

## Carbon dioxide removal studies in the Netherlands

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### **Abstract**

An explorative research programme on CO<sub>2</sub> removal has been carried out in the Netherlands. The goal of this programme was to obtain a better understanding of the technical and economic feasibility of the recovery of CO<sub>2</sub> from flue gases and synthesis gases and the sustainable storage of CO<sub>2</sub> outside the atmosphere.

As far as CO<sub>2</sub> recovery from power plants is concerned, options based on coal gasification with CO<sub>2</sub> recovery turn out to be most energy-efficient. Of the remaining recovery options chemical absorption from flue gases, using amines, seems most promising. A number of recovery options based on membrane technologies have been identified, but most of them still require considerable development.

In manufacturing industry, attractive options for CO<sub>2</sub> recovery are available in refineries equipped with residue gasification, and in the ammonia fertilizer industry. More costly options were identified in the iron and steel industry and in the petrochemical industry.

CO<sub>2</sub> storage in aquifers is technically feasible. When injecting CO<sub>2</sub> in aquifers part of the water already present will be displaced. The main mechanisms for this displacement will be gravity segregation and viscous fingering, as was shown by simulation calculations. The Dutch subsurface contains a large number of aquifers that are potentially suitable for CO<sub>2</sub> storage.

### **1. INTRODUCTION**

In the period of 1991 to 1993 an explorative research programme on CO<sub>2</sub> removal has been carried out by a number of companies and research institutes in the Netherlands. The goal of this programme was to obtain a better understanding of the technical and economic feasibility of the recovery of CO<sub>2</sub> from flue gases and synthesis gases and the sustainable storage of CO<sub>2</sub> outside the atmosphere.

Before this research programme started a number of publications on

carbon dioxide recovery and storage had already been issued in the Netherlands with special emphasis on carbon dioxide removal from IGCC power plants and on storage of carbon dioxide in depleted natural gas fields. In the new research programme the main emphasis was on studying a range of techniques to recover carbon dioxide from gas streams in detail. Some studies were devoted to the recovery of carbon dioxide from industrial processes. One study explored the possibilities of CO<sub>2</sub> storage in aquifers. A separate study was directed at the calculation of the efficiencies and costs of complete power plants in a comprehensive way. A more extended overview of the results is given in [1].

The research programme was sponsored from various sources, the main ones being the Ministry of Housing, Physical Planning and Environment and the National Research Programme on Global Air Pollution and Climate Change. The total budget amounted to about 1.5 million Dutch guilders (1 Dfl = \$0.6 = ECU 0.45).

## 2. CO<sub>2</sub> RECOVERY BASED ON COAL GASIFICATION

It was confirmed that carbon dioxide recovery based on coal gasification shows the smallest decrease in efficiency of electricity production. The detailed analysis carried out by the research institute of the electric utilities, KEMA, showed that efficiencies of over 36% can indeed be attained in combination with carbon dioxide recovery (table 1). Two widely differing CO<sub>2</sub> recovery technologies were studied.

In the first case a shift reaction is applied after gasification resulting in a fuel gas mainly consisting of hydrogen and carbon dioxide. For separation of hydrogen and carbon dioxide a number of options were studied: freezing out the CO<sub>2</sub>, membrane separation, hydrogen recovery, physical absorption and chemical absorption. The best option is physical absorption (using selexol). By freezing out the CO<sub>2</sub> the required high degree of CO<sub>2</sub> recovery (to less than about 120 g/kWh) can not be attained. When this limitation would not be set, freezing out the carbon dioxide should certainly be taken into consideration. Using membranes at low temperatures is not attractive, mainly due to the high hydrogen loss. Combined with high-temperature gas clean up membrane applications may become of interest, although the membranes with the required high H<sub>2</sub>/CO<sub>2</sub> selectivities are still under development. Chemical absorption systems have a too high energy demand. Hydrogen recovery techniques showed considerable hydrogen losses.

The components for the favoured shift/selexol concept are commercially available but were never applied in this combination. It is concluded that the technology is ready for demonstration.

The second IGCC approach makes use of a gas turbine in which the fuel is combusted in a mixture of oxygen and recycled CO<sub>2</sub>. The

Table 1. Some key results for complete power plant concepts as calculated by KEMA. Preliminary cost estimates range from 60 - 80 Dfl per tonne of CO<sub>2</sub> avoided, being the lowest for the IGCC options. Electricity production costs are estimated to be 0.14 - 0.15 Dfl/kWh for the coal cases and 0.095 Dfl/kWh for the natural gas case.

Type of plant - method of recovery	Net conversion efficiency (%)	Specific CO <sub>2</sub> emission (g/kWh)
IGCC - CO <sub>2</sub> /O <sub>2</sub> -combustion (Texaco)	34.8	5
IGCC - CO <sub>2</sub> /O <sub>2</sub> -combustion (Shell)	36.0	30
IGCC - shift & physical absorption (Texaco)	36.4	139
Pulverized coal - chemical absorption (retrofit)	29.7	105
Natural gas fired combined cycle - chemical absorption	44.9	86
Reference coal fired power plant	42 - 43	800 - 820
Reference natural gas fired power plant	52	390

combustion products (mainly CO<sub>2</sub> and water) are expanded through the turbine section. After cooling in a heat recovery steam generator and removal of the water, the CO<sub>2</sub> is recycled to the gas turbine compressor. Part of the compressed CO<sub>2</sub> is used in the gas turbine combustion chamber, the remainder is exported. As CO<sub>2</sub> is the main working fluid in the gas turbine, the properties differ strongly from a conventional gas turbine. The results of integrating such a gas turbine in an IGCC plant are given in table 1. The main bottleneck for the application of this scheme is the fact that such a *CO<sub>2</sub>-gas-turbine* is not available at present. Starting such a costly development process is only justified if it gives clear (cost or efficiency) advantages above the IGCC/shift/selexol-process mentioned before.

### 3. CHEMICAL ABSORPTION/OTHER RECOVERY TECHNIQUES

As the future of coal gasification is still uncertain it is advisable to develop other CO<sub>2</sub> recovery techniques as well. A number of other options for CO<sub>2</sub> recovery was evaluated. In most cases chemical absorption, using amines, is the most attractive alternative.

For the recovery of CO<sub>2</sub> from flue gas of conventional coal-fired power plants the use of gas *separation* membranes is more expensive than chemical absorption. This is mainly due to the high power requirements for the compression of the flue gases. When chemical absorption is applied, the use of gas *absorption* membranes, is of interest. Gas absorption membranes are used in conjunction with chemical absorption liquids where the conventional absorption column is replaced by a membrane contactor. This modification could increase the conversion efficiency of the power plant by approx. 0.5%. This improvement is mainly due to a reduction of the pressure drop over the absorber. Gas absorption membrane systems, however, are still under development.

For natural-gas-fired combined cycle power plants the most cost-effective option also is chemical absorption, with an overall conversion efficiency of approx. 45%. An alternative is a power plant based on a gas turbine using combustion in a CO<sub>2</sub>/O<sub>2</sub>-mixture. Also a system based on methane reforming of natural gas (to a large extent similar to an IGCC plant) was investigated. However, it showed a low efficiency: about 37%.

#### 4. CO<sub>2</sub> RECOVERY IN MANUFACTURING INDUSTRY

Twenty plants in manufacturing industry with the largest CO<sub>2</sub> emissions in the Netherlands together are responsible for about 20% of the total Dutch CO<sub>2</sub> emissions. Main sectors are refineries, the iron and steel, petrochemical and fertilizer industries.

Carbon dioxide recovery can be accomplished in refineries equipped with a residue gasification unit. Residue gasification is expected to be a good solution in the development towards low sulfur oil products and deeper conversion. The gasification product is fed to a shift reactor in order to produce hydrogen for other refinery processes. The carbon dioxide that is co-produced can be recovered easily. In this way about one quarter of the CO<sub>2</sub> emissions in future refineries can be avoided.

Another attractive option is available in the fertilizer industry. In producing ammonia, which is one of the main feedstocks for fertilizer production approx. 50% of the CO<sub>2</sub> output of the fertilizer industry is already recovered. At present part of this amount is utilized, the remainder is vented to the atmosphere. CO<sub>2</sub> recovery can be applied on this stream by just compressing it to transportation pressures. Both for the refineries and the fertilizer industry estimated mitigation costs are in the order of 20 Dfl per tonne of CO<sub>2</sub> avoided.

More costly options were identified in the iron and steel industry: recovery of CO<sub>2</sub> from blast furnace gas; and in the petrochemical industry: the use of low-temperature waste heat (100 - 150 °C) for supplying the reboiler duty of a chemical absorption process.

## 5. STORAGE OF CARBON DIOXIDE

According to one of the studies, CO<sub>2</sub> storage in aquifers is technically feasible. When injecting CO<sub>2</sub> in aquifers part of the water already present will be displaced. The main mechanisms for this displacement will be gravity segregation and viscous fingering. Extended simulations of the behaviour of CO<sub>2</sub> have been carried out for sample reservoirs; in one of these aquifers 15,000 tonnes of carbon dioxide per day can be injected during 8 years. After this period CO<sub>2</sub> breakthrough is observed at the spillpoint. The Dutch subsurface contains a large number of aquifers that are potentially suitable. Taking a number of constraints into account the total aquifer storage capacity for CO<sub>2</sub> a prudent estimate of the storage capacity of 1.2 Gtonne CO<sub>2</sub> is made.

The main chemical effect of carbon dioxide in aquifers is its effect on carbonate chemistry. The decrease of the pH due to the dissolution of carbon dioxide will cause solution of carbonates. This effect is so small that weakening of the porous structure is not expected. However significant changes in permeability may occur. If the seal of the structural trap is a clay layer, drying of this layer could reduce its tightness. The costs of injection (departing from a delivery pressure of 110 bar) are estimated to be 0.7 and 1.2 Dfl per tonne of CO<sub>2</sub> injected for aquifers above and below 1000 m depth respectively.

## 6. CONCLUSIONS

As far as CO<sub>2</sub> recovery from power plants is concerned, options based on coal gasification with CO<sub>2</sub> recovery turn out to be most energy-efficient. Of the remaining recovery options chemical absorption from flue gases, using amines seem most promising. A number of recovery options based on membrane technologies have been identified, but most of them still require considerable development.

More than at present, attention should be paid to CO<sub>2</sub> recovery options outside the electricity production sectors, e.g. in manufacturing industry. Storage of CO<sub>2</sub> in aquifers seems to be technically feasible, but the total storage capacity, taking into account strict conditions, is limited.

It is felt that with respect to underground storage of carbon dioxide, especially in aquifers, the largest uncertainties exist. Further investigation of this option by reservoir simulations, laboratory experiments and field tests should have a high priority in further R&D planning.

## **7. REFERENCE**

- 1 K. Blok: Final report of the Integrated Research Programme on Carbon Dioxide Removal and Storage", Department of Science, Technology and Society, Utrecht University, The Netherlands.