The Range and Level of Impurities in CO$_2$ Streams from Different Carbon Capture Sources

Richard T.J. Porter[a],*, Michael Fairweather[b], Mohamed Pourkashanian[a] and Robert M. Woolley[b]

[a]Energy Technology and Innovation Initiative, School of Chemical and Process Engineering, University of Leeds, Leeds LS2 9JT, UK.

[b]Institute of Particle Science and Engineering, School of Chemical and Process Engineering, University of Leeds, Leeds LS2 9JT, UK.

* Corresponding author: Tel: +44 113 343 2481; fax: +44 113 246 7310

Email address: R.T.J.Porter@leeds.ac.uk (Richard T.J. Porter).

ABSTRACT

For CO_2 capture and storage deployment, the impact of impurities in the gas or dense phase CO_2 stream arising from fossil fuel power plants, or large scale industrial emitters, is of fundamental importance to the safe and economic transportation and storage of the captured CO_2. This paper reviews the range and level of impurities expected from the main capture technologies used with fossil-fuelled power plants in addition to other CO_2 emission-intensive industries. Analysis is presented with respect to the range of impurities present in CO_2 streams captured using pre-combustion, post-combustion and oxy-fuel technologies, in addition to an assessment of the different parameters affecting the CO_2 mixture composition. This includes modes of operation of the power plant, and different technologies for the reduction and removal of problematic components such as water and acid gases (SO_x / NO_x). A literature review of data demonstrates that the purity of CO_2 product gases from carbon capture sources is highly dependent upon the type of technology used. This paper also addresses the CO_2 purification technologies available for the removal of CO_2 impurities from raw oxy-fuel flue gas, such as Hg and non-condensable compounds. CO_2 purities of over 99 % are achievable using post-combustion capture technologies with low levels of the main impurities of N_2, Ar and O_2. However, CO_2 capture from oxy-fuel combustion and integrated gasification combined cycle power plants will need to take into consideration the removal of non-condensables, acid gas species, and other contaminants. The actual level of CO_2 purity required will be dictated by a combination of transport and storage requirements, and process economics.

KEYWORDS

Carbon capture and storage, CCS, Impurities, CO_2 quality

1. INTRODUCTION

The work presented in this paper originates in the CO_2QUEST project (CO_2QUEST, 2013), which aims to address the fundamentally important issues surrounding the impact of typical impurities in high pressure gas or dense phase transported CO_2 streams from fossil fuel power plants and other industries fitted with carbon capture and storage (CCS) technologies, upon the safe and economic transportation and storage of CO_2. The ultimate composition of the CO_2 stream captured from fossil fuel power plants or other CO_2 intensive industries and transported to a storage site using high pressure pipelines will be governed by safety, environmental and economic considerations. The project therefore aims to elucidate optimum levels of CO_2 purification for carbon capture processes in consideration of downstream impurity impacts on pipeline transport and geological storage, and the purification costs. To complement this, key gaps in knowledge relating to the impact of impurities on the chemical, physical and transport properties of the CO_2 stream under different operating conditions will be addressed.

Impurities in CO_2 captured from combustion based power generation with CCS can arise in a number of ways. Water is a major combustion product and is considered an impurity in the CO_2 stream. The elements inherently present in a fuel such as coal include sulfur, chlorine and mercury, and are released upon complete or incomplete combustion and form compounds in the gas phase which may remain to some extent as impurities in the CO_2 after it is captured and compressed. The oxidising agent used for combustion such as air may result in residual impurities of N_2, O_2 and Ar. These same impurities may also result from air ingress into the process. The materials and chemicals used for the CO_2 separation process, such as monoethanolamine in the case of post-combustion capture or selexol in pre-combustion capture, and their degradation products can also be carried over into the CO_2 stream constituting a further class of impurity.

Several reports, such as those from IEAGHG (June, 2011) and Farret et al. (2012), are based upon a literature review of public information and references, mainly concerning electric power plants. They show that quantitative references for actual impurities in product CO_2 streams are not very numerous and that most quantitative values are theoretical estimates using measurements from combustion processes as a base. Further works by the National Energy Technology Laboratory (NETL) (Matuszewski and Woods, 2012) and the Dynamis

project (de Visser et al., 2008) have provided recommended impurity limits for CO_2 stream components in studies of CO_2 capture utilisation and storage systems. Limits are suggested based upon a number of different factors and these quality guidelines may serve as a basis for conceptual studies. The presence of impurities in CO_2 can shift the boundaries in the CO_2 phase diagram to high pressures, meaning that higher operating pressures are needed to keep CO_2 in the dense phase. For pipeline and storage applications, the total concentration of the air derived non-condensable species (N_2, O_2 and Ar) should not exceed 4% due to the impact on compression and transport costs. In addition, these species can reduce the CO_2 structural trapping capacity in geological formations by a greater degree than their molar fractions (Wang et al., 2012a). Hydrogen may be present in pre-combustion capture derived CO_2 streams and is also believed to impact required pipeline inlet pressures significantly (Wetenhall et al., 2014). Enhanced Oil Recovery (EOR) applications require stricter limits, particularly O_2 which should be kept below 100 ppm due to it promoting microbial growth and reaction with hydrocarbons. CCS specifications for water are set in order to limit corrosion due to the formation of in situ carbonic acid (Cole et al., 2011), clathrate formation and condensation at given operating conditions. Reported guidelines for water vary widely and can be dependent on the concentration of other species present in the stream such as acid gases. Sulfur species (H_2S, COS, SO_2 and SO_3) pose a corrosion risk in the presence of water and should be removed to a certain level, and there are additional toxicity concerns for H_2S. There are however a number of technology approaches for removing sulfur species including newer developments for carbon capture applications. SO_3 can form in pulverised fuel plants that utilise post-combustion or oxyfuel combustion capture techniques, although this species reacts quickly with water so can be removed by water contacting units. NETL (Matuszewski and Woods, 2012) recommend that the target for SO_2 be 100 ppmv on the basis of its IDLH (Immediately Dangerous to Life or Health) level. NO_x species may be present in CO_2 streams as combustion by-products and also pose a corrosion risk due to nitric acid formation (Sim et al., 2013). There are a number of traditional and novel CCS approaches for NO_x limitiation. The IDLH limits of NO and NO_2 are 100 and 200 ppmv, respectively and a limit of 100 ppmv has therefore been proposed for CCS derived CO_2 streams. Amongst the numerous trace metal species that could be present in CO_2 streams, mercury receives attention due to its toxicity and corrosion effects on a number of metals. The well-established gas processing industry sets typical specifications of <0.01 $\mu g\ m^{-3}$ for mercury species and Kinder Morgan have specified limits of 0.3 gal/MMcf for CO_2 – EOR applications (de Visser et al., 2008).

Due its toxicity, limits have been suggested for carbon monoxide but these vary widely in the literature. The removal of particulates from CO_2 streams is driven by the need to prevent damage or fouling of equipment. Design parameters for particulates have been reported as 0 – 1 ppmv (Matuszewski and Woods, 2012); however, it may be possible to specify limits for certain particle size ranges. For other components that may be present in CO_2 streams (e.g., HCl, HF, NH_3, MEA, Selexol), little or no information is available to understand their downstream impacts on transport and storage and determine maximum allowable amounts. Further work is therefore required to understand the impacts of these species in transport and storage applications and to elucidate potential cross over effects.

The purpose of this paper and its place within the CO_2QUEST project is to define the range and level of impurities from the three currently available types of capture technology, namely: oxy-fuel combustion capture; post-combustion capture; and pre-combustion capture. A comprehensive and detailed review of predicted and measured CO_2 impurity levels in the different capture technologies has been made. In order to find optimum levels of CO_2 quality for given cases, a fundamental understanding of the origins of the impurities and the factors that control them is essential. Analysis is made of the different process parameters which affect CO_2 composition, including mode of operation of the power plant and of the technologies used for the separation of CO_2 and removal of impurities. The potential of CO_2 impurities from the utilisation of biomass for power is discussed and the impact of capture from other types of CO_2 intensive industries on the range and level of impurities is also analysed. The information presented in this paper can form a basis for undertaking full chain CCS techno-economic evaluations and risk analysis in order to find optimal CO_2 quality levels for different scenarios.

2. CLASSES OF CO_2 IMPURITIES BY ORIGIN

Impurities contained in the CO_2 streams from different carbon capture technologies may be classified broadly by origin into three main categories arising from fuel oxidation, excess oxidant/air ingress, and process fluids, as shown in Table 1. It is possible that impurity species arise from different sources, e.g. NH_3 may arise as an oxidation product or as a process fluid. The oxidation products listed in Table 1 derive from coal and/or biomass oxidation. These fuels are considered for use with CCS and produce a larger range and higher level of CO_2 impurities in comparison to those of CO_2 derived from natural-gas combustion with CCS.

(insert Table 1 here)

Major and minor complete oxidation products of coal and biomass form the common impurities of water, SO_x, NO_x and halogens. Partial oxidation products such as carbon monoxide (CO) and hydrogen sulfide (H_2S) may arise from fuel-rich conditions encountered in gasifiers as employed for integrated gasification combined cycles (IGCC). Volatiles comprising hydrogen and light hydrocarbons are formed from fuel devolatilization with heating. Biomass fuels contain higher levels of alkali metals in comparison to coal and could form a class of CO_2 impurities, the main species being chlorides, sulfates and hydroxides of potassium and sodium. Trace metals contained in fuel may be released to the gas-phase on combustion and propagate into the CO_2 stream. These metals may exist in the CO_2 stream in elemental or oxidised form such as mercury dichloride $HgCl_2$ and may require removal due to operational and environmental health reasons. Particulates in the form of ash and soot with polycyclic aromatic hydrocarbon (PAH) precursors are another type of oxidation impurity. Oxygen, nitrogen and argon are CO_2 impurities that can arise from excess oxidant used for combustion or air ingress into the boiler. The oxidant/air ingress species are referred to as 'inerts' by some authors. A final class of CO_2 impurities are the process fluids used for CO_2 separation such as monoethanolamine and selexol. Other contaminants may arise from the power plant or CCS process such as machinery lubricants or metals but are not discussed further in this analysis because no estimates or measurements have been made of these and they are not expected to be present in CO_2 streams in levels that would cause concern.

3. IMPURITIES ARISING FROM DIFFERENT COMBUSTION CAPTURE MODES

3.1 Oxy-fuel Combustion Capture Impurities

Oxy-fuel combustion refers to the combustion of a fuel in a mixture of oxygen and recycled flue gas (RFG), rather than using air solely as the oxidant. The recycle is required to moderate the otherwise excessively high flame temperature that would result from burning in pure oxygen. The oxy-fuel combustion capture process is shown in Figure 1. The flue gas produced from the process comprises mainly CO_2, N_2, O_2 and water (Table 2). The additional equipment required for the oxy-fuel combustion process in comparison to the air-firing mode is principally:

i. A cryogenic air separation unit (ASU) to provide high purity oxygen (95-99 % v/v) to the boiler.

ii. A CO_2 compression and purification unit for removal of water, particulate matter and other pollutant gases.

iii. A flue-gas recycle system with a recycle ratio of approximately 0.7. Recycled flue gas may be wet (retaining the moisture) or dry (dried and then recycled).

(insert Table 2 here)

(Insert Figure 1 here)

Oxyfuel-derived flue gas can contain a complex, interdependent mixture of impurities, including combustion by-products, excess oxygen and inert components from air introduced from the ASU or by air ingress into the process. Two recycle streams are needed to recycle approximately two thirds of the flue gas back to the combustion chamber. The primary stream is used for coal drying and transportation to the burner and should ideally be dry and desulfurised. The secondary recycle is used for the recirculation of the bulk of the flue-gas with several options existing for its location as indicated by the dashed lines in Figure 1 (Toftegaard et al., 2010). The secondary can be defined as a wet recycle, taken before the flue gas desulfurization (FGD), or as a dry recycle after FGD. FGD options therefore revolve around using a unit sized for recycled flue gas or much lower final exit flowrates with implications for capital and operating costs. The recycle has an added benefit of reducing NO_x levels via reburning in the combustion chamber. An additional consequence of reducing

volumetric flowrate and introducing recycled flue gas is an increase in SO_2 concentration in the flue gas (in ppm) but a lower emission rate of SO_2 (in mg MJ^{-1}) (Stanger and Wall, 2011). Recirculating the flue gas before FGD results in a 3-4 times higher concentration of SO_2, and other impurities not removed. This can have a negative impact on the FGD plant and therefore certain design and operation criteria should be observed (Faber et al., 2011).

Raw CO_2 flue gas can be dehydrated, purified and compressed prior to transportation off site. The power plant configuration, coal composition and mode of operation of power plant and CO_2 compression and purification unit will affect to a large extent the level of impurities in the CO_2 product stream. A cost- benefit analysis can be used to optimise the process and address the trade-off between the operation of the CO_2 compression and purification unit and other parts of the process like the air separation unit and the level of purity of the oxygen it produces. The analysis can also be used to assess whether traditional pollution-control devices are necessary, or if the pollutant removal requirements can be fulfilled by the CO_2 compression and purification unit. The level to which each impurity is required to be removed will depend upon a number of factors, such as: corrosivity, transport and storage economics, regulations, process requirements, toxicity, and constraints on geological storage. The different options for CO_2 compression and purification are reviewed in the following sub-sections.

3.1.1 CO_2 Compression and Purification Technologies for Oxy-fuel Combustion Capture

Currently available technology for CO_2 compression and purification utilise multistage compression and a combination of water or caustic soda scrubbing and phase separation for multi-pollutant removal. Figure 2 shows the first stage of raw oxy-fuel CO_2 stream cooling and compression to 30 bar (White et al., 2009).

(Insert Figure 2 here)

For the example process shown in Figure 2, the raw flue gas contains just over 70% CO_2 with the most abundant impurities being N_2, O_2, Ar and H_2O. The raw flue gas is sent to a direct-contact water scrubbing packed tower where water and soluble gases, such as SO_3 and HCl can be condensed out. A portion of the CO_2 leaving the tower is recycled to the boiler whilst

the rest is compressed to an intermediate pressure of 15 bar. The heat of compression is recovered using two heat exchangers for boiler feed-water heating and condensate preheating in the boiler steam system. Two more heat exchangers are used to provide cooling using cooling water before and after further compression to 30 bar. The 30 bar CO_2-rich flue gas then flows to the next stage for further drying, purification and compression.

There are a number of other options for the removal of O_2, N_2 and Ar from the CO_2 stream with varying costs and levels of CO_2 purity. In the double flash case (Figure 3), the raw CO_2 first passes through a dual bed thermally-regenerated dryer and then through two multi-stream heat exchangers which are each followed by flash separators, which separate liquid high purity CO_2 at low temperature from the inert impurities which remain in the gas-phase. The cooling for the heat exchangers is provided by the Joule-Thompson effect of returning liquid CO_2 streams passing through adiabatic throttles, expanding and evaporating. The CO_2 stream is further compressed and cooled for transportation at 110 bar. The CO_2 product stream reaches ~96 % purity with this approach, and this level of purity may be acceptable for general sequestration purposes. Power can also be recovered from the vent gas using a turbine.

(insert Figure 3 here)

Higher purity CO_2 is required for enhanced oil recovery (EOR) applications of CO_2, in particular, oxygen should be reduced to below 100 ppm in order to avoid oxidation of hydrocarbons and limit aerobic bacterial growth. In addition, N_2 and Ar increase the minimum miscibility pressure of oil and CO_2 in the subsurface and it is therefore desired to keep the concentration of these species to below 1 % v/v each. A distillation column can be used to purify the 30 bar CO_2 as opposed to the double flashing system as shown in the process flow diagram of Figure 4. Water is stripped prior to distillation by adsorption using molecular sieves, in order to avoid ice formation which can block heat exchangers and the distillation column. The raw CO_2 stream is cooled to -27 °C in a heat exchanger with cooling provided by an external refrigeration loop. The CO_2 stream then passes to a ten plate distillation column which is cooled by another refrigeration loop. The temperature at the top of the column is - 54 °C while the bottom is maintained at -10 °C. As shown in Table 3, the distillation case produces CO_2 at purities in excess of 99 %. In addition to the double flashing

and distillation cases, a triple flashing case has been proposed (Dillon et al., 2005) which can produce CO_2 of 98 %.

(insert Figure 4 here)

Process modifications at the pre-compression stage of Figure 2 (first compression train to 30 bar) have the potential to remove NO_x and SO_x using the 'sour compression' process. Air Products have patented this process (Allam et al., 2005) which is believed to be a variant of the lead chamber process. Reactions (1-5) are suggested as the main reaction pathways:

$$NO + \tfrac{1}{2}O_2 \rightarrow NO_2 \qquad\qquad\qquad (1)$$

$$NO_2 + SO_2 \rightarrow NO + SO_3 \qquad\qquad\qquad (2)$$

$$SO_3 + H_2O \rightarrow H_2SO_4 \qquad\qquad\qquad (3)$$

$$2NO_2 + H_2O \rightarrow HNO_2 + HNO_3 \qquad\qquad\qquad (4)$$

$$3HNO_2 \rightarrow HNO_3 + 2NO + H_2O \qquad\qquad\qquad (5)$$
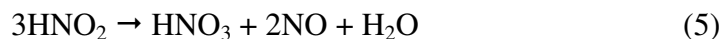
In this reaction scheme, NO acts as a catalyst for SO_2 oxidation, SO_2 is removed from the gas stream as H_2SO_4 and NO/NO_2 are removed as HNO_3. The process also has the potential to remove residual Hg via reaction with HNO_3. Elemental Hg is insoluble in water but may be captured as a nitrate which is $Hg(NO_3)_2$. The process is effectuated by the use of additional contacting columns in the first compression train to 15 bar, as depicted in Figure 5. A few seconds residence time in the contacting columns is believed to be sufficient to remove around 90 % of NO_x and all SO_2 prior to removal of N_2, O_2 or Ar (White et al., 2009). This process has been tested on a slip stream of flue gas from Vattenfall's 30 MW_{th} oxyfuel pilot plant in Schwarze Pumpe, Germany (White et al., 2013b).

(insert Figure 5 here)

The oxyfuel demonstration project at Schwarze Pumpe also adopted a similar flue gas conditioning system designed by Linde for the removal of SO_x, NO_x, water and mercury. A process flow diagram of the system has been reported by (Yan et al., 2011). In this process, the flue gas is first cleaned by conventional methods such as ESP, wet limestone FGD and flue gas condensation, and then passes to a separator for condensate removal. After this, the flue gas is fan-compressed to 1.25 bar to pass through a bed of activated carbon for mercury

removal. Mercury removal is carried out at low pressure in order to avoid the possibility of spontaneous combustion at higher pressures. After passing through the bed of activated carbon, the flue gas is compressed in two-stage screw-type compressors with interstage cooling and condensate removal to 22 bar and then sent to a dehydration unit for further water removal. After dehydration, the dried CO_2 is sent to a low temperature rectification column for liquefaction and purification. Separated gases consisting mainly of non-condensable O_2, N_2 and Ar are vented to atmosphere whilst a high purity product CO_2 leaves at the bottom of the column (Li et al., 2012).

A CO_2 purification process for producing high purity CO_2 from oxyfuel derived flue gas was used in the Callide oxyfuel demonstration project which was designed by Air Liquide, and a process flow diagram can be found in Spero et al. (2014). Similar to the Air Products process, upstream of the CO_2 Processing Unit (CPU) the flue gas was cooled and neutralised in a low-pressure scrubber which employs a water and caustic soda mix to remove SO_2, HCl, HF and NO_2. Residual particulates were then removed by passing the flue gas through a fabric filter. A four stage centrifugal compression system with interstage and after-cooling was used to compress to 22 bar (Li et al., 2012). Contaminants such as NO_2, converted from NO during the compression, and Hg (by reaction with the acidified water) were removed at the interstage steps. The flue gas was further cooled and washed with chilled water in a high pressure column and then dried in pressure-swing absorption column that uses recycled non-condensable gases, N_2, O_2 and Ar, separated from the CO_2 during the purification process for regeneration. After dehydration the CO_2 stream was liquefied and purified in a cold box which uses cryogenic distillation (Bourhy-Weber et al., 2013) with an ammonia refrigeration circuit to produce high purity CO_2. A test campaign at the Callide Oxyfuel processing plant was carried out in December 2012, to establish the behaviour and possible operational impacts of trace elements within. Sampling and measurements were carried out for solid inputs and outputs and gases at the stack exhaust (under both air and oxyfuel firing conditions) and at various points in the CPU using a variety of techniques for a range of common coal pollutants and trace metal species.

3.1.2   Oxy-fuel Process Parameters Affecting CO_2 Purity

Under the oxy-fuel combustion and capture operation, a number of process parameters will affect the level of purity in the final CO_2 product stream. These may comprise the mode of operation of the power plant and the carbon capture associated equipment. The ASU typically provides oxygen of purity in the range of 95 – 99 % v/v, and this parameter will impact on the levels of N_2 and Ar in the raw CO_2 flue gas stream. Higher O_2 purity from the ASU will come at a cost of increased ASU power requirement (kWh/ton O_2). Properties of the solid fuel used for combustion and power generation are defined with proximate, ultimate, ash and trace element analyses. These properties can affect CO_2 quality, such as high-sulfur coals leading to higher levels of SO_x in the CO_2 flue-gas stream. Alstom have made suggestions for different oxyfuel configurations and locations for an FGD unit based on coal sulfur content (Wang et al., 2009). For coals with sulphur content up to 0.5 %, an FGD out of the recycle loop and flue gas cooler are considered to be sufficient to treat the flue gas. For intermediate fuel sulfur levels of 0.5 – 1.0 %, it was considered that the FGD should be located inside the recycle loop thus removing the SO_2 before the flue gas is returned to the boiler. For fuels with high sulfur content (> 2 %), a high efficiency wet FGD within the recycle loop should be considered, with either an additional spray drying absorption system prior to fabric filter particulate removal or a wet ESP after the flue gas cooler (Stanger and Wall, 2011). Ash properties may affect the level of particulates in the CO_2 stream, while ashes with high calcium content can act as a sorbent for sulfur and reduce gas-phase SO_x. Levels of trace elements in coal including heavy metals such as Hg which can vaporise on combustion will have a direct effect on their level in the CO_2 flue gas stream.

The type and mode of operation of the boiler can also impact upon CO_2 quality. Boilers typically operate with oxygen excess, meaning that combustion products will be completely oxidised. The extent of oxygen excess will have a major impact upon the amount of oxygen in the CO_2 flue gas stream and other impacts on the levels of N_2 and Ar. Air leakage into the boiler and other parts of the process will impact on the levels of N_2, O_2 and Ar in the CO_2 stream and will be a greater problem for retrofit plants compared to new-build. The extent to which SO_2 converts to SO_3 in the boiler will affect the level and partitioning of SO_x in the flue gas and product streams. Reduced levels of char particle burnout can also lead to higher levels of impurities in the flue gas. Furnace temperature may have an impact on NO_x formation and the in-furnace NO_x control configuration will impact on nitrogen species

partitioning in the CO_2 product stream. Post-combustion NO_x controls such as selective catalytic reduction (SCR) can reduce the levels of NO_x in the CO_2 flue gas stream but any slip of ammonia from the process unit could become a CO_2 impurity. The efficiency of particulate control devices will have an impact on the particulate levels in both the flue gas and product streams. The efficiency of FGD units in removing SO_x, particulates and chloride species will also have an impact on CO_2 quality. The RFG ratio and position of the recycle will have an impact on the raw CO_2 stream composition although there is a growing consensus that dry recycles are preferential. Finally, the selection of raw CO_2 compression and purification technology options detailed in Section 3.1.1 can be considered to have the greatest impact on CO_2 quality, but capital and operation costs relating to the CO_2 unit purification energy (kWh/ton CO_2) will be an important factor in addition to transport and storage requirements.

3.1.3   Oxy-fuel CO_2 Impurities from Pulverised Coal

Table 3 gives details of the range and levels of impurities from oxy-fuel combustion capture from different authors and with different modes of applied purification, i.e. raw/dehumidified CO_2 and CO_2 obtained using double flashing or distillation phase separation technologies. Data used to compile the table are taken from the COORAL project (Kather and Kownatzki, 2011; Kather et al., 2013), a collaborative industrial paper (Wilkinson et al., 2001), a study from the Norwegian University of Science and Technology (NUST) by Pipitone and Bolland (2009), an IEA report (Dillon et al., 2005), a paper written by Air Products (White et al., 2009) and a report on the Callide oxyfuel demonstration project (Spero et al., 2014). Table 3 shows the raw/dehumidified CO_2 has a purity in the range of 74.8 – 85 %, with the main impurities being O_2, N_2 and Ar which arise from excess oxidant and air ingress. Acid gases of NO_x and SO_x form impurities at lower concentrations which may pose corrosion problems. Residual water is reported for two cases along with CO for one of the cases. The reported double flashing cases are in general accordance with CO_2 purities ~96 % v/v, where O_2 is reduced to just over 1 % v/v, N_2 is roughly 2 % v/v and Ar is roughly 0.5 % v/v. Certain levels of NO_x and SO_2 are reported for two of the double flashing cases but these species are reported to be completely removed using the Air Products sour compression process. The distillation case from the COORAL project (Kather and Kownatzki, 2011; Kather et al.,

2013) reports very high purity CO_2 at 99.94 % v/v; however, the CO_2 purity of the distillation case reported by Pipitone and Bolland (2009) is lower at 99.3 % v/v.

The level of CO_2 purity measured in the Callide oxyfuel project at both the raw CO_2 and final product stage have been reported (Spero et al., 2014). Prior to water removal, the raw CO_2 stream contained 50 – 57 % v/v CO_2 and 19 – 22 % v/v H_2O. Values of other reported impurity species in the raw CO_2 stream are comparable to the "raw / dehumidified" values given in Table 3 (i.e., 3-5 % v/v O_2, ~18 % v/v N_2, 20-200 ppm CO, 500-1000 ppm NO, 20-40 ppm NO_2, 800-1500 ppm SO_2 and 1-15 ppm SO_3). Hg concentrations were measured using a combination of an activated carbon sorbent-tube sampling method and by using continuous measurement techniques (Morrison et al., 2012). The level of Hg in the raw CO_2 stream was reported to be 0.3 – 0.5 ppb. The authors report that after CO_2 purification, analysis of the product CO_2 indicated high purity, exceeding 99.9 % (Table 3). The final CO_2 product was maintained between 1450 to 2300 kPa and a temperature of 246 K. Levels of metals, acid gases and mercury were found to be below the level of operational concern beyond the first low pressure scrubber with 80% of the mercury in the CO_2 flue gas being removed here and the final CPU process gas mercury concentration approaching the concentrations measured in ambient air (<2 ng m^{-3}). The level of most impurities in the final product CO_2 stream were at or below detection limits of the measurement devices (Li et al., 2012).

In the Schwarze Pumpe Oxyfuel demonstration project, the CO_2 flue gas composition at the different stages of processing (i.e., downstream of the ESP, FGD and Flue Gas Condenser (FGC)) have been reported by Anheden et al. (2011) and compositions of the final CO_2 product from the Air Products and Linde purification processes have been reported by (White et al., 2013a) and (Yan et al., 2011), respectively. Table 4 exemplifies the measured composition of the CO_2 flue gas streams at different plant locations and for 2 different compression and purification technologies from the Schwarze Pumpe Oxyfuel Pilot project. It can be seen that in this pilot plant high CO_2 concentrations of ~90 % on a dry basis could be achieved even upstream of the CO_2 compression purification plant. This is explained by the use of high purity oxygen (99.5 %) from the ASU, very good combustion behaviour, implementation of measures on boiler and ESP to reduce air ingress, use of a separate seal gas system and use of a separate oxidation tank for the oxidation of the gypsum slurry in the FGD process. Furthermore, it is believed that the concentrations of NO_x and CO can be

reduced in upstream stages of the process through further combustion optimisation (Anheden, 2011). The final product CO_2 quality from the Linde and Air Products processes is very high and claimed to be above 99.9 %, with low levels of some reported impurities (Table 4). It should be highlighted, that these high purity levels may not be necessary for transport and some storage applications and optimised purity levels are needed in order to lower the energy consumption and costs for CO_2 purification. Air Products have also reported a lower CO_2 product quality of 97.4 % CO_2 with impurities of 1.1 % O_2 and 1.5% N_2 which is assumed to be based on the double-flashing technique (Figure 3) (White et al., 2013a). During slipstream testing of the Air Products sour compression process for NO_x and SO_x removal, it was found that 80 % of the $NO + NO_2$ was removed at the point of exit from the 15 bar column (Figure 5); however, in certain situations, particularly high SO_2/NO_x ratios, some of the NO_x would convert to gaseous N_2O with the worst case scenario being compete conversion of $NO + NO_2$ to N_2O. Further work was recommended to understand this behaviour (White et al., 2013b).

(insert Table 3 here)

(insert Table 4 here)

3.2   Pre-combustion (IGCC) Capture Impurities

The pre-combustion capture process produces and traps CO_2 prior to the combustion phase. A general process flow diagram is shown in Figure 6. Solid fuel (coal/biomass) is converted to syngas in an oxygen blown gasifier via partial oxidation. The gasifier is supplied oxygen from an ASU similar to that used for oxy-fuel combustion and may be fed fuel using a slurry or a dry feed system. The syngas produced is a mixture of CO, H_2, CO_2 and H_2O. As the syngas is produced from sub-stoichiometric oxidation, partial oxidation products are produced in significant quantities, which is different to oxy-fuel and post-combustion capture where complete oxidation occurs. In the water-gas shift reactor, CO reacts with water to produce CO_2 and H_2. Different solvents can be used to remove sulfur mainly in the partially oxidised form of H_2S and smaller amounts of carbonyl sulfide COS. The removed syngas sulfur species can be converted to elemental form for sale using Claus and Beavon-Stretford plants. After CO_2 removal, the syngas stream is rich in H_2 and can be used to produce energy using a combined cycle gas turbine.

(insert Figure 6 here)

3.2.1   Pre-combustion Capture Process Parameters Affecting CO_2 Purity

Under the pre-combustion capture operation, a number of process parameters will affect the level of purity of the CO_2 product stream. The main effects relate to the operations used to generate and process the syngas into an H_2-rich stream. Changes to mode of operation of the power island section of the plant are not expected to greatly impact upon the CO_2 quality. Syngas production is usually operated in steady state, and flexible operation will be highly constrained by the operation of the ASU. Alternative methods of flexible operation are proposed including storing syngas or O_2, or co-firing syngas with natural gas (IEAGHG, June, 2012). The operation of the ASU and purity level of produced O_2 may have a small impact on the low levels of N_2 and Ar found in the CO_2 product stream. A more important impact on the CO_2 quality will originate from the fuel composition. In particular, the levels of sulfur in the solid fuel will dictate the levels of gas-phase sulfur species in the syngas produced by the gasifier, which is mainly in the form of H_2S with lower levels of COS which may carry through to the CO_2 product stream. The operation conditions selected for the gasifier including temperature, pressure, equivalence ratio and water or steam input, will affect the syngas composition which could propagate through to the CO_2 product stream. In addition, the level of ash carry-over and particulate removal efficiency will have an impact on the particulate levels in the syngas and CO_2 streams. The extent of sulfur loss to the solid particle phase will also have an effect on the sulfur levels in the syngas and ultimately in the CO_2 stream. In the water-gas shift reactor, COS can convert to H_2S, affecting the downstream sulfur partitioning due to solubility differences. The removal efficiency of H_2S and COS in the sulfur removal unit will affect the levels of sulfur species in the CO_2 product stream. The removal efficiency will be affected by process temperatures, residence times, loading rates and solvent selection. The extent to which CO is converted to CO_2 will also have an effect on the resulting CO_2 product stream, as will the CO_2 removal efficiency also be influenced by the process temperatures, residence times, loading rates and solvent selection. The selected solvent such as Selexol, can also form an impurity as volatility and in-place waterwash systems control the extent to which it may be carried over into the CO_2 product stream. The Selexol solvent consists of dimethyl ethers of polythene glycol and can also be used to remove both sulfur species and CO_2 from the syngas stream.

3.2.2　　　　　Pre-combustion (IGCC) CO_2 Impurities from Pulverised Coal

Table 5 gives details of the range and levels of impurities from pre-combustion capture from different authors and with different methods of CO_2 removal. Data used to compile the table are taken from the COORAL project (Kather et al., 2013), a European Communities (EC) guidance document on Geological Storage of CO_2 (E.C., 2011), a report by Linde on their CO_2 removal technologies (Prelipceanu et al., 2007), a report by the Energy Research Centre of the Netherlands (Walspurger and Dijk, 2012) and the findings of the French CO_2 Club (Anheden et al., 2004; Apps, 2006; Farret et al., 2012; Kather, 2009) that led to a report based on a literature review, through a working group of 8 experts from industry and from national research institutes. Levels of reported CO_2 purity from the COORAL project and the EC guidance document are in accordance with H_2 making up the most voluminous impurity. N_2 may be a significant impurity resulting from impure oxidant or air ingress. Ar and H_2O make up impurities at lower levels. Reported levels of sulfur species (predominantly H_2S) may vary widely – this may be explained by co-capture and separate capture configurations for H_2S and CO_2. In the IGCC co-capture configuration, H_2S and CO_2 are being captured in the same absorber, whereas in the separate capture configuration there are two absorbers. Although the solvent for capturing H_2S and CO_2 is the same in the separate capture configuration, process conditions in each absorber are optimised for each component producing CO_2 with a lower H_2S concentration (CO_2PIPETRANS, 2008) In the Linde Rectisol[®] case, absorption of H_2S and CO_2 occurs in one column, which is followed by two columns for separated desorption of CO_2 and then H_2S. Low concentrations of ash, NH_3, Cl and heavy metals such as Hg, As and Se, have also been reported in the CO_2 product stream. The sorption enhanced water-gas shift (SEWGS) is a technology that relies on a pressure swing adsorption cyclic process carried out at temperature in the range 350-450 °C, and has a high recovery at atmospheric or slightly above atmospheric pressure (Walspurger and Dijk, 2012). Purity from the SEWGS process has been reported to be above 99 %. The reported impurity levels from the French CO_2 club review generally agree with the other reported values. Low levels of additional impurities NO, SO_2, Ni, Pb, benzene and napthalene have also been reported in the CO_2 product stream (Anheden et al., 2004; Apps, 2006; Farret et al., 2012; Kather, 2009; Oosterkamp and Ramsen, 2008).

(insert Table 5 here)

3.3 Post-Combustion Capture Impurities

A simplified process flow-diagram for post-combustion CO_2 capture using amine solutions is shown in Figure 7. Combustion derived flue gas enters the absorber at the bottom of the column and bubbles up through an aqueous amine, such as monoethanolamine, or aqueous ammonia, at temperatures between 40 and 60 °C, where the CO_2 in the flue gas becomes chemically absorbed in the solution. The CO_2-scrubbed flue gas passes through a water wash to remove any entrained amine solvent before being vented to atmosphere via the stack. The CO_2 loaded 'rich' solvent leaves via the bottom of the absorber column where it is pumped to the regenerator or stripper via a heat exchanger and enters the column at the top. The stripper column is maintained at higher temperatures between 100 and 150 °C where the absorbed CO_2 can leave solution as a gas, where it then passes through a condenser and on for further processing. The CO_2 free 'lean' solvent is pumped back to the absorber column via the lean/rich amine heat exchanger and a further lean amine cooler unit, to bring it to the absorber temperature level.

(insert Figure 7 here)

3.3.1 Post-Combustion Capture Process Parameters Affecting CO_2 Purity

The effect of the mode of operation of the power generation section of a plant using post-combustion capture on the levels of CO_2 impurities shares some commonalities with those detailed for oxy-fuel combustion capture in section 3.1; i.e. fuel proximate, ultimate, ash and trace element analyses, boiler excess air, air leakage, furnace temperature, SO_2/SO_3 conversion, S retention in ash, burnout, in-furnace NO_x control configuration, SCR NO_x removal efficiency, electrostatic precipitator (ESP) removal efficiency and the efficiency of FGD at removing SO_x, particulates and chloride species. Lee et al. (2009) estimated the impurities included in the CO_2 stream from a post-combustion capture control unit with different combinations of air pollution control devices and different flue gas compositions. Published performance parameters from existing MEA based absorption processes and conventional air pollution control devices were used to estimate levels of acid gases and mercury vapour in the CO_2 product. Five different CCS power plant configurations were used as scenarios for the estimation of composition of CO_2 streams. These were:

1) No NO_x or SO_2 control.
2) No NO_x but SO_2 control with wet FGD scrubber.
3) NO_x control with Low NO_x Burners (LNB) / SCR and no SO_2 control.
4) NO_x control with LNB / SCR and SO_2 control with wet FGD scrubber.
5) NO_x control with LNB / SCR and SO_2 controlled to <10 ppmv SO_2 at inlet of MEA absorber.

Case 1 had the highest levels of acid gases in the CO_2 stream due to no SO_2 or NO_x controls being deployed. The results for cases 1 and 3 without wet FGD scrubbing indicated that up to 4 % w/w of SO_2 could be included in the separated CO_2 with no heat stable salt formation assumed. Cases 2 and 4 with a wet FGD system showed that SO_2 levels could be reduced to hundreds or thousands of parts per million by weight (ppmw) in the CO_2 product. Other acid gas impurities of NO_2, SO_3, and HCl were below 0.1 %. Mercury concentrations were greatly affected by the presence of wet FGD and were predicted to be below 30 ppbw when it is deployed. In case 5, 75 % of the SO_2 entering the capture system was assumed to have formed heat stable salts which may be removed by the reclaimer; under this case a minimum of 35 ppmw SO_2 was predicted to partition to the CO_2 product stream. The levels of other impurities (NO_2, SO_3, HCl, and mercury) in case 5 were also the lowest (<0.01%) because to achieve the high desulfurisation level of 10 ppmv at the absorber inlet, a secondary SO_2 polishing system is required which can co-remove soluble impurities by water contact. Case 5 is considered to be the most likely scenario for post-combustion capture systems due to the impacts of SO_2 on the degradation of sovents used for CO_2 capture.

The post-combustion capture process parameters themselves may be adjusted and this has the potential to affect CO_2 impurities. The CO_2 purity can be affected in different ways, for example, it is possible to operate a post-combustion capture facility over a range of CO_2 capture rates (85 – 95 %). The temperature of flue gas entering the amine plant can be varied between 30 – 50 °C to impact upon efficiencies, and the recycle rates of amines can also be adjusted along with stripper column temperatures and efficiencies. SO_2 polishing prior to entering the amine plant can be adjusted by varying water-wash concentration and flow rate, and SO_2 should be kept below 10 ppm before entry to the amine plant due to heat-stable salt formation. An increase in stripper pressure/temperature, an increase in CO_2 loading and a decrease in stripper overhead condenser temperature can also lead to an increase in CO_2 purity.

3.3.2   Post-Combustion Capture CO_2 Impurities

Table 6 gives details of the range and levels of impurities from post-combustion capture from different authors. Data used to compile the table are taken from the COORAL project (Kather et al., 2013), a European Communities guidance document on Geological Storage of CO_2 (E.C., 2011), and the findings of the French CO_2 Club (Anheden et al., 2004; Apps, 2006; Farret et al., 2012; Kather, 2009; Oosterkamp and Ramsen, 2008). The levels of reported CO_2 purity are in very good accordance and are very high at 99.6 – 99.8 % v/v. The impurity with the highest reported level in post-combustion capture derived CO_2 streams is N_2 which can arise from excess air in the boiler, air ingress into the process or possibly from NO_x conversion to N_2. The impurity with the second highest reported level is water, which will predominantly arise from the post-combustion solvent which contains around 30% amine in aqueous solution. Smaller amounts of Ar, NO_x, SO_x, CO, O_2, Cl, ash, trace metals and cyclic aromatics can also be present.

(insert table 6 here)

4. CO₂ IMPURITIES FROM THE UTILISATION OF BIOMASS FOR POWER

A possible renewable alternative for fossil-fuelled power plants is based upon the use of biomass. Biomass is co-fired with other fossil fuels, mainly coal, in many power plants and dedicated biomass is also used for small- and large-scale power generation. Existing coal plants can be converted to co-fire a large percentage of biomass, with white wood pellets or chips being the preferred choice of fuel by operators. The use of biomass in conjunction with CCS (Bio-CCS) is considered as an option that has the potential advantage of being carbon neutral or even carbon negative (Catalanotti et al., 2013). The substitution of coal for biomass, in whole or in part, can have an impact on the resulting CO_2 composition in CCS applications due to the altered fuel chemical composition. The chemical composition of biomass differs to that of coal, in that it generally contains less sulfur, fixed carbon, and fuel bound nitrogen, but more oxygen (Tumuluru et al., 2011). Derived flue gas from dedicated or co-firing plant boilers, or syngas from gasifiers in the case of IGCC, has proportionally decreased SO_2 emissions with an increasing biomass share in the thermal input (Williams et al., 2012). As for coal fired CCS plants, the amount of pollutants in the CO_2 product stream will be dictated to a large extent by the plant's pollution control and CO_2 purification equipment. As fuel bound nitrogen is the major source of NO_x in combustion plants, the formation of this pollutant may be expected to decrease with an increased proportion of biomass in the fuel input. In-furnace NO_x controls can be used with biomass but the larger particle size compared to coal may present a problem for reburning.

A disadvantage of using biomass is that a higher concentration of akali metal species can be found in derived flue-gases compared to using coal alone. The principal metal is potassium, but sodium species are also present. These species present slagging, fouling and corrosion problems, as well as pollutant formation issues (Hald, 1995). Elevated concentrations of alkali species in biomass derived flue-gases can occur due to their presence in usually higher quantities in the fuel and also due to differences in how these species are bound in biomass. Potassium is mainly released to the gas-phase as KOH and KCl; the latter being dominant when the fuel Cl content is high. KOH and KCl can undergo transformation in the gas-phase to form K_2SO_4. The condensation of alkali salts on fly ash produces a sticky particle layer which enhances deposition (Garba et al., 2012). Alkali salts exhibit a high degree of water solubility (Wang et al., 2012b), and their salt vapours may therefore be expected to mainly

condense on particles and deposit in-boiler or become dissolved in aqueous contacting systems present in the power plant rather than reach a product CO_2 stream in significant quantities. However, the control of fine particulate metal aerosols formed in biomass combustion systems may be more difficult to achieve, depending on their characteristics.

Fly ashes from biomass combustion can be characterised in two distinct fractions: coarse fly ash with particle diameters of 1 – 250 μm, and aerosols with particle diameters of 0.01 – 1.00 μm (Obernberger et al., 2003). The size distribution of fly ash shifts to finer particles with an increase in quantities of aerosols when there is an increase of biomass in the blended fuel input with coal, due to the fine size of the fuel minerals in the biomass and the prevalence of organically associated alkali and alkaline earth metals that are expected to form fine particles (Lind, 1999; Zygarlicke and Folkedahl, 2003). Increased aerosols pose a problem for conventional ESP particle control devices and aerosol penetration has been reported for the technology (Lind et al., 2003; Strand et al., 2002). The chemical composition of the formed aerosols almost exclusively depends on the chemical composition of the fuel and the release of metal species, sulfur and chlorine (Frandsen, 2005). Aerosols may also form from ZnO vapour by nucleation in the furnace. As the flue gas further cools, other ash forming compounds which are alkali sulfates (K_2SO_4, Na_2SO_4), alkali chlorides (KCl, NaCl) and heavy metal compounds (PbO, $PbCl_2$, $ZnCl_2$), condense on these particles. Alternatively, if insufficient ZnO seed particles are present, new particles form by nucleation from the primarily alkali compound ash forming vapours (Jöller et al., 2007). Particles from biomass combustion will consist of a soluble fraction, which include alkali metal salts: sulfates, carbonates and chlorides (Vainikka et al., 2011), and an insoluble fraction. Silicates and some other minerals are insoluble, and alkali bonded in silicates is less prone to volatilise and remains insoluble (Werkelin et al., 2010). PbO, $PbCl_2$ and ZnO are mainly insoluble. Pollutants from biomass can also include tar aerosols (Williams et al., 2012) which are amorphous, carbonaceous spherules with diameters typically between 30 and 50 nm. Tar aerosols are initially hygroscopic, but the particles become largely insoluble as a result of free radical polymerisation of their organic molecules (Pósfái et al., 2004).

At the time of writing, no estimates or measurements of the composition of CO_2 derived from Bio-CCS are available in the literature. The scope for aerosol particles to reach the product CO_2 stream will depend on a combination of the pollution control and CO_2 purification technology in the Bio-CCS plant and the aerosol characteristics such as size, density and

solubility. Further research is needed to investigate the range and level of impurities in Bio-CCS derived CO_2 streams and to define limits for transportation and storage on potentially deleterious substances.

5. INDUSTRIAL SOURCES OF CO_2

CO_2 emissions arising from non-power industrial processes are substantial. Apart from natural-gas sweetening, capture from these processes has not been tested on a large scale. Different processes must be considered individually for their suitability to CO_2 capture. Many of the major industrial emissions sources are suitable for CO_2 capture in terms of emissions per source and the concentration of CO_2 in waste gas streams. Implementation of CCS technologies for most industrial activities (e.g. boilers, iron and steel furnaces, and cement) requires a capture step applied to low concentration CO_2 streams. The technical feasibility of this in each case will depend upon the layout of the industrial plant. In some instances, industrial activities already apply some form of CO_2 removal or capture as an inherent part of the process and therefore emit a relatively pure CO_2 stream. These types of activities include natural gas processing, hydrogen production for ammonia and subsequent fertilizer production, and synthetic fuel production such coal-to-liquids and gas-to-liquids. Estimates and measurements of the ranges and levels of impurities in the CO_2 capture streams from industrial processes have limited availability. The following subsections provide brief descriptions of some of the main industries considered for CCS and present data of the derived CO_2 stream composition where possible.

5.1   Iron, Steel and Metallurgical Coke Production

The iron and steel industry is an energy-intensive activity and a major industrial CO_2 emitting sector, accounting for about 650 Mt of CO_2 per year. Steel production at an integrated iron and steel plant is accomplished using several related process, and emissions occur at each step of the production process. These processes include: 1) coke production; 2) sinter production; 3) iron production; 4) iron preparation; 5) steel production; 6) semi-finished product preparation; 7) finished product preparation; 8) heat and electricity supply; and handling and transport of raw, intermediate, and waste materials (Last and Schmick, 2011).

The vast majority of CO_2 emissions from steel production come from blast furnace stove stacks where the combustion gases from the stoves are discharged. The relative composition of blast furnace gas has been estimated to be roughly 60% N_2, 28% CO and 12% CO_2 (EPA, 2010). Post-combustion carbon capture applied to this dilute CO_2 exhaust stream is likely to

produce similar impurity estimates to those from the power sector. Metallurgical coke is used in blast furnaces to reduce iron ore to iron. Coke is produced by destructive distillation of coal in the oxygen free atmosphere of coke ovens until the most volatile components are removed, and these stack gases are a source of CO_2.

5.2   Cement Production

Production of cement is the largest industrial source of CO_2 emissions after the power sector, accounting for around 1000 Mt of CO_2 per year. Cement production involves the calcination of limestone and has large process emissions of CO_2. Furthermore, large quantities of heat energy are needed to drive the process which is usually derived from the combustion of fossil fuels. NO_x, SO_2, CO and CO_2 are the primary gaseous emissions in the manufacture of cement. Smaller quantities of VOCs, NH_3, chlorine and HCl may also be emitted (EPA, 1995). Emissions may also include partial combustion products. The concentration of CO_2 in the flue gases from cement production is 15-30% by volume, considerably higher than from fossil fuel power plants. Post-combustion capture technologies can therefore be applied to cement production plants.

5.3   Hydrogen and Ammonia Production

The production of hydrogen is the first step in the manufacture of ammonia using the Haber-Bosch process. Around half of all globally produced hydrogen is used to produce ammonia and 80% of ammonia manufactured worldwide is used to produce inorganic nitrogen based fertilisers. There are several processes for producing hydrogen from fossil fuel or biomass feed stocks, these include: steam reforming, auto-thermal reforming, partial oxidation and gasification. Technology selection depends on economics, feedstock source and plant flexibility. All involve the application of solid-fuel gasification or natural-gas reforming technologies to produce a syngas which is purified by a gas clean-up step to produce a reformed syngas mix of H_2. The water-gas shift reaction process converts syngas to a mixture of CO_2 and hydrogen in varying proportions. In the case of H_2 production, the CO_2 must be removed to produce a purified stream (Zakkour and Cook, 2010). As the process is quite

similar to pre-combustion capture, parallels may be drawn in terms of the composition of the produced CO_2 stream.

5.4   Natural Gas Processing

Natural gas typically undergoes processing prior to export to market. Natural gas reservoirs contain significant quantities of impurities, principally CO_2 and H_2S, and additional treatments must be applied to remove these which are usually amine or membrane separations. The processes produce high-purity CO_2 streams which can be stored. There are two operating natural gas plants that capture and store CO_2 from natural gas processing: these are the Sleipner plant in the North Sea and the In Salah plant in Algeria. CO_2 captured from natural gas processing is also used in several EOR projects in the USA. For the separation of CO_2 in natural gas processing, the co-absorption of hydrocarbons and H_2S and carry over to the CO_2 product stream may be an issue. In the Sleipner project, the CO_2 stream is 98% pure with the main contaminant being methane (E.C.C.S.D.P.N., 2012).

5.5   Lime Production

Lime is produced via the calcinations of limestone, dolomite or other mineral materials, and rotary kilns are the most prevalent type of kiln used in the process. CO_2, CO, SO_2 and NO_x are all produced in lime kilns, and emissions are affected by the properties of the fuel used to heat the kiln, the properties of the mineral feed material, the quality of the lime produced, the type of kiln used and the type of pollution control equipment employed. Toxic species in the exhaust gases from lime kilns are metals such as arsenic, cadmium, chromium, nickel and HCl (EPA, 2003). The exhaust gas from a lime kiln contains around 50 % CO_2 (Last and Schmick, 2011).

5.6   Other Processes

Other petrochemical processes, such as the production of ethylene and methanol are also amenable to CO_2 capture and storage. CO_2 can also be captured from processes involving biomass, such as the fermentation of sugar to produce bio-ethanol.

5.7 CO₂ Stream Compositions from Industrial Processes

Consistent information on the composition of CO_2 streams that could be captured from non-power industries is difficult to find for most industries, so here we rely on estimates given in an EC report (E.C., 2011) and in a report by the Pacific Northwest National Laboratory (Last and Schmick, 2011). Table 7 summarises the indicative compositions of CO_2 streams generated using post carbon capture from major non-power emitters of CO_2 which include an oil refinery, a cement plant, coke production and a lime kiln. The composition estimates from (E.C., 2011) are based on engineering calculations and make assumptions about flue-gas pre-treatment and capture processes. The estimates provided by Last and Schmick (2011) are based on a compilation of air pollutant emission factors by the EPA. The authors assumed that carbon capture technology would remove most of the air (N_2, O_2 and Ar) to produce a concentrated CO_2 stream with the same approximate ratio of other impurities to CO_2 as the original exhaust emission.

(insert Table 7 here)

6. Conclusions

Specifications for required CO_2 purity levels for transport and geological storage are currently uncertain. However, existing pipeline specifications and the experience being gained from current CCS projects will provide crucial insights for future regulation and purity requirements. Pipeline specifications for impurity levels are expected to be stricter than those of storage, particularly for species that can cause internal pipeline corrosion, such as SO_x, NO_x and water which increases CO_2 acidity, and species which cause fouling due to the formation of hydrates and clathrates. In this regard, the recommendations on CO_2 quality given by NETL can serve as a point of reference (Matuszewski and Woods, 2012).

Several reports, such as that by Farret et al. (2012) and reports from the IEAGHG (June, 2011) are based on a literature review of public information and references. They show that: a) such references are not very numerous and they contain mainly values that are only theoretical estimates based on measurements from combustion processes and not direct measurements on product CO_2 streams, and b) that there exists a core set of "basic" references, with most other open publications being based upon them and taking the same values.

The levels of impurities in CO_2 streams can vary widely depending on the level of fuel oxidation, i.e. gasification or complete oxidation, and on the characteristics of the fuel. Furthermore, in CO_2 capture technologies, the levels of most impurities can be reduced to low levels by adding additional or more intensive process operations. In this respect, recommended levels for transport and storage will in practice dictate actual impurity levels for hazardous or corrosive species. Levels for more benign species such as N_2 and Ar may be governed more by full CCS chain techno-economic evaluations. Table 8 summarises the main impurities from different CO_2 capture technologies. With the standard technologies for the different carbon capture technologies, the order of purity from the main carbon capture technologies are oxy-fuel (double flashing) ~96 % < pre-combustion ~98 % < post-combustion ~99.6 %. The highest concentration of impurities for oxy-fuel are O_2, N_2 and Ar, but SO_x and Hg may also be present to a certain level and be a cause for concern in relation to potential corrosion and toxicity issues. The main impurity of concern from pre-combustion is H_2S due to its corrosion potential, but H_2 may also be a species of significant concentration in the CO_2 product stream, leading to a relative increase in transport cost. For post-combustion

capture, impurity levels are lower than the other standard capture technologies (pre-combustion and oxyfuel double flashing), and N_2, H_2O and O_2 are seen to be the main impurities of highest concentration from this operation. Although oxy-fuel and pre-combustion standard capture technology options have higher levels of CO_2 impurities, there are options to push the technology in order to obtain higher purities of CO_2 but there will be implications for cost and capture rates.

(insert Table 8 here)

7. Acknowledgments

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9. Figure Captions

Figure 1. Possible configuration of an oxy-fuel power plant, ASU: air separation unit, SCR: selective catalytic reduction reactor (de-NO_x), ESP: electrostatic precipitator, FGD: flue gas desulfurization (Toftegaard et al., 2010).

Figure 2. Raw oxy-fuel CO_2 cooling and compression to 30 bar (adapted from White et al. (2009)).

Figure 3. Double flash case for O_2, N_2 and Ar removal from oxy-fuel CO_2 stream and compression to 110 bar (adapted from Dillon et al. (2005)).

Figure 4. Distillation case for O_2, N_2 and Ar removal from oxy-fuel CO_2 stream and compression to 110 bar (adapted from Pipitone and Bolland (2009)).

Figure 5. Raw oxy-fuel CO_2 compression with integrated SO_x and NO_x (adapted from White et al. (2009)).

Figure 6. Possible configuration of a pre-combustion capture (IGCC) power plant.

Figure 7. Process flow diagram for post-combustion CO_2 capture.

10. Table Captions

Table 1. Classes of potential CO_2 impurities by origin.

Table 2. Raw and product CO_2 compositions from basic oxy-fuel process (White et al., 2009).

Table 3. Oxy-fuel CO_2 impurities from pulverised coal. Sources: [a] (Kather and Kownatzki, 2011), [b] (Wilkinson et al., 2001), [c] (Pipitone and Bolland, 2009), [d] (Dillon et al., 2005), [e] (White et al., 2009), [f] (Kather et al., 2013), [g] (Spero et al., 2014) (* includes sour compression step prior to removal of inerts).

Table 4. CO_2 flue gas composition at different stages of the Schwarze Pumpe Oxyfuel Pilot Plant. Sources: [h] (Anheden et al., 2011), [i] (Yan et al., 2011), [j] (White et al., 2013a)

Table 5. Pre-combustion CO_2 impurities from pulverised coal. Sources: as Tables 3 and 4, and [k] (E.C., 2011), [l] (Prelipceanu et al., 2007), [m] (Walspurger and Dijk, 2012), [n] (Farret et al., 2012), [o] (Anheden et al., 2004), [p] (Apps, 2006), [q] (Kather, 2009), [r] (Oosterkamp and Ramsen, 2008) (‡summary of considered rectisol and selexol cases, *sorption enhanced water-gas shift, †average values of relevant sources).

Table 6. Post-combustion CO_2 impurities from pulverised coal. Sources: as Table 5 (†average values of relevant sources).

Table 7. Compositions of CO_2 streams generated using post carbon capture from major non-power emitters. Sources: as Table 3, and [s] (Last and Schmick, 2011)

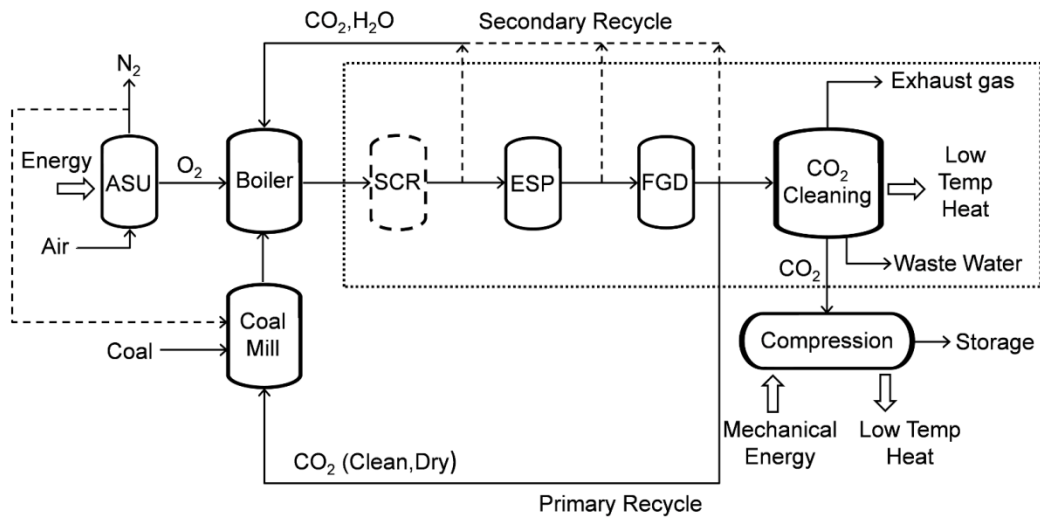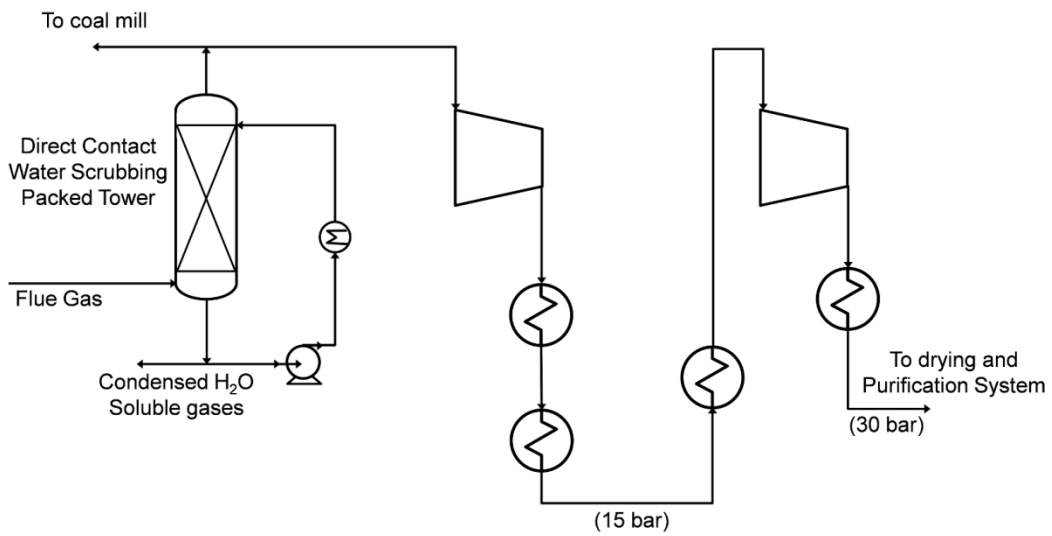Table 8. Summary of CO_2 impurities from different CO_2 capture technologies.

Figure 1

Figure 2

Figure 3
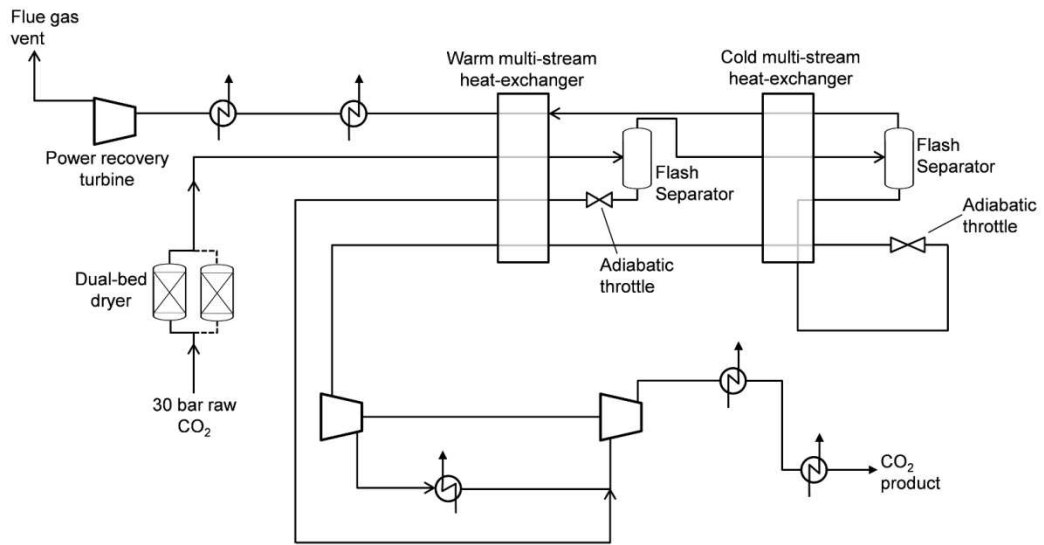
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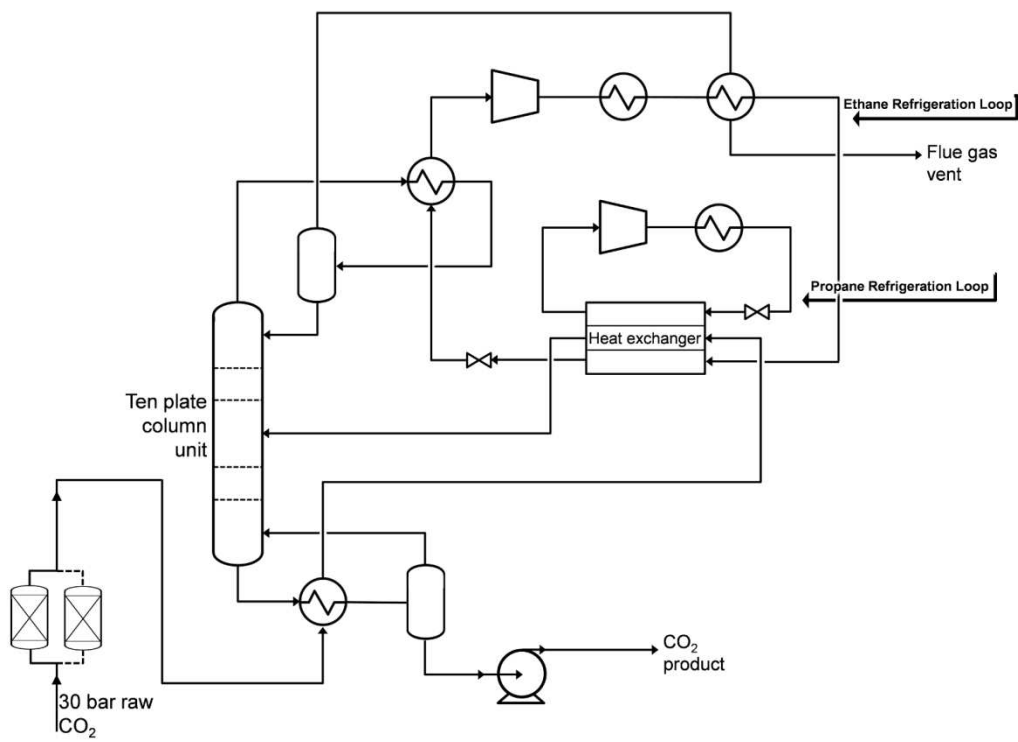
Figure 5
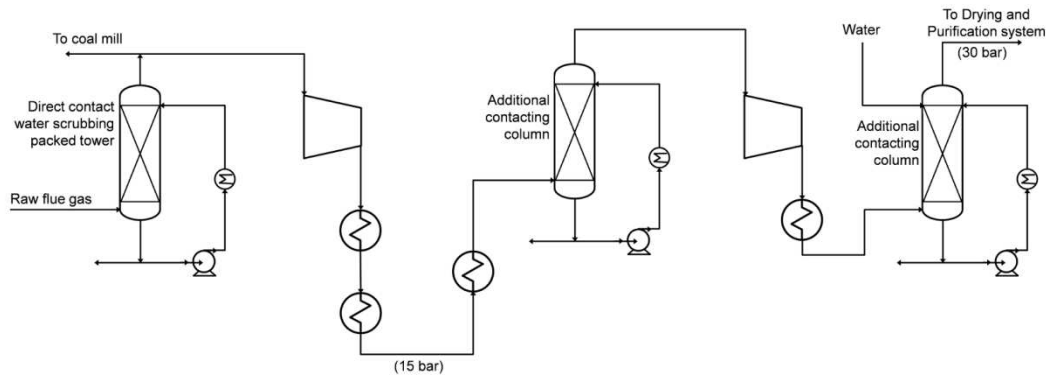
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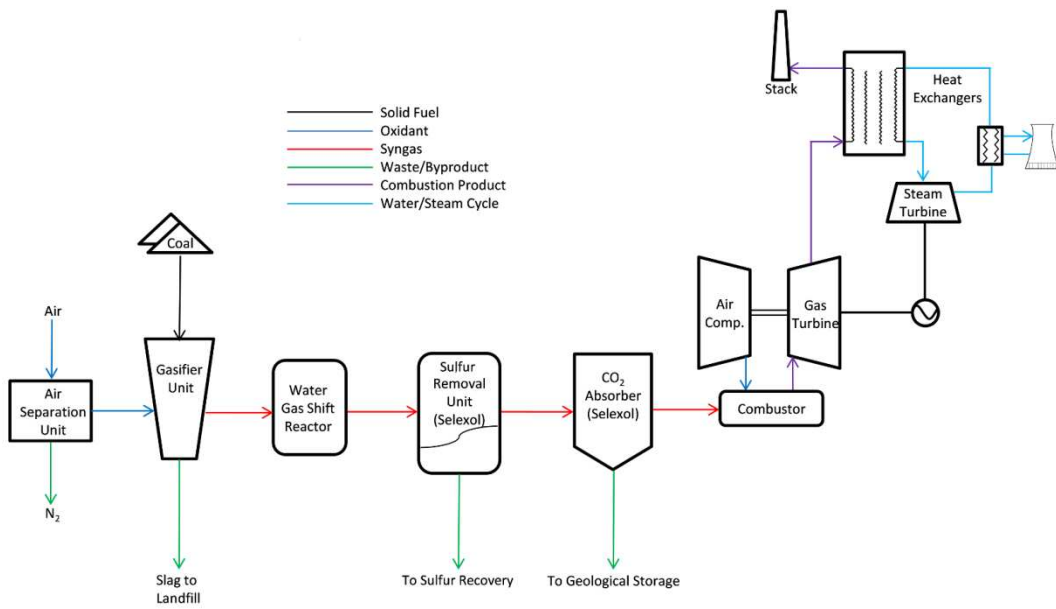
Figure 7
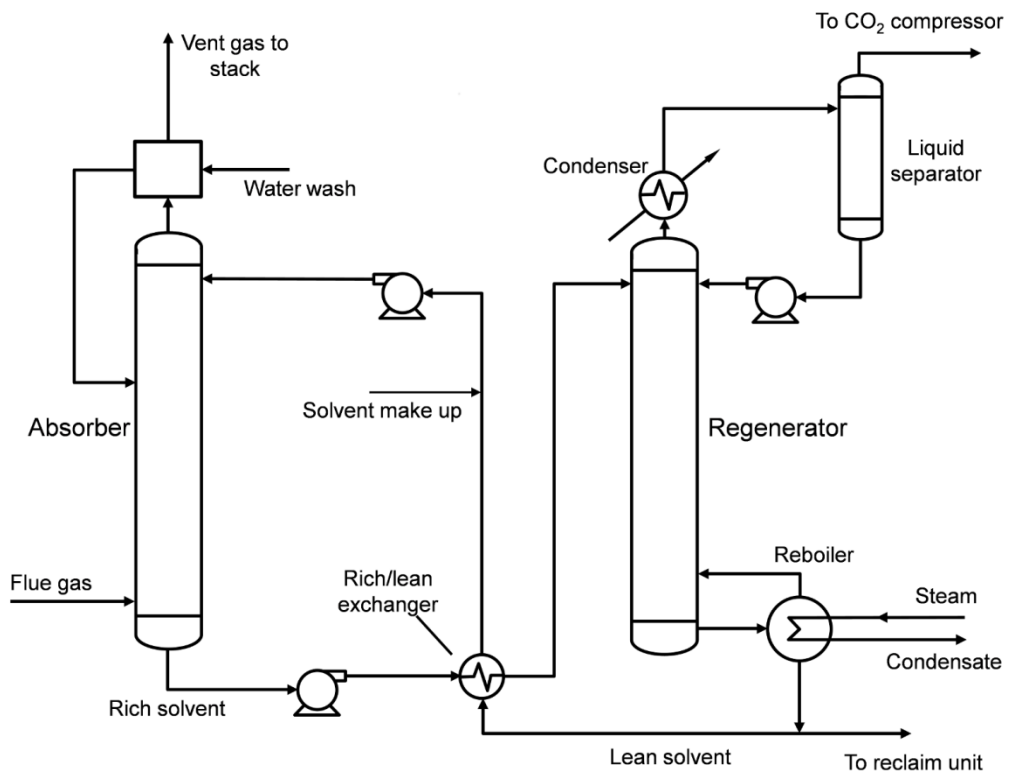
Table 1

Coal/biomass oxidation products	
Complete	**Partial**
H_2O, SO_x, NO_x, HCl, HF	CO, H_2S, COS, NH_3, HCN
Volatiles	**Biomass alkali metals**
H_2, CH_4, C_2H_6, C_3+	KCl, NaCl, K_2SO_4, KOH etc.
Trace metals	**Particulates**
Hg ($HgCl_2$), Pb, Se, As etc.	Ash, PAH/soot
Oxidant / air ingress	**Process fluids**
O_2, N_2, Ar	Glycol, MEA, Selexol, NH_3 etc.

Table 2

	Raw Flue Gas 35 ºC, 1.02 bar mol %	CO_2 Product 35 ºC, 110 bar mol %
CO_2	71.5	95.8
N_2	14.3	2.0
O_2	5.9	1.1
Ar	2.3	0.6
SO_2	0.4	0.5
NO	0.04	0.01
H_2O	5.6	0.0

Table 3

	Raw / dehumidified			Double flashing			Distillation		
	[a]	[b]	[c]	[d]	[e]*	[c]	[6]	[f]	[g]
CO_2 % v/v	85.0	77.19	74.8	95.84	96.3	96.7	99.94	99.3	> 99.95
O_2 % v/v	4.70	3.21	6.0	1.05	1.1	1.2	0.01	0.4	< 30 ppm
N_2 % v/v	5.80	15.49	16.6	2.03	2.0	1.6	0.01	0.2	Trace
Ar % v/v	4.47	4.03	2.3	0.61	0.6	0.4	0.01	0.1	Trace
NO_x ppm	100	-	709	130	0	150	100	33	< 5
SO_2 ppm	50	800	702	4500	0	36	50	37	< 0.1
SO_3 ppm	20	-	-	-	-	-	20	-	
H_2O ppm	100	0	1000	0	0	0	100	0	< 20
CO ppm	50	-	-	-	-	-	50	-	< 10

Table 4

	Downstream ESP	Downstream FGD	Downstream FGC	Linde Final Product	Air Products High Purity Final Product
	[h]	[h]	[h]	[i]	[j]
CO_2	64 % v/v	63 % v/v	87 % v/v	> 99.9 % v/v	99.9+
N_2, Ar	~ 3 % v/v	~ 3 % v/v	~ 4 % v/v	< 0.01 % v/v	207 ppm
H_2O (g)	~ 29 % v/v	~ 31 % v/v	~ 4 % v/v	< 5 ppmv	-
O_2	~ 3.5 % v/v	~ 3 % v/v	< 5 % v/v	< 0.001 % v/v	167 ppm
SO_2	~ 8000 mg/m^3	< 200 mg/m^3	< 100 mg/m^3	< 1 ppmv	-
SO_3	not reported	not reported	not known	< 0.3 ppmv	-
CO	< 200 mg m^{-3}	< 200 mg m^{-3}	< 200 mg m^{-3}	< 2 ppmv	-
NO_x	< 700 mg m^{-3}	< 700 mg m^{-3}	< 700 mg m^{-3}	3-10 ppmv	-
Temperature	443 – 463 K	343 K	303 K	not known	-

Table 5

	[6] ‡	[7] Selexol	[8] Rectisol®	[9] SEWGS*	[10, 11-14] †
CO_2 % v/v	98	98.1	95-98.5	> 99	
N_2 % v/v	$\leq$ 0.9	0.0195	< 1	< 1	0.0195
H_2 % v/v	$\leq$ 1	1.5	0.002	< 1	2.4
Ar ppmv	$\leq$ 300	178	150	< 1	1000
H_2O ppmv	10 – 600	378	0.1 – 10	500	5.07
H_2S/COS ppmv	$\leq$ 100	1700	0.2 – 20	1 – 5000	5968
CH_4 ppmv	100	112	100	< 1	
CO ppmv	400	1300	400	< 1	1667
CH_3OH ppmv	200	-	20 – 200		
Ash ppm		1.2			
NH_3 ppmv		38			
Cl ppmv		17.5			
Hg ppbv		0.068			1.1
As ppmv		0.0033			0.01
Se ppmv		0.01			0.017
NO ppmv					400
SO_2 ppmv					25
Ni ppmv					0.009
Pb ppmv					0.0045
Benzene ppmv					0.014
Napthalene ppmv					0.0008

Table 6

	[6] Amine PC plant	[7] MEA PC plant	[10, 11-14] French CO_2 Club †
CO_2 % v/v	99.8	99.7	N.I.
N_2 % v/v	0.045 (+Ar)	0.18	N.I.
CO ppmv			10
Ar ppmv		22	210
H_2O ppmv	100	640	N.I.
NO_x ppmv	20	1.5 (NO_2)	38.8
SO_x ppmv	10	< 1 (SO_2)	67.1 (SO_2)
CO ppmv	10		10
O_2 ppmv	150	61	N.I.
Cl ppmv		0.85	
Ash ppm		11.5	
Hg ppmv		0.00069	0.0028
As ppmv		0.0055	0.0022
Se ppmv		0.017	0.0122
Mn ppmv			0.0309
Ni ppmv			0.002
Pb ppmv			0.0011
Benzene ppmv			0.019
Napthalene ppmv			0.0012

Table 7

	[7] MEA Refinery Stack	[7] MEA Cement Plant	[15] Cement Kiln	[15] Coke Production	[15] Lime Production
CO_2 % v/v	99.6	99.8	99.00	99.4	99.52
N_2 % v/v	0.29	0.0893			
CO ppmv	1.2	1.2	1620	701	2000
Ar ppmv	11	11			
H_2O ppmv	640	640			
NO_x ppmv	2.5 (NO_2)	0.86 (NO_2)	3330	1690	1100
SO_x ppmv	1.3 (SO_2)	< 0.1 (SO_2)	4410	3030	1800
CO ppmv	1.2	1.2			
O_2 ppmv	35	35			
CH_4 ppmv				206	
Cl ppmv	0.41	0.41	65.7	26.8	
Ash ppm	-	5.7			
Hg ppmv		0.00073	0.1		
As ppmv	0.29	0.0029			
Se ppmv	1.2	0.0088			
VOC ppmv				96.9	
TOC ppmv			81		

Table 8

	Oxyfuel Combustion			Pre-combustion	Post-combustion
	Raw / dehumidified	Double flashing	Distillation		
CO_2 % v/v	74.8-85.0	95.84-96.7	99.3-99.4	95-99	99.6 – 99.8
O_2 % v/v	3.21-6.0	1.05-1.2	0.01-0.4	0	0.015 – 0.0035
N_2 % v/v	5.80-16.6	1.6-2.03	0.01-0.2	0.0195 – 1	0.045 - 0.29
Ar % v/v	2.3-4.47	0.4-0.61	0.01-0.1	0.0001-0.15	0.0011 – 0.021
NO_x ppmv	100-709	0-150	33-100	400	20 - 38.8
SO_2 ppmv	50-800	0-4500	37-50	25	0 - 67.1
SO_3 ppmv	20	-	20	-	N.I.
H_2O ppmv	100-1000	0	0-100	0.1 - 600	100 – 640
CO ppmv	50	-	50	0 - 2000	1.2 - 10
H_2S/COS ppmv				0.2 - 34000	
H_2 ppmv				20-30000	
CH_4 ppmv				0-112	