CHAPTER 17

THE GAS-, COKE- AND TAR INDUSTRY

CHARACTERISTICS OF THE WASTE WATER

In the process of coke carbonization three principle products are obtained: gas, coke and tar.

The waste water produced during the carbonization and gasification of fuel and from tar distillation may be classified in four basic groups:

1. Water used for quenching the coke discharged from the ovens.
2. Waste water produced during cooling and washing of the gas.
3. Waste water formed during the purification of by-products.
4. Waste water produced in conjunction with the tar distillation.

Relatively large amounts of waste water are produced. The amount per unit mass of fuel is depending on several factors: the kind of fuel, degree of purification of gas and by-products and the extent of re-cycling.

A general figure for the water consumption is 15-30 m^3/ton of coal treated (Sierp, 1959), but by re-circulation it is possible to reduce this figure by a factor of up to 100.

The waste water is complex and has a variable composition. Table 17.1 shows the composition of waste water from the carbonization of coke and from tar distillation. As seen the waste water contains several toxic components. Phenol, which is in a rather high concentration, is far from being as toxic as cyanide, however.

TABLE 17.1

Composition of waste water from the carbonization of coke and from tar distillation (mg/l), (Sierp, 1959)

Component	Coke works	Tar distillation
N (total)	5000-15000	15-4000
Free ammonia	2000-12000	20-1000
Carbon dioxide	3000-14000	0
Hydrogen sulphide	300-5000	2-50
Cyanides	50-2000	0-20
Thiocyanates	50-1200	0-800
Phenols	500-3000	50-2500
Pyridines	100-500	0-20
pH	8-9.5	5-12

Waste water problems of this industry

Table 17.2 shows the toxic concentration and the LD_{50} value (50% of experimental animals will die at this concentration) for fish for some of the most toxic components found in these types of waste water (the data are mainly from Kemp et al., 1973).

TABLE 17.2

Toxic concentrations and LD_{50} values for fish

Component	Formula	Toxicity limit (mg/l)	LD_{50} (mg/l)
Cyanides	HCN	0.05	0.2
Ammonia	NH_3	<0.5	0.5
Hydrogen sulphide	H_2S	0.5	3
Phenol	C_6H_5OH	3	10
Benzene	C_6H_6	2	18
Pyridine	C_5H_5N	100	>500
Chlorine	Cl_2	0.05	0.2

Discharge of raw waste water from these industries may cause serious complications because of the high concentration of organic material. The permanganate value is 30 to 150 times that of domestic sewage and the oxygen balance in the receiving water may be seriously upset. The insoluble pollutants, especially tar, form a surface layer which hinders the access of oxygen from the air. Finer suspended particles clog the gills of fish making it impossible for them to survive.

A considerable amount of dissolved oxygen is also consumed by sulphurous compounds, mainly sulphide, in addition to their very harmful effect on fishlife.

The life of a stream may undergo a fundamental change if phenolic waste water is introduced into it.

The lower lethal limits for phenols with respect to fish are as follows (Nowacki et al., 1953):

p-Cresol	4-5 mg/l
Phenol	6-7 "
1.2,6-Xylenol	7-9 "

The dependence of the time necessary to cause the death of fish upon the concentration of phenol in water is given in Table 17.3.

TABLE 17.3

Time recorded for fish (tench) to die in relation to concentration of phenol (Nowacki et al., 1953)

Phenol concentration in water (mg/l)	(Time in minutes) Fish are agitated	Fish swim on one side	Fish swim with belly upwards	Fish die
100	2	4	5	8
80	2	4	7	11
60	3	6	8	12
40	4	8	11	17
20	9	38	145	378
15	70	100	210	520
10	130	250	720	1030
8	170	310	950	1830
6	410	450	1730	3220
5	still alive after 4 days			

The results presented in Table 17.3 were obtained by experiments carried out with tench weighing 15 g each. The water temperature was 20°C.

Animal plankton are even more sensitive to phenol than fish. It is known that toxic constituents when present in a mixture, may act in a different way. The resultant toxicity need not always be an additive property and the deviation may be in various directions. Thus, while examining the toxic effect of phenol upon fish, it was found that mixtures of cresylic acid and p-cresol act additively, whereas a non-lethal dose of xylenol increases the toxicity of p-cresol. Similarly, the toxicity of p-cresol is increased by non-lethal doses of potassium cyanide, whereas the toxicity of potassium cyanide is not increased by the addition of non-lethal doses of p-cresol.

Apart from the toxic effect of phenols their presence in rivers impart odour and taste to the flesh of the fish. It has been found that as little as 1 mg/l of phenol causes deterioration in the taste of fish meat. If chlorophenols are present this value falls even below 0.1 mg/l.

Furthermore, a pronounced and undesirable effect is displayed by phenol on potable water. Concentrations as small as 0.1-0.2 mg/l may be detected by the taste. When the water is sterilized by chlorination the chlorophenols formed are perceptible at a concentration as low as 0.005 mg/l.

Table 17.4 summarizes the threshold concentrations of various phenols and their chlorinated derivatives.

TABLE 17.4

Odour threshold of phenols before and after chlorination

Compounds	Odour threshold concentration (mg/l)	Odour threshold concentration after chlorination (mg/l)
Phenol	18	0.001
Cresols	0.0025	0.0001-0.001
Thymol	0.23	0.05-0.1
Naphthol	70	0.5-1.0
Xylol	40	-
Creosote (technical)	0.12	0.01-0.05

The toxicity of ammonia to fish is dependant on the pH, or rather it is the free ammonia (NH_3) and not the ammonium ion, NH_4^+, which is toxic (Spotte, 1970).

Different values for the lethal concentrations of ammonia are given in the literature. About 0.05 mg/l of free NH_3 seems to be a reasonable limit to use in practice.

As the pK_a for the ammonium ion is 9.2, the limit for the total ammonium concentration ($NH_4^+ + NH_3$) is 0.05 mg/l at pH 9.2, 0.5 mg/l at pH 8.2 and 5 mg/l at pH 7.2.

Activated sludge treatment

As the waste water has a high concentration of organic material, it is possible to use the activated sludge method for the waste water, but a biological culture, adapted to the waste water, must be used (Wurm, 1970) and (Chamber, 1961). Phenol-oxidizing bacteria, such as Vibrio and Pseudomonas, thiocyanate-oxidizing bacteria such as Thiobacillus and nitrifying bacteria such as Nitrobacter must be present.

The biological oxidation of weak ammoniacal liquor from coke plants has been studied intensively. Is has been found that it is possible to oxidize phenol, thiocyanate and ammonium to reduce cyanide, but it was necessary to acclimatize the activated sludge plant (Kustenbader et al., 1969).

The preferred temperature range is 25-35°C. The pH must often be adjusted before the biological treatment and it is generally necessary to add nutrients. The optimum ratio of BOD_5 to nitrogen and phosphorus is 100:15:1. It means that phosphorus is needed. Furthermore, magnesium sulphate and iron chloride must be added as small amounts of magnesium, iron and sulphate must be present (Meisner, 1953).

As the concentration of ammonia is quite high complete nitrification will not take place in a one-step biological treatment. Consequently, a two-step biological treatment must be used if a complete nitrification is required.

The biological oxidation of phenol as a function of time of aeration is shown in Fig. 17.1 for a relatively small phenol concentration.

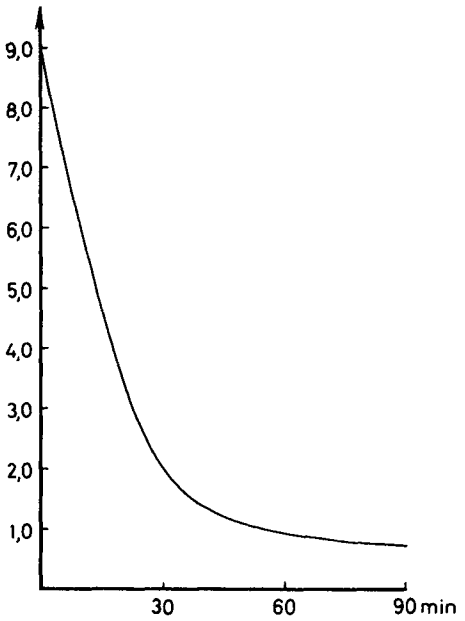
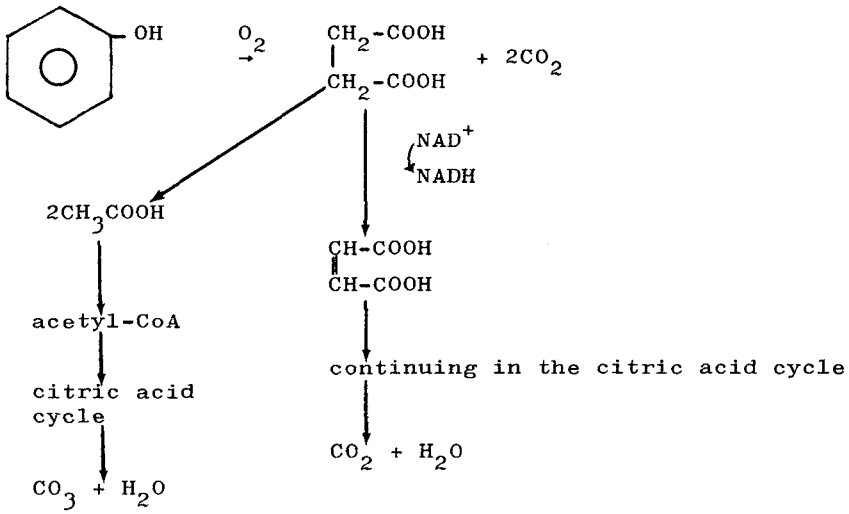


Fig. 17.1. The biological oxidation of phenol as a function of time of aeration.

If we compare with the analytical data in Table 17.1, it is seen that a rather long aeration time is needed in most cases, which again involves a rather large investment (Hall et al., 1959).

A two-step biological treatment of 1000 m^3 waste water/24h with a phenol concentration of 500 mg/l will require an expenditure as high as $. 500,000. The waste water considered in this case has a BOD_5 of about 1500 mg/l. This means that the investment/kg BOD_5 is more than $. 300, which is slightly higher than the corresponding investment for the biological treatment of municipal waste water.

The biological oxidation of phenol follows the processes



The intermediates formed will be oxidized by the citric acid cycle to carbon dioxide and water or transformed to acetic acid, which is oxidized to acetyl-CoA into the citric acid cycle.

Extraction

Extraction can be used for the recovery of phenols and other organic material present in the waste water (Wurm, 1962). As extraction media benzene, isopropyl ether, butyl acetate and the higher alcohols are needed (Husmann, 1965). A survey of the distribution coefficients for the various solvents which can be used for the extraction of phenols are shown in Table 17.5.

The extraction process removes a mixture of phenols, cresols, xylenols and pyridine bases from the waste water. This mixture is called raw phenol. A counter-current extraction followed by distillation for recovery of the solvents is the process generally used (Kaiser, 1955). The raw phenol, which is produced after distillation of the solvents can be separated into the different components by further distillation (Gutzeit et al., 1959). If the waste water contains more than 2 g/l of raw phenol, it is profitable to use countercurrent extraction before biological treatment of the water.

TABLE 17.5

Distribution coefficients of phenols

Solvent	Distribution coefficient
Light gasoline	0.2
Benzene	0.2
Diethyl ether	17
Dipropyl ether	17
Butyl alcohol	19
Isopropyl ether	20
Tricresyl phosphate	28
Ethylacetate	36
Isopropyl acetate	45
Butyl acetate	49
Xylenyl diphosphate	60
Mixture of higher alcohols	12

The Pott-Hilckenstock method, which is commonly used in Germany, separates the phenol from the solvent by washing out with sodium hydroxide. The sodium phenolate formed is treated by carbon dioxide to produce free phenol and sodium carbonate. The sodium carbonate is treated with lime, whereby sodium hydroxide is regenerated and returned to the process.

The composition of the sodium phenolate solution obtained by the Pott-Hilckenstock method is given in Table 17.6 (Bernacki, 1957).

TABLE 17.6

Composition of sodium phenolate obtained by the Pott-Hilckenstock method

Component	Content (%)
Phenols	40
Organic bases	0.1
Tar, oils	0.2
Total sodium hydroxide	18
Free sodium hydroxide	2
Water	40

Other methods

Plants for tar distillation are often smaller than coke works and since phenol extraction plants and biological treatment plants require rather large imvestments, it will not be possible for smaller tar distillation plants to solve their waste water problems along the lines given above.

In such plants it is often advantageous to separate the waste water. The waste water can be split up into the following categories:

a) Waste water containing emulsion of organic material.

b) Waste water containing phenols.

c) Waste water containing other impurities.

By treating the three types of waste water separately by rather simple processes (Husmann, 1965), it is possible to achieve a certain level of purification with smaller investment.

The type a) waste water can be treated by sedimentation or flotation and sometimes by addition of emulsion-breaking compounds. A substantial part of the biological oxygen consumption can be eliminated in this way.

Type b) the waste water containing phenol can be extracted by solvents and since only small amounts of waste water are considered the extraction plant will not require large investment.

Type c) the remaining waste water can be treated by the addition of calcium hydroxide together with a flocculating agent such as iron(II)sulphate. A considerable amount of the organic material will be precipitated, including arsenic-containing organic compounds which is important to remove for the receiving water or for a later biological treatment process at the municipal waste water plant.

From the investigations of Eisenhower (1971) it is clear that the complete ozonation of phenols to carbon dioxide and water cannot be achieved economically, even at elevated temperatures. However, the first stage of the oxidation is sufficient to satisfy pollution control problems, as 98% of the phenol can be removed by using only 5 moles ozone/mole phenol.

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