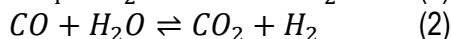




Paint it Blue (Part I): Hydrogen Production by Steam-Methane Reforming

Hydrogen's main use is as feedstock for synthesis of other components such as ammonia. However, using hydrogen as a fuel has gained lots of interest lately as a vector to decarbonize energy-intensive and hard-to-abate sectors (e.g., power and transportation). Nonetheless, most of the hydrogen production comes from fossil-based feedstocks such as natural gas and coal. Steam Methane Reforming (SMR) is the state-of-the-art H₂ production process, and is responsible for more than half of global H₂ production.

SMR involves the reaction of hydrocarbons comprising natural gas with steam at high pressure and temperature (typically 20–40 bar and 800–950°C) to produce syngas in an *endothermic* reaction (Eq. 1). To increase hydrogen production, the coproduced CO is further reacted with more steam in the so-called water-gas shift reaction (Eq. 2). This reaction is *exothermic* and occurs at much lower temperature than the reforming reaction. All reactions proceed using catalytic reactors.



The overall reaction shows that, stoichiometrically, for each mole of CH₄ four moles of H₂ can be produced. On the other hand, one mole of CO₂ is inherently produced. Stoichiometrically, that accounts for 5.5 kg of CO₂ per kg of H₂ produced. Nevertheless, since the reforming reaction (Eq. 1) is endothermic, natural gas is usually also used as a fuel to provide the required heat. When this extra CO₂ emission is accounted for, aligned with conversion inefficiencies, it is estimated that up to 10 kg CO₂ are emitted per kg of H₂ [1].

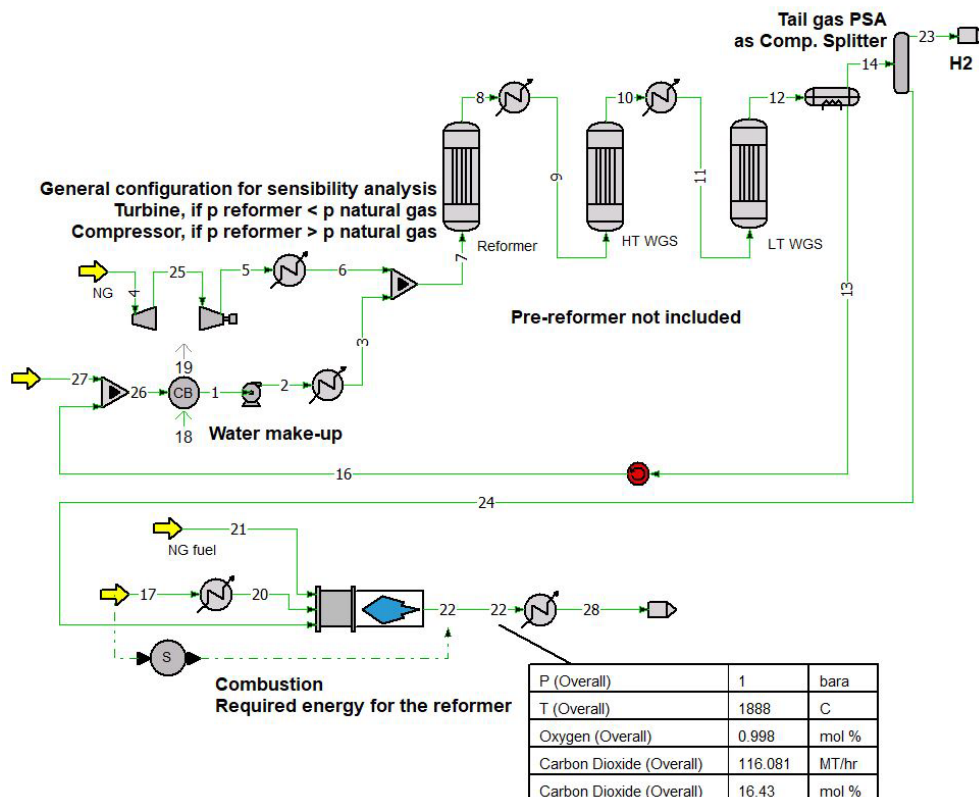
To be considered a low carbon fuel, the CO₂ emitted from the

SMR process must be captured and properly stored (CCS). If CCS is applied to SMR, the hydrogen is labeled as blue hydrogen (and gray if no CCS is applied).

In this issue of the Contactor™, OGT | ProTreat® is used to simulate the process of SMR to identify the influence of operating parameters on H₂ production, energy requirements and opportunities to apply CO₂ capture.

Case Study

For illustration, we assume that the gas is available at 1 atm and 25°C with a composition of 95.6% CH₄, 2.8% C₂H₆, 0.8% C₃H₈, 0.3% iC₄H₁₀ and 0.5% CO₂. The natural gas flow (as feedstock) is set to 3,000 kmol/h while the steam-to-natural gas mole ratio was set to 3. As shown in the Flow Diagram below, the gas is compressed, heated, and mixed with steam at the same temperature (600°C) and pressure (15 bara) before entering the reformer reactor. The outlet temperature of the reformer was set, and the duty calculated by ProTreat. The



gas leaving the reformer is cooled before entering the shift reactors. These are high- and low-temperature reactors with inlet temperatures set to 350 and 200°C, respectively. All reactors were modelled as Gibbs reactors. The gas leaving the last shift reactor is cooled to 35°C and sent to a Pressure Swing Adsorption (PSA) unit to purify the H₂ up to 99.99% at an efficiency of 90% (modelled as a component splitter).

The pressure and outlet temperature of the reformer was varied from 15 to 35 bar and 700 to 950°C, respectively. The amount of natural gas required for combustion was optimized for every case to match the reformer duty. The temperature of the flue gas leaving the reformer was set to 1025°C.

Results

The reformer outlet temperature and pressure are the most important parameters in the reforming reaction. According to Le Chatelier's Principle, increasing the temperature will increase the hydrogen production while increasing the pressure will decrease it. As seen in Figure 1, the simulations were able to predict this behavior. It is seen that the CH₄ conversion increases almost linearly with the outlet temperature up to a point where the H₂ production approaches the stoichiometric limit and the curve starts to level off. At higher pressures, higher temperatures are required to increase conversion. This reflects in the need for more energy.

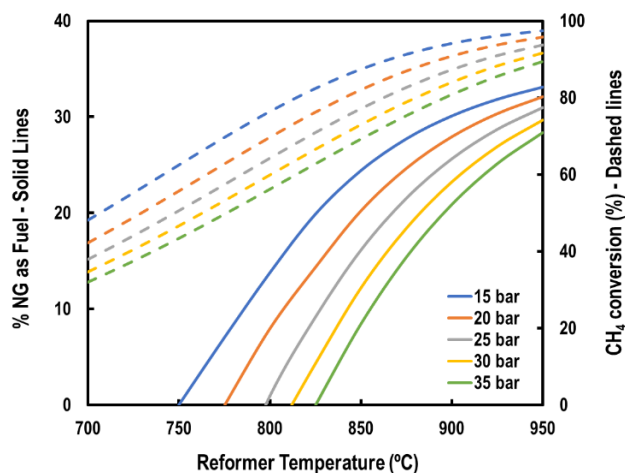


Figure 1. Reformer performance at varying temperature and pressure. Solid lines representing the % of natural gas required as fuel (left y-axis). Dashed lines representing the methane conversion (right y-axis).

As seen, there is a trade-off between conversion and energy input. The H₂ production process is usually designed to use up to 20% of the available natural gas as fuel (and CH₄ conversions around 80%). For low conversion rates, the PSA tail gas is rich in methane which is

enough to provide the energy required, but at an undesirable H₂ production rate.

From gray to blue

For H₂ from SMR to be considered a low carbon fuel, a CCS plant must be implemented along with the SMR plant. There are essentially three points where the capture unit can be placed: (i) after the gas shift cooler, (ii) on the tail gas of the PSA, and (iii) on the flue gas of the reformer.

If CO₂ capture is performed at conditions (i) and (ii), only a fraction of the total CO₂ emitted could be captured as the CO₂ emissions from flue gas accounts for only about 33% of the total emission.

In our example, the tail gas is recycled to the burner to use the H₂ that is absorbed, unreacted CO and CH₄ content to recover the energy from this stream as heat. Thus, the configuration that can maximize the removal of carbon is capturing the CO₂ from the flue gas. That would account for both the CO₂ produced in the reactors and the CO₂ produced in the reformer burners.

The result is an enriched post-combustion capture and amine-based process can be implemented successfully. In the second part of this article, a CO₂ capture process will be analyzed for turning gray H₂ into blue.

Conclusions

ProTreat was successfully used to simulate the SMR process. The simulations provide duties and stream compositions that can be further refined for more thorough energy analysis (and steam production potential) and to properly design the capture process.

References

[1] Front. Energy Res., 18 August 2020 Sec. Hydrogen Storage and Production.

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