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Hydrogen production from natural gas: Auto-thermal reforming and CO_2 Capture

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We study the hydrogen production by the Auto-Thermal Reforming (ATR) process coupled with a CO_2 capture using an MonoEthanolAmine (MEA) aqueous solution and the methanation process as means of hydrogen purification technique. Under several fixed assumptions on operating conditions, we found that the large-scale production of 99mol% pure hydrogen can be reached and depends strongly on the operating temperature at the ATR and the CO_2 removed in the capture step. High purity hydrogen streams derive from a high carbon capture in the absorption column that avoids further parasitic methanation reactions.

1. Introduction

Combustion of fossil fuels is the main source of carbon dioxide, accounting for 90% of the annual emissions. These fuels are mainly consumed in three activity sectors: transport, heating and power generation. The emission reduction on the power generation sector is probably the most effective measure to reduce the accumulation of CO_2 in the atmosphere. Therefore, remarkable efforts focused on the development and techno-economical feasibility of several processes for CO_2 capture from power plants (Klemeš et al. 2007, Kanniche et al., 2010 and Amann and Bouallou, 2009). Nevertheless, for future development of energy infrastructure, either for power generation, transport fuelling or to a lesser extent industrial application, hydrogen appears as a relevant energy carrier that might replace fossil fuels.

Accounting for the limited natural availability of hydrogen and assuming an energy future driven by constraints on greenhouse gas emissions, current methods for hydrogen production need to evolve and importantly decrease their emissions of CO_2. The Steam Methane Reforming (SMR) and the Partial OXidation of hydrocarbons (POX) are by far the most relevant processes in terms of hydrogen production capacity and economic competitiveness compared to electrolysis and other novel technologies. The latter refers to promising processes, such as Thermo-chemical Cycles and High Temperature Electrolysis, that head towards large demonstration stages but still need time to become commercially available due to technical and economic challenges (Rivera-Tinoco, 2009). For SMR and POX, processes that are likely to remain a dominant large scale

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hydrogen production technology in the nearby future, it has been proposed to capture and storage (CCS) the CO_2 generated. Reviewed and collected data for electricity and hydrogen production technologies and possible combinations with CO_2 capture methods are presented by the IEA (1996), Klett et al. (2002) and National Research Council (2004). The conversion efficiency of conventional large-scale SMR facilities varies between 74 and 85% (IEA, 1996 and Klett et al., 2002), however, relatively few studies have been performed to assess efficiency loss and costs associated with CO_2 capture. The CO_2 can be captured from the furnace off-gas by means of a monoethanolamine (MEA) unit, or alternatively, it can be captured by installing an methyl-diethanolamine (MDEA) unit between the shift reactor and the PSA unit. Although this has not been applied to date, MDEA is proven technology.

SMR can be combined with POX resulting on a process referred to as Auto-Thermal Reforming (ATR). Basically, steam and oxygen (or air) is injected into the reformer, causing the reforming and oxidation reaction to occur simultaneously. The exothermic POX reaction provides the necessary heat to the endothermic SMR reaction. The convenience of ATR derives from the higher CO_2 partial pressure in furnace exhaust that enables to capture more economically the gas than in a conventional exhaust stream from the SMR furnace. Investment costs of oxygen-blown ATR are about 15–25% lower than fired tubular reformers, but the costs of oxygen supply make ATR less attractive than SMR even for large-scale plants (650 MW-H_2) (Rostrup-Nielsen and Rostrup-Nielsen, 2002). The highlights on ceramic Ion Transport Membranes (ITM) for oxygen production with an ATR reactor open new possibilities for high-efficient and low-cost hydrogen production with CO_2 capture on the long term (Simbeck, 2005). For low-cost hydrogen production, membrane costs need to be reduced (Middleton et al., 2003). K. Damen et al., (2006) provide the ranges in efficiency and investment costs for the different routes of hydrogen production from natural gas with CO_2 capture. According to the author, for the short term large-scale SMR with a chemical absorption unit (MDEA) will prevail and, on the longer term, technologies such as large-scale ATR-ITM with a chemical/physical absorption unit after the shift will rise. Annual operating and maintenance (O&M) costs for SMR/ATR systems with CO_2 capture are estimated between 3 and 6% of total plant costs (IEA, 1996, Klett et al., 2002, National Research Council, 2004).

Within the scope of sustainable hydrogen production, in this work we will focus only on the ATR process supplied by natural gas and coupled to a Carbon Capture (CC) process. We assumed natural gas as consisting only of methane. The natural gas is firstly oxidized into syn-gas (CO and H_2) in a catalytic furnace. Then, CO reacts in presence of water to produce CO_2 and H_2 by a catalytic shift reaction. Carbon dioxide is at the end captured by amines through an absorption process. Hydrogen recovered after CC is purified by means of methanation in a catalytic reactor. The simulation of the process is performed with the software Aspen Plus^{TM}.

2. Auto-Thermal Reforming

The ATR process consists on the natural gas oxidation and shifting, in which the feedstock reacts (catalytically) with oxygen, in sub-stoichiometric conditions, and steam in a single reactor.

Stepwise and total SMR reactions are following:

$$CH_4 + H_2O \rightleftharpoons CO + 3H_2 \qquad \Delta H_{(298K)} = 206\ kJ.mol^{-1} \tag{1}$$

$$\underline{CO + H_2O \rightleftharpoons CO_2 + H_2 \qquad \Delta H_{(298K)} = -41\ kJ.mol^{-1} \qquad (2)}$$

$$CH_4 + 2H_2O \rightleftharpoons CO_2 + 4H_2 \qquad \Delta H_{(298K)} = 165\ kJ.mol^{-1} \tag{3}$$

The partial oxidation exothermic reaction in which natural gas is partially oxidised is the following:

$$CH_4 + ½\ O_2 \rightleftharpoons CO + 2H_2 \qquad \Delta H_{(298K)} = -36\ kJ.mol^{-1} \tag{4}$$

The Redlich-Kwong-Soave model is used in the simulation of the ATR (Carlson, 1996) as it is suitable for mixtures of non-polar to moderately polar compounds and suits for processes at high temperature and pressure.

3. The capture of CO_2 and hydrogen purification

The field of large-scale CO_2 capture is undoubtedly dominated by absorption processes, using an amine solvent, for which temperature and pressure values are limited by the CO_2 triple point conditions. We considered that the flue-gas exiting the shifters is introduced into the absorption columns and reacts with an aqueous solution of MEA at 30 wt%. On the basis of available information of the complex reactions of CO_2 absorption in amine solutions (Abu-Zahra et al., 2007) we simulated the chemical absorption of CO_2 under the assumptions deriving of the electrolyte NRTL model (Amman, 2007). The operating conditions of the absorption column are 1.1 atm, 313 K and the MEA solution with a flow of 54 kmol/s. The latter allows the removal of 85% of carbon dioxide according to Alie et al. (2005). The outlet liquid stream of solvent is afterwards treated in order to regenerate the MEA and separate carbon dioxide which is then purified and compressed for storage. The latter is achieved by the dehydration process of CO_2 by TriEthylene Glycol (TEG) that was simulated accounting for the state equation Peng Robinson (PR), as recommended by Hyprotech (Øi and Tyvand Selstø, 2002). The operating conditions that enable the regeneration column to reach an α factor near to 0 are set at 3.2 atm and 373 K. Further details are presented by Amann (2007). The CO_2 concentration at the column outlet stream is 98 mol%. The gas stream rich in hydrogen is sent into a methanation reactor in order to fully convert the undesirable CO_2 into methane following the inversed reforming reaction. This reaction enhances the separation of hydrogen, which reaches a 90 % purity, but consumes part of hydrogen of the stream.

4. Overall results

4.1 ATR results

In Figure 1 we present the flowsheet of the process studied and simulated. Inside the dashed rectangle of the mentioned figure we highlight the ATR process equipment. The natural gas (CH_4) and compressed steam stream and the stream containing oxygen are preheated in the heat exchanger B2 up to 923K and 873 K, respectively. This equipment (B2) supplies the heat required by means of the hot syn-gas that is generated in the ATR and which is further cooled in the exchanger B4 down to 620 K. At this temperature, the syn-gas enters the first Shift reactor (Shift-ht) in which CO is partially converted to CO_2 and H_2. The next step attempts to reach total conversion of CO into CO_2 in a second Shift reactor (Shift-lt) at a lower temperature reached by cooling the stream down to 470 K (heat exchanger - B5). Inside the ATR reactor the working pressure is 40 atm and the oxygen flow is calculated on the basis of the required outlet temperature of the reactor, fixed at 1323K. Additional operating conditions include flows and temperatures of natural gas and steam streams at 2917 kmol/h and 4680 kmol/h, and 363 K and 613 K respectively. The catalysts used are in the first Shift reactor are generally iron and chromium oxide based. For the Low Temperature shift reactor (Shift-LT), the catalysts used are generally copper based (Amann, 2007).

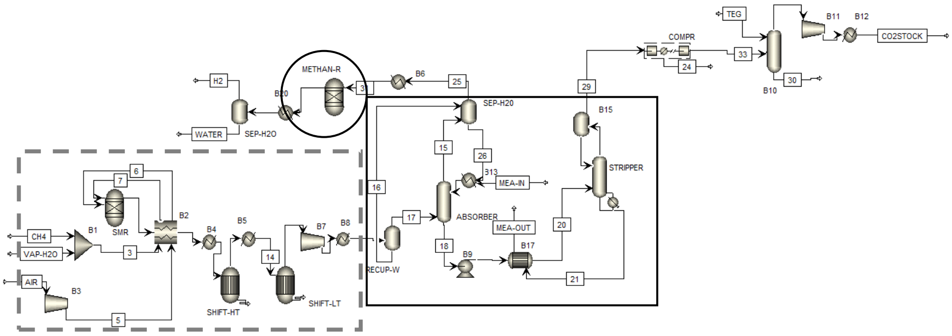

Figure 1 Flow sheet of the hydrogen production process by the Auto-Thermal Reforming coupled to a Carbon Capture and methanation process

The maximum operating conditions for an ATR system were reported by Christensen and Primdahl (1994) and we considered them in order to simulate a reference case. Simulation results are presented in Table 1.

Table 1: Composition in the outlet streams of the ATR and shifters

Compound	Flow (kmol/h)	
	ATR	Shifters
O_2	2.8×10^{-12}	0
CH_4	48.8	48.8
CO	2073.6	109.7
CO_2	794.8	2758.7
H_2	6091.6	8055.6
H_2O	4325.2	2361.3

4.2 CO_2 capture and hydrogen results

Inside the solid-lined rectangle and circle of Figure 1 we highlight the CO_2 capture system and the methanation process equipments. Estimations show that hydrogen production rate and purity strongly depend on the remaining CO_2 in the hydrogen rich stream exiting the absorption column. The higher the concentration of CO_2 incoming the methanation reactor, the higher the amount of hydrogen is consumed to produce methane; hence the lower purity of the hydrogen is obtained. It is strongly recommended to increase the CO_2 capture in the absorption column in order to avoid the decrease on hydrogen purity. The study of CC impact on hydrogen production and purity was performed and results are condensed in Figure 2.

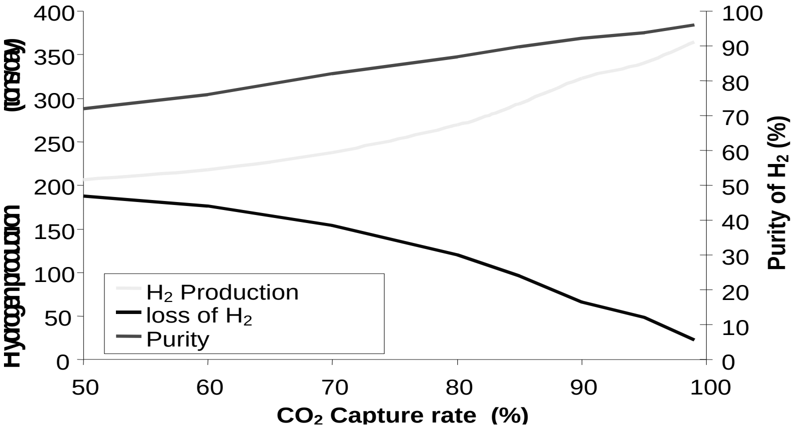

Figure 2 Hydrogen purity and production as function of CO_2 captured in the absorption column

When the capture of CO_2 increases up to 99 %, respectively the purity and production capacity at the facility increase up to 98 % and 360 t/d. The latter diminishes the hydrogen lost in parasitic methanation reactions down to 20 t/d from originally 180 t/d if only 50% of the CO_2 is captured in the absorption column. The results obtained are as promising as Mambre (2009) presented, however and although high purity and production capacities are reached, we suggest to be aware that methanation is still on the development phase and its competitiveness has not been proven at large-scale facilities.

5. Conclusion

We performed the impact assessment of operating conditions on the hydrogen production by means of the ATR process coupled with a CC system and purification by methanation process. The reactions taking place in the ATR allow higher conversion of natural gas into hydrogen when the operating temperature is near to 1200 K. Concerning the purification of hydrogen; we found that an increase in the CO_2 capture in the absorption column reduces the methane to be produced during the methanation reaction, which enhances the hydrogen purity and rate. The production of 90mol% pure hydrogen can reach a flow of 300 t/d from a feedstock of 13 kg/s methane, 24 kg/s water, and 15 kg/s air and the process remains flexible to a wide range of required hydrogen purities up to 99%.

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