Evaluating technology options to mitigate greenhouse gas emissions

IEAGHG Technical Review

2017-TR3

March 2017

Reference data and Supporting Literature Reviews for SMR Based Hydrogen Production with CCS

IEA GREENHOUSE GAS R&D PROGRAMME

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The IEA Greenhouse Gas R&D Programme has recently published two reports covering the topic of CCS in SMR based hydrogen manufacture.

The first published study in the sequence was:

IEAGHG Report 2017-02 – Techno-Economic Evaluation of Deploying CCS in Standalone (Merchant) SMR Based Hydrogen Plant using Natural Gas as Feedstock/Fuel, February 2017.

Hydrogen is a key raw material to other energy intensive industries. Globally, nearly 90% of the hydrogen produced industrially is consumed by the ammonia, methanol and oil refining industries. In the future, hydrogen could play an important role in the decarbonisation of space heating (i.e. industrial, commercial, building and residential heating) and transport fuel (i.e. use of fuel cell vehicles).

Currently, the steam methane reformer (SMR) is the leading technology for H_2 production from natural gas or light hydrocarbons. Modern SMR based hydrogen production facilities have achieved efficiencies that could reduce CO_2 emissions down to nearly 10% above its theoretical minimum. Further reduction of CO_2 emissions from hydrogen production would only be possible by the integration of CCS.

This study has provided an up-to-date assessment of the performance and costs of a modern SMR based H_2 plant with and without CCS producing 100,000 Nm3/h H_2 and operating as a merchant plant (i.e. standalone plant - without any integration to an industrial complex).
The study presented the economics of deploying CCS in an SMR based hydrogen plant capturing CO_2 from the (a.) shifted syngas, (b.) PSA's tail gas or (c.) SMR's flue gas. Each capture option was evaluated using IEAHG's standard assessment criteria against a Base Case (i.e. H2 plant without CCS).

Unlike other studies in the series, the capture of CO_2 from an SMR plant is a commercial operation. This is one of the main sources of industrial and food grade CO_2 in the market globally. However, only 3 sites around the world have demonstrated the integration of CO_2 capture with CO_2 transport and storage. These include (a.) the Port Arthur Project in the USA, (b.) the Quest Project in Canada, and (c.) the Tomakomai Project in Japan.

The second study was:

IEAGHG Report 2017/03 Techno-Economics of Deploying CCS in a Natural Gas Based Production of Methanol and Ammonia/Urea, February 2017

Ammonia/urea and methanol production are the pillars of the basic chemicals industry worldwide. Ammonia/urea is an important commodity used in the agriculture (fertiliser) and food industry. Whilst methanol is an important feedstock in production of various chemicals and fuel used in our daily lives. Globally (except for China), these commodities are mainly produced from NG or light hydrocarbons.

It should also be noted that both urea and methanol production (combined) are the largest users of CO_2 second only to CO2-EOR, globally.

The study presented a detailed baseline information of the performance and cost of deploying CO_2 capture in a SMR Based HyCO plant using natural gas as feedstock / fuel and operating as a captive plant (i.e. integrated within an industrial complex) with an aim to evaluate the cost of capturing additional CO_2 from the SMR's flue gas.

As background to these two published study the contractor AmecFosterWheeler undertook three technical reviews which provided both key reference data and supporting information for technology decisions made for the two main published studies.

The 3 Technical Reviews are combined in this report as reference material for members and others reading the main reports.

The technical Reviews undertaken were:

1. A review of the **Current State-of-the-Art Technologies for Hydrogen Production.** Presented as Annex 1 of this Technical Review document

   The aim of the review was to highlight the key features of the different hydrogen production processes commercially deployed worldwide. In particular, the different process characteristics, plant performance, points of CO_2 emission and relative CO_2 concentration of the leading hydrogen production technologies are presented.

2. A review of **Technologies for CO_2 Capture from Hydrogen Production Unit's.** Presented as Annex 2 of this Technical Review document.

   The aim of this review was to provide a general overview of the state-of-the-art of technologies that are commercially available for capturing the carbon dioxide (CO_2), mainly in connection with hydrogen production.

3. A Review of **Ongoing Major Demonstration Projects for CO_2 Capture from Hydrogen Production Unit's.** Presented as Annex 3 of this Technical Review document.

   The purpose of this technical review is to provide an overview of the major on-going Demonstration CCS projects applied to SMR Hydrogen Plants with a focus on the CO_2 capture system. In particular, the technical approach used for the design and execution of the Demonstration plants and the relevant peculiarities are outlined.

   The following CCS demonstration projects were considered in the review:

   - The Port Arthur Project (Air Products)
   - The QUEST Project (Shell)
   - The Tomakomai Project (JCCS ltd/METI)
   - The Port Jerome Project (Air Liquide)

   The information included in the review was collected from the public domain and integrated, where available, with comments received from the Companies involved in the relevant projects, with the aim of including the most recent public data available about each demo project at the time of publication of the review, September 2016.

   For each of the demonstration projects the information reported includes:

   - a description of the project (e.g.: location, scope of work, objective)
   - latest information on the status of the project (timeline, project phases etc.),
   - CO_2 capture technology brief description
   - and a table summarizing key plant performance data.

Client : IEAGHG
Project Name : Techno-economic Evaluation of H_2 Production with CO_2 Capture
Document Name: Technical Review (Part 1): Current State-of-the-Art Technologies for Hydrogen Production
FWI contract : 1BD0840A

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APPROVED BY : G. Collodi

Date	Revised Pages	Issued by	Checked by	Approved by

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1. Introduction

Globally, nearly 90% of the hydrogen produced is consumed by the ammonia (about 50%), methanol and oil refining industries. Other major users include the metal, glass, electronics, food, and other chemical and petrochemical industries. In the future, hydrogen could play an important role in the decarbonisation of transport fuel (i.e. use of fuel cell vehicles).

In the near term, the growth in the demand for hydrogen is driven by the oil refining industry. Hydrogen is used in several oil refining processes such as hydrocracking, hydrodesulphurization and isomerization. Demand for hydrogen in this sector is continuously growing due to the introduction of stricter environmental regulations requiring the use low sulphur gasoline, diesel and marine fuels. Additionally, to address the declining quality of crude oil, hydrogen is an important ingredient in the processing of heavier crude to meet the increasing demand for lighter products.

The economics of hydrogen production are determined by several factors such as cost and quality of the feedstock, and utilities.

More than 95% of the hydrogen produced is obtained from fossil fuels (natural gas, refinery off-gases, heavy refinery residues, petcoke, coal, and others). Other sources could include water (via electrolysis), renewables, as well as by-product from other chemical processes.
Hydrogen used in industries could be in the form of high purity hydrogen (i.e. with greater than 99+% purity), or a mixture of hydrogen and carbon monoxide also known as HyCO gas.

Besides hydrogen, the conversion of fossil fuels to hydrogen also produces significant amount of CO_2 as by-product. Environmental concerns regarding the reduction of CO_2 emissions from energy intensive industries (including hydrogen production) should be expected in the future.

Currently, most of the modern hydrogen production facilities have achieved efficiency that could reduce CO_2 emissions down to nearly 10% above its theoretical minimum. Further reduction of CO_2 emissions from hydrogen production would only be possible by integration of CO_2 capture and storage system.

To understand the cost of deploying CO_2 capture system in a hydrogen production plant, IEA Greenhouse Gas R&D Programme commissioned Amec Foster Wheeler to undertake the "Techno-Economic Evaluation of Hydrogen Production with CO_2 Capture".

This report is the first part of deliverable for Task 1 providing a Technical Review presenting an overview to the "Current State-of-the-Art Technologies for Hydrogen Production".

The review would highlight the key features of the different hydrogen production processes commercially deployed worldwide. In particular, the different process characteristics, plant performance, points of CO_2 emission and relative CO_2 concentration of the leading hydrogen production technologies are presented.

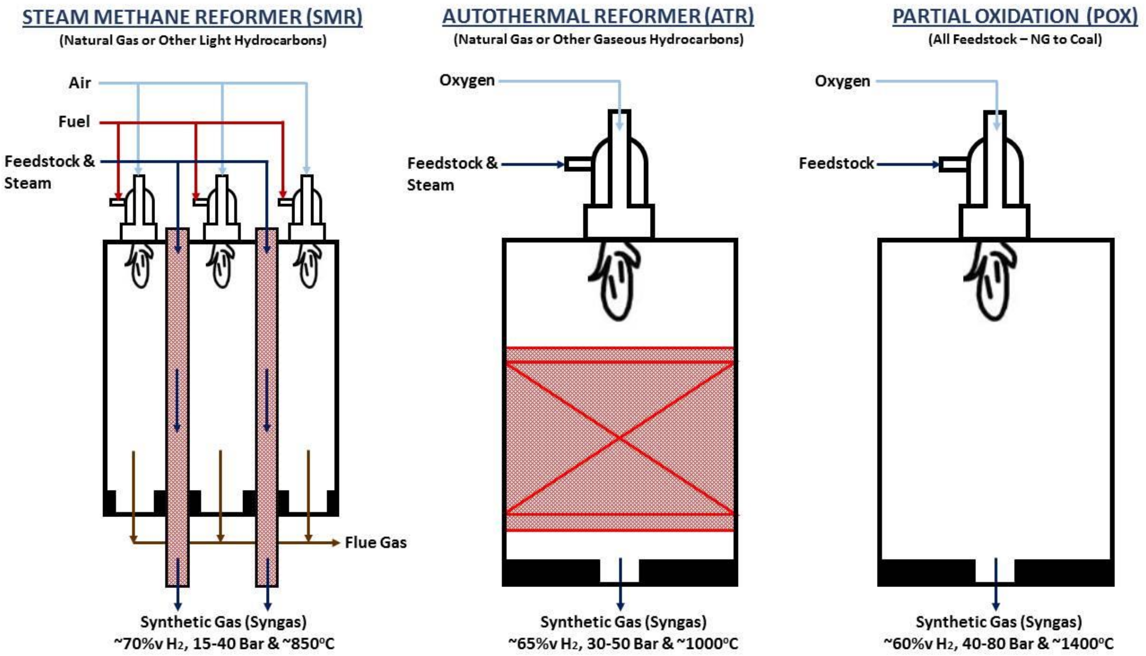
2. Review of the current State of The Art Technologies for Hydrogen Production

2.1. Overview

Several technologies producing hydrogen from fossil fuel at industrial scale (i.e. greater than 5000-10000 Nm^3/h) are available in the market. Currently, the leading technologies are:

- Steam Methane Reformer (SMR)
- Auto-thermal Reformer (ATR)
- Partial Oxidation (POX)

Figure 1 below illustrates the simplified schematic representation of these processes



The selection of the most appropriate technology is dependent on the following:

- type of feedstock available,
- required hydrogen production capacity, and
- economics of the generated by-products (i.e. steam and/or electricity)

For cases where generation of high purity hydrogen is the main scope of the Unit, the use of SMR is typically predominant, compatibly with the type of feedstock available. On the other hand, the use of the other two technologies (POX and ATR) is commonly associated with the additional requirements for power generation, steam export and/or syngas/HyCO production for further conversion processes

2.2. Steam Reforming (SMR) - based Hydrogen Production

2.2.1. Process Description

Nowadays, steam methane reforming (SMR) remains to be the leading technology for production of hydrogen in the oil refining, chemical and petrochemical industries.

The basic process of converting natural gas or other light hydrocarbons into hydrogen in a SMR Plant consists of the following steps:

- Feedstock Purification
- Pre-reforming (Optional)
- Steam Reforming
- Shift Reaction/Syngas Heat Recovery
- Raw Hydrogen Purification

Feedstock Purification

In addition to methane, the natural gas also contains small percentage of heavier hydrocarbons, CO_2 and nitrogen; and few ppm of sulphur and chloride compounds. Some of these components sulphur, chloride and olefin) are detrimental to the downstream catalysts; therefore, need to be removed when present.

Feedstock purification consists of two steps: (a.) hydrogenation of organic sulphur and chloride compounds; and olefins removal; and (b.) removal of H_2S and HCl.

The first step involves the hydrogenation of the organic sulphur (typically mercaptans or other more complex sulphur species) and organic chloride compounds. These are converted to H_2S and HCl respectively through a bed of CoMo/NiMo catalyst in the presence of H_2.

Although unlikely to be found in the lighter feedstock such as natural gas, any olefins present in the feed should be removed; as they could cause the risk of carbon formation on the steam reforming catalyst. Thus, with heavier feedstock (e.g. naphtha, LPG) containing some olefins, the hydrogenation step should also ensure that olefins are removed via saturation through the CoMo/NiMo catalyst.

The second step involves the absorption of the H_2S as zinc sulphide in the bed of ZnO. If chloride compounds are present, a layer of sodium alumina adsorbent is installed on top of the ZnO bed to take care of the HCl removal.

Both steps require a temperature of about 350-370^{o}C.

Pre-Reforming (Optional)

In the case of using multiple or heavier feedstock and/or for larger capacities SMR (typically above 60000 Nm^3/h), an adiabatic catalytic pre-reforming is installed upstream of the primary reformer.

The pre-reforming step catalytically converts ethane and other heavier hydrocarbons in the desulphurized and pre-heated feed to produce an equilibrium gas mixture containing methane (~60%), hydrogen (~20%) and carbon oxides (remaining balance[1])

The reaction is carried out adiabatically over a high activity nickel based catalyst at a temperature of around 500°C.

Pre-reforming provides the following benefits to the downstream primary reforming process: (a.) reduces the heat load of the primary reforming furnace, (b.) increases the tubes life of the reformer, (c.) lowers the feed steam to carbon ratio, and (d.) allows higher inlet feed temperature with minimal risk of carbon deposition.

In transferring some of the reformer duty from the primary reformer to the pre-reformer, the process efficiency is improved; and the size of the primary reformer heater is reduced.

Steam Reforming

In the steam reforming furnace, the mixture of steam and methane reacts inside the metallic tubes filled with nickel based catalyst. The most essential reaction is the endothermic steam-methane reaction producing carbon monoxide and hydrogen.

$$CH_4 + H_2O \rightarrow CO + 3H_2$$

This reaction is limited by equilibrium. The maximum conversion of methane increases with (a.) increasing temperature and (b.) increasing steam/methane ratio in the feed; but conversion decreases with increasing pressure.

The steam reforming catalyst is also active with respect to the exothermic water gas shift reaction:

$$CO + H_2O \leftrightarrow CO_2 + H_2$$

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[1] About 19-19.5% CO_2 and 1-0.5 % CO

The overall steam reforming process converting the methane to raw synthesis gas (syngas) is strongly endothermic; thus a large amount of heat is required.

As the reactants (i.e. methane and steam) pass through the catalyst inside the tubes, the heat required is normally supplied to the reaction by heating the banks of high alloy metallic tubes containing the nickel catalyst in a fired radiant furnace. Typical furnace configuration could be shown in Figure 2.

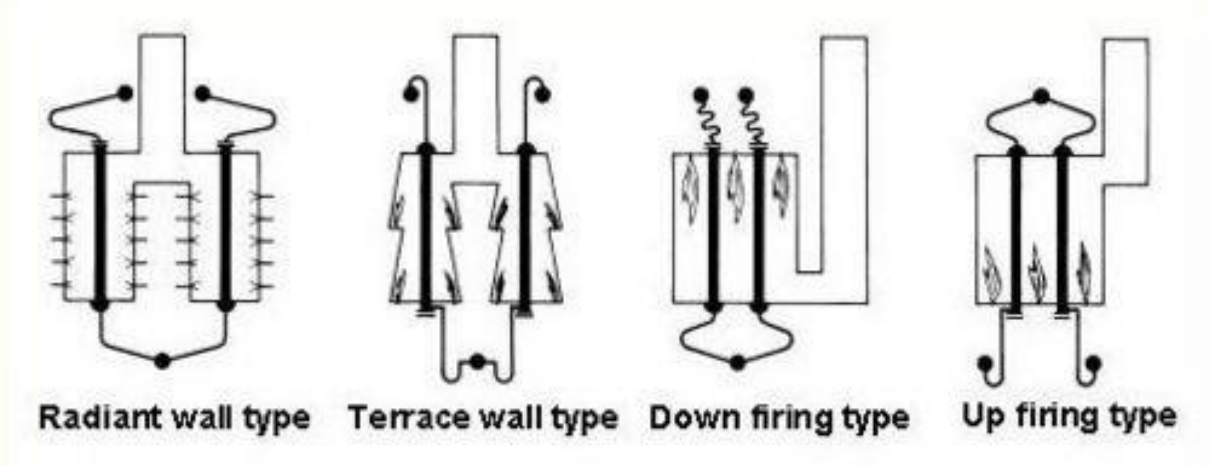


Figure 2: Typical furnace configuration of an SMR

Shift Reaction/Syngas Heat Recovery

Gas leaving the primary reformer usually has about 12% of its potential hydrogen in the form of carbon monoxide. To realise this potential, the carbon monoxide should be shifted by its exothermic reaction with residual steam to produce the additional hydrogen and carbon dioxide.

Typically, the gas composition of the syngas coming from the primary steam reformer is in equilibrium with respect to the water – gas shift reaction. After cooling of the syngas in the shift reactor to about 350°C by raising steam, further shift reaction would take place at lower temperature over a selective catalyst where the equilibrium reaction favours the CO conversion to H_2 and CO_2.

Generally, high temperature shift (HTS) catalyst is used in the shift reactor. This is an iron based, copper promoted catalyst that only requires a minimum steam to dry gas ratio at the reactor inlet; thus avoiding any unwanted side reactions (such as Fischer Tropsch reactions) across the shift catalyst.

For primary reformers designed with lower steam to carbon ratios, a more active copper based iron free catalyst (MTS catalyst) is used; and the reaction takes place at lower temperature (typically at 260-290°C).

Due to its formulation, the MTS catalyst normally produces certain amount of methanol in the shift effluent that needs to be stripped from the process condensate in order to meet the necessary requirements for export steam quality.

The water-gas shift reaction is always an equilibrium limited reaction and typically there is enough steam present in the gas to reduce the carbon monoxide to approximately 3%v (dry basis).

Following the shift reaction step, the process gas, containing about 17% carbon dioxide (dry basis), is cooled down to about 35-40°C whilst heat is recovered to generate steam, to preheat the boiler feed water and the condensate separated from the raw hydrogen.

Overall, the SMR-based hydrogen plant produces steam in excess to the requirement of the steam reforming reactions. The excess steam produced is usually made available and exported. Such amount of steam is generally accounted as a credit in the energy efficiency calculation (See Section 2.2.4).

Raw Hydrogen Purification

In modern hydrogen plants, the final hydrogen purification is accomplished via Pressure Swing Adsorption (PSA) system.

PSA system can produce up to 99.999% pure hydrogen with a recovery ranging from 70-95%.

The concept of PSA unit involves the adsorption of the impurities in a hydrogen stream onto the micro or meso-porous materials. The adsorbent materials can be zeolites, activated carbons, silica and alumina gels. The hydrogen stream is passed through a packed bed at relatively high pressure in order to produce purified hydrogen at the required pressure.

The basic PSA unit consists of vessels operating cyclically on an adsorption, depressurization, purging, pressurization cycle.

The impurities separated from the hydrogen are collected in the tail gas which provides the bulk of the steam reformer fuel. More detailed information about the Pressure Swing Adsorption System are described in Section 2.7.1. of this review.

2.2.2. *Block Flow Diagram*

The block flow diagram (as shown in Figure 3) illustrates the different sections of the SMR Hydrogen Plant.

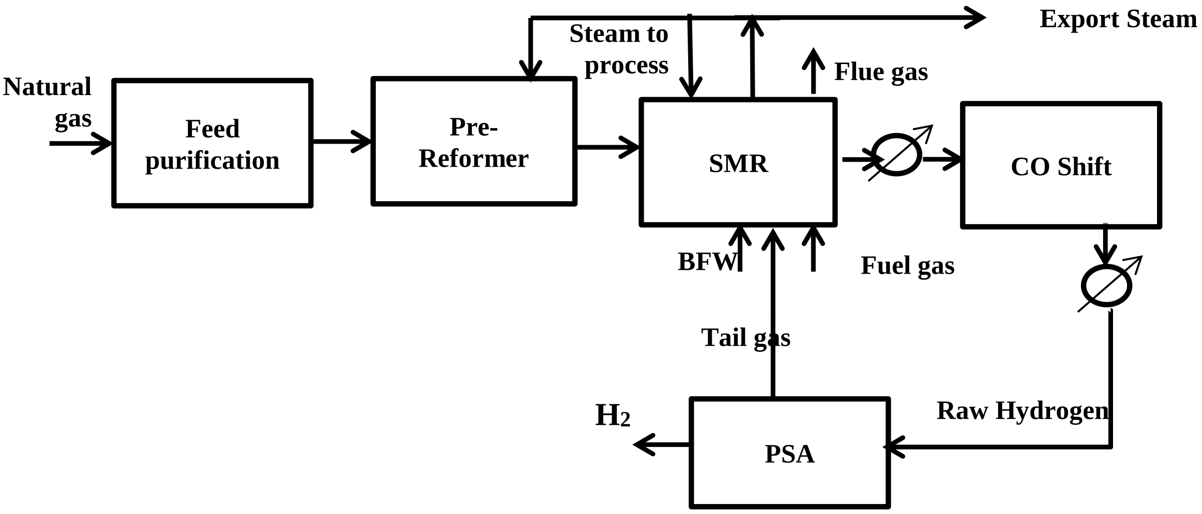


Figure 1 – BFD of SMR Hydrogen Plant

2.2.3. *CO_2 Balance in SMR Hydrogen Plant*

In a modern steam reforming hydrogen plant fed by natural gas, up to approx. 60% of the total CO_2 produced is contained in the shifted gas. The CO_2 is then separated from the H_2 in the PSA system thus ending up in the PSA tail gas.

Normally, the PSA tail gas (containing approx. 15% CO and 9% CH_4) provides most of the fuel of the SMR and is burned together with the additional fuel. Therefore, the remaining 40% of the CO_2 comes from the product of the combustion of the additional fuel required by the SMR and the CO and CH_4 present in the tail gas.

Typical CO_2 flow rates and partial pressures for a 100,000 Nm^3/h Hydrogen plant are reported in the following Table 1.

Table 1 – Typical H_2 plant CO_2 balance

Stream	CO_2 concentration (% mol) wet basis	CO_2 flow rate (kmol/h)	CO_2 partial pressure (bara)	CO concentration (% mol) wet basis	CH_4 concentration (% mol) wet basis
Raw H_2 (PSA inlet)	15.0-16.4	1,000-1,100	3.40-3.7	4.0-5.0	3.0-3.5
PSA tail gas	45.1-50.4	1,000-1,100	0.60-0.67	14.5-15.0	8.5-9.5
SMR flue gas	19.0-19.5	1,850-1,930	0.20	N/A	N/A

2.2.4. Energy Performance

The impact of major process parameters on SMR Hydrogen Plant Efficiency is outlined in the Table 2 below:

Table 2 – Impact of major process parameters

Parameter	**More/Less**	**Impact**
Steam to Carbon Ratio	Less (Lower)	Greater Energy Efficiency Less Fuel consumption More feed consumption More Steam export
Exit Reformer Temperature	More (Greater)	Greater Energy Efficiency More fuel consumption Less feed consumption More Steam Export SR more expensive
Inlet Reformer Temperature	More (Greater)	Less Fuel consumption Less steam export SR less expensive
Air Pre-heating Temperature	More (Greater)	Greater Energy Efficiency Less fuel consumption Less Steam export SR more Expensive

For a Hydrogen Plant the energy efficiency is calculated according to the following formula:

$\underline{\text{(Feedstock (GJ/h) + Fuel (GJ/h) – Steam export (GJ/h)) / 1000 Nm}^3\text{/h } H_2 \text{ product}}$

Typical efficiency values range from 12.39 to 16.32 GJ/1000Nm^3

The efficiency value is influenced by size, feedstock and plant configuration.

2.2.5. *References for Licensors and largest capacity Plants*

The top SMR hydrogen technology providers include the following companies:

- Amec Foster Wheeler
- Haldor Topsøe
- Linde
- Technip
- Udhe

The listed companies above generally provide full–service Engineering, Procurement and Construction (EPC) that have extensive experience in building integrated hydrogen plants around their proprietary reforming units.

Table 3 present the lists of the top 5 largest single train SMR hydrogen plants.

Table 3 – World's largest single train SMR hydrogen plants

Owner	Plant Name	Location	Capacity [Nm^3 /h]	SMR Licensor
Tuapse Refinery	U-34 *	Sao Francisco do Conde, Brasil	240000	Technip
Kuwait National Petroleum Co Ksc	CFP2*	Mina Abdulla, Kuwait	203500 (per train, 3 trains)	Haldor Topsøe
JSC Bashneft NOVOIL	HPU	Ufa, Russia	165000	Amec Foster Wheeler
TUPRAS	HPU*	Izmit, Turkey	160000	Technip
Abu Dhabi Oil Refining Company (Tarter)	Hydrogen 2 UNIT 1300	Ruwais, U.A.E	151000	Haldor Topsøe

*Under construction

2.3. Auto Thermal Reforming (ATR) - based Hydrogen Production

2.3.1. Process Description

Auto Thermal Reforming is a catalytic technology, essentially a combination between Steam Reforming and Partial Oxidation (POX). The heat generated from the exothermic POX reaction is used for supplying the heat needed for the endothermic SR reaction during operation.
The following sections are integrated in an ATR based Hydrogen production Unit:

- Air separation unit
- Feedstock Purification and Preheating
- Pre-reforming (optional)
- ATR
- Shift Reaction/Syngas heat recovery
- Hydrogen Purification

Air separation Unit

The air separation unit integrated into an ATR based hydrogen plant has the same characteristics as the one integrated into a POX based hydrogen plant, therefore for description of this unit refer to section 2.4.1-Air separation unit.

Feedstock Purification

Feedstock processed in a ATR based Hydrogen plant are of the same nature as the ones used in a SMR based Plant. For a description of the purification step refer to section 2.2.1-Feedstock Purification.

Pre-reforming

Integration of pre-reforming into a ATR based Hydrogen Plant increases flexibility with reference to feedstock processing. For characteristic of pre-reforming reference can be made to section 2.2.1-Pre-reforming.

ATR

The ATR unit is a refractory-lined pressure vessel containing a burner, a combustion chamber and a catalyst bed. Once the reactor is at operating temperature, hydrocarbon feedstock, steam and air are all fed into the reactor in the same step.
In the combustion chamber, partial oxidation reaction takes place and the generated heat is utilised for the endothermic steam reformer reaction. In the lower section of the

reactor (loaded with reforming catalyst, nickel based) the steam reforming and shift conversion reactions occur as the gas passes through the fixed bed, generating a gas mixture of H_2 and CO. The Autothermal Reformer is described by two reaction zones: a combustion zone and a catalytic steam reforming zone. The behaviour of the Autothermal Reformer is determined by a set of chemical reactions in each of the zones which are below listed:

- Combustion zone:

$C_nH_m + n/2\ O_2 \rightarrow n\ CO + m/2\ H_2$
$CH_4 + 1/2\ O_2 \rightarrow CO + 2\ H_2$
$H_2 + 1/2\ O_2 \rightarrow H_2O$
$CO + 1/2\ O_2 \rightarrow CO_2$

- Catalytic steam reforming zone:

$CH_4 + H_2O \leftrightarrow CO + 3H_2$
$CO + H_2O \leftrightarrow CO_2 + H_2$

Shift Reaction/Syngas Heat Recovery

For description of the water gas shift section refer to paragraph 2.2.1-Shift Reaction with the following considerations with reference to the differences between the two Technologies:

- In the ATR unit the amount of CO produced due to the partial oxidation of hydrocarbons is higher than that formed due to the reforming reactions; hence the H_2/CO ratio is lower than the one in the SMR Plant. This results in an additional load on shift reactor.
- The CO_2 amount at the exit of the Shift section is less in the ATR based Plant compared to the SMR. This is because the higher operating temperature in the ATR restricts the exothermic water gas shift reaction.
- In The ATR, the amount of oxygen fed stoichiometrically consumes the hydrogen part of the feed hydrocarbon not contributing to hydrogen production. Even though the process steam required for reforming at the inlet of the ATR unit is less when compared to SMR based Plant, additional steam is needed at the inlet of the shift section for a similar CO slip.

Hydrogen Purification

For a description of the Raw Hydrogen Purification section and main difference with SMR hydrogen Plants refer to section 2.4.1- Hydrogen Purification.

2.3.2. *BFD*

The following Block Flow Diagram (Figure 2) illustrates the typical sections included in an ATR based Hydrogen Plant

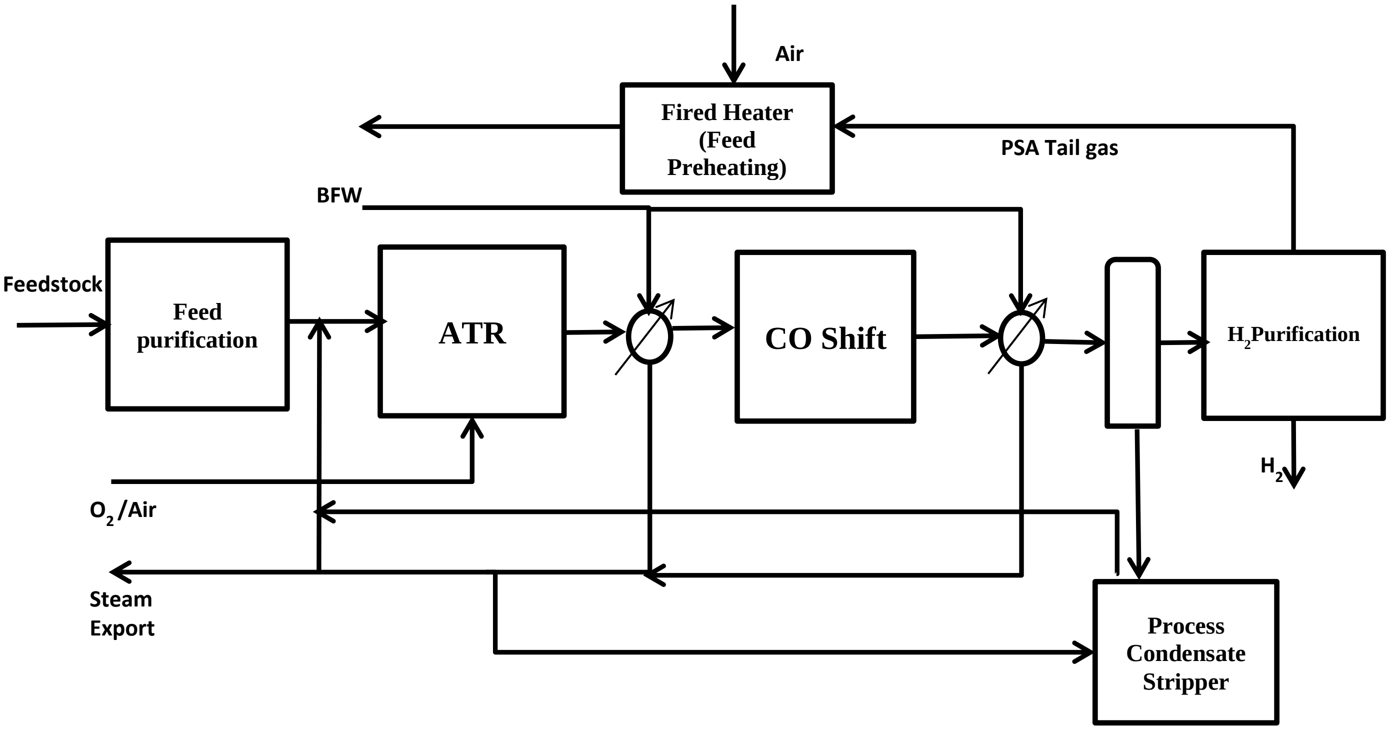


Figure 2 –BFD of ATR Hydrogen Plant

2.3.3. *CO2 Balance in ATR Hydrogen Plant*

In an ATR plant 100% of the total CO_2 produced is contained in the PSA tail gas. At last, all the CO_2 ends up in the flue gas of the Fired Heater. (See Figure 2 above)

The below Table 11 shows the simplified CO_2 balance for a ATR based hydrogen plant (100000 Nm^3/h H_2 capacity) based on natural gas feedstock.

Table 11 – Typical H_2 plant CO_2 balance

Stream	**Equivalent CO_2 flow (kmol/h)**	**Main carbon component (%mol dry basis)**
Syngas from ATR (H_2: 63%)	1966	CO: 30% CO_2: 5% CH_4: 1.37%
Shifted syngas (H_2: 72 %)	1966	CO: 0.2% CO_2: 26.5% CH_4: 1 %
PSA tail gas (H_2: 23%)	1966	CO: 0.6% CO_2: 71.5% CH_4: 2.8%
H_2 (99.5% purity)	-	-

2.3.4. *Energy Performance*

For an ATR based hydrogen Plant, assuming the Plant configuration shown in section 2.4.2 and the following process parameters:

Table 12 – Typical ATR-based H_2 plant balance

Parameter	Unit	Value
H_2 production	Nm^3/h	100000
Feed consumption (Natural Gas)	Kg/h	26729
HP Steam Export (steam conditions: 395 C, 42.2 barg)	Kg/h	58730
NG LHV	KJ/kg	49034

and according to the following formula to calculate the Hydrogen plant efficiency:

$$\underline{(\text{Feedstock (GJ/h)} - \text{Steam (GJ/h)}) / 1000\ \text{Nm}^3/\text{h}\ H_2\ \text{product}}$$

the resulting value is 9.2-10.5 GJ/1000 Nm^3.

2.3.5. *References for Licensors and largest capacity Plants*

The list of the top ATR technology providers includes the following Companies:

- Haldor Topsøe
- Lurgi (Air Liquide)
- Davy Process Technologies (JM)
- KBR
- Udhe

The ATR-based hydrogen plant is a scheme that may have an economic justification in case of very large production, probably >200000 Nm^3/h. There is not as a common position among the various ATR technology providers on this subject, and there is not ATR-based plant dedicated to large hydrogen production.

However, there are large syngas production based on ATR, for example in case of GTL (Fischer-Tropsch) plant, where potentially most of the H_2+CO contained might end up as pure hydrogen product.

As an example, the Oryx GTL in Qatar produces approx. 577000 Nm^3/h of syngas in a single Topsøe ATR trains, in this case sent to F-T synthesis.

2.4. Partial Oxidation (POX) - based Hydrogen Production

2.4.1. *Process Description*

Partial Oxidation is a viable and competitive technology for hydrogen or more in general chemical production via syngas from low quality feedstock, such as heavy residue, and from solid feedstock as coal. The POX technology combines the flexibility to process a wide variety of low quality feedstock with high conversion efficiency and minimizing impact to the environment with the possibility to easily design the plant for poly-generation as the syngas intermediate product can be converted into a variety of chemicals and power.

The key and initial process step of the plant is the feedstock gasification. Gasification is the partial oxidation of any fossil fuel to a gas, often identified as synthesis gas (syngas), in which the major components are hydrogen and carbon monoxide. It can be applied to solid, liquid and gaseous feedstock such as coal, petroleum coke, residual oils and LPG, naphtha and natural gas. The gasification agents used in the gasification process are oxygen or air and, usually, steam. The choice of oxygen or air depends on a number of factors such as the reactivity of the feed material, the purpose for which the gas is to be used and the type of gasifier. Steam helps the mixing of feed and oxidant and acts as a temperature moderator, as the reactions of steam with carbon are endothermic. Syngas generated by gasification is cleaned from acid gas components and treated to meet the proper temperature and pressure conditions and composition required by the hydrogen production unit.

The process for producing Hydrogen via POX technology includes the following units:

- Air separation unit
- Feedstock storage and handling (mainly for solid feedstock)
- Gasification Island
- Gas processing system (including acid gas removal)
- Sulphur recovery unit and Tail Gas Treatment
- Hydrogen Purification

Air separation Unit

The technology currently used for large oxygen (and nitrogen) production in gasification plants is based on the distillation of atmospheric air at cryogenic temperatures to separate it into an oxygen-rich stream and a nitrogen –rich stream.

The Air Separation Unit (ASU) is designed to produce high pressure oxygen for the gasification and a small quantity of low-pressure oxygen for the Sulphur Recovery Unit (SRU). Nitrogen is also produced at different pressure and purity levels, depending on its final use and the gasification technology.

The ASU configuration best suited for a gasification plant for hydrogen production is a low pressure scheme with pumped liquid oxygen (LOX).

The ASU mainly consists in the compression, pre-cooling and purification of ambient air, the cold production section (cold box) and the distillation section typically based on multiple (two or three) columns at different pressure level.

The ASU is an electric or steam-driven system that does not utilize any external fuel.

This technology has been known for over 100 years and at present it is the most cost-effective one, with a number of international companies able not only to offer lump sum turnkey plants, but also often willing to build, own and operate the plant by themselves.

Gasification Island

A large number of gasification processes are commercially available on the market.

Depending on the flow regime inside the gasifier, the gasification process can be classified into moving bed or fixed bed gasification, where fuel is fed at the top while oxygen and steam at the bottom, fluidised bed gasification where solid feedstock is suspended in the gas stream, and entrained flow gasification.

In this type of gasifier, the feedstock flows co-currently with the oxidising agents (O_2 and steam). Residence time is very short, between 0.5 and 5 seconds; the temperature inside the gasifier is uniform and very high, from 1300°C to over 1500°C. At these temperature conditions the syngas product contains only very small amounts of methane (0.1-0.3% vol.).

For this reasons, the entrained gasifiers are the preferred option when syngas is used in most of the chemical synthesis, including hydrogen production. In addition, entrained flow gasifiers have higher flexibility in processing a large variety of fuels, solid and liquid, and they can achieve in a single train large capacities, thus resulting in an overall investment cost lower than the other technologies.

As for the above, this section is focused on the entrained flow gasification technology.

Entrained flow gasifiers differ in the way for recovering the large amount of sensible heat in the hot syngas: the waste heat boiler (WHB) type and the water quench type.

•	**WHB type**:	Recovery of gasifier sensible heat can be made in a waste heat boiler, downstream of the gasifier, generating high pressure steam;
•	**Quench type.**	Syngas is cooled down through a water quench inside the gasifier and subsequent recovery of the degraded heat in external waste heat boilers, producing medium and low pressure steam

The waste heat boiler system improves the energy efficiency, but the quench system permits to remove efficiently solids from the raw gas before entering the downstream facilities. In addition, water quench is attractive when syngas requires CO shifting to increase the H_2/CO ratio, as for the hydrogen production case via shift reactions. In fact, CO shift requires the addition of large amounts of water in the gas, which can be done conveniently in the quench. Most of the main gasification technology licensor are able to provide both solutions depending on the gasification plant final product (power or chemical).

For the solid gasification, two types of feed systems are in use in the different entrained flow gasification technologies: slurry feed and dry feed.

•	**Slurry feed:**	based on pumping a slurry of feed (e.g. pulverized coal) in water;
•	**Dry feed.**	based on pneumatic transport of the feed.

Wet type is less suitable in the case of coals with large water contents like lignite and sub-bituminous coal.

The most prominent entrained flow gasification technologies to be integrated in a POX based hydrogen plant are listed in the Table 4 below.

Table 4 – Entrained flow gasification technologies

Gasification licensor	oxidant	Heat recovery	Feed system
General Electric Energy (GE)	Oxygen blown	quench type / radiant syngas cooler	slurry feed
Shell	Oxygen blown	WHB type / partial quench	dry feed
Siemens	Oxygen blown	quench type	dry feed
Uhde – Prenflo	Oxygen blown	WHB type / quench type	dry feed

Conoco-Phillips (E-GAS)	Oxygen blown	WHB type	slurry feed
Mitsubishi	Air blown	WHB type	dry feed

Among the above listed licensor, General Electric Energy and Shell have developed also the technology for partial oxidation of gaseous feedstock, mainly natural gas but also light hydrocarbon.

The gasification island is composed of several units, mainly the feedstock handling and pressurisation, the gasifier reactor, the heat recovery section, the syngas scrubber, the by-product (mainly grey water, slag and/or ash) separation and collection for disposal and the gasification water treatment. The type and the configuration of the units within the gasification island vary significantly depending on the gasification technology licensor and on the feedstock type (heavy residue, solid feedstock or gas).

The core system of the gasification island is the gasifier reactor. Pressurised feedstock is fed to the gasifier burners, with steam and oxygen from the air separation unit.
The amount of oxygen added to the gasifier is limited so that only partial oxidation occurs, converting the feedstock into a syngas product as per the reaction described below, and a residual slag by-product. The syngas consists of hydrogen, carbon monoxide, carbon dioxide, hydrogen sulphide and small amounts of other compounds. The hot syngas from the gasifier chamber is quenched or sent to the downstream WHB for heat recovery and finally sent to a water scrubbing system to remove any remaining particulates from the syngas before being delivered to the downstream gas processing system for treatment as further described below.
The main gasification by-product is slag resulting from the molten feedstock ash and/or the residual soot. In most of the gasification processes, the slag exits the gasification section in a slurry water phase. The slag and water are separated and most of the water is recycled back to the gasification process, after being treated.

Gasification chemistry

The gasification is a non-catalytic, auto-thermal process where the hydrocarbon feed is partially oxidized with oxygen and steam to produce syngas, mainly composed of hydrogen and carbon monoxide.
The main gasification reactions between the reactant streams are listed below:

$$C_nH_m + n/2\ O_2 \rightarrow n\ CO + m/2\ H_2 \qquad (1) \quad \text{(exothermic)}$$
$$C_nH_m + n\ H_2O \rightarrow n\ CO + (m/2+n)\ H_2 \qquad (2) \quad \text{(endothermic)}$$
$$C_nH_m + n\ CO_2 \rightarrow 2n\ CO + m/2\ H_2 \qquad (3) \quad \text{(endothermic)}$$

To reach and maintain the required reaction temperature, part of the hydrocarbon feed is fully oxidized according to the following strongly exothermic reaction:

$C_nH_m + (n+m/4)\ O_2 \rightarrow n\ CO_2 + m/2\ H_2O$ (4) (exothermic)

The four main gaseous species present in the gasifier (CO, CO_2, H_2 and H_2O) are in equilibrium at the gasification temperature according to the water shift reaction, which is mildly exothermic when moving to the hydrogen and carbon dioxide:

$CO + H_2O \leftrightarrow CO_2 + H_2$ (5)

The feedstock is immediately dried and pyrolysed as it enters the reactor. In fact, at the outlet of the gasification burner the fuel is heated by radiation from the flame and by mixing with hot syngas. Vaporization and cracking of the volatile matters take place in this stage.

As soon as the ignition temperature is reached, part of the feed reacts with oxygen according to the highly exothermic reaction (4). Practically, the whole oxygen available is consumed in few microseconds. The remaining portion of the feed, which has not been oxidized, reacts with the combustion products from reaction according to the mildly endothermic reactions (2 and 3).

It is essential that all reactants inside the gasifier are intimately mixed in order to avoid local excessive temperatures and to balance the thermal effect of the exothermic and endothermic reactions. The final thermal equilibrium of the system is reached when the temperature is in the range 1300°C to 1500°C. The steam fed to the gasifier mixed with the oxygen stream acts as a temperature moderator and participates to the above gasification reactions.

Finally, the hydrogen and carbon dioxide content in the gas increases due to the shift reactions (5), with a mild exothermic effect that penalizes the gasification efficiency.

In the final gasification stage, shift reaction (5) and reforming reactions takes place:

$CO + 3H_2 \leftrightarrow CH_4 + H2O$ (steam reforming)

$2CO + 2H_2 \leftrightarrow CH_4 + CO2$ (CO_2 reforming)

At the high gasification temperatures of entrained flow gasifiers, the equilibrium of these reactions is strongly shifted to the left, thus the CH4 content of syngas from entrained flow gasifiers, operating at very high temperatures, is very low, between 0.1 and 0.3 % vol (dry basis).

Other secondary reactions occurring in this gasification stage are:

$C + H2O \leftrightarrow CO + H_2$ (water gas reaction)

$C + CO2 \leftrightarrow 2CO$ (Boudouard reaction)

C is the residual soot which can reacts according to the above mildly endothermic reactions only if there is sufficient residence time, which is not the case in entrained flow reactors.

Gas processing System

The raw syngas from the gasification island is routed to the gas processing system.

The final purpose of the gas processing system is to product a contaminant free, hydrogen-rich syngas to be fed to the downstream PSA for hydrogen production. Syngas is hot, generally humid, and contaminated with acid gases (e.g. CO_2 and H_2S) and other species like carbonyl sulphide (COS), mercury (Hg), hydrogen cyanide (HCN) and ammonia (NH_3), that needs to be removed before sending the syngas to the PSA for hydrogen production.

Three possible ways to produce hydrogen from syngas have been identified, mainly differing for the process used for increasing the hydrogen content in the syngas stream to be fed to the PSA: membrane or shift (clean or sour).

- **Membrane + PSA**

  The raw syngas from the gasification island is cooled in waste heat boilers, recovering heat while generating steam at medium and low pressure level before being sent to the acid gas removal (AGR) unit for H_2S removal. If the AGR system is not capable to treat the COS, a hydrolysis reactor is required upstream the cooling section. The clean syngas is fed to a membrane system separating the syngas into two streams: a hydrogen-rich permeate stream to be sent to the PSA for final hydrogen purification and a non-permeated hydrogen depleted stream. This configuration is typical of hydrogen and power coproduction plant, due to the significant amount of hydrogen depleted syngas from the membrane that is typically used as fuel in gas turbines. The description refers to the block flow diagram 1 shown in the following paragraph 2.4.2.

- **Clean shift + PSA**

  The raw syngas from the gasification island is cooled in waste heat boilers, recovering heat while generating steam at medium and low pressure level before being sent to the acid gas removal (AGR) unit for H_2S removal. The clean syngas is sent to the clean shift section for the catalytic conversion of CO and water to H_2 and CO_2, in order to increase the hydrogen content in the syngas to be fed to the PSA. The description refers to the block flow diagram 2 shown in the following paragraph 2.4.2.

- **Sour shift + PSA**

  The raw syngas from the gasification island is sent to a sour shift section for the catalytic conversion of CO and water to H_2 and CO_2, in order to increase the syngas hydrogen content. The hot syngas is cooled down in waste heat boilers, recovering heat while generating steam at different pressure level.

> The shifted gas is sent the AGR for the removal of the acid gas (H_2S and CO_2). This configuration is particularly suited for carbon capture application as both CO_2 and H_2S can be selectively removed from the syngas. The clean hydrogen-rich gas is fed to the downstream PSA system for final purification. The description refers to the block flow diagram 3 shown in the following paragraph 2.4.2.

The acid gas stream from the AGR is sent to a sulphur recovery unit (SRU) for sulphur production and recovery. The resulting tail gas is recycled back to the AGR.

Acid gas removal (AGR)

The primary purpose of the Acid Gas Removal (AGR) unit is the removal of acid gases, H_2S (and CO_2), to a level compatible with the plant environmental limits and/or the requirements of the downstream units. Besides being a key unit for meeting the environmental performance of the plant, the AGR section is also a capital intensive unit and a large consumer of energy.

The accurate selection of the process and solvent type for making the capture of the acid gases is important for the performance of the entire gasification plant. Several different technologies are commercially available for the AGR. The detailed description of these technologies and solvent, commercially available and suited for hydrogen production plant, is included in the Technical Review #2 of the present report.

Shift

As in the hydrogen plant based on SMR technology, CO shift unit is considered in order to convert carbon monoxide and water to hydrogen and carbon dioxide, in accordance to the following reaction, increasing the hydrogen content in the syngas:

$$CO + H_2O \rightarrow CO_2 + H_2$$

The equilibrium constant for the water-gas shift is a function of the temperature, with greater shift occurring at lower temperature. As the shift reaction is exothermic and heats the gas as CO shifts to CO_2, it tends to inhibit the conversion. While the shift reaction is favoured at low temperatures, the reaction rates and the catalyst reactivity at low temperature are low, so commercial water gas shift reactors generally operate at a practical compromise temperature, where the catalyst proves most effective.

The conventional shift reaction takes place into two consecutive stages, with intermediate cooling for syngas pre-heating and steam generation between them. A two-stage process is generally required to reach an overall CO conversion higher than 85-90%. Hot syngas from the first reaction stage preheats the saturated syngas from the scrubber up to the minimum temperature required for the operation of the CO shift catalyst (higher than 260°C).

In order to maximize the conversion of the CO, the injection of steam might become necessary, in particular for non-water quenched gasification technology, to maintain the water content in the syngas higher than the minimum level required for proper catalyst operation.

Downstream of the CO shift reactors, syngas is cooled in a series of waste heat boiler, generating steam at different pressure level.

Mercury removal

Depending on the feedstock, the hydrogen production plant based on POX technology may include a mercury removal system to eliminate mercury from the syngas before being fed to the final purification step in the PSA. This system uses sulphur-impregnated activated carbon beds capable of removing almost all the mercury in the syngas stream. The mercury removal package is typically located immediately upstream of the Acid Gas Removal unit, allowing operation of the system in its optimum conditions and enhancing the downstream AGR system performance and solvent life due to mercury and other contaminants removal.

Sulphur recovery unit

The Sulphur Recovery Unit (SRU) processes the main acid gas from the AGR unit, together with other small flash gas and ammonia containing off-gas streams coming from other units. The SRU consists of two Claus Units, each sized for approximately 100% of the maximum sulphur production in order to assure a satisfactory service factor. Low-pressure oxygen or enriched air is used as oxidant of the Claus reaction.

Hydrogen Purification

The final hydrogen purification is achieved in a Pressure Swing Adsorption (PSA) system, fed by hydrogen rich gas from the gas processing units, in order to obtain high purity hydrogen (> 99.5%).

The PSA system is in principle identical to the one included in the SMR-based hydrogen plant (section 2.2.1) and described in section 2.7.1.

The differences are mainly related to the operating pressures that, in case of POX, are higher than in SMR case both at the inlet, and at the tail gas side, where a pressure of 0.3 barg (typical for a PSA in SMR-based hydrogen plant) is too low to be used as fuel gas. In the POX case, in fact, there is not a furnace capable to use such a low pressure fuel, and therefore the tail gas pressure is at a higher value (1 barg or more) in order to limit the tail gas compressor energy consumption, without penalising too much the PSA hydrogen recovery.

Another difference is that the syngas originated from POX unavoidably contains nitrogen (together with the oxidant) and this component may have an impact in the hydrogen purity.

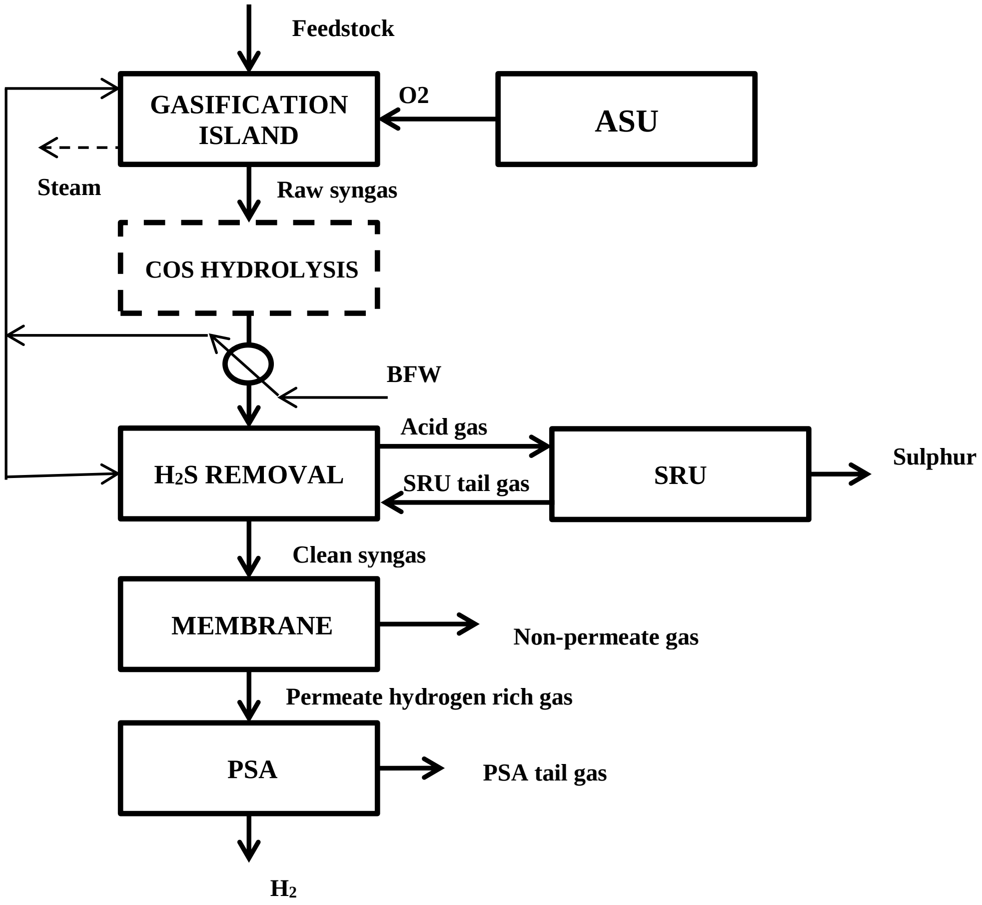
Gaseous vs. Liquid/Solid Feedstock's for POX

The partial oxidation of a gaseous feedstock like natural gas is relatively simple compared to that of liquids or solids. In particular, there is no feed handling and preparation, being the case similar to the ATR discussed in the previous section.
The natural gas does not contain ash, heavy metals (mercury might be present at ppb levels), thus simplifying or eliminating the soot water/grey water treatments and avoiding complicated system for ash removal. The amount of sulphur is generally much lower than in case of liquid/solid feedstock's (ppm vs. pct.) and this sulphur could be removed either upstream or downstream the POX reactor: the AGR is by consequence simpler. The low amount of sulphur exiting the POX reactor (if not removed upstream) may originate an acid gas from AGR with a low H_2S concentration (10% mol. or lower) and the possibility to feed this gas into a traditional Claus SRU should be investigated.
From an economic point of view, the advantage of natural gas POX only comes when no-purpose built oxygen plant is required, or when a CO-rich syngas is desired (these considerations are valid also for ATR).

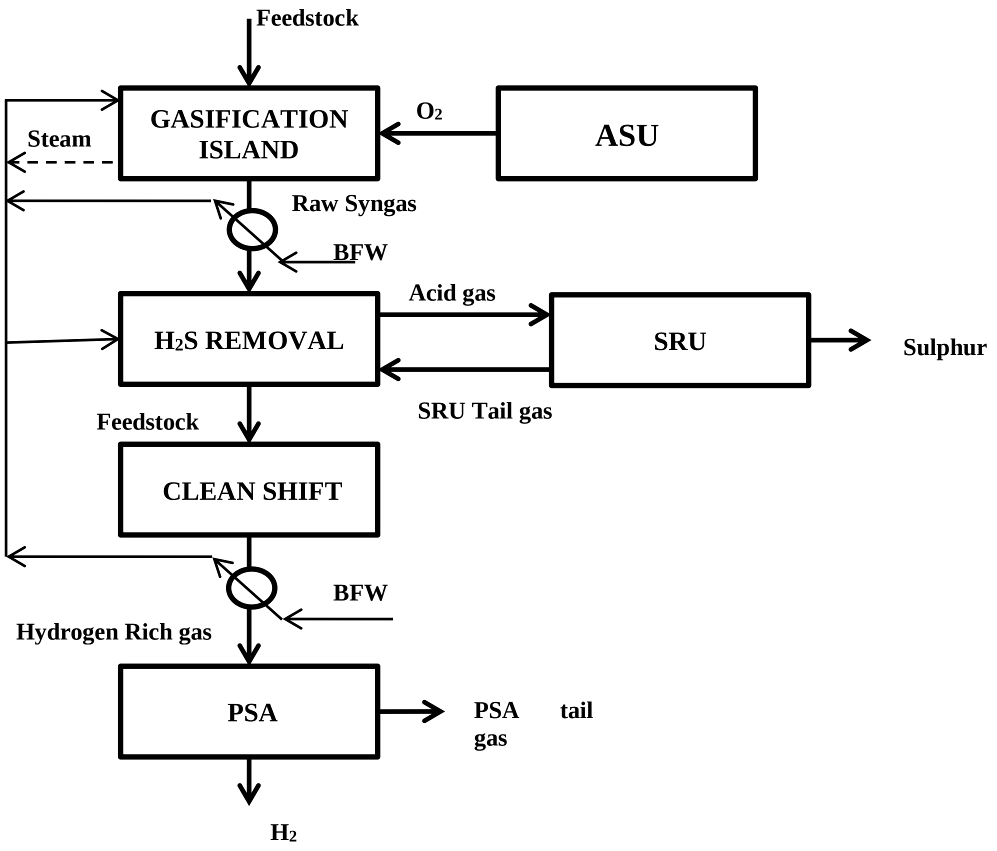
2.4.2. *BFD*

The three ways to produce hydrogen from syngas from a POX unit identified in the previous section are illustrated in the following Blok flow diagrams.

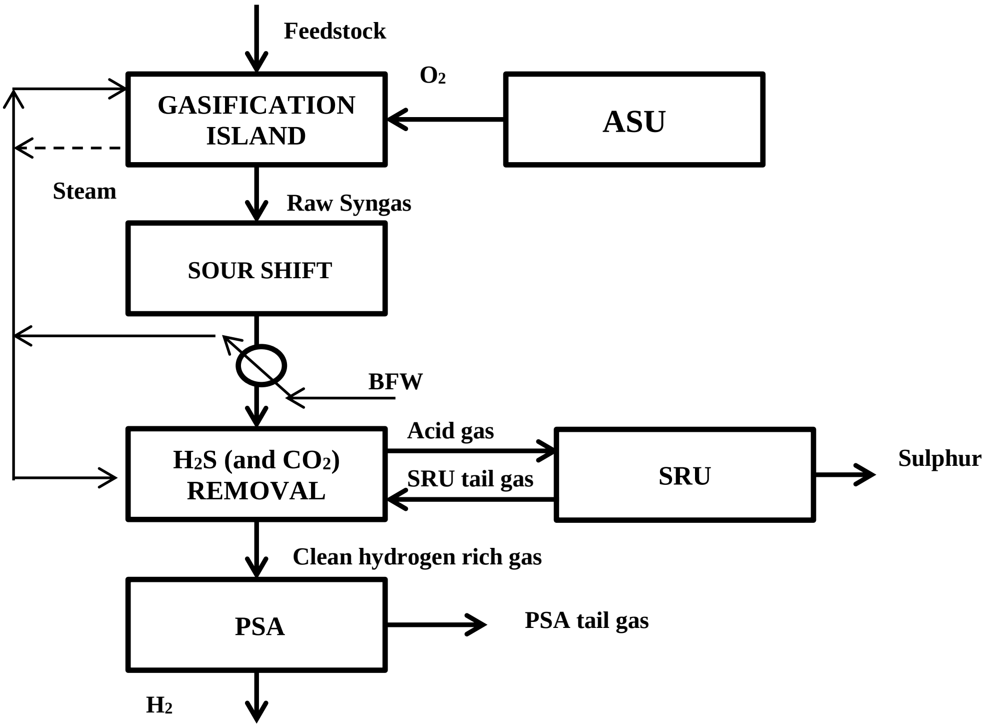
BFD 1: Membrane + PSA



BFD 2: Clean shift + PSA



BFD 3: Sour shift + PSA



2.4.3. CO_2 Balance in POX Hydrogen Plant

With reference to the BFD shown in the above section 2.4.2, the following tables summarise the carbon balance (expressed as equivalent molar CO_2 flowrate) for each of the different hydrogen production scheme identified. Figures are referred to 100,000 Nm^3/h of hydrogen production.
It has to be noted that in a POX hydrogen plant, not all the carbon content of the feedstock goes in the syngas exiting the gasification unit, as a small amount of unconverted carbon remains (0.5-1.0%) in the slag by-product. Due to the small amount of this unconverted carbon, the balance summarised in the below tables is based on the carbon content of the syngas.

Option 1: Membrane + PSA

In a POX hydrogen plant based on membrane + PSA process for hydrogen production, most of the carbon remains in the non-permeate gas separated in the membrane, while the residual remains in the permeate stream and finally in the PSA tail gas. The below Table 5 shows the simplified balance is case of VR gasification, where around 85% of the carbon contained in the syngas goes in the non-permeate stream.

Table 5 – Typical CO_2 balance. Option 1

Stream	**Equivalent CO_2 flow (kmol/h)**	**Main carbon component (%mol dry basis)**
Clean syngas (H_2: 40-45%)	22,470	CO: 45-50% CO_2: 6-8% CH_4: 0.5%
Non-permeate (H_2: 35%)	19,470	CO: 55-60% CO_2: 6-8% CH_4: 0.5%
Permeate H_2-rich gas (H_2: 65%)	3,020	CO: 25% CO_2: 10% CH_4: 0.5%
PSA tail gas (H_2: 25-30%)	3,020	CO: 50-55% CO_2: 20-25% CH_4: 0.5%
H_2 (99.5% purity)	-	-

It has to be noted that, the amount of hydrogen product being fixed, the membrane process requires a higher amount of syngas (compared to Options 2 and 3) and consequently of feedstock and related amount of carbon, due to the significant amount of non-permeate syngas. This stream is normally used as fuel in a combined cycle plant, as the membrane process is normally used in IGCC plant with combine hydrogen and power production.

Option 2: Clean shift + PSA

In a POX hydrogen plant based on clean shift + PSA process for hydrogen production, the carbon in the syngas goes into the PSA off-gas. Part of the CO_2 in the raw syngas eventually separated H_2S removal is returned to the gas processing plant within the tail gas stream. The below Table 6 shows the simplified balance for a POX plant based on quench gasification of coal.

Table 6 – Typical CO_2 balance. Option 2

Stream	**Equivalent CO_2 flow (kmol/h)**	**Main carbon component (%mol dry basis)**
Clean syngas (H_2: 35-40%)	3980	CO: 40-45% CO_2: 15-20% CH_4: 0.5%
Shifted syngas (H_2: 40-45 %)	3980	CO: 0.5-1.0% CO_2: 30-35% CH_4: 0.5%
PSA tail gas (H_2: 10-15%)	3980	CO: 1-1.5% CO_2: 80-83% CH_4: 0.5%
H_2 (99.5% purity)	-	-

Option 3: Sour shift + PSA

In a POX hydrogen plant based on sour shift + PSA process for hydrogen production, the carbon balance is similar to the clean syngas case. However, as the acid gas removal is foreseen downstream the shift where most of the CO is already converted into CO_2, this scheme is the best suited for capturing the CO_2. In this case, as shown in the below Table 7, most of the CO_2 is recovered in the AGR and sent to plant BL as a separate stream.

Table 7 – Typical CO_2 balance. Option 3

Stream	**Equivalent CO_2 flow (kmol/h)**	**Main carbon component (%mol dry basis)**
Raw syngas (H_2: 35-40%)	3980	CO: 40-45% CO_2: 15-20% CH_4: 0.5%
Shifted syngas (H_2: 40-45 %)	3980	CO: 0.5-1.0% CO_2: 30-35% CH_4: 0.5%
CO_2 stream from AGR (H_2: < 2%)	3580	CO_2: 98% CO: 0.2%
H_2-rich gas from AGR (H_2: 85-90%)	400	CO_2: 5% CO: <1%
PSA tail gas (H_2: 45-55%)	400	CO: 4-5% CO_2: 25-30% CH_4: 1%
H_2 (99.5% purity)	-	-

2.4.4. *Energy performance*

The POX hydrogen plant energy balance shall take into account the following consumption/production:

- Feedstock consumption
- Electric power consumption
- Fuel gas (PSA tail gas) production
- Steam generation

All the above items vary significantly depending on the following:

- Hydrogen production process (shift or membrane)
- Feedstock
- Gasification technology.

The gasification technology and the feedstock have an impact, not only on the fuel consumptions directly related to the gasification island (e.g. feedstock consumption, steam generation), but also on the ASU electric consumption as the oxygen demand varies with the gasification and the feedstock type. A minor impact is related to the technology for acid gas separation.

This section focuses on the hydrogen production process based on the shift option as dedicated to hydrogen production whist the membrane can be selected only in case of huge co-production of exported syngas/power.

The below Table 8 summarises the main consumption/production figures for a 100,000 Nm^3/h POX hydrogen plant based on sour shift + PSA.

Table 8 – Main consumption/production figures

Hydrogen production 100,000 Nm^3/h (300 MWth LHV basis)	
Feedstock consumption, MWth LHV basis	450-540
Electric Power consumption, MWe	35-45
Steam generation, MWth	30-70
Fuel gas production, MWth LHV basis	40-50

It has to be noted that, while in the steam reformer the PSA tail gas is used as bulk fuel for the SMR itself, the PSA off-gas of the POX plant shall be used in a dedicated power plant for power and steam generation in order to close the steam and electric power balance of the whole POX plant.

In most of the POX plant, the PSA off-gas and the steam generated (in particular in plant based on WHB/radiant quench gasification technology) are adequate to cover the whole POX plant power demand, as shown in the below performance table (Table 9), relevant to a coal fired radiant syngas cooler gasification technology[2].

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[2] IEAGHG, *CO_2 capture at coal based power and hydrogen plant*, Report 2014/03, July 2014

Table 9 – Performance summary

POX H_2 Plant Performance Summary **(Power island: off-gas fired boiler)**		
INLET STREAM		
Coal Flowrate (as received)	t/h	75.0
Feedstock thermal energy	**MWth (LHV)**	**539**
OUTLET STREAM		
Hydrogen flowrate	Nm^3/h	100,000
Thermal Power of Hydrogen	MWth (LHV)	298
Thermal Power of offgas to boiler island	MWth (LHV)	45
ELECTRIC CONSUMPTION/GENERATION		
Power plant gross power output	MWe	55
Plant power consumption	MWe	42
Excess power to the grid	**MWe**	13

Considering a POX plant where the power / steam / off-gas fuel are closed without any import/export, the energy efficiency can be expressed as:

$$\underline{\text{Feedstock (GJ/h) / 1000 Nm}^3\text{/h H}_2\text{ product}}$$

Typical efficiency values range from 15.9 to 19.3 GJ/1000 Nm^3 of H_2.

2.4.5. *References for Licensors and largest capacity Plants*

The top entrained flow gasification technology licensor to be integrated in a POX based hydrogen plant are listed below:

- Shell
- General Electric
- Siemens
- Mitsubishi Heavy Industries
- E-Gas

Table 10 – Large capacity POX hydrogen plants

Owner	Location	Feedstock	Capacity	Gasifier Licensor	Final Product
Linde North America	LaPorte, USA	Natural gas	4,800,000 Nm^3/h as Syngas (existing facilities) + 2,400,000 Nm^3/h as Syngas (planned in 2015)	GE	Chemicals
Qatar Petroleum	Qatar	Natural gas	3,300,000 Nm^3/h as Syngas	Shell	Liquid fuels
Reliance Industries Ltd.*	Jamnagar, India	Petcoke	2,720,000 Nm^3/h as Syngas	E-Gas	Power/Chemicals
Shell	Pernis, NL	Visbreaker residue	112000 Nm^3/h	Shell	Power/Steam /H_2
SARLUX	Sardinia, Italy	Visbreaking tar	60000 Nm^3/h	GE	Power/Steam /H_2
Coffeyville Resources	Coffeyville, Kansas, USA	Petcoke	~84000 Nm^3/h	GE	Hydrogen for Ammonia
Saudi Aramco*	Jazan, KSA	Vacuum residue	100000	Shell	Power/H_2

*Under design/construction

2.5. Syngas Technology Comparison

The following Table 13 summarizes the main characteristics of the three Hydrogen production technologies described in the previous paragraphs

Table 13 – Syngas technology comparison

Technology		SMR	ATR	POX
Principles	Reaction	Gaseous	Gaseous	Gaseous & Heterogeneous
	Catalytic	yes	yes	no
	Heat Supply	Indirect (firing)	Direct (O2)	Direct (O2)
Feed		Natural Gas, Refinery Off-Gas, LPG, Naphtha	Natural gas, Refinery Off- Gas, Partially Reformed Gas	Natural Gas, Refinery Off-gas, Coal, Heavy Oil, Petcoke, Residue
Reforming	Equipment	Externally heated catalyst filled tubes in a furnace	Refractory lined reactor	Refractory lined reactor
	Pressure, barg	15-40	30-50	40-80
	Temperature, °C	750-950	950-1050	1200-1400
	Steam/Carbon ratio mol/mol	1.8-3.0	1.0-2.0	0.1-0.5
	H_2 in syngas , mol% (Dry basis)	73-68	63-65	35-45
	H_2/CO in syngas mol/mol	3.5-5.5	2.5-3.5	1.5-2.0
	CO_2 in syngas, mol% (Dry basis)	7-10	30-35	6-20
	CO_2 in syngas, shift outlet mol% (Dry basis)	15-20	25-30	30-35
	CH_4 in syngas, mol% (dry basis)	2-6	1-3	0.2-1

Syngas Cleaning		-	-	Soot scrubbing & washing, H2S removal, sulphur production unit

2.6. Hydrogen Production and COGEN

Nowadays, the importance of high flexibility and efficiency is growing in the worldwide market of hydrogen and more in general of the chemical production from syngas (HyCO market) in the refinery and in the petrochemical/chemical sectors. The final goals are reducing the plant capital and operating costs and the plant emission in order to respect the more stringent environmental regulation and lower the carbon emission.

At the same time, power plants must face with the challenges of the liberalized electricity market and the requirement to respond to the daily and seasonal variation of the electricity demand.

Drivers for these requirements are related to the floating of the fuel and electricity prices and the growing importance of the economic issue particularly in the current scenario of the global economic crisis.

The combined production of different products represents one of the most effective approaches to improve plant economics and reduce the global emissions.

In particular, the co-production of hydrogen, electricity and steam can be achieved in a poly-generation plant or integrating the hydrogen production plant with a cogeneration power plant.

The poly-generation plant is generally a gasification based plant, where the generated syngas is partly used for hydrogen production in PSA or for power generation in a syngas fired combined cycle, with the ability to vary the electricity-to hydrogen output keeping the plant at base-load depending on the electricity demand, with significant economic advantages. For detailed description of the co-production of power and hydrogen in a POX-based poly-generation plant reference can be made to IEAGHG report 2014/03 '*CO_2 capture at coal based power and hydrogen plant*'.

A SMR hydrogen plant can be combined and integrated with a power plant for combined steam and power production (COGEN unit). In this case, the hydrogen demand and the SR plant configuration (in particular the steam generation pressure) are the drivers for the selection of the COGEN unit capacity and consequently the amount of produced steam/power and also configuration.

The different alternative configuration of an integrated SMR based Hydrogen Plant with a COGEN unit are described in section 2.2.1 of this Technical Review.

2.6.1. *Advantages of hydrogen and power coproduction*

The main advantages of the combined production of hydrogen, power and steam in a poly-generation plant or in an integrated hydrogen and COGEN plant are listed below.

- **Integrated project execution.**

  It is simpler and less expensive to build a single integrated plant that produces H_2, steam and power compared to several stand-alone facilities. A single project provides engineering design and construction cost savings, furthermore some redundant equipment can be eliminated. Many utilities such as boiler feed-water, firewater, condensate return and wastewater disposal can be shared. Likewise, the electrical substation, cooling tower, control room maintenance and supplies warehouse can be combined.

- **Economy of scale**

  The production of H_2, steam and power can be highly capital intensive, in particular for coal/heavy residue POX plant. A poly-generation plant lead to a significant capital cost saving, in particular if the required amount of each product is not large enough to justify the development of a dedicated facility. The syngas production line is sized to meet the requirement for the production of both hydrogen and power, reducing the capital cost by designing a single larger plant.

- **Improved energy efficiency.**

  The overall plant efficiency can be improved by exploiting the possible integration between the power island or the COGEN and the syngas/hydrogen plant.

  Considering an IGCC with combined hydrogen production, the PSA offgas can be fired in the HRSG supplementary firing syngas and the cold condensate from the combined cycle can be pre-heated against syngas in the gas processing line, saving steam in the power island and also reducing the cooling water required for the syngas cooling.

  In a SMR integrated with a COGEN unit based on a gas turbine, energy efficiency is improved by introducing the gas turbine exhaust into the radiant section of the SMR, reducing stack heat losses. Additionally, secondary benefits include reduced total radiation losses, improved back end heat recovery and reduced cooling water flow. The energy consumption for an integrated SMR cogeneration configuration can be about 20% less compared to similarly sized stand-alone SMR and cogeneration facility.

- **Enhanced reliability**

  As result of the key role played by hydrogen within the refinery, its availability is a critical parameter in selecting plant configuration. The reliability of a SMR is typically high and it is not affected in an integrated plant due to the installation of dedicated design feature (e.g. bypass).

  On the other hand, a POX based poly-generation plant can achieve a high availability on hydrogen as the more critical equipment for the overall reliability (i.e. the gasifier) is oversized with respect to the hydrogen production. In case of critical equipment failure, the priority is given to the hydrogen production increasing the POX plant availability to figures similar to the ones related to the SMR.

- **Flexibility**

  The poly-generation plant allows to vary the electricity-to hydrogen output within a selected design range keeping the plant at base-load depending on the electricity demand and consequently of the electricity selling price, with significant economic advantages. For detailed assessment of the advantages of poly-generation plant for enhancing plant operating flexibility and for plant capabilities to operate efficiently in the variable electricity market shall be made to IEAGHG report 2012/06 '*Operating Flexibility of power Plant with CCS*'.

- **Environmental performance.**

  An integrated design results in reduced CO, CO_2, NO_x and VOCs emissions due to more efficient fuel utilization compared to stand-alone hydrogen and cogeneration Plants.

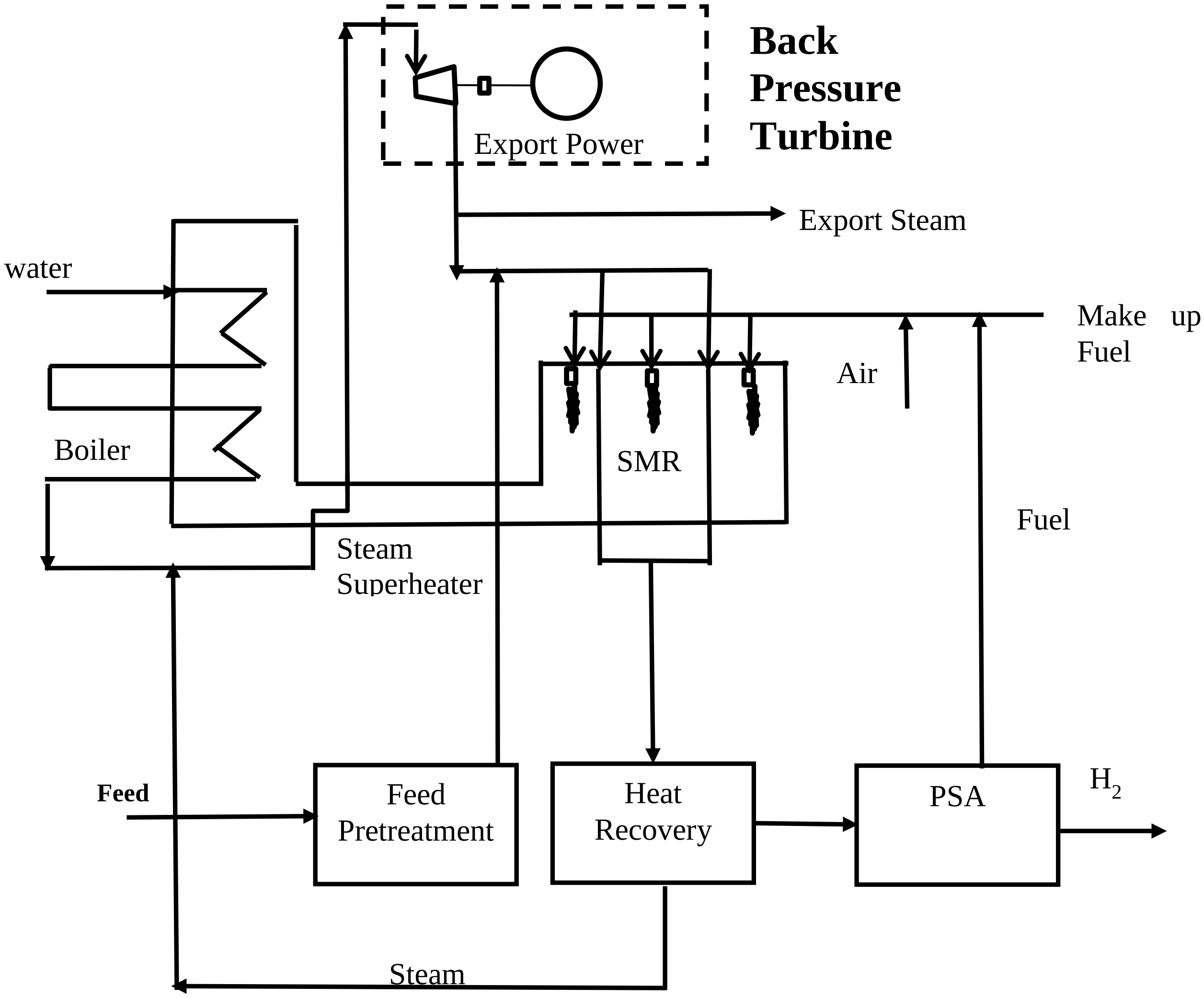
- **Operation and maintenance synergy**

  The total manpower needs are reduced as a result of the combination of the skills employed in power generation and steam methane reforming processes, therefore a single team can operate and maintain all plant equipment from one control room.

2.6.2. Power generation Options

Several options for power generation can be integrated into a SMR Hydrogen plant. Typical alternatives for integrating COGEN system within the SMR hydrogen Plant scheme are listed and described below:

- Back Pressure Turbine:
  In this configuration all of the steam is produced within the hydrogen plant at higher pressure and it is throttled down to lower) in a back pressure turbine producing power A small part of the generated power is consumed for Plant needs whilst the remaining is available to export to the refinery or local grid.
  The figure below shows the simplified BFD for a Hydrogen Plant integrating a topping turbine.



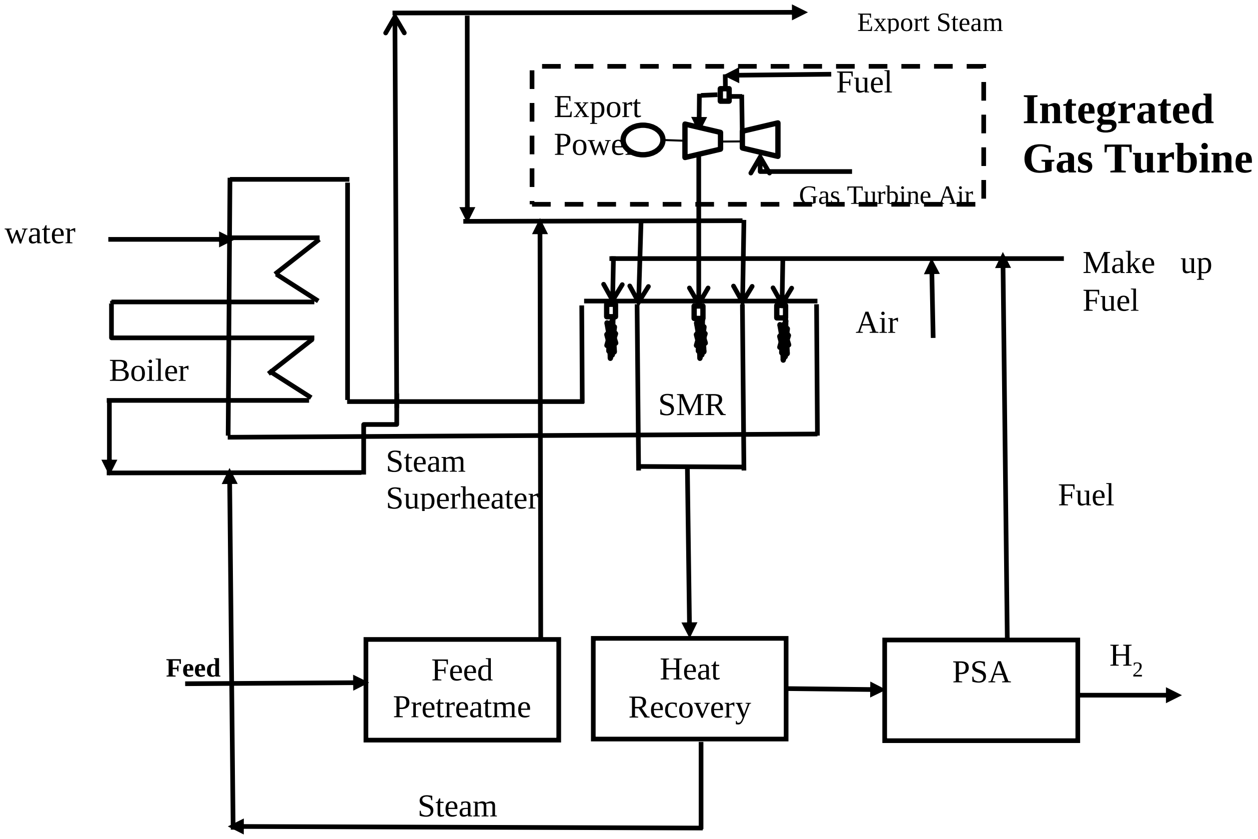
- Integrated Gas Turbine

In this configuration the exhaust from a gas turbine enters the radiant section of the reformer. This gas serves as combustion air to the reformer and, since this stream is hot, reformer fuel consumption is decreased. The convection section replaces the heat recovery steam generator in a cogeneration design. Once heat is recovered, the cooled gas enters an induced-draft fan and leaves via the stack. Steam raised in the convective section can be put through either a back pressure or condensing turbine for power generation.

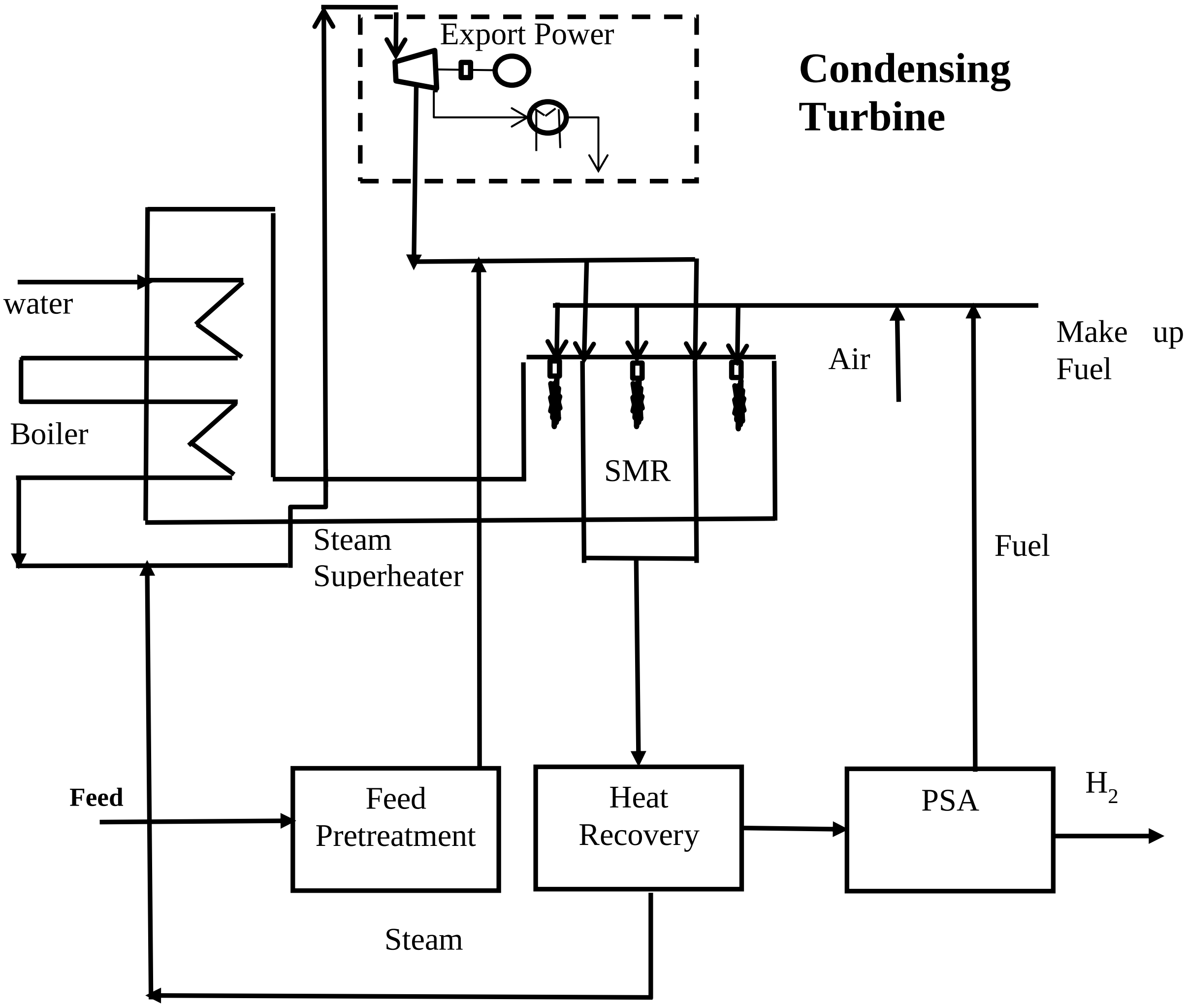
In this configuration, the steam produced in the Hydrogen plant does not need to be upgraded to higher pressure, Natural gas is instead fired in the gas turbine and the resulting produced power is partially used for the SMR Hydrogen plant needs and the rest exported to the refinery or local grid.

This system can be designed such that production of hydrogen can continue in the event of loss of power generation units through the integration of fresh air inlets into the SMR.Hydrogen Plant This allows outages of the gas turbine for maintenance and repair of the turbine generator. Separately, a gas turbine exhaust bypass system allows the gas turbine to be decoupled from the reformer so that, in the event of a reformer trip, the gas turbine can operate and continue to produce electricity.

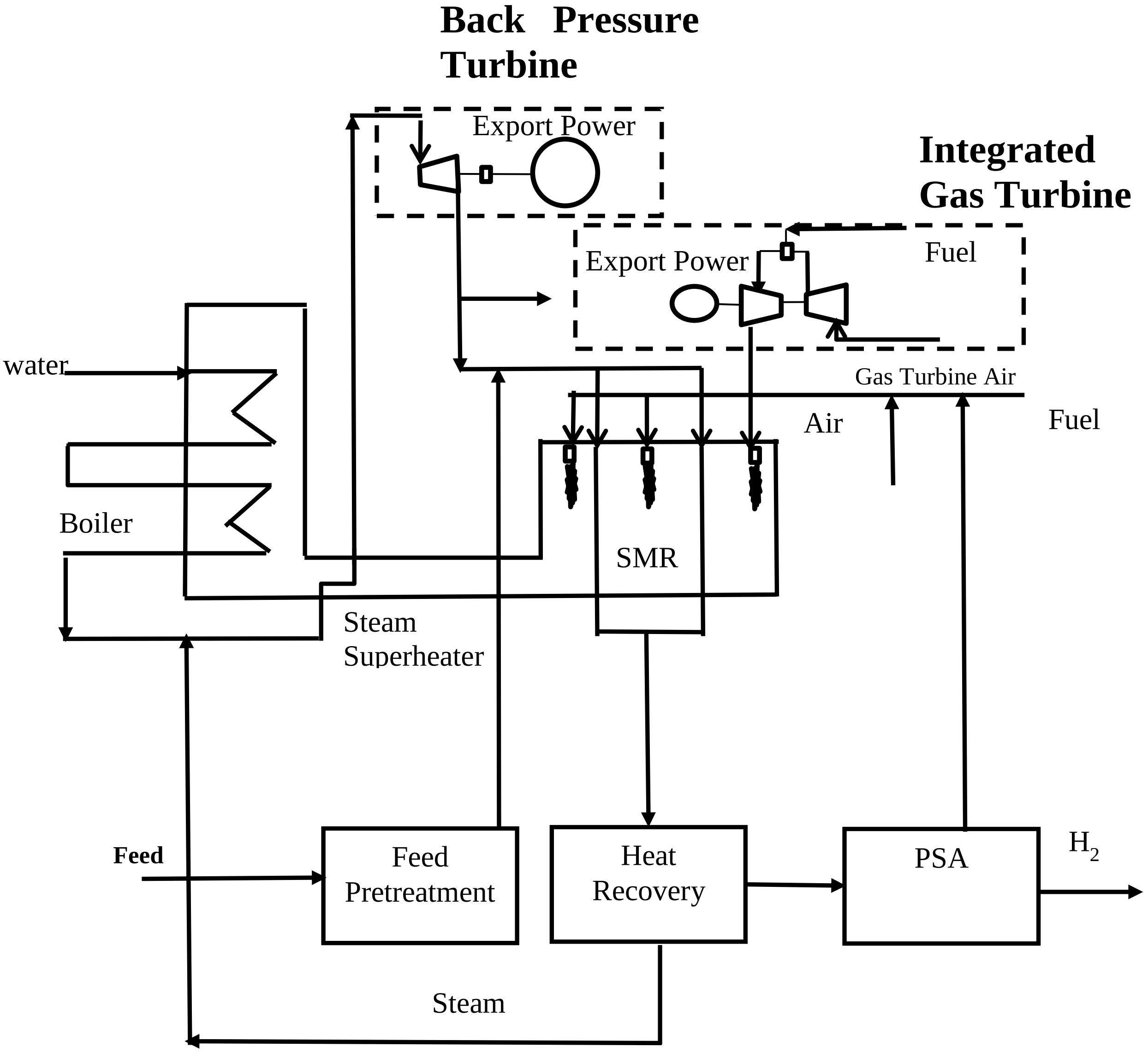
The figure below shows the simplified BFD for a Hydrogen Plant integrating a gas turbine.



- Condensing Turbine
  In this configuration, all of the steam is produced within the SMR Hydrogen Plant at higher. By condensing the export steam, it is possible to convert the sensible and latent heat in steam to power. A small part of the generated power is consumed for plant needs and the rest is available for export to the refinery or local grid. This configuration results in zero export steam. With a condensing turbine it is possible to vary the amount of condensing steam, Consequently, steam production can be decoupled from power generation to meet specific customer needs.
  The figure below shows the BFD for a Hydrogen Plant integrating a condensing turbine



- Back Pressure Turbine and Gas Turbine
  This configuration is a combination of back pressure turbine and gas turbine. Power production is a combination of power production of topping turbine case and of gas turbine case. All of the steam is produced at higher pressure. In this configuration appropriate bypasses can be incorporated into the plant design to decouple hydrogen production from power production.



2.6.3. CO$_2$ emissions

The base case developed in TASK 3 of this Study considers an SMR based Hydrogen Plant integrating power and steam generation units. Refer to TASK 3 for information about CO$_2$ emissions point and CO$_2$ balance data of SMR based Hydrogen Plant with COGEN.

2.7. Hydrogen Recovery and Purification

After Shift conversion the syngas contains about 17% of carbon dioxide (dry basis) and needs to be purified in order to reach the required purity of the hydrogen product. Hydrogen Plants built before the late 1970s incorporated CO$_2$ removal and methanation step in order to purify the hydrogen product. These “old style” Hydrogen Plants could reach Hydrogen product purity not higher than about 97%. Nowadays PSA technology has become the preferred option as it provides higher energy efficiency and higher purity hydrogen.

2.7.1. Pressure Swing Adsorption

Pressure Swing adsorption is the principle process to achieve hydrogen purity levels required in refinery applications (Figure 3).

PSA System can be considered the industry standard for production of high purity hydrogen from streams containing 60 to 90 mol percent hydrogen.

PSA systems can produce 98 to 99.999 percent hydrogen stream with a recovery of 70 to 90 percent.

Pressure Swing Adsorption technology is based on physical binding of gas molecules to adsorbent material. The respective force acting between the gas molecules and the adsorbent material depends on the gas composition, type of adsorbent material, partial pressure of the gas component and operating temperature. The separation effect is based on different in binding forces to the adsorbent material. Highly volatile components with low polarity such as hydrogen are practically non- absorbable as opposed to molecules as CO, CO$_2$ and N$_2$, hydrocarbons and water vapour. Consequently, these impurities can be adsorbed from a hydrogen containing stream and high purity hydrogen is recovered.

The adsorbent material can be zeolites, activated carbons, silica and alumina gels.

Pressure Swing Adsorption process works at basically constant temperature and uses the effect of alternating high pressure and low pressure to perform adsorption and desorption. Since heating or cooling is not required, short cycles within the range of minutes are achieved.

The adsorption step is carried out at high pressure, typically in the range of 10 to 40 bar until the equilibrium is reached. At this point no further adsorption capacity is available and the adsorbent material needs to be regenerated. This regeneration is done by lowering the pressure to slightly above atmospheric pressure resulting in a respective decrease in equilibrium loading. As a result, the impurities on the adsorbent material are desorbed and the adsorbent material regenerated. The amount of impurities removed from a gas stream within one cycle corresponds to the difference of adsorption to desorption loading. After termination of regeneration, pressure is increased back to adsorption pressure value and the process starts again from the beginning.

Some hydrogen is purged with the impurities into the fuel system which can be used to fire the reformer furnace. The pressure fluctuation in the purge gas to fuel is evened out in surge drums.

To provide continuous hydrogen supply minimum four adsorption vessels are required.

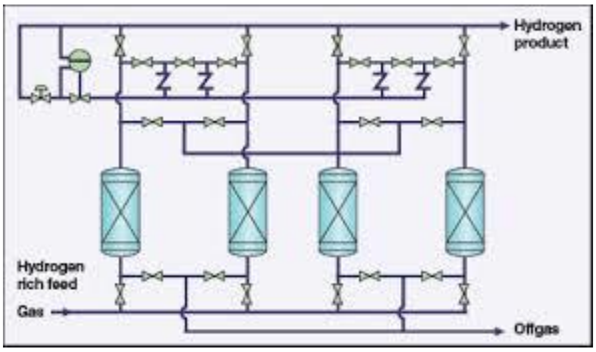


Figure 3 – Typical 4-beds PSA scheme (source:UOP)

2.7.2. *Chemical Absorption*

A detailed description of Chemical Absorption based purification processes is provided in Technical Review 2, section 2.1.1-2.1.2.

2.7.3. *Physical Absorption*

A detailed description of Chemical Absorption based purification processes is provided in Technical Review 2, section 2.1.1-2.1.2.

2.7.4. Membranes

Membrane separation system can be used to recover hydrogen from refinery streams. Membranes are a pressure driven process, where a semi-permeable layer is used to selectively separate hydrogen from other impurities. Membrane processes are continuous unlike PSA (which is cyclical). Membranes are mainly used in smaller scale applications because of the scalability of PSA processes.

Hydrogen separation membranes represent an attractive solution for achieving both economical hydrogen production and CO_2 separation, depending on the particular situation or opportunity. They have certain advantages when compared to other recovery technologies in cases where high recovery and less stringent purity are required. In addition, the can operate at moderate pressure and temperature with notable exceptions for the latter. Membranes require less maintenance because the lack moving parts and have less complex control systems than most other hydrogen purification technologies. The on-stream lifetime of a membrane depends on the nature of the feed stream. Streams containing compounds that can react with or foul the membrane will result in significantly shorter lifetime.

Polymers are currently the primary material utilized for refinery separation processes. They currently offer the greatest cost to performance ratio. However, the feed must undergo a pre-treatment process in order to allow the membrane to separate efficiently.

All condensates and water vapour must be removed prior to membrane. Membranes coupled with PSA are one of the possible options for producing hydrogen from a POX based Hydrogen Plant. More details about this specific application can be found in section 2.3.1 of this review.

Section 2.4 of Technical Review 2 reports additional information on membrane application for H_2 purification.

2.7.5. VPSA

VPSA (Vacuum Pressure Swing Adsorption) is a technology similar to PSA, but the final depressurization step is carried out under vacuum, thus requiring a vacuum pump. This technology has some application in air separation in order to obtain a oxygen-rich stream, in the range of 90% purity, as depicted in the Figure 4 below.

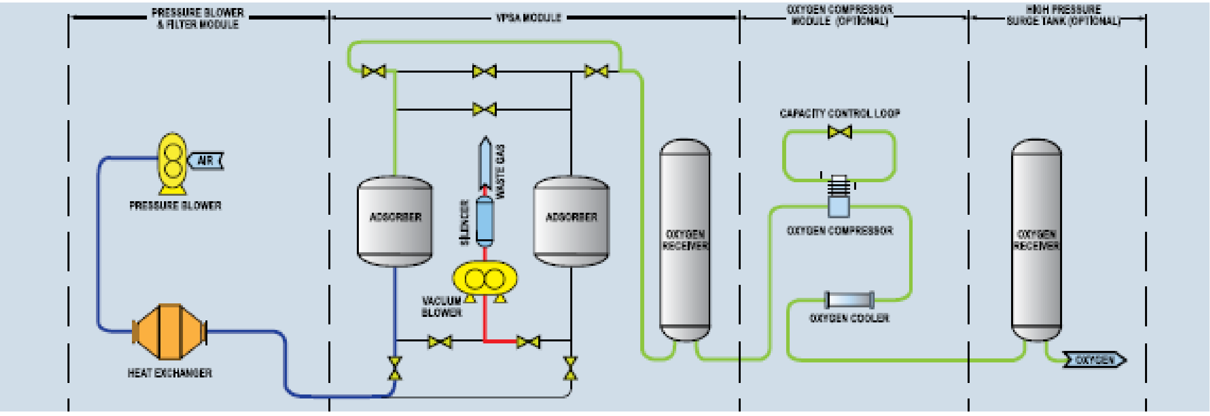


Figure 4 – Air separation via VPSA (source: AirSep)

When the inlet operating conditions (pressure and temperature) are near-ambient, the technology is simply called VSA.

VPSA may be applied for hydrogen recovery in place of the standard PSA.
The only advantage of a VPSA is the increased hydrogen recovery. For a large steam reformer PSA, the normal hydrogen recovery would be 89% ±1%, while a VPSA would achieve around 94-95% hydrogen recovery. This would give a slightly higher CO_2 concentration in the tail-gas from around 50 to 60%.

By increasing the hydrogen recovery, the tail gas calorific value is reduced which, in turn, leads to a higher consumption of supplementary fuel and reduced efficiency.

The disadvantages for VPSA are:

1. Level of complexity, in fact as well as cycling the absorbers we have to cycle the vacuum pump.

2. Higher capital cost: adsorbers, adsorbent is similar to positive pressure PSA, but vacuum pumps are needed probably a building to house them and the valve skid.

3. Higher running cost, high power consumption.

4. Higher plot requirements, need space for vacuum pumps.

5. High maintenance and lower reliability.

VPSA is seldom adopted today in hydrogen plants; however some Chinese mfr. has VPSA in reference list, both as new installation or revamping of standard PSA.

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APPROVED BY	:	G. Collodi

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TABLE OF CONTENT

1. Introduction

In the scientific community it is generally acknowledged that to manage the risk of climate change, substantial reduction in carbon dioxide emissions from power production and other high carbon intensive emitting industries is required.

More widely, it can be stated that CCS is the only technology currently available or on the horizon that can de-carbonize sectors, in addition to the energy-segment, such as refinery, cement, or iron and steel.

Scope of this Technical Review 2 is to provide a general overview of the state-of-the-art technologies that are commercially available for capturing the carbon dioxide (CO_2), mainly in connection with hydrogen production.

2. Review of technologies for CO_2 capture from Hydrogen Production Unit

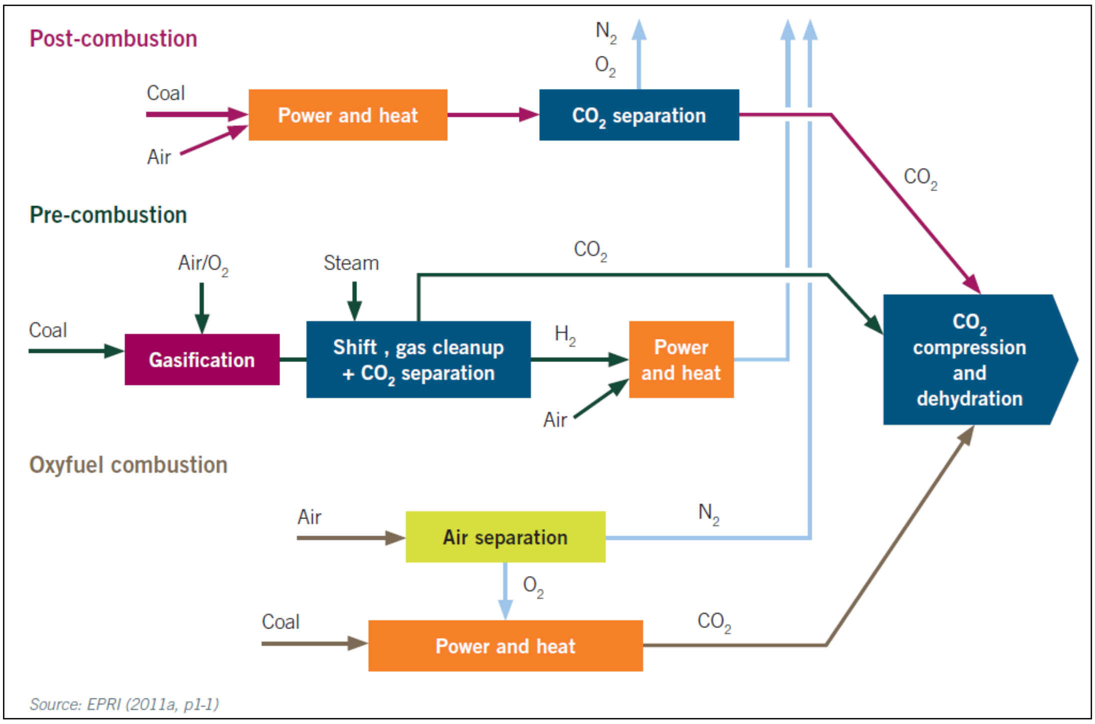
2.1. Description of CO_2 capture options

2.1.1. *Process types*

The most important de-carbonization schemes that can be adopted for capturing the CO_2 in conventional power plants can be grouped as follows:

- ✓ Pre-combustion processes;
- ✓ Post-combustion processes;
- ✓ Oxy-combustion processes.

Depending on the type of plant and on the carbon sequestration technology, CO_2 capture units can be differently integrated into traditional plants configurations, as shown in the following Figure 2.1 for coal-based power plants (and also applicable to power plants firing different feedstock).



Source: EPRI (2011a, p1-1)

Figure 2.1: Main CO_2 separation schemes for coal-based power plants

All the considerations made for power plants are applicable also when the main product is hydrogen, with the peculiarities indicated in the following paragraphs, where appropriate. The Section 2.2 specifically addresses the CO_2 capture technologies applied to SMR/ATR hydrogen plant.

Post-combustion technologies foresee the CO_2 capture downstream the combustion section. In this case, carbon dioxide is contained in the hot flue gases, for example from the Steam Reforming furnace, together with other products and inerts from the combustion (N_2, H_2O, O_2, SO_2, etc.). Gas pressure is nearly atmospheric and CO_2 partial pressure for the stream is generally low (around 10-15%vol).

In pre-combustion processes, CO_2 is usually removed from a stream of raw synthetic gas, or syngas, derived from a steam reforming, an autothermal or a gasification process, containing H_2, CO, CH_4, H_2S (depending on the type of feedstock and technology), N_2, H_2O and other trace elements components. The syngas typically passes through one or two shift reaction stages (to increase the amount of H_2 and reduce that of CO) and different cooling steps, before entering the Acid Gas Removal (AGR) section, where carbon dioxide and sulphur components are separated.

Oxy-combustion processes differ from traditional combustion ones because the combustant is not constituted by air but by a stream of high purity oxygen. The use of high purity oxygen involves the installation of an Air Separation Unit (ASU) and special design precautions shall be taken for the boilers, but this technique allows generating a stream of flue gases mainly composed by water, carbon dioxide and a small amount of inert gas (mainly O_2, N_2, Ar). Therefore, with oxy-combustion technologies carbon dioxide partial pressure in the flue gases is much higher than in traditional combustion units. Final CO_2 purification consists in several steps for water removal by condensation and TSA and finally inert gas removal by cryogenic separation of liquid carbon dioxide.
Being specific for power plant applications, for the scope of the present study oxy-combustion is not further assessed.

In more general term, the most common processes nowadays available for acid components (including CO_2) removal from a gas stream can be classified as follows:

- Absorption processes: they are characterized by a solvent washing process for separation of sour component from the gas. Depending on the type of solvent, the process can be a chemical absorption, a physical absorption, or a hybrid type of absorption. For both the pre- and post-combustion processes, absorption is the most quoted technology for capturing the CO_2 from a gas stream (syngas in case of pre-combustion or flue gas in case of post-combustion) and further details on the types of solvents can be found in section 2.1.2.

- Adsorption processes: in this kind of processes the gas comes into contact with the adsorbent solid surface, which makes the acid gas removal from the stream, thanks to chemical bonding interactions between the gas and the solid phases. Typical process configurations are Pressure Swing Adsorption (PSA) and Temperature Swing Adsorption (TSA). The adsorbent is characterized by a high surface capacity to improve contact with the gas stream and by high selectivity for acid components to be removed. However, the use of adsorption techniques is not economically attractive for large-scale post-combustion processes, due to the low pressure of the gases and their relevant low driving force. This is also valid for the large-scale pre-combustion processes, because a significant part of hydrogen and nitrogen would pass in the CO_2 stream, thus corresponding to a non-negligible thermal loss in the plant.

- Other removal processes: the main acid gas removal processes differing from absorption and adsorption are cryogenic separation and membranes.
  Cryogenic separation operates at extremely low temperature to separate carbon dioxide up to certain purity. This kind of process is typically used in combination with oxy-combustion technologies for inert gas removal after water separation as the flue gas stream is almost totally composed by carbon dioxide, as further analysed in section 2.1.3 of this report.
  Membrane separation is based on a selective permeation principle, allowing the acid gases to diffuse through the membrane. This is not a commercially fully developed technology yet and it is still undergoing a research and development phase. It will be further discussed along with other emerging technologies in section 2.4 of this report.

2.1.2. *Solvent types for absorption processes*

An appropriate selection of the process and solvent type is a key factor for the performance of the whole plant, since CO_2 capture units heavily affect the internal energy demand.

For heavy residue / coal fired plants, the presence of sulphur in the feed can be significant and in this case the washing processes shall be capable either to capture H_2S from the syngas in gasification plants with pre-combustion capture, or to face with the presence of SOx in the flue gases in boiler based power plant with post-combustion capture and oxy-combustion process.

As above stated, in absorption processes the acid components contained in a gas stream are removed by means of a solvent washing process. The typical absorption configuration foresees two main process steps:

- *Absorption*, in which the gas is deeply contacted with the clean solvent and the acid components are transferred to the liquid phase;
- *Desorption/stripping*, in which the rich solvent is regenerated with the removal of the previously absorbed acid gases by means of suitable pressure and temperature variations.

Several different solvent washing processes are commercially available both for pre- and post-combustion capture of the CO_2. They can be grouped into the following main categories:

- ✓ *Chemical solvents*;
- ✓ *Physical solvents*;
- ✓ *Physical-chemical or hybrid solvents*.

With ***chemical solvents,*** the carbon dioxide to be removed from the gas stream chemically reacts with the solvent forming new product components. The reaction is reversed and the acid gases are released during the solvent regeneration process.

Chemical solvents are capable to remove high amounts of CO_2 at low partial pressure, i.e. before the solvent gets saturated with the acid gas and loses absorption capacity (Figure 2.2).

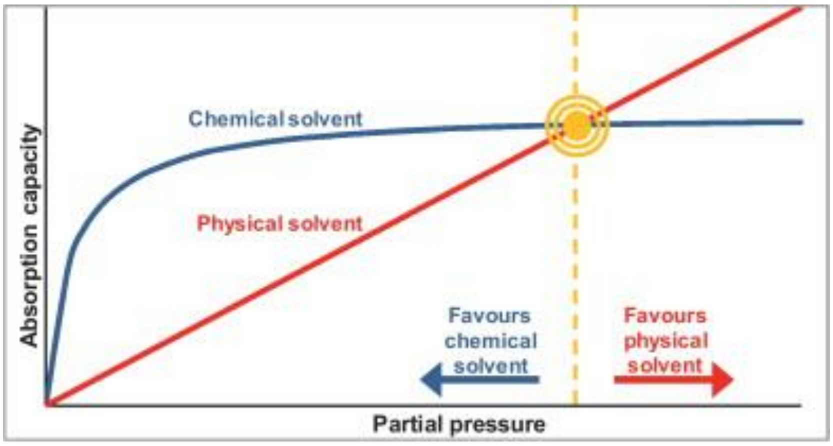


Figure 2.2: Absorption capacity of chemical and physical solvents

As shown in the above figure, chemical absorption process is not much dependent on the CO_2 partial pressure in the gas stream.

Solvent regeneration is usually operated by means of temperature increase, sometimes in combination with flashing sections.
Usually, chemical solvents are characterized by low investment costs, but on the other hand they suffer from high energy requirements for regeneration and from chemical degradation in presence of oxygen and other impurities (e.g. COS and C_2S for MEA). Chemical solvents include many *amines*, *hot potassium carbonate*, *ammonia* or *amino acids*.

Amines are organic compounds derived by ammonia (NH_3) in which one or more of the hydrogen atoms are replaced by an organic group. Depending on the number of alkyl groups bonded to the nitrogen atom, amines can be classified as either primary (e.g. MEA), secondary (e.g. DEA), or tertiary (e.g. MDEA).

MEA (or monoethanolamine, Figure 2.3) is the most common primary ammine used for CO_2 sequestration; it is characterized by one ethanol group replacing one of the ammonia hydrogen atoms.
It shows high reactivity with CO_2 and is thus effective at removing virtually all carbon dioxide, but requires a large quantity of heat for regeneration, because of the strong chemical bonds created during the CO_2 removal process.

Secondary amines are less reactive with carbon dioxide if compared to primary ones, due to their more complex molecular structure. They are suitable for CO_2 removal processes from gas streams with less stringent product specifications. One example is

DEA (or diethanolamine, Figure 2.3) in which two of the hydrogen atoms of the ammonia are replaced by ethanol groups. It requires less regeneration heat with respect to MEA but it is not capable to reduce the carbon dioxide content in the gas to significantly low levels.

Tertiary amines are used when a certain acid gas selectivity is required, but their utilization is not advisable with low acid gas partial pressure or when a deep CO_2 removal efficiency has to be achieved, due to their lower reactivity with CO_2 if compared to primary and secondary amines. MDEA (or methyl-diethanolamine, Figure 2.3) is one of the most frequently used tertiary amines, requiring a pressure higher than approximately 20 barg. It is formed by a nitrogen atom bonded to 1 methyl and 2 ethanol groups. MDEA requires very low regeneration energy and is particularly selective with H_2S, but is characterized by a slow reaction rate, if compared to primary and secondary amines, being absorption rate strictly controlled by resistance to mass transfer resistance in the liquid phase. It is therefore often associated to a reaction promoter, typically piperazine, which is highly reactive with CO_2 (kinetic is about ten times faster than with MEA). Since only small concentrations of piperazine are needed to enhance absorption rates, penalizations in terms of energy requirement for solvent regeneration are limited.

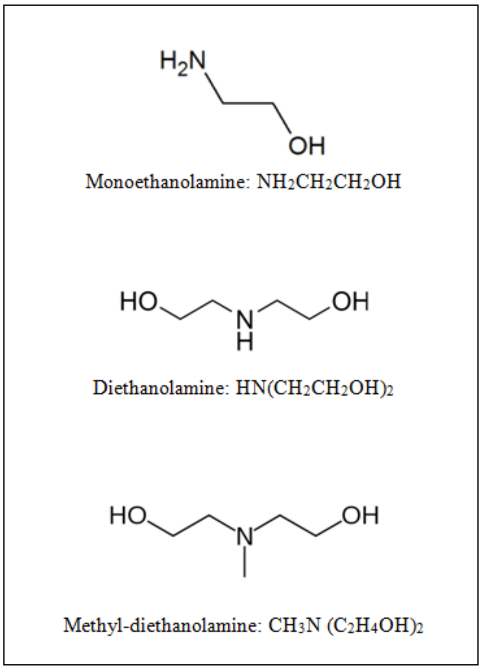


Figure 2.3: Main primary, secondary and tertiary amines

In addition to the above mentioned amines, there are other forms of amines like the sterically hindered amines, where the amino group is attached to a tertiary carbon atom. For instance, 2-amino-2-methyl-1-propanol (AMP) is a commercially available sterically hindered form of MEA. Another sterically hindered amine, which is used in the industry, is 2-amino-2-methyl-1,3-propanediol (AMPD). AMPD has a similar chemical structure to AMP, where one of the -H is replaced by -OH.

The absorption of CO_2 by a *Hot Potassium Carbonate* solution is a chemical reaction where the CO_2 reacts with the dissolved potassium carbonate forming potassium bicarbonate, according to reaction [1], proceeding left to right, while by heating, the potassium bicarbonate is decomposed, releasing the CO_2 and restoring the potassium carbonate, proceeding right to left.

$$CO_2 + H_2O + K_2CO_3 = 2KHCO_3 \quad [1]$$

The CO_2 absorption is enhanced by the presence of an activator (e.g. glycine, DEA). Since the formation and decomposition of potassium bicarbonate is controlled by the law of chemical equilibrium, potassium carbonate and bicarbonate co-exist in the solution. It is customary to express as Fractional Conversion (FC) the content of bicarbonate present as carbonate.

Ammonia is used as a solvent in an aqueous solution and is capable of capturing the CO_2 from flue gases through ammonium bicarbonate formation. Ammonia processes are usually operated at atmospheric pressure but require cooling of the feed gas below ambient temperature. The main advantage in the use of ammonia as a solvent is the lower energy requirement for regeneration if compared to amines. On the other hand, the risk of solvent entrainment in the carbon-free gases is higher and should be carefully evaluated. Moreover, it has to be highlighted that, according to literature data, the reactivity of ammonia is significantly less than amines.
Therefore, in order to obtain an adequate mass transfer for an efficient CO_2 absorption in ammonia based systems, packed columns shall be taller than amine systems, leading to a higher capital cost requirement for the capture unit.

Amino-acids (e.g. glycine and taurine) are used in the form of salt solution, with negligible vapour pressure and low sensitivity to the oxygen degradation. They also show good reactivity with carbon dioxide, comparable to that of amines. This solvent has low environmental impact and is easy to handle, if compared to ammonia or amines.
However, development work of these systems is well behind that of conventional amines and significant testing is still required before arriving to large, commercial scale plants.

Physical solvents capture CO_2, H_2S and/or other acid gases by dissolving these molecules into the liquid phase, without changing their chemical composition (no chemical reactions happen). Physical absorption process takes place in accordance with the Henry's law, which states that "at a constant temperature, the amount of a given gas dissolved in a given type and volume of liquid is directly proportional to the partial pressure of that gas in equilibrium with that liquid". Therefore, these solvents are favoured at elevated operating pressure (greater than 30 barg) and at high CO_2 partial pressures in the gas stream, as it is possible to see from above Figure 2.2.
In physical absorption processes, in order to improve the solvent effectiveness, the absorption step usually takes place below ambient temperature while the regeneration of the solvent is mainly achieved by means of pressure reduction, with a small heat contribution. In carbon capture applications, CO_2 is flashed at various pressures, in order to reduce the compression work and parasitic power load associated to sequestration.
Even if the investment cost is usually higher for physical solvents, their low regeneration energy consumption is one of the advantages with respect to chemical ones.

Selexol®, *Genosorb*®, *Rectisol*® and *Purisol*® are typical examples of physical solvents.

Dimethyl ether of polyethylene glycol (DEPG) is the physical solvent utilized in the *Selexol*® absorption process. In addition to CO_2, it is able to selectively remove H_2S and other sulphur compounds.
Selexol absorption process is typically used for high pressure gas application (greater than 25-30 bar) with high acid gas partial pressures (e.g. syngas treating). Depending on the type of application, the product purity can be more or less severe; the process complexity varies accordingly and chillers to cool the solvent below ambient temperature are often required.
UOP is the reference technology Licensor of the Selexol® process.

Genosorb® is a solvent with composition and characteristics almost identical to Selexol® and is commercialized by Clariant.

Rectisol® process uses methanol (CH_3OH) to remove acid gases from a stream. It is particularly suitable for high pressure and high CO_2 concentration applications. For this reason, it is one of the most common removal processes when extremely high purities of the CO_2 are required or in case of high carbon capture rates. Consequently, its most obvious and natural application is in chemical plants based on syngas feed.
Methanol is a quite economical solvent, showing no particular issues related to impurity contamination or material selection. It is also selective to H_2S, which can be removed separately form CO_2. On the other hand, Rectisol process is rather complex

and requires chilling equipment to reach the desired operating temperature (-40°C/-60°C), leading to an increase in the plant investment cost.
Linde and Lurgi (Air Liquide) are the reference technology Licensors of the Rectisol® process.

Purisol® process uses NMP or N-Methyl-2-Pyrrolidone as a solvent. Its applications are mostly relevant to gas desulphurization processes, being NMP selectivity for H_2S much higher if compared to CO_2. As for the other above mentioned physical solvents, the process is usually performed below ambient temperature.
Lurgi (Air Liquide) is the reference technology Licensor of the Purisol® process.

Physical-chemical or hybrids solvents, which combine the high treated-gas purity offered by chemical solvents with the flash regeneration and lower energy requirements of physical solvents. Sulfinol, as an example, is a mixture of sulfolane (a physical solvent), diisopropanolamine (DIPA) or MDEA (chemical solvent), and water. Hybrid solvent processes usually do not require refrigeration, but are still able to keep the heat consumption low with respect to pure chemical solvents.
Shell is the reference technology Licensor of the Sulfinol® process.

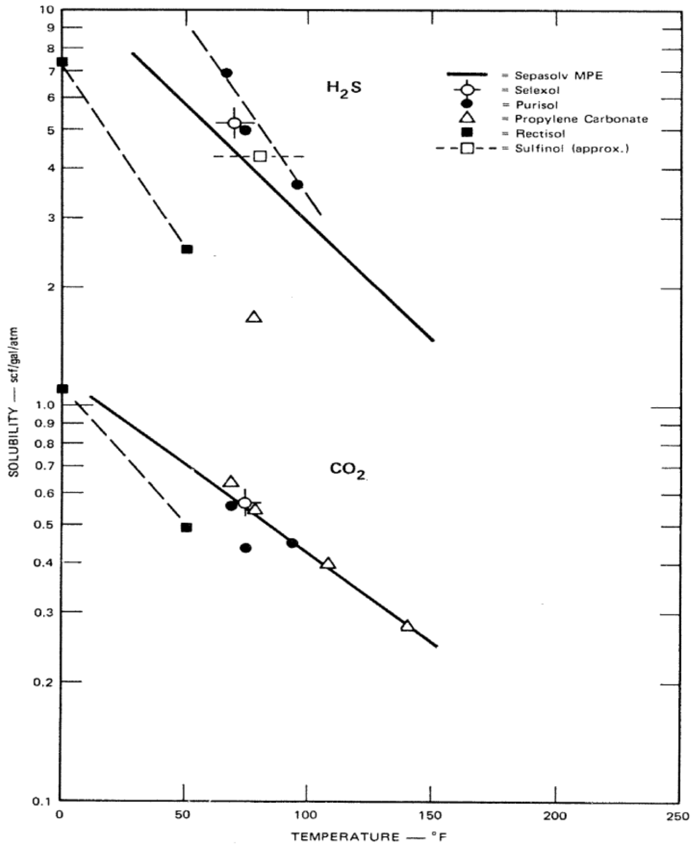


Figure 2.4: Solubility data on H_2S and CO_2 in various solvents [DOE/NETL-2007/1281]

Figure 2.4 shows equilibrium solubility data for CO_2 (and H_2S) in various representative solvents. The solubility is expressed as standard cubic feet of gas per gallon liquid per atmosphere gas partial pressure. The figure illustrates the relative solubility of CO_2 (and H_2S) in different solvents and the effects of temperature. It also shows an order of magnitude higher solubility of H_2S over CO_2 at a given temperature and that the acid gas solubility in physical solvents increases with lower solvent temperatures.

2.1.3. Types of cryogenic purification

Another technique to remove CO_2 from a gas stream is to cool it down to cryogenic temperatures, to liquefy, and to separate it from other components. These processes are particularly suitable when oxy-combustion technologies are applied, since the flue gas stream from the boiler is mainly constituted by water and carbon dioxide, with a limited amount of inert gas.

Depending on the CO_2 final destination and use (e.g. EOR, storage or industrial use), the purity requirements of the CO_2 rich stream leaving the power plant may be different:

- A simple compression of the flue gases could be made separating most of the water, but in this case the carbon dioxide purity would not be greater than 90-92%, due to the presence of inert gas and water traces in the feed stream.
- Cryogenic purification (generally including two flash stages) is a separation process that is normally applied to get CO_2 high purity grades (95-98%).
- If particularly severe specifications are required (>99% CO_2 purity) distillation columns can be integrated to cryogenic purification process.

The following Figure 2.5 shows the main CO_2 properties, which shall be carefully considered in the design of cryogenic purification systems (e.g. triple point).

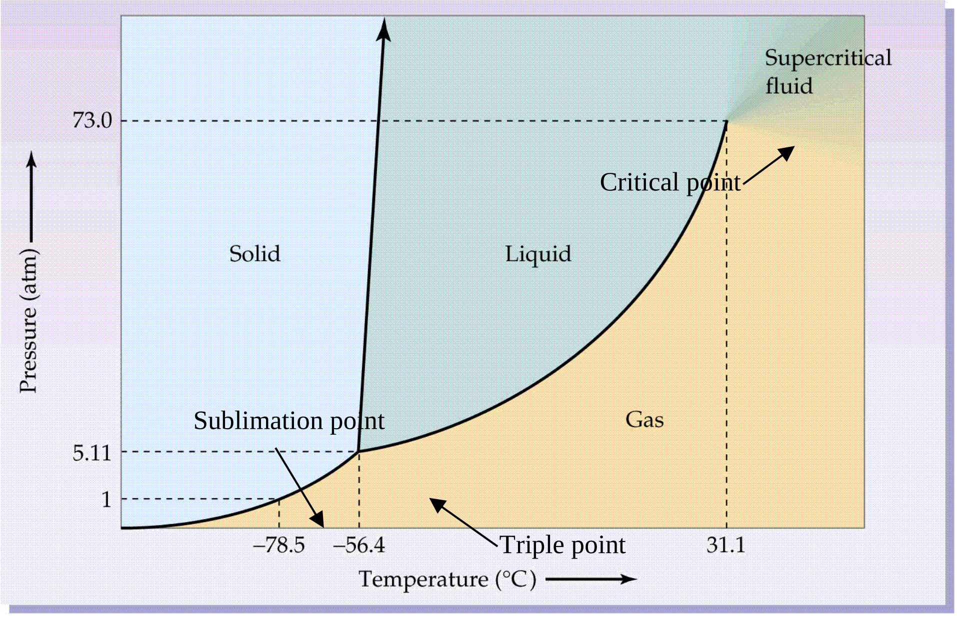


Figure 2.5: CO_2 phase diagram

The process based on an “auto-refrigerated cycle”, uses the expansion of the gases generated and compressed in the process to make the cooling of the flue gases. Although there are not yet many industrial applications, the use of this process will likely increase in the next years because it shows several advantages with respect to the use of a conventional refrigeration cycle, namely lower investment cost and lower energy demand.

Nowadays several Companies (e.g. Air Liquide, Air Products, Linde and Praxair) have developed and tested at pilot/demo plant scale the auto-refrigerated technology for the cryogenic CO_2 purification process applied to oxy-fired boiler flue gas. Further development and demonstration is required to fully validate the processes at commercial scale.

The Figure 2.6 refers to the typical process flow diagram for cryogenic purification of an oxy-combustion exhaust gas, which can be used for the production of a CO_2 rich stream with purity greater than 95% by volume.

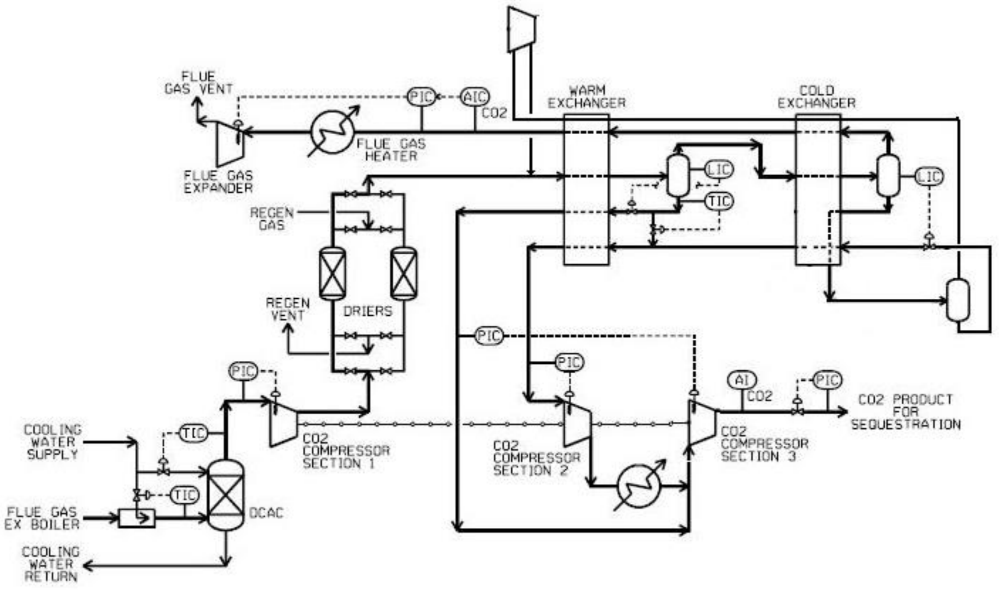


Figure 2.6: CO_2 purification section (“Auto-refrigerated cycle”)

Air Liquide has developed two cryogenic purification technologies specifically designed for steam-methane reforming (SMR) and blast furnaces processes:

- Cryocap^{TM} H_2

- Cryocap^{TM} Steel.

A simplified process flow diagram of an SMR Unit with Cryocap^{TM} H_2 is illustrated in Figure 2.7.

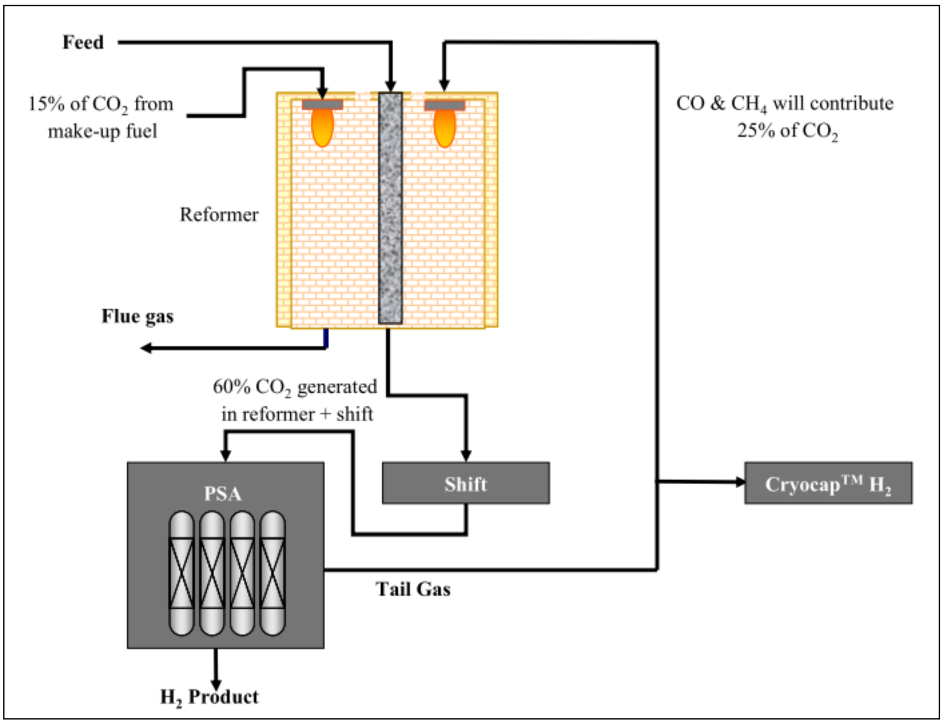


Figure 2.7: Simplified process flow diagram for SMR plant with Cryocap^{TM} H_2

Air Liquide has developed its Cryocap™ H_2 technology in order to capture CO_2 from the PSA tail gas. Actually, the high concentration of carbon dioxide in this stream (nearly to 45%) makes CO_2 separation by cryogenics an attractive option.

Air Liquide recently launched the first Cryocap™ H_2 project at Port Jérôme, France.

For a more detailed analysis of this Air Liquide demo project, please refer to Technology Review 3 of this Study.

When applied to PSA tail gas, rather than to flue gas from oxy-combustion, the main difference is the gas composition, that in case of PSA tail gas includes, in addition to CO_2 and N_2 (if present in the feedstock) also hydrogen, methane and carbon monoxide;

on the other hand there is no oxygen, argon, NO_x and SO_x. Water vapor is present in both streams, in different amounts.

In both cases the gaseous streams are compressed to a pressure at which CO_2 may be separated by liquefaction at -50/-55°C, therefore a dehydration step is required in both cases upstream the cold box to avoid water freezing. The off-gas (incondensable) after CO_2 separation, in case of PSA tail gas, has increased its heating value and hydrogen concentration, with potential advantages in terms of efficiency and economics. In addition, in order to enhance hydrogen recovery and CO_2 capture, the incondensable gas from the cold box can be processes in a dedicated membrane system.

2.2. State of the Art technologies for CO_2 capture from SMR /ATR Hydrogen Plant

2.2.1. *Where to capture CO_2 in a SMR Hydrogen Plant*

In the Technical Review 1, Section 2.2.3., it has been reported the typical CO_2 balance in a 100,000 Nm^3/h SMR Hydrogen plant. As shown, CO_2 is present (with different amounts and concentrations) in three plant locations:

- ✓ PSA inlet (syngas)
- ✓ PSA tail gas
- ✓ SMR flue gas.

It is theoretically possible to capture the CO_2 from any of the above locations, or their combination.
The following figure schematically depicts these three options.

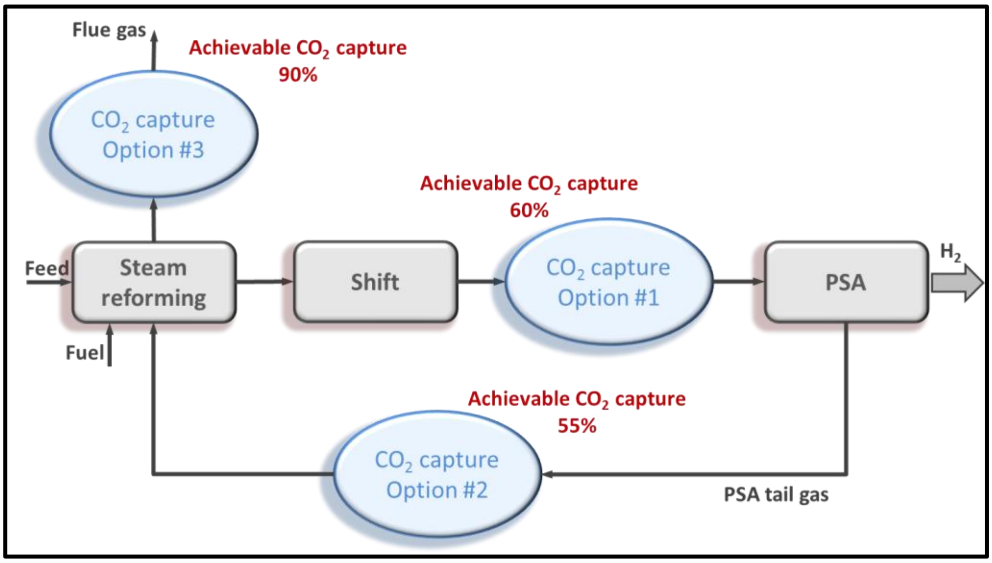


Figure 2.x: CO_2 removal locations

The approx. total CO_2 potentially removed (ηCO_2) from the three locations, calculated with the formula:
ηCO_2 (%) = 100 x (1 – CO_2 in flue gas after rem./CO_2 in flue gas without CO_2 rem.)
is reported in the table overleaf:

CO_2 removed from:	CO_2 removed from each stream (%)	Overall ηCO_2 (%)
1.PSA inlet (syngas)	100	60
2.PSA tail gas	90	55
3.SMR flue gas	90	90

It is also possible, in principle, to combine CO_2 removal 1 or 2, with 3 (from flue gas), and obtain an overall ηCO2 of about 96 and 94% respectively.
In all cases the CO_2 is obtained at high purity (>99% dry basis).

When a traditional plant is retrofitted with the addition of CO_2 removal 1, the steam reformer burners have to be checked for the new tail gas composition which, being poorer in CO_2, has a higher tendency to NO_x formation, with the consequence that low-NO_x burners and/or space for a future installation of a de-NO_x catalytic system in the convection section of the heater, could be considered at the design stage. As a consequence of the retrofit the PSA will have some capacity margin due to the reduced inlet flow rate after CO_2 removal.
Instead, no pre-investment is needed in case of retrofit of a traditional plant with the addition of CO_2 removal 3, however additional ducting and ID fan addition/replacement shall be considered when the unit is added to the SMR plant.

For the scope of this study only the removal options from syngas and from flue gas will be considered. The removal option from PSA tail gas is considered not economic compared to the others, though it is subject of investigation by various technology providers (see Technical Review 3).

2.2.2. *Pre-combustion Options*

The separation of CO_2 in pre-combustion applications from SMR/ATR units is the easiest and the most referenced amongst the different carbon capture technologies, as it is already performed in a number of standard industrial processes. For example, in natural gas production, CO_2 is separated from the natural gas during processing. Similarly, in industrial plants that produce ammonia or hydrogen, CO_2 is removed as part of the process.

In pre-combustion applications, all the different types of solvents could theoretically be used for the capture of the CO_2.
Physical absorption systems are generally more capital intensive than the equivalent chemical processes, but the major advantage is that they are less sensitive to impurities

in the feed, which on the contrary may degrade an amine. In a syngas produced via SMR/ATR, however, impurities are not present.

As far as CO_2 partial pressure in the syngas, it must be noticed that it increases with the presence of CO shift stages in the syngas treatment line downstream the reforming. In fact, in a shift reactor the following chemical reaction takes place:

$$CO + H_2O \rightarrow CO_2 + H_2$$

increasing both the amount of hydrogen and of CO_2 in the shifted gas stream.

As already explained in section 2.1, physical solvents are favoured by high acid gas partial pressures, while chemical absorption solvents operate with low CO_2 partial pressures. Therefore, depending on the syngas treatment line, both types of solvent could be suitable in pre-combustion applications.

In case of chemical solvent use, since the common operating pressure of the solvent washing unit is approximately 30 barg, the recommended solvent type is generally the tertiary amine (MDEA), which has been already extensively used in the market for low/medium CO_2 capture rates.

Hot Potassium Carbonate solution may be an economic alternative to MDEA. Such solution, used for example by UOP-Benfield, Giammarco-Vetrocoke, or Catacarb, has several references in ammonia plants where CO_2 removal is part of the process.

Several companies have gained significant experience in the past years in pre-combustion CO_2 capture processes on numerous chemical plants in commercial operation, using chemical, physical and hybrid solvents. A list of the most quoted technology suppliers is the following:

Chemical solvents:

UOP/DOW:	Amine Guard FS (UCARSOL®).
BASF:	aMDEA.
LINDE:	aMDEA.
UOP:	Hot Potassium Carbonate (Benfield®)
GIAMMARCO-VETROCOKE:	Hot Potassium Carbonate
EICKMEYER & ASSOCIATES:	Hot Potassium Carbonate (Catacarb®)

Physical solvents:

UOP/DOW:	DEPG (Selexol®)

• **LURGI (AIR LIQUIDE):**	Methanol (Rectisol®)/ Purisol®
• **LINDE:**	Methanol (Rectisol®)
• **CLARIANT:**	Genosorb®

Hybrid:

• **SHELL:**	Sulfinol®

2.2.3. *BFD Pre-combustion*

The following description makes reference to a typical chemical solvent-based pre-combustion process, designed for the removal of CO_2 from a syngas stream. The simplified unit configuration is shown in Figure 2.118 and refers to a Hot Potassium Carbonate-based unit, typically used in syngas application like ammonia or hydrogen plants.

Similar design principles also apply to other physical and chemical solvents, being at least one absorption column and one regeneration column always required when operating with solvent washing processes. In section 2.3.2. a typical physical solvent-based (Rectisol) unit is described, in an application where simultaneous removal of CO_2 and H_2S is required.

The absorption of CO_2 by a Hot Potassium Carbonate solution is a chemical reaction where the CO_2 reacts with the dissolved potassium carbonate forming potassium bicarbonate, according to reaction [1], proceeding left to right, while by heating, the potassium bicarbonate is decomposed, releasing the CO_2 and restoring the potassium carbonate, proceeding right to left.

$$CO_2 + H_2O + K_2CO_3 = 2KHCO_3 \quad [1]$$

The CO_2 absorption/regeneration process, in the simplest industrial configuration (Fig. 2.8), comprises one absorption column (absorber), where the CO_2 is washed out of the synthesis gas under pressure by a counter-current flow of the aqueous solution containing, in the main, potassium carbonate (lean solution) and one regeneration column (stripper), in which the aqueous solution containing, in the main, potassium bicarbonate (rich solution) is depressurised and heated to the boiling point, producing steam, which is used to strip-out in counter-current the CO_2 from the solution exit from the absorber.

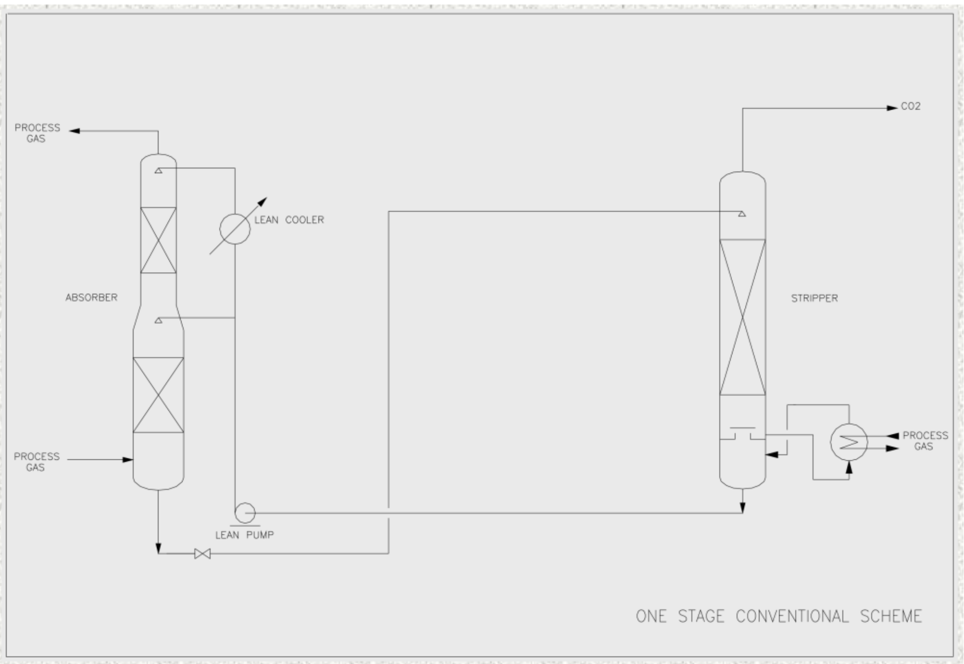


Figure 2.8: One-stage conventional scheme (source: Giammarco-Vetrocoke)

The lean solution is circulated by a pump from the bottom of the stripper to the top of the absorber, while the rich solution is fed back again to the top of the stripper by let-down of the pressure prevailing at the absorber bottom.

The lean solution feeding the absorber is split into two streams: the main portion to the midpoint and the remainder deeply cooled so as to reduce the CO_2 partial pressure to the extent required to achieve a CO_2 slip of 1,000 ppmv max., to the top.

An improvement to the previous scheme is the adoption of two solution circulation pumps, by which the main portion of the regenerated solution (semi-lean solution), withdrawn from a mid-point of the stripper, separately feeds the mid-point of the absorber, while the remainder, after a more thorough regeneration in the bottom section of the stripper (lean solution) and final cooling, feeds the top of the absorber, where, owing to the much lower CO_2 partial pressure, a CO_2 slip of 500 ppmv or less is normally achieved. A saving of about 10% on the regeneration heat requirement is achieved by this scheme.

A further improvement to the conventional schemes in response to the growing demand for energy savings is the implementation of a low-level heat regeneration scheme. The adopted technology is based on the installation of a flash tank operating at a lower pressure than the stripper. Here steam flashes off the lean or semi-lean solution and is recompressed to the stripper by steam ejectors or mechanical recompression. A saving of about 20% on the regeneration heat requirement is achieved by these schemes.

Other schemes with two separate strippers working at different pressures – a high pressure (HP) stripper and a low pressure (LP) stripper are available, with a saving of about 40% on the regeneration heat requirement.

Often, in case of pre-combustion CO_2 removal from a syngas originated from a steam reforming configuration, operating at a pressure in the range of 25-30 barg, a chemical or hybrid solvent is preferred over a physical one, due to the relatively low CO_2 partial pressure. This is indeed the standard solution adopted in the ammonia plants where aMDEA, Giammarco-Vetrocoke and Benfield are most frequently chosen.
From an energy point of view all units require heat input from outside, either from process gas reboiler alone, or/and partially with LP steam. The aMDEA process shows slightly lower energy consumption, but both Giammarco-Vetrocoke and Benfield have comparable low-energy schemes. Practically no differences are present in CO_2 removal efficiency (that is close to 100% of CO_2 present in the syngas) and purity.

2.2.4. *Post-combustion Options*

For post-combustion applications, the solvents that are commonly considered for the capture of the CO_2 are of chemical type only. This is due to the low pressure of the flue gases, which results in a low partial pressure of the carbon dioxide, thus making the use of physical and hybrid solvents not economically advantageous.

All the chemical solvents listed in the previous sections can be used in post-combustion applications, and more specifically the following ones:

- MEA,
- Sterically hindered amines,
- Ammonia,
- Amino-acid.

However, amongst the amine-based solvents, MEA and the sterically hindered amines have been already extensively used for CO_2 removal in different commercial applications. On the other hand, ammonia and amino-acid processes are not well developed, but their performances are promising.

Actually, whilst there is a number of theoretical Licensors that could provide chemical-based solvents, there are in practice few that are capable to offer a technology that is reliable for medium and large scale operation, since not many commercial applications processing large volumetric flows, like gas turbine-based and boiler-based plants, have been developed yet.

The most quoted companies that could offer chemical solvents for CO_2 capture from flue gases are, in alphabetical order, the following, divided by type of solvent.

MEA

- **CB&I:** ABB Lummus offered a MEA scrubbing technology on the original Kerr Mc Gee process. This technology, which was the first used on a coal flue gas, was then acquired by Chicago Bridge & Iron Co. (CB&I) in November 2007. CB&I and Lummus together now offer various processes for cleaning of hydrocarbon gases, including CO2 capture.

- **FLUOR:** it offers the Econamine FG Plus (EFG+) process. This is a development of the MEA based ECONOAMINE process developed by Dow and acquired by Fluor.

  The following Table 2.1 shows the main reference plants of Fluor for the Econoamine FG^{SM} process. Overall, there are about 24 commercial plants worldwide that use this technology.

  The most significant power application is at Florida Power & Light’s licensed plant at the Bellingham Energy Center in Bellingham, Mass, which captured about 320 tons per day of carbon dioxide from the exhaust of the natural gas – fired power plant. This plant has been in operation from 1991 to 2005 and is the only commercial-scale application, operated on gas turbine flue gas.

  Fluor has made several tests, at a small scale, on coal flue gas as well as gases from heavy fuel oil. It has also to be noted that Fluor and E.ON Energie AG (E.ON) have formed a strategic partnership for the development of a slipstream carbon capture pilot plant in northern Germany. Fluor’s Econamine FG Plus^{SM} technology is applied to demonstrate removal of carbon dioxide from flue gas at E.ON’s Wilhelmshaven coal-fired power plant (3 t/h CO_2 capture level). The project construction was completed, fully commissioned and put into operation in 4Q12. Recent updates show that several tests are going to be performed at the pilot plant in the next years. Aim of the testing is to validate energy saving arrangements relevant to absorber inter-cooling and lean vapor recompression and to evaluate the effect of sudden changes on plant operating conditions. During test phase, the effect of single perturbations on plant stability and performance will be measured. Some of the parameter tests include: varying the steam rate to the reboiler, varying the chemical rate in the direct contact cooler, and operating the stripper at different pressures.

From the considerations made in this section, it is evident that Fluor shows a high level of maturity in the field of capturing CO_2 from flue gases of natural gas fuelled plants, while having relatively lower experience with coal.

Location	Source	Plant purpose
Carisbad, New Mexico	Flue gases from NG fired boiler	Enhanced Oil Recovery (EOR)
Lubbock, Texas	Flue gases from NG fired boiler	EOR
Israel	Heavy fuel oil fired boiler	Food industry
Altona, Australia	Flue gases from NG fired boiler	Food industry
Botany, Australia	Flue gases from NG fired boiler	Food industry
Quito, Ecuador	Light fuel oil	Food industry
Manila, Philippines	Light fuel oil	Food industry
Argentina	Steam reformer	Urea plant feed
San Fernando, Philippines	Light fuel oil	Food industry
Uttar Pradesh, India	Gas fired reformer furnace	Urea plant

Location	Source	Plant purpose
Sichuan Province, PRC	Gas fired reformer furnace	Urea Plant
Bellingham, Mass.	Gas turbine exhaust	Food Industry
Osaka, Japan	LPG	Demo plant
Yokosuka, Japan	Coal mixture heavy fuel oil	Demo plant
Chiba, Japan	Refinery gas mixture heavy fuel oil	Food industry
Barranquilla, Colombia	Natural Gas (other info not reported)	Food industry
Rio de Janeiro, Brazil	Steam Reformer	Methanol production
Cairo, Egypt	Light fuel oil	Food industry
Santo Domingo, Dom. Rep.	Light fuel oil	Food industry
Sudrigiu, Bhor County, Romania	Fuel oil	Food industry
Sao Paolo, Brazil	Gas engine exhaust	Food industry
Brazil	NG, heavy fuel oil	Food industry
Spain	Gas engine exhaust	Food industry
Barcelona, Spain	Gas engine exhaust	Food industry
Various	Gas engine exhaust	Food industry
Singapore	Steam reformer	Food industry

Table 2.1:Fluor Econoamine FG^{SM} – Main reference plants [www.fluor.com/econamine/Pages/projectsites.aspx]

- **HTC Energy**: it offers the Purenergy CCS Capture System^{TM}, which is a pre-engineered, pre-built and modularly constructed unit, using a technology developed in the University of Regina, based on an amine solvent.

The following Table 2.2 shows the main reference plants of HTC Energy for their amine-based solvent. HTC has not yet commercial plants, whilst they have pre-engineered, pre-built and modularly constructed a system that is capable of capturing approximately 3,000 t/d of CO_2.

Owner	Location	Start operation	Source	Size (t/d)	Plant purpose
Doosan Power Systems	Scotland	2010	Coal and others	1	Pilot plant
Doosan Power Systems	UK	2012	Coal Fired Power Station	100	Pilot plant

Table 2.2: HTC Energy – Main reference plants [www.htcenergy.com/mediaCenter]

It is noted that HTC Energy have gained a significant experience on CO_2 injection and monitoring from the largest Enhanced Oil Recovery (EOR) project in the world, the Encana oil field near Weyburn, Saskatchewan, which started to inject CO_2 in 2001. HTC worked on the original design of the project and developed protocols that are used in this sector.

Doosan Power Systems (DPS) is developing a competitive PCC technology for application on coal and natural gas fired power plants based on Amine HTC PCC technology, for commercialization by 2020. Doosan Power Systems has, over the past 30 months, retrofitted two PCC pilots, firstly to its 160 kWt Emissions Reduction Test Facility (ERTF), located in Renfrew (Scotland) and secondly a 15MWt PCC plant (CCPilot100+) to the SSE owned Ferrybridge Power Plant in Northern England.

From the considerations made in this section, it can be drawn that the HTC process has not yet commercial plants in operation, though their capabilities are good with regardless the full chain of CCS, from capture to injection and monitoring.

- **AKER:** it offers, through its subsidiary Aker Clean Carbon, an amine-based solvent for CO_2 capture from various flue gases types.

  Aker Clean Carbon has started to work on pre-combustion carbon capture technologies, delivering the Sleipner CO_2 platform to Statoil in 1996, capturing 3000 t/d of carbon dioxide from high-pressure natural gas for injection in the Utsira aquifer.

  Then, Aker started focusing on post combustion and, as of today, its operational experience is from six alternative amine based carbon capture pilots and demo plants, as highlighted in Table 2.3.

Plant name and owner	Location	Start	Source	Size	Plant purpose
Karsto K-lab, Statoil	Norway	1998	Natural Gas	Gas engine	Pilot
Castor/CESAR programme	Esbjerg, Denmark	2006	Coal fired power plant	1 t/h of CO_2	Pilot/ demonstration
MTU, Gassnova	Risavika, Norway	2008	Natural gas	60 kg/h of CO_2	Pilot
MTU, Scottish Power	Longannet, UK	2009	Coal fired power plant	180 kg/h of CO_2	Pilot/ demonstration
Solvit, SINTEF	Norway	2010	Propane gas	Burner	Pilot (ongoing)
MTU, Southern Company	Alabama, USA	2010	Coal fired power plant	180 kg/h of CO_2	Pilot/ demonstration
EnBW	Heilbronn, Germany	2011	Coal + bio	Pilot	Pilot
TCM Company (European CO_2 Technology Center Mongstad)	Mongstad, Norway	2011	Exhaust Gases from a Residue Catalytic Cracker (RCC) and NG Combined Heat and Power (CHP) Plant	100 t/d of CO_2	Demo plant

Table 2.3: Aker Clean Carbon – Main reference plants [http://www.akercleancarbon.com]

Regarding R&D programs, Aker Clean Carbon started in 1996 and in 1998 built a pilot plant in Kartso for capturing CO_2 from gas power. More recently, Aker invested about 75 MEuro in R&D programmes and is leading SOLVit, which is a major scientific research and development programme to produce improved amines for the carbon dioxide capture processes. This programme was launched together with Sintef, an independent research organization, and the Norwegian University of Science and Technology NTNU. The programme was launched in Norway in August 2008 and will run for eight years.

Aker developed also a “Mobile Test Unit (MTU)” in 2008 (Norway), that is a complete capture process module with the size of a transport container, capable of testing different flue gases and various operating parameters. The process module is 40 meters length and 2.6 m tall, with a CO_2 capture capacity of 180 kg/h from coal and 60 kg/h from gas power. This module was then moved to Longannet (Scotland) in 2009, to demonstrate and qualify the technology by testing the process for the first time on coal-based flue gas. In June 2010, the MTU moved to Alabama, US where it performed test campaigns at the National Carbon Capture Center (NCCC), hosted by Southern Company. The MTU is actually at the Mongstad Test Center to support testing of the solvent.

Finally, Aker Clean Carbon has also patented a method to minimize amine emissions to atmosphere, using a cleaning-bath as the last step in the treatment of the exhaust.

Noteworthy, is the Technology Centre at Mongstad (TCM) in Norway. The facility’s total capacity is 100 tons of CO_2 captured per day, it was put in operation in 2011 and the test results will be valid for direct scale-up to full scale CO_2 capture plants. First tests started using MEA as a solvent and were aimed at heat and material balance validation, but recently MEA has been replaced with one of Aker proprietary formulated solvents. For the next months, operation of the plant will be dedicated to a qualification program of the full-scale Mongstad project using Aker solvent, developed to minimize environmental impact and steam consumption.

From the considerations made in this section, it is evident that Aker Clean Carbon shows a good level of maturity in the field of capturing CO_2 from flue gases. It is also evident that Aker has made significant investments in R&D’s programmes, with the objective of reaching for post-combustion processes the same level of maturity as for pre-combustion natural gas sources.

- **CANSOLV:** it offers a combined SO_2/CO_2 scrubbing process, using 2 different amine-based solvents in a thermally integrated system. Cansolv is a subsidiary of Shell Global Solutions group.

Table2.5 shows the main reference plants of Cansolv (part of Shell Global Solutions Group), which also offer, if required, an integrated system for combined sequestration of SO_2 and CO_2. Not many referenced plant are available for this pioneer technology, but encouraging results are expected from its first applications.

In January 2013 the Aberthaw Power Station pilot plant started operation, capturing a carbon dioxide flow rate of 50 tons per day, corresponding to about 90% capture rate and to essentially 100% SO_2 captured. Cansolv will now initiate a research and development program in this site focused on further optimization of the process and demonstrating the advantages of new generation solvents.

But the most important Cansolv project is SaskPower Boundary Dam, Canada, which started operation in September 2014. It is the first commercial scale application for the technology and the first post-combustion capture project of its kind in the world, sequestrating 1 million tons CO_2 per year that will be used for enhanced oil recovery purposes.

As the only provider of amine based SO_2 and CO_2 scrubbing technologies, Cansolv may offer an integrated solution that uses the same technology to sequentially scrub SO_2 and CO_2 in one system. Since the two processes are very similar, this technology can benefit of several advantages relative to internal synergies for energy recovery.

Cansolv developed a concept of regenerable amine scrubbing technology, based on the application of 2 different di-amine solvents, Cansolv DS for SO_2 removal, and DC-105^{TM} for CO_2 removal. A typical scheme of Integrated SO_2/CO_2 scrubbing system is show in Figure 2.9.

The most significant heat integration is achieved at the top of the SO_2 regeneration column, where the hot SO_2 stream condensation produces heat that can be used to provide part of the CO_2 solvent regeneration energy.

The integrated SO_2/CO_2 scrubbing system allows avoiding the installation of a wet FGD unit (typically used for SO_2 abatement and subject to limestone/gypsum market availability). The SO_2 stream from integrated sequestration can be used to produce saleable sulfuric acid in a dedicated unit.

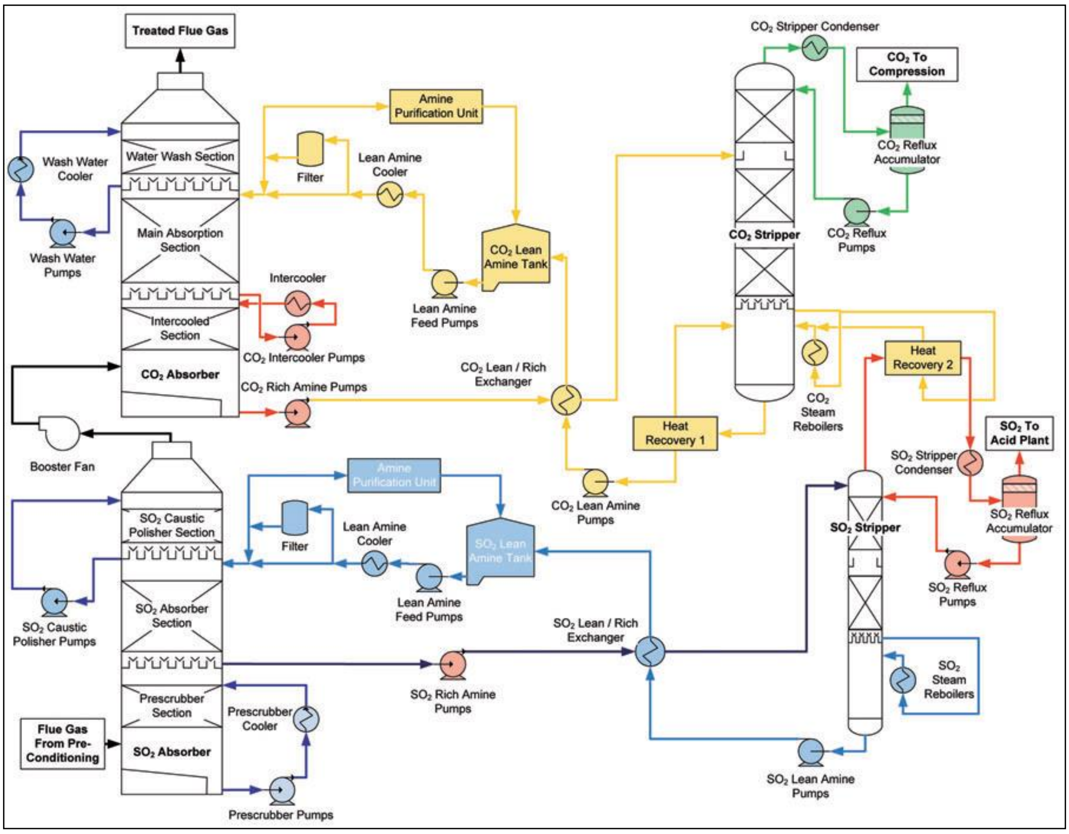


Figure 2.9: Cansolv Integrated SO_2/CO_2 scrubbing system

Owner	Location	Start operation	Source	Size	Plant purpose
RWE NPower	Wales	2013	Coal Power station	50 t/d	Demo plant
SaskPower	Canada	2014	Lignite-Coal Fired Power Station	1 million t/ year	Full scale plant

Table2.4: Cansolv – Main reference plants [www.cansolv.com]

Sterically hindered amines

- **MHI**: Mitsubishi Heavy Industries (MHI) offers the KS-1 process, based on a formulation of sterically hindered amines, which is a joint development between MHI and the Kansai Electric Power Company (KEPCO).

  The following Table 2.5 shows the main reference plants of MHI for their sterically hindered amine-based solvent.

Owner	Location	Start operation	Source	Size (t/d)	Plant purpose
Petronas Fertilizer(Kedah) Sdn Bhd)	Kedah Darul Aman, Malaysia	October 1999	NG fired steam reformer flue gas	200	Urea plant
'A' chemical company	Fukuoka, Japan	October 2005	NG and heavy oil fired boiler flue gas	330	General use (Several Industries)
Indian Farmers Fertiliser Co-Operative Ltd.	Aonla, India	December 2006	NG fired steam reformer flue gas	450	Urea plant
Indian Farmers Fertiliser Co-Operative Ltd.	Phulpur, India	December 2006	NG fired steam reformer flue gas	450	Urea plant
Nagarjuna Fertilizers and Chemicals Limited	Kakinada, India	March 2009	NG fired steam reformer flue gas	450	Urea plant
Gulf Petrochemical Industries Co.	Bahrain	December 2009	NG fired steam reformer flue gas	450	Urea plant

Owner	Location	Start operation	Source	Size (t/d)	Plant purpose
Petrovietnam Fertilizer and Chemicals Corporation	Phu My, Vietnam	2010	NG fired steam reformer flue gas	240	Urea plant
Ruwais Fertilizer Industries	Abu Dhabi , United Arab Emirates	2010	NG fired steam reformer flue gas	400	Urea plant
Engro Fertilizers Limited	District Ghotoki, Pakistan	2010	NG fired steam reformer flue gas	340	Urea plant
Southern Company and MHI	Plant Barry, Alabama, USA	2011	Pulverised Coal (PC) boiler flue gas	500	Saline aquifer storage

Table 2.5: MHI KS-1 – Main reference plants [www.mhi.co.jp/en/products/detail/km-cdr_experiences.html]

MHI currently has six (6) commercial plants in operation in the chemical and fertilizer industry, up to 450 tons/day, while other three are under construction. As MHI has already gained a significant experience on the capture of CO_2 from natural gas steam reformer flue gases, they have decided to test in two pilot plants the capture of carbon dioxide from coal fired flue gases. In these testing facilities, MHI completed more than 6,000 hours of near-continuous operation.

The tests have demonstrated that the energy requirement of this solvent ranges from 2.6 to 3.2 GJ/ton CO_2 captured. In addition, different parameters have been tested, specifically for the coal, like influence of dust or of SOx impurities in the gas.

MHI has also developed with Southern Company a demonstrative plant in USA, Plant Barry, trying to close the gap now exiting between gas fired and coal fired CCS plants, with the purpose of having a coal fired CCS plant in commercial operation on a large scale by 2015. This plant successfully started capturing CO_2 (500 t/day, the world’s largest unit using MHI KM-CDR technology) in June 2011 and sequestrating the CO_2 underground in August 2012. Several test campaigns, performed since the beginning of the project, were aimed at heat and mass balance validation, emission monitoring, performance optimization and dynamic response for load following. Recent updates highlight that the testing program is proceeding, in order to validate long-term reliability for the equipment and high impurity loading related to alternative coal burning.

From the considerations made in this section, it is evident that MHI has gained considerable commercial experience in CO_2 capture from natural gas-fired boilers and is ready to provide large scale, single train commercial CCS plants.

Ammonia

- **ALSTOM**: it is the only referenced company that is developing an ammonia-based solvent process, using a solution containing ammonium carbonate (Chilled Ammonia Process, CAP).

  The following Table 2.3 shows the main reference plants of Alstom for the Chilled Ammonia Process (CAP). The table shows that, up to now, the chilled ammonia has been used for pilot and demo plants only. In fact, Alstom's R&D programmes are concentrated to have ammonia, as well as amine, available as early as 2015 for full commercial deployment.

  After a phase of laboratory tests and a testing facility at SRI International, Alstom planned a series of field demonstration projects to test the technology at the We Energies Pleasant Prairie power plant (unit 1 and 2). This test facility has confirmed the technical viability of the chilled ammonia process, demonstrating full system operation on flue gas from coal-fired boiler, CO_2 capture rate and solvent regeneration.

  Another similarly sized pilot plant is installed at E.ON's Karlshamn power plant in Sweden, to test capture from an oil-fired auxiliary boiler that burns high sulphur content fuels.

  Tests, mainly on energy and cost requirements, are made in AEP's Mountaineer site, located in West Virginia. Another validation facility is at Statoil's Mongstad Technology Centre in Norway, as already shown in the previous section. The pilot plant was inaugurated in May 2012 and is now completing tests aimed at technology validation. These projects will be the basis to have the Chilled Ammonia Process ready for commercialization by year 2015.

Owner	Location	Start operation	Flue gas source	Size (t/d)	Plant purpose
EPRI, Alstom	We Energies Pleasant Prairie, Wisconsin, USA	June, 2008	Pulverised Coal (PC) boiler flue gas	15,000 t/y	Pilot plant
E.ON Thermal Power	Karlshamn, Sweden	April 2009	Boiler combusting high-sulphur fuel oil	45	Pilot plant
DOW, Alstom	South Charleston, USA	July, 2009	Coal fired industrial boiler	1,800 t/y	Pilot plant
American Electric Power (AEP)	New Haven, West Virginia, USA	September,2009	Pulverised Coal (PC) boiler flue gas	300	Demo plant
TCM Company (European CO_2 Technology Center Mongstad)	Mongstad, Norway	2012	Exhaust Gases from a Residue Catalytic Cracker (RCC) and NG Combined Heat and Power (CHP) Plant	100	Demo plant

Table 2.3: Alstom Chilled Ammonia Process – Main reference plants [www.power.alstom.com/home/about_us/strategy/clean_power_today/carbon_capture_storage_ccs/pilots_and_demonstrations]

:

One disadvantage of this process is that ammonia is classified as toxic and dangerous for the environment. As such, ammonia slip in the flue gas shall be carefully considered in the design of the plant, likely leading to need of an additional absorber/stripper section to abate ammonia slip in the treated gas, thus penalizing both the unit energy demand and the capital cost of the unit. Moreover, according the publications available in literature, it is generally recognized that ammonia shows lower reactivity compared to amines, resulting in the requirement of tall packed columns to promote turbulence and reduce liquid-film resistance to CO_2 absorption. It has to be also noticed that chilling the NH_3 to reduce volatility and slip further penalizes the solvent reactivity.

From the considerations made in this section, it can be drawn that the Chilled Ammonia Process (CAP) by Alstom is not in a complete state of maturity yet. However, demonstration facilities are well planned, as well as the programme testing. Based on Vendors claims, preliminary results are encouraging, even if more data and experience are needed to see how this technology will compete against traditional amines.

Amino-acid

- **SIEMENS**: it is the only referenced company that is developing an amino-acid salt solution process for the chemical absorption of the carbon dioxide.

The following Table 2.4 shows the main reference plant of Siemens for their amino-acid salt solution. The table shows that this solution has just started to be used at a pilot plant level only, while a demonstrative plant was planned for Fortum in Finland by 2015; however, this project discontinued.

Owner	**Location**	**Start operation**	**Flue gas source**	**Size (t/d)** (1)	**Plant purpose**
EON, Siemens (POSTCAP project)	Staudinger, Germany	August 2009	Pulverised Coal (PC) boiler flue gas	1.0	Pilot plant

(1) Assuming 90% plant load factor.

Table 2.4: Siemens – Main reference plants [Science Direct, Energy Procedia (2009) 1043-1050]

In addition to the project mentioned in this table, Siemens is also adapting its process for CO_2 capture to the special conditions prevalent in combined cycle power plants for the Norwegian utility Statkraft, also looking at the operation with frequent load changes and fewer integration options for low temperature heat from the capture plant.

Siemens has also signed an exclusive agreement for R&D collaboration with the Netherlands Organization for Applied Scientific Research (TNO). The main objective of this collaboration is to faster the development of the technology and implement a full-scale demo plant by 2014.

Siemens is also undergoing a concept study aimed at qualifying Siemens PostCap™ technology for the installation of a full-scale integrated CO_2 capture plant at Mongstad Technology Centre facility.

From the considerations made in this section, it can be drawn that the amino-acid salt solution by Siemens is not yet in a complete state of maturity. However, based on Vendors claims, preliminary results are encouraging, even if more data and experience are needed to see how this technology will compete against tradition ones.

2.2.5. BFD Post-combustion

The following description makes reference to a simplified typical process flow diagram of the CO_2 capture unit, shown in Figure 2.10, which refers to a MEA solvent-based post-combustion process.

In terms of process configuration and operating principles, all the commercially available technologies using MEA are similar. The main equipment is mostly “open-art” systems and could be designed and built by anyone, following the good engineering practise.

The same design principles also apply to the other chemical solvents (ammonia, amino-acid salts or MDEA), though features that are unique for these solvents are discussed earlier in the report.

As shown in Figure 2.10, the CO_2 capture unit is mainly composed of one washing column and one absorption column, followed by a regeneration stripper, exchangers and pumps.

Before entering the downstream CO_2 absorption column, the flue gas from the boiler shall be cooled in a washing column or scrubber, lowering the particulate concentration and the water content in the flue gas but in particular the SO_2/SO_3 content to the level required not to have solvent degradation.

Downstream the scrubber, the flue gas is fed to the absorption tower by a flue gas blower. The gas entering the absorption column is contacted with a lean solvent solution, to allow CO_2 capture from the stream entering the unit.

Before leaving the column, the cleaned gas is scrubbed with make-up water to remove the entrained solvent and avoid any dispersion to the atmosphere.

From the bottom of the columns, the rich solvent is heated in a regenerative cross exchanger against the hot stripper bottom and sent to the regeneration column, which is mainly composed of a stripping and a rectification section. Steam is necessary to provide heat for solvent regeneration in the stripper.

The vapour at the top of the column is cooled and separated in a K.O. drum, generating the rich CO_2 stream, which flows to the CO_2 compression, while condensed water is partially returned to the column as reflux.

The lean solvent at the bottom of the stripping column is pumped back to the absorption, after final cooling against cooling water.

Different commercially available processes contain additional features to achieve a high degree of thermal integration in the unit, in order to minimize the stripping load, thus maximizing the efficiency, though resulting in a higher investment cost, like:
- Absorber inter-cooling;
- Inter-heating in the regenerator;
- Lean vapour recompression and optimization of lean/rich solvent heat exchange.

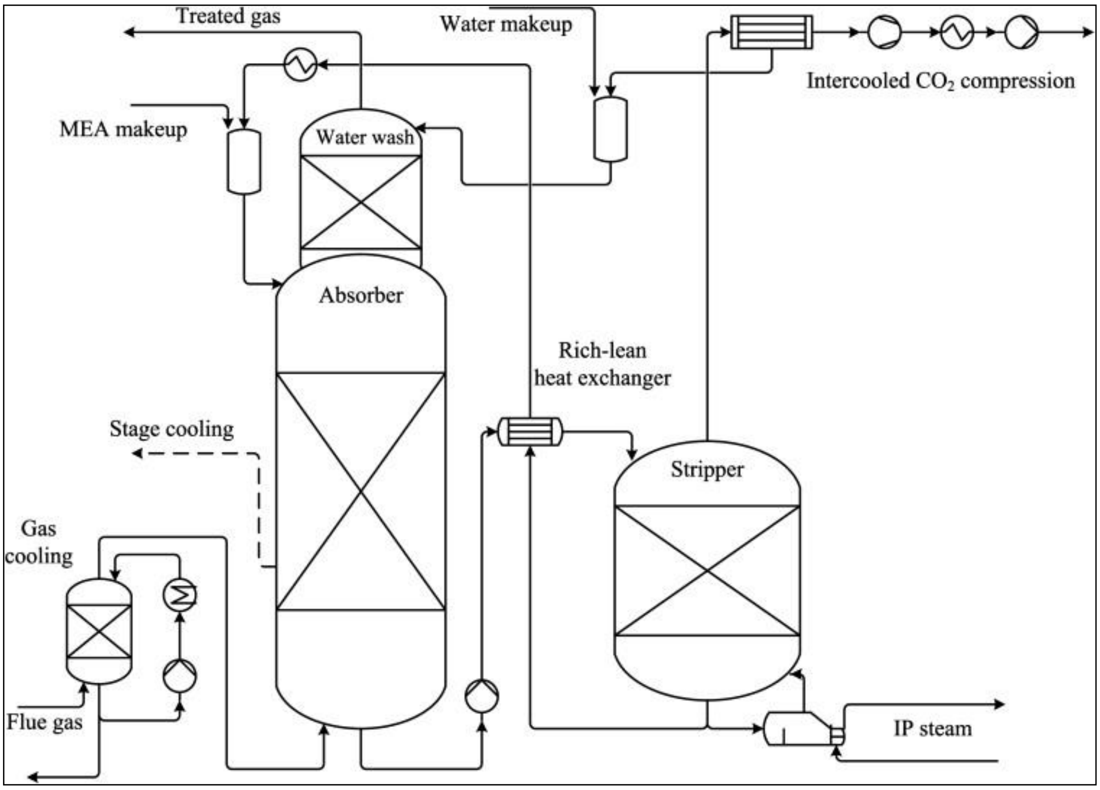


Figure 2.10: Typical process configuration for a CO_2 absorption and desorption unit

From a capture performance point of view, all the technologies mentioned in the previous sections have the capability to reach high CO_2 capture rates, normally ranging from 85 to 95% of the carbon present in the flue gas feed, as well as to produce the carbon dioxide at different levels of purity, typically ranging from 90 to 99% by volume. Therefore, all these technologies can meet the most stringent environmental requirements on Carbon Capture and Storage (CCS).

The major part of energy demand in a CO_2 capture plant is the stripping heating, required by the reboiler of the stripping column to regenerate the solvent. This information is generally covered by secrecy agreements that each Licensor require to Clients, when asked to bid for a specific project. The information available in the technical literature, or in the conference proceedings, shows quite a large range of variation of this parameter. This information is also strictly dependant on the author of the paper or presentation. In fact, many of these works are made by the same Licensors, with the purpose of publicizing its own product.

Therefore, it is not always possible to link a specific Licensor to a unique energy requirement, whilst it is possible to provide the expected range of variation for each solvent-type.

The following Table 2.5 shows the expected energy consumption ranges of the chemical solvents investigated in the previous section.

For the amine-based solvents, there is a range of energy requirement that can be considered valid for all the different Licensors. However, it is noted that most of the before mentioned Licensors are investing in different R&D's programmes, with the main objective of reducing the energy requirements. Therefore, it is likely to say the energy requirements of the MEA-based solvents will decrease in the next years.

Solvent type	Licensor	Energy requirement (GJ/ton CO_2 removed)
Amine based	Aker, Cansolv, Fluor, HTC Energy, MHI	2.5 – 3.2
Ammonia	Alstom	Data Not Available (1)
Amino-acid salt solution	Siemens	2.7

(1) Alstom states that preliminary testing results confirm the energy penalty is approximately 5% lower than a conventional amine-based solvent [Alstom web site].

Table 2.5: Expected energy consumption range of chemical solvents

Regarding the chilled ammonia process from Alstom, though a specific energy requirement is not available in the technical literature, the energy saving stated by Alstom can be justified by the fact that the chilled ammonia requires less low-pressure steam for absorbent regeneration. This is due to the lower heat of reaction and the higher operating pressure of the regenerator, which results in a lower water vaporization and less sensible heat loss because of the higher CO_2 load in the solvent and hence lower circulation rate. In addition, electric power saving is expected for the CO_2 compressor, because absorption is at low pressure, while regeneration occurs at 10-20 bar, thus decreasing the load of the first compression stages. In this sense, the expected energy demand of the compressor can vary from 85-90 kWe/ton CO_2 for the atmospheric processes to 35-40 kWe/ton CO_2 for the chilled ammonia. However, it is noted that this advantage is generally offset by the additional power required for the flue gas cooling, as the process requires to bring the temperature down to around 20°C instead of the 30-40°C generally considered for the other processes. Moreover, an additional absorber/stripper section maybe required to abate ammonia slip in the treated gas, thus further penalizing the unit energy demand.

2.3. State of the Art technologies for CO_2 capture from POX Hydrogen Plant

2.3.1. *Pre-combustion Options*

Many of the pre-combustion options for CO_2 capture from POX Hydrogen Plant are identical to those from SMR/ATR described in section 2.2.1. The main difference between a syngas originated by a SMR/ATR or by a POX hydrogen plant is the presence of sulphur compounds in the latter case. In fact the catalytic processes involved in SMR/ATR units require the total removal of sulphur compounds before the steam reforming reactions take place.

The presence of sulphur in the syngas requires some additional consideration to what indicated in section 2.2.1.

Typically, when removal of both H_2S and CO_2 is required from the syngas, in conjunction with high carbon sequestration rates, physical solvents like Rectisol® or Selexol® are preferably selected.

In IGCC plants for power production, the sulphur compounds are to be removed from the syngas to a level compatible with the plant environmental limits. This is also valid for POX hydrogen plant as the H_2S not removed from the syngas does not affect hydrogen purity as it remains in the PSA tail gas, which is normally used as fuel.

Selexol® solvent is capable to reach H_2S levels in the treated syngas, in the standard plant configuration, around 2 ppmv, which is more than adequate for meeting the environmental limits.

If lower H_2S content in the purified gas is required as in chemical production trains including a catalyst sensible to sulphur poisoning, or for almost complete removal of carbon dioxide, then Rectisol® solvent is generally applied.

With respect to other amine solvents, MDEA is particularly selective towards H_2S, reaching levels in the treated syngas around 20 ppmv. If more stringent limitations were imposed, it would be necessary to install an additional AGE (Acid Gas Enrichment) unit downstream the AGR, where through another absorber/stripper process H_2S content in the purified syngas can be further reduced. Alternatively, as said, a physical solvent could be considered.

Hot Potassium Carbonate solution is not suitable for H_2S absorption.

2.3.2. *Pre-combustion*

The following description makes reference to a typical Rectisol-based unit, designed for the removal of H_2S and CO_2 from a syngas stream. The simplified unit configuration is shown in Figure 2.11 and is typically used in polygeneration plants with stringent purity requirements.

Similar design principles also apply to other physical and chemical solvents, being at least one absorption column and one regeneration column always required when operating with solvent washing processes.

As shown in Figure 2.11 for the Rectisol washing process, the CO_2 capture unit is mainly composed of a H_2S and CO_2 absorber, followed by a CO_2 production column and by a solvent regeneration stripper.

Before entering the absorption column, the syngas from the treatment line is cooled in a multiple gas exchanger against CO_2 and treated syngas streams.

Syngas is subsequently fed to the absorber, where it is washed by lean solvent (methanol) entering the top of the column. Refrigeration capacity needs to be supplied to the column, which is operating at sub-zero temperatures, in order to allow proper impurity removal from the syngas.

CO_2 and H_2S are dissolved into the solvent by means of a physical absorption process, while treated syngas with very low impurity contents exits the top of the column. Cleaned syngas at very low temperature is preheated against raw syngas, before being fed to downstream process units.

Rich solvent from the bottom of the absorber and semi-lean solvent from an intermediate stage of the column are fed to the CO_2 production column, where rich solvent is partly flashed to free dissolved acid gases. Sulphur compounds in the flashed gas stream are removed by semi-lean solvent washing in the upper part of the column. Pure CO_2 exits the top of the column and is preheated against raw syngas before supplying to the compression train.

From the bottom of the CO_2 production column, the rich solvent is heated in a regenerative cross exchanger against the hot stripper bottom and sent to the regeneration column. Steam is necessary to provide heat for solvent regeneration in the stripper.

The vapour at the top of the column is a H_2S rich stream, which typically flows to a Claus unit for elemental sulphur recovery.
The lean methanol at the bottom of the stripping column is pumped back to the absorber, after cooling against rich solvent.

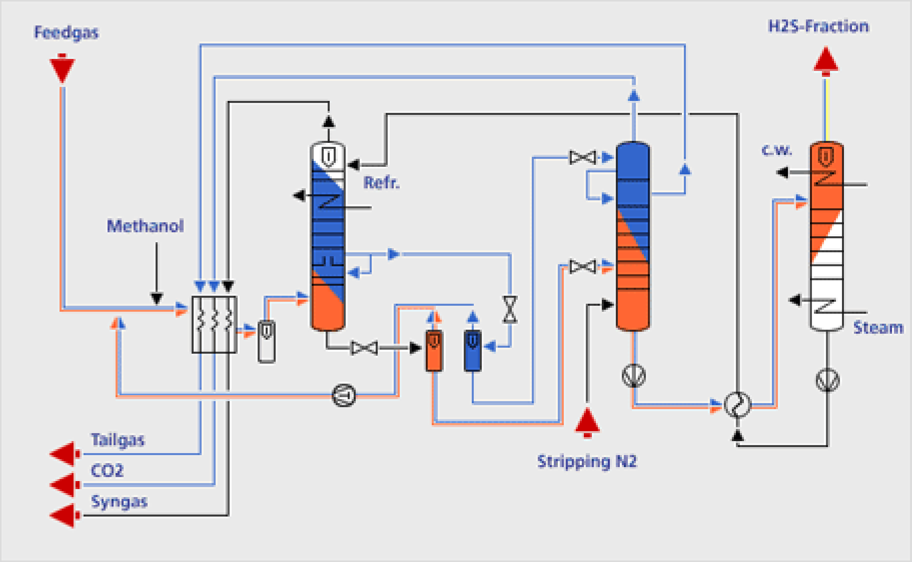


Figure 2.11: Typical process configuration for a Rectisol unit (source: Linde AG)

Although resulting in a higher investment cost, different commercially available configurations contain additional features to achieve a high degree of thermal integration in the unit and different pressure CO_2 streams, in order to minimize the stripping load and the compression train consumptions, thus maximizing plant efficiency.

2.3.3. *Air Blown vs Oxygen blown POX reactors*

The gasification processes require an oxidant for the partial oxidation reaction. There are essentially two alternatives: 1) air, and 2) oxygen, which has to be separated from the nitrogen in the air at considerable cost. A third alternative, oxygen-enriched air, is essentially a mixture of the two.

Historically, the first partial oxidation systems operated with air. The idea of operating with pure oxygen was only realized in the 1930s after the introduction of large-scale commercial cryogenic oxygen plants.

In that period between 1935 and 1985, most of the gasification plant were built for chemical application and consequently were operated with high purity oxygen (>90mol% O_2) mainly due to the fact that the presence of large quantities of nitrogen originating from the air was detrimental to the downstream chemical synthesis process.

These considerations of downstream chemistry do not apply to power applications, i.e. IGCC plants, which have developed along with the increasing efficiencies of gas turbines. The main advantage of the air-blown gasification technology is the reduction of the ASU size and consequently power demand and capital cost. On the other hand, the gasification and the gas treatment units are to be size for more than twice the capacity with respect to the oxygen-blown gasification. Energy requirement for syngas purification also increases.

As a result of the above, typically oxygen-blown technology is preferred in large-scale IGCC projects. For small-scale IGCC projects (<50MWe), mostly operating with biomass or waste, the decisions have tended to favour air because the initial investment of an ASU is not justified by savings on the much smaller equipment and the improved efficiency of oxygen operation.

In some case a project-specific evaluation might be required, for example when using oxygen-enriched air, and/or when the syngas is used for ammonia production, where nitrogen is a desirable component.

2.3.4. ASU and POX Unit integration options

The integration of ASU with the POX unit is relevant in case of an IGCC and specifically with the gas turbine (GT) of the combined cycle unit.
For the cases discussed under the scope of this study there are no specific integration options between ASU and POX when dedicated to H_2 production with or without CO_2 capture.

For sake of completeness the ASU-GT integration options are here below briefly summarized.

There are several possible degrees of integration between the air separation plant and the gas turbines.

In the case of total integration, 100% of the air required by the air separation is supplied by bleeding some of the air from the discharge of the gas turbine compressor. Depending on the gas turbine frame this air can be available at approximately 14 barg, therefore the air separation plant is a high pressure type, delivering oxygen and nitrogen at 5 bar. Oxygen is -compressed/pumped and used in gasification, while nitrogen is -compressed and re-injected in the syngas to replenish the mass deficit, caused by the air bleeding, and, at the same time, reduce NOx formation during combustion by lowering the flame peak temperature.

Alternatively the air separation plant can be "stand-alone", not integrated, with its own air compressor delivering air to the cryogenic process at the minimum pressure required to meet the energy demand of the unit.
In this case the selection of the ASU configuration (low pressure or high pressure) mainly depends on the amount of nitrogen required by the syngas-fired combined cycle.

In case nitrogen is used for both syngas dilution and NOx control in the gas turbine, a significant amount of nitrogen is required. In this case high pressure configuration is preferred as the large compression energy required to feed respectively the gasifier and the gas turbine with the low pressure nitrogen product more than offset the increased consumption of the air compressors. As an alternative, syngas humidification can be foreseen for NOx control, reducing the amount of nitrogen required. In this case, low pressure configuration can be selected.

A design, which is intermediate between these two cases, is the partially integrated air separation. Air is partly supplied by the gas turbine and partly by a separated air compressor. The percentage of air required by the air separation, which is supplied by the gas turbine, is taken as the degree of integration. Also in this case the air separation plant operates at high pressure, thus reducing the compression energy of oxygen and nitrogen.

2.4. Emerging Technologies for CO_2 capture from Hydrogen Plant

This part of the report provides a general overview of two promising technologies that are currently under development and for which there are no large-scale plants in commercial operation yet.

The novel technologies objects of the following sections are:

- Membranes for O_2, H_2 or CO_2 separation;
- Chemical Looping.

2.4.1. *Membranes for O_2, H_2 and CO_2 separation*

Description of the process

Recent researches are involved in the development of membranes used to separate *oxygen* from air and membranes able to separate hydrogen from syngas. It is thought that these innovative membranes will play a key-role in the development of CO_2 emission-free fossil fuel plant.

In order to provide pure oxygen to the GT combustion chamber or combustion reactors, an alternative to the cryogenic ASU is the Ionic Transport Membrane (ITM), which is currently being developed and envisaged as being commercially available in the medium term. The membranes consist of inorganic mixed metal oxides such as persovskites, which are capable of both electronic and oxygen ionic conductivity when operated at high temperature (typically 800-900°C). This gives high permeability and selectivity for efficient separation of oxygen from air.

The system is essentially being developed for Integrated Gasification Combined Cycle (IGCC) power systems, but is applicable also to any combustion application that uses oxygen such as oxy-fuel processes and autothermal reforming. The cost of producing oxygen by this method is potentially 30% lower than the present oxygen production costs and has the potential to improve overall system efficiency and economics.

On the other hand, *hydrogen* membrane could be used also to produce pure hydrogen in carbon-free power plant and in electricity/hydrogen co-generative plants. Using membranes, CO_2 can be removed from shifted syngas (e.g. gasification process, methane autothermal reforming and methane steam reforming) to obtain high-purity hydrogen stream.

The configuration shown in the following Figure 2.12 employs a H_2 Separation Membrane Reactor (HSMR) integrated in an ATR reactor to shift the equilibrium of the reaction toward the products. This solution allows moving toward products equilibrium of steam reforming and water gas shift reactions. The main advantage arising from this configuration is that the ATR can operate at a lower S/C ratio, since the Fe based catalyst for the water-gas shift reactor (which sets specific limits on the S/C) is no more required just because of the enhancement of the shift reaction achieved inside the HSMR. Two other advantages can also be achieved: the H_2 production is increased and a higher CO_2 concentration in the stream at the reactor outlet is obtained, making the CO_2 separation process less energy consuming.

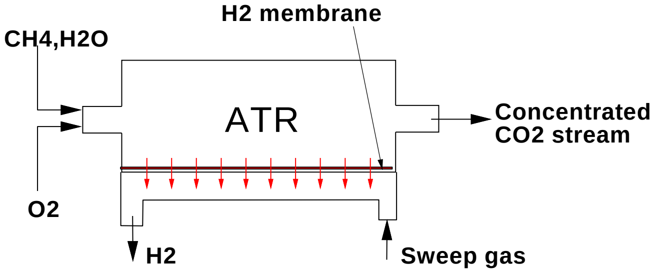


Figure 2.12: Schematic representation of hydrogen selective membrane applied to ATR reformer.

IGCC and pre-combustion power plants may also take advantage by simultaneously applying oxygen transport membranes and hydrogen separation membrane water gas shift reactors instead of conventional components. The combined effect of these substitutions could provide an efficiency increase valuable as 3 to 5 percentage points.

Studies estimates that coal oxy-fuel combustion, based on pressurized circulating fluidized bed boilers fed with oxygen produced by mixed electrolytic transport membrane modules, has a net efficiency 4 to 5 percentage points higher than competing solutions based on cryogenic air separation units.

In the field of *carbon dioxide* removal, there are promising new membrane technologies for both pre and post-combustion applications.
Figure 2.13 shows an application of Polaris™ membrane by MTR, proposed to recover 90% pure CO_2 from a SMR syngas, in two stages. Nearly 75% of the CO_2 contained in the syngas can be recovered.

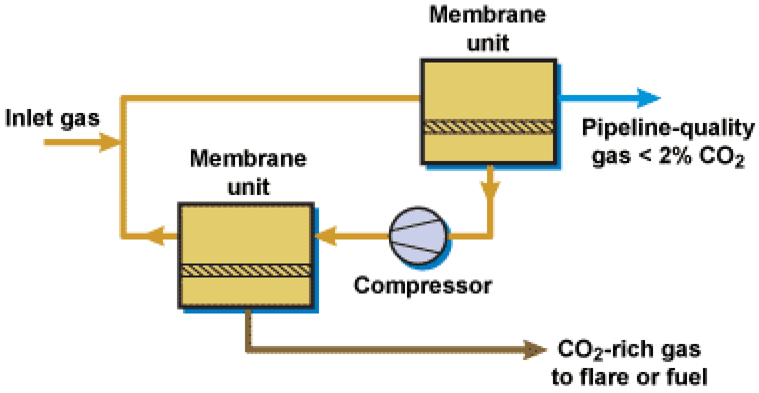


Figure 2.13: Schematic representation of CO_2 removal with membranes (source: MTR)

Development status

In the last decade different projects have been undertaken by several research laboratory and company involved in membrane construction and air separation units installation. Important effort in realizing such devices has been given by companies like Praxair and Air Products in conjunction with US Department of Energy (DOE).

Meanwhile, other projects financed by the European Community (e.g. ENCAP project under 6th Framework Programme and DECARBit project under 7th Framework Programme) and involving large research organizations such SINTEF have made steps forward in the definition of the membrane formula and construction technique.

World-wide activities are now focused on the development of more efficient membranes in combination with cost-effective supporting concepts. Scope of the undergoing researches is to provide commercial available separation membrane in the next decade, overcoming the actual problems of cost reduction and membrane support mechanical resistance. With this scope, a new European Community 7th Framework Programme has started in 2010 involving different European university laboratories and companies such as Sulzer and Amec Foster Wheeler itself.

The program foresees the use of new plasma deposition technique for membrane preparation and the technical and economical assessment of membrane-integrated plants at large scale. First results are encouraging and show some potential advantages with respect to benchmark technologies.

2.4.2. Chemical Looping

Chemical Looping Combustion (CLC) is an emerging technology that enables the CO_2 capture without the high efficiency loss of other carbon capture technologies. CLC employs a circulating solid such as metal oxide to carry oxygen from the combustion air to the fuel. Direct contact between the combustion air and fuel is avoided, and the flue gas is free of N_2.

As shown in the following Figure 2.14, the CLC system is composed of two reactors: an air and a fuel reactor.

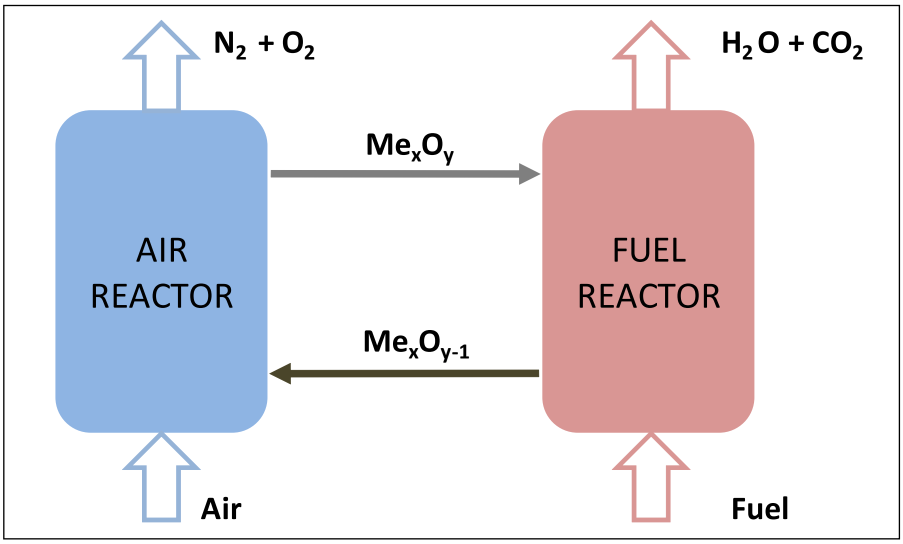


Figure 2.14: CLC system

The fuel is introduced in the fuel reactor, which contains a metal oxide, Me_xO_y. The fuel and the metal oxide react according to:

$$(2n+m)\ Me_xO_y + CnH_{2m} \rightarrow (2n+m)\ Me_xO_{y-1} + m\ H_2O + n\ CO_2 \quad [1]$$

The exit gas stream from the fuel reactor contains CO_2 and H_2O. The reduced metal oxide (Me_xO_{y-1}) is transferred to the air reactor where it is re-oxidized:

$$Me_xO_{y-1} + \frac{1}{2} O_2 \rightarrow Me_xO_y \qquad [2]$$

Depending on the metal oxide and fuel used, the first reaction is often endothermic, while the second reaction is exothermic. Anyway the total amount of heat evolved from both reactions is the same as for normal combustion, where the oxygen is in direct contact with the fuel. Therefore the air, which oxidizes the metal oxide, produces a flue gas containing only N_2 and some unused O_2. On the other hand, the outgoing stream from the fuel reactor essentially contains CO_2 and H_2O.

The advantage of chemical-looping combustion compared to normal combustion is that CO_2 is not diluted with N_2, but obtained in a separate stream without the need of any active separation of gases. Because water can be easily separated by condensation, CO_2 can then be captured with a much lower energy penalty than for other capture concepts.

From a thermodynamic point of view, one of the major differences between CLC and conventional combustion is that the oxygen carrier materials effectively limit the maximum combustion temperature (800-1200°C). These temperature limitations affect the efficiency of the power cycle.

CLC in Autothermal Reforming

Chemical looping autothermal reforming, often referred to simply as Chemical Looping Reforming (CLR), utilizes the same basic principles as CLC.

CLR could be described as a process for partial oxidation of hydrocarbon fuels (rather than complete oxidation as in CLC), where a solid oxygen carrier is used as a source of undiluted oxygen. This would eliminate the need for expensive and power demanding air separation.

CLR is operated at under stoichiometric conditions, i.e. insufficient air is added to the air reactor to completely oxidize the fuel added to the fuel reactor.
In the air reactor, the reaction [2] will occur, just as in CLC. All added oxygen will be consumed, so the depleted air will consist of only N_2.

In the fuel reactor, some fuel may become completely oxidized to CO_2 and H_2O via the reaction [1], but the larger share should react according to the reaction of partial oxidation using oxygen from the oxygen carrier:

$$C_nH_m + n\ MeO \rightarrow n\ CO + \tfrac{1}{2}m\ H_2 + n\ Me$$

The outlet from the CLR fuel reactor consists of syngas, which could be used as feedstock for chemical processes or for production of H_2. Steam or CO_2 can be added to the fuel to enhance the relative importance of steam reforming, or CO_2 reforming.

This could be useful if syngas with a H_2 to CO ratio that differs from the hydrogen to carbon ratio of the fuel is desired.

Development status

The technical development of CLC started during the late 1980's. Initial research activities were focused on the material development of oxygen carriers and power plant process integration studies. Laboratory-scale and pilot scale tests have also been conducted to evaluate the reactivity of Fe and Ni based oxygen carriers in a fluidised-bed CLC system. Tests of a reactor system at a 10 kW-scale are ongoing at Chalmers University of Technology in Sweden, while Alstom has completed engineering studies and bench-scale tests on the chemical looping process.
Nowadays, primarily in Europe and with efforts in the US and Asia, intensive academic research programs are mainly concentrated on finding the appropriate metal oxides (such as Fe, Ni, Co, Cu, Mn and Cd based oxide) for different fuels. There is also a growing interest in using CLC for solid fuels although involves more complex systems, because the direct reduction reaction of the solid fuel with the oxygen carrier is more difficult when compared with gas/solid reactions.

Thus far more than 600 materials have been tested and the technique has been successfully demonstrated in chemical-looping combustors in the size range 0.3 – 50 kW, using different types of oxygen carriers based on the metals Ni, Co, Fe, Cu and Mn. From these tests it can be established that almost complete conversion of the fuel can be obtained and 100% carbon capture with almost pure CO_2 is possible.

However, this technology is not mature yet and it has not been demonstrated on large scale. For this reason experimental engineering data are required to obtain for performance and economic evaluation for CLC system design. Moreover, further research and development is especially needed to develop high temperature and more resistant oxygen carrier and to clarify the deactivation of the oxygen carrier due to carbon deposition and other chemical phenomenon.

To investigate the use of new material in a fixed bed reactor, a research project co-financed by the EU under the 7th Framework Programme (FP7) has started in 2011, involving universities and companies like Sintef and Amec Foster Wheeler itself. Research is progressing well and a pilot plant in the Elcogas IGCC plant of Puertollano will also be realized in order to test the technology.

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APPROVED BY : G. Collodi

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1. Introduction

Over the past years a number of demonstration CCS projects have been developed around the world with the aim to provide valuable information, assist in the design of large CO_2 capture plants and to advance the understanding of CO_2 behaviour in the subsurface.

The objectives of the CCS demonstration projects can be summarized as follows:

- Demonstrating the technical feasibility of a particular technology
- Gaining operational experience and economic information
- Gathering data to support the development of large scale projects.

The purpose of this technical review is to provide an overview of the major on-going Demo CCS projects applied to SMR Hydrogen Plants with a focus on the CO_2 capture system. In particular, the technical approach used for the design and execution of the Demo Plants and the relevant peculiarities are outlined.

The general available options for CO_2 capture from SMR Hydrogen Plants are described in Technical Review 2.

The information included in the following sections has been collected from the public domain and integrated, where available, with comments received from the Companies involved in the relevant project, therefore reports the most recent public data available about each demo project.

2. Review of On-going Major Demo projects for CO_2 capture from Hydrogen Production Unit

2.1. Overview

The next sections outline the reviews of the following CO_2 capture projects:

- Port Arthur Project (Air Products)
- QUEST Project (Shell)
- Tomakomai Project (METI of Japan, JCCS)
- Port Jerome Project (Air Liquide)

For each demo project review the information reported in the next sections includes: a description of the project (e.g: location, scope of work, objective) latest information on the status of the project (timeline, project phases etc..), CO_2 capture technology brief description and a table summarizing key plant performances data.

The initial information retrieved from the public domain about each project has been organized according to the above mentioned structure and emailed to specific contacts from Air Products, Shell, JCCS/RITE and Air Liquide.
Feedback from the Companies involved in the relevant project has been received, except in case of Air Liquide, and used to integrate the preliminary information and finalise the reviews.

The four demo plants can be schematically categorized as follows:

DEMO PLANT	SOURCE OF CO_2	CAPTURE TECHNOLOGY
Port Arthur Project	Syngas from SMR	V(P)SA
QUEST Project	Syngas from SMR	Amine wash
Tomakomai Project	PSA Off-gas	Amine wash
Port Jerome Project	PSA Off-gas	Cryogenic + Membrane

2.2. Port Arthur Project (Air Products)

2.2.1. Project Description

In June 2010 Air products was selected to design, construct and operate a system to capture CO_2 from two SMR Hydrogen Plants Located within the Valero Refinery in Port Arthur, Texas.

The CO_2 removal Technology is retrofitted to the existing SMR Hydrogen plants (215 MM scfd H2 capacity) which produce hydrogen from natural gas to assist in the manufacture of petrochemicals and making of cleaner burning transportation fuels by refinery customers on the Gulf Coast hydrogen pipeline network.

The project also includes a 30MW cogeneration unit to supply make up steam to the SMR's and operate the VSA and compression equipment.

The recovered, purified and compressed CO_2 is supplied for injection into enhanced oil recovery (EOR) projects in Texas.

The main objective for this CO_2 capture process is to demonstrate an advanced technology that captures and sequesters CO_2 emissions from large scale industrial sources into underground formations. Moreover this project is supposed to provide real world data illustrating the true cost of CO_2 capture and sequestration.

Map shows Denbury's Green CO2 Pipeline. Data source is Denbury, December 2011, CO2 Flooding Conference

2.2.2. *Project Status*

The CO_2 capture project is being executed in three phases and is proceeding on schedule.

Phase 1: established the definitive project basis and has been completed

Phase 2: covers the design and construction of the project

Phase 3: entails operation of the project through the end of the demonstration period.

Civil work initiated in October 2011. Mechanical construction began in January 2012 and electrical and instrumentation construction began in June 2012. The CO_2 capture system was put on stream in December 2012 (PA-2) and March 2013 (PA-1).
Full capacity was achieved in April 2013 and 1,355,000 tons of CO_2 were delivered through the end of September 2014.

The demonstration period will continue until end of September 2017.

2.2.3. *Technology Description*

Air Products Port Arthur CO_2 Project is a new technology to recover anthropogenic CO_2 for utilization by Danbury in enhanced oil applications.

CO_2 is captured and purified from syngas stream produced in two SMR Hydrogen Production Units.

The figure below shows the integration of the CO_2 capture facility within the existing SMR Hydrogen Plants.

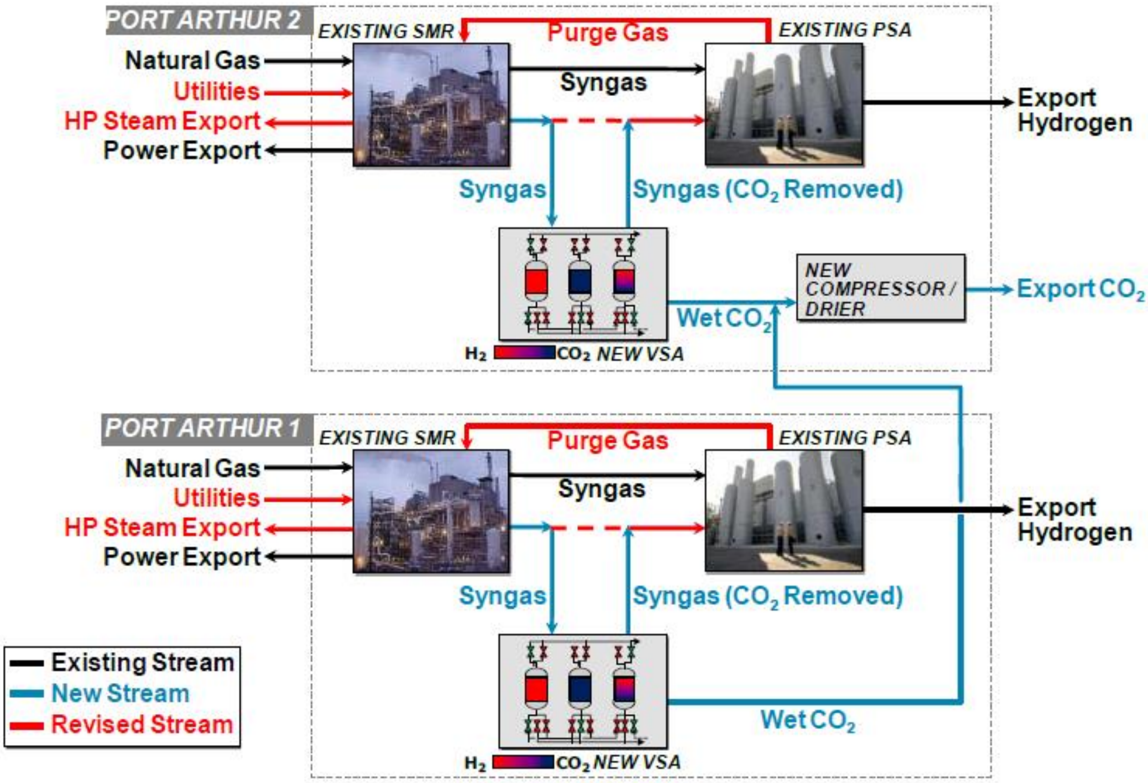
The facility utilizes a proprietary-designed CO_2 vacuum swing adsorption (VSA) system that is retrofitted to each of the two existing SMR Hydrogen Plants trains (PA-1 and PA-2). Each VSA unit is designed to remove more than 90% of the CO_2 contained in the reformer PSA feed gas. Sweet syngas (CO_2 removed) will be returned from the VSA system to feed the existing SMR hydrogen PSA. CO_2 produced from the VSA units will be compressed and dried in a single train located at PA-2.

VSA System (PA-1 and PA-2): CO_2 containing syngas from the steam-methane reformer and cold process condensate separator is routed to VSA system. The CO_2 contained in the process gas of the PA-1 and PA-2 SMRs will be removed with multiple VSA units. Each VSA unit includes a series of vessels filled with adsorbent to selectively remove one or more components from the feed gas. In this case, the feed gas is the raw hydrogen stream from the SMR plants upstream of the existing hydrogen PSA.

CO_2 compressor and dryer (PA-2): Raw CO_2 exits the two trains of the VSA systems after cooling and is combined at the suction of the first stage of an eight stage, integrally –geared centrifugal compressor. Each of the first five compressor stages is followed by an intercooler, which also includes an integral separating section to remove condensate, which is mainly water.

Condensate from the first five intercoolers is combined in a common vessel and piped to the existing plant waste sump. A portion of the PA-2 condensate can be sent to the tri-ethylene glycol (TEG) dryer system, where it serves as water makeup, thereby reducing the overall water requirements of the plant by recycling.

CO_2 exiting the fifth stage intercooler is sent to a TEG drying system, where the water is removed. After drying, the CO_2 is sent to the sixth stage section, where the final compression occurs in stages 6, 7 and 8. After final cooling following the eight stage, the CO_2 exits the battery limits and enters the CO_2 pipeline at over 2000 psig,


Simplified CO_2 Capture Block Flow Diagram

2.2.4. *Key parameters*

The table below summarizes the performances achieved by the integration of CO_2 capture system within the two SMR Hydrogen Plants (PA-1 and PA-2).

		100% Load
HPU		
Feedstock		natural gas
Fuel	t/h	NA
Hydrogen export (PA-1)	t/h	105 MMscfd
Hydrogen export (PA-2)	t/h	110 MMscfd
HP Steam (co-produced)	t/h	1-2 MM lb/hr
Flue gas production	t/h	NA
CO_2 Capture Plant		
Flue gas feed	t/h	NA
Vent Gas to Atmosphere	t/h	NA
CO_2 export	t/h	approx. 1 MM ton/yr.
Utilities		
Import Power	MW	NA
HP Steam feed (condensate all returned)	t/h	NA
Cooling Water circulation (internal)	t/h	NA
Import Water	t/h	NA
Waste Water	t/h	NA
Carbon Balance		
Total carbon in Feed	t/h	NA
Total carbon in CO_2 export	t/h	NA
Carbon Capture Rate	%	90 (from syngas)
Total CO_2 captured	t/h	NA
Total CO_2 emitted	t/h	NA

NA=data not available

2.2.5. References

- *Air Products: Success in advanced separation and CO_2 processing for EOR*-John Palamara, Galip Guvelioglu, Steven Carney Air Products and Chemicals, Inc. Presented at the 19th Annual CO_2 Flooding Conference, December 11-13,2013 Midland, Texas

- *CO_2 capture from SMRs: A Demonstration project*-W Baade, S.Farnand, R-Hutchison and K. Weltch, Hydrocarbon Processing, September 2012.

- Correspondence between Amec Foster Wheeler and Vince White (Air Products) dated 06/01/2015

2.3. Quest Project (Shell)

2.3.1. Project Description

QUEST is a fully integrated carbon capture and storage (CCS) project that is being led by Shell Canada Energy, on behalf of the Athabasca Oil Sands Project. This is a joint venture among Shell Canada Energy (60%), Chevron Canada Limited (20%) and Marathon Oil Canada Corporation (20%). The project includes the capture, transportation, injection, storage and monitoring of CO_2. CO_2 is captured from three Hydrogen Units located in the Scotford Upgrader in Fort Saskatchewan, Alberta, Canada.

The Project is designed to capture and store up to 1.2 megatonne of CO_2 per year (stream day).

2.3.2. Project Status

The Project milestones are as follows:

Complete government funding agreements	End 2010
Regulatory approval	Q1 2012
Design/Construction	2012/13/14
Commissioning and Start up	2015

2.3.3. Technology description

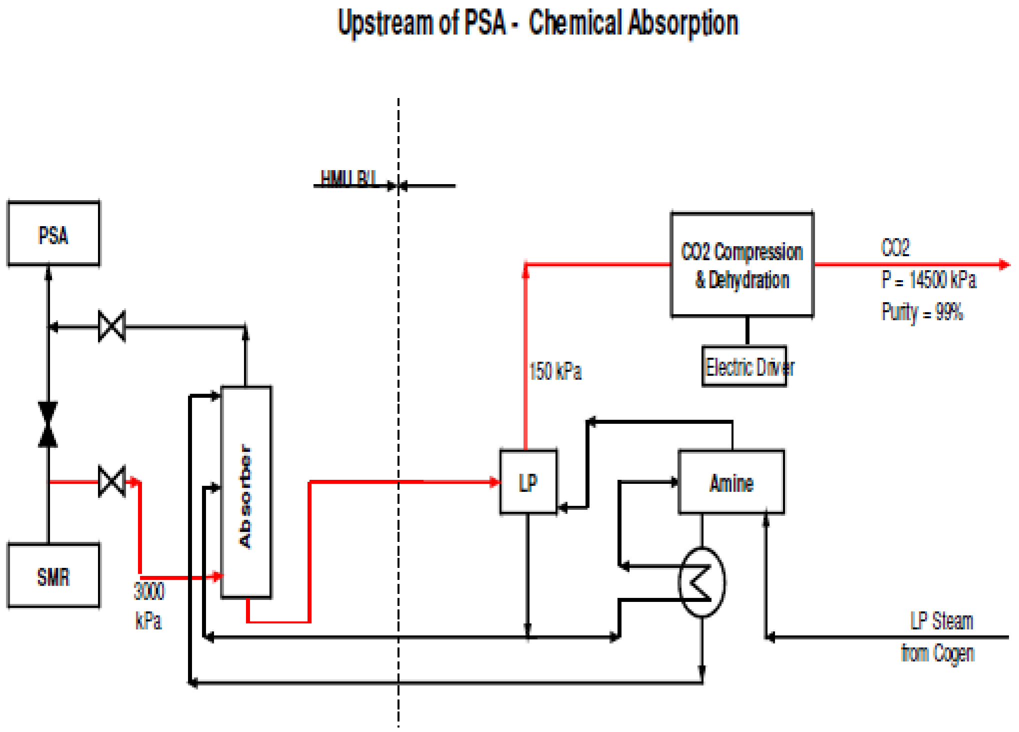
An absorber vessel will use an amine solvent to capture the CO_2 from the syngas of three Hydrogen Units, and then the CO_2 will be released from the amine by heating. The CO_2 will be compressed, dehydrated into a dense fluid and transported by pipeline to an injection location approximately 80 kilometres north of the Shell Scotford upgrader.

The CO_2 will be stored permanently in a geological formation called Basal Cambrian Sands, located two kilometres below the surface of the earth.

The CO_2 is captured upstream of the H_2 purification unit (PSA) where the typical raw process gas composition is 17% CO_2, 74% H_2, 6% CH_4, 2% CO and <1% of N_2 & H_2O (vol basis).

CO_2 is removed via absorption system based on a commercially proven activated Amine (Shell ADIPX).

Final purity of captured CO_2 is over 99% downstream the dehydration unit.
The figure below shows the integration of the CO_2 capture facility within the existing SMR Hydrogen Plants



Simplified CO_2 capture Block Flow Diagram

Key parameters

The table below summarizes the performances achieved by the integration of CO_2 capture system within the three SMR Hydrogen Plants

		100% Load
HMU		
Feedstock	t/h	105
Fuel	t/h	94
Hydrogen export HPU 1	t/h	11.8
Hydrogen export HPU 2	t/h	11.8
Hydrogen export HPU 3	t/h	13.8
HP Steam (co-produced)	t/h	438
Flue gas production	t/h	1016
CO_2 Capture Plant		
H_2 raw gas feed to Capture	t/h	267
H_2 rich gas from Capture to HMU-PSA	t/h	116
CO_2 export	t/h	150
Utilities		
Import Power (including CO_2 Compression)	MW	21
LP Steam feed (condensate all returned)	t/h	63
Cooling Water circulation (internal)	t/h	5850
Import Water	t/h	12
Waste Water	t/h	23
Carbon Balance		
Total carbon (CO_2) in Feed	t/h	183
Total carbon in CO_2 export	t/h	150
Carbon Capture Rate	%	82%
Total CO_2 captured	t/h	150
Total CO_2 emitted	t/h	33

2.3.4. References

- *Quest Carbon Capture & Storage Project*-Carbon sequestration Leadership Forum, Warsaw, October 2010
- *Quest CCS Project*- Natural Resources Canada
- Correspondence between Amec Foster Wheeler and Lily Gray (Shell) dated 23/01/2015

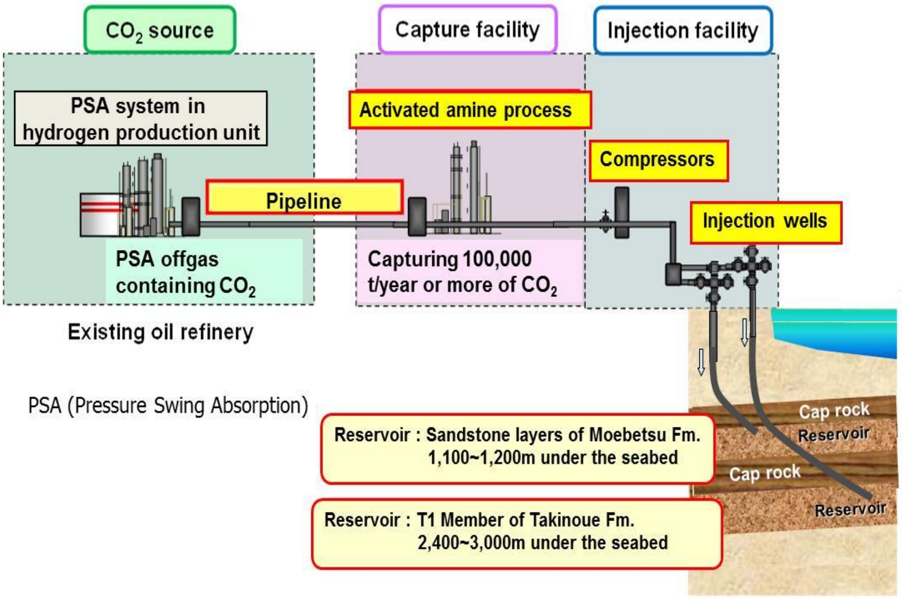
2.4. Tomakomai Project (METI of Japan, JCCS)

2.4.1. Project Description

The Tomakomai CCS Demonstration project was endorsed by Japan's Ministry of Economy, Trade and Industry (METI) in February 2012 based on an evaluation of geological conditions in the Tomakomai area which indicated it was suitable for CO_2 storage.
The project aims to demonstrate an overall CCS system from capture to storage as a foundation for commercializing CCS from 2020. The emission source for the project is a Hydrogen Plant at Idemitsu Kosan's Hokkaido Refinery situated at Tomakomai port. The flow scheme below shows CO_2 source and facilities included in the Tomakomai CCS Demo Plant.

In addition to the CO_2 capture system from Hydrogen Plant, a gas treatment technology (licensed by BASF) will be used to remove CO_2 from a gas stream from a refinery close to the location of the Demo Plant

Flow Scheme of CCS Demonstration Project



2.4.2. *Project Status*

Design and construction of the facilities, drilling of wells and preparation for operation began in 2012 with CO_2 injection planned to begin in 2016. CO_2 injection is planned to take place for three years to 2018 after which environmental monitoring will continue for two years post injection.
Performance testing of the BASF gas treatment Technology is scheduled to be completed at the beginning of 2016.

2.4.3. *Technology description*

The Hydrogen Production Unit (HPU) at Idemitsu Kosan's Hokkado Refinery supplies PSA off gas to a new-build capture plant via a pipeline.

At the capture plant, gaseous CO_2 of 99% purity will be produced by an amine scrubbing process at a rate of 100,000 tonnes per annum or more from the PSA off gas. The plant design is based on 200,000 tonnes maximum per annum.

The CO_2 removal technology utilized in Tomakomai Project is an absorption process via amine solvent where the carbon dioxide to be removed from the gas stream chemically reacts with the solvent forming new product components. The reaction is reversed and the acid gases are released during the solvent regeneration process.

The gaseous CO_2 will then be sent to the CO_2 injection facility next to the capture plant where it is compressed and injected into two different offshore reservoirs by two deviated injection wells.

With the technology from BASF, carbon dioxide will be removed from a gas stream which, after the treatment process, will consist of mainly hydrogen and methane and will be used to produce utilities such as steam and electricity in the same CCS Plant. Annually the unit is designed to capture about 200000 tons of CO_2.

2.4.4. *Key parameters*

The table below summarizes the performances achieved by the new-build capture plant adjacent to the Hydrogen Plants at Idemitsu Kosan's Hokkaido Refinery.

		100% Load (Design rate)
HPU		
Feedstock	t/h	NA
Fuel	t/h	NA
Hydrogen export	t/h	6.00 as 100% H_2
HP Steam (co-produced)	t/h	NA
Flue gas production	t/h	NA
CO_2 Capture Plant		
CO_2 gas feed (PSA off gas)	t/h	28.24 (CO_2=25.32 t/h)
Treated gas from Absorber(Fuel gas)	t/h	2.91 (CO_2=0.02t/h)
CO_2 export (CO_2 storage)	t/h	26.25 (CO_2=25.30t/h)
Utilities		
Import Power	MW	0.49 (for amine pumps) *
HP Steam feed (condensate all returned)	t/h	10.4 as LP steam to amine reboiler
Cooling Water circulation (internal)	t/h	465 (delta temp=10 deg C)
Import Water	t/h	0.92
Waste Water	t/h	zero
Carbon Balance		
Total carbon in Feed	t/h	6.91 as C
Total carbon in CO_2 export	t/h	6.90 as C
Carbon Capture Rate	%	99.9
Total CO_2 captured	t/h	25.30 as CO_2
Total CO_2 emitted	t/h	0.02 as CO_2

*Power for the PSA off gas compression upstream of CO_2 absorption is not included because the compression is to attain a simulated CO_2 partial pressure same as the PSA upstream gas. The CO_2 absorption could not be conducted upstream of PSA due to area limitation inside the refinery.

2.4.5. References

- *Tomakomai CCS Demonstration project in Japan*- Masanori Abe Japan CCS Co., Ltd, 2014 International CCS Conference, Taipei, Taiwan, May 19th 2014

- *The Tomakomai CCS Demonstration Project*-The global status of CCS, 2014

- *Tomakomai CCS Demonstration Project in Japan, 2014 Update* - GHGT-12 International Conference, Austin, USA, October, 2014

BASF gas treatment technology supports Japan first scale Carbon dioxide Capture and storage demonstration project

- Correspondence between Amec Foster Wheeler and Ryozo Tanaka- Research institute of Innovative Technology for the Earth (RITE) dated 24.12.2014

2.5. Port Jerome Project (Air Liquide)

2.5.1. *Project Description*

Port Jerome project is the first Cryocap ^{TM} project launched by Air Liquide and is an application of CPU (Cryogenic Purification Unit) Technology to capture CO_2 from Hydrogen Plants.

Cryocap ^{TM} system in Port Jerome Plant will remove the CO_2 from the PSA tail gas and will have a capacity of approximately 300 t of CO_2 per day. The system will demonstrate technologies up scalable to 2000 t CO_2 per day.

The CO_2 will be produced as a food grade liquid, demonstrating the ability to reach purity levels high enough for even the most stringent specifications.
The CO_2 concentration in the PSA is sufficient to make CO_2 separation by cryogenics an attractive option. Focusing CO_2 capture on this stream reduces specific cost. This is due to its relatively high concentration compared to the flue gases generated by the burners used to heat the furnace.

This project shows that very limited revamp is necessary in order to implement CRYOCAP ^{TM} H_2. For instance no revamp was required on the burner side or on the furnace convection section side. Moreover the overall thermal SMR plant efficiency will be increased by retrofitting this technology thanks to the higher hydrogen recovery from the syngas.

2.5.2. *Project Status*

Following extensive preliminary studies and FEED, in 2013 Air Liquide launched the execution phase of its Cryocap^{TM} H_2 project. Start-up is planned at the beginning of 2015.

2.5.3. *Technology description*

Air Liquide has developed its Cryocap ^{TM} H_2 technology in order to capture CO_2 from the PSA Tails gas (off gas).

This technology uses cryogenic purification to separate the CO_2 from the off gas of the PSA. This is followed by membrane separation in order to simultaneously increase the CO_2 capture rate and the SMR productivity as hydrogen recovery from syngas is increased.

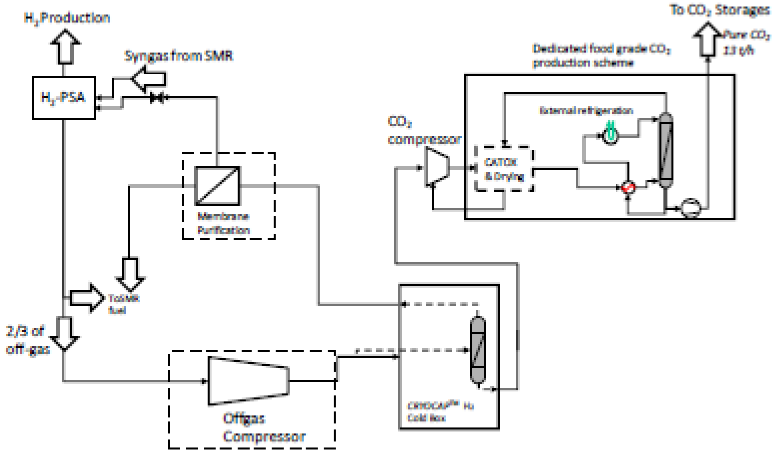
The figure shows the process flow diagram for Port Jerome plant integrating Cryocap system. Key parts of the process are here below described:

- **Off gas compression and drying** : The off gas is compressed with a 8 stage high efficiency centrifugal machine to a pressure at which CO_2 may be separated by liquefaction at around -50 ^{o} C , close to the triple point.
- **Cryogenic purification of CO_2:** A cryogenic process is used to separate and purify CO_2. This will include partial condensation and distillation of CO_2. Special care is taken regarding risk of freezing CO_2 in the cold part.
- **Membranes:** The non-condensable gases are then passed through a membrane system which enables additional H_2 and CO_2 to be recovered. The use of proprietary membranes from Air Liquide Membrane Division (MEDAL) will demonstrate high CO_2 recovery and extra hydrogen production.
- **H_2 PSA integration:** the hydrogen separated from the Membranes is recycled to PSA boosting the overall recovery of hydrogen from syngas. This step requires modification of the control system (adaptation of the cycle) and this re-programming had to be included in the project.

CO_2 recovery rates on the off gas in excess of 95% are attainable.

Therefore, the Cryocap ^{TM} H_2 Unit has been designed not only for high capture rates, but also to recover the remaining H_2 from the off gas. In this way the process economics and efficiency are optimised since H_2 can be sold as a high value product instead of being used as low value substitute for natural gas.

Typically, an increase in H_2 production of 10-20% may be attained for a given SMR compared to Plant without Cryocap^{TM} H_2.



Simplified BFD for Port Jerome plant with Cryocap^{TM} H_2

2.5.4. *Key parameters*

The table below summarizes the performances achieved by the integration of CO_2 capture system within the SMR Hydrogen Plants.

		100% Load
HPU		
Feedstock	t/h	14.2
Fuel	t/h	1.4
Hydrogen export HPU	t/h	4.5
HP Steam (co-produced)	t/h	33.1
Off gas production	t/h	36.1
CO_2 Capture Plant		
H_2-PSA Syngas feed	t/h	35.4 (CO_2=22.8t/h)
Off Gas to SMR burners	t/h	12.5 (CO_2=9.2t/h)
CO_2 export	t/h	13.0
Utilities		
Import Power	MW	NA
HP Steam feed (condensate all returned)	t/h	0.6
Cooling Water circulation (internal)	t/h	400 (delta T =10°C)
Import Water	t/h	0
Waste Water (returned to SMR)	t/h	0.1
Carbon Balance		
Total carbon (CO_2) in syngas Feed	t/h	6.24
Total carbon (CO_2) in off gas to burners	t/h	2.50
Total carbon (CO_2) in CO_2 export	t/h	3.56
Carbon (CO_2) Capture Rate	%	>95 from off-gas (target)
Total CO_2 captured	t/h	13.0
Total CO_2 emitted	t/h	28.4

2.5.5. References

- *Oxycombustion for carbon capture on coal power plants and industrial processes: advantages, innovative solutions and key projects, ScienceDirect*-Nicolas Perrin, Richard Dubettier, Frederick Lockwood, Philippe Court, Jean-Pierre Trainer, Claire Bourthy-Weber, Michel Devaux - GHGT-11 International Conference

- *CO_2 capture from H_2 plants: implementation for EOR*, *ScienceDirect*- Paul Terrien, Frederick Lockwood, Ludovic Granados, Thomas Morel, Air Liquide Global E&C Solutions - GHGT-12 International Conference, Austin, USA, October, 2014

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