

Hydrogen Production via Steam Reforming with CO₂ Capture

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Hydrogen demand in refineries is increasing vigorously due to the stringent transportation fuel specifications, furthermore the interest in the so-called hydrogen economy developed in the recent years put the hydrogen as energy carrier in the centre of a growing interest.

More than 95% of the hydrogen for refinery use is nowadays produced via hydrocarbon steam reforming, where Foster Wheeler plays an active role both as a technology and steam reforming furnace (the Terrace Wall™) supplier.

Depending on the quality of the feedstock (natural gas, rich gases, naphtha, etc.), one ton of hydrogen produced will also produce 9 to 12 tons of CO₂.

As a consequence, from carbon emissions point of view, besides the optimisation of the hydrogen balance (Stockle and Bullen, 2008) and the improvements in production technologies, CO₂ capture is also an option to be considered.

The paper will examine the possibilities of CO₂ capture in a steam reforming based plant, and its impact on the economics of hydrogen production.

1. The Steam Reforming Hydrogen Plant

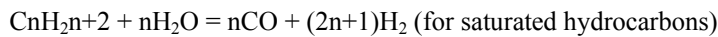
For many years, steam methane reforming (SMR) has been the leading technology for generation of hydrogen in refining and petrochemical complexes.

The steam reforming plant consists of four basic sections (Bressan et al., 2009):

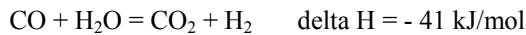
- The first is feedstock treatment where sulphur and other contaminants are removed.
- The second is the steam methane reformer, which converts feedstock and steam to syngas (mainly hydrogen and carbon monoxide) at high temperature and moderate pressure. In case of multiple or heavy feeds and/or for large capacities, an adiabatic, catalytic pre-reforming step is foreseen upstream the SMR.
- The third section is the syngas heat recovery and incorporates CO shift reactor/s to increase the hydrogen yield.
- The final section is the raw hydrogen purification, in which modern plants employ a pressure swing adsorption (PSA) unit to achieve the final product purity.

In addition to the core process sections, compression is often needed to raise the feedstock and product hydrogen pressures.

The reforming reaction between steam and hydrocarbons is highly endothermic and is carried out using specially formulated nickel catalyst contained in vertical tubes situated in the radiant section of the reformer. The simplified chemical reactions are:



In the adiabatic CO shift reactor vessel, the moderately exothermic water gas shift reaction converts carbon monoxide and steam to carbon dioxide and hydrogen:



The PSA purification unit removes from the hydrogen, by adsorption, CO, CO₂ and CH₄ gases.

SMR is a mature technology and is now less likely to yield any large step changes in economic benefit from technological developments. Marginal economic improvements are the order of the day.

2. The CO₂ Balance in the Hydrogen Plant

In a modern steam reforming hydrogen plant fed by natural gas, up to approx. 60% of the total CO₂ produced is contained in the shifted gas (and then in the PSA tail gas), while the remaining 40% is the product of the combustion of the additional fuel gas required by the steam reformer. At last, all the CO₂ ends up in the flue gas of the SR heater. (See Figure 1 below)

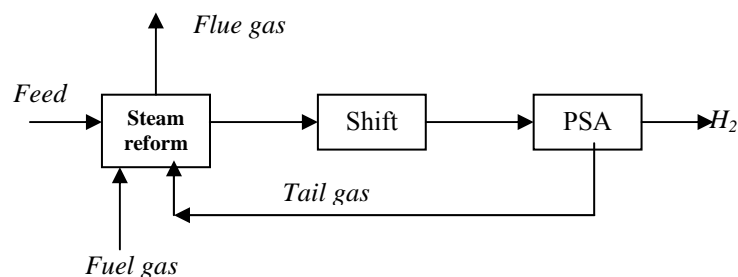


Figure 1 – Simplified H₂ block flow diagram

Typical CO₂ flow rates and partial pressures for a 100,000 Nm³/h (89.5 MMSCFD) Hydrogen plant are reported in the following Table 1.

Table 1 – Typical H₂ plant CO₂ balance

Stream	CO ₂ concentration (% mol)	CO ₂ flow rate (kmol/h)	CO ₂ partial pressure (bara)
Raw H ₂ (PSA inlet)	15.0	1,000	3.40
PSA tail gas	45.1	1,000	0.60
SR flue gas	19.0	1,850	0.20

It is clear from this example that one ton of hydrogen produced will also produce about 9 tons of carbon dioxide.

The CO₂ could be captured from any of these three streams (see Figure 2), with removal efficiency of about 90% (from PSA tails gas and from SR flue gas) and up to more than 99% (from raw H₂ at higher pressure).

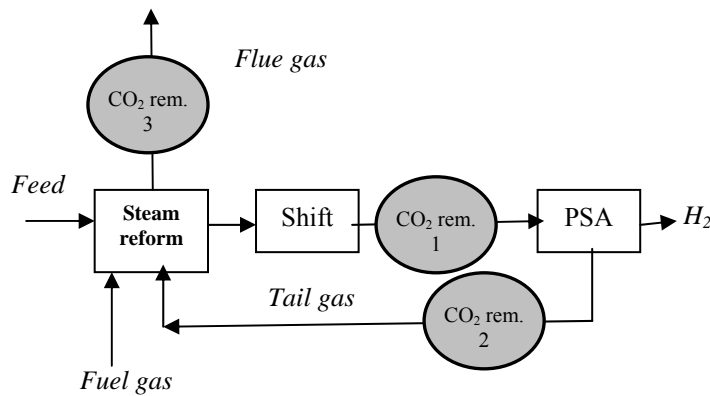


Figure 2 – CO₂ removal locations

The total CO₂ potentially removed (η_{CO_2}) from the three locations, calculated with the formula

$$\eta_{CO_2} (\%) = 100 \times (1 - \text{CO}_2 \text{ in flue gas after rem.} / \text{CO}_2 \text{ in flue gas without CO}_2 \text{ rem.})$$

is reported in Table 2.

Table 2 – Achievable CO₂ removal

CO ₂ removed from:	CO ₂ removed from each stream (%)	Overall η_{CO_2} (%)
1.Raw H ₂ (PSA inlet)	100	60
2.PSA tail gas	90	55
3.SR flue gas	90	90

It is also possible, in principle, to combine CO₂ removal 1 or 2, with 3 (from flue gas), and obtain an overall η_{CO_2} of about 96 and 94% respectively.

3. CO₂ removal technologies

There are several and different available technologies for CO₂ removal, at different stage of development and commercialisation. The next paragraphs will quickly review such technologies and their application. For sake of simplicity, the review is here limited to the CO₂ removal cases 1 and 3, yet recognising the potential carbon capture also from PSA tail gas.

3.1 CO₂ removal from syngas (raw H₂)

The CO₂ removal from syngas is performed at relatively high total pressure (25-30 barg) and CO₂ partial pressure (3-4 bara). There are several technologies available, most of them being used in ammonia plants CO₂ removal section, or in the “old fashion” hydrogen plant, before the introduction in the market of the PSA technology for hydrogen purification.

Main technologies include:

- Amines (MEA, MDEA, aMDEA);
- Hot potassium carbonate;
- Physical solvents (PEGE, Methanol);
- Membranes.

The first three categories use liquid solvents in an absorption/regeneration sequence. The “chemical” solvents in this application are generally less expensive than the “physical” ones and allow an almost complete removal of the CO₂; depending on plant layout, the CO₂ stream is made available at high purity (say >98.5% vol) and at a pressure of 0.5-1.5 barg. Membranes performances in terms of removal efficiency and purity are expected to be lower.

When a traditional plant is retrofitted with the addition of such removal unit, the steam reformer burners have to be checked for the new tail gas composition which, being poorer in CO₂, 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 CO₂ removal.

Licensors active in these technologies include: BASF, Giammarco-Vetrocoke, Linde, Lurgi, UOP, etc.

3.2 CO₂ removal from flue gas

As indicated in Table 1, the CO₂ present in the steam reformer flue gas has a very low partial pressure (about 0.2 bara) and the flue gas actual volumetric flow is 20 times or more the raw syngas volumetric flow (m³/h). These two factors and the presence in the flue gas of components like oxygen, sulphur, NO_x, dust, makes the CO₂ removal from this stream generally more complicated and expensive. Nevertheless its quantity is very high (see Table 1) and its capture is being considered an environmental and economical challenge.

Main technologies include:

- Amines (MEA, MDEA, “hindered” amines);
- Chilled ammonia;
- Membranes.

The basic principles of CO₂ removal from flue gas are the same as from raw hydrogen, but the experience is so far limited. The environmental concern related to the GHG emissions is determining a growing interest for this application in many industries, for example in the power sector.

In practical terms a CO₂ removal of 85 - 90% is an acceptable target, and the CO₂ is also in this case obtained at high purity and low pressure.

No pre-investment is needed in case of retrofit of a traditional plant, however additional ducting and ID fan addition/replacement shall be considered when the unit is added to the SMR plant.

Licensors active in these technologies are: Axens, Fluor, GTC, MHI, MTR etc.

4. Case study

In this chapter we will examine an example of the economic impact of a CO₂ removal unit (from raw hydrogen and from flue gas) when added to a SMR hydrogen plant. The technologies considered are in both cases amine based, using in-house simulations and available technical documentation. Different technical solutions may of course lead to different results, especially considering the different level of maturity of the technologies involved.

The selected hydrogen production is 150,000 Nm³/h (134.3 MMSCFD) from natural gas. The CO₂ removal efficiency from raw H₂ and from flue gas is considered 100% (rounded off) and 90% respectively. The pure CO₂ stream is then compressed to 150 barg for sequestration, EOR or other utilisation (out of the scope of the study).

The economics of the alternatives are evaluated through the “abatement cost” concept.

“Abatement cost (AC)” is defined as the incremental cost of a low-emission technology compared to the reference case, measured as € per ton CO₂ abated emission (ICCA, 2009).

$$AC = \frac{(\text{Full cost of CO}_2 \text{ efficient alternative}) - (\text{Full cost of reference solution})}{(\text{CO}_2 \text{ emissions from reference solution}) - (\text{CO}_2 \text{ emissions from alternative})}$$

The full cost of the alternatives includes investment cost (calculated over 25 years at 5% discount rate), operating costs and possible cost (energy) savings generated by the use of the alternatives.

Other economic data:

Natural gas price = 14 – 28 €/Gcal (5 – 10 \$/MMBtu)

Steam price = 7 – 14 €/ton

Electric power price = 60 €/MWh

A plant equivalent availability of 95% (8,300 h/y) is assumed.

The results are summarized in following Table 3.

Table 3 – CO₂ capture comparison and results

	No CO ₂ capture	CO ₂ capture 1 (raw H ₂)	CO ₂ capture 3 (flue gas)
CO ₂ abated emission (t/h)	0	66	110
NG consumption (Gcal/h)	Base	-29	unchanged
Steam consumption (t/h)	Base	+107	+142
Power consumption (MW)	Base	+8.5	+16
Investment cost (MM€)	Base	45	167
AC (€/t CO ₂ abated emission)	0	31 - 36	43 - 52

The two AC values per each CO₂ capture case refer respectively to the low and high values assumed for the Natural Gas (and for steam).

The “abatement cost” so calculated, compared with the CO₂ trading price or carbon tax, is an indicator of the profitability of the initiative.

These values (carbon tax) have shown fluctuations in the last years and are now (last quarter 2009) in the range of 10 ÷ 20 €/ton CO₂.

Several web sites deal with carbon market, e.g. www.pointcarbon.com, and other listed in the References at the end of the paper (Komanoff, 2008).

5. Conclusions

The analyses performed in this study lead to the following conclusions:

- CO₂ emissions from SR hydrogen plants are significant and have the potential to impact the economics of hydrogen production.
- CO₂ capture technologies are available and applicable to SR hydrogen plants. Experience of removal from syngas is consolidated. Fewer references are present in the removal from flue gas, but technology and interest is growing.
- From an economic point of view, with the assumptions indicated in the previous paragraph, the CO₂ abatement cost from flue gas is substantially higher than from raw H₂, and in both cases higher than the current carbon tax.
- Investment costs for the two alternatives have an approximation inherent in this kind of studies, however macroeconomic variables like interest rates, carbon market or socio/political decisions may have a highest impact than the error margins, and may heavily affect the economics of the proposed solution.

References

- Bressan L., Collodi G. and Ruggeri F., 2009, Hydrogen generation for modern refineries, Hydrocarbon Engineering, November 2009.
- ICCA, 2009, Innovations for GHG reductions, A life cycle quantification of carbon abatement solutions enabled by the chemical industry.
- Komanoff C., 2008, A question of balance; Finding the optimal carbon tax rate, www.carbontax.org.
- Stockle M., Bullen T., 2008, Integrate refinery carbon dioxide reduction plans plant-wide, Hydrocarbon Processing, November 2008.