



# **CO<sub>2</sub> ABATEMENT BY THE USE OF CARBON- REJECTION PROCESSES**

**Report PH3/36  
February 2001**

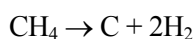
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**Title:** CO<sub>2</sub> Abatement by use of carbon-rejection processes  
**Reference number:** PH3/36  
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**Other remarks:**

## **Background to the study**

It has been suggested that processes that recover energy from the hydrogen content of fossil fuels and reject the carbon content as a solid would be potentially attractive methods of avoiding CO<sub>2</sub> emissions. Such processes avoid the need to capture and store CO<sub>2</sub> for many years in a safe repository, although something would have to be done with the solid carbon. The key reaction required is thermal decomposition, or ‘cracking’, of a fossil fuel; in the case of methane it is represented as follows:



In the case of natural gas, the rejected carbon contains nearly 50% of the energy in the feed. Hydrogen carries the remainder of the energy so the energy efficiency of this type of process as a means of producing hydrogen will be, at most, approximately 50% (in theory). In practice, the efficiency could be significantly less as the reaction is endothermic and requires a large energy input. Other hydrocarbons have a higher carbon-to-hydrogen ratio than methane and so would produce more carbon, and the process would have a lower efficiency.

Given the above limitations, some researchers have concluded that, for such a process to be of interest, the rejected carbon has to be used rather than just stored indefinitely. In which case the process would be a co-producer of energy and a carbon product. There are 2 major suggestions for the use of the carbon:

- (a) in established uses for carbon black.
- (b) in the metallurgical industry.

Alternatively, the thermal decomposition of methane could be integrated with the production of other energy products. For example in the Carnol process, carbon is rejected and the hydrogen produced is reacted with CO<sub>2</sub> to make methanol. The CO<sub>2</sub> is recovered from power generation. It has been suggested that such integrated processes result in a net reduction in CO<sub>2</sub> emissions when compared to ‘stand-alone’ processing of oil for transport fuels and power generation from fossil fuels. A similar concept involving the reuse of CO<sub>2</sub> to make methanol was examined in report PH3/13; it was found that, compared to stand-alone power plant with CO<sub>2</sub> capture, there was not a large reduction in emissions by reusing CO<sub>2</sub> for producing methanol as a transport fuel. The recommendation of that study was that the process should be reassessed only as a ‘fall-back’ option, if difficulties are encountered with large-scale CO<sub>2</sub> storage.

## **Approach adopted**

The study is focused on natural gas processing, as other fossil fuels are likely to be less attractive. For calibration purposes, it also includes an assessment of the use of coal in a Carnol-type process.

Processing options based on combustion of the rejected-carbon are outside the scope of work for this study; they do not avoid CO<sub>2</sub> storage, are not well defined, and would require extensive process development.

There are three components to the study:

- Carbon-rejection processes are reviewed and assessed for their potential as hydrogen producers.
- Current and potential future markets for carbon are assessed.
- A Carnol-type process, integrating thermal decomposition of methane with the production of methanol and electricity, is assessed.

The study was done by ECN, Petten, The Netherlands, assisted by Maarten van der Burgt, a consultant.

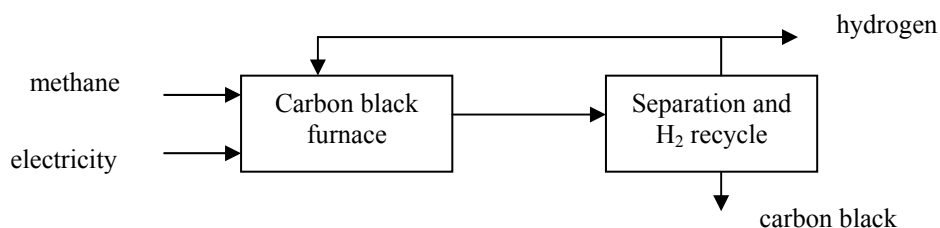
The overall objective was to assess carbon-rejection schemes as means of CO<sub>2</sub> emission abatement.

## Results and discussion

### carbon-rejection processes and the production of hydrogen

The report reviews established processes in which carbon is produced; they are primarily dedicated to the production of carbon black.<sup>1</sup> Almost all the world's carbon black production is produced by the furnace black process in which aromatic hydrocarbons are cracked in hot flue gas at atmospheric pressure. With the exception of the relatively expensive acetylene black process (used when a pure graphite is required), none of the established carbon black process are suitable for the co-production of hydrogen and carbon. For example, in the furnace black process, the hydrogen is burnt to supply heat to the cracking reaction.

The introduction of plasma arc based technology for carbon black production provides an alternative means of producing hydrogen. The best known example of a plasma arc carbon black process is the Kværner process. A 20 000 tonne/year carbon-black plant with a 6 MW plasma torch was scheduled for start-up at the time this report was written. The process is simple in concept (see figure S1).



**Figure S1: Kværner process for the production of carbon black and hydrogen**

The efficiency of the Kværner process is high (93%) - if the thermal value of the carbon product is included. But if hydrogen is regarded as the only 'energy' product, the process efficiency is 49%. The energy efficiency of the process is lower still if the efficiency of producing the electricity is taken into account. So, the Kværner process is not an efficient way of producing hydrogen from methane - a steam-methane reformer can produce hydrogen with an efficiency of 76% (Report PH2/2).

Theoretical schemes, based on a thermal decomposition process for the production of hydrogen and carbon from methane, have been suggested as a way of avoiding the need for electricity. It is concluded in the report that such schemes will have a similar efficiency to the Kværner process and would probably be more expensive.

The economic attractiveness of the Kværner process depends on the value of the carbon product. The process could be a competitive way to produce hydrogen if the carbon produced has a significant value. The key question is how much carbon black could be sold at a significant price, if very large quantities of it were produced. The current US price of furnace carbon black is approximately \$800/tonne. If the carbon produced in the Kværner process can be sold at even \$300/t, the cost of hydrogen becomes

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<sup>1</sup> The term carbon black refers to a range of products made by partial combustion or thermal decomposition of hydrocarbons.

competitive with steam-methane reforming but if the carbon-black has zero value, the cost of hydrogen production is 12.5\$/GJ (at a natural gas costs of 2\$/GJ). For comparison, in report PH2/2 it was shown that the cost of hydrogen production in a conventional steam-methane reformer is approximately 4\$/GJ (gas at 2\$/GJ), rising to approximately 6\$/GJ if the process is modified to capture CO<sub>2</sub>.

The Kværner process does produce a significant amount of hydrogen, approximately 0.3 tonnes of hydrogen per tonne of carbon. If the carbon black produced can be sold at current market prices, the process is potentially an economic way of producing hydrogen without emitting CO<sub>2</sub> to atmosphere. The next stage of the study is an examination of the markets for carbon.

### **market potential for carbon black**

A large market for carbon is needed if emissions of CO<sub>2</sub> are to be reduced considerably by deployment of carbon-rejection processes.

The existing carbon black market, approximately 8 million tonnes/year, is very small compared to the global emission of approximately 6000 million tonnes of carbon per year from use of fossil fuels<sup>2</sup>. The production of hydrogen for use as an energy source, combined with traditional uses for carbon black cannot, therefore, be expected to make a major contribution to a reduction in global emissions of CO<sub>2</sub>. However, it is possible that new large markets could develop.

Various potentially large markets for carbon are discussed in the report. The overall conclusion is that the only potentially substantial application is for iron ore reduction. This potential market would replace pulverised coal injection, which is used to reduce coke consumption. The maximum potential consumption is estimated to be 125 million tonnes of carbon/year. A direct reduction in emissions is not achieved as the carbon is used as a reducing agent and is emitted to atmosphere as CO<sub>2</sub>. The emission reduction which would be achieved depends on what happens to the fuel that would otherwise have been used. The maximum reduction in emissions is achieved if all the fuel displaced would no longer be used. However, some of the fuel displaced may be a waste product that has to be burnt less effectively thus giving less net emissions reduction. The report concludes that it is not likely that this market would be taken up to any great extent. In the event of major action to reduce CO<sub>2</sub> emissions, natural gas could be used for direct reduction of iron ore (see report PH3/30); this would lead to a 3 to 4 fold decrease in CO<sub>2</sub> emissions per tonne of iron.

The overall conclusion is that there is a very large difference between the quantity of CO<sub>2</sub> produced from fossil fuels and any potential market for carbon black. The only potentially significant market, at 125 million tonnes of carbon per year, is equivalent to approximately 2% of global carbon emissions. Even this limited market for iron ore reduction is unlikely to be taken up completely in the event of major action to limit CO<sub>2</sub> emissions as there are alternative approaches, such as the direct reduction of iron ore with methane.

### **integrated processing**

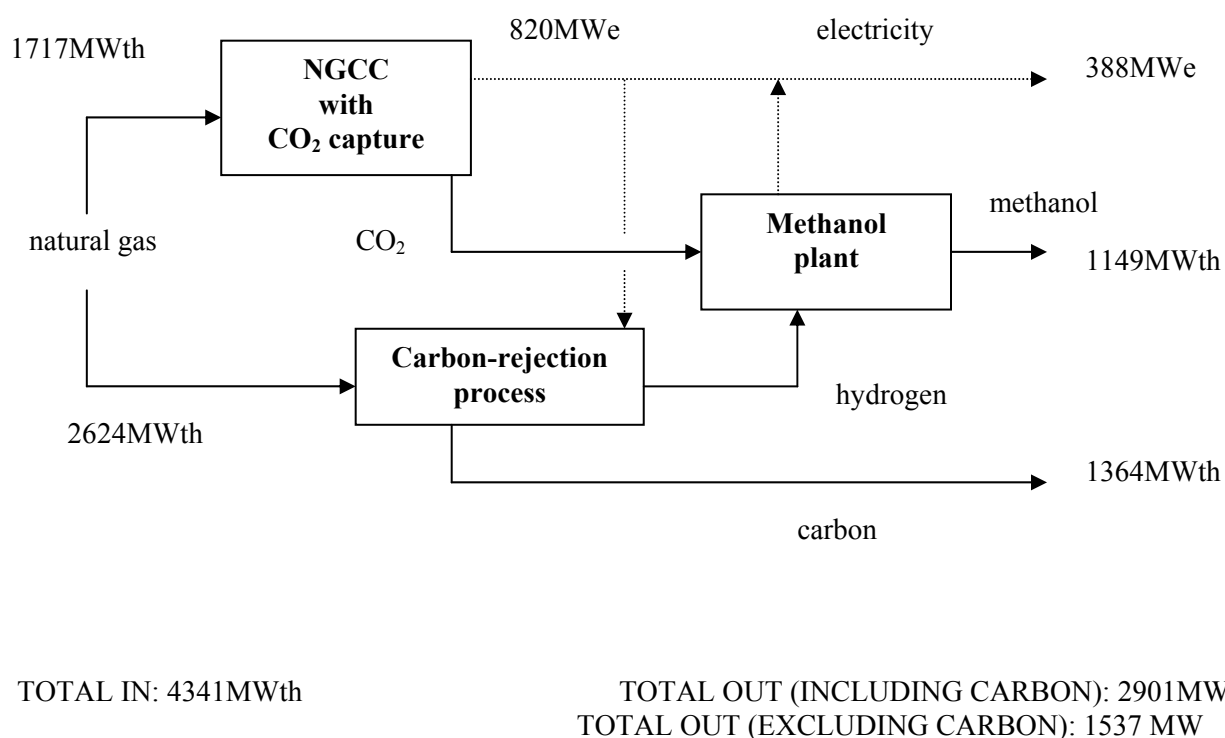
As an alternative to seeking a major market for a process in which both carbon black and hydrogen are produced, it has been suggested that a process which integrates decomposition of methane with the production of methanol and electricity could be an effective method of reducing CO<sub>2</sub> emissions. In this case the carbon would be disposed of as a by-product which may, or may not, have a significant value. The method of disposing of large amounts of carbon is not identified.

The integrated process assessed in the report is based on a Camol-type process as suggested by Steinberg (see references in main report); the Kværner process is used to generate hydrogen and produce carbon black. It has been suggested that such processes result in a net reduction in CO<sub>2</sub> emissions when compared to 'stand-alone' processing of oil for transport fuels and power generation from fossil fuels.

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<sup>2</sup> 1995 figure from IEA 'World Energy Outlook'

Details of the process are given in the main report. A combined cycle power station provides electricity for export and for the carbon black process. CO<sub>2</sub> is captured from the power station flue gas. The CO<sub>2</sub> is combined with hydrogen produced in the carbon black process to make methanol. Production of methanol from CO<sub>2</sub> and hydrogen is not an established commercial process but there is considerable research activity in this area. The overall efficiency of the process is 35% (LHV), if only the methanol and electricity are regarded as saleable (energy) products. The process is illustrated in figure S2.



**Figure S2: Carnol-type process based on use of Kværner carbon black process**

There are 3 products in the integrated process: electricity, methanol and carbon black. Only 9% of the input energy is converted to net electricity production. The process cannot, therefore, be regarded as a realistic option for production of decarbonised electricity on a global scale. The process is primarily a way of producing transport fuel – approximately 3 times more energy is contained in the methanol than in the electricity.

A coal version of the Carnol-type process was also assessed; it requires a net import of electricity and is therefore not viable as a power generation process. It is unlikely to be competitive with more conventional processing as a route to methanol production.

The report contains an economic analysis of the Carnol-type process. The cost analysis is quite complicated because there are 3 ‘products’: carbon black, methanol, and electricity. Various cost sensitivities are assessed.

As discussed earlier, there is no market for the carbon produced at the scale necessary for a Carnol-type process to have an impact on global CO<sub>2</sub> emissions. In the unlikely event that all the carbon could be sold at current price levels, the cost of CO<sub>2</sub> avoided is still quite high (\$62/tCO<sub>2</sub>) compared to alternative greenhouse gas mitigation options.

The coal route is more unattractive than the natural gas route and is not discussed here.

As noted above, the Carnol-type process is primarily a way of producing a transport fuel. IEA GHG has not done sufficient work to establish the cost of CO<sub>2</sub> abatement in road transport but some useful comparisons can be made with the earlier work on methanol (report PH3/13) and hydrogen (report PH2/2):

- Conversion of natural gas to methanol does not, in itself, bring about a reduction of CO<sub>2</sub> emissions. Methanol releases 65 kgCO<sub>2</sub>/GJ as opposed to 55 kgCO<sub>2</sub>/GJ for natural gas.
- Approximately 60% of the carbon entering the Carnol-type process is converted to carbon black in the Kværner processing unit; a further 34% is captured in the power station. Integrating these processes and producing methanol does not add to the amount of carbon captured compared to operating them as stand-alone processes. A similar conclusion was reached in the earlier work on a process involving the reuse of captured CO<sub>2</sub> (report PH3/13).
- It was concluded in an earlier report (PH2/2) that hydrogen is an expensive form of energy unless some added value is gained in its use. Combining hydrogen produced in the Kværner process with captured CO<sub>2</sub> in order to produce methanol reduces the efficiency of the process still further, and hence increases the cost per unit of energy (the methanol produced contains only 76% of the energy that was in the hydrogen used to make it).
- The direct production of methanol from natural gas is an established process in which one molecule of methane is reacted to produce one molecule of methanol ( $\text{CH}_4 + \text{O} \Rightarrow \text{CO} + 2\text{H}_2 \Rightarrow \text{CH}_3\text{OH}$ ). If methanol is the only, or the dominant product, the addition of intervening processing steps, such as power generation and carbon-rejection, does not change this basic relationship, and is therefore not able to lead to a major reduction in the amount of carbon in the product per unit of energy.

### **Expert Group and other comments**

Detailed comments on the report were received from a number of reviewers, including Professor Steinberg.

The main points raised were:

- A thermal process for methane decomposition could be more efficient than an electrically-driven process.
- Work on the lean-burn of natural gas in oxygen leads to claims by some that this technology would be considerably cheaper than the Kværner process. We are not able to verify this at present.
- It was suggested that potential uses for large amounts of elemental carbon should be sought. ‘Way-out’ ideas, such as use as a soil enhancer, might be established. This particular one does not appear very likely to help, as the economic value of soil carbon is small compared to carbon black and it can be accumulated at a low cost by soil management techniques.
- It was suggested that the ‘C-fix’ activity of Shell could be a major market for carbon. The idea is that instead of burning heavy oil residues, or converting them in a gasifier, they would be used as a cement substitute to make a ‘carbon-concrete’. The carbon-rich residue acts like cement. The idea looks good as a potential way of disposing of oil residues and reducing emissions of CO<sub>2</sub> from their use. However, it is questionable whether carbon from the Kværner process would bind aggregates in the same way as heavy oil residues as there is no pitch content. A better option would seem to be to use methane to replace combustion of heavy oil residues and use the residues to make ‘carbon-concrete’ as proposed by Shell.
- Also on concrete, another reviewer pointed out that research is in progress on the use of carbon-fibre reinforced concrete. (Carbon fibre is made by charring a filament of a suitable hydrocarbon, so the process is quite different to carbon black production.)

The comments were passed to the contractor who incorporated them as appropriate in the report.

## **Major conclusions**

The major conclusions are as follows:

1. Most carbon black processes are not suitable for the co-production of hydrogen and carbon. Of the commercially available processes, the Kværner process is the most attractive. It is possible that advanced thermal dissociation processes could be more attractive than the Kværner process but such processes are very speculative.
2. There is a large difference between the quantity of carbon potentially available from fossil fuel power stations and any existing market for carbon. Applications have been identified for processes that co-produce hydrogen and carbon. However, a major new use for large quantities of carbon is needed to make such processes significant as a major CO<sub>2</sub> abatement option. For this to compete with other abatement options, the user must be prepared to pay for the carbon.
3. Without significant income from sale of the carbon, the production of hydrogen in this way costs twice as much as production by steam reforming with capture of the CO<sub>2</sub> produced.
4. Processes integrating electricity generation with the production of carbon black and hydrogen are not options for abatement of CO<sub>2</sub> emissions from power generation on a global scale, because less than 10% of the input energy is converted to net electricity production. Even if the carbon could be sold at current market prices (which seems unlikely), the cost of avoiding emissions would be more than that of options such as capture of CO<sub>2</sub> with underground storage.
5. The main product of Carnol-type processes is methanol. IEA GHG has only done limited work on reducing CO<sub>2</sub> emissions from transport, so we do not have benchmarks for comparison of such options. If large-scale reduction of CO<sub>2</sub> emissions from transport was found to be much more expensive than reducing emissions from power generation, schemes in which methanol is a co-product might be of interest.

## **Recommendations**

It is recommended that IEA GHG do no further work on carbon rejection processes for CO<sub>2</sub> abatement in power generation.

A study of the CO<sub>2</sub> abatement options applicable to heavy oil residues should be considered.

When IEA GHG has established the cost and effectiveness of leading CO<sub>2</sub> abatement options relevant to road transport, it will be possible to put it in context options based on methanol production from CO<sub>2</sub> captured in power plant.

## **Assessment of Carbon-rejection processes as a method of CO<sub>2</sub> abatement**

IEA Greenhouse Gas R&D Programme  
United Kingdom

P.E. Lugten  
D. Jansen  
M.J. van der Burgt  
A. Carp

1.1 Revisions		
A		
B		
Made by:	Approved:	ECN Clean Fossil Fuels
P.E. Lugten	D. Jansen	
Checked by:	Issued:	
M. Weeda	C.A.M. van der Klein	



## Justification

The IEA Greenhouse Gas R&D Programme (IEA GHG) funded the study. They undertake a range of studies aimed at avoiding the emissions of greenhouse gases to the atmosphere. The scope of the study was specified in the Technical Study Specification: IEA/CON/99/51

## Keywords

CO<sub>2</sub> abatement, carbon rejection, carbon black, hydrogen, Kvaerner process, Carnol process, petroleum coke, iron production, methanol.

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## 2. EXECUTIVE SUMMARY

The objective of this study was to evaluate the competitiveness of carbon rejection schemes as means of CO<sub>2</sub> abatement. Traditional carbon rejection schemes for the production of carbon black and modern plasma arc processes were reviewed. The results of this study show that the Kvaerner plasma arc process is the only efficient process for carbon rejection and hydrogen production.

Kvaerner claims a thermal efficiency of 92,3 % (LHV) . The products are pure hydrogen and high quality carbon black. Drawback is the high power demand.

The main advantage of the process is that it is a simple process that is flexible in terms of carbon black quality and produces hardly any emissions. The economic data of the process show that for zero cost of carbon black the hydrogen will cost almost US\$ 1500 per ton. This is in accordance with data published in ref.[4].

For CO<sub>2</sub> abatement it is required to find a substantial outlet for the carbon produced. The only application is for iron ore reduction, which requires 300 million tons per year of carbon. However because of quality requirements it is not expected that metallurgical coke can be replaced by carbon black. A possible market for carbon black can be replacement of coal used as pulverised coal injection in a blast furnace. With a 100 % penetration on a global scale, this would result in a maximum consumption of 125 million tons per year. The current world consumption of carbon black amounts only 8 million tons per year. New market applications like the production of solar grade silicon have a small potential volume. Because of the limited market applications of carbon black, the use of carbon-rejection processes have no substantial contribution to the abatement of CO<sub>2</sub>.

The Kvaerner process is used as a basis to assess the attractiveness of the Carnol process as a means of CO<sub>2</sub> abatement. The Carnol process consists of three integrated processing steps. (A.) Hydrogen production by the Kvaerner process, (B) a fossil fuel fired power plant in which CO<sub>2</sub> is captured and (C) a methanol production plant where carbon dioxide is catalytically hydrogenated into methanol. The products of the Carnol process are electricity, methanol and carbon. Methanol is used as a transport fuel. The reject carbon produced is not used in the Carnol process. It is either sold or stored.

Natural gas will be used in the hydrogen generation process. For power generation two cases were assessed viz. power generation by coal and by natural gas.

The overall thermal efficiency of the Carnol process based on the heating values of methanol and carbon is 66% (LHV). In case only the heating value for methanol is accounted for the thermal efficiency drops to 30% (LHV) .

Because the Carnol process on basis of a coal-fired power plant requires a net import of power this concept is not viable. Results of the process evaluation are presented in the block diagrams in chapter 5.

When in the Carnol process power is generated by natural gas the thermal efficiencies are respectively 67% (LHV) and 35% (LHV). In this concept the Carnol process exports power. Although this concept is workable, the total process has the disadvantage of low overall efficiency.

Based on the results developed from the economical evaluation the cost of reducing CO<sub>2</sub> emissions based on the Carnol process are US\$ 95 per ton CO<sub>2</sub> avoided in case power is generated by coal firing.

In case gas firing is used for power generation the cost is US\$ 61 per ton CO<sub>2</sub> avoided.

Carbon-rejection processes, including the Carnol process, have no substantial contribution to the CO<sub>2</sub> abatement because of the low production volume, due to the limited market applications of carbon black.

There is an enormous discrepancy between the CO<sub>2</sub> that is produced in fossil fuel fired power stations and the potential carbon black market. To substantially reduce the emission of CO<sub>2</sub>, coal in power plants should be replaced by natural gas.

### 3. INTRODUCTION AND STUDY SCOPE

#### 3.1 Introduction

As an alternative to the capture and storage of CO<sub>2</sub>, it has been suggested that processes which recover energy from the hydrogen content and reject the carbon content of fossil fuels as a solid would be potentially attractive methods of avoiding CO<sub>2</sub> emissions.

Such processes avoid the need to store CO<sub>2</sub> for many years in a safe repository. The key reaction involved is thermal decomposition of a fossil fuel. In case of methane decomposition roughly 50% of the energy remains in the rejected carbon and is not recovered. Any version of this process that only makes use of the hydrogen product will therefore have at most a theoretical efficiency of 50%. In practice the efficiency is likely to be significantly less as the reaction is strongly endothermic, 75 % of the input mass is rejected as carbon. Some researchers have come to the conclusion that, for such a process to be of interest, the rejected carbon has to be used rather than just stored indefinitely. There are 2 major suggestions involving use of the carbon, which are assessed as part of this study:

- Use the carbon in established uses for carbon black.

- Use the carbon in the metallurgical industry.

An alternative application of this technology which will also be assessed in this study has been suggested by Steinberg [ref. 5, 6]. In his proposed “Carnol process”, the thermal decomposition of methane is integrated with the production of other energy products. Carbon is rejected and the hydrogen produced is reacted with CO<sub>2</sub> recovered from power generation to make methanol. The integrated process claimed to result in a net reduction in CO<sub>2</sub> emissions compared to conventional processing of oil for transport fuels, together with power generation from fossil fuels.

The overall objective of this study is to assess the competitiveness of carbon rejection schemes as means of CO<sub>2</sub> abatement.

#### 3.2 Scope of work

The scope of work for this study is specified in 3 tasks which are summarised below.

(The complete study scope is given in the Technical study specification IEA-CON-99-51).

##### Task 1

In this task different types of carbon rejection processes will be assessed to establish their performance and costs.

The current and future world market potential for carbon black will be assessed. The world market will be compared to worldwide CO<sub>2</sub> emissions from fossil fuels.

##### Task 2

The potential use of carbon black in the metallurgical industry will be assessed.

##### Task 3

In this task the attractiveness of the Carnol process as a means of CO<sub>2</sub> abatement will be assessed. The reject carbon produced is not used in the Carnol process, it is either stored or sold. Methanol is used as transport fuel. Natural gas will be used in the hydrogen generation process and coal in the power generation. An alternate case will illustrate the effects of using natural gas in both the hydrogen production and the power generation step.

The results will include derivation of the costs of reducing CO<sub>2</sub> emissions. (\$ per ton CO<sub>2</sub> avoided)

## 4. CARBON REJECTION PROCESSES

### 4.1 Introduction

There can be little doubt that carbon rejection is often a more attractive route towards CO<sub>2</sub> abatement than CO<sub>2</sub> storage. Not for reasons of efficiency but because it is more generally applicable, less risky and involves less complicated processes.

Hydrocarbon feedstock's have the advantage that by thermal-cracking virtually pure carbon and hydrogen are produced. In the furnace black process this hydrogen is immediately combusted and thus helps to supply the heat for the endothermic cracking reactions. In the thermal black process hydrogen could be produced. However because the process is operated semi-continuously at atmospheric pressure, hydrogen is used as fuel gas for preheating the checkerboard.

Natural gas is of course the feedstock giving the highest co-production of hydrogen. In case there is a market for hydrogen, and natural gas is available, the use of the latter feedstock becomes even more attractive. It should be mentioned though that methane is one of the most stable hydrocarbon molecules and therefore a more difficult nut to crack than other feedstock's used for carbon-black production.

It is possible that, in the interbellum between the present fossil fuel era and an era in which renewable sources will supply most of the energy, cracking of natural gas will play a major role as a source of hydrogen, even in case the carbon will have to be disregarded and sequestered.

New processes that are presently under development are based on plasma arc and catalytic processes that operate at lower temperatures. The pros and cons of these developments are discussed below.

### 4.2 Plasma arc based process for carbon rejection

#### 4.2.1 Introduction

The use of electricity as an energy source in chemical reactions is sometimes unavoidable. In case e.g. elements as aluminium, sodium and phosphorus that have to be produced from compounds with a very high energy of formation, electricity must be used. The use of electricity in a process involving the conversion of a fuel into another fuel should be viewed with some caution. In a chemical conversion of a fuel into another fuel such as coal to syngas, syngas to Fischer-Tropsch products, etc. one loses always 20-25% of the combustion value of the feedstock. This is inherent to the thermodynamics of the process. Using electricity, being exergetically the highest value product, for a chemical reaction does not improve this situation as electricity itself is in most cases generated by the combustion of a fossil fuel with a maximum efficiency of (only) 60%.

However, the plasma arc process has in the first place to compete with the furnace black process that does not have a high efficiency. Moreover the plasma arc process is claimed to be more flexible towards producing carbon-blacks of different qualities and further pure hydrogen is produced as a by-product, which has important consequences as will be discussed below.

#### 4.2.2 Kværner process

The best known example of a plasma arc process is the **Kværner** process (see Figure 1) in which a hydrocarbon is split into carbon and hydrogen. Using a pure hydrocarbon feedstock

such as desulphurised natural gas for the production of carbon-black for reducing top grade quartz sand, a very high-grade silicon is produced. After removal of the carbon from the silicon it is claimed to be suitable for the production of solar cells. Currently a 20,000-ton/year carbon-black plant in Canada featuring a 6 MW plasma torch is being started up. Natural gas or aromatic rich hydrocarbons are used as feedstock's. Assuming optimistically a feedstock consisting of methane that is preheated to 500 °C and gases leaving the reactor at 1100 °C the theoretical thermal efficiency defined as Lower Heating Value (LHV) of the products over that of the feedstock plus the electricity is 93.4% (see Figure 2). This is only marginally higher than the 92.3% reported by **Kværner** for their process, which implies that they use an efficient feed/product heat exchange (see Figure 3).

Assuming the same thermal efficiency the relevant flows of mass and energy for the **Kværner** process using the IEA natural gas are given in Figure 4. These data are normalised for the hydrogen required for converting the CO<sub>2</sub> collected from the 362 MW<sub>e</sub> coal fired power station into methanol.

Taking the same efficient plasma furnace and electricity generated in a natural gas fired combined cycle power station with an efficiency of 56.2% (LHV), the efficiency defined as the LHV of the hydrogen and carbon produced over that of the natural gas required for both the plasma furnace and the combined cycle power station reduces to 82.4%.

The power required for the plasma arc process can also be generated by burning part of the hydrogen produced instead of burning additional natural gas in the combined cycle station. This results in a zero carbon dioxide emission process but reduces the efficiency to 76.6 %. However, because virtually pure hydrogen is available as a fuel it may be assumed that in the distant future the power will be generated in fuel cells having an efficiency of 80 %. This increases the latter figure of 76.6 % to 88.9%, which is very high for a chemical reaction in which electricity is used. These figures are equal or even better than for paper processes in which a heat carrier is used to accomplish the cracking, which may reach efficiencies of about 80%. Moreover such heat carrier processes have still to be developed and are much more complex and therefore more capital intensive than the plasma arc process. Further power can be generated from non-fossil sources and/or from large efficient power stations that take full advantage of the economy of scale that adds to the flexibility of the **Kværner** process.

The main advantages of the **Kværner** process are that it is a simple process that is flexible in terms of the carbon-black quality and that both the carbon and the hydrogen produced are of a very high purity. More specifically it has the following qualities.

- When the carbon is used for the reduction of high purity quartz sands the silicon produced is claimed to be, apart from some carbon that has to be removed, of a quality as required for solar cells. As the silicon is the most important cost item in the production of PV cells this could have a large impact on the large-scale use of solar energy.
- In a renewable world electricity and hydrogen will be used for many purposes such as iron ore reduction where now fossil hydrocarbon fuels are used. The **Kværner** process fits very well in such a scenario.
- The hydrogen produced in the **Kværner** process is of such a quality that it can be used directly in fuel cells. In case the hydrogen is used to produce the electricity for the **Kværner** process via the fuel cell route the scope of this process is greatly enhanced.
- The **Kværner** process can operate at a pressure of maximum 6 bar that reduces compression energy of the hydrogen produced.
- The **Kværner** process itself produces virtually no emissions.



#### 4.2.3 Economics of the **Kværner** process

The economics of the **Kværner** process are given in Figure 5. The numbers are based on a capital cost of US\$ 527,4 x 10<sup>6</sup>/ y for a plant producing 1,19 x 10<sup>6</sup> ton/y carbon- black and 361,4 x 10<sup>3</sup> ton/y hydrogen.

The data show that for a zero cost of carbon-black the hydrogen will cost almost US\$ 1500/ ton, whereas for a zero cost of hydrogen the carbon-black will cost about 450 US\$ / ton.

In case the carbon-black will have to be sequestered and thus having a negative cost of say – 200 US\$/ton, the cost of hydrogen will increase to about 2150 US\$/ton.

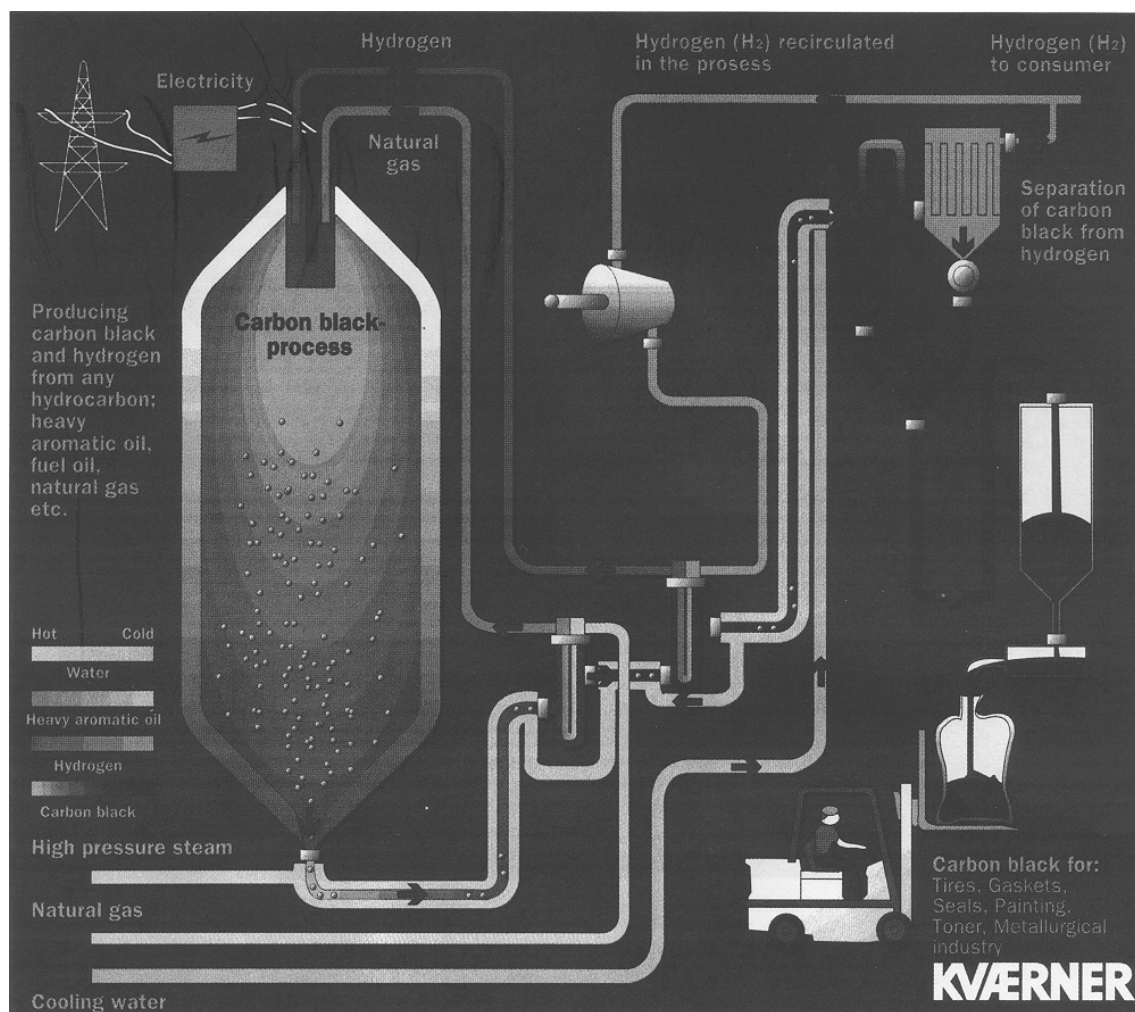


Figure 1. Flow sheet of the Kvaerner Carbon Black and Hydrogen process.

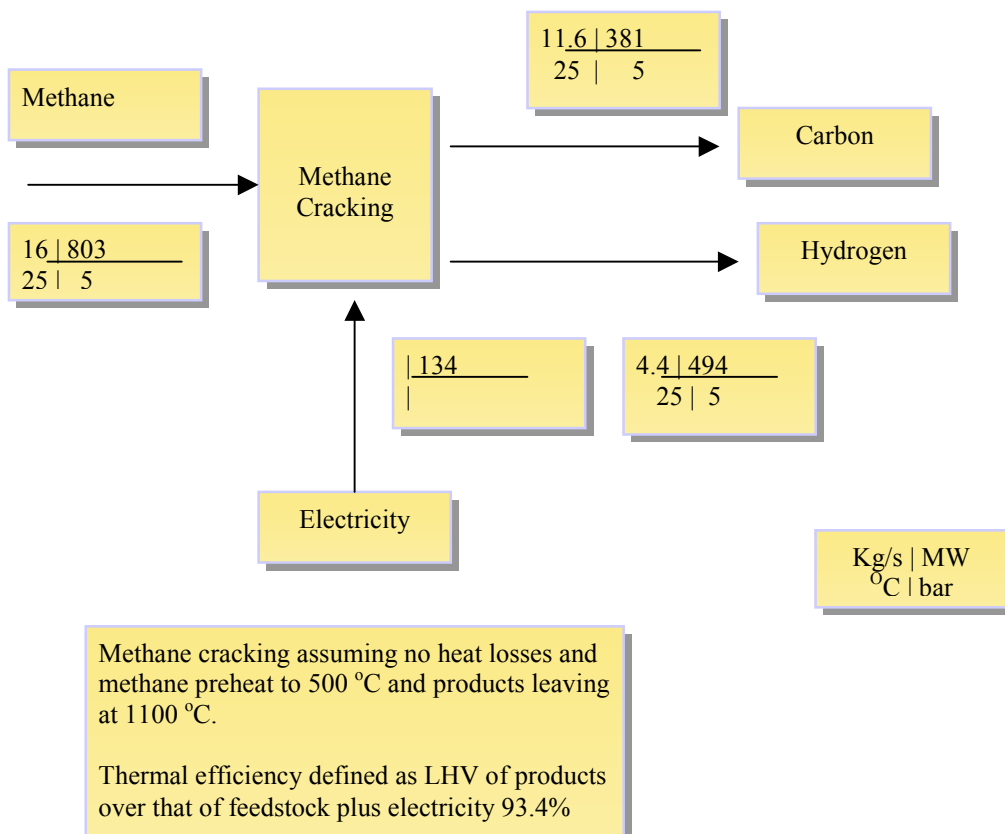


Figure 2. Process data theoretical methane cracking.

The process data indicate that 134 MW electrical energy is needed for the methane cracking. The theoretical electrical input for the methane cracking at 1100 °C is 72.6 MW. However, the products (carbon and hydrogen) are leaving the reactor with a temperature 1100 °C. The total amount of sensible heat in the product streams is 84.1 MWth. In this case part sensible heat of the hydrogen product stream (23 MWth) is used to preheat the methane to 500 °C. The other 61.1 MWth is not used. Of this 19.6 MWth is the sensible heat of the carbon black.

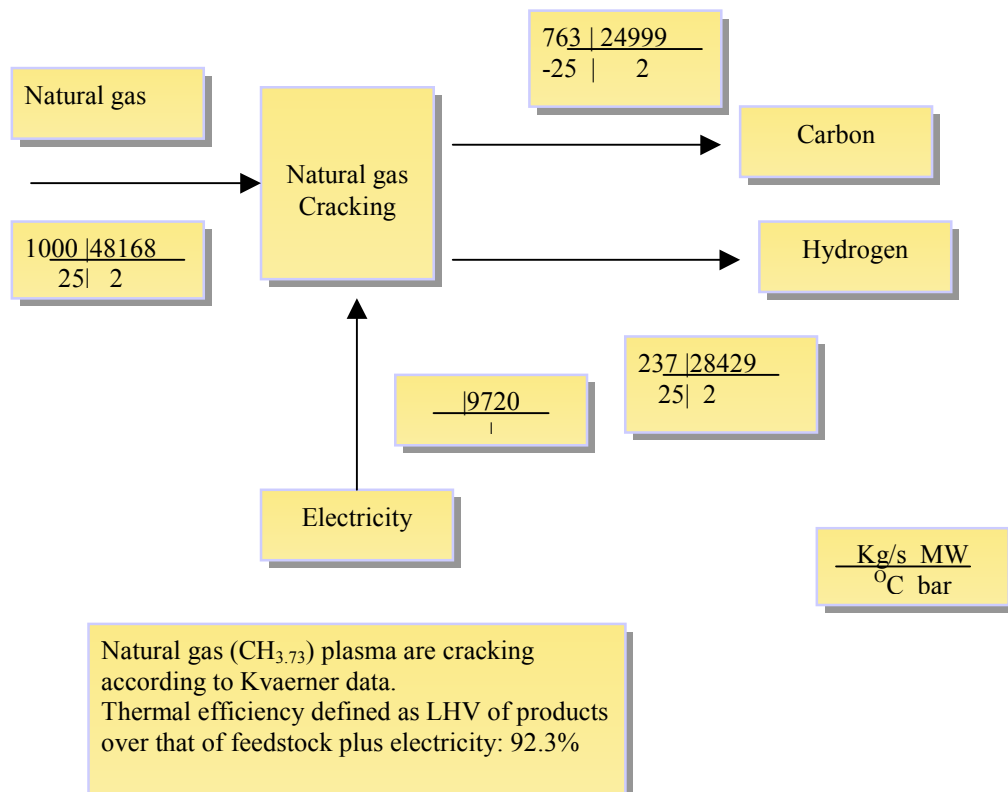


Figure 3. Kvaerner process data natural gas cracking.

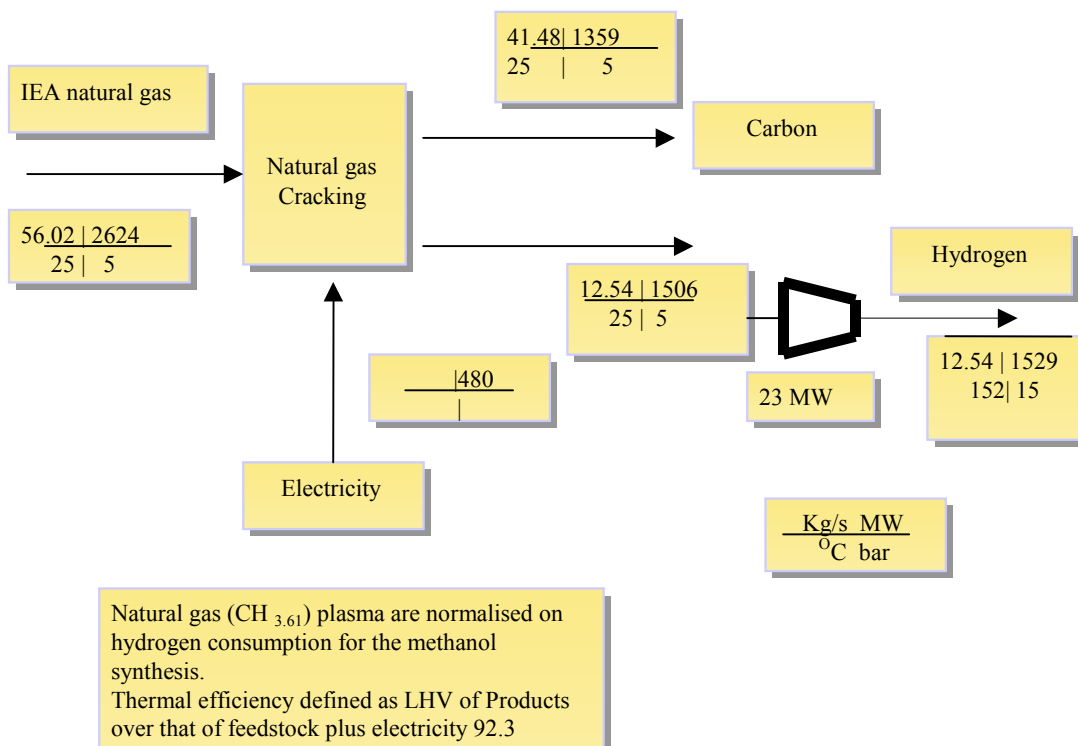


Figure 4. Kvaerner data IEA natural gas cracking (normalised hydrogen production 12.54 kg/s).

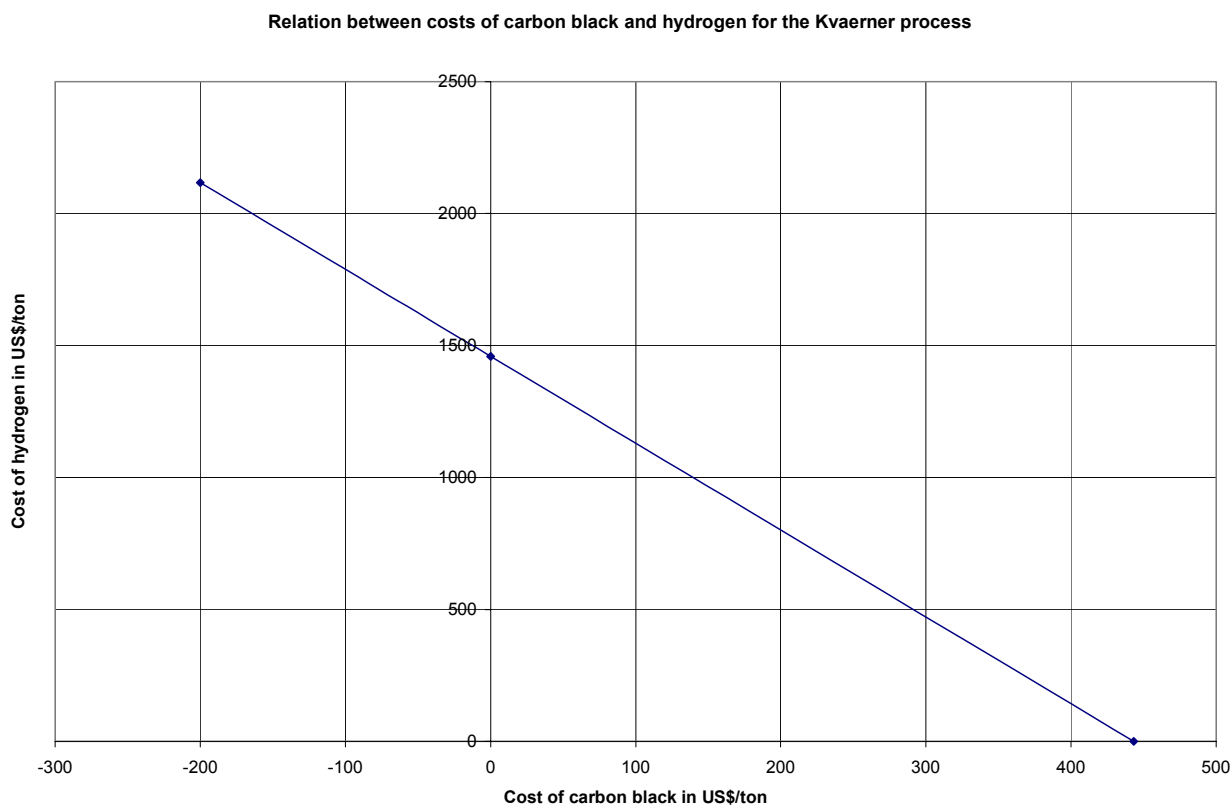


Figure 5. *Relation between costs of carbon black and hydrogen for the Kvaerner process.*

## 4.3 Description of traditional carbon-black processes

### 4.3.1 General

All large-scale commercial carbon-black processes are rather inefficient and comprise further developments of rather crude technologies. Much has been done in newer designs to improve the environmental aspects of the processes but little has been done to make use of e.g. the co-produced hydrogen. With the exception of the acetylene black process all existing commercial processes are unsuitable for the co-production of hydrogen. One of the reasons is that all these processes operate at atmospheric pressure. Other problems are that the process is not fully continuous (the thermal black process) or that the hydrogen is contaminated with nitrogen and combustion gases (furnace black). In the acetylene black process hydrogen can be co-produced but the route via acetylene to make hydrogen is very inefficient.

### 4.3.2 Furnace black

Furnace black (see Figure 6) is produced by thermal decomposition of carbon rich hydrocarbons. Almost all carbon-black in the world (95% of the 8 million tons/year) is produced as so-called furnace black. In this process aromatic refinery streams such as heavy catalytically cracked cycle oils, ethylene cracker residues and streams from extraction processes as e.g. used for lubricating oil production are used as a feedstock. In the process these feedstocks are injected as small droplets into hot flue gases produced by burning an auxiliary fuel. It is a fully continuous process with a yield of 45-65% of the theoretical. The lower yields are obtained in case large aggregates of carbon-black are produced at relatively high temperatures and the higher yields in case small aggregates are produced requiring lower temperatures.

The process is carried out at atmospheric pressure, temperatures ranging from 1200-1700 °C and residence times of a few milliseconds to several seconds. The reactor effluent consisting of flue gases and carbon-black are quenched by the injection of water and subsequently the carbon-black is separated from the gas by a combination of cyclones and bag filters.

Another form of furnace black process, also called the **thermal black** process, comprises a semi-continuous process generally based on natural gas as a feedstock (see Figure 7). The reactors (generators) contain a checkerboard of refractory bricks, which are heated to a temperature of 1300 °C by burning natural gas. The combustion air is then cut off and the natural gas supply continues resulting in its cracking to carbon and hydrogen. By combining various (3 or 4) reactors it is possible to obtain a continuous gas production. The gas and carbon-black are separated as described above for the furnace black process. The carbon-black produced has a large particle size but shows little agglomeration. Further it has a low surface area.

Other processes are the **lampblack** process, and the **acetylene black** process based on acetylene as a feedstock. These processes play a minor role in the bulk carbon-black market.

#### 4.3.3 Lampblack

Lampblack is the oldest way of producing carbon-black. It is based on the incomplete combustion of coal tars and petroleum residues such as anthracene and creosote oils in open pans.

#### 4.3.4 Acetylene black

The acetylene carbon-black process is interesting as it is based on the exothermic decomposition of acetylene at temperatures of 1000-1500°C. The co-produced hydrogen is generally flared or used for heating purposes in other parts of the industrial complex into which the process is integrated. The product is very pure and graphitic in nature. It is packaged in various grades having bulk densities of (only) 100-200 kg/m<sup>3</sup>.

### 4.4 Catalytic pyrolysis

Catalytic processes are mostly based on cracking and direct or indirect partial oxidation. In order to produce directly a pure gas, thermodynamics predict that even at atmospheric pressures a temperature of 1100 °C or higher is required. At such temperatures the reactions proceed already so fast that catalysts can do little to enhance them. Further catalyst stability is often problematic at temperatures above 1000°C. Moreover such catalytic processes are more complex than the Kvaerner process.

### 4.5 Direct thermal cracking

M. Steinberg [9] suggests a thermal decomposition process of methane for the production of hydrogen and carbon black. The reason for this is that the use of electricity, even when it is produced in an efficient combined cycle power plant significantly reduces the overall thermal efficiency. In principle this is correct. However, all very high temperature processes have the problem that both the products and the flue gases from the indirect heating leave the process at essentially the process temperature or an even somewhat higher temperature. Heat exchange at temperatures above 600 °C requires already very expensive high nickel steels and above 850 °C steel heat exchangers are not available. This implies that above 500-600 °C heat exchange becomes energetically not very effective. Working at temperatures below 1100°C for methane cracking is useless as even at atmospheric pressure thermodynamically such temperatures are

already theoretically required to obtain a hydrogen purity of over 98%. This immediately implies that the molten tin option is out for that reason in case reasonably pure hydrogen has to be produced. Calculations were made for schemes for methane cracking using heat as proposed by Steinberg [9] because these could be more efficient than using power to drive a chemical process. Even when operating with power recovery and not looking at the very high equipment cost, the best theoretical schemes based on natural gas as the feedstock and using part of the produced hydrogen as fuel had only efficiencies of about 42% based on the net hydrogen production. This is about the same efficiency that can be obtained with the much lower capital cost **Kværner** process using “CO<sub>2</sub>-free” electricity.

#### 4.6 Conclusion

It can be concluded that the Kvaerner plasma arc process is the only efficient process for carbon rejection and hydrogen production. The traditional carbon-black processes are inefficient and crude technologies. Calculations on basis of direct thermal cracking of methane as proposed by Steinberg show that only an efficiency of 42% based on the net hydrogen production is possible. This is about the same efficiency that can be accomplished with the Kvaerner process.



### Furnace Black Process

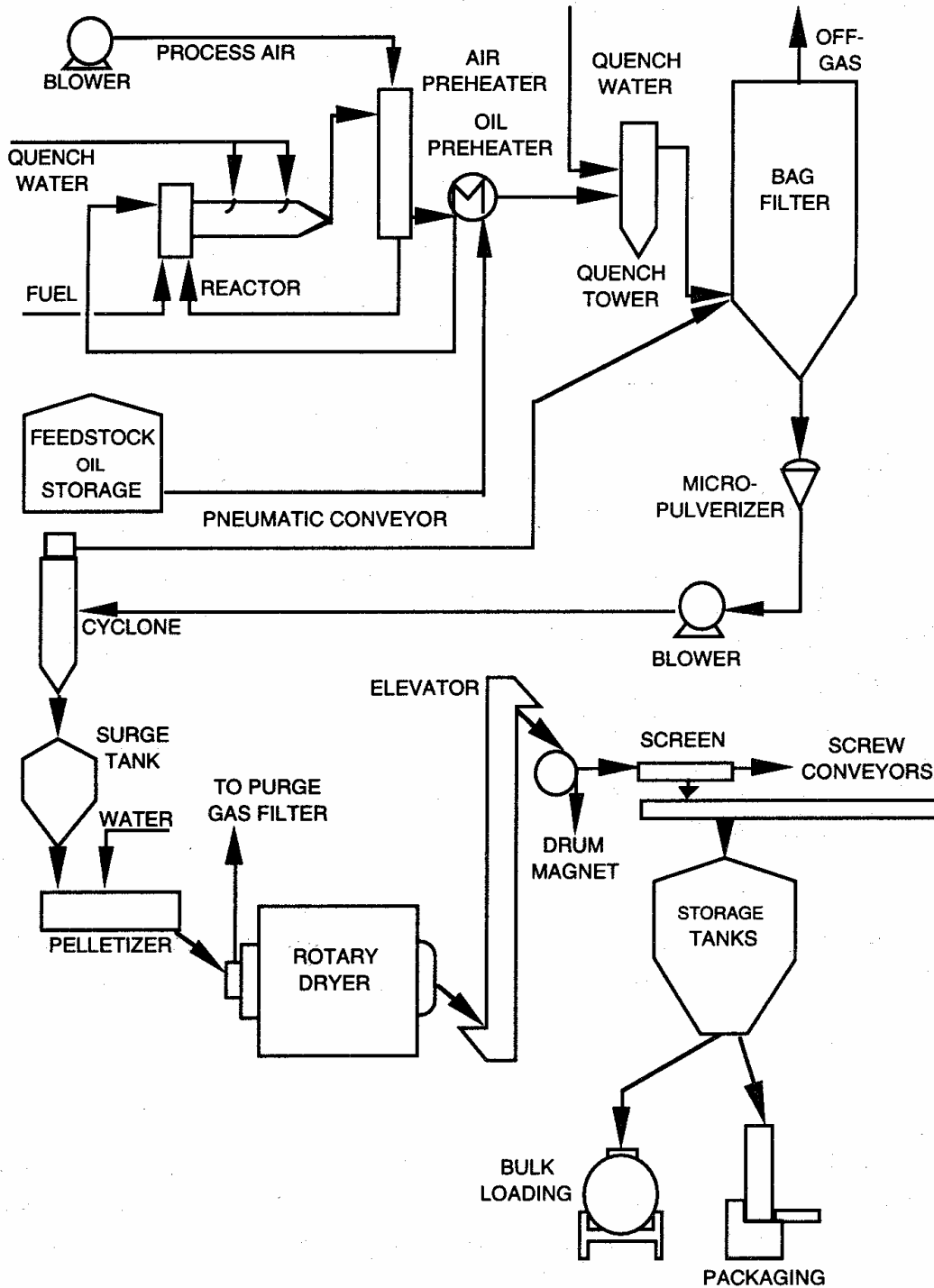


Figure 6. Furnace black process.

## Thermal Black Process

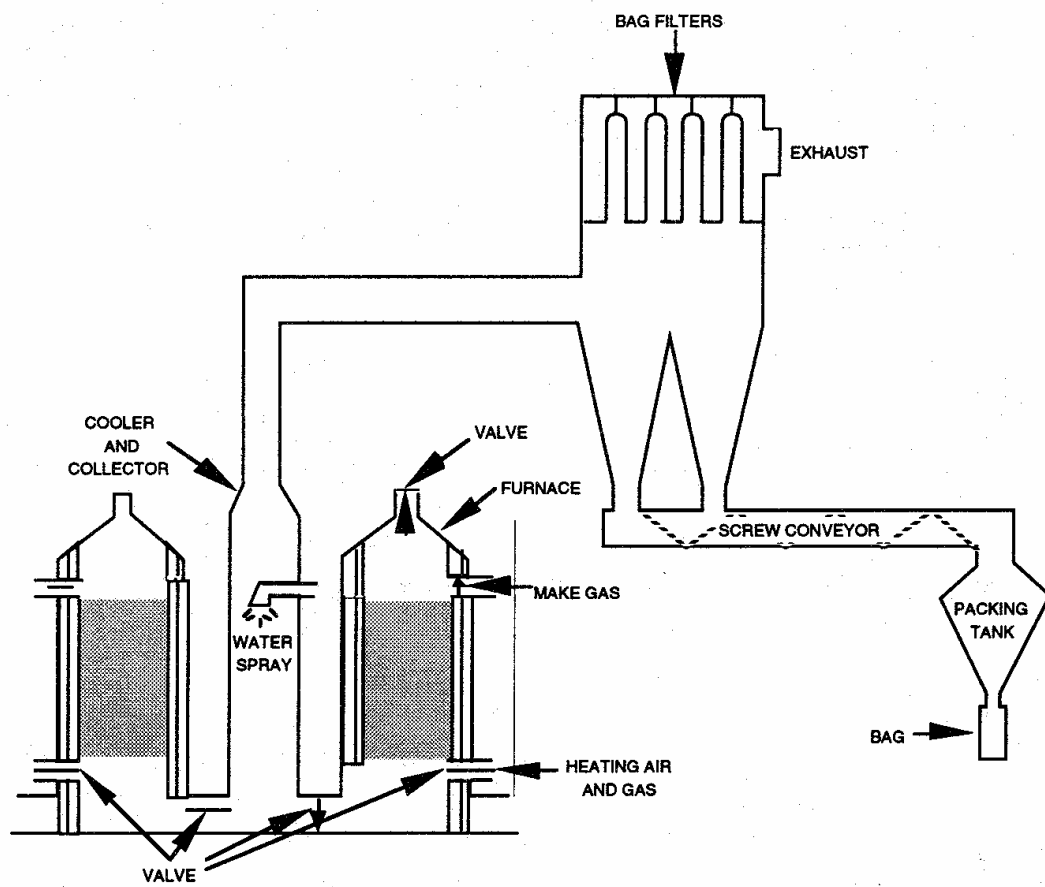


Figure 7. Thermal black process.

## 5. THE CURRENT AND FUTURE MARKET POTENTIAL FOR CARBON BLACK

### 5.1 Introduction

In case of carbon rejection it would of course be advantageous if a market could be found for the carbon. The only large scale use of carbon for non-combustion purposes is iron ore reduction, for which 300 million tons per year are required. The traditional carbon black market requires only 8 million tons per year.

All other markets for non-fuel application in which carbon is used consume only about 13 million tons per year mostly in the form of petroleum coke.

Some additional data illustrating this problem are given in the table below.

<b>Important relative mass flows in the world</b>		
	<b>Ton/y</b>	<b>Relative mass</b>
<b>Fossil fuels (ff)</b>	<b><math>10 \times 10^9</math></b>	<b>100</b>
<b>Carbon from ff</b>	<b><math>8 \times 10^9</math></b>	<b>80</b>
<b>CO<sub>2</sub> emission</b>	<b><math>30 \times 10^9</math></b>	<b>300</b>
<b>Chemicals</b>	<b><math>3 \times 10^8</math></b>	<b>3</b>
<b>Ceramic building materials</b>	<b><math>10-15 \times 10^8</math></b>	<b>10-15</b>
<b>Iron</b>	<b><math>5 \times 10^8</math></b>	<b>5</b>
<b>Carbon for iron ore reduction</b>	<b><math>3 \times 10^8</math></b>	<b>3</b>
<b>Carbon black market</b>	<b><math>8 \times 10^6</math></b>	<b>0.08</b>
<b>Waste biomass</b>	<b><math>10-20 \times 10^9</math></b>	<b>100-200</b>

These figures illustrate the problem of utilising “waste” streams derived from fuels.

The only substantial markets for fuel derived waste are in the building- and iron and steel industry.

### 5.2 The current market for carbon black

The current world market for carbon black amounts to only 8 million tons per year.

Of the world consumption of carbon black 70% is used in the production of tires and tire products. Roughly 20 % goes into other rubber products such as hose, belting, mechanical and molded goods. The remainder ( nearly 10%) is being used in plastics, printing ink and miscellaneous applications.

The long term growth rate of carbon-black consumption is expected to run closely parallel to that of the rubber industry (ref. [7]) which is 1.5-2.0% per year. This expectation could be optimistic though in case carbon- black in tires will be more and more replaced by silica. The use of cleaner automotive Diesel fuels (lower sulphur and soot emissions) will make that the

wear of tires will then become responsible for most of the carbon/soot emission from traffic and will hence promote the use of silica for this purpose.

The US prices for furnace carbon black are in the range of 40 ¢ per lbs. This means a price of US\$ 800-900 per ton.

### 5.3 The potential use of carbon black in the metallurgical industry (coke consumption for raw iron production)

The main use of carbon in the metallurgical industry is the coke consumption of the raw iron production in blast furnaces. The world raw iron production (1998) is about 580 million ton. The world production of metallurgical coke is about 305 million ton. So an average coke consumption of about 525 kg per metric ton of raw iron would result. However technological differences cause a wide spread: Coke consumption of an individual blast furnace is expressed in terms of standard reduction entity (SRE). Most modern blast furnaces will show a coke consumption of 475 to 480 kg of SRE per ton raw iron. This can be in the form of coke only or in a combination of coke and an alternative source like pulverised coal injection (PCI) heavy fuel oil or natural gas. Most modern blast furnaces use one of these as a means to reduce coke consumption. At CORUS (Hoogovens IJmuiden) the level of PCI achieved is 220 kg/ton and this reduces the coke consumption to a level of 310 kg SRE per ton. In the blast furnace process coke serves three main functions: it supplies the carbon for the carbothermal reduction of the ore, it forms the structure that supports the charge in the BF and the porous nature allows the gas-solid phase reactions of the reduction process to take place. The heat required is mainly generated by the PCI and provided by the hot blast stoves that preheat the air. For above reasons the iron and steel industry has a record of tight quality specification for the coke and the coking coal used for its production. Because of above quality requirements it is not expected that metallurgical coke can be replaced by an alternative made from carbon black.

However because of the cost of coke and the fact that the coke battery is one of the major pollutants in the industry the iron industry has always been keen on methods to reduce the coke consumption hence the adoption of PCI. Carbon black can be used to replace the PCI coal if the structure will not cause it to clog the injection lines. The maximum level reached by PCI is about 220 kg per ton raw iron production. With a 100% penetration on a global scale this would result in a maximum consumption of 125 million ton per year. The value of this should be estimated at the cost of the coal replaced. This consumption will not give a direct contribution to the CO<sub>2</sub> emission as the carbon is used as a reduction agent.

When there is a wish for CO<sub>2</sub> abatement, the future iron ore reduction will take place via direct reduction. In this process, natural gas is used instead of coal-coke. This leads to a 3-4-fold decrease in CO<sub>2</sub> emission per ton iron and requires a lower investment than the blast furnace route. Note: in this case there remains no market for carbon black as replacement for PCI coal.

### 5.4 Carbon black as petroleum coke replacement

#### **Use of petroleum coke in metallurgy, world market for petroleum coke.**

Petroleum coke is a by-product from the oil industry. It can be considered as a sink for the many waste products generated during the refinery processes. Therefore the quality of petroleum coke has always been a secondary feature.

The current petroleum coke production amounts to 50 million metric ton (1998). The average annual market growth has been 4.5% per year since 1980.

This trend is expected to continue into the following century.

Three factors influence both the quality and quantity of petroleum coke production.

- The increasing demand of transportation fuel.
- The tighter environmental regulations imposed on these fuels.
- The deteriorating quality of the feedstock.

For this reason it is expected that the growth of the petroleum coke production will be mainly in the inferior qualities.

#### 5.4.1 Fuel grade petroleum coke

Raw petroleum coke is produced either in the flexicoker, in the fluid bed system or in the delayed coking process. The last process is most common and yields a product with superior structural properties. 80% of world petroleum coke production is concentrated in North America. The petroleum coke is classified in three product qualities: Sponge coke (high percentage volatiles), Shot coke (high level of asphaltenes) and needle coke. The first two are sold as fuel (fuel grade petroleum coke). The higher quality of sponge and needle coke is used in the production of electrodes and other carbon or graphite products. Currently 75% of world petroleum coke production about 37.5 million ton per year is sold as fuel grade petroleum coke to the cement industry and recently in an increasing volume to the power industry. Current fuel grade petroleum coke prices show an average level of 80% of the average crude oil prices. European deliveries of fuel grade petroleum coke to the cement industry are reported to have an average price of less than \$20 per metric ton. The volume of the petroleum coke market remains less than one percent of the world coal market.

#### 5.4.2 Non fuel use of petroleum coke

Of the world production of 50 million tons per year of petroleum coke, 12.5 million ton per year is sold as non fuel petroleum coke to the SiC manufacturers and as anode grade petroleum coke to the metallurgical industry. Also some other graphite products are sold outside the metallurgical industry. The SiC manufacturing uses green petroleum coke. The metallurgical industry uses calcined petroleum coke that is much more expensive. The following lists the non-fuel products from petroleum coke in increasing cost.

For the Silicon carbide industry a premium quality of green needle coke is used. The specifications include low metal levels especially for Fe and Al, a sulphur level below 4%, a low shot percentage and specified baking properties. The process releases two molecules of CO per molecule of SiC formed to the exhaust system. The CO can be recovered for power generation but this will release the resulting CO<sub>2</sub> to the atmosphere. The current petroleum coke market for the SiC production is about 0.6 million metric ton per year. The current price level for this quality petroleum coke is \$30 to 40 per metric ton.

For the anodes of the aluminium smelters and for the electric arc furnace electrodes the prime properties of the petroleum coke is its ability to be graphitized, i.e. when heat treated under pressure it will assume a structure that approximates that of graphite. The denser the material is and the lower the coefficient of thermal expansion gets the better. Therefore the volatile matter content and the amount of shot are important. For the aluminium smelter anodes typical properties for the calcined petroleum coke are: 0.5% ash, and Vanadium and Nickel levels of 200 ppm Silicon 0.02% and Sulphur 2.5%. Further the electrode material is subjected to a reactivity test towards air and towards the CO<sub>2</sub> atmosphere that exists in the smelter reactivity should be minimal. All carbon of the anodes will eventually be released to atmosphere as CO<sub>2</sub>. The production of one kg of aluminium consumes about 0.4 kg of calcined petroleum coke; the metallurgical consumption is 0.38% the balance is attrition. The Petroleum coke consumption for the anode fabrication is forecast to increase to more than 8 million metric ton in 2000. The current price level of calcined petroleum coke is between \$300 and \$375 per metric ton.

For the Electric arc furnace electrodes the same type of requirements are given only with tighter specifications. Typical properties for the calcined petroleum coke are: 0.15% ash, 10 ppm Vanadium, 20-40 ppm Nickel, 0.04% Silicon and 1.0% Sulphur. Specific consumption's as low

as 2 kg per ton of EAF steel are quoted. All carbon will eventually be released to atmosphere as CO<sub>2</sub>. The Petroleum coke consumption for the electrode fabrication is forecast to increase to about 1.3 million metric ton in 2005. The current price level of calcined petroleum coke is between \$300 and 375 per metric ton. (I have not found evidence of a price difference but we must assume the higher level will apply to the tighter requirements for the EAF electrode manufacturing).

Other carbon and graphite products like refractory linings of blast furnaces and electrodes for the production of metallic silicon and phosphorus are not reviewed in detail. It is assumed that those applications will form the balance of the quoted consumption figures and that the petroleum coke quality will be similar to the EAF electrodes.

#### 5.4.3 Penetration of Carbon black into the petroleum coke market

1. Penetration into the fuel grade market segment will yield a price not higher than \$20 per ton. However penetration in this market will not give any changes in the likely CO<sub>2</sub> emissions.
2. Penetration into the SiC production market is questionable. This market requires a moisture level of 8% for dust abatement purposes also a grain size of around 3 mm is specified for handling purposes. Further the market is only 600,000 ton per year at a price level of around \$30 to 40 per ton.

Penetration into the anode and electrode market is possible if the carbon black material is graphitizable. Calcination is an important step in the production. The vibrating bulk density VBD of the calcined coke must be greater than 86 g/100cc. The porosity of the calcined coke should be low. The absence of ash and metal content can be considered to be of advantage however a certain sulphur level reduces the reactivity (air and carboxyl). If carbon black succeeds to penetrate into the anode metallurgical petroleum coke market, the maximum volume would be around 8 million metric ton at a price level between \$300 and \$ 375 per ton. This penetration would not result in a likely shift in CO<sub>2</sub> emission level from the processes involved. There are however some improvements possible in the emission levels of other pollutants like SO<sub>2</sub> and H<sub>2</sub>S.

#### 5.5 Special new markets for carbon black

A new market for carbon black could be the production of solar grade silicon. This product will require equal quantities of ultra clean quartz and silicon carbide to form pure silicon.

The silicon carbide can be made using carbon black produced by the Kvaerner CB&H process. Optimistic forecasts of the total volume of the solar grade silicon market show an increase from the current 2000 ton per year to 5000 ton per year in 2006.

5000 ton of silicon would require only about 3200 ton of carbon black.

#### 5.6 Handling of pure carbon

Pure carbon is commercially used in two main forms: carbon-black and graphite.

In carbon-black type processes both products are produced as a very fine fluffy powder and for this reason they are mostly pelletised in order to make them amenable to transportation. This pelletisation adds substantially to the cost of this product, but as long as it is used in relatively (to fuels) high added value products such as tires or used for the production of solar cells this is not a problem. However, as soon as such a material has to compete with low cost industrial fuels such manufacturing steps become an economic obstacle.

The bulk density of pelletised carbon black is about 360 kg/m<sup>3</sup> which makes that also in this form transport is still expensive. Even in the pelletised form the product is very prone to attrition. Careful attention has therefore to be paid to minimising the handling of carbon-black by e.g. avoiding transport over large distances. Another aspect concerns possible health risks.

Now that the emissions of soot from Diesel engines are scrutinised because their possible health hazard it is logical that also other carbon-blacks are faced with the same problem.

## 5.7 Conclusion

In case of carbon rejection it is required to find a substantial outlet for carbon that is co-produced as a result of cracking a hydrocarbon.

The only substantial application for carbon black is for iron ore reduction.

This market requires 300 million tons per year of carbon. However because of quality requirements, namely the structural strength of the carbon black to support the charge in the blast furnace, it is not expected that metallurgical coke can be replaced by an alternative made from carbon black.

A possible market for carbon black can be the replacement of coal used as pulverised coal injection (PCI) in a blast furnace. With a 100 % penetration on a global scale, this would result in a maximum consumption of 125 million ton per year.

Furthermore, when there is a real wish for CO<sub>2</sub> abatement the future iron ore reduction will take place via direct reduction, where natural gas is used instead of coal/coke. This leads to a 3-4-fold decrease in CO<sub>2</sub> emission per ton iron and requires a lower investment than the blast furnace route. In this case there remains no market for carbon black as replacement for PCI coal. The current world consumption for carbon black amounts only 8 million tons per year mainly in the production of tires and tire products.

If carbon black could succeed to penetrate into the metallurgical petroleum coke market the maximum level would be 8 million tons per year.

Other new market application of carbon black, like solar grade silicon, has only a small potential volume.

It can hence be concluded that there is an enormous discrepancy between the CO<sub>2</sub> that is produced in fossil fuel fired power stations and the (potential) carbon-black market.

## 6. ASSESSMENT OF THE CARNOL PROCESS AS A MEANS OF CO<sub>2</sub> ABATEMENT

### 6.1 Process background

The Carnol process consists of three integrated processing steps. (M.Steinberg ref.[5] and [6]).

(A) Hydrogen production as in the carbon –rejection process.

(B) A fossil fuel fired power plant in which CO<sub>2</sub> is captured.

(C) A methanol production plant from hydrogen and CO<sub>2</sub>.

The products of the Carnol process are: electricity, methanol and carbon. Methanol is used as a transport fuel. The reject carbon produced is not used in the Carnol process. It is either sold or stored.

Natural gas will be used in the hydrogen generation process, in this case the Kvaerner process is used. For the generation of power two cases were studied, viz. power generation by coal and power generation by natural gas. This is because the Carnol process is thought to be a possible way of allowing the continued use of coal in power generation.

### 6.2 Carnol process

#### 6.2.1 Design basis Carnol process

The design of the Carnol process is based on a coal fired power plant with CO<sub>2</sub> capture. The concept is coal fired power generation with a super critical steam cycle with CO<sub>2</sub> capture from the flue gas. The plant is described in the (draft) report: “Assessment of leading technology options for abatement of CO<sub>2</sub> emissions”, by Stork Engineering Consultancy B.V. (ref. [1]). The power plant has a fuel input of 1098 MW and a power production of 362 MWe. This plant is equipped with an absorber/stripper combination where 85% of the CO<sub>2</sub> is removed from the flue gas using a MEA solution. The MEA solution chemically binds the CO<sub>2</sub>. CO<sub>2</sub> is removed by applying heat. The washed flue gas leaves the absorber column onto the atmosphere. The CO<sub>2</sub> leaves the stripper and is compressed and cooled down. The amount of CO<sub>2</sub> captured is 85,6 kg/sec. The not captured portion of the CO<sub>2</sub> leaves the plant as flue gas (14,9 kg/sec.)

The amount of CO<sub>2</sub> captured is the basis of the capacity of the Carnol process.

The Kvaerner process as described in chapter 3 produces hydrogen required for the conversion of CO<sub>2</sub> into methanol. The capacity of the plant is 12.55 kg/sec hydrogen which is required to convert the available CO<sub>2</sub> into methanol.

The methanol synthesis takes place in the methanol plant at a pressure of 50 bara. Details of the process are given in figure 5.3.

#### 6.2.2 Summary process results Carnol process (Case Coal fired power plant)

Results of the process calculations are presented in figure 5.1. In the diagram mass- and energy streams are given.

As can be seen from the diagram in the case of a coal fired power plant the power produced by the power plant is not enough to satisfy the power demand of the CB&H ( Kvaerner ) process. Although the methanol process produces 71 MW electricity, a net power import of 70 MWe is required.

The production of the Carnol process is 209 t/h methanol and 149 t/h carbon black. Water is a by-product. The overall thermal efficiency of the process based on the heating values of methanol and carbon is 66%(LHV). In case only the heating value for methanol is accounted for the thermal efficiency drops to 30% (LHV).



Because the Carnol process on basis of a coal-fired power plant requires a net import of power this concept is not workable.

### 6.2.3 Summary process results Carnol process (Case Gas Fired power plant)

An alternative to the coal fired Carnol process is a case in which power is generated by a gas fired power plant. For this case power generation in a combined cycle was selected with partial flue gas recycling. Flue gas exiting the HRSG passes through an absorber /stripper combination where 85% of the CO<sub>2</sub> is removed using a MEA solution. CO<sub>2</sub> is stripped from the solution, compressed and cooled down.

The plant is specified in reference [1]. The net efficiency is 47,8% (LHV).

Because the CO<sub>2</sub> production of the described gas fired power plant is 69,5 kg/sec. This does not meet the for the mass balance required amount of 85,6 kg/sec. For this reason this plant was scaled-up to an CO<sub>2</sub> output of 85,6 kg/sec.

Results of the process calculations are presented in figure 5.2. In the diagram mass en energy streams are given. As can be seen from the diagram in case of a natural gas fired power plant there is a net output of power from the total Carnol system. Power produced by the power plant is in excess to satisfy the power demand of the CB&H (Kvaerner) process.

The net production of the Carnol process is 388 MWe, 209 t/h methanol and 149 t/h carbon black.

The production of methanol and carbon black are in both cases the same because the design basis is a net production of 85,6 kg/sec CO<sub>2</sub> by the power plant. Water is a by-product. The overall thermal efficiency of the process based on the heating values of methanol and carbon is 67%(LHV). In case only the heating value for methanol is accounted for the thermal efficiency drops to 35% (LHV).

The concept of the Carnol process on basis of a natural gas fired power plant is workable. The disadvantage of the concept is the low overall thermal efficiency.

Furthermore there is no substantial contribution to the CO<sub>2</sub> abatement.

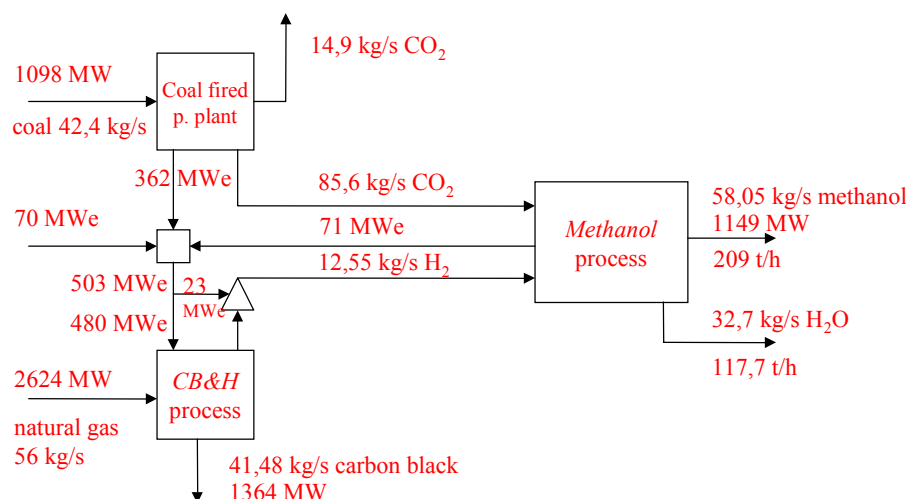


Figure 5.1 Carnol Process, Case: Coal Fired Power Plant

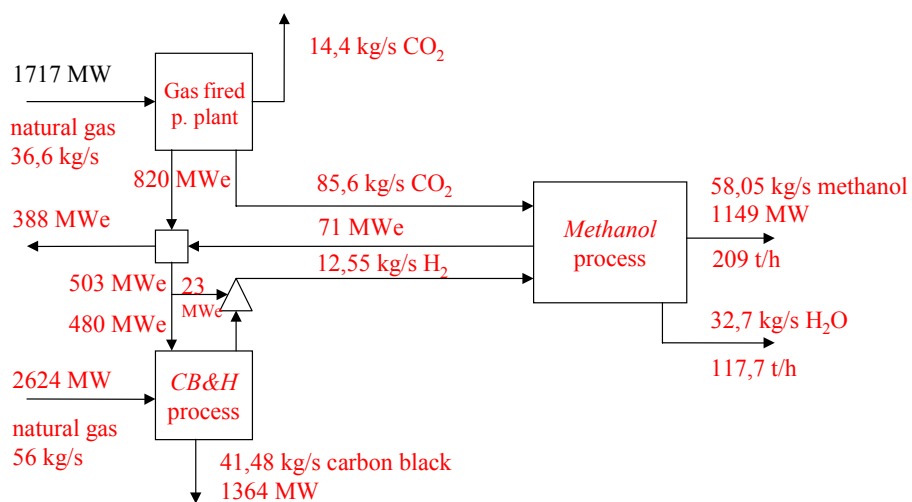


Figure 5.2 *Carnol Process, Case: Natural Gas Fired Power Plant*

## 7. ECONOMIC EVALUATION CARNOL PROCESS

### 7.1 Introduction

For the economical evaluation of the Carnol process the technical and financial assessment criteria are used as described in the Technical specification Appendix 1 of the IEA Greenhouse Gas R&D programme.

Cost estimates are based on data supplied in reference 1 for the coal and natural gas fired power plants. For the CB&H process Kvaerner Oil & Gas (ref.2) supplied the data for cost estimate.

The methanol synthesis plant investment was estimated on basis of historical investment data available from the methanol synthesis plant located in Delfzijl Holland.

For DCF calculations real rates of return of 10% are used. To illustrate the sensitivity a discount rate of 5% is also quoted.

### 7.2 Economic evaluation Carnol process

The following tables present an overview of the economic evaluations of the Carnol process.

Table A-1 presents the results of the case with a coal-fired power plant. The economic evaluation is based on the assumption that methanol is valued as transport fuel at a price of \$ 150 per ton. The resulting cost of the carbon black is \$ 350 per ton. Consequently, the cost per ton CO<sub>2</sub> avoided amounts \$ 95.

The cost of CO<sub>2</sub> capture in a power plant amounts 35-45 \$ per ton CO<sub>2</sub>. This compares favorably with the cost for CO<sub>2</sub> capture in the Carnol process.

Table A-2 presents the results of the case with a natural gas fired power plant. On the same assumption regarding the methanol price, the resulting cost of the carbon black is \$ 225 per ton and the cost per ton CO<sub>2</sub> avoided amounts \$ 62. In this case the cost are lower compared to the previous case because in this case there is a net export of power.

Tables A-3, A-4, A-5 and A-6 present the plant economic data of respectively a coal fired power plant, a natural gas fired power plant, the carbon black & hydrogen plant (Kværner process) and the methanol synthesis plant.

Table A1

Table A.1

**Economic evaluation overview****Case: CARNOL process with coal fired power plant**

Discount rate		0,05	0,10	1/year	
Hours per year	8000 hrs/year				
Natural gas price	2,0 \$/GJ				
Coal price	1,5 \$/GJ				
Capital requirements					
Coal fired power plant		742,4	773,8	M\$	
Carbon black & Hydrogen plant		1730,4	1764,4	M\$	
Methanol synthesis plant		501,2	511,1	M\$	
Total capital requirements		2974,1	3049,2	M\$	
Plant life	25 year				
Annuity factor		0,07008	0,10894	1/year	
<b>Yearly capital costs</b>		<b>208,4</b>	<b>332,2</b>	<b>M\$/year</b>	
Operating costs					
Coal fired power plant		41,0	41,0	M\$/year	
Carbon black & Hydrogen plant		60,1	60,1	M\$/year	
Methanol synthesis plant		18,9	18,9	M\$/year	
<b>Yearly total operating costs</b>		<b>120,0</b>	<b>120,0</b>	<b>M\$/year</b>	
Fuel costs					
Coal fired power plant		47,4	47,4	M\$/year	
Carbon black & Hydrogen plant		151,1	151,1	M\$/year	
<b>Yearly total fuel costs</b>		<b>198,6</b>	<b>198,6</b>	<b>M\$/year</b>	
<b>Yearly power costs</b>		<b>18,1</b>	<b>18,1</b>	<b>M\$/year</b>	70 MWe @ 0,0323 \$/kWh, with CO2 removal
<b>Grand total yearly costs</b>		<b>545,1</b>	<b>668,9</b>	<b>M\$/year</b>	
<b>Revenues from methanol sales</b>		<b>250,8</b>	<b>250,8</b>	<b>M\$/year</b>	58,05 kg/s @ 0,15 \$/kg, see note.
<b>Nett yearly costs</b>		<b>294,3</b>	<b>418,1</b>	<b>M\$/year</b>	
<b>Carbon black production</b>		<b>1,195</b>	<b>1,195</b>	<b>MTon/year</b>	41,48 kg/s
<b>Carbon black production costs</b>		<b>246,4</b>	<b>350,0</b>	<b>\$/ton</b>	
<b>Costs of CO2 avoided</b>		<b>67,2</b>	<b>95,4</b>	<b>\$/ton CO2</b>	152,09 kg/s CO2

Note: methanol price related to 28 \$/bbl crude, petrol value 1.6 x crude, heating value corrected, LHV petrol = 41.3 MJ/kg, LHV methanol = 19.8

Table A2

Table A.2

**Economic evaluation overview****Case: CARNOL process with natural gas fired power plant**

Discount rate			0,05	0,10	1/year	
Hours per year	8000	hrs/year				
Natural gas price	2	\$/GJ				
Capital requirements						
Natural gas fired power plant			583,9	595,4	M\$	
Carbon black & Hydrogen plant			1730,4	1764,4	M\$	
Methanol synthesis plant			501,2	511,1	M\$	
Total capital requirements			2815,6	2870,8	M\$	
Plant life	25	year				
Annuity factor			0,07008	0,10894	1/year	
<b>Yearly capital costs</b>			<b>197,3</b>	<b>312,8</b>	<b>M\$/year</b>	
Operating costs						
Natural gas fired power plant			28,4	28,4	M\$/year	
Carbon black & Hydrogen plant			60,1	60,1	M\$/year	
Methanol synthesis plant			18,9	18,9	M\$/year	
<b>Yearly total operating costs</b>			<b>107,4</b>	<b>107,4</b>	<b>M\$/year</b>	
Fuel costs						
Natural gas fired power plant			98,9	98,9	M\$/year	
Carbon black & Hydrogen plant			151,1	151,1	M\$/year	
<b>Yearly total fuel costs</b>			<b>250,0</b>	<b>250,0</b>	<b>M\$/year</b>	
<b>Grand total yearly costs</b>			<b>554,7</b>	<b>670,2</b>	<b>M\$/year</b>	
Revenues						
Methanol sales			334,4	334,4	M\$/year	58,05 kg/s @ 0,2 \$/kg, see note.
Power sales			67,0	67,0	M\$/year	388 MWe @ 0,0216 \$/kWh, <u>without</u> CO2 removal
<b>Yearly total revenues</b>			<b>401,4</b>	<b>401,4</b>	<b>M\$/year</b>	
<b>Nett yearly costs</b>			<b>153,3</b>	<b>268,8</b>	<b>M\$/year</b>	
<b>Carbon black production</b>			<b>1,195</b>	<b>1,195</b>	<b>MTon/year</b>	41,48 kg/s
<b>Carbon black production costs</b>			<b>128,3</b>	<b>225,0</b>	<b>\$/ton</b>	
<b>Costs of CO2 avoided</b>			<b>35,0</b>	<b>61,4</b>	<b>\$/ton CO2</b>	152,09 kg/s CO2

Note: methanol price related to 28 \$/bbl crude, petrol value 1.6 x crude, heating value corrected, LHV petrol = 41.3 MJ/kg, LHV methanol = 19.8 MJ/kg

Table A3

Table A.3 **Plant economic data**Unit: **Coal fired power plant with CO2 removal**

Fuel usage, LHV	1098	MWth
Nett efficiency	0,330	-
Power production	362,3	MWe
Fuel price	1,50	\$/GJ
Hours per year	8000	hr/year

Remarks:

Overnight construction costs (OCC)	608,4	M\$	Specific costs \$/kWe = 1679 (ref. 1)	
Fees	12,2	M\$	2 % of OCC	
Land purchase, site preparation	30,4	M\$	5 % of OCC	
Contingencies	60,8	M\$	10 % of OCC	
<b>Total installed costs</b>	<b>711,8</b>	<b>M\$</b>		

Allowances during construction

Discount rate		0,050	0,100	1/year
1st year	0,20	0,221	0,242	
2nd year	0,45	0,473	0,495	
3rd year	0,35	0,350	0,350	
Construction period factor		1,043	1,087	

<b>Total capital requirement</b>	<b>742,4</b>	<b>773,8</b>	<b>M\$</b>
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Operating costs

Maintenance				
coal handling	8,8	M\$/year	4 % of	36 % of OCC
remaining capital exp.	7,8	M\$/year	2 % of	64 % of OCC
Labour	4,1	M\$/year	(ref. 1)	
Waste disposal	1,9	M\$/year	(ref. 1)	
Chemicals & consumables	6,3	M\$/year	(ref. 1)	
Insurance & taxation	12,2	M\$/year	2 % of OCC	
<b>Total operating costs</b>	<b>41,0</b>	<b>M\$/year</b>		

<b>Fuel costs</b>	<b>47,4</b>	<b>M\$/year</b>
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Table A4

Table A.4 **Plant economic data**

<b>Unit:</b>		<b>Natural gas fired power plant with CO2 removal</b>			
Fuel usage, LHV	1717	MWth			
Nett efficiency	0,478	-			
Power production	820,0	MWe			
Fuel price	2,00	\$/GJ			
Hours per year	8000	hr/year			
Remarks:					
Overnight construction costs (OCC)	489,3	M\$			Specific costs \$/kWe = 596,7 (ref. 1)
Fees	9,8	M\$			2 % of OCC
Land purchase, site preparation	24,5	M\$			5 % of OCC
Contingencies	48,9	M\$			10 % of OCC
<b>Total installed costs</b>	<b>572,5</b>	<b>M\$</b>			
Allowances during construction					
Discount rate		0,05	0,10		1/year
1st year	0,40	0,420	0,440		
2nd year	0,60	0,600	0,600		
Construction period factor		1,020	1,040		
<b>Total capital requirement</b>	<b>583,9</b>	<b>595,4</b>	<b>M\$</b>		
Operating costs					
Maintenance	9,8	M\$/year			2 % of OCC
Labour	3,0	M\$/year			(ref. 1)
Waste disposal	0,0	M\$/year			(ref. 1)
Chemicals & consumables	5,8	M\$/year			(ref. 1)
Insurance & taxation	9,8	M\$/year			2 % of OCC
<b>Total operating costs</b>	<b>28,4</b>	<b>M\$/year</b>			
<b>Fuel costs</b>	<b>98,9</b>	<b>M\$/year</b>			

Table A5

Table A.5 **Plant economic data**

<b>Unit:</b>		<b>Carbon black &amp; Hydrogen plant</b>			
Fuel usage, LHV	2624	MWth			
Fuel price	2,00	\$/GJ	Natural gas		
Hydrogen production	12,55	kg/s			
Carbon black production	41,48	kg/s			
Power requirement	480	MWe			
Hours per year	8000	hr/year			
Remarks:					
Overnight construction costs (OCC)	1450,0	M\$			Specific costs \$/ton C = 1210 (ref. 2)
Fees	29,0	M\$			2 % of OCC
Land purchase, site preparation	72,5	M\$			5 % of OCC
Contingencies	145,0	M\$			10 % of OCC
<b>Total installed costs</b>	<b>1696,5</b>	<b>M\$</b>			
Allowances during construction					
Discount rate		0,05	0,10		1/year
1st year	0,40	0,420	0,440		
2nd year	0,60	0,600	0,600		
Construction period factor		1,020	1,040		
<b>Total capital requirement</b>	<b>1730,4</b>	<b>1764,4</b>	<b>M\$</b>		
Operating costs					
Maintenance	29,0	M\$/year			2 % of OCC
Labour	2,1	M\$/year			(ref. 1)
Waste disposal	0,0	M\$/year			(ref. 1)
Chemicals & consumables	0,0	M\$/year			(ref. 1)
Insurance & taxation	29,0	M\$/year			2 % of OCC
<b>Total operating costs</b>	<b>60,1</b>	<b>M\$/year</b>			
<b>Fuel costs</b>	<b>151,1</b>	<b>M\$/year</b>			



Table A6

Table A.6 **Plant economic data**

Unit:	Methanol synthesis plant			
Feed CO2	85,6	kg/s		
Feed H2	12,55	kg/s		
Production Methanol	58,05	kg/s		
Power production	71	MWe		
Hours per year	8000	hr/year		
Remarks:				
Overnight construction costs (OCC)	420,0	M\$	Based on investment Methanol Synthesis Delfzijl	
Fees	8,4	M\$	2 % of OCC	
Land purchase, site preparation	21,0	M\$	5 % of OCC	
Contingencies	42,0	M\$	10 % of OCC	
<b>Total installed costs</b>	<b>491,4</b>	<b>M\$</b>		
Allowances during construction				
Discount rate		0,05	0,10	1/year
1st year	0,40	0,420	0,440	
2nd year	0,60	0,600	0,600	
Construction period factor		1,020	1,040	
<b>Total capital requirement</b>	<b>501,2</b>	<b>511,1</b>	<b>M\$</b>	
Operating costs				
Maintenance	8,4	M\$/year	2 % of OCC	
Labour	2,1	M\$/year	(ref. 1)	
Waste disposal	0,0	M\$/year	(ref. 1)	
Chemicals & consumables	0,0	M\$/year	(ref. 1)	
Insurance & taxation	8,4	M\$/year	2 % of OCC	
<b>Total operating costs</b>	<b>18,9</b>	<b>M\$/year</b>		
<b>Fuel costs</b>	<b>N.A.</b>	<b>M\$/year</b>		

## 7.3 Sensitivity analysis

### 7.3.1 Carnol process: case coal fired power plant

The sensitivity analyses show how the cost of carbon black react to varying methanol and natural gas prices.

The following graphs show the results of these calculations for the Carnol process based on a coal fired power plant.

Figure 6.4.1 shows that at low methanol prices the cost of carbon black increases substantially. In case the methanol price is reduced to 0,10 \$/kg (base case price methanol 0,15 \$/kg), the cost of carbon black will increase from \$ 350 per ton to \$ 425 per ton.

Figure 6.4.2 shows the effect of the natural gas price on the cost of carbon black.

An increase of the natural gas price from \$ 2 / GJ to \$2,5 / GJ will only marginally effect the price of carbon black. The price of carbon black will increase from \$ 350 per ton to \$ 380 per ton.

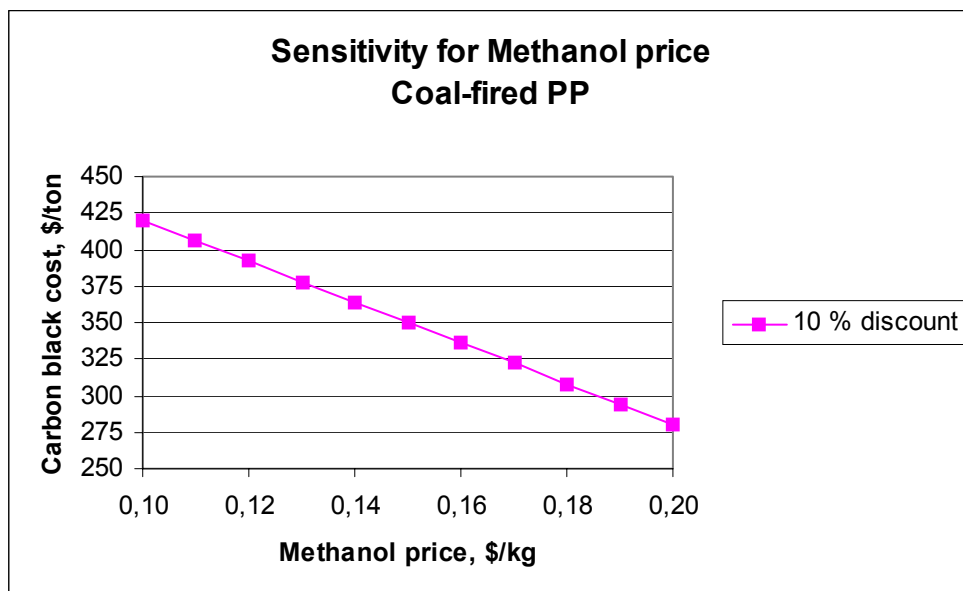


Figure 6.4.1 Carbon black price versus methanol price.

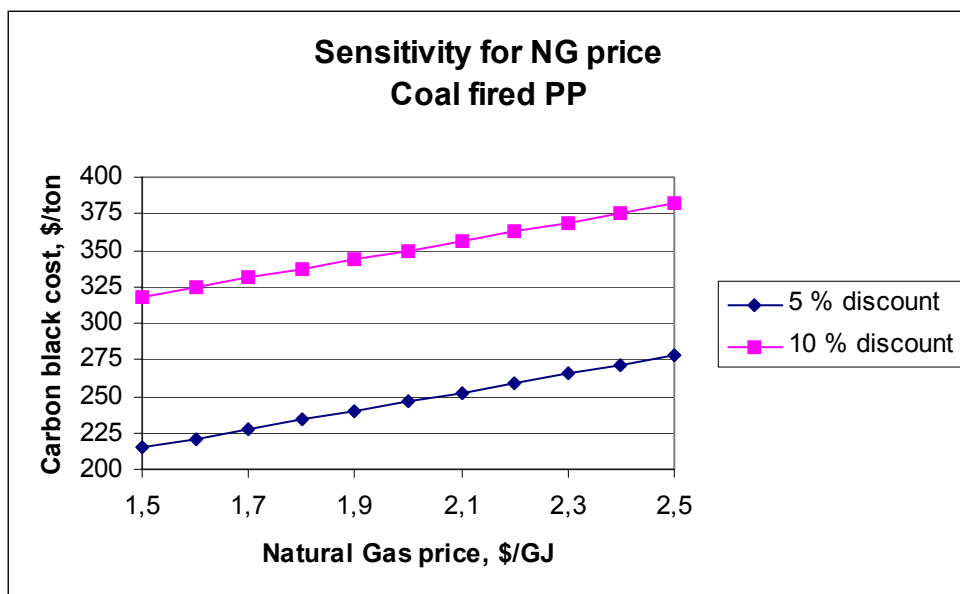


Figure 6.4.2 Carbon black price versus natural gas price.

### 7.3.2 Carnol process: case gas fired power plant

The sensitivity analyses show how the cost of carbon black react to varying methanol and natural gas prices.

The following graphs show the results of these calculations for the Carnol process based on a gas fired power plant.

Figure 6.4.3 shows that at low methanol prices the cost of carbon black increases substantially. In case the methanol price is reduced to 0.10 \$/kg ( base case price methanol 0.15 \$/kg) , the cost of carbon black will increase from \$ 300 per ton to \$ 360 per ton.

Figure 6.4.4 shows the effect of the natural gas price on the cost of carbon black.

An increase of the natural gas price from \$ 2 / GJ to \$ 2.5 / GJ will have a substantial effect on the price of carbon black. The price of carbon black will increase from \$ 225 per ton to \$ 275 per ton.

The reason for this is the fact that in this case both hydrogen and CO<sub>2</sub> are produced from the feedstock gas.

This is different from the previous case where only hydrogen is produced from gas.

In figure 6.4.5 shows the effect of the natural gas price on the cost of carbon dioxide avoided.

At a nominal gas price of \$ 2 / GJ the cost of carbon dioxide avoided amount \$ 62 per ton.

At a gas price of \$ 2.5 / GJ the cost of carbon dioxide avoided increases to \$ 76 per ton.

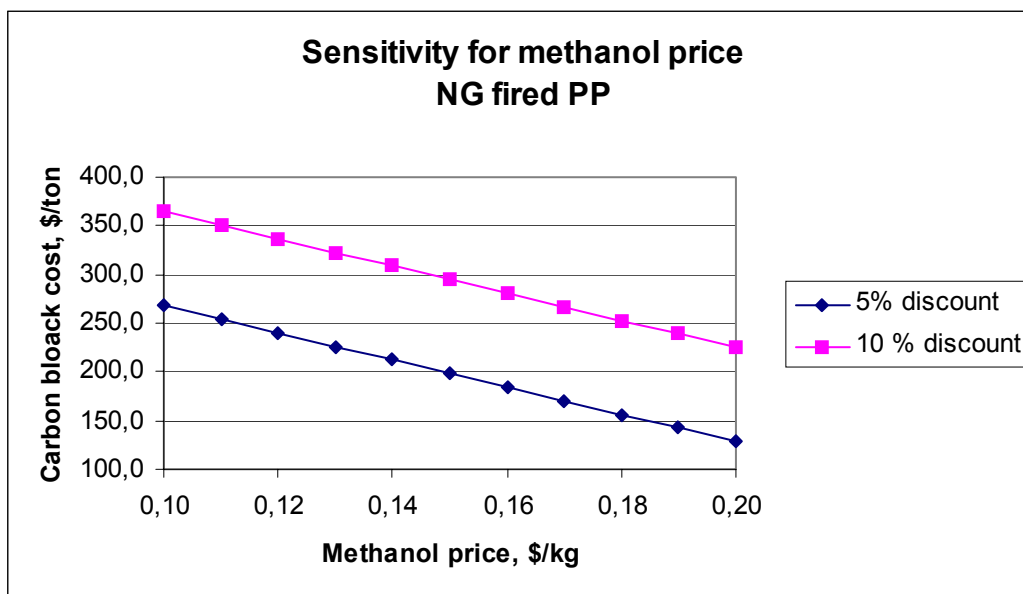


Figure 6.4.3 Carbon black price versus methanol price.

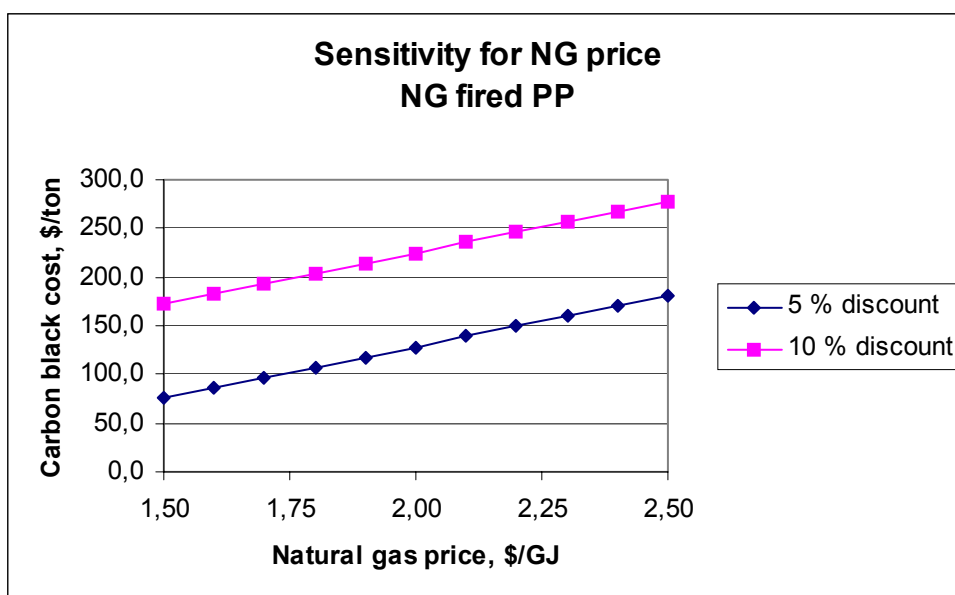


Figure 6.4.4 Carbon black price versus natural gas price.

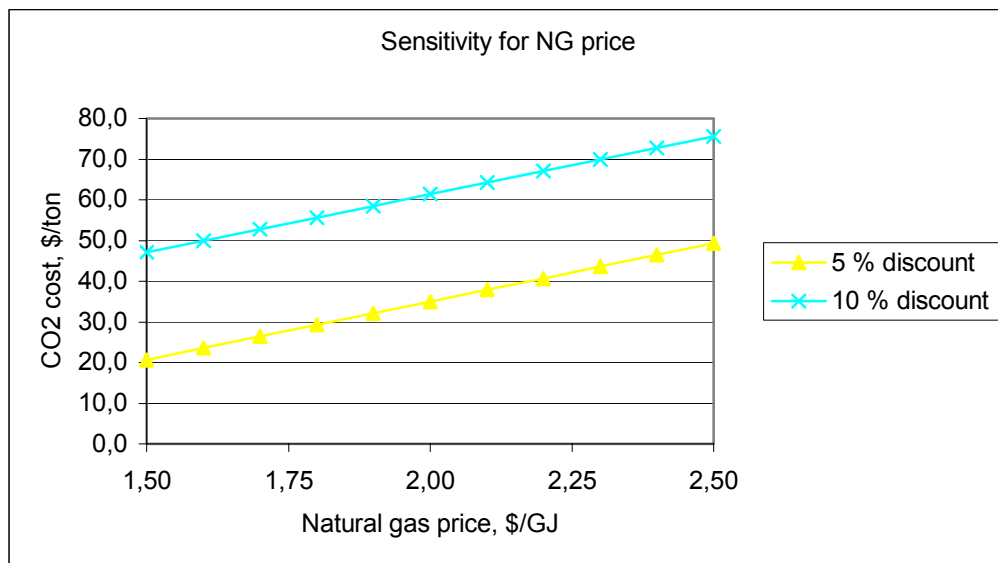


Figure 6.4.5 Cost of CO<sub>2</sub> avoided versus natural gas price.

## 7.4 Conclusion

Because the Carnol process on basis of a coal-fired power plant requires a net import of power, this concept is not workable. The overall thermal efficiency, based on the heating values of methanol and carbon is 66 % (LHV). In case only the heating value of methanol is accounted for, the thermal efficiency drops to 30 % (LHV).

When in the Carnol process, power is generated by natural gas, the thermal efficiencies are respectively 67 % (LHV) and 35 % (LHV). In this concept the Carnol process exports power. Although this concept is workable, the total process has the disadvantage of low overall efficiency.

## 8. REFERENCES

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## APPENDIX 1. METHANOL SYNTHESIS

### 1.1 Methanol synthesis background

The amount of CO<sub>2</sub> captured (85,6 kg/sec.) is the basis of the capacity of the Carnol process. The hydrogen production facility ( Kvaerner process fig.4 ) is designed to produce the required amount of hydrogen ( 12,55 kg/sec.) to convert the available amount of CO<sub>2</sub> into methanol. This is accomplished in the methanol synthesis plant where CO<sub>2</sub> is catalytically hydrogenated. The methanol synthesis takes place at low pressure (50 bar) according to the following chemical reaction:



The state of the art technologies use carbon monoxide and hydrogen as feedstock for the production of methanol. By replacing carbon dioxide by carbon monoxide in the synthesis, the carbon conversion efficiency decreases.

Saito et al. (Ref.[8]) have investigated the methanol synthesis from hydrogen and pure CO<sub>2</sub> with a Cu/ZnO multi-component catalyst at moderate pressures ( 50 bar) and temperatures (250°C). The hydrogenation reaction was carried out in a packed-bed reactor with a feed ratio H<sub>2</sub>/CO<sub>2</sub> = 3.1. No additional energy was required due to the exothermic character of the reaction. The catalyst showed good methanol activity and selectivity. The catalyst was highly active and stable for a long period. The main products were methanol, CO and water. Methane and dimethylether were also detected in the products, but the selectivity for the by-products was less than 0,1 %.

As the conversion of CO<sub>2</sub> to methanol at reaction equilibrium is very low, experiments were carried out in a recycle reactor, which showed a higher conversion. In a gas phase methanol synthesis from CO<sub>2</sub> and H<sub>2</sub> a large quantity of unconverted gas should be recycled. 1.2 Process description methanol synthesis.

### 1.2 Process description methanol synthesis

Refer to Block Diagram fig. 1.1 that depicts the conversion of CO<sub>2</sub> and H<sub>2</sub> into methanol.

Hydrogen from the Kvaerner process, which is available at a pressure of 15 bara, is compressed to the required process pressure of 55 bara. Carbon dioxide is available at battery limit at 55 bara. (The design of coal fired power plant with CO<sub>2</sub> capture assumes a CO<sub>2</sub> pressure of 110 bara, pressure benefit is accounted for in the energy balance of the methanol synthesis plant).

Make up gas is mixed with the recycle gas and preheated with the hot outlet stream from the reactor to a reaction temperature level of 225°C.

Because the reaction is strongly exothermic, the temperature rise is limited to 25°C by injection of cold gas at several points in the reactor.

The hot outlet stream is cooled with the incoming gas stream. Heat is removed by generating MP steam. This steam is used as heating medium for the methanol distillation.

By cooling with cooling water the temperature of the reactor outlet stream is further reduced to 40 °C. By reducing the pressure to 5 bara, gas and liquid (methanol and water) are separated in a liquid gas separator.

Gas from the separator, mainly hydrogen and carbon dioxide, are routed back to the recycle compressor.

A portion of the gas is purged and routed to a combined cycle unit for power generation.

The liquid from the separator (raw methanol) is routed to a two columns distillation system. In the first column mostly referred to as topping column light ends are expelled overhead. The

bottom product is fed to the refining column in which the pure methanol is obtained at the column top and water in the column bottom. Some high boiling compounds are withdrawn from a side outlet below the feed tray.

The process was simulated with the Aspen Plus flow-sheeting program.

Stream data were generated by simulating the process with the flowsheeting program AspenPlus. Stream numbers refer to block diagram fig. 1.1.

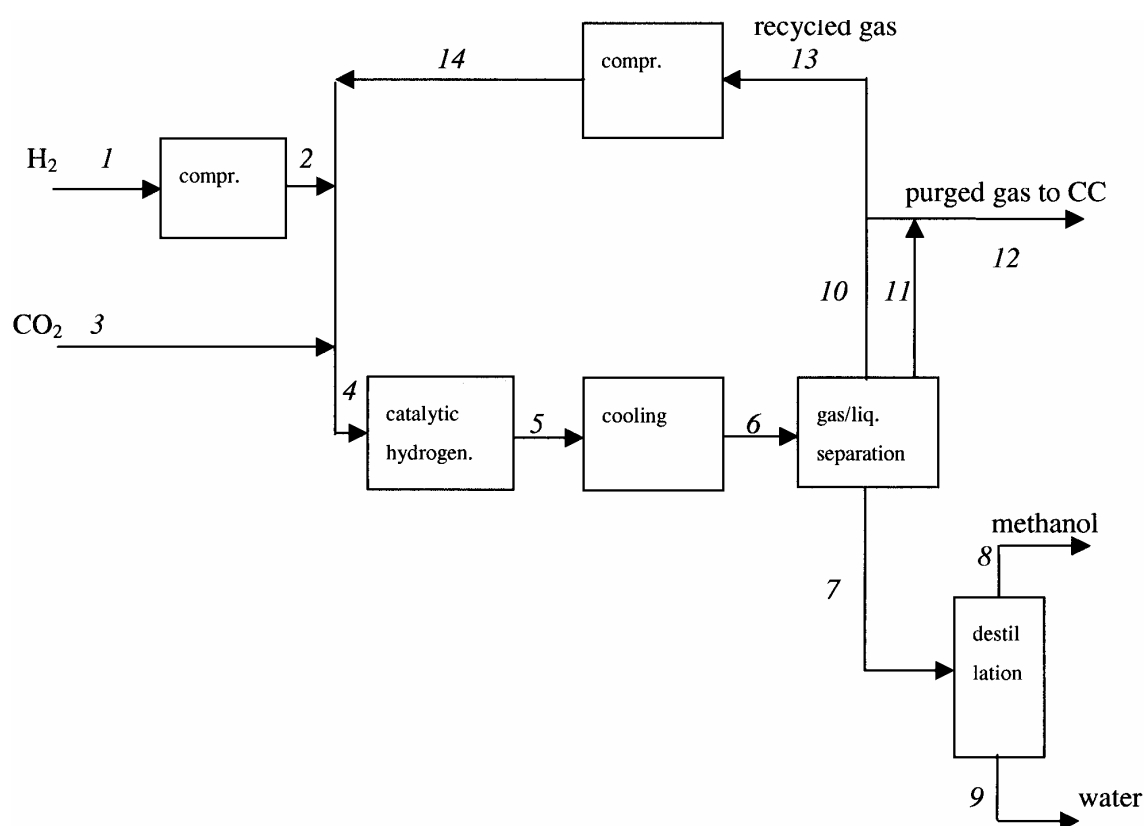


fig. 1.1 the basic process scheme of catalytic hydrogenation of CO<sub>2</sub>.



<b>Table A-1</b> <b>Stream data methanol synthesis</b>							
Component	Stream number and description						
	1 H <sub>2</sub> from Kværner plant	2 H <sub>2</sub> feed into recycle gas	3 CO <sub>2</sub> feed into recycle gas	4 Feed reactor	5 Reactor product	6 Reactor product to g/l separator	7 Crude methanol
	Mol%	Mol%	Mol%	Mol%	mol%	mol%	Mol%
H <sub>2</sub>	100	100	0	84.83	77.95	idem	0
CO <sub>2</sub>	0	0	100	13.4	9.67	←	0
Methanol	0	0	0	0.3	5.57		49.7
CO	0	0	0	1.4	1.6		0
H <sub>2</sub> O	0	0	0	0.07	5.2		50.3
Methane	0	0	0	0	0		0
Total kg/s	12.55	12.55	85.60	313.7	313.7	313.7	90.74
Bar abs.	15	55	55	55	50	50	1.6
°C	40	129	40	59	250	40	40
Mol wt.	2.01	2.01	44.0	8.1	8.97	8.97	24.99
MW	41.78	64.83	-749.2	-1800	-1800	-1890	-740

<b>Table A-1, cont.</b> <b>Stream data methanol synthesis</b>							
Component	Stream number and description						
	8 Methanol	9 Water	10 Off gas 1	11 Off gas 2	12 Purge gas	13 Recycled gas	14 Recycled gas ex. Compressor
	mol%	Mol%	mol%	mol%	mol%	mol%	Mol%
H <sub>2</sub>	0	0	87.1	4.8	84.7	87.1	87.1
CO <sub>2</sub>	0	0	10.6	93.72	13.0	10.6	10.6
Methanol	100	traces	0.4	1.1	0.4	0.4	0.4
CO	0	0	1.8	0.17	1.8	1.8	1.8
H <sub>2</sub> O	traces	100	0.1	0.2	0.1	0.1	0.1
Methane	0	0	0	0	0	0	0
Total kg/s	58.05	32.69	221.9	1.09	7.41	215.58	215.58
Bar abs.	1.0	1.0	50	50	50	50	55
°C	58	45	40	160	44	40	52
Mol wt.	32	18	7.09	41.77	8.07	7.09	7.09
MW	-300	-430	-1140	-9.45	-43	-1110	-1100

## APPENDIX 2. CRACKING OF VARIOUS FEEDSTOCKS FOR THE PRODUCTION OF HYDROGEN AND CARBON

### 1.1 Thermal cracking of various feedstock's

In case hydrogen is the desired product methane is a nice feedstock because of its high hydrogen content but it is a difficult (hydrocarbon) nut to crack. Therefore also benzene, naphthalene and anthracene have been studied as feedstock's for thermal cracking (see table below). However it appears that the latter two feedstock's also require temperatures of 1100 °C in order to obtain hydrogen purities of over 98-99%. In the table below some comparative data are given including data for a bituminous coal and for biomass.

The energy required for cracking is much lower for the highly aromatic feedstock's than for methane and certainly in case carbon is the required product such feedstock's are much to be preferred. But also for hydrogen the energy required for cracking methane is the highest.

The cost of the feedstock will probably determine which feedstock will become the winner.

For all the above feedstock's high temperatures of 1100 °C are thermodynamically required in order to produce reasonable pure hydrogen. Reducing the temperature to 900 °C reduces the hydrogen purity to about 97% for benzene, naphthalene and anthracene and to below 95% for methane. These figures are all for 5 bar pressure. In order to avoid excessive compression costs it is unlikely that lower pressures will be applied although –at least thermodynamically- these result in somewhat higher purities.

At such high temperatures the reactions are already proceeding pretty fast. This fact together with the thermodynamically requirement of a high temperature for purity reasons makes that there is little scope for catalytic processes for these applications. Much the same applies to coal or heavy oil gasification. When the gas is to be used as syngas temperatures of at least 1300 °C are required in order to produce a gas with a low CO<sub>2</sub> content and without tarry by-products.

### 1.2 Cracking of oxygen containing feedstock's

Cracking of oxygen containing feedstock's as coal and biomass (which is but a very young coal) is more complex than cracking of pure hydrocarbons. The main difference is that no conditions exist at which a more or less pure hydrogen stream can be produced. The gas always contains 30-50% mole CO that implies that for the production of hydrogen a shift conversion is required. For syngas applications very little or no shift conversion is required. Further sulphur compounds have to be removed and as well as other impurities as nitrogen compounds and compounds of trace elements. The carbon that is produced always contains all the ash present in the feedstocks.

### Thermal cracking of various feedstocks

Feedstock	Methane	Benzene	Naphtalene	Anthracene	Bituminous Coal	Dry biomass
Preheat feedstock, °C	500	500	500	500	25	25
Temperature, °C	1100	1100	1100	1100	1000	900
Pressure, bara	5	5	5	5	1	1
Hydrogen, %mole	98.4	99.2	99.3	99.4	70.6	53.4
CO, %mole	0	0	0	0	27.1	45.1
H <sub>2</sub> / feedstock, Kg/kg <sup>*)</sup>	0.24	0.076	0.062	0.056	0.08	0.11
Carbon/ Feedstock, Kg/kg	0.73	0.92	0.93	0.94	0.53	0.22
Energy per kg H <sub>2</sub> , MJ <sup>*)</sup>	34.2	13.5	22.0	16.0	36.3	35.1
Energy per kg carbon, MJ	11.5	1.1	1.5	1.0	5.5	17.5

<sup>\*)</sup> For coal and biomass the CO is included and expressed as kg H<sub>2</sub> equivalent assuming that for each mole of CO one mole of H<sub>2</sub> is produced.

## APPENDIX 3. BASIC DATA

### 1. Process data

#### 1.1 Natural gas specification

<b>Components</b>	<b>volume %</b>
Methane	83.9
Ethane	9.2
Propane	3.3
Butane +	1.4
CO <sub>2</sub>	1.8
Nitrogen	0.4
Sulphur (as H <sub>2</sub> S)	4 mg/Nm <sup>3</sup>
LHV	46.899 MJ/Nm <sup>3</sup>

The original specification gives a lower heating value of 36.25 MJ/Nm<sup>3</sup>. This is not consistent with the given component specification.

The gas specification is based on a pipeline quality gas from the southern part of the Norwegian off-shore reserves.

#### 1.2 Coal specification

<b>Proximate analysis</b>	<b>weight %</b>
Coal (dry, ash-free)	78.3
Ash	12.2
Moisture	9.5
Gross CV	27.06 MJ/kg
Net CV	25.87 MJ/kg

The coal specification is based on a open-cut coal from eastern Australia.

#### 1.3 Methanol

Heating value: 19,8 MJ/kg

#### 1.4 Efficiency of power generation (LHV)

##### 1.4.1 Natural gas fired combined cycle

Electrical efficiency = 56.2 %.

##### 1.4.2 Natural gas fired combined cycle with CO<sub>2</sub> capture

Electrical efficiency = 47.8 %.

##### 1.4.3 Coal fired power plant with CO<sub>2</sub> capture

Electrical efficiency = 33.0 %.

### 2. Economic data

Gas price: \$ 2.0 / GJ.

Coal price: \$ 1.5 / GJ.

Methanol price: \$ 150 / ton.

Power cost: \$ 0.0323 / kWh.

For the economical evaluation the technical and financial assessment criteria are used as specified in the IEA Technical Specification, appendix I.