



GHGT-9

Recovery of Carbon Dioxide and Hydrogen from PSA Tail Gas

Satish Reddy^{a*}, Sunil Vyas^a

^a Fluor Enterprises, Incorporated, 3 Polaris Way, Aliso Viejo, CA 92698, USA.

Abstract

As refineries attempt to expand their production and reduce their carbon footprint, a process capable of recovering incremental hydrogen and capturing carbon dioxide has tremendous value. Fluor's patented process, CO₂LDSepSM, is a cost effective technology that is able to recover residual hydrogen and CO₂ from a Pressure Swing Adsorption (PSA) tail gas. The CO₂LDSepSM process is very useful as a retrofit strategy in an existing refinery.

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Carbon Dioxide Capture; CO₂LDSepSM, incremental hydrogen recovery, liquid carbon dioxide, food grade carbon dioxide.

* Corresponding author. Tel.: +1-949-349-4959; fax: +1-949-349-2898.
E-mail address: satish.reddy@fluor.com.

1. Introduction

Most modern hydrogen plants use a PSA to recover hydrogen from a shifted syngas. PSA's are able to recover between seventy five to greater than ninety percent of the overall hydrogen in the syngas. Therefore, the rest of the hydrogen remains unrecovered and is burned as fuel gas.

The CO₂LDSepSM process recovers hydrogen, high pressure liquid CO₂, and a fuel gas as products from the PSA tail gas. The CO₂ liquefaction uses compression, cooling, and expansion of the PSA tail gas to recover between fifty and ninety percent of the CO₂ in the feed. No solvents are required. Once the CO₂ is recovered, the remaining gas stream is enriched in hydrogen. This gas is sent to another PSA to recover an incremental amount of hydrogen.

If the desired CO₂ recovery is high, supplemental refrigeration may be used. Also if food-grade CO₂ production is desired, the liquid CO₂ can be purified in a reboiled stripper to a purity of 99.99 wt%. No external steam is required to achieve the stripping.

The CO₂ product is available as a liquid, which allows for low energy consumption when high pressures of product CO₂ are desired.

2. Process Description

A typical hydrogen plant process consists of four steps: 1) reforming, 2) waste heat recovery, 3) shift reaction and cooling, and 4) purification. A block flow diagram of a hydrogen plant is shown in Figure 1 below.

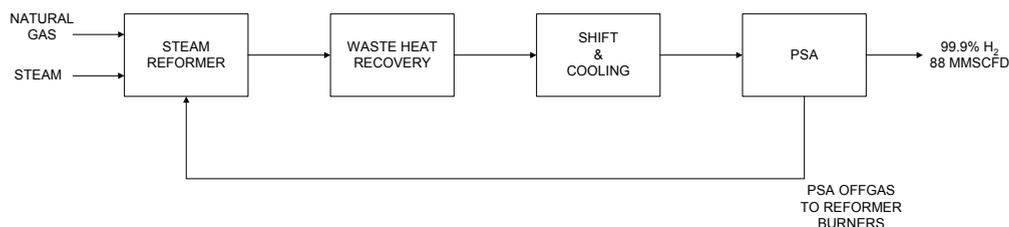


Figure 1 – Typical Hydrogen Plant

In most hydrogen plants, the purification process consists of a PSA unit to recover hydrogen from the shifted syngas. PSA's recover between 75-90+% of the incoming hydrogen. The concentration of hydrogen in the PSA feed gas and, to a lesser extent, the feed gas pressure are factors that affect the recovery rate. A PSA can produce hydrogen at a purity of 99.99+ wt%. The PSA off-gas is at slightly above atmospheric pressure and has the following typical composition:

- Carbon Dioxide 50-55 mol%
- Hydrogen 24-26 mol%
- Methane 15-20 mol%
- Water 0-5 mol%
- Carbon Monoxide 0-2 mol%

PSA off-gases are ideally suited to be used as a fuel gas in the hydrogen plant's reformer. However valuable, unrecovered hydrogen still exists in this stream. If refineries can recover this hydrogen, they can utilize it to expand their overall production and profitability.

Additionally, refineries are becoming more focused on limiting their carbon dioxide emissions for environmental reasons. By implementing the $\text{CO}_2\text{LDSep}^{\text{SM}}$ process on the PSA off-gas, refineries can increase their production and reduce their carbon footprint by recovering hydrogen and carbon dioxide.

Figure 2 shows a typical hydrogen plant with the $\text{CO}_2\text{LDSep}^{\text{SM}}$ process.

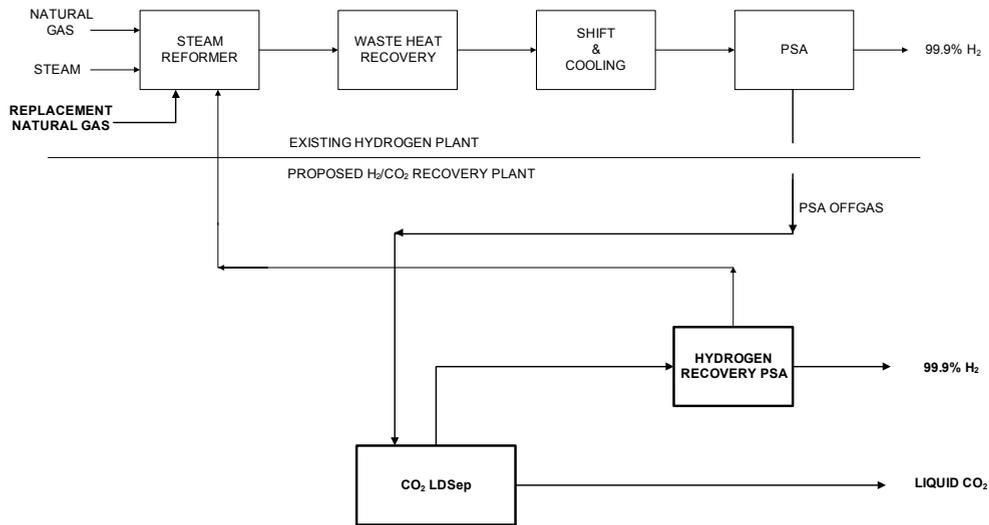


Figure 2 – Typical Hydrogen Plant with $\text{CO}_2\text{LDSep}^{\text{SM}}$ process

The following description of the $\text{CO}_2\text{LDSep}^{\text{SM}}$ process corresponds to Figure 3 shown below.

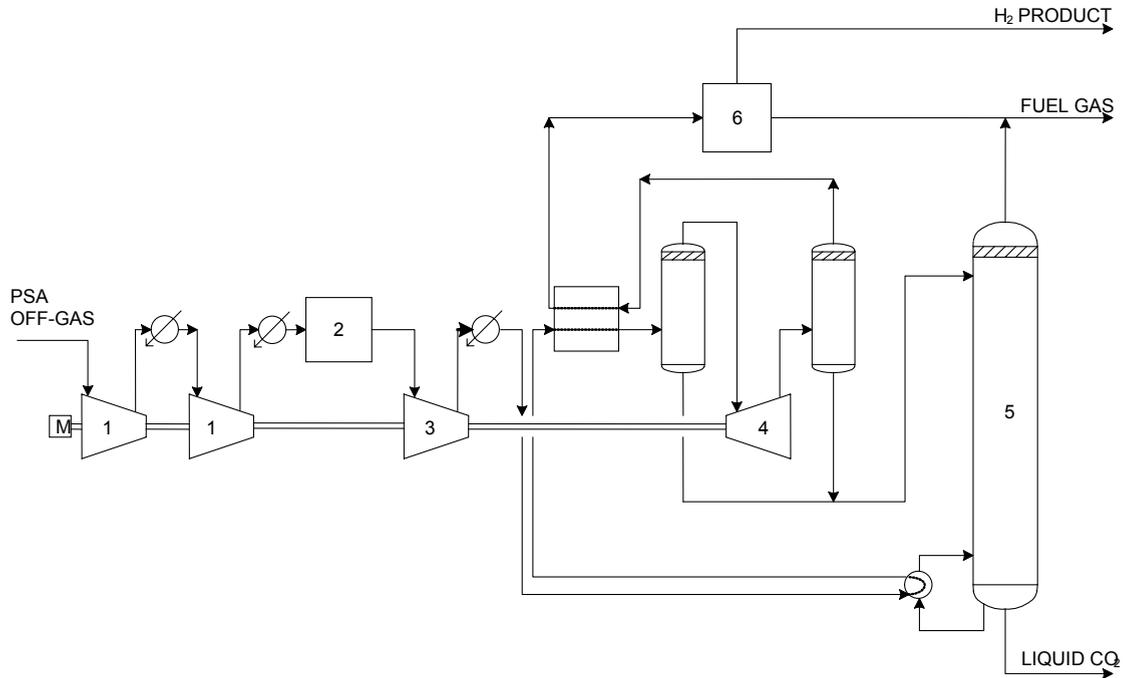


Figure 3 – Typical CO₂LDSepSM process for PSA Off-gas

The off-gas from the PSA unit in the existing hydrogen plant enters the CO₂LDSepSM plant and is compressed in the Feedgas Compressor (1). The compressed feedgas is then dried (2), further compressed (3), cooled, and expanded (4). The compression/expansion services may be accomplished in a single integrally geared compressor package. The autorefrigeration effect of expanding the CO₂ causes a portion of the CO₂ to be removed through liquefaction. Supplemental refrigeration may be used, if the desired CO₂ recovery is high, but is not required. If food-grade CO₂ production is desired, the liquid CO₂ can be purified in a reboiled stripper (5) to a purity of 99.99 wt%. The CO₂ product is available as a pumpable liquid, which allows for low energy consumption when high pressures of CO₂ are desired for Enhanced Oil Recovery (EOR).

The hydrogen-enriched gas leaving the CO₂LDSepSM Unit is sent to the Hydrogen Recovery PSA (6), where high-purity hydrogen is separated from the carbon oxides, methane, and other impurities.

The off-gas stream from the new Hydrogen Recovery PSA along with the overhead from the stripper, if applicable, can be routed to the reformer furnace where it is blended with replacement natural gas fuel and combusted.

As can be seen in Figure 3, the CO₂LDSepSM process utilizes a single compression/expansion unit to accommodate all of the services. An integrally geared centrifugal compressor consists of impellers mounted on pinions which run on a main gearbox. Each pinion is capable of having two impellers attached and can, therefore, accommodate two stages of compression. A pinion can also be used for a single stage of expansion. The ability to have so many services on a single machine, render an integrally geared compressor a good fit for the CO₂LDSepSM process. These machines are compact and require relatively low maintenance when compared to other types of compressors. Some pictures of integrally geared compressors are provided in Figures 4 and 5 courtesy of Atlas Copco and MAN Turbo.

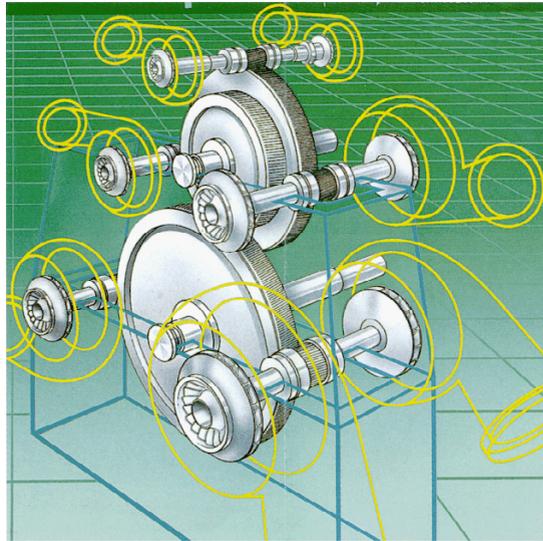


Figure 4 – Integrally Geared Compressor



Figure 5 – Integrally Geared Compressor

3. Performance & Other Applications

The CO₂LDSepSM process was initially designed to recover hydrogen and CO₂ from PSA off-gas. However, the CO₂LDSepSM process can also be used to recover CO₂ from a variety of streams. The process of liquefying the CO₂ and the type of equipment used is similar for each application.

Pure CO₂ streams often need to be liquefied and pumped to a high pressure for Enhanced Oil Recovery (EOR) or CO₂ sequestration. The CO₂LDSepSM process is able to liquefy pure CO₂ with low energy consumption compared to conventional methods.

Flue gas from an oxyfuel boiler contains large amounts of CO₂. The CO₂LDSepSM process is able to recover approximately 85% of the incoming CO₂ and produce a liquid product.

In the Gasification process, syngas is generated and then can be shifted to contain mostly CO₂ and H₂. The CO₂LDSepSM process can be implemented to recover the CO₂ and purify the H₂ for various uses. For this application, a two-stage CO₂LDSepSM process is implemented to maximize recovery and efficiency.

Table 1 shows the various applications and their respective performance numbers.

Table 1 - CO₂LDSepSM typical performance for various applications

	Feed CO ₂ (mol%)	CO ₂ Recovery (%)	Power (kWh/tonne CO ₂ recovered)	H ₂ Recovery (%)
CO ₂ Liquefaction Unit	96.5	99.6	152.1	-
Oxyfuel Boiler Exhaust	79.9	85.0	224.3	-
PSA Off-Gas	41.0	63.1	419.7	74.8
Gasified Syngas	42.0	88.3	105.5	87.2

4. Conclusions

The CO₂LDSepSM process is a simple and efficient process that uses proven equipment to recover carbon dioxide and, if desired, hydrogen. The process has low energy consumption and does not require any solvents. The simplicity of the process allows for a low equipment count using equipment that is familiar to operators. In addition, external refrigerants are not required for most applications. The CO₂LDSepSM process's various applications make it ideal for all recovering and liquefying carbon dioxide.

The CO₂LDSepSM process was originally designed to recover carbon dioxide and hydrogen from PSA off-gas. Refineries who implement the CO₂LDSepSM process will be able to increase their production and reduce their overall carbon footprint.