

CO₂ Capture Technologies and Opportunities in Canada

**“Strawman Document for CO₂ capture and Storage (CC&S)
Technology Roadmap”**

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1. Introduction

Currently 90% of the world's primary energy requirement is supplied by fossil fuels, causing rising emissions of greenhouse gases (GHGs) and related concerns over global warming and climate change. CO₂ is by far the most important of the GHGs, being responsible for about 64% of the enhanced greenhouse effect. As a result of anthropogenic CO₂ emissions, atmospheric concentrations have risen by 30% from pre-industrial levels of 280 ppm to 360 ppm today, primarily as a consequence of fossil fuel use. However, at the current state of development, and the levels of risks and cost of non-fossil energy alternatives such as nuclear, biomass, solar energy, *etc.*, these energy sources cannot meet our need for energy fed by fossil fuels. Additionally, any rapid change to non-fossil energy sources, even if it were possible, would result in large disruptions to the existing energy supply infrastructure with substantial consequences to the global economy. Some may argue that hydrogen could be a substitute for fossil energy. But it should be noted that currently most of the hydrogen produced commercially originates from fossil fuels. Per unit of heat generated, more CO₂ is generated by producing H₂ from fossil fuels than by directly burning those fossil fuels. Emission-free H₂ production by water electrolysis, powered by renewable or nuclear sources is as yet not cost-effective (Hoffert et al., 2002).

Given their inherent advantages such as availability, competitiveness and ease of transport, fossil fuels, which account for 80% of Canada's primary energy demand (96% in Alberta and Saskatchewan-see Figure 1), are expected to remain a major component of Canada's energy supply in the near future (CEO, 1999).

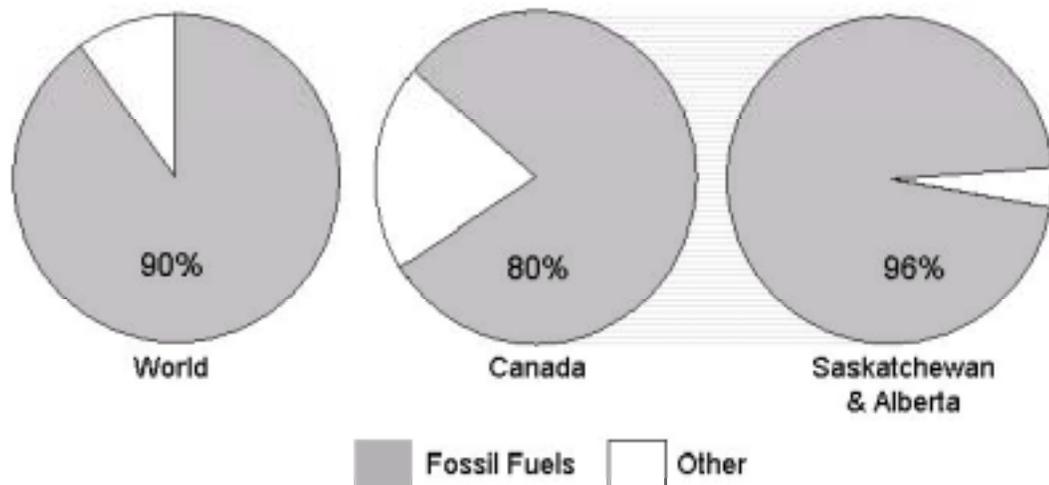


Figure 1: Sources of primary energy in the World and Canada

Figure 2 shows the rising gap between Canada's Kyoto target and Business as usual scenario (BAU). It is estimated that in the Kyoto compliance period (2008-2012), this gap will increase to the tune of 240 Mt of CO₂ equivalent (Pearson, 2003). Through ratification of the Kyoto Protocol, the Government of Canada is committed to cap GHG emissions to an average of 6% below the 1990 level. The immediate challenge for Canada (in particular, Alberta and Saskatchewan) is to reduce CO₂ emissions into the atmosphere while minimizing any associated

negative economic impacts. Thus to meet mid-to long term CO₂ reduction targets, cost effective CO₂ capture from fossil fuels uses and subsequent sequestration options need to be evaluated in Canadian context.

Within the mandate of technology road-mapping exercise on CO₂ capture and storage, this paper provides a status review of the existing and emerging technology options for the capture of CO₂ from large point source emissions in Canada.

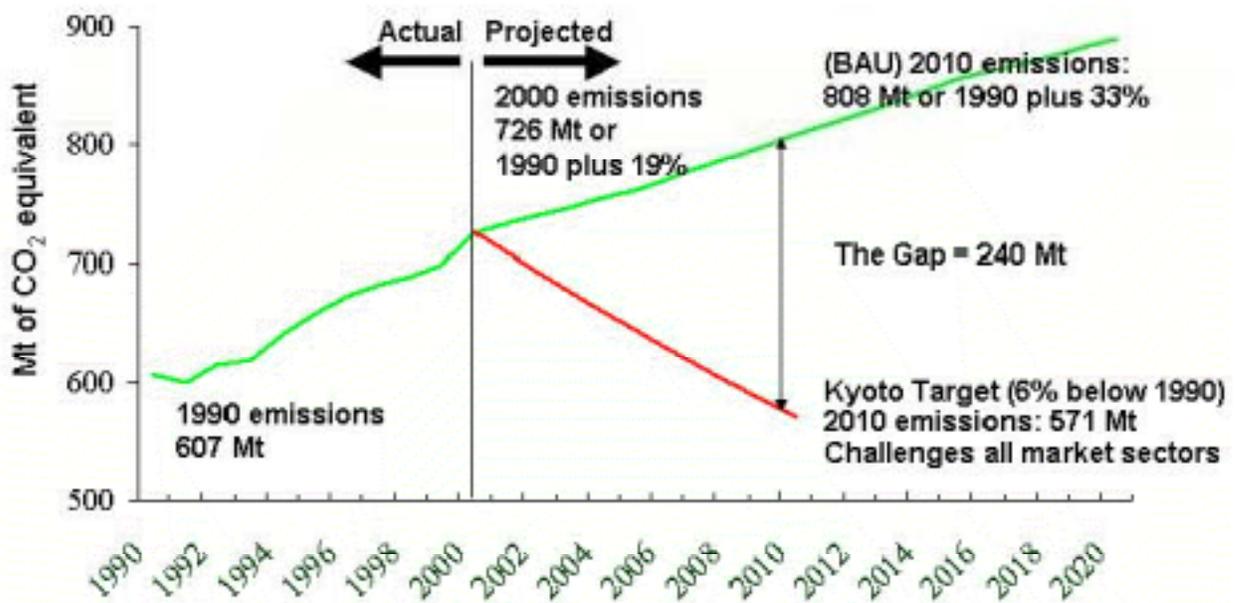


Figure 2: Canada's Kyoto challenge

2. CO₂ emission profiles in Canada

Figure 3 and Figure 4 give a break-up of Canada's GHG emission profile for industrial and upstream oil and gas sector (CEO, 1999). Over a period of 1997-2010, while the industrial sector shows a growth of 9 % in GHG emissions, the growth rate in upstream oil and gas sector is to the tune of 21 %. Current estimates show that, out of total 293 Mt of non-transportation and non residential CO₂ emissions in 2000, electricity generation and the industrial sector accounts for 110 Mt and 116 Mt respectively. The remainder (67 Mt) comes from the extraction and processing of petroleum, bitumen and natural gas, including refining and fugitive emissions. Most of these emission sources are located in the Western Canadian Sedimentary Basin (WCSB) (CEO, 1999).

The profile of CO₂ emissions in WCSB is different from the national and other regional profiles, for two reasons that are linked to the nature of the basin itself. First, the WCSB is a major North American hydrocarbon producer, accounting for 94% of Canada's oil and 99% of Canada's gas production (CERI, 2002). Secondly, the abundance of inexpensive fossil fuels (particularly coal) in Alberta and Saskatchewan encourages CO₂ intensive thermal power generation. In contrast, generation capacity in the rest of Canada is mainly hydroelectric or nuclear, producing no CO₂

directly.

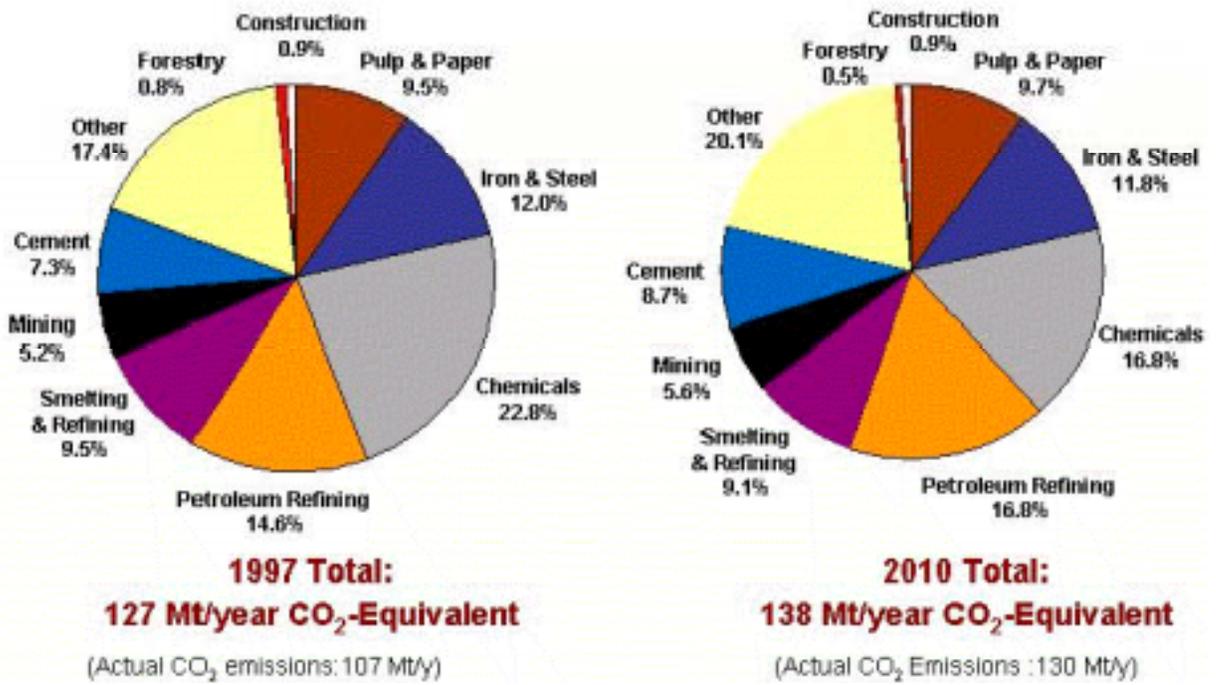


Figure 3: Canada's emission profile : industrial sector (CEO, 1999)

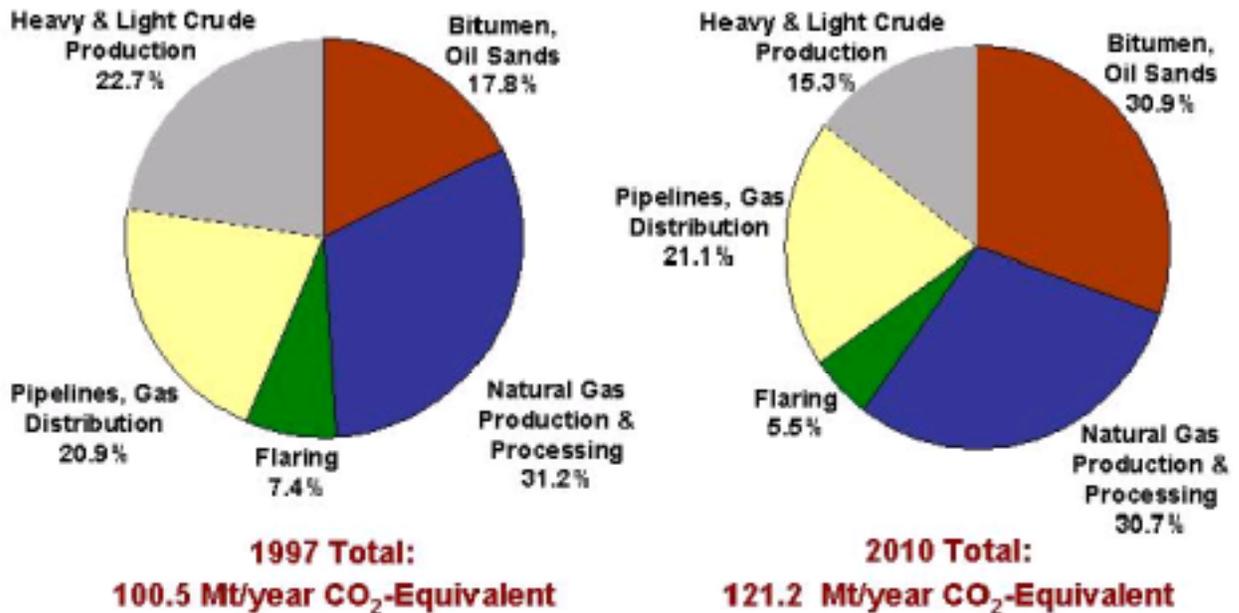


Figure 4: Canada's emission profile: upstream oil and gas sector (CEO, 1999)

3. How to capture CO₂

The objective of CO₂ capture is to produce a concentrated stream of CO₂ which can be transported and sequestered underground or in deep oceans. The CO₂ capture concept is not new to industry. The capture processes have been widely applied in the natural gas processing and chemical processing industries for over 60 years and existing practice is to vent it to atmosphere. The concept of capture for the purpose of sequestration, including the power generation sector is relatively new. Figure 5 gives an idea about CO₂ capture pathways in a broad spectrum of fossil energy conversion processes including power generation.

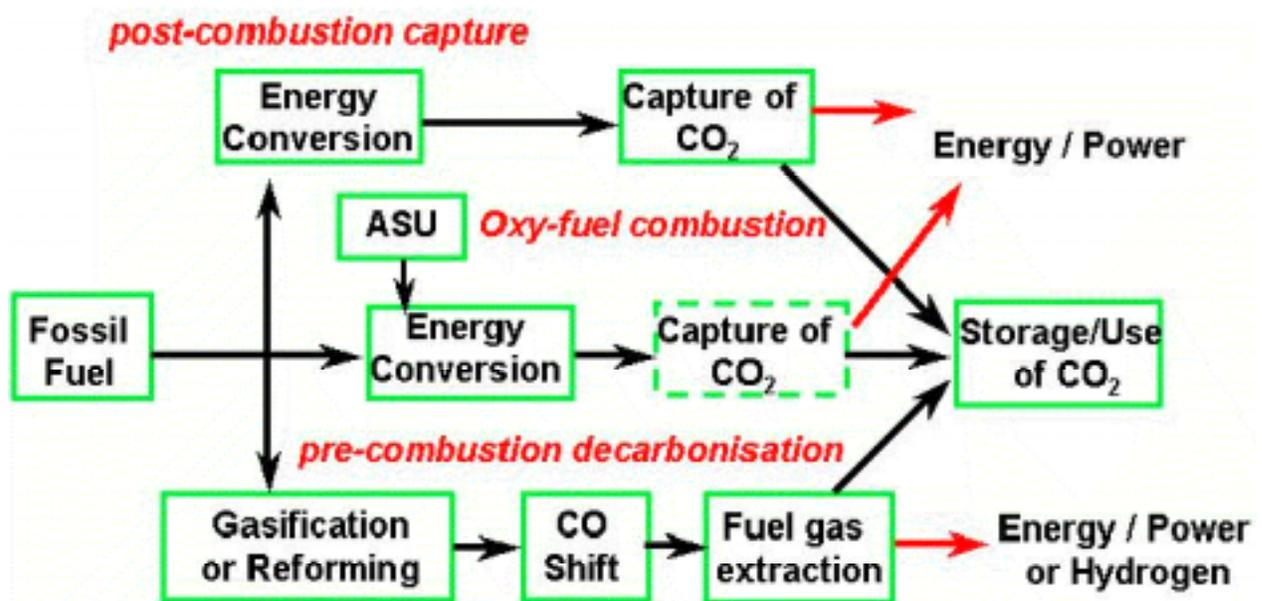


Figure 5: CO₂ capture pathways in fossil energy conversion processes

In general CO₂ capture can be divided into three categories:

3.1 Post-combustion capture:

Capture of CO₂ in the downstream of a carbonaceous fuel based combustion unit is referred as post-combustion capture process. Conventional process heaters and industrial utility boilers fit into this category. In these processes, the fossil fuels are combusted in excess air, resulting in a flue gas stream which contains lean concentrations of CO₂ (12-15 v/v% for modern coal fired power plants and 4-8 v/v% for natural gas fired plants). In some of cases, such as cement kilns and blast furnaces where flue gases contain process related CO₂ also, the CO₂ concentration in the flue gases may vary from 14-33%. CO₂ from the post combustion flue gases can be captured by a variety of techniques such as absorption by amines, membrane separation and cryogenic separation etc. Under the current state of technology, only absorption and to some extent membranes are considered to be economically viable technologies. These issues will be discussed further in Section 4 and section 5.

3.2 Oxy-fuel combustion:

CO₂ capture method through oxy-fuel combustion is a variant of post combustion capture process. However removal of nitrogen from the air in the oxidant stream produces highly concentrated flue gas stream (>80 v/v% CO₂) which can be easily concentrated further through simple gas purification techniques such as cryogenic separations. Although the oxyfuel processes such as RILEE (Recycle Incineration Low Exhaust Emission) process that involves the oxy-fuel burners for treating non-ferrous scrap, have been widely applied, their application in process heaters, in large industrial utility boilers and gas turbines is relatively a new concept and will require comprehensive breakthroughs in terms of low cost oxygen production techniques and combustion in oxygen rich environment. Section 4 and section 5 will discuss these issues in further details.

3.3 Pre-combustion capture:

The pre-combustion capture process is basically a de-carbonization of carbonaceous fuels. In this case, through gasification (controlled oxygen or air) or through steam reforming, the fuel is converted to carbon mono-oxide (CO) and hydrogen (fuel gas). Subsequently, CO is converted to CO₂ through shift conversion process resulting a stream rich in CO₂ and H₂. The concentration of CO₂ in this stream is around 25-40% and the total pressure is typically in the range of 2.5-5 MPa. Thus the partial pressure of CO₂ in the pre-combustion capture is very high compared to post-combustion method, making it much easier to separate through techniques such as solvent scrubbing etc.

4. Types of CO₂ capture technology

Most CO₂ capture technologies themselves are not new. Specialized chemical solvents were developed more than 60 years ago to remove CO₂ from impure natural gas, and natural gas operations continue to use these solvents today. In addition, several power plants and other industrial plants use the same or similar solvents to recover CO₂ from flue gases for application in the food processing and chemical industries. Finally, a variety of alternative methods are used to separate CO₂ from gas mixtures during the production of hydrogen for petroleum refining, ammonia production and in other industries (Anderson and Newell, 2003).

The selection of a technology for a given capture application depends on many factors i.e. partial pressure of CO₂ in the gas stream, extent of CO₂ recovery required, sensitivity to impurities, such as acid gases, particulates, purity of desired CO₂ product, capital and operating costs of the process, the cost of additives necessary to overcome fouling and corrosion where applicable the environmental impacts (White et al., 2003).

Based upon the method of CO₂ removal, capture technologies can be broadly classified into the following categories (also see Figure 6):

1. Chemical/physical solvent scrubbing
2. Adsorption
3. Cryogenic
4. Membranes

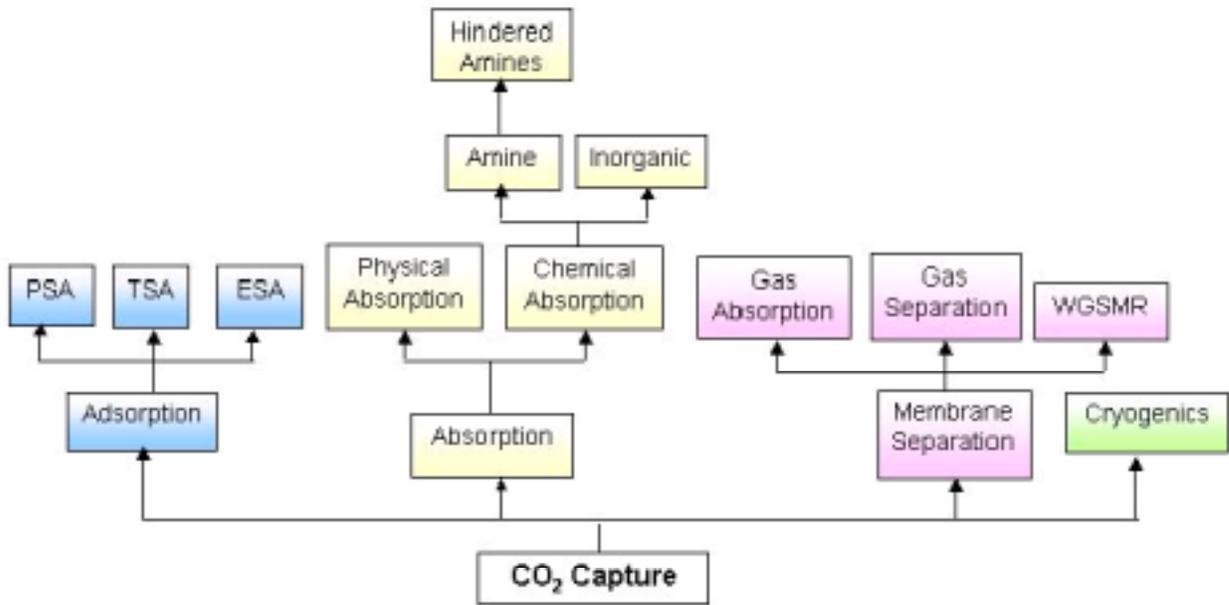


Figure 6: Strawman of CO₂ capture technologies

4.1 Chemical/physical absorption

Chemical and or physical absorption processes are widely used in the petroleum, natural gas and chemical industries for separation of CO₂. The solvent capacity of an absorbed gas is a function of its partial pressure in the absorption unit (Thambimuthu,1993; Kohl and Nielsen, 1997). In physical absorption, the solvent capacity or loading, which initially follows Henry's law (for ideal non interacting gas mixtures), assumes an almost linear dependence on the gas partial pressure. In chemical absorption, the solvent loading assumes, a non-linear dependence on partial pressure and is higher at low partial pressures. At the concentrations approaching the saturation loading of the solvent, chemical absorption decreases sharply. Large increases in the partial pressure of the absorbed gas result in a very small increase in the solvent loading. This behaviour is caused by an effect akin to weak physical absorption and usually arises from gas absorption in the aqueous component of the solvent used in the process. Thus, the retention capacity of a chemical solvent in a chemical absorption process is much higher at low partial pressures, whereas the converse is true for physical absorption(Thambimuthu,1993). The primary method of regeneration in physical absorption occurs by a simple pressure reduction in the system. This method of regeneration reduces the operating costs. In chemical absorption, heating or reboiling is necessary for solvent regeneration and may be cost effective if the process has large supply of low cost and sufficiently high temperature heat or steam available to it. However with much higher chemical solvent loading capacities, the solvent circulation rates are much lower, with high capital cost savings.

Table 1 lists the most common industrial CO₂ scrubbing solvents and their process conditions.

4.1.1 Chemical Absorption:

The majority of chemical solvents are organic amine based. Stoichiometric manipulation of this group has led to the development of sterically hindered amines, which enhances the absorption capacity of the solvent. Alternative inorganic solvent systems are Na/K carbonates and aqueous ammonia processes.

Prior to CO₂ removal the CO₂ containing stream is cooled and particulates and other impurities are removed as far as possible. It is then passed into an absorption vessel where it comes into contact with the chemical solvent, which absorbs much of the CO₂ by chemically reacting with it to form a loosely bound compound. The CO₂ rich solvent from the bottom of the absorber is passed into another vessel (stripper column) where it is heated with steam to reverse the CO₂ absorption reactions. CO₂ released in the stripper is compressed for transport and storage and the CO₂ free solvent is recycled to the absorption vessel. CO₂ recovery rates of 98% can be achieved, and product purity can be in excess of 99% (Wilson, 1992).

4.1.1.1 Organic solvents

4.1.1.1.1 Amines

Three classes of amines, basically primary, secondary and tertiary, are generally used as organic chemical solvents. Monoethanolamines (MEA) are more reactive than secondary amines and hence dominate the CO₂ capture market (Thambimuthu, 1993).

Amine scrubbing technology has been established for over 60 years in the chemical and oil industries, for removal of hydrogen sulphide and CO₂ from gas streams. This experience is largely on natural gas streams and/or with chemically reducing (primarily oxygen deficient) gases but there are several facilities in which amines are used to capture CO₂ from flue gas streams today, one example being the Warrior Run coal fired power station in the USA, where 150 t/d of CO₂ is captured (Thambimuthu et al., 2002).

The main concerns with MEA and other amine solvents are corrosion in the presence of O₂ and other impurities, high solvent degradation rates from reaction with SO₂ and NO₂ and the large amounts of energy required for regeneration. As much as 80% of the total energy consumption in an alkanolamine absorption process occurs during solvent regeneration (White et. al, 2003). These factors generally contribute to large equipment, high solvent consumption and large energy losses. New or improved solvents with higher CO₂ absorption capacities, faster CO₂ absorption rates, high degradation resistance and low corrosiveness and energy use for regeneration are needed to reduce equipment sizes and capital and operating costs.

Table 1: Commercial CO₂ scrubbing solvents used in industry.

Absorption process	Solvent	Process conditions	Developer/ licensor
Physical Solvent			
Rectisol	Methanol	-10/-70°C, >2 MPa	Lurgi and Linde, Germany; Lotepro Corporation, USA
Puisol	n-methyl-2-pyrrolidone (NMP)	-20/+40°C, >2 MPa	Lurgi, Germany
Selexol	dimethyl ethers of polyethylene glycol (DMPEG)	-40°C, 2-3 MPa	Union Carbide, USA
Fluor Solvent	Propylene carbonate	Below ambient temperatures, 3.1-6.9 MPa	Fluor, El Paso, USA
Chemical Solvent			
<i>Organic (Amine Based)</i>			
MEA	2.5 n monoethanolamine and chemical inhibitors	~40°C, ambient-intermediate pressures	Dow Chemical, USA
Amine Guard (MEA)	5 n monoethanolamine and chemical inhibitors	~40°C, ambient-intermediate pressures	Union Carbide, USA
Econamine (DGA)	6 n diglycolamine	80-120°C 6.3 MPa	SNEA version by Societe National Elf Aquitaine, France
ADIP (DIPA & MDEA)	2-4n diisopropanolamine 2 n methyldiethanolamine	35-40°C, >0.1 MPa	Shell, Netherlands
MDEA	2 n methyldiethanolamine		
Flexsorb/ KS-1, KS-2, KS-3	Hindered amine		Exxon, USA; M.H.I.
<i>Inorganic</i>			
Benfield and versions	Potassium carbonate & catalysts Lurgi and Catacarb with arsenic trioxide	70-120°C, 2.2-7 MPa	Lurgi, Germany; Eickmeyer and Associates, USA; Giammarco Vetrocoke, Italy
Physical/ Chemical Solvents			
Sulfinol-D and Sulfinol-M	Mixture of DIPA or MDEA, water and tetrahydrothiophene (DIPAM) or diethylamine	>0.5 MPa	Shell, Netherlands
Amisol	Mixture of methanol and MEA, DEA, diisopropylamine (DIPAM) or diethylamine	5/40°C, >1 MPa	Lurgi, Germany

4.1.1.1.2 Sterically hindered amines

Sterically hindered amines are amines in which a bulky alkyl group is attached on the amino group. As a consequence the reactivity is different from the alkanolamines. Sterically hindered amines currently used in absorption processes are 2-amino-2-methyl-1-propanol (AMP), 1,8-pmethanediamine (MDA) and 2piperidine ethanol (PE). They were originally developed by Exxon. (Veawab et al., 2002).

The advantage of sterically hindered amines over alkanolamines is that only 1 mol of the sterically hindered amine, instead of 2 mol of alkanolamine, is required to react with 1 mol of CO₂. Thermal degradation occurs at temperatures higher than 478 K. Sterically hindered amine systems can have lower heats of absorption/regeneration as compared with MEA. This makes these types of amines potential candidates for CO₂ removal in power generation systems. (White et. al, 2003)

Another set of sterically hindered amines are KS-1. KS-1 has a lower circulation rate compared to MEA, (because of its higher lean to rich CO₂ loading differential), lower regenerative temperature (383K), and lower heat of reaction with CO₂. KS-1 has been used in a commercial gas scrubbing operation in Malaysia to produce a pure CO₂ stream for urea production” (Mimura et al., 2000).

4.1.1.2 Inorganic solvents

The non-organic based chemical solvents include potassium, sodium carbonate and aqueous ammonia. Among these, potassium carbonate has the dominant market share. The potassium carbonate process can be used in various configurations. Generally these process configurations are accompanied by minor changes in the solvent and catalytic additives used in the process. Overall the system uses an aqueous solution of about 20-40% wt% of the potassium salt. The absorption of CO₂ shows an equilibrium behaviour that is favourable even at temperatures (typically 70-120°C) close to the atmospheric boiling point of the solvent. Consequently, it is possible to operate the process with a relatively low incremental heat input for solvent regeneration or gas desorption. This feature normally eliminates the use of the heat exchangers used to cool the solvent flow between the regenerator and absorption column. The popular Banfield process is a split flow version of the basic potassium carbonate process used at moderate gas pressures of around 2.2 MPa.

4.1.1.2.1 Ammonia

Most recently ammonia has been tested as a sorbent for CO₂. It has been observed that the maximum CO₂ removal efficiency by NH₃ absorbent can reach 99% and the CO₂ loading capacity can approach 1.2 kg CO₂ /kg NH₃ (Yeh at al, 2002). On the other hand, the maximum CO₂ removal efficiency and loading capacity by MEA absorbent were 94% and 0.40 kg CO₂ /kg MEA (White et. al, 2003). At pH=11.0, when the total ammonium carbonate concentration is 0.1 M, ammonia equilibrium vapor pressure is 0.0034 atm, and CO₂ removal efficiency is observed to be 100% from an initial 12% CO₂ in flue gas (Huang and Chang, 2002).

However, the concerns with this technology include the highly volatile nature of ammonia. Also this technology lacks in the regeneration of ammonia from its carbonate salts (Huang and Chang, 2002). Capability of anion-exchange resins to regenerate ammonia from ammonium bicarbonate as well as the feasibility for the regeneration of resin by heated water and collection of CO₂ are being tested. Released ammonia will react with the remaining ammonium bicarbonate to form ammonium carbonate, which results in the resin's inability to completely regenerate ammonia. A new scrubbing system has been proposed where CO₂ in flue gas, along with the acid gas pollutants, SO₂, NO_x, HCl and HF, could be removed in a regenerable scheme (Yeh et al, 2002). The key advantage to the process is that the thermal energy consumption for the CO₂ regeneration is expected to be significantly less than the MEA process. (White et. al, 2003)

The thermal energy requirement is approximately 50% less in a dual alkali system using ammonia to absorb CO₂ and anion-exchange resins to regenerate ammonia for reuse than using amine to absorb CO₂ and steam stripping to dissociate the resulting carbamates. (Huang and Chang, 2001).

The major drawback of inorganic solvents lies in the fact that they may release Na, K and V in the product gas that could promote deposition, erosion and corrosion in gas turbines and fuel cells. Others such as arsenic trioxide are potent chemicals hazardous to plant and animal life.

4.1.2 Physical absorption

The physical solvents are ideally suited for the removal of CO₂ from fuel gases with high vapour pressure (mostly in reducing atmospheres). These physical solvents combine less strongly with CO₂. The advantage of such solvents is that CO₂ can be separated from them in the stripper mainly by reducing the pressure, resulting in much lower energy consumption. Table 1 gives an idea about the main physical solvents that could be used for CO₂ capture (Thambimuthu, 1993). These are basically cold methanol (Rectisol process), dimethylether of polyethylene glycol (Selexol process), propylene carbonate (Fluor process) and n-methyl-2pyrrolidone (NMP-purisol). Physical solvent scrubbing of CO₂ is well established, e.g. in ammonia production plants. Majority of physical absorption solvents are based on organic solvents with high boiling points and low vapour pressures. Other than methanol, most of these solvents can be used at ambient temperatures without appreciable vaporization losses, but may require special water washing stages to mitigate solvent losses.

In general, all physical solvents must have an equilibrium capacity for absorbing CO₂ several times that of water and a lower capacity for removing other primary constituents of the gas stream. They must have low viscosity, low or moderate hygroscopicity, and low vapor pressure at ambient temperature. They must be non corrosive to common metals as well as non reactive with all components in the gas stream. (White et. al, 2003). The technology development needs for physical solvents are similar in principle to those for chemical solvents. In particular, there is a need for higher efficiency gas-liquid contactors and solvents with lower energy requirements for regeneration (Thambimuthu et al. 2002).

4.1.3 Hybrid absorption processes

Hybrid absorption processes use solvents which offer a combination of chemical and physical absorption. Processes currently used with coal syngas for removal of CO₂ and sulphur

compounds are the Shell Sufinol[®] process and Amisol[®] process developed by Lurgi (Collot, 2003).

In its original form the shell Sufinol process uses sufolan (tetrahydroehiophene dioxide) as the organic solvent and an amine solvent, DIPA (di-isopropanolamine) with 15% water. Shell has also developed M-Sufinol[®] in which the amine solvent is MDEA instead of DIPA. The main difference between the sulfinol[®] unit and an alkanolamine unit is that sulfinol[®] unit tolerates a much higher acid gas loading (twice as much as the standard MEA unit) before becoming corrosive (Collot, 2003).

The Amisol[®] process is based on a mixture of methanol and either MEA or DEA as the chemical component and a small percentage of water. Another version which is particularly suited for the removal of large quantities of CO₂ uses MDEA as the chemical solvent component.

4.2 Adsorption

The intermolecular forces between gases such as CO₂ and the surface of certain solid materials permit separation by adsorption. Selective adsorption of the gases depends on temperature, partial pressures, surface forces and adsorbent pore size. The solid adsorbents, such as activated carbon and molecular sieves are normally arranged as packed beds of spherical particles. The process operates on a repeated cycle with the basic steps being adsorption and regeneration. In the adsorption step, gas is fed to a bed of solids that adsorbs CO₂ and allows the other gases to pass through. When a bed becomes fully loaded with CO₂, the feed gas is switched to another clean adsorption bed and the fully loaded bed is regenerated to remove the CO₂. In pressure swing adsorption (PSA), the adsorbent is regenerated by reducing pressure. In temperature swing adsorption (TSA), the adsorbent is regenerated by raising its temperature and in electric swing adsorption (ESA) regeneration takes place by passing a low-voltage electric current through the adsorbent.

Both PSA and TSA are commercially available technologies and are used in commercial H₂ production, bulk separation of O₂ and in the removal of CO₂ from natural gas (McKee, 2002). A combination process of pressure and temperature swing adsorption (PTSA) has been tested at the bench scale and pilot scale levels by Tokyo Electric Power Company (TEPCO) & Mitsubishi Heavy industries respectively (Smith, 1999). Bench scale PTSA tests selected an adsorbent zeolite Ca-X(β) for having a high capacity and selectivity. Pilot-scale test from a power station burning coal/oil mix and a flue gas with a concentration of 10.8% CO₂ generated a recovery of 90% CO₂. Using PTSA compared to PSA reduced the power consumption required for separation by 11% (Smith, 1999)

ESA which is commercially not ready, holds promise as a possible advanced CO₂ separation technology that uses less energy than other processes. The material used in ESA for separation of CO₂ is basically carbon fiber composite molecular sieve(CFCMS). The Oak Ridge National Laboratory in USA is developing a novel ESA process which adsorbs amongst the other gases CO₂ from syngas from low hydrogen-to-carbon ratio fuels on a carbon fiber molecular sieve with a monolithic structure. After saturation of the carbon fibre adsorbent with CO₂, immediate desorption of the adsorbed gas is accomplished by applying low voltage across the adsorbent. The efficacy of the ESA process for gas separation has been studied at pressures up to 2 MPa and temperatures up to 100°C. A CO₂ uptake of 45% (wt) has been demonstrated at a pressure of 2 MPa and a temperature of 25°C (Klara and Srivastava, 2002; Collot, 2003).

Further details on CO₂ removal by adsorption technologies and studies of possible adsorbents for IGCC applications can be found in [Smith \(1999\)](#).

Adsorption is not yet considered attractive for large-scale separation of CO₂ from flue gas because the capacity and CO₂ selectivity of available adsorbents is low. However, it may be successful in combination with another capture technology. Adsorbents that can operate at higher temperatures in the presence of steam with increased capacity and improved selectivity are needed ([Thambimuthu et al., 2002](#)).

4.3 Cryogenic

Cryogenic separation is widely used commercially for purification of CO₂ from streams that already have high CO₂ concentrations (typically >50%). It is not normally used for dilute CO₂ streams such as flue gas from coal/natural gas fired boilers as the amount of energy required for refrigeration is uneconomic for the plant. Cryogenic separation has the advantage that it enables direct production of liquid CO₂, which is needed for economic transport, such as transport by ship or pipeline. The most promising applications for cryogenics are expected to be for separation of CO₂ from high pressure gases, such as in pre-combustion capture processes, or oxyfuel combustion in which the input gas contains a high concentration of CO₂.

4.4 Membranes

A membrane is a barrier film that allows selective and specific permeation under conditions appropriate to its function. With regards to CO₂ capture, two types of membranes systems are considered:

4.4.1 Gas separation membranes

Gas separation membranes rely on differences in physical or chemical interactions between gases and a membrane material, causing one component to pass through the membrane faster than another. Various types of gas separation membranes are currently available, including ceramic, polymeric and a combination of two (hybrid). The separation of the gases rely on solubility or diffusivity of the gas molecules in the membrane - differences in the partial pressure from one side of the membrane to other acts as a driving force for gas separation (as shown in Figure 7).

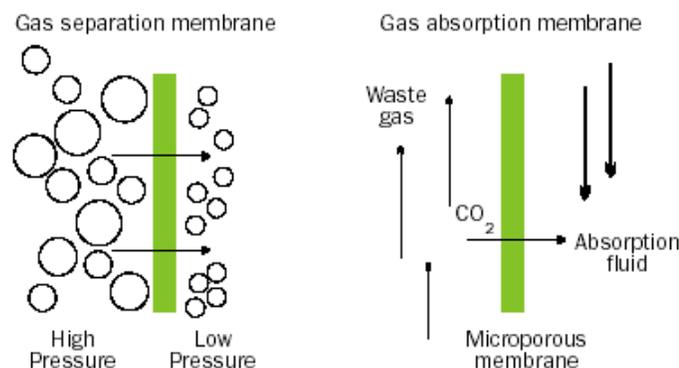


Figure 7: Principles of gas separation and gas absorption membranes ([McKee, 2002](#))

2.4.1 Gas absorption membranes

Gas absorption membranes are micro-porous solid membranes that are used as contacting devices between gas flow and liquid flow. The CO₂ diffuses through the membrane and is removed by the absorption liquid, which selectively removes certain components from a gas stream on the other side of the membrane. In contrast to gas separation membranes it is the absorption liquid (not the membrane) that gives the process its selectivity (McKee, 2002).

Los Alamos National Laboratory is developing a high temperature polymeric membrane with better separation performance by supporting a polybenzimidazole (PBI) film on a sintered metal support. The PBI possesses excellent chemical resistance, a high glass transition temperature (450°C) and good mechanical strength. This type of membrane is highly selective and is able to operate at flue gas conditions (Klara and Srivastava, 2002).

Several membranes with different characteristics may be required to separate high-purity CO₂. Membranes could be used to separate CO₂ at various locations in power generation processes, for example from fuel gas in IGCC or during combustion in a gas turbine. However membranes have not been optimized for the large volume of gas separation that is required for CO₂ capture. Membranes cannot usually achieve high degrees of separation, so multiple stages and/or recycle of one of the streams is necessary. This leads to increased complexity, energy consumption and costs. Much development is required before membranes could be used on a large scale for capture of CO₂ in power stations.

5. CO₂ capture opportunities in Canada

Although the electricity generation, industrial sector and fossil fuel processing industry contributes to only 54% of total CO₂ emissions during 2000, they are potential stationary sources, well suited for large scale CO₂ capture and storage applications. Among them power plants are the clearest contenders. But the other energy intensive industries like oil and gas refining, hydrogen and ammonia processing, iron and steel manufacturing and cement production also combust large quantities of fossil fuels and have significant CO₂ emissions. In addition to those combustion sources, some of these sectors produce non-combustion CO₂ rich by-product process streams for which the incremental cost of capture and storage is very low.

5.1 Electricity Generation

CO₂ emissions from electric power generation in Canada have been estimated to be approximately 110 Mt CO₂ /year which is 20% of Canada's total CO₂ emissions in 2000 (CEO, 1999). In order to meet Canada's Kyoto commitments, it is anticipated that carbon capture might find an early application in Canadian electric power generation. As discussed in section 3, all three methods i.e. post-combustion capture, pre-combustion capture and oxyfuel combustion can be effectively applied in electricity sector.

4.1.1 Post-combustion capture

Although, one can suggest to compress and store the flue gas underground but at the scale of power plants, the energy required for compression would be very large and more over the underground reservoirs would quickly become full. It is therefore necessary to separate the CO₂ from the flue gas which contains a lion's share of nitrogen.

As the CO₂ partial pressure in flue gas is significantly low, the best proven technique for post combustion capture of CO₂ at present is to scrub the flue gas with an amine solution in a chemical absorption process. The amine from the scrubber is heated by steam to release high purity CO₂ and the CO₂-free amine is then reused in the scrubber. However, some additional measures are needed to minimize contamination of the CO₂ capture solvents by impurities in the power station flue gas, such as sulphur and nitrogen oxides. In many respects, post-combustion capture of CO₂ in a power station is analogous to wet flue gas desulphurisation (FGD) techniques, which is widely used on coal and oil fired power stations to reduce emissions of SO₂. Another advantage of post-combustion capture systems in power station is that they can operate in a plug and play mode with the existing fleet of pulverized coal power plants and natural gas fired plants without significant changes in the upstream systems. Under prevailing uncertainty in the regulatory norms, this gives tremendous flexibility to existing utilities operators.

However, the low concentration of CO₂ in power station flue gas means that a large volume of gas has to be handled, which results in large equipment sizes and high capital costs. A further disadvantage of the low CO₂ concentration is that powerful chemical solvents have to be used to capture CO₂ and regeneration of the solvents to release the CO₂ requires a large amount of energy. If the CO₂ concentration and pressure could be increased, the CO₂ capture equipment would be much smaller and different physical solvents could be used, with lower energy penalties for regeneration.

4.1.2 Pre-combustion capture

Energy or power generation processes where pre-combustion capture can be applied include IGCC (integrated gasification combined cycle) plants fuelled by coal, residual oil and petroleum coke, but these plants do not yet have long continuous operating times, causing concerns for reliability and availability. With the addition of CO₂ capture, one of the novel aspects is that the fuel gas feed to the gas turbine is essentially hydrogen. The hydrogen will be diluted using nitrogen or steam to reduce emissions of nitrogen oxides from the gas turbine combustors. It is expected that it will be possible to burn hydrogen in an existing gas turbine with little modification, however this is not a demonstrated technology. Nevertheless there are a large number of existing IGCC plants such as in refineries where hydrogen rich fuels are used in the gas turbines. (Thambimuthu et al., 2002)

5.1.3 Oxy-fuel combustion

If fuel is burnt in pure oxygen in an existing industrial boiler, the flame temperature is excessively high, so some CO₂-rich flue gas would be recycled to the combustor to make the flame temperature similar to that in a normal air-blown combustor.

The nitrogen-free combustion process can benefit from a highly reduced flue gas volume (around one fifth to one third) leaving as the exhaust stream from the process and is highly rich in CO₂ with much lower flue gas treatment costs. For existing boilers, a retrofit technology involving partial flue gas recycle (FGR) may be considered. In this approach, nitrogen is basically replaced by CO₂ and the boiler heat transfer profiles remain close to the existing air-fired process. On the other hand for new plants, the oxy-fuel combustion strategy would include advanced, compact boilers with low or zero flue gas recycle, resulting in significant reductions in the boiler dimensions and capital and operating costs.

The advantage of oxygen-blown combustion is that the flue gas has a CO₂ concentration of above 80%, compared to 4-14% for air blown combustion, so only simple CO₂ purification is required.

Currently, the major energy and cost penalty in oxyfuel combustion arises from oxygen production in cryogenic air separation units. New technology development for oxygen production targets the commercial development of novel oxygen transport membranes (OTMs) for air separation, that may be available within the Kyoto compliance period of 2008-2012 (Miller, 2003). With the advent of commercial scale air separation modules based on OTMs, oxyfuel combustion is likely to be an attractive option for capturing CO₂ in existing and new pulverized coal fired units.

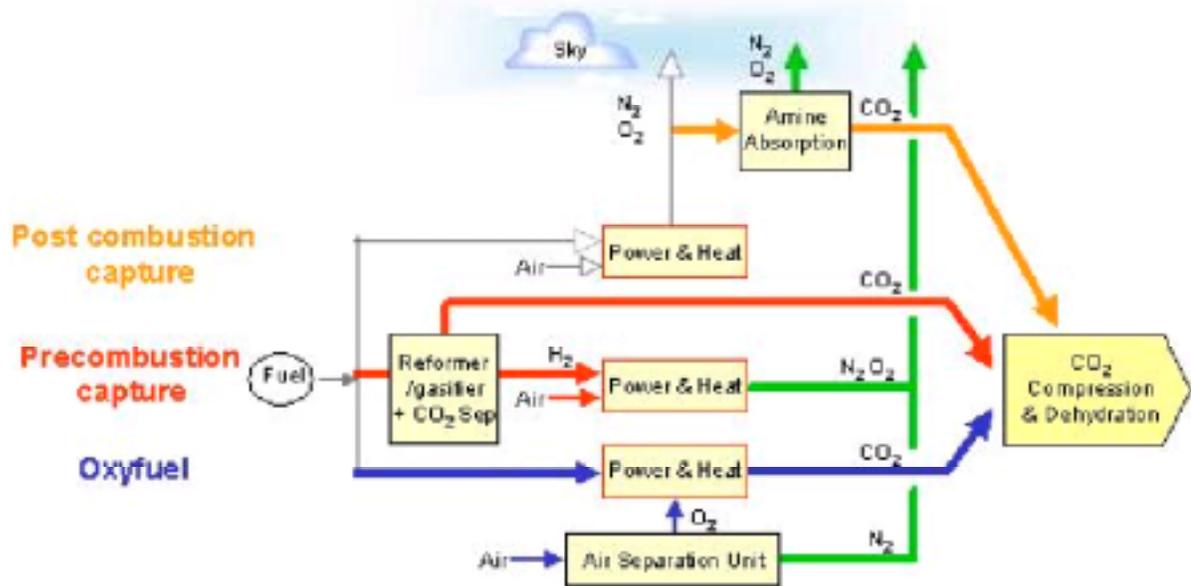


Figure 8: A simple schematic diagram of combustion based power cycles with CO₂ capture options

Figure 8 provides a generic picture of carbon capture in electricity generation.

5.1.3.1 Novel oxy-fuel capture concepts

Unlike the oxy-fuel capture technique discussed above, few promising variants of oxy-fuel combustion are still in conceptual stages of development. These concepts also rely on the production of pure CO₂ streams from fuel combustion, facilitating CO₂ removal with minor purification of the gas stream.

5.1.3.1.1 MATIANT Cycles

These power cycles are based on variations of the oxygen combustion approach. For example in the MATIANT cycle, CO₂ produced from fuel combustion in oxygen and recycled CO₂ (oxy-fuel combustion) is used as the working fluid, replacing nitrogen in the air. The excess CO₂ generated in the process is extracted through simple valves. This avoids the need for CO₂ capture from a

Turbine (HAT) concept (Brandvoll and Bolland, 2002). The major development issue associated with chemical looping combustion is development of a metal oxide material that is able to withstand long term chemical cycling and is resistant to physical and chemical degradation from impurities generated from fuel combustion.

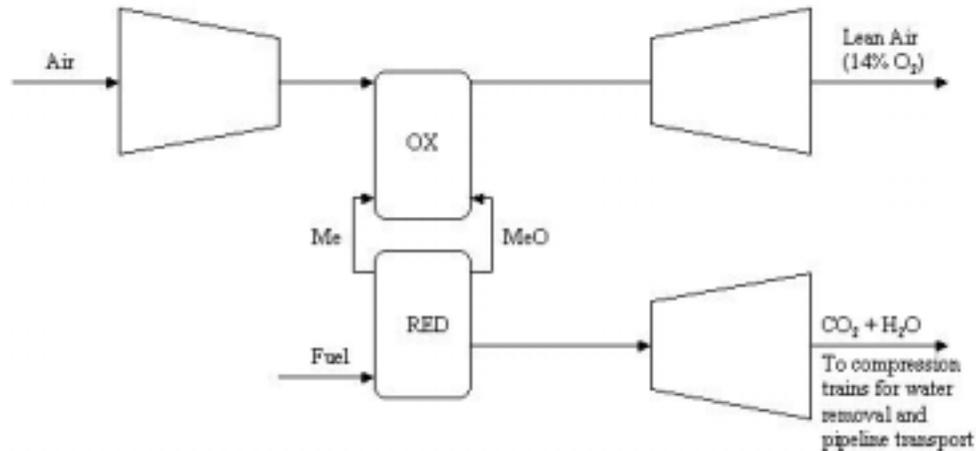


Figure 11: The Chemical Looping Combustion (CLC) principle

5.2 CO₂ capture opportunities in non power-sectors

5.2.1 Iron and steel production

About 60% of global steel production is from primary integrated steel mills but these mills account for over 80% of CO₂ emissions from steel production (IEA GHG, 2000a). According to recent estimates, using available capture technologies, this sector alone can help reduce global CO₂ emissions by 4% at a cost of US\$ 10-19/t CO₂ (Gielen, 2003)

The Canadian iron and steel sector is composed of four integrated steel plants with coke ovens, blast furnaces, and basic oxygen furnaces, one non-integrated plant operating a basic oxygen furnace, and 11 non-integrated plants operating electric arc furnaces. Canada's iron and steel sector was the 13th largest steel producer in 2000 with production of 16.5 million tonnes or two percent of world production (Environment Canada and CCME, 2002).

Direct GHG emissions from steel plants were 14.5 Mt in 1996 or 2% of Canada's total GHG emissions. Virtually all emissions were CO₂ from the fossil fuels used in ore smelting/reduction and in combustion. The two main sources of GHG emissions are the coal and natural gas used in iron and steel production. Integrated steel producers are estimated to account for 85% of steel industry GHG emissions. The largest sources of CO₂ come from coke oven gas and blast furnace gas (Issue Table, 2000)

About 70% of the carbon input to an integrated steel mill is present in the blast furnace gas, which is used as fuel gas within the steel mill. Blast furnace gas typically contains 20% by volume CO₂ and 21% CO, with the rest being mainly N₂; its pressure is typically 2-3 bar. CO₂ could be captured before or after combustion of this gas. The CO₂ concentration after combustion

in air would be about 27% by volume, significantly higher than in the flue gas from power stations. The higher flue gas CO₂ concentration can reduce the energy penalty of capture depending on the type of CO₂ capture technology deployed. Other process streams within a steel mill may also be suitable candidates for CO₂ capture, before or after combustion, for example the off-gas from an oxygen-steel furnace contains typically 70% CO and 16% CO₂. Blast furnace gas composition is changing because of increasing injection of coal, natural gas and plastic waste into existing furnaces (Gielen, 2003). As these fuels reduce the temperature in the blast furnace, the effect is balanced by 50-75 kg of oxygen injection per ton of iron. The oxygen enrichment decreases the N₂ concentration in the off gas and concentrations of CO, CO₂ and H₂ increases (see Figure 12).

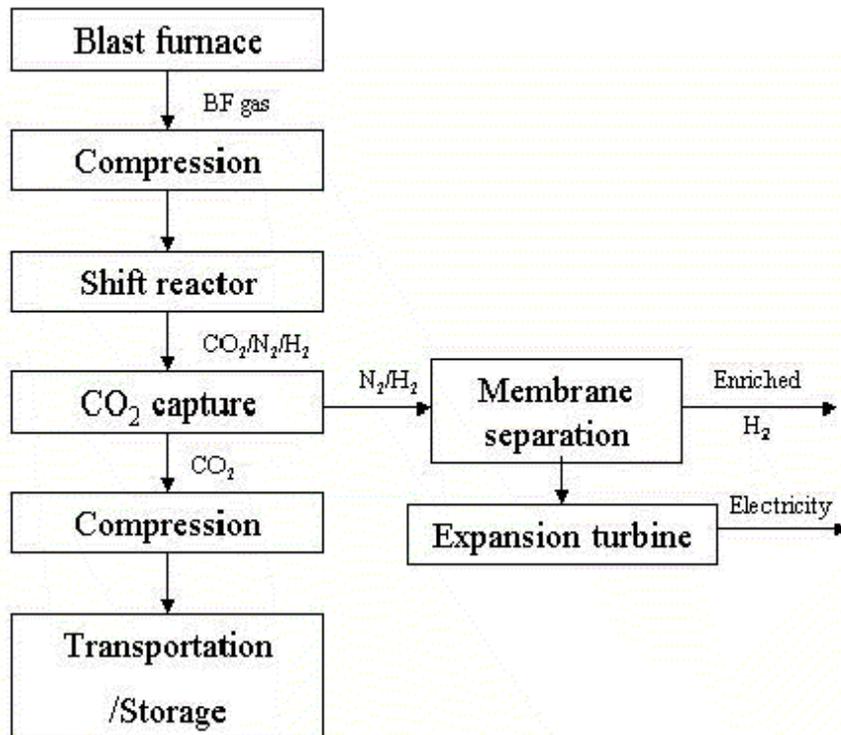


Figure 12: CO₂ capture from a conventional blast furnace

CO₂ capture is already widely applied in the iron and steel industry in the production of Directly reduced Iron (DRI) in order to enhance the flue gas quality. CO₂ is removed from the reduction gas and the reduction gas is recycled for DRI production. A typical example of DRI process coupled with a gasifier is shown in Figure 13 .

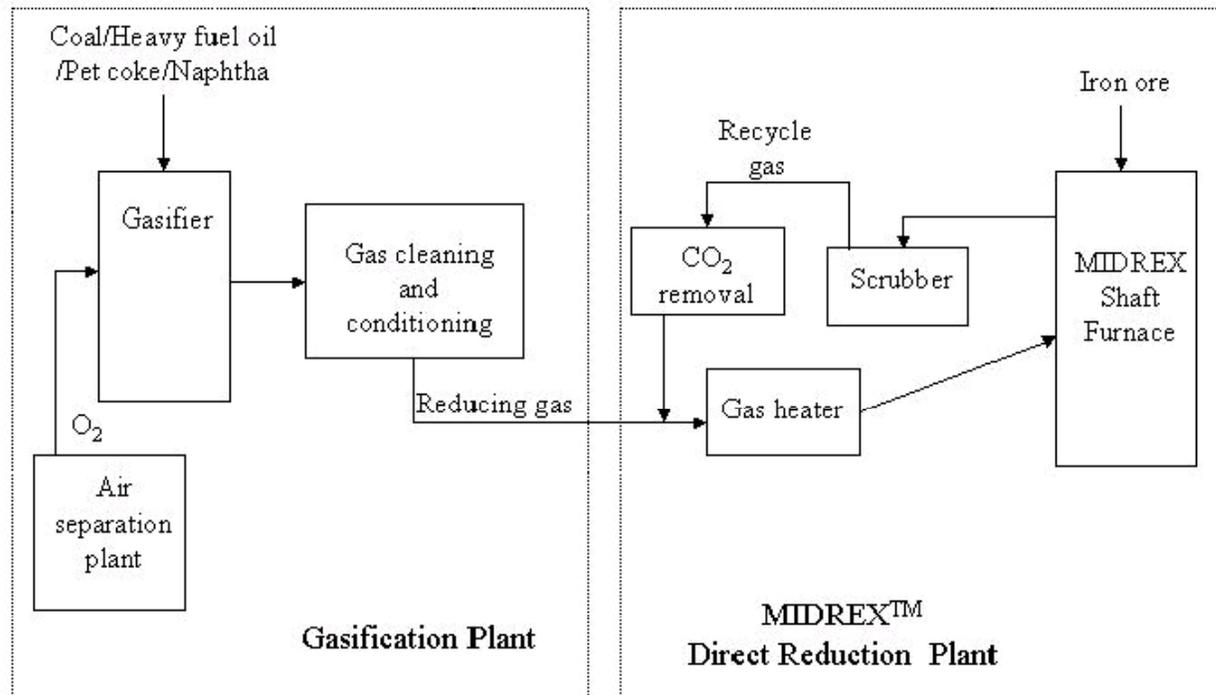
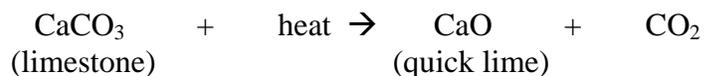


Figure 13: DRI process coupled with gasification and CO₂ removal (Cheeley, 2000)

5.2.2 Cement production

The annual capacity of Canadian cement industry is over 14.5 million tonnes of cement. Total CO₂ emissions are 8 million tones/yr. (Canadian Cement Council, 1994; Humphrey and Mahasenan, 2002)

Cement is made in two basic types of process: wet, in which the raw materials (limestone and silica) are ground in water and fed to the kiln as a slurry; and dry, in which the raw materials are ground and fed into the kiln as a dry powder where the calcinations process takes place:



Preheater and precalciner kilns are modern fuel-efficient refinements of the dry process where considerable heat is recovered from the exhaust gases (Canadian Cement Council, 1994). The wet process is less fuel-efficient and generates more CO₂ emissions than the dry process because of the need to remove the added water from the raw mix. The Canadian cement industry is technologically advanced, and more than 80% of its production capacity is of the energy efficient dry process and precalciner/ preheater types. (Canadian Cement Council, 1994).

As discussed above, the production of cement and lime requires two main ingredients, each of which contributes to CO₂ emissions. The first source of CO₂ emissions is the combustion of fossil fuels to heat the kilns. Currently a large section of Canadian cement manufacturers use natural gas in the kilns. However because of fluctuating prices of natural gas, cement plants intend to switch to coal as kiln fuel. The second source of CO₂ is chemical reaction (as shown above), calcinations, that occurs in the kiln. Process-related CO₂ normally accounts for more than half of the total CO₂ emissions and this proportion is expected to increase in future due to energy

efficiency improvements. In the conventional coal based cement manufacturing processes, the concentration of CO₂ in the flue gas stream may vary from 14 % (in heaters and boilers) to 33 % in the calcinators. The CO₂ concentration of flue gases in cement industry is higher than in power generation processes, so cement kilns could be suitable for CO₂ capture. CO₂ could be captured using amine scrubbing but the large quantities of low grade heat required for amine regeneration are normally unavailable at cement works (Thambimuthu et al. 2002). Combined heat and power plants would have to be built at the site to provide the heat. It may be quite possible to use oxyfuel combustion in cement kilns but the effects of a higher CO₂ concentration in the flue gas on the process chemistry would need to be assessed.

5.2.3 Hydrogen/Ammonia production

Large quantities of hydrogen is widely used in petroleum refining, ammonia synthesis and in the upgrading of raw bitumen extracted from the oil sands in the Western Canadian Sedimentary Basin (WCSB). Production of refined petroleum products from oil sand bitumen requires 5-10 times the amount of hydrogen compared to conventional crude. With the projected expansion of oil sands operations in WCSB, hydrogen demand for oil sand sector alone is likely to quadruple to 2 billion scf/day by 2010 (Keith, 2002; Thambimuthu, 2003). This will be equivalent to 20% of current world production of H₂ for refining applications. This scenario is likely to place Alberta with the world's largest concentration of hydrogen plants and possibly an attractive opportunity for low cost CO₂ capture. Currently all commercial hydrogen production in WCSB comes from steam methane reforming (SMR) of natural gas. According to projected growth rate of hydrogen production, the SMR and water-gas-shift will produce around 13 Mt CO₂/year by 2010. In the prevailing regime, Benfield and PSA processes are used for purification of H₂ streams. The Benfield process is a conventional process and involves two shift reaction stages followed by CO₂ removal through chemical absorption (Section 2.1.1.2), producing a high purity hydrogen stream as shown in Figure 14. The off gas contains basically 47% CO₂ and 52% water which can be easily removed through condensation followed by CO₂ compression .

The Pressure Swing Adsorption (PSA) process which uses a PSA unit instead of a solvent to purify the product hydrogen, is emerging as the process of choice as it involves only a high temperature shift conversion and provides a very high purity of (>99.5%) H₂ stream as shown in Figure 7. Although the off gas contains sufficiently high concentration of CO₂ (46%), the presence of methane (20%), hydrogen (23%) and CO (10%) makes CO₂ capture a little cumbersome and may require selective chemical, physical absorption or oxyfuel combustion of the fuel gas to additionally remove CO₂. Under the current practice, in PSA plants, for synergic reasons, the residual off gas stream (after hydrogen removal) is mixed with other fuel gases and then combusted as fuel.

4.2.4 Natural gas processing

Raw natural gas varies widely in composition and is rarely suitable for pipeline transportation. Natural gas (NG) may contain 0-30% CO₂ by volume. In addition to this, raw natural gas may contain significant amount of other impurities such as H₂S and nitrogen. In fact MEA solvents were developed 60 years ago specifically for this purpose. The mean CO₂ concentration of natural gas produced in Canada is currently about 2.5 %, implying that the total production of well CO₂ is around 9 Mt CO₂/year, equivalent to about 1.5 % total Canadian CO₂ emissions (Keith, 2002). Since NG production in Canada is likely to rise by 50% by the next decade, the

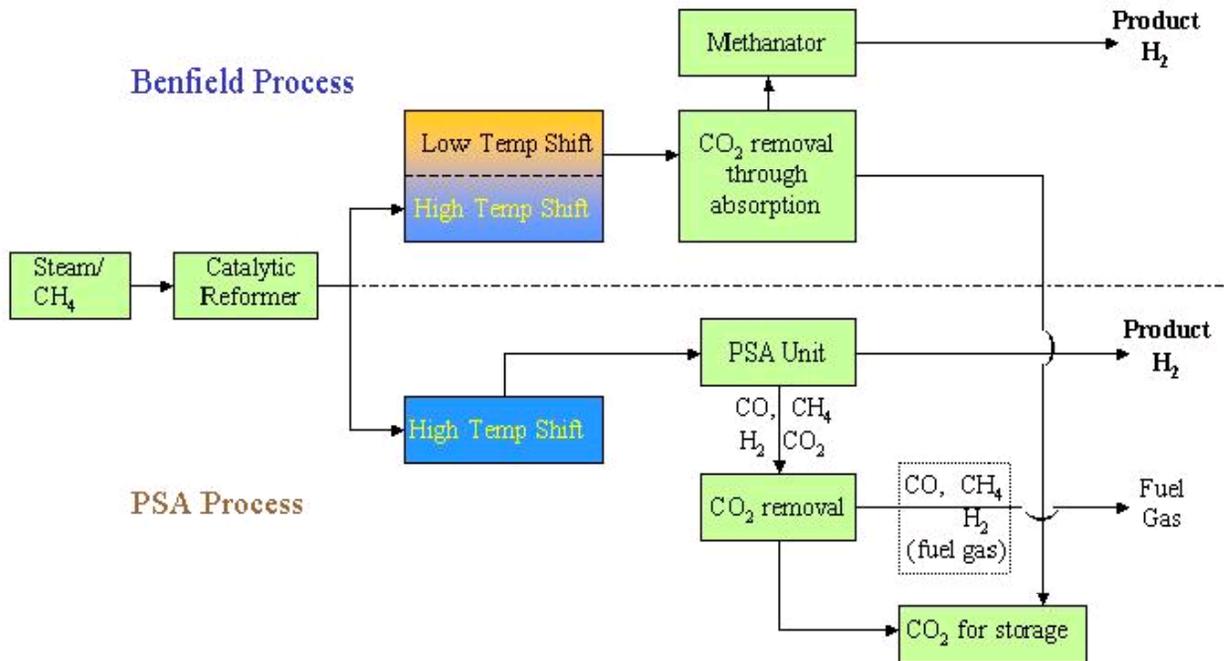


Figure 14: Hydrogen production from Natural Gas: Benfield and PSA process

NG well CO₂ production is likely to rise to 14 Mt CO₂/year, which will be equivalent 2.3 % of total CO₂ emission in Canada (CEO, 1999). Under existing practice, while treating natural gas to meet piping specifications, this CO₂ is captured but is vented to atmosphere. Figure 15 shows a typical process sheet for natural gas processing. This shows the option of onsite acid gas injection (AGI) involving CO₂ onsite sequestration with the H₂S removed from the gas.

5.2.5 Oil refining

The refinery is essentially a carbon/hydrogen manipulator, tailoring and reshaping molecules and boiling ranges to meet the production needs of particular fuels.

All emissions from the refinery itself originate from the feedstocks used. These feedstocks are mainly crude oil(s) to be processed plus other imported feedstocks such as natural gas for steam or hydrogen plants. Figure 16 shows CO₂ emissions profile for two typical 100 000 bpsd refineries, one hydrocracking (HCK) based, the other fluid catalytic cracking (FCC) based. Both refineries are designed to produce EU specification products (Philips, 2002).

Figure 8 above indicates that emissions are dominated by those resulting from burning of fuel in fired heaters, power production and utilities (80-84%). In practice, refineries have a large number of process heaters scattered with in the plant area. These heaters emit flue gases with CO₂

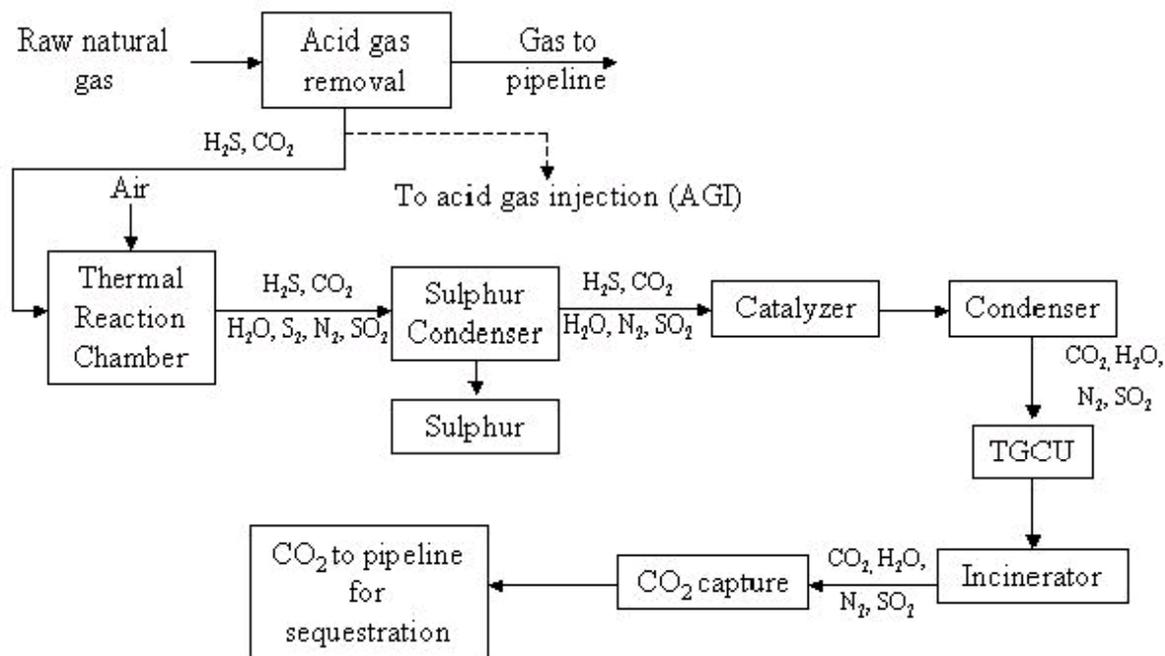


Figure 15: Natural gas processing plant with CO₂ capture and sequestration

concentrations of 4-14% depending upon the fuel used. This makes CO₂ capture more difficult, extremely expensive or even impractical. However, there is potential for capture of CO₂ produced from power generation, hydrogen production and utilities within the refinery complex, which represents approximately half the refinery CO₂ emission.

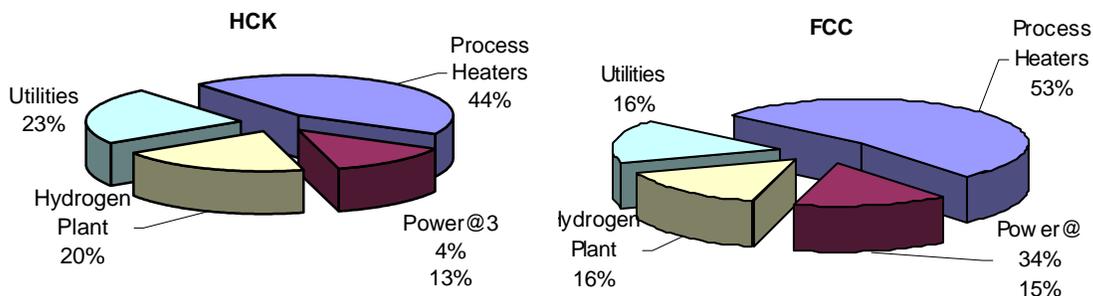


Figure 16: Distribution of CO₂ emissions in refineries

Thus the CO₂ capture options in a refinery (IEA, 2000b) include:

- Capture from fired heater flue gases using a regenerable amine solvent.
- Use of oxygen produced in an air separation unit (ASU) to burn the heater fuel (oxy-fuel combustion). Flue gas is re-circulated to control the combustion temperature. Another important application of oxyfuel combustion could be the fluid catalytic cracking (FCC) units in the refineries. Under existing practice, the spent catalyst is regenerated using combustion (in air) to get rid of coke that collects on the catalyst during FCC process. The resulting flue gas contains low concentration of CO₂ (see Figure 17). The use of pure oxygen in de-coking of the catalysts will result in highly concentrated streams of CO₂. However the effect of pure oxygen on the catalyst activity has to be studied.
- Use of a hydrogen-rich fuel gas in the fired heaters. CO₂ capture takes place before the fuel is burnt. The H₂-rich fuel gas is made from the refinery-produced gases supplemented by natural gas

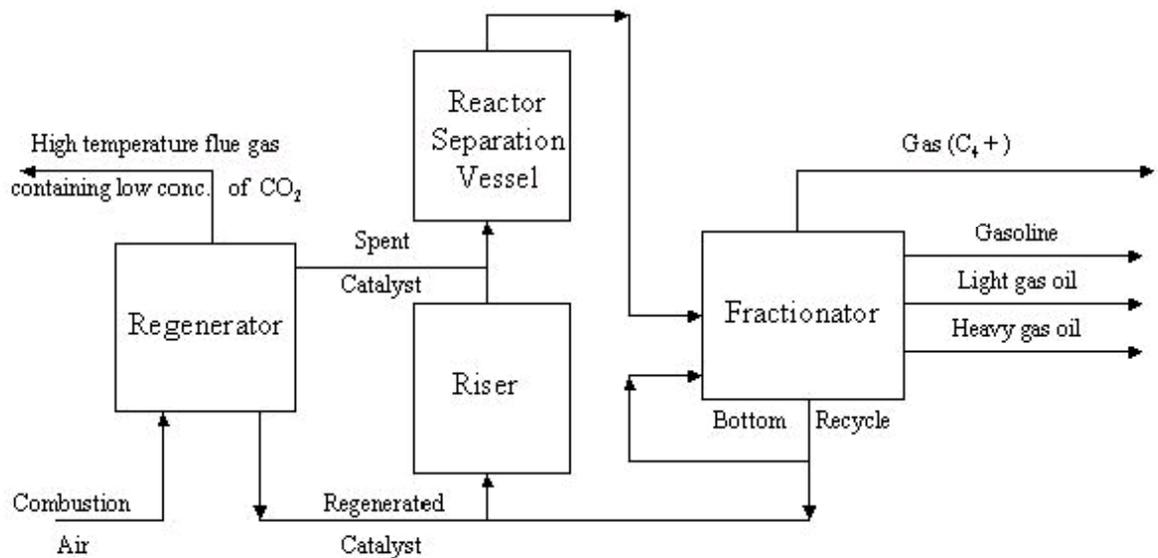


Figure 17: Fluid catalytic cracking (FCC) process

It is interesting to note that following issues influence the above options;

1. Fuel replacement
2. The need for hydrogen

In the past the driving force behind fuel replacement has been SO₂ reduction. However, it can be seen from Figure 18 that fuel switching from heavy oil to natural gas has a relatively small impact on CO₂ emissions (only 20%). However it puts enormous pressure on dwindling natural gas supplies which can be otherwise used as a raw material for hydrogen production for upgrading the refinery products. According to conservative estimates, approximately 10 tones of CO₂ per tonne of hydrogen is produced irrespective of the manufacturing process used. Also as

discussed before, use of hydrogen as fuel causes more CO₂ emissions than raw fuel directly (Hoffert et al., 2002). Hence for process heating, refineries have to look for fuels other than hydrogen or natural gas and have to install the appropriate CO₂ capture devices.

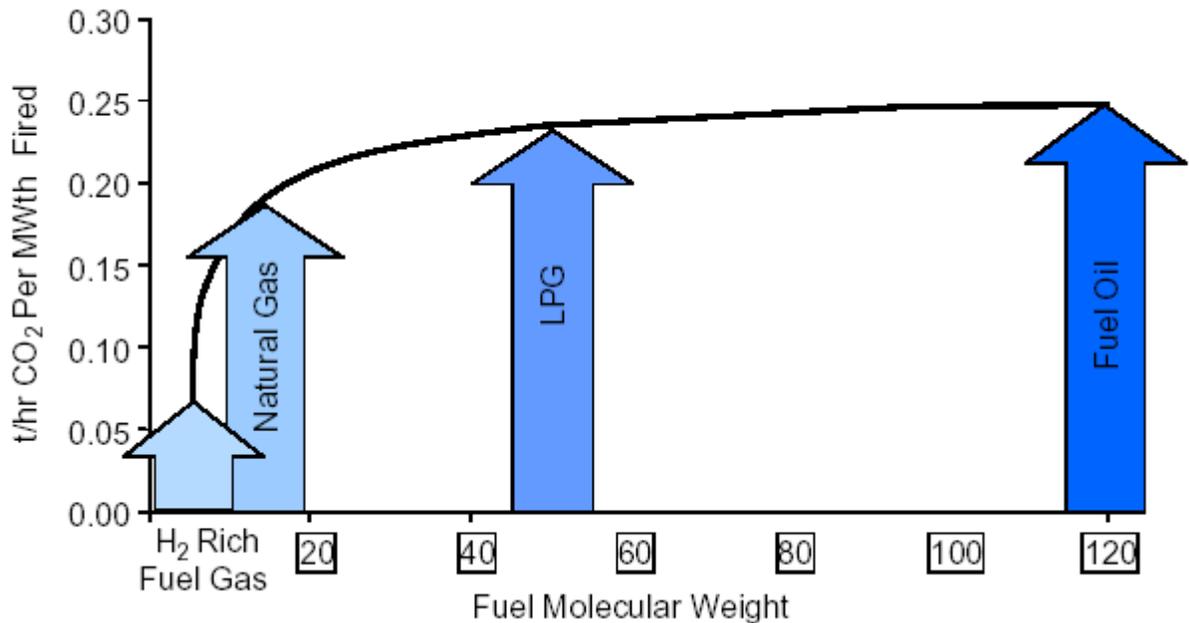


Figure 18: CO₂ emissions: Impact of fuel switching in a refinery (Philips, 2002)

5.3 CO₂ capture costs for various sectors

Generally, the cost of CO₂ capture and the concentration of CO₂ in the capture stream have an inverse relationship. High purity CO₂ sources are by far the most attractive candidates for capture. However as shown in Figure 19 the bulk of the potential streams in the WCSB consist of relatively dilute CO₂ concentrations, with only 5 % of CO₂ available from relatively high purity sources.

The significant contribution of coal fired power plants is reflected in the large 10-20 % CO₂ concentration category. Virtually all of the CO₂ from the leanest (<10% CO₂) streams is associated with natural gas-fired operations.

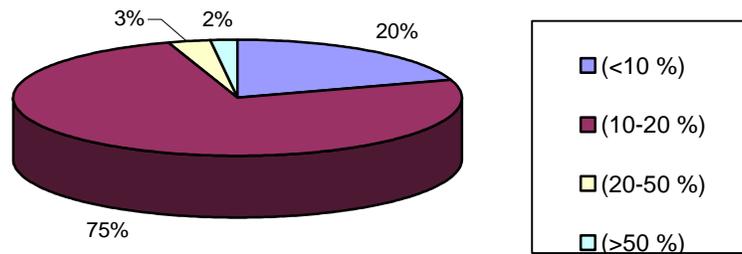
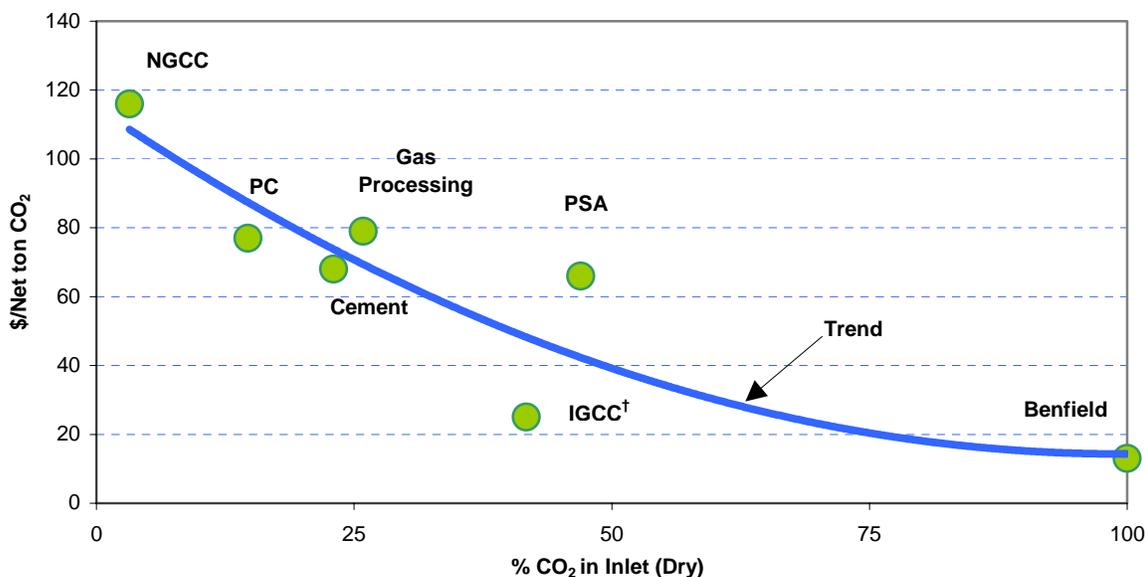


Figure 19: Concentration based distribution of CO₂ emissions in WCSB: Total emissions: 141 Mt/year (CERI, 2002)



† Conc. in the downstream of shift reactor

Figure 20: Net capture cost vs % CO₂ in the inlet stream

Figure 20 shows the typical capture cost for various processes and sectors as a function of CO₂ concentration in the emission stream (inlet for CO₂ capture plant) (SNC-Lavalin, 2002). Higher concentrations of CO₂ discharge in the IGCC and Benfield process (hydrogen production) result in a reduced cost of CO₂ capture. In general, the overall cost of CO₂ avoided decreases with the increase in CO₂ conc. at the inlet of capture plant. Table 2 shows the sector wise cost of CO₂ capture and the unit process involved therein. The low concentration streams involving chemical solvent scrubbing exhibit higher orders of the cost compared to cost incurred in the Benfield process, oxyfuel combustion and IGCC. As the low concentration streams share a larger fractions

of total CO₂ emissions, these streams will need to be addressed in the Kyoto compliance regime (2008-2012) and beyond. As CO₂ capture matures into an industry, the advances in the development of oxygen transport membranes (OTMs) for oxygen production, or new amine compounds (such as the KS –series as discussed in the earlier sections) and their optimization with the overall plant operations will reduce the cost of CO₂ extraction from the low partial pressure streams.

6. Future trends

Although the CO₂ capture concept is widely practiced in the petroleum and natural gas processing industry, the concept of capture in power generation and process heating (especially in lean and oxidizing environments) and its sequestration is relatively a new concept. Presently, a large chunk of Canadian CO₂ emissions belong to this lean CO₂ streams from coal/natural gas fired conventional utilities or from industrial heaters. This poses challenges in terms overwhelming capture costs.

The current Canadian fossil fuel based energy infrastructure depends heavily upon natural gas which can be easily transported from one region to another. This results in distributed and lean streams of CO₂ emission, making it tedious to capture CO₂ at each source. However with the dwindling reserves of gas and oil, this situation is likely to change in the future. In the post Kyoto compliance regime, such that in the period 2015 and beyond, a hydrogen based zero emission energy infrastructure is likely to gain momentum. However, in the absence of any major breakthrough in public perception of the potential risks of nuclear energy technology, most of the hydrogen will likely be supplied from fossil fuels. The Western Canadian Sedimentary Basin which is rich in coal and oil sands is likely to feed most of Canada's fossil energy needs and would become one of the largest hub of hydrogen production in the world. Thus, the fuel decarbonisation processes for hydrogen production would produce relatively concentrated CO₂ streams (see Figure 21). This is likely to provide synergetic opportunities for low cost CO₂ capture and its in-situ storage in the WCSB. This scenario will get a further boost from any breakthrough in conventional or new membrane separation technologies or advanced solid state CO₂ capture technologies such as PSA and ESA.

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Table 2 : Cost* of CO₂ capture-by sector (CNC-Lavalin, 2002)

No.	Sector	Fuel/Raw Material	Unit Process Selected								Unit Cost Net basis \$/ton	Remark
			Cooling	FGDSU	Caustic Wash	Gas Shift	CO ₂ separation -MHI	CO ₂ -Selexol	CO ₂ MEA	Compression		
1	Combined Cycle	Natural Gas	X				X			X	116	
2	PC	Coal	X	X			X			X	77	
3	IGCC	Coal				X		X		X	25	
4	O ₂ -fuel	Coal	X	X						X	10 [†]	Stromberg (2003)
5	Cement	Coal	X				X			X	68	
6	Iron & Steel	Coal	X				X			X	53 ^{††}	Anderson and Newel (2003)
7	Hydrogen Production											
8	-Benfield	Natural Gas	X							X	13	
9	-PSA	Natural Gas					X			X	66	
10	Refinery	-	X				X			X	-	
11	Gas Processing	-	X	X			X			X	79	

* Unless mentioned, figures are in Canadian \$

† Cost in Euro/ton

†† Cost in US\$/ton