Feed Flexibility of CH_4 Combined Reforming for Methanol Production

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Abstract

Natural gas with high CO_2 content is a readily available resource, whose application for synthesis gas (syngas) production through dry reforming is strictly limited to processes that require low H_2/CO ratios. In a recent work we have demonstrated that methanol production through a process scheme based on combined reforming of methane (with CO_2+H_2O) becomes a viable alternative from both technical and economic viewpoints. The use of an H_2 separation membrane, as well as a partial H_2 reinjection into the loop reactor, has been considered for the syngas composition adjustment to stoichiometric conditions ($M \cong 2$). The reformer and the methanol synthesis reactor were assumed at thermodynamic equilibrium conditions, i.e. at 950°C and 20 bar for the former, and at 250°C and 71 bar for the latter. By using a natural gas feed containing 30% CO_2 and $H_2O/CH_4 = 2$, it is feasible to operate the synthesis reactor with a lower recycle ratio, as well as a CO_2 concentration close to the one employed in industrial practice. Under the operating conditions mentioned above, the use of combined reforming for methanol synthesis turns out to be economically advantageous over the classical steam reforming process.

In this work a study of the feed flexibility for combined reforming is carried out taking into account the existence of gas fields with CO_2 contents higher than 30%. Feed mixtures containing 35% and 40% CO_2 were analyzed, while maintaining the operating conditions for the reformer (P, T, H_2O/CH_4) and the synthesis reactor (P, T, M). For comparative purposes, a methanol plant producing 400,000 mtpy was considered. A higher CO_2 content in the feed does not significantly alter the CH_4 conversion, but increases the CO_2 conversion and lowers the H_2/CO ratio. Consequently, it is necessary to increase the separation and reinjection of H_2 to keep stoichiometric conditions in the synthesis reactor. However, a moderate increase in CO_2 concentration in the synthesis reactor cannot be avoided. It is also shown that the recycle ratio should be markedly reduced in order to achieve stable operation. This situation reduces the operating cost of the recycle compressor. On the other hand, the flow of $CH_4 + CO_2$ to the reformer should be increased for a constant methanol production, which in turn affects the reformer's energy balance. The main operating costs of the methanol plant, with respect to the reference case ($CO_2/CH_4 = 0.43$), grow for $CO_2/CH_4 = 0.55$ and $CO_2/CH_4 = 0.67$ by 9.5% and 25%, respectively. This preliminary technical and economic analysis shows that combined reforming of natural gas with CO_2 content up to 40% is a feasible process to produce methanol without CO_2 removal.

Keywords: CO_2/CH_4, methanol, CO_2 removal, energy, natural gas.

1. Introduction

More than 40% of the world's conventional gas reserves are estimated to lie in reservoirs that contain significant amounts of Hydrogen Sulfide (H_2S) and CO_2 (Duissenov, 2013). Natural gas (NG) with a high CO_2 content can be found in many different places all around the world at various regions of economic interest, such as Indonesia (Suhartanto *et al.*, 2000), the Colorado Plateau on the South of the United States (Allis *et al.*, 2001), Norway (Nørstebo *et al*., 2012) and also Argentina (Morales *et al.*, 2002; Crotti *et al.*, 2007; Indrebø, 2010). As some of these fields are located far away from the main NG processing areas, they are usually kept in reserve.

For the recovery of NG Liquids cryogenic processes are nowadays preferred (Mehra *et al.*, 1999; Kidnay *et al.*, 2006). Under low temperature conditions CO_2 might solidify, hence obstructing pipes and other equipment items. Then, prior to NG fractionation, the addition of a CO_2 removal stage becomes necessary. Moreover, in Argentina the highest allowable CO_2 content for transportation and domestic use is limited to 2%, since CO_2 contributes not only to lower NG's heat capacity, but also to cause corrosion. Therefore, processing NG with a high CO_2 content in order to obtain conventional NG is difficult and above all uneconomical. Without requiring a previous CO_2 removal, it might be interesting to employ the NG stream with its high CO_2 content as a feedstock for the production of higher value derivatives.

Over the last few years the production of liquid fuels or methanol through the Combined Reforming (CR) process (with CO_2 + H_2O) of NG has gained special interest (Song *et al.*, 2006; Roh *et al.*, 2008), due to the employment of two of the most important greenhouse gases: CO_2 and CH_4. CR allows obtaining synthesis gas (syngas) with a higher H_2/CO ratio than the one obtained in Dry Reforming (DR), while avoiding the troublesome carbon formation. In Cañete *et al.* (2014) we have shown that for a NG feed with 30% CO_2, it is economically feasible to produce methanol through CR without the need of a partial CO_2 removal. In this work, the effect of higher CO_2 concentrations in the feed gas on the main process and the corresponding economic parameters are analyzed.

2. Methodology

The simulation of the scheme shown in Figure 1 was made by means of GAMS software (Brooke *et al.*, 2014), where both the reformer and the synthesis reactor were considered to operate at thermodynamic equilibrium conditions. For these calculations the Gibbs-free-energy minimization method was employed, also taking into account carbon formation for the reformer. Table 1 shows the main operating conditions for both the reformer and the methanol synthesis reactor.

Table 1. Simulation parameters

Unit	Inlet Temp. (°C)	Outlet Temp. (°C)	Inlet Pressure (Bar)	Pressure Drop (Bar)	Thermal Efficiency (%)
Reformer	600.0	950.0	20.0	0.0	50.0
Synthesis reactor	255.0	255.0	71.0	3.0	----

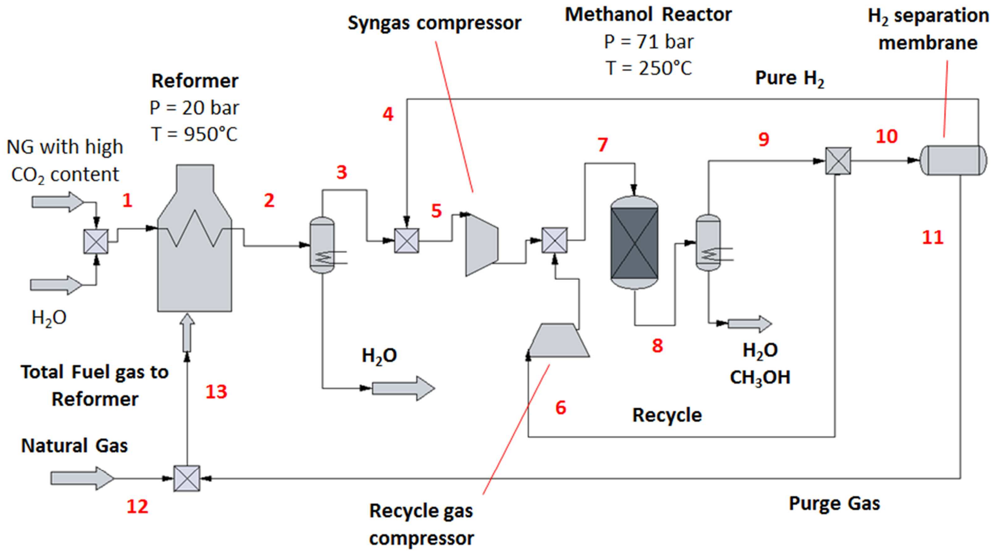

Figure 1. Simplified process scheme

For this analysis a methanol production of 400,000 metric tonnes per year (mtpy) has been set. The simulations aim at analyzing the effect of the CO_2/CH_4 feed ratio on the process scheme and their impact on the overall energy balance. The M module ($M = H_2\text{-}CO_2/CO+CO_2$), which is commonly employed to characterize the obtained syngas, was fixed in 2.05 after H_2 reinjection (Stream 5 in Fig. 1). This number is close to the stoichiometric value ($M = 2$) and was determined to be a suitable composition for methanol synthesis (Cañete *et al.*, 2014).

An important design parameter that has been set free was the CO_2 concentration at the methanol reactor inlet Although a high value has a negative effect over methanol synthesis kinetics (Lim *et al.*, 2009; Rahman, 2012), it is inconvenient to set an upper limit for this composition since in this analysis the requirement of a CO_2 separation stage is intended to be avoided. However, the resulting CO_2 concentrations were closer to the one employed at industrial practice. For example, Lim *et al.* (2009) have concluded that the maximum methanol concentration obtained with a $Cu/ZnO/Al_2O_3/ZrO_2$ catalyst corresponds to a CO_2 concentration around 10%. A common value for the reformer efficiency (50%) was established by Dybkjaer (1995). It relates the total heat transferred to reaction (the one required for heating the feed up to the outlet temperature level plus the heat of reaction) to the total heat generated by fuel combustion.

It is important to remark that both purge gas flow (Stream 11 in Fig. 1) and recycle gas flow (Stream 6 in Fig. 1) have strong influence on the overall energy balance. Therefore, they affect the economy of the process.

3. Results and discussion

For CO_2/CH_4 feed ratios of 0.55 and 0.67 and $H_2O/CH_4 = 2.1$, Tables 2 and 3 show the effect of CO_2 content on the CH_4 and CO_2 conversions, as well as on the compositions of the main streams for the methanol plant. It can be envisaged that a higher CO_2/CH_4 ratio implies a growth in the consumption of feed gas and fuel gas (Stream 12 in Fig. 1). The pure H_2 flow to be separated at the membrane unit (Stream 4 in Fig. 1) is also higher. NG with higher CO_2/CH_4 ratio shows a major tendency for DR, resulting in higher CO_2 conversion (X_{CO2} in Tables 2 and 3) at the reformer unit and a syngas with lower H_2/CO ratio. Meanwhile, CH_4 conversion (X_{CH4} in Tables 2 and 3) is only slightly altered by changes in CO_2/CH_4 feed ratio.

Table 2. Computational results (CO_2/CH_4 = 0.55: 35% CO_2 in NG)

Stream*	Flow (Kmol/h)	Composition (vol%)						XCH_4 (%)	XCO_2 (%)
		CH_4	CO_2	CO	H_2	H_2O	CH_3OH		
1	4770.0	0.274	0.151	0.0	0.0	0.575	0.0	93.9	31.7
2	7229.8	0.011	0.068	0.202	0.478	0.241	0.0		
4	1034.0	0.0	0.0	0.0	1.0	0.0	0.0		
5 (M = 2.05)	6521.4	0.012	0.075	0.224	0.688	0.0	0.0		
6	7600.0	0.117	0.127	0.051	0.705	0.0	0.0		
7	14121.4	0.076	0.097	0.130	0.697	0.0	0.0		
8	10964.9	0.098	0.106	0.043	0.590	0.019	0.144		
11	595.9	0.320	0.346	0.140	0.193	0.0	0.0		
12	935.0	0.994	0.006	0.0	0.0	0.0	0.0		
13	1530.9	0.732	0.138	0.055	0.075	0.0	0.0		

*The stream identification numbers correspond to Fig. 1

Table 3. Computational results (CO_2/CH_4 = 0.67: 40% CO_2 in NG)

Stream*	Flow (Kmol/h)	Composition (vol%)						XCH_4 (%)	XCO_2 (%)
		CH_4	CO_2	CO	H_2	H_2O	CH_3OH		
1	5020.0	0.265	0.177	0.0	0.0	0.558	0.0	94.9	36.4
2	7537.8	0.009	0.075	0.21	0.459	0.247	0.0		
4	1482.0	0.0	0.0	0.0	1.0	0.0	0.0		
5 (M = 2.05)	7158.0	0.009	0.079	0.221	0.690	0.0	0.0		
6	4620.0	0.046	0.165	0.069	0.720	0.0	0.0		
7	11778.0	0.024	0.113	0.161	0.702	0.0	0.0		
8	8626.6	0.033	0.135	0.056	0.575	0.018	0.183		
11	806.4	0.117	0.48	0.199	0.204	0.0	0.0		
12	1200.0	0.994	0.006	0.0	0.0	0.0	0.0		
13	2006.4	0.642	0.196	0.08	0.082	0.0	0.0		

*The stream identification numbers correspond to Fig. 1

Figure 2 shows partial methane conversion for DR and SR reactions. It is evident that a higher CO_2/CH_4 feed ratio produces a higher CH_4 partial conversion by DR and a slightly lower methane partial conversion by SR.

The feed with a higher CO_2/CH_4 ratio also implies a lower recycle ratio (Stream 6/Stream 5 in Fig. 1) that is beneficial for the economy of the process, since diminishing the recycle ratio leads to less compression work at the methanol reactor loop. Even when syngas compression requirement slightly increase with CO_2/CH_4 ratio, a considerably lower value appears for the recycle stream because of the significant reduction in recycle ratio. It is also shown that the CO_2 concentration at the methanol reactor inlet also increases with CO_2/CH_4 ratio, which might be detrimental for methanol production. As mentioned before this concentration is commonly limited to a maximum of approximately 10% (Lim *et al.*, 2009; Rahman, 2012), which is close to the figures shown in Tables 2 and 3 (Stream 7 in Fig. 1).

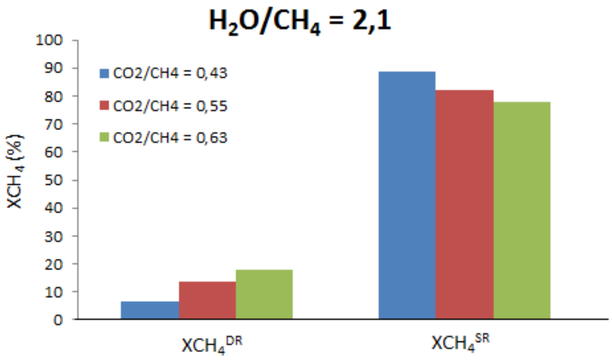

Figure 2. CH_4 partial conversion for DR and SR reactions dependence on CO_2/CH_4 ratio for a feed gas with H_2O/CH_4 = 2.1

In this work the considered CO_2 emissions account for the amount present in the flue gas at the reformer unit. For a conventional 400,000 mtpy methanol plant based on SR, CO_2 emission rounds 367 tpd (tonnes per day). In contrast, for CR the CO_2 emissions are approximately 1495 tpd and 1945 tpd for CO_2/CH_4 = 0.55 and CO_2/CH_4 = 0.67, respectively. There is a net CO_2 production for each alternative of 735 tpd and 1007 tpd, respectively. Total fuel gas (Stream 13 in Fig. 1) for SR is rich in H_2 (≈ 80%, v/v), while fuel gas for CR is almost exclusively composed of CH_4 (60% - 75%). Due to this fact, for CR a significant amount of CO_2 is yielded through CH_4 combustion.

The main operating costs for the process scheme shown in Fig. 1 are those related to the NG requirement (as feedstock and fuel gas), as well as costs arising from recycle and syngas compressor operation. Compared with CO_2/CH_4 = 0.43, the operating costs rose steadily in a 9.5% and 25% for a feed gas with CO_2/CH_4 = 0.55 and CO_2/CH_4 = 0.67. Besides, in comparison with SR, these costs increased to about 2.1% and 14.3% thus indicating that the CR alternative would still remain competitive, even for CO_2 content in NG higher than 30%. In short, while capital costs of a CR plant are considerably lower than those for SR, operating costs are only slightly higher for CR.

4. Conclusions

Natural gas with a high CO_2 content is a promising resource for the production of valuable derivatives, like methanol. For a scheme plant where H_2 is partially separated and reinjected to the inlet of the methanol loop, augmenting CO_2/CH_4 ratio in the feed gas produces an increase in the CO_2 conversion at the reformer because of a major contribution from DR reaction. Methane conversion is only slightly altered with changes in CO_2/CH_4 ratio. The increase in CO_2/CH_4 ratio leads to higher NG consumption (as feed gas and fuel), higher H_2 separation rate, higher CO_2 concentration in the syngas and a lower recycle ratio. The latter reduction results in less operating costs as a consequence of lower compression requirements. The operating costs for CO_2/CH_4 = 0.55 and CO_2/CH_4 = 0.67 are approximately 9.5% and 25% higher than the alternative design with CO_2/CH_4 = 0.43, while these costs become 2.1% and 14.3% higher than that for SR. Then, the Combined Reforming of NG with CO_2 content up to 40% is a feasible process to produce methanol without CO_2 removal.

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