APPLICATION NOTE

INDUSTRIAL PROCESS & EMISSIONS

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PROCESS: CARBON CAPTURE AND STORAGE

INTRODUCTION

Carbon Capture and Storage (CCS) technologies aim to capture carbon dioxide (CO_2) emissions from power plants and heavy industry before transporting it by pipeline or ship and storing it underground in, for example, empty oil and gas fields. The driver behind this method is to reduce the mass of CO_2 that enters the atmosphere and contributes to global warming and ocean acidification. The technology can be used in energy production facilities, and other industrial processes, wherever large CO_2 quantities are produced. Different CCS technologies allow retrofitting to existing plants and integrating in new plants.

Carbon Capture and Usage (CCU) aims to use the captured CO_2 emissions as a source for manufacturing of fuels, carbonates, polymers and other chemicals, and contribute to a circular economy. In general, CCU is less advanced in the industrial application than CCS and requires continuing research and development. That said, CCU is already used on an industrial scale in the European Union (EU) in the fertilizer industry for the production of melamine and urea-based glues and resins, with around 1.8 Mtpa (millions of tonnes per annum) of CO_2 captured from steam methane reforming (SMR) during the ammonia (NH_3) production [Fertilizers Europe/ European Gas Regulatory Forum, 2019]. CCU is also used in the production of calcium carbonate, where CO_2 reacts with NH_3 to produce lime which can be mixed with calcium nitrate to produce calcium ammonium nitrate, a popular nitrogen fertilizer used in the EU.

Due to the CO_2 emissions exceeding the current expectations of CO_2 usage market development, CCU is considered a complementary alternative to CCS only. Depending on the source the expected market potential is approximately 200 $MtCO_2$/y for CO_2 utilisation [Aresta et al. 2013] and approximately 14,000 $MtCO_2$/y emission [Boot-Handford et al. 2014]. The technology is currently still in the development stage, but pilot projects are already in effect, and more are planned over the next decade. Depending on the literature source the expectation is to capture up to 85-90% of CO_2 emissions. Currently, multiple sites are already active or planned within the EU (Figure 1) and worldwide. To meet climate neutral ambitions, CCS and CCU efforts will be increased significantly over the next few years.

USEFUL LINKS

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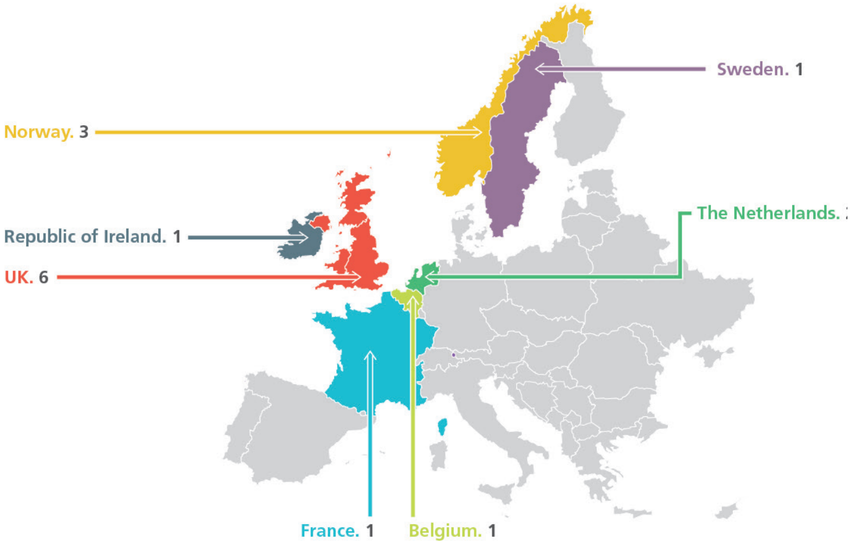


Figure 1. Active/planned CCS projects in Europe

CCS and CCU can be further broken down by the method and placement of the capture technology. Figure 2 is a diagram representing a summary of the following CCS and CCU applications. Figures 3-5 show these methods in more detail.

Post-Combustion Capture

CO_2 can be captured from the flue gas of a combustion process. This can be flue gas coming from any (pressurized) combustion in a boiler, gas turbine or industrial process yielding CO_2. In many cases, the flue gas is first cleaned, with trace components like sulfur dioxide (SO_2) and hydrogen chloride (HCl) being removed to prevent malfunctioning of the capture process. Various capture mechanisms, or combinations of them, can be applied, including phase separation, selective permeability and sorption. The latter mechanism, sorption, is the most widely utilized mechanism at large point sources. This mechanism encompasses chemical or physical absorption and adsorption. In the CO_2 capture processes based on this mechanism, a sorption medium, or a sorbent, is used. When these sorbents are in solution, they are called solvents. The current research, development and demonstration focus is on using chemical and physical solvents to separate the CO_2 from the gas stream. Retrofitting existing plants with CO_2 capture will likely be done with a chemical absorption based post-combustion capture technology. After CO_2 is captured from the flue gas, the inert gases, for example nitrogen (N_2), oxygen (O_2) and argon (Ar) in the flue gas are vented to atmosphere. Traces of CO_2 will be present in the vented gas due to the efficiency of the capture process being less than 100%.

The research, design and development (RD&D) focus in post-combustion capture is aimed at reducing energy requirement and capital cost through developing and adapting solvents, optimizing the required process installations and integrating the capture system within the process. The application of the capture process on contaminated flue gases, for example flue gases from coal fired power plants, is already commercially applied (Strazisar, Anderson et al. 2003). However, large-scale CO_2 capture, as well as dealing with the contaminants in the flue gas, remains a challenge.

Pre-Combustion Capture

Pre-combustion capture comprises a group of technologies that removes CO_2 before the combustion of the fuel. This requires a carbonaceous fuel to be broken down into hydrogen (H_2) and carbon monoxide (CO), i.e. syngas. To make CO_2 capture with high efficiencies possible, the syngas that is formed after steam reforming or partial oxidation/gasification has to be 'shifted' after it is cleaned. The 'shift reaction', or 'water gas shift' (WGS) reaction, yields heat and a gas stream with high CO_2 and H_2 concentrations. The CO_2 can then be removed with chemical and physical solvents, adsorbents and membranes. CO_2 traces can be present in the H_2 stream.

For the near-term it is expected that chemical or physical solvents (or a combination) are used for the CO_2 removal. The CO_2 removal step yields relative pure CO_2 and a gas stream with a high H_2 and low carbon content. The latter can be used for power production in, for example, a (modified) gas turbine. The gas with reduced carbon content can, after further purification, also be used in the production of synfuels, the refining of hydrocarbons, or to produce chemicals (IPCC 2005).

For solid and liquid fuels, pre-combustion CO_2 capture can be applied in an IGCC (Integrated Gasification Combined Cycle) power plant. For gas fired power generation with pre-combustion capture other concepts are being studied (Ertesvag, Kvamsdal et al. 2005; Kvamsdal and Mejdell 2005; IEA GHG 2006c; Kvamsdal, Jordal et al. 2007).

The technology to capture CO_2 from the syngas generated in a gasifier can be considered proven technology, is commercially available and has been used for several decades in other applications than for electricity production. Examples include H_2, NH_3 and synthetic fuel production (Nexant Inc. 2006). Also, reforming and partial oxidation of (natural) gas are already widely applied, for example in the production of H_2 in the NH_3 production process.

The pre-combustion concept has not yet been proven in an IGCC power plant. Proving its reliability and effectiveness in power plant concepts is therefore one of the main RD&D targets. In addition, improving the efficiency of the WGS step and integration of this process with CO_2 capture is also an area of research.

Oxyfuel Combustion

Oxyfuel combustion is based on denitrification of the combustion medium. The nitrogen is removed from the air through a cryogenic air separation unit (ASU) or with the use of membranes. Combustion thus takes place with nearly pure oxygen. The result is a flue gas containing mainly CO_2 and water. Trace components like oxides of nitrogen (NOx) and SO_2 can be present. The CO_2 is purified by removing water and impurities. The remaining small amounts of N_2, O_2 and Ar are vented off, but can contain traces of CO_2. The production of O_2 requires a significant amount of energy, which results in a reduction of the efficiency of the power plant. Further, the purification and the compression of the CO_2 stream also requires energy.

The combustion with O_2 is currently applied in the glass and metallurgical industry (Buhre, Elliott et al. 2005; IPCC 2005; M. Anheden, Jinying Yan et al. 2005). Oxyfuel combustion for steam and power production using solid fuels has been at present only proven in test and pilot facilities. Oxyfuel combustion can also be applied in natural gas fired concepts. Power cycles for gaseous and solid fuels, however, vary significantly.

Although there are no significant differences compared to air firing of solid fuels, the combustion process and optimal configuration of the burners are considered to be the most important hurdles to overcome. In addition, the design and configuration of the flue gas cleaning section and CO_2 purification section are challenges for the short-term. For the gas fired concepts, system integration and development of critical components hinder direct application on a commercial scale. Examples of critical components are the turbines and combustors for the near- and medium-term options and, additionally, the fuel reactors for the concepts in the longer term.

Capture from Industrial Process

This group of technologies is often mentioned as the early opportunity for CCS at relative low cost. The total reduction potential due to CO_2 capture from these point sources is, however, considered to be rather limited. Examples for industrial processes include the production of cement, iron and steel, ethylene (oxide), NH_3 and H_2. In addition, CO_2 can be captured from natural gas sweetening processes and from refineries (IPCC 2005). The capture processes applied are, in general, the same technologies as already described above.

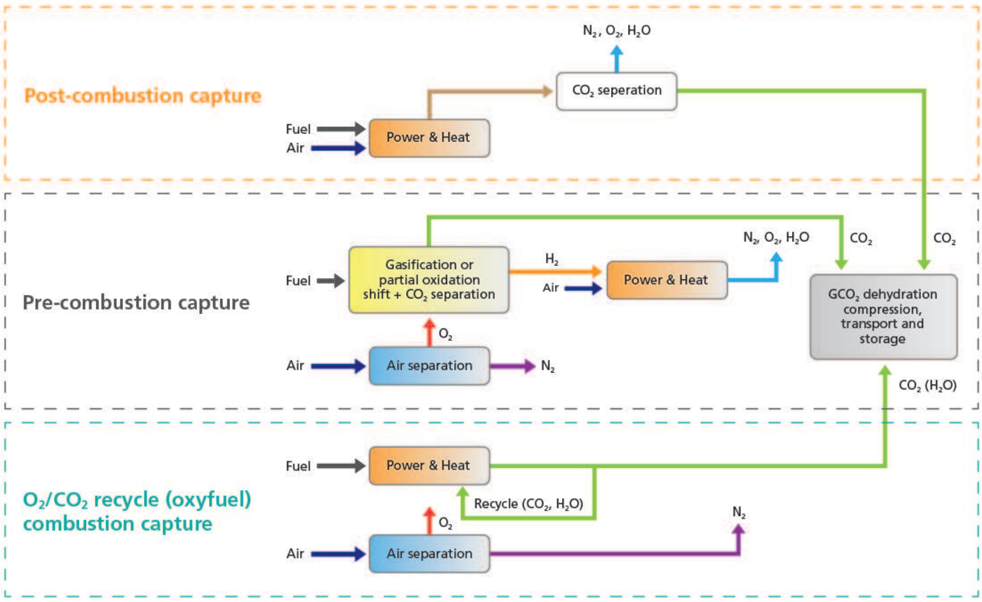
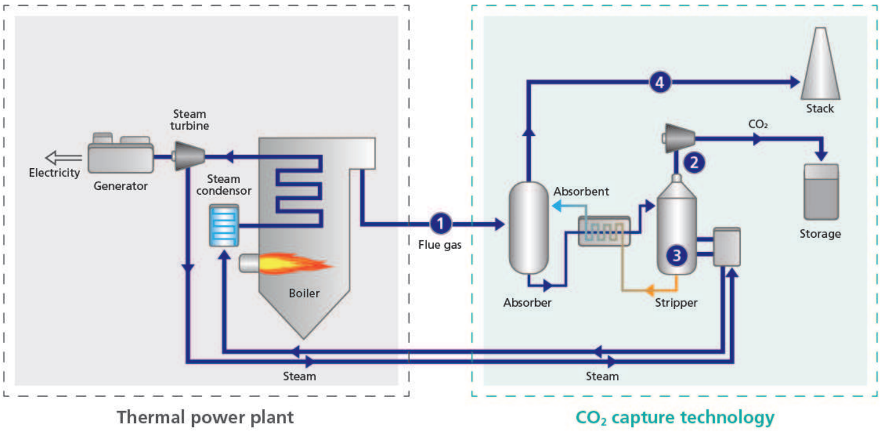


Figure 2. Schematic of the three main principles of CO_2 capture technology



Combustion control as usual in an (unmodified) power plant.

1. Fluegas (SO_2, NOx, H_2O, O_2, CO, CO_2)
    - Potentially SOx stripper/NH_3
2. CO_2 stream to storage via compressor (H_2O, CO_2)
3. Lean amine stream (CO_2 slip)
4. Fluegas to atmosphere (CO_2, SO_2, NOx, O_2, amine/THC)

Figure 3. Post-combustion CCS – measurement points

Typically operated with Integrated Gas Combined Cycles (IGCC). Up to CO_2 capture similar to SMR.

1. CO_2 Stripper – Lean absorbent stream (CO_2 slip)
2. CO_2 Stream to storage via compressor (CO_2, H_2O)
3. H_2 rich fuel gas to gas turbine (or fuel cell)
4. Fluegas to atmosphere (O_2, N_2, H_2O, NOx)

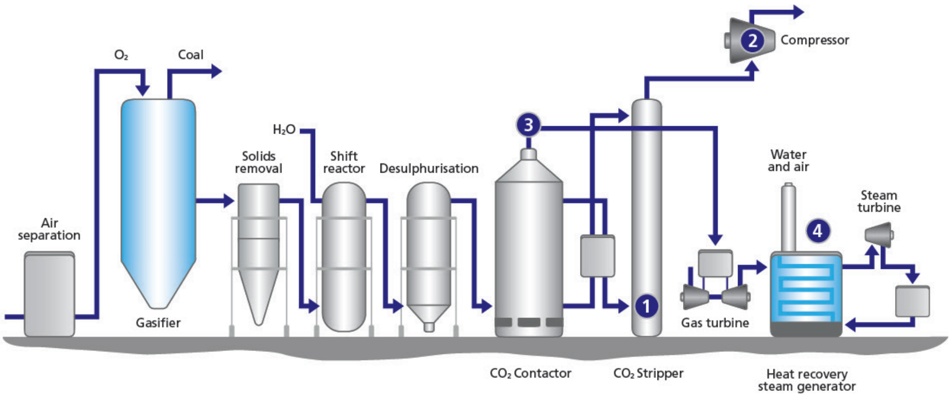
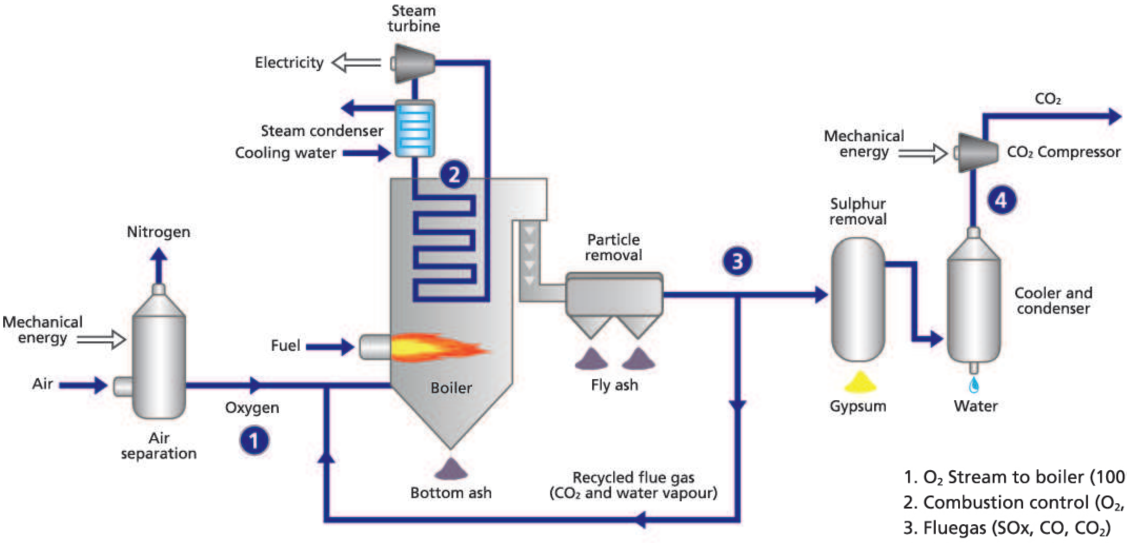


Figure 4. Pre-combustion CCS – measurement points



1. O_2 Stream to boiler (100%)
2. Combustion control (O_2, CO)
3. Fluegas (SOx, CO, CO_2)
4. CO_2 stream outlet cooler/condenser (H_2O, CO_2)

Figure 5. Oxyfuel-combustion CCS – measurement points

PROCESS MEASURING POINTS

Figures 3–5 show the position of typical measuring points in the CCS process, excluding the process control points on SMR/power plant the CO_2 is derived from. Tables 1-3 below list the respective gas analysis requirements together with the typical ranges and Servomex analyzers suited for each measurement. At present, the reported capture efficiency of the above-mentioned capture processes range from 95 to >99%. This means up to 5% of the CO_2 is still vented to the atmosphere at the capture installation, either through direct emission to the atmosphere or through indirect emissions from degassing of the water from the dehydration step at compression.

Installation location	Gas Measured	Measuring Range	Application	Servomex Analyzer
Flue gas from power plant	CO_2 CO NOx O_2 SO_2 H_2O	20% 500/3,000 ppm 500/3,000 ppm 25% 100/2,000 ppm (1) 30%	Emissions	SERVOPRO 4900 Multigas SERVOTOUGH SpectraExact 2500
CO_2 stream capturing/product	CO_2 SO_2 H_2O	100% (2) 100 ppm 70 ppm	Quality	SERVOTOUGH SpectraExact 2500 SERVOPRO DF745SG SERVOPRO MultiExact 4100 (3) SERVOPRO AquaXact 1688
Lean absorbent stream from CO_2 stripper	CO_2 (slip)	1%/10%	Process control	SERVOTOUGH SpectraExact 2500 SERVOPRO MultiExact 4100
Pipeline/temporary storage	CO_2 H_2S H_2O O_2 NH_3	4% (4) 100 ppm 70 ppm 21% 10 ppm	Safety	SERVOTOUGH SpectraExact 2500 SERVOPRO MultiExact 4100 SERVOPRO DF-745SG SERVOPRO AquaXact 1688
Flue gas to stack	CO_2 CO NOx O_2 SO_2	5% (5) 100/1,000 ppm 500 ppm 25% 100/2,000 ppm	Emissions	SERVOPRO 4900 Multigas
CO_2 Storage	CO_2 O_2	4% (4) 21%	Safety	SERVOTOUGH Oxy 1900 SERVOTOUGH SpectraExact 2500 SERVOPRO MultiExact 4100

(1) To increase efficiency of CO_2 absorbent desulfurisation can be used. Range 0-2,000 ppm SO_2 at inlet, range 0-100 ppm SO_2 at outlet.

(2) Uncertainty <1.5% as per MRG (EU, 2010), Annex I or <2.5% for transferred CO_2 from the capture installation MRG (EU, 2010), Annex XVI.

(3) ME4100, DF only if area classified as safe area.

(4) OSHA PEL 0.5% CO_2 and permanent damage expected >4%. Storage Directive (EU, 2009), monitoring if CO_2 leakage is damaging the environment or human health. MRG (EU, 2010), Annex XVI, uncertainty <2.5% for transferred CO_2 from the capture installation, in the transport network and to the storage site. Servomex can only offer measurement of decompressed CO_2 (gaseous).

(5) CO_2 concentration in vented (flue) gases in post-combustion capture processes.

Table 1. Post combustion measurement points

Installation location	Gas Measured	Measuring Range	Application	Servomex Analyzer
Flue gas to stack	CO_2 NOx O_2 SO_2	5/10% 500 ppm 25% 100/2,000 ppm	Emissions	SERVOPRO 4900 Multigas
CO_2 stream to storage (product)	CO_2 H_2S CO SO_2	100% (3) 1-2% (1) 300-4,000 ppm (1) 100 ppm	Quality	SERVOTOUGH SpectraExact 2500 SERVOPRO AquaXact 1688
Pipeline/temporary storage	CO_2 H_2S H_2O O_2	4% (2) 100 ppm 70 ppm 21%	Safety	SERVOTOUGH SpectraExact 2500 SERVOPRO MultiExact 4100
CO_2 Storage	CO_2 O_2	4% (2) 21%	Safety	SERVOTOUGH Oxy 1900 SERVOTOUGH SpectraExact 2500 SERVOPRO MultiExact 4100

(1) Pre-combustion carbon capture only.

(2) OSHA PEL 0.5% CO_2 and permanent damage expected >4%. Storage Directive (EU, 2009), monitoring if CO_2 leakage is damaging the environment or human health. MRG (EU, 2010), Annex XVI, uncertainty <2.5% for transferred CO_2 from the capture installation, in the transport network and to the storage site. Servomex can only offer measurement of decompressed CO_2 (gaseous).

(3) Uncertainty <1.5% as per MRG (EU, 2010), Annex I or <2.5% for transferred CO_2 from the capture installation MRG (EU, 2010), Annex XVI.

Table 2. Pre combustion measurement points

Installation location	Gas Measured	Measuring Range	Application	Servomex Analyzer
O_2 stream (ASU)	O_2	100%	Quality	SERVOTOUGH OxyExact 2200 SERVOPRO MultiExact 4100
Combustion control	CO O_2	1,000 ppm 50%	Process Control	SERVOTOUGH Laser 3 Plus (1), SERVOTOUGH FluegasExact 2700 (modified)
Flue gas	CO_2 CO NOx O_2 SO_2	80% 500/3,000 ppm 500 ppm 25% 100/2,000 ppm	Process Control	SERVOPRO 4900 Multigas
CO_2 stream outlet cooler (product)	CO_2 SO_2 H_2O O_2	100% (4) 100 ppm 70 ppm 5% (2)	Quality	SERVOTOUGH SpectraExact 2500 SERVOPRO DF-745SGMax SERVOPRO AquaXact 1688
Pipeline/temporary storage	CO_2 H_2S H_2O O_2 NH_3	4% (3) 100 ppm 70 ppm 21% 10 ppm	Safety	SERVOTOUGH SpectraExact 2500 SERVOPRO MultiExact 4100 SERVOPRO DF-745SGMax SERVOPRO AquaXact 1688
CO_2 Storage	CO_2 O_2	4% (3) 21%	Safety	SERVOTOUGH Oxy 1900 SERVOTOUGH SpectraExact 2500 SERVOPRO MultiExact 4100

(1) Control of O_2 >21% for Oxyfuel combustion is currently not available in-situ Laser 3 Plus.

(2) 3.7-4.1% N_2/Ar/O_2 in Oxyfuel derived dried CO_2

(3) OSHA PEL 0.5% CO_2 and permanent damage expected >4%. Storage Directive (EU, 2009), monitoring if CO_2 leakage is damaging the environment or human health. MRG (EU, 2010), Annex XVI, uncertainty <2.5% for transferred CO_2 from the capture installation, in the transport network and to the storage site. Servomex can only offer measurement of decompressed CO_2 (gaseous).

(4) Uncertainty <1.5% as per MRG (EU, 2010), Annex I or <2.5% for transferred CO_2 from the capture installation MRG (EU, 2010), Annex XVI.

Table 3. Oxyfuel combustion measurement points

APPLICATION Emissions

Incomplete combustion leads to higher carbon monoxide (CO) production, excessive particulate matter or smoke (measured as opacity), sulfur dioxide (SO_2) and oxides of nitrogen (NOx) when excess O_2 is present. These gases are detrimental to the environment and are regulated worldwide but to different levels in each country. Continuous emissions monitoring systems (CEMS) are generally required by most regulatory bodies as they attempt to rein in pollution emitted from power plants, both public and private. While every region applies their own rules for how the analyzers must function, which gases and levels must be monitored and how the data needs to be reported, most need to continuously monitor O_2 for reference and the pollutants SO_2 and NOx. CO, CO_2, and particulate matter (PM) may also be included depending on local requirements.

SERVOMEX SOLUTION

4900 Multigas

The 4900 Multigas analyzer is used to analyze SO_2, NOx, CO, CO_2 and O_2 in the stack prior to the flue gas emitting to the atmosphere. The 4900 Multigas is a multicomponent extractive analyser that can measure up to 4 components in a single chassis, so generally only one analyzer is needed for most CEMS gas analysis requirements. The analyzer requires a clean dry sample hence, a sample conditioning system is required which can be supplied by Servomex. The CEMS system typically consists of a sample probe, heated filter unit, heated sample line, pump and chiller with the sample flow control to match each analyser's requirement. If NOx is required, a NOx converter can be supplied which converts the nitrogen dioxide (NO_2) in the flue gas to nitric oxide (NO), thus enabling the 4900 Multigas to measure total NOx. Other components can also be added to the Servomex CEMS system package as required, such as flow monitors, dust monitors, and data loggers. The data logger is required to log and report the CEMS analysis in accordance with the local legislative requirements.

APPLICATION Quality

Because captured CO_2 is a useful product for the manufacturing of fuels, carbonates, polymers and other chemicals, its quality post capture requires close monitoring. If captured from a process such as coal-fired power generation, the captured CO_2 can contain traces of contaminants like sulfur dioxide (SO_2) and hydrogen sulfide (H_2S).

The measurement is made after CO_2 is captured in the stack, or after the methyl diethanolamine (MDEA) outlet, pre-transport to the CO_2 user.

SERVOMEX SOLUTION

SpectraExact 2500

MultiExact 4100

MonoExact DF310E

The SpectraExact 2500, in combination with a back pressure regulator, offers an accuracy of +/-0.2% between the range of 80-100% CO_2. Depending on the required accuracy, impurities of CO and SO_2 and, depending on range, H_2O could be offered.

Trace CO_2 and O_2 is available in the MultiExact 4100, with trace SO_2 currently offered in the 4900 Multigas.

For both the SpectraExact 2500 and MultiExact 4100 / 4900 Multigas, it will be necessary to compensate for any CO_2 in the background. Trace O_2 and lower traces of H_2O can also be offered with the SERVOPRO MonoExact DF310E and SERVOPRO DF-700 Series. Note, the DF series, as well as the 4000 series, can currently only be installed in safe area. All mentioned analyzers require a suitable sampling system which conditions the sample to analyzer requirements.

APPLICATION Safety

Monitoring traces of H_2S and H_2O in pipelines is required to avoid sweet and sour corrosion. Further, monitoring of CO_2 and O_2 in ambient air for safety of personnel in enclosed spaces around the pipeline/storage and to detect leakage is required.

SERVOMEX SOLUTION

DF-745SGMax

Currently, Servomex can offer a safe area solution for trace H_2O measurement in CO_2 with the DF-745SGMax. The trace level tuneable diode laser (TDL) provides high stability measurements through minimal moisture contact with optical elements. Detection range of 0-100 ppm with an accuracy +/-5% of reading or +/-5 ppb (whichever is greater). Factory calibrated, the zero-drift performance delivered by the high stability TDL requires no ongoing calibration, while the non-depleting sensor technology never needs replacing. In closed environments which allow sampling, the Oxy 1900 (paramagnetic) for O_2 and SpectraExact 2500 (infrared) for CO_2 can be used for hazardous area installation. The SpectraExact 2500 offers an accuracy of +/-1%of the scale for the measurement of CO_2. The Oxy 1900 offers a measurement range of 0-25% O_2 with an accuracy of +/-0.05% O_2 or better.

In closed environments which allow sampling and are rated as general-purpose area, the MultiExact 4100 can be used for O_2 and CO_2 measurement. Suitable sampling systems which condition the sample to analyzer requirements are needed. The measurement ranges for monitoring CO_2 storage/network for leakage should be selected in compliance with OSHA recommendation considering damage to environment or human health.

APPLICATION Combustion Control (Oxyfuel)

The oxyfuel reaction relies on the oxidation of fuel with near pure O_2 rather than the traditional combustion air. The use of pure O_2 means no N_2 is introduced to the process to form NOx, and thus this is a good strategy for reducing emissions, aside from the fact it can be expensive and more of a safety hazard. Fuel and O_2 are fed into the boiler/furnace/heater where combustion takes place as normal. Because the combustion process is not perfect, excess O_2 is required to ensure that there is complete combustion, however, too much will reduce the combustion efficiency due to increased heat loss to the atmosphere. Conversely if there is too little O_2 the combustion efficiency will fall dramatically since the fuel is not being completely burnt and not all the energy is being released. This will also result in an even greater environmental impact as CO and other hydrocarbons will also be emitted, thus the importance for optimization of the excess air at the minimum level required for complete combustion, ensuring that combustion efficiency is optimized and emissions are minimized. Due to changes in output demand, aging equipment, varying fuel composition, atmospheric conditions and process conditions, this optimum operating point varies. By continuously monitoring the amount of oxygen and combustibles in the flue gas, prompt adjustments can be made to the boiler control system to maintain peak efficiency.

SERVOMEX SOLUTION

FluegasExact 2700

Traditional zirconia technology cannot often be utilized for oxyfuel excess O_2 measurement, as the technology can typically only measure up to 21% O_2. This is due to the fundamentals of how the technology operates (with the reference side of the zirconia being exposed to ambient air containing 21% O_2. When the sample side and reference side are equal at 21% O_2, the sensor output is zero).

The SERVOTOUGH FluegasExact 2700 flue gas analyzer, however, can be modified using special software to operate at a range of 0-50% O_2, even with the zirconia reference being exposed to ambient air. There is little to no detriment to analyzer performance and safety concerns are addressed by the analyzers integral and standard flame traps that protect all routes back to process.

The FluegasExact 2700 can monitor both O_2 and combustibles (COe). O_2 is measured using zirconium oxide sensor technology. A thick film catalytic sensor optimized for CO is used to detect ppm levels of combustibles and monitor breakthrough, the point the process runs out of O_2 available to fully burn the fuel, thus producing high levels of CO. To enable preventative maintenance, an optional flow sensor is available that monitors the flow up the analyzer's probe and through the sensors. These sensors are housed in a sensor head mounted on the process wall to which a sample is aspirated via a sample probe.

WE’RE READY TO HELP

WHATEVER YOUR GAS ANALYSIS REQUIREMENTS, WHEREVER YOU ARE

These analyzers are not intended for any form of use on humans and are not medical devices as described in the Medical Devices Directive 93/42EEC.

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