EDGAR CO_2 purity: type and quantities of impurities related to CO_2 point source and capture technology: a Literature study

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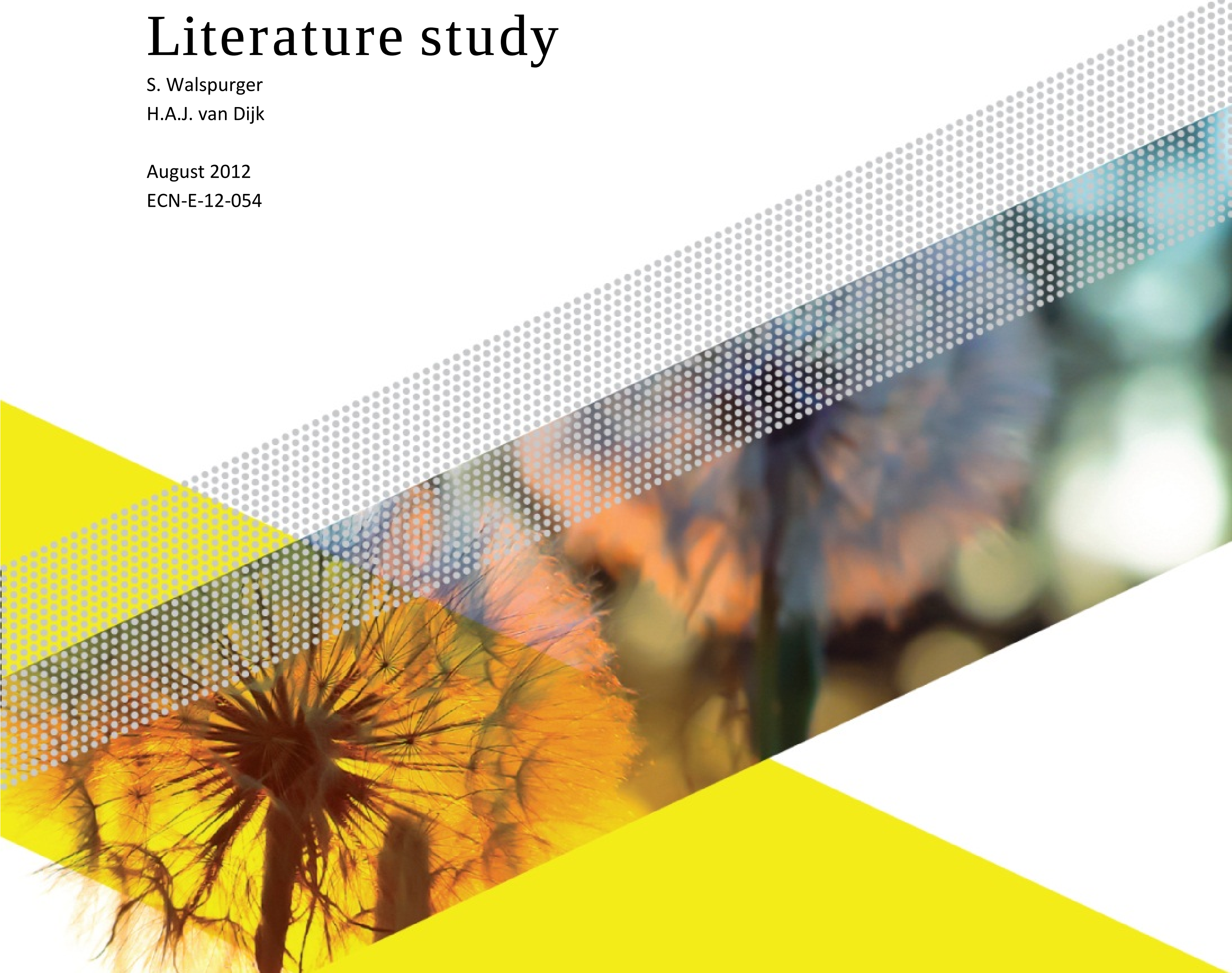

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Abstract

Carbon capture and storage (CCS) is an important tool that will contribute significantly to CO_2 emissions abatement both in power and industrial sectors. Capture technologies as well as transport and distribution infrastructure development need to be carried on to ensure efficient CO_2 separation and safe transport to storage sites. This study aimed at identifying, and when possible quantifying, the impurities present in CO_2 streams resulting from various CO_2 capture plants, such that challenges in development of appropriate materials and cleaning technologies for future CCS infrastructure may be anticipated. In its first part, the study provides a description of the characteristics of the different CO_2 capture technologies with respect to their response to different type and quantity of impurities, striving for describing realistic combinations of point sources and capture technologies. Composition of CO_2 gaseous streams was found to be highly dependent upon the type of CO_2 point source and the removal technology selected. In most of the capture processes, most impurities concentration may be minimised by fine tuning of process operation. However plant economics eventually govern the impurity level in the CO_2 stream. For mature technologies such as absorption by chemical or physical solvents lower impurity levels were found to be theoretically quite low, but when energy spent for regeneration is lowered, or when 2nd generation capture with lower energy requirement are considered, the impurity level in CO_2 stream increases. Accordingly, the report also addresses the conditioning technologies that are available or need to be developed for removal of traces elements such as mercury, volatile compounds and other condensable and points at technologies to be developed, especially in the sulphur compounds removal from CO_2. In its final part the report addresses the quantification of future specification and concludes based on literature study that pipeline specifications (for transport) may actually be more stringent than storage specifications. The report conclusion is presented as a table which summarized quality range that can be anticipated for a number of relevant processes that may be implemented in the power sector and in the industrial sector.

Contents

Summary

This study provides an in-depth description of CO_2 stream quality that is to expected in a Carbon Capture and Storage (CCS) context, such that needs for development of appropriate infrastructure may be anticipated. The summary of literature data shows that composition of CO_2 gaseous streams vary significantly as a function of CO_2 point source such like power plants flue gas, fuel gas, land-fill gas and digester gas streams and also depend strongly upon the recovery technology to be used. In general, it clearly appears that plant economics eventually govern the impurity level that will be actually found in the CO_2 stream. While CO_2 purity higher than 97% may be reached with most of the first generation solvent scrubbing systems, the use of less energy intensive 2nd generation capture technologies such as solid sorbents and membrane separation unit may induce higher impurities levels in CO_2, while decreasing the energy requirement for CO_2 separation. As a result the report also addresses the conditioning technologies that are available or need to be developed for removal of traces elements such as mercury, volatile compounds and other condensable compounds, as complementary cleaning technology to CO_2 capture technologies. Finally the report tentatively establishes a relation between current pipeline specifications which may actually impose most of the criteria on CO_2 quality specifications and the proven separation performances of available CO_2 capture technologies. If post-combustion capture on power plant flue gas is to dominate CO_2 capture technology in the future, as a result of the possibility of retro-fitting existing power plants, main contaminants will be nitrogen and oxygen and concerns about poisonous or harmful contaminant are not of concern. However, if CO_2 capture from industry is to be implanted sulphur contaminants, fuel contaminants and CO contaminant must be taken into account and adequately abated.

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Objectives

The present literature study aims at a description of the composition of the CO_2 gaseous streams captured from the major CO_2 point sources that include power plants flue gas, fuel gas, land-fill gas and digester gas streams. Since it appears that CO_2 quality depends both upon the source and upon the recovery technology to be used, the study provides a description of the characteristics of the different CO_2 capture technologies with respect to their response to different type and quantity of impurities, striving for describing realistic combinations of point sources and capture technologies. Furthermore an analysis of the expected CO_2 product composition for the identified realistic combinations of point sources and capture technologies is listed at the end of the report to draw more attention on the conclusive results of this report.

Various CO_2 point sources were considered as high potential candidates for CO_2 capture technology implementation in agreement with literature data. Most studied point sources for electricity production include:

- pulverized coal power plants;
- natural gas fired power plants;
- coal based integrated gasification combined cycle.

Other important non-power point sources are:

- coal-to-liquids (CTL, mostly Sasol plants in South Africa);
- blast furnaces and steel industry;
- cement industry;
- oil refineries;
- ammonia plants;
- bio-digesters, landfill and waste water treatment plants.

The first part describes in more details the processes that have been considered in this study. The report is organised such that CO_2 streams purity are discussed for each relevant gas cleaning and CO_2 removal technologies that have been selected among absorption, liquefaction, high temperature separation and drying technology.

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CO_2 stream purity from absorption-based technologies

2.1 Impurities in CO_2 separated by chemical absorption

2.1.1 Chemical absorption in power plants

CO_2 capture technologies have been considered for implementation on large point-sources such as coal power plants and fossil fuel fired power plants. As a priority, supercritical coal fired power plants (supercritical pulverised coal combustion, see Flowchart in **Figure 1**) which are currently the standard most efficient commercial coal fired power plants, have been considered for CO_2 capture technology integration. Chemical solvent scrubbing technologies are the most mature technologies for the so called post-combustion CO_2 capture. Before considering the quality of CO_2 streams that is to be expected to be obtained from such an installation it is essential to recognize that coal quality mostly influences impurity level in the flue gas. It then determines the characteristics of the subsequent flue-gas cleaning processes and the CO_2 capture process.

At first, coal quality impacts indeed directly or indirectly the flue gas composition that needs to be processed in post-combustion CO_2 capture unit. The main components of typical flue gas are CO_2, N_2, O_2 and H_2O, together with pollutants such as SO_x, NO_x, particulates, HCl, HF, mercury, other metals and other trace organic and inorganic contaminants. Many coal-fired power plants have dedicated units to remove these major pollutants prior to the CO_2 capture unit. This concerns well-established conversion/separation processes (see **Figure 1**) such as Selective Catalytic Reduction (SCR) for nitrous oxides abatement, Electro Static Precipitation (ESP) for fly-ash and dust removal, ceramic filters and/or and cyclones, and Flue-Gas Desulphurisation (FGD) for sulphur removal. In a power plant equipped with CO_2 capture unit, these various processes need adaptation because most of the pollutants remaining downstream

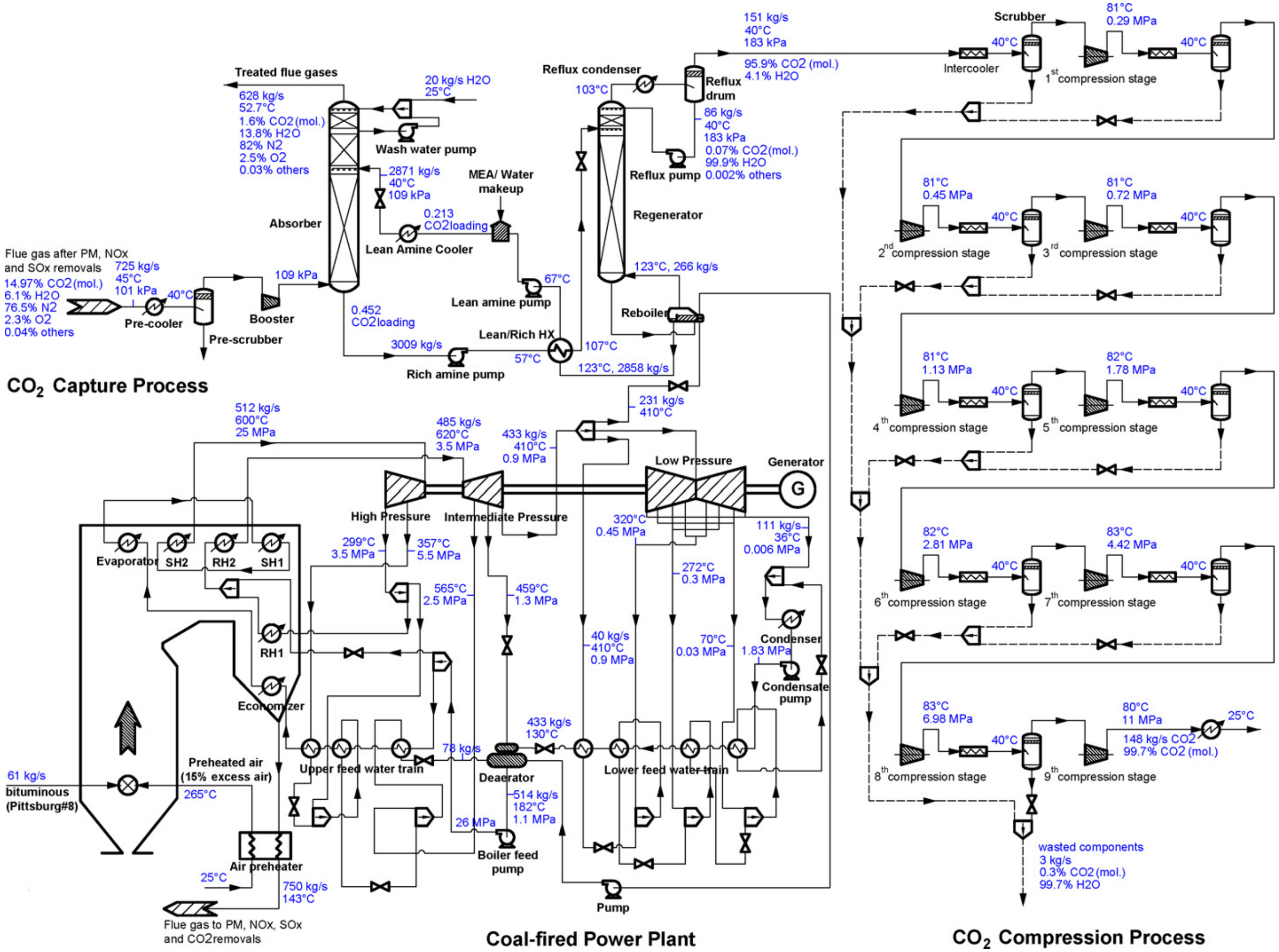

Figure 1: Flow diagram of 800 MWe supercritical pulverized coal power plant with CO_2 capture and compression unit [2]

these processes will be absorbed in the chemical solvent used for CO_2 separation. This can result in the formation and accumulation of heat stable salts, and increase the requirement for solvent filtering, regeneration and replacement, impacting seriously the operability and the economics of the capture units. NO_x is unlikely to be a major problem since it may be removed to an acceptable level by normal SCR processes. On the contrary SO_x must be removed at a higher removal rate than the ones normally achieved by Flue Gas Desulphuriser (FGD) since the amine compounds of scrubbing solvent are quite sensitive to the presence of acid gases and potential oxidants. Chemical absorption of CO_2 by aqueous alkanolamine scrubbing system (depicted in the upper part of **Figure 1**) is indeed currently the technology that is the closest to a possible commercial deployment for CO_2 removal from flue gas at ordinary pressure with CO_2 concentration between 5 and 15% [1].

For instance at the Niederaussem CO_2 capture pilot plant, a pre-scrubber system has been implemented between the existing FGD unit and the CO_2 capture pilot unit which consists of a direct contact cooler where sodium hydroxide is added to the cooling water to remove extra acid gas contaminant such as SO_x and NO_x which are usually still present at 50-100 ppm downstream FGD [3,4]. This precaution has been taken to avoid fast degradation of alkanolamine based solvent. Note that although state-of-the art wet FGD might be sufficient to reach SO_x level below 20 ppm, amine scrubbing CO_2 capture plants economics might impose lower levels and thus an additional unit.

In general, chemical absorption by e.g. alkanolamine aqueous solution or simply by water is used to remove acid gases and also other trace compounds such as NH_3, higher hydrocarbons, HCN, organic sulphur and metals when necessary. However some trace elements compounds of the raw gas to be treated may react with the alkanolamine aqueous solution or with other soluble compounds and cannot be removed by regeneration. In this case, accumulation issues may eventually lead to clogging, foaming, corrosion and solvent losses. This affects the separation unit performance and generally leads to a CO_2 selectivity decrease which definitely alter the CO_2 stream purity. For instance, many commercial solvents encounter accumulation problems with organic sulphur compounds and cyanides [5]. In specific cases COS is also present in the flue gas and its reaction with MEA results in non-regenerative products. Rate of formation of these products is slower with DEA (diethanolamine) and other advanced amines such as DIPA (di-isopropylamine). Sulfinol (DIPA+Sulfolane) is presented as a very efficient option for removal of COS. In general other mercaptans do not appear to lead to degradation products formation. In contrast, heat stable acids produce heat stable salts by interacting with amines. They may be generated by reaction with oxygen or by thermal degradation of the amine and may accumulate in the solution. Constant concentration of active amine may be reached by implementing reclaimers. Commercial techniques include distillation under vacuum or atmospheric pressure, ion exchange and electrodialysis. Soda ash or sodium carbonate is usually added to release the amine but they also may not accumulate more than 10 wt% in the circulating solution. Filters remove solid particles from side stream purification units. Adsorption by activated carbons may be used to prevent foaming due to surface active contaminant or emulsified high molecular weight organic compounds. Degradation products may be removed from amine solutions by distillation of a small sidestream (0.5 to 2 % of the main stream). Remediation methods abound both in the open literature and patent literature and will not be discussed further in this report.

Once the inlet stream of a monoethanolamine MEA scrubbing-type installation has been considered, the outlet stream treatment options must be taken into account and may offer opportunities for further cleaning when necessary. A water wash for both decarbonized flue gas (absorber outlet) and CO_2 stream (stripper-regenerator outlet) is generally used to prevent alkanolamine loss by vaporization and further contamination of both streams. CO_2 is stripped from the alkanolamine aqueous solution using heat supplied by a re-boiler, delivering a wet warm stream at the outlet of the regenerator which needs to be condensed for aqueous alkanolamine solution recovery and recycle to ensure operation continuity. Note that while condensing water, soluble acid gas may concentrate as well and water soluble impurities may be recovered at this point. Theoretically absorption with aqueous amine solutions can be designed to capture from 85 – 95 % of the CO_2 in the flue gas and produce a CO_2 with a high purity of > 99.95 %. Both recovery rate and CO_2 purity require optimization since there are no theoretical limitations on these parameters [6]. Due to the very high selectivity of amine for acid gas the concentration of inert gases is kept extremely low. However, one must keep in mind that loss of selectivity due to any problems evoked earlier may contaminate significantly CO_2 stream with nitrogen mostly.

In general there is a lack of information on CO_2 purity levels that are achieved in pilot units, although all consortia carrying out demonstration experimental work on these facilities indicate that they are currently studying this issue [7]. Kather et al. [8] have released a case study on CO_2 impurity level for postcombustion capture with various amine scrubbing configurations. **Table 1** summarizes the numbers available from a presentation of results obtained in the German project COORAL [8].

Table 1: CO_2 purity from postcombustion CO_2 capture, considered in the COORAL project

Component		Case 1-3
CO_2	%	99.8-99.9
O_2	ppm	150-300
N_2+Ar	ppm	450-900
NO_x	ppm	20-40
SO_2	ppm	10-20
H_2O	ppm	100-600
CO	ppm	10-20

Alkanolamine scrubbers are also used in the chemical industry to separate CO_2 from process gas such as in ammonia production, in oil refining, in iron production when the MIDREX process is used. CO_2 purity delivered by alkanolamine scrubbing plant from these applications may be affected by the same potential problems cited for the power from coal case, although clogging and accumulation issues are less severe because of the higher quality of the streams used in chemical industry (less particles, less dust).

2.1.2 Chemical absorption in Natural Gas processing

Natural Gas treatment before pipeline injection aims at removing acid gas, inerts and water. When CO_2 and H_2S concentrations are low, alkanolamine aqueous scrubbers are preferred options since methane losses are kept small thanks to poor solubility of methane in aqueous phase. If CO_2 and H_2S concentration are high, regeneration of solvent becomes high and alkanolamine scrubber may only be used when economics are better than competitive processes such as Benfield (aqueous carbonates) or Selexol. In this case CO_2 may be recovered with significant H_2S contamination and staged scrubbing processes must be envisaged to clean CO_2 from Sulphur compounds before transport. A similar conclusion may be drawn for CO_2 removal from biogas when alkanolamines are used, which again depends on the economics of the plant.

2.1.3 Chemical absorption in biogas

Biogas from anaerobic fermenters is composed of CH_4, CO_2 and small amounts of H_2S and NH_3. Traces of N_2, H_2, organic sulphur and halogenated hydrocarbohydrates may also be present together with steam (vapour pressure corresponding to the digester temperature) and siloxanes (coming from soap and detergents decomposition mainly) in particular in sewage treatment plants or landfill sites [9]. Other typical impurities present in landfill gas are listed in **Figure 2**. Firstly, a water wash is applied to remove most of the soluble compounds, and then a separation with alkanolamines may be carried out. H_2S may be separated from CO_2 in a downstream process with an available tail-gas treatment process described in a separate report [10]. In this case the purity of recovered CO_2 is highly dependent upon the selected H_2S-CO_2 separation process and careful consideration of process design is necessary. A lot of facilities producing biogas choose for less costly water absorption biogas cleaning which enters the physical absorption category.

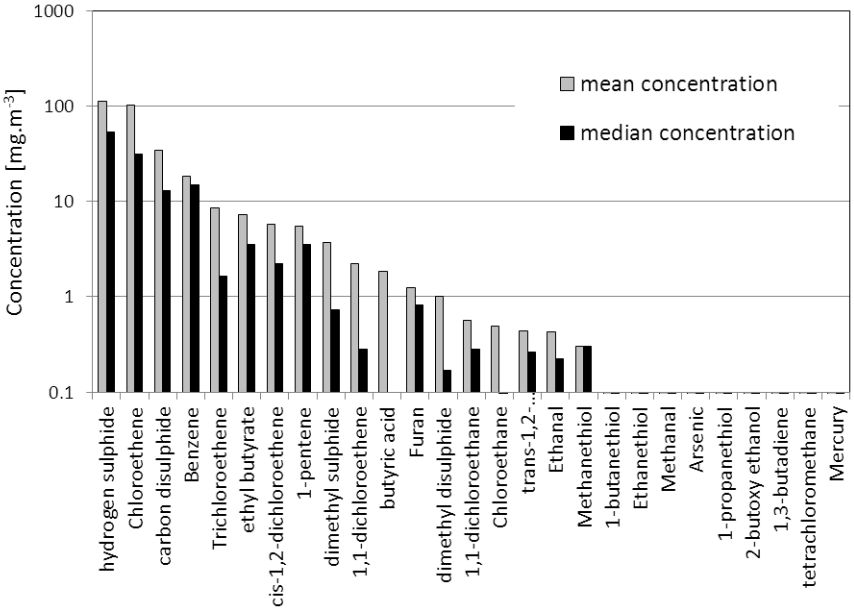

Figure 2: Typical UK Municipal solid waste landfill Gas composition [11]

2.2 Impurities in CO_2 separated by physical absorption

2.2.1 Physical absorption in biogas

Water scrubbing is used to remove CO_2 and H_2S by physical absorption (solubilisation). Usually biogas is pressurised and fed to the bottom of a packed column in which water is fed from the top, in counter-current mode. Water may be regenerated and recirculated if the economics of the plant make it necessary. In case CO_2 is recovered it comes with other soluble impurities and the obtained gas stream must undergo further cleaning operations before transport, which may impact the biogas production costs significantly. If H_2S concentration is high it is recommended to selectively remove it first thanks to the higher solubility of H_2S in water.

In an alternative scheme, biogas may be cleaned using polyethylene glycol scrubbing (Selexol-type) which is a physical absorption process very similar to the water-based one, see **Figure 3** [12]. Higher solubility of acid gases in polyethylene-glycol enables energy saving by decreasing the workload on pumping system and impurities may be separated and concentrated after regeneration of the solvent in the stripper. Landfill gas impurities (see **Figure 2**) are removed by a first Selexol stage which may be followed by a second Selexol stage in which CO_2 is removed to get sufficiently high CH_4 purity and suitable energy value gas stream for injection into the distribution grid. CO_2 stream obtained by Selexol has a purity that is dependent on the staging of the installation which directly impacts the investment and operational costs of a Selexol unit. The CO_2 stream may thus contain traces of H_2S and methane.

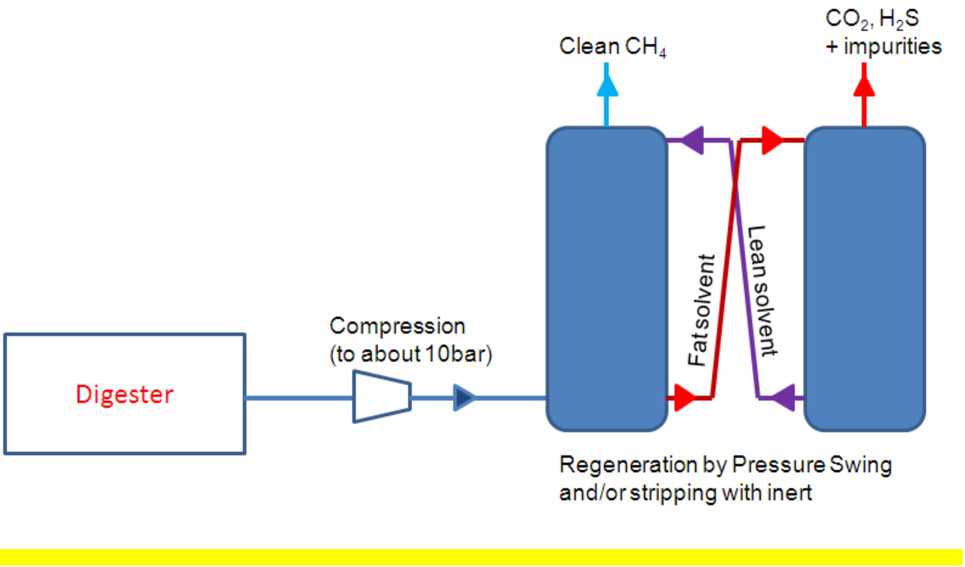

Figure 3: Traditional flowsheet Biogas upgrading by physical absorption of acid gas [12]

2.2.2 Physical absorption in industrial gas treatment

Physical absorption processes are of particular interest for separation of CO_2 from pressurized gaseous streams since the driving force for solubilisation is higher when concentration is higher. Hence the use of physical solvent has gained popularity for

Natural Gas processing, especially with the soaring LNG market. Processes using physical solvent are also preferred in coal gasification based industry such as Coal to Liquids (Sasol uses Rectisol technology for instance) and Ammonia from coal because of the potential low H_2S (sub ppm) and/or CO_2 slips achievable. Besides, physical solvents are foreseen as key technologies enabling pre-combustion CO_2 capture in coal gasification based power plants such as Integrated Gasification Combined Cycle (IGCC) which are recognised as an attractive option to afford CO_2 capture with a lower energy penalty than conventional post-combustion technologies. Before elaborating on CO_2 purity that is to be expected from available physical solvent technologies, we describe hereunder what may affect the performances of these separation technologies in a typical plant such as Puertollano, which is one of the two demonstration plants of this type in Europe.

2.2.3 Physical absorption in power plants

Like in the case of CO_2 recovery from combustion plant (c.f. §2.1) gasification plants fuel gas composition vary with the fuel quality that is used. For instance the Puertollano ELCOGAS IGCC [13] plant uses mixture up to 50% pet coke from a Repsol refinery (5.5 wt%S) and coal and the Buggenum IGCC plant tests co-feeding of coal and biomass. At Puertollano the current plant layout is designed such that (without CO_2 capture unit) the fuel gas stream is depleted from sulphurous compounds, first by catalytic conversion of COS to H_2S and then eliminating H_2S with MDEA (tertiary amine with high selectivity for H_2S) scrubbing at relatively low temperature. MDEA is regenerated in a stripper at about 100°C. However when pre-combustion CO_2 capture is considered in such a plant physical absorption is the most suitable option thanks to the relatively high pressure of the gas stream to be treated. Unlike natural gas where hydrocarbons co-absorption may be a problem, syngas streams are perfectly suited for physical solvents. This makes the physical solvents especially attractive for syngas feed containing more than 5 bar CO_2, although it may suffer from potential accumulation problems very similarly to the alkanolamine scrubbers. Rectisol (Lurgi GmbH, Linde AG) is by far the preferred purification process for coal, heavy oils and waste gas produced by gasification, when deep desulphurisation is a must before chemical conversion. A worldwide capacity of more than 100 units corresponding to 75 % of the coal gas to be treated was listed in 2006 [9,14]. Rectisol has the demonstrated ability to separate troublesome HCN, aromatics, organic sulphur and gum forming hydrocarbons impurities. Moreover the use of methanol at low temperature (-60 to -75°C) as solvent facilitates dehydration of the gas and allows obtaining syngas or hydrogen with H_2S concentration <0.1 ppm and CO_2 concentration close to 1 ppm [15]. Hence Rectisol has become the major use purification process in ammonia, methanol, hydrogen, SNG, Fischer-Tropsch and oxo alcohols production. The plant configuration, however, may be quite intricate by the necessary hot column regeneration for water removal, naphtha stripping and methanol regeneration [5]. On the CO_2 recovery side, the relatively high methanol vapour pressure may involve some contamination of CO_2 stream which needs to be controlled carefully. Linde claims >98.5 % CO_2 purity at CO_2 recovery rate between 90-97 % with H_2S <10 mg/m^3 (<7 ppm) and water <1 ppm with a stage stripper Rectisol design [16].

A competitive process is Selexol which uses dialkyl ethers of polyethylene glycol at typical operating temperatures ranging from 0°C to 175°C. A worldwide capacity of 110.10^6 m^3/d was listed in 2006 with main applications for natural gas and syngas purification and more recently for landfill gas purification, as described earlier in this report.

Although high capacities for H_2S and CO_2 may be reached at lower temperatures, the actual practical operating window of Selexol strongly depends on the viscosity. Selexol is currently mostly used for either combined CO_2 and H_2S removal or the selective removal of H_2S. It may be used for bulk CO_2 removal in a double stage process when the CO_2 concentration is high compared to H_2S [17]. UOP licences the processes and develops it for new applications and possible CO_2 capture. **Table 2** has been taken from a presentation by Santos (IEAGHG) on the influence on CO_2 purity of the use of Selexol and Rectisol [16,18]. Very pure CO_2 streams may be obtained at the cost of optimisation whose feasibility and viability rely upon plant economics once again.

Table 2: CO_2 purity from postcombustion CO_2 capture, considered in the COORAL project

Gas component	Selexol IGGC standard [18]	Selexol IGGC advanced (UOP)	Rectisol IGCC standard	Rectisol IGCC advanced (Linde) [16]
CO_2	98.1%	99.7%	95%	>98.5%
H_2	1.5%		20ppm	
N_2	195 ppm		0.2% to 4% (with N_2 stripping)	< 1%
Ar	178ppm		150ppm	
Sulphur Comp.	0.17%	2ppm	20ppm	2-10ppm
CO	0.13%	100ppm	400ppm	
CH_4	112ppm		100ppm	
MeOH			100-200ppm	20ppm (water wash)
H_2O	376ppm		10ppm	< 1ppm

Competitor Purisol process using NMP (N-methyl-2-pyrrolidone) as solvent is also used in the industry for H_2S separation and is particularly well suited to the purification of high pressure, high CO_2 synthesis gas for gas turbine IGCC systems because of its high selectivity for H_2S.

Sulfinol (Shell) which is a hybrid physical/chemical solvent is particularly adapted for high efficiency removal of sulphur compounds such as H_2S, COS and other mercaptans and for deep CO_2 removal on compressed gas stream (LNG in particular, CO_2<50 ppm). Over 200 units were reported in operation or under construction in 1999 [19]. In the specific case of LNG, acid gases are removed then the gas is dehydrated and finally mercury is removed.

As highlighted in the previous sections the main concern for CO_2 capture by absorption is further removal of sulphur from the main CO_2 stream. Although it may be achieved by modification of the flow charts for Rectisol and Selexol and by adding intermediate separator devices in the regeneration loop, some other systems based on sulphur species direct catalytic conversion may be envisaged. For instance US4332781 discloses the removal of H_2S and COS from hydrocarbon gas stream with first removal of H_2S by scrubbing with aqueous solution of regenerable oxidizing reactant (MOX with M=Fe, Mn or Cu and OX=(poly)chelates). COS containing stream is hydrolysed and H_2S may be removed again by absorption [20]. In US5104630 COS is converted by contacting with warm aqueous alkanolamine and H_2S is further removed by absorption in alkaline solution. Polishing zinc oxide bed may be used to get rid of the last traces of sulphur compounds [21]. Praxair's patent US2007/0148069 discloses a process that allows CO_2 and O_2 removal. O_2 is removed by oxygen scavenging material (or gas) before the CO_2 rich solution is heated up to prevent degradation of amines by oxygen at high temperature [22]. EP0698577 uses activated alumina to first hydrolyse COS with excess steam compared to COS. H_2S is then oxidized with a non regenerable iron oxide (or Ni or Mn) which is discarded after saturation with S leading to deactivation and replaced by fresh material. Fe sulfide is accepted for disposal in landfill [14]. Further literature data are reported in a separate report by van Dijk [10].

3

CO_2 stream purity from adsorption technologies with solid sorbent

3.1 Low temperature adsorption for post-combustion

Recovery of CO_2 in flue gases containing 15-35% of CO_2 such like in steel production, lime production and even coal fired power plants is possible by Pressure Swing Adsorption technologies since CO_2 is strongly adsorbed on many adsorbents [23]. However desorption under vacuum is necessary to enable sufficiently high cyclic capacity and high CO_2 recovery. JFE steel corporation in Japan has developed a 2-stage vacuum swing process for blast furnace gas that allows recovering high purity CO_2 at relative modest recovery rates (<70%) in the first stage, while CO is recovered in a second stage and recirculated to the blast furnace [24]. In a patent issued in 2010 JFE has proposed a novel 2-stage separation which consists of first removal of H_2 - N_2 in a first PSA unit and subsequent CO_2 - CO separation in a dedicated second PSA [25]. CO_2 streams captured by this technology contain some amount of CO that must be taken into account in the health and safety regulation framework for gas transport. Vacuum swing adsorption is also envisaged for CO_2 recovery from power plant flue gas although some technological barriers such as working CO_2 capacity of adsorbents in the presence of humidity still need to be solved [26-29]. In these VSA processes high CO_2 purities may be reached at the expense of relative low recovery rate [30]. At fixed high recovery rate the CO_2 stream will anyway contain considerable amounts of N_2 (in the % range) and possibly oxygen which may have to be removed at the compression stage before for transport.

Flue gas contains up to 10-15 % water vapour which must be removed by using guard beds or layered adsorbent beds in the PSA unit. To avoid these additional complexity and derivate costs a CO_2 water resistant sorbent is highly desirable. Supported solid amines are a relatively new type of sorbents which have high CO_2 capacity when water is present in the flue gas [31]. These materials have attracted a lot of attention since their development by the NASA to equip space shuttles and submarines [32]. CO_2 removal by temperature swing adsorption is usually considered as the best option for these sorbents which show a high CO_2 adsorption enthalpy (chemisorption) although some recent studies highlighted the opportunities to use PSA as well. For instance operation about 80°C was found to be suitable for CO_2 recovery from flue gas with CO_2 partial pressure around 100 mbar, using mostly the carbamate to bicarbonate equilibrium with a relative low adsorption enthalpy (50 $kJ.mol^{-1}$) [33]. Although the CO_2 selectivity of the material is rather high, the envisioned PSA cycle would need adaptation with extra step such as rinsing to allow reasonable CO_2 purity. CO_2 must be further dried before compression.

In contrast, the use of supported amine with temperature swing adsorption has been further developed and appears to be the preferred option over pressure swing. The sorbent stability seems to be high enough to sustain long term cyclic operation, although this needs more verification work. Important parameters are the presence of oxygen, the type of amine (primary, secondary, tertiary), and the method of functionalization at the support surface (anchoring, impregnation, or even polymerization in the porous structure of the support [34,35,36,37]). The excellent CO_2 selectivity enables reaching rather high CO_2 purity, which still depends on the process design options and particularly the stripping gas chosen for the regenerative step. Relevant studies in this field suggest to use CO_2 regeneration which has the advantage of yielding concentrated CO_2 but limit the working cyclic capacity and possibly the lifetime of the material [38,39]. Regeneration by using steam stripping is another option that allows recovery of concentrated CO_2 after steam condensation but which may also affect the stability of materials by (poly)amine leaching or support alteration [40,41]. Finally a sufficiently small stream of inert such as air or N_2 in case an ASU is available may also be suited for regeneration needs, whether it is for meeting fluidization requirements or provide a driving force to extract CO_2 out of the regenerator. In this last option a few % of inert will be found in the CO_2 stream and must be taken into account for compression, transport, sequestration or reuse.

Usual impurities such as SO_x and NO_x are more reactive than CO_2 and will thus be trapped by the supported amines and lead to steady deactivation of the sorbent in practice. Beside improvement of the FGD operation, regeneration strategy may be implemented to recover these species, or make-up flow of new fresh material to replace the contaminated one may be implemented, at the expense of higher operational costs. CO_2 recovered by this method is thus contaminated by N_2 and must be dried before compression. Note that leaching of amine functionality is not tackled by most of the study and may deserve further attention [42]. Finally process design work has identified dual circulating fluidized beds as the most suited reactor concept to achieve more advantageous mass and energy balances. Although high CO_2 recovery with high purity may theoretically be obtained, one should not underestimate the N_2 or air contamination of the CO_2 stream by cross contamination due to the necessary interconnection between adsorber and desorber when applying fluidized beds.

3.2 Low temperature adsorption for pre-combustion

As mentioned in section 2.1 solvent absorption technology is currently the preferred option considered for pre-combustion CO_2 capture. Nevertheless physical solvent scrubbers are expensive and require significant utility consumption during operation leading to a high energy use for CO_2 capture.

On pressurized feed, Pressure Swing Adsorption processes operate between 2 pressures, without need for vacuum installation, and allow simpler installation than thermal cyclic process in the absence of heat requirement for desorption. For CO_2 separation the operations are indeed equilibrium driven since CO_2 is selectively adsorbed by a number of materials as heavy product. PSA technology has been developed and extensively used at commercial scale for hydrogen purification, which is carried out downstream steam methane reforming unit by PSA unit to obtain 99.999^{+}% purity. Air Products developed Gemini 9 and 8 to allow simultaneous production of pure hydrogen and carbon dioxide from reformer off-gases [43]. The concept comprises a PSA unit for H_2O and CO_2 removal and another PSA train to remove CO_2, CO, N_2 and CH_4 from H_2. According to simulations H_2 may be recover at 86% rate with 99.999% purity while CO_2 may be recovered at 86 % rate with 97.0%+ purity. CO_2 is then contaminated by some amount of CO, and CH_4 mostly after dehydration. Air Products [44] has recently developed a H_2 production with CO_2 capture technology based on PSA processes operating under sour conditions which lowers the capture cost by 25%. The sour-PSA concept delivers pure H_2 and the tail gas contains CO_2 and H_2S and other sour gases with some amount of H_2 and CO. The tail gas is combusted in a low BTU-sour oxy-combustion unit that is developed in parallel by Air Products. A subsequent innovative compressor/separator unit, also developed by Air Products, allows further purification of CO_2-rich stream from SO_x and NO_x via the formation of H_2SO_4 and HNO_3, see gas conditioning chapter 5 for more details. Theoretically high CO_2 purity could thus be reached by this cascade of novel technologies, which is however not corroborated by experimental data so far.

3.3 Purity of CO_2 recovered with high temperature sorption

In power generation and other relevant industrial applications using gaseous fuels obtained either by gasification of coal - biomass or by methane reforming separation at high temperatures and high pressures, sorption processes at high temperature are among the best options to reduce the energy penalty induced by the CO_2 capture. The major reason are that cooling/reheat would be avoided between the water-gas shift section and gas turbine, while the steam would be preserved in the hot and pressurized hydrogen stream, contributing to power generation [45,46]. Combined CO_2 sorption and fuel processing step such as steam methane reforming and/or water-gas shift reactions are innovative promising pre-combustion decarbonisation technologies. Thermodynamics of sorption enhanced steam methane reforming (SESMR) have revealed that it would be rather difficult to achieve high enough methane and CO conversion while operating SESMR at sufficiently low temperature (400-450°C) for reasonable reactor design and costs [47]. Sorption Enhanced Water-Gas Shift (SEWGS) on the other hand is a technology ready for pilot scale that is capable of producing simultaneously pressurized and hot H_2 with high recovery rate and CO_2 with high recovery at atmospheric or slightly above atmospheric pressure [48]. The SEWGS technology relies on a Pressure Swing Adsorption cyclic process carried out at temperature in the range 350-450°C. The sorbent material used in SEWGS shows excellent performance under extended cyclic operation [49] and is capable of adsorbing simultaneously CO_2 and H_2S and desorbing it [50].

The performance of such sour SEWGS have been assessed experimentally and have been simulated by models which showed that any CO_2 purity may be obtained, very similarly to normal PSA technology. For instance Manzolini et al. have considered based on thermodynamic model that recovered CO_2 stream would contain 98% CO_2 and 0.9% N_2 and 1.1% H_2 after thorough drying in the clean case, with syngas from natural gas reformer [51]. In sour SEWGS isolated CO_2 is recovered together with the total amount of H_2S initially present in the feed, which may be at concentration up to 0.1-2% and may require a supplementary separation device before CO_2 is transported and stored.

4

CO_2 purity in CO_2 capture using membrane technology

4.1 Separation type versus capture process

Membranes are advanced technology considered for CO_2 capture. Various types of membranes exist and depending on the capture process different types of separation are required [52,53], see **Figure 4**.

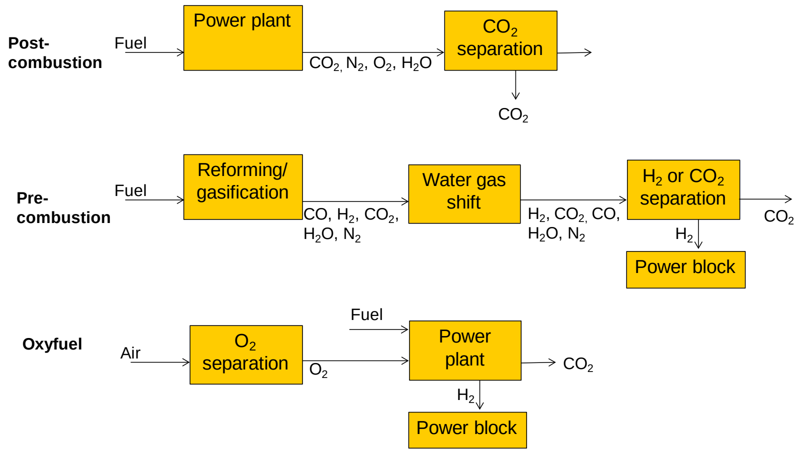

Figure 4: Location of membrane separation process in the three types of capture process

For post-combustion CO_2 capture the CO_2 selective membrane must remove CO_2 from a stream comprising mainly N_2, CO_2 and water. For pre-combustion capture the fuel is first transformed into syngas (reforming for gaseous fuels and gasification for solid fuels) followed by a shift step. The obtained CO_2-rich syngas then passes the membrane reactor where the membrane separates between H_2 and CO_2 from a mixture of H_2, CO_2 and water, possibly containing CO and N_2. This can be done either by separating H_2 from the mixture, or by separating CO_2 from the mixture. In oxy-combustion the membranes separate oxygen from air, which is then used in an oxy-combustion power block.

4.2 Basic principles in membrane separation

A membrane is a selective barrier between two process streams. The basic lay-out of a membrane unit is depicted in **Figure 5**. The membrane has a feed inlet, and an optional sweep inlet. It has two outlets, one for the permeating species, and one for the retentate stream. Membranes can be classified into organic or inorganic, porous and non-porous membranes.

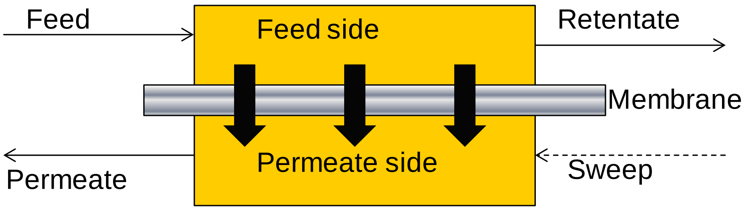

Figure 5: Basic lay-out of a membrane unit

The driving force for membrane permeation is the difference in chemical potential between the permeating component i at the feed side of the membrane and on the permeate side. In gas separation the driving force is related to the partial pressure of component i. A measure for how fast a component permeates through the membrane is the permeance, which is the amount of component i permeating per unit of membrane surface area, divided by the driving force. Often membranes are not totally selective towards one component, which means that more than one component permeates through the membrane. The selectivity of a membrane is defined as the difference in permeation rate between two components at equal driving force. At the process level, the apparent selectivity depends also upon the membrane-module connection (the sealing) and the general robustness of the module. Finally the recovery is defined as the relative amount of the permeating component removed by the membrane.

4.3 Membranes for Natural gas treatment

Membrane technology is used for high CO_2 content natural gas processing on offshore platforms where gas pressure is high and plant footprint and maintenance are an issue. CO_2 selective polymer membranes are typically considered for this application. However membrane units with a reasonable staging and recirculation configuration will not be able to reach high CO_2 removal rates and CO_2 permeate will contain some hydrocarbons (1-3%) and possibly H_2S which needs to be removed with another scrubbing (solvent) or cryogenic technology. In addition, most of the polymers used for these membranes suffer from swelling in the presence of CO_2 which lead to severe alteration of both gas permeances and separation selectivity.

4.4 Membranes for pre-combustion capture

Membranes for pre-combustion capture should separate mainly between H_2 and CO_2. Two membrane categories can be considered in principle, H_2 selective membranes and CO_2 selective membranes [54].

H_2 selective membranes
For H_2 selective membranes several types of membranes can be considered [52,55]:

- *Dense polymeric membranes* work with a solution/diffusion mechanism and operate at low temperature. The glassy type is the most advanced, is commercially available [56], and has the advantage of a higher selectivity. The rubbery type has a higher permeance but a lower selectivity.
- *Microporous ceramic membranes* work on the basis of molecular sieving (Knudsen diffusion). The membranes can be based on alumina, silica, zirconia, titanium oxide or zeolites.
- *Dense metallic membranes* work with a solution/atomic diffusion mechanism in the metal matrix, and are theoretically 100% selective towards H_2. This type of membrane is based on Pd-alloys or other hydride species, and is currently at pre-commercial development stage.
- *Porous carbon membranes* work on the basis of surfaces diffusion and molecular sieving at high temperature.
- *Dense ceramic membranes* work on the basis of a solution/diffusion (proton conduction) mechanism at high temperature and are theoretically 100% selective. Materials considered are e.g. $SrCeO_{3-\delta}$ [57] and tungstate-based mixed oxides..

The polymeric membranes operate at low temperature <100°C and can only be used downstream the reforming/gasification and shift reactor. The other types of membrane work at higher temperatures allowing possible integration with the reforming/gasification reactor. For all H_2 selective membrane, H_2 is removed from the feed gas while the CO_2 stream is obtained as the retentate stream. Both from a technical as well as from an economical viewpoint it is not possible to remove all H_2 from the feed stream. The retentate will therefore contain H_2 typically in the range 1-10% depending on how much effort is spent for reaching high recovery hydrogen, although values are usually not disclosed in literature data. Moreover the retentate contains all the contaminants present in the feed stream, including N_2 and Ar from the reforming/gasification step as well as CH_4. In addition there is some CO that could not be converted in the shift step. All impurities that are not tolerated by the membrane, such as H_2S in coal gasification, have to be removed upstream the membrane unit to very low levels (preferably at ppm level, at most 20ppm) and therefore will not be present in the CO_2-rich retentate, at a significant concentration.

A CO_2 clean-up section is therefore required to remove these species from the CO_2 stream. Options considered here are combustion of the H_2 with oxygen, CO_2 cryogenic distillation or physical absorption unit to remove contaminants from the CO_2 [58]. The combustion with oxygen will eliminate H_2, CO and CH_4, but since the O_2 has only a limited purity, some N_2 will be added. Moreover some O_2 will be added as well since a small surplus of O_2 is generally used to ensure combustion of H_2 and CO. Cryogenic distillation and physical absorption will give a very pure CO_2 stream, but the amount of CO_2 captured is reduced unless recycling of this stream is applied (See also chapter 4 on this topic).

On the permeate side the sweep gas may be steam or nitrogen (which is available if the system has an air separation plant to supply oxygen for the reforming/gasification step). When N_2 is used as a sweep gas, the partial pressure of N_2 is higher at the permeate side than the feed side, N_2 is expected to permeate from the permeate side to the feed side when porous membranes are used, resulting in contamination of the CO_2 stream. Assessing the amount of CO_2 captured and CO_2 purity requires complex modelling of the capture process and the partial pressure profiles in the membrane unit. For instance, a study by Ku [59] on H_2 separating membranes in IGCC showed that the H_2/N_2 selectivity specification must be constrained to rather high values to avoid dilution of the CO_2. The target values given were a H_2/N_2 selectivity of 64 for a 90% hydrogen recovery and 21 for a lower recovery of 70%. This illustrates the degree of interdependency of parameters from one to another and how intricate the assessment of CO_2 capture rate and purity may be.

CO_2 selective membranes

For CO_2 selective membranes fewer types of membranes are being considered [60,61,62]. Given that the molecular size of hydrogen is much smaller than that of CO_2, facilitated transport is required to prevent H_2 from permeating in the envisaged application.

- *Polymeric membranes* use an ethylene oxide building block having a high affinity for CO_2, thereby favouring the permeation of CO_2 over other gasses. Reported selectivities are still quite low (CO_2/N_2 selectivity <9 [53] and 15.5 [63])
- *Functionalized zeolite and alumina membranes* are porous membranes. Conventional porous membranes are not selective towards CO_2 since the Knudsen diffusion mechanism favours H_2 permeation rather than CO_2 permeation. However it is possible to increase the affinity for CO_2, albeit with a rather poor selectivity (around 10 at 140°C).
- *Absorption enhanced membranes* for selective transport of CO_2 as CO_3^{2-} ions at high temperature. Materials considered are *e.g.* Li_2ZrO_3 in a porous matrix. These membranes theoretically are 100% selective, but experimentally much lower values of 4-5 are observed [60].
- *Ionic liquid membranes* consist of anions and cations in liquid phase, and have no significant vapour pressure. In principle, they can be absorbed in a matrix forming a membrane. Theoretically high selectivity towards CO_2 may be achieved by selecting functionalized cations with high affinity for CO_2. However since also other components than CO_2 are absorbed in the liquid, they usually have a limited selectivity. Ionic liquid membranes are in an early development stage.

Ideal 100% selective CO_2 membranes will give a totally pure CO_2 stream. However, the CO_2 purity will be affected when the selectivity is lower. Depending on the CO_2/H_2 selectivity CO_2 may be contaminated with considerable amounts of non-condensable H_2 also permeating through the membrane. Cascading may be used to reach higher CO_2 purity in the permeate in a second stage, while returning the retentate to the first stage feed.

Other impurities next to H_2 include N_2, Ar, CH_4 and unconverted CO for gasification/reforming that are present in the syngas. Traces of non-removed H_2S could permeate and end-up in the CO_2 permeate. If the H_2S removal is downstream the membrane unit, the H_2S selectivity is more critical to avoid H_2S to be present in significant amounts in the CO_2.

Franz et al. [63] have published an extensive analysis on the variables affecting CO_2 purity including membrane selectivity, capture ratio, and membrane surface area distribution over two stages. They found that for a single stage membrane the CO_2/H_2 selectivity must be above 150 to achieve a CO_2 purity target of 95%. With a cascade concept the selectivity should be above 60. A second study on the CO_2 purity for pre-combustion H_2 selective membranes has been conducted by Grainger et al. [64]. Using a combination of series and cascade units and a membrane with an assumed CO_2/N_2 selectivity in the range 100-133, CO_2 purities of 95% to 97% appeared to be achievable for both sweet and sour syngas feed in the absence of H_2S permeation. Considered selectivities are well above the state of the art for any type of CO_2 membranes mentioned above. Therefore, CO_2 permeating membranes are not likely to be applied for CO_2 capture in the near future.

4.5 Membranes for post-combustion capture

Membranes for post-combustion capture separate mainly between CO_2 and N_2/O_2. Because the separation is carried out at low CO_2 partial pressure, the driving force for CO_2 membrane separation is very low compared to pre-combustion separation cases. Post combustion membrane separation requires thus huge membrane surface area to compensate for low driving force, and make therefore this technology less likely to be implemented, unless highly selective materials are available. The following membrane types are currently considered [62,65,66].

- *Polymeric membranes* use a solution/diffusion transport mechanism where chemical interaction of the CO_2 with the polymer favours CO_2 permeation over that of N_2. Especially glassy polymers can be considered here, with a large variety of polymer types [67]. Generally, polymeric membranes exhibit inverse permeance/selectivity behaviour; in other words, selectivity to different gas pairs increases as the gas permeance decreases. Selectivities up to 50 are found in literature with polyimide membranes but also other types such as poly(ethylene oxide)-based membranes.
- *Porous inorganic membranes.* These membrane include zeolite, alumina and silica membranes separate CO_2 by a Knudsen diffusion mechanism, in combination with using functionalized pore surfaces. Usually there is a trade-off between selectivity and permeance. For instance CO_2/N_2 selectivities up to 120 have been shown for the best performing membranes with very low permeance. This membrane technology is still at an early development stage.
- *Hybrid membranes* combine the advantages of inorganic and polymer membranes, or combinations of organic membranes. Nonporous polymeric membranes give good selectivity but poor permeance and porous inorganic membranes give high permeance but poor selectivity.
- *Carbon membranes* are manufactured by carbonizing hollow fibres of cellulose acetate. Modelling show that at a CO_2 recovery of 67%, a CO_2 purity of 88% could

be achieved. A high surface area would be required leading to costs of CO_2 capture of 200 €/ton$_{CO2}$.[65].
- *Facilitated transport membranes* comprise a carrier (metal ions, amines or enzymes) with a special affinity toward a target gas molecule and this interaction controls the rate of transport. With amines 98% CO_2 selectivity has been achieved at 95% CO_2 recovery [65].

N_2 impurity

In post-combustion membrane capture the driving force for N_2 permeation is much higher than for CO_2 permeation because flue gasses are quite diluted (5-20% CO_2 in N_2 or O_2-lean air). While inlet N_2/CO_2 concentration ratio is around 5 outlet conditions are to be higher than 50 at capture ratio higher than 90%. Given the low selectivities currently observed for CO_2 selective membranes, single stage separation will result in significant amounts of N_2 in the CO_2. Lin [68] showed that for a CO_2/N_2 selectivity of 50 and a 1-stage vacuum process a CO_2 purity of only 63% is achieved at 70% CO_2 recovery. For higher purity multi-stage processes are required, providing a CO_2 purity of 88%. Zhao [69] showed that there is significant impact from the process conditions. Depending on vacuum level, number of stages, degree of separation, and flue gas recycle, between as low as 40% and as high as 95% CO_2 purity were found for a CO_2/N_2 selectivity of 43. These process parameters have also a significant impact on membrane surface area required and efficiency penalty.

Other impurities

Depending on the location of the membrane, before or after the gas cleaning, some amount SO_x and NO_x could theoretically permeate with the CO_2, as well as Ar and O_2. These are expected to be at trace level, if the membrane is placed downstream the gas cleaning. Non condensable Ar, O_2 and N_2 may be partly removed by flashing during CO_2 compression stage.

4.6 Membranes for oxy-combustion capture

In oxy-combustion capture the membrane separation is between O_2 and N_2. The oxygen is then used for oxy-combustion of the fuel in the power plant. Porous membranes are not suitable for the separation given the low difference in kinetic diameters between O_2 (3.46 Å) and N_2 (3.64 Å). The types of membranes considered are [56,60]:
- *Polymer membranes.* These membranes work by absorption/diffusion and are applied on a large scale for industrial N_2 and enriched air production. State-of-the art are polyimide membranes having O_2/N_2 selectivities from 9 to 19.8, depending on membrane permeance. In general this type of performance is suitable for N_2 production containing low amount of oxygen (0.5 to 5%) and membrane technology dominate small scale application in this field (<50t/d). For oxygen air enrichment (OAE), these membranes allow only limited oxygen enrichment (up to 50%) in single stage membrane reactors and are therefore not foreseen to compete with cryogenic or adsorption based technologies for high grade O_2 production [56]. Nevertheless OAE with membrane could find advantageous application in low quality coal gasification.
- *Ion transport membranes (ITM).* These dense inorganic membranes work at high temperature (>700-1000°C) and consist of a Perovskite material. Oxygen is

transported as O^{2-} through the dense separation layer, which also serves as an electron conductor. The membrane is theoretically 100 % selective.

N_2 impurity

CO_2 purity will depend on the purity of the fuel as well as that of the oxygen. With 100% pure oxygen, as could be produced in theory with ITM membranes no contaminants will originate from the oxygen the only contaminants will originate from the fuel and from possible air ingress. This will include N_2 from a natural gas feed, N_2 from air and N_2 from N contained in the coal. For polymer membranes, single stage units will cause a significant dilution of the CO_2 with N_2. Cascading will be required to produce sufficiently pure oxygen, leading to larger investments and efficiency penalties.

Other impurities

For natural gas impurities in the CO_2 that originate from the fuel could be inerts such as N_2 and in lesser amount Ar in the natural gas. For coal power plants a gas clean-up consists of SCR-DeNO$_x$, FGD-DeSO$_x$ and electrostatic precipitators, removing sulphur oxides, dust, and nitrous oxides and to some extend halogen compounds and heavy metals. However, the removal efficiencies of SCR and FGD are not 100%, so some low levels contaminants will be present in the CO_2 product going to the gas conditioning section.

4.7 CO2 purity and membrane technologies

At the current stage of development it is quite difficult to associate accurate and meaningful CO_2 purity data that can be reached with each of the membrane processes described in this chapter. For most cases reaching high purity CO_2 will be achieved either by cascading membrane reactors or by combining membrane reactors with other separation technologies such as pressure swing adsorption, solvent scrubbing or cryogenic separation. Rather than giving a tentative table on achievable CO_2 purity that could be misleading, we have chosen to describe a number of gas cleaning technologies for gas conditioning for further transport and storage in the next chapter that may be considered for upgrading CO_2 stream obtained from membrane separation units and any other technology that does not enable reaching sufficient CO_2 purity grade to meet specifications.

5

Gas conditioning

Prior to transport of the CO_2 product, the captured CO_2 stream generally needs conditioning, consisting minimally of drying and compression. In general, CO_2 transport via pipelines or ships is considered. For pipeline transport, CO_2 is compressed to supercritical state (typically 80-150 bar), while ship transport involves liquid CO_2 (typically near the triple point, 6.5 bar and -51°C) [70]. The gas conditioning system has to deal with 3 types of components: water, volatiles and condensables. The presence and concentrations of these 3 types of components varies widely as a function of the capture technology used.

5.1 Gas conditioning in oxy-fuel combustion

Gas conditioning technologies are mostly studied for the oxyfuel CO_2 capture route. This process is indeed considered as one of the most promising processes for carbon capture from coal fired power plants due to its specific advantages. Chemical looping cyclic processes are also very promising in that respect and have been developing quite fast recently. The oxyfuel process consists of coal combustion by oxygen supplied by an Air Separation Unit (ASU) and assisted by recirculated flue gas (to control flame temperature and O_2 concentration). Thereby the CO_2 concentration in the flue gas may reach values of about 80–90 vol% (dry basis). Impurities originate from air ingress, ASU performance, fuel composition and combustion conditions. Their quantity varies strongly upon combustion stoichiometry. NO_x and SO_x can be reduced to low very level by usual cleaning processes such as FGD and SCR [71]. As a first step, Air Products [72] mentions a water wash step to remove particles and soluble gasses such as HCl and SO_3. This washing essentially does not remove SO_2, SO or NO_x.

While residual oxygen amounts usually at 2.8 vol% in the air blown combustor effluent, the oxygen level in oxyfuel combustion depends mostly on oxygen excess used for the combustion and recycle rates and may be around 5 vol% in normal operation [71,73]. According to Kather et al. most of the combustion facilities operate under slightly lower pressure than the atmospheric pressure to ensure that no non-treated flue gas escapes from the facility [73]. As a result air enters the system and contaminates the flue gas at a level of 3% for newly built facilities up to 10% for older plants. This clearly affects greatly the CO_2 concentration in oxyfuel plant exhaust gas and leads also to question on the oxygen purity specification delivered by the ASU. Since ASU plant operation is energy-intensive and the energy requirements increase exponentially with O_2 purity for high purity levels (95%$^+$), there must be a trade-off between O_2 impurity level allowed after the ASU and impurity levels induced by the air ingress.

The flue gas composition focussing on impurity levels for oxy-coal combustion, using 3 different coal types, has been assessed by modelling [74]. The studied system contained flue gas recycle (FGR) to the boiler, but no flue gas desulphurisation (FGD) nor NO_x reduction technology (Selective Catalytic Reduction, SCR). Representative compositions of CO_2-rich flue gas entering the gas conditioning system are given in **Table 3**. Since the mentioned NO_x and SO_2 levels are valid for a system without any FDG or SCR, these levels should be considered as maximum levels. When extensive FGD, SCR treatments and water knock-out are included into the scheme, a system analysis of Hu and Hua [75] reports rough numbers on flue gas compositions as summarized in **Table 4**. Indeed, FGD and SCR seem to be capable of significantly abate the NO_x and SO_2 levels within the fuel gas entering the gas conditioning system.

Table 3: CO_2-rich flue gas compositions in oxy-coal without FGD and SCR unit [74]

		UK Bituminous	Pittsburgh #8	Sub-bituminous
CO_2	% dry	90.3	90.3	91.2
O_2	% dry	5.2	5.2	5.1
N_2/Ar	% dry	3.5	3.5	3.3
NO_x	ppm dry	9400	9300	2500
SO_2	ppm dry	1100	930	730
H_2O	%	11.6	12.1	21.3

Table 4: CO_2-rich flue gas compositions in oxy-coal with FGD and SCR unit [75]

		Fuel gas for gas conditioning
CO_2	%	94
O_2	%	1.7
N_2	%	2.3
NO_x	ppm	30
SO_2	ppm	5
H_2O	%	1.9

Besides system studies, a good indication of the effectiveness of FGD systems in oxy-coal systems are provided by actual measured SO_2 levels. In the Vattenfall Schwarze Pumpe Oxyfuel pilot plant the SO_2 level of the flue gas recycle (FGR) is in the order of 7500 ppm, while the total SO_x content entering the gas conditioning system is <15 ppm [76]. The FGR is taken upstream the FGD system. Considering global sulphur removal, besides SO_x reduction within the FGD unit, significant amounts of sulphur are also removed by deposition on ashes within the boiler and electrostatic filters because of the flue gas recirculation system, normally not present in air-fired plants (pulverized coal). For NO_x control, it is considered not to rely on SCR systems, but to test $DeNO_x$ options within the gas conditioning system. This will be discussed in more detail in section 5.5.

5.2 Mercury removal

Mercury is present in coal and any heavy feedstocks in general. In any power generation option and thus any CO_2 capture plant, Mercury emissions are to be controlled for environmental reason in the near future. For Oxyfuel combustion, Mercury is not only an environmental issue but also an operational issue which may cause dramatic failure in case mercury accumulate in the system (Moomba gas processing incident [77]). Some contaminants usually present in relatively high concentrations such as chlorine and sulphur together with the combustion characteristic of the coal both influence minor contaminants usually present at very low concentrations such as Hg and more precisely its speciation throughout the process. A significant proportion of the oxidised mercury can be recovered as bottom ash at the bottom of burners or boilers. More severe issue are encountered for trace elements such as elemental Hg that are rather difficult to remove from the gas phase. In contrast, gaseous oxidized Hg ($HgCl_2$, HgO, HgS…) or Hg particles formed upon combustion can be captured rather easily in existing air pollution control devices. In the presence of Cl, gas phase equilibrium conditions favour the formation of $HgCl_2$ at flue gas cleaning temperatures. However the oxidation of Hg^0 is kinetically limited by the homogeneous and heterogeneous reaction rates [78]. SO_2 reduces the homogeneous oxidation of Hg in flue gas and can inhibit the sorption and oxidation of Hg^0 by carbon surface upon SO_3 or sulphate groups' formation [79]. Unburned carbon in fly ash appears to be a key parameter in the heterogeneous oxidation of Hg^0. Hence, the Hg capture efficiency is usually decreased with lower ranked coals and also with a decreased amount of unburned carbon in coal ash [80].

5.3 Drying

Free water accelerates corrosion, especially in the presence of CO_2 and other acid components such as H_2S, NO_2 and SO_2. Furthermore, ice and hydrate formation during gas conditioning can cause damage or even plugging of process equipment. Therefore, drastic drying is required prior to CO_2 transport. For instance in Natural Gas conditioning for transport the quantity of water in saturated gas at various pressures may be estimated using the correlation of McKetta and Wehe or the well-known one from McCarthy [5]. Unlike NG, the saturated water concentration content of liquid CO_2 increases with increased pressure, see **Figure 6** from the Dynamis project. The illustrated water content can change upon the presence of other impurities.

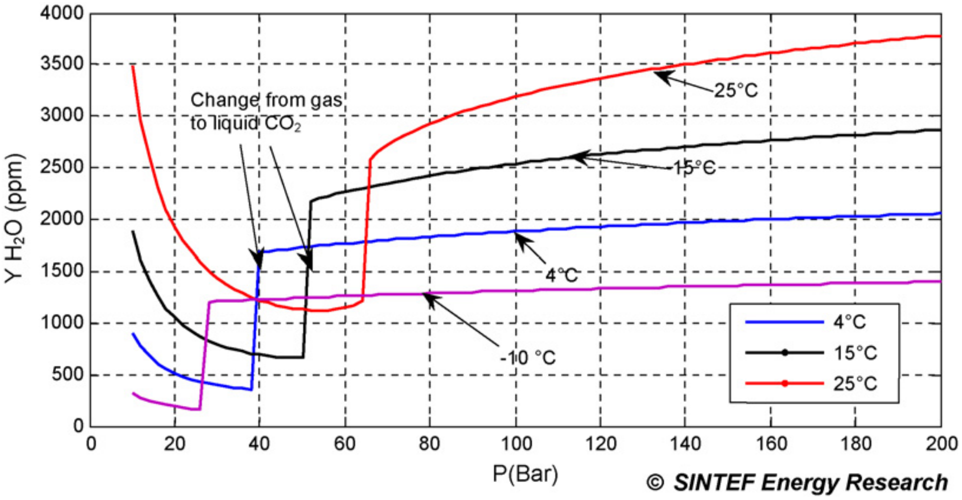

Figure 6: Water content at saturation of CO_2 at different temperatures [81]

Most of the water is already removed during the compression/cooling stage and with correct design <500 ppm H_2O contents in CO_2 can be reached [70]. Further drying to single digit values then requires a dedicated dehydration processes. Commercially available processes are based on absorption by hygroscopic liquids or reactive solids or adsorption by activated solid desiccant. Shell developed a glycerol process, which is more attractive than commonly used glycol for high pressure or supercritical CO_2. At these pressures glycerol is only slightly soluble in CO_2 ($3.2\ 10^{-2}$ kg/km^3) in strong contrast with glycols which are typically 35 to 75 times more soluble albeit with a comparable drying capability.

In conclusion, drying to <50 ppm is relatively easily achieved. Dissolution of CO_2 in water decreases with increasing temperature and decreasing pressure. All the water separated during compression should therefore be collected in a final atmospheric pressure drum. The CO_2 loss via the condensate is therefore limited at <0.4% of the total CO_2 feed stream.

Recently, the potential of cryogenic condensation of water and freezing of CO_2 ice was investigated [82]. A good separation of N_2, steam and CO_2 could be obtained, reaching high CO_2 capture ratios of 99%. A cheap cold utility, however, is required for the process to be economically attractive. Moreover, the fate of impurities was not investigated to a large extend. H_2S was shown to end up in the CO_2. Clean-up of the CO_2 is therefore likely to be required in such a process.

5.4 Volatile components

Volatiles are components with low boiling points, such as N_2, Ar, O_2, H_2, CO, NO and CH_4. The content of these components in the CO_2 product can be decreased by flashing or distillation. When applying flashing, a CO_2 recovery of >90% and a CO_2 purity of 95% is readily achieved [83,84,85]. Using distillation, however, the CO_2 purity can be boosted to >99%. As for standard distillation, the condenser duty determines the amount of CO_2

in the purge stream and the reboiler duty the purity of the CO product. As a rule of thumb, a single column system would result in a molar CO_2 content of the purge at best equalling the molar content of impurities of the column feed. It may be interesting to redirect this purge stream back into the capture process aiming at reducing the loss of CO_2 and fuel components. This is particularly interesting in case the amount of inerts is small *i.e.* if the impurities mainly consist of (unconverted) fuel components such as CH_4, H_2 and CO.

The separation of CO_2 from a H_2-rich syngas in an IGCC by means of low temperature separation (-56°C, albeit not cryogenic) has been studied within the Decarbit project [86]. Prior to the low-temperature separation, the syngas is desulphurised, shifted and dehydrated, resulting in a feed consisting of 54% H_2, 38% CO_2, 1.7% CO and 5.7% N_2+Ar at 35 bar. First, the syngas has to be compressed to typically 110 bar. Active cooling is done via propane and ethane cycles. Using either multiple flashing or distillation, a CO_2 purity of 98.7% is reached at 75% CO_2 recovery and a specific energy consumption of 360 $kJ.kg^{-1}CO_2$. Later optimization [87] allowed a 99+% CO_2 purity at 85% CO_2 recovery and a specific energy consumption of 330 $kJ.kg^{-1}{}_{CO2}$.

5.5 Condensable components

Condensable components, having a boiling point in the same range as CO_2, typically are propane, ethane, H_2S, NO_2 and SO_2. Accordingly, these components cannot easily be removed by flashing or distillation and will end up in the CO_2 product unless additional cleaning is applied. Propane and ethane are unlikely components when considering combustion processes, but might be present in syngas generated by reforming or gasification in pre-combustion capture schemes when CO_2 capture is performed using membranes or physical solvents. In oxy-fuel schemes, where the entire flue gas stream would be treated in the gas conditioning system, cooling and CO_2 compression are preceded by $DeNO_x$ and Flue Gas Desulphurization (FGD) units to avoid clean-up processes within the gas conditioning section.

Pipitone and Bolland [85] include a desulphurization unit within their gas conditioning section consisting of a wash step using sea water. They consider fuel gasses coming from oxy-fuel plants using either natural gas or pulverized coal. The pressurized sea water washing step reduces the SO_2 levels from a few 100 ppm down to 30 ppm. Besides, Air Liquide considers adsorption for SO_x removal using Ca-based or Na-based sorbents within the gas conditioning section [83].

Air Products [72,88,89] describes a system in which the flue gas from an oxyfuel plant is first compressed wet and passed through several reactors where the SO_x and NO_x are converted to H_2SO_4 and HNO_3 using the residual O_2 in the flue gas. The NO_x present promote SO_2 oxidation to H_2SO_4. Following SO_2 removal, NO_x conversion to HNO_3 is done. The Hg is converted into $HgNO_3$. Air Products claims to reach around 90% removal of SO_x and NO_x. The treated flue gas is then fed to the “standard” drying and volatiles removal units. The compositions of the raw flue gas as well as the CO_2 product resulting from “standard” drying and volatiles removal and the CO_2 product with their system are listed in **Table 5**. A similar approach for NO_x removal has been described by the Vattenfall group [76,90]. In their system, however, the SO_x content of the flue gas entering the gas conditioning system is <15 ppm due to prior extensive desulphurization and $DeNO_x$ within the compression system is the main focus.

Table 5: Raw and product CO_2 composition for oxyfuel [72]

	Raw flue gas composition [mol%]	CO_2 composition [mol%]	
		standard drying and volatile removal	Air Products process
CO_2	71.5	95.8	96.3
N_2	14.3	2.0	2.0
O_2	5.9	1.1	1.1
Ar	2.3	0.6	0.6
SO_2	0.4	0.5	0.0
NO	0.04	0.01	0.0
H_2O	5.6	0.0	0.0

Besides Babcock-Hitachi has also developed a proprietary catalytic systems to remove efficiently both SO_3 and Hg before compression, which was verified both in oxyfuel and combustion with air [91].

5.6 Energy requirement during gas conditioning

For oxy-fuel plants, the specific energy requirements for the gas conditioning is in the order of 100-200 kWh/t captured CO_2 (=360-720 kJ/kgCO_2), see **Figure 7** [70,83,85]. Note that gas conditioning covers CO_2 enrichment by flashing or distillation, CO_2 compression, and drying. At a feed pressure of 1 bar, the higher the initial CO_2 purity, the lower the energy consumption, reaching about 90 kWh/t captured CO_2 (=324 kJ/kgCO_2) for pure (atmospheric pressure) CO_2 streams. This value represents the energy consumption associated with CO_2 compression of 100% pure CO_2 at 1 bar. Logically, at a certain CO_2 feed purity, the higher the inlet pressure, the lower the energy requirement for the gas conditioning system.

Figure 7 illustrates the sensitivity of the energy requirement for the drying and volatile removal system for the initial content of volatiles and the captured CO_2 stream pressure. P1 is the standard system with compression, distillation and drying, P2 without distillation and S1 with additional liquefaction. As expected, the energy requirement increases with volatile content and decreases with increasing pressure of the captured CO_2 stream. Moreover, volatile removal via distillation only adds considerably in case the volatile content is very high. Additional liquefaction will always cost extra.

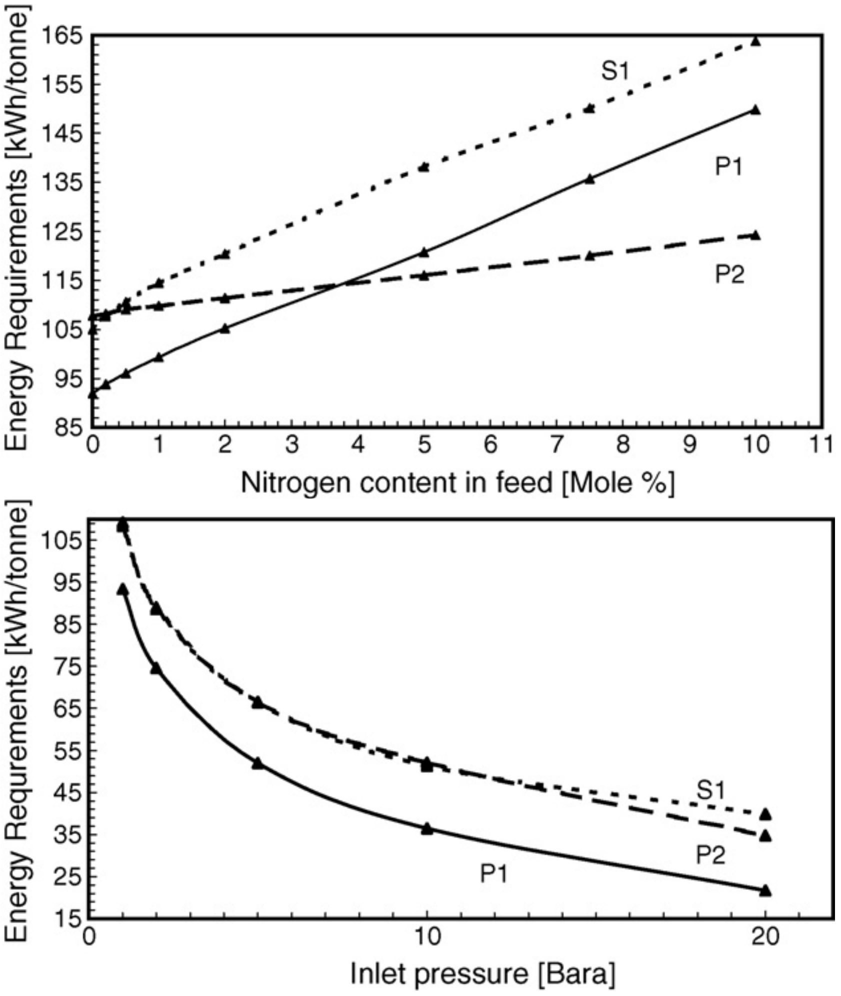

Figure 7: Energy requirement for the gas conditioning section as a function of the initial volatile content at a total pressure of 1 bar (upper graph) and as a function of the inlet pressure at a given CO_2 purity for 3 systems (lower graph) [70]. P1: compression, distillation, drying; P2: compression, drying; S1: compression, distillation, drying, liquefaction

5.7 Concluding remarks on gas conditioning

Although the gas conditioning system is most often discussed for the CO_2 purification of oxyfuel flue gasses [72,84,85,87], the system can also be applied for other captured CO_2 streams [70]. Aspelund and Jordal [70] include other CO_2 capture systems from natural gas fired processes, *e.g.* amine scrubbing, O_2-membrane oxy fuel, chemical looping, and membrane pre-combustion capture. The conditioning technologies described herein can therefore be used for the refining of CO2 streams originating from various sources, when cleaning is necessary, for transport, storage or utilization for instance.

An interesting study by Pipitone and Bolland [85] investigated two cold-temperature gas conditioning systems for CO_2 purification from volatile components, both for NG-fired and pulverised coal fired oxy fuel plant. Prior to the treatment, the CO_2 stream was desulphurized by means of cold seawater contact, reducing SO_2 from 130 ppm for NG and 702 ppm for coal to <30 ppm. The results are listed in **Table 6**. It can be seen that high capture ratios and CO_2 purities may be obtained, especially when using distillation. Nevertheless, significant amounts of O_2 are present, likely too high for EOR but allowable for aquifer storage. It is also observed that the condensables SO_2 and NO_2 are concentrated in the CO_2 product.

Table 6: Compositions of CO_2 captured stream before and after cold temperature purification for NG and pulverised coal oxy-fuel plant [85]

		Captured CO_2		double flashing		distillation	
		NG	Coal	NG	Coal	NG	Coal
CO_2 recovery	%	100	100	96	88	95	87
CO_2	%	88	75	96	97	99	99
H_2O	%	0.2	0.2	-	-	-	-
Ar	%	5.7	2.3	2.0	0.4	0.5	0.1
N_2	%	3.7	16.4	0.8	1.6	0.04	0.2
O_2	%	2.2	6.0	0.8	1.2	0.2	0.4
SO_2	ppm	30	25	34	35	25	37
NO	ppm	148	703	53	150	10	32
NO_2	ppm	1	-	1	1	1	1

6

CO_2 purity for transport

DYNAMIS was a European project that aimed at establishing recommendations for CO_2 purity for Transport and Storage for European CCS projects to ensure safe transport, durability of the transport infrastructure and finally effective and efficient use of the transport capacity [81]. In general it is considered that requirements for CO_2 transport will turn out to be more stringent than those for EOR or storage [92]. The authors issued the following simplified **Table 7**. Note that the EBTF recommendations are very similar and provide a comparison with storage purity recommendation (see http://caesar.ecn.nl/fileadmin/caesar/user/documents/D_4.9_best_practice_guide.pdf)

Table 7: Simplified summary of DYNAMIS CO_2 quality recommendations

Component	Recommended concentration	Criteria used for recommended level
H_2O	500 ppm	Design and operation considerations
H_2S	200 ppm	Health and safety considerations
CO	2000 ppm	Health and safety considerations
SO_2	100 ppm	Health and safety considerations
NO_2	100 ppm	Health and safety considerations
CH_4	Aquifer: <4 vol% EOR: <2 vol%	ENCAP proposed limit
N_2	< 4 vol%	ENCAP proposed limit
Ar	< 4 vol%	ENCAP proposed limit
H_2	< 4 vol%	to be minimized
CO_2	> 95.5 %	

The water level in CO_2 has to be low enough such as it prevents the risks for formation of free water leading to corrosion and hydrates leading to fouling. Limits for H_2S, CO, SO_2 and NO_2 are set by health and safety considerations, rather than by technical limits to assure safe transportation. In this project only a limited amount of effort has been dedicated to analyse the impact of O_2. The recommended limit for O_2 was set to 100 – 1000 ppm although there is a lack of information regarding the underground effects of

O_2. Besides, the maximum total volume of volatile gases (N_2, H_2, CO, CH_4, O_2, Ar) was set to 4 %. Regarding the amount of volatile impurities, a rough estimation of the extra compression work it imposes for the compression of CO_2 from 14.5 to 150 bar was estimated to vary linearly with the impurity concentration in CO_2 such as 2.5 % for 1 % O_2, 3.5 % for 1 % H_2 and 1.5 % for 1 % N_2 [92]. The effect of CH_4 on the solubility of water in CO_2 is significant, but not harmful for transportation of CO_2 at concentrations of CH_4 below 5 % and a maximum water level of 500 ppm.

Other significant studies on CO_2 quality requirements for systems with CO_2 capture, transport and storage have been carried out by researchers at Vattenfall (NUON main shareholder). Anheden *et al.* [93,94] have listed impurities that are to be considered for deeper removal. In the list water content has been identified to be an issue especially in case of CO_2 liquefaction (-50°C) which is required for transport by ship. Risk of hydrate formation with CH_4, H_2S and SO_2 have also been pointed out. A recent study showed that SO_2 indeed enhances the formation and the stabilization of hydrates and possibly clathrates, whereas NO_2 has an insignificant role on hydrates formation equilibrium. Interestingly the authors suggest that acidification due to the presence of both components may be more problematic than their hydrates formation enhancement effects. Water interaction with CO_2, H_2S or SO_2 could lead to corrosion problems. The presence of Ar, H_2, or O_2 could lead to two phase flow related problems. According to the authors effective complete dehydration is a key condition that could influence and soften the restrictions on the other chemical contaminants less stringent. On a relative scale post-combustion capture options appear to be less problematic than IGCC and oxyfuel.

Aspelund *et al.* [70] proposed a simplified table with the composition of the captured CO_2 stream for different natural gas fired power plant concepts defined in a previous study by Kvamsdal *et al.* [95], see **Table 8**. Note that low level impurities such as H_2S, NO_x and SO_x are not mentioned. The processes can be subdivided into 3 categories:

1. Virtually pure wet CO_2 with traces of amines and minor fractions of inerts, resulting from amine scrubbing (both pre- and post-combustion), SOFC+GT, AZEP and CLC.
2. Wet CO_2 containing non-combustible volatiles, resulting from oxy-fuel applying ASU.
3. Wet CO_2 containing inerts and combustible volatiles, resulting from pre-combustion membrane processes, SEWGS and ATR+amines as well as probably CLC processes, since they probably do not have full fuel conversion.

Moreover, note that the N_2, Ar and O_2 content of oxy-fuel process is likely higher than mentioned in this table because of air ingress, especially for retrofit plants. Also, with oxy-coal combustion a much larger inerts+O_2 content of up to 15% is mentioned [83,85], of which up to 5% is O_2.

Table 8: Gas composition of CO_2 stream in various capture design [70]

	CO_2	H_2O	H_2	CO	N_2	O_2	CH_4	Ar	P (bar)	T (°C)
Amine (post-comb.)	94.4	5.6	0	0	0	Traces	0	0	1.01	35
ATR (pre-comb., amine)[a]	98.2	1.8	0	0	0	0	0	0	1.01	16
Water cycle (WC)	59.7	32.8	0	0.01	2.81	1	0	3.59	0.045	13
S-Graz	61.7	30.9	0	0	2.91	0.85	0	3.69	1.01	337
Oxyfuel CC	93.8	4.2	0	0	0.28	1.38	0	0.35	1.01	30
SOFC + GT	35.9	63.8	0	0	0.26	0	0	0	1.01	439
AZEP HP	35.9	63.8	0	0	0.26	0	0	0	15.38	248
AZEP LP	35.9	63.8	0	0	0.26	0	0	0	1.01	111
CLC[b]	34.7	65.1	0	0	0.28	0	0	0	1.01	415
MSR-H2 HP	62.4	35.5	0.92	0.57	0.45	0	0.12	0	63.94	578
MSR-H2 LP	62.4	35.5	0.92	0.57	0.45	0	0.12	0	1.04	98

a In reality, a 1% level of H_2 and other components like CO, CH_4, N_2 and Ar can be expected.

b Incomplete fuel conversion is probably a more realistic assumption.

Beside water content all these studies confirmed the importance of lowering the volatile compounds in CO_2 stream to be stored. Yan *et al.* [94] therefore carried out a techno-economical study on the impact of non-condensable gas on CCS by assessing the CCS cost of three grade CO_2 streams, namely, 87 %, 96 % and 99 % purity. The capture investment cost increased from 87>96>99 although the increase from 87 to 96 was kept quite low thanks to the use of conventional separation processes compared to the increase from 96 to 99. In sharp contrast 87 % case showed a significant pipeline diameter increase leading to a significant cost increase on the transport that may be amplified by transport distances. Non condensable concentrations of less than 4 % may be considered as a reasonable CO_2 purification level for general cost balance in the CCS chain.

A novel approach in oxy-fuel power plants is the compression and purification of CO_2 (compression and purification unit, CPU) via liquefaction at cold temperatures. Air Liquide claims that during cooling and compression it is possible to remove the impurities from the flue gas at the most economical point between low pressure (close to atmospheric pressure) and high pressure, thus obtaining very high CO_2 purity (99.99 %+) at a reasonable cost. **Table 9** specifies typical flue-gas compositions for 2 oxy-fuel plants.

Table 9: Estimated flue gas compositions (mole fractions) from new & retrofit oxy-combustion coal power plants using Illinois No. 6 coal

Compounds	New Oxy-fuel plant	Retrofit oxy-fuel plant
Ar	0.031	0.025
CO_2	0.70	0.58
H_2O	0.17	0.17
N_2	0.082	0.18
O_2	0.025	0.041
SO_2	0.0001	0.001
NO_x	0.0000	0.0004
CO	0.0000	0.0001

Finally NETL (US) has recently published a short report on recommended CO_2 purity for transport and storage to be taken into consideration in system analyses [96]. The data were based on literature analysis mostly. Essentially the authors recommend considering CO_2 purity of at least 95% such like the one in DYNAMIS conclusions. Besides impurity levels are all comparable to DYNAMIS (see **Table 7**) at the exception of a more stringent 300 ppm limit for water and 35 ppm for CO. In the case of CO_2 utilization for EOR it is recommended to consider more stringent limits on O_2 level (100 ppm) to avoid both uncontrolled exothermic reaction in the reservoir and aerobic bacteria proliferation at the injection point.

7

Conclusions

CO_2 purity specifications that capture units must supply to CO_2 transport infrastructure for eventual underground storage remains largely unknown yet. Nevertheless existing specifications of pipeline operators and current practice observed in demonstration projects may give insights for anticipating upcoming regulations and purity requirements. It is usually anticipated that pipeline specifications will be more stringent than storage ones, especially for the compounds that may lead to pipeline corrosion (namely acid gas such as SO_x and NO_x, water that enhances the acidity of CO_2) and fouling issues (formation of hydrates). To this respect the recommendations given by the DYNAMIS project give a widely accepted reference.

The impurity content of CO_2 streams delivered by capture units varies widely as a function of the process producing CO_2 as an end product (combustion, gasification, fermentation etc…), as a function of the feedstock quality and the CO_2 capture technology itself. Moreover in most of the capture processes most impurities concentration may be minimised by fine tuning of process operation. However plant economics eventually govern the exact amount of impurity level that will actually be found in the CO_2 stream. Therefore common sense calls for considering recommendation levels rather than achievable levels. For mature technologies such as absorption by chemical or physical solvents lower impurity levels are available from existing facilities or demonstration plants in operation. In contrast predictions are more difficult for technologies at development stage, such as membrane separation reactors and hot gas cleaning in general. **Table 10** summarizes the CO_2 purities that may be reached by various technologies and the impurity level that is to be found in the respective stream. If post-combustion capture technologies are to dominate, as a result of the possibility of retro-fitting existing power plants, it is pretty clear that main contaminants will be nitrogen and oxygen and concerns about poisonous or harmful contaminant are less acute. However if CO_2 capture from industry is to be implemented the table clearly shows that sulphur contaminants, fuel contaminants and CO contaminant must be taken into account.

Table 10: CO_2 purity anticipated from various capture units and various optimization cases

Gas component	post-combustion	Pre-combustion				Oxyfuel
	Amine Scrubbing	Selexol IGGC [18]	Rectisol IGCC [16]	Amine scrubbing [70]	Sour SEWGS	Oxyfuel + double flashing [85]
CO_2	99.8-99.9	98.1-99.7	95-98.5	>97.2	> 99	97
H_2	-	1.5%	20ppm	<1%	<1%	-
O_2	150-300 ppm	-	-	-		1.2%
N_2	450-900 ppm (incl. Ar)	195 ppm	< 1% (stripping)	<1%	<1%	1.6% 150 ppm NOx
Ar	See N_2	178ppm	150 ppm	<1%	<1%	0.4%
Sulphur Comp.	10-20 ppm (SO_2 mostly)	2<H2S<1700 ppm	0.2-20 ppm	H_2S<200 ppm For 2-stage plant	<5000 ppm to ppm level with H_2S stage	35 ppm SO_2
CO	10-20 ppm	100<CO<1300 ppm	400 ppm	<1%	<1%	-
CH_4	-	112ppm	100 ppm	<1%	<1%	-
MeOH	-		20-200 ppm			-
H_2O	100-600 ppm	376ppm	0.1-10 ppm	1.8	500 ppm (drying step)	-

8

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