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CO_2 capture from H_2 plants: implementation for EOR

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Abstract

Hydrogen plants are a significant source of CO_2 in refineries. More precisely, the hydrogen plant is one of the largest emitters in a typical refinery. Therefore CO_2 capture from hydrogen plants has become a particular point of attention for refining and industrial gas companies such as Air Liquide, who owns and operates numerous hydrogen plants throughout the world.

Typical hydrogen plants use steam methane reforming technology and provide concentrated streams of CO_2 that can potentially lead to lower CO_2 capture costs than in other industries.

One Air Liquide solution for CO_2 capture from SMR plants is called CRYOCAP™ H_2. 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. Extra hydrogen production ranges from 10 to 20%.

A first opportunity for the development of this technology can be the EOR (Enhanced Oil Recovery) application. Indeed, as will be shown, this technology offers CO_2 capture costs low enough and at the right locations for such usage. This should also allow the cost of capture to be further reduced and accelerate the technology adoption as a way to reduce CO_2 emissions associated with geological storage.

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Keywords: CO_2, CCS, EOR, CPU, H2, refineries

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1. Introduction

Development of technologies for CCUS needs to happen in various sectors simultaneously. Whereas the main sector will be carbon capture from fossil fuel power plants, it might not be the most economical to start with. It makes sense to start with sources where the cost of capture can be the lowest first. Typically hydrogen plants are an example of such sources. CRYOCAP™ H_2 is a solution for CO_2 capture from hydrogen production plants. It offers a very cost efficient (both in terms of CAPEX and OPEX) for the CO_2 capture from refineries.

The CRYOCAP™ line of products has been developed over the last ten years. CRYOCAP™ H_2's development has been very fast and it is now reaching commercial level with the first industrial reference ready for start-up soon.

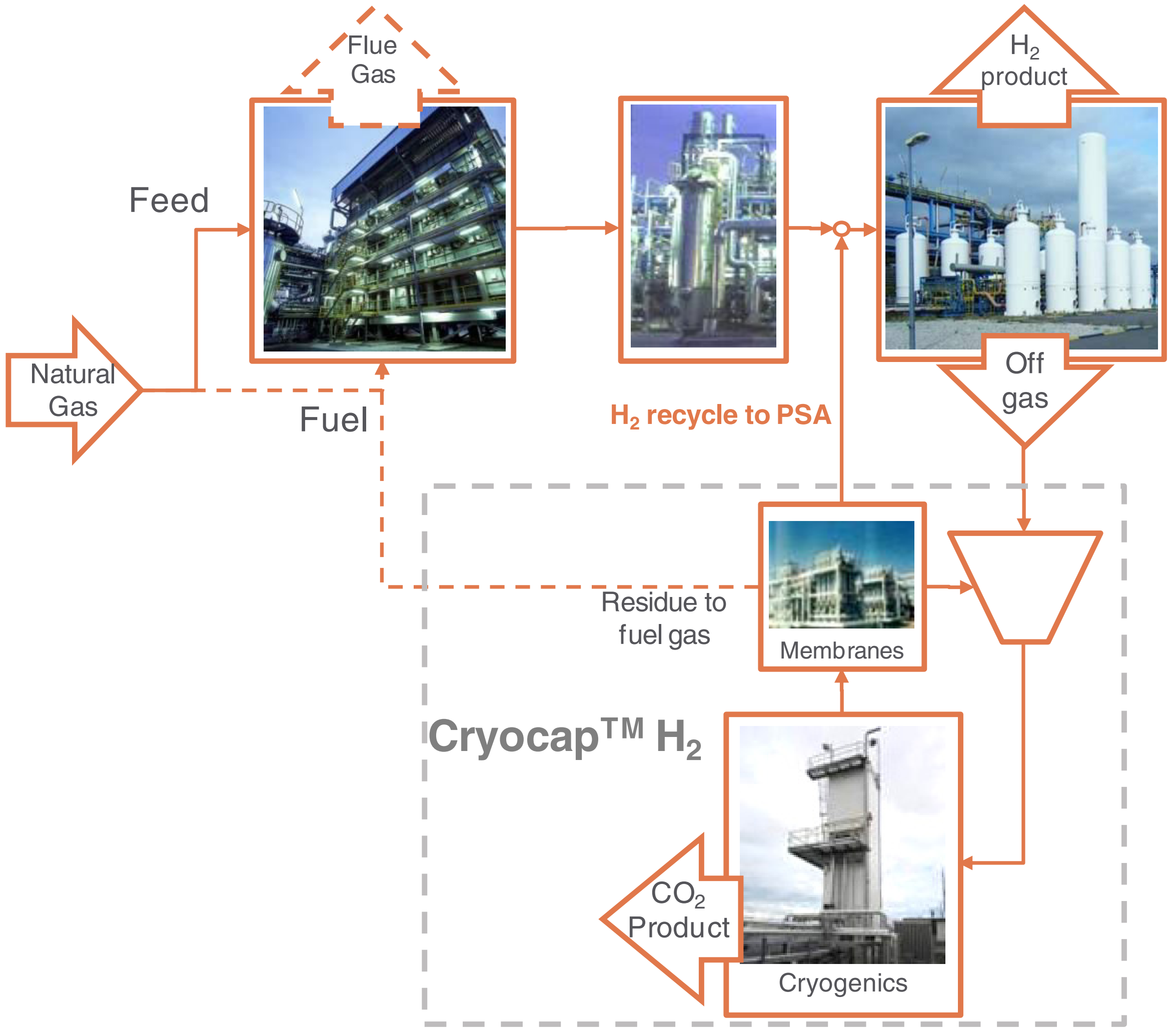

Fig 1. Process block flow diagram of *CRYOCAP™* H_2 technology

As shown in figure 1, the concept is to co-produce CO_2 and additional hydrogen in a traditional SMR plant. The first step is a compression of the PSA off-gas, followed by cryogenic purification to separate the CO_2 under pressure. CO_2 can be produced at very high pressure with limited re-compression energy. The next step is a multi-stage membrane separation in order to simultaneously increase the CO_2 capture rate and the SMR productivity (hydrogen recovery from syngas is increased – see figure 1 above). Extra hydrogen production ranges from 10 to 20%. The membranes used are MEDAL™ membranes, offering both high efficiency and low CAPEX.

The overall CO_2 recovery from syngas is typically higher than 97% whereas the overall hydrogen recovery from syngas is typically higher than 98%.

Because a part of the CO_2 emitted from a hydrogen plant comes from combustion, it is not possible to reach 100% capture in the plant. Indeed, roughly only 2/3 of the CO_2 can be captured with this technology (this is a so-called partial capture solution). However it was shown in previous papers ([1]), that the incremental cost of capture of the last third of the CO_2 produced is very high. This technology has been compared in this article against other partial capture solutions, which are themselves clearly more economical than total capture solutions.

2. Technology Readiness – Port-Jérôme: first industrial reference

The technology is being fast tracked to industrial demonstration and the first reference is currently under construction at Port Jérôme, France. Most of the critical equipment has now been installed and it will be ready for start up at the beginning of 2015.

Building on experience from cryogenic purification units for other applications, Air Liquide has been through a detailed engineering and execution phase for this industrial project. 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. Figure 2 shows a process flow diagram for the process. Since the product is food grade CO_2, the process actually includes some extra steps that will not be required for typical EOR product specifications. On the other hand, all of the required blocks for EOR application are included in the design.

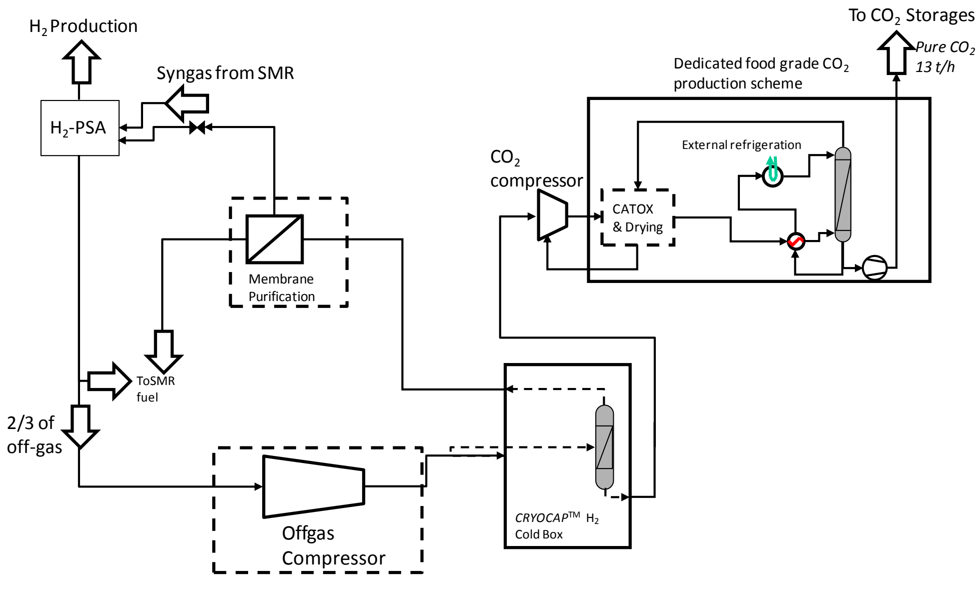

Fig 2. Process flow diagram of the Port-Jérôme plant

The Port-Jérôme project will demonstrate all the key parts of the process:

- **Off-gas compression and drying:** An 8 stage high efficiency centrifugal machine will be used and drying using a TSA.

- **Cryogenic purification of CO_2:** A cryogenic process will be used to separate and purify CO_2. This will include partial condensation and distillation of CO_2. Special care was taken regarding risk of freezing CO_2 in the cold part.
- **Membranes:** The use of proprietary membranes from Air Liquide's membrane division (MEDAL) will enable demonstration of high CO_2 recovery and extra hydrogen production.
- **H_2 PSA integration:** Hydrogen is recycled to PSA boosting the overall recovery of hydrogen from syngas. This requires modification of the control system (adaptation of the cycle) and this re-programming had to be included in the project.

All main technology blocks for Cryocap™ H_2 will be demonstrated at Port-Jérôme on a small industrial scale.

This project showed 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. The integration of a centrifugal machine with the PSA has also been a challenge but was validated after modelling by dynamic simulation and site data analysis. Indeed cyclic variations of composition and pressure need to be taken into account in the specifications of the compressor.

Another side benefit is that the overall thermal SMR plant efficiency will be increased by retrofitting with CRYOCAP^{TM} H_2 technology. This is mostly a consequence of the higher hydrogen recovery from the syngas.

3. CRYOCAP™ H_2 as a solution for CO_2 Enhanced Oil Recovery (EOR)

Drawing from its long experience as an hydrogen plant operator and owner, as well as a technology provider, Air Liquide performed detailed comparisons of available CO_2 capture solutions.

To illustrate this comparison, a case study for Steam Methane Reformers (SMR) producing 100 kNm^3/h in US Gulf Coast is presented here, with the following assumptions:

- Eletricity price: \$60/MWh
- Natural gas price: \$4/MMBTU
- Product: Supercritical CO_2 at 150bara

The main competition for CRYOCAP^{TM} H_2 technology is aMDEA absorption on syngas. This technology is the state-of-the-art technology for CO_2 separation from SMR plants. Figure 3 shows the results from this comparison between those two technologies.

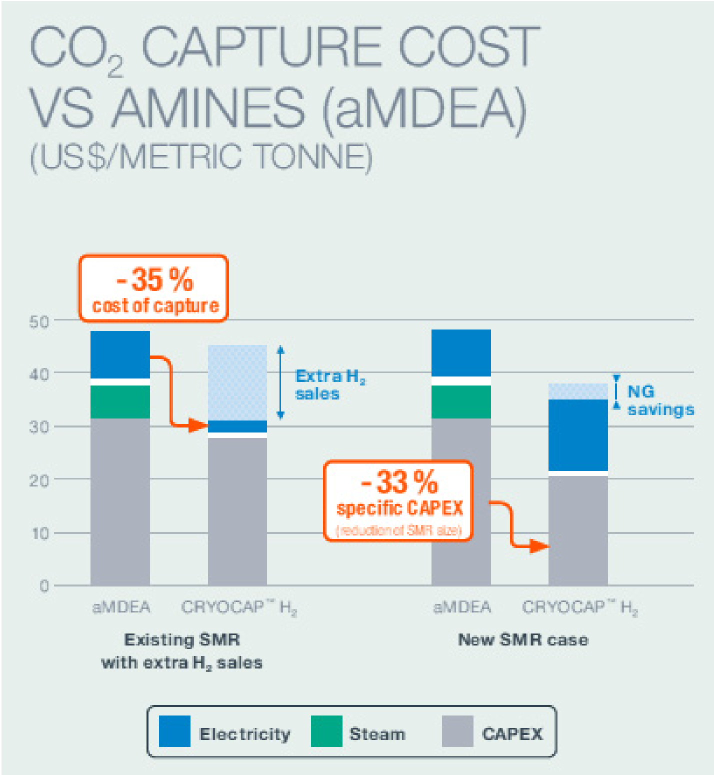

Fig 3. CO_2 capture cost comparison

As illustrated in figure 3, the price of CO_2 that can be reached with Cryocap™ H_2 is below $40/tonne of CO_2 and can be up to 40% cheaper than aMDEA solutions (depending on various assumptions such as retrofit or green field cases, price of utilities and value of hydrogen).

This cost of capture also makes the H_2 PSA off-gas on SMR plants one of the cheapest 'untapped' sources of CO_2.

The competitiveness of this cryogenic CO_2 capture method makes it a perfect fit as a CO_2 EOR source. In particular, some regions in the world such as the US Gulf Coast include CO_2 EOR infrastructure as well as a number of refineries and hydrogen plants where this technology could be implemented. The example of the Gulf Coast region is illustrated on figure 4, making the proximity between sources and sink clear.

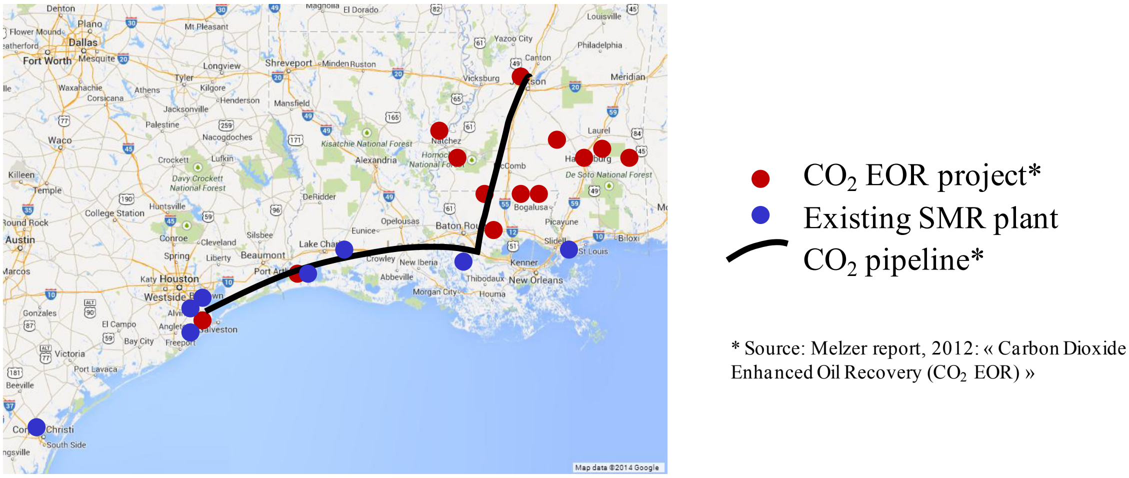

Fig 4. Proximity of sources and sinks in the US Gulf Coast region

Cryocap^{TM} H_2 now combines a sufficient level of maturity and competitive CO_2 production cost making it an attractive option for EOR use in such regions.

4. Conclusion

It was shown that the Cryocap^{TM} H_2 technology has the potential to reduce CO_2 emissions with no (or limited to the first large project) intervention from governments because of the low cost of capture that can be reached and the match with current requirements for CO_2 EOR, for instance on the US Gulf Coast. This can be achieved in the short term because of the maturity level of the technology. It can also been seen as an enhancer for massive adoption of CCS as a CO_2 mitigation technique, enabling reducing cost of capture in other domains such as oxy-combustion for power plants with carbon capture using similar cryogenic CO_2 separation (CPU).

Acknowledgements

References

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