

**The potential for  
application of CO<sub>2</sub>  
capture and storage  
in EU oil refineries**



# The potential for application of CO<sub>2</sub> capture and storage in EU oil refineries

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## ABSTRACT

CO<sub>2</sub> Capture and Storage (CCS) is a potential route to large scale reduction of CO<sub>2</sub> emissions to the atmosphere from large power generation and manufacturing facilities. It does, however, raise a number of technological, economic and legal challenges. This report reviews the state of knowledge in the areas of transport and storage of CO<sub>2</sub>, to focus mainly on CO<sub>2</sub> capture in oil refineries. Sources of refinery CO<sub>2</sub> emissions, the capture technologies that can potentially be deployed in that environment and the particular issues facing refiners in the application of CCS are discussed from both a technological and an economic point of view. One important conclusion is that the volumes and unit locations for CO<sub>2</sub> production in refineries are not conducive to CCS projects in individual refineries and will require alliances with other large CO<sub>2</sub> producers, particularly the power industry, in order to be commercially justified.

## KEYWORDS

CCS, carbon dioxide, capture, refinery, processes, hydrogen, geological, storage, aquifer, EOR, EGR

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## SUMMARY

### *Refinery CO<sub>2</sub> emissions in perspective*

Oil refineries require energy to convert crude oil into marketable products. In the process they emit CO<sub>2</sub> through both fuel burning and production of the hydrogen required by the conversion processes. The refining sector currently produces approximately 6% of total European industrial CO<sub>2</sub>, i.e. 3-4% of all anthropogenic emissions in Europe.

Individual refineries are fairly large CO<sub>2</sub> emitters but are still, in general, smaller emitters than power plants. Unlike the latter, refineries emit CO<sub>2</sub> from a multiplicity of dispersed and often relatively small sources which adds a level of complexity to the capture process, particularly for post-combustion capture technologies.

Refinery CO<sub>2</sub> emissions are dominated by those from process furnaces and utilities. In practice heat and power plants within the refinery are the largest single sources, as a moderately complex refinery may have 20 to 30 separate process heaters often spread over a fairly large area.

With the exception of some hydrogen plants, CO<sub>2</sub> is emitted in flue gases and off-gases with fairly low CO<sub>2</sub> concentrations, in the order of 3 – 12 %v/v CO<sub>2</sub>.

### *Refinery CO<sub>2</sub> capture and associated combustion technologies*

There are essentially two routes to CO<sub>2</sub> capture: either leaving the combustion technology unchanged and capturing from large volumes of flue gases with low CO<sub>2</sub> concentrations or changing the combustion technology to directly create highly concentrated CO<sub>2</sub> streams.

Capture from flue gases relies on existing chemical absorption technology but would have to be deployed at an as yet undemonstrated scale. Impurities and contaminants commonly found in flue gases would also present technical challenges. Major breakthroughs in the absorption technology are needed to achieve larger cost and energy reductions. It is critical that there is a mechanism in place which provides incentives to implementers of early demonstration CCS projects, such that the industry can benefit from experience and reduce the cost of future projects.

Capture is not only costly from a capital perspective but also requires a large amount of extra energy mostly for desorbing CO<sub>2</sub> from the solvent, which in itself would lead to extra CO<sub>2</sub> emissions. There is therefore a significant distinction to make between “CO<sub>2</sub> avoided”, i.e. the amount of CO<sub>2</sub> emissions prevented from reaching the atmosphere, and “CO<sub>2</sub> captured”, i.e. the total amount of CO<sub>2</sub> captured and compressed for transport. CO<sub>2</sub> avoided is calculated as the difference between the CO<sub>2</sub> captured and the CO<sub>2</sub> generated by the capture and compression process.

Alternative combustion technologies include oxy-fuel combustion and pre-combustion. Oxy-fuel combustion involves replacing air by pure oxygen thereby eliminating nitrogen from flue gases. It has not been widely deployed in industry thus far and brings significant technological challenges. It has gained interest mostly in the power industry for grass roots power stations and industries such as glass, iron and steel. Retrofitting the larger number of individual refinery process heaters will be complex and possibly expensive. Pre-combustion consists of partially or

completely decarbonising the refinery fuel to burn hydrogen. In practice it consists of gasification of a heavy feedstock or conversion of fuel gas to syngas followed by conversion to hydrogen via the shift reaction. Although the full decarbonised fuel chain is not utilised today, the process building blocks are available as commercial technologies. These, however, can be complex and expensive installations. Retrofitting refinery heaters to burn hydrogen-enriched fuel gas could require extensive modifications, depending on the hydrogen concentration.

Whatever the option selected, CO<sub>2</sub> capture would result in high cost and significant extra energy consumption and CO<sub>2</sub> emissions. Adding large capture facilities with hitherto untested technology at the required scale could also affect the reliability of refinery installations. Although some of the developments in CCS for the power sector could be implemented in the refining sector, there is a need for projects incorporating technology developed to address the specific challenges of refineries (specific impurities, lack of free space, high reliability, low retrofitting impact, energy consumption and energy integration).

Since energy integration is much easier on power plants (which are steam and electricity producers) than in refineries (which will need to install new utilities plants for the CCS energy demand), the need for improvement in energy consumption for CCS technology will be greater in refineries than in power plants, requiring special effort and support to be given to developing technologies that tackle this problem.

### **CO<sub>2</sub> transport**

CO<sub>2</sub> can be transported in bulk either as a supercritical liquid in pipelines or as a refrigerated liquid in ships. There is relevant commercial experience for both. For large quantities and short to medium distances pipeline is the most cost-effective transport method. Shipping is unlikely to be justifiable long term except for very long distances and coastal or near coastal locations.

Quality specifications for the CO<sub>2</sub> streams will need to be developed addressing all relevant impacts including corrosion. Transport and handling of large quantities of CO<sub>2</sub> near populated areas will raise safety, and therefore public acceptance, issues.

Because of the cost and complexity of major pipeline projects, it will make economic and practical sense to build large pipelines serving several users, most probably around large single emitters such as power stations or in industrialised areas.

### **CO<sub>2</sub> storage**

Large amounts of CO<sub>2</sub> can potentially be stored in various geological formations in Europe. Most of the potential CO<sub>2</sub> storage capacity in Europe is located offshore (68% of the total).

Storage in deep saline aquifers is the most promising in terms of capacity. CO<sub>2</sub> can also be permanently stored in fully depleted oil and gas fields which are generally well known and documented, although storage capacity would be less than in aquifers.

CO<sub>2</sub> injection into oil and gas fields for Enhanced Oil/Gas Recovery (EOR/EGR) is a fully developed technique through which some CO<sub>2</sub> can be retained. In contrast with North America where EOR and EGR are widely practised, it is anticipated that the use of CO<sub>2</sub> for EOR/EGR is unlikely to be economic in Europe if the crude price is consistently below 100\$/bbl.



The integrity of storage sites will need to be continuously monitored using a range of techniques and protocols, many of which are already well known.

### ***Refinery CCS costs***

The cost of refinery CCS is expected to be significantly higher than the current estimates of \$60-80 (43-57 €) per tonne CO<sub>2</sub> avoided for CCS in coal-fired power plants. The estimated cost of capture (typically about 80% of the total CCS cost) will vary widely, depending on each refinery's size, complexity and location. The capture cost is also highly dependent on the fraction of the total emissions to be captured, as refineries usually have a small number of large emission sources and a large number of smaller, low concentration sources. The capture cost for the first 50% of the total CO<sub>2</sub> emissions of a large, complex refinery has been estimated by Shell [19] at 90-120 € per tonne CO<sub>2</sub> avoided (2007 basis). The cost will be considerably higher for capture of the remaining 50% of emissions. Smaller, less complex refineries would not benefit from the economy of scale and unique configuration of the refinery in the Shell study. Taking into account the costs of transport, storage and monitoring, and escalating to 2010 prices, the total CCS cost estimate for the Shell example refinery would be in the range 132-178 € per tonne CO<sub>2</sub> avoided (2010 basis).

Transport of the captured CO<sub>2</sub> to storage sites would require additional investment in pipeline infrastructure. Based on a 200 km pipeline, investment for transport could be in the region of 220 M€ (2009 basis) although actual cost per tonne transported would be highly dependent on volume. The development of shared infrastructure with other large emitters could significantly improve the economics of CO<sub>2</sub> transport.

With the current lack of experience of large-scale CCS projects in refineries and therefore limited understanding of the cost implications, there are wide variations in published cost estimates. Power station demonstration projects will partially address this lack of experience and highlight the major technology issues. Building on this experience, refinery pilot and demonstration projects could then help to assess the most attractive technologies and to improve the understanding of the true cost of CCS in refining and its potential applicability in particular refining applications.

A detailed estimate of refinery CCS costs is beyond the scope of this report, requiring rigorous analysis of a wide range of variables in order to place the costs in their proper context. CONCAWE could consider the possibility of publishing a second report in the future with details of costs based on third-party estimates of a range of refinery configurations.



## 1. INTRODUCTION

CO<sub>2</sub> Capture and Storage (CCS) is one of the most promising routes to large scale reduction of CO<sub>2</sub> emissions to the atmosphere. Its deployment at large scale would make it possible to continue using fossil energy resources while meeting the challenging emission reduction targets that are widely believed to be necessary to avoid serious climatic consequences. A recent report by McKinsey and Company [18], states that CCS is the largest single lever for abating oil and gas emissions, if enough resources – both in terms of capital and engineering capacity – are made available.

CCS does, however, raise a number of technological, economic and legal challenges.

Technologies to collect, separate/capture, transport and inject CO<sub>2</sub> in geological structures are known and have all been applied in commercial ventures. Nonetheless, the scale required for widespread application of CCS and the need to combine all steps into a seamless chain raises significant technological, practical and regulatory challenges.

CCS will require capture equipment, transport infrastructure, injection and monitoring facilities – bringing high complexity and cost. Beside the extra investment costs there will also be additional operating costs as CCS will require additional resources, particularly energy. The extra expenses can only be justified if CO<sub>2</sub> has a sufficiently high long term price.

Underground storage of CO<sub>2</sub> over centuries raises specific legal issues regarding ownership, liabilities etc. Although governments and international institutions, particularly in Europe are working on the development of appropriate legal frameworks, operators do not currently have a clear picture of their short and long term legal positions.

This report focuses on the specific challenges faced by oil refineries in Europe for the capture of the CO<sub>2</sub> they emit during their normal operations, the availability of suitable storage sites within reasonable distances and the development of a transport infrastructure. Information in this report is based on various literature sources, particularly the comprehensive 2005 IPCC special report [1]. Some sources are already a few years old and, although technology has not evolved much over the period, costs have increased significantly.

After a short introduction to oil refineries and a discussion of their sources of CO<sub>2</sub> (**Section 2**), the main focus of this report is covered in **Section 3**: CO<sub>2</sub> capture technologies in a refinery environment. This is followed by brief reviews of transport and storage options (**Sections 4 & 5**) and the availability of storage sites in Europe, particularly looking at the possible implications for the quality of the required CO<sub>2</sub> streams. **Section 6** summarises the factors affecting cost and highlights the difficulties inherent to an assessment of the total cost of refinery CCS projects. Finally **Section 7** discusses specific issues that are considered crucial to the successful development of large scale integrated CCS projects.

## 2. REFINERY CO<sub>2</sub> EMISSIONS IN PERSPECTIVE

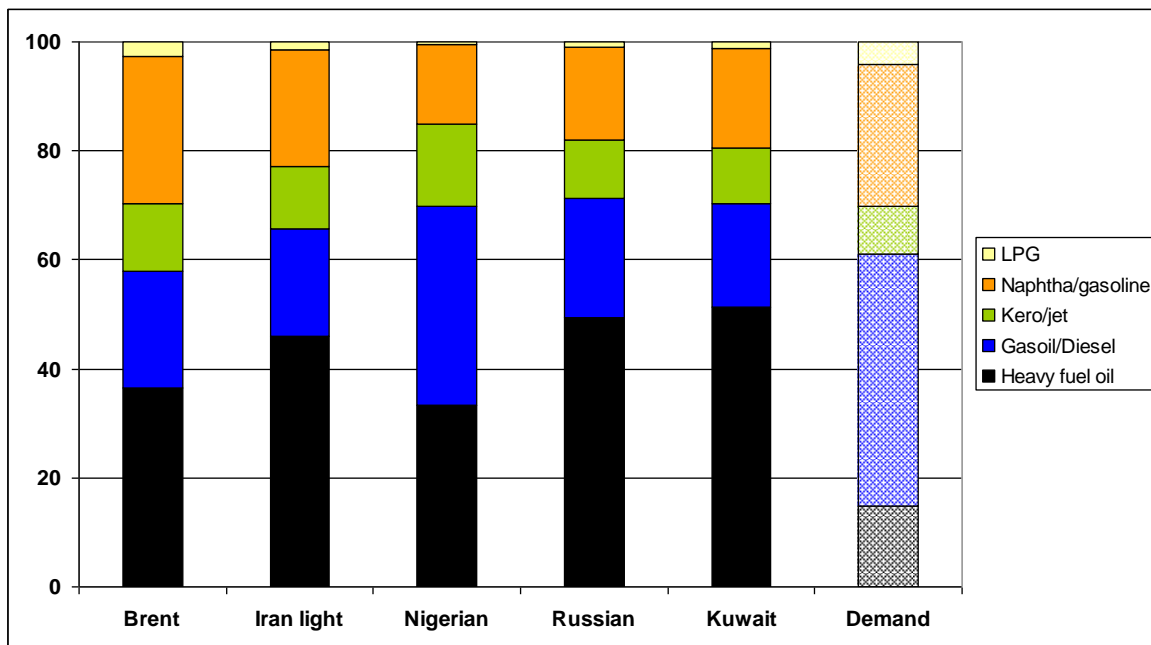
### 2.1. OIL REFINERIES, ENERGY AND CO<sub>2</sub> EMISSIONS

The purpose of an oil refinery is to turn crude oil into fit-for-purpose marketable products to be used as fuels, as feedstocks for the petrochemical industry and, in special applications, as lubricants, asphalts and solvents.

All crude oils are different ranging from the very light to the very heavy with very low to very high sulphur content. Over the years, demand for light products such as road or air transport fuels or petrochemical feedstocks have increased while markets for heavy fuel oils have decreased. The quality requirements of finished products has also gradually become much more stringent as illustrated for instance by the reduction of sulphur in transport fuel in Europe by two orders of magnitude within roughly a decade. At the same time the worldwide average crude oil has gradually become heavier and contains more sulphur.

As a result there is an increasing mismatch between the quantity and quality of products that can be directly distilled from crude oil and the market demand. As shown in **Figure 1**, even light crudes such as Brent (from the North Sea) do not contain the desired proportions of light and heavy components to match the EU market demand.

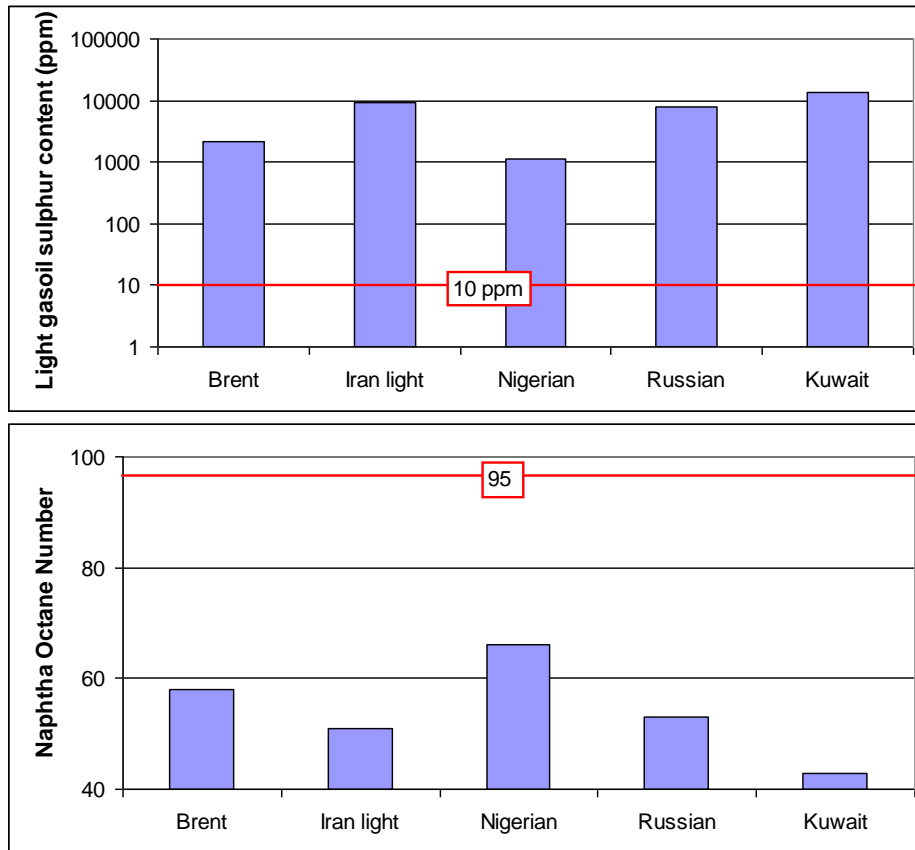
**Figure 1** Crude oil composition (in %wt) does not match the demand barrel



**Figure 2** illustrates the gap of two to three orders of magnitude between the sulphur content of virgin<sup>1</sup> gasoil and the EU diesel fuel 10 ppmw limit, as well as the low octane rating of virgin naphthas compared to what is required in automotive gasoline.

<sup>1</sup> The term "virgin" designates products that are distilled from crude oil but are otherwise unprocessed

**Figure 2** The quality of virgin products does not match market requirements



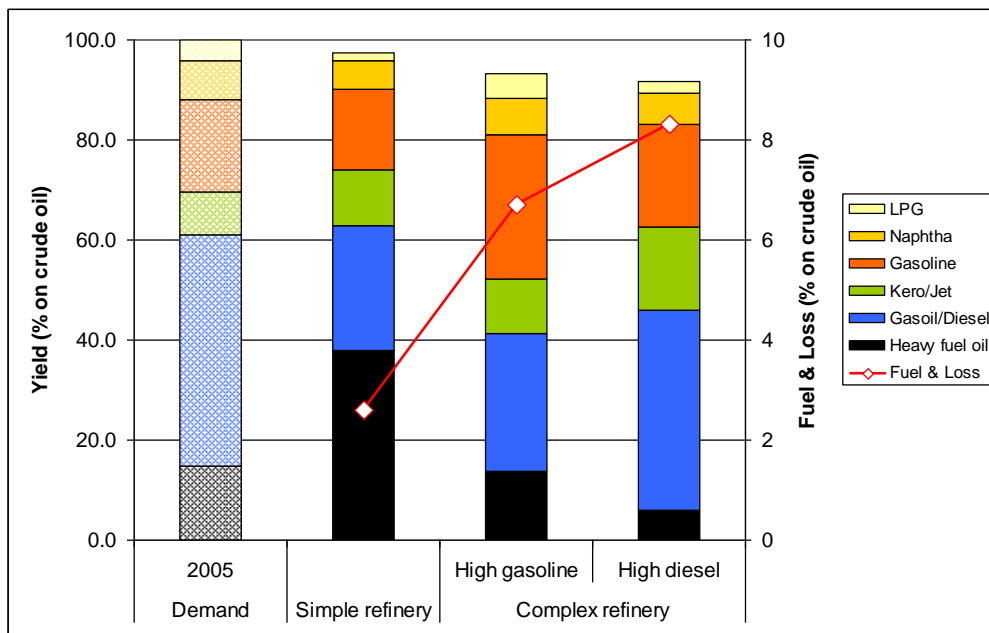
Refineries have therefore to fulfil several tasks:

- Separate the different fractions available in crude oils,
- Increase the yield of desired fractions through “conversion” or “cracking” of heavy molecules to match market demand,
- Achieve the desired quality of finished products by appropriate treating, reshaping of molecules and blending of components.

Many refineries also manufacture “specialty” products such as lubricating oils, bitumen, and solvents. In addition, many sites include or are integrated with petrochemical plants producing such products as aromatics and light olefins.

The resulting product package is significantly lighter than the original crude oil, contains much less impurities such as sulphur, and has a higher hydrogen to carbon ratio. Achieving this requires energy for physical separation, for key chemical reactions such as cracking of heavy molecules and production of hydrogen. **Figure 3** shows the relationship between product yield and energy consumption. A more complex refinery better matches market demand but has a higher energy consumption. EU refineries consume on average 6.5 to 7% of the calorific value of their crude intake (called “Fuel & Loss”) although actual values range from as low as 2-3% to over 8% depending on the actual complexity of each particular refinery.

**Figure 3** Complex refineries are needed to meet demand but require more energy



Refineries generate most of the energy they need internally through combustion of low value hydrocarbon by-product streams. Many refinery processes generate mixtures of light hydrocarbons (methane and ethane) which have little commercial value as such and have largely to be used as fuel on the premises. The Fluid Catalytic Cracking (FCC) process, used in many refineries worldwide and in Europe, generates its own energy by burning the coke deposited on a circulating catalyst during the cracking reaction. The balance of refinery fuel needs is provided by a combination of internally produced liquid components (mostly heavy residues) and/or imported streams such as natural gas. The latter is often used in order to meet air emissions regulations particularly with regards to SO<sub>x</sub> and particulate matter. In addition many refineries either import or export electric power and sometimes heat.

Combustion of hydrocarbons generates CO<sub>2</sub> and is responsible for the bulk of refinery CO<sub>2</sub> emissions. The relationship between energy consumption and actual CO<sub>2</sub> emissions depends on the type of fuel burnt, on the portion of the energy that is self-generated rather than imported and whether additional energy is exported.

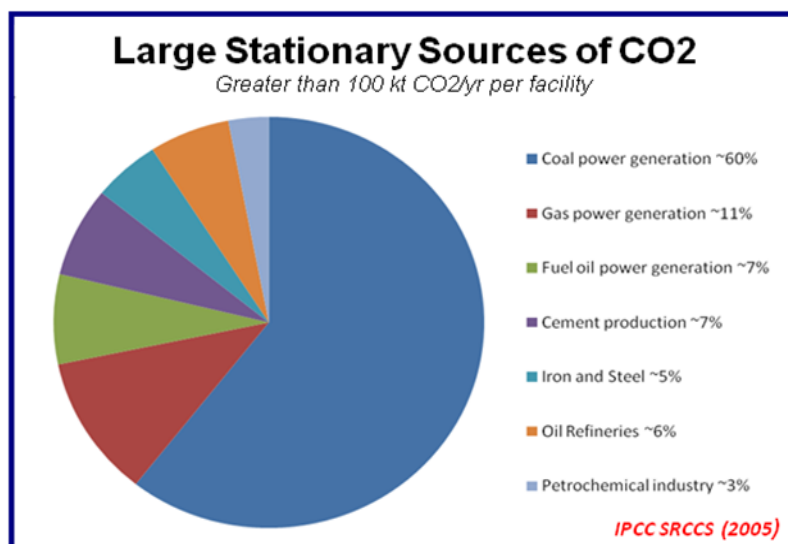
In addition to combustion, refineries generate CO<sub>2</sub> through decarbonisation of hydrocarbon molecules to produce the hydrogen needed to remove impurities such as sulphur or nitrogen and to saturate aromatics and/or olefins e.g. for the production of high quality diesel fuel. Traditionally refineries have generated hydrogen in the catalytic reformer which increases the octane rating of virgin naphtha by dehydrogenating linear and cyclic paraffins to aromatic molecules. The increasing need for more and cleaner light products, particularly diesel fuel, has increased the demand for hydrogen beyond what catalytic reformers can produce and refineries have gradually resorted to dedicated hydrogen production. By far the most widely used process for hydrogen production is methane steam reforming. Some refineries use partial oxidation of heavy residues to produce a mixture of carbon monoxide and hydrogen (so-called "synthesis gas") with subsequent conversion of the former to hydrogen and CO<sub>2</sub> by reaction with water vapour (the

“CO shift” reaction). These processes emit both “combustion” CO<sub>2</sub> (to supply the heat of reaction) and “chemical” CO<sub>2</sub> from decarbonisation of the hydrocarbon feedstock. Total emissions are in the region of 10 tonne CO<sub>2</sub> per tonne of hydrogen produced depending on the actual feedstock used.

EU refineries collectively emit some 140 to 150 Mt/a of CO<sub>2</sub> corresponding to just over 200 kg of CO<sub>2</sub> per tonne of crude processed on average. As in the case of energy, there are large variations between refineries and this number should only be used as a generic indicator of the CO<sub>2</sub> intensity of EU refineries rather than a metric applicable to individual plants. A moderately complex refinery with a capacity of 150,000 bbl/d will typically produce around 1-1.5 Mt/a of CO<sub>2</sub>. In refineries without hydrogen production facilities all emissions are from combustion (including FCC coke). “Chemical” CO<sub>2</sub>, as released by the decarbonisation of hydrocarbons, can be a very significant proportion of the total emissions of refineries with large hydrogen production facilities. On average it currently represents about 10% of total EU refinery emissions.

Although oil refineries are large CO<sub>2</sub> emitters, comparable to other heavy industries such as cement or iron and steel, all these are dwarfed by the power sector whose emissions are an order of magnitude larger (unlike the hydrocarbon fuels produced by a refinery, electricity is a fully decarbonised energy carrier for which all emissions occur at the production stage). As shown in **Figure 4**, power generation accounts for 78% of emissions from heavy industry in the EU compared to 6% from refineries. Individual power plants are also generally much larger emitters than individual refineries. A typical 1 GW power plant will emit around 4 Mt/a CO<sub>2</sub> if gas-fired and between 8 and 10 Mt/a if coal-fired, compared to typically 1-1.5 Mt/a for a medium size refinery.

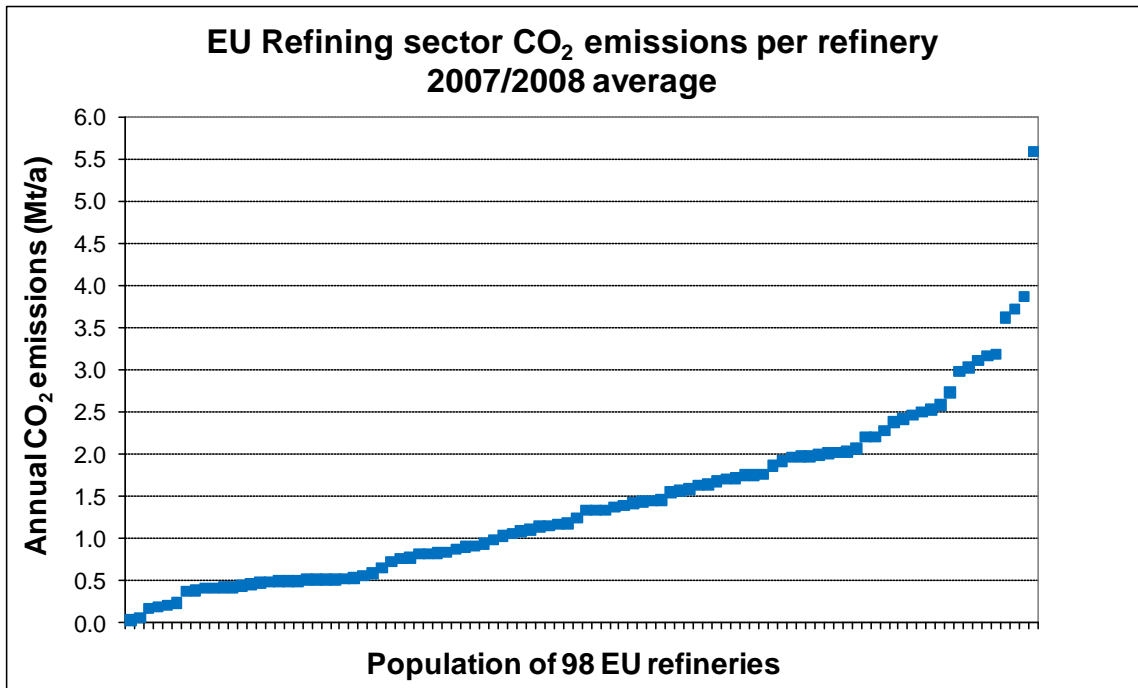
**Figure 4** EU large stationary sources of CO<sub>2</sub>



The range of CO<sub>2</sub> emissions from EU refineries is a reflection of the great diversity of their size and complexity. This is illustrated in **Figure 5**, showing the average emissions of each of the 98 mainstream EU refineries over the 2007-2008 period. The first quartile of EU refineries emit less than 550 kt/a CO<sub>2</sub>, and 50% of refineries emit less than 1.3 Mt/a. Only 8 refineries emit more than 3 Mt/a. The smallest and

least complex refineries are at the left of the graph. The CO<sub>2</sub> emissions from these refineries are very low but they are nevertheless greater than zero.

**Figure 5** CO<sub>2</sub> Emissions of EU refineries



**2.2. CURRENT AND FUTURE EU REFINERY CO<sub>2</sub> EMISSIONS**

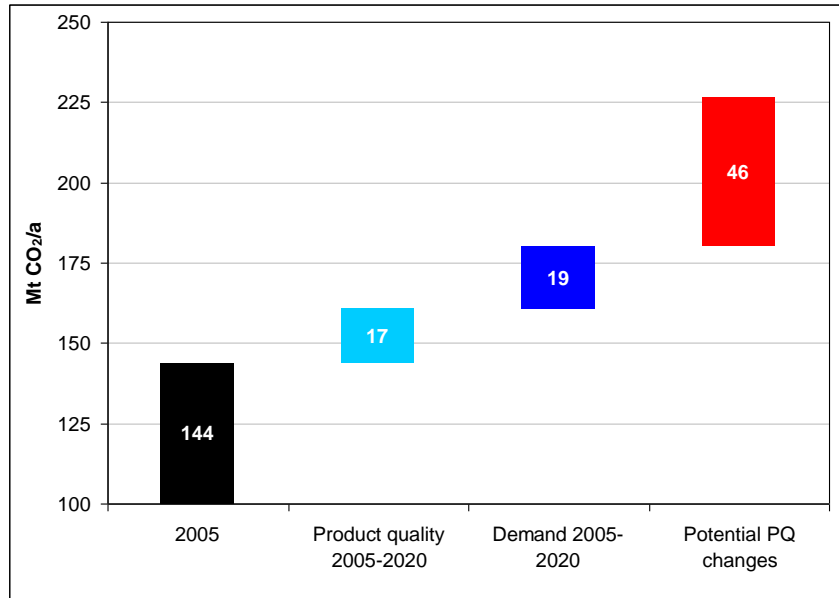
As mentioned above, EU refineries collectively emit 140-150 Mt/a of CO<sub>2</sub>. This has been increasing over the years under the combined influence of slowly increasing total product demand and much more stringent product quality requirements. This has happened worldwide but a factor peculiar to Europe is the very high, and still increasing, demand for “middle distillates” (gas oils, diesel fuel and jet fuel) relative to gasoline. This has created a serious imbalance between these two main product groups resulting in additional energy consumption and therefore CO<sub>2</sub> emissions.

In a 2008 study [2], CONCAWE simulated the foreseeable evolution of EU refinery CO<sub>2</sub> emissions based on independent demand projections and either already agreed or currently proposed product quality changes. **Figure 6** shows the forecast emissions in 2020 compared to 2005, with the increase broken down between product quality and demand changes and without any mitigation measures.

The trend is clearly upwards and could be exacerbated by additional product quality changes (shown in red) such as the conversion of all bunker fuels to distillates which, although they have not been legislated or formally proposed, have been debated.

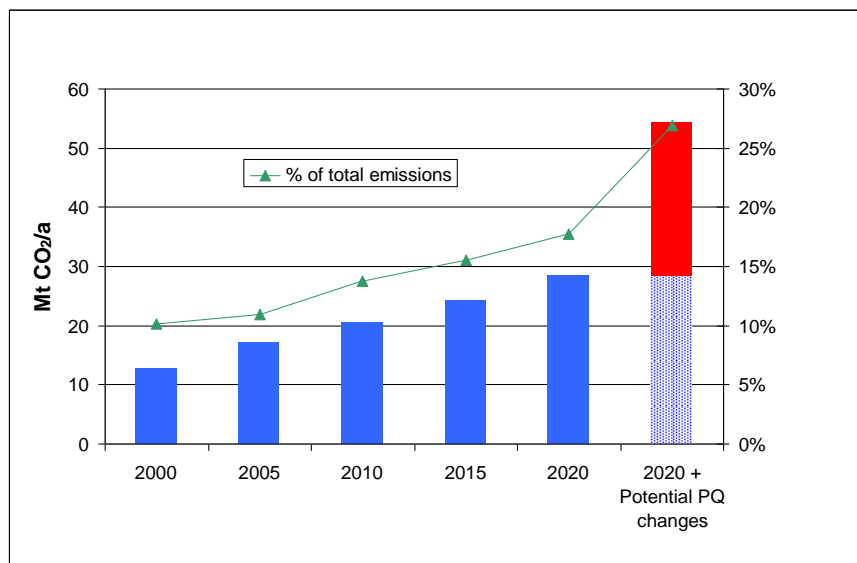


**Figure 6** Forecast EU refinery CO<sub>2</sub> emissions in 2020 (no mitigation measures)



Part of the increase is due to the increasing demand for hydrogen as the products demanded by the market become gradually lighter and more desulphurisation is required. This is illustrated in **Figure 7** which shows the evolution of the “chemical” CO<sub>2</sub> emissions which are set to increase by 65% by 2020 compared to 2005 to reach 15% of total emissions.

**Figure 7** “Chemical” CO<sub>2</sub> emissions from hydrogen production in EU refineries



There are relatively few mitigation measures available to the refiner. Energy efficiency improvement is of course first and foremost and will contribute some reduction. While fuel substitution (burning lighter fuels) and processing lighter crude

oils may produce reduction for a given refinery, it would be unlikely to result in genuine global emission reductions as they would mostly cause “shuffling” of fuel or crude oil types, particularly between regulated and unregulated regions of the world. A full analysis of these options is given in CONCAWE report 8/08 [2].

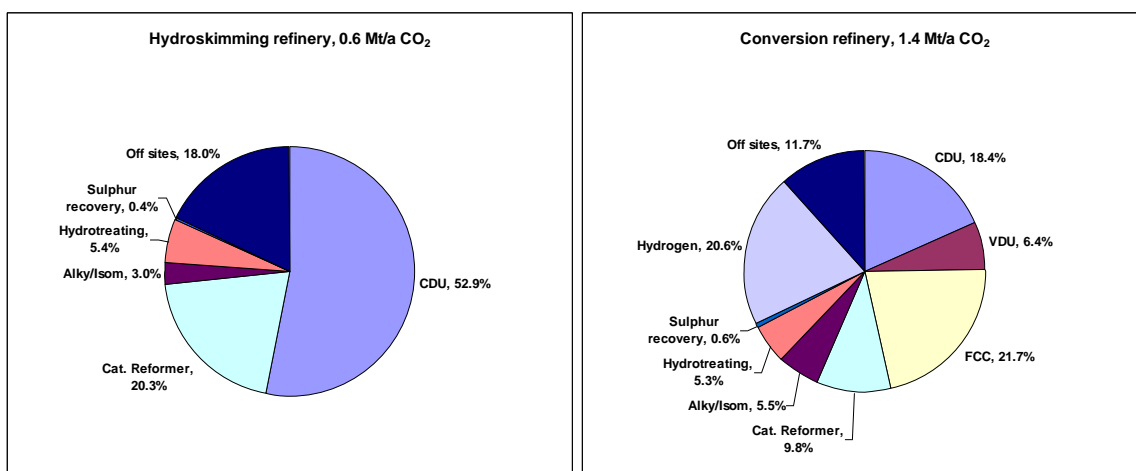
CCS is also an option and the specific issues related to refineries are discussed in the following sections of this report.

### 2.3. PHYSICAL SOURCES OF REFINERY CO<sub>2</sub>

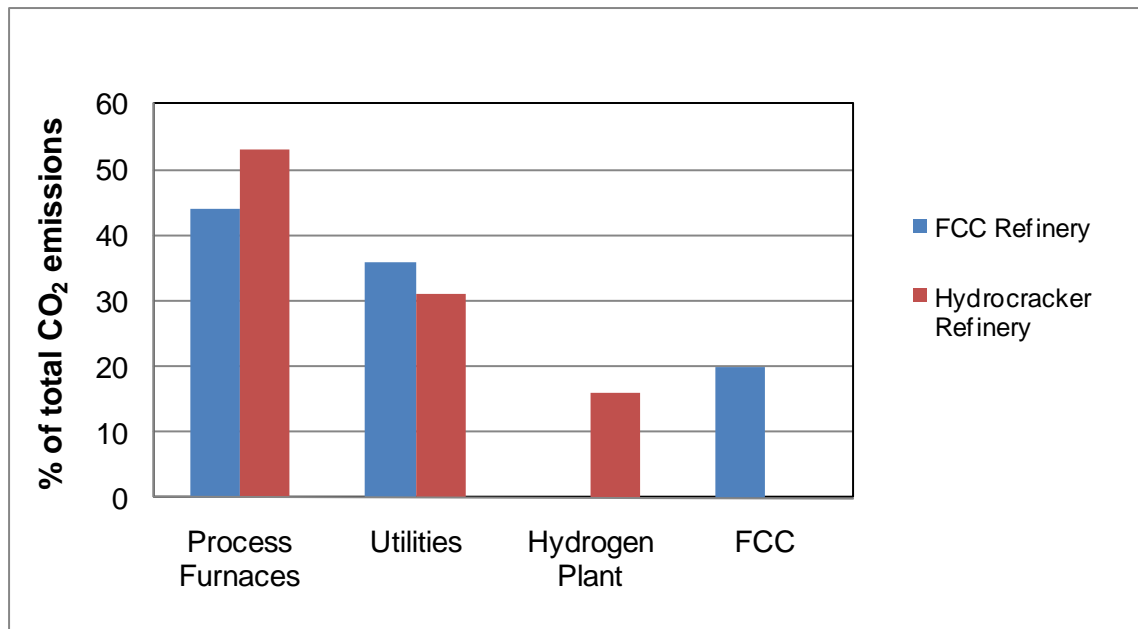
As described above, refinery CO<sub>2</sub> emissions come from fuel combustion to supply energy for the refining processes and the production of process hydrogen. Fuel combustion is the main source. **Figure 8** gives an idea of the relative contribution of the different processes in a simple (“hydroskimming”) and complex 150 kbb/d refinery. The simple refinery is dominated by the crude distiller while FCC and hydrogen plant are the largest contributors in the complex refinery.

In practice fuel is consumed in process furnaces that directly provide heat to the process units and in utility boilers or other devices (such as gas turbines) that generate electricity and steam for use in pumps, compressors, heat exchangers etc. Hydrogen plants add to the total both through combustion of the fuel required to provide the heat of reaction and through decarbonisation of the hydrocarbon feed into “chemical” CO<sub>2</sub> as discussed later. Process heaters generate the largest proportion of the total energy requirement and therefore of CO<sub>2</sub> emissions, the actual share depending on the configuration and original design of the refinery. A typical split between process heaters, utility boilers and hydrogen plant is shown in **Figure 9** for two common conversion refinery configurations based on either catalytic cracking or hydrocracking. These broad categories are analysed in some more detail below.

**Figure 8** Refinery CO<sub>2</sub> emissions breakdown by process (% m/m)  
(These figures are based on total energy requirement including allocation of utilities)



**Figure 9** Typical distribution of CO<sub>2</sub> emissions by source in a complex refinery



**2.3.1. Utilities (electric power and process steam generation)**

Refineries require high amounts of electric power and steam, mostly internally generated although many sites import at least some power. Power and steam export is increasingly common as more and more refineries become equipped with highly efficient combined heat and power plants (CHP also known as co-generation plants), taking advantage of the fact that they can make use of relatively low pressure steam from back pressure turbines. In the last 20-30 years, refineries have recognized the value of replacing simple steam boilers by gas turbines which use either excess refinery gas or imported natural gas to directly produce electric power. More electricity and medium pressure steam is produced by passing the high pressure exhaust gases through a conventional turbine (so-called combined cycle) or they can alternatively be used to supply high temperature process heat. With such CHP systems thermal efficiency can be increased up to 80%.

In all cases these plants are fairly large and emit CO<sub>2</sub> from a single stack albeit as part of the flue gases i.e. in diluted form (typically 4-15% v/v depending on the fuel used). They tend to be among the largest single point sources in refineries.

**2.3.2. Process heaters**

Although process heaters collectively form the largest category of emitters, in practice a moderately complex refinery may have 20 to 30 process heaters ranging from 2 to 250 MW (while a site with petrochemicals may have many more), often spread over a fairly large area especially in larger and older sites with many process units built at different times. This potentially makes end-of-pipe recovery of CO<sub>2</sub> logistically and technically difficult as well as expensive. In some more favourable cases flue gases from a number of furnaces are ducted to a smaller number of common stacks although these are often physically far away from each other.

Process heaters also emit CO<sub>2</sub> in a diluted form as part of the flue gases.

### 2.3.3. Carbon rejection processes (FCC and continuous cokers)

Coke produced during cracking of the oil feed in these processes is burned to generate heat of reaction.

In the FCC surplus heat can be used to generate steam and electricity. Because nearly pure carbon is being burned the concentration of CO<sub>2</sub> in the flue gases is relatively high (about 20% v/v). They can also contain high levels of SO<sub>2</sub> (originating from sulphur in the feed) as well as catalyst dust.

In the continuous coker, there is a lot of surplus heat and the coke is partially burned with steam and air to produce a gas mixture of H<sub>2</sub>, CO, CO<sub>2</sub> and nitrogen. This is similar to a POX unit described later but uses air rather than oxygen and the process operates at low pressure. This “low Joule gas” also contains high levels of H<sub>2</sub>S, other sulphur compounds and coke particles which are scrubbed out before distribution to a number of the larger refinery furnaces where the H<sub>2</sub> and CO are burned to water and CO<sub>2</sub>. Here again the concentration of CO<sub>2</sub> in the final flue gases is relatively high because virtually only carbon is involved.

### 2.3.4. Hydrogen production

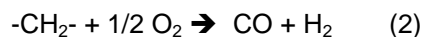
Refineries generate some hydrogen through dehydrogenation of naphtha to high octane gasoline blending components. Whereas this used to be the only source of hydrogen in refineries (and still is in a number of them), the increasing need for hydrodesulphurisation of middle distillates and, more recently the development of hydrocracking and residue hydroconversion have made it necessary to generate additional hydrogen.

The most widespread process is steam reforming where a light hydrocarbon feed combines with steam at high temperature and in the presence of a catalyst into carbon monoxide and hydrogen.



In the majority of cases the feed is natural gas i.e. methane but excess refinery gas, LPG or naphtha can also be used.

Alternatively the hydrocarbon can be “partially oxidised” (i.e. burned in an oxygen deficient atmosphere) according to



In this case the feed is usually heavy residual streams or petroleum coke and the plant is known as a “POX” (partial oxidation) unit. Pure oxygen is used rather than air.

The water gas “shift” reaction converts then water and CO into more hydrogen and CO<sub>2</sub>.



These processes are energy intensive whatever the combination as breaking the hydrocarbon bonds and decomposing water require a lot of energy (which can be released when hydrogen is burned, recombining with oxygen to produce water). The laws of thermodynamics are such that more energy has to be supplied than specifically required by the reaction. Some of the waste heat can be recovered to generate steam. CO<sub>2</sub> is therefore produced both as a result of the decarbonisation of the feed (“chemical” CO<sub>2</sub>) and through burning fuel to sustain the reaction. The total amount of CO<sub>2</sub> produced in proportion to hydrogen is a function of the type of feed. For steam reforming the average is about 10 t CO<sub>2</sub> / t hydrogen, roughly equally split between feedstock for the chemical reaction and fuel required to supply heat to the 750-800°C process temperature.

Following the shift reaction CO<sub>2</sub> needs to be removed from the CO<sub>2</sub>/H<sub>2</sub> mixture to produce the high purity hydrogen stream normally required for downstream processes. For the stoichiometric reaction the concentration of CO<sub>2</sub> in the CO<sub>2</sub>/H<sub>2</sub> stream is quite high from 25% v/v for methane reforming to 33% v/v for partial oxidation. In practice it is less because the stream also contains unconverted hydrocarbons and CO. CO<sub>2</sub> removal can be effected by absorption in a solvent (usually an amine) or, as is now state-of-the-art, with a more energy efficient molecular sieve system. In the former case a high purity CO<sub>2</sub> stream is produced (up to 99%) that would just need drying and compression to be transported to a storage site. In the latter case the waste stream contains a mixture of CO<sub>2</sub>, hydrogen, CO and hydrocarbon and the CO<sub>2</sub> concentration is typically in the 50% v/v range so that further separation would be required to prepare a CO<sub>2</sub> stream suitable for transport and storage.

Some refineries operate oxygen-based residue gasification (POX) units which can be used for hydrogen production. More details of this technology are given in **Section 3.2.3**. For hydrogen production up to 15 t CO<sub>2</sub> / t hydrogen are generated, significantly more than for steam reforming as described above on account of the heavier feeds and the relatively higher proportion of hydrogen originating from the hydrocarbon feed rather than from water. The process produces a high purity CO<sub>2</sub> stream.

### **2.3.5. Sulphur recovery**

Sulphur recovery units are designed to partially oxidise H<sub>2</sub>S recovered from sour refinery gas by amine scrubbing to make elemental sulphur. The basic “Claus” process only recovers 93-97% of the sulphur releasing the balance as SO<sub>2</sub>. Environmental regulations have led refineries to install additional “tail gas” units which boost sulphur recovery to above 99%. The combined sulphur recovery complexes produce some CO<sub>2</sub> partly through its co-absorption with H<sub>2</sub>S in amine scrubbers, the presence of 1-2% hydrocarbons in feed streams and mainly from burning fuel gas in the tail gas unit and its incinerator. Flue gas from the incinerator can have a high level of SO<sub>x</sub> as well as oxygen. Again, the CO<sub>2</sub> volumes are a small proportion of the total.

### **2.3.6. Flaring**

The flare is the ultimate “safety valve” of a refinery. If something goes wrong in one of the process units and particularly those operating at high pressure there needs to be an outlet available immediately to safely dispose of the gaseous hydrocarbon inventory in that plant. Safety flaring is infrequent and unpredictable. The flare is also used during plant shutdowns to safely depressurise equipment. A continuous

small pilot flame is required to ensure ignition of the material to be disposed of. In total flaring represents a very small proportion of refinery emissions, in the order of 1.5%. Because of its irregular and by essence unpredictable nature and because it is a safety feature, it would be impractical to consider any CO<sub>2</sub> recovery from the flare exhaust.

**Table 1** shows typical properties of the various refinery sources of CO<sub>2</sub>. All CO<sub>2</sub> containing streams are only available at or close to atmospheric pressure. When originating from flue gases they have a low CO<sub>2</sub> concentration. Hydrogen plants produce the streams with highest CO<sub>2</sub> content when using solvent absorption. This technology, however, tends to be replaced by the more efficient physical absorption (Pressure Swing Adsorption or PSA) which delivers a less concentrated off-gas containing some hydrogen and unconverted hydrocarbons, normally recycled as fuel to the process heater.

**Table 1** Typical properties of refinery CO<sub>2</sub> emission sources

<b>Emission sources</b>	<b>CO<sub>2</sub></b> % v/v	<b>Oxygen</b> % v/v	<b>SO<sub>2</sub></b> ppmv	<b>Other contaminants</b>
Gas Fired Process/Utility Furnaces <sup>(1)</sup>	3-6	2-6	10-20	SO <sub>3</sub>
Oil Fired Process/Utility Furnaces <sup>(2)</sup>	7-12	2-6	50-600	SO <sub>3</sub>
FCC Regenerator Stack	8-12	1-2	1000-15,000	Catalyst Dust, CO, SO <sub>3</sub>
Hydrogen via steam reforming:				
Solvent absorption	95-99 <sup>(3)</sup>	0	0	Clean
PSA	40-50	0	0	CO, H <sub>2</sub>
Hydrogen via residue gasification (POX)	95-99 <sup>(3)</sup>	ppm levels	ppm levels	H <sub>2</sub> S, COS
SRU Incinerator	2-7	1-8	200-6000 <sup>(4)</sup>	COS, CS <sub>2</sub> , Sulphur, SO <sub>3</sub>

Notes

- (1) Assuming refinery gas at < 200 ppmv H<sub>2</sub>S
- (2) Assuming heavy fuel oil at up to 1% m/m sulphur
- (3) From solvent regenerator
- (4) High variation depending on type of tail gas unit

### 3. REFINERY CO<sub>2</sub> CAPTURE AND ASSOCIATED COMBUSTION TECHNOLOGIES

There are essentially two routes to CO<sub>2</sub> capture: either leaving the combustion technology unchanged and facing the challenge of large volumes of flue gases with low CO<sub>2</sub> concentrations or changing the combustion technology to directly create highly concentrated CO<sub>2</sub> streams.

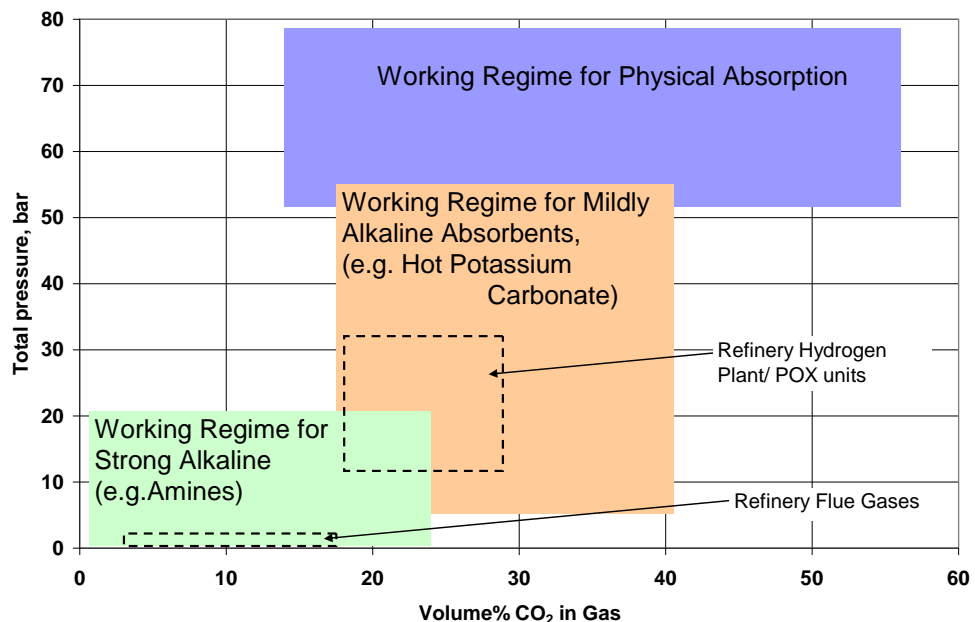
#### 3.1. CAPTURE TECHNOLOGIES FOR EXISTING STREAMS

There are a number of well proven technologies for scrubbing CO<sub>2</sub> out of a gas stream, developed in such processes as hydrogen manufacture (see **Section 2.3.4**). They are all solvent absorption processes with different variants depending on CO<sub>2</sub> partial pressure:

- Physical processes where CO<sub>2</sub> is forced in to various chemical solutions require CO<sub>2</sub> partial pressures of at least 20 bar (e.g. 70 bar total pressure and CO<sub>2</sub> content above 30%).
- Mildly alkaline solvents such as potassium carbonate solutions or certain amines require a much lower CO<sub>2</sub> partial pressure, in the order of 2 bar (e.g. total pressure of 10 bar and 20% CO<sub>2</sub>). This is used in older type hydrogen plants.
- Highly alkaline solvents such as Monoethanolamine (MEA) can be used at even lower pressures.

**Figure 10** maps out the CO<sub>2</sub> removal technologies that would be suitable for different combinations of CO<sub>2</sub> partial pressure and CO<sub>2</sub> concentrations.

**Figure 10** Technology selection for CO<sub>2</sub> absorption



As can be seen, because of the relatively low pressure at which most of the CO<sub>2</sub>-containing gas streams are available, refinery capture technologies are limited to chemical absorption (amine or hot potassium carbonate), with the exception of capture from hydrogen plants. In practice only amine-based processes (virtually all MEA currently) are effective at the low CO<sub>2</sub> partial pressures of flue gases.

Ease of capture is a function of CO<sub>2</sub> partial pressure. From H<sub>2</sub> plant/POX Units, capture efficiency would be 98% or better. Capture from flue gas would probably be around 90%. The potential variation in CO<sub>2</sub> partial pressures depending on fuel burned would lead to a variable recovery. Design to deal with a large variety of fuel types could lead to significant additional investment.

### 3.1.1. Flue gas CO<sub>2</sub> capture processing scheme

Practical recovery of CO<sub>2</sub> from flue gas is sufficiently different from other gas treating applications such as natural gas and refinery gas sweetening and purification of ammonia and hydrogen plant synthesis gas that it requires its own specialized processes. Candidate processes must be effective at low CO<sub>2</sub> partial pressure and tolerate oxygen and NO<sub>x</sub>. Flue gases (including those in refineries) can also contain SO<sub>x</sub>, soot and fly ash. Issues relevant to these 'bad actors' are further discussed in **Appendix 2**.

There are flue gas scrubbing technologies in use today, though mostly on a much smaller scale than would be required for CO<sub>2</sub> capture from a refinery and with different objectives (mostly SO<sub>x</sub> removal). Amongst other issues, many of the trace bad actors may be more of a problem than has been so far evaluated.

The most likely processing scheme for flue gas CO<sub>2</sub> capture in refineries would be similar to that shown in **Figure 11**, i.e.

- I. Flue gas is cooled with water in a quench column, also reducing water content and with NaOH/Na<sub>2</sub>CO<sub>3</sub> injection to remove SO<sub>x</sub> compounds, fly ash etc.,
- II. A blower is used to overcome plant pressure drop,
- III. CO<sub>2</sub> is removed from the cooled flue gas in a MEA absorber,
- IV. The reduced CO<sub>2</sub> content flue gas is vented to atmosphere,
- V. The rich amine solution is routed to the regenerator where it is heated to separate CO<sub>2</sub> from the amine solution.

There may also be a need for a NO<sub>x</sub> reduction step which is unclear at present.

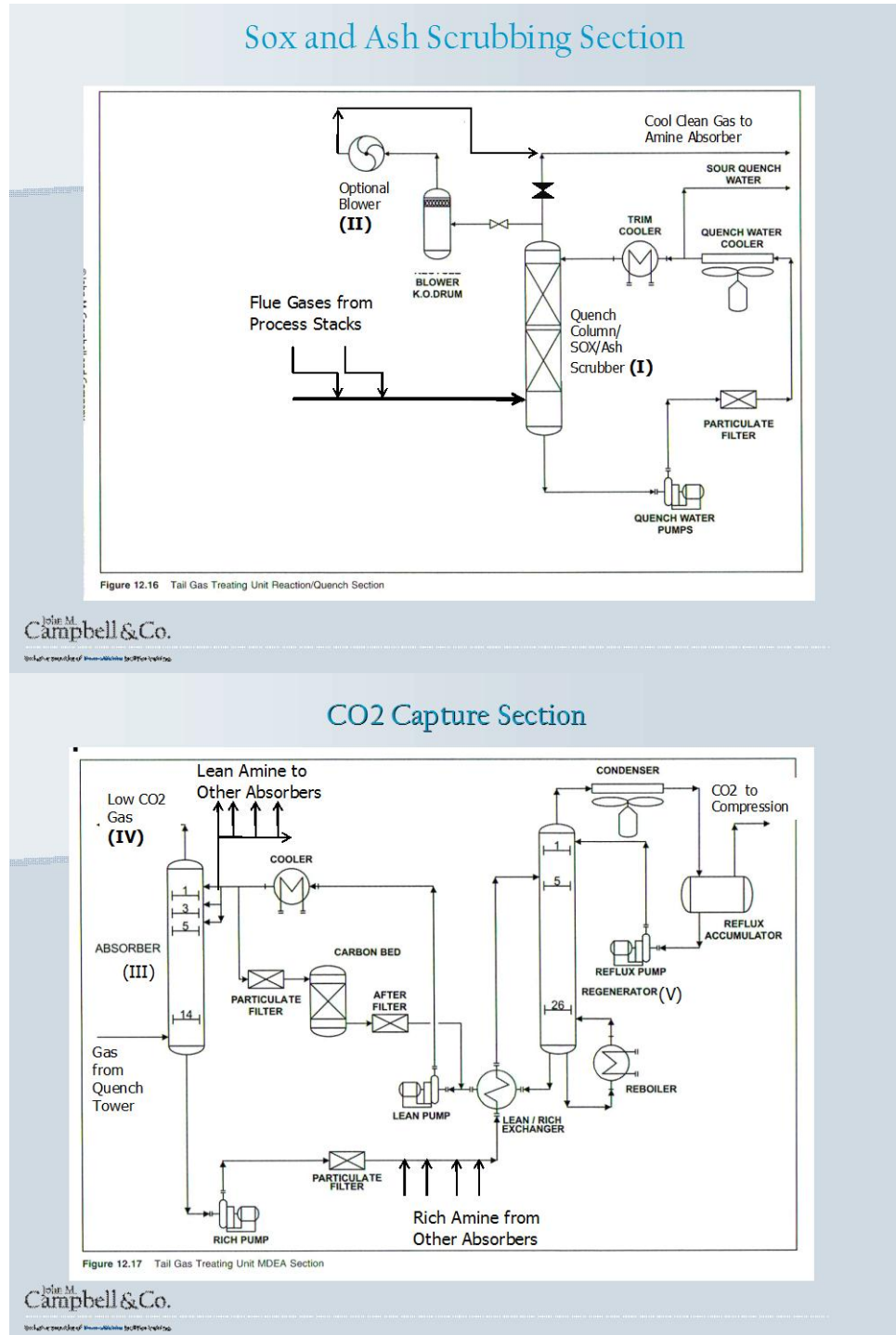
#### 3.1.1.1. Energy consumption

Low pressure absorption processes that are effective in removing CO<sub>2</sub> today are also those which require the most energy input, mostly to regenerate the circulating solvent. In fact solvent regeneration is likely to account for the largest portion of the total energy required for capture if not for the whole CCS chain. The reaction energy between solvent and CO<sub>2</sub> represents 30-40% of the total energy required. Regeneration energy needs to be minimised by developing solvents with high capacity and relatively low reaction energy. The ability to use low-value heat sources (mostly low temperature) is also a way to reduce overall energy consumption as it opens the possibility to use waste heat. In already heat integrated energy-efficient refineries such waste heat may however not be available and the majority of the additional energy required for capture will have to be supplied by



extra fuel. In other words capture in itself will generate more CO<sub>2</sub> emissions. This is an important point that will be further highlighted later when discussing the distinction between CO<sub>2</sub> avoided and CO<sub>2</sub> captured.

**Figure 11** Schematic of a Possible Flow Diagram for Refinery CO<sub>2</sub> Capture Used by permission of John M Campbell & Co.



**3.1.1.2. Reliability, Technical complexity and additional risk**

Addition of any equipment to refinery processes brings with it a potential deterioration of overall plant reliability. This would be a significant consideration on choice of technology to be applied. Additional investment is required to ensure continued operation of the base facility without CO<sub>2</sub> capture i.e. large by-pass lines/valves and significant materials of construction issues. Because of unknowns in CO<sub>2</sub> capture at present there would need to be a period of operation of the capture plant to allow reliability to be assessed. As pointed out in a study done by a major contractor for the CO<sub>2</sub> Capture Project (CCP) [14] ducting flue gas around the site and linking several furnaces together implies additional safety risks. Operations such as start-up and shutdown of individual furnaces could be significantly more complex and therefore more prone to mishaps and incidents. Effective technology development and demonstration projects are critical to improve the understanding of these issues and to develop mitigating actions to minimise the risks.

**3.1.2. Energy requirement and increase of CO<sub>2</sub> footprint: CO<sub>2</sub> captured v. CO<sub>2</sub> avoided**

Depending on assumptions made on CO<sub>2</sub> concentration, solvent efficiency, operating pressures etc., the energy required to capture all CO<sub>2</sub> emitted would represent 20 to 30% of the total existing refinery energy consumption and would therefore increase CO<sub>2</sub> emissions by a similar percentage. Estimating the typical energy requirement for capture at 3.5 GJ/t CO<sub>2</sub> captured and the energy for compression to pipeline/storage conditions at 0.7 GJ/t CO<sub>2</sub> captured, the capture and compression of 1 t CO<sub>2</sub> would represent an additional energy consumption of 4.2 GJ, producing additional CO<sub>2</sub> emissions of about 0.273 t CO<sub>2</sub> per t CO<sub>2</sub> captured (assuming a typical EU refinery emission factor of 0.065 t CO<sub>2</sub>/GJ).

The aim of CCS is to “avoid” venting CO<sub>2</sub> to atmosphere. In the above example, in order to “avoid” 100 t of CO<sub>2</sub> being vented one would have to consume energy leading to the generation of an additional 27.3 t of CO<sub>2</sub> that would also need to be captured, generating in turn an additional 7.5 t of CO<sub>2</sub>, and so on. The need to emit more CO<sub>2</sub> in order to avoid what is emitted in the first place creates a “roll up” effect illustrated in **Table 2**.

**Table 2** Example of captured CO<sub>2</sub> build up v. CO<sub>2</sub> avoided

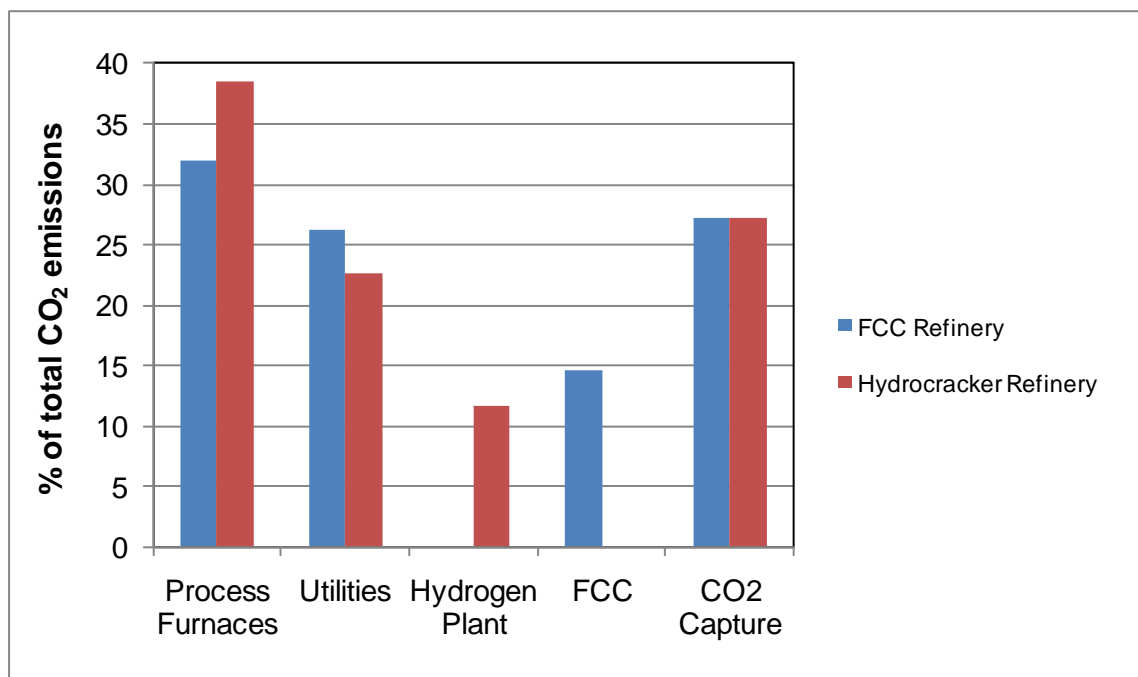
CO <sub>2</sub> to be avoided	100 t	Cumulative CO <sub>2</sub> to be captured
Additional CO <sub>2</sub> generated to capture		
100 t	27.3	127
27 t	7.5	135
7 t	2.0	137
2 t	0.6	137
0.6 t	0.2	137

All figures in t CO<sub>2</sub>

There is therefore a fundamental distinction to make between **CO<sub>2</sub> avoided** which is relevant to the aim of CCS and **CO<sub>2</sub> captured** which is what CCS must achieve. In the above example for every 100 t of CO<sub>2</sub> we initially wish to “avoid”, 137 t need to be captured i.e. the CO<sub>2</sub> to be captured is nearly 40% more than the CO<sub>2</sub> to be avoided in the first place.

CO<sub>2</sub> emissions by source for the two types of conversion refineries would now be as in **Figure 12** i.e. CO<sub>2</sub> capture could be the greatest contributor to refinery CO<sub>2</sub> production.

**Figure 12** Refinery CO<sub>2</sub> sources including additional CO<sub>2</sub> for capture



This has important consequences on required resources and their attendant costs in terms of the facilities to be built and of energy consumption. In effect to avoid the CO<sub>2</sub> produced by a plant, one would have to build a facility capable of capturing 40% more CO<sub>2</sub> although this may be reduced through process optimisation, improvements in capture technology etc.,

CCS would significantly increase refinery energy consumption i.e. require more energy resources to supply the same amount of final energy to consumers. This is a potentially serious issue in the context of limited energy resources, particularly fossil sources.

**3.1.3. Plant dimensions and physical footprint**

The equipment required would be massive. Assuming all flue gas is gathered by a system of ducting as in the CCP report [14] to a single capture plant, the overall plot size required for the capture plant only would be very large. The large amine absorber and regenerator vessels may not be transportable and may have to be constructed on site. The preferred material for these vessels is likely to be lined concrete.

There are a few existing MEA-based flue gas treating plants ranging in size from 90 to 1000 t/d of CO<sub>2</sub> recovered [15]. The main limitation to scaling up is the maximum diameter of the absorber vessel. Scrubbing equipment size depends on flue gas volume and not just on tonnes of CO<sub>2</sub> recovered. The CCP report [14] estimates that four absorber columns of 10.3 m diameter would be required to capture 2 Mt/a of

CO<sub>2</sub> (about 5700 t/d) in a medium complexity UK refinery, representing about 55% of its combustion emissions. This assumed that the flue gases from nine selected combustion sources (out of a total of twenty potential sources) are gathered into two separate ducting systems, each leading to two parallel absorber columns. The alternative would be a multiplicity of smaller absorbers distributed in the refinery.

Additional utilities equipment would be required to supply the energy needs of the capture and compression process. This would add significantly to the total footprint of the CCS plant, which could severely limit CCS deployment in refineries with space restrictions.

The above figures are only illustrative. In reality each refinery site would have to carry out its own feasibility and design study based on the specific configuration of the site.

#### **3.1.4. Expected technology learning curve and areas for cost reduction**

Scrubbers and absorbers are already commonplace in refineries and a wealth of know-how and detailed operating experience is available. This could be in a way an advantage but also means that there is limited scope for large performance improvements in such a mature technology. The very size of the equipment to be operated would probably be a challenge though, as would be the integration with the drying and compression systems.

As mentioned above solvent regeneration is the largest contributor in energy terms and this is an area where further improvements could be expected with more efficient use of existing solvents (e.g. lower solvent circulation rate) or development of new ones. Certain solvents may be better suited to specific conditions such as higher CO<sub>2</sub> concentrations when scrubbing off gas from a hydrogen plant. They may also allow use of cheaper construction materials or corrosion inhibitors could be used. As amine regeneration requires relatively low temperature heat (140-150°C), there may be some opportunities to identify underused sources of such low level heat although most of these have already been accounted for in modern refineries.

MEA strength and loading can have a significant impact on investment and energy requirements and would have to be optimised. Higher MEA concentrations allow a higher pick up of CO<sub>2</sub> for a given circulation rate hence allow smaller equipment but lead to more corrosion issues so that more of the system has to be upgraded from carbon steel to stainless steel. 15 to 20% m/m MEA in water is common. A reclaimer can help eliminate degradation products and heat stable salts. With sufficiently high grade materials, good monitoring and constant use of the reclaimer up to 25% m/m MEA solutions can be used. The reclaiming operation does not result in the use of more energy as the steam generated is used as stripping medium in the regenerator tower.

It is unclear at present whether it would be better to combine several refinery flue gases and treat a single large stream or have absorbers for each stack or group of stacks with one or two common regenerators. This arrangement would allow troublesome scrubbers to be isolated as necessary or change routing of rich amine to one absorber or another e.g. one amine system for relatively clean flue gas and another for more difficult to scrub gases. Amine circulation piping would be relatively small compared with that required for ducting flue gas. On the other hand the multiplication of scrubbers would significantly complicate the whole system and would likely increase investment. The best solution is likely to be very site specific.

### 3.2. ALTERNATIVE COMBUSTION TECHNOLOGIES

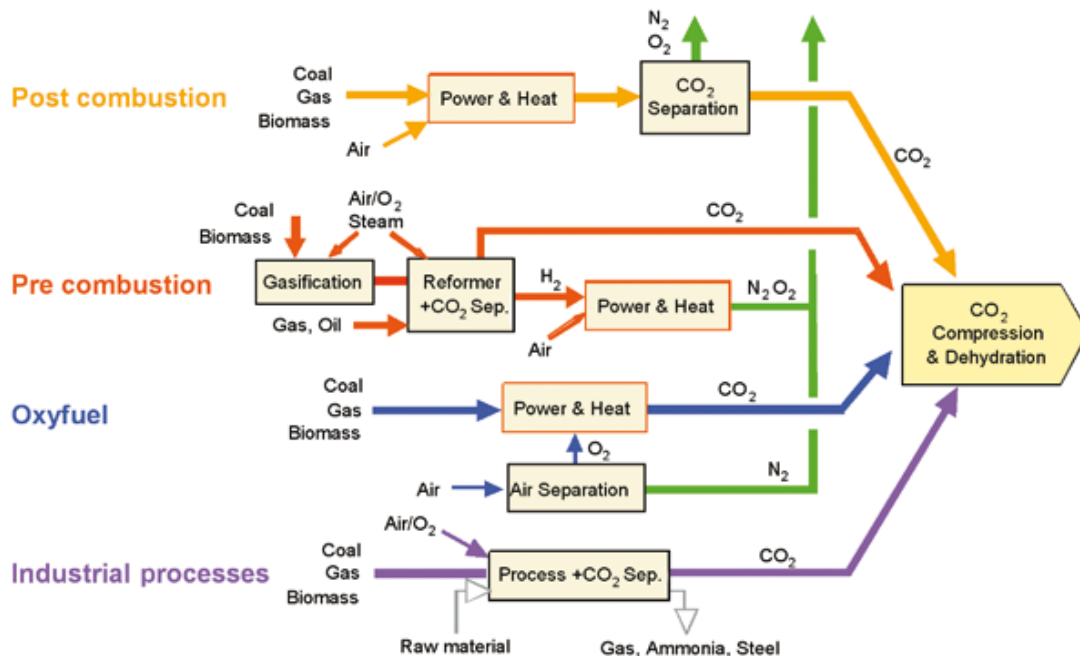
Up to the present, combustion has largely used atmospheric air as the source of oxygen. As a consequence the combustion products (CO<sub>2</sub> and water) are diluted by large amounts of nitrogen. CO<sub>2</sub> capture from such flue gases is termed Post-Combustion. The drawbacks of this have already been alluded to above i.e. large volumes of gases only available at atmospheric pressure, with low concentrations of CO<sub>2</sub> and with SO<sub>x</sub>, nitrogen, oxygen and other gases, making it difficult to generate a high purity CO<sub>2</sub> stream from them.

A number of alternative combustion technologies are intended to reduce the volume of flue gas (by eliminating N<sub>2</sub>), increase CO<sub>2</sub> content of the waste gas and increase total pressure of the flue gases. There are in principle two ways of achieving this:

- Replace air by pure oxygen: this is known as oxyfuel combustion.
- Convert the hydrocarbon fuel into hydrogen before burning it in boilers and process heaters and directly recover the high concentration CO<sub>2</sub> stream: this is known as pre-combustion capture.

The various routes are shown in **Figure 13** alongside post-combustion and other industrial processes.

**Figure 13** Combustion Technologies  
(Source: [1], figure 3.1)



In terms of energy efficiency there is however no silver bullet. If energy is saved at the capture stage this is compensated by the extra energy required to produce the hydrogen in pre-combustion and separate oxygen from air in oxyfuel combustion. Averaging estimates collected in the IPCC report [1] indicate that, for a refinery situation using a mixture of refinery gas and fuel oil, loss in efficiency would be 25,

29 and 31.5% for post-, pre- and oxyfuel combustion respectively. A further report by McKinsey [16] considers that, for the study cases they assumed, overall cost of CO<sub>2</sub> avoided would be broadly similar for all three for a grass roots power station.

### 3.2.1. Oxyfuel combustion

Oxyfuel combustion eliminates nitrogen from flue gas by combusting the fuel in pure oxygen. The combustion temperature is very high (about 3500°C) and, because of material limitations and also to control NO<sub>x</sub> emissions, has to be reduced to about 1900°C in a conventional fired boiler/heater or 1300-1400°C if a gas turbine is used. This is done by recycling cooled flue gas or condensate back to the combustion chamber. The net flue gas, after cooling to condense water vapour, contains between 80 and 93% CO<sub>2</sub> depending on the fuel used and the particular oxyfuel combustion process. Higher CO<sub>2</sub> concentrations are unlikely to be attainable, due to the need to maintain a certain level of excess oxygen and the inevitable ingress of some nitrogen originating from tramp air or from the fuel gas. This concentrated CO<sub>2</sub> stream can be dried, further purified and compressed before delivery into a pipeline for storage. Purification would not be a simple task. Concentrating the flue gas would also concentrate a number of impurities and trace elements originating from the fuel. Residual inert gases from the oxygen would have to be limited in order not to create problems with compression.

There are several well tried technologies to produce oxygen from air, including cryogenic distillation, adsorption using multi-bed pressure swing units and polymeric membranes. For applications involving less than 200 t/d of oxygen the adsorption system will be most economic. For larger applications, which would include refinery power station boilers, cryogenic air separation is the preferred choice. Whatever the technology, the high amount of energy required to manufacture oxygen<sup>2</sup> would generate extra CO<sub>2</sub> equivalent to 25-30% of the combustion emissions. The stoichiometric oxygen demand for the typical UK refinery in the CCP report [14] would be about 5300 t/d to produce the 2 Mt/a of CO<sub>2</sub> captured, corresponding to 55% of the refinery's combustion emissions. This would require an oxygen production capacity exceeding the largest oxygen plants built to date (about 3500 t/d [1]), although the industry is studying the feasibility of building larger plants. Where refineries are physically close together or close to a power plant, an oxygen facility could be built and operated by a separate specialist company and the oxygen production shared as is currently often done with hydrogen.

There is considerable interest in this technology from the power industry particularly for coal burning. Semi-commercial scale trials are planned but practical full commercial application is probably 10-15 years away.

For FCC unit catalyst regenerators the CCP Capture Team [25] is developing a pure oxyfuel approach where the regenerator combustion air is replaced by pure oxygen diluted with recycled high-purity CO<sub>2</sub> to maintain thermal balance and catalyst fluidisation. Further testing is planned to determine the impact of the high CO<sub>2</sub> content in the flue gas on equipment corrosion, thermal balance, catalyst attrition and coke burn rate. The test results should help to establish whether it is possible to retrofit an existing FCC regenerator for oxyfuel operation, which would incur additional capital and operating costs for an air separation plant, recycle gas conditioning system and compression of the recycle gas.

<sup>2</sup> The EIGA [21] Benchmark specific electricity consumption is 400 kWh<sub>e</sub> / tonne Oxygen

Pure oxyfuel combustion in refinery furnaces results in different flame shapes and firing characteristics. Flue gas recycle is usually required to control flame temperature. In addition the combustion firebox must be sealed to avoid air ingress and dilution of the produced CO<sub>2</sub>. Although it could be considered for new refinery installations, retrofitting would be considerably more challenging. The design of process furnaces is in many cases specific to the process with tailored flame heat release profiles and heat flux limitations. Many furnaces are natural draft and would need extensive modifications. Generally, sealing the fire box and downstream heat recovery systems would be difficult. Most furnaces would probably need extensive modifications and possibly rebuild, so with the number of smaller process furnaces spread around a large conversion refinery the cost would again be high. The economics may be more favourable for large steam boilers.

The flue gas would be hot, essentially at atmospheric pressure and would still contain potential contaminants so would need to be scrubbed by an alkali wash incorporated in a Direct Contact Cooler/Water Condenser. Water treatment and circulation would be a major undertaking particularly with any commercial fuel other than natural gas. CO<sub>2</sub> recovery could be close to 100% versus 80-90% for a post-combustion system though inerts removal may lower the final oxyfuel recovery.

Some aspects of the technology are new and it is possible that costs will decrease as know-how improves with time. An alternative which may be worth studying would be to use post-combustion in combination with oxygen-enriched air to reduce nitrogen in the flue gas of conventional furnaces. This would reduce the size of flue gas contacting equipment although energy cost for amine regeneration would not change.

### 3.2.2. Chemical Looping Combustion

This is a variation on oxyfuel combustion consisting of circulating one of several possible compounds (such as an iron compound) acting as an oxygen carrier between the combustion chamber where it delivers oxygen for the hydrocarbon combustion and an "oxidiser" where the material is returned to its oxidised state. The process could be similar to an FCC with continuous fluidised circulation of the oxygen carrier. This would avoid the costly and energy-intensive oxygen production and result in higher overall thermal efficiency as there would not be the same heat release/high temperature problem that results from straightforward oxyfuel combustion [1,17]. Promising trials of up to 300 hours have been made with the circulating materials. This technology is, however, still very much at the R&D stage, and no industrial demonstration is expected in the near future.

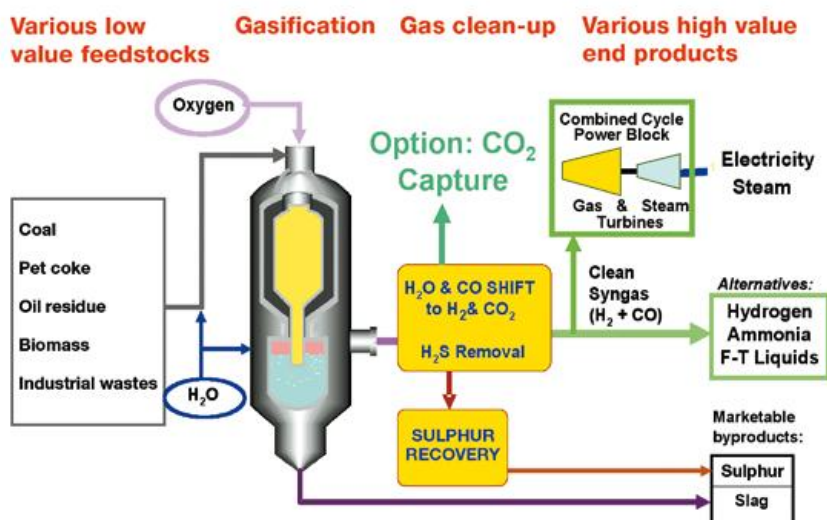
### 3.2.3. Pre-Combustion capture systems

Pre-combustion means removal of carbon from hydrocarbons so that only hydrogen is left to use as fuel. The carbon is converted to CO<sub>2</sub> but at a much more useful pressure and concentration.

In such plants the carbonaceous feed is "gasified" i.e. partially burnt with steam and oxygen to produce a mixture of CO, CO<sub>2</sub> and H<sub>2</sub> (so-called synthesis gas or "syngas"). This process is called Partial Oxidation (POX) when used in refineries. After removal of sulphur compounds and other impurities the syngas can be used to various ends such as production of electricity in a gas turbine, methanol or liquid hydrocarbons via the Fischer-Tropsch synthesis but also to produce hydrogen via the shift reaction described in **Section 2.3.4**. CO<sub>2</sub> produced in the partial oxidation

step and the shift step can be scrubbed out via a physical or chemical process delivering a CO<sub>2</sub> stream at relatively high pressure and concentration which makes capture easier. The scrubbing processes applied would be essentially the same as those described for refineries in **Section 2.3.4**.

**Figure 14** Simplified schematic of a gasification process showing options with CO<sub>2</sub> capture and electricity, hydrogen or chemical production (Source: [1], figure 3.14)



If syngas is turned to hydrogen all CO<sub>2</sub> becomes available in concentrated form. If it is first scrubbed of CO<sub>2</sub> and then used for electricity production CO<sub>2</sub> produced in the combustion of CO becomes “post-combustion” CO<sub>2</sub>. **Figure 14** shows a simple flow scheme of the whole process.

Partial Oxidation technology has been employed for 20-25 years and there is significant operating experience with it. In Europe there are about 10 operating units in oil refining, petrochemicals and utilities generation. Most plants produce electricity exclusively although some co-produce methanol and hydrogen. Overall this technology is very expensive to install and relies on the availability of very cheap feedstocks which tend to be high in carbon content i.e. high CO<sub>2</sub> producers.

If this technology was to be used to decarbonise refinery fuel i.e. burn hydrogen in process heaters, modifications would be required to those heaters and to the refinery fuel distribution system, depending on the hydrogen content of the fuel gas.



## 4. CO<sub>2</sub> TRANSPORT

CO<sub>2</sub> can be transported as a gas, liquid or solid. To aid understanding of how CO<sub>2</sub> will be transported and stored, some background on its nature and physical properties is given in **Appendix 1**.

For large quantities and short to medium distances pipeline is the most cost-effective transport method. The alternative is shipping but this is unlikely to be justifiable long term except for very long distances and would only be practical for coastal or near coastal CO<sub>2</sub> emitters and off-shore or near-shore storage sites.

Transport and handling of large quantities of CO<sub>2</sub> near populated areas will raise safety and therefore public acceptance issues. CO<sub>2</sub> is odourless, invisible and heavier than air and could accumulate in low points such as natural valleys or cellars and underpasses causing asphyxiation of human and animal life.

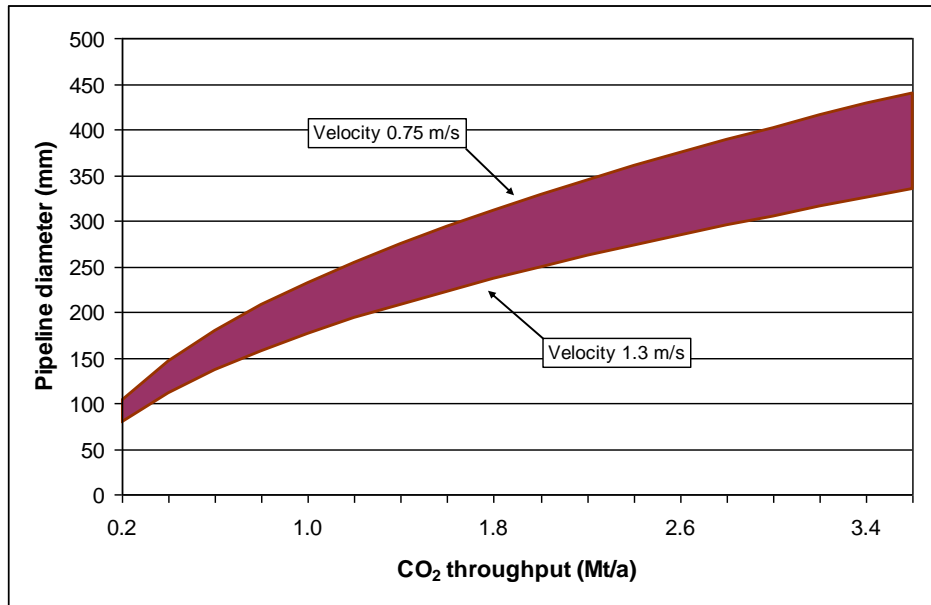
### 4.1. PIPELINES

In relation to EOR activities in North America, considerable experience has been gained for transporting CO<sub>2</sub> in pipelines over distances of the same order of magnitude as would be required for CCS in Europe (say up to 500 km, see **Section 5.3.1**). There are numerous long distance pipelines throughout Europe carrying natural gas, crude oil, refined products or chemicals so the basic technology and operational aspects of such pipelines are well known.

In pipelines CO<sub>2</sub> is transported as a supercritical fluid (dense phase) at pressures that need to remain in excess of 80 bars at all points of the pipeline. In practice all dense phase CO<sub>2</sub> pipelines in existence today operate at 130-140 bars, allowing for increased volume transport as well as ensuring that, with topography changes, the fluid is certain to remain in a single dense phase. More than 3000 km of pipelines covering distances of up to 800 km have been in continuous service for up to 30 years in North America [1] servicing over seventy EOR projects. Europe currently has one short gas phase line in The Netherlands providing CO<sub>2</sub> from the Shell Pernis refinery to local greenhouses, and Statoil has constructed a dense phase CO<sub>2</sub> pipeline for offshore sequestration of CO<sub>2</sub> captured at the Snøhvit LNG terminal. Several smaller European lines are being considered for various demonstration projects.

The design of a pipeline for transporting a given flow is always an economic compromise between size, pressure, number of recompression stations etc. Based on velocity data derived from four pipelines used in North America for EOR [1], **Figure 15** shows the pipeline size that would be needed for the typical range of refinery CO<sub>2</sub> production. The largest US CO<sub>2</sub> pipeline has a diameter of 760 mm, is 800 km long and has been designed to carry up to 20 Mt CO<sub>2</sub>/a i.e. equivalent to two to three 1000 MW power stations. In the typical UK refinery described in the CCP report [14], the capture of 55% of the CO<sub>2</sub> emitted by combustion sources would lead to capture and transport of 2 Mt/a of CO<sub>2</sub>. This would require a pipeline of about 300 mm diameter. Assuming a typical length of 200 km, an inlet pressure of minimum 125 bars would be required to guarantee 80 bars at the end of the pipe. The corresponding electrical power consumption for compression can be estimated at 0.30 GJe/t CO<sub>2</sub> or some 22 MWe for the total volume. Intermediate pumping stations may be required in some cases for longer distances and/or difficult topography.

**Figure 15** Estimated pipeline size required as function of CO<sub>2</sub> throughput



In contrast to some areas in North America, routing of pipelines to avoid areas of population would be much more difficult in Europe. Even though the safety and leakage record of European pipelines is excellent [12] obtaining rights of way may raise significant opposition and public concern making pipeline projects more difficult, expensive and subject to delays as well as increasing the regulatory requirements for monitoring and possibly quality specifications.

For this reason and also because pipeline costs per tonne of CO<sub>2</sub> are strongly impacted by scale (see **Section 6.2**), pipelines involving large volumes of CO<sub>2</sub> collected from several sources should be favoured. Collaboration between refineries and power stations and/or other large CO<sub>2</sub> emitters would be desirable to realise economies of scale. In other words a common pipeline infrastructure designed to match sources with storage locations would be much more practical and cost effective than a series of one-off projects with dedicated transport and storage facilities. Such “backbone” infrastructure would, however, require huge up-front investments and require a high level of cooperation between emitters and regulatory authorities, possibly in different countries.

Carbon steel would be adequate for CO<sub>2</sub> transport systems although it would be critical to keep the system dry to avoid potentially severe corrosion. Corrosion monitoring techniques including in-line inspections would need to be used extensively with special preventative measures for non piggable lines.

**4.2. TRANSPORT BY SHIP**

CO<sub>2</sub> is commonly transported by ship in liquid form at low temperature. In Northern Europe, 4 small CO<sub>2</sub> tankers, similar to LPG vessels, distribute liquid CO<sub>2</sub> derived from ammonia plants to food producers [1]. There have been studies done by Norwegian tanker lines funded by Statoil and supported by work provided to the IPCC Special Study on CCS [1]. Large tanker applications have been studied but

practical applications may be difficult to identify as ship transport only becomes economic over long distances well in excess of 1000 km.

Ship transport requires on shore support infrastructure:

- Liquefaction facilities: The largest of these built to date is 350 kt/a of CO<sub>2</sub> [1, 13].
- Loading/Unloading facilities: These facilities would be very similar to that required for LPG shipments with equally similar costs.
- Refrigerated storage: Assuming 10 days storage, this would require 6-8 spheres of 8-10,000 m<sup>3</sup> capacity for a typical 150 kbb/d conversion refinery.
- Regasification / compression facilities at the point of injection.

The number of ships required would depend on ship size, sailing and turnaround times. The semi-refrigerated type is preferred by ship designers. Standard design semi-refrigerated LPG carriers transport 22,000 m<sup>3</sup> at a design point around -50°C and 7 bars. Cost estimates for CO<sub>2</sub> carriers vary widely, within a range of 17-45 M€ for a 20 kt tanker at 2008 costs. Charter rates of €25,000 /day are expected at 2008 prices. With speeds of 20-30 km/h a number of such tankers would be needed to cover loading/unloading and sailing time [1]. For a 1000-2000 km trip, probably three would be needed.

For the typical distance required in Europe (500 km), the overall cost of CO<sub>2</sub> transport by ship would be approximately twice the pipeline cost. Shipping would only become cost-competitive for distances greater than 1000 km. It is assumed that the receiving facility would bear the (relatively low) cost of converting the low pressure/ low temperature CO<sub>2</sub> to a high pressure supercritical fluid for injection purposes.

Carbon dioxide tankers and terminals are clearly much less of a fire or explosion risk than those handling hydrocarbons, but there is an asphyxiation risk in case of a large CO<sub>2</sub> release. Based on the record of LPG and natural gas tankers this risk is considered very low [1].

An added factor for the handling (loading/unloading) operation and transport of CO<sub>2</sub> is that it must be kept dry at all times to avoid corrosion. This requires additional facilities and attention to operating procedures to avoid ingress of any moisture.

#### 4.3. CO<sub>2</sub> STREAM QUALITY REQUIREMENTS FOR TRANSPORT

For transport, the main concerns are public safety, corrosion and energy consumption. European and National regulations exist with respect to toxicity and flammability for transport of gases by any means including pipelines. These are currently seen to be sufficient to regulate the transport of CO<sub>2</sub> as long as H<sub>2</sub>S levels are very low. Even in the rural environment of West Texas, pipelines have H<sub>2</sub>S limits ranging from 20 to 200 ppm. Europe would probably require the H<sub>2</sub>S level and any other noxious gas to be similar.

Currently there is no commonly recognised quality standard for transport of CO<sub>2</sub> streams. However, some CO<sub>2</sub> pipeline operators in the US have established quality specifications deemed necessary for safety and to satisfy the needs of seller, transporter and user. **Table 3** is a pipeline specification for a US facility. An EU standard will need to be developed.

**Table 3** Example of a CO<sub>2</sub> Stream Quality Requirement for pipeline transport  
(CORTEZ PIPELINE. Courtesy Kinder Morgan)

Component	Number	Units
Carbon Dioxide	>95	Mole%
Free Water	None	
Water vapour	<630	ppm v/v
Hydrogen Sulfide	<20	ppm m/m
Total Sulfur	<35	ppm m/m
Nitrogen	<4	Mole%
Hydrocarbon	<5	Mole%
Hydrocarbon Dew Point	<29	°C
Oxygen	<10	ppm m/m
Glycol	< 42	l/MNm <sup>3</sup>
Liquid Glycol	None	
Temperature	48.9	°C

Other commercial pipelines impose similar specifications, sometimes allowing higher sulphur content such as the Canyon Reef Carriers Pipeline for which both the H<sub>2</sub>S and total sulphur limits are 200 ppm.

Establishing a uniform, consistent quality specification will need to be addressed by owners, operators and responsible parties for the pipelines and storage facilities. The criteria developed in the US can serve as a starting point to which additional requirements can be added to address Europe specific circumstances. One of these is the location of pipelines in densely populated areas which will necessitate additional safety procedures that may not be required in the US.

The above specification mostly addresses potential contaminants. In addition the CO<sub>2</sub> concentration will need to be at least 90% v/v and probably closer to 95 % because of compression requirements. One European operator has stated that there should be no more than 3% v/v N<sub>2</sub> + Argon. If the CO<sub>2</sub> content was reduced to 75% v/v, power requirement would increase by 33 % to reach a pressure of 190-200 bars.

A fully fledged quality specification will require assessment of the impact of all non-CO<sub>2</sub> compounds in the fluid stream on the entire fluid stream, the transport system and the storage site. In addition to potential issues with individual gas streams, consideration would need to be given to potential synergistic effects. For instance mixing two gas streams respectively containing high H<sub>2</sub>S and some oxygen could create elemental sulphur with the potential for severe corrosion, accumulation of solid sulphur and blockages. Currently the main concern over oxygen is potential stimulation of microbial action.

## 5. CO<sub>2</sub> STORAGE

Although CO<sub>2</sub> storage is not the main focus of this report, the aim of this chapter is to briefly introduce and discuss the various options that have been proposed and identify any issues (e.g. quality) that may have to be taken into account at the capture stage.

Underground storage in geological formations is by far the most studied and developed concept. Other options have been proposed such as “mineralisation” but these are less likely to play a role, at least in the medium term.

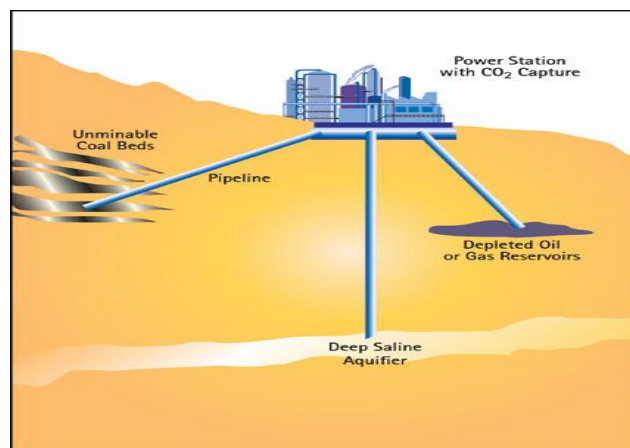
### 5.1. POTENTIAL GEOLOGICAL FORMATIONS FOR CO<sub>2</sub> STORAGE

The general concept behind CO<sub>2</sub> underground storage involves maintaining the CO<sub>2</sub> at elevated pressure in a so-called “supercritical” state i.e. a form that is a combination of high density gas and liquid. Under such conditions CO<sub>2</sub> has a density of 500 to 800 kg/m<sup>3</sup> (depending on pressure/temperature) compared to about 2 kg/m<sup>3</sup> as a gas at atmospheric pressure. In other words 250 to 400 times more CO<sub>2</sub> than at atmospheric pressure can be stored in a given volume. Three main options are being considered for underground CO<sub>2</sub> storage (**Figure 16**):

- Deep saline aquifers
- Depleted or abandoned oil and gas fields
- Unexploited deep coal seams and enhanced coalbed methane recovery (ECBM)

**Figure 16**

Main geological storage options  
(Courtesy of the IEA Greenhouse Gas R&D Programme)



There is a broad consensus among geologists working in this field that there is considerable scope for underground storage of CO<sub>2</sub>, and easily for 50+ years at current and forecast production rates [1,3]. Currently there are very few sites used specifically to store CO<sub>2</sub> particularly long term. Several large scale trials, shown in **Table 4**, are being carried out to test the practicability of the main storage options.

**Table 4** CO<sub>2</sub> Trial Storage Sites –Completed, Ongoing or Planned [1]

Project name	Country	Project Start	Injection rate, tCO <sub>2</sub> / day	Anticipated Storage (tCO <sub>2</sub> )	Reservoir Type
Weyburn	Canada	2000+	1500	20,000,000	EOR
In Salah	Algeria	2004+	2000	17,000,000	Gas field
Sleipner	Norway	1996+	3,000	20,000,000	Saline formation
K12B	Netherlands	2004+	100	8,000,000	EGR
Frio Brine	U.S.A	2005-6	150	3000	Saline formation
Fenn Big Valley	Canada	1998	50	200	ECBM
Qinshui Basin	China	2003	30	150	ECBM
Nagakoa	Japan	2004-5	20	10,400	ECBM
Recopol	Poland	2003+	1	10	ECBM
Gorgon	Australia	2009	~ 10,000	129,000,000	Saline formation
Snøhvit	Norway	2008	2,000	unknown	Saline formation
Rousse	France	2009	200	150,000	Depleted gas field

In spite of the extensive experience already gained through these activities there are still many technological uncertainties related to long term storage of very large quantities of CO<sub>2</sub>. The resulting costs are therefore also uncertain. Although storage costs are very likely to be much lower than capture costs, they are the most uncertain. Secure containment over long time periods needs to be demonstrated with potential for leakage via old or new wells, new or reactivated geological faults or sideways migration. When also considering permitting, ownership, liability issues and public perception issues, storage is clearly the area of the CCS chain that presents the highest risks.

### 5.1.1. Deep Saline Aquifers

These aquifers are huge volumes of salt water permeating through mainly sandstone. The water is not potable and cannot be used for either soil irrigation or desalination plant feed. These formations have by far the largest potential for long term storage of CO<sub>2</sub> but are the least characterised [1,4,5]. In the first demonstration of this type of CO<sub>2</sub> storage designed specifically for climate change mitigation purposes, about 1 Mt/a of CO<sub>2</sub> has been injected at 1000 m into a deep saline aquifer in the Sleipner field (Utsira area of the North Sea) over the last 10 years. Under a related international monitoring project undertaken by BP, Statoil, EU, the IEA Greenhouse Gas R&D Programme and the Norwegian Government various tests including 3-D seismic surveys of the area have been carried out and no escape of CO<sub>2</sub> has been detected.

### 5.1.2. Oil and Gas fields

CO<sub>2</sub> injection in oil and gas fields has been practiced for many years as part of Enhanced Oil Recovery (EOR) or Enhanced Gas Recovery (EGR) programmes. This technology is used to increase production and/or prolong the life of oil and gas fields nearing depletion (which generally occurs after about 30% of the oil or 60 to 80% of the gas has been recovered). CO<sub>2</sub> injection is practiced in addition to or after water injection below the reservoir (flooding) with the aim of increasing reservoir pressure to push oil out of the rock structure. In addition to maintaining gas pressure in the reservoir, CO<sub>2</sub> permeates through oil containing rock pores, reducing the oil viscosity and stimulating flow markedly. The effect of CO<sub>2</sub> injection is felt after 1-2 years. This technology really only results in partial storage, as 40-60% of the CO<sub>2</sub>

injected resurfaces with the crude oil. However that CO<sub>2</sub> can be separated at high pressure in production facilities and recycled.

In gas reservoirs, CO<sub>2</sub> starts to mix with natural gas, causing dilution. At some point, EGR loses economic attractiveness as the cost of separating CO<sub>2</sub> from the gas becomes prohibitive.

In North America, a total of about 500 Mt CO<sub>2</sub> has been injected in a number of EOR projects since the 70s. A 2008 survey [6] showed a large increase in on shore CO<sub>2</sub> injection projects for EOR in North America although EOR with CO<sub>2</sub> only accounts for 3.6% of total oil production. A very active major company in the CO<sub>2</sub> gathering, pipeline and supply business reports that EOR with CO<sub>2</sub> in the USA is currently limited by the supply of CO<sub>2</sub> [6]. A report by the joint taskforce of the UK & Norwegian governments indicated that there is little incentive for EOR with CO<sub>2</sub> in the UK & Norway offshore sectors with a crude oil price at \$100/bbl or less [7]. If the oil price is sustained above this value there may be an incentive for EOR.

As oil and gas fields become truly depleted after EOR they are abandoned and capped. The geological structure may then be used for permanent CO<sub>2</sub> storage. Their location and capacity is known based on the volume of oil and gas extracted. In general, the trapping ability of the geological structure should be secure as it has held oil and gas under pressure for millions of years. However, extraction of the oil and gas may have caused some changes to the rock structure so survey work is still required to ensure the integrity of the reservoirs. The original extraction wells have normally been plugged so new wells for injection and monitoring would need to be drilled.

Abandoned and capped oil or gas production facilities, with piping and platforms removed, are likely to be much more difficult and expensive to re-commission for CO<sub>2</sub> storage service or EOR. If such structures are to be used for storage then arrangements need to be made to 'mothball' them until ready to start receiving CO<sub>2</sub>. This will require consultation between several parties, viz.

- Potential CO<sub>2</sub> producers,
- Oil and Gas Producers operating oil and gas reservoirs,
- Companies active in CO<sub>2</sub> trading,
- Local/National governments who will need to put necessary legislation in place with respect to long term storage of CO<sub>2</sub>-rich streams on - and transport through - their territories,
- International bodies that will need to develop legislation for long term storage outside national territorial waters. This would be similar to agreements/legislation with respect to transport and disposal of hazardous wastes a few decades ago.

These issues are currently being debated for all geological storage methods.

### 5.1.3. Storage in Deep Coal Seams

Deep coal seams which cannot be mined constitute an additional CO<sub>2</sub> storage alternative. In this case, CO<sub>2</sub> would be injected at high pressure at typically 1000 m depth into the coal seams where it would permeate through coal, displacing methane (Enhance Coal Bed Methane, ECBM) which would be recovered for use. Although some CO<sub>2</sub> is recycled, there is some permanent storage of CO<sub>2</sub>. A trial of

this method of CO<sub>2</sub> storage is currently underway in the **Recopol** project in Poland [8].

#### 5.1.4. **Shallow exhausted or unused coal mines**

Some commercial companies are looking at this as an easily achievable storage method. As with depleted oil and gas fields, subsequent coal recovery could result in release of the CO<sub>2</sub> or require transfer to another storage structure. Leakage of CO<sub>2</sub> through the coal fields appears to be an issue as the fields can be highly fractured and there have been numerous mine workings in past centuries, often poorly recorded. This method has little support from national governments or potential CO<sub>2</sub> producers.

#### 5.1.5. **Salt caverns**

Numerous salt caverns are in use around the world, particularly in North America and Europe, for storing oil, LPG and natural gas. These caverns can occur naturally but most are man-made by dissolving salt with hot water in naturally occurring high density salt deposits. The technology is well known and widely applied. Care is taken to maintain good separation of individual caverns. Seismic checks are carried out to ensure integrity of the caverns. Generally the caverns are relatively small but could be used for temporary storage of small batches of CO<sub>2</sub> pending transport to permanent storage sites.

### 5.2. **OTHER STORAGE OPTIONS**

#### 5.2.1. **Reaction of CO<sub>2</sub> with minerals**

CO<sub>2</sub> reaction with e.g. silica is a possible means of tying up CO<sub>2</sub> as mineral carbonates. This could be seen as the ultimate long term storage i.e. many centuries, with no potential for leakage. Currently this method is mostly in the early research phase and large scale trials are not at a true planning stage. Estimated costs are the highest of all potential storage options.

### 5.3. **POTENTIAL STORAGE IN THE EU**

The **Gestco** project [9] produced a first inventory of anticipated storage capacity in EU countries which participated in the project (**Table 5**). This points out to sufficient storage capacity to cover in the order of 100 years of current CO<sub>2</sub> emissions. It has to be emphasised though that these numbers are based on a high level survey of geological formations rather than detailed assessments of individual reservoirs. The feasibility of storage in any particular reservoir will require a thorough assessment including the ability of the formation to retain CO<sub>2</sub>, the risk of geological instability such as earthquakes etc. It is likely that eventual usable capacities will be significantly reduced compared to these preliminary figures.



**Table 5** Estimated storage in Oil, Gas and Saline Aquifers in Some European Countries  
(Source: **Gestco** Project, 2004 [9])

Country	Storage Capacity (Mt CO <sub>2</sub> )		Emissions (Mt CO <sub>2</sub> /a) (Based on ETS reporting)	Potential Storage (years)		
	Oil & Gas fields	Saline aquifers		Oil & Gas fields	Saline aquifers	Total
Germany	2,500	33,000	474	5	70	75
Denmark	800	16,000	26	31	615	646
France	800	27,000	131	6	206	212
UK (North Sea)	10,000	15,000	251	40	60	100
Greece		2,500	71	0	35	35
Norway	12,500	12,700	113	111	112	223
Netherlands	11,000	2,000	80	138	25	163
<b>Total</b>	<b>37,600</b>	<b>108,200</b>	<b>1,146</b>	<b>33</b>	<b>94</b>	<b>127</b>

A more comprehensive survey published in 2009 by the **GeoCapacity** project [10] includes 25 European countries. It gives a total conservative European storage capacity of 117 Gt, of which 96 Gt in deep saline aquifers, 20 Gt in depleted hydrocarbon fields and 1 Gt in unmineable coal beds. Offshore Norway accounts for approx. 25% of the total capacity, mainly in deep saline aquifers. This total storage capacity corresponds to 62 years of storage of the 1893 Mt CO<sub>2</sub>/a of European emissions from large point sources (>0.1 Mt/a per source).

A noteworthy result of the GeoCapacity project is the high proportion of offshore storage capacity: about 68% of the total available storage capacity identified in the GeoCapacity GIS database is offshore. This will have a significant impact on the cost of pipelines and other infrastructure.

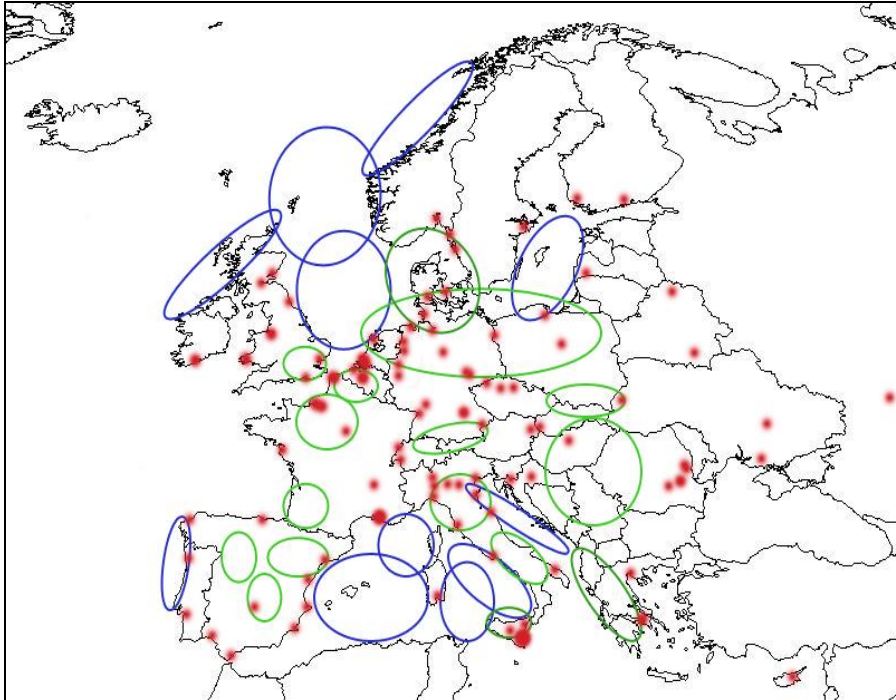
### 5.3.1. Geological storage locations in relation to EU refineries

**Figure 17** shows refineries and potential sedimentary basins storage sites. The red dots represent refineries or groups thereof (e.g. in Sicily, Antwerp and Rotterdam). Areas bounded in green and blue are potential storage areas, on-shore and off-shore respectively. The sedimentary basin areas shown, although relatively well known, have not been mapped in detail in all cases. As mentioned in the previous section, more investigation is required to prove that all or parts of such sedimentary basins are suitable for long term storage. Nevertheless the map suggests that, in general in Europe, there are potential storage areas relatively close to refineries i.e. within 500 km.

This distance is well within the experience range built up in the US for CO<sub>2</sub> transport for EOR (see **Section 4**). The relative location of refineries and storage areas may in some cases involve trans-boundary transport which could raise issues even within the EU.

Some National Governments, for example Spain, have already reserved areas both on- and off-shore of their territories which are potential storage sites close to refineries and other industrial CO<sub>2</sub> producing areas.

**Figure 17** Location of EU Refineries and Potential CO<sub>2</sub> Storage Areas [3]



#### 5.4. CO<sub>2</sub> INJECTION

Amongst oil and gas producers there is a considerable body of expertise in injecting CO<sub>2</sub> in underground reservoirs and monitoring its behaviour in relation to EOR and EGR mostly in North America.

Maintaining CO<sub>2</sub> in dense (supercritical) phase requires a pressure of 80 bars or more. If CO<sub>2</sub> is diluted with incondensable gases like nitrogen or argon, total pressure needs to be proportionally higher. The degree of purification then becomes a question of economics, its cost being compared with that of extra compression power and equipment design pressure.

For storage, CO<sub>2</sub> stream quality issues are long term effects of trace components and the potential impact of CO<sub>2</sub> release on the safety of personnel and the public near storage sites. As yet there is no specification for CO<sub>2</sub> streams to be stored but there are likely to be limits regarding oxygen which could lead to microbial growth and any compounds that could react over time e.g. SO<sub>2</sub> with H<sub>2</sub>S to form elemental sulphur. There are also likely to be restrictions on mixing of gas streams particularly, from a legal point of view, anything that could be considered a waste material being added to the CO<sub>2</sub> stream.

There is no experience with geological storage of CO<sub>2</sub> captured from furnace flue gas. Potential issues with trace contaminants need to be addressed in conjunction with transport requirements to develop a European specification for transport and storage.

## 5.5. LONG TERM MONITORING OF STORAGE

CO<sub>2</sub> storage sites will need to be monitored mainly in relation to leakage or potential leakage of CO<sub>2</sub> to atmosphere. There are several potential techniques and protocols considered and used today [1]:

- Seismic surveys to track CO<sub>2</sub> movements and detect faults or potential faults in the surrounding geological structure,
- Peripheral detection drill taps as the storage volume increases,
- Use of tracers in the stored CO<sub>2</sub>,
- Physical methods such as pressure measurement,
- Atmospheric concentration measurements around the storage sites.

Whichever method is used there will be an associated cost. Companies involved in storage will select one or several methods most probably in consultation with regulatory Authorities. Oil and gas producers tend to favour their standard practice of seismic surveying. CO<sub>2</sub> injection for EOR in North America has given operators there a high degree of confidence in their ability to track movements of CO<sub>2</sub> in oil and gas fields. The Statoil trial in the Sleipner field has demonstrated the ability to monitor CO<sub>2</sub> movement seismically in a saline aquifer and now the entire operation is considered "routine business". So far there is no legislation prescribing one or several specific techniques.

## 6. COST OF CCS

Most estimates of the cost of CCS have been based on power plants. In particular, current cost estimates for CCS in coal-fired power plants are in the range of 60-80 \$/t (43-57 €/t) of CO<sub>2</sub> avoided [20]. CONCAWE member companies concur that with the possible exception of emissions from hydrogen production units, the cost of CCS for refineries can be expected to be considerably higher than for power plants, particularly with respect to capture, for a number of reasons already alluded to in **Section 3** and further discussed below. The likely cost of CCS in refineries will also be much higher than the current price of CO<sub>2</sub> permits under the EU ETS and particularly when compared to the figure of 30 €/t CO<sub>2</sub> which is routinely used for economic evaluations at the 2020 horizon. Even if there were cost reductions through experience building and cost breakthroughs, implementing CCS would not be achievable at this CO<sub>2</sub> price.

### 6.1. CAPTURE COSTS

The capture cost is highly dependent on the fraction of the total emissions to be captured, as refineries usually have a small number of large emission sources and a large number of smaller, dispersed, low concentration sources. A report by Shell [19] estimates the capture cost for 50% of the total CO<sub>2</sub> emissions of one of the largest and most complex EU refineries at 90-120 €/t CO<sub>2</sub> avoided (2007 basis). The cost will be considerably higher for capture of the remaining 50% of emissions. Smaller, less complex refineries would not benefit from the economy of scale of the refinery in the Shell study.

The cost of capture for refineries is affected by a number of additional factors which contribute to making the cost higher than in power plants.

- **Scale:** The annual CO<sub>2</sub> emissions of EU Refineries lie in the range 0.4 Mt/a to 2.7 Mt/a (10-90 percentile). The biggest emitter of all the EU refineries emits about 5.6 Mt/a CO<sub>2</sub>, while 50% of refineries emit less than 1.3 Mt/a each. Refineries are small emitters by comparison with power plants. The largest five EU coal-fired power plants produce an average of about 28 Mt/a CO<sub>2</sub> (Source: European Pollutant Release and Transfer Register). Economies of scale are therefore likely to benefit CCS costs for power plants considerably more than for refineries.
- **Distributed and diverse sources:** Power plants have a single type of flue gas emitted from a single stack (or possibly two or three stacks for the very large ones). Refineries can typically have 20 to 30 different CO<sub>2</sub> emission sources, ranging widely in size, location, flue gas concentration and types of contaminants. These sources generally emit to the atmosphere through individual stacks, which are scattered throughout the refinery site. Gathering these sources into a centralised capture facility requires considerable investment in large cross-section ducting and induced draft fans, with additional energy requirements, often in situations where space is severely restricted.
- **Range of CO<sub>2</sub> concentrations:** The wide range of possible CO<sub>2</sub> concentrations in refinery flue gases depending on the fuel burned (natural gas, refinery gas, liquid fuel and FCC coke), many of which result in CO<sub>2</sub> concentrations well below the typical level of 10-13% v/v in coal-fired power plants, will determine capture equipment sizes, rangeability and control system

requirements. This generally results in a more complex capture system than in a power plant where the flue gas concentration is relatively stable.

- **Utilities:** A large power plant can be de-rated to provide the energy required for the capture process. This is not possible for refinery units. Therefore, the capture cost needs to account for the investment in dedicated utilities equipment required to generate the additional steam and electricity, as well as the related operating costs.
- **Brownfield projects:** CCS deployment in EU refinery industry will consist entirely of retrofits, since no grassroots refinery projects are foreseen due to the limited growth in total product demand. Brownfield projects will have higher complexity and higher associated costs than grassroots projects. This contrasts with the situation in the EU power industry where grassroots power plant projects are planned to replace older power plants and meet the growing demand for electricity in Europe.
- **Economic premises:** The cost per tonne of CO<sub>2</sub> is highly dependent on the discounting premises used to annualise the capital investment cost. Power plants, which operate in a stable and predictable market, are usually premised at annual capital charges of typically 7-8% of capital cost. Refinery plants operate in a much more volatile and less predictable market with intrinsically higher discount rates and capital charges. For the same investment cost this difference alone can significantly increase the cost of CCS for refineries in €/t CO<sub>2</sub> avoided. Other economic assumptions such as tax charges can further increase this difference.
- **Fuel cost:** In a refinery the marginal fuel consumed to supply energy for capture unit utilities is likely to be natural gas, whereas the marginal fuel in many power plants is likely to be coal. The resulting difference in additional fuel costs is likely to penalise the cost of capture for refineries in €/t CO<sub>2</sub> avoided.

CONCAWE has reviewed the available estimates from published literature (shown in **Table 6**), consultants and internal member company work. The wide range of these estimates highlights the need to allow for the specific context of each case, in terms of the relative size and complexity of the refinery, the variance in size of emission source streams, the variety of CO<sub>2</sub> concentrations within those streams, and the geographic dispersion of those sources across a large refinery plot.

**Table 6** Post-combustion Capture costs in refineries from literature

Reference	Estimation year	Process Unit/Technology	Cost (€/t CO <sub>2</sub> avoided)	Cost (\$/t CO <sub>2</sub> avoided)
RCI [26]	2009	Post-Combustion (Heaters)/Amines	110-130	
CCP2 [14]	Mid2008	Post-Combustion (Boiler)/Amines	96	
ERM [27]	2009	Post-Combustion (Heater, Boiler)/Amines		114-192
CCP2 [14]	Mid2008	Post-Combustion (FCC)/Amines	85-112	
Shell [19]	2007	Post-Combustion/Amines	90-120	

The estimated cost of capture varies widely, particularly for refineries on account of the large number of technology-related unknowns. Although the process unit operations are existing technologies used in gas treating, large-scale CO<sub>2</sub> capture from combustion products will involve the application of these technologies in a much harsher environment and on a scale for which there is currently no practical experience.

Additional factors that should be borne in mind when comparing literature cost estimates are the differences in reference year, uncertainties concerning the fraction of refinery emissions captured in each case, different economic assumptions (i.e. discount factor, capital charge factor, time horizon, etc.), and different equipment lists depending upon the extent to which utilities and related infrastructures can be integrated into the existing refinery. Furthermore, the inherent uncertainties in feasibility level cost estimates can lead to considerable deviations in completed project capital and operating costs for commercial-scale demonstration projects compared to the original project cost estimates.

The escalation of capital costs for commercial-scale demonstration projects has illustrated that the finished project can be vastly more expensive than suggested by the bulk of literature estimates to date. For example, it has been reported that the estimated cost of the Mongstad large-scale test facility has risen significantly since the original 2006 estimate. Admittedly, this is a technology demonstration plant, but it underscores the uncertainty – both technical and economic – in estimating the cost of capture.

In view of the huge size of the equipment, retrofitting to an operating refinery would be a major engineering, construction and economic challenge. The installation of major equipment and extensive ducting in an operating refinery would lead to extensions of normal shutdowns involving large parts of the refinery, with consequent production losses and negative economic impact. There would also be a number of specific design issues to be considered such as how to handle any potential backpressure on operating furnaces and safety aspects of connecting

furnaces together. Detailed evaluation could lead to very much higher costs and every refinery will probably be different in this respect.

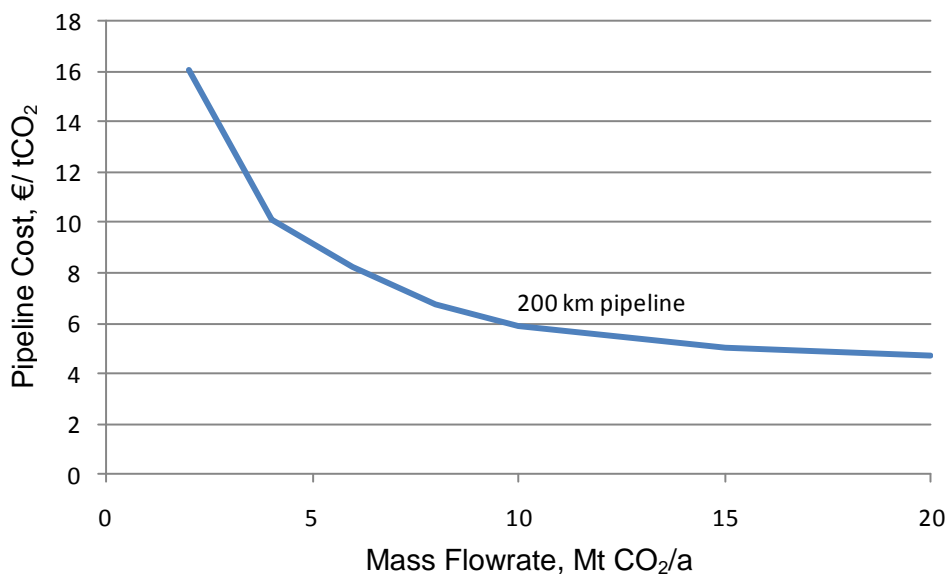
CONCAWE is considering the possibility of launching a separate study to produce a detailed independent cost estimate that is representative of capture from refinery units, with the intention of publishing this in a separate report in due course.

## 6.2. PIPELINE INVESTMENT

The cost per tonne of CO<sub>2</sub> transported by pipeline is very much related to the size of the operation. In general large pipelines are more cost-effective than smaller ones. Without including compressors, a 300 mm onshore pipeline would cost 1.1 M€/km at 2009 prices [11], assuming costs similar to the US and an exchange rate of 1.4 \$/€. This is an average number with a wide spread because pipeline costs are very sensitive to the terrain and environment in which they are to be laid. A 200 km line would then cost about 220 M€ for the 2 Mt/a CO<sub>2</sub> captured (1.4 Mt/a CO<sub>2</sub> avoided) from the typical UK refinery in the CCP study [14]. Unless this investment could be shared with other large emitters, it would be a major barrier to phased CCS implementation in refineries (e.g. 5-10% of the total from a conventional hydrogen plant) because the small initial volumes would have to support the total cost of a much larger transport infrastructure. Long offshore lines are likely to be a factor of 2-3 higher and short offshore lines a factor of 10 higher. As noted in **Section 5.3**, the majority of available storage capacity in the EU is offshore (68% of the total), which suggests that the majority of pipelines will be offshore and average costs will be higher than the above estimate.

**Figure 18**

**Pipeline Transport Cost**  
 2009 US average cost correlation [11] with 15% capital charge, 1.4 m/s maximum velocity, 8000 h/a operation, 1.4 \$/€. Energy costs and booster stations not included.



According to **Figure 18** flow rates of at least 5-10 Mt/a of CO<sub>2</sub> would be required to bring unit costs down to manageable levels. No single refinery in Europe would generate this amount of CO<sub>2</sub> so collaboration between refineries and preferably with

power stations and/or other large CO<sub>2</sub> emitters would be necessary to justify building such pipelines. Implementation of a common “backbone” pipeline infrastructure may also facilitate access to large remote storage sites. Infrastructure of this kind would require huge initial investments and a high level of cooperation between various economic actors as well as with governments and civil society.

The 200 km pipeline investment cost of 220 M€ for the 2 Mt/a captured (1.4 Mt/a avoided) in the above example UK refinery amounts to about 23 €/t CO<sub>2</sub> avoided, based on a 15% annual capital charge. Including fixed operating costs (at 3% of capital cost) this would increase to 28 €/t CO<sub>2</sub> avoided. This would of course be significantly less if the pipeline was shared.

### 6.3. STORAGE

Compared with CO<sub>2</sub> capture, storage costs are relatively low but are the most uncertain. Most of the cost arises from drilling injection wells. Public perception of storage under areas of population may be negative so that, although more expensive in terms of CO<sub>2</sub> transport and well drilling, offshore geological storage may be a more acceptable solution. Projected costs for injection /storage, prorated from the IPCC report [1] range from €1 - €12 /t CO<sub>2</sub> stored. The lower figure assumes that existing onshore extraction facilities such as depleted oil and gas reservoirs are used for CO<sub>2</sub> injection. The higher figure assumes new offshore drilling into the deeper saline aquifers. For Europe the higher end of the range is more likely.

### 6.4. MONITORING

Monitoring costs updated to 2008 from the IPCC report [1] are estimated to be 0.1-1.0 €/t CO<sub>2</sub> stored. As yet there is no clear indication of which methods would be employed. The upper end of the range would particularly apply to offshore storage.

### 6.5. ENERGY COST

As mentioned in **Section 3.1.2**, extra energy is required, mostly for capture and to a lesser extent for compressing CO<sub>2</sub> for transport and injection. The total energy requirement for capture and compression was estimated at 4.2 GJ/t CO<sub>2</sub> captured. Small energy consumptions are also associated with storage and monitoring, estimated at 0.16 GJ/t CO<sub>2</sub> captured. With an assumed crude oil price of 50 €/bbl (70 \$/bbl) and commensurate energy price (5.6 €/GJ, i.e. 65% of crude price) the total energy cost for capture, compression and storage of 2 Mt/a CO<sub>2</sub> (1.4 Mt/a CO<sub>2</sub> avoided) in the CCP study [14] UK refinery example would amount to 49 M€/a, or 35 €/t CO<sub>2</sub> avoided. This figure would of course be subject to potential large variation with the general cost of energy. It may also be possible to reduce the energy consumption if waste heat is available at the site at a sufficiently high temperature to integrate into the capture unit.



## 7. OVERALL VIEW OF REFINERY CCS PROJECTS

As already outlined, there are several technologies postulated for CCS for each element in the chain. **Table 7** summarises the state of technological readiness for each of the elements as viewed by IPCC experts. Clearly there is still a long path to be walked until even the “mature” technologies required for CCS can be widely deployed at full commercial scale.

**Table 7** Technical readiness for the elements of CCS  
(Source: [1], Table TS1)

CCS Element	Technology Type	Research	Demonstration	Economically Feasible under specific Conditions	Mature
Capture	Industrial Separation i.e. H <sub>2</sub> plant, Ammonia, Natural Gas				X
	Post Combustion			X	
	Pre-Combustion			X	
	Oxy Fuel Combustion		X		
Transportation	Pipeline				X
	Shipping			X	
Geological Storage	Enhanced Oil Recovery.( Practiced but not solely so far for storage)				X
	Gas or Oil Fields			X	
	Saline formations			X	
	Enhanced Coal Bed Seams		X		
Mineral Carbonation	Natural Silicate materials	X			
Industrial Use	Various small high purity quantities				X

### 7.1. BARRIERS AND CHALLENGES TO IMPLEMENTING REFINERY CCS PROJECTS

CCS will require investment in new equipment that will be physically very large and represent a considerable financial burden that can only be recouped through selling (or not having to buy) carbon emitting permits. Before this can be done the three components of capture, transport and storage have to be in place. This is particularly challenging for several reasons. We have seen that, particularly for relatively small emitters such as refineries, transport infrastructure will likely have to be shared. In addition owners/operators of storage sites and emitters are likely to be different economic entities. As a result a number of conditions will need to be fulfilled for full-scale CCS to develop, including :

- Real understanding that CCS is a very long term undertaking i.e. at least 20-30 years for capture and much more for storage,

- Long term partnerships between emitters, transportation companies/ storage owners and regulators,
- Leadership for development and operation of the massive CO<sub>2</sub> gathering infrastructure by major emitters,
- Clear market signals of the long term value of CO<sub>2</sub> and the mechanisms to determine the value such as taxation or penalties,
- Confidence in the long term soundness of the technologies used,
- Clear delineation of responsibilities and liabilities particularly for the long term.

## 7.2. ADDITIONAL RESOURCE REQUIREMENTS

As we have seen in **Section 3**, the infrastructure required for retrofitting CCS in an existing refinery will be massive. This would not only concern capture equipment itself, but also additional offsite and utility systems that would be required to meet the considerable extra energy demand.

The detailed refinery study done in [14] assumed gathering of all refinery flue gases in four large amine absorbers. The scale of the required facilities is illustrated below.

- 2 km of ducting with a cross-sectional area of up to 9 m<sup>2</sup>
- 10 MW and 15 MW blowers to route flue gases through the scrubbing system
- 4 amine absorbers of 10.3 m diameter
- 1 regenerator of 10.4 m diameter

Other sites could be very different. In particular, the required length of ducting will strongly depend on the refinery layout.

There would be process safety issues related to ducting flue gases at low pressure level and interconnecting heater fire boxes via the duct system. Operating issues such as shutdown and isolation of individual furnaces would need to be addressed.

A number of environmental issues could also arise such as

- Visible plumes from cooling tower water vapour and decarbonised flue gas
- High dissolved solids in scrubbing water blow down
- 150 t/week spent amine from reclaiming which may require incineration

A new utility complex would be required, as shown in **Table 8**.

**Table 8** Utility plant additions required for 1.4 Mt CO<sub>2</sub>/a avoided  
(Source: [14])

Utility	Units	Quantity	Plant Description
Steam	t/h	480	CHP plant
Power	MW	72	CHP plant
Cooling Water	m <sup>3</sup> /h	18139	Two cooling towers
Natural Gas	MW	396	Direct import for CHP firing
Water	t/h	1025	Direct import for system make-up

### **7.3. OTHER ISSUES AND CONSIDERATIONS**

#### **7.3.1. Legal Issues**

At present, few countries have specifically developed legal and regulatory frameworks for onshore CO<sub>2</sub> storage. Relevant legislation includes petroleum-related legislation, drinking-water legislation and mining regulations. In many cases, there are laws applying to some, if not most, of the issues related to CO<sub>2</sub> storage. Specifically, long term liability issues have not yet been addressed. Monitoring and verification regimes and risks of leakage may play an important role in determining liability, and vice versa. As with the climate change problem, long term perspective is essential to a legal framework for CCS. In some countries the property and sub-surface rights of all those affected must be considered. States may exercise geological control of CO<sub>2</sub> storage within their jurisdiction and probably will have a responsibility to ensure that activities do not cause damage to the environment within the jurisdiction of other States.

Currently, there are several treaties (notably the UN Convention on the Law of the Sea, and the London and OSPAR Conventions) that could apply to the offshore injection of CO<sub>2</sub> into marine environments (both into the ocean and the geological sub-seabed). All these treaties were originally drafted without specific consideration of CO<sub>2</sub> storage. Amendments to the OSPAR convention (relating to the northeast Atlantic region) and the London Protocol in 2007 specifically prohibit storage of CO<sub>2</sub> in the sea water column and on the seabed but allow storage in sub-seabed geological formations, provided a permit is granted. The permitting requirements include the completion of an impact assessment and the determination of monitoring requirements. The transboundary export of CO<sub>2</sub> was prohibited under Article 6 of the London Protocol until an amendment was agreed in October 2009, permitting the export of carbon dioxide for disposal provided an agreement or arrangement has been entered into by the countries concerned.

Further clarification is required with regard to the international legal framework for CO<sub>2</sub> transport and storage, notably the transboundary liability issues raised by CCS projects.

Legislation specific to the EU entered into force on 25 June 2009 in Directive 2009/31/EC on the geological storage of CO<sub>2</sub>. The EU CCS Directive establishes a legal framework for the environmentally safe geological storage of CO<sub>2</sub>. The implementation of the Directive requires the transposition into legislation in each EU Member State by 25 June 2011. The EU Commission published four guidance documents on 31 March 2011 to support Member States in the implementation of the Directive and ensure a uniform implementation across Europe.

#### **7.3.2. Public Perception**

Assessing public perception of CCS is challenging because of the relatively technical and "remote" nature of this issue. The very few studies conducted to date indicate that the public is generally not well informed. If information is given in the context of other climate change mitigation options, the handful of studies carried out so far indicate that CCS is generally regarded as less favourable than other options, such as improvements in energy efficiency and the use of non-fossil energy sources.

Acceptance of CCS, where it occurs, is characterized as “reluctant” rather than “enthusiastic”. In some cases, this reflects the perception that CCS might be required because of a failure to reduce CO<sub>2</sub> emissions in other ways. There are indications that geological storage could be viewed favourably if it is adopted in conjunction with more desirable measures.

Recent experiences have highlighted the difficulties involved in addressing the concerns of communities to obtain public engagement in CCS projects. Some common strategies have emerged that contribute to successful engagement, but the approach needs to be tailored to each project to allow for specific regional or community attributes. Guidelines are becoming available to assist project developers in planning successful public engagement activities for CCS projects. These include the World Resource Institute guidelines [22] and the US DOE/NETL Best Practices manual [23].

Guidelines aimed specifically at the European context include the Public Engagement report from the European CCS Demonstration Project Network [24].

## 8. CONCLUSIONS

Successful deployment of CCS will require simultaneous development of efficient capture technologies, extensive transport infrastructure and secure CO<sub>2</sub> storage sites.

The specificity of oil refinery CCS projects will be mostly related to capture. Although refineries are fairly large CO<sub>2</sub> emitters as an entire site, these emissions come from a number of discrete sources, often spread over a large area and with different gas compositions. This makes efficient capture more complex and expensive than is the case for single-source sites such as power stations. As a result, it is estimated that about 50% of the combustion CO<sub>2</sub> emissions in most refineries are produced by sources that are likely to be too small and dispersed to be practically and economically captured.

Retrofitting CO<sub>2</sub> capture to a refinery would be a highly complex operation and would require very large equipment in the form of flue gas ducting, absorbers, solvent regenerators etc.

Although alternatives such as oxy-fuel combustion or pre-combustion capture cannot be ruled out, post-combustion capture i.e. capture of CO<sub>2</sub> from conventional flue gases is the most likely scenario for refineries in the foreseeable future.

Irrespective of the technology selected, CCS will significantly increase the energy footprint of the installation to which it is applied. The majority of the additional energy will be required for capture. CO<sub>2</sub> compression for transport will also add to the energy bill. In itself, this additional energy demand will cause more CO<sub>2</sub> to be emitted so that for a given amount of CO<sub>2</sub> really “avoided” considerably more will need to be captured (about 40% more in refinery projects).

Transport infrastructure, mainly in the form of pipelines, will need to be developed for large volumes in order to be cost-effective. Most refineries are not large enough emitters in this respect and would have to team-up with other emitters in order to develop viable projects.

In the near term, storage in depleted oil and gas fields is the most likely option, based on the extensive geological knowledge of such formations and on the experience built up with Enhanced Oil and Gas Recovery. In the longer term deep saline aquifers offer the largest capacity and most secure sites. Although legislation is being developed, there are still many issues related to long term ownership and liabilities that need to be resolved.

The total cost per tonne of CO<sub>2</sub> avoided for capture and compression in a typical EU refinery would be significantly higher than current estimates of 60-80 \$/t CO<sub>2</sub> avoided (43-57 €/t) for CCS in coal-based power plants, and higher still than the current cost of CO<sub>2</sub> permits under the EU-ETS which would serve as the benchmark for justifying projects.

Projects incorporating technology developed to address specific challenges in refineries (specific impurities, lack of free space, high reliability, low retrofitting impact, energy consumption and energy integration) will be critical to reducing total costs through experience-building and facilitating the selection of the appropriate technology for the variety of emission sources.

## 9. GLOSSARY

AMP	2-amino-1-methyl-1-propanol
CCP	CO <sub>2</sub> Capture Project
CCS	CO <sub>2</sub> Capture and Storage (also Carbon Capture and Storage)
CHP	Combined Heat and Power (also called Co-Generation)
CO	Carbon Monoxide
CO <sub>2</sub>	Carbon Dioxide
COS	Carbonyl sulphide
CS <sub>2</sub>	Carbon disulphide
DEA	Diethanolamine
ECBM	Enhanced Coal Bed Methane Recovery
EGR	Enhanced Gas Recovery
EOR	Enhanced Oil Recovery
ETS	Emissions Trading System
EU	European Union
FCC	Fluid Catalytic Cracking
FGD	Flue Gas Desulphurisation
GHG	Greenhouse Gas
H <sub>2</sub>	Hydrogen
H <sub>2</sub> O	Water
H <sub>2</sub> S	Hydrogen Sulphide
HCl	Hydrogen Chloride
HF	Hydrogen Fluoride
IEA	International Energy Agency
IGCC	Integrated (Coal) Gasification Combined Cycle
IPCC	Intergovernmental Panel on Climate Change
LNG	Liquefied Natural Gas
LPG	Liquid Propane Gas
MEA	Monoethanolamine
N <sub>2</sub>	Nitrogen
NO <sub>x</sub>	Nitrogen Oxides
O <sub>2</sub>	Oxygen
OSPAR	<b>O</b> slo and <b>P</b> aris Convention for the Protection of the Marine Environment of the North-East Atlantic
POX	Partial Oxidation (unit) i.e. gasification
ppmv	Parts per million, volume basis

ppmm	Parts per million, mass basis
PSA	Pressure Swing Adsorption, a process to purify hydrogen
SO <sub>2</sub>	Sulphur Dioxide
SO <sub>3</sub>	Sulphur Trioxide
SO <sub>x</sub>	Sulphur Oxides, SO <sub>2</sub> , SO <sub>3</sub>
SRU	Sulphur Recovery Unit (also known as Claus unit)
t	tonne

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## 11. LINKS TO ADDITIONAL CCS INFORMATION

1. Carbon Sequestration Leadership Forum: <http://www.cslforum.org>
2. Carbon Capture & Storage Association (CCSA): <http://www.ccsassociation.org>
3. Climate Action Network Europe (CAN-E): <http://www.climnet.org>
4. The European Network of Excellence on the Geological Storage of CO<sub>2</sub> (CO<sub>2</sub>GeoNet): <http://www.co2geonet.com>
5. Carbon Dioxide Knowledge Sharing Network (CO<sub>2</sub>NET): <http://www.co2net.com>
6. Cooperative Research Centre for Greenhouse Gas Technologies (CO<sub>2</sub>CRC): <http://www.co2crc.com.au>
7. Research project on underground storage of CO<sub>2</sub> in Aquifers (CO<sub>2</sub>STORE): <http://www.co2store.org>
8. European Technology Platform for Zero Emission Fossil Fuel Power Plants (ZEP): <http://www.zeroemissionsplatform.eu>
9. European Commission Climate Action - Carbon Capture and Geological Storage: [http://ec.europa.eu/clima/policies/lowcarbon/ccs\\_en.htm](http://ec.europa.eu/clima/policies/lowcarbon/ccs_en.htm)
10. Stanford University Global Climate and Energy Project (GCEP): <http://gcep.stanford.edu>
11. The Global Carbon Project (GCP): <http://www.globalcarbonproject.org>
12. International Energy Agency (IEA) - Carbon Dioxide (CO<sub>2</sub>) Capture and Storage (CCS): <http://www.iea.org/Textbase/subjectqueries/cdcs.asp>
13. Intergovernmental Panel on Climate Change (IPCC) Carbon Dioxide Capture and Storage: <http://www.ipcc-wg3.de/publications/special-reports/special-report-on-carbon-dioxide-capture-and-storage>
14. IPIECA The global oil and gas industry association for environmental and social issues: <http://www.ipieca.org/topic-issue/carbon-capture-and-storage>
15. World Energy Council: <http://www.worldenergy.org>
16. Global CCS Institute (GCCSI): <http://www.globalccsinstitute.com>

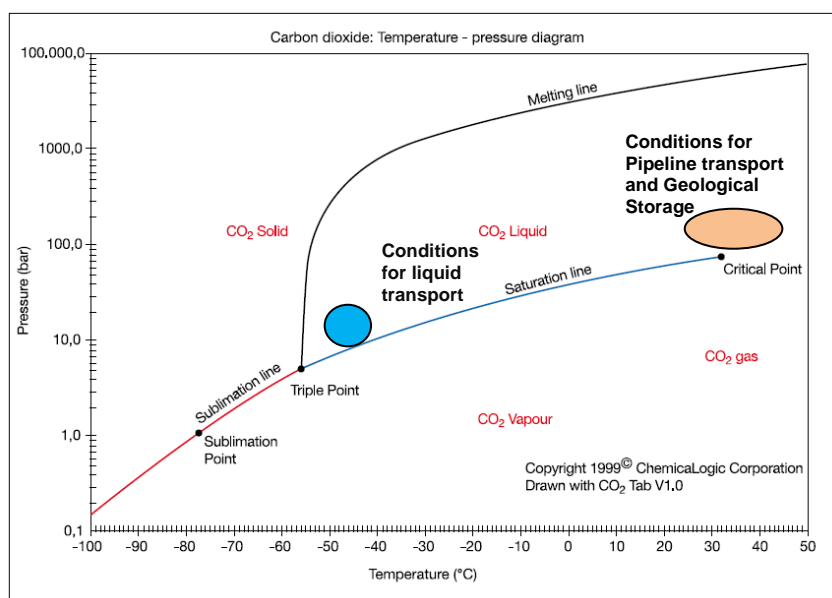
## APPENDIX 1: PROPERTIES OF CARBON DIOXIDE

Carbon dioxide is a chemical compound of two elements, carbon and oxygen, in the ratio of one to two; its molecular formula is CO<sub>2</sub>. It is present in the atmosphere in small quantities (370ppmv) and plays a vital role in the Earth's environment as a necessary ingredient in the life cycle of plants and animals. During photosynthesis plants assimilate CO<sub>2</sub> and release oxygen. Anthropogenic activities which cause the emission of CO<sub>2</sub> include the combustion of fossil fuels and other carbon containing materials, the fermentation of organic compounds such as sugar and the breathing of humans. Natural sources of CO<sub>2</sub>, including volcanic activity, dominate the Earth's carbon cycle. CO<sub>2</sub> gas has a slightly irritating odour, is colourless and is denser than air. Although it is a normal, if minor, constituent of air, high concentrations of CO<sub>2</sub> can be dangerous.

### Physical properties of Carbon Dioxide

At ambient temperature and pressure, carbon dioxide is a gas. The physical state of CO<sub>2</sub> varies with temperature and pressure as shown in **Figure A1-1** – at low temperatures CO<sub>2</sub> is a solid; on warming, if the pressure is below 5.1 bar the solid will sublime directly into the vapour state. At intermediate temperatures (between -56.5°C, the temperature of the triple point, and 31.1°C, the critical point), CO<sub>2</sub> may be turned from a vapour into a liquid by compressing it to the corresponding liquefaction pressure (and removing the heat produced). At temperatures higher than 31°C (if the pressure is greater than 73.9 bar, the pressure at the critical point), CO<sub>2</sub> is said to be in a supercritical state where it behaves as a gas; indeed under high pressure, the density of the gas can be very large, approaching or even exceeding the density of liquid water. This is an important aspect of CO<sub>2</sub>'s behaviour and is particularly relevant for its storage and transport. Heat is released or absorbed in each of the phase changes across the solid-gas; solid-liquid and liquid-gas boundaries (see **Figure A1-1**). However, the phase changes from the supercritical condition to liquid or from supercritical to gas do not require or release heat. This is useful for the design of compression facilities since this property can be exploited to avoid the need to handle the heat associated with the liquid-gas phase change.

**Figure A1-1** Phase diagram for CO<sub>2</sub>



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## APPENDIX 2: CHALLENGES IN CAPTURING CO<sub>2</sub> FROM FLUE GAS

### CO<sub>2</sub> Capture with Amines

**Monoethanolamine (MEA)** has a long history of commercial CO<sub>2</sub> recovery with various feeds including flue gases. MEA that does not contain additives (also called “uninhibited MEA”) is generally limited by corrosion problems to about 15-20% m/m MEA.

Furthermore, many applications rely on the presence of hydrogen sulphide in the feed to provide a passivating layer of iron sulphide and reduce carbonic acid corrosion. This protection is absent in flue gas systems where H<sub>2</sub>S is not present. The low MEA concentration raises the reboiler duty substantially. For example, the reboiler duty increases 20% when the MEA concentration decreases from 30 to 15% m/m. The required pump power increases even more. Since the reboiler heat duty is the most important key to operating costs, this is a significant handicap. However, there are four licensed units that use 15-20% m/m MEA to recover CO<sub>2</sub> from coal-fired flue gas. The plant capacities vary between 180 and 720 t CO<sub>2</sub>/day. Some corrosion inhibitors in conjunction with a quantitative oxygen and NO<sub>x</sub> removal system allow the MEA concentration to be raised to 25-30% m/m.

MEA is the cheapest amine and although it is degraded by high temperature the losses are manageable. Keeping the MEA system clean is the greatest improvement that can be made. The cheapest way to do this is with a thermal reclaimer which requires use of caustic soda and increased operator involvement as it is a batch process. The waste stream is a mix of MEA, sodium salts, polymer material and corrosion products for which an outlet is needed. Use in Sour water strippers is not an option because of the MEA content. Ion exchange processes to reclaim the MEA are available and work very well in refinery acid gas service units. They are expensive and also have a sodium salts rich stream which needs to be disposed of. It is possible that several refineries or indeed power stations could operate a common reclaiming process.

**Sterically Hindered Amines.** Kansai Electric Power Company (KEPCO) and Mitsubishi Heavy Industries have been developing a proprietary hindered amine called KS-1 as an MEA replacement for flue gas applications. KS-1 has a lower circulation rate (due to its higher lean to rich CO<sub>2</sub> loading differential), lower regeneration temperature (110°C), and 10-15% lower heat of reaction with CO<sub>2</sub>. It is non-corrosive to carbon steel at 130°C in the presence of oxygen. A second sterically hindered amine, AMP (2-amino-1-methyl-1-propanol), may have similar properties to KEPCO's KS-1. The first commercial plant using KS-1 for Petronas Fertilizer Kedah Sdn Bhd's fertilizer plant in Gurun Kedah, Malaysia is now in operation.

### Problem areas in amine scrubbing of flue gases

**Low CO<sub>2</sub> partial pressure.** Flue gases and engine exhausts have very low CO<sub>2</sub> partial pressures because they are typically available at or near atmospheric pressure with CO<sub>2</sub> concentrations of typically 3 to 13% v/v. Many acid gas treatment processes operate at hundreds of bar and cannot remove CO<sub>2</sub> at less than about 0.1 bar partial pressure. These high-pressure processes can be used by compression of the flue gas to the normal operating pressure followed by recovery of a portion of the compression energy in expanders; however the overall energy consumption invariably results in unattractive economics. Commercial absorbents active enough for recovery of dilute CO<sub>2</sub> from atmospheric pressure gas are monoethanolamine (MEA) and other primary amines including the newly developed hindered amines.

**Oxygen.** Oxygen can cause corrosion and solvent degradation problems. Carbon steel is desirable from a cost standpoint, but it can rapidly corrode in the presence of oxygen, especially in hydrogen sulphide-free CO<sub>2</sub> recovery systems. Also, uninhibited alkanolamines such as diethanolamine (DEA) and MEA can be excessively degraded in an oxygen environment. Some

licensed processes employ an inhibitor to both passivate the metal and inhibit amine degradation. It is claimed that flue gas streams need at least 1.5% v/v oxygen to maintain inhibitor activity. Alternate approaches include the use of expensive alloys or the removal of all the oxygen with a combination of a near-stoichiometric burner waste heat boiler and a catalytic reactor. Another alternative, continuous addition of an oxygen scavenger to the solvent system, has not been commercially demonstrated.

**SO<sub>2</sub>.** Flue gases can contain significant concentrations of SO<sub>2</sub> unless natural gas or very low sulphur fuels are being fired. SO<sub>2</sub> reacts irreversibly with MEA to produce non-reclaimable corrosive salts that are very detrimental to plant operation. For MEA-based processes, it is less expensive to install a SO<sub>2</sub> scrubber than to accept the solvent losses when the flue gas contains more than 10 ppmv SO<sub>2</sub>. Coal fired boilers produce the highest concentrations of SO<sub>2</sub>, often 300 to 5000 ppmv before flue gas desulphurisation (FGD), but even oil firing can produce 1000 ppmv SO<sub>2</sub>. The limestone or wet lime FGD systems in large power boilers today achieve SO<sub>2</sub> reductions in the 90-95% range. Therefore, even the flue gas from a low-sulphur liquid or solid fuel, or from a limestone FGD system needs further SO<sub>2</sub> removal. The 10 ppmv SO<sub>2</sub> requirement is met by using the active alkali metal neutralizing agents, caustic soda or soda ash, in a relatively inexpensive spray scrubber

**Sulphur trioxide, SO<sub>3</sub>,** like SO<sub>2</sub>, leads to solvent loss and a sulphuric acid aerosol in wet scrubbers. Furthermore, less than one-third of the SO<sub>3</sub> may be removed by the SO<sub>2</sub> scrubbing system unless a special mist eliminator is used. Therefore, most of the remaining SO<sub>3</sub> will form heat stable salts in the absorber. The fraction of SO<sub>x</sub> which forms SO<sub>3</sub> is a function of combustion, fuel composition, and flue gas processing factors, but SO<sub>3</sub> typically accounts for a few percent of the total sulphur. Minimization of SO<sub>3</sub> is a furnace design issue preferably handled upstream of the SO<sub>2</sub> scrubber.

**Fly Ash** in the CO<sub>2</sub> absorption solvent may cause foaming in the absorber and stripper, scaling and plugging of equipment, erosion, crevice corrosion, and increased solvent loss through chemical degradation and physical association with removed sludge. Furthermore, fly ash may create significant difficulties in the upstream SO<sub>2</sub> scrubber. If the fuel produces fly ash, the particulates should be removed upstream of the SO<sub>2</sub> scrubber. A coal fired boiler flue gas has a typical loading of 4.5 g/m<sup>3</sup> (dry basis) that amounts to about 20 t/d of fly ash per 1000 t/d CO<sub>2</sub>. It is recommended that the loading be reduced to 0.013 g/m<sup>3</sup> requiring a removal efficiency of about 99.7% m/m.

**Soot** presents a special problem in the absorber. Soot derived from firing gas or very light fuel oils does not cause problems and passes harmlessly through the absorber tower. However, soot derived from heavy fuel oil stabilizes an amine mist above the CO<sub>2</sub> absorption zone that is not captured in the water wash zone. In this instance, a special mist eliminator must be employed in the absorber to capture the micron-sized MEA mist particles.

**Nitrogen oxides, NO<sub>x</sub>,** have never created problems in FGD units, however they have led to corrosion of steel and amine degradation in other plants. NO<sub>x</sub> is best controlled through control of the peak flame temperature in the boilers. The chief culprit in NO<sub>x</sub> is NO<sub>2</sub>, which reacts to form nitric acid in the amine solvent and ultimately heat stable salts. However, typically only 10% of the NO<sub>x</sub> is NO<sub>2</sub> and only a fraction of the NO<sub>2</sub> gas is absorbed in the solvent. NO<sub>x</sub> can be a problem in the CO<sub>2</sub> product if it is to be used in the food and beverage industry and steps must be taken in the liquefaction unit for its removal.

**High Flue Gas Temperature.** Hot flue gases can cause solvent degradation and decrease absorber efficiency. The flue gas must be cooled to a water dew point of 50°C before entering the absorber. This is accomplished either in the SO<sub>2</sub> scrubber, if present, or in a direct contact water cooler.

## Other processes for CO<sub>2</sub> recovery from flue gases

This section surveys other processes that have been proposed for CO<sub>2</sub> recovery from flue gas. CO<sub>2</sub> can also be recovered by caustic soda, ammonia, and various other weak acid-alkali salts. Additional processes are available for applications involving EOR where CO<sub>2</sub> is to be produced rather than removed. Pure oxygen boilers and oxygen-blown gasifier derivatives can produce a nitrogen-free flue gas without CO<sub>2</sub> separation.

**Higher Pressure Absorption Processes.** Flue gases from refinery processes are only available at atmospheric pressure. This is a severe handicap for processes that require higher pressures for absorption. This limitation is foremost on physical solvents, such as the UOP Selexol™ process, where CO<sub>2</sub> recovery is directly proportional to the partial pressure of the CO<sub>2</sub> in the feed gas. This limitation also applies to a lesser degree to the less reactive chemical solvents, including methyldiethanolamine (MDEA), diethanolamine (DEA), diisopropanolamine (DIPA), triethanolamine (TEA), and hot potassium carbonate, and also to molecular sieves, membranes, and cryogenic separation (Ryan-Holmes process). For these processes, the driving force for CO<sub>2</sub> absorption and the cyclic loading between absorption and desorption will be insufficient for economical CO<sub>2</sub> recovery. These processes have some advantages in terms of improved solvent stability and reduced energy input for CO<sub>2</sub> desorption, but compression costs to put the flue gas into the operational range are prohibitive.

**Hot Potassium Carbonate.** Hot potassium carbonate (HPC) or "Hot Pot" is effectively used in many ammonia, hydrogen, ethylene oxide and natural gas plants. To improve CO<sub>2</sub> absorption mass transfer and to inhibit corrosion, proprietary activators and inhibitors are added. These systems are known as "activated hot potassium carbonate" (AHPC) systems. The most widely licensed of these are the UOP Benfield™ process, with over 600 units worldwide and the Catacarb™ process, with over 100 units. Other commercial processes are the ExxonMobil Flexsorb™ process, which uses a hindered amine activator, and the Giammarco-Vetrocoke process, which uses an organic activator. The processes are designed for bulk CO<sub>2</sub> removal from high pressure streams but also produce CO<sub>2</sub> of high purity. The "hot pot" family of processes requires a feed CO<sub>2</sub> partial pressure of about 700 kPa for full loading. The Benfield and Catacarb processes are commercially offered for applications at a minimum CO<sub>2</sub> partial pressure of 300 to 450 kPa.

**Membranes.** Membranes suffer from both the cost of compression and heat exchange to obtain a high pressure feed and in that they produce an impure CO<sub>2</sub> product. There are currently no commercial applications of membranes for recovery of CO<sub>2</sub> from flue gases, though they have been used in Upstream projects to recycle CO<sub>2</sub> from the associated gas. The presence of fly ash and the effects of trace components such as SO<sub>x</sub>, NO<sub>x</sub>, HCl, and HF are also potential complications.

**Ionic Liquids** are organic salts with low melting points (typically below 100°C) and negligible vapour pressure. They show good solvent properties for many substances including CO<sub>2</sub>. Thus, ionic liquids have been investigated as an alternative to capture CO<sub>2</sub> from flue gases as they have most of the advantages of commercial solvents. Typical ionic liquids are composed of imidazolium, pyridinium, ammonium or phosphonium cations with a wide variety of anions to tailor their properties as solvents. Despite the general promise of ionic liquids in gas treatment, research groups are facing three obstacles which hinder the use of ionic liquids:

- Although molar capacity is good, absorption capacity on a volume basis is low.
- Absorption and desorption kinetic rates are low because of their high viscosity
- They cannot compete with amines on a cost basis

Research is still ongoing and some recently developed ionic liquids are claimed to show improved performance. However recent publications indicate that ionic liquids are not going to play a significant role in capturing CO<sub>2</sub> in the near future.





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