

CHEMICAL ECONOMICS - CARBON DIOXIDE EXTRACTION - PART 1

Central to many of the approaches to greenhouse gas mitigation is the removal of carbon dioxide from gaseous emissions so it does not add to the greenhouse burden of the atmosphere. When extracted the gas can be sequestered in deep underground storage facilities. In the extreme, there are now several proposals to extract the gas from the atmosphere for geo-sequestration. In this paper I will discuss the current practice and economics of carbon dioxide separation from streams of mixed gases in industry. In a later paper, I will discuss some of the issues relating to carbon dioxide removal from exhaust gases of power generating facilities.

Carbon dioxide is found as a waste (unwanted) gas in a wide variety of streams in the hydrocarbon processing and chemical industry and there are a wide variety of methods used to remove it. Generally this is accomplished by process plant illustrated in Figure 1. The gas to be treated flows into the base of tower A at pressure and rises against a descending stream of absorbent. The treated gas (carbon dioxide depleted) exits the top of the tower. Absorbent loaded with carbon dioxide exits the base of the tower and is pumped to a regenerator tower B where the carbon dioxide is desorbed from the absorbent, often by boiling the absorbent by means of a heater C, and exits the top of the tower. Regenerated absorbent is pumped to the top of tower A.

Most commonly absorbent regeneration is accomplished by heat (boiling the absorbent) and to optimise efficiency of the process the streams passing between the towers pass through heat-exchangers.

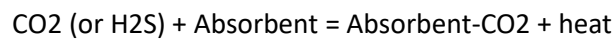
The choice of absorbent (process) is determined by the nature of the gas being treated. Some processes use physical absorbents with the rate and efficiency of absorption of carbon dioxide being determined by Henry's law. In the Table is a list of common components in gases to be treated., together with their normal boiling points - the value for carbon dioxide is computed. For design purposes, the process is built around the removal of a key gas (carbon dioxide) to a specified level. A consequence of this is that, to a first approximation, gases present with higher boiling point are also removed. For example, in the case of carbon dioxide removal, any hydrocarbons present with a higher boiling point will also be stripped from the gas.

An early process (Rectisol™) uses methanol which is chilled (to typically -40°C) so the process requires refrigeration plant. This process is good at handling highly fouled gases from gasifiers and the like and is able to strip out high boiling hydrocarbons and tars. The choice of a low boiling solvent such as methanol facilitates separation from these materials and methanol recycle. Originally used in coal gasifiers such a process would be used to clean gases from bio-gasification of renewable feedstock such as wood-waste and bagasse. Newer processes use higher boiling solvents to avoid the refrigeration requirement or mixed absorbents to improve selectivity.

To a large extent, membrane processes operate by a similar manner (Figure 2). High pressure carbon dioxide containing gas enters one side of a unit separated into two by a membrane. Carbon dioxide "dissolves" in the membrane and passes through the membrane to the low pressure side of the unit. Adequate separation efficiency is improved by operation of multiple units in series and

recompressing and recycling the tail gases. Problems arise when the gas to be treated contains higher boiling compounds which also dissolve and degrade the membrane, such as aromatics. This has occurred in carbon dioxide rich natural gas in central Australia.

In many instances, hydrogen sulphide removal is also required along with the carbon dioxide. As Table 1 shows, hydrogen sulphide will also be removed with physical absorbents. However, both of these gases are acid gases and there are a large number of processes which use this fact to improve removal efficiency by using an alkaline absorbent. These processes get over the limitations of Henry's Law absorption capacity and kinetics by chemically reacting the acid gases. As will be appreciated the choice of absorbent is limited by the need to form a salt which can be easily reversed in the regenerator.



Application of heat in the regenerator liberates the acid gases. Alkanolamines are widely used for this purpose in removing carbon dioxide and hydrogen sulphide from natural gas. In this use, heavier hydrocarbon are first removed upstream so they do not interfere with the process.

Another absorbent used is hot potassium carbonate (the Benfield Process) which forms a bicarbonate upon contact with carbon dioxide. This process is commonly found in ammonia synthesis plants where ample steam is available for process operation (near 100°C) and absorbent regeneration. Overall, the processes is less energy intensive than amine or physical solvent type processes and ammonia synthesis gases (nitrogen and hydrogen) are effectively insoluble in the hot potassium carbonate solution which minimises losses.

The economics of gas treatment and the choice of the process to be used are strongly dependent on the nature of the gases to be treated. At one end of the spectrum lie the Rectisol type process which can, more or less, treat any gas. Minimising losses and extracting and separating unwanted products such as hydrocarbons and tars, requires a lot of process equipment and hence high capital cost. At the other extreme, chemical absorption processes are well established for treating gases with relatively few unwanted species.

Most natural gas contains some carbon dioxide. To date this is usually extracted and exhausted to atmosphere. Only recently as fields higher in carbon dioxide are developed have there been proposals for carbon dioxide geo-sequestration. The Gorgon field in WA (10 to 20% carbon dioxide) is a case in point where the developers (Chevron) remove and geo-sequester carbon dioxide so that the final gas meets specifications for production of LNG or pipeline transmission to Perth (typically 2% carbon dioxide). However, high carbon dioxide content fields in central Australia (25% or more carbon dioxide) and newer developments in Bass Strait (Kipper >10% CO₂) still exhaust extracted carbon dioxide to the atmosphere.

Difficulties of mass carbon dioxide removal are illustrated by the case of the East Natuna gas field in the Indonesian sector of the South China Sea (the West Natuna field provides gas to Singapore). The East Natuna field is one of the largest undeveloped gas fields known. It was discovered in 1973 and is thought to contain over 200Tcf (trillion cubic feet) of gas, unfortunately with a carbon dioxide content of about 70% (volume) which has to-date precluded its development. Proposals to develop the field have gone through many iterations with one proposal to lower the carbon dioxide content

by membranes and re-injecting the carbon dioxide requiring double the usual off-shore facilities (dedicated off-shore carbon dioxide removal and geo-sequestration platforms).

In a following article I will discuss the issue of carbon dioxide removal from flue gas prior to geo-sequestration.

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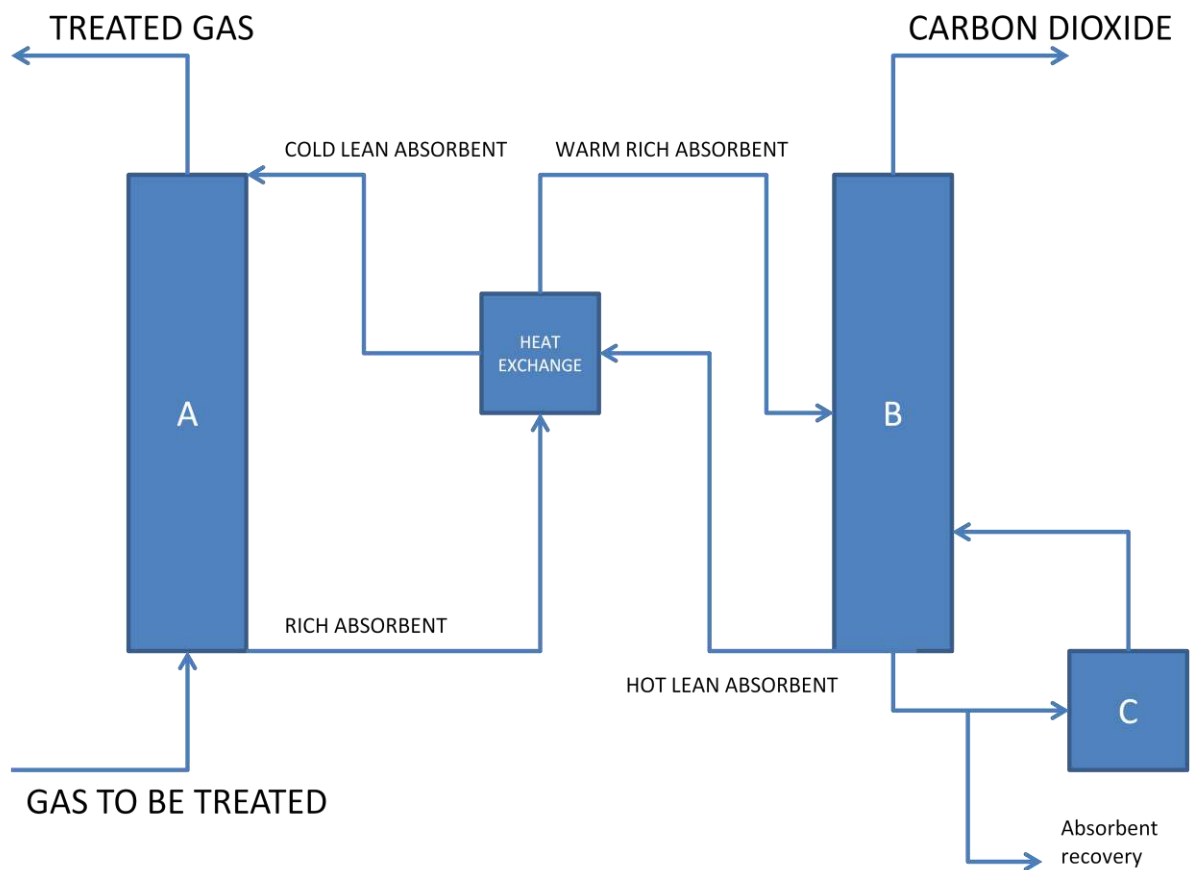


Figure 1: Schematic for carbon dioxide removal from industrial gases

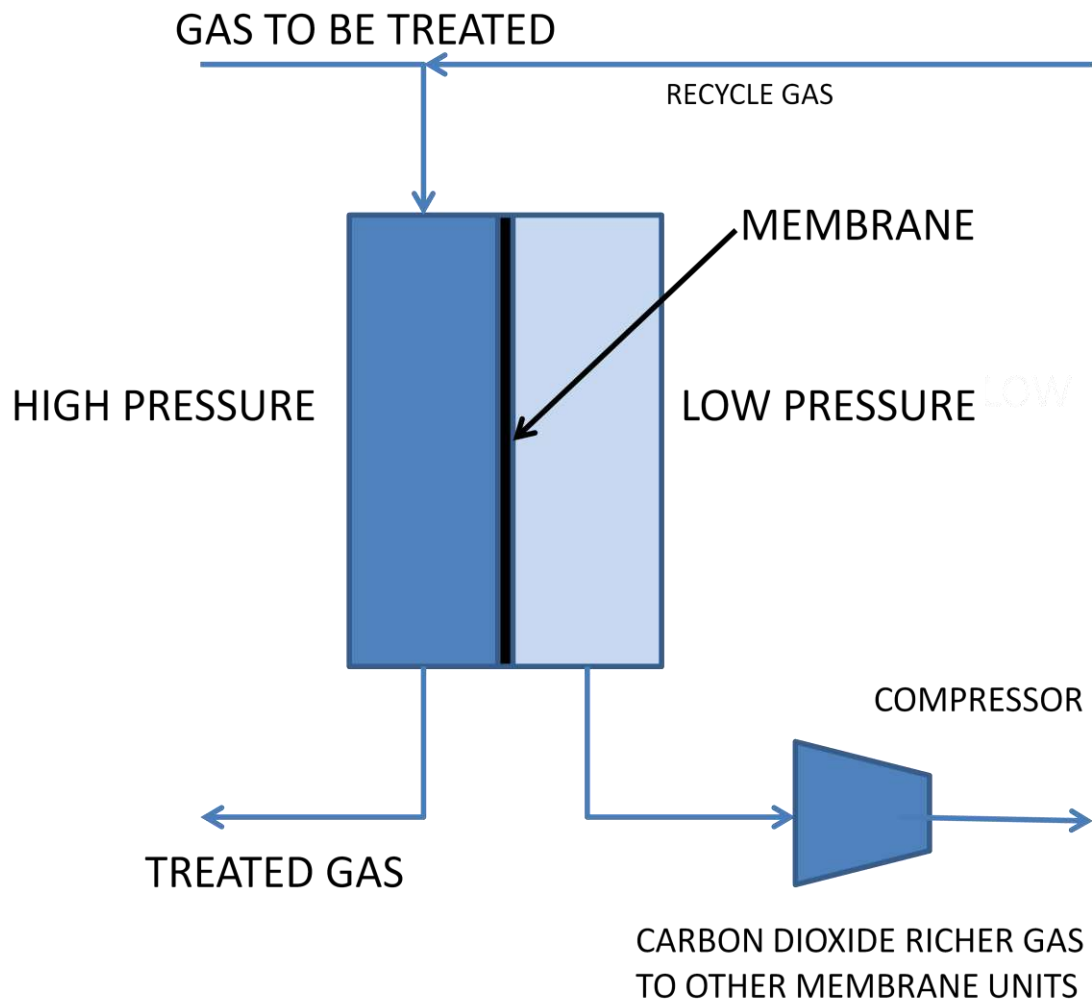


Figure 2: Schematic for membrane processes

Table 1: Boiling points of gases pertinent to CO2 removal

		bp (K)
H2		20.4
N2		77.4
CO		81.7
O2		90.2
CH4		112
CO2	computed	175
C2H6		184.6
C2H2		188.4
H2S		213.5
COS		223
C3H8		231.1
NH3		240
i-C4H10		261.4
SO2		263.2
n-C4H10		272.7
CH3SH		279.1
NO2		294.3
HCN		299
i-C5H12		301
EtSH		308.2
n-C5H10		309.2
CH3SCH3		310.5
CS2		319
n-C6H14		341.9
C6H6		353.2
c-C6H12		353.8
n-C7H16		371.6
H2O		373.2
n-C8H18		398.8