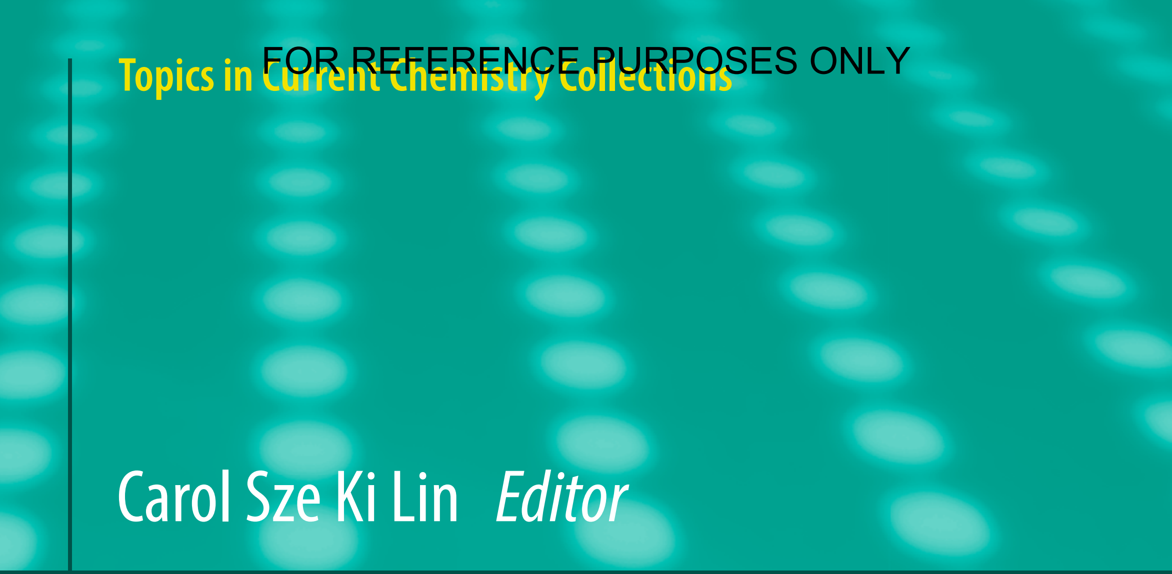

Topics in Current Chemistry Collections

Carol Sze Ki Lin *Editor*

Chemistry and Chemical Technologies in Waste Valorization

Springer

Topics in Current Chemistry Collections

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The goal of each thematic volume is to give the non-specialist reader, whether in academia or industry, a comprehensive insight into an area where new research is emerging which is of interest to a larger scientific audience.

Each review within the volume critically surveys one aspect of that topic and places it within the context of the volume as a whole. The most significant developments of the last 5 to 10 years are presented using selected examples to illustrate the principles discussed. The coverage is not intended to be an exhaustive summary of the field or include large quantities of data, but should rather be conceptual, concentrating on the methodological thinking that will allow the non-specialist reader to understand the information presented.

Contributions also offer an outlook on potential future developments in the field.

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Editor

Chemistry and Chemical Technologies in Waste Valorization

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Ragnhild Dragøy Whitaker • Sileshi Gizachew Wubshet
Vânia G. Zuin

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Editor
Carol Sze Ki Lin
School of Energy and Environment
City University of Hong Kong
Hong Kong, China

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Contents

Preface

Increasing demand for consumer goods from an exploding world population is placing enormous strain on the resources needed by the worlds manufacturing industries. Traditional resources have often been from non-renewable sources located in relatively accessible regions, but these are finite, their exploitation non-sustainable, and they are becoming scarce. At the same time, the wastes generated in manufacturing and in use of the articles of today's society have been allowed to accumulate in rapidly filling landfill sites or disposed of in other environmentally harmful ways.

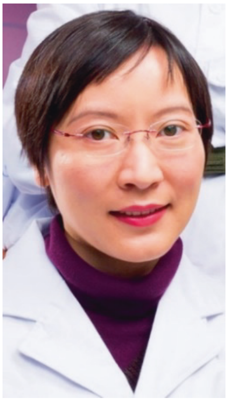
As the Editor in this special issue of Topics in Current Chemistry entitled 'Chemistry and Chemical Technologies in Waste Valorization', I have selected relevant works from worldwide respected and well-known leaders on this hot topic. The aim of this collection is to familiarize chemists with techniques and technologies used in waste valorization, and to show that chemistry plays an important role in transforming waste to useful resources.

Prof. Juan Carlos Colmenares's contribution deals with the use of sonocatalysis which is related to the use of a catalytic conversion method assisted by ultrasound energy [1]. This constitutes an alternative way for biomass upgrading. The possibility of combining catalysis with sonication provides an effective conversion method for lignocellulosic wastes. His review highlights recent progress and methods based on catalysis assisted by ultrasound energy for the transformation of lignocellulosic biomass into valuable products. Whereas Prof. Gordon McKay's contribution deals with various waste printed circuit board (WPCB) treatment methods as well as recycling techniques of WPCB divided into direct treatment (landfill and incineration), primitive recycling technology (pyrometallurgy, hydrometallurgy, biometallurgy and primitive full recovery of NMF-non metallic fraction) and advanced recycling technology (mechanical separation, direct use and modification of NMF). These topics are reviewed and analyzed based on their advantages and disadvantages [2]. Also the evaluation criteria are discussed including economic, environmental and gate-to-market ability. His review indicates the future research direction of WPCB recycling should focus on a combination of several techniques or in series recycling to maximize the benefits of process.

Prof. James Clark presents an overview on some of the more recent developments in processing the three main components of biomass—carbohydrates, lipids, and proteins for green materials, as well as case studies that bring these technologies and materials together into final products for applied usage [3]. Similarly, Prof. Mubofu Egid reports the valorisation of cashew nut shells liquid (CNSL) via various chemical reactions for the production of industrially important chemicals and materials [4]. The reactions involved in these transformations include transfer hydrogenation reactions, isomerization reactions, metathesis reactions, carbonylation reactions, polymerization reactions, isomerizing metathesis reactions, and isomerizing carbonylation reactions. Dr. Diana Lindberg's contribution covers all the important aspects of achieving optimal utilization of proteins in residual raw materials, such as heads, bones, carcasses, blood, skin, viscera, hooves and feathers originating from the fisheries, aquaculture, livestock and poultry sectors [5]. Her review includes industrially applied technologies such as freezing/cooling, acid preservation, salting, rendering and protein hydrolysis. In this regard, it is important to achieve stable production and quality through all the steps in the manufacturing chain, preferably supported by at- or online quality control points in the actual processing step. If aiming for the human market, knowledge of consumer trends and awareness are important for production and successful introduction of new products and ingredients.

Dr. Nattha Pensupa's contribution provides an overview of valorization of textile waste to value-added products, as well as an overview of different strategies for sugar recovery from cellulosic fiber and their hindrances [6]. Prof. Zheng Sun presents a critical review of recent technological developments in the production of chemicals and other materials from microalgae grown using different types of waste. A range of novel approaches are examined for efficiently capturing CO_2 in flue gas via photosynthetic microalgal cultivation. Strategies for using microalgae to assimilate nitrogen, organic carbon, phosphorus, and metal ions from wastewater are considered in relation to modes of production [7]. Lastly, Prof. Vania G. Zuin presents a review on green and sustainable separation of natural products from agro-industrial waste [8]. Her review discusses the concepts of green and sustainable separation of natural products, with highlights of the main studies conducted on this topic over the last 10 years. The principal analytical techniques (such as solvent, microwave, ultrasound and supercritical treatments), byproducts (e.g., citrus, coffee, corn and sugarcane waste) and target compounds (polyphenols, proteins, essential oils, etc.) are covered. These include the emerging green and sustainable separation approaches towards bioeconomy and circular economy contexts.

The guest editor would like to express her appreciation and gratitude to the Topics in Current Chemistry editorial office (Springer) for their kind invitation to compile this comprehensive topical collection on **Chemistry and Chemical Technologies in Waste Valorisation**. I would also like to extend my most sincere gratitude to thank all the authors and reviewers who contributed to the publication of this topical collection. It was a pleasing experience to work with them on this topical collection. Last but not least, I sincerely thank the publishing editors, Elizabeth Hawkins and Charlotte Hollingworth and assistant editor, Na Xu, who patiently and kindly took us through the development of this topical collection over the past two years to achieve this impressive final result, which would not have been possible without such support.



Carol Sze Ki Lin
School of Energy and Environment
City University of Hong Kong
Tat Chee Avenue, Kowloon, Hong Kong

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REVIEW

Sonocatalysis: A Potential Sustainable Pathway for the Valorization of Lignocellulosic Biomass and Derivatives

Ewelina Kuna[1] · **Ronan Behling**[2] · **Sabine Valange**[2] · **Gregory Chatel**[3] · **Juan Carlos Colmenares**[1]

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Abstract Lignocellulosic biomass represents a natural renewable chemical feedstock that can be used to produce high value-added chemicals and platform molecules. Nowadays, there are extensive studies on a variety of aspects concerning the valorization of lignocellulosic biomass into desirable products. Among the current technologies for biomass conversion some require extreme conditions along with high temperatures and pressures. Therefore, major technological innovations based on more economical and environmental methodologies are currently developed both in academic laboratories and in industry. In this context, ultrasound-assisted catalysis constitutes an alternative method offering new strategies to upgrade biomass. The possibility of combining catalysis with sonication indeed provides avenues that are worth exploring for the valorization of lignocellulosic compounds into value-added chemical feedstocks. In this mini-review, the available sonochemical systems are first presented, with a focus on the most important ultrasonic parameters, which is intended to provide a mechanistic background. Next, this contribution aims to provide insight into the most recent developments along with prominent examples in the field of sonocatalysis applied to the chemical transformation of lignocellulosic biomass and its derivatives.

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✉ Gregory Chatel
gregory.chatel@univ-smb.fr

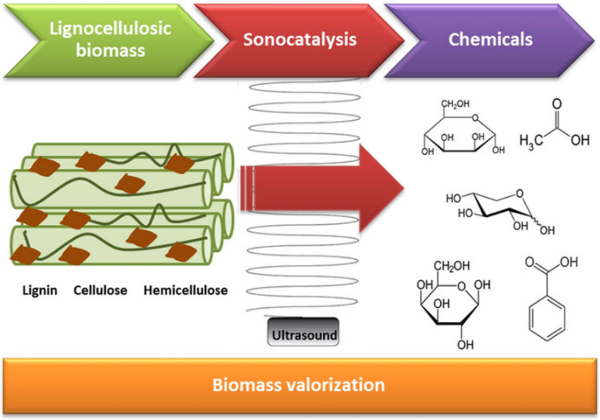
✉ Juan Carlos Colmenares
jcarloscolmenares@ichf.edu.pl

[1] Institute of Physical Chemistry, Polish Academy of Sciences, Kasprzaka 44/52, 01-224 Warsaw, Poland

[2] Institut de Chimie des Milieux et Matériaux de Poitiers (IC2MP), Université de Poitiers, CNRS, ENSIP, B1, 1 rue Marcel Doré, 86073 Poitiers Cedex 9, France

[3] Univ. Savoie Mont Blanc, LCME, F-73000 Chambéry, France

Graphical Abstract



Keywords Sonochemistry · Sonocatalysis · Biomass upgrading · Lignocellulosic waste valorization · Lignocellulose depolymerization

1 Introduction

The worldwide accessibility of biomass undoubtedly plays a fundamental role in sustainable energy production. In favorable circumstances, around 25% of global energy requirements can be supplied by biomass [1]. The enormous potential of plant materials resides in the presence of lignocellulosic residues coming from forest residues, energy crops, municipal and industrial wastes [2]. This type of renewable resource is now increasingly used for the production of value-added chemicals and transport fuels [3]. Nevertheless, plant dry matter possesses a sturdy structure, which complicates the effective conversion process of lignocellulosic biomass into platform chemicals. Lignocellulose is a recalcitrant biopolymer composed of the semi-crystalline polysaccharide cellulose, the polysaccharide hemicellulose, and the three-dimensional amorphous phenylpropanoid lignin polymer [4, 5]. The conversion of lignocellulosic feedstock leads to the production of a variety of added value platform chemicals, including phenolic compounds (*p*-coumaryl alcohol, coniferyl alcohol, and sinapyl alcohol), aliphatic acids (formic acid, acetic acid, levulinic acid), and furan aldehydes (hydroxymethyl furfural) [6]. It is worth mentioning that the accessibility to desired products is dependent on biomass pretreatment methods, which have a significant influence on the production of their derived feedstocks for further valorization strategies. Notwithstanding, the selection of the most favorable pretreatment process depends predominantly on the target molecule and many other factors such as economical and environmental aspects [7]. The depolymerization process of lignocellulosic biomass includes physical, chemical, and biological treatments, as well as various combinations thereof (Fig. 1) [7–9]. The physical pretreatment of biomass as a first step for

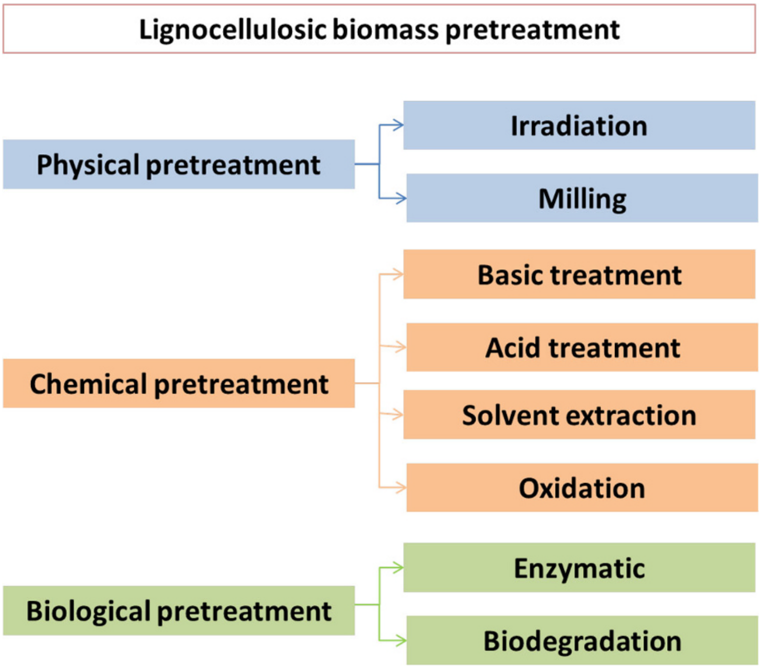


Fig. 1 Methods for pretreatment of lignocellulosic biomass. (Adapted and modified from Ref. [9])

further upgrading is achieved by mechanical comminution of lignocellulosic materials through a combination of chipping, grinding, or milling. In the particular case of cellulosic biomass, such physical process leads to a size reduction due to a decrease of both the degree of polymerization and the crystallinity, resulting in the increase of the mass transfer and the improvement of the hydrolyzation reaction. However, the energy consumption required for physical treatment is higher than the theoretical energy content available in lignocellulose, which makes it prohibitively expensive for large-scale uses [10]. An alternative for deconstructing lignocellulosic biomass is chemical pretreatment. This method is based on catalytic processes such as acid/alkaline hydrolysis, oxidative delignification, cracking, reduction reaction, among others [11]. Acid pretreatment allows converting hemicellulose into monomeric sugars (e.g. glucose, xylose) and soluble oligomers, whereas alkaline hydrolysis renders lignin recoverable. Delignification of lignocellulosic biomass can also be performed by treating in the presence of oxidizing agents (e.g. hydrogen peroxide, ozone, and oxygen) [12]. In most of these cases, catalysis increases the efficiency of the process and is responsible for the major effects achieved by pretreatment [13]. The application of catalysts provides a more effective approach in biological processing, where the yield of hydrolysis is relatively low along with long pretreatment times. Enzymatic hydrolysis can also be improved by combining ultrasonic pretreatment with the organosolv process. Ultrasound has the potential to enhance the separation and hydrolysis of lignocellulosic materials [12]. By contrast, the combined use of organic solvents (including ionic liquids) or their mixtures with water was shown to enhance dissolution of biomass and increase depolymerization rates [14].

The immensity of available pretreatment methods creates opportunity to choose those which enable downstream processing of lignocellulosic biomass. Recovered carbohydrate polymers such as cellulose and hemicellulose can further be transformed into fermentable sugars and then into fuels or feedstock chemicals. Valuable products can also be obtained from lignin through development and integration of current and new technologies such as sonocatalysis, heterogeneous photocatalysis, or microwave-assisted conversion [15, 16]. According to a classification proposed in previous papers [8, 17] a simplified summary of conversion strategies is given in Fig. 2. Thermal technologies can be used to produce solid feedstocks (e.g. biochar), liquids (e.g. oils and viscous tars), and gaseous products. However, methods such as pyrolysis and gasification require large energy inputs due to the high processing temperatures. Chemical conversion techniques (e.g. catalyzed depolymerization, hydrotreating, oxidation, liquid-phase reforming) constitute a more energy efficient and environmentally sustainable way to valorize biomass [17].

In the present review, we focus on the recent literature advances on sonocatalytic valorization of lignocellulosic biomass and their platform molecules. It is evident that catalysis is regarded as a key route enabling technology for pretreatment and conversion of lignocellulosic biomass [8]. Over the past few years, research on the development and optimization of highly active and selective catalytic systems has been an ongoing activity to overcome drawbacks associated with harsh chemical conditions, low yield production, and high processing cost [18]. Additionally,

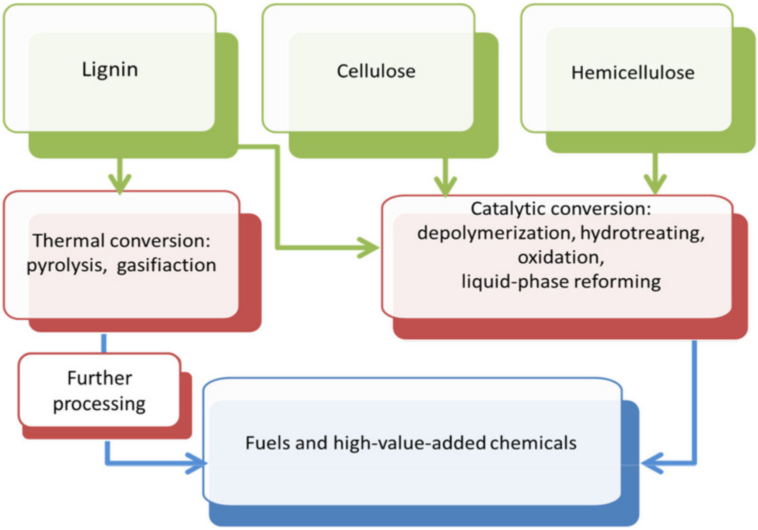


Fig. 2 Biorefinery strategies for lignocellulosic biomass valorization to fuels and chemicals. (Adapted and modified from Refs. [8, 17])

sonochemical-assisted reactions offer opportunities to develop environmentally friendly and cost-effective processes for biomass upgrading [4, 19].

2 Generalities on Sonochemistry

Sonochemical effects arise from cavitation, which is defined as the phenomenon of formation, growth, and implosive collapse of bubbles under the influence of an ultrasonic field in liquids [20, 21]. Cavitation can be categorized into various forms (acoustic, hydrodynamic, optic, and particle cavitation) depending on the method of generation and associated ultrasonic/experimental parameters (frequency, acoustic power, shape of the reactor, solvents, temperature, pressure, etc.). Acoustic and hydrodynamic cavitation may generate physical and chemical changes in solution in contrast to optic and particle cavitations. Numerous “hot spots” can be created by acoustic and hydrodynamic cavitation due to the accumulation of a huge amount of energy which in turn results in immense pressures and temperatures [22, 23]. The pressure fluctuation induced by changing the geometry of the flow system produces hydrodynamic cavitation, while the pressure fluctuation in the passageway of sound waves induced acoustic cavitation [24].

Acoustic cavitation takes place within collapsing bubbles (gas-phase chemistry), on the outer side of the bubbles (solution-phase chemistry) and at the liquid–solid interface (physical modification) [21]. The chemical and physical effects of ultrasound eventuate from the cavitation phenomenon and not from direct interaction between chemical species and ultrasonic waves [21, 25]. The chemical effect of ultrasound is the consequence of the implosive collapse of microbubbles, producing free-radicals, whereas the physical effects are the result of shock waves

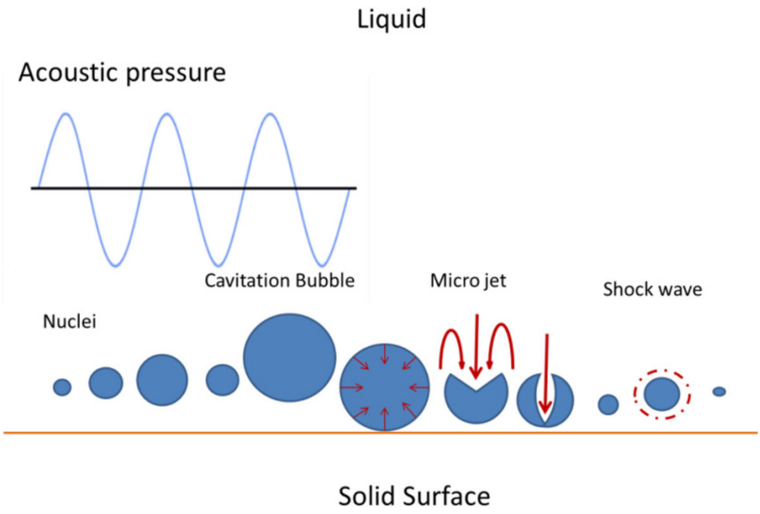


Fig. 3 Acoustic cavitation mechanism

and microjet generated during symmetric and asymmetric cavitation, respectively (Fig. 3) [26].

The rate of motion of ultrasound is significantly greater than the molecular scale [23]. Generally, when the sound velocities in a liquid are around 1000–1500 m s^{-1} the power ultrasound (in opposition to diagnostic ultrasound, particularly used in medical imaging) can oscillate from approximately 10 to 10^{-4} cm over the frequency range of 20–2000 kHz [21, 22]. The compression and expansion waves put the liquid under dynamic tensile stress. As a result, the local pressure decreases adequately below the saturated vapor pressure and initiate cavitation [21, 27]. Microbubbles present in a liquid absorb energy from ultrasound waves and undergo a rapid overgrowth leading to violent collapse. The final stage of implosion is almost adiabatic and provides extreme conditions [21, 28].

2.1 Homogeneous and Heterogeneous Sonochemical Systems

Sonochemical reactions can be classified into three categories, namely homogeneous sonochemistry of liquids, heterogeneous sonochemistry of liquid–liquid or liquid–solid systems, and sonocatalysis (which involves the aforementioned systems) (Fig. 4) [29, 30]. Homogeneous systems include radical reactions, which are accelerated by sonication and that follow via radical or radical-ion intermediates [32]. In this case, the chemical bonds are broken under the high temperature and pressure generated during cavitation [24]. The short-lived chemical species are turned back to the bulk liquid and react with other species [32]. Sometimes homogeneous sonochemistry followed by secondary reactions taking place in the liquid, especially in the case of compounds of low volatility, which can interact with

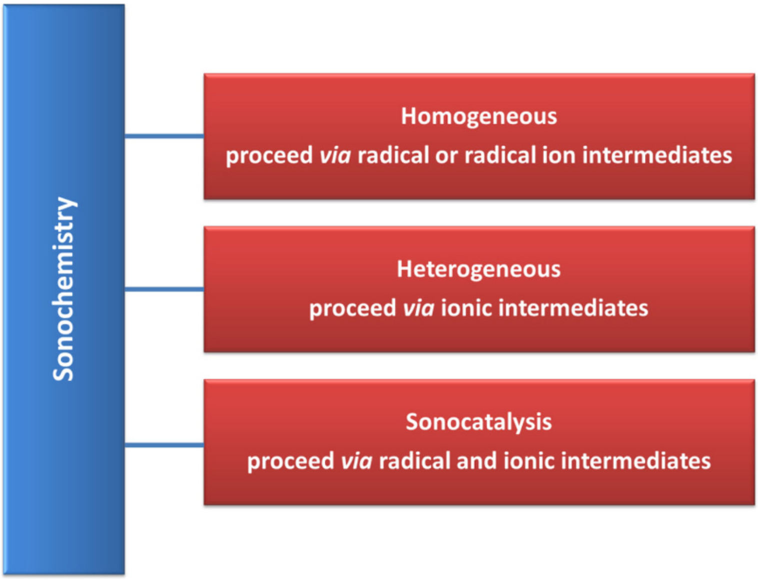


Fig. 4 Classification of sonochemistry reactions

radical species produced from solvent sonolysis [33]. In homogeneous systems, where the surroundings are uniform, the cavity remains spherical. Cavity collapse in heterogeneous system may proceed via two fundamentally different mechanisms such as microjet impact and shock wave damage. Deformation in the cavity is caused by asymmetric motions of the molecules in liquid during cavity collapse. The expanded bubble's potential energy is converted into kinetic energy of a high-speed liquid jet that passes through the bubble's interior and pierces the opposite bubble wall. The available energy is predominantly handed over to the accelerating jet rather than the bubble wall itself [34, 35]. High energy concentration can cause an intense damage to the boundary surface. The stress fracture on the surface can be invoked by shockwaves generated through cavity collapse in the liquid. The impingement of microjets and shockwaves form the localized erosion, which is in charge of ultrasonic cleaning and another sonochemical effects such as particle size reduction or improved mass transfer on heterogeneous reactions [24]. In heterogeneous systems, the use of ultrasound accelerates chemical reactions, drawing on mechanical effects of cavitation. The dynamics of the cavity collapse changes dramatically when cavitation takes place in a liquid nearby a solid surface [32]. The imposition of the heterogeneous and homogeneous sonochemistry includes a radical and an ionic reaction mechanism. Indeed, depending of the ultrasonic frequency (see Sect. 2.2), the sonication enhances radical formation and mechanical effects (e.g. mass transfer) [30].

2.2 More Important Parameters in Sonochemistry

The selection of ultrasonic parameters (such as frequency, acoustic power, temperature, pressure, solvent, design of reactors, etc.) is a crucial issue in order to optimize the system and thus influence efficiency of a chemical process. There are different ways to optimize these parameters depending on the target experimental outcome; they can be chosen by taking into account the data concerning studies on bubble cavitation characteristics [36]. The problem connected with cavitation distribution and quantification might be addressed by using different experimental or theoretical mapping techniques [37]. The basic aspects of each method, their applicability, pros and cons have been highlighted by Sutkar and Gogate [37, 38]. Their analysis allows one to determine the behaviour of cavitational activity regarding reactor geometry over a range of operating parameters [24]. In order to estimate mutual relation, bubble dynamics analysis has been also employed by other researchers [37, 39]. The study includes quantifying the correlation between the pressure and temperature linked with cavity implosion as a function of intensity, frequency, and initial radius of the nuclei [24].

The cavity dynamics is defined by two elements: the maximum magnitude accomplished by the cavity before implosion (that determines the pressure and temperature generating during collapse) and the lifetime of the cavity (that defines the distance travelled by the cavity from the place where it is formed) [37, 40]. Both elements are of paramount importance for the design of sonochemical reactors and should be optimized by appropriately adjusting the various geometric and operating parameters [37]. The reactor design has significant effects on the cavitational activity, in terms of the reactor and horn tip diameters (including the ratio of both diameters) and the position of the horn tip immersed in the liquid [24, 41].

Another factor that has an influence on the cavitation is the amount of energy, which is supplied to the bulk solution. The power dissipation rate varies on the extent of temperature growth, which causes direct changes in the gas solubility and vapour pressure, generating active cavitation sites. Energy efficiency is expressed by the amount of energy dissipated into the liquid and is generally calculated by a calorimetric method (monitoring the temperature as a function of time allows to estimate the acoustic power) [24, 37].

The effect on the bubble cavitation is directly connected to the frequency of the ultrasound. We can distinguish frequencies at low range (20–80 kHz) and high range (>150 kHz) [42]. High frequency does not promote the occurrence of active cavitation, because of insufficient duration of the ultrasonic cycle, which is required for the growth, radial motion, and collapse of bubbles. The short-lived bubble can boost the concentration of free radicals and may have a higher probability to get out the cavitation site to the bulk mixture. Compared to lower frequency ultrasound, high ultrasonic frequencies produce less violent cavitation and lead to chemical effects. Low frequencies are responsible for physical effects, where rapid cavitation leading to enormous temperatures and pressures at the cavitation site [43]. It is noteworthy that physical properties of the liquid phase have also many effects on ultrasonic cavitation. Relative low volatility, viscosity, and high surface tension of liquid solvents are preferred for favoring efficient cavitation [37]. Active cavitation occurs also in heterogeneous sites in liquids such as impurities, gas microbubbles, non-volatile additives, etc. [36].

The physical and chemical effects produced by ultrasonic cavitation in a liquid phase provide extreme local conditions such as immense local heating ($\sim$5000 °C), pressures ($\sim$1000 atm), and heating/cooling rates (10^{10}°C s^{-1}) [34]. Microjet streams and shock waves created by cavitation promote better energy and mass transfer, which has an impact on accelerating chemical reaction, increasing conversion, improving the yield, and enhancing the selectivity in both homogeneous and heterogeneous systems [44]. For this reason, sonochemistry has found wide applications in chemical synthesis used for the preparation of nanostructured materials (e.g. hybrid lignocellulosic materials) [45] and modification of inorganic materials (e.g. clay minerals) [46]. Additionally, the benefits of the use of ultrasound in organic synthesis are also highlighted by interesting review articles [47–49]. Some key examples where synthetically useful sonochemical organic transformations carried out in homogenous and heterogeneous conditions include: hydrolysis [50], cycloaddition (e.g. Diels–Alder reaction) [51], coupling (e.g. Suzuki reaction, Mitsunobu reaction) [47], isomerization (e.g. glucose to fructose) [52], alkylation [53], esterification [54], and polymerization reactions [55].

3 Ultrasound-Assisted Catalysis for Lignocellulosic Biomass Valorization

3.1 Principles of Sonocatalysis

The combination of sonochemistry with catalysis can be used to accomplish a number of chemical reactions with convenient workup conditions (e.g. shorter reaction times) in contrast to more conventional methods [56]. Heterogeneous reactions follow via ionic intermediates provoked by mechanical effects, whereas radical reaction enhanced mainly by sonication. In the case when radical and ionic mechanisms lead to other products, ultrasound might promote the radical reaction, which can also provide new synthetic pathways [30]. The fundamental rule of sonocatalysis is diffusion and sorption of the main components on a solid surface followed by a series of heterogeneous chemical reactions on active sites [57]. In a heterogeneous reaction system, the improvement of chemical reaction is mainly caused by physical effects. The physical phenomena improve mass transfer from turbulent mixing and acoustic streaming, generate cavitation erosion at liquid–solid interfaces, and are responsible for deformation of solid surfaces (Fig. 5) [25].

The effect of ultrasonic irradiation on a heterogeneous catalyst may cause physical and chemical modifications (e.g. changes in crystallization, dispersion, and surface properties, as well as changes on catalytic reactivity during reaction (Fig. 5) [58]. The chemical rate increases due to enhancement of external transport phenomena and the increase in temperature at the catalyst surface. Acoustic

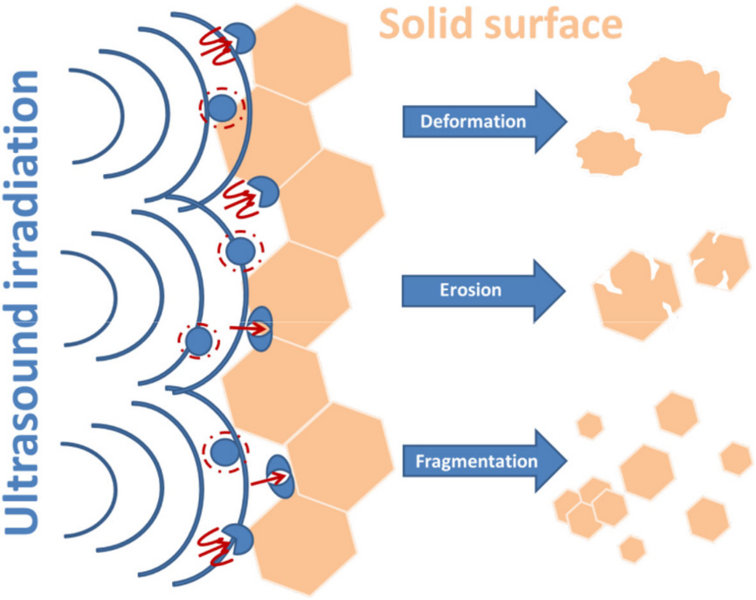


Fig. 5 Effect of ultrasound irradiation on a heterogeneous catalyst surface

cavitation can induce the breaking of the catalytic particle and gives more accessibility to the internal surface for the reagents. In the gas–liquid-solid system (e.g. hydrogenation reactions) sonication increases the interphase surface and favors the removal of outer oxide or other passivating layers from the catalyst surface [49].

3.2 Homogenous and Heterogeneous Sonocatalysis

The application of ultrasound in homogeneous and heterogeneous reaction systems in the presence of catalysts is viewed as a convenient technique for lignocellulosic valorization. Catalysis assisted by ultrasound includes a variety of reactions such as hydrolysis, hydrogenation, oxidation [59]. Sonication improves hydrolysis of lignocellulosic materials into sugars and their subsequent fermentation into bioethanol. The main reason for enhanced conversion is the substantial improvement of mass transfer in reacting systems, as well as the activation of chemical and biological catalysts [37]. Yunus et al. reported that the acid hydrolysis of palm oil to xylose was increased from 22 to 52% under ultrasound pretreatment (20 kHz, 2 kW), in comparison to silent conditions (Table 1; Entry 1) [60]. An improvement of the reaction rate under ultrasound (25 kHz, 600 W) was noticed also by Choi and Kim during the acid-catalyzed hydrolysis of starch (Table 1; Entry 2) [61]. Ultrasonic energy can have a direct influence on hydrolysis and fermentation reactions of cellulosic materials, while the application of ultrasound with enzymes accelerates saccharification and the fermentation rate [36]. Cavitation effects enhance the transport of enzyme macromolecules to the surface of the substrate, whereas the substrate surface is opening up to the action of enzymes due to the mechanical effect of cavitation [4, 62]. Additionally, the sono-assisted enzymatic conversion of cellulose performed in solvents such as ionic liquids (ILs) yielded high performances by promoting high conversion, yield, and selectivity [36]. The combination of ultrasound with ILs has indeed recently attracted much interest for lignocellulosic biomass valorization [36]. For example, enzymatic hydrolysis of lignocellulose assisted by ultrasound (45 kHz, 100 W) in imidazolium-based ionic liquid media improves cellulosic conversion from 75 to 95% [63] and saccharification ratio to 92% from 55% [64] in 60 min (24 kHz, 35 W). The benefits of ultrasound-assisted enzymatic processes are the enhanced solvation and the increased reactivity of biomass reactants, coupled to reactions taking place at lower temperature within shorter time and with less requirement for acid or base catalysts [36].

The nature of solvents fulfils a crucial role in the lignocellulose depolymerization process. In some cases, ionic liquids were used only selectively to dissolve lignin rather than hemicellulose or cellulose [65]. For example, the catalytic hydroprocessing of lignin under ultrasound conditions resulted in a higher efficiency when conducted in an ionic liquid (1-butyl-3-methylimidazolium acetate) in comparison to organic solvents and water. Considerable enhancement in conversion up to 90% was noticed with nano-Ni and NiO nanosheets catalysts [66]. The conversion rate and the mass distribution of products depends on the procedure used for the pretreatment (acidic or alkali) of lignin. This means that in most cases, acidic extraction leads to a larger extent of depolymerization reaction (Table 1; Entry 3)

Table 1 Homogeneous and heterogeneous sonocatalytic biomass valorization

Entry	Process	Catalyst	Substrate	Sonochemical parameters	Experimental details	Sonocatalytic behaviour	References
1	Hydrolysis	2% sulphuric acid (aqueous solution)	Oil palm empty fruit bunch	2 kW (20 kHz)	Reaction time 15, 45, 60 min Solvent H_2SO_4 concentration (2%) Temperature 25 °C	The highest yield of xylose (58%) was obtained under ultrasound irradiation (90% amplitude) during 45 min, whereas without ultrasonic pretreatment yield was equal to 22%	[60]
2	Hydrolysis	1–5% sulphuric acid (aqueous solution)	Starch Maltose Maltotriose	600 W (25 kHz)	Reaction time 100 min. Solvent dilute sulfuric acid (1–5 wt%) Temperature 90–100 °C	The reaction yield in the presence of ultrasound is higher than in the reaction without sonication (increased ~75 % at 90 °C)	[61]
3	Hydroprocessing	Fe_3O_4 (NiAlO) x Fe_3O_4 (NiMgAlO) x	Miscanthus (lignin, glucose, xylose, arabinose, galactose, mannose, extractives, and ash)	(35 kHz)	Reaction time: 6 h/24 h. Solvent: ethyl acetate/methanol/ionic liquid [BMIM]OAc Temperature room temperature/180 °C	Catalysts exhibited a slight activity whereas considerable growth in conversion (up to 90% under US irradiation) was noticed on nano-Ni (0) and NiO (111) nanosheets samples	[66]
4	Degradation	Rutile- TiO_2 Anatase-TiO_2 Montmorillonite Clay (MMT), ZnO and Fe_3O_4	2-hydroxyethyl cellulose	100 W (24 kHz)	Reaction time 100 min Solvent water Temperature 25 °C	The sonocatalytic activity (rate constants) of nanoparticles catalysts increases in the following order: Fe_3O_4, Rutile-TiO_2, ZnO, Anatase-TiO_2, and MMT	[68]

Table 1 continued

Entry	Process	Catalyst	Substrate	Sonochemical parameters	Experimental details	Sonocatalytic behaviour	References
5	Sonophotocatalytic Degradation	TiO_2	Chitosan	30–90 W (24 kHz)	Reaction time 60 min Solvent water Temperature: 25 °C	In 60 min (at loading catalyst: 0.1–0.6 g/L) rate constant is modified in the range of 0.354–1.134 ($mol^{1.7}$ $L^{-1.7}$ min^{-1} × 10^{-9}) while for the sonocatalytic degradation from 1.737 to 2.654 ($mol^{1.7}$ $L^{-1.7}$ min × 10^{-9})	[69]
6	Hydrolysis	Hydrochloric acid	Corn starch	Not provided by the authors	Reaction time 90 min Solvent hydrochloric acid Temperature 100 °C	The optimum conditions (levulinic acid yield 23%) were achieved during first 90 min at 100 °C with acid concentration (4.5 mol/L) and the ratio of liquid: solid (15:1 mL/g)	[72]
7	Oxidation	$FeCl_3/HNO_3$ (various Lewis acids)	A mixture of benzyl alcohols	120 W (35 kHz)	Reaction time 10–25 min Solvent acetone Temperature room temperature.	Ultrasound enhances chemical reactions and allows to obtain the complete conversion of benzyl alcohol into aldehyde during first 10 min reaction. However, continuation of the reaction over 20 min does not improve the yield (94%) and leads to other oxidized byproducts (e.g. benzoic acid)	[73]
8	Oxidation	TEMPO/NaBr/ NaClO	Cotton linter pulp	300 W (40 kHz)	Reaction time 24 h Solvent water Temperature 25 °C	Ultrasonic-assisted by TEMPO oxidation allows obtain high carboxylate content (1.66 mml/g) cellulose nanocrystals (the widths 5–10 nm; the lengths 100-400 nm)	[74]

Table 1 continued

Entry	Process	Catalyst	Substrate	Sonochemical parameters	Experimental details	Sonocatalytic behaviour	References
9	Oxidation	Au/SiO_2	D-glucose	(35 kHz)	Reaction time 60 min Solvent: 30% hydrogen peroxide Temperature room temperature	The application of ultrasound provides high conversion (~100%) and selectivity (~80% into gluconic acid) and eliminates consequent reaction by products (fructose, mannose, glycolaldehyde, sorbitol, and maltose)	[79]
10	Hydrogenation	Raney-Ni Cu/SiO_2 Cu/ZnO/Al_2O_3	D-fructose	0–50 W	Reaction time: 120 min Solvent – Temperature 70–110 °C	In the case of Raney-Ni catalyst, reaction selectivity was slightly lower at 30 W (47%) than under silent conditions (51%) and reactions carried out with 10 W (50%) and 50 W (50%)	[80]

[66]. Additionally, work by Napoly and co-workers shows that it is possible to obtain vanillin-based monomers with yield equal to 0.51 wt% in the presence of a tungsten-based catalyst and an oxidizing agent such as H_2O_2 [67]. Na_2WO_4 acted as the most promising catalyst, which promoted an effective system, where ultrasound generated sufficient oxidation conditions (20 kHz, 11 W) and involved strengthened oxidative coupling of phenoxy radicals [67].

A relevant study about the degradation of cellulose was recently published by Taghizadeh (Table 1; Entry 4) [68]. The degradation behaviour of 2-hydroxyethyl cellulose was conducted in the presence of a variety of heterogeneous catalysts (such as titanium oxide, montmorillonite clay, zinc oxide, and iron oxide) under ultrasound irradiation (24 kHz). Sonolytic degradation (without catalyst) increases with increasing of ultrasonic power (in the range of 30–90 W); however, it is remarkably lower in comparison to the efficiency of the sonocatalytic degradation. The results obtained revealed that the combined use of catalysts and US irradiation improved the degree of cellulose depolymerization. Among all the catalysts tested, the most efficient was Fe_3O_4, which provided a better ability for radical generation through electron transfer between the metal ion and the water molecules during the sonication process. The possibility of combining ultrasound irradiation with heterogeneous photocatalysis was also studied by the same research group (Table 1; Entry 5) [69]. The complete degradation of chitosan (with cellulose-based structure) was achieved during 1 h in the presence of titanium oxide at 24 kHz. In this case, sonophotocatalysis enhanced the production of reactive radicals as well as increasing the active sites of the catalyst surface.

Behling et al. recently investigated the low frequency (20 kHz) ultrasound-assisted aqueous-phase oxidation of vanillyl alcohol to vanillin using a heterogeneous Co_3O_4 catalyst with hydrogen peroxide as the primary oxidizing agent under mild reaction conditions (low temperature and atmospheric pressure). The outcome of this work was that the ultrasound-assisted catalytic reaction is faster (4x), more selective (2.3x), and more efficient (2.7x) than the corresponding reaction carried out under silent conditions [70]. Additionally, a large decrease of the overall energy consumption was observed under ultrasound (36 vs. 288 kJ). Moreover, from an environmental point of view, green metrics indicators such as the E factor and the process mass intensity (PMI) calculated for both activation systems clearly showed the benefit of the ultrasound-mediated reaction [70]. The ultrasound-microwave assisted process is also an interesting approach for lignocellulosic biomass valorization. The simultaneous microwave (100 W) and ultrasound irradiations was shown to improve the hydrolysis reaction rates of glucose [71] and corn starch [72] (Table 1; Entry 6) in 60 min. In both cases, the reaction yield to levulinic acid was high (49 and 23% from glucose and corn starch, respectively) in comparison with those reported in the open literature.

Kardos and Luche [42] have investigated interesting approaches to obtain high value-added chemicals through the conversion of biomass feedstocks such as polymeric carbohydrates to lower weight molecules. In the case of polysaccharides, the partial or total depolymerization has to be taken into account. Hydrolytic procedures, already mentioned before, have been widely examined to accomplish this aim. Nevertheless, particular attention should be paid to oxidation reactions. For example, glucose being selectively oxidized into glucuronic acid in the presence of iron sulfate under ultrasound irradiation (100 kHz), whereas hexoses are oxidized to the corresponding uronic acids. It is interesting to note that this type of reaction cannot be performed without oxygen or acoustic activation [42].

The sonocatalytic oxidation of primary benzyl alcohols into the corresponding aldehydes was reported by Naik et al. [73]. They noted that the mixture of HNO_3/$FeCl_3$ provides high yields (80–94%) of aldehydes within 10–25 min (Table 1; Entry 7). Reactions carried out under silent conditions showed fourfold lower rates and yields than those performed under sonication. The application of ultrasound (35 kHz, 120 W) gave excellent yields with short reaction times and allowed to avoid over-oxidized products.

The work of Qin et al. [74] showed that the TEMPO/NaBr/NaOCl oxidation system assisted by ultrasound (40 kHz, 300 W) can be used to prepare cellulose nanocrystals with high carboxylate content from cotton linter pulp (Table 1; Entry 8). This is consistent with the study carried out by Brochette–Lemoine et al. [75]. The results of these investigations indicated that the rate of the oxidation of methyl α-D-glucopyranoside or sucrose was increased in the presence of ultrasound. Moreover, the reaction can then occur without the commonly used sodium bromide owing to the ability of ultrasound to generate the active oxidizing species during the catalytic cycle. Additionally, sonication accelerated the oxidation reaction, especially when the frequency of ultrasound was increased from 20 up to 500 kHz [76]. In order to scale up the oxidation of cellulose, Paquin et al. [77] proposed the use of a continuous flow-through system instead of the classical standard batch mode. The flow-through reactor increased the reaction rate ($\sim$36%) in comparison to the batch reactor while decreasing the overall energy consumption ($\sim$87%) [4].

Another reaction worth interest for the industry is the production of gluconic acid from D-glucose. Rinsant et al. [78] have described a way to selectively oxidize glucose via a sono-Fenton process with hydrogen peroxide in the presence of iron (II) sulfate as catalyst. In contrast to preconceived ideas, they proved that sonochemistry does not constitute an "intensive energy consuming" technology. Furthermore, the energy consumption could be minimized when ultrasound-based processes are optimized. Energy consumption (under ultrasound) was lower than that attained under conventional reactions. Remarkably high conversion ($\sim$100%) and selectivity ($\sim$95%) values were obtained only after 15 min (20 kHz, 0.25 W mL^{-1}). This example on D-glucose oxidation relies on the efficient combination of an eco-friendly oxidant (hydrogen peroxide) and ultrasound, which constitutes a promising strategy for the valorization of biomass. In the same strategy of sugar oxidation by sonocatalysis, Bujak et al. [79] observed that silica-supported gold catalysts are extremely active and selective for D-glucose oxidation to gluconic acid at ambient temperature and under ultrasound conditions (35 kHz) (Table 1; Entry 9). The application of ultrasound is of crucial importance to provide not only high conversion of glucose into gluconic acid with 100% yield, but also high reproducibility.

The effect of sonication (26, 78 and 130 W cm^{-2}) on D-fructose hydrogenation in the presence of heterogeneous catalysts was examined by Toukoniitty et al. [80]. The reaction rate and selectivity were investigated at various conditions of temperature (70–110 °C), pressure (10, 30, and 50 bar), and ultrasonic power (0–50 W) (Table 1; Entry 10). The application of sonication during the hydrogenation reaction considerably accelerated the reaction rate in the presence of the Cu/SiO_2 catalyst. High temperature and pressure had a moderate effect on the catalyst activity whereas the variation of nominal ultrasonic power input effectively improved the reaction rates.

4 Challenges and Future Perspectives

In most cases, combining catalysis with sonication has interesting effects on reactions course. In the present mini-review, we have shown that the use of sonocatalysis allows avoiding harsh chemical conditions, along with reducing reaction times and improving heat and mass transfer, thereby increasing chemical rate constants, yields, and selectivities. Hence, the ultrasound-assisted catalysis can be successfully applied for the pretreatment and chemical conversion of lignocellulosic biomass and its derivatives in a variety of processes such as hydrolysis, oxidation, and hydrogenation reactions. The recent studies on the use of ultrasound to assist catalytic reactions have clearly shown great advantages and technological potential of this concept for the chemical industry, especially when thinking about processes under flow. More significant scientific breakthroughs for biomass valorization are expected to occur in this innovative field in the near future. Last, but not least, and continuing in the same lines, the important role of ultrasound on photocatalysis (ultrasound and photocatalysis together) for the valorization of lignocellulosic biomass and its derivatives might be also a promising research avenue worth broad interest in the huge spectrum of possibilities offered by lignocellulose-based processes, for instance, sonophotocatalytic proof concepts for: lignocellulosic biomass depolymerization [81], biohydrogen [82], and biomethane production [83].

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REVIEW

Waste Printed Circuit Board (PCB) Recycling Techniques

Chao Ning[1] · Carol Sze Ki Lin[2] · David Chi Wai Hui[1] · Gordon McKay[1,3]

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Abstract With the development of technologies and the change of consumer attitudes, the amount of waste electrical and electronic equipment (WEEE) is increasing annually. As the core part of WEEE, the waste printed circuit board (WPCB) is a dangerous waste but at the same time a rich resource for various kinds of materials. In this work, various WPCB treatment methods as well as WPCB recycling techniques divided into direct treatment (landfill and incineration), primitive recycling technology (pyrometallurgy, hydrometallurgy, biometallurgy and primitive full recovery of NMF-non metallic fraction), and advanced recycling technology (mechanical separation, direct use and modification of NMF) are reviewed and analyzed based on their advantages and disadvantages. Also, the evaluation criteria are discussed including economic, environmental, and gate-to-market ability. This review indicates the future research direction of WPCB recycling should focus on a combination of several techniques or in series recycling to maximize the benefits of process.

Keywords Waste printed circuit board · Recycling techniques · Pyrometallurgy · Hydrometallurgy · Mechanic separation · Performance evaluation

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✉ Gordon McKay
gmckay@qf.org.qa

[1] Chemical and Biomolecular Engineering Department, The Hong Kong University of Science and Technology, Hong Kong SAR, Hong Kong

[2] School of Energy and Environment, The City University of Hong Kong, Tat Chee Avenue, Hong Kong SAR, Hong Kong

[3] College of Science and Engineering, Hamad bin Khalifa University, Education City, Qatar Foundation, Doha, Qatar

Abbreviations

EEE	Electrical and electronic equipment
WEEE	Waste electrical and electronic equipment
PCB	Printed circuit board
WPCB	Waste printed circuit board
MF	Metallic fraction of printed circuit board or waste printed circuit board
NMF	Non-metallic fraction of printed circuit board or waste printed circuit board

1 Introduction

Electrical and electronic equipment items (EEE) including MP3, cell phones, and tablets have been the indispensable necessity of peoples' daily lives while past decades have witnessed the rapid growth of EEE manufacturing industries. Currently, the production rate of EEE is estimated to be between 8.3 and 9.1 million tons per year in 2005 with an increasingly rapid growth rate due to technology updates, making it the dominant manufacturing industry in the world [1, 2]. The rapid development of EEE has given rise to the blooming of the printed circuit board manufacturing industry, which produces the core components of electrical and electronic equipment [3, 4]. Meanwhile, the accelerating upgrading of these industries also shortens the life span of EEE from around 5 years to as short as 2 or 3 years [5, 6]. This is an accelerating process, with an annual rate of 3–5% according to an EU report in 2000 [7]. Consequently, it is not difficult to realize the fact that the amount of waste electrical and electronic equipment (WEEE), as the result of EEE jettisoning, is increasing at an overwhelming rate. It is estimated that currently the amount of WEEE production is nearly 45 million tons yearly worldwide with an annual growth rate of 7–10% [8].

The printed circuit board (PCB) is considered to be the core part in most kinds of EEE (see Table 1). It is estimated that global production of printed circuit boards (PCBs) was around \$50 billion in 2010 and reached nearly \$60 billion in 2012 with a market growth rate of 1.7% [10, 11]. However, the mass disposal of WEEE generates a huge stream of waste printed circuited board (WPCB) into municipal solid waste, which was produced in large amounts which increase significantly every year (Fig. 1). Although WPCB only occupies a small portion around 3–6% of

Table 1 Main components of typical WEEE [9]

Typical WEEE	Main components
Refrigerator	Tubes, liners, condenser, wires, refrigerant
Air conditioner	Heat exchanger, motor, compressor, copper pipe, PCBs, wires, refrigerant
Washer	Tub, drain hose, motor, wires, salt waste
Television	Deflection yoke, demagnetized coil, speaker, PCBs, wires, CRT, LCD
Computer	Speaker, battery, storage medium, PCBs, wires, CRT, LCD
Printer/duplicator	Roller, toner, PCBs, wires, toner cartridge

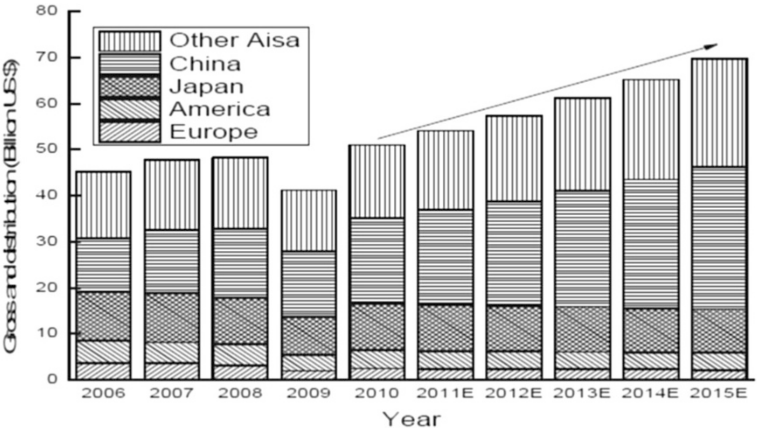


Fig. 1 PCBs increasing based on the global gross [11]

the total WEEE generated worldwide, the immense total WEEE amount still made it considerable [8, 12]. WPCB can be either directly treated, which includes landfill and incineration, or the recycling of WPCB by various kinds of technologies is also an alternative [13–18]. Compared to direct treatments, recycling is more favorable due to both environmental and economical consideration given the enrichment of materials in WPCB. It is regarded as a secondary resource since the concentration of precious metals, organic resins, or polymers in WPCB is normally ten times higher than rich non-renewable are (sometimes even hundred times higher) [19]. Therefore, recycling is not simply reduction of waste but the reuse of resources with better economic feasibility and less environmental impact.

The USEPA (United States Environmental Protection Agency) has identified seven major benefits when scrap iron and steel are used instead of virgin materials (Table 2). Using recycled materials in place of virgin materials results in significant energy savings (see Table 3 [20]). Also, the European Commission launched the 2002/96/EC Directive, known as the WEEE Directive, which came into effect on February 13, 2003, with the aim of achieving up to 70–80% recovery of electrical and electronic equipment [15]. Therefore, recycling is not only for the purpose of resource refining, more importantly, it can reduce the toxic pollution emitted in the initial manufacturing process, which will make a significant benefit difference in remediation costs.

Current recycling methods includes pyrometallurgy and hydrometallurgy, which have a long history and wide application [21–23]. Biometallurgy as an emerging technology also takes up a certain share of the WPCB recycling market [24–26]. Many studies have been done to improve the performance or cut the cost of these techniques. However, the inherent drawbacks are very obvious for these techniques, including the irritation to the environmental intensive energy consumption. Therefore, new advanced technologies are in great demand due to the requirement of technology with high safety and economic feasibility. Mechanical separation was developed due to the requirement for a high-purity metallic fraction of WPCB (MF)

Table 2 Recycled materials energy savings over virgin materials

Materials	Energy savings (%)
Aluminum	95
Copper	85
Iron and steel	74
Lead	65
Zinc	60
Paper	64
Plastics	>80

Table 3 Benefits of using scrap iron and steel

Benefits	Percentage
Saving in energy	74
Saving in virgin materials use	90
Reduction in air pollution	86
Reduction in water use	40
Reduction in water pollution	76
Reduction in mining wastes	97
Reduction in consumer wastes generated	105

and it can achieve good separation performance for real-use applications [27–30]. Recently, the use of the non-metallic fraction (NMF), which was forgotten in the past, is becoming the concern of researches including both the direct use or the modification of NMF [31–35].

However, a unanimous blind spot among the majority of works is the environmental emission analysis, which is a very serious problem derived from WPCB treatment. Several studies have been done on the evaluation of the emissions or discharge [5, 15]. Common pollutants generated from WPCB treatment or recycling include heavy metals, secondary particulates, PBDD/Fs, and PCDD/Fs, which have been studied and their toxicities are regarded as obstacles to WPCB recycling. However, emissions with lower toxicity, especially bromide in the form of hydrogen bromide or bromide, did not receive adequate attention. Despite the relatively low harm these emissions possess compared to dioxin-like organic compounds or heavy metals, the jeopardy they show is still a significant threat to human health that requires detailed studies and further treatment. Moreover, the complexity of WPCB's composition creates the scenario that specific analysis targeting certain pollutants is available while an overall review of emissions impact is still absent. Therefore, this overall emission impact study and strategy needs more effort.

Other than the discussion of emission, another issue mentioned previously is concerned with the techniques that focus mainly on general WEEE treatment methods. Nevertheless, WPCB shares several similarities with WEEE in terms of composition and chemical characteristics, the minor differences between them still requiring the development of better process techniques for WPCB treatment [36–38]. The common composition of EEE is shown in Table 4 while the detailed

Table 4 Main materials found in EEE [39]

Material	Percentage
Ferrous	98
Non-ferrous	28
Plastics	19
Glass	4
Wood	1
Other	10

discussion of WPCB will be presented in a later section. Therefore, the techniques for WEEE can be applied to WPCB but may not acquire ultimate efficiency. Actually, compared with WEEE, the composition of WPCB is more or less more consistent, since the outer casing for WEEE varies with different kinds of EEE, for example, the refrigerator or television while most WPCB has no relationship with the outer casing, making WPCB simpler for treatment or recycling. Thus, the specific design and analysis for WPCB treatment or recycling is indispensable in order to obtain the maximum sustainable environmental and economical benefits.

Herein, the lack of a summary on current techniques due to the upgrading of techniques as well as the absence of systematic emission analysis claims that an overall review of this field is imperative. Also, with the development of technologies, the overlapping of chemical, mechanical and physical treatments is very obvious, thus a new criteria is necessary for sorting and evaluating the interdisciplinary recycling and treatment techniques. In this work, the treatment and recycling techniques of WPCB are categorized according to their recovery rate and both existing and emerging techniques are reviewed and discussed. The performance of WPCB recycling techniques is evaluated from both an economic and environmental perspective. Moreover, the concept of "gate to market ability" is introduced for a more profound understanding of the feasibility of WPCB recycling techniques.

2 Characterization of WPCB

The composition of WPCB varies, since the source, components, and manufacturing processes of the WPCB maybe very different [40]. Generally, the composition of currently used PCBs is classified as glass fiber reinforced epoxyresin (FR-4), which is normally used for small electronic equipment or a paper laminated phenol is resin (FR-2) used in home appliances [41, 42]. Also, during the manufacturing process, carbonaceous compounds including brominated flame retardants and dyes are added in order to improve the flame resistance and visual recognition ability. In Table 5, it is obvious that WPCB mainly consists of MF and NMF. It is generally accepted that WPCB contains around 30% metallic fraction and 70% non-metallic fraction by weight [43, 44]. However, what needs to be clarified is that the percentage of noble metals in WPCB has been decreasing in recent years with the upgrading of technologies [45].

It is widely accepted that WPCB is comprised of a heterogeneous mixture [39, 46–48]. The heterogeneity originates from two aspects, which are the

Table 5 Composition of a populated PCB [36]

Components of WPCB	Percentage
Non-metal (e.g., epoxy resin, glass, etc.)	>70
Copper	~16
Solder	~4
Iron, ferrite (from transformer cores)	~3
Nickel	~2
Silver	0.05
Gold	0.03
Palladium	0.01
Other (bismuth, antimony, tantalum, etc.)	<0.01

heterogeneity of different PCB brands including the use of cellulose paper reinforced phenolic resin or glass fiber reinforced epoxy resin and heterogeneity in the morphology of a PCB due to the presence of metal plating [49]. However, if an adequate amount of WPCB is collected and pulverized into fine powder, empirically rules of the composition of WPCB can still be identified by comparing them globally. This is the so-called "pseudo-homogenous" effect, which means that the individual composition of a certain WPCB item will vary from others, while the bulk composition of all WPCB items will still share similarities, as shown in Table 6.

Generally, the uncertainty of WPCB composition hampers the systematic treatment or recycling of WPCB, since the complexity of it interferes with each component [59]. Therefore, pulverization is a very important pretreatment part for mixed WPCB recycling and treatment techniques since the higher pseudo-homogeneity is more favorable for easier application in overall treatment.

3 Direct treatment methods—landfill and incineration

The types of technologies for WPCB recycling are increasing with the development of research and thus the old category for technologies sorting is no longer applicable. Some processes divide the technologies to thermal or non-thermal, or

Table 6 Materials composition of several common used printed circuit boards

Metals/Ref.	[15]	[50]	[51]	[52]	[53]	[54]	[55]	[56]	[57]	[58]
Cu/%	36.4	16.0	33.87	18.29	19.187	32.5	19.60	31.95	26.8	19.19
Au/%	–	0.025	0.0007	0.011	0.013	0.004	–	–	0.008	0.007
Ag/%	–	0.100	0.04	0.018	0.0704	0.3	0.0034	0.34	0.33	0.01
Al/%	8.7	5.0	2.57	–	4.011	3.7	2.34	11.11	4.7	7.06
Pb/%	3.8	2.0	4.96	2.31	0.385	–	0.30	2.41	–	1.01
Pd/%	–	0.010	0.0012	–	0.0028	–	0.0016	–	–	–
Sn/%	4.6	3.0	0.153	3.92	0.689	0.9	0.17	1.78	1.0	2.03
Cd/%	–	–	0.00002	–	–	–	–	–	0.015	–
Total	53.5	33.14	41.59	24.55	24.36	37.40	22.42	47.59	32.85	29.31

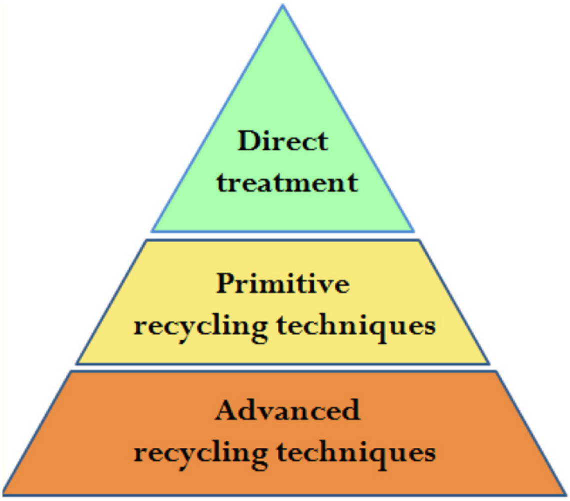


Fig. 2 Hierarchy figure of the WPCB treatment and recycling techniques

some divide into chemical treatment or mechanical treatment, others divide them by the atmosphere of the reaction or some divide them into hydrometallurgical processing or pyrometallurgical processing [16, 60, 61]. In this review, the treatment and recycling techniques for WPCB are classified according to their recovery degree (Fig. 2). Direct treatment including landfilling and incineration means that no or only the energy of WPCB was recovered while primitive recycling means the simple recycling of MF, while the NMF ended up in disposal or limited non-hazardous treatment. Advanced recycling includes two parts: separation methods without damage to the NMF and the direct use or modification of NMF. It is highly convincing that this classification can better describe the current situation of WPCB recycling and provide a basis for an overall treatment perspective instead of focusing on only one or two areas.

3.1 Landfill

Landfill is a WPCB treatment method with a long history and wide application worldwide because of simplicity in operation. However, the land for WPCB disposal is thereby regarded as wasteland and normally incapable of being exploited again in predictable decades, which is not suitable for countries/communities where there is a lack of land space. In addition, the environmental issues aroused by WPCB landfilling such as the leachate formation in landfill sites and evaporation of hazardous substances raise safety concerns. It is reported that almost 70% of the heavy metal in landfill sites come directly from WEEE, which indicates that a considerable part of heavy metals actually come from WPCB [62]. Concurrently, the co-landfilling of WPCB with various kinds of municipal solid waste makes the formation of leachate containing brominated toxic compounds and heavy metals possible due to the reactions during the landfilling process [13, 14]. The synergic pollution will contaminate the atmosphere, soil, and ground water, and this has been proven by several research groups.

Heavy metals including lead and mercury are identified in landfill sites. Lindberg et al. identified total gaseous mercury (TGM), monomethyl mercury (MMM), and dimethyl mercury (DMM) in the landfill gas in Florida, USA [63]. The results show that the mean concentration of TGM is 7190 ng/m^3 and MMM is 6 ng/m^3. It should be emphasized that DMM, a form of extremely toxic organic mercury, was also observed in landfill gas with a concentration of 30 ng/m^3. Spalvins et al. also identified lead in the leachate in landfill sites with a concentration of 0.007–0.066 mg/l [64]. Other than heavy metals, PCDE(polychlorinated diphenyl ethers)/PBDE(polybrominated diphenyl ethers) were also discovered in landfill sites by Osako et al. [65]. Samples from seven different landfill sites in Japan were collected and analyzed. Landfill sites in operation or closure within 1 year show the presence of several kinds of hazardous compounds, especially obvious is the higher concentration of brominated flame retardants and the derivatives. TBBPA with concentration from n.d. to 620,000 pg/l and PBDE-47, -99, and -100 with the total concentration from n.d. to 4000 pg/l were detected in the raw leachate from different landfill sites. More dangerously, the hazards of landfill leachate and gas are not only limited to the landfill site because they will propagate though aquatic systems or rain fall and cause the spread of contamination. Wong et al. found that even in the downstream of the small-scale landfill site of a Chinese processing village, a certain amount of metals can still be detected including Cd (n.d. to 10.3 mg/kg), Cu (17.0–4540 mg/kg), Ni (12.4–543 mg/kg), Pb (28.6–590 mg/kg), and Zn (51.3–324 mg/kg) [66]. This indicates the possibility of toxic substance migration, which makes the condition of landfill sites much worse.

It summary, landfilling is currently considered an improper way to treat WPCB due to the environmental concerns it brings about, and actually the function of it is to use land resources to remedy hazardous WPCB, which is a waste of resources for both soil and WPCB. Therefore, stricter policies and regulations have been imposed on simply landfill WPCB in many countries and more environmental benign treatment methods are required [67–71].

3.2 Incineration

Incineration means the combustion of WPCB by converting its calorific value to energy and emitting the gas directly or after treatment with the purpose mainly to remove the non-metallic fraction part (around 70 wt%) [72, 73]. It has the advantages of significantly reducing the volume of WPCB by 50%, and also the calorific value of WPCB is relatively high compared to municipal solid waste, which is around 9.9×10^4 kJ/kg [15, 16]. Therefore, it readily satisfies the minimum incineration calorific value for waste, which is roughly 5000 kJ/kg. Currently in the world, incineration is still widely used in American, Asia, and Europe due to the simplicity of the process. However, during the combustion of WPCB, toxic emissions including heavy metals, fly ash, polychlorinated dibenzo-*p*-dioxins/polychlorinated dibenzofurans (PCDD/Fs) and polybrominateddibenzo-*p*-dioxins and dibenzofurans (PBDD/Fs) are released into the atmosphere in the absence of post-purification [74, 75]. Cadmium, copper, nickel, lead, and zinc will be vaporized according to the order of their melting points and released into the atmosphere [76]. Unfortunately, incineration is an ideal place for the formation of PCDD/Fs and PBDD/Fs due to the presence of halogens and an oxidizing atmosphere as well as incomplete combustion [77–79]. Additionally, in incineration, copper in WPCB will play the role of catalyst for dioxin formation in the presence of brominated flame retardant [5]. This all contributed to the high emission amount of PBDD/Fs, as high as 130,000 ng/g, which is very high compared to other investigations [80]. Also, the amount of PBDD/Fs exceeds PCDD/Fs significantly due to the abundance of bromide in WPCB. Other gaseous pollutants including Br_2, HBr, CO, and NOx also attract considerable concern about them.

Ni et al. has conducted high-temperature WPCB incineration in a tube furnace and found that high-temperature combustion favors the removal of PBDD/Fs, which can release maximum 99.9% bromide into flue gas in the form of HBr or Br_2 with much lower toxicity compared with PBDD/Fs [79]. Also, the temperature needs to exceed 1200 °C in order to reduce the formation of CO and ensure the completely decomposition of brominated flame retardant (Fig. 3). However, the high temperature will slightly favor the formation of NOx from 690 mg/Nm^3 (800 °C) to 790 mg/Nm^3 (1400 °C) that exceeds the emission standard value of 500 mg/Nm^3. In spite of HBr and Br_2having a lower toxicity, they still need further treatment like adsorption to avoid the emission to local atmosphere.

Other than the gaseous emission that incineration releases, there is still the solid-phase residue of the incineration that is termed “bottom ash,” which will be landfilled or processed for further treatment. There are significantly enriched heavy metals in the bottom ash including copper (35.8–1295 mg/kg), Pb (226.3–606.6 mg/kg), and Cd (0.87–7.46 mg/kg), which makes the safe disposal of it become a troublesome issue [76]. Normally, a vitrification process at a temperature of 1500–1600°C is typical for the treatment of bottom ash [82].

Therefore, incineration as a treatment method for WPCB is not an environmentally friendly option considering the toxic emissions. Also, the construction of an incineration plant is a major expenditure for local governments. Actually, as these side effects were revealed by the emerging researches, the use of existing incineration plant or planning for future incineration plants was seriously affected in many countries. Public concerns and acceptability were more attracted to the recycling instead of simple treatment of WPCB.

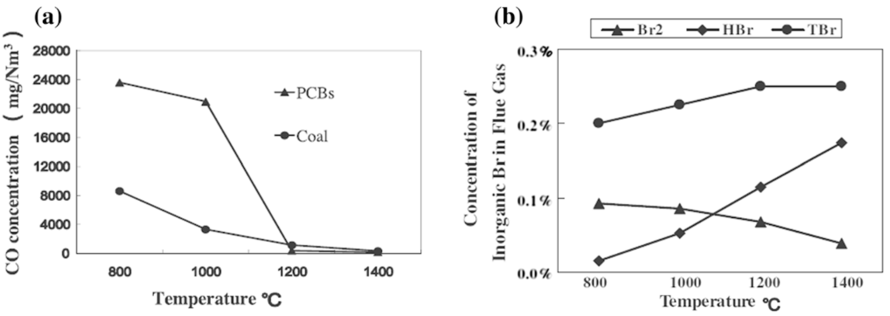


Fig. 3 Effects of temperature on CO emission (**a**) and HBr/Br_2 emission (**b**) (excess air factor = 1.3, high temperature zone residence time = 0.25 s)

4 Primitive Recycling Techniques

4.1 Partial Recovery of Metallic Fraction from WPCB

4.1.1 Pyrometallurgy Recycling Techniques

Pyrometallurgy recycling techniques are conducted by decomposing WPCB in the absence of air or the presence of an inert atmosphere. It is a very important and mature technology for WPCB recycling and numerous works have been done on this. Although pyrometallurgy shares similarities with incineration, they are still distinct and separate techniques. The main difference between pyrometallurgy and incineration is that the purpose of incineration is simply reducing the volume of WPCB and to, achieve partial heat recovery though the incineration of WPCB when the heat released is adequate, whereas the purpose of pyrometallurgy focuses more on resource recovery, which includes the concentrating of MF and other materials out of the WPCB feedstock by decomposing NMF to low molecular weight organic compound-formed liquid or gas. This also leads to the result that unlike incineration, the operation cost for pyrometallurgy is normally much higher than incineration due to maintaining the absence of oxygen from the process. More comparisons of incineration and pyrolysis in detail are listed in Table 7.

In pyrometallurgy, the process is typically divided into two stages. In the first stage, the WPCB starts to decompose due to the intensive heat input and the release of volatile organic compounds. The second stage is the formation of char due to the pyrolysis of polymer inside the structure [6]. Therefore, temperature is a very critical variable in pyrometallurgy such that low temperatures (<400 °C) will favor the formation of liquid products while high temperatures (>800 °C) will help the breakage of high molecular weight compounds, thus producing more small organic molecular [15, 83, 84]. Also, the pyrolysis of WPCB is extremely dangerous while the temperature is low (lower than 800 °C) and the absence of an inert atmosphere since there will be PBDD/Fs formation [85]. Normally, the absence of air is relatively difficult to ensure, especially in large-scale applications, thus the production of PBDD/Fs is a serious issue for low-temperature pyrolysis.

As for the pyrolysis products, some pyrolysis reactions can produce pyro-oil or pyro-gas, which has the potential to be used as fuel or chemical material source, but the complexity and uncertainty of it greatly hampers its application [15, 16]. Also, the products of pyrometallurgy have been characterized by several groups and HBr, by-products of brominated phenols, PCDD/Fs, PBDD/Fs have been found in pyrolysis products, which has the side effects of aquatic toxicity, carcinogenicity, and mutagenicity [17, 18, 86–89]. As for the pyro-solid, which is the inorganic components left after pyrolysis normally generates a huge amount of acidic effluents, will jeopardize the aquatic environment and cause side effects to human health [90]. As a result, the majority of research only focuses on the recovery rate of WPCB without overall consideration of the environmental impact analysis.

Pyrolysis of commercial WPCB has been done in an autoclave at 500 °C for 30 min and the pyro-liquid, pyro-gas, as well as pyro-solid were collected [15]. The

Table 7 Comparison between incineration and pyrolysis [81]

Aspect	Incineration	Pyrolysis
Dioxins and furans emissions	Incineration produces dioxins that are released in air and remain also in the solid material	Pyrolysis has a reduced production of dioxins
Bromine recovery	Incineration achieves complete bromine evolution in combustion gases. There is a risk of formation of elementary Br2	Bromine evolves part in the gas and part in pyrolysis oil. Bromine recovery could be an important aspect for the pyrolysis plant
Tin recovery	With incineration tin solder recovery is not possible	Tin solder recovery is possible with pyrolysis
Heat recovery	Incineration will release more heat than pyrolysis	Pyrolysis products will have 70 and 40%, respectively, of the raw material heating value (respectively for RAMs and CPUs)
Heavy metals emissions	Incineration results in the emission of mercury and cadmium	Pyrolysis process has reduced emissions of heavy metals

yields of pyro-liquid, pyro-gas, pyro-solid, and char derived from the pyrolysis of polymeric materials were 16.2, 7.3, 76.5, and 5.8%, respectively. However, the value of these pyrolysis products is very limited since the pyro-solid contains a high content of heavy metals including Cu (36.4 wt%) and Pb (3.8 wt%), which is not capable of being recovered and actually requires further treatment. Also, the pyro-liquid contains a certain amount of Br and Cl, which is hazardous to human health, and is not clarified in the paper. Guan et al. also studied the pyrolysis products of WPCB and the GCV value of pyro-liquid was found to be around 29 MJ/kg, which is around the same level as coal, which is normally 30 MJ/kg [16]. However, the Br inside the pyro-liquid will hamper the usage of it, which must undergo removal before application. The main components of pyro-gas are hydrogen, carbon monoxide, carbon dioxide, and methane at 500 °C. However, there still are some bromorganic molecules inside, which will affect the usage of the pryo-gas. Therefore, we can conclude that the failure of separation with Br is a serious challenge for the application of pyro-liquid and pyro-gas. Thus, Terakado et al. used metal oxide including ZnO, Fe_2O_3, La_2O_3, CaO, and CuO as the fixation of Br in pyrolysis process and the results show a significant reduction of HBr as well as bromorganic compounds emission [91]. The deficiency is that metal oxide was used as additive and still in the end bromide salt requires further treatment.

Guo et al. has done the pyrolysis in 500 °C and 71.60 wt% solid residue, 18.23 wt% tar, and 10.71 wt% gas were obtained from this process [92]. The main component of the pyro-gas is CO, CO_2, propylene, and small bromorganic molecules like bromomethane and bromopropane. The calorific value of pyro-gas is 2.386 MJ/kg, which is quite low comparing to natural gas (38.93 MJ/kg), together with the difficulty in direct application due to bromide inside the gas. The pyro-tar and pyro-solid have been investigated and been found to have a certain amount of metal and bromide, reducing its environmental friendliness. The energy balance was calculated and it shows that only 35% of the heat required for pyrolysis is capable of recovery from the pyrolysis products, which means an additional heat source is necessary for the process.

Cayumil et al. has done high temperature pyrolysis from 800 to 1350 °C [93]. After this process, they obtained a slag phase, tin–lead (~40% Sn, ~8% lead, and ~45% copper)-rich metallic phase and copper-rich phase (~85% copper), which has relatively high purity. However, there are still 22–25 wt% of slag phase which has not be recycling and the crucial point is that there is still certain percentage of metal inside this slag phase, which means that although this process is very energy-intensive, there is still a considerable amount of toxic solid waste produced (Fig. 4).

To remedy the drawbacks of a high pyrolysis temperature and side reaction occurrence, vacuum pyrometallurgy techniques have recently been developed as an advanced technology for pyrometallurgy recycling techniques, since it has the advantages of low operation temperature and a reduction in the intensity and occurrence of side reaction or reformation of hazardous materials [94–96]. However, the strict vacuum requirement calls for a separation before vacuum metallurgical methods.

Anjan Kumari et al. conducted vacuum pyrometallurgy followed by solvent extraction to recycle various kinds of product after vacuum pyrolysis at 300 °C for 4 min due to the enhanced performance of pyrolysis under high vacuum [88]. This is a very systematic process that has the advantage to recycle fuel oil, fuel gas, sulfuric acid, Cu, Ni, and Fe. Therefore, the emission of toxic gas will be reduced significantly since the recovery section takes a big percentage of the total composition of WPCB feedstock. Details about this process are shown in Fig. 5. However, attention to the bromide is still not be given, since the process does not contain a step for bromide removal and TEHA dissolved in kerosene is used as the extraction solvent, which will also have the side effect of emission.

Zhou et al. found that the assistance of pre-separation will improve the efficiency of the process [49, 97]. The pretreatment is mainly aimed at separate solder and other electronic components. They performed the vacuum pyrolysis at 600 °C for 30 min under a vacuum lower than 1.5 kPa. However, the pretreatment was conducted at 183 °C, which needs an energy input as they are using an oil bath, which is not comparable to the result of separation of solder although the composition of solder remains almost unchanged. For the pyrolysis part, the pyro-

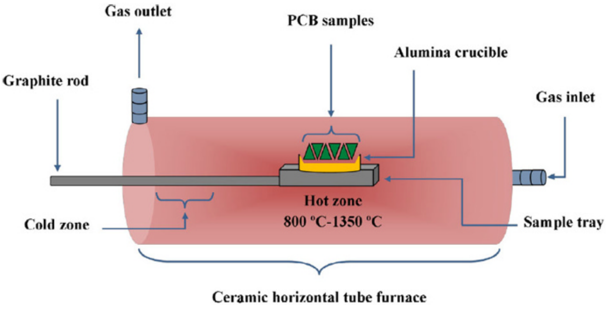


Fig. 4 Typical design of pyrolysis equipment [91]

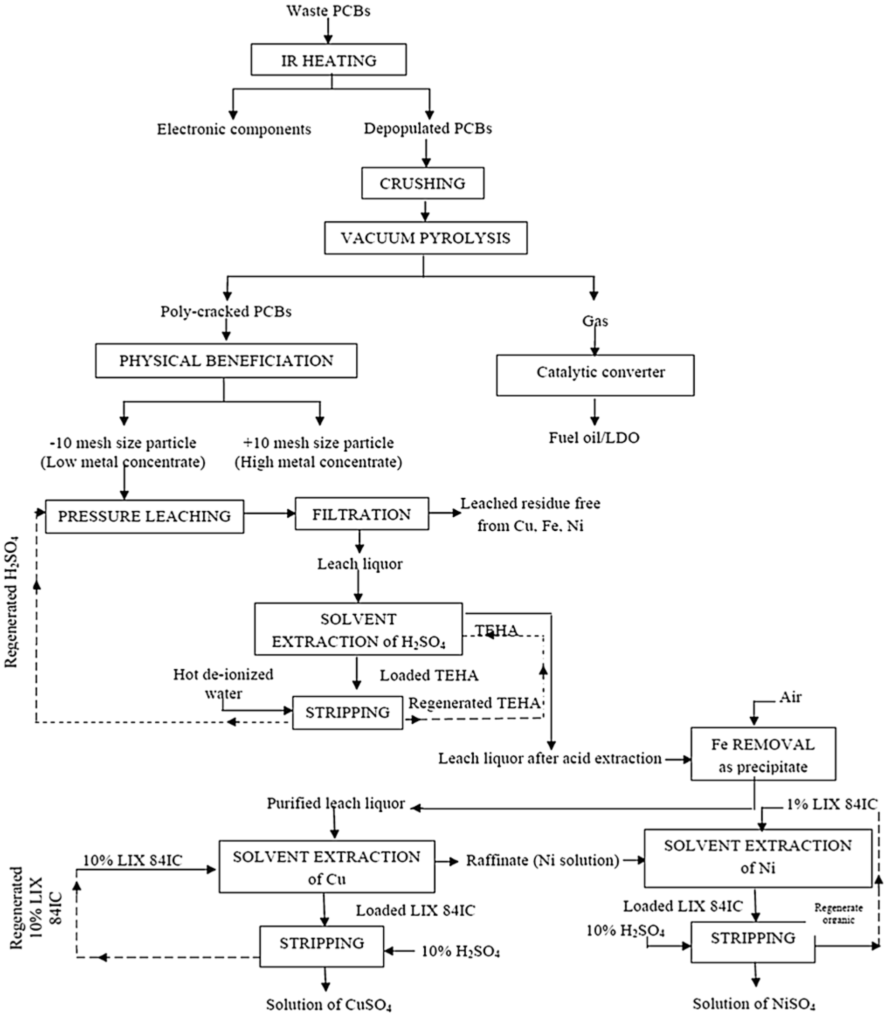


Fig. 5 Complete process flow sheets for recovery of base metals from waste PCBs [116]

oil it produced has unknown composition, which cannot be used for any refinery. Li et al. studied the vacuum pyrometallurgical process at low temperatures and concluded that vacuum (less than 1000 Pa) will significantly improve the performance of recycling by significantly reducing the activation energy from 127.87 and 115.36 kJ mol^{-1}to 53.59 kJ mol^{-1}, which significantly improves the outcome of the process [60].

However, the drawbacks of vacuum pyrometallurgy techniques are very obvious, namely, the requirement of a high vacuum. Although vacuum equipment is used in industry, the vacuum degree needed for the vacuum pyrometallurgy technique calls for expensive equipment and good air tightness, since the failure to guarantee high vacuum degree will lead to the incomplete pyrolysis of WPCB, causing hazardous emissions and side reactions in the process. Therefore, the application of this process is seriously hindered due to its low economic feasibility.

Summarily, pyrometallurgy recycling techniques can recycle most of the MF at the cost of ruining the NMF. Also, the burn off of the nonmetallic fraction will not only produce bromorganic compounds and other toxic emissions, but it will also give around 20–25% ash content, which will have a certain percentage of heavy metals and need a further workload to perform disposal or refining [51]. A remediation method is to do the dehalogenation either no later than the pyrolysis process, or in the upgrading of the pyrolysis products [82, 98]. However, it may add further workload and cause the reduction of the yield and value of the pyrolysis products. Moreover, copper or lead in the feedstock will function as collectors of other metals, which will result in the output of unknown alloy from pyrometallurgy instead of pure metal that require further refining [99].

4.1.2 Hydrometallurgy recycling techniques

Hydrometallurgy recycling techniques make use of solvent leaching using cyanide, thiourea, thiosulfate, halide, and recycling the metallic fraction (mainly copper and gold) from WPCB feedstock [100–102]. Compared to pyrometallurgy, hydrometallurgy recycling techniques are more accurate, highly predictable, and easily controlled, which makes it the most competitive technique for WPCB recycling currently with the assistance of mechanical crushing as pretreatment [103].

Kinoshita et al. use nitric acid as a leaching reagent and they used two rounds of leaching in the first round Ni was extracted with a concentration of 279 mg/l at 363 K for 72 h and in the second round Cu was extracted with a concentration of 3220 mg/l at 363 K for 6 h [102]. The Au was obtained by filtration of the leachant and separated in the form of flakes. The metal-rich solution was forward extracted and backward extracted by organic solvent and 4.0 M nitric acid, respectively. The recovery rate is high and selective recovery was achieved. However, the process takes a long time and it produces waste water containing an organic phase and a strong acid, which is a common issue in hydrometallurgy recycling techniques. Similarly, Park et al. use aqua regia as the leaching agent to extract palladium, silver, and gold from WPCB feedstock [50]. The recovery of palladium in the form of $Pd(NH_4)_2Cl_6$ precipitation is 93 wt%. Gold nanoparticles were obtained by organic solvent extraction using dodecanethiol and sodium borohydride with a recovery rate of 97 wt%. Silver stays stable in aqua regia and was recovered without further treatment with a recovery rate of 98 wt%. The recovery rate is very high as well as the purity of the metal they collected. However, the usage of strong acid and organic solvent decrease the environmental evaluation of this process.

Therefore, despite the advantages of the hydrometallurgical treatment methods, a serious issues is that they produce a lot of highly toxic waste water containing cyanides or halides, which is extremely hazardous for both soil and water bodies [104]. Moreover, non-cyanide or non-halide leaching solvents like thiourea or thiosulfate have disadvantages including low-stability, high cost, and high consumption of extracting reagent [21–23]. Corrosion also causes problems for

Table 8 Comparison of different kinds of leaching solvent

Leaching solvent	Advantages	Disadvantages
Acid and mix acid [103–105]	High dissolution rate	Corrosive, high concentration of acid needed
Cyanide [106, 107]	Low cost, high stability, low dosage	High toxicity, slow leaching rate
Thiourea [53, 108, 109]	Low toxicity	Difficulty in recovery, high cost
Thiosulfate [110–112]	High selectivity, nontoxic, and non-corrosive	Sensitive to pH change
Halide [113]	High leaching rate, good selectivity	High cost, environmental irritation
Hydrogen peroxide [114, 115]	Low toxicity	Need acid assistance

the equipment when several kinds of leaching reagents were applied. More details are shown in Table 8 below.

Also, the leaching process normally takes a long time to obtain metal-rich solution due to the slow leaching rate, which makes the process a time-consuming one. Therefore, studies that reinforce the driving force and accelerate the leaching rate have been studied including using electrochemistry, pre-pyrolysis, supercritical extraction, and mechanical treatment [52, 54, 99, 117, 118]. Havlik et al. studied the hydrometallurgical process with pre-combustion, in which WPCB was leached in 1 M HCl solution after combustion in air for 15 to 60 min in 500–900 °C [99, 119]. The results showed that the pre combustion at 900 °C will significantly improve the leaching of copper from the WPCB feedstock due to the conversion of Cu to Cu_2O, which dissolves more preferable in HCl. However, the pre-combustion leads to the difficulty in extracting tin since Sn is oxidized to form SnO_2, which is very stable in acid with minimal leaching. Therefore, the efficiency of hydrometallurgy was seldom enhanced even without considering the emission during combustion process.

Fogarasi et al. used mediated electrochemical oxidation to recover copper from WPCB and high purity copper (99.04%) was obtained with 63.84% current efficiency [52]. However, a sludge was still produced with certain concentrations of copper and lead (49.37 and 32.49 wt%, respectively); this issue needs further work. Also, the fate of NMF was not clarified, as well as the bromide inside the NMF. Kim et al. use electro-generated chlorine to leach metals from WPCB feedstock [120, 121]. Copper as well as noble metal was obtained together due to the high oxidation potential they gained in the process. In the first stage, the recovery of Cu is 94.91% and in the second stage the recovery rate of Au is 93.06%. Then the metal ions can be collected by an ion-exchanger with efficiency around 97%. However, the feedstock used is already after dismantling and sorting therefore it has very high metal concentration (Cu 66 wt% and Au 0.045 wt%), which is not comparable to the raw WPCB feedstock, making the research not representative for all kinds of WPCB. Also, although the acid solutions as well as the low concentration solution are recycled back after ion exchange, the problem of discharge still exists since the halide is concentrated in the process if it is applied to WPCB with a high NMF content as well as the low pH of the solution. Silvas et al. used magnetic separation before the leaching test and they recovered 90 wt% Al, 40 wt% Zn, 8.6 wt% Sn in the first leaching stage using sulfuric acid media and 100 wt% Cu, 60 wt% Zn, and 10 wt% Al in the second stage using oxidant [54]. It is supposed that the recovery rate is very high due to the assistance of mechanical separation and this could be a possible way for future work. However, the fate of NMF was not mentioned in this paper and remains a potential pollutant.

Summarily, hydrometallurgy recycling techniques are easy to apply and simple to operate. However, the problem that cannot be avoided or ignored is the discharge of leachate as well as the pollutants since these techniques do not incorporate the recycling of NMF. The process is mainly undermining the structure of NMF and emits them, which not only wastes the useful part of NMF but also converts them into pollutants. Another issue that should be highlighted is that the recovery rate for hydrometallurgy recycling techniques is full recovery. Therefore, there will be a certain amount of heavy metal present in the effluent in the form of free ions, which will reinforce the hazardous content of it. So an upgrading of current hydrometallurgical recycling techniques is urgently required to stop the wild application of it.

4.1.3 Biometallurgy recycling techniques

Biometallurgy recycling techniques use microorganisms including bacteria or fungi to treat WPCB [122]. Commonly used bacteria include mesophilic chemolithotrophic, cyanogenicor moderately thermophilic bacteria [25, 26, 123, 124]. The mechanism of biometallurgy recycling techniques is similar to hydrometallurgy recycling techniques since they all incorporate the process of leaching. However, instead of adding leaching reagents, biometallurgy recycling techniques normally use the chemicals produced by the microorganism itself, including organic/inorganic acids, cyanide, or sulfate ions. After leaching, the metal ions will form complexes or precipitates and thus they are separated from the culture broth for direct use or further refining. It has the advantages of only a small volume of waste water discharge and is environmental benign compared to hydrometallurgy, which generally requires a high dosage of toxic chemical reagents. Besides, certain kinds of bacteria are capable of reducing brominated flame retardants in the pathway shown in Fig. 6, which is rarely achieved in other recycling techniques [122, 125].

Liang et al. used a mixed culture of *Acidithiobacillus thiooxidans* and *Acidithiobacillus ferrooxidans* to recover copper from WPCB fine powder [123]. The bacteria can oxide elemental sulfur added to sulfuric acid for bioleaching and then extract the metal from the broth. The highest recovery rate (98.37%) was obtained with the condition of pH value 1.56, elemental sulfur S^0 5.44 g/l and 16.88 g/l $FeSO_4 \cdot 7H_2O$ concentration. However, the increase of WPCB addition in culture from 18 to 32.4 g/l will cause a sharp drop in the copper recovery rate from 98.3 to 87.2%. Also, the fate of NMF was not mentioned in this work and remains a potential hazardous material. Ilyas et al. used moderately thermophilic bacteria to recover metals and conducted the process in a column test [124]. The recovery rate for Zn, Al, Cu, and Ni is 80, 64, 86, and 74%, respectively, which already meets the requirements of industrial-scale implementation for recycling of MF of WPCB. It is also noticed that NMF will contribute to the alkalinity which will affect the leaching of metal ions, requiring washing before conducting the culture stage. However, in

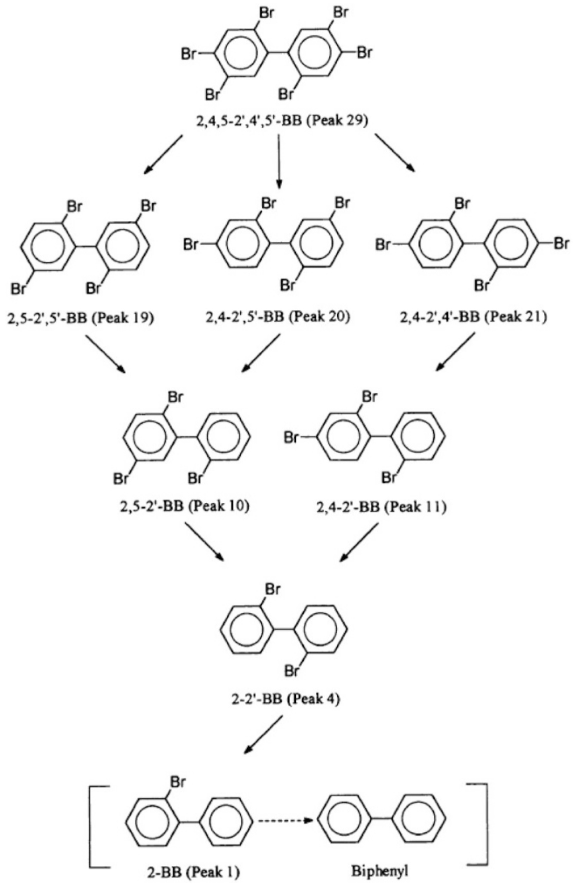


Fig. 6 Proposed pathway for the reductive debromination of 2,4,5-2′,4′,5′-BB in Firemaster by Pine River and Hudson River sediment microorganisms. Debromination of 2,2′-BB was only observed for a pyruvate plus Aroclor 1242 enrichment obtained from Hudson River sediment microorganisms

this process, Pb and Sn along with other metals will form precipitates in the column, not only preventing the recycling of metals but also causing potential blockages of the column. Yang et al. used *A. ferrooxidans* to study the factors affecting the mobilization of copper in the bioleaching process [125]. The higher concentration of Fe^{3+} from 0.64 to 2.13 g/l in the stock solution will bring to the increase of copper leaching in 12 h from 34.53 to 79.75%. As a similar result was observed that copper recovery decreased from 99.06 to 88.40% in 48 h when the pH value increased from 1.5 to 2.0. Therefore, it is noticed that the concentration of Fe^{3+} as well as the pH value have a very obvious effect on copper leaching. Ting et al. used two cyanide-producing bacteria, *Pseudomonas fluorescens* and *Chromobacterium violaceum* to extract gold and copper from WPCB and the recovery rate was around 27 and 20% for gold and copper [126]. In a two-step extraction, the recovery rate for gold and copper was increased to around 30 and 24%, respectively.

However, biometallurgy recycling techniques require a lot of nutrients for microorganism enrichment and metal extraction. The addition of an Fe source is necessary for copper extraction since the solubilization of copper needs the presence of Fe^{3+} according to reaction (1). Also, the ferrous ion is the energy source for *A.*

ferrooxidans, which is an aerobic and autotrophic bacterium according to reaction (2).

$$\mathrm{Cu}^0 + 2\mathrm{Fe}^{3+}_{(\mathrm{aq})} \rightarrow 2\mathrm{Fe}^{2+}_{(\mathrm{aq})} + \mathrm{Cu}^{2+}_{(\mathrm{aq})} \tag{1}$$

$$4\mathrm{Fe}^{2+} + \mathrm{O}_2 + 4\mathrm{H}^+ \rightarrow 4\mathrm{Fe}^{3+} + 2\mathrm{H}_2\mathrm{O} \tag{2}$$

Also, the low extraction rate in high WPCB dosage due to the limitation in air distribution and oxygen mass transfer hinder the application of the biometallurgical treatment method [127]. Moreover, normally microorganisms are vulnerable to heavy metals, thus the growth of them will be inhibited due to the toxicity of metals [128]. Although some bacteria or fungi can adjust to the condition after prolonged adaptation time and achieve a good recovery rate, the time required for this adaption is extremely long (more than a week) [129]. Furthermore, the recovery period for biometallurgical treatment is much longer than pyrometallurgy or hydrometallurgy recycling techniques, which affected the positive evaluation of process. Also, normally the WPCB feedstock needs to be a fine powder with a particle size around 100 μm or even lower to ensure adequate surface contact, which will consume a lot of energy in the early stage [130].

4.2 Summary of partial recovery of metallic fraction from WPCB

From the above-mentioned techniques, partial recovery of the metallic fraction from WPCB processes will benefit metal recovery, which incorporates the most valuable components inside WPCB. The application of partial recovery of metallic fraction from WPCB still exists in many developing countries trapped by the fact of lacking funding. Differences still exist among pyrometallurgy, hydrometallurgy, and biometallurgy in terms of cost, efficiency, harmful effect, as well as the time for recycling as shown in Table 9.

Pyrometallurgy shows the best performance in efficiency and time for recycling since it can significantly remove the non-metallic fraction in WPCB by thermo-decomposition. However, the high energy consumption and construction cost also make it the most expensive technique. Additionally, the toxic emissions and residues generated in the process cause considerable harmful effects to the environment if performed without proper treatment. Compared to pyrometallurgy, hydrometallurgy and biometallurgy have much less environmental impact since the pollution is confined mostly in the liquid phase. Nevertheless, the driving force in hydrometallurgy and biometallurgy is not comparable to pyrometallurgy, thus making them extremely time-consuming techniques although their cost is several times lower than pyrometallurgy. Summarily, the partial recovery of metallic fraction from WPCB by the above methods has obvious drawbacks. It is imperative to develop further full recovery techniques for WPCB to improve the current methods of WPCB recycling.

Table 9 Comparison of different kinds of partial recovery of metallic fraction techniques

Technique	Cost	Efficiency	Harmful effect	Time for recycling
Pyrometallurgy	High	High	High	Short
Hydrometallurgy	Low	Medium	Medium	Medium
Biometallurgy	Medium	Low	Low	Long

4.3 Primitive full recovery from WPCB

Despite diversity possessed by MF recycling techniques, a common drawback shared by them is the absence of NMF treatment, which will give rise to the toxic emission including brominated organic compounds, secondary particulates, and other kinds of pollutants. A simple mass balance concept implies the less recycled, the more emitted. Therefore, techniques focusing not only recycling the MF but also achieving the safe disposal of NMF simultaneously are reviewed next including supercritical fluid extraction, plasma treatment and hydrothermal method [131–133].

Huang et al. used DC arc plasma to treat printed circuit boards, which decomposed the WPCB in molten bath at 1400–1800 °C in a DC arc furnace [131]. The product for this process is homogenous and vitreous slag and small molecular gases including HCl, H_2S, NO_X, and SO_2. Although the safe disposal of solid residue is achieved, it produces a certain amount of air pollution and the energy consumption is huge due to the high temperature and long duration time. Xiu et al. has conducted a series of studies using supercritical fluid including supercritical water (SCW) and supercritical methanol (SCM) to recycle WPCB [134–138]. For the SCM recycling, most kinds of heavy metals are converted to metal oxides with around 100% conversion, except for Mn and Ni, since near 50% of them enters in liquid phase. The copper extracted from WPCB will undergo an eletrokinetic (EK) process and can be synthesized to nanoparticles, which functions as a photocatalyst [139]. The degradation of NMF also happens with the formation of phenol and phenol derivations, which is the main composition of liquid product (~55%). Xing et al. also used SCW to detoxify bromorganic compounds inside WPCB and achieved maximum debromination rate of 97.8% [55, 140]. The bromide was concentrated in water in the form of hydrogen bromide. Also, the bromine-free oil with main components consisting of phenol (58.5%) and 4-(1-methylethyl)-phenol (21.7%) was collected. Moreover, copper was recovered in the purities of near 95% with a recovery rate as high as 98.11%. However, supercritical technologies need high temperature (above 400 °C) and high pressure (higher than 20 MPa). Therefore, the utilization of this process needs a good-quality equipment, which increases the cost significantly. Yin et al. used hydrothermal technology to decompose brominated epoxy resin in WPCB and achieved more than 80% decomposition rate and obtained a liquid with the main composition of phenol, which can be used as a chemical material [141]. Also, after this treatment, WPCB can be used to recover MF with a much lower emission. However, the feature of hydrothermal technology determines that the operation capacity is very limited; in this work, 0.1 g WPCB per batch, which is not applicable for large-scale operations.

Summarily, despite the fact that the previously mentioned technology can recycle MF with the safe disposal of NMF, the energy and effort put into this process is not proportional to the output, which is only the MF. Also, although the safe disposal of NMF will not cause further pollution, a considerable amount of resource inside NMF is wasted after all. Therefore, the separation of MF and NMF and further recycling of NMF is necessary for the consideration of sustainable resource recovery. For this, the effective separation for MF and NMF is indispensable for the purpose of more detailed and efficient recycling.

5 Advanced Recycling Techniques

5.1 Mechanic Separation of MF and NMF

Based on the previous Sects. 1, 2, 3, 4, it can be concluded that a common drawback shared by the primitive recycling technologies is the lack of attention given to the NMF-70% by weight of the WPCB, which fundamentally blocks the recycling or upgrading of NMF due to the loss of mechanical or chemical structure and properties. Therefore, separation of MF and NMF without damage to the structure of NMF is the precondition for NMF recycling and itself is also regarded as one type of recycling since the MF separated from the feedstock can be sold to the market directly. With the development of technologies, the method for MF and NMF separation has changed from manual disassembly to more advanced technologies. Mechanical separation methods take the advantages of the differences in density, magnetism, and electro-conductivity, and have become increasingly important in the recycling of WPCB [27–30]. Since the composition of NMF indicates that most chemical separation techniques will damage the properties of NMF and bring difficulties to further treatment operations, mechanical separations stand out although in some situations they were regarded as assistance processes for pyrometallurgy or hydrometallurgy techniques. Still it is an efficient recycling method which offers great potential, especially with the development of electrical conductivity-based separation [53]. Also, with the development of the automation industry, the mechanical separation also involves automatic or semi-automatic application [11]. These techniques can relieve the situation a lot by separating the MF and NMF of WPCB with a high efficiency and good purity. Therefore, it makes it possible to treat MF and NMF separately and it brings about the selling of high-purity MF to the market and also directing recycling and modification of NMF from WPCB as two potential ways to treat the NMF part of WPCB. Also, the separation of MF and NMF avoid potential interactions of NMF in further treatment stages because the metals in MF can catalyze unwanted side reactions of NMF.

5.2 Density-based Separation

Density-based separation uses the differences of particles size and density to separate the MF and NMF and various equipment items were developed, as shown in Fig. 7 [27]. This method has a long history dating back to the jigging method,

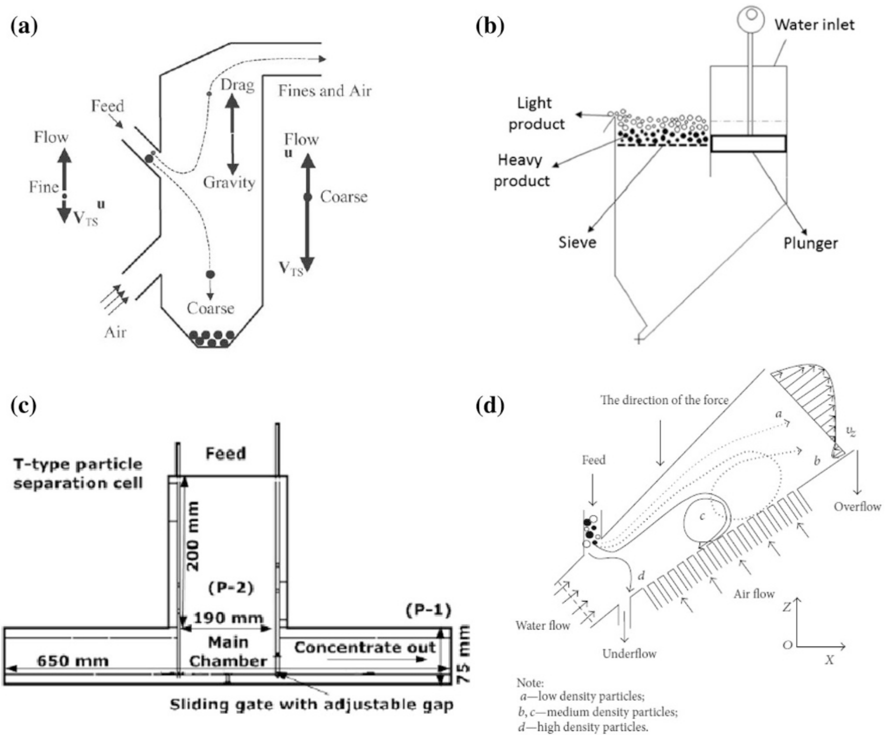


Fig. 7 Schematic illustration of several kinds of density-based separation methods: **a** air classifier, **b** laboratory scale Harz jig, **c** T-type vertical vibration separation cell, and **d** inflatable tapered diameter separation bed

which used a plunger to hit the bottom of the feedstock to give a force to kick the light particles out, thus preserving the heavier ones. Sarvar et al. used wet jigging to separate WPCB feedstock and the recovery rate of metal content for coarse-size, middle-size, and small-size fractions are 95.6, 97.5, and 85%, respectively [142]. However, low grades around 70% were obtained and a significant part of gold is lost at the flotation process. Currently, air classification is a popular method based on the fact that the particles suspended in the gas stream will be separated due to the gravity and drag forces experiencing in opposite directions [28]. The heavier particles will gain larger terminal settling velocity and move towards the bottom of air steam while light particles go to the opposite side, which is the top of the column. Eswaraiah et al. used an air classifier to separate the WPCB and recover 96.7% copper in the sink and 98% plastics and glass fibers in the float [143]. However, there is still 70.94% of other materials in the sink, which makes the purity of copper only 26.77%. Habib et al. [144] also use vertical vibration to separate MF and NMF from WPCB feedstock and they obtained a MF fraction as a combination of Cu (~50%), Fe(~10%), Sn(~10%), Zn(~8%), Pb(~8%), as well as some NMF. Also, the NMF fraction includes 65% NMF and 25% Cu as well as a certain amount of metals. The advantages of density-based separation are the simplicity of its equipment and low energy consumption while the common problem is low product purity, adding workload and difficulty to further refine [145].

5.3 Magnetic-based separation

Magnetic-based separations can achieve the recovery of ferromagnetic metals such as aluminum from non-ferrous metals and other non-magnetic contents with a permanent or electro-magnet. An eddy current separator is a mature technology for magnetic-based separation that can efficiently separate aluminum from non-ferrous contents, as shown in Fig. 8 [29]. When the feedstock passes over the separator, aluminum will be affected by the eddy current generated by the rotation of the magnets inside the shell at high speed, which causes them to be surrounded by a magnetic field. Therefore, the particles will be repelled away from the magnet much further due to the polarity between the two magnetic fields, thus the separation between them and NMF is achieved. Zhang et al. used an eddy current separator to recovery aluminum from electronic scrap and achieved more than 90% aluminum recovery rate with a purity around 85% for a single pass [146]. Yoo et al. used a two-step magnetic separation to recover MF from WPCB and from the first magnetic separation at 700 Gauss, 83% of the nickel and iron was recovered in the magnetic fraction. The second magnetic separation at 3000 Gauss increased the total amount of nickel recovery but caused a drop of the nickel purity from 76 to 56% [58].

However, not all MF can be separated out through eddy current separation because only material with a high σ/ρ can be separated out, where ρ is the density of the material and σ is the electrical conductivity of material. Table 10 shows the materials that can be separated by an eddy current separator, from which it is obvious that aluminum is the most easily separated material while stainless-steel, plastic, and glass have a zero value for the conductivity-to-density ratio, meaning it is not applicable to separate them by an eddy current separator [147].

5.4 Electronic conductivity-based separation

Electronic conductivity-based separation focuses on the difference in the electrical conductivity between MF and NMF, which is normally related to corona

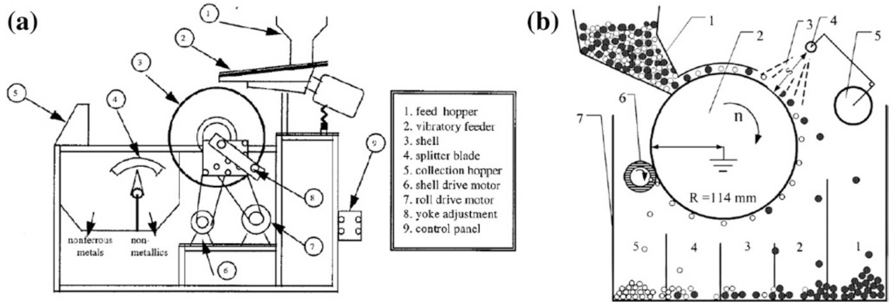


Fig. 8 Schematic illustration of eddy current separator (**a**) and corona electrostatic separator (**b**)

Table 10 Materials that can be separated by an eddy current separator, and their properties

Materials	σ ($10^{-8}/\Omega$m)	ρ (10^3 kg/m^3)	σ/ρ (10^3m$^2/\Omega$kg)
Al	0.35	2.7	13.1
Zn	0.17	7.1	2.4
Ag	0.63	10.5	6
Cu	0.59	8.9	6.6
Brass	0.14	8.5	1.7
Pb	0.05	11.3	0.4

σ electrical conductivity, ρ density, σ/ρ ratio of electrical conductivity to density

electrostatic separation in PCB recycling that fits the condition well, as shown in Fig. 8 [30]. The sample feed in the separator will be bombarded by the high-voltage electrostatic field generated by a corona electrode and electrostatic electrode. Now, the MF will be neutralized quickly as they contact the earthed electrode and leave the rotating roller while the charged NMF are pinned by the electric image force to the rotating roller and move with the rotating roller, finally falling into the holding tanks.

Li et al. used corona electrostatic separation with the pretreatment of pulverization of WPCB feedstock to successfully separate the MF and NMF of WPCB and achieved a high recovery rate (more than 90%) along with high capacity (0.5-1 t/h) with no obvious side effects compared to fluidized bed separation, which has wastewater discharge or air-current separation with a dust-releasing issue [19, 148]. The MF has very high purity and can be sent to a smelting plant directly or with minimal refining. Jiang et al. has designed a new two-roll electrostatic separator that takes advantage of the force of gravity to pass the mixture to the second step for recycling of metals and nonmetals from waste printed circuit board [149]. The production capacity was significantly increased for maximum 50% with 45% reduction of middling products. However, mechanical processes for recycling WPCB normally needs to undergo at least two steps, including coarse crushing and fine pulverizing and especially during fine pulverizing, the temperature will increase up to almost 300 °C [150]. Dust and ash is a common issue for mechanical separation and although it can be avoided by using personnel protective equipments, it still adds to the cost of the process, which makes the economical feasibility of this energy-intensive process even worse. Therefore, an upgrading of NMF to make value-added products is necessary to remedy the expenditure of energy and equipments cost. Also, noble metals will be lost in the crushing process since they will attach on the surface of nonmetallic fraction and cannot be recycled [49].

5.5 Directly Recycling of Nonmetallic Fraction from WPCB

At the beginning, the purpose of recycling of NMF from WPCB is simply to avert the potential hazardous environmental impacts when they end up in landfill or incineration. The composition of NMF is a random combination of epoxy resin and glass fiber. The reuse of NMF is hindered due to understanding of the chemistry of them. Therefore, it is common to be directly used as filler, concrete, and modifier, which means the NMF was used without any forms of modification and is a low value-added material [31–35, 151–154].

Guo et al. has done a series of studies on the feasibility of replacing wood flour in the production of phenolic moulding compound (PMC) using the NMF of WPCB [151, 152]. The addition of NMF can significantly improve the impact strength and heat deflection temperature (HDT) and reduces flexural strength and Raschig fluidity of the phenolic moulding. Notably, the increase of the content of NMF will sharply reduce Raschig fluidity. Therefore, the optimum content for adding NMF is considered to be 20 wt%, in which condition the flexural strength is 70 MPa, the Charpy notched impact strength is 2.4 kJ/m^2, the heat of deflection temperature is 168 °C, the dielectric strength is 3.9 MV/m and a Raschig fluidity of 103 mm. These criteria all meet the national standard. In addition, they did economic analysis, which shows that the addition of NMF can save the cost for the producers of PMC. However, if the cost-saving can cover the energy consumption of corona electrostatic separation is not clear. The authors claim the market price of NMF is for free, which is not correct in the current market. They also study the possibility of producing nonmetallic plate (NMP) from NMF of pulverized WPCBs by hot-press forming with the addition of a resin paste as a bonding agent [31, 32]. The maximum content of NMF in reproduction nonmetallic plate (RNMP) can be as high as 40 wt%. However, the RNMP showed excellent mechanical properties with impact strength of 5.8 kJ/m^2 and flexural strength of 65.1 MPa when NMF added was 20 wt%. Yokoyama and Iji also investigated the use of NMF as filler in the reproduction of resin-type construction materials and the comparison of mechanical properties of these materials with those of reference materials with silica powder was conducted [33]. The NMFs in the materials show reinforcement in mechanical strength and thermal expansion properties of the epoxy resin mold, which has better performance than talc, calcium carbonate, and silica. This is probably because of the compatibility between the NMFs and the epoxy resin matrix, and also the incorporation of glass fiber.

Niu and Li used recycled waste PCBs for cement solidification, which is actually a method to use the waste PCBs as a raw material for concrete [154]. It is proved that the cement solidification can be significantly improved in terms of the compressive strengths (4.89 MPa for slag cement and 7.93 MPa for Portland cement) and the impact resistance of 200 (maximum) of NMF can turn it into strong monoliths. The leaching test shows that the leaching of Pb in the raw material can be effectively prevented (<5 mg/l) even under an acidic environment.

Zheng et al. used NMFs as reinforcing fillers in PP composites [153]. The NMFs are modified by a silane-coupling agent KH-550 and PP powder S1003 is applied as the matrix polymer. NMF and PP powder are pre-mixed and the products are obtained by extruding. The mechanical characterization shows that the ensile strength, tensile modulus, flexural strength, and flexural modulus are significantly improved 28.4, 62.9, 87.8, and 133.0%, respectively, by the adding of NMF. The optimum content of the NMF added is 30 wt% based on technical, environmental, and economical consideration.

However, Lu et al. found that PCB can be liberated effectively with a size between 0.5 and 1.2 mm while for a better recovery ratio the over-pulverized phenomenon is very serious. This limits the further use of the glass fibers that are the support material of PCB (~50 wt%) [155]. The mechanical properties of NMF were sacrificed in order to achieve a high metal recovery rate. Therefore, the direct reuse of NMF is seriously influenced due to this phenomenon. A more advanced technology of NMF modification is indispensable.

5.6 Modification of Nonmetallic Fraction from WPCB

The direct recycling of NMF can help solve the disposal problem of NMF. However, it is still weak for them to compensate for the high operation cost of the MF and NMF separation due to the low value-added products they produced by NMF. With the requirement to better use NMF, which takes more than half of the weight of NMF, the modification of NMF followed by the upgrading was studied by many research groups [156–160].

One thought for the modification is based on the thought that NMF is a carbon source for potential reuse considering the high content of carbon in its composition due to the addition of epoxy resin or other polymers. Normally, the carbon content in NMF is between 30 and 40%, which varies with the source of WPCB [161]. Ke et al. first pyrolyzed the NMF of WPCB in the temperature range 500–800 °C and used physical or chemical activation to obtain activated carbon [156]. Physical activation with H_2O as an activation reagent produced granular activated carbon with a surface area as high as 1019 m^2/g and pore volume 1.1 cm^3/g while chemical activation with KOH as activation regent obtain the same product with higher surface area of 3112 m^2/g and a pore volume of 1.13 cm^3/g.

Rajagopal et al. used the activated carbon prepared by physical activation with CO_2 subsequent to pyrolysis of NMF of WPCB to and apply it in supercapacitor [157]. The NMF activated at 850°C for 5 h shows the highest surface area of 700 m^2/g as well as 0.022 cm^3/g pore volume. Electrochemical characterization of the activated carbon prepared under optimum conditions, shows a specific capacitance of 220 F/g at the current density of 30 mV/s and 156 F/g at the current density of 100 mV/s, which is comparable to activated carbon prepared by other methods. Also, the activated carbon has an energy density of 15.84 Wh/kg at 850 W/kg, which is very high compared to commercially available supercapacitors based on activated carbons that have an energy density ranging from 4 to 5 Wh/kg with power density values of 1 to 2 kW/kg [162]. Moreover, the retention value of the activated carbon was studied to be 98% for over 1000 cycles.

Hadi et al. has developed a thermal-alkaline activation process to functionalize NMF to produce an aluminosilicate adsorbent for heavy metals uptake from waste water [158]. The NMF was mixed with potassium hydroxide solution and activated in 300 °C to develop the porosity of NMF which is a non-porous material. After activation, equilibrium isothermal adsorption tests show that the modified novel material called ANMF had a high uptake capacity for Cu(2.9 mmol/g), Pb(3.4 mmol/g), Zn(2.0 mmol/g), which is much higher than commercial adsorbents used in industry. Xu et al. studied the factors affecting the adsorption capacity including contact time, initial cadmium ion concentration, pH, and adsorbent dosage when this material is used for cadmium uptake [159]. The results showed that pH has an important effect on the uptake capacity for cadmium and the maximum uptake capacity for cadmium is 2.1 mmol/g obtained when $pH = 4$. Modeling of the adsorption was also done in this work and several isothermal equations have been studied while the Redlich–Peterson model shows the best fitting. Moreover, the activation mechanism as well as the optimization of reaction condition was done by Ning et al. [160]. The factors affecting the pore-development process were studied including reaction temperature, impregnation ratio, and reaction time, and the results shows that reaction temperature and impregnation ratio has a significant effect on the structure of ANMF during the reaction while reaction time has no significant effect. This provides a possibility for the porous structure tuning for the NMF of WPCB, which will significantly enlarge the potential applications of NMF as a catalyst, adsorbent, and filter support.

Summarily, the modification of NMF to make value-added products can greatly improve the value of NMF. Thus, the value added to NMF can possibly compensate for the high cost derived from mechanical separation.

6 Perspectives on Recycling Technologies

6.1 Economy Perspective

The economy perspective is always very important, or of first priority for the evaluation and implementation of a recycling technique. The process, which is cost-effective, will have a better chance to be commercialized especially in developing countries due to the lack of sufficient funds for WPCB recycling. Obviously, landfill and incineration has limited economical benefit even without the concern about the treatment of the hazardous substances they emit. The construction and administration costs of landfill sites or incineration plants are large expenses with a scant return. This is also a reason for the reduction in the current application of these two techniques for WPCB treatment. Pyrometallurgy and hydrometallurgy recycling techniques can achieve partial recycling of WPCB by recovery of MF from the feedstock. However, the intensive energy consumption in pyrometallurgy is ascribed for the main expense in the whole process. The energy power in the process is around 0.2–4 kW, varying with the different processes, while sufficient data is not available for these techniques since most works were conducted at the laboratory scale and energy analysis is absent for most of the studies [148]. However, the normal pyrolysis temperatures are from 400 °C to 800 °C, and the post gas treatment equipment normally needs the temperature higher than 1200 °C and no doubt consumes a considerable amount of energy. For hydrometallurgy recycling techniques, the chemical reagents used including cyanide, halide, acid, or other chemicals takes a considerable and indispensable percentage of the cost. Also, in hydrometallurgy, water is used as leaching media and solvent on a large scale, which also contributed to the operation cost.

Furthermore, as the decrease of percentage of noble metal in the WPCB is due to manufacturing upgrading, the driving force for recycling MF from WPCB is decreasing, since previous works focus on the benefit of metal recovery. Recycling of NMF is a potential way to remedy the cost on energy and/or chemical cost. However, the precondition for NMF recycling is the homogenization of the WPCB, which means the pulverization of WPCB feedstock by shredders and hammer mills, which also requires energy and equipment cost. A fine size of NMF (around 0.1 mm) is typical for the recycling of NMF in many studies. While in both pyrometallurgy and hydrometallurgy recycling techniques, the structure of NMF was totally decomposed, the recycling of NMF is therefore not applicable. In some types of mechanical separation, the structure or composition of NMF was preserved with a meager effect on the chemical and mechanical properties. Nevertheless, the direct use is not enough to add adequate value to compensate for the cost required to preserve their structure. Therefore, the upgrading and recycling of the value-added non-metallic fraction are attracting more and more researchers.

6.2 Environmental Perspective

The environmental perspective is another important issue that affects the evaluation of the WPCB recycling techniques. A general rule for emissions is that the more material recycled, the less will be emitted. Therefore, the focus of a technique should not only be on the performance of the recovery rate of specific components like copper or noble metals, but also the fate of the remaining part due to the potential emissions they may have, especially for gaseous emissions. The environmental emissions can be divided into primary pollution, which comes from the WPCB, and secondary pollution, which is emitted during the treatment or recycling process.

For primary pollution, heavy metals including Cu, Pb, Cd are of great concern. They can enter the environment in the form of leachate in landfill or vapor in incineration or some pyrometallurgy recycling techniques without proper purification. It can cause the distortion of the human body as well as various other hazardous effects; the presence of PBDD/Fs and PCDD/Fs is a critical health issue when their presence in the vapor will cause cancer. They mainly form due to the oxidizing atmosphere and the presence of metals as catalyst.

However, the majority of public attention is still paid to the emissions of NOx, SOx, or VOCs, while some kinds of pollutants are ignored due to their relatively low toxicity, like Br and HBr. Yet low toxicity does not equal being environmentally friendly. The vast emissions still cause damage to individual hygiene [19]. Bromide is a hazardous material source with obviously inadequate attention, it is even claimed as harmless in a few studies [5, 15]. Bromide concentration in WPCB is relatively high ($\sim$ 4%) due to the addition of brominated flame retardants [163]. The decomposition of brominated flame retardants happens in the recycling process while bromide still remains in the form of several kinds of bromide or bromorganic compounds including HBr, bromomethane, and bromophenol (Fig. 9). However, research shows that bromide, especially HBr, has a very bad effect on human health, since it can cause health problems and is accumulated in the human body and is difficult to degrade. Therefore, to achieve complete recycling and elimination, emissions are the ultimate objective of the environmental impact of WPCB recycling techniques.

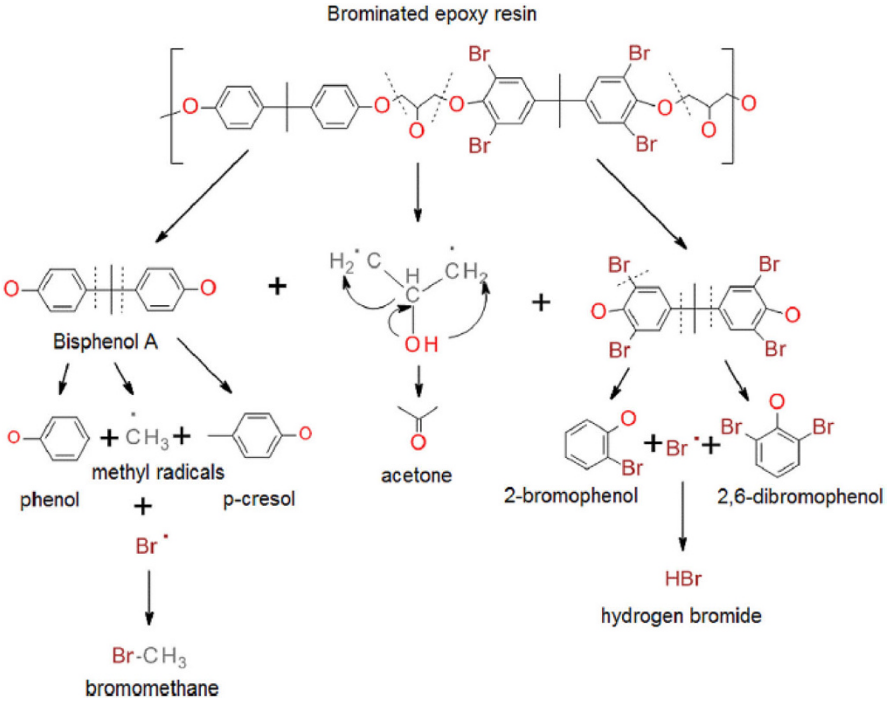


Fig. 9 Possible decomposition pathway of brominated epoxy resin according to the products generated [51]

6.3 Gate-to-Market Ability Perspective

Previously, the evaluation of a recycling technique is always based on economic and environmental perspectives. However, for a real application, it is not a two-sided choice while sometimes a technique is both cost-effective and environmentally friendly and does not mean that this process has high feasibility since the product's status is not well clarified. In previous research, a common mentioned concept is the recovery rate, which means the percentage of materials recovered from feedstock, in weight or volume percentage. Yet with deeper understanding and the real need for resources, the recovery rate is not comprehensive enough to describe the extent of recycling due to the fact that it is not capable of reflecting the required purity of the products, as for some techniques the recovery rate is very high (>90%) while the product purity is particularly low, including several components with concentrations between 20 and 40%. These products are actually incapable of being used or sold to the market directly, which need further separation or refining. However, in the evaluation of the process, the cost and environmental effects are not ascribed to the technique itself but are transferred to the uncertain downstream treatment. Thus, the performance of the technology can be overestimated or underestimated. Therefore, in this work, a new criteria was first raised named "gate-to-market ability", which means the ability of the products to be sold or used in a real industry application

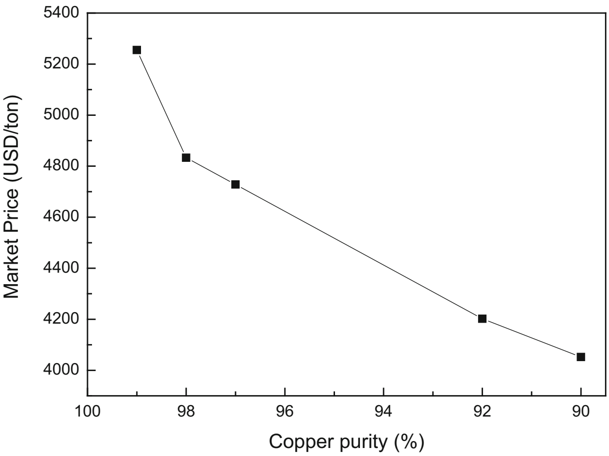


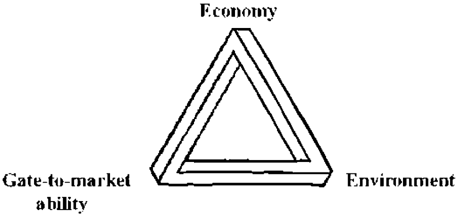
Fig. 10 Market price of copper with different purity (collected on January 21, 2016)

after it has been produced by the technique. It is obvious that the purity of the products will be significantly affected by their gate-to-market ability of them, for some recycling produces even a slightly lower purity will cause them to be discarded.

The market price of copper, a common recycling product of WPCB, is seriously affected by their purity, as shown in Fig. 10 where the prices of copper were collected from several copper markets over the world on January 21, 2016. It can be concluded from the figure that a small decrease in purity (from 99 to 90%) will cause a sharp drop in the unit price of around 22.89% when the purity is decreased. However, the copper recovered from the above-mentioned technology is normally around 70%, except corona electrostatic separation, which means the margin of profit is cut a lot or even not applicable without further refinery. The following process will add both an economic and environmental burden to the techniques. Therefore, gate-to-market ability is a criterion independent of economical and environmental perspective and plays an important role in the evolution of the feasibility of the process.

Normally, hydrometallurgy recycling techniques will give low gate-to-market ability due to the form of products, which are normally alloys. Generally, hydrometallurgy recycling techniques and mechanical separation can provide products with good gate-to-market ability since the products of these processes can

Fig. 11 The relationship for three factors on technology evaluation. This triangle actually does not exist, indicating the impossibility of achieving these three criteria simultaneously



achieve high purity beyond 90%, which reduces the difficulty of further application. Still, co-precipitation in hydrometallurgy will reduce the gate-to-market ability since the product will have several kinds of components inside.

7 Conclusions

WPCB is dangerous waste, but at the same time a rich resource for various kinds of materials. The recycling technologies of WPCB divided into direct treatment (landfill and incineration), primitive recycling technology (pyrometallurgy, hydrometallurgy, biometallurgy and primitive full recovery of NMF), and advanced recycling technology (mechanic separation, directly use and modification of NMF) were studied and analyzed to access their advantages and disadvantages. This review shows that direct treatment has advantages on their simplicity of treatment but the environmental problem is a big issue for them. Primitive recycling techniques achieve a certain extent of recycling, mainly the MF of WPCB. However, the energy consumption as well as the waste gas and water emission still remain a problem for the application of them. Advanced recycling techniques can separate the MF and NMF of WPCB with minimum effects on the environment with a good gate-to-market ability while the energy consumption is huge for them. Therefore, the direct use and modification of NMF was studied to remedy the cost from the energy consumption and become the concern of WPCB recycling.

To summarize, a triangle figure of economy perspective, environmental perspective, and gate-to-market ability perspective can be set as shown in Fig. 11. However, the discussion indicates that the three criteria cannot be satisfied with one simple technique. Therefore, the future research direction of WPCB recycling should focus on the combination of several techniques or in series recycling since the drawback of a process could have a chance to be remedied by one of the techniques and the evaluation should be conducted on the whole process until the products satisfy the market standard.

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REVIEW

Chemical Valorization of Cashew Nut Shell Waste

E. B. Mubofu[1] **· J. E. Mgaya**[1]

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Abstract Cashew nut shells are agro-wastes produced from cashew nut processing factories and contain about 30–35 wt% oil called cashew nut shell liquid (CNSL). This liquid is a mixture of four potential compounds, namely anacardic acid, cardanol, cardol and 2-methyl cardol. Various reactions have been developed to convert the components of cashew nut shell liquid into industrially important chemicals, and these materials are herein described. Such reactions employed in the transformation include transfer hydrogenation reactions, isomerization reactions, metathesis reactions, carbonylation reactions, polymerization reactions, isomerizing metathesis reaction, and isomerizing carbonylation reactions. Through these descriptions, one realizes that cashew nut shells are not a waste, but they are rather a good source of a potential liquid, CNSL, which is a promising renewable resource for synthesizing various industrial chemicals.

Keywords Cashew nut shells · Cashew nut shell liquid · Agro-wastes

1 Introduction

Cashew (*Anacardium occidentale*) is a tree native to Brazil, and it was introduced to other parts of the world in the sixteenth century, mainly with the intention of soil conservation. From its intended purpose to check soil erosion, the crop became a major foreign exchange earner in most countries [1, 2]. It is primarily

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✉ E. B. Mubofu
ebmubofu@udsm.ac.tz; ebmubofu@gmail.com

[1] Chemistry Department, University of Dar es Salaam, P.O. Box 35061, Dar es Salaam, Tanzania

grown on the continents of Asia, Africa and South America. Asian countries mainly include India, Vietnam, Indonesia, Philippines, Malaysia, Thailand and Sri-Lanka. The African countries producing cashew include Côte d'Ivoire, Nigeria, Tanzania, Mozambique, Kenya, Benin, Guinea-Bissau, Mozambique, Ghana, Senegal and Madagascar. Latin American countries producing cashew consist of Brazil, Columbia, Costa Rica, Honduras and El Salvador [2]. Cashew is mainly grown for its nuts, which have a well-established market in the United States and European Union countries with a great variety of uses. The other product, cashew apple, is generally processed and consumed locally.

Global cashew nut (with shells) production has increased every year until 2013, when the production reached 4.44 million tonnes compared to 3.21 million tonnes in 2005 (Fig. 1).

Cashew nuts consist of 35–45% kernels and around 55–65% shells. The cashew nut shells contain about 15–30% dark reddish brown viscous liquid called cashew nut shell liquid, and it is located in the honeycomb structure (Fig. 2).

The cashew kernels (edible nuts) are obtained from the raw nut after removal of the cashew shells. The extraction of the kernels from the nuts is traditionally done by putting the nuts in an open pan over an open fire and stirring continuously to avoid scorching. The roasted nuts are then thrown into sand to extinguish the fire. This makes the shell brittle, less corrosive and easy to break to remove the kernel. On an industrial scale, roasting is done by putting the nuts in a hot oil bath and then heating to 192 °C for about 90 s depending on the size of the nuts. During the roasting process, the cells of the shell break allowing CNSL to flow from the shells into the bath.

Cashew nut shell liquid (CNSL) is a byproduct of cashew nut processing factories with a composition of four unsaturated phenolic compounds namely anacardic acid, cardanol, cardol and traces of 2-methyl cardol (Fig. 3).

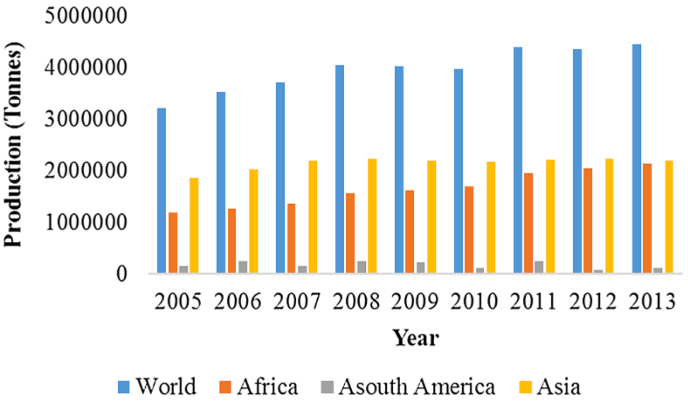


Fig. 1 Production and percentage share of cashew nut (with shells) by major producing regions Faostat 2016

Fig. 2 Picture of cashew nut shells showing a honeycomb structure

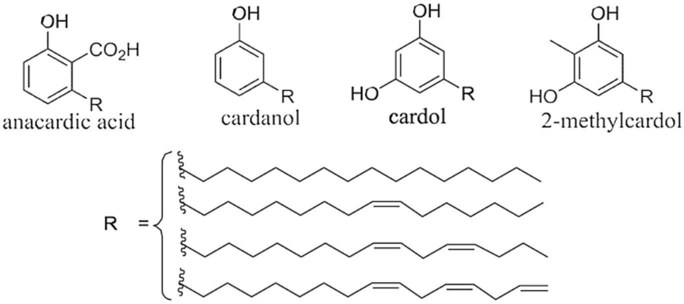


Fig. 3 Components of cashew nut shell liquid

2 Extraction of Cashew Nut Shell Liquid from the Cashew Nut Shells

Generally three methods are available for extraction of CNSL from cashew nut shells. The methods are solvent extraction, thermal extraction and mechanical extraction. The composition of CNSL differs depending on the method of extraction. Natural CNSL, which is extracted by using cold solvents or mechanical extraction contains anacardic acid (60–65%), cardanol (10–15%), cardol (20%) and traces of 2-methylcardol. On the other hand, technical cashew nut shell liquid is extracted by roasting the cashew nuts at higher temperature causing decarboxylation of most anacardic acid to cardanol as a major component (60–65%). Other CNSL components include cardol (15–20%), polymeric materials (10%) and traces of 2-methylcardol [3].

3 Solvent Extraction of CNSL

Solvent extraction is the best method when CNSL rich in anacardic acid is a target and generally yields more CNSL compared to other methods. Solvent extraction can be carried out via various approaches such as static solvent extraction [4], soxhlet extraction [5, 6], ultrasonic extraction, two-step extraction [7], subcritical water (SCW) extraction [7], and supercritical carbon dioxide [8, 9]. Common solvents used in the extraction of CNSL include petroleum ether, carbon tetrachloride, hexane, cyclohexane, diethyl ether, xylene, ethyl acetate, toluene, ethanol, methanol and acetone. Polar solvents have been reported to give high amounts of extracted CNSL than non-polar solvents [10].

4 Thermal Extraction of CNSL

Thermal extraction involves roasting the nuts at 180–185 °C, which breaks the cells of the shell and cause the oil to ooze out of the shell. Thermal extraction can be achieved via open pan roasting, drum roasting and hot oil roasting. These higher temperatures used in the extraction, decarboxylate anacardic acid into cardanol. This makes the thermal extraction approach applicable if cardanol-rich CNSL is the target. The open pan roasting method the oil is removed by charring causing most of CNSL liquid being wasted. This method is generally not suitable considering the difficulty in collecting the oil. The hot oil bath method on the other hand is the most suitable method considering the viability of CNSL collection. In this method, the shells are immersed in a tank containing CNSL at high temperature. The cells of the shell break and lose their oil thereby increasing the volume of the oil in the tank [11, 12].

5 Mechanical Extraction Process

Mechanical method (screw press method) is a straightforward and quick method of extracting CNSL. It involves putting the raw cashew nut shells into a hydraulic screw press followed by exerting high pressure to release CNSL from shells [12]. An extraction experiment using this method was performed elsewhere [11] using a tapered compression screw, feeding rollers of transversal zigzag surface type and cylindrical casing with 2-mm diameter holes. The yield of CNSL extracted was reported to be between 20.65 and 21.04% containing 42% cardol, 47% anacardic acid and 3% Cardanol [13, 14]. One of the setbacks of this method is that the residues remaining after extraction still contained significant proportions of CNSL. Moreover, CNSL obtained via this method had higher levels of impurities and higher viscosity [13].

6 Applications of Cashew Nut Shell Liquid

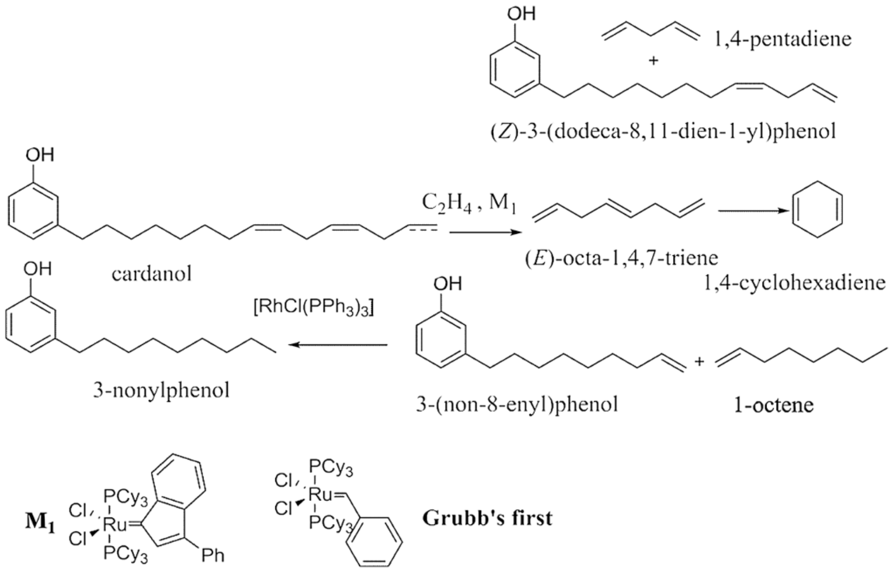
CNSL have found a wide array of applications in various sectors. In the construction sector, CNSL is used for cementing floors to prevent chemical damage. In the laminating industry, CNSL is used to reduce brittleness and improve the flexibility of laminates. In the foundry industry, CNSL is a substitute for linseed oil in the manufacture of foundry core oil used as a binder. In automobiles, CNSL resins are used in brake lining. In the coating sector, CNSL is used in the production of curing agents for special epoxy hardeners and epoxy resins. Other applications of CNSL are as antioxidants, bactericides, fungicides, disinfectants, insecticides, dispersing and emulsifying agents, dye stuffs, ion exchange resins, surfactants, stabilizers, and curing agents.

7 Chemical Transformation of Cashew Nut Shell Liquid

The components of cashew nut shell liquid have functionalities in their structure that present several possibilities of converting it into industrial useful chemicals. The presence of double bond in their structure for instance allows chemical transformations via metathesis [15, 16], carbonylation [17], isomerization [18], ozonolysis [19], and polymerization reactions [20, 21]. In addition, the presence of phenolic group on these compounds allows transformation via esterification [22, 23] reactions, as well as reaction with aldehydes such as formaldehyde [23]. This review attempt to highlight techniques that have been developed in transforming cashew nut shell liquid components into valuable chemicals of diverse industrial interests.

8 Metathesis Reactions of Cardanol

The discovery of well-defined organometallic complex catalysts in olefin metathesis has led to a wide application of the reaction in research and industries for synthesis chemicals of interest. In appreciation to the contribution and the importance of metathesis reaction in organic synthesis, the 2005 Nobel Prize in Chemistry was awarded to the pioneers of olefin metathesis; Yves Chauvin, Robert H. Grubbs, and Richard R. One application where olefin metathesis is highly promising is in the transformation of biomasses such as plant oils into polymers and industrial fine chemicals [24, 25]. Investigations on metathesis reactions of cardanol have shown that industrially useful chemicals such as 1-octene and 3-nonylphenol can be synthesized by the metathesis reaction of cardanol with ethylene (ethenolysis) using the first generation catalysts (Scheme 1) [15]. Immobilized Hoveyda-Grubbs type Zhan catalyst (ZC) and Grubbs second generation catalysts on mesoporous materials have also been reported to be highly active



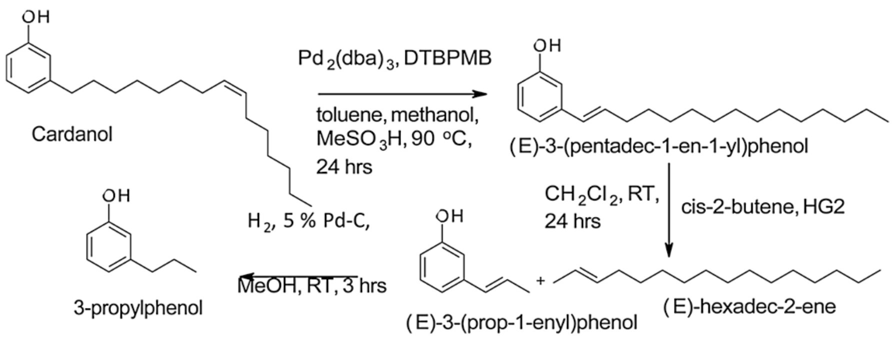
Scheme 1 Catalysed cardanol ethenolysis reaction

and selective in ethenolysis reaction of cardanol achieving TONs up to 2075 [16]. Immobilized catalysts are designed to enhance separation of products and catalysts.

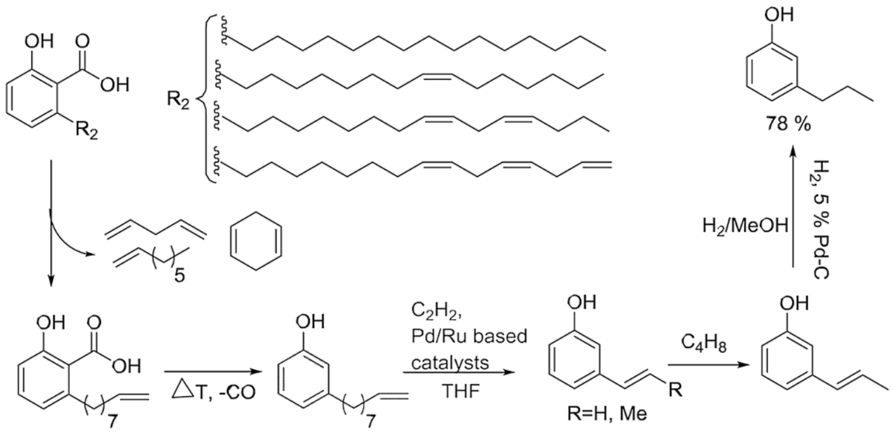
9 Isomerization-Metathesis Reactions

The double bond at the C8 of the 15-carbon alkyl chain of cardanol can be isomerized to either side of the chain using a suitable catalytic system such as Pd/H^+/DTBPMB. The isomerization reaction of cardanol produces double-bond positional isomers with a double bond located at any position in the chain (C1–C15), and the major isomer (40%) is that with the double bond at C1. The double bond of this isomer is a major product because it is stabilized by the conjugation of the benzene ring. Metathesis reaction of this isomer with cis-2-butene using a Hoveyda-Grubbs second-generation catalyst produces (E)-3-(prop-1-en-1-yl) phenol. Hydrogenation reactions of the latter product using 5% Pd/C produces 3-propylphenol (Scheme 2), which is a kairomone component used in tsetse fly traps [26].

Further optimisation on the synthesis of 3-propylphenol from cardanol have been achieved [27] by doing a one pot isomerisation metathesis reaction (Scheme 3). The reaction involves conversion of cardanol mixture (triene, diene and monoene) to 3-(non-8-enyl) phenol (98% purity) via ethenolysis and distillation. This is followed by isomerising cross-metathesis of the 3-(non-8-enyl)phenol with short-chain olefins in the presence of Pd-based isomerisation catalyst ($[Pd(\mu\text{-}Br)(tBu_3P)]_2$) and a Ru-metathesis catalyst (Hoveyda type NHC catalyst) to produce 3-(prop-1-enyl)



Scheme 2 Synthesis of 3-propylphenol from cardanol

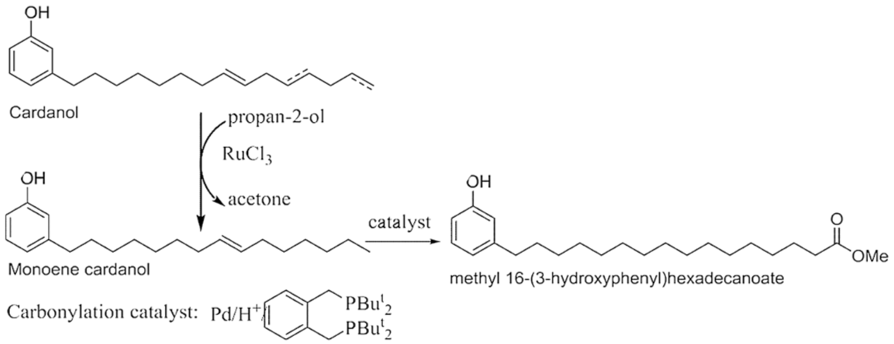


Scheme 3 Synthesis of 3-propylphenol via isomerising-metathesis of 3-(non-8-enyl) phenol

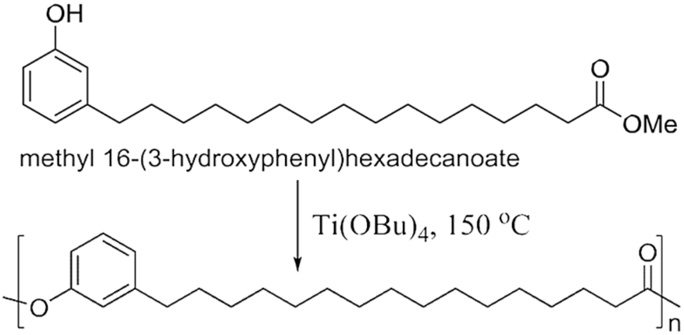
phenol. Hydrogenation of the resulting phenol afford 3-propylphenol in good yield (78%) [27].

10 Isomerising-Carbonylation Reactions

The presence of the double bond in the alkyl chain of anacardic acid and cardanol brings about very interesting isomerization chemistry. These double bonds can be isomerized using appropriate catalytic systems such as Pd/DBPMB/MSA to form the double bond reaching the terminal end can be trapped by carbonylation in the presence of methanol to form an ester function [17]. Carbonylation of the internal double bond leads to formation of a branched ester. However, for bulk ligands such as DTBPMB, only double bonds reaching the terminal part are trapped by carbonylation to form linear esters. Bulk ligands such as DTBPMB enable a selective carbonylation towards linear esters. The catalytic system of Pd/DTBPMB/MSA has been reported to



Scheme 4 Synthesis of methyl 16-(3-hydroxyphenyl)hexadecanoate from cardanol

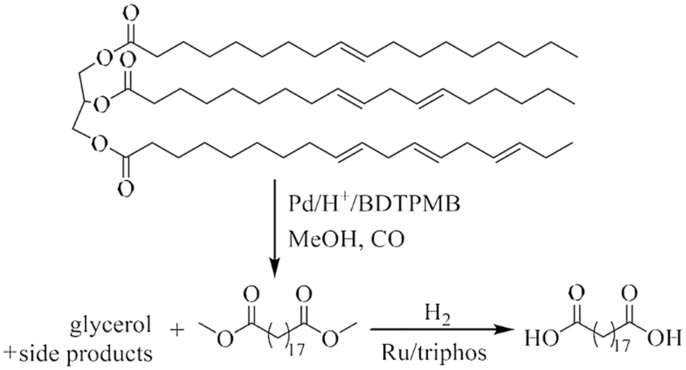


Scheme 5 Polymerisation of methyl 16-(3-hydroxyphenyl)hexadecanoate

be very effective for carbonylation of terminal and internal alkenes to produce linear esters in extremely high selectivity (99%) [28–31]. Similar carbonylation with this catalytic system on cardanol has produced methyl 16-(3-hydroxyphenyl) hexadecanoate (Scheme 4), which is a potential bifunctional monomer for synthesis of fire retardant polymers [17].

The potential advantage of methyl 16-(3-hydroxyphenyl) hexadecanoate synthesized from methoxycarbonylation of cardanol is that it is a bifunctional monomer that can be polymerized without the need of a second monomer (Scheme 5).

For other plant oils, methoxycarbonylation usually produce α-ω diesters which must be reduced to form dialcohols. The diesters are then copolymerized with dialcohols to form polyesters (Scheme 6) with properties more or less similar to polyethylene [28, 29].



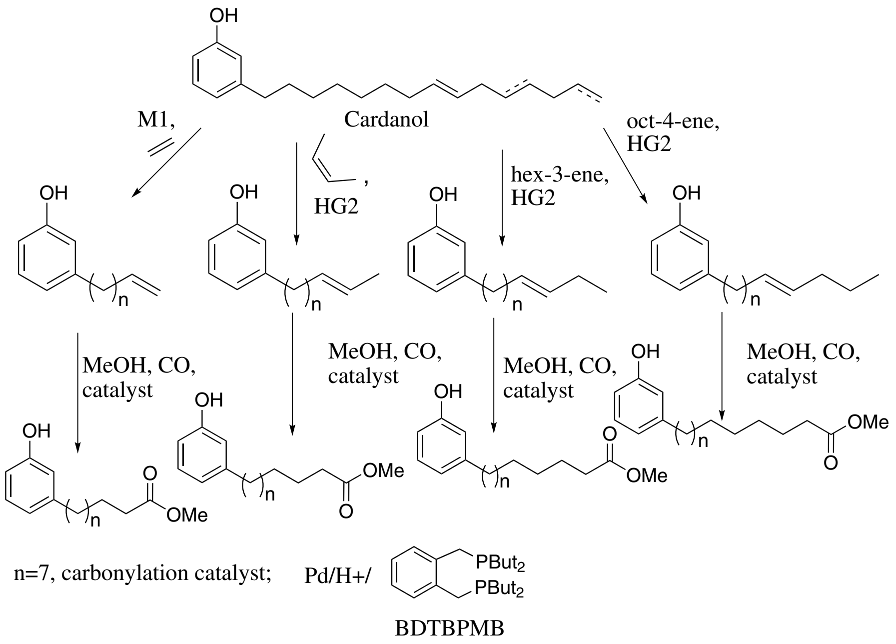
Scheme 6 Methoxycarbonylation of natural oils and the subsequent reduction of diesters

11 Metathesis-Carbonylation Reaction

An application of cardanol derived bifunctional monomers is to make fire retardant polymers. Polymers are organic compounds, thus they burn easily when exposed to intense heat. One way to synthesize intrinsic fire retardant polymers is to incorporate aromatic groups in the polymer backbone. Cardanol derived bifunctional monomers have phenyl group which qualify them for synthesis of fire retardant polymers [32, 33]. This implies that the greater the density of aromatic groups in the polymer backbone, the more heat resistant is the polymer. This can be achieved by shortening the C-15 alkyl chain of cardanol. Metathesis reaction of cardanol with symmetrical alkenes such as ethylene, cis-2-butene, trans-3-hexene and trans-4-octene produces shorter chain alkenylphenols consisting of C-9, C-10, C-11 and C-12, respectively (Scheme 7). Carbonylation of these derivatives produces shorter chain bifunctional monomers [17]. Polymerization of these monomers produce polymers that are intrinsically fire retardants due to their higher density of aromatic groups incorporated in the polymer chain. This is expected because the thermal stability and char yield of polymers containing aromatic groups in their backbone increase with the relative number of aromatic groups in the main chain. The high thermal stability of aromatic based polymers prevents the decomposition of polymers into combustible gases under intense heat, hence prevent the polymer from burning. On the other hand, char formation reduces polymer flammability by acting as a physical barrier to gaseous combustible products. The char has low thermal conductivity and therefore formation of char layer over the exposed surface, acts as thermal insulation to protect the polymer from burning [34].

12 Polymerization Reactions of Cardanol

Cardanol, which is the major component of technical CNSL has been the centre of attraction in the polymerisation reactions for the production of phenolic resins, epoxy resins, vinyl ester resins, phenalkamines and polyols [35–38]. The long

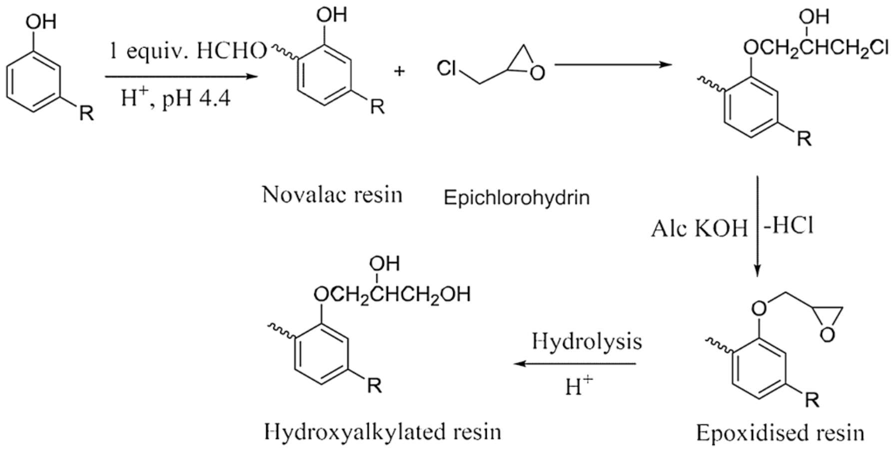


Scheme 7 Synthesis of shorter chain bifunctional monomers from cardanol

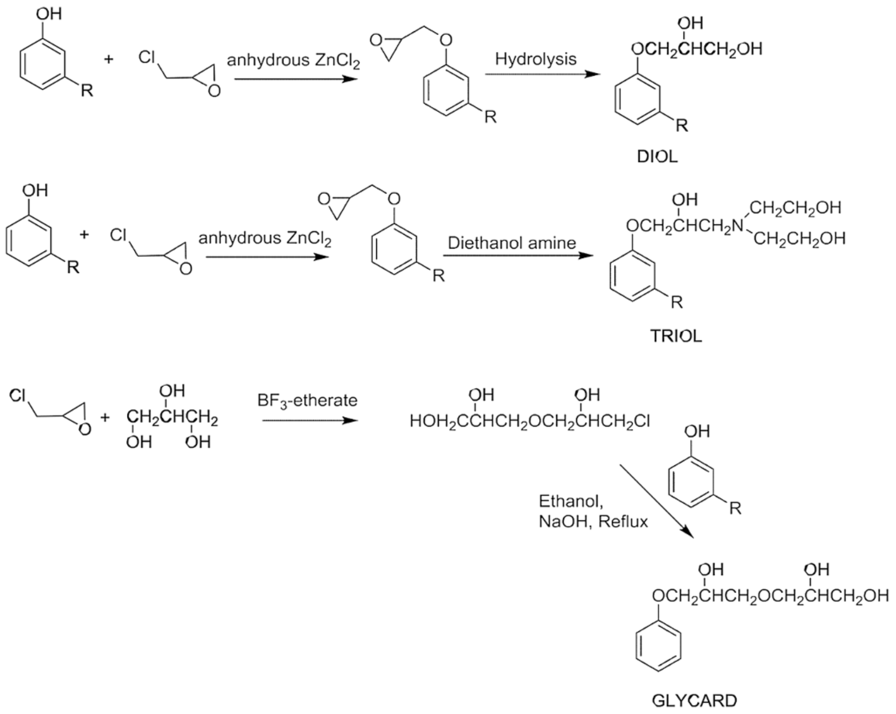
15-carbon alkyl chain in the meta position of the phenolic ring of cardanol offer attractive properties such as good processability and high solubility in organic solvents. Because of the phenolic group in cardanol, most cardanol derived resins are, therefore, fabricated using aldehydes [39–42]. The reaction takes advantage of the phenolic nature by reacting it with aldehydes such as formaldehyde to form phenolic resins. For instance, condensation of cardanol with formaldehyde (1:1 mol ratio) in the presence of sebasic acid catalyst affords a novalac-type phenolic resin. Epoxidation and hydrolysis of this resin, forms polyol, which can be condensed with other commercial polyol such as polypropylene glycol-1200 (PPG-1200) and hexamethylene diisocyanate to make polyurethanes (Scheme 8). More reactions on preparation of polyols from cardanol are summarized in (Scheme 9) [35].

13 Preparation of Chalcogenide Nanoparticles

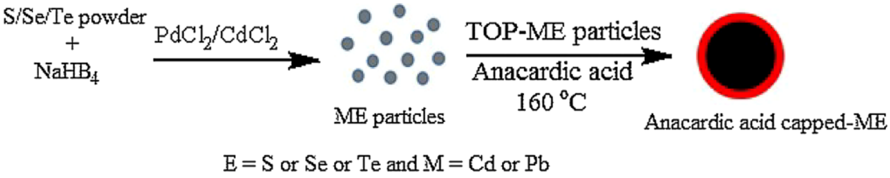
The increase in environmental concerns has forced researchers to focus on green chemistry with great emphasis on the utilization of nontoxic chemicals, environmentally benign solvents and renewable materials. Recently, the field of nanotechnology have started focussing on green renewable chemicals for the generation of inorganic nanostructures and other nanomaterials. Anacardic acid, which is the major component of non-technical cashew nut shell liquid, has proven to be an effective capping agent in the fabrication of nanoarchitectures (Scheme 10) [44]. A recent study by Mubofu et al. [45]



Scheme 8 Formation of the hydroxyalkylated resin using cardanol [43]



Scheme 9 Various routes to synthesis of polyols from cardanol [35]



Scheme 10 Reaction scheme for the synthesis of anacardic acid capped ME nanoparticles [44]

reported the use of cashew nut shell liquid extracts for the synthesis of metal chalcogenides (cadmium and lead sulfide, selenide and telluride) nanoparticles via a solution-based technique. The synthesized metal chalcogenide nanoparticles had well-defined size and morphology comparable to those obtained using other capping agents under similar reaction conditions. The suitability of cashew nut shell liquid and its isolate, anacardic acid, in nanoparticle synthesis is associated with their chemical structures, easy availability, nontoxicity, low cost, non-food competition, high boiling point and high viscosity. Other naturally occurring green chemicals that have been used as capping agents to fabricate nanoparticles are castor oil/ricinoleic acid [46], olive oil [47, 48], and oleic acid. [49].

14 Activated Carbon and Biomass Briquettes

The cashew nut shells remaining after removal of cashew nut shell liquid have the potential to be used in the production of activated carbon and biomass briquettes.

Activated carbon is a form of carbon processed to have small, low-volume pores that increase the surface area available for adsorption or chemical reactions. Historically, activated carbon has been mainly used for removal of unwanted color pigments, removal of odor and for various catalytic functions. However, with the advancement of activated carbon process capability, activated carbon has found more applications in industrial, pharmaceutical, chemical and environmental; for adsorption of unwanted chemicals, to neutralize toxic compounds, food purification, soil enrichment and carrier of chemical catalysts.

Biomass briquette is small block of compressed coal dust or other combustible biomass material such as charcoal, rice husk, bagasse, ground nut shells, municipal solid waste, sawdust, wood chips, peat, or paper used for fuel especially in the developing world, where cooking fuels are not as easily available. The raw materials are compressed into briquette in order to burn longer and make transportation of the goods easier. Cashew nut shells are known to have high energy content which qualifies them as potential raw materials for making biomass briquette.

15 Conclusions

The diversity of chemical transformation techniques available for converting CNSL into useful industrial chemicals has proven that cashew nut shells are important and potential resource. The presence of double bonds and a phenol functionality in the components of cashew nut shell liquid offer unique properties for the derivatization of CNSL components into vital industrial raw materials or finished products. This paper has briefly shown how cashew nut shells can be valorized into CNSL, which in turn can be used as a renewable bio-based resource for the production of several chemicals such as tsetse fly attractants, bifunctional monomers and polymers, 1-octene, 3-nonylphenol and detergents. This diversity of chemicals from CNSL components signifies that CNSL is a potential alternative to petroleum-based starting materials for the production of wide range of industrial materials. The fact that cashew nut shells are obtained as wastes from cashew nut processing factories means they do not compete with food production, hence they are a cheap and environmentally friendly resource of chemicals.

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REVIEW

Valorisation of Biowastes for the Production of Green Materials Using Chemical Methods

Thomas I. J. Dugmore[1] · **James H. Clark**[1] · **Julen Bustamante**[1] · **Joseph A. Houghton**[1] · **Avtar S. Matharu**[1]

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Abstract With crude oil reserves dwindling, the hunt for a sustainable alternative feedstock for fuels and materials for our society continues to expand. The biorefinery concept has enjoyed both a surge in popularity and also vocal opposition to the idea of diverting food-grade land and crops for this purpose. The idea of using the inevitable wastes arising from biomass processing, particularly farming and food production, is, therefore, gaining more attention as the feedstock for the biorefinery. For the three main components of biomass—carbohydrates, lipids, and proteins—there are long-established processes for using some of these by-products. However, the recent advances in chemical technologies are expanding both the feedstocks available for processing and the products that be obtained. Herein, this review presents some of the more recent developments in processing these molecules for green materials, as well as case studies that bring these technologies and materials together into final products for applied usage.

Keywords Green chemistry · Biomass · Waste valorisation · Microwave

1 Introduction

1.1 Global Drivers

Sustainability is a much-used modern day buzzword that encompasses economic, social, and environmental values, i.e. the three pillars of sustainability. Sustainable

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✉ Thomas I. J. Dugmore
tom.dugmore@york.ac.uk

[1] Green Chemistry Centre of Excellence, University of York, York, North Yorkshire YO10 5DD, UK

development is development that meets the needs of the present without compromising the ability of future generations to meet their own needs [1]. However, the last one hundred years has seen global population multiply fourfold to 7.4 billion, global economic output increase more than 20-fold, and global material consumption increase eightfold. To date, about 72 billion metric tonnes (Gt) of materials are being consumed by humanity per annum and this number is projected to reach 100 Gt by 2030 [2].

Because of its abundance, ease of extraction and versatility, crude oil has been the primary feedstock for fuels and materials in modern day society for over a century [3]. Liquid fuels for the automotive industry is the most prolific use of crude oil; in the USA, fuels account for 76% of consumption as of 2014 [4]. However, many other materials are also derived from crude oil, most notably plastics (accounting for 6% of total oil consumption [5]), but pharmaceuticals, lubricants, adhesives, cosmetics, and food additives (and many others) are all typically manufactured from crude oil [6]. The manufacture of many of these products also requires the use of solvents, which are also largely crude-oil derived and account for ~1% of consumption [5, 7]. The outputs of chemical manufacturing are a success story reflected by the vast number articles and goods used in modern-day society that cater for daily well-being and lifestyle.

However, whilst crude oil may be the cornerstone of our established chemical industries it is a finite resource and its continued use represents a major environmental burden. Crude oil typically takes millions of years to form from biomass and migrate to reserves that are easy to tap [8–11], however as of 2013, our consumption is roughly 90,000 barrels per day (14.3 billion litres) [12]. Current estimates of remaining known reserves is between 900 and 1350 billion barrels [13]; although it should be noted that reporting figures do not always distinguish between proven reserves and probable reserves [14] and independent consensus from several reports has advised revising these figures downwards [15–18]. Crude oil consumption exceeded discovery in the late 1970s and on current consumption rates, crude oil is projected to run out approximately between 2080 and 2100 [13, 19]. Additionally, there are rising concerns about the environmental impact of extracting, refining, and using crude oil. Greenhouse gas (GHG) emissions are amongst the primary concerns; if we are to limit global warming to no more than 2 °C by 2020, then over 80% of coal, 50% of gas, and 30% of oil reserves are un-burnable [20]. Additionally the safety of the extraction/refining processes themselves are also of concern due to the environmental impact of oil spills [21]. Furthermore, increasing legislation, in particular REACH (Registration, Evaluation, Authorisation, and Restriction of Chemicals) in the European Union and its counterparts in other parts of world will certain raw materials' availability, supply chains, and businesses [22].

In order to maintain worldwide quality of life and development levels, it is, therefore, imperative to access a clean, sustainable feedstock for our chemicals, materials, and energy. This led to the development of the biorefinery concept, whereby biomass, as opposed to crude oil, is the refinery feedstock and subsequently processed to separate the material into different fractions (such as biogas, sugars, proteins, oils, and cellulosic residues) before further processing into useful, marketable products and energy [23–27].

Whilst this concept enjoyed an initial surge in popularity in the mid-2000s, a number of problems soon arose—most notably in the use of biofuels. As fuel accounts for the largest consumption of crude oil, it is perhaps inevitable that biofuels were one of the first and fastest-developing bio-products to emerge [28–30]. The two most prominent biofuel processes at the time were fermentation to produce bio-ethanol to replace petroleum [25] and transesterification of vegetable oils with methanol to produce fatty acid methyl ester (FAME) biodiesel to replace mineral diesel [25, 28, 30–33].

The biggest problem that arose was the objection to using food-grade crops to produce fuels with malnutrition still being a global issue in what become popularly known as the "food vs. fuel debate" [34]. However, with biodiesel in particular, a number of operational problems with the fuels themselves started to become apparent. Vehicles, in particular, equipped with diesel particulate filters observed reduced engine performance over time due to injector clogging [35–37] and lubricant fouling [37–41] amongst others. This became largely attributed to polyunsaturated fats polymerising at higher temperatures and forming reactive oxygen radicals at moderate temperatures which in turn attacked the engine lubricant [40, 42]. Meanwhile, saturated fats, due to their higher melting points, solidify at temperatures unsuitable to the majority of European and North American environments, particularly during winter [43, 44].

Meanwhile, our current global society is suffering from escalating waste problems, which is becoming increasingly important and alarming in less developed and developing countries such as the BRICS (Brazil, Russia, India, China, and South Africa) and MINT (Mexico, Indonesia, Nigeria, and Turkey) nations, as well as in developed countries. The UN's new sustainable development agenda sets key targets to reduce waste and also to protect natural resources, which are to be achieved by 2030 [45]:

- To manage and use natural resources sustainably and efficiently;
- To halve per capita global food waste at the retail and consumer levels and reduce food losses along production and supply chains, including post-harvest losses;
- To reduce waste generation substantially through prevention, reduction, recycling, and reuse;
- To ensure that people everywhere have the relevant information and awareness for sustainable development and lifestyles in harmony with nature;
- To support developing countries to strengthen their scientific and technological capacity to move towards more sustainable patterns of consumption and production.

To be truly sustainable, a more holistic approach to the biorefinery concept is required. As well as being renewable, an ideal feedstock also needs to be available on the timescales and volumes required for production. The means of processing it to a product should also be environmentally benign where possible, whilst ensuring that the product is still fit for purpose. The end of life of the product, as well as any waste generated during the process also requires attention. The now-famous 12

Principles of Green Chemistry developed by Anastas and Warner [46] in 1998 provided a good set of guidelines of how to produce chemical products and materials in an environmentally benign fashion. However, legislation is also coming in fast in other areas related to supply of feedstocks and handling of waste—most notably REACH (in the case of chemical feedstock for the former [22]) and the Waste Framework Directive (for the latter [47]) in Europe.

1.2 Unavoidable Agri-Supply and Food-Supply Chain Wastes: An Interesting Renewable Resource

The twin problems faced by modern society of unsustainable dependence on non-renewable fossil resources (escalating demand with respect to supply) and escalating waste problems has the potential to be addressed by employing certain unavoidable wastes as raw materials. Unavoidable wastes such as agri- and food-supply chain wastes that arise from primary and secondary processing contain a wide range of highly functional molecules and are therefore prime candidates to be valuable raw materials for biorefineries for the generation of high-value products.[1] Processes using renewable feedstocks are often closer to being carbon neutral compared with those of the conventional petrochemical routes [48, 49].

Even assuming that 100% of arable land is used for food production, the same efficiency is not the case for the crops themselves. Across the entire food and farming industries there are losses from harvest, through processing, all the way to retail, catering, and home consumption. This is in no small part due to inefficiency (spills, storage, etc.), but also nearly every crop has parts that are inedible to humans and therefore subsequently consigned to waste. For filter coffee production for instance, the pulp, and hull of the coffee beans are removed at harvest, during the roasting process the silverskins (or chaff) fall off, and finally, at the point of consumption boiling water is passed over the ground coffee to extract the flavour, leaving the grounds themselves behind as residues [50–52]. Whilst inedible to humans (and in the case of spent coffee grounds, to animals, notably ruminants [53] as well due to the presence of theobromine [50]), many of these residues still contain many functional materials and chemicals. For instance, relating to the food vs. fuel concept, spent coffee grounds also contain good amounts of oil (10–15% [50, 51])—Table 1 compares the oil yield of spent coffee grounds (SCG) to other typical oilseed crops. Several studies have successfully converted this oil to biodiesel which complies with both EN and ASTM standards [54–58] and London, UK, has now seen its first commercial SCG biodiesel plant open in 2014 [59].

However, even after the oil has been extracted, this still leaves the remaining residues behind, which account for >80% of the overall mass. SCGs have also been researched as solid fuels [56, 72, 73], but higher value applications for the solid portion to be researched have included: adsorbents for metal ions [74], capture of dyes [75, 76], and CO_2 [77], extraction of antioxidants [78–83], as a growth medium for edible mushrooms [84] and fungal strains to release phenolic compounds [85].

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[1] High value in this context means additional to economic value created from liquid biofuels (bioenergy) within the context of a biorefinery.

Table 1 Typical oil content of various oilseed crops (wet basis)

Oilseed crop	Typical oil yield (%)
Spent coffee grounds	10–15
Chia	32–38 [60]
Corn	5–15 [61, 62]
Linseed	34–43 [63]
Olive	5–25 [64]
Rapeseed (Canola)	35–50 [65–67]
Soybean	10–20 [68, 69]
Sunflower	25–45 [70, 71]

Whilst, due to their high volumes, agri-residues have attracted a large amount of research interest, it is important to note that they are not the only source of biowastes. Forestry, for instance, also generates large amounts of wastes from tree felling in the form of smaller branches, leaves, needles, etc., which are removed before the larger tree logs are used for wood and paper [86]. Municipal maintenance and gardening also generate waste biomass in the form of pruning, grass cuttings, and hedge trimmings—generally considered (alongside household waste) as municipal solid waste (MSW) (sometimes termed organic fraction municipal solid waste, OFMSW) [87, 88]. Whilst composition varies, biomass still comprises largely the same types of major molecules (proteins, carbohydrates, and lipids) with lesser amounts of speciality molecules.

Both established and emerging global economies view waste as a bioresource for our next generation energy, chemicals, or platform molecules and materials, lessening the burden on crude oil, as of strategic importance. (Bio)waste as a resource has been recognised of national importance by the UK government following their 2015 report, “Building a high value bioeconomy: opportunities from waste” [89] as a result of the House of Lords Science and Technology Committee report, “Waste or resource? Stimulating a bioeconomy” [90] published a year earlier, both evoking the need for a UK bioeconomy for future sustainable development. The reports highlight a significant market for renewable chemicals, already estimated to be $57 billion worldwide and forecast to rise to $83 billion by 2018. Similarly, the United States Department of Agriculture (USDA) BioPreferred program reports that a bio-based economy contributes a total of $369 billion to the U.S. economy each year, while four million jobs were supported, directly and indirectly, by the bio-based economy [91]. Small and medium enterprises (SMEs) are an important driver for new growth as the EU bioeconomy (not restricted to waste feedstocks) has a turnover of about €2 trillion, employs around 22 million people, mainly in rural areas and often SMEs, and represents 9% of total employment in the EU. Each euro invested in EU-funded bioeconomy research and innovation is estimated to enable €10 of value added in bioeconomy sectors by 2025 [92].

Biorefineries will emerge alongside new infrastructure technologies. Some biorefineries will be standalone, others integrated with traditional petro-refineries, for maximum resource re-use. The best biorefineries will be those that are feedstock flexible, thus functioning all year round. New process intensification methodologies will need to developed in order to maximise resource and reduce waste as chemical manufacturing "does more and better with less". Unavoidable food supply chain waste (UFSCW) represents an interesting "waste as a resource" option due to its high volume, chemical richness, and heterogeneity.

1.3 High Value Applications

Whilst food vs. fuel dominated the early biofuels debate, it is important to note that the biorefinery concept extends far beyond fuels, both in terms of products to be produced, as well use of the entire feedstock. Examples of research beyond fuels into the solid portion of spent coffee grounds have already been given, but it is important to note that in the context of the biorefinery, for example, production of adsorbents for metal ions should be in addition to oil extraction. As with the petroleum industry, the feedstock should be processed to produce a range of products rather than honed in on one single product. As crude oil is the core feedstock for a range of materials besides just fuels, it is important that in order to succeed the oil refinery, the biorefinery should achieve the same goals. In fact, fuels from biomass should arguably be a last resort for two reasons.

The first is the concern about GHG emissions. Whilst biomass is renewable, as it is carbonaceous, burning it for energy still emits CO_2 as part of the combustion process. As plants continually take in CO_2 to produce energy and materials, the carbon emissions offset far more than for fossil fuels and are sometimes viewed as "theoretically" carbon neutral. However, once the full life cycle is taken into account beyond simply the carbon of the plant to include farming equipment, pesticides, conversion to fuel, etc., burning of biofuels still contributes a net increase in carbon emissions and can even be higher if, for instance, forests are cleared to grow biofuel crops [93–95].

The second is about efficient use of feedstocks. There exist a number of alternative ways to generate renewable energy such as solar, wind and hydroelectric. However, these sources cannot directly generate the carbon building blocks necessary to build the materials and products needed by society. As synthetic chemistry (whether for a single, pure product, polymer, or composite) essentially involves taking smaller, simple molecules and assembling them into larger, more complex ones, it is seen as wasteful to take biomass, which is already full of large, complex molecules and then burn it to reduce it back down to CO_2—one of the simplest carbon-containing molecules. We should look to use the inherent structure and functionality provided by nature's biopolymers and chemicals of life rather than trying re-synthesise from petroleum-based building blocks. Hence, making innovative use of currently low-value, underutilised biorenewable waste streams, especially unavoidable losses resulting from industrial practices (e.g. manufacturing, recycling) for the production of bio-derived chemicals, fuels, and other value-added functional materials is particularly important and attractive. Such waste valorisation practices also represent an imperative grand research challenge and a promising topic globally from both an environmental and economic point of view.

Herein, this review explores the major components of unavoidable terrestrial waste biomass, namely agri- and food waste. The first part will describe some of the advances in chemical technologies that allow processing of these components into higher value application materials. Secondly, some case studies where several aspects of these technologies are being brought together to help realise a “true” biorefinery where no part of the feedstock is lost to waste will be covered. Since polymers are the second largest product market after fuel, a significant amount of the materials and applications covered will fall into this category. This is to be a generic overview of some of the main processing means developed in the last few years and not intended to be exhaustive.

2 Carbohydrates

Of the three main biomass building blocks, carbohydrates are the most hydrophilic; as they are essentially hydrates of carbon, carbohydrates possess a hydroxyl group on every carbon atom to provide a high degree of polarity and hydrogen bonding. In biomass, carbohydrates mainly fall into two categories—simple sugars (monosaccharides) and dimers or polymers of those sugars (polysaccharides) with the remainder being derivatives of these. Of the simple sugars, the most abundant is glucose, which exists in two forms, α- and β-glucose, (structures shown in Fig. 1) with the only difference being the hydroxyl group at the $1'$ position being either axial or equatorial. As glucose possesses six carbon atoms, it is classed as a hexose; the remaining hexose sugars are all analogous to glucose, again differentiated by the hydroxyl groups at the other positions being axial or equatorial. Other than hexose sugars, there are also pentose sugars which consist of five membered rings rather than six membered rings, again with the position of the hydroxyl groups determining the isomers [96].

2.1 Sugars

Since the simple sugars are so similar in structure, processing them using many “broad-brush” techniques is relatively easy. As sugars are also a primary energy source for many non-photosynthetic cells, fermentation to ethanol (for fuel or alcoholic beverages) has long been a means of converting sugars to other products [97–99]. As the process of fermentation involves the production of several intermediates [100], as do many other metabolic processes, many recent advances in sugar valorisation utilised fermentation to other target molecules, particularly platform molecules—those identified as being a set of basic chemical building blocks for synthesis into a wider range of molecules. Notable ones include lactic acid [101, 102], succinic acid, and levulinic acid [103]—structures shown in Fig. 2—although more will be covered throughout this review.

Lactic acid production via fermentation is an extremely well-known process, which was reported by Luedeking and Piret as early as 1959 using glucose as a feedstock and *Lactobacillus* bacteria [104]. Since then, through a combination of selective breeding of bacteria and enhancements of work-up and isolation

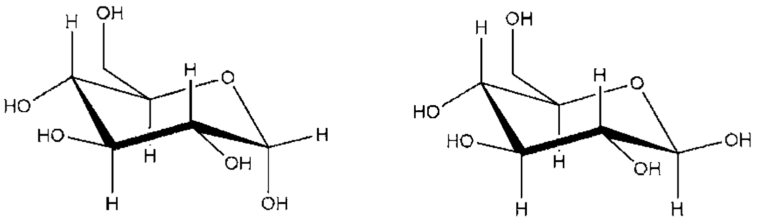


Fig. 1 α- and β-glucose, the most abundant sugars

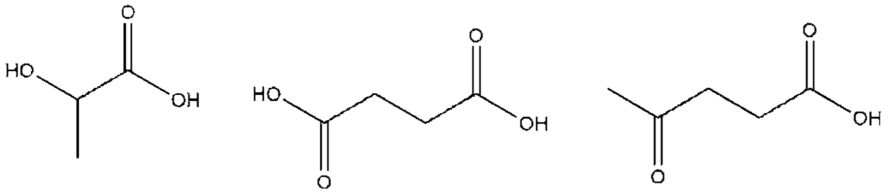


Fig. 2 From *left* to *right*: lactic acid, succinic acid, levulinic acid

techniques, the process has advanced considerably; a particular high point coming in 1996 with Linko and Javanainen reporting a yield of 98% from glucose using *Lactobacillus*—although several purification steps were still required to isolate the lactic acid from the broth [105]. As it possesses both an acid and alcohol moiety, lactic acid polymerises into polylactic acid (PLA) with relative ease. Polylactic acid is a well-established bio-based polymer, which is favoured for its biodegradability and compostability. It can, therefore, be used in many packaging and coating applications where biodegradability is desired, but is unsuitable for others—notably food packaging—due to its permeability and biocompatibility [106].

Succinic acid and levulinic acid are relatively more recent developments in the field (though receiving an increasing amount of attention). Originally, production of succinic acid (traditionally known as "spirit of amber") was via the distillation of amber; it is also petrochemically produced from butane. It was identified by Zeikus in 1999 [107] for its potential to be produced from fermentation, albeit with low yields of around 45 g/L unless using specific bacteria from the *Succinogenes* species. It was identified in 2004 by the USDA as "one of the renewable building block chemicals with the greatest technical feasibility and commercial potential" [108], and the last few years has seen a surge in publications on its production. Levulinic acid was also mentioned as one of the 12 key platform molecules in the same report—it is traditionally produced from heating sugars in the presence of dilute acid [109]. Levulinic acid, therefore, has the longest history of bio-derivation, the key green chemistry driver for a switch to enzymatic production, in this instance to remove the mineral acid waste stream left over; to this end acidic ionic liquids have also been investigated [110].

Succinic acid is a popular choice as a platform molecule as just a few chemical steps allows conversion into a range of different molecules; Fig. 3 provides a (non-exhaustive selection). These include:

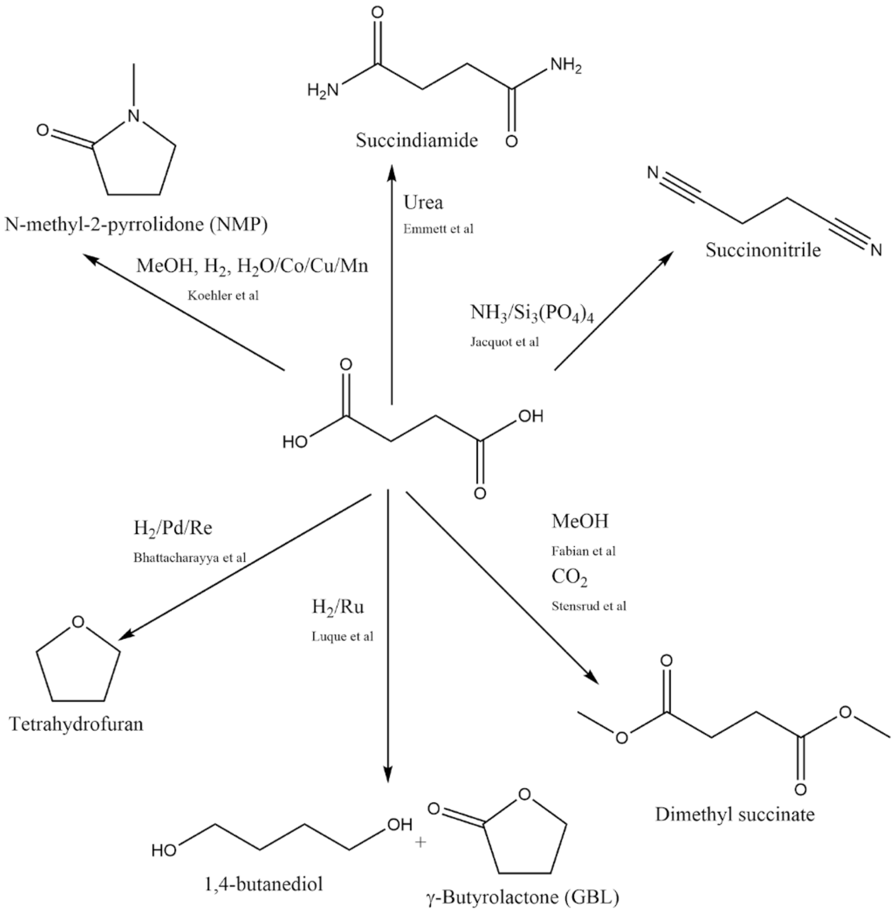


Fig. 3 The chemical structure of succinic acid and a selection of conversions that can be performed on it [112–121]

- Common manufacturing solvents, such as tetrahydrofuran and *N*-methyl pyrrolidone (NMP), although the latter is becoming strongly discouraged through REACH);
- Succinonitrile, a widely used electrolyte for Li-ion batteries (commonly produced by reacting toxic hydrogen cyanide with acrylonitrile [111]);
- Monomers for plastic production, such as 1,4-butanediol and succindiamide—although it is a di-acid, succinic acid itself is a monomer for polymer production.

As a di-acid, polyesters are one of the most prominent polymer classes to which SA can be a monomer. In addition to SA, there are a many other di-acids that can be produced through fermentation including malic acid, maleic acid, and itaconic acid (structures shown in Fig. 4)—all of which can be converted to the subsequent diols.

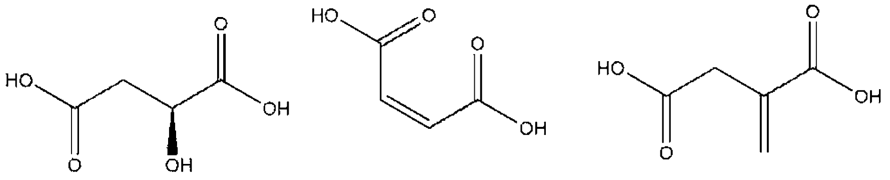


Fig. 4 From *left* to *right*: malic acid, maleic acid, and itaconic acid

Many of these molecules can be and are produced from petrochemical feedstocks (e.g. SA is produced by oxidation of butanediol, which is in turn produced by reacting ethyne with formaldehyde); therefore, in addition to bio-derivation, one of the advantages of using these platform molecules is that it avoids the use of toxic or otherwise harmful oxidation agents. Polyesters from combinations of these platform molecules have been successfully achieved in a number of studies using standard poly-esterification methods, such as with Ti(IV) tetra-*tert*-butoxide as a catalytic initiator [122] and through Michael additions using 1,3-dicarbonyls to produce a more complex branched network [123]. The resulting resins have had a range of properties reported, e.g. polydispersities from 2.8 to 85, molecular weight distribution from 8300 to 350,000 Da and glass transition temperatures from −51.2 to 135.4 °C—all of which further increased with Michael additions. Whilst the range of properties is promising, the authors did note two unwanted side reactions—isomerisation of itaconate units and saturation of C=C bonds—highlighting a need for good control measures in scale-up.

Whilst not typically produced chemically, polyhydroxyalkanoates (PHAs) are another class of linear polyesters worthy of mention—ones where the alcohol and acid moiety are on the same molecule. Many bacteria produce them as a means of carbon/energy storage from sugars and lipids. As previously noted, there are a wide range of different monomers, which can be produced from sugar fermentation there is similarly a wide range of polymers and resulting properties, which can be produced [124]. One of the most common is poly-(*R*)-3-hydroxybutyrate (P3HB), which typically employs glycerol as a feedstock; therefore, the lipids section will cover this in more detail.

One issue with the use of sugars for production of platform molecules is obtaining them from the respective biowastes. Solubilisation and extraction methodologies to extract sugars from complex matrices, such as pressing, ultrafiltration, and hot acid extraction have all been trialled [125, 126], but increasingly, free sugars in mixtures have also been studied for direct fermentation. Table 2 presents a range of substrates, bacteria, and yields of succinic acid and lactic acid reported from various studies. The results show many high (>70%) yields, indicating the potential for such a biorefinery concept to be adaptable to many different types of biowastes. It is worth noting that whilst lactic acid yields are notably generally superior to those from succinic acid, this is partly attributed to the fact that lactic acid fermentation is a much more established technology than succinic acid fermentation; however, using mixed waste feedstocks is still a comparatively recent development in the field. This suggests that as technology

Table 2 A summary of some of the lactic acid and succinic acid yields from various food waste feedstocks

Feedstock	Bacteria	Yield (g/g)	Authors
Lactic acid			
Jackfruit seeds	*Streptococcus equinus*	0.62	Nair et al. [127]
Corn stover	*Lactobacillus pentosus* FL0421	0.66	Hu et al. [128]
Hydrolysed bakery waste	*Thermoanaerobacterium aotearoense LA1002-G40*	0.89	Yang et al. [129]
Sweet sorghum juice	*Bacillus coagulans*	0.92	Wang et al. [130]
Bakery waste	*Lactobacillus casei*	0.94	Kwan et al. [131]
Mixed food waste	*Lactobacillus casei*	0.94	Kwan et al. [131]
Succinic acid			
Cake	*Actinobacillus succinogenes*	0.25	Zhang et al. [132]
Pastry	*Actinobacillus succinogenes*	0.32	Zhang et al. [132]
Bread	*Actinobacillus succinogenes*	0.47	Zhang et al. [132]
Cane molasses	*Actinobacillus succinogenes*	0.55	Liu et al. [133]
Wood hydrolysate	*Mannheimia succiniciproducens MBEL55E*	0.56	Kim et al. [134]
Corn stalk	*Actinobacillus succinogenes*	0.66	Li et al. [135]
Cotton stalk	*Actinobacillus succinogenes*	1.23	Li et al. [135]

increases, or more efficient bacterial strains evolve, there is still very good scope for yields of succinic acid to increase over the next few years.

2.2 Starch

In addition to simple sugars, carbohydrates consist of a wide range of more complex polysaccharide molecules, with starch and cellulose the two most common. The main component of starch is simply long, linear chains of α-glucose polymerised through the 1 and 4 carbons—see Fig. 5.

There are several noted starch-rich food wastes. For instance, roughly 19% of the weight of a potato is starch [136]. Current global production of potatoes reached 360 million tonnes in 2013, with the UK alone producing 5.5 million tonnes [137].

Starch has been used for decades as a thickening agent, primarily for cooking, but also to produce gels for adhesion purposes. Most modern starch-based adhesives require some means of chemical modification (typically acid- or alkali- based) prior to their use, but have still generally been restricted by water-stability or inadequate mechanical properties for advanced applications. A more recent development by White et al. investigated the use of controlled thermolysis to achieve modification [138]. They used corn starch in water and heated above 100 °C under pressure (both thermal and microwave heating methods were used) to maintain water in its liquid form, also known as superheated or super-critical water [139]. Superheated water has lower polarity compared to liquid water under standard conditions and higher diffusivity; the effect on the starch is to cause the structure to swell, producing a highly porous network. Cooling the gel then "locks" the expanded network in place.

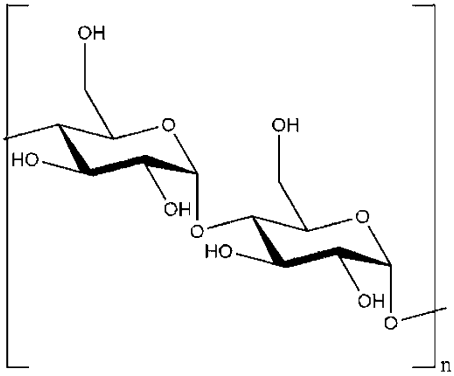


Fig. 5 The generic chemical structure for starch

The water is then "flushed out of" the matrix via solvent exchange in order to prevent collapse of the network. Acetylating the expanded starch gel with acetic or propionic anhydride then produces the final adhesive. This material is of interest as it expands the range of surfaces, notably metals, that can be bound using starch based adhesives [140]. However, the key property that differentiates this material from other adhesives is that is only exhibits adhesive properties within a certain temperature range, varying according to the binding surfaces [141]. This allows for selective bonding and de-bonding, therefore, enabling recycling at the end-of-life of the product. This has successfully been achieved in the production of carpet tiles [142]. At present, carpet tile production occurs by irreversibly binding the fabric layer to a bitumen base, leaving no option, but landfill at the end of life. By de-bonding via heating, the base is recovered for re-use with a different material, whilst the fibres can be recycled. This, therefore, represents a significant development for the production of green materials as it uses a renewable resource (starch), which is available in many waste streams from food production, prepares it without the use of harsh acids or alkalis, and enables the final product to be recyclable. Additionally, as starch is non-flammable, the resulting adhesive can produce the tiles without the addition of brominated flame-retardants that are required for many petroleum-based adhesives.

Another notable development for valorising starch has been the production of Starbon® materials—mesoporous carbonaceous materials derived originally from starch, but now from a variety of polysaccharides. This process, developed by Budarin et al. [143–145], involves heating starch in water under pressure, in the same manner as producing the initial expanded starch gel for switchable adhesives. The material is then doped with a catalytic amount of organic acid (e.g. *p*-toluene sulfonic acid) and then pyrolysed under controlled heating conditions (again to prevent collapse of the network) to 300–800 °C depending on the desired properties. The higher the temperature, the more hydrophobic the surface properties [146–150]. This process has also been shown to work on alginic acid—another polysaccharide material obtained from seaweed.

These materials are finding use as replacements for activated carbons (AC)—carbon allotropes modified to provide high surface areas. ACs are widely used in applications such as water purification, filtration, flue gas scrubbing, and catalytic supports. Budarin et al. estimated that the current market for them is almost 1 Mt per year [144]. Because of the high porosity, particularly mesoporosity (2–50 nm pores [151]) generated through the gelation process, these new materials have frequently shown superior properties as adsorbents compared to their AC counterparts—a trait largely attributed to allowing adsorbates easier access to the inner micropores for adsorption. The model that increased surface area on activated carbon allows for greater adsorption to the surface is well established, but Hsieh et al. questioned how much of the surface area was actually available for adsorption. i.e. the increase in surface area was not worthwhile if it simply involved making up micropores too small for adsorbants to fit in, particularly for larger molecules. From subsequent Langmuir and Dubinin–Radushkevich modelling they suggested that increased mesoporosity would allow for increased diffusion throughout the material to access more of the AC surface [152].

For instance, Parker et al. tested the adsorption capacity of Starbons® on a range of phenols [153]. S800 (starch derived and pyrolysed to 800 °C) with a surface area of 535 m^2/g was shown to have an adsorption capacity for phenol of 87 mg/g. This compares to 37 mg/g with a coconut coir pith AC with surface area of 470 m^2/g [154] representing a 2.35× increase in capacity with just a 1.13× increase in surface area. Apricot stone AC was shown to have a better adsorption capacity of 120 mg/g [155], but this required a surface area of 1306 m^2/g; an improvement of just 1.38x despite a 2.44× increase in surface area. A800 (alginic acid derived and pyrolysed to 800 °C) performed even better, demonstrating an adsorption capacity of 89 mg/g despite a surface area of just 265 m^2/g.

In a similar study, Garcia et al. tested the ability of Starbons® to adsorb metal ions. Au, Pd, Pt, Ir, Ni, Cu, and Zn were all tested and successfully adsorbed by S800, with partial success in the adsorption of Au—an adsorption capacity of >3000 mg/g was reported compared to just 62–100 mg/g on AC [155]. Adsorption for the other metals were similar to AC results; however, in another crucial observation, both Parker and Garcia were able then to desorb the selected phenol and metal species, presenting the opportunity not just to remediate wastewater, but also to recover materials of interest. The recovery of the platinum group metals is of particular relevance due to their scarcity in the earth's crust coupled with their increasing demand [156, 157]. A recent (2016) case study has been carried out by Tony et al. using Starbons to treat wastewater from commercial laundrettes [158].

The catalytic properties of these materials has also been successfully demonstrated. Because of their high adsorption capacity for metals, several studies exist using metal-based Starbon® catalysts. For instance Luque et al. have reported the successful use of supported metal nanoparticles on Starbon® for Rh, Ru, Pt, and Pd and their subsequent use in catalysing the hydrogenation of succinic acid and other platform molecules [114]. The team were able to achieve selectivity and conversions to their intended products of over 70% in less than 12 h with ruthenium being particularly effective—optimising reaction conditions led to over 90% selectivity and conversion for a range of organic acids [113]. Furthermore, they were able to tune their reaction conditions to achieve different target molecules. Other metal-centred catalytic studies have included Colmenares et al. work comparing the photocatalytic activity of TiO_2 on Starbon against other AC materials. Over a threefold increase in the rate constants was reported in all instances [159]. Ojeda et al. have also reported their ability to produce Fe, Co, and Cu containing Starbon® matrices via a similar method, though at the time of writing they have yet to test their activity on any reactions [160].

Several studies also demonstrate Starbons® to be effective as solid acid catalysts. Many chemical transformations such as esterifications, hydrolysis, and hydration of alkenes rely on the addition of a catalytic amount of acid, usually sulfuric acid. After removal of the solvent, the added acid remains in solution and thus generates large amounts of acidic waste. Binding the sulphate group to an insoluble support (such as AC) allows the catalyst to be then filtered off and recovered after the reaction, thereby both enabling recycling and preventing the generation of harmful waste. After developing the materials, one of the first applications demonstrated by Budarin et al. was for sulphonated solid acid catalysis on esterifying succinic acid and ethanol. The Starbon®-based materials showed nearly a tenfold improvement on reaction rates compared to other solid acid catalysts and a twofold improvement over aqueous sulphuric acid [161, 162]. Other platform molecules such as itaconic acid and fumaric acid have demonstrated similar trends [163–165]. The material is also proving successful on other acid-catalysed transformations including alkylation and acetylation [166] and even for complex substrates such as the Ritter reaction [167]. It is unclear at present why the increased porosity improves catalytic performance, though a likely explanation is that it is to similar reasons for the adsorption properties; increased pore volume leads to more exposed acidic sites.

Whilst in early phases, the material has also been trialled as a stationary phase for HPLC where it successfully separated a mixture of carbohydrates [168].

2.3 Cellulose

Cellulose, in a similar fashion to starch, is linked through β-glucose units at the 1 and 4 positions (see Fig. 6). Whilst the only difference between α- and β-glucose is that the hydroxyl group on the 1′ position isbeing axial and equatorial, respectively, this difference is key to very different resulting properties as it dramatically alters the bond angle between the two monomers and, by extension, the whole superstructure of the resulting polymer (as illustrated in Figs. 5, 6). Unlike starch, cellulose is insoluble in water, indigestible in many animals (including humans),

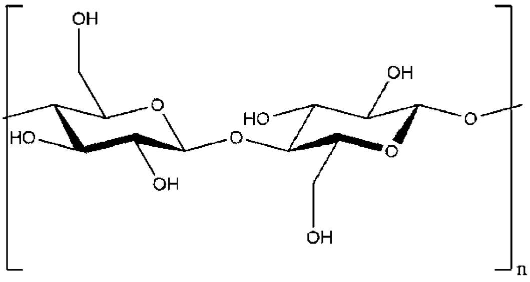


Fig. 6 The generic chemical structure of cellulose

and much more resistant to breakdown. For this reason, cellulose is a structural material in plants, rather than an energy store. Because it makes up the cell walls for the majority of plant cells, it is also the most abundant biopolymer on Earth.

Cellulose itself has a long history of applications in materials production, most notably as the raw material for paper and cardboard, as well as other materials such as cellophane and rayon. Since it is such a strong polymer, cellulose is very hard to break down without respective enzymes, which on one hand makes washing and recycling of the material relatively easy compared to some materials, but on the other can make it hard to process into other materials once recycling is no longer an option. In paper recycling for instance, the fibres get shortened in each recycling step, meaning after 5–6 stages the fibres are too short to be recycled into paper products anymore. One study addressing the valorisation of by-products from paper recycling came from Zhang et al. As with starch, cellulose also has a long history of usage in adhesive production. Zhang et al. investigated the microwave pyrolysis of waste paper and waste residues from the de-inking processes (e.g. fines and ink-sludges) used in paper recycling [169–171]. The standard products (depending on conditions) from microwave pyrolysis are biogas, biochar and a bio-oil, which itself comprises an aqueous and an organic fraction. When curing the organic fraction of the wastepaper bio-oil by hot-pressing between two aluminium plates, Zhang was able to achieve a maximum tensile strength of 2300 N for this adhesive—over twice as strong as the mandatory 900 N typically required for metal adhesion purposes. The de-inking residues did not fare as well, achieving only $\sim$600 N under the same conditions; however, Zhang noted the high amount of sugars and aromatics in the bio-oil suggesting the potential for this material (or the precursor) to be a feedstock for other carbohydrate valorisation methods, particularly 5-hydroxymethyl furfural (HMF) and 5-chloromethyl furfural (CMF) production.

In the context of green materials production from cellulosic biowastes, the production of the furan derivatives HMF and CMF (see Fig. 7) has also become a very interesting development.

Many biomass sources naturally produce HMF through the degradation of sugars and is another noted platform molecule—Fig. 8 provides a selection of molecules derived from it through simple chemical syntheses. Again, the function of these molecules varies considerably. 2-methyl THF is seen as a potential candidate to replace THF as a solvent [172], 2,5-dimethylfuran (sometimes abbreviated to DMF, not to be confused with dimethyl formamide) is a biofuel [173], 5-hydroxy-4-keto-2-pentenoic acid possesses an acid and alcohol group, making a monomer for polymer production [174], as is furan-2,5-dioic acid (FDA) as a di-acid. One of the key challenges for the biorefinery concept is the relative lack of aromatics compared to petroleum. Lignin from woody-biomass represents the most abundant source of

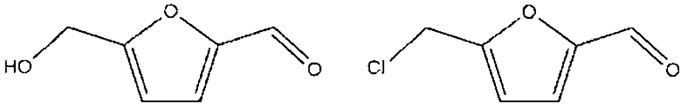


Fig. 7 The chemical structures of 5-hydroxymethyl furfural (HMF-*left*) and 5-chloromethyl furfural (CMF-*right*)

benzene-like rings; however, it is a non-uniform structure rendering it very difficult to break it down into uniform monomers or separate out bio-oils. HMF and CMF help address this challenge as they are, if not benzene-like, both based around aromatic rings.

FDA especially makes for an interesting case study in replacing petroleum-based molecules. Polyethylene terephthalate (PET) is one of the most abundant plastics in circulation and is the most abundant of all polyesters. It has a range of uses, but is most widely recognised for food and drink storage, notably in drinks bottles. The two monomers used to make PET are ethylene glycol and terephthalic acid (benzene 1,4-dicarboxylic acid)—structure shown in Fig. 9. Even though it is furan-based rather than benzene-based, FDA is otherwise extremely similar in structure to terephthalic acid and can be substituted in for producing a new polymer, polyethylene furanoate (PEF) [174]. PEF has not only been shown to be successful in replacing PET in many applications [176], but is also now in commercial production for plastic bottles [177].

However, it is not only the applications of HMF and CMF that make it especially interesting from a biorefinery perspective, but the ease at which it can be manufactured from a range of cellulose based biowastes. HMF production is relatively simple to achieve by dehydrating sugars [178], but from polysaccharides it can be trickier because it has the ability to form polymers itself. Furfural (and furfural derivative) production from sugars has been in place since the late end of the nineteenth century using acid catalysis (both homo- and heterogeneous) to eliminate water [175, 179], with pentoses forming furfural and hexoses forming HMF. However, yields were low (~50%) with polymer coatings on the reaction vessels noted. However, the fact that these polymers partially prevented corrosion of the vessel wall by the acid catalysts employed partially mitigates that point. Since then, many other processes have emerged to improve the yield and efficiency, such as the Agrifurane, Suprayield and Westpro-modified Huaxia Tech processes. However, they all typically employ high (150–240 °C) temperatures, and where

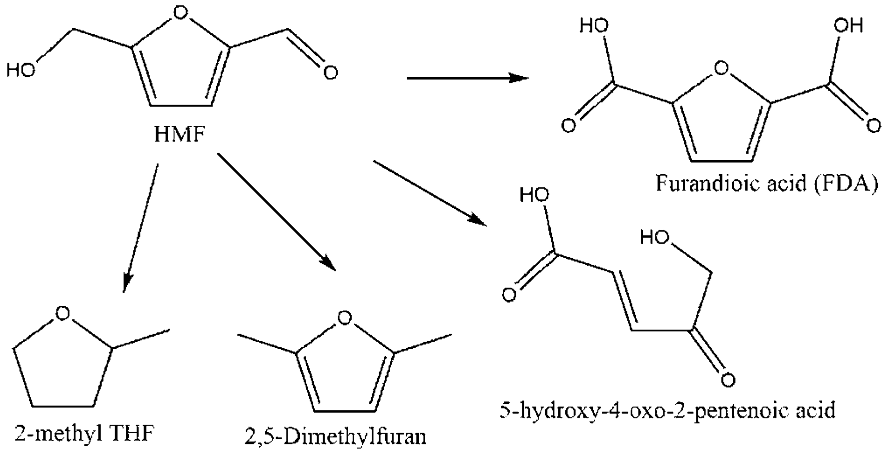


Fig. 8 HMF, *top left*, and a selection of molecules it can subsequently be transformed to [175]

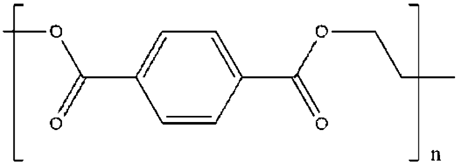


Fig. 9 The chemical structure of PET

polymerisation is prevented, furfural breakdowns to a mixture of molecules (including formaldehyde) instead[180].

However, a new process developed by Mascal et al. demonstrates the ability to address both the aforementioned problems. By heating sugars in a mixture of aqueous hydrochloric acid and dichloromethane the sugars are easily dehydrated to the furan moiety, but the Cl^- groups from the acid replace the hydroxyl group at the 5-position, thereby preventing the polymerisation route [181]. The newly formed CMF is non-water miscible and, therefore, separates out into a biphasic system, decanted and able to undergo the same reactions as HMF [182, 183]. This process has been demonstrated to work on simple sugars, and cellulose and corn stover have also been successful, providing yields of >75% with levulinic acid as the only major by-product, as opposed to polymer resins or unwanted breakdown products. The fact that the by-product in this case is another valuable platform molecule, therefore, enhances both the green and economic credentials of the process. This process has also been successful under microwave conditions, presenting an opportunity to green the process further by reducing the time and energy inputs [184]. The one drawback at present, however, seems to be the inability to replace dichloromethane as the production solvent.

Neither starch nor cellulose typically exist in the ideal "pure" forms given in Figs. 4 and 5. The starch shown in Fig. 4 is the linear amylose variety, but there can also be branching at the 6-position to another α-glucose molecule, which is the amylopectin variety. Most starch consists of different ratios of the two, but amylase enzymes easily break down most forms and the ratios tend to make little difference to the described methods. Cellulose, on the other hand, frequently occurs entwined with large amounts of hemi-cellulose and pectin. Hemi-cellulose is a complex polysaccharide comprised of an indeterminate number and types of sugar molecules. As such, it is very hard to categorise and separate and many of the described valorisation techniques tend to focus on either removal of it for purified cellulose, or to break it down and ferment/process it along with the cellulose.

2.4 Pectin

Pectins, however, are also becoming of interest for material properties. They are another group of complex polysaccharides present in non-woody biomass mainly in the primary cell wall and intercellular regions [185]. They are composed of an α-(1-4)-D-galacturonic acid polymer chain (sometimes esterified with a methyl group—see Fig. 10) which, when unbranched, is known as homogalacturonan (HG) or the "smooth region", and a "hairy" region, which comprises branched, neutral sugar chains (see Fig. 11).

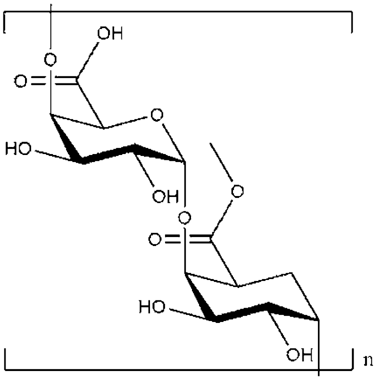


Fig. 10 The general chemical structure of pectin

The degree of esterification, level of branching, and, as with all polymers, average chain length and molecular weight distribution can all vary between biomass sources and can ultimately impact the overall properties [187]. Pectin extraction is a highly attractive valorisation method for fruit waste since pectin is present in high concentrations within fruit and has many applications within the food manufacturing industry for its ability to form a gel in water [188]. The degree of "smoothness" or "hairiness", the degree of esterification (DE), amount of galacturonic acid (GA) and uronic acid, viscosity, and average molecular weight [189] are all properties governing the potential gelling properties of the pectin. This availability along with guaranteed demand means that pectin extraction could be one of the most lucrative aspects of fruit biorefinery systems. However, as these parameters differ depending on the source, if extraction of pectin for use in the food industry is the goal, rigorous analysis is needed to determine these values.

Mango waste, especially the peel, has been shown to have great promise as a potential source of food grade pectin with extraction yields of up to 21% [190] and promising values for the GA and DE. Traditionally, mineral acids have been employed in the extraction of pectins; however, this conflicts with the principles of green chemistry [191], due to their hazardous nature, and also they are unselective, meaning pectins extracted using this method have high neutral sugar content [192]. This technique is also time consuming [193], and although a high yield is generally obtained, the long extraction times at high temperature leads to thermal degradation [194, 195] of the pectin, lowering the average molecular mass [189]. More green extraction methods have been explored including using ammonium oxalate or ultrasound- and microwave-assisted extraction (MAE) techniques with quoted pectin yields of up to 11.6% [193, 196]. These extraction techniques have all been shown to be more selective and less harsh, yielding non-degraded pectin in high yields with good values for the GA and DE, along with high molecular mass and viscosity [189].

The variety of uses for sugars and starch is interesting as it highlights the potential to derive platform molecules from carbohydrate waste, analyse using HPLC, and convert them to materials all from carbohydrate-based resources.

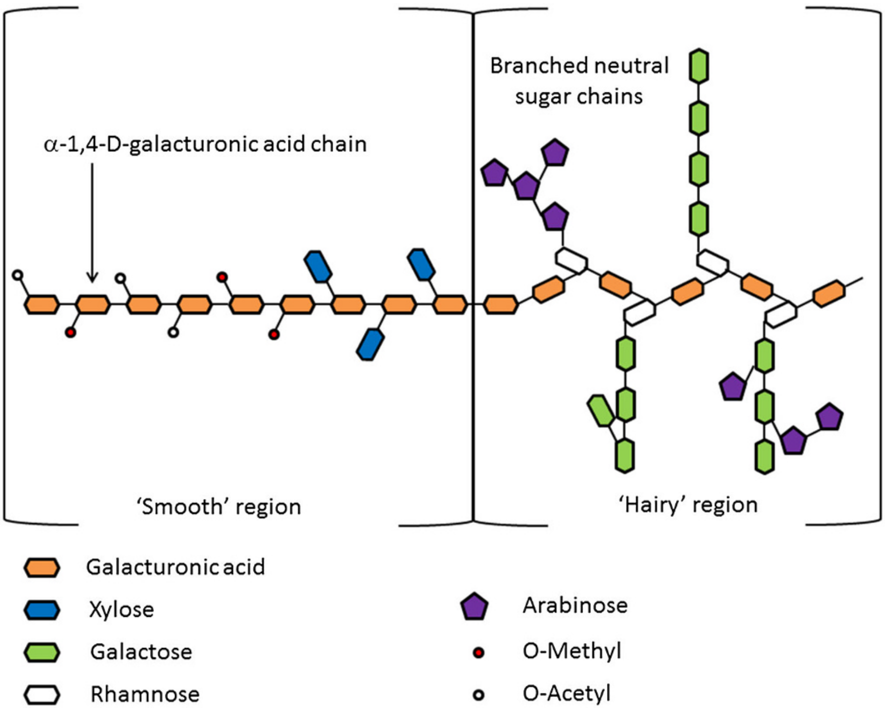


Fig. 11 General structure of pectin [186]

3 Lipids

Converse to carbohydrates, lipids are the most hydrophobic of the three macronutrients and used in biological systems primarily for energy storage and as water repellents/surfactants. The two principal components in lipid systems are glycerides and fatty acids. Triglycerides, where three fatty acids are bound to one molecule of glycerol via ester bonds, occur more frequently in edible vegetable and animal oils and fats. Phospholipids, similar to triglycerides, but with one fatty acid replaced by a phosphate group, are the principal components of cell membranes, responsible for maintaining an aqueous environment inside the cell by creating a hydrophobic environment outside [197]. Figure 12 shows the structures for both.

Figures 13 and 14 give the generic structures for fatty acids. Saturated fatty acids are essentially simply long chain, unbranched carboxylic acids where, generally, $n > 5$. The most common ones are $n = 8$ or 9 (16 or 18 carbons long). Unsaturated (both mono- and polyunsaturated) fatty acids also consist of one or more double bonds along the chain, always separated by one carbon atom (i.e. no conjugation) and always *cis*.

Extraction of lipids from biomass also typically requires solvent extraction with non-polar solvents. Hexane is a common choice, but is on ChemSecs SIN list as of 2016 [198], substances of very high concern, under the criteria set up by REACH (the Registration, Evaluation, Authorisation, and Restriction of Chemicals) [22].

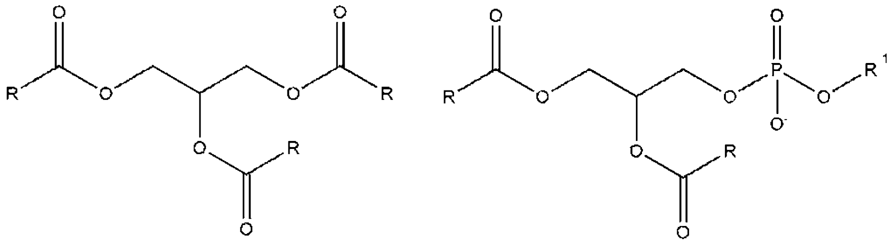


Fig. 12 The generic structure of triglycerides and phospholipids, the two most common lipid systems

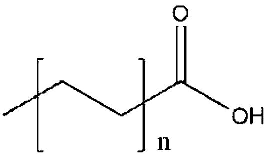
This being the case, heptane is a greener alternative (based on toxicity), which is becoming more attractive for this purpose due to similar solvation properties [185, 199, 200].

Supercritical CO_2 extraction is an interesting alternative green solvent to hexane. This is attractive since CO_2 is low cost, inflammable, relatively inert, has low toxicity and a wide range of solvent properties depending on its temperature and pressure [200]. The term supercritical refers to a fluid, which is under pressure and temperature greater than the critical point (see Fig. 15) meaning that the fluid exhibits the properties of the gaseous and liquid phase whilst being a single phase [201]. The density of the fluid is closer to that of the liquid, and as solubility increases with density, pressure, and temperature, supercritical fluids exhibit a large absorption capacity. The gaseous properties of the super critical fluid allow for efficient extraction due to its highly diffuse nature. Once the extraction is complete the extract can be easily collected by reducing the pressure in the collection vessel until the fluid becomes a gas again, causing the extractant to “fall” out of the solution, negating the need for solvent removal through more conventional methods. Table 3 provides a selection of oil yields from supercritical CO_2 from various feedstocks.

Another technique is use of subcritical water, previously mentioned in expanding starches. This allows for fast, cheap, green extraction [208] and low working temperatures [209]. Although the temperature is relatively high for water-based operations, the extraction method is so fast that it aids the retention of volatile and thermally sensitive components. This is where subcritical water extraction differs from classic steam distillation, because although steam distillation is run at 100 °C the run time is much longer, increasing the likelihood of compound degradation and loss of volatiles. Because the temperature of the water is increased, its polarity as a solvent decreases, allowing for extraction of compounds, which are not typically water soluble [210]. Subcritical water is generally cheaper than supercritical CO_2 because increasing the temperature of a system is cheaper than increasing the pressure. Table 4 provides a selection of yields from subcritical water extraction from various feedstocks.

As one of the roles of lipids in the cell is to partition aqueous and non-aqueous environments, it is unsurprising that one primary means of valorising waste oils is as surfactants. The most common form is base hydrolysis to form fatty acid salts, which form the bulk material for soaps (hence, the common name for the reaction is

Fig. 13 The generic structure of saturated fatty acids



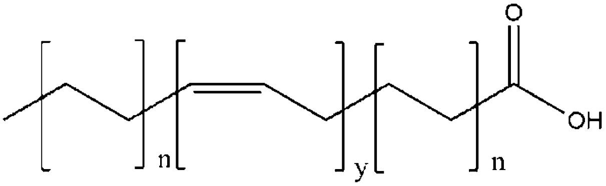


Fig. 14 The generic structure of unsaturated fatty acids

Fig. 15 Typical phase diagram showing subcritical and supercritical conditions

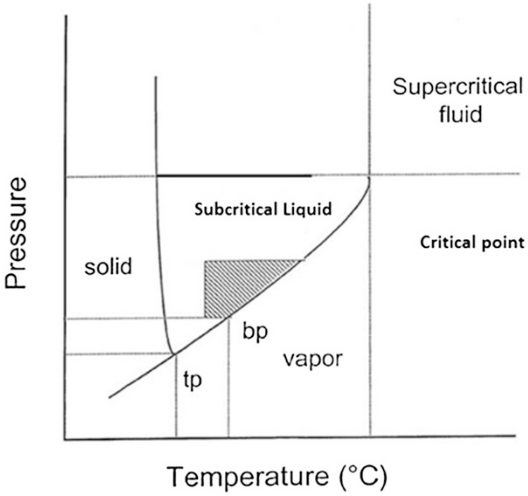


Table 3 A selection of oil yields from various feedstocks obtained from supercritical CO_2 vs conventional solvent extraction (CSE) yield

Feedstock	Temperature (°C)	Pressure (bar)	Yield (%)	CSE yield (%)
Soybean [200]	50	552	18.3	19.0
Wheat straw [202]	100	400	1.8	1.17
Corn leaves [203]	65	400	1.76	
Linseed [204]	70	550	25	38
Rosehip [205]	40	300	8.78	8.99
Lavender [206]	48	90	4.9	4.9
Rice bran [207]	100	620	20.4	20.5

Table 4 A selection of yields from various feedstocks obtained from subcritical water vs steam distillation (SD) yield

Feedstock	Temperature (°C)	Pressure (bar)	Yield (%)	CSE/SD yield (%)
Ziziphora [209]	150	60	1.56	1.32 (SD)
Cretan Oregano [211]	150	60	3.76	3.58 (SD) 3.62 (CSE)
Rosemary [212]	150	20	0.05	0.05 (SD)
Kava [213]	100	60	9	5.7 (CSE)
	175	60	10.4	
Marjoram [214]	150	5	1.24	0.244

"saponification"). However, the role of lipids as surfactants and emulsifying agents has attracted the attention of other fields as well. Do, Attaphong et al. studied the use of adding sulphate and phosphate groups to the acid head of free fatty acids to increase the hydrophilicity of the "head" end of the molecule. They were able to use them to make emulsions without the use of a co-oil with applications in cosmetics, vegetable oil extraction [215] (the latter is particularly relevant in light of the potentially upcoming restrictions on hexane) and viscosity modifiers for biofuels [216].

Another traditional use for animal and vegetable oils and fats prior to petroleum is as greases and lubricants to reduce friction between moving surfaces. Standards for performance in, e.g., engines have become more stringent since the advent of petroleum. In addition, there are many new applications, such as computer hard disks, that have emerged since the advent of petroleum, meaning that oils and fats cannot be directly applied to some traditional and novel applications, but require some form of processing first. Mobarak et al. investigated the long term stability (oxidative, hydrolytic, thermal, etc.) and properties of vegetable oils compared to their mineral counterparts [217]. They noted that vegetable oils were typically less thermally and oxidatively stable due to the presence of unsaturated fats. They also noted that they typically offered better lubricity during their lifespan, as well as lower volatility and, therefore, emissions. From this, they compared the different oil properties with industrial applications to suggest a "best-fit" for each. Since vegetable oils are major targets for automotive fuel in the form of biodiesel, it is perhaps unsurprising that the majority of literature on bio-lubricants have an emphasis on the same field—including the applications suggested by Mobarak. For instance, Bokade et al. studied the possibility of transesterification of vegetable oils to both biodiesel and bio-lubricants by altering the alcohol moiety [218]. They observed a lower conversion from triglycerides to monoesters as the alcohol chain length increased, but ultimately concluded that for *n*-octanol a 72% yield and 78% selectivity was still sufficient for the selected catalysts when considering the implications for being able to produce both commodities in the same process, same catalyst, etc. Salimon et al. attempted expand on this by using unsaturated fats to their advantage by adding other hydrophobic or hydrophilic groups to these sites and were, therefore, able to expand the usage of bio lubricants to other more advanced applications, notably as hydraulic systems and lightweight gas turbines [219].

Within the unsaturated fatty acids, the nature of the double bonds provides more options to perform chemistry on for higher value products. As with all double bonds, they are prone to autoxidation reactions [220]. However, in polyunsaturated fatty acids, as a carbon atom separates the double bonds, the double bonds are particularly prone to oxidation. This is because the process creates either an ion or radical intermediate that is stabilised by migration of one of the double bonds to form a conjugated system upon formation of the final product. Therefore, there is a strong thermodynamic driver due to the lowering the Bond Dissociation Energy of the allylic C–H bond [221–224] (mechanism shown in Fig. 16, where *R* is typically O_2, $RO_2\cdot$, or $RO\cdot$) [225].

Autoxidation of double bonds can also occur by direct addition across the double bonds to form epoxides [226–228]. The subsequent ring opening ability of epoxides from petroleum-based alkenes has long been exploited to create resins with a broad range of useful properties specific for application such as high strength, excellent corrosion and weather resistance, and excellent electrical insulation [229, 230]. Cross-linking agents are frequently used to open the epoxide rings and form a polymer matrix (structure shown in Fig. 17) [231].

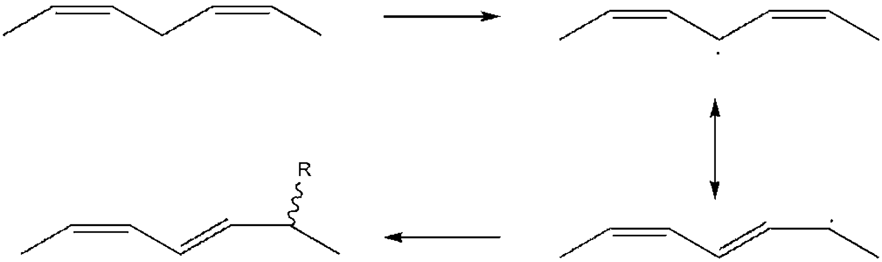


Fig. 16 The migration of double bonds

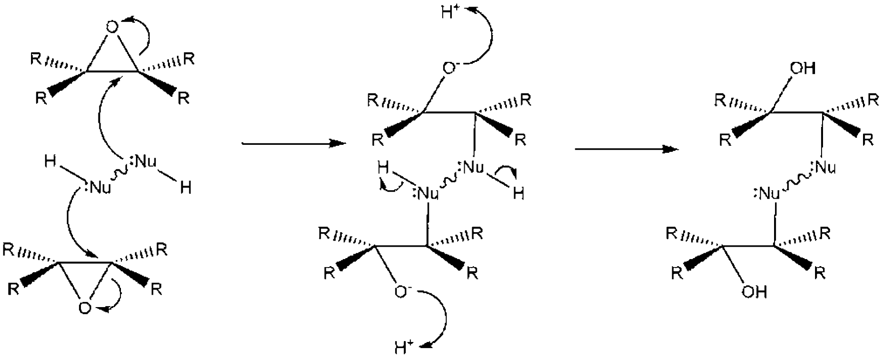


Fig. 17 Cross-linking mechanism to form epoxy resins

However, the energy required for epoxidation is greater than the energy required for breaking the allylic C–H bond [232]; therefore, in addition, a petroleum-based alkenes the process to make traditional epoxy resins also deploys more specific oxidising agents and/or heat. For instance, Prilezhaev process uses formic acid and hydrogen peroxide to form performic acid, which is then used to carry out the epoxidation of the alkene [233, 234]—Fig. 18.

As fats and oils have always been commodities, epoxy resins from vegetables are also established products. However, the cross-linkers used are often still petroleum derived. Commonly, amines are used as hardeners due to the nucleophilic nature of the electron-dense nitrogen. Aliphatic amines are more nucleophilic than aromatic amines (where the aromaticity will withdraw electron density from the nitrogen), therefore, frequently involving the use of ammonia in preparation. Amine-based cross-linkers, therefore, potentially expose workers to harmful substances at both the production and usage stages of the operation through ammonia and amines, respectively. Park and Lin also voiced concerns about inadequate electrical and heat resistance [235].

Stemmelen et al. tried to use cysteamine hydrochloride, a dehydrated analogue of cysteine, to add directly to the double bonds of fatty acids through the thiol moiety before using the amine moiety to open the epoxides on another fatty acid chain as a means of creating a bio-derived cross-linker [236]. However, the initial reaction requires dioxane as a solvent, with chloroform, hexane, and diethyl ether as alternatives, all of which are typically derived from petroleum and face severe restrictions under REACH.

Gerbase et al. synthesised several epoxy resins from soybean oil using a range of petroleum and bio-derived acid anhydrides (including succinic anhydride and maleic anhydride) that were able to display a range of thermal and mechanical properties, demonstrating a good degree of versatility; however, they still required the use of a tertiary amine (often trimethylamine) as a reagent [237]. Mahendran et al. carried out similar work with linseed oil, achieving similar results, but managing to replace the amine reagent with an imidazole catalyst [238].

In 2004, Park and Lin investigated the production of epoxy resins from soybean and castor oil without the use of a cross-linking agent, using only a catalyst, *N*-benzylpyrazinium hexafluoroantimonate (BPH—structure shown in Fig. 19) [239]. They reported that the resins both had a relatively low glass transition temperature, but a low coefficient of thermal expansion when compared to conventional diglycidyl ether of bisphenol A (DGEBA) resins synthesised under the same

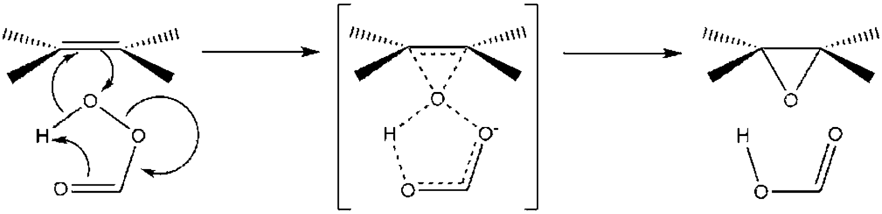


Fig. 18 The Prilezhaev process for forming epoxides

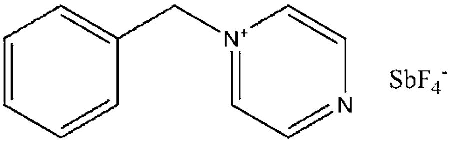


Fig. 19 The chemical structure of *N*-benzylpyrazinium hexafluoroantimonate, BPH

conditions [240, 241]. Similarly, in 2010, Altuna et al. synthesised pure epoxidised soybean oil (ESO) resins and DBEBA resins and mixtures of the two using a methyltetrahydrophthalic anhydride cross-linker and found that the glass transition temperature steadily decreased with an increasing amount of ESO. However, they also noted that the impact strength increased with a 40:60 mix of ESO:DGEBA, whilst the storage modulus remained relatively constant [242].

More recently in 2015, Ding et al. have reported using bio-based di-carboxylic acids as cross-linking agents for epoxidised linseed oil [243]. They observed that shorter acid chain length led to higher glass transition temperatures and better mechanical properties, but lower thermal stability.

The different properties resulting from the differing feedstocks and curing methods give the potential to produce a wide range of resins from lipids. Literature reviews on the subject seem to be largely positive, even if there are still issues to be resolved. Galià et al. [244] did an overview of vegetable oil-based polymers, highlighting deficiencies in flame retardant properties of pure vegetable oil epoxy resins and suggested that in order to obtain desired hardness properties, traditional cross-linkers used in petroleum resins would not be sufficient. They highlighted a need for novel resins to be developed. This was echoed by both Lu and Larock [245], who also noted that many of the cross-linkers needed for epoxy resins were still petroleum based. Tan and Chow [246] reported that epoxidised vegetable oil resins still needed to be blended with petroleum epoxy resins for many applications due to deficiencies in toughness and hardness. However, they also noted that advancements in oleochemical technology were addressing many of the shortcomings and concluded that "when being treated with proper curing agents, it is strongly believed that epoxidised vegetable oils have the potential to fully substitute current petroleum-based materials". To this end, Ding and Matharu [247] conducted a review of the different curing agents available from biomass and also noted a variety of modified lipid-based curing agents available, as well as from carbohydrates and proteins, suggesting a great potential to address the concerns noted in the previous two reviews.

The production of such composites dates back to as early as 1997, where Crivello et al. explored a composite using glass-fibre mixed with linseed oil, which they suggested for use in standard domestic applications such as roofing, culverts, and low-pressure pipework [248]. More recently, in 2014, Supanchaiyamat et al. reported using epoxidised linseed oil and expanded starch (from the aforementioned Starbon® process) to produce a fully bio-based composite with 227% improvement in tensile strength and 166% enhancement in Young's modulus, compared to those with no added starch, suggesting it as a replacement for vinyl based films [249].

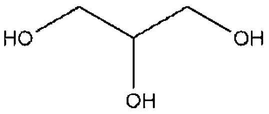


Fig. 20 Glycerol. The major by-product from biodiesel and soap production

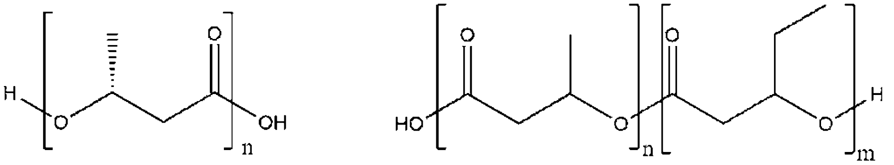


Fig. 21 The chemical structure of poly 3-hydroxybutyrate (PHB-*left*), the most common class of polyhydroxyalkanoates, and its *co*-polymer poly (3-hydroxybutyrate-co-3-hydroxyvalerate) (PHBV-*right*)

Other biopolymers from lipids have also been investigated. Polyurethanes, for instance, have been extensively studied by Petrovíc et al. by hydroxymethylating unsaturated acids—particularly oleic acids [250]. In his review, he noted the ability of ozonolysis of double bonds to produce diacids, aldehydes, and alcohols from double bonds for further polymerisation to polyurethanes and polyols [251]. He reported that the ability to select triglycerides with only one type of fatty acid allowed for greater control of mechanical properties, although noted that as all the major unsaturated fatty acids possess their first (counting from the acid moiety) double bond at the 9′ position, that ozonolysis or hydrolysis could achieve that required uniformity. However, he also cautioned that adding additional steps would inevitably drive up the cost of producing the material, which is undesirable for competing with cheap petroleum.

Overall, whilst there has been a large amount of research investigating the use of vegetable oils for bio-based polymers and resins, there is unfortunately no literature at the time of writing using these emerging technologies on waste oils such as used cooking oil or spent coffee oil. There has been research on applying these technologies to non-edible oils such as karanjia [252–254] and jatropha [255–257] with comparable results suggesting that the same technologies have the potential for application to waste oils—providing there is an appropriate amount of olefins to carry out the chemistry on. However, this is not confirmed at the time of writing, although Petrović did highlight the potential for fish oils to produce monomers via ozonolysis due to the high number of double bonds typically [251].

However, there has been a significant amount of work carried out on glycerol-based polymers, which is the primary waste product generated from soap production, biodiesel production, and any other process that cleaves the fatty acids from the triglycerides (structure shown in Fig. 20).

A relatively well-researched area is fermentation to a class of polymers known as (PHAs), most notably poly 3-hydroxybutyrate (PHB—structure given in Fig. 21, left) [258, 259]—structure shown in Fig. 20. PHAs, as mentioned before (with levulinic acid given as an example) are a common class of biosynthesised polymers, but PHB is of particular interest. As well as being the most common of all PHAs, it is biodegradable and biocompatible leading to its application in medical devices and implants, in particular when produced with 3-hydroxypentanoic acid to produce poly 3-hydroxybutyrate-*co*-3-hydroxyvalerate (PHBV—structure given in Fig. 21, right), which is sold under the trade name Biopol.

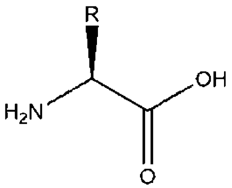
Because of the biorefinery concept, it is perhaps inevitable that the production of these from crude glycerol (as opposed to pure, commercial grade) has attracted research interest. Mothes et al. investigated the effect of common contaminating salts from biodiesel production on the yield of PHB from glycerol and showed that whilst a 5% NaCl contamination led to a 48% reduction in PHB yield, K_2SO_4 showed minimal effect. Furthermore, the molecular weight distribution was between 620,000 and 750,000 g mol^{-1} was comparable to that of commercial PHB, indicating a good potential for crude glycerol mixes to be used in existing manufacturing methods [260]. Comparing commercial methods, Naranjo et al. demonstrated that the yield of PHB using glycerol as the feedstock could be as high as 62%. This is the same as for sugarcane bagasse and only 2% lower than whey, and they subsequently suggested that, since glycerol is produced as a waste product, the profit margin for PHB from glycerol could be up to 20% higher than glucose-derived PHB [261]. In a more complete biorefinery structure, Kachrimanidou et al. demonstrated not only the production of PHB from crude glycerol, but also the production of PHBV from a mixture of crude glycerol, sunflower meal (the leftover residue from oil extraction in biodiesel production) and levulinic acid, thereby using all by-products from biodiesel production [262].

Other monomers from crude glycerol have included the work of Papanikolau et al. in the production of 1,3-propanediol using crude glycerol (65% purity). This was obtained from a mixed-feedstock biodiesel production plant, with the same study also demonstrating the production of citric acid from the same feedstock—itself an important nutrient for fermentation of many of the products outlined in the carbohydrates section [263]. Vivek et al. built upon this to enhance the propanediol yield to as high as 0.83 g per g of glycerol [264]. Another example is the production of acrylonitrile from glycerol by Calvino-Casilda et al. by using niobium-doped Sb_nV/Al_2O_3 catalysts [265].

4 Proteins

Of the three groups of macromolecules in biomass, proteins are arguably the most varied and complex. The main units of proteins are amino acids—essentially a carbon centre bonded to an amino group, a carboxylic acid group, a hydrogen atom, and an R group (see Fig. 22). The amino acids themselves join through amide bonds (more commonly known as peptide bonds in protein chemistry—see Fig. 23) between the amine and acid groups, but it is the R groups that are crucial for determining the nature of the protein. The R groups include other acids, amines, aliphatic chains, and aromatic rings providing a range of polarities and hydrophobicities. The sequence of the amino acids (primary structure) ultimately determines the (secondary and tertiary) structure and nature of the protein. In their review on

Fig. 22 An amino acid, the building block for proteins



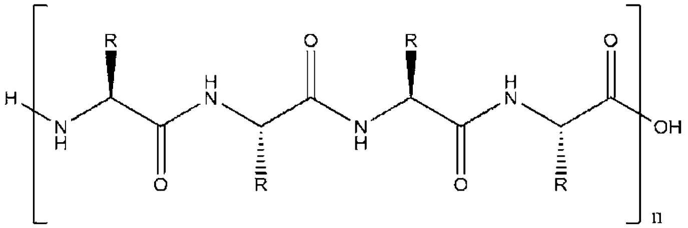


Fig. 23 A chain of amino acids linked via peptide bonds

isolation of vegetable proteins, Rodrigues et al. noted that “in theory, there is a limitless number of proteins with unique properties” [266].

Whilst the wide range of structures of proteins makes for a similar wide range of materials and products, they also make protein processing a very challenging task, as there is no “universal” approach. In addition, whilst rendering of fats and sugars for various purposes is established, protein extraction is a relatively new area. Nevertheless, there is still extensive research detailing the pros and cons of differing extraction and processing methodologies for different proteins, as well as their uses.

Most notably, as protein is a major macronutrient required by the body and traditionally consumed through meat, the rise in popularity of vegetarian and vegan diets has driven up the demand for plant-based proteins [267, 268]. Protease inhibitors from potatoes, for instance, are a very new development within the scope of potato valorisation. The protein obtained from potato is rich in lysine, which is one of the essential amino acids; because of this, potato protein is stated to be of higher quality than many other vegetable proteins [269, 270]. The protein quality is roughly 70% that of whole egg protein, as calculated using the EAAI (Essential Amino Acid Index) estimation of the amino acid composition [270, 271]. One interesting application for potato protein is because one of the protease inhibitors present (namely PI2) has been proven to be an appetite suppressant. It achieves this by inhibiting both trypsin and chemotrypsin, which constitute a negative feedback signal for cholecystokinin secretion, which creates a satiety feeling [269]. The study quoted that 82% of trypsin inhibition and 50% of chemotrypsin inhibition through potato protein is due to PI2. Kemin Health (marketing it under the trade name Slendesta®) has quoted that the required dose of PI2 needed to create the satiety effect is in the range of 300–600 mg and, therefore, can be taken in tablet form [272]. PI2 has a molecular weight of around 21 kDa and as such has scope to be separated via ultrafiltration; this system could theoretically be made to an industrial scale if PI2 separation was desired [273, 274].

A system has been developed that allows for PI2 concentration within the protein isolate; the separation of PI2 can be performed due to its relative stability concerning heat when compared to other potato proteins. PI2 is stable to above 70 °C, whereas patatin (another high concentration potato protein) is denatured and, therefore, precipitates out of solution at around 45–55 °C. This means that if the PFJ was heated to around 70 °C for a specified amount of time, the majority of the other proteins will precipitate out of solution, and the PJF could then be centrifuged to remove the precipitate and then the concentrated PI2 precipitated out using one of the different methods described above (ammonium sulphate, for example) [273, 274].

Within the field of chemistry, just as with carbohydrates and fats, another key use of proteins is the use of constituent amino acids as platform molecules. With the exception of glycine, where the R group is another hydrogen atom, all amino acids are chiral. However, unlike in traditional chemical synthesis, which produces both enantiomers in roughly equal amounts, in biomass the amino acids occur almost exclusively in the L-isomer. This makes them extremely useful in asymmetric synthesis either in introducing a chiral centre as part of the functional structure of the molecule or as a temporary attachment to create diastereomers and thus facilitate separation [275]. It should be noted, however, that the latter is frowned upon in terms of green chemistry, which seeks to avoid the use of temporary analogues, such as protecting groups—particularly if the unwanted enantiomer is then consigned to waste [46]. Nevertheless, asymmetric synthesis is an integral tool for synthetic chemists, particularly for drug development whereby one enantiomer may be inactive, or even harmful. The production of enantiomerically pure compounds similarly requires testing, purifying and quantifying in the production process. In order to interact differently with different enantiomers, many of the reagents and catalysts [276], HPLC stationary phases [277, 278], etc. often need to be in enantiomeric excess themselves, further highlighting the essential role of amino acids and proteins as platform molecules.

The field of health drug discovery has also highlighted other innovations for protein valorisation. Whey protein from cheese production is of particular interest in this field as it contains all 20 amino acids making it a very rich nutrient source for the body to construct its own proteins. Athletes and sportspeople will be familiar with the presence of whey protein powders in gyms and sports shops to enhance muscle growth [279–281], but the ability to help the body synthesise its own necessary proteins means it is also being investigated as an alternative to glucose as a drug-delivery media [282]. There has also been reported success in weight loss [283, 284], anti-cancer [285], tissue regenerating [286, 287], and anti-inflammatory medications [288]. Smithers has forecast a large growth in this field for whey protein; however, he noted the need to make use of emerging, non-thermal technologies, such as pulsed electric field [289], for extraction and isolation in order to make the applications cost-effective [290].

Collagen is another protein that has been studied for drug delivery purposes [291]. Collagen is the most abundant protein in animal bodies, providing the structural integrity for body tissue [292] and is a particularly abundant by-product from seafood production [293]. For applications, a drawback is that it is non-vegetarian friendly—although whey protein is similarly non-vegan friendly.

Keratin is another common polymer, which is of interest for its structural properties [294]. Keratin is an insoluble protein that makes up the exterior parts of animals such as hair, nails, claws, feathers, etc. Historically, the most prominent use of keratin has been the spinning of sheep's wool or other hair/fur for material such as woollen garments or angora. However, the harder keratin types, such as those that make up feathers are now becoming more of interest due to the quantities of waste feathers generated in the poultry industry. The proteins here are typically hard, insoluble, and mechanically strong—properties generally attributed to the high amounts of cysteine side chains able to provide "built-in" cross-linking groups via disulphide bonds—see Fig. 24.

Tanabe et al. studied the polymerisation of films from keratin in a similar manner to resins from lipids [295]. However, as before, the use of a cross-linking agent was required to get the highest tensile strength of the films; however, glycerol proved to be the best cross-linking agent, whilst films mixed with chitosan also demonstrated superior mechanical properties to keratin alone. As both these materials are discarded as biowastes in large quantities, this presents an interesting opportunity for an integrated biorefinery by using feedstocks from different sources. However, from a green chemistry perspective, the use of sodium dodecyl sulphate and, particularly, 2-mercaptoethanol to extract and prepare a solution of keratin is less desirable. Poole et al. investigated the use of both chicken feather keratin and wheat gluten for the production of protein fibres, comparing them to other natural (e.g. cotton and silk) and synthetic (e.g. nylon and polypropylene) fibres [296]. Whilst on the low end of the molecular weight distribution range required, feather keratin still showed all the required properties in terms of crystallinity, cross-linking sites, and ability to form threads. Wheat gluten showed a more desirable molecular weight distribution, but did not perform as well in the rest of the properties desired. Furthermore, feather keratin estimates suggest them to be available in up to five million tonnes annually in very consistent quality, and unlike Tanabe's work, did not require additional cross-linking agents. However, Poole et al. also noted the difficulty in solubilising the keratin that Tanabe had observed, suggesting the need for a green extraction method to be able to validate polymers and fibres from keratin as a "green" material.

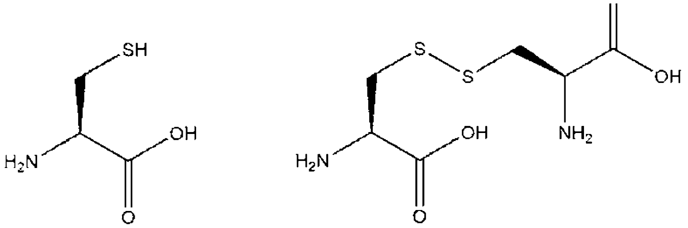


Fig. 24 The chemical structure of cysteine (*left*) and cross-linking with itself in a disulphide bond to form cystine (*right*)

5 Case Studies

5.1 Potatoes

This review so far has covered the different components of biomass and potential processing methods to different materials. In order to realise these concepts efficiently it is necessary to bring these methodologies together. This final section will look at some case studies, where (a) the different parts of a biowaste are refined into their respective materials, and (b) different materials are brought together to make finished products.

As mentioned earlier, 19% of a potato's composition by weight is starch [136], but they also contain proteins; roughly 2% by weight, as well as other higher value components such as protease inhibitors found within the potato protein; these have been shown to have an appetite suppressing effect on mammals [269, 297]. Figure 25 summarises the main steps in a theoretical bio-refinery system based on existing systems already utilised within the potato industry.

A summary of the potential steps is as follows:

1. Removal of dirt/sand
   Washing of the tubers with water to remove excess dirt and sand. This aids in maintaining operational integrity in the system by removing impurities that could damage fast moving machinery.
2. Tuber milling/rasping
   Milling of the tubers to open tissue cells allowing extraction of the starch. Optimisation of this step is required to achieve maximum tissue milling without negatively affecting later filtration steps. Sodium hydrogen sulphite is sometimes required at this point to prevent discoloration. Achievable throughput has been quoted to be in the range of 20–30 t/h [298].
3. Separation of potato fruit juice (PFJ)
   There are a variety of systems described in the literature for the separation of the protein rich potato fruit juice, the majority utilise some form of centrifuge based decanter system to separate the liquid phase containing soluble proteins from the pulp containing the insoluble starch fraction. Because of the need for excess water to wash the pulp to ensure maximum protein recovery, wastewater from the starch purification step later in the supply line can be used, allowing for the reduction of water used within the system.
4. Fibre extraction
   Separation of the pulp resulting from the PFJ separation into fibre and starch using centrifugal sieves, jet extractors, or centrisieves. It has been quoted that optimised methods can yield a >95% yield of starch with a maximum throughput of 30 t/h [298].
5. Starch de-sanding, refining, de-watering, and drying
   De-sanding of the crude starch using hydrocyclones and several washes to remove protein and other soluble components (this water is recycled earlier in the process). Drying of the purified starch happens through a variety of methods; the one quoted in the literature involves use of rotating vacuum filters

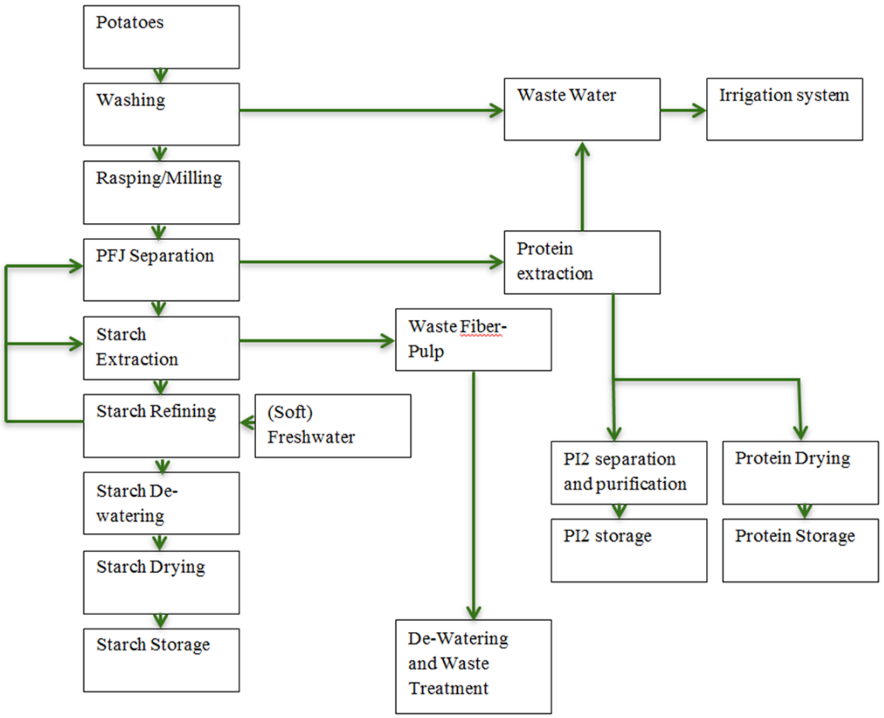


Fig. 25 Process flow for proposed potato bio-refinery [298]

to reduce water content to 38% followed by flash drying to reach a final water content of 20%. Any aggregates produced in the drying step are fed back into the milling step.

6. Pulp de-watering
   Drying of the waste fibre-pulp produced to aid in waste treatment.
7. Protein recovery
   Protein recovery is an attractive addition to the existing starch extraction procedure, as it uses one of the current waste streams as the starting feedstock—for example, the PI2 protein discussed earlier. The wastewater from the starch process needs processing to obtain the protein; research on different precipitation methods is summarised in Table 5. The different methods for precipitation result in protein with different properties, so there is scope to tailor the precipitation method to suit the proposed protein use. There is also the issue of waste management; some of these precipitation methods use acid and therefore would complicate waste treatment procedures.
   Summarised in the above table is the ratio of the various proteins in the extracted protein isolate. These are important to consider as they change the nature of the protein extracted. PFJ in its non-precipitated form has been quoted within the literature to contain 22.9–38% patatin, 45.6–56% protease inhibitors, and 9–23.7% higher molecular weight proteins; this variation is heavily

Table 5 Different protein yields and properties with regard to precipitation method [269]

Precipitation agent	Max protein yield (%)	Purification factor	Patatin (%)	PI 25–21 kDa (%)	PI 20–15 kDa (%)	PI <15 kDa (%)	HMW proteins (%)
Thermal/acid	90.2	0.74	37.9	0	20.2	31.3	10.7
Acid	64.7	1.26	11.1	9.9	15.3	17.4	46.4
$FeCl_3$	75.2	6.24	21.7	18.7	23.2	34.3	2.0
$MnCl_2$	16.8	1.52	20.4	0	30.9	44.2	4.6
Ethanol	55.2	3.79	37.7	8.0	22.4	26.5	5.4
$(NH_4)_2SO_4$	98.8	2.99	31.1	7.6	23.7	26.3	11.3

dependent on the variety of potato extracted [269]. As can be seen, the ratio of proteins in the isolate is heavily dependent on the precipitation method, with more thermally labile proteins such as patatin being more prone to precipitation via heat, whereas thermally stable proteins such as the protease inhibitors are more sensitive to other precipitation methods. This shows scope for tailored precipitation methods depending on the intended application for the protein isolate.

Another important factor to consider for use of extracted potato proteins as a food additive is the solubility in water. Once again, it is the protein precipitated using ammonium sulphate that performs particularly well here with solubility at pH 7.0 ranging from 78 to 89%; this indicates that the protein retains its conformational structure, proving that precipitation using ammonium sulphate is a soft technique (does not destroy/alter the protein).

8. Waste pulp and water

The waste streams produced from this system require consideration. There are two main avenues of waste from the above-described process, one is the aqueous waste stream, and one is the solid pulp waste stream. The amount of waste water is reduced by recycling the fresh water used in the starch refining step in previous steps; this allows for the reduction of water used down to 0.4 m^3/t of potatoes as quoted by Bergthaller et al. [298]. The unavoidable wastewater has the potential for re-use in the irrigation system used for growing the potatoes. The water stream will also be contaminated with the precipitation agent used to recover the protein isolate; this could potentially help in choosing the method of protein extraction; acidified water streams are obviously not desirable for crop irrigation, whereas use of ammonium sulphate (which is commonly used as a fertilizer) is more desirable. The waste fibrous pulp, however, requires further research into its potential valorisation routes.

9. Testing for glycoalkaloids

Testing the concentration of glycoalkaloids within the extracted protein is very important if the intention is to produce it as a food additive. Alkaloids are frequently toxic at relatively low doses, yet can still display potentially useful characteristics in pharmacology if the dosage is low enough—e.g. atropine, which is the poison found in *Atropa Belladonna* (Deadly Nightshade) [299], is also on the World Health Organization's list of essential medicines for a basic health system [300]. There have been many methods for determining glycoalkaloids reported in the literature including gas chromatography, thin layer chromatography, enzyme-linked immunosorbent assay, capillary electrophoresis, and MALDI-TOF MS. But the one method most used is HPLC [301]. Below is a brief summary of a typical HPLC assay for testing glycoalkaloid content in either the extracted starch or protein. Potato glycoalkaloids can be extracted using dilute acetic acid and sodium sulphite, the powdered protein is homogenised in this solution for 2 min, and the solid residue removed via centrifugation. The solution is then purified using solid phase extraction; HPLC analysis can then be carried out and using external standards, the concentration of both α-solanine and α-chaconine can be obtained [301].

5.2 Citrus Fruits

Another significant case study in the use of a combined biorefinery is on citrus fruits, which includes oranges, lemons, limes, grapefruits, and tangerines. In 2013–2014 the major citrus producing countries, such as Brazil, China, India, US, EU-27, Mexico, Egypt, Turkey, and South Africa, produced around 140 million MT of these fruits, of which 60% were oranges [137]. Worldwide figures estimate that over 30% of citrus fruit produced (40% in the case of oranges) is processed by the food industry each year, as opposed to going directly to retail. This processing, including juicing and canning, generates large quantities of citrus peel waste (19 million tonnes annually). On top of this, and even though the harvesting season is fixed in specific locations worldwide [302], citrus fruits are grown and harvested around the globe on either side of the equator throughout the year, ensuring a constant supply of citrus peel waste that has the potential to be used as a bio-refinery raw material for valorisation purposes.

Citrus peel waste accounts for 50% of the whole fruit [303] and contains up to 80% water [304, 305]. It has been recognised as an interesting source of dietary fibre, natural antioxidants, food colorants, and flavours and is of particular interest given the variety of compounds it contains. Major components of dry citrus peel waste are cellulose (up to 37%), pectin (up to 23%), sugars (up to 23%, including glucose, fructose, sucrose, and xylose; dry weight basis), and up to 11% hemicellulose [304]. Other components also present in dry citrus peel include lignin (up to 10%) [305], flavonoids (up to 4.5%), and up to 4% of essential oil [306], mainly composed of D-limonene and often referred as citrus essential oil.

Amongst these compounds, D-limonene and pectin are the most attractive for industrial production, but the recovery of other compounds such as flavonoids and sugars are nowadays gaining importance for the reasons outlined previously. The production of D-limonene from waste citrus peel normally takes place after the essential oil extraction by traditional methods like cold pressing or steam distillation once the juicing process has finished [303, 307, 308]. The two different processes yield respectively a high purity/food grade and a technical grade of D-limonene as the latest involves the use of lime as a dewatering agent [305], hence limiting the final cellulosic-based end product to toxic cattle feed supplement [309]. On the other hand, pectin is traditionally extracted by acidic hydrolysis once the juice extraction process has concluded, generating quantities of acidic waste water [310, 311]. Still, this is not generally a by-product of the juice production industry as the inclusion of these extraction steps highly depends on the level capital available for investment, the required pay-back period and the juicing equipment used [312]. Moreover, the several washing and purification stages also involved make pectin production a wasteful and polluting process (particularly if the precipitation of pectin uses aluminium salts).

These conventional methods show some disadvantages related to high energy costs and long extraction times, and, according to the literature, the overall juicing process is becoming unprofitable and ineffective and would benefit from further improvements as current citrus waste processing is based upon processing technology that is at least 70 years old [309]. Scientists have, therefore, been developing greener and more efficient methodologies to be used in alternative biorefinery concepts to (1) increase production efficiency and (2) contribute to environmental preservation.

Clark et al. have recently developed a new biorefinery concept to combine all these extraction methods in an integrated process to be applied at industrial scale with the intention to bring together various new technologies [313]. As mentioned previously, conventional techniques tend to require hazardous solvents or additives to carry out a successful extraction of products from citrus peel waste. Thus, a methodology to produce a wide range of marketable products and relying on green solvents and techniques and able to cope with wet feedstock would be advantageous. Here lies the advantage of the microwave protocol compared to other techniques. Recently, microwave technology has gained increased industrial interest in the food sector since it (1) can be applied directly to the desired biomass without any need of solvent or pre-treatment (i.e. drying); (2) allows a rapid and homogeneous heating; and (3) is adaptable for continuous processes and easily scalable [314]. This is a key factor for future industrial scale applications given the importance of citrus peel drying costs. The scalability of this technology has been proved in different studies and has shown important advantages over traditional methods [315]. These features allow microwave technology be applied to different systems in order to obtain more flexible processes, leading to lower energy consumption and environmental impact [316].

Microwave heating has been previously used as a faster, more efficient and cost effective alternative for the extraction of higher quality D-limonene [317, 318] and pectin [319–321] from citrus peel waste. However, most of these individual methods still involve the use of additives and/or additional pre-treatment steps.

The methodology developed by Clark et al. [313] shows that it is possible to treat fresh waste orange peel (WOP) through three steps without involving additional chemicals for subsequent extraction: (1) D-limonene using microwave energy, (2) sugars and flavonoids after washing the residual citrus peel with hot ethanol, and (3) pectin following a pressurised microwave extraction under acid-free conditions, finally to end up with a cellulose-based solid material, and resulting in an innovative zero-waste biorefinery concept.

5.3 Bio-Boards

Coming from the other angle, the final case study presented gives an example of where the differently processed parts of several biowastes are brought together to make a finished product. MDF and particle boards are very highly used in furniture construction—the UK is estimated to produce over three million tonnes annually [137]. The process typically involves using chipped wood or other lingo-cellulosic substance being pressed or moulded into panels and bound together in place with urea–formaldehyde as a binder. The current issues associated with this process are:

1. Competition for virgin wood for other purposes coupled with the need to preserve forests.
2. Petroleum is the current source for urea–formaldehyde.
3. Formaldehyde is currently listed as a "probable carcinogen" and is continually emitted from the boards through their lifespan [322].

A joint project between the Universities of Bangor and York, as well as several private companies investigated using waste wheat straw as an alternative raw material for particleboards and manufacturing them in a greener manner. First, the wheat straw is de-waxed, with one portion of the straw going for biomass burning for renewable energy and the other directly to make the boards. Potential applications for the waxes include a variety of coatings, plasticisers, and cosmetic bases amongst others [323–326]. Meanwhile, the ashes from the biomass burning then have the silicates extracted with sodium- or potassium-based alkali solutions [327, 328]. The resulting silica solutions can then subsequently be used as the binder for the wheat straw alongside either whey protein or glycerol with the resulting boards pressed in the same manner as conventional particleboard [329]. The resulting boards have been assessed to meet all EN criteria and now produced at scale [330]. With the wax extracted for various purposes and the wheat straw used either directly in the board itself or via the power station as ash, this strategy represents full usage of wheat straw in a biorefinery concept. In addition, it demonstrates the "big picture" of biorefineries by integrating products resulting from the biorefinery of other biowastes, e.g. whey protein from dairy effluent or glycerol from biodiesel/soap production. The process is summarised in Fig. 26.

6 Concluding Remarks

Overall, the prospects for using waste biomass from existing industrial processes—notably food production—as the source for many of our materials is becoming increasingly close to realisation. Sugars and other carbohydrates are arguably the easiest and most versatile of the three main biological macromolecules due to their relative similarity in structure (allowing for more broad-stroke techniques) and the fact that they are already used a feedstock for bacterial cultures for many existing fermentation processes. The range of molecules produced includes platform

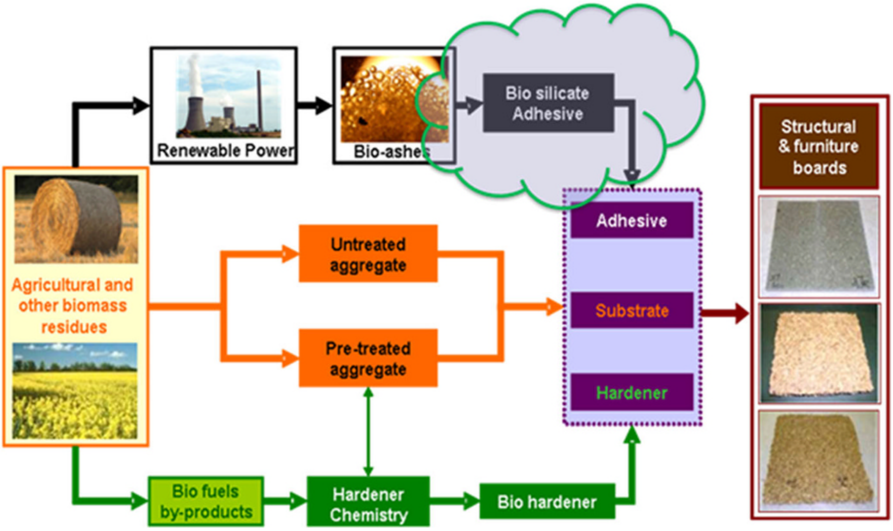


Fig. 26 The schematic overview of the production of bio-boards [330]

molecules for the production of materials, monomers capable of polymerisation directly to materials and solvents used for the processing stages.

Lipids present less versatility, but again their similarity in structure allows for the application of a number of broad-stroke techniques and their hydrophobicity makes them useful as replacements for a number of crude oil applications such as surfactants, lubricants, waxes, and polymers.

Proteins represent a class of materials in their own right due to the structures and functions they provide in biological systems. However, because of this they are by far the most diverse of the three macromolecules and are arguably the hardest to develop a processing method for due to the lack of broad-brush techniques available to carbohydrates and lipids. Extraction, in particular, is a major barrier to overcome in order to achieve processing to green materials. However, there are a number of promising developments in this field and their diversity represents significant promise for versatility in the range of materials that could arise from the biorefinery concept.

The case studies presented highlight the ability to utilise all parts of biomass sequentially in the biorefinery concept as well potential for different fractions to come together when producing new materials. They also illustrate that the minor components of biomass, such as vitamins and minerals, are also important when considering refining biomass, as they also represent the potential to be feedstocks for niche applications.

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REVIEW

Valorization of Proteins from Co- and By-Products from the Fish and Meat Industry

Tone Aspevik[1] · **Åge Oterhals**[1] · **Sissel Beate Rønning**[2] ·
Themistoklis Altintzoglou[3] · **Sileshi Gizachew Wubshet**[2] ·
Asbjørn Gildberg[3,4] · **Nils Kristian Afseth**[2] ·
Ragnhild Dragøy Whitaker[3] · **Diana Lindberg**[2]

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Abstract Large volumes of protein-rich residual raw materials, such as heads, bones, carcasses, blood, skin, viscera, hooves and feathers, are created as a result of processing of animals from fisheries, aquaculture, livestock and poultry sectors. These residuals contain proteins and other essential nutrients with potentially bioactive properties, eligible for recycling and upgrading for higher-value products, e.g. for human, pet food and feed purposes. Here, we aim to cover all the important aspects of achieving optimal utilization of proteins in such residual raw materials, identifying those eligible for human consumption as co-products and for feed applications as by-products. Strict legislation regulates the utilization of various animal-based co- and by-products, representing a major hurdle if not addressed properly. Thorough understanding and optimization of all parts of the production chain, including conservation and processing, are important prerequisites for successful upgrading and industrial implementation of such products. This review includes industrially applied technologies such as freezing/cooling, acid preservation, salting, rendering and protein hydrolysis. In this regard, it is important to achieve stable production and quality through all the steps in the manufacturing chain, preferably supported by at- or online

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The original version of this article was revised: The spelling of the fourth author was incorrect. The correct name is Themistoklis Altintzoglou.

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✉ Diana Lindberg
diana.lindberg@nofima.no

[1] Nofima AS, P.B. 1425 Oasen, 5828 Bergen, Norway

[2] Nofima AS, P.B. 210, 1431 Ås, Norway

[3] Nofima AS, P.B. 6122 Langnes, 9291 Tromsø, Norway

[4] Ildervegen 27, 9017 Tromsø, Norway

quality control points in the actual processing step. If aiming for the human market, knowledge of consumer trends and awareness are important for production and successful introduction of new products and ingredients.

Keywords Food and feed applications · Enzymatic hydrolysis · Downstream processing · Bioactivity · Analytical chemistry · Consumers

Abbreviations

ABPs	Animal by-products
BAPs	Bioactive peptides
BSE	Bovine spongiform encephalopathy
EU	European Union
FTIR	Fourier-transform infrared
TSE	Transmissible spongiform encephalopathy

1 Introduction

The rapid growth, urbanization and increasing prosperity of the world population demand improved utilization of existing protein sources along with development of new and sustainable food production. The global demand for protein is expected to double by the year 2050. This is due to not only population growth but also increased recognition of the important role of protein in a healthy diet in general and especially for children and the growing elderly population [1]. Fish and meat products are important protein sources in the human diet and contain essential amino acids, minerals and vitamins. In industrial fish and meat processing, the main goal is to process the main products, such as fillets, chops and mince. However, these processes generate huge amounts of protein-rich residual raw materials. About 40–60 % of the total weight of animals and fishes are classified as residuals. This includes heads, bones, carcasses, blood, skin, viscera, hooves and feathers, depending on the species. Much of this material has great potential for higher-value applications in food and feed. This review focusses on how to increase the value of such material derived from livestock, poultry, fisheries, and aquaculture sectors. Such residuals can be divided into co-products, which can be used for human consumption, and by-products, which cannot (Fig. 1). Applications of by-products are strictly regulated; this review provides an overview of the most important European regulations. Moreover, it presents more established industrial processes, e.g. ensilage and rendering, as well as emerging processes, i.e. enzymatic hydrolysis, for processing of fish and meat co- and by-products. When selecting the most suitable process for each specific situation, a trade-off is possible. Established processes, with relatively easy production and low investment cost, represent a somewhat restricted product segment. On the other hand, more complex technology often requires higher investment cost, but allows for wider end markets and possibly higher market price for some products. The available volume, its quality and nutritional properties, together with current legislation, regulate the potential use and processing demands for residual raw materials. In

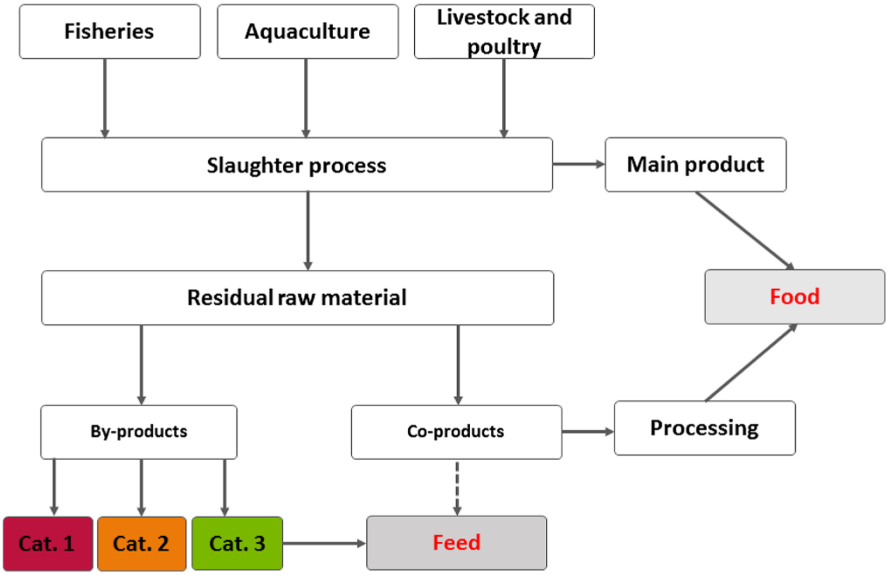


Fig. 1 Process from fisheries and farming of fish and livestock to co-products and by-products. Co-products are defined herein as residual raw materials from the slaughter process that still have food-grade quality and can be used for food. Other material not suitable for human consumption, for commercial or safety and/or regulatory reasons, is defined as by-products, separated into three categories (*1*–*3*) based on their origin and potential use in feed applications

addition, market demand, consumer acceptance, feasibility, technology awareness, the required level of process control, and the available infrastructure influence the choice of the most beneficial and cost-effective process.

2 Volumes and Nutritional Values

The total global production of fish from aquaculture and fisheries in 2014 is estimated to be 128 million tons (Table 1) [2]. About 70 million tons of fish are processed as main products globally, indicating that residual raw materials constitute more than half of the entire fish weight. It is important to stress that, in some cases, discarded fish are not included in reporting of volumes of residual raw materials and hence represent large lost values, estimated at 7.3 million tons [3]. In Norway, white fish and pelagic fisheries resulted in 43 and 12 % residual raw materials in 2015, respectively [4]. Here, the most underutilized materials consist of heads, intestines and roe from whitefish, and blood from aquaculture processing [4]. Another example is tuna processing, where reported values range from 50 to 55 %, or up to 70 % [5].

Looking at meat, total production has reached more than 263 million tons annually [6]. Table 2 presents production of some major types of livestock together with the percentage of by-products resulting from processing of these species in Norway [7–9]. Other figures from the USA on the portion of residuals generated, given in live weight of livestock, are 49 % from cattle, 44 % from pigs, and 37 %

Table 1 Summary of production of freshwater, marine and diadromous (living in fresh and salt water) fishes in 2014

Continent	Inland waters		Marine areas				Aquaculture value (USD 000s)
	Sub-total all production (ton)	Sub-total aquaculture (ton)	Sub-total all production (ton)	Sub-total aquaculture (ton)	All production (ton)	Aquaculture (ton)	
Africa	4,527,980	1,682,039	5,455,976	12,814	9,983,955	1,694,852	3,573,168
Americas	1,607,879	1,076,073	13,870,982	1,018,460	15,478,861	2,094,533	11,112,732
Asia	47,557,457	40,319,666	38,759,848	3,388,124	86,317,305	43,707,790	73,760,477
Europe	831,604	477,051	14,205,697	1,820,109	15,037,301	2,297,160	12,099,014
Oceania	20,165	4,432	1,281,690	63,124	1,301,856	67,557	756,601
Summary					*128,127,276*	*49,861,891*	*101,301,993*

Data based on Food and Agriculture Organization of the United Nations (FAO) global production statistics [2], divided into continental and global data with a subset showing aquaculture production

Table 2 Production summary of major types of livestock by continent in 2014 based on Food and Agriculture Organization Corporate Statistical Database (FAOSTAT) data [8]

Continent	Cattle 1000 head	Pigs 1000 head	Sheep 1000 head	Chickens 1000 head	Turkeys 1000 head
Africa	312,327	34,332	340,749	1,809,059	23,658
Americas	508,942	169,902	86,074	5,436,151	312,477
Asia	491,020	590,548	536,251	11,923,472	14,575
Europe	122,011	185,546	130,118	2,114,988	110,786
Oceania	40,226	5346	102,432	126,014	1377
Summary world	1,474,526	985,673	1,195,624	21,409 683	462,873
By-product (%)[a]	60	37	63	51	45

The final row shows the percentage of residual raw materials resulting from slaughter of each type of livestock based on Norwegian data [9]

[a] Figures based on the assumption that everything not sold as meat from the animals can be considered as by-product

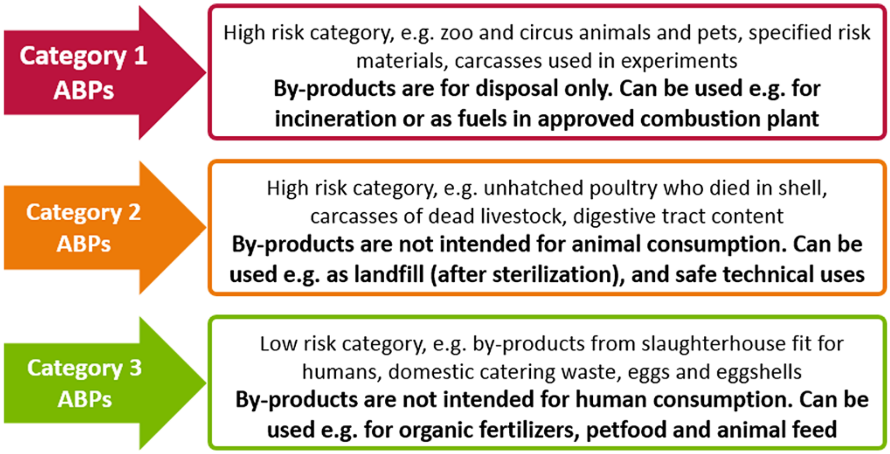
from broilers [10]. Independent of the particular percentages, as seen for fish above, the amount of residual raw material is directly related to the physiology of each species; For example, pig slaughter results in low amounts of residuals because large parts of the skin and fat contain substantial amounts of easily solubilized collagen, used as a binding ingredient in sausages and other mixed products. For cattle, almost 20 % of the residual material consists of bones. Bone marrow contains large amounts of protein and was considered an excellent feed ingredient before the bovine spongiform encephalopathy (BSE) scandal in 1992. Nowadays, marrow bone is regulated as a specified risk material for destruction.

All these residual raw materials represent a different set of possibilities and challenges that it is important to investigate and solve before successful industrial processing. Although a large part of this biomass is utilized today in many countries, significant quantities are still under- or unutilized. Both animal and fish residuals have excellent nutritional value, and this material contains large amounts of high-quality protein, lipid, micronutrients and minerals that could be better utilized towards human consumption and other kinds of product. The protein content of meat-based residuals is generally 10–23 g per 100 g raw material, with porcine chitterlings and brains at the lower end and ears, feet and liver at the top end [11]. The protein in these different organs has different nutritional value and is more or less accessible, which is important from a processing perspective.

3 Regulatory Framework

The laws and regulations governing collection, transport, storage, handling, processing, use and disposal of residual raw materials are often-overlooked factors that severely influence the number of applications available for processing of this material. It is outside the scope of this review to cover all regulations worldwide; rather, we exemplify their importance by reference to European Union (EU) legislation. When material is found to be unfit for food but suitable for feed, it is classified as an animal by-product (ABP) and must be processed at appropriate by-product plants, according to EU regulations. After the material has reached such a facility, it can no longer be upgraded for food use. It is therefore imperative that as much as possible of residual raw materials is handled according to food hygiene regulations if the intended use is processing for human consumption.

The EU has developed an elaborate legislation framework governing the use of residual raw materials from fisheries, aquaculture, livestock, and poultry industries. The type and quality of each residual material are of utmost importance for its further processing possibilities and define its use for food or feed applications, according to the hygiene rules for food of animal origin [12]. Raw materials that do not meet the general rules for food hygiene or are classified as not suitable for human consumption are regulated by the rules of ABP regulations [13] and implementation of health rules for animal by-products and derived products not intended for human consumption [14]. ABPs can be divided into three categories (1–3; Fig. 2) based on their origin and potential risk to public and animal health and the environment. No ABPs can be used for human consumption, and only low-risk, category 3 by-products can be used for feed production. Some animal parts are not eligible for either food or feed use and are classified as category 1, specified risk materials. These include bone marrow, spinal cords and brains from cattle, sheep and goats, and sick and dead animals [13]. Category 3 by-products are further classified according to their origin, i.e. ruminants or non-ruminants, due to the risk of transmissible spongiform encephalopathy (TSE). A compilation of regulations for use of different category 3 ABPs in feed is presented in Table 3. ABP [13] together with TSE regulations [15] are major components of the EU's strategy to eradicate feed-borne crises such as BSE in cattle, foot and mouth disease and dioxin contamination. The main objective of these regulations is to protect the population and farmed animals from any health risks related to contamination by infectious microorganisms or heat-stable bacteria-derived toxins (e.g. histamine and enterotoxins).



High risk category, e.g. zoo and circus animals and pets, specified risk materials, carcasses used in experiments

By-products are for disposal only. Can be used e.g. for incineration or as fuels in approved combustion plant

High risk category, e.g. unhatched poultry who died in shell, carcasses of dead livestock, digestive tract content

By-products are not intended for animal consumption. Can be used e.g. as landfill (after sterilization), and safe technical uses

Low risk category, e.g. by-products from slaughterhouse fit for humans, domestic catering waste, eggs and eggshells

By-products are not intended for human consumption. Can be used e.g. for organic fertilizers, petfood and animal feed

Fig. 2 Brief summary of by-products included in each of three animal by-product (ABP) categories regulated in the EU, and examples of some approved uses of ABPs in each category [13]

Table 3 Overview of category 3 animal by-product material from different animals suitable for feed use according to TSE regulation [15]

	Ruminants	Non-ruminants	Fish	Pets and fur animals
Processed protein from ruminants	✘	✘	✘	✔
Processed protein from non-ruminants	✘	✘	✔	✔
Blood from ruminants	✘	✘	✘	✔
Blood from non-ruminants	✘	✔	✔	✔
Hydrolyzed protein from ruminants	✘	✘	✘	✔
Hydrolyzed protein from non-ruminants	✔	✔	✔	✔
Collagen and gelatin from ruminants	✘	✘	✘	✔
Collagen and gelatin from non-ruminants	✔	✔	✔	✔
Fishmeal	✘	✔	✔	✔

Production plants that process category 3 by-products must comply with the general hygiene requirements provided in ABP regulations [13] and have a documented pest control program. Materials that have not received specific heat treatment during start-up or leakage must be either recirculated through the applied heat treatment step, collected and reprocessed, or discarded. The health rules regarding ABPs [14] describe several processing methods approved for heat treatment of category 3 by-products, based on methods 1–5 and 7 for material originating from domestic animals and methods 1–7 for aquatic animals (Table 4). The different heat treatment operation conditions are based on the following critical control parameters: (1) raw material particle size, (2) achieved core particle temperature level, (3) pressure, (4) duration of heat treatment and (5) in case of chemical treatment, the achieved pH level. In the case of fish processing, the material rapidly becomes tender as muscle proteins coagulate and disintegrate when exposed to mechanical forces in a cooker, strainer, screw-press or screw conveyor. Based on experience, reduction of particle size prior to the heat treatment step is not required to achieve uniform temperature throughout fish material [16]. Moreover, high shear forces during grinding might cause fat separation problems due to formation of emulsions and should be avoided if not needed.

4 Post-harvesting Handling, Industrial Processing and Analysis of Meat and Fish Residual Raw Materials

Both meat and fish residual raw materials represent a rich supply of easily available nutrients. However, they have high moisture content and are therefore easily spoilt in presence of microorganisms. Microorganisms can contaminate such materials via the fish and animals themselves, e.g. from the gastrointestinal tract or by contamination from hooves and/or hide and skin. Contamination can also come from the processing environment, e.g. due to poor employee hygiene or process facility cleansing routines. The commonest type of contamination is bacterial, but yeast and molds can also contaminate meat products. A broad battery of techniques are used post-harvesting for preservation of meat- and fish-based products [17], also

Table 4 Approved alternative methods for heat treatment of category 3 animal by-products [14]

Method	Particle size (mm)	Core temperature (°C)	Time (min)	Pressure (bar)	pH	Batch	Continuous
1	50	>133	20	3		×	×
2	150	>100	125	NS		×	
	150	>110	120	NS		×	
	150	>120	50	NS		×	
3	30	>100	95	NS		×	×
	30	>110	55	NS		×	×
	30	>120	13	NS		×	×
4[a]	30	>100	16	NS		×	×
	30	>110	13	NS		×	×
	30	>120	8	NS		×	×
	30	>130	3	NS		×	×
5[b]	20	>80	120	NS		×	×
	20	>100	60	NS		×	×
6[c]	50	>90	60	NS	<4.0	×	×
	30	>70	30	NS	<4.0	×	×
7[d]	NS	>76	20	NS		×	×
	NS	>70	20	NS		×	×

NS not stated

[a] Carver–Greenfield process, i.e. heating in a vessel with added oil

[b] The by-products must be heat coagulated and mechanically pressed to remove water and fat before final heat treatment

[c] Animal by-products originating from aquatic animals or aquatic invertebrates only

[d] Method approved by Norwegian authorities (wild fish >70 °C, aquaculture fish >76 °C; Nygård [16]), or any method authorized by the competent authorities complying with the following microbiological standards: *Clostridium perfringens* absent in 1 g product after heat treatment, *Salmonella* absent in final product ($n = 5$; $c = 0$; $m = 0$; $M = 0$), *Enterobacteriaceae* ($n = 5$; $c = 2$; $m = 10$; $M = 300$ in 1 g)

being valid for by- and co-products [18]. In industrial processing, conservation can be done before processing, but it can also be coupled with processing methods, e.g. in the case of fish silage. Conservation can also be minimized or potentially excluded in cases where the slaughterhouse is close by or even connected to the processing facility for residual materials. This ensures valorization of absolutely fresh residual raw materials.

4.1 Chilling and Freezing

Chilling and freezing are preferred methods in the meat and poultry industry to preserve the quality of main products. Cooldown is performed after processing and removal of the main product. By- and co-products from both fish and meat can be handled in the same way to preserve their quality, and chilling/freezing is easily facilitated in established slaughterhouses. Plate freezing equipment is applied to block-freeze mixed residuals sold as wet feed to the fur animal industry.

Fish residuals present some additional problems associated with conservation. Psychrotrophic microorganisms, which can grow at temperature as low as −5 °C, are present in fish from cold waters, affecting the temperature needed for effective conservation. Furthermore, the amount of microorganisms present in the digestive system of many fish species is dependent on season. Some smaller fish species such as capelin, herring, anchovy and sprat have high hydrolytic enzyme activity caused by active feeding on zooplankton during some periods of the year. Such species are prone to autolytic degradation and enhanced bacterial spoilage due to tissue softening and belly burst, which can be prevented by chilling.

Chilling of fish and residual raw materials onboard the fishing vessel is challenging. Many chilling techniques involve addition of water or ice to obtain heat transfer. Modern large-scale fishing vessels are normally equipped with active chilling systems based on circulation of refrigerated sea water or in combination with refrigerated fresh water to reduce salt uptake by fish. Low salt uptake is important to comply with fishmeal specifications regarding salt and ash content. Disinfection of pipes and the chilling system by ozone injection [19] or other antimicrobial agents improves the quality of recirculating water before addition of captured fish. This industrial practice has significantly improved the quality of pelagic fish caught for production of fishmeal and oil for use in animal feed, especially when combined with the optional addition of acetic acid. Chilling by addition of crushed ice is also possible but difficult to apply in large-scale operations. A promising option is production of ice slurry by partial freezing of sea water [20]. This technology results in pumpable ice and a very high chilling rate due to the content of small ice crystals and high cooling capacity. Excess blood-water generated by the above chilling technologies is generally drained off and pumped at sea. A novel cooling approach, avoiding addition of water, is use of solid carbon dioxide [21]. The choice of cooling medium and technology depends on several factors including the scale of the operation, the need for chilling to ensure quality before further processing, investments and energy consumption.

4.2 Organic Acid Preservation and Fish Silage

Preservation of meat- and fish-based foods using low-molecular-weight acids has been known for centuries [22]. Lactic, acetic, propionic, citric and benzoic acid are all organic acids used as food preservatives as well as being food ingredients, adding to their value and usefulness. This conservation principle is based on dissociation of the organic acid after diffusion through the microbial cell wall. This reduces the cytoplasmic pH, and in combination with accumulation of acid anions, inhibits cellular functions [22, 23].

Lactic and acetic acid are used to prevent contamination of freshly slaughtered beef carcasses after removal of hides and before or after evisceration [17]. Production of fish silage using organic acids is a well-established method in Scandinavia for preserving proteins and obtaining value-added products from fish raw material that would otherwise not be utilized. Fish silage can be described as a liquid product that develops when all or parts of the fish are treated with acid [24]. Use of fish silage in fish and animal feed has been widely studied, and it is regarded as a well-suited protein source [25, 26]. For preparation of fish silage, the raw material must preferably be crushed or ground and the mixture stirred to ensure good contact between the raw material and added acid. At acidic pH <4.5, enzymes naturally present in fish viscera degrade and liquefy the fish tissue without risk of bacterial spoilage [26]. A schematic overview of the production of crude silage is shown in Fig. 3. Further downstream processing of crude silage is covered in Sect. 4.5.2.

The rate of autolysis is determined by the content and activity of digestive enzymes, pH and temperature. Most commonly, formic acid is used, producing a stable silage at pH of about 4.0–4.5. Antioxidants, such as ethoxyquin, are added to prevent oxidation of fish oil. Production of fish silage is a relative simple and low-cost technology, but requires strict process control to avoid growth of spoilage bacteria. Moreover, this approach can be adapted to operations of any scale, and the final products are stable and can be stored for long periods. In Norway, production of fish silage is the main technique used for preserving marine by-products [4]. The final product is not suitable for human consumption, and silage technology should preferably be based on fish and residuals found unfit for food production. Although there have been reports of ensiling of chicken intestines [27], we are not aware of examples of industrial implementation of this technology for preservation of ABPs.

4.3 Salting and Production of Fish Sauce

Fish sauce is used as a condiment in large areas of South-East Asia. Conservation during production is achieved by addition of sea salt to fish raw materials. The mixture is stored for several (6–12) months at ambient (normally tropical) temperatures, until a clear, amber water solution, rich in hydrolyzed protein and salt, can be recovered. Very few microorganisms can survive and grow at such high salt concentration, and after a couple of months of storage, only low numbers of harmless halophilic bacteria are present. In addition to hydrolyzed protein and free amino acids, this liquid also contains short-chain fatty acids and aldehydes, adding cheesy and meaty aromas to the dominant sharp, salty taste [28]. To obtain good product stability, the amount of salt added to the fresh raw material must be in the range of 1:3–1:2 by weight. Normally, industrial production is performed in square concrete tanks covering large flat areas close to fishing harbours. In principle, fish sauce can be produced from most kinds of fish raw materials. Lean raw materials are

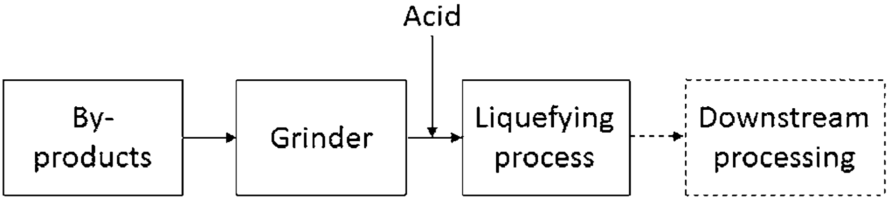


Fig. 3 Simplified illustration of silage process. The raw material must be ground for good contact with acid. At acidic pH, enzymes present in fish viscera degrade and liquefy fish tissue without risk of bacterial spoilage due to the low pH. The silage gradually liquefies due to the activity of tissue-degrading enzymes naturally present in the fish, mainly in viscera. Silage can either be used as is (crude) or be further processed (Fig. 5)

more suitable than fat raw materials, since the oil fraction does not contribute significantly to the volume of sauce recovered. Although fish sauce is normally produced from tropical fish species, pilot-scale experiments in Spain, Canada and Norway have shown that good-quality fish sauce can also be obtained from temperate- and cold-water fish species. Presence of intestinal tryptic enzymes, however, is of premium importance to achieve good protein hydrolysis and sauce recovery. There are considerable variations in the level of intestinal enzymes in small pelagic species, particularly in those from temperate and cold waters. To compensate for low levels of tryptic enzymes, suitable amounts of minced intestines from carnivorous white fishes can be added, since the intestines of such fishes always contain high levels of tryptic enzymes [29]. The major application of fish sauce is as a salting and flavouring condiment for vegetable dishes.

4.4 Rendering

Processing of animal and fish by-products is based on a common main principle called rendering technology. The raw material is heated to a temperature defined by legislation to eliminate any pathogenic bacteria, i.e. >70 °C for fish raw material and >100 °C for ABPs [14]. The main products from the rendering process are a protein powder and fat/oil. In this process, raw material is heat-coagulated followed by mechanical dewatering and separation steps to extract the oil phase, followed by thermal dewatering steps to concentrate the solubles and obtain dried high-protein powder [30, 31]. Such industrial-scale operations worldwide are fairly standardized, although some technology and process layout differences exist depending on the type of raw material and target product quality [32].

A general outline of the operation of such units for processing conventional fishmeal and oil is shown in Fig. 4. After heat treatment to 90–95 °C in a continuous screw cooker, the fish raw material is run over a strainer to remove free water and oil phase before entering a screw press. The compression ratio, normally 1:3.5–1:4 in a fish press, causes fish oil and water to be squeezed out of the coagulated material and through the sieve plates. The water and oil together with solubles and fine particles are collected in the bottom of the press and mixed with the oil/water phase removed by the strainer. The combined liquid streams are heated to above 90 °C and run over a decanter centrifuge to remove suspended fine solids before oil separation using a disc centrifuge.

4.5 Protein Hydrolysis

Protein hydrolysis is a method commonly used to extract proteins from meat and fish residuals. It involves breaking down proteins into smaller and more water-soluble peptides and free amino acids. The term “hydrolysis” literally means reaction with water, and protein hydrolysis requires presence of water molecules. The main purpose of hydrolysis is to increase protein recovery and the yield of valuable components. Protein hydrolysis can be achieved by chemical or enzymatic processes.

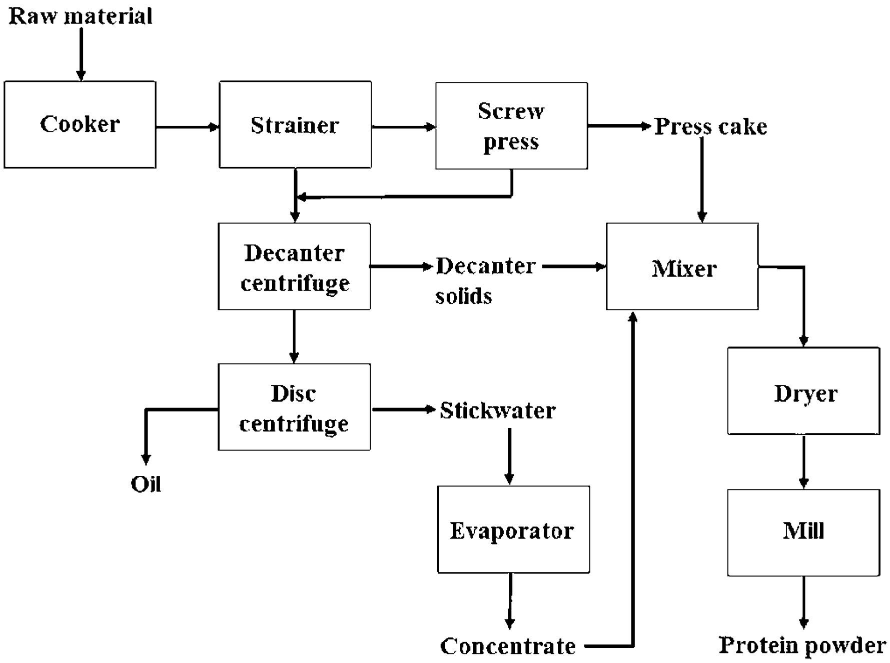


Fig. 4 Simplified process flow diagram showing the main unit operations applied in the wet rendering process. The raw material is cooked before entering the strainer. Decanter and disc centrifuges separate the solids, oil and stickwater phases. The stickwater is evaporated to a concentrate, mixed with the solids (press cake and decanter solids) and eventually dried to protein powder. The process conditions applied depend on the raw material and are listed in Table 4

4.5.1 Chemical Protein Hydrolysis

Chemical processing includes use of acid or alkali to cleave peptide bonds. Acidic protein hydrolysis is most commonly and frequently used to produce flavour enhancers from vegetables. Hydrolyzed vegetable protein is produced by treating the protein source with mineral acid (usually 4–6 M HCl) at 100–130 °C for 4–24 h followed by neutralization with NaOH [33, 34]. Alkaline hydrolysis is a straightforward process starting with protein solubilization by heat treatment followed by addition of alkaline agents (calcium, sodium or potassium hydroxide), adjustment of the temperature to a desired set point (usually 25–55 °C) and hydrolysis for several hours to achieve the desired hydrolysis product. Alkaline hydrolysis is less common in food and feed applications because of negative effects on the nutritive protein quality when using alkali. Thermal processing at alkaline pH can result in formation of toxic substances such as lysinoalanine, leads to racemization of L-amino acids to undesired D-amino acids and partly destroys the amino acids arginine, tyrosine, lysine, cysteine and threonine [35, 36].

Even though acid hydrolysis is preferred over alkali hydrolysis, the acid process can also influence the nutritive value of protein: the essential amino acids tryptophan and cysteine are destroyed, and glutamine and asparagine are converted to glutamic acid and aspartic acid [37]. Moreover, neither acid nor alkali hydrolysis is specific, and both generate large amounts of salt in the final product after the neutralization process. In general, processes based on chemical hydrolysis yield hydrolysates with reduced nutritional quality and poor functionality that are restricted to use as flavour enhancers [36]. Chemical hydrolysis involves use of highly corrosive acid or base and requires glass-lined stainless-steel reactors that can withstand high pressure and temperature [37].

4.5.2 Enzymatic Protein Hydrolysis

Production of protein hydrolysates using protein-digesting enzymes, i.e. proteases, is a very promising alternative for valorization of proteins from meat and fish by- and co-products for different markets. The process used in this technology is regarded as mild and results in high product yield without prejudicing nutritional quality by e.g. destroying amino acids as seen with chemical hydrolysis. Enzymatic hydrolysis decreases the molecular weight of intrinsic proteins and peptides and increases the number of ionizable groups, resulting in new peptides that are smaller and more water-soluble than the intact proteins [38]. A typical hydrolysis process is characterized by an initial rapid burst phase where the substrate is in excess. As the enzymatic hydrolysis reaction progresses, the reaction rate levels off. This can be explained by reduced enzyme activity caused by one or a combination of the following factors: change in reaction pH, fewer peptide bonds available for cleavage [39], substrate [40] and product inhibition [41], as well as the possible presence of protease inhibitors in the substrate [42].

Enzymatic hydrolysis can be performed either by use of (endogenous) enzymes that occur naturally in the substrate or by addition of commercially available (exogenous) enzymes. Production of fish silage is essentially endogenous enzyme protein hydrolysis using visceral digestive enzymes. As described in Sect. 4.2, the organic acid preserves the fish by-products, but lowering the pH also serves to activate digestive proteases from the fish. Use of endogenous enzymes is seen as an inexpensive and mild process; however, it usually requires long hydrolysis times and results in nonspecific hydrolysis. Hence, use of exogenous enzymes is considered the best choice for producing food-grade protein hydrolysates, as the process is highly specific and reproducible and may enable tailoring of well-defined hydrolysate products. Generally, the additional cost associated with use of the latter type of enzymes is considered justifiable in the enzymatic hydrolysis industry. This is because the specificity and higher reproducibility enable production of products with potential to reach higher-paying markets, compared with products based on e.g. rendering or ensiling. There are a vast array of commercially available proteases, and a judicious choice should be made with regards to enzyme performance and cost [43].

Proteins are complex substrates containing peptide bonds with different accessibility to enzymatic cleavage [44]. Proteases are ubiquitous and exhibit a huge diversity of action, e.g. in terms of substrate selectivity, where individual proteases cleave the peptide bond, and regarding pH and temperature preference [45]. In processing of protein-rich materials, protease selection is based on both product parameters, such as peptide size distribution, and the protein source [37]. Processing parameters also determine product outcome, e.g. enzyme-to-substrate ratio, pH and processing time. Careful optimization of these parameters enables development of products with selected properties.

A simplified protein hydrolysis process flow diagram is shown in Fig. 5. The raw material is minced and diluted with water to ensure good mixing and enzyme access [46]. Proper dilution can prevent product inhibition and maximize product yield, but added water is also a factor influencing processing costs associated with the drying process. A compromise between the desired product yield and the amount of water to be removed is imperative. The pH of the enzymatic hydrolysis process is often selected based on the optimum for a given protease [47]. However, adjusting the pH requires acid or base, which can result in high levels of salt in the final hydrolysate. This may reduce the nutritional value of the product and, if possible, should be avoided. At the end of the reaction, enzyme activity is terminated by its irreversible denaturation by heating to above 90 °C for at least 10 min. The crude hydrolysate is separated by a three-phase decanter into an oil, water and solid phase. The water phase constitutes water-soluble protein hydrolysate that can be concentrated in an evaporator followed by drying in a spray dryer. The solid phase contains bones and insoluble proteins that can be used in production of bone meal.

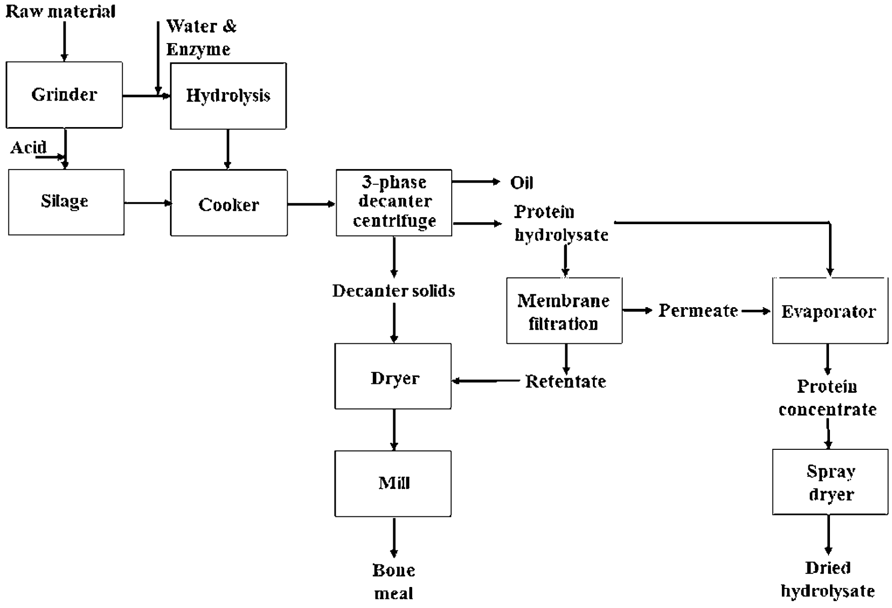


Fig. 5 Simplified process flow diagram showing the main unit operations applied in a hydrolysis process. The raw material is ground and mixed with water and enzyme, and the hydrolysis process is run using predefined time and temperature conditions. In case of silage production, acid is added to the raw material followed by hydrolyzation using inherent proteolytic enzyme activity at ambient temperature. Enzyme activity is terminated by cooking, and the crude hydrolysate is separated by three-phase decanter centrifuge into oil, soluble peptides and amino acids, and solid phases. The solids are dried and milled into bone meal. The protein hydrolysate can be membrane-filtrated to achieve desired a molecular weight distribution of peptides and eventually evaporated and dried to obtain dry protein hydrolysate

4.6 Analysis

Valorization of proteins from by- and co-products is, in most cases, based on heterogeneous raw materials with substantial and uncontrollable variation in quality. It is crucial to develop a production process that is robust towards raw material quality and variations in order to produce a stable product. An essential first step is thus evaluation of the raw material composition (e.g. fat, protein, moisture and ash). The Kjeldahl nitrogen method for protein determination is a commonly used analytical approach based on classical wet chemistry. The method provides figures for the total nitrogen content in a sample, providing the protein content after multiplication by a suitable nitrogen-to-protein conversion factor. Food matrices contain other nitrogenous organic compounds that will influence the determination of the true conversion factor, such as non-protein amino acids and nucleotides. Substrate-specific nitrogen-to-protein conversion factors have been calculated for poultry by-products, meat and bone meal, and Atlantic salmon head and backbone residuals [43, 48]. Another important parameter for characterization of raw material is the amino acid composition. Amino acid analysis is typically performed using chromatographic methods and can provide important knowledge about the nutritional properties of the raw material.

The above analytical measurements are performed offline and typically on a small representative sample from a batch of raw material, and the heterogeneity of meat- and fish-based products poses a significant challenge for representative sampling. Rapid and non-destructive spectroscopic techniques such as fluorescence, Raman and near-infrared spectroscopy have been demonstrated to be valuable tools for characterization of raw materials and products in terms of gross composition [49, 50]. Such approaches are expected to be essential for enzymatic protein hydrolysis in the future, where novel strategies for optimization and monitoring are used to obtain robust processes and products with defined quality.

One of the main control parameters in protein processing is the measured extent to which protein has been degraded. In this respect, measurement of the degree of hydrolysis, i.e. the percentage of cleaved peptide bonds, is a widely used approach for monitoring enzymatic protein hydrolysis. Another valuable parameter used for characterization of protein hydrolysates is the molecular weight distribution of the peptides. Unlike the degree of hydrolysis, which is always relative to the starting material, the molecular weight distribution is a direct measure of the peptides and proteins present. A major limitation of both of these measurement techniques is their laborious sample treatment and lengthy analysis time, limiting their use in industrial settings and as potential online monitoring tools. Recently, it was shown that Fourier-transform infrared (FTIR) spectra are useful for characterization of enzymatic protein hydrolysates [51, 52]. This technique has promising potential as an on- or at-line process monitoring tool for measurement of degree of hydrolysis. In the future, FTIR could thus be a valuable tool in industrial hydrolysate production by providing online process control, optimization possibilities and thus stable product quality.

Thorough characterization of individual peptides is also a very important aspect, especially if the chemistry of a given product is to be related to a specific sensory or biological activity. In such cases, chromatographic fractionation and mass spectrometry has been shown to be a powerful technique for unequivocal elucidation of peptides [53].

4.7 Scale-Up of Bioprocesses

Many of the processes used to convert fish and animal residuals to higher-value products are developed at laboratory scale and demonstrated at pilot scale. When developing new products from these biomasses, many processes fail to meet significant challenges in the transition from laboratory to industry scale. Thus, the upscaling steps need to be carefully planned already at the start of product development. The scale-up phase is commonly called the demonstration phase, where a prototype product can be produced, capital and operating costs of the process calculated and the product tested in the market. This is an important step in bioprocess development. One of the reasons for these challenges is the chemistry during process scale-up, where differences in mixing, shear rate, and mass and heat transfer result in differences in how the biomass is processed compared with small-scale processes. In addition, production of process inhibitors that are effective at large but not small scale can be experienced [54, 55]. Another challenge is the economics of the demonstration phase, which is referred to as the "valley of death" in product development. There is a lack of available risk capital to perform this step, and limited access to demonstration plants that can be used to test processes. Demonstration plants are needed to reduce the risk and cost of the demonstration phase. It is too risky for most developers to invest in a full-scale facility before the process or market acceptance has been demonstrated. A solution that has been successful in many countries is the establishment of publicly financed demonstration plants. Here, flexible plants are built and constructed to accommodate a large variety of different processes. In such plants, many different developers can test and demonstrate their process and the product in the market. Due to the flexibility of such plants, operating and capital costs can be estimated; however, loss of biomass and process yield will likely occur when using such flexible plants, which can be improved in a plant specially designed for one process. Still, publicly financed demonstration plants have been and will be important for continued commercialization of new biomasses towards new products [56].

5 Applications

Co- and by-products from fish and animal processing have great potential for use in food and feed products, as well as for other markets. For human consumption, it is important that residuals are not classified as ABPs. As described in Sect. 2, in general, co- and by-product materials contain high amounts of protein, with essential amino acids, vitamins and minerals.

5.1 Food Ingredients

Fish and meat co-products have several applications in food ingredients, if the process implements systems such as good manufacturing practice (GMP) and hazard analysis and critical control point (HACCP) [57]. Variety meats and other parts of animals that are traditionally considered edible, such as kidneys, liver and oxtail, can be used directly for human consumption. Collagen-rich material such as animal hides and bones and fish skin are used for gelatin production. In Norway, dried cod heads, co-products from the stock- and klippfish industry, and meat-rich salmon trimmings and backbones are sold for different food applications. There are also many different applications of blood in food production, e.g. as an emulsifier, stabilizer or clarifier [58, 59]. However, to use animal blood for human consumption, it must be extracted using special equipment in direct contact with a cooled tank to avoid contamination [60].

For some time now, production of enzymatic protein hydrolysates has attracted interest for use in human nutrition. The process is mild and does not impair the nutritional quality of the original protein substrate. Protein hydrolysates may have several applications as food ingredients, e.g. as emulsifiers or foaming agents. Other applications are in specialized adult nutritional formulas, e.g. in diets for the elderly who need extra protein supplements to maintain their body weight, formulas for infants with allergies to intact food proteins or with congenital metabolic disorders, and nutraceuticals [61–64]. A current drawback with production of protein hydrolysates is the generation of bitter and unpalatable tastes during the hydrolysis process. Bitter taste is mainly ascribed to small peptides of less than 1000 Da with hydrophobic and/or aromatic amino acids [65]. Not only the presence of hydrophobic and aromatic amino acids, but also the amino acid peptide sequence is important for the intensity of such bitter taste. Based on the hydrolytic specificity of the protease chosen, it may be possible to produce hydrolysates with different bitter potency from the same substrate [66]. It may also be possible to remove the bitter taste using different debittering techniques [67], although such techniques may be challenging in industrially relevant applications [68]. In general, restricting the hydrolysis to reach a low degree of hydrolysis with a broad molecular weight distribution will reduce the formation of bitter taste [66]. In addition to formation of bitter taste, protein hydrolysates have flavours related to the raw material, i.e. fish, chicken, meat etc., which influence the overall flavour profile. These flavours are not related to the protein, but rather water-soluble compounds present in the substrate [66].

5.2 Feed

Use of processed animal proteins in fish feed has several advantages compared with currently used plant proteins, as plant-derived feed ingredients may contain anti-nutrients and allergenic proteins [69]. Meat and bone meal and fishmeal are the final products from rendering of animal and fish by-products, respectively (Sect. 4.4). These are excellent feed sources due to their high content of essential proteins, minerals and vitamins. However, especially meat and bone meal may be subjected to large variations in nutritional quality. This is mainly caused by variations in the composition of the raw material and the harsh rendering temperatures applied [70, 71]. In addition, raw materials rich in bone will result in meal with high ash content, which is associated with low protein digestibility.

As described in Sect. 4.5.2, enzymatic protein hydrolysis results in two fractions with usable peptide content. One is a water phase with soluble peptides, and the other is a solid phase containing insoluble proteins and minerals. Both are frequently used as feed, although with large price differences. Protein hydrolysates have favourable formulation properties for animal feed, such as high solubility over wide ranges of pH and ionic strength, and a set of positive nutritional properties, including feeding stimulation and palatability enhancement, facilitated adsorption of e.g. labile and insoluble amino acids, and presence of beneficial hormone-like peptides [72]. As mentioned above, feed production is an area subject to a strict regulatory framework; a relevant review of the European regulatory framework and potential uses of ABPs for feed was published recently [73].

The potential valorization of proteins from fish residuals is not fully exploited [74]. In general, fish protein products have many applications within feed for the aquaculture sector and monogastric land animals such as weanling pigs, poultry and pets. The use and importance of fishmeal in the aquaculture sector have grown substantially over the last decades [75], and there is huge potential for increased fishmeal production from underutilized sources for this sector. Meat and bone meal from pigs and poultry may also have greater potential as feed ingredients within the aquaculture sector. In Europe, use of ABPs in fish feed has been restricted due to the risk of TSE, but these restrictions were lifted in 2012 for non-ruminant protein meal [76]. Recent studies evaluated the effects of poultry and porcine by-products as feed ingredients for Atlantic salmon and found that ABP material can provide about 50 % of dietary protein without negative effects on growth. Moreover, use of ABP protein did not show any severe negative effects on gut health, which is often a problem with plant-based diets [77, 78].

Piglets show greater preference for feed that includes either dried hydrolyzed porcine protein or fishmeal compared with other protein-rich feeds, e.g. soybean protein, wheat gluten and sweet milk whey. Feed based on fishmeal got the highest score at inclusion level of 50 g per kg, with high preference for feeds including hydrolyzed porcine protein over a wide inclusion range (50–200 g per kg) [79].

5.3 Pet Food

Companion animals, such as cats and dogs, represent additional consumption of protein via human purchasing. As such, this also represents an additional indirect protein need for humans. To ensure sustainable pet ownership in the future, pet food must be sustainable and affordable and effectively satisfy the requirements for good animal health and well-being [80]. In general, all category 3 by-product material is suitable for pet food production (Table 3). In production of wet pet food, only residuals that are eligible for human consumption (i.e. co-products), but found unfit for various reasons, can be used [13]. Pet food formulas are either dry, semi-dry or wet, and protein content varies between 10 and 50 %, with wet foods at the lower and dry food at the upper end [81].

Meat and bone meal products derived from rendered ABPs are used by many pet food producers. However, their popularity is declining due to several reasons, including the name of the product and its perceived association with TSE risk. Also, poultry meal is a widely used protein ingredient in pet foods. In general, poultry protein meals are well utilized by dogs and cats and make up a large share of the total protein in many premium pet foods [82]. Protein hydrolysates of both animal and fish origin are also increasingly utilized for pet food applications. These hydrolysates contain short peptides and free amino acids that might act as feeding stimulants and palatability enhancers [71, 83]. Moreover, protein hydrolysates might have hypoallergenic [84] and bioactive properties (as discussed below), making them interesting pet food ingredients for companion animals with special needs.

5.4 Health-Promoting Products

By- and co-products from the fish and meat industry are rich sources of biologically active molecules with potential health-promoting effects. Such bioactive molecules can be included in e.g. food (nutraceuticals) and as active ingredients in cosmetics (cosmeceuticals). Bioactive peptides (BAPs) are short chains of amino acids with hormone- or drug-like activity that modulate physiological functions through interactions with specific therapeutic targets [85]. Numerous BAPs derived from co-products have been proven to exhibit a wide range of positive health effects, with most such research focussing on blood pressure lowering, blood sugar regulation, and anti-microbial and anti-oxidant activities [86–88]. In addition to a specific therapeutic function, peptides may have other beneficial effects; for example, rats fed with hydrolyzed fish protein showed reduced visceral adipose tissue mass [89], and peptides derived from collagen were shown to increase muscle mass and strength in elderly men [90]. BAPs from by-products can also have a positive effect on collagen production, which makes them attractive ingredients in cosmeceuticals for wound healing and skin aging [91].

A standard process for evaluating the health-promoting potential of BAPs comprises several stages of analysis involving both in vitro and in vivo experiments. Ideally, to validate the bioactivity of a given bioactive peptide, human intervention studies are necessary. However, such studies are expensive and typically conducted after selecting a potent candidate through a rigorous screening process. The majority of screening experiments for BAPs are performed using in vitro assays including enzymatic assays, cell cultures, genomic tests and in vitro digestion stimulation. Candidates identified through such screening exercises are further evaluated using animal models and eventually human intervention studies (Fig. 6).

A large proportion of the reported bioactivities of meat and fish protein hydrolysates are based on either chemical or enzyme-based bioassays. BAPs in food must be absorbed in the intestine during digestion, and enter the bloodstream to exert their physiological effect, although some peptides may act locally in the

Fig. 6 Comprehensive method platform for testing health-promoting ingredients, from preliminary in vitro digestion models, bioactivity screening assays, to extensive human intervention studies

stomach or intestine. After absorption, BAPs can act on a given therapeutic target as a single molecule or synergistically [92]. BAPs from different meat and fish processing co-products have been shown to possess bioactivities towards key therapeutic targets related to diseases such as diabetes, obesity and coronary heart disease [53, 93–95]. Cell models can provide additional knowledge after preliminary bioactivity screening assays, including endogenous effects, dose-response and target organ. Some peptides exert their effect on muscle development, while others influence liver, bone, angiogenesis, inflammation etc. It is therefore vital to use different types of cell model when examining such bioactivity effects.

5.5 Other Applications

It is important to stress that there are a huge number of applications for products based on meat and fish residual raw materials that are not covered above. Protein hydrolysates based on both chemical and enzyme production can be used as growth media in areas of fermentation and biotechnology for production of pharmaceuticals and recombinant proteins, as well as in diagnostic media [96]. Blood from various animals has also shown antioxidant and antimicrobial activity [97]. Also, bovine serum albumin extracted from blood is an important tool in microbiology and many enzyme assays. Various enzymes extracted from livestock livers are used in many biotechnology applications, e.g. several types of dehydrogenases and catalase from bovine liver and porcine liver esterase. Aside from being an excellent feed source, poultry feathers can be used for a range of non-food applications [98]. Examples span electrical and electronic applications, composite materials, oil adsorbents and generation of micro- and nanoparticles. Meat and bone meal and fat from the rendering process may also be used as fertilizers and biodiesel or as raw materials for the chemical industry, respectively [99].

6 Utilization of Co-products towards Consumer Products

In valorization of meat and fish by- and co-products, the human consumption market has been specifically challenging to reach. In the meantime, consumers are becoming increasingly concerned about the environment and sustainability. This trend is expected to continue or even increase in the future, with consumers aiming to influence industries via their consumption pattern, i.e. food, and particularly protein production [100]. Being an integral part of the value chain, consumers influence both the levels of food waste and the acceptance of value-added co-products [101]. Still, challenges remain regarding regulations and the feasibility of introducing products for human consumption in terms of supply, control and economics [56]. Only minor efforts have been made so far to understand the best approaches for upgrading fish- and animal-based co-products to lucrative products for human consumption [102].

Fish- and animal-based by- and co-products can be used in development of new products or to replace ingredients in existing products. Much of this work is following an “industry push” strategy, where products are tested with consumers after most product development decisions have already been made [103]. Currently, there is a lack of awareness regarding the need for consumer acceptance, which is of utmost importance for market success of potential products based on ingredients from new sources [104, 105]. Thus, poor product development strategies can lead to product failure. To improve this strategy, implementation of systematic product testing will likely increase the chance of market success [106].

Information about products and production methods have repeatedly been shown to influence consumer choices [107]. Studies on use of added-value compounds usually rely on analytical and sensory testing processes that do not take into account the consumer perspective [108]. In rare cases, consumer acceptability studies are included, but usually on end products and without providing information about the origin of the ingredients [109]. When excluding information about origin in use of trained panels or consumers for tasting of food products, it is hard to estimate the actual acceptability of a product by consumers in the real market. Provision of relevant information as part of a balanced communication strategy could increase consumer demand for products with proteins from production methods with reduced environmental impact [110].

Consumers have adequate knowledge on how to use food ingredients and supplements, but besides segments of particular interest, they are rarely aware of product production methods [111, 112]. When new products or ingredients are presented to the market, consumers become more alert and curious regarding their origin [113]. This concern has been one of the main barriers to e.g. use of ABPs or genetically modified ingredients in salmon feed, despite the potential benefits [114]. Considering the fact that consumer acceptance varies and changes with exposure to products and information, it is possible to achieve potential improvement of products without sacrificing quality [115].

When consumers analyze their food choices, they are confronted with trade-offs between convenience, health and sustainability that may challenge their final decisions [116]. Thus, communicating one positive element of a product, such as “sustainability” or “using the whole animal”, should not come in the way of aspects such as “food safety”, “health”, “convenience”, “hedonic expectations” etc. In fact, it is more probable that products will be chosen by consumers if all positive elements of the product are combined with production information in a holistic and transparent reputation-building strategy. Such a strategy could be successful when used in combination with targeting of consumers that are interested in functional foods and likely to seek additional information about the product [117].

Despite continuous improvements, there has been an increase in public concerns about livestock and aquaculture production, due to food crises and the environmental impact of production practices [118]. This has led consumers away from consumption of meat proteins in favour of plant proteins [119]. An expected positive trend in the near future is that consumers will demand fish that is farmed under safe and controlled conditions in clean waters [120]. Therefore, any information supplied to consumers should focus on trust building, with transparent and balanced communication. This type of approach could establish a fertile ground for introduction of new products and ingredients in the market for human consumption, such as products based on sustainable co-products from fish and animals.

7 Challenges and Future Trends

There are a growing number of initiatives in the context of the foreseen transition from an oil-based economy to a bioeconomy. This includes concomitant awareness of consumers, producers and governments about the importance of recovery and recycling of what was previously regarded as waste. In many countries worldwide, research funding is being directed towards finding new methods to optimize recovery and exploitation of intrinsic raw material components, preferably using a biorefinery approach to enable maximum utilization. There is immense potential for growth when it comes to increased valorization of fish- and animal-based co- and by-products. As more products reach the market, producers will start competing for what are now inexpensive starting materials, and one can expect higher prices for residual materials in the future. At the same time, producers must be able to rely on a stable supply of raw materials to obtain the predictability required for production.

Many of the technologies described above form the basis of established industries, with well-established processing operations and well-known markets. Enzymatic protein hydrolysis represents an up-and-coming, relatively new industry based on a highly enabling technology, showing great promise based on published research. However, when implemented in industrial practice, results show that there are challenges related to controlling the number of variables that affect the properties and quality of the final product. This includes raw material variations, processing parameters such as pH, time, choice of enzyme and inactivation method in protein hydrolysis, choice of downstream unit operations and choice of drying method. Current industrial practices rely on traditional and established analytical tools for quality parameter evaluation. However, this methodology cannot provide the fast feedback required for production of products with specific properties. In the future, nondestructive spectroscopy-based technologies could be valuable tools for industrial production of protein hydrolysates, by providing online process control, new optimization possibilities and reduced product quality variation.

Considering the predictions of future food shortages, it makes sense to strive to use as much of high-quality meat and fish co-products for human consumption as possible. There is increasing interest in upgrading such residual materials for human consumption; however, consumer acceptance and preferences should be known and targeted before products reach the market. Sometimes the desired market growth is hindered by a lack of synergy among stakeholders, and a lack of common vision. Achieving perfect collaboration among all stakeholders is challenging, but increased cooperation will lead to shared vision, strategic planning, targeted communication and overall image improvement.

Image improvement forms the foundation for societal acceptance, and vice versa, societal perceptions can also inform strategic decisions of stakeholders towards image improvement and positive reputation. Based on systematic research, stakeholders will reach a point where there is less "waste products" and "residual raw materials" but rather optimized utilization and processing of all resources.

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Compliance with Ethical Standards

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REVIEW

Integration of Waste Valorization for Sustainable Production of Chemicals and Materials via Algal Cultivation

Yong Chen[1,2,3] · Li-ping Sun[1,2,3] · Zhi-hui Liu[1,2,3] · Greg Martin[4] · Zheng Sun[1,2,3]

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Abstract Managing waste is an increasing problem globally. Microalgae have the potential to help remove contaminants from a range of waste streams and convert them into useful biomass. This article presents a critical review of recent technological developments in the production of chemicals and other materials from microalgae grown using different types of waste. A range of novel approaches are examined for efficiently capturing CO_2 in flue gas via photosynthetic microalgal cultivation. Strategies for using microalgae to assimilate nitrogen, organic carbon, phosphorus, and metal ions from wastewater are considered in relation to modes of production. Generally, more economical open cultivation systems such as raceway ponds are better suited for waste conversion than more expensive closed photobioreactor systems, which might have use for higher-value products. The effect of cultivation methods and the properties of the waste streams on the composition the microalgal biomass is discussed relative to its utilization. Possibilities include the production of biodiesel via lipid extraction, biocrude from hydrothermal

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Yong Chen, Li-ping Sun and Zhi-hui Liu equally contributed to this work.

✉ Zheng Sun
zsun@shou.edu.cn

[1] International Research Center for Marine Biosciences, Ministry of Science and Technology, Shanghai Ocean University, Shanghai 201306, China

[2] Key Laboratory of Exploration and Utilization of Aquatic Genetic Resources, Ministry of Education, Shanghai Ocean University, Shanghai 201306, China

[3] National Demonstration Center for Experimental Fisheries Science Education, Shanghai Ocean University, Shanghai 201306, China

[4] Department of Chemical and Biomolecular Engineering, University of Melbourne, Melbourne, VIC 3010, Australia

liquefaction, and bioethanol or biogas from microbial conversion. Microalgal biomass produced from wastes may also find use in higher-value applications including protein feeds or for the production of bioactive compounds such as astaxanthin or omega-3 fatty acids. However, for some waste streams, further consideration of how to manage potential microbial and chemical contaminants is needed for food or health applications. The use of microalgae for waste valorization holds promise. Widespread implementation of the available technologies will likely follow from further improvements to reduce costs, as well as the increasing pressure to effectively manage waste.

Keywords Biomass utilization · Metabolic pathways · Culture systems · Bioenergy · By-products

1 Introduction

Industrial development and intensified agricultural production have given rise to serious pollution problems from waste gas, wastewater, and solid waste. In general, waste gas is discharged directly into the atmosphere, and this large amount of untreated gas exacerbates global warming. It is well known that the main cause of global climate change is the uncontrolled discharge of greenhouse gas, which is largely the result of human activity and industrial production [1]. CO_2, an important component of waste gas pollution, is derived from the burning of fossil fuels and solid waste [2, 3]. Excess nutrients (such as nitrogen and phosphorus) in wastewater can lead to eutrophication and ecological imbalance [4]. The direct damage from eutrophication includes three main aspects: (1) reduced biodiversity, such as the loss of dominant species; (2) damage to the water environment, such as increased toxicity; and (3) changes in the physical properties of water, such as increased turbidity. According to Dodds et al. [5], the economic cost of water eutrophication in the United States is approximately $2.2 billion per year. At the same time, an outbreak of cyanobacteria will indirectly affect the health of residents in proximity to the affected water, and hinder the development of tourism [6]. Heavy metal pollution from wastewater is also a serious concern. For example, the total amount of wastewater discharged from China increased from 65.9 billion tons to 73.5 billion tons between 2011 and 2015. The emissions of phosphorus and nitrogen in the wastewater remained constant, while heavy metal components (e.g. Cr, As, Pb, Hg) increased each year (Fig. 1). Food waste is considered the most important category of solid waste. In Hong Kong, for example, food waste accounts for about 36–40% of municipal solid waste [7]. In daily life, this waste produces odor or mildew, further threatening sanitation and health. In addition, as Hartmann and Ahring [8] pointed out, soil-buried food wastes are an important source of greenhouse gas emissions. Landfill gas is mainly produced by the degradation of organic waste, and is composed primarily of methane (40–70% by dry volume). Methane has a thermal effect 20 to 25 times that of CO_2, further exacerbating the greenhouse effect [9].

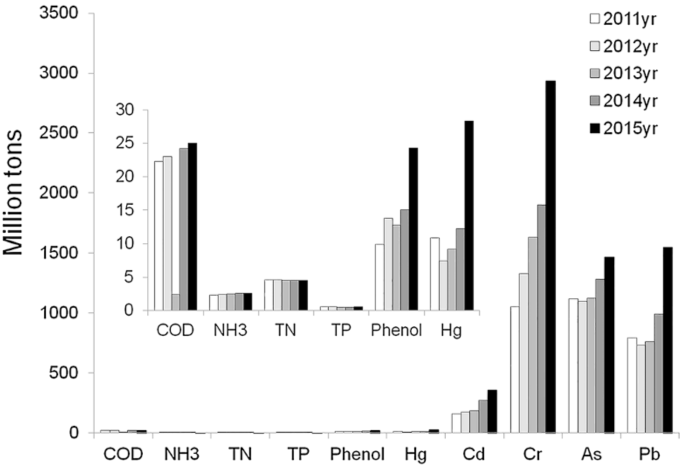

Fig. 1 Wastewater composition in China 2011–2015

Traditional waste disposal methods largely comprise physical and chemical processes such as burial, filtration, sedimentation, and anaerobic fermentation. Compared to these methods, algae, and especially microalgae, have shown advantages in the efficient absorption of gaseous substances (such as CO_2) from waste gas, or the removal of nitrogen, phosphorus, and toxic metal components from wastewater [10, 11]. The use of algae to treat sewage can overcome adverse effects such as secondary pollution, potential nutrient loss, or suboptimal water use caused by traditional waste disposal methods. At the same time, microalgae can effectively clean water by removing eutrophic nitrogen, phosphorus, and other nutrients [12]. Nitrogen that is removed from wastewater by bacterial nitrification/denitrification alone is released in the form of nitrogen gas, whereas algae treatment can effectively deposit nitrogen in useful biomass. The economic viability of algae culture depends on the cost of the water source and the fertilizer and organic carbon used [13]. The use of microalgae culture strategies to make use of waste for the production of useful chemical and material products helps to reduce costs and promote environmentally sustainable development. For example, sugar, protein, oil, and fatty acids contained within the algal biomass can be used as raw materials for chemicals, materials, and energy alternatives [14]. In particular, the oil from microalgae can be converted into biodiesel via transesterification, and fatty acids can be converted into synthetic plasticizers [15, 16], surfactants [17], or other chemical products [18]. Starch can be a sugar platform for fermentation [19] or hydrolyzed to produce polyols [20]. In this paper, we first summarize different types of waste, considering the means by which microalgae can absorb, metabolize, and transform this waste to promote their own growth. Second, we explore different cultivation methods/systems and the effects of microalgae on waste purification. Finally, we discuss the prospect of bioenergy.

2 Waste and Nutrient Sources for Algal Growth

Of the many sources of waste, microalgae are most suitable for treating large point-sources of flue gas, wastewater, or organic waste. This section will describe how microalgae use these three types of waste as resources for their growth.

2.1 Flue Gas as Carbon Dioxide Feedstock

Much of the global CO_2 emissions from flue gas are discharged directly into the atmosphere [1, 21]. The use of flue gas as an inorganic carbon source can promote algal growth, diverting the release of CO_2 into useful biomass. Photosynthetic growth of microalgae can be significantly enhanced by the addition of flue gas to the culture medium [22]. The provision of CO_2 means the growth is not limited by carbon availability (as it is if relying solely on atmospheric CO_2), allowing full utilization of the solar energy resource. The overall process involves the chemical reduction of CO_2 via the Calvin–Benson cycle, to produce organic carbon that can be used for cellular biosynthesis. This is an energy-intensive process that is fueled by photosynthesis. The mechanisms of CO_2 assimilation and utilization in microalgae are complex. As shown in Fig. 2, CO_2 in the flue gas dissolves in the liquid growth medium as CO_2 molecules, carbonates, or bicarbonate ions. CO_2 molecules are able to cross the cell membrane through free diffusion, whereas carbonates and bicarbonates are a class of charged ions that must be actively transported into the cell. Carbonic anhydrase located in the chloroplast is used to produce CO_2 efficiently, which is a kind of CO_2 concentrating mechanism that

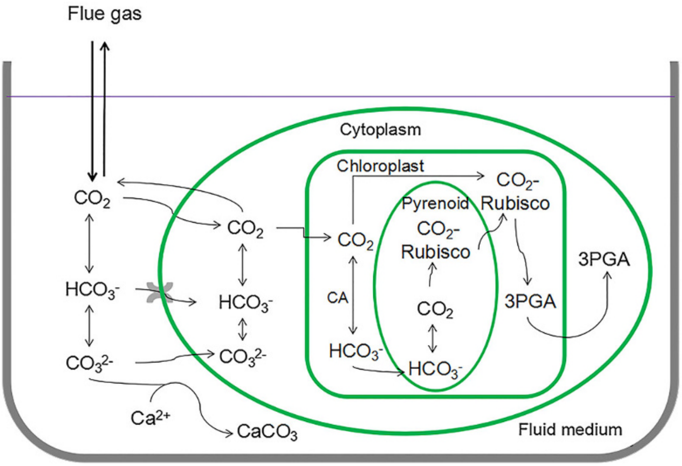

Fig. 2 Pathway of inorganic carbon uptake, conversion and storage in algae [23–25]. Carbon dioxide molecules, carbonates, or bicarbonate ions in the culture medium enter the cells in different ways. The carbonic anhydrase on the chloroplast captures carbon dioxide and binds to the RuBisCO located in the protein core via condensation to produce unstable intermediates. It is then cleaved into 2 molecules of 3-phosphoglycerate, and the resulting 3-phosphoglyceraldehyde is involved in the metabolism in cytoplasm. *CA* carbonic anhydrase

occurs under low CO_2 concentrations [23]. CO_2 and ribulose-1,5-bisphosphate carboxylase/oxygenase (RuBisCO) condense into unstable intermediates, and cleave into 3-phosphoglycerate; the phosphoglycerate kinase in the matrix catalyzes the transfer of phosphate groups to produce 3-phosphoglyceraldehyde, which can either be used to synthesize starch or other carbohydrates for energy storage, or be funneled directly into glycolysis to release energy for the cells [24, 25].

Many research efforts have been dedicated to investigating how to best combine algal growth with flue gas utilization. The traditional approach is to sparge CO_2 bubbles to cultures. Almashhadani et al. [26] created bubbles within the medium by using a fluidic oscillation diffuser, while Fan et al. [27] used a kind of polyvinylidene fluoride hollow fiber membrane to generate microbubbles. It is worth mentioning that with these methods, much of the CO_2 may be lost to the atmosphere. Some researchers have suggested the use of membrane reactors to minimize CO_2 loss. In this case, CO_2 was dissolved directly into the medium rather than in the form of bubbles. For example, Kim et al. [28] employed a type of polyurethane and polyethylene membranes to deliver flue gas into algal medium. However, this method cannot avoid energy waste. In a study by Nole et al. [29], CO_2 was first absorbed in a solid sorbent and then stripped into a sodium carbonate solution to produce a bicarbonate solution. A CO_2-selective membrane was subsequently used to transfer dissolved CO_2 into seawater through contact between two liquids. The seawater was ultimately used as carbon source in photoreactors. Although this approach avoided the energy demand of solvent regeneration, a series of unit operations were difficult to realize. Zheng et al. [30] proposed a novel approach: in this case, CO_2 was absorbed into a potassium carbonate solvent and the gas was desorbed into microalgal medium via a non-porous polydimethylsiloxane hollow fiber membrane. This approach dramatically reduced the cost of capture. In addition to developing delivery technologies, many studies have investigated the biological response to flue gas, including the effects of different concentrations of CO_2 and flue gas contaminants. For example, Tang et al. [31] examined the carbon utilization efficiency of *Scenedesmus obliquus* and *Chlorella pyrenoidosa* at different CO_2 concentrations (0.03–50%). At a concentration of 10%, the carbon fixation efficiencies of *Scenedesmus obliquus* and *Chlorella pyrenoidosa* were 0.288 and 0.26 g L^{-1} day^{-1}, respectively. Yoo et al. [32] recently reported biomass yields of 0.077 and 0.203 g L^{-1} day^{-1} for *Botryococcus braunii* and *Scenedesmus*, respectively, cultured using 5.5% CO_2 of waste gas. However, Hauck et al. [33] found that excessive CO_2 in waste gas hindered the growth of algae. This may result from the lower pH due to the dissolution of CO_2. Concentrations of NOx, SO_2, and other substances tended to vary in relation to the CO_2 concentrations of the flue gas (Table 1). The percentage of CO_2 was continuously measured, and the concentrations of other components in flue gas were found to be decreased to the same extent. The effects of these contaminants have been studied. Although sulfur is indispensable for algal growth, sulfur dioxide has been reported to be toxic to some microalgae [35]. It is well known that SO_2 directly interferes with CO_2 fixation (inhibition of RuBisCO by SO_3^{2-}), energy metabolism (inhibition of mitochondrial ATP production by SO_3^{2-}), and the formation of organic sulfonates in plants [36]. However, few mechanisms leading to toxicity have been revealed in

Table 1 Mean concentration of components in flue gas with different CO_2 concentrations [24, 34]

Components of flue gas (%)	CO_2 concentration (%)		
	11.37	6.71	2.50
NO_x	45	26.6	9.9
SO_2	36.1	21.3	7.9
CO	0.45	0.27	0.1
TOC	0.714	0.421	0.157
Other toxic substances[a]	4.39	2.6	0.976

[a] Other toxic substances were mainly composed of HCl and Hg

microalgae. Thus far, studies on the biochemical effects of SO_2 are limited to its ability to act as a reducing or oxidizing agent. NO has been considered an important messenger in plant defense signaling against photo-inhibition and plant death. It is unclear whether NO plays a similar role in microalgae or affects algal physiological features. According to Nagase et al. [37], the lipid and starch content of microalgae exhibited no difference with and without the addition of NO. To date, no studies have elaborated the effects of NO present in flue gas on the growth of microalgae [38].

2.2 Assimilation of Nitrogen Sources from Wastewater

Wastewater comes from industrial, municipal, and agricultural sources. As shown in Table 2, the major pollutants in industrial wastewater are heavy metals and chemical oxygen demand (COD), the composition of which are complex and varied. For example, food production leads to large amounts of biodegradable organic matter, colloids, acids, and alkali salts, whereas the chemical industry produces wastewater with problematic concentrations of lead and mercury. Agricultural wastewater mainly includes fertilizer run-off including organic phosphorus and pesticide products that have strong toxicity. Municipal sewage generally includes suspended solids, organic matter, and other nutrients. After primary and secondary treatment processes, the largest amount of pollutants remaining in wastewater are nitrogen and phosphorus-based nutrients. In general, nitrogen and phosphorus (e.g. nitrates, urea, and phosphates) are common chemical elements that are widely present in the various types of wastewater environments described above.

Microalgae purify wastewater through nitrogen and phosphorus absorption and utilization. During autotrophic growth, photosynthesis removes dissolved CO_2, promoting an increase in the pH, which in turn promotes the precipitation of orthophosphate, and thus indirectly removes phosphorus. At the same time, phosphorus can also be phosphorylated into ATP, phospholipids, and other organic substances. As CO_2 is the carbon source for microalgae, nitrogen is typically the growth-limiting nutrient. It is directly absorbed by algal cells and converted into biomass components including proteins. As shown in Fig. 3, nitrogen sources such as ammonium salts, urea, and purines are largely assimilated in three ways [52–55]: (1) Nitrate and nitrite have active transport systems, and ammonium can be assimilated intracellularly [56]. (2) Urea is decomposed into bicarbonate and

Table 2 Typical chemical characteristics of industrial, municipal and agricultural wastewater

Sources	Chemical components				Heavy metals								Other toxic substances		Refs.
	COD	TN	NH_3-N	TP	Al	As	Cd	Cr	Cu	Hg	Pb	Ni	Phenol	Organ-phosphorus	
Industrial wastewater	–	–	–	–	√	√	√	–	√	√	√	√	–	–	[24, 39–42]
	–	–	–	–	√	√	√	–	√	√	√	√	–	–	
	–	–	–	–	√	√	√	–	√	√	√	√	–	–	
	–	–	–	–	√	√	√	–	√	√	√	√	–	–	
	√	–	√	√	–	–	–	√	–	–	–	–	–	–	
Municipal wastewater	–	√	–	√	–	–	–	–	–	–	–	–	–	–	[43–49]
	√	–	√	–	–	–	–	–	–	–	–	–	–	–	
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	√	–	√	√	–	√	√	–	–	–	√	–	–	–	
	√	√	–	√	–	–	–	–	–	–	–	–	–	–	
Agricultural wastewater	√	√	–	√	–	–	–	–	√	–	√	√	√	√	[50, 51]
	–	–	–	√	√	√	√	√	√	√	√	√	–	–	

√ Detected, – undetected

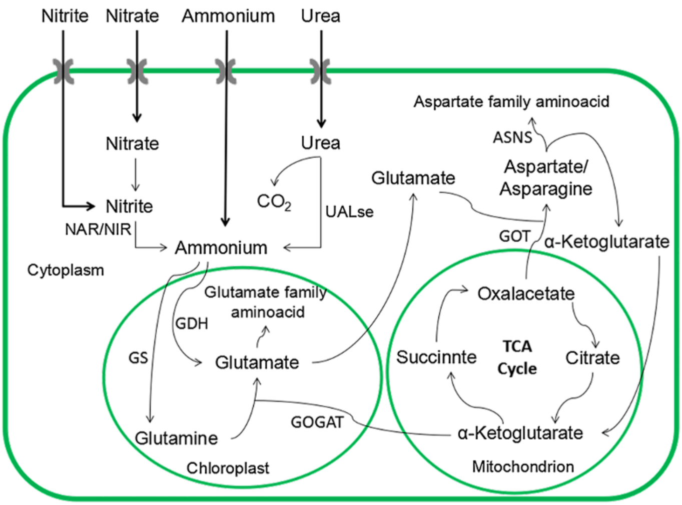


Fig. 3 Metabolism model of nitrogen sources in algae [52–55]. The ammonium salt is catalyzed by glutamate synthase in the chloroplast to produce glutamine, and synthesizes two molecules of glutamate with α-ketoglutaric acid from the endoplasmic reticulum under the catalysis of glutamate synthase. In addition, glutamate dehydrogenase directly catalyzes ammonium and α-ketoglutaric acid to generate glutamate. The glutamate from these two sources can further synthesize the glutamate family amino acid. Chloroplast-derived glutamate enters the cytoplasm, and through the catalysis of glutamic-oxaloacetic transaminase, a transamination reaction with oxaloacetic acid synthesizes aspartic acid. Powered by ATP and under the action of aspartyl synthase, this generates an aspartate family amino acid and releases α-ketoglutaric acid. *NAR* nitrate reductase, *NIR* nitrite reductase, *UALse* urease and urea carboxylase, *GS* glutamine synthetase, *GOGAT* glutamate synthase, *GDH* glutamate dehydrogenase, *GOT* glutamic oxalacetic transaminase, *ASNS* asparagine synthetase

ammonium salts [55]. (3) Ammonium salts in the external environment can cross cellular membranes via a group of transporters (belonging to the ammonium transporter family). In the chloroplast, the ammonium salts are converted to glutamine and combined with α-ketoglutaric acid to form two molecules of glutamate (GS/GOGAT pathway) [57, 58]. In addition, under the catalysis of glutamate dehydrogenase, glutamate can be obtained from ammonium and α-ketoglutaric acid (GDH pathway) [59]. Through the GS/GOGAT or GDH pathway, ammonium is incorporated into glutamate and reacts with oxaloacetate to produce aspartic acid, and is further transformed into asparagine. The resulting glutamine, glutamate, aspartate, and asparagine provide a material basis for the synthesis of intracellular organic nitrogen (proteins, nucleic acids, and chlorophyll).

Microalgae also adsorb heavy metals through complex reactions or ion exchange. The metal cations in wastewater can be in complexes with negatively charged functional groups in proteins, lipids, and polysaccharides in the cell, such as –COOH, R-SH, and phosphates (Table 3). In addition, some metal cations in wastewater replace protons on the cell walls of algae, while the remainder of the metal ions adsorb on the cell wall surface by electrostatic attraction or coordinate bonding. Studies have shown that alginate and sulfates in polysaccharides have a significant ion exchange capacity [72]. The use of active immobilized microalgae

Table 3 Functional groups combined with heavy metals in algae

Heavy metals	Strains	Functional groups	Refs.
Cu	*Chlorella vulgaris*	–COOH	[60]
	Cladophora fascicularis	–COOH, $–NH_2$, –OH	[61]
	Sargassum sp.	–COOH, $–NH_2$, –OH	[62]
Cr	*Chlamydomonas reinhardtii*	–COOH, $–NH_2$, –OH	[63]
	Sargassum sp.	–COOH, $–SO_3H$, $–NH_2$, –OH	[64]
Pb	*Spirogyra* sp.	–COOH, $–NH_2$, –OH	[65]
	Spirulina maxima	$–NH_2$, –OH	[66]
Cd	*Sargassum fluitans*	–COOH	[67]
	Spirulina sp.	–COOH, $–P_2O_3$	[68]
Zn	*Ulva fasciata* sp.	–COOH	[69]
Al	*Padina pavonica*	–COOH, $–NH_2$, –OH	[70]
Ni	*Chlorella vulgaris*	–COOH	[71]

can bind a large part of metals to live or dead cellular surfaces, which is further desorbed by acid treatment. On the other hand, the absorbed heavy metals are stored in different cytoplasmic structures of microalgae, and the trace amounts of essential heavy metals participate as co-factors in enzymatic processes in microalgal cells [38]. Although microalgae have shown high uptake capacity and were able to detoxify various heavy metals at lower concentrations [73], higher concentrations of heavy metals are still toxic [74]. For example, Douskova et al. [75] found that mercury from untreated flue gas was detrimental to microalgae. When the concentration of Cu^{2+} rose to 2 mg L^{-1}, it even inhibited the waste removal capability and growth of *Chlorella sorokiniana* [76].

2.3 Metabolism of Glucose from Food Waste

Food waste is defined as products from the production, processing, wholesale, and consumption of food [77], and consists primarily of oil, sugar, protein, vitamins, and phosphates (Table 4). The content of carbohydrates, protein, and oil is typically in the range of 30–60%, 10–20%, and 10–35%, respectively. Macromolecular organic matter food waste can undergo a series of degradation processes. Complex cellulose and starch can be decomposed into glucose or glucose oligomers. Proteins and lipids can be degraded into peptides, amino acids, and fatty acids. These small organic substances can eventually dissociate into inorganic forms of nitrogen and phosphorus. These highly degraded forms of food waste can then potentially be utilized by microalgae. For example, Gao et al. [86] reported that heterotrophic cultures of *Chlorella protothecoides* grown with enzymatic hydrolysates of sweet sorghum juice yielded dry cell weight and lipid content of 5.1 g L^{-1} and 52.5%, respectively, which are higher than those using glucose as a carbon source. A similar study was reported by Li et al. [87], in which *Chlorella pyrenoidosa*

Table 4 Gross composition of various types of food waste

Sources	Typical composition of food waste (w/w %)						Refs.
	Carbohydrates	Lipids	Protein	Total nitrogen	Phosphate	Total fatty acids	
Dried meal from food waste	33.5–62	19–35.2	7.1–17	1.25–2.98	1.5–1.7	–	[78]
Bread waste	59.8	–	8.9	1.56	Trace	–	[79]
Bakery waste	62	19	4.2	0.76	1.5	11.5	[80]
Canteen waste	42.7	6.2–6.7	10.5–11.2	–	1.6	–	[81, 82]
Wheat flour	71.8–73.15	–	10.7–11.2	1.83	0.158–0.24	–	[83, 84]
Molasses	48–58	–	–	0.2–2.8	0.02–0.07	–	[85]

– Undetected

cultivated under light intensity of 40 μmol $(m^2s)^{-1}$ with rice straw hydrolysates also exhibited rapid growth and high oil content. Therefore, organic waste may be considered a potential nutrient source for microalgal cultures.

Glucose is the most commonly used organic carbon source in heterotrophic or mixotrophic regimes. As shown in Fig. 4, uptake of extracellular glucose is driven by a specific transporter to facilitate diffusion or synergistic transmembrane entry into the cells. Through phosphorylation of glucose, glucose-6-phosphate is formed and is then catalyzed by a series of mutase and dehydrogenase reactions to produce two molecules of pyruvate. Synthesized pyruvate enters the mitochondria to participate in the tricarboxylic acid (TCA) cycle: pyruvate is assembled and combined into acetyl coenzyme A, and the coenzyme complex provides oxaloacetic acid with two carbon atoms to form citric acid. The citric acid becomes isocitric acid through isomerization, and then undergoes oxidized decarboxylation to form α-ketoglutaric acid. It is subjected to further oxidative decarboxylation to become succinic acid, and is then converted to form oxaloacetic acid. The TCA cycle is the central hub of biological metabolism, and produces intermediate products that can be used as sources for other biosynthetic reactions. For example, citric acid can be converted into fatty acids or cholesterol, and α-ketoglutarate and oxaloacetic acid can be involved in amino acid biosynthesis [55, 88].

Compared to autotrophic algae, heterotrophic algae are more likely to metabolize glucose through the pentose phosphate pathway (PPP) [13, 89]. The PPP is thought to be an important mechanism for the decomposition of glucose. As shown in Reaction Scheme (1), glucose-6-phosphate is hydrolyzed and dehydrogenated to ribulose-5-phosphate. Ribulose-5-phosphate then forms xylulose-5-phosphate by epimerase, and glucose-6-phosphate can be regenerated by trans-ketone and trans-aldehyde. Ribose-5-phosphate is converted to pyruvate. Glycerol aldehyde-3-phosphate and fructose-6-phosphate, an intermediate produced by the PPP, enters the glycolytic pathway and serves as a link to the glycolysis pathway.

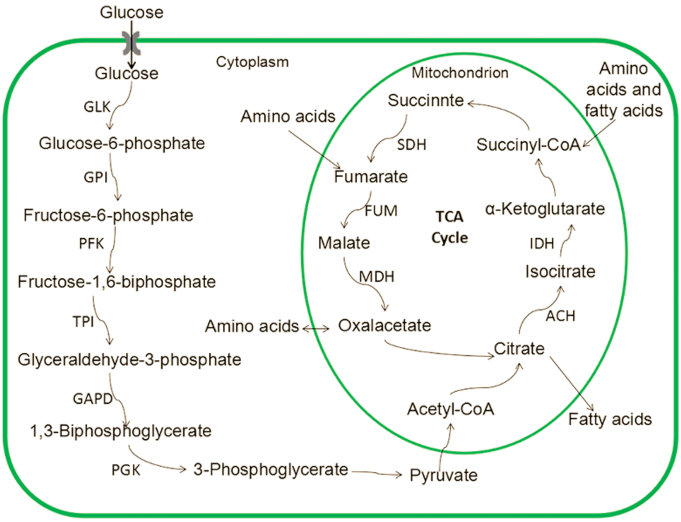


Fig. 4 Assimilation of glucose in algal cells [55, 88]. Glucose is phosphorylated to glucose-6-phosphate at position 6; phosphoglucose isomerase is catalyzed to fructose-6-phosphate, and is further phosphorylated to fructose 1,6-diphosphate. This substance is cleaved into one molecule of dihydroxyacetone phosphoric acid (dihydroxyacetone phosphoric acid can be converted to glyceraldehyde-3-phosphate) and one molecule of glyceraldehyde-3-phosphate. The resulting glyceraldehyde-3-phosphate is oxidized to 3-phosphoglycerate and then to 2-phosphoglycerate. Dehydrated under the action of enolase to produce phosphoenolpyruvate, it is finally converted to pyruvate and produces an ATP. Pyruvate is then oxidized in the mitochondria and involved in the citric acid cycle. *GLK* glucokinase, *GPI* glucose phosphate isomerase, *PFK* phosphofructokinase, *TPI* triose phosphofructokinase, *GAPD* glyceraldehyde phosphate dehydrogenase, *PGK* phosphoglycerate kinase, *ACH* aconitate hydratase, *IDH* isocitrate dehydrogenase, *SDH* succinate dehydrogenase, *FUM* fumarate hydratase, *MDH* malate dehydrogenase

$$\begin{aligned}&3G\text{luose - 6 - phosphate} + 6NADP^{+} + 5NAD^{+} + 5Pi + 8ADP \rightarrow \\ &5P\text{yruvate} + 6NADPH + 3\mathrm{CO_2} + 8H^{+} + 5NADH + 2\mathrm{H_2O} + 8ATP\end{aligned} \tag{1}$$

In heterotrophic culture, more ATP is generated by glucose than autotrophic and mixotrophic modes in which energy is supplied by light [13]. In heterotrophic mode, glucose is metabolized as a substrate for ATP synthesis through respiratory pathways, i.e. glycolysis, PPP, and TCA cycle. Yang et al. [13] noted that 90% of the glucose metabolism in *Chlorella pyrenoidosa* was derived from the PPP, in complete darkness, and with glucose as the sole carbon source. Similarly, the PPP is a major metabolic form of sugar metabolism in heterotrophic cultures of cyanobacteria *Synechocystis* spp. [89, 90].

3 Microalgae Cultivation in Relation to Waste Utilization

In the years since Oswald proposed the idea of using algal cells to remove nitrogen and phosphorus from sewage, we have witnessed the rapid development of treatment technologies based on algal cell culture [91, 92]. High-rate algal ponds

(HRAPs), photobioreactors, and other microalgae culture devices have emerged and are gradually advancing toward application. There have been a number of comprehensive reviews covering this topic [93, 94], and here we briefly introduce the application of common open/closed culture systems and the advantages of pollutant removal with microalgae.

3.1 Open Microalgae Culture Systems

Open microalgae culture systems are reactors open to the environment using sunlight as energy [95], which have the advantage of low energy consumption, low infrastructure investment, low operating cost, and easy operation [96]. They are suitable for culturing the algal cells that grow fast and tolerate extreme environments (e.g. high concentrations of sodium bicarbonate and high salinity).

These open systems include large-scale pools, open tanks, round culture tanks, and HRAPs [96]. The most widely used system is the HRAP [91, 97, 98]. When integrating HRAP with wastewater treatment, an "algal–bacterial symbiotic system" is employed, which can achieve the simultaneous removal of many nutrients [94]. In the treatment of sewage, the symbiotic system is a more energy-efficient alternative to conventional removal processes, enabling the removal of nutrients without the need for mechanical oxygenation [99]. In symbiotic algal–bacterial systems, aerobic–heterotrophic bacteria oxidize and decompose organic pollutants in the wastewater. The resulting metabolic products provide a good source of carbon, nitrogen, and phosphorus to support algal photosynthesis. Microalgal photosynthesis uses CO_2 to produce O_2, which in turn is consumed for the respiration of bacteria. In addition to O_2 and CO_2 that can be exchanged between microalgae and bacteria, heterotrophic bacteria metabolize the organic carbon produced from algae to produce CO_2, NH_3, PO_4^{3-}, H_2O, and other substances, and these substances are used to enhance microalgae growth and reproduction [93, 100].

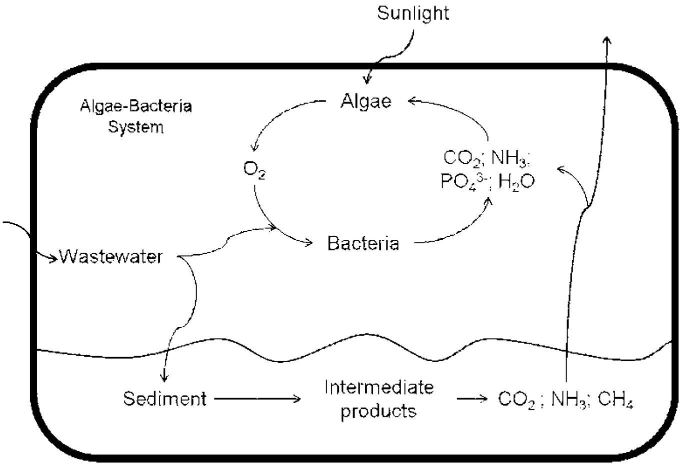


Fig. 5 Algal–bacterial symbiotic system

As shown in Fig. 5, sewage sediment produces volatile acids and other intermediates via the metabolism of bacteria; the sediment releases CO_2, NH_3, and CH_4 (CO_2 and NH_3 can be recycled into the algae culture, and CH_4 can be directly used as a clean energy) after being completely decomposed by bacteria. Studies have shown that algae (cyanobacteria)–bacteria combination systems have better growth and decontamination capacity than conventional algal culture systems [101]. Mujtaba and Lee [47] demonstrated a symbiotic algal–bacterial association in a process designed for wastewater treatment. The performance of inorganic nutrient (nitrogen and phosphorus) and organic pollutant removal was investigated using a co-culture system to treat municipal wastewater with different inoculum ratios of suspended activated sludge to alginate-immobilized microalgae *Chlorella vulgaris*. The results showed different removal efficiency for different inoculation rates (sludge/microalgae), and the biomass of algal cells increased from 0.03 to 0.05 g L^{-1} day^{-1} in the co-culture system with a low inoculation rate. These results indicate the existence of optimal inoculation in the co-culture system for the efficient removal of contaminants from the effluent. Liu et al. [46] further confirmed that the "algae–bacteria–effluent co-culture system" improved the removal efficiency of COD and total phosphorus (TP) in wastewater centrate, providing a promising route for the treatment of wastewater by improving nutrient removal and biomass production.

HRAPs have been shown to be effective for nutrient removal in many countries, including the United States, Germany, France, New Zealand, Israel, South Africa, Singapore, India, Bolivia, Mexico, and Brazil [93, 102]. In terms of waste utilization, depending on the product specifications, these ponds can potentially use sources of nitrogen and phosphorus from relatively clean wastewater sources. In addition, the ponds need to be provided with CO_2, which can be from flue gas if located close enough to a point CO_2 source [103]. While the scale is small for specialized high-value products, meaning the benefits for mitigating climate change are minimal, if biofuel production can be made economically viable, significant amounts of CO_2 could be used [104]. However, the HRAP approach also has limitations. For example, growth conditions are difficult to control [105] and are susceptible to the effects of climate; algal biomass is low [106]; and the system can be more easily contaminated by other algae species, bacteria, and protozoa than closed systems.

3.2 Closed Microalgae Culture Systems

Closed microalgae culture systems refer mainly to microalgae photobioreactors, and have been designed in tubular [107], flat-tank [108], bubble column, and serpentine [109] configurations. Compared to open culture systems, photobioreactors can better control algal cell growth conditions to achieve higher productivity and reduce contamination by other algae [110, 111]. In addition, the cost of subsequent separation and purification can be reduced somewhat if a higher titer can be obtained. However, construction and operating costs are high, and there are significant technical requirements in expanding the reactor size [112].

In general, the use of a microalgae photobioreactor coupled with wastewater treatment and product output includes the following steps: (1) Design and development of the microalgae photobioreactor. The optimized devices with high efficiency and low cost are developed based on the physiological and ecological characteristics of target microalgae; and factors such as light, pH value, and temperature that are essential for microalgae growth should be considered. (2) Pretreatment of sewage. Sewage containing nitrogen and phosphorus usually needs to be pretreated to meet microalgae culture requirements. The main purpose of pretreatment is to minimize or remove the substances that are toxic or have an inhibitory effect on microorganisms. (3) Separation of treated water and algal cells. The microalgae and water bodies in the photosynthetic reactor are generally separated using membrane separation technology, and the "clear water" purified by microalgae is obtained at the outlet of the system. (4) Collection and extraction of algal biomass to produce biodiesel and other products [113, 114]. Various researchers have investigated the use of PBRs for wastewater treatment. For example, Hom-Diaz et al. [115] used a microalgae photobioreactor to treat toilet waste, removing 30–80% of pharmaceutically active compounds. García et al. [116] developed a conventional photobioreactor for biogas scrubbing applications by rationally combining the photobioreactor with hypoxia-aerobic algal–bacterial symbiosis to improve the domestic wastewater nitrification–denitrification process. Results showed that this innovative process configuration enhanced the rates of total nitrogen and phosphorus removal by assimilation of biomass, and also supported CO_2 and H_2S removal to achieve efficient upgrading of biogas. Cheng et al. [48] found that oleaginous microalgae *Tribonema minus* could grow in a photobioreactor with sewage containing industrial phenol contaminants. The contaminants in the biomass were immobilized, and could then be used as a raw material for bioenergy production.

In addition to the conventional PBRs, closed microalgae culture technology includes activated algae systems and algae immobilization technology. The activated algae system is used to produce high-concentration algal fluid, which is then inoculated in a photobioreactor through an artificial strengthening technique, and the wastewater subsequently used as culture medium [117]. Algae immobilization technology involves the use of embedding or adsorption methods to collect algae cells on a carrier, which is typically a natural macromolecule gel carrier (such as agar and calcium alginate) or an organic synthetic polymer gel carrier (such as polyvinyl alcohol [PVA] or polyacrylamide [ACAM]). Advantages of this technology, including high concentrations of algal cells, fast reaction speeds, high removal efficiency, and easy harvesting, have led to its wide adoption for wastewater treatment [94].

3.3 Microalgae Cultivation with Anaerobic Digestion Effluents of Waste

The application of food waste as feedstock in the cultivation of microorganisms allows the recycling of waste matter by assimilation in biomass and the use of metabolites of microorganisms for production of energy, materials, and chemicals [81]. In addition, it is a clean method for the disposal of food waste to produce biogas through anaerobic digestion because of its low environmental impact, economic benefits, and high load-carrying capacity for waste minimization [118]. Han et al. [85] assessed the techno-economic feasibility of dark fermentative hydrogen production from molasses, and concluded that the payback period was 6.9 years when the hydrogen-producing plant was scaled up to 50 m^3. A later study investigating a novel bioprocess combining solid-state fermentation and dark fermentation for hydrogen production suggested that the payback period of the plant would be 5 years, with an internal rate of return of 20.2% [119]. Ji et al. [120] cultured *Scenedesmus obliquus* in Bold's basal medium containing 0.5–10% (v/v) of food wastewater, and Heo et al. [121] cultured *Tetraselmis suecica* in seawater-diluted food waste. They both found that microalgae culture had a significant effect on the removal of contaminants (e.g. TN, TP, NH_3-N) in the waste, and the yields of microalgal biomass were significantly improved. Shin et al. [122] diluted anaerobically digested food wastewater effluent with the primary effluent of municipal wastewater and then cultured *Scenedesmus bijuga* to purify food wastewater and produce biodiesel. Microalgae can also be cultured with other solid waste. For example, Singh et al. [123] cultivated three algae strains (*Chlorella minutissima*, *Chlorella sorokiniana*, and *Scenedesmus bijuga*) using 6% (v/v) anaerobic digestion effluent of poultry waste, and found that the biomass growth rate increased significantly, with phosphorus removal rates of 60 and 80%, respectively. Similarly, Cai et al. [124] cultured *Synechocystis* sp. and *Nannochloropsis salina* with an artificial seawater medium containing 3–24% (v/v) anaerobic digestion effluent. The results showed that this algal culture method not only removed nitrogen and phosphorus, but also increased the algal biomass, which is consistent with the results obtained by Singh et al. [123].

With the promotion of biogas projects in large and medium-sized farms, the production of biogas by anaerobic digestion of microalgae is becoming increasingly widespread. Han et al. [125] developed a combination of solid-state fermentation and batch fermentative hydrogen production from food waste, and the highest yield was 52.4 mL H_2/g of food waste. Alberto et al. [126] used two-step fermentation to study the potential of algae as a resource for methane production. Subsequently, Li et al. [127] proposed that combining microalgae culture and purification of biogas slurry could achieve the dual effect of microbial biomass transformation and environmental treatment. Based on this concept, Xu and Li [128] explored biogas production technology of anaerobic digestion with blue-green algae in Taihu and large-scale farm manure, and laid the foundation for methane production from pig manure and other fecal waste. As shown in Table 5, the methane/biogas yield, expressed as liters (L) of methane/biogas produced per gram (g) of volatile solids (VS), was between 0.117 and 0.366 L g^{-1} VS, indicating that methane/biogas yields vary according to different algae strains and anaerobic digestion conditions. These results suggest that large-scale biogas/methane production has the potential for expansion using a combination of microalgae culture and environmental management.

Although anaerobic digestion of microalgal biomass may be energy efficient [137], the costs would likely be prohibitive. Microalgae oil extraction for biodiesel production can also be energy efficient [138]. However, pyrolysis oil technology

Table 5 Anaerobic digestion process conditions and biogas/methane yield of algae

Microalgae	Cultivation	Anaerobic digestion process conditions	Methane/biogas yield (L g^{-1} VS)	Refs.
Stigeoclonium sp., *Monoraphidium* sp., *Nitzschia* sp., *Amphora* sp.	Wastewater	20 days (37 °C, continuous test)	0.180 (CH_4)	[129]
Chlorella vulgaris	Non-sterile effluent from UASB (swine manure)	24 days (37 °C, batch reactor)	0.364 (biogas) 0.228 (CH_4)	[130]
Hydrodictyon reticulatum	Secondary wastewater	25 days (35 °C, batch reactor)	0.170 (CH_4)	[131]
Rhizoclonium	Drainage water	28 days (53 °C, batch reactor)	0.230–0.240 (L CH_4/g TS)	[132]
Chlorella vulgaris	Swine wastewater, nitrified secondary effluent	25 days (mesophilic conditions, batch reactor)	0.366 (biogas) 0.229 (CH_4)	[133]
Pediastrum sp., *Micractinium* sp., *Scenedesmus* sp.	Primary settled sewage	14–16 days (37 °C, CSTR reactor)	0.179 (CH_4)	[134]
Scenedesmus obliquus, *Chlorella vulgaris*	Primary treated urban wastewater	46 days (35 °C, batch reactor)	0.172 (biogas) 0.117 (CH_4)	[135]
Algal biomass	Primary treated wastewater	15 days and 20 days (35 °C, continuous test)	0.130 and 0.170 (CH4)	[97]
Algal biomass	Sewage	28 days (38 °C, batch reactor)	0.340 (methane)	[136]

VS volatile solids, *TS* total solids, *CSTR* continuously stirred tank reactor, *UASB* up-flow anaerobic sludge blanket

requires dehydration, drying, and subsequent processing, thus demanding a sizable energy investment. The production of biogas by anaerobic digestion of microalgae does not require strict product separation or the extraction of oil and lipids [139]; their main product, methane, is captured in the gas phase. During fermentation, many macromolecules (proteins, lipids, and sugars—all parts of the microalgae structure) are used [140].

It may be possible to integrate a number of these waste utilization strategies. For instance, the nutrients in wastewater, such as organic nitrogen or phosphorus, can be mineralized to feed the microalgal culture [141]. The biological methane produced can be burned to produce heat and electricity, upgraded, and injected into natural gas grids or used as automotive fuels [136, 142–144]. CO_2 can be isolated and used for high-concentration open microalgal culture. The original microalgae biomass and other biofuel residues can also be used for anaerobic digestion for material recycling and cost reduction [131, 145]. It is important to note that residues of algae

Table 6 Removal efficiency of NH3-N, TN, TP (PO_4^{3-}), and COD, and the maximum biomass accumulation by microalgal cultures

Microalgae	NH_3-N	TN	TP (PO_4^{3-})	COD	Final biomass concentration/ productivity	Refs.
Chlorella PY-ZU1	73%	–	95%	79%	4.81 g L^{-1}	[153]
Chlorella PY-ZU1	99%	–	99%	68%	4.30 g L^{-1}	[118]
Chlorella sp.	100%	75.7–82.5%	62.5–74.7%	27.4–38.4%	–	[152]
Synechocystis sp. *Nannochloropsis salina*	82.5–100%	71.2–100%	83.6–100%	–	0.21 g L^{-1} day^{-1}	[124]
Scenedesmus spinosus SHOU-F7	88.82%	93.25%	97.57%	–	–	[154]
Scenedesmus obliquus SHOU-F21	95.84%	87.78%	97.96%	–	–	
Chlorella vulgaris SHOU-F28	97. 18%	52.38%	96.61%	–	–	
Chlorella ellipsoidea SHOU-F20	96.74%	62.42%	91.51%	–	–	
Oocystis solitaria SHOU-F5	97.50%	91.73%	96.74%	–	–	
Synechocystis sp. LX1	–	98%	98%	–	0.11 g L^{-1}	[155]
Scenedesmus obliquus	–	75%	12%	–	0.41 g L^{-1}	[120]
Scenedesmus bijuga	–	90.7%	90.5%	66.4%	1.49 g L^{-1}	[122]
Tetraselmis suecica	99.0%(NH_4^{+})		52.3%	–	2.00 g L^{-1}	[121]
Neochloris aquatica CL-M1	96.2%	–	–	81.7%	6.10 g L^{-1}	[156]
Chlorella vulgaris JSC-6	91.3%	–	–	70%	3.96 g L^{-1}	[157]
Chlorella pyrenoidosa	91.2%	–	–	55.4%	0.3 g L^{-1}	[158]
Chlorella zofingiensis	–	81.03%	–	79.84%	2.962 g L^{-1}	[159]
Chlorella vulgaris	–	97%	80%	–	2.97 g L^{-1} day^{-1}	[43]
Neochloris oleoabundans	98%	–	–	Negligible	0.63 g L^{-1}	[160]
Neochloris oleoabundans	95%	–	–	Negligible	0.125 g L^{-1}	[161]
Neochloris oleoabundans	99%	–	–	Negligible	2.10 g L^{-1}	[162]

– Undetected

after anaerobic production of biogas (biogas slurry and biogas residue) can be used directly as natural fertilizers or can be further processed [105, 146].

3.4 Changes in Inorganic Chemical Components and Accumulation of Algal Biomass

In general, wastewater, food waste, and effluents from farms are rich in various chemical elements. Studies have shown that microalgae can effectively reduce the COD and adsorb heavy metals to purify pollutants [147–149].

3.4.1 Nitrogen and Phosphorus Removal and Biomass Accumulation

Nitrogen and phosphorus (nitrite, nitrate, ammonium, and urea) are common chemical elements or components present in wastewater and waste materials. The nitrogen removed by microalgae is largely synthesized into algal protein and other active substances. Phosphorus in waste sources can also be directly absorbed by microalgal cells and converted into ATP, phospholipids, and other organic substances through various phosphorylation methods [94, 150, 151]. Studies have shown that microalgae can effectively accumulate nitrogen and phosphorus into biomass [118, 122, 152]. As shown in Table 6 (data are the maximum values of

Table 7 Metal and metal ion removal by microalgae culture

Inorganic composition		Microalgae	Refs.
Heavy metals	Pb Co Hg Cd As Cu Ni	Diatoms species, *Chlorella vulgaris*, *Desmodesmus insignis*, *Nannochloropsis salina*	[39, 118, 149, 167, 171, 172]
Trace metals	Zn Fe Mn Mo	*Chlorella vulgaris*, *Chlorella* PY-ZU1	[118, 149, 167]
Metal ions	Cu^{2+} Hg^{2+} Pb^{2+} Cr^{+} Cd^{2+} Mn^{2+} Zn^{2+}	*Dicrateria* sp., Charophyte, *Chlorella vulgaris*, *Chlamydomonas reinhardtii*	[169, 173–176]

experiments), a few studies achieved over 90% removal of nitrogen and phosphorus, with the commonly studied algae species including freshwater *Scenedesmus*, *Chlorella*, and *Spirulina*. Thus microalgae cultures can remove nitrogen, phosphorus, and other substances as a means of water purification, while accumulating new biomass that can be used for bioenergy or other applications.

The use of microalgae to remove nitrogen and phosphorus from partially treated sewage is currently under intensive study [163], as the advantages of CO_2 fixation, nitrogen and phosphorus removal, and microalgae biomass production [164, 165] become more attractive. In addition, the use of microalgae to treat sewage can overcome the drawbacks of high-energy nitrogen removal processes and suboptimal nutrient recovery with traditional sewage treatment methods [150]. However, although it is generally considered to be relatively cost-effective, simple, and feasible, this method has yet to be widely adopted.

3.4.2 Metal Removal by Microalgae Culture

Heavy metals are stable and toxic at low levels, passing through the food chain, endangering the growth and reproduction of aquatic organisms and causing a variety of human diseases [166]. Many studies have shown that microalgae can be widely used for biosorption of heavy metals and other pollutants [39, 149]. Rugnini et al. [167] demonstrated the potential for employing green microalgae for bioremediation of metal-polluted water, given their ability to grow in the presence of high metal concentrations and to remove them efficiently. Hala and Sjahrul [168] studied the biosorption of Zn^{2+} and Cd^{2+} ions by *Nannochloropsis salina*, reporting removal efficiency of 96 and 93%, respectively. With regard to bioremediation of radioactive metals (e.g. Th, U and Ra), toxic heavy metals (e.g. Cd, Cu, Hg and Pb), and economically valuable metals (e.g. Ag, Au, Pt and Co), many studies using microalgae have been reported [149, 167, 169]. For example, Napan et al. [170] introduced 14 inorganic contaminants (As, Cd, Co, Cr, Cu, Hg, Mn, Ni, Pb, Sb, Se, Sn, V, and Zn) into the media of *Nannochloropsis salina* culture. Trace contaminant analysis showed that Cd, Co, and Mn were absorbed at rates greater than 90%, while As, Cr, Cu, Ni, and Pb were absorbed at 50 to 90%, and Sb and V were absorbed at less than 50%. As shown in Table 7, different microalgae can remove different metal elements or metal ions, with *Chlorella* species the most extensively tested to date.

3.5 Changes in Organic Chemical Components in Microalgae Culture

Studies have shown that cultivation using wastewater and food waste can increase the productivity of lipids in microalgal cultures. Yu et al. [177] tested ten microalgae strains cultivated in diluted anaerobically digested effluent kitchen waste, and found that the biodiesel produced from lipids extracted from these strains had better functional properties (presumably due to an improved fatty acid profile) than those cultivated on regular growth media. Liu et al. [154] used pig farm wastewater for microalgae cultivation, and found that the amounts of 16:0 and 18:3 n3 (fatty acids suitable for biodiesel production) were higher than those grown on regular media across 15 microalgae strains. Furthermore, the protein content of algae was significantly higher in the cultures grown in wastewater-enriched media. Pleissner et al. [178] confirmed that heterotrophic cultures of *Schizochytrium mangrovei* and *Chlorella protothecoides* using pure food waste hydrolysate as medium produced biomass of up to 14 g L^{-1}. In this study, the content of lipids, protein, and docosahexaenoic acid (DHA) in *Chlorella pyrenoidosa* was increased significantly, while the content of oleic acid, linolenic acid (ALA), and carbohydrate remained unchanged. Thus microalgae can use waste to synthesize their own biomass. CO_2 in air and waste gas streams can be used as a carbon source, inorganic and organic nitrogen can be used for protein synthesis, and phosphorus and phosphates can be used for nucleotide and phospholipid synthesis, thereby increasing the biomass of algal cells. The resulting lipids, proteins, and carbohydrates can be further used as valuable products.

4 Development and Application of Value-Added Products of Microalgae

Fuels such as biodiesel, ethanol, biogas, and methane can be produced from lipids and carbohydrates, and the remaining protein-rich material can be processed into animal feed. In addition, other higher-value compounds, such as DHA and astaxanthin, in the algal cells can be extracted to develop chemicals or materials (Fig. 6).

4.1 Production of Biodiesel from Microalgal Lipids

Biodiesel can be produced from triacylglycerols (TAGs) that accumulate in the microalgae. This requires cell disruption and lipid extraction. Since most of the

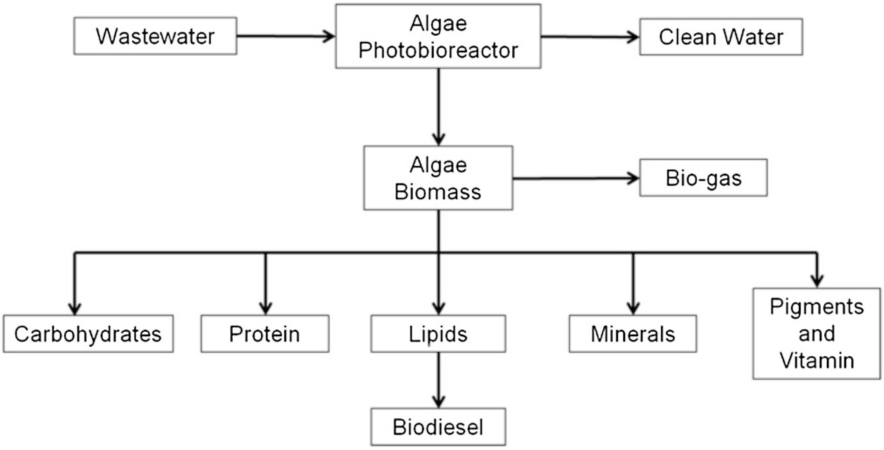


Fig. 6 Overview of algae-derived products

Table 8 Advantages and disadvantages of different types of catalysts for transesterification of oils to biodiesel

Types	Advantages	Disadvantages	Applicable raw materials	Refs.
Homogeneous base catalyst	Mild reaction conditions; high catalytic activity; wide application range; fast reaction rate	More sensitive to free fatty acids and water contents in sample; easy saponification; poor reproducibility	Feed oil containing no free fatty acids or water	[195]
Homogeneous acid catalyst	Less sensitive to free fatty acids; high product yield	Easily corrodes equipment; difficult recycling; high cost	Food waste oil	[196, 197]
Heterogeneous base catalyst	Easy to separate, recyclable; high activity; high efficiency	Toxic; slower reaction rate than homogeneous base catalyst	–	[196]
Heterogeneous acid catalyst	Less sensitive to free fatty acids; easy to separate and reduced corrosion	High cost and low activity compared with the liquid acid	–	[198, 199]
Biological enzymes	Environmentally friendly and low cost	Slow reaction rate	Waste cooking oil	[200]
Supercritical method	High phase solubility; fast reaction rate	High temperature and pressure; high production cost	Various types	[196]
Co-solvent method	Fast reaction rate and easy to recover	Risk, toxicity	Vegetable oil, waste edible oil, animal fat	[196, 201]

– Unknown

microalgal cells have rigid cell walls, rupture of algal cells prior to solvent contact can greatly improve the resulting lipid yields [179, 180].

4.1.1 Disruption of Microalgal Cells

Cell disruption can be achieved by mechanical methods such as bead milling [181], ultrasonication [182], and high-pressure homogenization [180], and non-mechanical methods involving microwave heating [183] and chemical or enzymatic hydrolysis [181]. Although cell disruption can be achieved by various techniques, few are

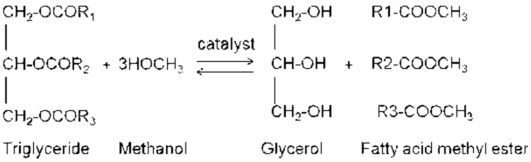


Fig. 7 The process of triglyceride transesterification reaction (R1, R2, and R3 are hydrocarbon chains of fatty acids) [205]

feasible for process-scale implementation. One of these, high-pressure homogenization, is a particularly promising technique for microalgal rupture. The process is not only effective in aqueous environments (excluding the need for energy-intensive drying), but it can also be expanded for processing large volumes [184, 185]. For example, Halim et al. [186] reported that high-pressure homogenization demonstrated high efficiency in disrupting the microalgae *Chlorococcum* sp., and the technique has also been used successfully for *Nannochloropsis* sp. (up to 25% w/w solids) [187].

4.1.2 Extraction of TAG as a Biodiesel Feedstock

In addition to the disruption of microalgae, the extraction of lipids is an important step in the preparation of biodiesel. Extraction techniques include organic solvent extraction, supercritical fluid extraction, and thermal cracking, all of which require the algae to be dried [188]. However, the drying pretreatment not only extends the biodiesel production cycle, but also affects lipid extraction efficiency. Cooney et al. [189] utilized the heat of vaporization for the drying step, and reported an energy load of up to 391.6 MW. In order to avoid the high energy input, novel wet routes including subcritical water extraction and in situ lipid milking have been proposed [188]. Olmstead et al. [180] reported effective extraction of wet algae to TAG through contact of the concentrated paste with hexane through impeller mixing, which achieved recovery of up to 70% w/w of the total lipids and was able to be performed at mild temperatures.

4.1.3 Conversion of Lipids to Biodiesel

Transesterification is the conventional and most commonly used method for producing biodiesel from vegetable oil. As shown in Table 8, the preparation of

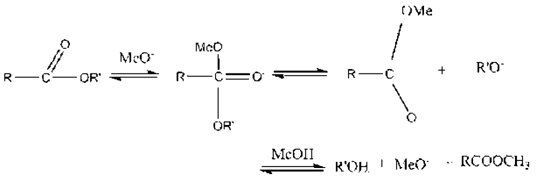


Fig. 8 The mechanism of alkali-catalyzed transesterification reaction (R and R′ are hydrocarbon chains of fatty acids) [203]

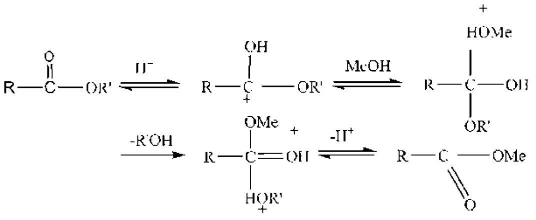


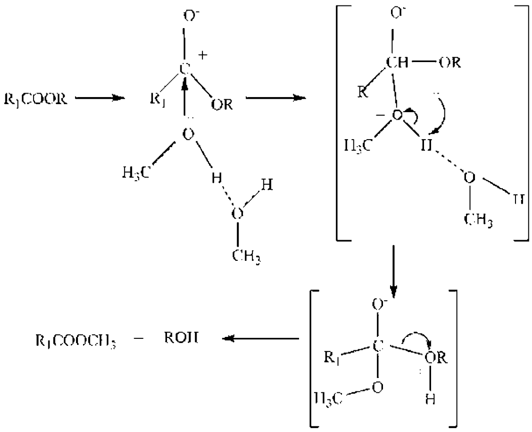
Fig. 9 The mechanism of acid-catalyzed transesterification reaction (R and R′ are hydrocarbon chains of fatty acids) [203]

biodiesel by transesterification can be divided into different types, and different catalysis methods have their unique advantages and disadvantages. Generally, transesterification is the reaction of an ester and an alcohol under the catalysis of an acid or alkaline to produce a new ester and new alcohol, i.e. the alcoholysis of the ester [190, 191]. Transesterification reduces the molecular weight of TAG oil to about one-third of the original, reduces the viscosity by a factor of about 8, improves fuel volatility, and produces a fuel with specifications close to those of mineral diesel [192]. It has certain advantages over petrochemical diesel: (1) high combustion efficiency—the oxygen content of biodiesel accelerates the combustion process and decreases its oxidation potential; (2) favorable lubricity—there is a significant improvement (about 30%) in lubricity when less than 1% of biodiesel is added to conventional diesel fuel; (3) fast biodegradability—biodiesel degrades approximately four times as fast as petrodiesel, mainly due to its low oxygen content [193, 194].

As shown in Fig. 7, transesterification is a multi-step reaction in which triglycerides are converted to esters (biodiesel) and glycerol (by-product). However, different catalysts have distinct catalytic mechanisms. (1) As shown in Fig. 8, alkali-catalyzed transesterification (alcoholysis) is a nucleophilic substitution reaction [202]. Alcohol first forms an anion MeO^- in the alkaline environment, and MeO^- then attacks the first carboxyl carbon atom of the raw material glycerol ester Sp2 hybrid, and a nucleophilic addition reaction forms the intermediate of a tetrahedral structure. This intermediate reacts with the alcohol to regenerate the anion MeO^-, and finally the intermediate rearrangement produces a fatty acid ester and diglyceride [203]. In this reaction, the alkoxy anion formed in the first step is a true catalyst that promotes the progress of the reaction. (2) As shown in Fig. 9, the carboxyl groups on the triglycerides form protonated carbons and undergo nucleophilic reactions with the alcohols to give the tetrahedral intermediates. The resulting tetrahedral intermediates are formed by elimination reaction, and finally produce new fatty acids ester. (3) The preparation of biodiesel by supercritical transesterification refers to the transesterification reaction of alcohols and algal oils in supercritical conditions, and belongs to nucleophilic reactions [204]. The O atoms on methanol attack the positively charged carbon atoms to form intermediates, and the H atom of the intermediate alcohol species is then transferred to the alkyl group of the triglycerides to form another intermediate, thereby obtaining the transesterification product (Fig. 10).

Hydrothermal liquefaction (HTL) refers to the thermochemical conversion of wet biomass material into an oily product (i.e. liquid bio-oil) under high-temperature and high-pressure (200–350 °C, 5–20 MPa) conditions. This technology, originally used to process straw and macroalgae, is now considered a promising technology for microalgal bio-oil production. HTL conversion efficiency is related to many factors, such as temperature, reaction time, algal species, and catalyst. In contrast to traditional transesterification methods for producing biodiesel, HTL converts lipids and carbohydrates to oil, but in the process degrades protein and other higher-value components of the microalgae [205]. The destruction of protein and other high-value biomass components may be less an issue for microalgae grown on wastewater, which precludes their use as an animal or human food source or

Fig. 10 The mechanism of supercritical transesterification (R and R1 are hydrocarbon chains of fatty acids) [204]



supplement. Another concern with the conversion of high-protein biomass using HTL, however, is the contamination of the oil by nitrogen compounds.

As shown in Fig. 11, HTL is a process that involves a series of chemical reactions [205–207]. At lower temperatures (0–100 °C), protein, lipids, and carbohydrates in the microalgae are hydrolyzed to produce amino acids, fatty acids, reducing sugars, and other intermediates. In the 100–200 °C range, the intermediate products undergo further reaction, such as amino acid decarboxylation and deamination, fatty acid decarboxylation, and bond re-forming reactions in reducing sugars, as well as the formation of amines, acids, hydrocarbons, and epoxy compounds, among others. Above 200 °C, further fatty acid amination and

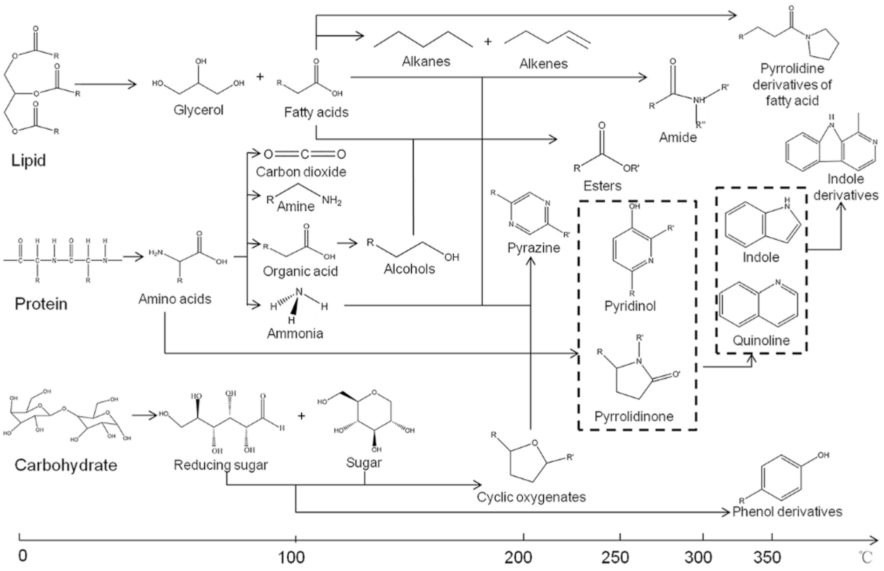


Fig. 11 Reaction process of HTL of low-lipid microalgae. Modified from Gai et al. [213]

esterification reactions occur, as well as the Maillard reaction of amino acids and reducing sugars and the formation of aliphatic amines, esters, and a variety of nitrogen oxycarbonyl compounds. Therefore, temperature plays a key role in microalgae HTL bio-oil production and its quality, and the choice of temperature is critical for industrial production safety and economy. Several studies have reported the effect of temperature on the yield and quality of biofuel, with results showing that the largest volume of bio-oil was obtained in a range of 250–375 °C [206–211]. Meanwhile, the components of feedstock, to a large extent, determine the chemical properties and yields of biocrude oil [212]. Results reported by Zou et al. [210] showed that low-fat, high-protein *Nannochloropsis* sp. and high-fat, low-protein *Chlorella* sp. could be effectively converted into biological crude oil, with maximum reported yields of 55.0 and 82.9%, respectively. HTL may be a promising technology for converting wet algae biomass, particularly when grown from waste sources that preclude the use of the biomass for high-value applications such as food or feed. However, the resulting biocrude still has higher oxygen and nitrogen content (5–15% and 5–10%, respectively) than traditional petroleum fuels, which would affect the bio-oil heat value and release nitrogen oxides into the atmosphere during the combustion process. Therefore, physicochemical modification is still needed to remove the bio-oil oxygen and nitrogen in order to improve the quality of biocrude.

4.2 Application of Microalgae in the Production of Other Energy Sources

In addition to biodiesel or bio-oil, the production of biogas (methane) or bioethanol from microalgal biomass is possible. This can be done either using the whole biomass or by converting the biomass remaining from biodiesel production. For instance, after extracting the oils used for biodiesel production, the remaining algae residue can be used as raw material to obtain methane via anaerobic digestion [214]. This can be accomplished with wet microalgae and can be combined directly with existing digester technology available in many wastewater treatment plants. The major limitation to this approach is the low commercial value of biogas fuel, which has hampered the adoption of biogas production from microalgal biomass.

Today’s most widely used biofuel is ethanol. Most ethanol is produced from so-called first-generation feedstock such as sugarcane or corn, although progress continues in second-generation lignocellulosic ethanol production [215]. An alternative is the use of microalgae as a source of ethanol. Microalgae are able to accumulate starch that can be depolymerized to glucose as a raw material for fermentation to ethanol [216]. In addition, microalgae cell walls are typically composed of polysaccharides such as cellulose. Since cell walls are a residue from microalgae oil extraction, it is possible to convert the polysaccharide into ethanol fuel using cellulosic ethanol technology. In addition, cyanobacteria have been genetically modified to produce ethanol directly during photosynthetic growth, a process brought to scale by the company Algenol [215].

Ethanol production from starch or other polysaccharides involves hydrolysis into fermentative sugars, followed by fermentation to ethanol. The hydrolysis process usually consists of a pretreatment step, such as dilute acid hydrolysis, followed by enzymatic saccharification. The fermentation to ethanol is usually performed using yeast, after which the ethanol is recovered by distillation. A similar process has been applied to microalgae biomass saccharification. Ashokkumar et al. [217] studied microalgae *Scenedesmus bijugatus* under different H_2SO_4 concentrations and temperature conditions, while other parameters (reaction time and solids concentration) remained unchanged. The authors found that after lipid extraction, the saccharification rate of the remaining biomass was the highest under the conditions of 2% H_2SO_4 concentration and 130 °C. In other studies, Nguyen et al. [218] reported an ethanol yield of up to 29 g ethanol/g microalgae in acid-pretreated *Chlamydomonas reinhardtii*, and Wang et al. [219] reported that treatment with 3% H_2SO_4 at 121 °C for 45 min resulted in the highest sugar yield in the hydrolysate of microalgae biomass.

The production of ethanol from microalgal biomass is simpler than from lignocellulosic feedstock, in that it has no lignin or hemicellulose (which contains 5-carbon sugars that are more challenging to ferment) [220]. However, additional difficulties arise in producing microalgal biomass, including the low initial concentrations, susceptibility to culture failure, and the capital costs of the growth ponds. In addition, the ethanol concentration in the fermentation broth can be quite low for microalgal biomass, as the concentration and sugar content is less than in conventional feedstock. This increases distillation cost and energy consumption, which is currently a major limitation to the economic feasibility of algal ethanol production [221].

4.3 Application of Microalgae as Protein Feed

A large number of studies have shown that algae protein can replace fish meal or soy protein in feed formulations [222–224]. While this can be used for terrestrial animals, the application of microalgae in aquatic feed is particularly attractive, given that microalgae are the natural base of the aquatic food chain, and contain required nutrient components such as omega-3 fatty acids and carotenoids [225].

The species of *Spirulina* have high nutritional value, with protein content of up to 60–70% and relatively low cellulose content that is easily digested and absorbed. *Spirulina* can be used directly as feed for aquatic animals [226] or indirectly as feed additives [227] to promote animal growth [228] or enhance animal immunity [229]. The Di Aisheng company has built *Spirulina* farms in Thailand with an annual output of 150 t, up to 60 t of which is used as bait or feed for aquatic animals [230]. Moreover, several studies have reported that *Chlorella*, which has low crude fiber content and high protein content, can be used as feed or feed additives for livestock or aquaculture animals [231–233]. Zhang and Meng [234] utilized municipal wastewater sludge to culture *Spirulina* and *Chlorella*, with results showing biomass, protein, and essential and non-essential amino acid content that was nearly the same as that obtained from microalgae grown in traditional culture media.

4.4 Integrated Development and Application of Other Components of Microalgae

In addition to being rich in oil, microalgae are rich in wholesome substances such as omega-3 fatty acids (eicosapentaenoic acid [EPA] and DHA). For example, EPA not only has a significant effect in preventing cardiovascular disease [235] and muscular dystrophy [236], but also exhibits anti-inflammatory activity [237] and regulates immunity [238]. Yuan et al. [239] suggested that phycobiliproteins and carotenoids had similar biological activity including antioxidant, anticancer, and antidiabetic properties. In another study, polysaccharides showed antioxidant or antibacterial effects on organisms [240]. Depending on the oil extraction method, the ω-3 fatty acids and pigments will either be extracted with the oil or remain with the algae residue [180, 241, 242], in which the polysaccharides and proteins will reside. These substances can be isolated and purified for the purpose of animal or human nutrition. However, the issue of food safety is a serious concern for algae culturing from waste. Ma et al. [243] utilized dairy plant wastewater and brewery anaerobic-treated wastewater to cultivate *Spirulina*. Their study found that several key parameters, including the content of protein, water, ash, and heavy metals, nearly met the national standard of food-grade *Spirulina* in China (GB/T 19919-1997). In this case, the use of wastewater was found to reduce the cost of *Spirulina* production, without compromising the quality of *Spirulina* products, which suggests the possibility of repurposing food industry wastewater.

5 Conclusions and Future Perspectives

A growing body of literature and recent developments suggest that microalgae cultivation is a valid option for waste recycling that is technically feasible and may contribute to sustainable economic development. Microalgae can capture CO_2 in waste gas and metabolize different forms of nitrogen, phosphorus, and carbon in wastewater to produce useful biomass. For waste applications, open cultivation systems such as raceway ponds or HRAPs are more efficient than closed photobioreactors, as they are more economical at a large scale. Microalgae can be effective in absorbing heavy metals in wastewater components, helping to achieve water purification. The biomass produced during the assimilation of these wastes acts as the raw material that can be converted into biofuels and other high-value-added products.

The source of waste influences the biochemical composition and growth rate of microalgae. Inhibition or augmentation of growth is possible through provision of the basic metabolic needs of the microalgae. Since the composition of waste varies, careful characterization is necessary before fermentation. Additionally, the use of waste for microalgae cultivation requires consideration of contamination by bacteria, viruses, protozoa, and heavy metals, which may influence how the cultivated biomass can be utilized, particularly with respect to feed applications. Developing a better understanding of how growth on wastewater affects the safe application of biomass as feed is an area requiring further research. Whether bioactive substances (such as astaxanthin and DHA) extracted from sewage-cultured microalgae can be made safe for application to foods, cosmetics, and other industries must be explored in future studies.

While the use of microalgae for waste valorization has enormous potential, it is yet to be fully realized. As pressure mounts for the establishment of responsible waste management strategies, the feasibility of implementing microalgal solutions will improve. Continued technological developments and scientific advances will also lead to more viable industrial microalgal processes. Many of the applications of microalgae for waste treatment involve open growth systems that allow multiple species to grow as consortia. Advances in internet monitoring systems may also be applied to microalgae cultivation practice. The use of modern biological tools such as metabolomics will improve our understanding of these complex microalgal communities, enabling the development of more productive and robust processes. Much recent progress has been made on developing efficient downstream processes to convert microalgal biomass into useful products. However, further improvements to dewatering, lipid extraction, and biomass conversion technologies would all be beneficial.

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Compliance with ethical standards

Ethics Approval and Consent to Participate Not applicable.

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Conflict of Interest Yong Chen, Li-ping Sun, Zhi-hui Liu, Greg Martin, and Zheng Sun declare that they have no conflict of interest.

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REVIEW

Recent Trends in Sustainable Textile Waste Recycling Methods: Current Situation and Future Prospects

Nattha Pensupa[1,2] · **Shao-Yuan Leu**[3] · **Yunzi Hu**[1] · **Chenyu Du**[4] · **Hao Liu**[3,5] · **Houde Jing**[3] · **Huaimin Wang**[1] · **Carol Sze Ki Lin**[1]

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Abstract In recent years, there have been increasing concerns in the disposal of textile waste around the globe. The growth of textile markets not only depends on population growth but also depends on economic and fashion cycles. The fast fashion cycle in the textile industry has led to a high level of consumption and waste generation. This can cause a negative environmental impact since the textile and clothing industry is one of the most polluting industries. Textile manufacturing is a chemical-intensive process and requires a high volume of water throughout its operations. Wastewater and fiber wastes are the major wastes generated during the textile production process. On the other hand, the fiber waste was mainly created from unwanted clothes in the textile supply chain. This fiber waste includes natural fiber, synthetic fiber, and natural/synthetic blends. The natural fiber is mostly comprised of cellulosic material, which can be used as a resource for producing bio-based products. The main challenge for utilization of textile waste is finding the method that is able to recover sugars as monosaccharides. This review provides an

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✉ Carol Sze Ki Lin
carollin@cityu.edu.hk

[1] School of Energy and Environment, City University of Hong Kong, Tat Chee Avenue, Kowloon, Hong Kong

[2] Department of Agro-Industry, Faculty of Agriculture, Natural Resources and Environment, Naresuan University, Phitsanulok 65000, Thailand

[3] Department of Civil and Environmental Engineering, The Hong Kong Polytechnic University, Kowloon, Hong Kong

[4] School of Applied Sciences, University of Huddersfield, Huddersfield, UK

[5] State Key Laboratory of Pulp and Paper Engineering, South China University of Technology, 510640 Guangzhou, China

overview of valorization of textile waste to value-added products, as well as an overview of different strategies for sugar recovery from cellulosic fiber and their hindrances.

Keywords Bioconversion · Hydrolysis · Pretreatment · Recycling · Textile waste · Valorization

1 Introduction

1.1 The Global Textile Market

The textile industry is one of the oldest and the largest industries in the world [1]. With the increase of world's population, there is an increase in the demand for textile products. In 1950, the FAO reported that 3.7 kg of textile fiber per person has been consumed and the figure continuously increased to 11.1 kg of fiber per person in 2007 [2, 3]. The great demand will, of course, lead to a high volume of textile fiber production. Around 70.6 million tons of textile fibers were produced worldwide in 2007 and the production trend was gradually increased to 90.8 million tons of textile fibers in 2014 [4]. The global textile and apparel market is predicted to grow at a compound average growth rate of 3.7% per year and to exceed 100 million tons by 2025 [5, 6].

Textile industry enlargement has a significant influence on the global economy. In 2002, industrial textile trade accounted for $400 billion worldwide, representing 6% of world trade [7]. In 2012, the industrial textile trade increased to $1.8 trillion dollars worldwide [8]. China and India are the top two textile producers worldwide. China is the world's largest clothing exporter, in which the textile industry accounts for around 54% of the world's total production. China's industrial textile value reached $755 billion in 2012, which was 12.7% higher than in the previous year [9]. Meanwhile, Indian textile trade value is $108 billion dollars, which contributes to around 4% of Indian gross domestic product (GDP) [10]. So far, the United States is the biggest importer of textile products. Their textile import value was approximately $151 billion in 2012 [8].

Natural fiber has been introduced as a raw material for the textile production in prehistoric times [2]. It has been a dominant material in the textile industry for many years. In the 1800s, scientists created synthetic fibers such as viscose, rayon, nylon, and polyester. These synthetic fibers have affected the natural fiber production and trends in consumption. Forsythe and Thomas [11] reported that cotton blended with synthetic fiber has higher customer preference compared with mono-fiber textiles. This led to an increasing demand for synthetic fiber in textile production. During 2007 to 2010, the demand for synthetic fiber increased by 4.3 million tons with market share expanding from 55.5 to 60.1%, while other fiber consumption, such as cotton, wool, and cellulosic fiber decreased to 1.7, 0.28, and 0.38 million tons, respectively [12]. Synthetic fiber production nowadays is greater than that for natural fibers [2]. Therefore, synthetic fiber is another material that needs to be focused on.

In summary, the current textile global market is mainly derived an apparel product with the synthetic fiber. The increasing household outcomes, particularly, in developing countries is promoting the development of the textile market [13]. A new pattern of consumption has appeared in recent years, for example, fast fashion strongly influences the purchase of textile products. Therefore, the increasing consumption of the textile and the apparel is a foreseeable future.

1.2 Textile waste and its environmental problems

Textile industry enlargement affects the environment, as around 10–20% of all textile products are considered to be wasted [14]. The annual textile waste in China, the United Kingdom, and the United States is estimated to be 26.0, 1.0, and 12.4 million tons, respectively [4, 15, 16]. In Hong Kong, the situation is also serious, and approximately 293 tons of textile waste are generated daily [17]. Fast fashion leaves a pollution footprint on which each step in textile life cycle carries potential environmental problems and hazards [18]. Furthermore, textile production processes require a high volume of water, energy, and chemicals. The growth of the textile industry has led to a subsequent increase of textile waste. Textile waste can be categorized into two main groups, i.e., *pre-consumer textile waste*, which is the waste generated during the textile production processes; and *post-consumer textile waste*, which is the waste created during consumer use and disposal. The pre-consumer textile waste component is related to the textile raw material, since the raw material to produce textiles can be classified into three main groups, which are *cellulose fiber, protein fiber*, and *synthetic fiber* [19]. Cellulose fiber is made from plant materials such as cotton, flex, hemp, and ramie. Protein fiber is produced from animals including wool, angora, cashmere, and silk, and synthetic fiber is made from petroleum-based chemicals such as polyester, nylon, spandex, acrylic, and polypropylene. Each type of raw material needs a specific kind of dyeing chemicals and materials in the production process, and therefore its by-product would create another stream of textile waste.

Cotton is one of the main raw materials among all fiber types owing to its large share in the textile market [20]. Around 25 million tons of cotton was produced annually, and 24% of total cotton production are grown in China [21]. This makes China the top ranking cotton producer in the world (Table 1), but most of the cotton is used domestically, due to the high demand for cotton in the textile industry. Cotton cultivation requires a high input of water, pesticides, insecticides, and fertilizers in order to obtain high productivity, and his has a negative effect on the environment.

The textile-production process using cotton as a raw material starts with cotton fiber being spun into yarn. The yarn is then converted into fabric by weaving or knitting, which is then dyed and printed. Therefore, the pre-consumer textile waste of cotton textile products is cotton gin trash during the preparation of yarn and thread, the dyeing material, and chemicals that dissolve in the wastewater, which are capable of harming human health and having a negative effect on the environment.

Table 1 Top ten cotton-producing countries in 2015/2016 (in thousands of metric tons) [21]

Rank	Country	Year			
		2010	2012	2014	2016
1	China	5970	6281	6532	5748
2	India	5683	6071	6426	4790
3	United States	3941	3413	3553	2806
4	Pakistan	1869	2312	2308	1524
5	Brazil	973	1673	1524	1285
6	Uzbekistan				827
7	Turkey				577
8	Australia				566
9	Turkmenistan				294
10	Burkina				239

The post-consumer textile waste is mainly disposed clothes, which contain a mixture of materials. Since the post-consumer textile waste is not easily decomposed [22], it accumulates and occupies space, and may lead to infectious diseases, attract pests, and spread odors in the environment. Therefore, these can cause environmental problems without proper waste management [23, 24].

1.3 Textile Waste Management

Currently, the eco-fashion market has attracted a great deal of attention, which indicates the rising concerns of textile consumers on environmental friendly fashion products [25]. Consequently, the environmental performance of textile manufacturers and suppliers is under unprecedented attention. The environmental management system (EMS) is one of the criteria in green textile strategies [26, 27]. In 1990, the International Organization of Standardization (ISO) has set up ISO 14000 to the textile process for identification, measurement, and control of environmental impact that may cause from any activity in the production chain [28]. Waste management is an important procedure in that system. Textile waste management has played an important role in order to prevent the expansion of textile waste. The idea of textile management is to prevent waste. Waste prevention refers to reducing the quantity of waste and using harmless substances as materials in the production process. Since the 1990s, numerous EMS have been developed for textile customers to assess the suppliers' operational performance, for example, the Green Dragon Environmental Management Standard in the UK and Global Recycling Standards for textiles and clothing [29]. By 2014, over 324,148 textile firms/suppliers distributed in 155 countries had adopted ISO 14000 [30].

Textile waste can be classified into two main groups by physical characteristics, which are wastewater and solid waste. Their chemical compositions and waste-management methods are presented in Sects. 2 and 3.

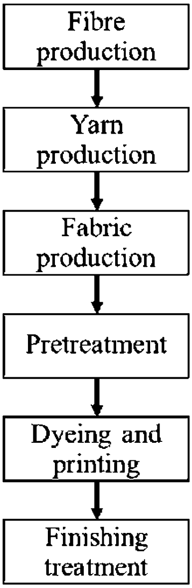

Fig. 1 The textile production process

2 Wastewater from the Textile Industry

2.1 Chemical Composition

The textile industry is one of the top three water-wasting industries in China: around 2.5 billion tons of wastewater were discharged every year [9]. About 700 l of water are used to produce 1 kg of textile [31]. Water is used to rinse or remove unwanted chemicals out of the fabric and it also uses as a chemical carrier to the fiber. Around 17–20% of industrial water pollution is contributed by the textile industry [32].

The quantity of chemicals found in the effluent from the textile production process is related to the type of fiber and its processing method. In order to characterize the chemical compounds in the wastewater from the textile industry, understanding the production process of a textile product is necessary. As shown in Fig. 1, the production process can be divided into six steps: fiber production, yarn production, fabric production, pretreatment, dyeing and printing, and finishing treatment.

2.1.1 Fiber Production

The chemicals used in the fiber production of each type of fiber are different. For cellulose fiber production, the chemicals that are normally used are pesticides, insecticides, and fertilizers, where natural resources are not sufficient for growing plants. While the protein fiber required the chemical to control parasites in animals and after the fiber has been shredded, the scouring chemicals to clean the fiber are needed. For synthetic fiber production, the petroleum oil is used as a feedstock. Pigment and dyes are normally applied in this step.

2.1.2 Yarn Production

The fiber is then spun into yarn. This step needs spinning oil in order to increase the strength of the fiber and reduce the friction force during spinning.

2.1.3 Fabric Production

Fabric is made from knitting or weaving the yarn. The sizing chemical and lubricant are added for preventing the yarn from breaking during the process.

2.1.4 Pretreatment

The pretreatment is a step that prepares the fabric for the dyeing process. This step contains multiple processes, such as de-sizing, scouring, bleaching, and mercerizing. The de-sizing process aims for removal of the sizing chemical (starch) and improvement of absorbency. The sizing chemical is removed by dilute mineral acid (0.25–0.5%) or oxidative agents are applied. However, the de-sizing chemical may affect cellulose fiber in cotton fabric. Therefore, an environmentally friendly de-sizing agent, such as amylase enzyme, is applied in order to remove the sizing agent without fiber damage. Then the washing process is carried out to remove dirt and impurities. The wax, fats, pectin, and lubrication oil are removed by using hot aqueous sodium hydroxide together with the surfactant in scouring process. Before the dyeing and printing step, a bleaching process is required in order to achieve the degree of desired whiteness of the fabric. The common chemical agents used in the bleaching process are sodium hypochlorite, sodium chlorite, and hydrogen peroxide. These oxidative agents can degrade cellulose in cotton fabric as well as decolorize the cotton [33]. Therefore, bio-bleaching by using peroxidase enzymes (DeniLite enzyme) process was created. This process can improve the durability of textiles due to the mild condition of bleaching process [34]. Lastly, a high concentration of sodium hydroxide (18–24%) is usually used in the mercerizing process to improve fabric properties, for instance, tensile strength, fabric hygroscopicity, dye absorbency, luster, and dimensional stability [35]. The strong alkali in the mercerization process causes fiber swelling, untwisting of fiber, and reorientation of cellulose structure leads to improved fabric properties.

This pretreatment step requires a number of chemicals, such as detergents, bases, solvents, enzymes, and bleaching reagents to make the fabric more suitable for dyeing and printing.

2.1.5 Dyeing and Printing

Several chemicals have been commonly used in dyeing and printing processes. Jegatheesan et al. [36] reported that around 700,000–1,000,000 tons of dyes was used for the textile industry and 280,000 tons of dye was disposed into the textile

Table 2 Fiber, their specific dye type, and the amount of unfixed dye in wastewater stream [37]

Fiber	Dye type	Unfixed dye (%)
Wool and nylon	Acid dyes/reactive dyes for wool	7–20
	Pre-metallized dyes	2–7
	After chromes	1–2
Cotton and viscose	Azoic dyes	5–10
	Reactive dyes	20–50
	Direct dyes	5–20
	Pigment	1
	Vat dyes	5–20
	Sulfur dyes	30–40
Polyester	Disperse	8–20
Acylic	Modified basic	2–3
Polypropylene	Spun dyed	N/A

N/A data is not available

wastewater. Dyes and chemicals used in the textile industries are specific for different type of fiber (Table 2). Cellulose fiber requires reactive dyes, direct dyes, naphthol dyes, and indigo dyes, while protein fiber prefers acid dyes and Lanaset dyes. Dispersed dyes, basic dyes, and direct dyes are used to dye synthetic fibers [19]. Hasanbeigi [37] reported that almost 80% of dye can stay on the fabric, and the typical dyes found in textile wastewater are shown in Table 2. Binders and polymeric resins are used to enhance the binding of the pigments in the fabric matrix, and then the unfixed pigments are removed by detergents (i.e., alkylaryl-sulfonates, sulfated alkylphenolpolyglycols, alkylphenol ethoxylates, sodium palmitate, and sodium stearate) in the washing process. The chemicals discharged into the water are one of the huge environmental problems as they can cause hemorrhage, ulceration of skin, nausea, severe irritation of skin, and dermatitis [19]. Additional environmental impacts include an increase of biochemical oxygen demand (BOD) and chemical oxygen demand (COD) and blockage of sunlight, and subsequently an effect on the growth of photoautotrophic microorganisms. Therefore, the unfixed dyes in the wastewater need decolorization and detoxification before disposal into the environment.

2.1.6 Finishing Treatment

This step is a process that adds a special property to the fabric, such as flame retardance, enhanced water resistance, and antibacterial treatment by using specialty chemicals. For example, halogenate or phosphor bases are added to generate flame-retardant fabric, whereas wax or silicone are added to improve water resistance of fabric.

These specialty chemicals used in the finishing treatment are shown in Table 3. These chemicals are applied to coat the fabric, and the residues after the coating

Table 3 Specialty chemicals used in the finishing treatment step [38]

Fabric property	Chemicals
Handle modification	Softeners: polyethylene, quaternary ammonium compounds, silicones, and polyurethanes
	Stiffeners: starches resins, polyvinyl acetate, polyvinyl alcohol
Crease resistance (anti-wrinkling, easy care)	Formaldehyde based
Antistatic treatment	Cationic softeners, polyglycols
Anti-pilling	Resins
Antibacterial/anti-odor treatment	Biocides such as silver, triclosane
Water repellence	Waxes, silicones, fluorocarbons
Oil/soil repellence	Oil/soil repellents based on fluorocarbons
Flame retardance	Flame retardants: halogenated or phosphor based
Protective coatings	Acrylates, polyurethanes, silicones, PVC with plasticizers
Garment treatments for fashion	Potassium permanganate, sodium hypochlorite, calcium hypochlorite, sodium hydrosulfite, potassium dichromate, formaldehyde resins, cationic softeners, cationic silicone softeners

process are discharged as an effluent. Consequently, this leads to environmental pollution.

In summary, the wastewater from the textile production process contains a variety of chemicals, such as dyes and chemicals that used in the process. Ammonia nitrogen and urea are from dyes, raw material, and process (Batik fabric production process requires urea). The typical total nitrogen is around 300 mg/l [39]. Phosphorous in wastewater come from phosphor detergent used in washing and scouring. Sulfide is another compound that is usually found in wastewater. It originates from sulfur, which is a kind of cheap and qualified dye. When oxygen has been removed, sulfur is converted into sulfide [40]. Sulfide is very toxic to the environment, and therefore it has been banned in some countries. In general, the wastewater from the textile industry is characterized by high value of BOD (>200 mg/l), COD (>700 mg/l), pH (>11) and color [41–43]. Moreover, in the process of pretreatment, the pH of dyeing wastewater remains between 10 and 11 when treated by alkali. This chemical's intense condition is harmful to marine life.

2.2 Textile Wastewater Management

Textile production consumes a high volume of water. Depending on the production process, 200–700 l of water could be used to produce 1 kg of fabric [19, 31]. The water is used for applying chemicals onto a textile and rising unwanted chemicals from a textile product. Wastewater from the textile industry contains a high level of chemical compounds. Therefore, wastewater treatment is required to reduce the chemical concentration before disposal to the environment.

2.2.1 Wastewater Treatment

Wastewater treatment can be classified into three techniques, which are physical treatment, chemical treatment, and biological treatment. Each techniques suitable for specific compounds. Most of the dyes used in textile processes are non-biodegradable compounds, therefore, physical and chemical treatments are applied. While the textile wastewater also contains high values of COD and BOD, the presence of particulate matter, oil, and grease in the effluent, can be eliminated by combining all physical treatment, chemical treatment, and biological treatment techniques together.

Physical treatment. Physical treatment is always the first step in wastewater treatment. The effluent from the textile industry contains suspended solids, excessive quantities of oil, grease, and gritty materials. Therefore, the effluent needs to pass through a coarse screened sieve for the removal of large-sized materials such as yarns, lint, pieces of fabrics, and fibers. Then a fine sieve is applied to screen the suspended particles out of the effluent.

Floating particles are removed by mechanical flocculation. This method uses a paddle to stir the effluent at low mixing rate. The small particles bind together and form heavier particles, which can be settled and subsequently removed.

Membrane filtration is an alternative to clarify the textile effluent. It has the ability to remove some particles including dyes from the textile effluent. However, this technique is non-economical, because the membrane may be at risk of clogging, resulting in membrane displacements.

Sun et al. [44] studied wastewater treatment by using radiation. Results showed that the COD value of wastewater decreased from 211.7 to 182.8 mg/l by applying 12 kGy of electron beam radiation.

Chemical treatment. The first step to treat the textile dyeing wastewater is to adjust its pH value, since most dyeing water is alkaline. Multivalent cations are added for neutralization. Then coagulation/flocculation agents are applied to settle the floating particles and decolorize the textile wastewater.

Alum (aluminum sulfate) and ferric chloride are common chemicals used in the coagulation/flocculation process. Over 89% of phosphorous from the effluent and 10–100 mg/l of suspended solids are removed when 90 mg/l of alum and ferric chloride are added [45]. Polyaluminium chloride (PACl), polyaluminium ferric chloride (PAFCl), polyferrous sulfate (PFS), and polyferric chloride (PFCl) are also effective chemicals used in the coagulation/flocculation of wastewater [46].

Ozonation is another technique to degrade organic compounds. Ozone is a strongly oxidizing agent. It forms a reaction at –OH group in the chemicals present in the effluent. This results in reducing COD, color, toxicity, and pathogens, and improves wastewater biodegradability and the coagulation-flocculation processes [47]. Roy et al. [41] reported that ozone treatment with 40 g O_3/m^3 for 30 min can reduce the COD value from 203 to 123 mg/l.

Fenton reaction is a chemical treatment process that uses an oxidizing agent to break down toxic chemicals that cannot be degraded in nature. Hydrogen peroxide (H_2O_2) is normally added in order to generate hydroxyl radicals. Then acidic solution ($pH = 2$–3) containing Fe^{2+} ions is added. This is called a “Fenton reaction". Lin and Peng [48] reported that the Fenton reaction has the ability to reduce the COD in textile wastewaters by approximately 80%.

Biological treatment. Physical and chemical treatments such as membrane filtration, coagulation, and chemical oxidation are conventional techniques that are normally used to remove unwanted materials from the effluent [49]. These techniques also have drawbacks, such as high cost and also generate toxic intermediates. Biological treatment is an alternative way to clean the wastewater. Biological treatment is a process that use enzymes or whole cells from microorganisms to degrade or remove the unwanted compounds from the textile wastewaters [50]. Generally, biological treatment is placed after physical and chemical treatment, as it requires a mild operation condition. Babu et al. [43] reported that most chemicals used in the finishing step are eliminated by adsorption or sedimentation in the biological treatment. However, some microorganisms such as *Galactomyces geotrichum*, *Saccharomyces cerevisiae*, and *Trichosporon beigelii* can degrade dye substances under anaerobic condition [49, 51–53].

Fu and Viraraghavan [54] reported a promising biological treatment process using microorganisms that has a high potential for dye removal. Most biological treatment processes use monoculture to absorb dyes from wastewater [50, 55–58]. Przysta et al. [59] investigated biological treatment by using a mixture of fungal species (*Pleurotus ostreatus*, *Gloeophyllumodoratum*, and *Fusarium oxysporum*). The result showed that after 96 h of treatment, the mixtures of fungal strains were less effective in the dye-removal process than single strains used separately. Monoculture of *P. ostreatus, G. odoratum*, and *F. Oxysporum* resulted in 95.5, 84.6, and 79.2% of dye removal, respectively. The co-culture of *P. ostreatus* and *G. Odoratum* removed 74.3% of dyes, while the co-culture of *P. ostreatus* and *F. oxysporum* removed only 32.2% of dyes. The efficacy of dye removal is related to many factors such as, microbial species, hazardous chemical substances present in the effluent, operating conditions, and retention time.

Abadulla et al. [60] proposed the biological treatment of using laccase to remove dyes in textile wastewater. *Trametes hirsuta* and a purified laccase were used to degrade triarylmethane, indigoid, azo, and anthraquinonic dyes. The results showed that up to 80% of anthraquinonic dyes were removed from the waste effluent. The laccase enzyme in biological treatment has a high decolorization rate, but it cannot degrade all reactive dyes. Since laccase is an enzyme, high anionic strength conditions may lead to enzyme deactivation. Tauber et al. [61] applied laccase with ultrasound technique to improve the decolorization rate. Results showed higher dye degradation rates when combining these two techniques. Laccase demethylated the dye (Acid Orange 52) and the ultrasound attacked the –OH group in the dye compound.

The biological process includes aerobic, anaerobic, and combinations of these two that can be subdivided into suspended and attached growth systems. However, these processes require a large amount of space for storage and a long retention time compared to physical and chemical treatments [62].

Another way to deal with wastewater issues is to avoid using harmful substances in the textile production process [63]. Kant et al. [32] proposed a green textile production concept which applies harmless or biodegradable substances in the process, for instance, applying a natural material such as olive mill wastewater, rutin (flavonoid), fennel leave, and mangrove bark as natural dye in dying process [64–67]. In the bleaching step, hydrogen peroxide or ozone are applied instead of chlorine, which is a strongly toxic chemical generated during the bleaching step. Since it can operate in cool conditions and ozone can increase oxygen and water into the wastewater [32]. Furthermore, bio-bleach or enzyme treat on textile is an alternative way to support green textile concept [68]. Bees wax, aloe vera, and vitamin A are good finishing agents in terms of flame retardance in the finishing step. Potato starch or carboxymethylcellulose can be used as a sizing agent instead of polyvinyl alcohol (PVA) [32]. The development of this idea requires more exploration.

3 Solid Waste from Textile Industry

3.1 Chemical Composition

The pre-consumer textile wastes in the textile production process are shown in Table 4. The solid form of pre-consumer textile waste contains biodegradable substances such as fiber waste, yarn waste, fiber lint, and fabric scrap. These substances can be recycled into new raw materials and they can decompose in nature, since they are organic matter.

The post-consumer textile waste is a mixture of natural fibers, synthetic fibers, and other substances, such as metallic zippers, acrylic buttons, wood buttons, shell buttons, and metallic snap fasteners, which make it hard to degrade [69]. Post-consumer textiles can be reused, but they mostly go to municipal landfill or incineration. These textiles accounted for about 13 million tons of the solid waste but only 15% was recovered in 2010 [70, 71]. Although textile waste contains organic substances, landfill of textile waste requires space and takes a relatively long time to decompose (6 months–20 years) [72, 73]. The degradation rate is related to the fabric component and landfill environment [72]. Cotton fabric showed 50–70% weight loss after 3 months of landfill [74] and wool takes 6 months to decompose [75]. Synthetic fibers, especially polyester, is a biodegradable-resistant fiber. There was no evidence of microbial degradation found after 4 weeks of landfill under by Fourier transform infrared spectroscopy observation [76] and only 20% weight loss was shown after 3 months of landfilling [74]. Furthermore, landfilling may release toxic substances, and it can generate methane, which contributes to the global warming issue. Therefore, these accumulated wastes lead to an environmental problem.

The conventional method for treatment of solid waste from textile industry is landfill or incineration [77]. However, this treatment is not favor, in some area of Europe (Germany, Austria, Sweden, Denmark, Belgium, the Netherlands, and Switzerland) and North America since the releasing leachate from textile landfill may contaminate the surface water and underground water source may cause adversely affect human health [14]. Furthermore, the methane formation during decomposing of organic substance can cause greenhouse gas emissions.

Table 4 Examples of waste materials generated during the cotton textile production process [35, 43]

Step	Process	Wastewater	Solid wastes
Fiber preparation	Fiber preparation	Little or no wastewater generate	Fiber waste
Yarn production	Yarn production	Spinning oil	Sized yarn, fiber waste, cleaning and processing waste
Fabric production	Sizing	BOD, COD, metals, cleaning waste, size	Fiber lint, yarn waste
	Knitting/weaving	Little or no wastewater generated	Yarn and fabric scraps, off-spec fabric
Pretreatment	Desizing	BOD from water-soluble sizes, synthetic size, lubricants, biocides, anti-static compounds	Fiber lint, yarn waste, cleaning materials such as, wipes, rags, and filters, cleaning and maintenance wastes containing solvents
	Scouring	Disinfectants and insecticide residues, NaOH, detergents, fats, oils, pectin wax, knitting lubricants, spin finishes, spent solvents	Little or no solid waste generated
	Bleaching	Hydrogen peroxide, sodium silicate, or organic stabilizer, high pH	Little or no solid waste generated
	Mercerizing	High pH, NaOH	Little or no solid waste generated
Dyeing and printing	Dyeing	Metals, salt, surfactants, toxics, organic processing assistance, cationic materials, color, BOD, sulfide, acidity/alkalinity, spent solvents	Little or no solid waste generated
	Printing	Suspended solids, urea, solvents, color, metals, heat, BOD, foam	Little or no solid waste generated
Finishing	Finishing	BOD, COD, suspended solids, toxics, spent solvents	Fabric scraps and trimmings

Incineration is another practical treatment that is widely used to handle textile waste since textile wastes have high energy contents [78]. However, incineration may cause dioxin emissions during a high-temperature process. The dioxin has long term accumulated in environment and food chain. This group of chemicals was found to have an adverse effect on human health such as damage to the immune system, interference with the hormone system, and also in causing cancer [79]. This led to the conclusion that textile incineration has a high potential to produce toxic compounds. Even though this treatment can reduce 95–96% of waste mass, toxic compound formation is still an environmental concern.

In order to minimize textile waste and prevent the expansion of textile waste, simple waste management such as recycling can be applied. Recycling is another strategy that can reduce the waste stream and generate an alternative income at the

Table 5 Recycled products from textile waste

Substrate	Product	Reference
Lyocell fabric (modified cellulose)	Adsorbent fiber for heavy metal adsorption	[82]
Cotton and textile ash wastes	Bricks	[81]
Cotton and limestone powder wastes	Bricks	[83]
Textile waste ash and basaltic pumice	Bricks	[84]
Cotton waste	Chipboards	[85]
Waste cotton fibers	Nanoparticle	[86]
Waste cotton fabrics	Microcrystalline cellulose	[87]
Waste cotton fibers	Thermoplastic matrix	[88]
Cotton/polyester blend fabrics	Reinforced composites	[89]
Cotton waste fiber	Reinforced composites	[90]
Woven fabric	Reinforced composites	[91]
Plain woven PET and cotton (65/35%) fabrics	Composites	[92]
Waste cotton fabrics	Composites	[93]

same time. The pre-consumer textile waste; by product from textile production process such as cotton residues, wool residues, yarn residues and fiber residues has a potential to be recycled. It can be used as a raw material to produce other products or it can go to reprocess again. However, reprocessing may decrease yarn properties. Wanassi et al. [80] reported that recycled cotton yarn has shorter fiber than new yarn and therefore the recycled cotton yarn has less tensile strength compared to new cotton yarn. On the other hand, post-consumer textile waste is a mixture substance. The recycling of post-consumer waste is first categorized by type of material, as textile waste may contain a cotton, wool, silk, nylon, olefin polyester, and other materials like button, metal hooks, and plastic materials. The categorized wastes are sold for recycling industry or for clothing reprocess. The cotton waste is sold to brick kilns factories [81, 82]. Pure cotton waste can be used to produce medical textiles and superabsorbent polymer. Wool residues are normally recycled by blending with new wool to create new textile products. The metal scrap is sold in the junk market from where it is resold to recycling industries. The plastic material is sold to chemical industries for refilling. There are many products that are made from textile waste (see Table 5). For example, composite material is normally produced from textile waste due to textile waste in brick may increase tensile strength into material. Moreover, brick production has less concern about organic content and heavy metal in the material. Adsorbent material is another product that is usually made from textile waste since the original properties of fiber are suitable for absorption. After being modified by physicochemical methods, it gains more absorption efficacy. A more detailed explanation about textile recycling is provided in Sect. 5.

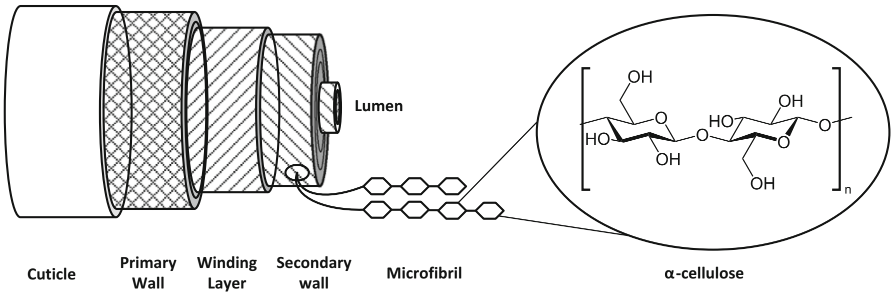

Fig. 2 Microstructure of the cotton fiber at various scales (the dimension of the cell wall is not to scale; the direction of microfibril alignment is not based on a real image). This diagram was re-plotted based on the previous publications of Anderson and Kerr [95] and Gordon and Hsieh [22]

4 Enzymatic Hydrolysis of Cellulose

4.1 Basic Structure of Cellulose

Cotton is the most widely used natural fiber in textile products [12]. Cotton fibers are collected from the boll of the *Gossypium* genus plants [94]. The basic structure of the native cotton fiber is shown in Fig. 2. A cotton fiber is a very long plant cell constructed within a multi-layered cell wall structure. The microstructure and the fundamental physiochemical characteristics of the layered cotton fiber cell wall have been investigated in detail previously [22, 95]. In summary, lumen is originally the "living" part of the cell, filled with liquid and protected by the cuticle, primary wall, winding, and secondary walls. In each layer of the cell wall, the microfibrils form into spiral bundles and align at different directions corresponding to the fibril axis of the cotton cell [94, 95]. The mature cotton fibers are dried cells, in which the lumen becomes a hollow space inside the collapsed cell wall.

The major constituent of the cotton fiber is α-cellulose, which contributes to nearly 100% of the secondary wall (i.e., with a high degree of polymerization, DP of 14,000) and 30% in the primary wall of the cotton fiber (i.e., DP between 2000 and 6000). The rest of the components are hemicelluloses and other trace elements [22].

The long cellulose chains are constructed in different orders in the microfibrils as illustrated in Fig. 3a. In the crystalline zone, cellulose chains are well organized and linked among each other under a specific order by hydrogen bonds and van der Waals forces; and an amorphous structure of which the microfibrils are twisted or less ordered [96]. Amorphous cellulose is more easily hydrolyzed by cellulase and has often been considered the "weak points" of the cellulose fiber in higher plants [97].

4.2 Cellulase

Cellulase is generated from various types of bacteria and fungi, such as *Cellulomonas fimi* and *Thermomonospora fusca* [98], and filamentous fungi belonging to the genera *Trichoderma* (i.e., *T. viride, T. longibrachiatum, T. reesei*)

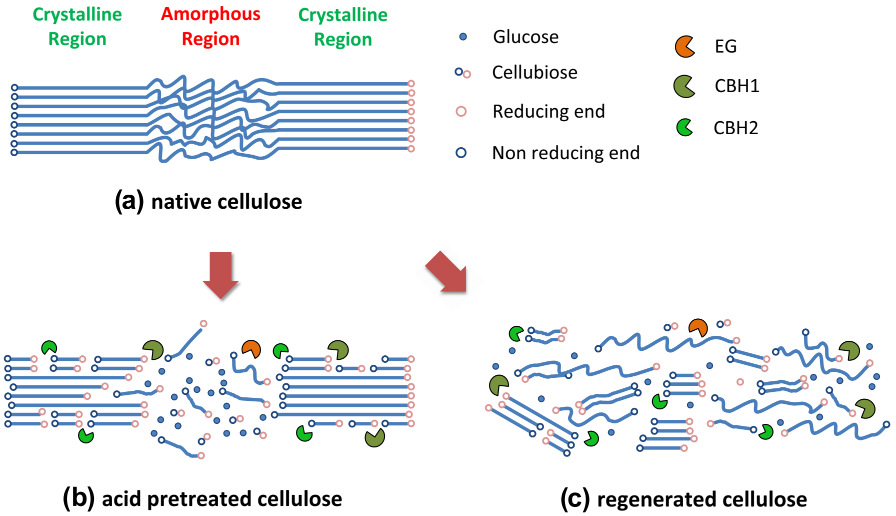

Fig. 3 Schematic diagram of the enzymatic hydrolysis processes of the native cotton cellulose before pretreatment (**a**); cellulose after acid pretreatment (**b**); and regenerated cellulose after freezing soda pretreatment (a hypothetical phenomenon generated based upon the dissolution-regeneration mechanisms) (**c**)

and *Aspergillus* [99]. *Trichoderma* is the most widely studied fungal genera for commercial production of cellulase [100–102].

Cellulase is an enzyme complex that is composed of several monoenzymes, i.e., β-1,4-endoglucanases (EGs), exoglucanase or β-1,4-cellobiohydrolase (CBH), and β-glucosidase (BGs), which are highly specified for enzymatic hydrolysis of cellulose [103, 104]. Some of the key cellulases and their affecting areas to the cellulose fiber are shown in Fig. 3. The synergetic reaction of enzymatic hydrolysis has been detailed in many studies [103, 105]. Briefly, EGs are reactive in cleaving the β-1,4-glucosidic bonds when binding randomly with the amorphous cellulose. This reaction creates new chain ends in the microfibrils. CBH (including CBHI and CBHII to target on the reducing end and non-reducing ends of the cellulose chain, respectively) further cut the bonding alone the chain and gradually release the cellobiose in the hydrolysate. Finally, BGs hydrolyses the cellobiose into glucose.

4.3 Factors Hindering the Enzymatic Hydrolysis

As enzymatic hydrolysis is carried out by the enzymes complex the efficiency and product yield of the synergetic reaction follows the basic criteria like all the heterogeneous catalytic reactions. Cellulase needs to bind with the specific site on the cellulose first and then the reaction can take place [106]. The specific binding sites on the cellulose fibers need to be as “accessible” as possible to the correlated cellulase [107]. Meanwhile, the function and reactivity of the enzymes (e.g., the mass ratios of the three basic cellulases, as mentioned in Sect. 4.2) should match the properties of the substrate, and the hydrolysis should be carried out under the appropriate environment, i.e., appropriate pH and temperature [108]. The key factors affecting the performance of enzymatic hydrolysis can be classified into two categories, the enzyme-related and substrate-related factors [109]. As the enzyme-related factors have been intensively studied [107] and the cellulosic fiber is a high purity component, only the substrate-related factor of cotton fiber is discussed in this review, as our project mainly focuses on textile waste treatment. The following sections summarize the most dominating substrate-related factors affecting enzymatic hydrolysis of cotton fiber.

4.3.1 *Cellulose Crystallinity*

Cellulose crystallinity (measured and expressed as the crystallinity index, CrI) and degree of polymerization (DP) are two most significant parameters affecting the efficiency of enzymatic hydrolysis. It has long been recorded that the initial reaction rate of enzymatic hydrolysis can increase with decreasing CrI of the cellulose samples [110, 111]. Therefore, pretreatment is essential to enzymatic hydrolysis of cellulose fiber with high CrI. For example, CrI was reduced significantly during mechanic pretreatment, e.g., twin screw extrusion [112], effectively while simultaneously changing the substrate properties, such as decrease of particle size or increase of accessible surface area [113], which furthermore increased the rate of hydrolysis. Also, it has been observed in chemical pretreatment methods, such as alkaline pretreatment, could reduce the CrI of the substrate [114].

4.3.2 *Degree of Polymerization*

The number of AGUs or DP are indicators of the mean chain length of the cellulosic fibril [115]. In purified cotton linter, the average DP is between 1000 and 3000 [116]. DP is strongly related to the other properties of the substrate such as CrI. During enzymatic hydrolysis, EGs target on less organized internal cellulose chains, which has a main role in decreasing DP. Cellulose DP ascribes to the increased recalcitrance of the remaining crystalline cellulose in the hydrolysate [117].

4.3.3 *Surface Area of Substrate/Feedstock Particle Size/Porosity*

Surface area and particle size are essential factors that can influence the enzymatic hydrolysis process. Increasing surface area or reducing particle size to increase the accessibility of cellulose to enzyme is the main focus of all types of pretreatment [118]. The influence of surface area and particle size on enzymatic hydrolysis could be even more crucial than the CrI under certain conditions [119]. Furthermore, the pore size of the substrate, created after pretreatment, is also a factor in enzymatic hydrolysis [120]. In most cases, the internal area of lignocellulose substrate is much larger than the external area, which blocks the accessibility of enzyme in the pores [121]. Therefore, increasing the porosity has the ability to boost the hydrolysis to some extent.

4.4 Pretreatment

Pretreatment is a primary step in increasing the cellulose accessibility to cellulase [107, 113]. A significant number of studies have been carried out on the pretreatment of textile fiber for resource recovery, and the major scopes with research outcomes are summarized in Table 6. The basic pretreatment approaches can be classified into four categories, i.e., chemical (acid, alkali, and ionic liquid), biological, physical (milling and grinding), and physico-chemical processes. Different pretreatment processes may result in different types and levels of structural modification and improve enzymatic hydrolysis after different mechanisms [114], which will be summarized in the following sections.

4.4.1 Acid Pretreatment

Acid pretreatment is currently the most widely studied and applied approach for the pretreatment of cellulose fiber and other related feedstock. The key mechanisms of the acid pretreatment to the decomposition of the microstructure of cellulose fiber and its impacts on enzymatic hydrolysis are illustrated in Fig. 3b. During the acid pretreatment process, the amorphous region of cellulose can be hydrolyzed to short saccharide chains, cellobioses, and some glucose, while the crystalline regions with more reducing ends and non-reducing ends can be exposed to the enzymes, which facilitates the enzyme to perform the degradation process. Meanwhile, formic acid was found to be useful in breaking down the hydrogen bonds between the chains of the cellulose molecules, causing swelling of the fibers, and "crush" the crystalline lattice of the microfibrils [136]. The sugar yield of acid-induced hydrolysis of cellulose fiber increases with increased dosages of acid, higher cooking temperature, and longer retention time. Complete conversion of cellulose to sugar is possible based upon the severity of pretreatment.

Acid pretreatment was conducted under two concentration ranges based on the needs of applications and the treated feedstock. Concentrated acid pretreatment has been carried out by using 60–90% of acid and dilute acid processes usually involve the use of acid at 0.5–15% in the pretreatment liquid [137]. Sulfuric acid or phosphoric acid pretreatment have been applied to improve both direct hydrolysis and enzymatic hydrolysis [122, 124]. Chu et al. [122] showed that cotton cellulose (at 30–70 g/l concentration) can be completely dissolved in 55% sulfuric acid at 40 °C, resulting in reasonable sugar yield between 64.3 and 73.9%. Shen et al. [123] used 85% phosphoric acid to treat the cotton-based textile wastes and achieved a 79.2% sugar recovery at 50 °C after 7 h. On the other hand, dilute acid pretreatment has been commonly applied for treating cellulose and other biomass [138, 139]. The process has often been conducted at higher temperature than the concentrated acid processes at 95 °C [127], 121 °C, or even higher temperature [126]. The cooking time of the processes is usually less than 30 min, followed by enzymatic hydrolysis after pH neutralization. The optimal pH for the enzymatic hydrolysis processes is approximately 4.8–5.0.

Acid pretreatment provides a simple solution to direct hydrolysis of simple cellulose such as cotton and textile wastes, but some concerns have been raised due

Table 6 Published pretreatment methods on cotton/polyester separation and enzymatic hydrolysis

Substrate	Solid content	Chemical	Pretreatment conditions	Hydrolysis condition (if applied)	Results	Reference
Cotton cellulose	30–70 g/l	55% H_2SO_4	40 °C		The reduced sugar yields from 64.3 to 73.9%	[122]
Cotton-based textile waste		85% H_3PO_4	50 °C, 7 h		79.2% sugar recovery	[123]
100% cotton liner and polyester/cotton blended shirt (40/60%)	5.20%	85% H_3PO_4	50 °C, 120 min	50 °C, 2.5% solids loading, pH 5.0, 10 FPU cellulase	4.6–7.7 mg/ml sugar yield, ethanol 0.4 g/g glucose	[124]
Cotton waste	2.50%	3% H_2SO_4	121 °C, 30 min	50 °C, 5% solids loading, pH 5.0, 0.52 U/ml cellulase	400 mg/ml sugar yield and 8.9 g/l ethanol yield	[125]
Cotton waste	1.50%	1.1% H_2SO_4	121 °C, 30 min	45 °C, 5% solids loading, pH 4.5, 0.52 U/ml cellulase	90 ml/l ethanol yield	[126]
Cotton cloth (mercerized cotton, Tencel, cupra, rayon, and polynosic)	0.20%	10 N H_2SO_4	95 °C, 1 min follow 10 min stirring		Complete cotton and polyester separation	[127]
Cotton linter/jeans	1 g/20 ml	12% NaOH	0 °C, 180 min	50 °C, 3% solids loading, pH 5.0, 60 FPU cellulase	0.48 g ethanol/g textile	[128]
Orange 50/50 polyester/cotton & blue 40/60 polyester/viscose blend	5%	85% *N*-methylmorpholine-*N*-oxide	120 °C, 120 min	50 °C, 3% solids loading, pH 5.0, 20 FPU cellulase	48 (85%) and 50 (89%) g ethanol/g, respectively	[129]
Blended knitting yarn (50% cotton/50% polyester) waste	10%	20 g/l $MgCl_2$ and 4 g/l $Al_2(SO_4)_3$	20 °C followed by 180 °C steaming		Highest degradation rate (95.47%) of cotton component	[130]
Greige cotton print cloth fabric	1% (3 g)	Cellulase EBT		1 g/l concentration, 108 FPU/ml, 50 °C, pH 4.8, 4 h with agitation	7% weight loss, reduce sugar 25.8 mg/g cotton	[131]
Denim 100% cotton fabric	3%	Genzyme SL		2% concentration, 55 °C, pH 5.5,40 min	5% weight gaining due to more shrinkage in warp direction	[132]

Table 6 continued

Substrate	Solid content	Chemical	Pretreatment conditions	Hydrolysis condition (if applied)	Results	Reference
Mercerized taffeta (100% cotton)	1%	100 mg/g *Trichoderma reesei*, Cellusoft L (CMC activity 25.8 mg/ml)	50 °C, 120 min	0.1 M acetate buffer, pH 5.0, at 50 °C.	100% total weight loss under mechanical agitation	[133]
Mercerized taffeta (100% cotton)	4%	100 mg/g *Trichoderma reesei*, Cellusoft L (CMC activity 25.8 mg/ml)	50 °C, 360 min	0.1 M acetate buffer, pH 5.0, at 50 °C.	100% total weight loss under mechanical agitation	[133]
Taffeta mixture (66% cotton and 34% polyester)	4%	200 mg/g *Trichoderma reesei*, Cellusoft L (CMC activity 25.8 mg/ml)	50 °C, 540 min	0.1 M acetate buffer, pH 5.0, at 50 °C.	50 and 45% in total and insoluble weight loss	[133]
Undyed 100% cotton T-shirts	2%	Ionic liquid (IL) 1-allyl-3-methylimidazolium chloride ([AMIM]Cl)	110 °C, 90 min	50 °C, 5% solids loading, pH = 5.0, 3.3U/ml cellulase	Highest sugar yield 94%	[134]
50/50 polyester/cotton blend yarn	2%	AMIMCI	120 °C, 360 min		100% dissolution and cotton/polyester separation	[135]

to its more stringent requirements of reactors/container to prevent corrosion at elevated concentrations and low recyclability of acid reagents. Both of these factors can considerably increase the operation cost and environmental concern of the overall biorefinery process. Meanwhile, high severity acid pretreatment (i.e., high acid doses, high temperature, and extended reaction time) can often promote the conversion of carbohydrates to form into sugar dehydration by-products (i.e., furan-type inhibitors; 5-hydroxy methyl-furfural and 2-furfuralaldehyde), which are harmful to the downstream fermentation processes at high concentration [118, 140, 141].

4.4.2 Alkali Pretreatment

Alkali pretreatment process is another commonly applied process to decompose the structure of the cotton fiber. The key function of alkaline to cellulose, as illustrated in Fig. 3c, is the swelling effect, which breaks down the inter and intra chains of cellulose molecules, resulting in more amorphous regions for enzymatic hydrolysis [139]. Sodium hydroxide (NaOH) [128, 142], potassium hydroxide (KOH) [143], and calcium hydroxide [$Ca(OH)_2$] [144, 145] are commonly used chemicals for alkaline pretreatment. Alkaline pretreatment is known for its saponification and salvation reaction to destroy the organized structure of the cellulose, which reduce the DP and CrI of the cellulose and create more porous space for enzymatic hydrolysis [118].

The sugar yields after sodium hydroxide at high temperature, i.e., 121 °C [142], room temperature, and freezing temperature [128], have been investigated in many previous works. The pretreatment condition of 121 °C and 15 psi is not widely promoted from an economic perspective of industry, even though it can largely improve the enzymatic hydrolysis [142]. Pretreatment under room temperature seems to be a more reasonable method for large-scale application.

Cellulose dissolution at low temperature by using NaOH seems to be an applicable approach to break the crystallinity region of cellulose to some extent. Many derivative and non-derivative cellulose dissolution solvents have been studied. Only non-derivative solvent like NaOH is proven to have the ability to regenerate dissolved cellulose for enzymatic hydrolysis [146]. NaOH/urea aqueous solution was found to directly dissolve cellulose at freezing temperature and to increase enzymatic hydrolysis efficiency based on the earliest proposed cellulose dissolution mechanism [147]. Sodium hydroxide hydrates could penetrate the amorphous region of cellulose and destroy the crystallized region; therefore this process increases the dissolution of cotton cellulose [148, 149]. The function of urea is to be a component of a system including NaOH hydrates–urea–free water–cellulose form a special solution. Soda in the solution serves as a cutting tool to destroy the inter- and intra- hydrogen bonds between cellulose molecules, and urea hydrates prevent the re-association of cellulose molecules by acting as a hydrogen bond donor and receptor in the solvent [150]. Although with many benefits for the alkali pretreatment, the long processing time, low solid-to-liquid ratios during pretreatment, and needs of neutralization of pretreated substrate, may somehow hinder the wide application of the process. These problems may be overcome by the high recyclability of the reagents in the spent liquor, which also needs to be tested in the near future.

4.4.3 Ionic Liquid

The pretreatment by using ionic liquid (ILs) has drawn a significant amount of attention recently. ILs are an organic salt that consists of organic cations and relatively smaller inorganic anions in a liquid phase at room temperature, and their melting point is below 100 °C [151]. There are mainly two factors that lead to the various properties of ILs: the cation structure (the symmetrical array, the influence of alkylphosphonate, and hydrophobic groups) and the anion delocalization degree [152]. Previous researchers also proved that the composition of lignocellulosic biomass changes scarcely while its structure alters significantly through ILs pretreatment [151]. Some ILs have shown outstanding characteristics for industrial application, i.e., high chemical and thermal stabilities, liquid form in wide range of temperature, low vapor pressure, and low viscosity operation, which reduces the cost of mixing [153].

Among all the investigated ILs, some non-derivative hydrophilic ionic liquid, for instance, 1-butyl-3-methylimidazolium chloride (BMIMCl) and 1-ethyl-3-methyl imidazolium diethyl phosphate (EMIMDEP) have shown the capability of dissolving cellulose [154]. Because the hydrogen bond in ILs arranged between non-hydrated chloride ions and sugar hydroxyl proton in a 1:1 ratio, which disrupts the non-covalent bonding of cellulose and other components [155]. After the ILs pretreatment process, the dissolved cellulose can be regenerated by adding anti-solvents such as water, ethanol, or acetone [154]. The regenerated cellulose through ILs pretreatment has more homogeneous microfibrils than original cellulose, while the DP and polydispersity remains with no significant changes [156].

ILs has been tested in the pretreatment of certain cotton or textile wastes, although its feasibility in large-scale application is still unclear and needs further investigation. Hong et al. [134] used a 1-allyl-3-methylimidazolium chloride ([AMIM]Cl) IL to treat undyed 100% cotton T-shorts. After 90 min of pretreatment at 110 °C, a high sugar yield (94%) was achieved by using a reasonable amount of cellulase. De Silva et al. [135] further used the same IL to treat a 50:50 blend PET/cotton yard at a longer cooking period (6 h) and higher temperature (120 °C). The cotton was effectively dissolved and regenerated in the anti-solvent and formed into fiber films after regeneration. The PET was completely recovered after the process.

The key limiting factors hindering the applicability of ILs are high production cost and environmental toxicity [157]. The current price for ([AMIM]Cl) IL is approximately $22–26 USD per gram (chemical grade, Sigma-Aldrich). Furthermore, complete removal of ILs should be conducted after the pretreatment process, as its residue has shown a substantial negative influence on enzyme hydrolysis [158]. Finally, in terms of operation and processing, the IL/cellulose mixture is difficult to handle in the existing reactor systems due to its increasing viscosity, which will significantly increase the operation cost of the overall processes and need to be overcome in further investigations [158].

4.4.4 Supercritical Fluid

Supercritical fluid is a phase of reagents of which both gas and liquid phases coexist under a specific pressure and temperature [159]. It shows liquid-like density and gas-like diffusing/penetrating ability to solid materials. Among all the supercritical fluids, supercritical carbon dioxide, which has a critical temperature at 31 °C, has shown to be suitable for pretreatment of cellulosic feedstock [159]. Supercritical carbon dioxide (SC-CO_2) has been widely used as an extraction solvent [160]. In aqueous solution, CO_2 forms carbonic acid and can improve the hydrolysis of polymers. CO_2 molecule is similar in size to the molecules of water or ammonia, and therefore they can penetrate through the same pathway to the small pores of the cellulose.

CO_2 has even been used to modify steric structures of some cellulases to improve their stability, solvent tolerance, and reactivity [161]. Saka and Ueno [162] investigated the direct conversion of various types of celluloses (including cotton linter) in supercirtyical water (500 °C, 35 MPa) into glucose and found that cellulose can be hydrolyzed to a similar level as acid or enzymatic hydrolysis, without the difficulties occurred by using those hydrolyzing techniques. Muratov and Kim [163] studied the performance of enzymatic hydrolysis of cotton fibers in supercritical CO_2 (120 atm, 50 °C, 48 h) and found that the productivity of the glucose increased by 20%, as in atmosphere. As commercial-scale supercritical CO_2 treatment has been seen in textile industries (such as for dyeing), similar technology and equipment could be worthwhile to be explore further for the treatment of textile wastes in the future.

5 Valorization of Textile Waste

In the 1990s, the waste valorization concept attracted attention worldwide since waste disposal is becoming a serious issue. Nowadays, waste valorization is not only concerned with efficacy of waste handling but also with the management of recycling programs. Valorization of waste is defined as a process activity that is aimed at reusing, recycling, or composting wastes to produce value-added products or sources of energy [164]. It is considered as a business opportunity as well as a sustainable way for chemical production. Textile recycling has the potential to make a huge environmental and economic impact. Valorization of textile waste is divided into two main types: valorization of wastewater and valorization of solid waste from textile industry.

5.1 Valorization of Wastewater from the Textile Industry

Textile wastewater is comprised of toxic pollutants such as dyes, heavy metals, and surfactants. Furthermore, wastewater composition changes according to the processing step. These toxic chemicals in textile wastewater are harmful to ecosystems, so most of the studies were focused on wastewater treatment rather than valorization of textile wastewater. Even though wastewater contains hazardous chemical compounds, it also contains organic components, which can be converted into value-added compounds via bioconversion processes.

5.1.1 Bioconversion of Wastewater to Value-Added Products

Due to the inhibitory effect of toxic chemicals in textile wastewater, there have been very few studies conducted on valorization of textile wastewater via bioprocesses (Table 7).

Opwisa and Gutmanna [170] have demonstrated a biological conversion of sugar in textile wastewater into biogas without any wastewater treatment. Results showed that biogas, which contains 60% of methane, was generated and COD in wastewater decreased around 85%. There is no evidence for microbial growth suppression by trace elements presented in wastewater. However, applying advanced oxidation processes as a wastewater treatment on biogas production has improved biogas productivity. Apollo et al. [171] investigated the effect of UV treatment of textile wastewater on biogas production via an anaerobic digestion system. Results showed that the treated wastewater has improved methane content in biogas of around 25–50%.

There are a few studies on using textile wastewater for biohydrogen production. Li et al. [169] investigated the feasibility of using textile wastewater as a raw material to produce biohydrogen. Result showed that just only 0.04 to 1.04 mol H_2/mol hexose was obtained from non-treated textile wastewater. Then wastewater activated carbon was applied in order to remove toxic chemicals. Result found that 1.37 mol H_2/mol hexose was obtained from treated textile wastewater.

On the other hand, Lay et al. [168] studied the bioconversion of textile wastewater without any pretreatment to remove toxic chemicals. They reported that 66 ml of bio-hydrogen was produced from textile wastewater surplus with starch via anaerobic fermentation. The biohydrogen contained 32.2% of H_2, corresponding to a hydrogen yield of 1.56 mol H_2/mol hexose with hydrogen production rate of 1.14 l/l/day. Moreover, ethanol, butanol, and acetic acid were generated as by-products at the same condition. This study found that the optimal textile waste concentration for producing bio-hydrogen was around 8–17 g COD/l. This indicated that pretreatment is required in order to reduce COD level and to remove toxic chemicals, which may have a negative affect on microbial cells. Consequently, it can improve productivity of the bioconversion process.

Unlike the bioconversion process, hazardous compounds have less concerned in thermal process. Therefore, Kipçak and Akgün [172] proposed an alternative method to generate energy via gasification of textile wastewater. The experiment was performed at high temperature (450–600 °C) under a constant pressure (25 MPa) for 150 s. Results showed that 1 ml of textile wastewater can generate 1.23 ml of syngas, which comprises 3.02% hydrogen, 38.93% methane, 4.33% ethane, 0.10% propane, 0.01% propylene, 7.97% carbon monoxide, 27.22% carbon dioxide, and 8.00% nitrogen.

Table 7 Overview of bioconversion of textile wastewater to value-added products via bioprocesses

Valorized product	Productivity (production rate)	Fermentation mixture	Microorganism	Fermentation type	Remark	Reference
Biogas	55.7 l/g COD (312 L/day)	Sago: textile dyeing wastewater at ratio of 70:30	Unknown microorganisms from the anaerobic digester treating sago effluent	Anaerobic digestion	88.5% COD removal	[165]
	90.8 l/g COD (1.65 L/L d)	Textile wastewater	Granular sludge	Anaerobic digestion	85% COD removal 20-l reactor	[166]
	3.3 l/g COD (7.2 l/day)	30% of synthetic dye and 70% of synthetic starch wastewater mixing	Mixed consortium from the anaerobic digester treating tapioca starch effluent	Anaerobic digestion	81% COD removal	[167]
Biohydrogen	1.56 mol H_2/mol hexose	Textile wastewater supplemented with starch and inorganic nutrients	Cow dung	Anaerobic fermentation	32.2% H_2	[168]
	1.37 mol H_2/mol hexose	Treated textile wastewater	Wastewater treatment sludge (*Clostridium butyricum* and *Klebsiella oxytoca*)	Dark fermentation	The wastewater was hydrolyzed by β-amylase. Inhibitors were removed by activated carbon and cation exchange resin. Ethanol and acetic acid were obtained in liquid phase	[169]

5.2 Valorization of Solid Waste from the Textile Industry

The solid waste from the textile industry may consist of a single type of fiber or multiple types of fiber depending on the processing step and end product. The waste that contains a single type of fiber is preferred, as their recycling process is simpler. Organic compounds in solid waste can be used as a raw material to produce desired products via bioconversion processes. On the contrary, thermal and chemical processes can convert both organic and inorganic compounds to value-added products.

5.2.1 Thermal and Thermochemical Conversion Processes

Conventional thermal processing refers to the combustion of solid waste and its conversion into energy. Since solid waste from the textile industry contains a high energy content, it can be used as a raw material to generate heat energy. Ryu et al. [78] reported that a mixture of cotton and polyester contained energy content of 16 MJ/kg. Combustion of the blend fabric at 700 °C for a few minutes could generate a high heat energy content gas stream at 1100 °C as the air flow rate of 819 kg/m^2/h (0.186 m/s).

Briquette is another product created from the conventional thermal process. Briquette is a solid fuel that is normally made from woody material. Solid waste from the textile industry can also be used as a raw material to produce briquette. Drying and densification processes are required because solid textile waste is bulky and contains high moisture. Once the textile waste is compacted, it can be used for co-combustion with solid fuel, since it contains a similar compound compared to the briquette that is obtained from coal [173] (Table 8).

The thermal processes that is performed at high temperature with inadequate oxygen could generate carbon monoxide, which is a greenhouse gas. Therefore, a thermochemical conversion process, such as pyrolysis, was applied. Pyrolysis is referred to the decompositional process with high temperature in absence oxygen condition. The absence of oxygen was controlled by nitrogen, which was used as the carrier gas to provide an inert atmosphere. Products from pyrolysis are various, such as activated carbon fiber, char, bio-oil, and syngas (as shown in Table 9). The variation of product is related to pyrolysis condition. William and Reed [174] investigated the effect of pyrolysis condition on the production yield (activated carbon from natural fiber textile waste). The results indicated that the pyrolyzed product at high temperature has improved surface area of activated carbon [174]. Nahil and William [175] investigated activated carbon production from acrylic compound in textile waste via pyrolysis. They reported that the retention time of pyrolysis also affects surface area generation. Results found that pyrolyzed product at 700 °C and steaming at 900 °C for 1 h had a surface area of around 500 m^2/g activated carbon, while pyrolysis at 700 °C and steam at 900 °C for 2 h can increase the surface area up to 752 m^2/g activated carbon.

Many textile-recycling studies have applied chemical substances in the process in order to improve properties of product. For instance, applying sulfonication technique on cotton lint can create absorbent material that can remove lead ions [179]. Cotton

Table 8 Composition of briquettes derived from textile waste and coal [173]

Feedstock	Textile waste	Coal
Ultimate analysis (%w/w daf)		
Hydrogen	6.52	5.7
Carbon	65.07	84.0
Sulphur	0.23	2.6
Nitrogen	16.14	1.5
Oxygen	12.04	6.06
Chlorine	–	0.14
Proximate analysis (%w/w)		
Ash (db)	1.98	6.6
Moisture (ar)	2.41	6.3
Heating values (MJ/kg)		
Lower heating value (ar)	26.37	29.97
Higher heating value (ar)	27.79	31.18

daf dry ash free basis

Table 9 Effect of pyrolysis condition of production yield

Substrate	Pyrolysis condition	Product	Reference
Cotton fibers	700 °C and nitrogen flow of 60 ml/min	72 wt% of oil, 13.5 wt% of gas, and 12.5 wt% of char	[176]
Natural fiber			[177]
Hemp	450 °C and steam activated at 800 °C	44.6 wt% of oil, 28.7 wt% of gas, and 28.5 wt% of char	
Flax		52.2 wt% of oil, 22.8 wt% of gas, and 25.1 wt% of char	
Jute		59.6 wt% of oil, 15.9 wt% of gas, and 24.6 wt% of char	
Coir		47.4 wt% of oil, 18.2 wt% of gas, and 34.4 wt% of char	
Abaca		48.1 wt% of oil, 23.6 wt% of gas, and 28.6 wt% of char	
Acrylic textile	800 °C and steam activated at 900 °C	Activated carbon	[178]
Acrylic textile	700 °C and steam activated for 2 h	Activated carbon	[175]

lint pyrolyzed at 550 °C surplus with sodium hydroxide generated a high surface area of activated carbon compared to an ordinary pyrolysis at the same temperature [180]. Jieying et al. [181] also supported that chemical $(NH_4)_2HPO_4$ added during pyrolysis affected the surface area of activated carbon. Table 10 shows the various physicochemical processes used for valorization of solid waste from textile industry. Several studies were carried out in which the textile waste was mixed with other solid waste for upgrading the physical properties of the derived products [182–186]. These modified materials are often used as construction materials (e.g., concrete, gypsum,

Table 10 Valorization of solid waste from textile industry via physicochemical process

Raw material	Process	Product	Reference
Textile waste, sunflower stalk, stubble fibers	Mix and high pressure	Thermal insulation material	[182]
Textile production wastes	Hot molding	Heat-insulating tiles	[184]
Textile waste, glass fiber	N/A	Lightweight concrete	[186]
Recycled textile fibers	Hot molding	Gypsum and cork	[183]
Waste cotton linter	Reactive liquid Si infiltration	Porous SiC ceramics	[187]
Short-fiber textile waste	Mix with wood fiber, organic synthesis	Fiber plates	[185]
Non-woven waste	As reinforcement to mix with raw material	Polypropylene, low-density polyethylene	[188]
Cotton waste garments	Dissolve and spun	Regenerated cellulose fibers	[189]
Textile loom waste	Graft co-polymerization	Highly absorbent polymer	[190]
Waste textiles	Co-combustion with coal	As energy supply	[173]
Textile sludge and waste glass	Hot molding	Bricks	[191]
Cotton woven waste	Carbonization and activation temperature are 700 and 800 °C	Activated carbon fibers	[181]
Cotton linters	NaOH at 350 °C (weight ratio of 1:3 for CLs/NaOH), the sample continued to be heated at 550 °C and maintained at this temperature for 1 h	Activated carbon	[180]
Native cellulose cotton fibers	Graft copolymerization of polyacrylonitrile (PAN) and then by insertion of phenyl thiosemicarbazide moieties	Chelating fibers	[192]
Cotton linter	Sulfonation	Adsorbent for high-efficiency removal of lead(II)	[179]

tiles, bricks), porous materials like activated carbon or ceramics [174, 175, 187], and absorbent materials [80, 188–190].

5.2.2 Bioconversion Process

Biochemical transformation via fermentation is a very attractive route for utilizing textile waste. Textile waste, especially cotton, is typically composed of 88–96% cellulose, with the remaining portions consisting of proteins, pectin, and wax [128, 193]. Therefore, it is possible to hydrolyze the cotton by enzymatic or chemical methods to obtain glucose, and then ferment it into value-added products (Table 11).

Table 11 Overview of valorization of textile waste via bioconversion processes

Substrate	Valorized product	Productivity	Pretreatment	Saccharification	Fermentation type	Microorganism	Reference
100% cotton red T-shirt and black T-shirt Blue 40/60 polyester/cotton blend shirt	Bacterial cellulose	1.88 g/l	Acid	Enz	SmF	*Gluconacetobacter xylinus*	[195]
100% cotton T-shirt	Bacterial cellulose	10.8 g/l	Ionic liquid	Enz	SmF	*Gluconacetobacter xylinus*	[134]
Purple and rose-red and green bed sheet	Bacterial cellulose	14.2 g/l	Ionic liquid	Enz	SmF	*Gluconacetobacter xylinus*	[197]
Purple and rose-red and green bed sheet	Cellulase	5.3 U/ml cellulase	Ionic liquid	Enz	SmF	*Gluconacetobacter xylinus*	[197]
A cotton–polyester waste textile	EtOH	70% yield	Alkaline solvent	Enz	SSF	*Saccharomycescerevisiae*	[194]
Cotton-based materials	EtOH	83% of the theoretical yield (0.42 g/g)	Acid	Enz	SSF	*Saccharomyces cerevisiae* CCUG 53310	[128]
Blue jeans	EtOH	86% of theoretical yield (0.44 g/g)	Acid	Enz	SSF	*Saccharomyces cerevisiae* CCUG 53310	[128]
Cotton-based materials	Glucose	Glucose yield of 85%	Alkali	Enz	N/A	N/A	[128]
Orange 50/50 polyester/cotton blend size: 3 × 3 cm^2	Biogas	Methane yield of 62.1%	Ionic liquid	Enz	AnD	Thermophilic bacteria from municipal solid waste digester	[129]
Orange 50/50 polyester/cotton blend size: 3 × 3 cm^2	EtOH	Ethanol yield 94.4%	Ionic liquid	Enz	SSF	*Saccharomyces cerevisiae* CCUG 53310	[129]
Blue 40/60 polyester/viscose blend size: 3 × 3 cm^2	Biogas	Methane yield of 56.8%	Ionic liquid	Enz	AnD	Thermophilic bacteria from municipal solid waste digester	[129]

Table 11 continued

Substrate	Valorized product	Productivity	Pretreatment	Saccharification	Fermentation type	Microorganism	Reference
Cotton waste	Biogas	Methane yield of 77.8%	N/A	N/A	AnD	Microbial in animal dung	[24]
Blue 40/60 polyester/viscose blend size: 3 × 3 cm^2	EtOH	Ethanol yield of 88.8%	Ionic liquid	Enz	SSF	*Saccharomyces cerevisiae* CCUG 53310	[129]
Wool textile residues	Biogas	0.43 N m^3/kg	Thermal	Enz	AnD	Bacteria from biogas plant	[200]

EtOH ethanol, *AnD* anaerobic digestion, *SmF* submerge fermentation, *SSF* simultaneous saccharification and fermentation, *Enz* enzymatic hydrolysis

Many studies have demonstrated that textile wastes can be converted into ethanol [128, 129, 194]. However, since the yield in the enzymatic hydrolysis of untreated waste was low, it is necessary to develop a suitable pretreatment process for the textile waste. Jeihanipour et al. [129] reported that textile waste pretreated by ionic liquid can achieve high ethanol yield (>70%).

Kuo et al. [195] proposed a process for the bacterial cellulose production via combination of enzymatic saccharification and *Gluconacetobacter xylinus* fermentation. After 7 days of static cultivation, 1.8 g/l bacterial cellulose pellicle was obtained. Hong et al. [134] used 1-allyl-3-methylimidazolium ([AMIM]Cl) to enhance the pretreatment process and obtained 10.8 g/l bacterial cellulose by using *Gluconacetobacter xylinus*. Furthermore, Adnan et al. [196] and Guo et al. [197] also investigated the possibility of producing both bacterial cellulose and cellulase from waste fiber sludge and waste textile, respectively. In addition, *Gluconacetobacter xylinus* was used for bacterial cellulose, and *Trichoderma reesei* was used for cellulase production.

Biogas production from textile waste via anaerobic digestion is an alternative route to utilize solid waste from textile industry. This process has less requirement on toxic compound removal, therefore the textile waste can be used directly in an anaerobic digestion process. Nevertheless, the pretreatment is needed in order to obtain high methane concentration. Rajendran and Balasubramanian [198] reported that ionic liquid-treated jeans can generate 600 ml of methane/day, while untreated jeans generated only 200 ml of methane/day. It was also found that a basic dye (Rhodamine-B) can be removed during anaerobic digestion [199].

Sections 5.2.1 and 5.2.2 demonstrate that the valorization of solid waste from textile industry via thermal process, physicochemical process, and bioconversion process can improve energy security and decrease pollution.

6 Challenges of textile waste valorization

As illustrated in Sect. 5.2.1, three main methods have been used for valorization of textile waste: (1) mechanical processing of textile waste for reuse in different applications; (2) decomposition via pyrolysis and/or hydrolysis to convert textile waste into basic chemicals, monomers and/or fuels; and (3) incineration to generate heat and power [201, 202].

The collection and separation of various kinds of textile wastes is one of the key challenges [203]. In the USA, the Trans-America Trading Company, with a capacity over 12 million pounds of textile waste per annum, has to spend enormous time and human power to separate more than 300 categories of textile waste by different size, composition, and fiber types [18]. An efficient textile waste collection system and a mechanical screening network are essential preconditions for large-scale textile valorization.

Based on current techniques discussed in this review, not all types of textiles are suitable for valorization. For cellulose fibers like fiber made from cotton, recycling by valorization could contribute to water conservation and waste water reduction, as cotton is one of the most water- and pesticide-dependent crops [18]. In contrast, for many polymers, especially for blending polymers, the energy required for fiber manufacturing from raw material is usually relatively lower than that to be used in recycling them from textile waste [204]. The synthetic polymers with similar melting points are difficult to be separated for respinning [201]. Also, the valorization process involves both the consumption of a certain amount of chemicals and the generation of pollutions (e.g., waste water). Therefore, the environmental benefit of textile waste valorization is still arguable [203]. The textile wastes with complex contents are difficult to be recycled in valorization. For example, carpet is a recalcitrant material and it is filled with thermoset materials (e.g., styrene-butadiene latex rubber), therefore, it could not be reshaped or re-melted [203]. The recycled materials from carpet usually lack suitable applications, hence most of them are discarded in landfills [202, 203]. Further investigations into more efficient and cleaner techniques are necessary.

Another challenge in textile waste valorization is the revenue obtained from the valorization process. With the technology development, the cost of raw materials and the prices of textile goods are both declining, which certainly will impair the attraction of investment on waste valorization [16, 18].

Overall, valorization of textile waste is promising but it has to face certain challenges. As a resolution, environmental accounting tools, such as life cycle assessment, should be applied to evaluate the environmental and economic benefits in waste valorization. In this way, the environmental impact and relative benefit in a cradle-to-grave process of textile products could be estimated with systematic data [203]. Moreover, favorable policies and the increasing consumers' appreciation of industry's effort on waste reduction should be the top priority on the agenda, with full support by the local government and policy-makers.

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REVIEW

Green and Sustainable Separation of Natural Products from Agro-Industrial Waste: Challenges, Potentialities, and Perspectives on Emerging Approaches

Vânia G. Zuin[1,2] · **Luize Z. Ramin**[1]

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Abstract New generations of biorefinery combine innovative biomass waste resources from different origins, chemical extraction and/or synthesis of biomaterials, biofuels, and bioenergy via green and sustainable processes. From the very beginning, identifying and evaluating all potentially high value-added chemicals that could be removed from available renewable feedstocks requires robust, efficient, selective, reproducible, and benign analytical approaches. With this in mind, green and sustainable separation of natural products from agro-industrial waste is clearly attractive considering both socio-environmental and economic aspects. In this paper, the concepts of green and sustainable separation of natural products will be discussed, highlighting the main studies conducted on this topic over the last 10 years. The principal analytical techniques (such as solvent, microwave, ultrasound, and supercritical treatments), by-products (e.g., citrus, coffee, corn, and sugarcane waste) and target compounds (polyphenols, proteins, essential oils, etc.) will be presented, including the emerging green and sustainable separation approaches towards bioeconomy and circular economy contexts.

Keywords Green and sustainable extraction · Sustainable separation · Green analytical techniques · Biomass waste · Biorefinery · Bioeconomy and circular economy

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✉ Vânia G. Zuin
vaniaz@ufscar.br; vania.zuin@york.ac.uk

[1] Department of Chemistry, Federal University of São Carlos, Rod. Washington Luís, km 235, São Carlos 13565-905, Brazil

[2] Green Chemistry Centre of Excellence, University of York, North Yorkshire YO10 5DD, UK

1 Introduction

Currently, it can be observed that global sustainability challenges are all closely interconnected, such as pollution, climate change, biodiversity loss, poverty, energy, and food security. As stated by Liu et al. [1], only holistic and disruptive approaches integrating various components of human and natural systems are effective in identifying and proposing suitable solutions for these challenges, especially those related to research, development, and innovation (RD&I) in interdisciplinary and transdisciplinary studies. To exemplify this systemic view, Fig. 1 illustrates the Earth surface that, based on the "Dymaxion map" (the Fuller Projection Map), shows the planet as a continuum without splitting any continents, seas, and oceans, where cycles are integrated through flows of matter, energy, and information [1, 2]. Here, Brazil, China, the Caribbean, and Africa interact across space, time, and organizational levels in many ways. For instance, the expansion of soybean production aggravates deforestation in Brazil, but also provides food and feedstock to China. The food trade between both countries also affects other areas, including the Caribbean and Africa. Dust particles from the Sahara Desert, also increased due to unbalanced agricultural practices, can reach the Caribbean and have an impact on coral reefs and soil fertility, diminishing tourism in this region. In addition, nutrient-rich particles from Africa can reach Brazil, improving its forest productivity.

According to the Director-General of the Food and Agriculture Organization (FAO) of the United Nations [3], after years of progress, world hunger has increased since 2015. Around 60% of the world's starving people are from countries affected by conflict and climate change, including northeast Nigeria, Somalia, South Sudan, and Yemen with 20 million people, often suffering extreme climatic events such as droughts and floods. Not surprisingly, some of the FAO's top priorities for the next

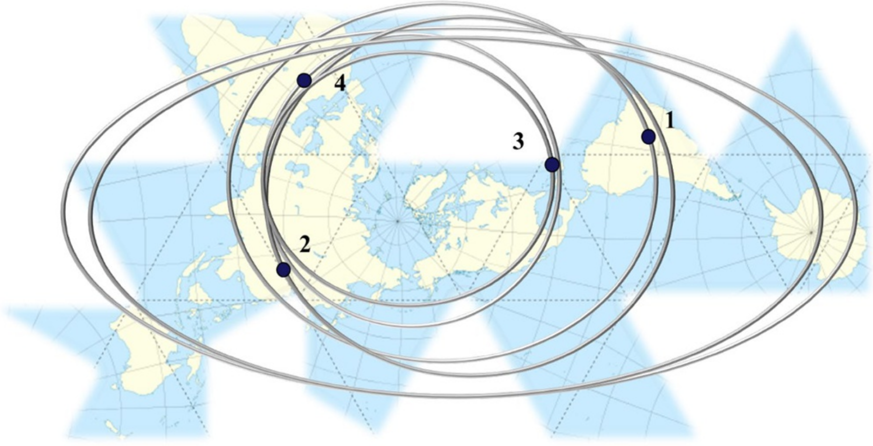


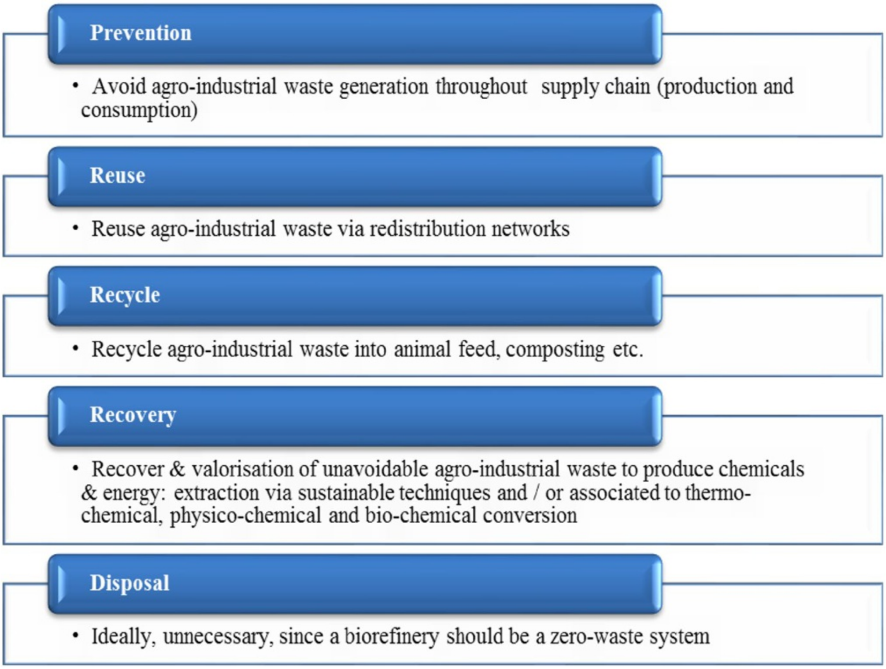
Fig. 1 Representation of an integrated planetary flow system based on the Dymaxion map, emphasizing some coupled cycles related to food production and socio-environmental impacts among (1) Brazil, (2) China, (3) the Caribbean, and (4) the Sahara Desert. Adapted from [1]

2 years include topics such as sustainable agriculture, climate change mitigation and adaptation, water scarcity and support of subsistence rural practices, and fisheries and forestry [3, 4]. The challenges related to this demanding context can be intensified and better understood when taking into account that the world population is expected to increase by about 30% over the next 35 years, reaching more than 9.5 billion people in 2050 and 11.2 billion in 2100 [5].

As pointed out by Xia et al. [6], the global food waste of approximately 1.3 billion tons per year is shocking in this context and, although it should be avoided or minimized, it cannot be completely prevented nowadays. Primary and secondary processing generates unpreventable food supply chain waste. This can be due to a number of factors along the supply chain, differing by the commodity and country in question. In general terms, developing countries such as some African countries suffer the greatest loss during the early, upstream part of the primary processing, corresponding to 75% of food losses during production and postharvest. Various initiatives, e.g., building better infrastructure through knowledge transfer (more efficient storage and transport technologies) and improving collaboration and market opportunities in the food supply chain could have a positive role. In industrialized countries, waste occurs especially in the consumption stage, accounting for 50% of overall loss of crops in some countries of North America, Europe, and Oceania. In this case, together with educational and cultural actions, other aspects such as developing legislation to make date labels more user-friendly for consumers (sell-by, best-before, and consume-by), redesigning packaging characteristics (avoiding the “buy 1 get 2” offers) and retailer marketing strategies should be considered [7].

It is estimated that around 140 billion tons of biomass from the agricultural sector are generated every year in the world [8, 9], and a considerable part is recognized as waste and not conflicting with food availability, e.g., leaves, roots, stalks, bark, bagasse, straw residues, seeds, wood and animal residues. Using alternative strategies to avoid additional losses and produce several high value-added chemicals could minimize the volume of non-renewable materials used today (i.e., roughly 50 billion tons of fossil fuels), enough to greatly reduce greenhouse gas emissions and dependence on non-sustainable resources. Therefore, considering their available volume and practically low costs locally and globally, associated to rich function, structure and chemical heterogeneity, all agro-industrial waste should also be considered for their chemical and material potential, as well as a source of energy [10–13].

An important proposal related to waste hierarchy as a framework for residue management can be seen in Fig. 2 [14, 15], which was reformulated to include agro-industrial waste. In this case, the agro-industrial waste hierarchy has a different meaning from top to bottom, since all biomass is valued as raw material. ‘Prevention’ is an intrinsic part of optimized processes, avoiding overproduction. Therefore, the least probable option is ‘disposal’ as the supply chain is designed to attend sustainable consumption, using all bio-based material generated. Here, sustainable production also includes eco-efficiency, cleaner and green productivity, whereas sustainable consumption allows greener choices to be made by individuals based on eco-procurement, supply chain management, waste minimization, recycling, and resource efficiency measures. Both sustainable production and consumption comprises ‘life-cycle thinking’, aiming at preventing problems shifting from one



- Avoid agro-industrial waste generation throughout supply chain (production and consumption)
- Reuse agro-industrial waste via redistribution networks
- Recycle agro-industrial waste into animal feed, composting etc.
- Recover & valorisation of unavoidable agro-industrial waste to produce chemicals & energy: extraction via sustainable techniques and / or associated to thermo-chemical, physico-chemical and bio-chemical conversion
- Ideally, unnecessary, since a biorefinery should be a zero-waste system

Fig. 2 The agro-industrial waste hierarchy modified from [15]. The main idea is to promote sustainable production and consumption systems through zero-waste biorefinery

life-cycle stage to another, one geographical area or environmental compartment to another.

One of the most important and cited references highlighting the advances in genetics, biotechnology, process chemistry, and engineering that has helped establish a new manufacturing concept to convert renewable biomass into valuable fuels and products, known as biorefinery, was published by Ragauskas and collaborators in the mid-2000s [16]. According to these authors and other researchers [16, 17], integrating biomass and biorefinery technologies has the potential to develop sustainable bio-based energy and materials leading to a new manufacturing paradigm (Fig. 3).

In fact, this paradigm is currently connected to other strong concepts, i.e., bioeconomy and circular economy; the latter is described as an industrial system that is restorative by intention and design. This idea replaces the end-of-life notion with regeneration, focusing on the use of renewable energy, elimination of toxic chemicals, reutilization, return and eradication of “waste through the superior design of materials, products, systems, and business models” [18, 19].

As can be noted, new generations of biorefinery combine innovative biomass resources from different origins, chemical extraction and purification and/or synthesis of biomaterials, biofuels and bioenergy via benign processes. From the very beginning, the identification and quantification of all potentially high value-added

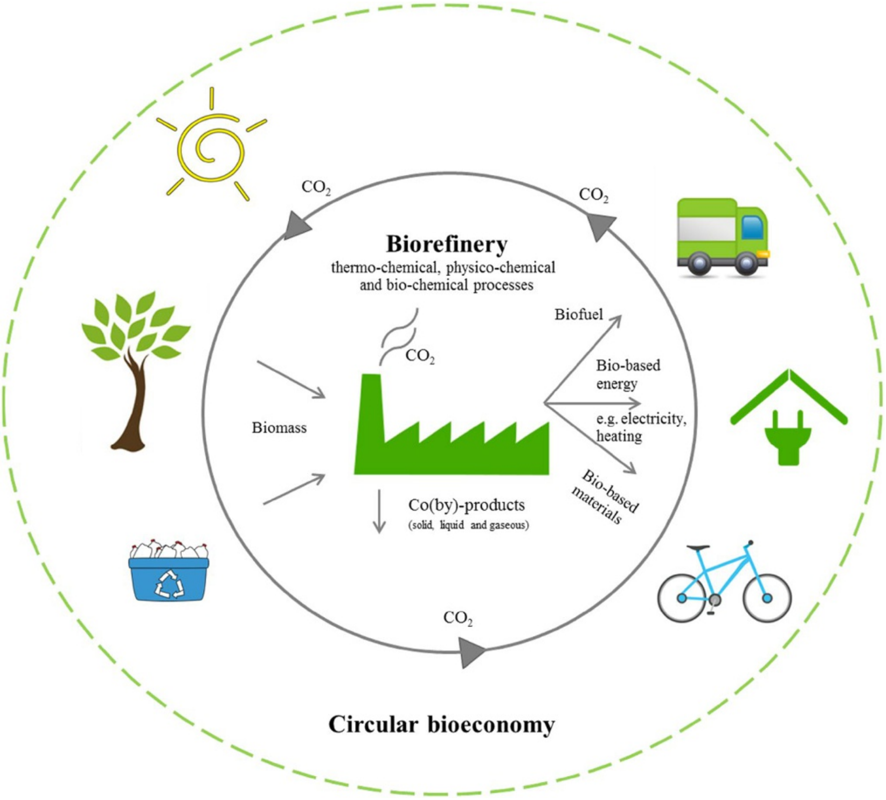


Fig. 3 Holistic biorefinery model integrating biomass, biofuel, biomaterials and bioenergy cycle, based on green and sustainable technologies in the scope of bioeconomy and circular economy. Updated and expanded from [16, 17]

compounds that could be removed from the available renewable feedstocks requires another analytical approach, also connected to green chemistry [20, 21].

2 From Green to Sustainable Separation: Towards Holistic, Flexible, and Zero-Waste Biorefineries

More recently, green extraction and purification have been presented as methods based on establishing processes that reduce energy consumption, using solvents and renewable materials, as well as ensuring a safe and high-quality fraction/product [22]. The aim of their application is to obtain natural products from industrial waste, which is considered a highly attractive initiative [23].

However, a more adequate term for such extraction and purification processes towards vanguard biorefineries could be sustainable separation, adding to the previous green definition, the notion of innovation across all sectors that allows for increased value in a wide sense, enhancing human and environment benefits and providing economically accessible technologies also advantageous to industry and large scale processing systems. It includes another dimension related to the generation of more creative and healthy jobs, contributing to the construction of a positive long-term sustainability agenda, encompassing bio-circular economy, environmental and social justice [24–27].

Sustainable separation can be defined as a holistic approach grounded on the circular and flexible design and application of renewable benign materials and auxiliaries (including bio-derived solvents, solid phases, membranes) and processes [rooted on green analytical techniques and sustainability metrics and indices, e.g., life cycle analysis (LCA), chemometrics, and other interdisciplinary indicators]. The aim is to optimize the tuneable use of energy, time, reagents, devices, scale, yield and number of steps to extract, fractionate, purify or even modify the components of interest from bio-derived waste during these in situ processes, ensuring analytical reproducibility, efficiency, selectivity robustness and scalability, with online evaluation regarding measurable objectives to create safer, healthier, and more efficient products, processes, and services under fair conditions, commercially available at accessible and just prices [28–30].

Natural products are among the most attractive value-added chemicals to be considered, which can be classified as organic compounds formed by living systems divided into three main categories: (1) compounds that occur in all cells and have a central role in their metabolism and reproduction (nucleic acids, amino acids, and sugars), also known as primary metabolites; (2) high-molecular polymeric materials which form cellular structures (cellulose, lignins, and proteins) and; (3) chemicals which are characteristic of a limited number of species, called secondary metabolites [22, 30]. Many of these bioactive compounds (e.g., alkaloids, terpenoids, and phenols) have been extensively used as medicine, nutraceuticals, flavors, fragrances, cosmetics, food additives, antimicrobials, bio-pesticides, etc. However, among the biggest challenges for biomass utilization is establishing benign methods to separate, purify and modify it into chemicals, fuels, and new materials. This is partially due to, with rare exceptions, the small amounts which are lower than 0.01% of the dry weight of vegetal, associated to possible product inhibition issues, large raw material variability, feed detoxification (when necessary), instability of the target compound (or fractions) and its presence in a complex mixture [23, 30].

It is well known that the separation steps, especially extraction, correspond up to 40–80% of the total costs of most common chemical processes currently used. From the point of view of a holistic biorefinery, separation has attracted more and more attention [31]. For instance, for natural products, solvent-based extraction is one of the best options nowadays considering the nature of many bio-based chemicals and matrices, and also the fact that other separation methods, such as those based on chromatography or membranes, do not have the same advantages taking into account commercial scales [32].

It is expected that high value-added components from biomass waste such as essential oils, polyphenols, and other food or medicinal-related products are extracted first, followed by polysaccharides, lignocelluloses or waxes via advanced separation and depolymerization processes. Among them, green solvents in general, supercritical CO_2, subcritical water, microwave (MW)-assisted acidolysis and gas-expanded liquids have been mentioned [33]. Green solvents offer important separation advantages, including near-supercritical or supercritical fluids, which have outstanding mass transport properties, polarity, and easiness of solvent removal after extracting the compound of interest [34]. Another interesting solvent is water, but the range of compounds that are soluble in this medium is quite limited. Nevertheless, the use of subcritical water has been demonstrated to be advantageous for organic modification to depolymerize, hydrolyze, gasify, and carbonize biomass to produce bioactive compounds, sugars, biogas, and other valuable solids [16, 35].

Integrating two or more green techniques combining different strategies has played an important role in overcoming the main drawbacks of a single technique towards sustainable separation. For instance, for high-pressure solvent extraction in which the extractants do not reach supercritical conditions, the temperature, time, and solvent consumed can be dramatically reduced associating ultrasound-assisted treatment [28, 36]. In fact, more attention has been paid to green extraction, purification, or modification of natural products derived from agro-industrial waste nowadays, opening up new opportunities for sustainable approaches designed for bioeconomy and circular economy models. The aim of this paper is to present an overview of the design and application of green and sustainable separation of natural products for vanguard zero-waste biorefineries. The main analytical techniques and procedures described over the last 10 years will be described in detail, showing the potentialities, challenges, and perspectives in this topical and emergent scenario.

3 High Value-Added Approaches for Green and Sustainable Separation of Natural Products from Waste: What can be Observed from the Literature?

More recently, trends in green and sustainable extraction, fractionation and purification techniques have largely focused on minimizing the use of solvents, energy and materials that are intrinsically benign to human health and the environment [37]. In order to analyze the *status quo* and perspectives related to natural product separation from waste, a systematic literature review was conducted using the ISIS Web of Knowledge platform (reviews and papers) from 2006 to 2017, combining the descriptors “natural product” and “green extraction/separation” (or “sustainable extraction/separation” or “eco-friendly extraction/separation”) and “waste” (or “residue”). Figure 4 shows the number of publications during this period. There were more than 160 research papers and reviews that, to the best of our knowledge, are reasonably representative to show the strongest tendencies in this field over the last decade. It can be clearly observed that there has been an increase in the number of manuscripts over the last 10 years, covering the principles, advances, and applications of these green methods.

The obtained data reflect the growing interest and potential of green and sustainable methods to separate natural products from waste. One tendency observed in particular was the innovative ways to remove (integrating extraction, purification and/or modification in the same integrated system) and use such compounds in more

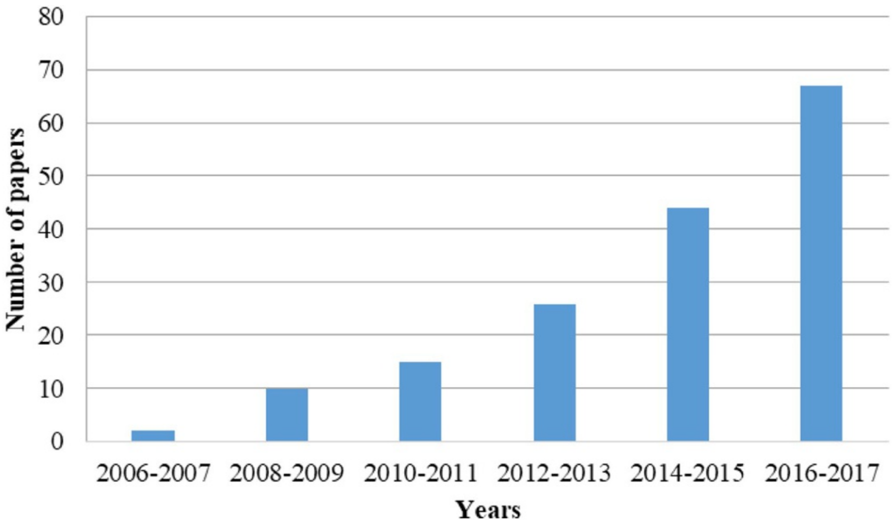


Fig. 4 Number of publications per year focusing on green and sustainable separation (extraction, fractionation and purification) of natural products from waste (ISIS Web of Knowledge, January 2006 to December 2017)

contemporary sectors, promoting human and environmental health instead of general and old-fashioned remediation [19, 38]. As a result, new applications for food, nutraceutical, and agricultural sectors have been further explored, based on their advantageous properties as natural colorants, flavors, aromas, antioxidants, antifungals, bioformulations (bio-pesticides) or simply their use as precursors to generate other compounds for similar uses. Some details related to patents, (non-) clinical trials, sustainable indicators, scaling-up, regulatory, agro-industrial variability and availability, traceability, seasonality, good laboratory and manufacturing practices, additional economical and marketing issues have also been discussed.

Table 1 presents the research papers and reviews published during this period, highlighting their main focus, the green or sustainable techniques/approaches adopted, raw materials (mostly agro-industrial waste) and target compounds studied. The most common raw materials described as chemical feedstocks were waste derived from plants, for instance, food, mainly fruits (citrus, mango, papaya, grape, passiflora, banana, tomato, olive), grains (corn, soybean, sunflower, coffee) and other abundant materials (sugarcane bagasse, tea, wood bark, rice and wheat straw). Additional issues that affect the quality of the final products were also discussed, namely the procedure used for waste collection, selection, storage, drying, matrix characteristics (particle size, shape, specific surface area and porosity). The latter aspects play an important role in extraction efficiency due to the mass and heat transfer processes. Understanding the nature of raw material is crucial to avoid negative influences impacting the quality and yield during the removal of the target compounds, e.g., caused by co-extracted contaminants or due to the presence of some

Table 1 Research papers and reviews focusing on green and sustainable separation of natural products from agro-industrial waste published from January 2006 to December 2017 (ISIS Web of Knowledge)

Year	Crop	Waste stream	Target compounds	Geographical location	Green or sustainable separation approach	References
2017	Olives	Olive kernels	Phenolic compounds and oil	France and Spain	Aqueous liquid solid extraction (LSE), mechanical expression (ME), supercritical CO_2 (SC-CO_2) and gas-assisted mechanical expression (GAME)	Gas-assisted mechanical expression (GAME) for the selective recovery of lipophilic and hydrophilic compounds from olive kernel [145]
2017	Figs	Leaves	Bioactive compounds	China	Deep eutectic solvent with microwave and ultrasound extraction Time: 10 min (MW) and 60 min (US) Temperature: 40–80 °C Power: 250 W (MW) and 700 W (US)	Enhanced and green extraction polyphenols and furanocoumarins from Fig (*Ficus carica* L.) leaves using deep eutectic solvents [136]
2017	*Polygonum multiflorum*	Herbal raw materials	Stilbene glycoside and anthraquinones	China	Ionic liquids with ultrasonic extractor Time: 1–120 min Power: 40–120 W	Sequential extraction and separation using ionic liquids for stilbene glycoside and anthraquinones in *Polygonum multiflorum* [131]
2017	Several sources	Not defined	Mostly bioactive compounds	Spain	Review Critical overview about the greenness of water as extraction solvent	Water as green extraction solvent: Principles and reasons for its use [146]
2017	Pomelo	Flavedo	Essential oil	China	Microwave irradiation Power: 240–700 W Time: 24 min	A process to preserve valuable compounds and acquire essential oils from pomelo flavedo using a microwave irradiation treatment [52]
2017	*Selaginella doederleinii*	Not defined	Biflavonoids	China	Ionic liquids and microwave-assisted extraction Power: 300–700 W Time: 30–50 min Temperature: 40–60 °C	Optimization of ionic liquid-assisted extraction of biflavonoids from *Selaginella doederleinii* and evaluation of its antioxidant and antitumor activity [132]

Table 1 (continued)

Year	Crop	Waste stream	Target compounds	Geographical location	Green or sustainable separation approach	References
2017	*Pogostemon cablin*	Leaves	Essential oils	Indonesia	Microwave-assisted hydrodistillation (MAHD) and solvent-free microwave extraction (SFME) Power: 600 W (MAHD) and 264 W (SFME) Time: 66 min (MAHD) and 45 min (SFME); solvent: water	Comparison of conventional and microwave-assisted distillation of essential oil from *Pogostemon cablin* leaves: analysis and modeling of heat and mass transfer [147]
2017	*Juglans regia* L.	Fresh male flowers and unripe walnut seeds	Phenolic content and water-soluble polyphenols	Italy	Microwave-assisted extraction Frequency: 2.45 GHz Max. power: 500 W Solvent: ethanol/water Temperature: 60–100 °C Time: 6–30 min	Process intensification by experimental design application to microwave-assisted extraction of phenolic compounds from *Juglans regia* L. [148]
2017	Walnuts	Walnut de-pellicle	Flavonoids	China	Macroporous resins Pretreated with 5% HCl and 5% NaOH solutions	Recovery of flavonoids from walnuts de-pellicle wastewater with macroporous resins and evaluation of antioxidant activities in vitro [149]
2017	Ginseng	Roots	Bioactive compounds	Brazil	Sequential extraction system using ethanol followed by water Temperature: 333 K Time: 5–240 min	Techno-economic evaluation of obtaining Brazilian ginseng extracts in potential production scenarios [150]
2017	Food ingredients and natural products	Not defined	Nutraceutics, cosmetic, pharmaceutical, and bioenergy applications	France	Review current knowledge on ultrasound-assisted extraction	Ultrasound-assisted extraction of food and natural products. Mechanisms, techniques, combinations, protocols and applications. A review [151]

Table 1 (continued)

Year	Crop	Waste stream	Target compounds	Geographical location	Green or sustainable separation approach	References
2017	Coffee	Coffee chaff	Antioxidants	Portugal	Solid–liquid extraction and multi-frequency multimode modulated (MMM) Frequency: 19.8 kHz Power: 250 and 500 W Time: 60–600 s	Multi-frequency multimode modulated technology as a clean, fast, and sustainable process to recover antioxidants from a coffee by-product [152]
2017	Apples	Wild apple fruit dust	Bioactive compounds, polyphenolic antioxidants	Serbia	Microwave-assisted extraction Time: 15–35 min Ethanol conc.: 40–80% Irradiation power: 400–800 W	Microwave-assisted extraction of wild apple fruit dust production of polyphenol-rich extracts from filter tea factory by-products [153]
2017	Wood	Wood biomass	Lignin oligomers	China	Microwave-assisted treatment with deep eutectic solvent Solvent: choline chloride and oxalic acid dehydrate Temperature: 80 °C Power: 800 W Time: 3 min	Efficient cleavage of lignin-carbohydrate complexes and ultrafast extraction of lignin oligomers from wood biomass by microwave-assisted treatment with deep eutectic solvent [137]
2017	Wood	Oak wood from cooperage by-products	Furanic compounds, *cis*- and *trans*- B-methyl-*y*-octalactones, terpenes and norisoprenoids, benzenic compounds	Spain	Pressurized liquid extraction Solvent: water, ethanol/water (80:20) and ethyl lactate Temperature: 60–120 °C Pressure: 10.34 MPa Flush volume: 60% Purging time: 80 s	Extraction of natural flavorings with antioxidant capacity from cooperage by-products by green extraction procedure with subcritical fluids [154]
2017	*P. armeniaca, P. persica, P. domestica, Triticum aesativum*	Fruit and vegetables seeds and peels	Phenolic compounds	Pakistan	Ultrasonic water bath Solvent: 65% (v/v) ethanol (methanol and acetone) Extraction time: 30 min Temperature: 50 °C	Extraction and quantification of phenolic compounds from *Prunus armeniaca* seed and their role in biotransformation of xenobiotic compounds [71]

Table 1 (continued)

Year	Crop	Waste stream	Target compounds	Geographical location	Green or sustainable separation approach	References
2017	Lignocellulose materials	Lignocellulosic biomass such as crops or forestry residues	High value-added bio-based products (e.g., bioethanol, biogas, acetic acid, acetic acid, or activated carbon)	Mexico and Pakistan	Review Focus on transformation based on syngas platform (thermochemical platform) and sugar platform (biochemical platform)	Lignocellulose: a sustainable material to produce value-added products with zero-waste approach [155]
2017	Olives	Olive by-product (paté)	Fatty acids and phenolic compounds	Spain and Italy	Soxhlet extraction (percolation with petroleum ether, under reflux)	Macro and micro functional components of a spreadable olive by-product (pate) generated by new concept of two-phase decanter [156]
2017	Tucumã palm fruit	Tucumã's endocarp	Cellulose	Brazil and USA	Alkaline extraction (135 °C, autoclave, 2 bar, 2 min, 20% of aqueous NaOH, 1:30 straw to liquor (g/ml), 30 min)	New approach for extraction of cellulose from tucuma's endocarp and its structural characterization [115]
2017	Grapes	Seeds	Resveratrol	China	Subcritical water extraction Pressure: 0.5–1.5 MPa Time: 20–30 min Temperature: 130–170 °C	Optimization of subcritical water extraction of resveratrol from grape seeds by response surface methodology [100]
2017	Mango, rambutan, santol	Peels	Antioxidant activity	Thailand	Solid–liquid extraction Ethanol (95%)	Study effect of natural extracts on the antioxidant activity in pork balls [157]
2017	Tomatoes	Pericarps without seeds	Nutrient-rich antioxidant ingredients	Portugal, Spain, Ireland	Microwave extraction (600 rpm, 200 W) Time: 0–20 min Temperature: 60–180 °C Ethanol conc.: 0–100% Solid/liquid ratio: 5–45 g/l	Valorization of tomato wastes for development of nutrient-rich antioxidant ingredients: a sustainable approach towards the needs of today's society [158]

Table 1 (continued)

Year	Crop	Waste stream	Target compounds	Geographical location	Green or sustainable separation approach	References
2017	*Citrus latifolia*, *Rubus* sp., *Origanum vulgare* and *Heterotheca inuloides*	Peel and broken down vegetable material	Fatty acids and antioxidants compounds	Mexico, Belgium	SC-CO_2 Extraction time: 1 h Flow: 25 g/min Pressure: 10–40 MPa Temperature: 35–60 °C Co-sol.: 0–8 g/min Percent flow: 0–32%	Thermodynamics and statistical correlation between supercritical CO_2 fluid extraction and bioactivity profile of locally available Mexican plant extracts [159]
2017	Pomegranates	Peels	Carotenoids	Greece	Ultrasound-assisted extraction (139 W, 20 kHz); solvents: vegetable oils Extraction time: 10–60 min Temperature: 20–60 °C	Green ultrasound-assisted extraction of carotenoids from pomegranate wastes using vegetable oils [72]
2017	Pomegranates	Both edible and non-edible parts	Polyphenols	Greece	Semi-automatic extractor Solvents: H_2O, β-CD, HP-β-CD Extraction time: 363 min Temperature: 25 °C	Green extraction of polyphenols from whole pomegranate fruit using cyclodextrins [121]
2016	Quince	Leaves	Natural dyes and bioactive compounds	Romania	Aqueous extraction Extraction time: 60–240 min Temperature: 4–100 °C	Dyeing and antibacterial properties of aqueous extracts from quince (*Cydonia oblonga*) leaves [160]
2016	Corn	Steep liquor	Vanillic acid, *p*-coumaric acid, ferulic acid, sinapic acid and quercetin	Spain, Portugal, and Italy	Liquid–liquid extraction Solvents: chloroform (56 °C, 60 min) Ethyl acetate (25 °C, 45 min)	A multifunctional extract from corn steep liquor: antioxidant and surfactant activities [161]
2016	Palm	Oil palm empty fruit bunches	Cellulose with polypropylene as biocomposite material	Malaysia, Pakistan	Ultrasonic treatment (40 kHz) solvent: hydrogen peroxide Extraction time: 1–3 h Room temperature	Autoclave and ultra-sonication treatments of oil palm empty fruit bunch fibers for cellulose extraction and its polypropylene composite properties [73]
2016	Tomatoes	Seeds and peels	Carotenoids/proteins	Tunisia and Germany	Supercritical CO_2 extraction 80 °C, 400 bar, 4 g CO_2/min for 2 h	Biorefinery cascade processing for creating added value on tomato industrial by-products from Tunisia [82]

Table 1 (continued)

Year	Crop	Waste stream	Target compounds	Geographical location	Green or sustainable separation approach	References
2016	Black tea	Black tea processing waste	Antioxidant and antimicrobial phenolic compounds	Turkey and USA	Solvent extraction Solvents: H_2O, ethanol Extraction time: 2 h Temperature: 70 °C	Black tea processing waste as a source of antioxidant and antimicrobial phenolic compounds [46]
2016	Rapeseed	Rapeseed oil cakes	Protein- and lignin-rich fractions	France	Ultrafine miffing and electrostatic separation Solvents: NaOH, diethylether, hexane Extraction time: 5 h Temperature: 60 °C	Chemical- and solvent-free mechano-physical fractionation of biomass induced by tribo-electrostatic charging: separation of proteins and lignin [139]
2016	Sunflower	Seeds	Sunflower protein-based ingredients	USA	Review Green pigmentation associated with the interaction of sunflower protein and oxidized chlorogenic acid (CGA) by outlining the sunflower oil and protein meal market, CGA reactions contributing to greening, methods for CGA extraction, and the effect of processing on sunflower protein quality and the greening reaction	Chlorogenic acid oxidation and its reaction with sunflower proteins to form green-colored complexes [162]
2016	Passion fruit	Peels	Pectin	Malaysia	Acidic and enzymatic extraction Citric solution, celluclast Extraction time: 30–120 min Temperature: 35–85 °C	Comparison of acidic and enzymatic pectin extraction from passion fruit peels and its gel properties [107]
2016	Red grape	Pomace	Polyphenols and anthocyanin pigments	Greece	Ultrasound-assisted extraction (140 W, 37 kHz) Solvent: aqueous glycerol Extraction time: 60 min Temperature: 45 °C	Development of a green process for the preparation of antioxidant and pigment-enriched extracts from winery solid wastes using response surface methodology and kinetics [74]

Table 1 (continued)

Year	Crop	Waste stream	Target compounds	Geographical location	Green or sustainable separation approach	References
2016	Orange and lemon	Fresh and waste peel	Pectin and D-limonene	Portugal and Italy	Microwave Solvent: water Extraction time: 1 h Temperature: 80 °C	Eco-friendly extraction of pectin and essential oils from orange and lemon peels [53]
2016	Coffee	Spent coffee grounds	Oil	China	Ultrasonication extraction Solvent: hexane Extraction time: 15–75 min	Effect of oil extraction on properties of spent coffee grounds-plastic composites [98]
2016	Tomato	Waste of tomato paste plants	Lycopene	Iran and Canada	Microemulsion technique (MET) Solvents: water, saponin: glycerol, surfactant: lycopene Extraction time: 30 min Temperature: 25 °C	Enhanced lycopene extraction from tomato industrial waste using microemulsion technique: optimization of enzymatic and ultrasound pre-treatments [163]
2016	Red capsicum (*Capsicum annuum*)	Processing residue	Carotenoids	India	Enzymatic liquefaction Pectinase, viscozyme L, cellulose extraction Time: 1 h Temperature: 60 °C	Enzyme-assisted extraction of carotenoid-rich extract from red capsicum (*Capsicum annuum*) [108]
2016	Rice	Husk	Cellulose	India	Eco-friendly method montmorillonite, LiOH, H_2O_2 Extraction time: 6 h Temperature: 80 °C	Extraction of cellulose from agricultural waste using montmorillonite K-10/LiOH and its conversion to renewable energy: biofuel by using *Myrothecium gramineum* [122]
2016	Tea (yarrow and rose hip)	By-products from filter-tea factory	Chlorophylls and carotenoids	Serbia	Supercritical fluid extraction Extraction time: 5 h Temperature: 40 and 60 °C Pressure: 100–300 bar CO_2 flow rate: 0.194 hk/h	Extraction of minor compounds (chlorophylls and carotenoids) from yarrow-rose hip mixtures by traditional versus green technique [83]

Table 1 (continued)

Year	Crop	Waste stream	Target compounds	Geographical location	Green or sustainable separation approach	References
2016	Corn, sugarcane, sorghum, pearl millet, green gram, groundnut sesame	Bagasse, stover, stalk and shell	*Para*-coumaric acid (pCA)	India and USA	Alkaline hydrolysis pH 3, alkali conc.: 0.5–4 M Hydrolysis duration: 4–24 h Sugaring-out for separation of pCA from hydrolysate	Extraction of *p*-coumaric acid from agricultural residues and separation using ‘sugaring out’ [116]
2016	Winery	Grape wastes and by-products	Antioxidant compounds and polyphenols	Denmark, China, France and Brazil	Review Conventional (solid liquid extraction, heating, grinding, etc.) and non-conventional (pulsed electric fields, high voltage electrical discharges, pulsed ohmic heating, ultrasounds, microwave-assisted extractions, sub- and supercritical fluid extractions, as well as pressurized liquid extraction) methods	Green alternative methods for the extraction of antioxidant bioactive compounds from winery wastes and by-products: a review [164]
2016	1st to 3rd generation biodiesel feed-stocks	Mostly microalgae	Biodiesel	Malaysia and Japan	Review Integration of enzymatic reactors with supercritical fluid technology	Green biodiesel production: a review on feedstock, catalyst, monolithic reactor, and supercritical fluid technology [84]
2016	*Jatropha curcas*, oil palm	Seeds, empty fruit bunch	Bio-oil	Malaysia	Microwave extraction Solvent: water Extraction time: 60–140 min Power: 200–700 W	Green bio-oil extraction for oil crops [54]
2016	Green tea	Green tea residue	Protein	The Netherlands	Alkaline protein extraction Solvent: NaOH Extraction time: 2 h Temperature: 95 °C	Improving yield and composition of protein concentrates from green tea residue in an agri-food supply chain: effect of pre-treatment [117]

Table 1 (continued)

Year	Crop	Waste stream	Target compounds	Geographical location	Green or sustainable separation approach	References
2016	Eucalyptus wood	Eucalyptus chips	Hemicelluloses	Uruguay	Green liquor extraction Solvents: water and green liquor (Na_2CO_3, Na_2S, and NaOH) extraction time: 30–150 min temperature: 100–160 °C	Integrated forest biorefineries: green liquor extraction in eucalyptus wood prior to kraft pulping [123]
2016	Watermelons	Juice	Lycopene	Brazil	Microfiltration, diafiltration, reverse osmosis α-Al_2O_3 membranes T1-70 (35 °C) Polyamide composite membranes (35 °C, 60 bar)	Integrated membrane separation processes aiming to concentrate and purify lycopene from watermelon juice [140]
2016	Larch wood	Sapwood, heartwood, bark and branches	Phenolic compounds	Slovenia	Pressurized hot water Extraction time: 30 min Temperature: 100 °C	Isolation of phenolic compounds from larch wood waste using pressurized hot water: extraction, analysis and economic evaluation [165]
2016	Tomatoes	Pomace	Lycopene	Iran	Microemulsion technique H_2O and surfactants Extraction time: 30 min Temperature: 35 °C	Microemulsion-based lycopene extraction: effect of surfactants, co-surfactants, and pretreatments [166]
2016	Melons	Rind	Carbohydrates, phenolic compounds, and fatty acids	Spain	Solvent extraction Solvent: cyclohexane, ethanol Extraction time: 2 h Microwave radiation: 190 °C, 20 min, 200 W	Microwave heating for the catalytic conversion of melon rind waste into biofuel precursors [167]
2016	Tomatoes, fungus *Blakeslea trispora*	Processing waste	Lycopene	Greece	Review Emphasis on final product safety and ecofriendly processing (solvent extraction, SFE, MAE, high-pressure processing, ultrasound, electrical methods)	Natural origin lycopene and its “green” downstream processing [168]

Table 1 (continued)

Year	Crop	Waste stream	Target compounds	Geographical location	Green or sustainable separation approach	References
2016	Oranges	Peel	Pectin	Italy	Conventional hydrodistillation, MAE, US Solvents: water Extraction time: 5–155 min Temperature: 90–333 °C	Novel configurations for a citrus waste based biorefinery: from solventless to simultaneous ultrasound and microwave-assisted extraction [55]
2016	Lemons, olives, onion, red grape, coffee, and wheat	Peel, leaves, solid wastes, pomace, spent filter and bran	Polyphenolic compounds	Greece	Ultrasound extraction (140 W, 37 kHz) eutectic mixtures Extraction time: 90 min Temperature: 80 °C	Novel glycerol-based natural eutectic mixtures and their efficiency in the ultrasound-assisted extraction of antioxidant polyphenols from agri-food waste biomass [75]
2016	Potatoes	Peels	Polyphenolic antioxidants	Greece	Ultrasound extraction (140 W, 37 kHz) Solvents: ethanol and glycerol Extraction time: 90 min Extraction temperature: 50–80 °C	Optimization of a green ultrasound-assisted extraction process for potato peel (*Solanum tuberosum*) polyphenols using bio-solvents and response surface methodology [76]
2016	Grapes	Seeds	Grape seed oil	Croatia	Supercritical CO_2 Extraction time: 90 min Temperature: 35–64 °C Pressure: 158–441 bar CO_2 flow rate: 1.94 kg/h	Optimization of supercritical CO_2 extraction of grape seed oil using response surface methodology [85]
2016	*Crocus sativus*	Petals (underutilized bulk agro-waste)	Phenolic compounds	Iran	Subcritical water extraction Extraction time: 20–60 min Temperature: 120–160 °C	Optimization of the subcritical water extraction of phenolic antioxidants from *Crocus sativus* petals of saffron industry residues: Box–Behnken design and principal component analysis [101]
2016	Bananas	Peels	Antioxidants	Malaysia and Turkey	Solvent extraction Solvents: acetone, ethanol, hexane, methanol, H_2O Extraction time: 1–5 h	Optimization of extraction parameters on the antioxidant properties of banana waste [47]

Table 1 (continued)

Year	Crop	Waste stream	Target compounds	Geographical location	Green or sustainable separation approach	References
2016	Pea vine	Pea vine waste	Potential platform molecules (5-hydroxy furfural; ethanoic acid); sugars (levoglucosenone, rhamnose, xylose, fructose); biopolymer with pectinaceous and starch-like characteristics	United Kingdom	Pseudo-subcritical water extraction Temperature: 125–175 °C Pressure: 20–60 bar Flow rate: 1–5 ml/min	Potential utilization of unavoidable food supply chain wastes-valorization of pea vine wastes [6]
2016	Keratin-containing products stored in large waste deposits	Processing waste	Keratin	Romania	Review Keratins solubilization (protected and unprotected methods) followed by dehydro-thermal, physical-type bonding or chemical treatments	Practical ways of extracting keratin from keratinous wastes and by-products: a review [169]
2016	*Taxus baccata* L.	Case study based on European yew	10-deacetylbaccatin III (10-DAB)	Germany	Review Theoretical approach in thermodynamics and process modelling as an alternative process design	Process design for integration of extraction, purification and formulation with alternative solvent concepts [170]
2016	Olives	Olive mill waste water	Biophenols (hydroxytyrosol and tyrosol)	Italy	Liquid–liquid extraction Solvents: *n*-hexane, EtOAc	Quick assessment of the economic value of olive mill waste water [171]
2016	Olives	Olive mill waste water	Tyrosol	Spain, United Kingdom and Spain	Hydrophobic ionic liquids Solvents: ILs Extraction time: 2 h Temperature: 303–323 K	Recovery of tyrosol from aqueous streams using hydrophobic ionic liquids: a first step towards developing sustainable processes for olive mill wastewater (OMW) management [133]
2016	Cupuassu	Seeds	Cupuassu butter (phenolic content/tocopherols/fatty acids)	Brazil	Supercritical CO_2 extraction Temperature: 50 and 70 °C Pressures: 20–40 MPa	Supercritical CO_2 extraction of cupuassu butter from defatted seed residue: experimental data, mathematical modeling and cost of manufacturing [86]

Table 1 (continued)

Year	Crop	Waste stream	Target compounds	Geographical location	Green or sustainable separation approach	References
2016	Coffee	Spent coffee grounds	Oil fraction	Portugal, Brazil, Portugal	Supercritical CO_2 Extraction time: 1 h Temperature: 55 °C Pressure: 250 bar Flow rate: 15 kg/h	The green generation of sunscreens: using coffee industrial sub-products [87]
2016	Ginger	Not defined	Essential oil, phenolics, fibers and phenolic acids	France	Microwave hydrodiffusion and gravity processing (MHG) and UAE Solvents: water Extraction time: 83 and 90 min Temperature: up to 100 and 50 °C	Towards a “dry” bio-refinery without solvents or added water using microwaves and ultrasound for total valorization of fruit and vegetable by-products [56]
2016	Passion fruit	Passion fruit seeds and passion fruit seed cake (the residue from the seed oil production by cold pressing)	Oil and extract with promising antioxidant and antimicrobial activities	Brazil and USA	SFE, LPE, MAC, UE Solvents: sCO_2, hexane, ethyl acetate, ethanol, H_2O Extraction time: 45 min–7 days temperature: room temp.– 50 °C	Valorization of passion fruit (*Passiflora edulis* sp.) by-products: sustainable recovery and biological activities [88]
2016	Wood	Broken pallets, crates, and waste timber from building and demolition works	Renewable energy source	Romania	Review Overview of the technical and economic opportunity of using wood waste as a renewable energy source	Wood waste as a renewable source of energy [172]
2015	Plants of spontaneous flora, cultivated plant, and wastes resulted in agricultural and food industry	General bio-derived materials	Polyphenols	Romania	Review Microwave-assisted extraction (MAE), supercritical fluid extraction (SFE), and ultrasound-assisted extraction (UAE)	A comparative analysis of the ‘green’ techniques applied for polyphenols extraction from bioresources [173]

Table 1 (continued)

Year	Crop	Waste stream	Target compounds	Geographical location	Green or sustainable separation approach	References
2015	Onion	Onion solid wastes	Polyphenol- and pigment-enriched extracts with antioxidant activity	Greece	Ultrasound extraction (140 W, 37 kHz) Extraction time: 60 min Temperature: 45 °C	A green ultrasound-assisted extraction process for the recovery of antioxidant polyphenols and pigments from onion solid wastes using Box–Behnken experimental design and kinetics [174]
2015	Six types of plant fibers (bast, leaf, seed, straw, grass, and wood) and animal fibers and regenerated cellulose fibers	Seed (coir) and animals (chicken feather) as they are secondary or made from waste products	Fibers	Sweden	Review Dew, stand, cold and warm water, steam, enzyme, mechanical, ultrasound chemical and Surfactant retting	A review of natural fibers used in biocomposites: plant, animal and regenerated cellulose fibers [175]
2015	Non edible vegetables	Seeds	Biodiesel	Egypt	Review	A review on green trend for oil extraction using subcritical water technology and biodiesel production [102]
2015	Neem	Neem seed cake (NSC)	Neem Protein (NP)	USA	Alkaline extraction Solvents: H_2O and NaOH Extraction time: 60 min Temperature: 75 °C	Bio-based polymeric resin from agricultural waste, neem (*Azadirachta indica*) seed cake, for green composites [118]
2015	Oranges	Peel	Essential oil, polyphenols and pectin	Algeria and France	MHG, UAE, MAE Solvents: “in situ” water Extraction time: 25 and 3 min Temperature: 59 °C	Bio-refinery of orange peels waste: a new concept based on integrated green and solvent free extraction processes using ultrasound and microwave techniques to obtain essential oil, polyphenols and pectin [57]

Table 1 (continued)

Year	Crop	Waste stream	Target compounds	Geographical location	Green or sustainable separation approach	References
2015	Corn, sugarcane, sorghum, soybean, rice, barley, potato, other lignocellulose, vegetable oils, oilseed	By-products (bagasse, straw, cobs, stalks, stover, grass etc.)	Biofuel, 1,3-propanediol, succinic acid, adhesives, solvents, surfactants, ethyl lactate, erucic acid, amylose ethers, among others	Denmark	Review Focus on integrating sustainability assessment procedures and tools (LCA and evaluation approaches)	Biorefining in the prevailing energy and materials crisis: a review of sustainable pathways for biorefinery value chains and sustainability assessment methodologies [144]
2015	Agro-industrial products	Agro-industrial co-products	Phenolic compounds	Brazil	Solid-state fermentation, even as friendly enzyme-assisted extractions	Biotransformation and bioconversion of phenolic compounds obtainment: an overview [176]
2015	Cashew-nut	Husk	Natural dyes	India	Enzyme-assisted extraction cellulase and pectinase Solvent: water Extraction time: 60–180 min pH 9.5	Cashew-nut husk natural dye extraction using Taguchi optimization: green chemistry approach [109]
2015	Beet	Sugar beet pulp	Monosaccharides present in hydrolyzed SBP pectin: L-rhamnose, L-arabinose, D-galactose and D-galacturonic acid	United Kingdom	Centrifugal partition chromatography ascending mode, 1000 rpm Mobile phase flow rate: 8 ml/min	Centrifugal partition chromatography in a biorefinery context: separation of monosaccharides from hydrolyzed sugar beet pulp [141]
2015	Mangoes (*Mangifera indica* L.) and rye grains (*Secale cereals* L.)	Peels and grains	Alk(en)ylresorcinols (ARs)	Germany	Ultrasound-assisted extraction Solvent: dichloromethane Extraction time: 15 s cooled in ice bath	Development and validation of an HPLC method for the determination of alk(en)ylresorcinols using rapid ultrasound-assisted extraction of mango peels and rye grains [78]

Table 1 (continued)

Year	Crop	Waste stream	Target compounds	Geographical location	Green or sustainable separation approach	References
2015	Olives	Waste from olive oil production	High-added value compounds (polyphenols, fatty acids, coloring pigments (chlorophylls and carotenoids), tocopherols, phytosterols, squalene, volatile and aromatic compounds)	Spain, France, Morocco and Portugal	Review Conventional (solvent, heat, grinding) and non-conventional methodologies (ultrasounds, microwaves, sub- and supercritical fluid extractions, pressurized liquid extraction, pulsed electric fields and high voltage electrical discharges)	Emerging opportunities for the effective valorization of wastes and by-products generated during olive oil production process: non-conventional methods for the recovery of high-added value compounds [142]
2015	Asparagus	Dried segments (residues)	Antioxidant compounds	China	Solid–liquid extraction Solvents: acetone, methanol or ethanol Extraction time: 2 h Temperature: 70 °C	Extraction and analysis of antioxidant compounds from the residues of *Asparagus officinalis* L. [177]
2015	Grapes	Skin	Anthocyanins	Korea	Deep eutectic solvents (DESs) Extraction time: 45 min room temperature	Highly efficient extraction of anthocyanins from grape skin using deep eutectic solvents as green and tunable media [138]
2015	Green tea	Green tea leaf residue	HG pectin, RGII pectin, organic acids, cellulose and hemi-cellulose	The Netherlands	Alkaline extraction Solvents: 0.1 M NaOH Extraction time: 2 h (protein), 5 min–24 h (carbohydrates or lignin) Temperature: 95 °C	How does alkali aid protein extraction in green tea leaf residue: a basis for integrated biorefinery of leaves [119]
2015	Papaya (*Carica papaya* L.)	Processing waste	Lycopene	China	Ultrasound extraction (600 W, 40 kHz) Solvents: ethanol/ethyl acetate Extraction time: 15–40 min Temperature: 20–70 °C	Optimization of ultrasound-assisted extraction of lycopene from papaya processing waste by response surface methodology [77]

Table 1 (continued)

Year	Crop	Waste stream	Target compounds	Geographical location	Green or sustainable separation approach	References
2015	Carrots, green beans, leeks and celeriac	Vegetable waste streams (rejected carrots, carrot steam peels, green beans cutting waste, leek cutting waste and celeriac steam peels)	Pectin	Belgium	Alcohol insoluble residue Solvents: ethanol and acetone	Pectin characterization in vegetable waste streams: a starting point for waste valorization in the food industry [178]
2015	Berries of *A. melanocarpa*	Black chokeberry wastes	Antioxidants	France	Extraction-adsorption process Extraction time: 2–8 h Temperature: 22 °C	Pilot scale demonstration of integrated extraction-adsorption eco-process for selective recovery of antioxidants from berries wastes [179]
2015	Cashew nuts (CNS)	Shells	Anacardic acid	Tanzania	Review Focus on natural anacardic acids from CNS and other plants and their semi-synthetic derivatives as possible lead compounds in medicine	Potential biological applications of bio-based anacardic acids and their derivatives [180]
2015	Soy, sugarcane, tea	Soy sauce residues, sugarcane bagasse and tea dregs	Hemicelluloses	China	Ionic liquid Solvents: ionic liquids Extraction time: 1–5 h Temperature: 70–100 °C	Quantitative industrial analysis of lignocellulosic composition in typical agro-residues and extraction of inner hemicelluloses with ionic liquid [134]
2015	Tomatoes	Processing tomato	Nutritional bioactive compounds, lycopene	Italy	Biocompatible technology extraction	Recovery of tomato bioactive compounds through a biocompatible and eco-sustainable new technology for the production of enriched "nutraceutical tomato products" [181]

Table 1 (continued)

Year	Crop	Waste stream	Target compounds	Geographical location	Green or sustainable separation approach	References
2015	*Citrus sinensis* (Hamlin, Valencia, Pera riu and Pera Natal)	Albedo and flavedo	Flavanone	Brazil	Enzymatic process tannase, pectinase and cellulase Extraction time: 30 h Temperature: 40 °C pH 5	Simultaneous extraction and biotransformation process to obtain high bioactivity phenolic compounds from Brazilian citrus residues [110]
2015	Sunflower	Seeds	Oil- (fatty acids and their antioxidant capacities) and water-soluble phase (proteins, carbohydrates and phenolics)	Slovenia	Subcritical water extraction Extraction time: 5–120 min Temperature: 60–160 °C Pressure: 30 bar	Simultaneous extraction of oil- and water-soluble phase from sunflower seeds with subcritical water [103]
2015	Cereals, root crops, fruits, vegetables, oilseeds, meat, dairy products	Food waste	Nutritionally interesting compounds, chemicals and biofuels	Brazil	Review Sub- and supercritical technologies	Sub- and supercritical fluid technology applied to food waste processing [89]
2015	Agricultural biomass	By-products such as durian peel, mango peel, corn straw, rice bran, corn shell and potato peel	Bio-fuel, water soluble sugars and phenolic compounds	Malaysia and Nigeria	Review Sub-critical water	Sub-critical water as a green solvent for production of valuable materials from agricultural waste biomass: a review of recent work [182]
2015	Sugarcane	Sugarcane waste (rind, leaf and bagasse)	Wax/long-chain aldehydes and *n*-policosanols (nutraceutical compounds) triterpenoids	UK and Brazil	Supercritical CO_2 ($scCO_2$) Extraction time: 4 h Temperature: 50 °C Pressure: 350 bar Flow rate: 40 g/min	Sugarcane waste as a valuable source of lipophilic molecules [183]
2015	Mangoes	Peel	Pectin	Germany and Saudi Arabia	Hot-acid extraction Extraction time: 90 min pH 1.5	The arabinogalactan of dried mango exudate and its co-extraction during pectin recovery from mango peel [184]
2015	Coffee	Spent coffee grounds	Tannin compounds	Malaysia	Alkaline extraction Solvent: NaOH Extraction time: 30–90 min Temperature: 60–100 °C	The influence of extraction parameters on spent coffee grounds as a renewable tannin resource [185]

Table 1 (continued)

Year	Crop	Waste stream	Target compounds	Geographical location	Green or sustainable separation approach	References
2014	*Eucalyptus globulus* wood	Trimmings of *Eucalyptus globulus* wood veneers	Phenolic compounds	Spain	Aqueous two-phase extraction PEG 2000 and ammonium sulphate Extraction time: 30–390 min Temperature: 25–65 °C	Aqueous two-phase systems for the extraction of phenolic compounds from eucalyptus (*Eucalyptus globulus*) wood industrial wastes [124]
2014	Pomegranates	By-products after winemaking of pomegranate	(poly)phenolic compounds	Spain, Mexico and Italy	Extraction with MeOH 70% (v/v) and sonication	Assessment of pomegranate wine lees as a valuable source for the recovery of (poly)phenolic compounds [186]
2014	Citrus	Peel, pulp and seeds	Several value-added products, such as essential oils, pectin, enzymes, single cell protein, natural antioxidants, ethanol, organic acids, and prebiotics	Greece and Sweden	Review	Biotransformation of citrus by-products into value added products [187]
2014	Olives	Olive solid waste	Natural dye	Tunisia	Aqueous extraction in closed flasks Solvent: NaOH Extraction time: 15–120 min Temperature: 30–90 °C	Development and optimisation of a non-conventional extraction process of natural dye from olive solid waste using response surface methodology (RSM) [125]
2014	Coffee	Waste coffee grounds	Biodiesel production	United Kingdom	Suspended in fresh heptane room temperature	Effect of the type of bean, processing, and geographical location on the biodiesel produced from waste coffee grounds [188]
2014	Grapevine and hazelnut	Grapevine waste and hazelnut skins	Polyphenols content	Italy and France	UAE and MAE Solvents: ethanol, methanol, acetone, butanone, β-cyclodextrin Extraction time: 5–40 min Temperature: 20–60 °C	Efficient green extraction of polyphenols from post-harvested agro-industry vegetal sources in Piedmont [58]
2014	Bamboo	Raw bamboo culm	Lignin	Malaysia	Review Chemical and steam explosion methods	Extraction and preparation of bamboo fibre-reinforced composites [189]

Table 1 (continued)

Year	Crop	Waste stream	Target compounds	Geographical location	Green or sustainable separation approach	References
2014	Spruce	Spruce sawdust	Carboxylic acids	Finland	Alkaline extraction Solvents: Na_2CO_3 or $Na_2S.9H_2O$ Extraction time: 30 min + 30 min; Temperature: 80 °C up to 160 °C and 210 °C	Production of carboxylic acids from alkaline pretreatment byproduct of softwood [120]
2014	Variety of biomass sources (rapeseed, soybean, palm oil and nonedible feedstocks)	Preferably 2nd–4th generation feedstock (non-edible materials as bagasse, oil waste, microalgae, cyanobacteria and microbes)	Biodiesel	Malaysia	Review Supercritical fluid process and catalytic in situ or reactive extraction process	Integration of reactive extraction with supercritical fluids for process intensification of biodiesel production: prospects and recent advances [90]
2014	Cherries	Cherry seeds	Total phenolic content	Brazil and France	Pressurized fluid extraction (PFE) Solvent: anhydrous ethanol Extraction time: 2–10 min Temperature: 40–80 °C	Isolation by pressurized fluid extraction (PFE) and identification using CPC and HPLC/ESI/MS of phenolic compounds from Brazilian cherry seeds (*Eugenia uniflora* L.) [190]
2014	Corn	Corn stover	Lignin	USA	Protic ionic liquid (PIL) Extraction time: 24 h Temperature: 90 °C	Lignin extraction from biomass with protic ionic liquids [135]
2014	Oranges	Peel	D-limonene	United Kingdom	Microwave-assisted extraction 200 W, closed vessel Solvent: hexane Temperature: 70–110 °C	Microwave-assisted extraction as an important technology for valorising orange waste [59]
2014	Sweet Limes	Peel	Antioxidant phenolics	Pakistan	Enzymatic treatment Incubation time: 30–120 min Temperature: 30–75 °C pH 5 to 8	Optimization of enzyme-assisted revalorization of sweet lime (*Citrus limetta Risso*) peel into phenolic antioxidants [111]

Table 1 (continued)

Year	Crop	Waste stream	Target compounds	Geographical location	Green or sustainable separation approach	References
2014	Artichoke	Artichoke scraps	Phenolic compounds	Italy	Ultrasound-assisted extraction (UAE) Time: 60 min Solvent: water	Phenols and antioxidant activity in vitro and in vivo of aqueous extracts obtained by ultrasound-assisted extraction from artichoke by-products [79]
2014	*Cachrys pungens* Jan (Umbelliferae)	Aerial parts of *Cachrys pungens* Jan (Umbelliferae)	Bioactive compounds	Italy	Solvent extraction Solvents: methanol Extraction time: 72 h room temperature dark conditions	Phytotoxic activity of *Cachrys pungens* Jan, a Mediterranean species: separation, identification and quantification of potential allelochemicals [191]
2014	Wheat	Wheat straw	Major organic components (e.g., *N*-heterocycles, fatty acids, phenols and lignins)	Canada	Fast pyrolysis steel shots 475 °C	Wheat straw biomass: a resource for high-value chemicals [192]
2013	Cranberries	Cranberry juice and pomace	Polyphenolics	Canada and Mexico	Pilot scale methods Solvents: ethanol Extraction time: 24 h	Bioactivities of pilot-scale extracted cranberry juice and pomace [48]
2013	Fruits, vegetables, eggs, shrimp	Plant residues, industrial and post-harvest materials	Carotenoids	Mexico	Review Novel environmentally friendly solvents (e.g., ethyl lactate, bioethanol, vegetal oil, commercial enzymes)	Carotenoids extraction and quantification: a review [193]
2013	Tomatoes	Peels	Lycopene	Italy	Enzymatic-assisted extraction Temperature: 45 and 60 °C pH 4–5 and 9–10.5	Environmentally friendly lycopene purification from tomato peel waste: enzymatic-assisted aqueous extraction [112]
2013	Coffee	Coffee residue left after the preparation of the brew (spent coffee grounds—SCG)	Polysaccharides	Portugal	Alkali extraction Solvent: H_2O and 4 M NaOH Extraction time: 3 h Temperature: 20–120 °C	Extractability and structure of spent coffee ground polysaccharides by roasting pre-treatments [194]

Table 1 (continued)

Year	Crop	Waste stream	Target compounds	Geographical location	Green or sustainable separation approach	References
2013	Coffee	Spent coffee grounds	Lipids, oil	Iran	Soxhlet, UAE, MAE, SFE Solvents: petroleum benzene and *n*-hexane Soxhlet: 6 h, boiling temperature UAE: 45 min, ambient conditions MAE: 30 s, 200 and 800 W SFE: 200–250 bar, 40–60 °C, modifier (water, ethanol, hexane)	Extraction of lipids from spent coffee grounds using organic solvents and supercritical carbon dioxide [60]
2013	Forest Industry	Forest residues, including bark	Bioactive molecules	Canada	Review Green alternatives for the design, formulation, and manufacture of new products with applications in various markets (cosmetics, natural health products, biocides, adhesives, coatings)	Forest extractives, the 4th pathway of the forest biorefinery concept [195]
2013	Coffee	Spent coffee grounds (SCG)	Lipid fraction	Portugal and Brazil	Supercritical carbon dioxide Extraction time: 1 h Temperature: 55 °C Pressure: 250 bar CO_2 flow rate: 15 kg/h	From coffee industry waste materials to skin-friendly products with improved skin fat levels [91]
2013	Walnuts	Green husk	Natural compounds with antioxidant and antimicrobial properties	Spain and Portugal	Solvent extraction Solvents: water, methanol, ethanol Extraction time: 45 min room temperature	Influence of solvent on the antioxidant and antimicrobial properties of walnut (*Juglans regia* L.) green husk extracts [49]
2013	Coffee	Spent coffee	Antioxidants	Spain	Soxhlet, SPE, filter coffeemaker Solvents: water, ethanol, methanol Extraction time: 6–165 min Temperature: 80–100 °C	Influence of extraction process on antioxidant capacity of spent coffee [50]

Table 1 (continued)

Year	Crop	Waste stream	Target compounds	Geographical location	Green or sustainable separation approach	References
2013	Tomatoes	Peel	Fatty acids	France	Depolymerization 1.5 M KOMe overnight treatment at room temperature	Interfacial properties of functionalized assemblies of hydroxy-fatty acid salts isolated from fruit tomato peels [196]
2013	Coffee	Spent coffee grounds (SCG)	Polysaccharides	Portugal	Microwave superheated water extraction Extraction time: 5 min Temperature: 200 °C	Microwave superheated water extraction of polysaccharides from spent coffee grounds [61]
2013	Turkish red pine timber	Waste barks	Natural dye	Turkey	Natural dyestuff extraction machine Solvents: water and ethanol Extraction time: 24 h (osmosis)	Natural dye extraction from waste barks of Turkish red pine (*Pinus brutia* Ten.) Timber and eco-friendly natural dyeing of various textile fibers [126]
2013	Cotton, jute, flax, hemp, ramie and natural colorants	Wastes and manufacturing by-products	Fibres, polysaccharides, dyes and pigments, polyphenols, oils and other biologically active compounds	India	Review Conventional maceration, soxhlet, MAE, SFE, ultrasonic extraction	Perspectives for natural product based agents derived from industrial plants in textile applications: a review [197]
2013	Coffee	Spent coffee grounds	Natural antioxidants	Italy	Solvent extraction Solvents: H_2O, ethanol, Extraction time: 30 min Temperature: 60 °C	Recovery of natural antioxidants from spent coffee grounds [198]
2013	Feijoa fruits	Primarily skin and some flesh	Total soluble solids (TSS), pectin fibre content, total extractable PP content (TEPC) and total antioxidant activity	New Zealand	Accelerated solvent extraction Solvents: (acidified) water, ethanol Temperature: 20 or 50 °C	Utilisation potential of feijoa fruit wastes as ingredients for functional foods [127]
2012	Green tea	Green tea waste	Noncaffeine tea polyphenols	China	Water bath 20 min 90 °C	A novel way of separation and preparation non-caffeine tea polyphenols from green tea waste [199]

Table 1 (continued)

Year	Crop	Waste stream	Target compounds	Geographical location	Green or sustainable separation approach	References
2012	Larch	Larch wood-derived lignocellulosic residue	Arabinogalactan, pectin, and crystalline glucose	Russia	Water extraction Extraction time: 2–3 h Temperature: 60–80 °C	An eco-friendly technology for polysaccharide production from logging and sawing waste [128]
2012	Olives	Olive leaves	Oleuropein	Greece	SFE and PLE SFE: 30 MPa, 50 °C, 9.6 kg/h PLE: 10.34 MPa, 10 min, 40–150 °C Solvents: H_2O and EtOH	Development of a green extraction procedure with super/subcritical fluids to produce extracts enriched in oleuropein from olive leaves [92]
2012	Wood	Wood barks, obtained from pulp mills as industrial wastes	Natural phenolic polymers of tannins and lignin	France	Aqueous extraction urea and sulfite used as water-additives Extraction time: 1 h under reflux Temperature: 75 °C	Development of green adhesives for fibreboard manufacturing, using tannins and lignin from pulp mill residues [129]
2012	Wheat	Wheat milling by-products	High quality oil and vitamin E	Italy	Review Solvent extraction, mechanical pressing or the eco-friendly supercritical carbon dioxide (SC-CO_2) extraction technology	Durum wheat by-products as natural sources of valuable nutrients [200]
2012	Tree bark	Waste product from paper pulp industries	Antioxidants	Sweden	SFE, PFE, SLE Solvents: scCO_2, ethanol, H_2O Extraction time: 30 min–24 h Temperature: 70–180 °C	Extraction of antioxidants from spruce (*Picea abies*) bark using eco-friendly solvents [93]
2012	Timber	Empty fruit bunches	Fiber	Malaysia	Perspective paper	Fiber resin matrix composites: nature's gift [201]
2012	Oranges	Peel	Essential oil	United Kingdom	Steam distillation and microwave irradiation SD: water, 1 h MW: 12.5 min, 200 °C, power gradient from 400 to 1200 W	*p*-cymenesulphonic acid: an organic acid synthesized from citrus waste [202]

Table 1 (continued)

Year	Crop	Waste stream	Target compounds	Geographical location	Green or sustainable separation approach	References
2012	Black tea	Black tea wastes	Pancreatic lipase-inhibiting polyphenols	Japan	Hot-compressed water (HCW) ion-exchange water extraction temperature: 100–200 °C	Polyphenols extracted from black tea (*Camellia sinensis*) residue by hot-compressed water and their inhibitory effect on pancreatic lipase in vitro [203]
2012	Green tea	Green tea waste	Polyphenols	China	Liquid–liquid extraction Solvents: H_2O, glyceryl, triacetate, *n*-butanol, ethyl acetate Extraction time: 12 h + 2 h	Recovery of tea polyphenols from green tea waste by liquid–liquid extraction [204]
2012	Citrus	Peels	Polymethoxy flavonoids	China	Solvent extraction Solvents: methanol and ethanol Extraction time: 1–3 h Temperature: 65–85 °C	Study on the extraction technique of poly-methoxyflavonoids from citrus peels by using response surface methodology [205]
2011	Coffee	Husks	Caffeine	Spain	Supercritical CO_2 Extraction time: 20 min Temperature: 323 K Pressure: 60 bar CO_2 flow rate: 2–3 g/min	Extraction of caffeine from Robusta coffee (*Coffea canephora* var. Robusta) husks using supercritical carbon dioxide [94]
2011	Oranges	Peel	Essential oils	France and Tunisia	Microwave steam diffusion (MSDf) Extraction time: 12 min Temperature:100 °C	Microwave steam diffusion for extraction of essential oil from orange peel: kinetic data, extract's global yield and mechanism [62]
2011	Grape	Skins	Anthocyanins	Spain	Microwave-assisted extraction Solvents: H_2O, methanol Extraction time: 5–20 min Temperature: 50–100 °C	Microwave-assisted extraction of anthocyanins from grape skins [63]
2011	Tea (green, oolong and black)	Tea residues (green, oolong and black tea residues)	Phenolic compounds	Japan	Microwave-assisted extraction water under autohydrolytic conditions Extraction time: 2 min Temperature: 110–230 °C	Microwave-assisted extraction of phenolic compounds from tea residues under autohydrolytic conditions [64]

Table 1 (continued)

Year	Crop	Waste stream	Target compounds	Geographical location	Green or sustainable separation approach	References
2011	Sea Buckthorn (Hippophae rhamnoides	By-Products of juice production	Flavonoids	France	Solvent-free microwave hydrodiffusion and gravity (MHG) without addition of solvent or water atmospheric pressure	Solvent free microwave-assisted extraction of antioxidants from sea buckthorn (*Hippophae rhamnoides*) food by-products [206]
2011	Wheat	Wheat straw	Energy and CO_2 secondary metabolites including fatty acids, wax esters and fatty alcohols	England	Supercritical CO_2 extraction Temperature: 40–100 °C Pressure: 100–300 bar CO_2 flow rate: 40 g/min	Use of green chemical technologies in an integrated biorefinery [95]
2011	Olives	By-products generated during storage of extra virgin olive oil	Phenolic compounds, hydroxytyrosol, tyrosol, decarboxymethyl oleuropein aglycone, and luteolin	Italy and Spain	Solid–liquid and liquid–liquid extraction Solvents: n-hexane, methanol, H_2O Extraction time: 1 h	Wastes generated during the storage of extra virgin olive oil as a natural source of phenolic compounds [207]
2010	Tomatoes	Ground tomatoes without seeds	Lycopene	France and Algeria	Solvent extraction Solvent: D-limonene	Carotenoid extraction from tomato using a green solvent resulting from orange processing waste [208]
2010	Tea plant	Tea stalk and fiber wastes	Caffeine	Turkey	Supercritical CO_2 ethanol as co-solvent Extraction time: 1–5 h Temperature: 50–70 °C Pressure: 250 bar semi-continuous flow	Effect of ethanol content on supercritical carbon dioxide extraction of caffeine from tea stalk and fiber wastes [96]
2010	Portuguese elderberry	Pomace	Anthocyanins	Portugal	Supercritical CO_2 extraction Solvents: CO_2, water, ethanol Extraction time: 40 min Temperature: 313 K	Effect of solvent (CO_2/ethanol/H_2O) on the fractionated enhanced solvent extraction of anthocyanins from elderberry pomace [97]
2010	Green tea	Green tea waste	Polyphenols, total catechins, and reducing sugars	South Korea and USA	Solvents: cold water (25 °C), hot water (90 °C), sulfuric acid, hydrochloric acid and methanol Extraction time: 20 min 250 rpm	Effects of cellulase from *Aspergillus niger* and solvent pretreatments on the extractability of organic green tea waste [130]

Table 1 (continued)

Year	Crop	Waste stream	Target compounds	Geographical location	Green or sustainable separation approach	References
2010	Tea	Tea waste	Caffeine	Iran	Subcritical water extraction Temperature: 100–200 °C Pressure: 20–40 bar water flow rate: 1–4 g/min	Isolation of caffeine from tea waste using subcritical water extraction [104]
2010	*Citrus sudachi*	Peels	Flavones	Japan	Microwave-assisted extraction Solvents: methanol extraction time: 10 to 12 min	Microwave-assisted extraction and methylation of useful flavones from waste peels of *Citrus sudachi* [209]
2010	Mate (*Ilex paraguariensis*)	Mate residue	Compounds with antioxidant properties, such as phenolic acids and methylxanthines, such as caffeine	Brazil	Solvent extraction Solvent: methanol, H_2O, ethanol sonication for 15 min room temperature	Phenolic acids and methylxanthines composition and antioxidant properties of mate (*Ilex paraguariensis*) residue [210]
2010	Rice	Rice bran	Phenolic compounds as well as other valuable materials	Japan	Subcritical water Preheated oil: 100–180 °C, 10 min Preheated water bath: 180–360 °C, 10 min and 220 °C for 2–30 min	Production of phenolic compounds from rice bran biomass under sub-critical water conditions [105]
2009	*Citrus*	Peels	Essential oil	France and Algeria	Microwave hydrodiffusion gravity Extraction time: 15 min atmospheric pressure 500 W	A new process for extraction of essential oil from citrus peels: microwave hydrodiffusion and gravity [65]
2009	Kiwifruit	By-products derived from kiwifruit processing	Phenolics and pectin polysaccharides	New Zealand	Solvent extraction Solvents: water, ethanol Extraction time: 1 h room temperature	Evaluation of the extraction efficiency for polyphenol extracts from by-products of green kiwifruit juicing [211]
2009	Palm	Black liquor of oil palm waste	Lignin	Malaysia	Solvent extraction Chemical extractions: di-ethyl ether, alcohol-benzene mixture treatment with H_2SO_4 for 30–45 min	Exploring the antioxidant potential of lignin isolated from black liquor of oil palm waste [212]

Table 1 (continued)

Year	Crop	Waste stream	Target compounds	Geographical location	Green or sustainable separation approach	References
2009	Turkish tea plants	Tea stalk and fiber wastes	Caffeine	Turkey	Supercritical carbon dioxide Extraction time: 1–10 h Temperature: 55–75 °C increasing pressure up to 250 bar semi-continuous flow	Extraction of caffeine from tea stalk and fiber wastes using supercritical carbon dioxide [99]
2009	Rice	Rice bran	Oil (value-added materials such as amino acids, organic acids, and water-soluble saccharides)	Japan	Subcritical water preheated oil bath: 100–180 °C Preheated salt bath: 200–360 °C Reaction time: 5 min	Sub-critical water treatment of rice bran to produce valuable materials [106]
2009	Several biomass	Residues rich in ligno-cellulosics	Bio-based chemicals (e.g., succinic, lactic, fumaric L-malic, L-aspartic acids)	England	Review Focus on green chemical conversion of lignin into higher value chemicals	The integration of green chemistry into future biorefineries [21]
2009	Apple	Industrially generated apple pomace	Antioxidants and polyphenols	Ireland	Pressurized liquid extraction accelerated solvent extractor static extraction of 5 min Temperature: 75–193 °C	The optimization of extraction of antioxidants from apple pomace by pressurized liquids [213]
2008	Chicory, citrus, cauliflower, endive, and sugar beet	Plant by-products (chicory roots, citrus peel, cauliflower florets and leaves, endive, and sugar beet pulps)	Pectins	France and Finland	Enzymatic extraction Extraction time: 4 h Temperature: 50 °C	Extraction of green labeled pectins and pectic oligosaccharides from plant by-products [113]
2008	Tea (green, oolong, and black)	Green, oolong, and black tea residues	Polysaccharides, polyphenols, arabinose, galactose, xylose, catechins	Japan	Microwave heating Solvent: water Temperature: 110–230 °C	Microwave heating of tea residue yields polysaccharides, polyphenols, and plant biopolyester [66]
2008	Plant lipids	Plant oils and other natural lipidic phases	Phytosterols, vitamins	Czech Republic	Review Enzymes as efficient natural catalysts	Plant products for pharmacology: application of enzymes in their transformations [114]

Table 1 (continued)

Year	Crop	Waste stream	Target compounds	Geographical location	Green or sustainable separation approach	References
2007	Broccoli	Broccoli seeds	Natural sulforaphane	China and Australia	Liquid–liquid and solid-phase extraction Solvents: ethanol, hexane, ethyl acetate	Separation and purification of sulforaphane from broccoli seeds by solid phase extraction and preparative high-performance liquid chromatography [214]
2006	Tea	Tea waste	Caffeine	Turkey	Solid–liquid extraction solvents: hot water and chloroform Temperature: 370 K and 293 K	Solid–liquid extraction of caffeine from tea waste using battery type extractor: process optimization [215]

components in these matrices, such as water or high molecular weight compounds [39].

The decision concerning the best method to separate the compounds of interest from the raw material is dependent on several aspects, such as the characteristics of the target extracts and raw material (physical–chemical properties), available technology, required purity, selectivity, stability and, more importantly here, the greenness of the whole process. As can be seen in Fig. 5, the most cited techniques in these research papers were based on solvent/maceration (25% of the total), microwave (19%), ultrasonication (14.7%) and supercritical fluid processing (13%), followed by methods using ionic liquids (7%), enzymatic and subcritical fluid treatment (6%), as well as the association of two or more techniques.

According to the literature, the most widespread approaches for separating natural products from a number of matrices are based on liquid–liquid or solid–liquid extraction (LLE and SLE). Several greener alternatives have been proposed by replacing toxic or non-renewable organic solvents, as well as the extraction times. In some cases, solid-phase extractions (SPE) were also carried out and decreased both the amount of solvent and the number of extraction cycles, offering high enrichment factors [39, 40]. Actually, the mass transfer enhancement for SLE has been largely studied and applied, contributing to technology innovation, process intensification and integration, and energy saving, especially important for microwave, ultrasound, and high-pressure processing, for instance [41]. An overview of these techniques and related examples will be discussed in this section.

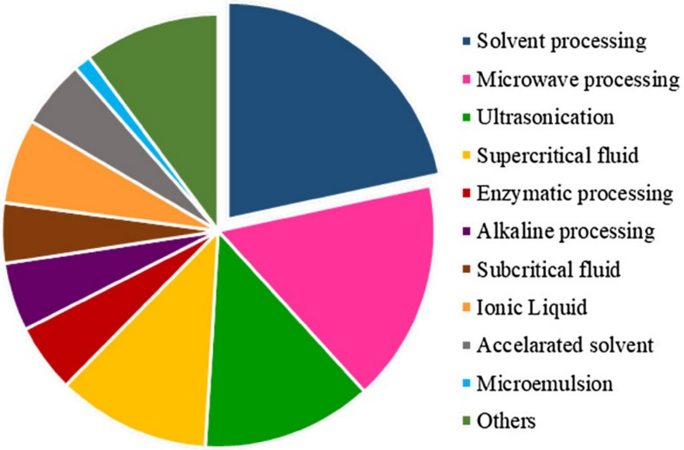


Fig. 5 Main green and sustainable techniques used to separate natural products from waste described in research papers (ISIS Web of Knowledge, January 2006 to December 2017)

3.1 From Conventional Solvent Separation to Enhancement Processing Approaches Over the Last 10 Years

Solvent processing is one of the most traditional methods to remove natural products from bio-derived materials. In this extraction approach, the raw material in adequate size is exposed to different solvents, mostly organic, which remove soluble components of interest. The samples are then usually centrifuged and filtered to separate the solid residue, and the extract is used in this way (as a food supplement or for preparing functional foods, for example) or treated after this step. Solvent extraction is attractive compared to other methods due to low cost and simplicity. However, this method does not always use benign solvents; it frequently requires an evaporation/concentration step for recovery, it usually demands large amounts of solvent and needs a long time to be carried out. Additionally, the possibility of thermal degradation of natural bioactive components is also possible due to the high temperatures used during the extraction process [42]. Despite this, it is largely used in industries, where solvent reuse is of great economic importance. In general, the raw material (in its liquid or solid form) is mixed with a solvent, and the separation kinetic of the target compounds is influenced by parameters such as the solvent ratio, pH, and temperature and, for SLE, the particle size. The solvent should be atoxic, non-flammable and stable at working conditions, ideally renewable and cheap, with low viscosity and an adequate boiling point, allowing for easier solvent removal from the extract/fraction [43]. Recently, several models have been proposed to predict the best solvents to be used in a specific case, which do not only take into account physical descriptors, such as enthalpy of vaporization, dielectric constant, refractive index, boiling point, etc., but also empirical descriptors to evaluate, for instance, intermolecular forces (specific and non-specific solute–solvent interactions, e.g., hydrogen bond donor and/or hydrogen bond acceptor, Van der Waals and ion/dipole forces). Purely theoretical descriptors have been also introduced, offering the most important advantage of not requiring any experiments, as is the case of the model known as quantitative structure property relationship (QSPR), able to predict 127 polarity scales for more than 700 solvents [44].

The solvent selection also depends on the physical–chemical proprieties of the compounds of interest, considering principally the selectivity and greenness degree of the process, aiming at obtaining high recoveries and the integrity of the target compounds. In general, the raw material stays in contact with the solvent for a certain period (from minutes to days), when the soluble compounds are transferred from the matrix to the extractor phase, usually by shaking the system. For SLE, the dispersion of the particles in the solvent is facilitated agitating them, optimizing their contact and accelerating the separation process. Traditionally, solvent treatment is performed at room temperature, although heating can promote higher recoveries to these compounds that are not thermosensitive. In some cases, LLE and SLE can be time-consuming, demanding further purification and concentration steps, which are their main drawbacks [41, 45].

Maceration using green and non-toxic solvents for the separation of natural products from plant-derived waste has been described over the last years (e.g., to remove dyes from quince leaves or catechins, theaflavins, gallic acid, and antioxidants in general from walnut green husk, cranberry pomace, black tea and banana processing waste). According to these studies, using water, methanol, ethanol or a mixture of them at 70–100 °C can be a low-cost, benign alternative for the recovery of high added-value compounds derived from residual biomass [46–49]. Scaling-up was also studied, whose results showed to be useful in determining industrial process feasibility and the economic value of polyphenols for commercial use, increasing the overall profitability of the cranberry industry [48].

Whenever possible, higher temperatures allow for higher mass transfer in a shorter time with lower energy consumption in general, resulting in better recovery efficiency than conventional systems [50]. As observed in Fig. 5, the second most cited green and sustainable separation process is based on microwave heating and can be considered a non-conventional technique nowadays. Heating is based on non-ionizing electromagnetic waves. Those between 0.915 and 2.45 GHz are used for industrial, scientific and medical applications. The overall principle of heating is rooted in its direct impact with polar materials/solvents and is dependent on ionic conduction and dipole rotation, occurring simultaneously in most cases. The increased temperature can overcome the natural product-matrix interaction caused by Van der Waals forces, dipole attraction, hydrogen bonding of the compounds of interest and active sites in the matrix. Therefore, thermal energy can disrupt both solute–solute and solute–matrix interactions, providing the activation energy required for the desorption process. The mass transfer of the compounds from the raw material to the solvent is also accomplished by convection and diffusion mechanisms, causing the explosion of plant cells and releasing their content into the liquid phase [51].

The eco-friendly removal of essential oils, pectin and polyphenols from a number of plant raw materials mediated by microwave irradiation has been described over the last years, paying special attention to citrus waste [52–66]. In fact, the orange juice processing industry can be considered more than a good case study. This sector is highly wasteful, generating 50% of waste from the total fruit/starting material (e.g., peel, bagasse, seeds and yellow water). Around 20 million tonnes of orange peel per year are produced worldwide, which consist of water (80%) and sugars, cellulose, hemicellulose, pectin and D-limonene (20%). Recently, it was shown using a mathematical model that D-limonene extraction consisted of a two stage diffusion process for a microwave (MW) heating approach: initial extraction from the exterior of cells followed by trans-membrane diffusion. Compared to other conventional extraction methods, it was found that the microwave treatment was more efficient, resulting in a higher overall yield due to the access to a higher amount of D-limonene [59].

The successful microwave-assisted solvent-free modification of pectin derived from citrus waste has also been reported [53]. These approaches not only allow for the separation of the major components of citrus peel, but they also add further value through the production of other high value-added products, such as pectin, D-limonene and a rare form of mesoporous cellulose which are produced in a single step, without added acid [67]. Along these lines, the concept of dry-biorefinery is gaining momentum, since valuable products can be recovered from plant by-products without adding solvents or water, using green processes such as MW [56].

Innovation relies on the separation of the target compounds from raw materials, which are rich in water, achieved without adding solvents or water, illustrating a circular systemic process; i.e., all materials and resources could be reintegrated into the integrated and zero-waste biorefinery [19]. Although very attractive, as expected, the design and use of real MW industrial scale equipment requires additional studies related to safety, corrosion and maintenance intervals [68].

The combination of two or more extraction/concentration methods is quite common in the literature (Table 1). As described by Boukroufa et al. [56], the removal of essential oil, polyphenols and pectin from orange waste was conducted using microwave and ultrasound technology, without adding any solvents. Essential oil separation was performed by Microwave Hydrodiffusion and Gravity (MHG), and thereafter the remaining water of this process was used as a solvent for the subsequent extraction of flavonoids and pectin. For polyphenol separation, ultrasound-assisted extraction (UAE) was used, and response surface methodology (RSM) using the central composite design (CCD) approach was used to investigate the influence of some variables. The CCD revealed that the optimized conditions of ultrasound power and temperature were 0.956 W/cm^2 and 59.83 °C giving a polyphenol yield of 50.02 mg GA/100 g dm, which, compared to conventional extraction, promoted an increase of 30% in the yield. Pectin was extracted by microwave-assisted extraction, resulting in a maximal yield of 24.2% for microwave power of 500 W (3 min), whereas traditional extraction provides18.32% (120 min). As can be seen, the combination of microwave, ultrasound and recycled water resulted in higher recoveries of the compounds of interest in a shorter time, so that a systemic loop/cycle could be closed using only the resources generated in the plant. This makes the whole process optimized in terms of time, energy savings, cleanliness and reduced amount of waste.

As can be noted, ultrasound has been widely utilized for helping to extract target components from waste plant-derived sources, reducing separation time, solvents, energy consumption and improving the product quality. The effectiveness of ultrasound is attributed to the cavitation phenomenon, assisting the solubilization of the compounds of interest into the solvent, enhancing their removal from the bulk raw material [69]. According to Chemat [70], the ultrasound waves (from 20 kHz to 10 MHz) pass through an elastic medium, inducing a longitudinal displacement of particles resulting in a succession of compression and rarefaction phases in this medium. Every medium has a critical molecular distance and, below this critical point, the liquid remains intact. However, above this distance, the liquid would break down, creating voids (cavitation bubbles) in the liquid. When the size of these bubbles reaches a critical point they collapse, releasing a large amount of energy. The estimated temperature and pressure at this time are estimated at 5000 and 2000 K atmospheres. This creates hotspots that accelerate the chemical reactivity into the medium, generating microjets directed towards the solid surface, also responsible for the general higher effectiveness of this technique, as the high pressure and temperature involved in the process destroy the cell walls of the plant matrices and their content can be released into the medium more easily.

Some new process aiming at agro-industrial waste application in food industries based on ultrasound-assisted extraction of natural products have been reported

[71–79], as is the case of carotenoid separation from pomegranate peels using different vegetable oils as solvents [72]. Sunflower and soybean oils were used as solvents and parameters such as time, temperature, solid/oil ratio used were analyzed considering the yield. It was found that the optimum mild operating conditions were: extraction temperature, 51.5 °C; peel/solvent ratio, 0.10; amplitude level, 58.8%; solvent, sunflower oil. Additionally, a subsequent separation of oil and carotenoids was not necessary, since the pigmented oil can be used as a carotenoid source in different commercial products in this format.

The green recovery of cellulose from oil palm bunches by autoclave-based and ultrasonication pre-treatments were successfully developed to replace the non-green chlorite method [73]. An ultrasonic process with hydrogen peroxide yielded 49% cellulose with 9.13% alpha-cellulose content and 68.7% crystallinity, as compared to 64% cellulose with an autoclave treatment. The cellulose/polypropylene composites generated with high tensile strength, high thermal stability, and low water and diesel sorption showed great potentials for conversion into eco-composite products such as polymeric material insulated cables for high voltage engineering, automotive parts, sports tools and other household or office items.

Another highly cited green and sustainable technique to isolate organic compounds from bio-based waste is based on supercritical fluid processing (Fig. 5). It is widely known that substances at temperatures and pressures near or above their critical points have exceptional solvent characteristics for analytical purposes. These supercritical fluids possess liquid-like solvating and gas-like diffusivity power, and other tuneable properties that can be adjusted varying temperature, pressure and the addition of other components acting as a modifier. Due to its gas-like low viscosity and high diffusivity, the supercritical fluid can easily penetrate into plant materials with a fast mass transfer rate. Possibly, the most important property of supercritical fluids for separation processes is diffusion, obtaining solubility and diffusion good enough to provide quantitative extraction yield [80, 81]. Carbon dioxide (scCO_2) is the fluid most widely used for extractions, with critical parameters of 31.1 °C and 73 atm (7.39 MPa), at relatively low operating conditions. It behaves as a nonpolar or polarizable solvent and low molar mass alcohols (co-solvents) are often added in small quantities to modify the solvent polarity. Because carbon dioxide can be depressurized to the gaseous state, the solvent is easily removed and supercritical fluid-based separation methods are easily coupled with subsequent analysis. Therefore, scCO_2 provides miscibility to the majority of natural products, availability and low cost, reliably high purity, negligible toxicity, facility for removal and reuse, resulting in many advantages for downstream processing in terms of product purification and/or catalyst recycling [80].

The approach using scCO_2 has been widely used for isolation and purification of chlorophylls, carotenoids, lipids, alkaloids, antioxidants from matrices such as filter tea, spruce bark, tomato and elderberry pomace, grape, passiflora, coffee and cupuassu seed waste [82–99]. In addition to the optimization of the separation process, some studies also aim to evaluate the techno-economic viability of large-scale commercial production, for example, to obtain cupuassu butter from cold-pressed seed residues, also evaluating the influence of thermodynamic and kinetic variables of yield, chemical composition and production costs of the extracts [86]. Optimal conditions related to extraction kinetics, chemical composition and production costs were 30–35 MPa and 50 °C. It was shown that the phenolic content (0.47–2.82 mg/g) was lower than those commonly found using other methods (20–23 mg/g). The high contents of tocopherols, as well as the unsaturated fatty acids (48%) compared to the saturated fatty acids (52%) present in the butter obtained by $scCO_2$ demonstrated its great potential as an ingredient in food, pharmaceutical and cosmetic industries. In addition, process intensification for biodiesel production involving supercritical fluids has been reported [84, 90]. Such approaches can allow biodiesel production without any addition of catalyst, or via catalytic in situ or reactive extraction process, combining the extraction and reaction phase together in a single operation unit. These studies also discuss both processes towards the future bio-refinery setup and more efficient use of all waste produced.

The use of fluids different to CO_2 has been described in the literature, but as they are usually organic solvents, they do not show any distinct advantages and often have high critical temperatures. Despite having a very high critical temperature, water shows unique properties in the subcritical region (200–300 °C), as a reduction in dielectric constant (20–30) and density (0.7–0.8 g/cm^3) compared to water at room temperature, improving its ability to dissolve nonpolar organic and inorganic compounds. Under these conditions, the water dissociation constant into hydroxide and hydrogen ions are more than three orders of magnitude higher, so that near-critical water acts as a self-neutralizing acid or base catalyst, avoiding salt waste generation. Moreover, using subcritical and supercritical water conditions greatly simplifies the product purification step in some cases, since nonpolar products are insoluble in water in lower temperatures [80, 100–106].

Other potential scalable approaches have been described, such as enzymatic [107–114], alkaline [115–120] and based on different types of aqueous media (e.g., cyclodextrins, montmorillonite K-10/LiOH, green liquor) [121–130]; ionic liquids [131–135], deep eutectic solvents [136–138], constituting alternative methods for the recovery of high added-value compounds from agro-industrial waste aiming at obtaining the best analytical, economical and socio-environmental compromise [139–142].

Based on the investigated literature [143], Table 2 summarizes the advantages and disadvantages of the four most cited green and sustainable techniques.

4 Conclusions

The establishment of vanguard biorefineries for bioeconomy and circular economy urgently demands innovation in green and sustainable separation for the recovery of natural products from agro-industrial by-products all over the world. Sustainable separation includes the idea of integrated valorization not only in an economic sense, but also strengthens other social and environmental dimensions, from small to large producing scales. According to the literature over the last decade, the number of studies in this field has grown significantly in recent years. New approaches incorporating holistic extraction and/or purification techniques, also integrating systemic chemical transformation through the design and use of renewable materials

Table 2 Advantages and disadvantages of different technologies that were most cited as green and sustainable techniques over the last 10 years

	Advantages	Disadvantages
Solvent processing	Inexpensive and simplicity; allows for solvent reuse	Does not always uses benign solvents; frequently requires an evaporation/concentration step for recovery; usually demands large amounts of solvent and long extraction time; possibility of thermal degradation
Microwave processing	Reduced extraction time; reduced solvent usage; improved extraction yield; simple and inexpensive	Not good when either target compounds or solvents are non-polar or volatiles
Ultrasonication	Inexpensive, simple and efficient; can reduce the operating temperature (good for thermolabile compounds); can be used with any solvent	Its efficiency may be linked to the nature of plant matrix; the active part of ultrasound inside the extractor is restricted to a zone located in the vicinity of the ultrasonic emitter
Supercritical fluid	Moderate extraction temperature (good for thermolabile compounds); rapid mass transfer (larger extraction rate); solubility of a chemical in a supercritical fluid can be manipulated; can eliminate concentration process; the solutes can be separated from supercritical fluids without losing volatiles due to its extreme volatility; additional filtration or centrifugation to remove solid residue is not necessary	Onerous operating conditions

and optimized processes should combine the best green analytical figures of merit with online evaluation of the whole production chain. These approaches should generate healthier and more efficient products, methods and processes at an affordable and fair cost.

Overall, solvent processing and its modification towards the enhancement of mass transfer to remove the compounds of interest from selected waste have been widely used (25%), also on industrial scales. Alternative extraction or purification methods have shown increasingly more applications, such as for microwave, ultrasonication and supercritical fluid processing. It was shown that a wide range of natural products and their derivatives are used mainly in food (as dyes, aromas, flavors) in medicines or green formulations in agriculture. According to the data available, one paradigmatic case largely studied is the valorization of citrus waste, representing more than 10% of all residues considered in the research papers.

Moreover, an emergent challenging topic is to evaluate biorefinery processing alternatives, i.e., sustainability assessment tools, for example LCA, which include parameters such as feedstock supply (to verify the suitability and adequacy of a potential biomass feedstock for the separation or transformation treatment), process performance (to assess the input–output balance of material and energy flows) and bio-based chemical production [144]. Therefore, the decision about the best separation approach takes into account various fundamental aspects and is based on green and sustainable assessment tools, considering the type of agro-industrial waste (e.g., quantity, periodicity, chemical variability, water amount, distance to the processing unit), the natural target products (chemical quality, purity, humidity, costs etc.) and available technologies.

Using sustainability indicators and tools will be increasingly demanded in this field, contributing to the greenness or sustainability of the whole processing system. The development of a sustainable separation method which provides better recovery efficiency will not only add value to the agro-industrial waste, reducing the overall manufacturing costs and the use of synthetic chemicals, but will also aggregate value to the whole production chain, including its final products. The emergence of bio-based industries is changing the current status of the producing systems, contributing to the current biomass residual losses. Based on the literature, the scenario for future research and innovation in green and sustainable separation for the recovery of agro-industrial waste is truly beginning, bringing together various areas and sectors towards more efficient and circular systems.

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ERRATUM

Erratum to: Valorization of Proteins from Co- and By-Products from the Fish and Meat Industry

Tone Aspevik[1] · Åge Oterhals[1] · Sissel Beate Rønning[2] · Themistoklis Altintzoglou[3] · Sileshi Gizachew Wubshet[2] · Asbjørn Gildberg[3,4] · Nils Kristian Afseth[2] · Ragnhild Dragøy Whitaker[3] · Diana Lindberg[2]

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The original version of this article unfortunately contained a mistake. The spelling of the fourth author was incorrect. The correct name is Themistoklis Altintzoglou.

The original article was corrected.

The online version of the original article can be found under doi:10.1007/s41061-017-0143-6.

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✉ Diana Lindberg
diana.lindberg@nofima.no

[1] Nofima AS, P.B. 1425 Oasen, 5828 Bergen, Norway

[2] Nofima AS, P.B. 210, 1431 Ås, Norway

[3] Nofima AS, P.B. 6122 Langnes, 9291 Tromsø, Norway

[4] Ildervegen 27, 9017 Tromsø, Norway