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Synthesis Gas Processes for Methanol Production via CH_4 Reforming with CO_2, H_2O, and O_2

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ABSTRACT: A conceptual design for the production of synthesis gas, suitable for methanol production, is presented. We propose the reforming of natural gas with high CO_2 content by using H_2O or H_2O-O_2 as coreactants. A thermodynamic analysis for two reforming processes is developed to get adequate operating conditions for the reformer. The flow scheme for the syngas-methanol plant, together with the corresponding mass balances, is presented. A H_2 separation process is considered for syngas composition adjustment. The methanol-loop reactor was also included in the analysis to take into account its close relationship with the reformer's energy balance. For a comparative study, the hypothetical expansion of an existing methanol plant based on steam reforming of natural gas was chosen. A fundamental economic study shows that combined reforming ($CO_2 + H_2O$) and tri-reforming ($CO_2 + H_2O + O_2$) of CH_4 are competitive processes, with lower operating and capital costs in comparison with steam reforming.

1. INTRODUCTION

Synthesis gas, which is also called syngas, is a H_2 and CO mixture of varying proportions. It is mostly employed as feedstock for the large-scale processes of ammonia and methanol production.

Synthesis gas is commonly produced by steam reforming (SR) of natural gas (NG), which is a proven catalytic process that leads to a high H_2/CO ratio (≅4.5). Over the last 2 decades, the CO_2 reforming of NG, which is also called dry reforming (DR), has been studied to a large extent as an alternative to produce syngas with a much lower H_2/CO ratio. The existence of numerous NG fields containing CO_2 in excess of 30% and the increasing availability of landfill gas give support to the importance of DR.

A major drawback of DR process is its tendency for coke formation over the catalyst, due to the larger C/O ratio and the absence of water. Consequently, numerous studies have been conducted in order to find active, stable catalysts for DR. Noble metals, like Pt supported on ZrO_2,[1,2] Rh on Al_2O_3,[3] Ce−Pd on α-Al_2O_3,[4] Ni−Ce on Al_2O_3,[5] Mo_2C supported on ZrO_2[6], and Ni supported on ceria,[7] have been shown to have good activity and stability for the DR process, at least under laboratory conditions. In spite of these encouraging results, DR's industrial applications are still very limited. The reason seems to be the rather low H_2/CO ratio (<1), which is generally obtained due to the occurrence of the reverse water−gas-shift reaction (RWGS). As mentioned by Ross,[6] this syngas ratio is only adequate for a small number of processes, like dimethyl ether or acetic acid synthesis. For the gas-to-liquid process, the ratio should be 2.0.

Methanol synthesis requires a higher value for this ratio and a feed gas containing H_2, CO, and CO_2 is commonly used. Although the reactions involved are still a matter of controversy, it may be assumed that methanol is produced by the hydrogenation of CO (reaction 1) and CO_2 (reaction 2). Therefore, the stoichiometric ratio $R = H_2/(CO + CO_2)$ is 2.5. In industrial practice the CO_2/CO ratio is about 0.5 or lower in order to limit the formation of H_2O and prevent the deactivation of the catalyst.[8] Consequently, the R ratio should be 2.3 and the H_2/CO ratio equal to 3.5. The M module, which is defined as $M = (H_2 - CO_2)/(CO + CO_2)$, is sometimes used in order to specify the syngas stoichiometry. On the basis of reactions 1 and 2, the optimum value should be M = 2.

$$CO + 2H_2 \leftrightarrow CH_3OH \qquad (1)$$

$$CO_2 + 3H_2 \leftrightarrow CH_3OH + H_2O \qquad (2)$$

As mentioned before, the use of the classic SR process to obtain syngas in methanol plants leads to a H_2/CO ratio higher than 4. Therefore, the resulting mixture contains a large excess of hydrogen. Both this condition and the low conversion to methanol due to equilibrium limitations require a large recycling of unreacted gas. In practice, a fraction of this stream is purged to eliminate inert components and it is used as a reformer fuel.

This scenario indicates the need to modify or complement the DR process aiming at considering the potential application of the emerging syngas for methanol synthesis. It is known that combining DR and partial oxidation can enhance hydrogen yield. Amin and Yaw[9] performed a thermodynamic equilibrium analysis to determine that a feed composition of $CH_4-CO_2-O_2$ = 1:1:0.2 at a minimum temperature of 727 °C was necessary in order to maximize the CH_4 conversion and to obtain a H_2/CO ratio of unity. Lower CO_2/CH_4 and larger O_2/CH_4 ratios were needed for higher H_2/CO values. They stated that a lower CO_2 conversion and H_2O formation are negative

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consequences of O_2 addition. However, oxygen presence helps to reduce the high energy demand of the reforming reactions, and unreacted CO_2 may be used for methanol synthesis. At this point it is necessary to remark that most of the reported thermodynamic analysis and laboratory scale tests have been performed at atmospheric pressure. The problem of carbon formation and the pressure effect were studied by Li et al.[10] for the autothermal CO_2 reforming of CH_4. They found that carbon formation decreases with an increase in O_2/CH_4 ratio and it increases with reaction pressure. By combining the partial oxidation of methane and CO_2 reforming, a H_2/CO ratio higher than one could be obtained for reaction temperatures below 627 °C. However, this reaction condition limited CH_4 and CO_2 conversions. At higher temperature, the H_2/CO ratio was equal to 1, as reported previously.[9]

An alternative to increase H_2 production and reduce CO concentration is the combination of DR and SR in the presence of oxygen (TR, tri-reforming) or in the absence of oxygen (CR, combined reforming). Van Keulen et al.[11] showed experimentally that the H_2/CO ratio can be varied between 5 and 2 by adjusting the CO_2/H_2O ratio from 0 to 1.2, respectively. They obtained similar results by using Pt/ZrO_2 or Pd/ZrO_2 catalysts at 800 °C. Pan[12] and Song and Pan[13] studied the dependence of the H_2/CO ratio on the concentration of reactants for TR and CR by thermodynamic equilibrium analysis, and they introduced the TR approach. Subsequent experimental work performed mainly on several supported Ni catalysts by TR at $T = 850$ °C and $P = 1$ atm demonstrated that H_2/CO values lay in the 1.7−2.0 range, which was close to equilibrium. More recently, several experimental catalytic studies[14−16] have successfully been carried out by means of CR in order to produce syngas for the gas-to-liquid process ($H_2/CO = 2$).

On the basis of these considerations, we have explored the employment of NG with a high CO_2 content to obtain syngas for methanol production. The potential of CR and TR processes to achieve this goal was analyzed by using thermodynamic equilibrium analysis and economic considerations. The hypothetical expansion of an existing methanol plant (YPF, Plaza Huincul, Argentina) to increase the production from 400 000 to 800 000 mtpy was chosen as a basis for a comparative study. This plant produces syngas by SR of NG at 880 °C and 20 bar, which is sent to a single Lurgi methanol reactor.[17] For large plants, adiabatic reactors in series with intercooling or combinations of water-cooled and gas-cooled reactors are recommended. Economical removal of the heat of reaction constitutes a permanent challenge in technological design for methanol synthesis.[18,19] Aasberg-Petersen et al.[20,21] have discussed the comparative costs related to various technologies.

In our analysis, a constant feed composition (CH_4, 70%; CO_2, 30%), a reformer temperature of 950 °C, and a total pressure of 20 bar were selected as basic assumptions. By using a higher temperature, the risk of carbon formation is reduced; therefore, the reformer may be operated with a lower steam/carbon ratio.

In order to adjust the syngas composition emerging from the reformer to the requirements of methanol production, several alternatives can be considered: the removal of CO_2 and H_2O, the H_2 enrichment by a subsequent WGS reactor, or the addition of H_2 recovered from the methanol-loop reactor. At this point it is important to mention that the main objective of this study was the thermodynamic and preliminary economic analysis of modified reforming processes. However, because of the strong interaction between the syngas generation and the methanol synthesis sections, both processes were considered, in order to close the mass and energy balances. For example, the amount of gas purged from the synthesis loop was employed to satisfy the energy demand in the reformer. In addition, the conversion of syngas to methanol by using low-pressure technologies is limited by thermodynamic considerations, forcing a large recycling of unreacted gas. For the simulation of the methanol reactor, a temperature of 255 °C, an inlet pressure of 71 bar, and a pressure drop of 3 bar were chosen as standard operating conditions.

2. METHODOLOGY

The equilibrium composition of reactant and products and the conversion of CH_4, CO_2, and H_2O were calculated by solving the thermodynamic equilibrium equations of the main reactions involved in DR, TR, and CR. For DR, the set of independent reactions comprising reactions 3, 4, and 5 was considered.

$$CH_4 + CO_2 \leftrightarrow 2CO + 2H_2 \quad \text{DR} \tag{3}$$

$$CO_2 + H_2 \leftrightarrow CO + H_2O \quad \text{RWGS} \tag{4}$$

$$2CO \leftrightarrow C + CO_2 \quad \text{Boudouard reaction} \tag{5}$$

Reaction 5 takes into account the feasibility of carbon formation by CO disproportionation. Regarding the problem of carbon formation, the endothermic CH_4 decomposition reaction ($CH_4 \leftrightarrow C + 2H_2$) is also relevant, particularly at high temperature. However, this equation is not independent because when coupled with the reverse of reaction 5, it leads to the main DR reaction (reaction 3).

For CR, H_2O was added to the CO_2-CH_4 mixture. Consequently, the main reactions considered were those of DR and SR of CH_4, i.e., reactions 3, 5, and 6.

$$CH_4 + CO_2 \leftrightarrow 2CO + 2H_2 \tag{3A}$$

$$2CO \leftrightarrow C + CO_2 \tag{5A}$$

$$CH_4 + H_2O \leftrightarrow CO + 3H_2 \quad \text{SR} \tag{6}$$

The WGS reaction is also expected, but it could be derived from a linear combination of the equations stated above. Finally, the TR of CH_4 was accomplished by the addition of O_2 and H_2O to the feed mixture. In this case, the major independent reactions involved were reactions 3, 5, 6, and 7. It is important to state that other expected reactions, like partial oxidation and WGS, were not included in this set because they can be derived by the proper combination of reactions 3, 6, and 7.

$$CH_4 + CO_2 \leftrightarrow 2CO + 2H_2 \tag{3B}$$

$$2CO \leftrightarrow C + CO_2 \tag{5B}$$

$$CH_4 + H_2O \leftrightarrow CO + 3H_2 \tag{6A}$$

$$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O \quad \text{Methane combustion} \tag{7}$$

In order to determine the equilibrium composition of the different sets of reactions, the equilibrium constants of reactions 3−7 were obtained at 950 °C by means of standard procedures.[22] The equilibrium equations were written as a function of the mole fractions of the participating components, including the fugacity coefficients and the total pressure. The

Table 1. Equilibrium Conversion and Product Distribution (v/v) for DR[a] (T = 950 °C; P = 20 bar; CO_2/CH_4 = 0.5)

X_{CH4} (%)	X_{CO2} (%)	CH_4 (%)	CO_2 (%)	CO (%)	H_2 (%)	H_2O (%)	C (%)	H_2/CO
83.5	89.7	5.2	1.6	23.1	47.6	5.1	17.4	2.1
(78.9)	(88.6)	(6.8)	(1.9)	(23.2)	(45.8)	(5.5)	(16.8)	(2.0)

[a] Values in parentheses were obtained by using the ASPEN PLUS 11.1 software.

corresponding sets of independent nonlinear equations were solved with Newton's Method by using Maple 11.[23] Another common procedure to determine the equilibrium composition of complex reaction systems is based on the minimization of the total Gibbs free energy. This method has been employed for the thermodynamic analysis of DR,[9,24,25] autothermal reforming,[10,26] and partial oxidation of CH_4.[9,24−26]

By using the Gibbs free energy minimization method we can obtain the equilibrium composition for a given component mixture at any selected set of operating conditions, without making any assumptions of the participating reactions. Only the reactants and expected products have to be specified. However, the knowledge of the main reactions involved is not only useful for the interpretation of the results but also good for guiding the selection of more convenient operating conditions. In this sense, the traditional method of the equilibrium constants, which is based on selected and well-known reactions, is helpful. A good agreement between the results obtained by both procedures indicates that all the major participating reactions have been considered.

Therefore, the solution of the thermodynamic equilibrium equations was verified by the Gibbs free energy minimization method. For these numerical calculations, the R-Gibbs reactor unit from Aspen Plus 11.1[27] was employed. The fugacities for the different components in the system were calculated through the Peng−Robinson equation of state.

We have used the Peng−Robinson equation of state because it is one of the most enhanced models in Aspen Plus. It also has a wide applicability range in terms of temperature and pressure and a large binary interaction parameter database. Moreover, the Peng−Robinson equation of state is regarded as suitable to handle systems containing hydrocarbons, water, air, and combustion gases.[28−30] In some other applications of interest,[10,24] the SRK equation of state has been employed, which is also usually used for the processes that contain hydrocarbons, water, and air.

3. THERMODYNAMIC ANALYSIS

3.1. Dry Reforming (DR). The main reactions included in the thermodynamic analysis were reactions 3, 4, and 5, assuming a CO_2/CH_4 feed ratio of 0.5, a reformer temperature of 950 °C, and a pressure of 20 bar. Although other feed compositions were explored, the selected CO_2/CH_4 ratio maximizes the production of H_2.[24] By solving the equilibrium equations, the expected conversion of reactants and the composition of the exit stream were obtained. The corresponding results are presented in Table 1.

These results show that a high similar level of CH_4 and CO_2 conversion could be obtained. The values could be higher if a lower operating pressure were assumed (X_{CH4}= 98.7%; X_{CO2} = 99.2% at 1 bar). The presence of water is due to the occurrence of reaction 4, which justifies the higher conversion of CO_2 relative to the one of CH_4. A significant amount of carbon is also formed, which is attributed to reaction 5. Consequently, a H_2/CO ratio of 2 is obtained. Although this is an appropriate syngas composition for the gas-to-liquid process, the amount of carbon formed is unacceptable for stable catalyst operation. It is well-known that the amount of carbon would be reduced if the reaction temperature were increased, but in that case the H_2/CO would decrease. Using a selective catalyst to eliminate or limit the participation of reaction 5 inevitably leads to a lower H_2/CO ratio.[4]

A comparison of the results obtained by solving the equilibrium equations and those computed by ASPEN allow us to predict a slightly lower CH_4 conversion, a lower H_2 production, and a higher H_2O production. These results may be attributed to the participation to a limited extent of other reactions, like methanation and methanol synthesis.[26]

3.2. Combined Reforming (CR). Taking into account the limitations of the DR process to obtain a H_2/CO ratio higher than one, the potential of CR was explored. Figure 1 shows how the equilibrium carbon composition (v/v, %) and the H_2/CO ratio change depending on H_2O/CH_4 ratio. In order to determine the amount of water to be added to the feed mixture it is important to take into account that a H_2O/CH_4 ratio greater than 2 enhances the production of H_2 due to the WGS reaction, leading to a higher H_2/CO ratio. It should be noticed that the formation of C is also avoided with this ratio.

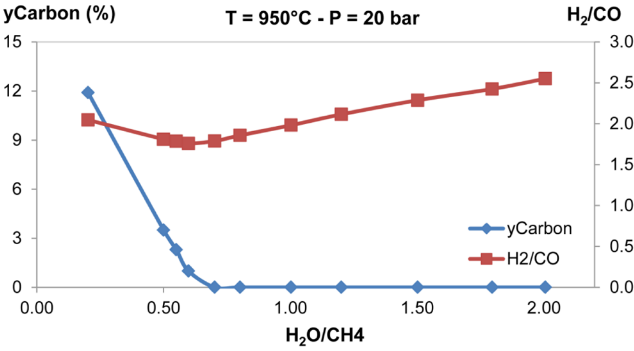

Figure 1. Carbon formation and H_2/CO ratio dependence on the H_2O/CH_4 ratio.

For a H_2O/CH_4 ratio higher than 0.85, no carbon is produced. Besides, from that point H_2/CO ratio grows with H_2O/CH_4 ratio but at the expense of a significant drop in CO_2 conversion. Consequently, a partial removal of CO_2 might be eventually necessary in order to adjust the syngas composition. For example, for a H_2O/CH_4 = 0.8, a CO_2 conversion of 72.7% is obtained, while for a H_2O/CH_4 = 2 only 27.3% is achieved. The latter is an adequate ratio, since the H_2/CO ratio is relatively high, and CO_2 conversion is not as low as to require CO_2 removal.

At this point it is important to note that higher water consumption implies considerably higher operating costs, since water fed to the reformer has to be heated up from ambient temperature to approximately 600 °C. Then, it is clear that the selected H_2O/CH_4 ratio depends on a trade-off between syngas composition requirements and economic considerations.

Table 2. Equilibrium Conversion and Product Distribution (v/v) for CR[a] (T = 950 °C; P = 20 bar; CO_2/CH_4 = 0.43; H_2O/CH_4 = 2.1; reformer feed = 28.3% CH_4, 12.2% CO_2, 59.5% H_2O)

X_{CH4} (%)	X_{CO2} (%)	CH_4 (%)	CO_2 (%)	CO (%)	H_2 (%)	H_2O (%)	H_2/CO	R
94.0	24.9	1.1	6.0	19.4	50.0	23.5	2.6	2.0
(93.5)	(24.8)	(1.2)	(6.0)	(19.3)	(50.0)	(23.5)	(2.6)	2.0

[a] Values in parentheses were obtained by using the ASPEN PLUS 11.1 software. C formation was not predicted.

The results presented in Table 2 show the behavior of a mixture with a CO_2/CH_4 ratio of 0.43 (30/70, v/v) and a H_2O/CH_4 ratio of 2.1. These values allow getting a syngas composition with a stoichiometric ratio close to the ideal value for methanol synthesis.

It is observed that the results obtained by calculation are in very good agreement with those from Aspen. The addition of H_2O suppresses the undesirable formation of C observed under DR conditions, while increasing the production of H_2 and lowering the one of CO. Consequently, the H_2/CO ratio became 2.6. The lower CO_2 conversion is explained by the predominance of the SR reaction and the WGS reaction, both favored by the relatively high concentration of H_2O. However, the amount of unreacted CO_2 is adequate for methanol synthesis. On the other hand, the H_2 concentration should be increased. One way to meet this requirement is the introduction of a WGS reactor operating at 350−400 °C, taking into account the presence of CO and H_2O in the mixture. However, an undesirable consequence of the WGS reaction is the production of CO_2 that forces a subsequent removal step. Another remarkable fact is that WGS reaction does not modify the M module.

A better option to adjust the syngas composition is the addition of H_2 recovered from the methanol-loop reactor after H_2O removal. The emerging process flow diagram for methanol production based on CR and hydrogen removal is shown in Figure 2.

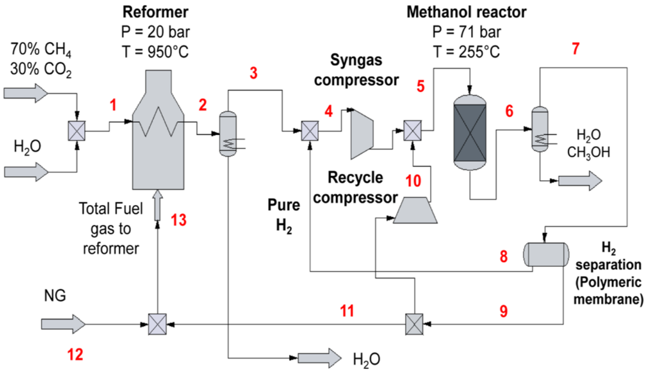

Figure 2. Simplified flow diagram of methanol-production process.

For the analysis carried out in this article, GAMS was chosen for the simulations because its earliest development was closely related to the field of economics. The synergy between economics, computer science, and operations research was the most important success factor in the system's development.[31] GAMS allows us to combine process simulation with economic or operating optimization in a relatively friendly, easy way. GAMS is especially useful for handling large, complex problems. This modeling platform is portable because it can also be linked to commercial simulators, such as Aspen Hysys. GAMS is widely recognized in process engineering, and this modeling environment has broadly been employed for process simulation in various fields. Jackson and Grossman[32] and Poth et al.[33] have successfully used GAMS modeling system for the MINLP simulation and optimization of single reactive distillation columns. Domancich et al.[34] also simulated a reactive distillation column for the production of MTBE by means of GAMS. This platform may not only be used as a process simulation tool itself. For example, Zhang et al.[35] have applied GAMS as supporting software in order to develop an optimum heat-exchange network with the objective of minimizing both utility and capital costs for a methanol plant. There are also some studies where GAMS has supported the thermodynamic analysis of different processes, through the employment of the Gibbs free energy minimization method. For instance, a thermodynamic analysis of steam reforming of ethanol and glycerine for hydrogen production was presented by Rossi et al.[36] Besides, Yancy-Caballero and Guirardello[37] dealt with the transesterification of soybean oil with both ethanol and methanol in order to improve the processes for biodiesel production.

Therefore, in this article a simplified model for the process shown at Figure 2 was developed in GAMS.[38] The equilibrium reactions in the methanol reactor were also adjusted by fugacity coefficients. The Aspen Plus RGibbs reactor unit was again employed to simulate a methanol reactor and to verify the results obtained in GAMS. The composition of the product stream and the amount of H_2 to be recovered were determined. The stoichiometric ratio equivalent to the M module at the loop entrance was fixed (R = 2.3, M = 2). In particular, the objective function to be minimized was defined as the NG amount necessary as a fuel to satisfy the energy balance in the reformer. This was accomplished by using a fraction of recycled gas (purge gas).

A heat-transfer efficiency of 80% in the reformer was assumed. Heat transfer efficiency has been considered in this work as the ratio of the "useful heat" in the process to the total heat generated by the fuel gas in the combustion. The so-called "useful heat" for a conventional steam reformer includes the heat supplied to the reaction, the heat required to raise the temperature to the reformer exit's level, the heat for feedstock preheating, and finally the heat for both the combustion air and fuel gas preheating. In our analysis we have only considered that 80% from the total heat generated by the fuel gas can be used, and thus this efficiency indicates that approximately 20% of the generated heat by the fuel gas during combustion is lost through the reformer's walls or through intermediate losses. For example, Dybkjaer[39] reports that the overall thermal efficiency of a steam reformer may approach 95%. Enforcing this concept, Padban and Vecher[40] inform an overall thermal efficiency of approximately 85%. In our case study, 50% of the total heat generated by the fuel gas was considered to be supplied to the reaction, which is also a common value.[39,40]

After methanol and H_2O separation, the H_2−CO−CO_2−CH_4 mixture was sent to a hollow fiber polymeric membrane unit[41] to separate H_2, which is a rather inexpensive process.

Table 3. Flow Rates and Gas Compositions (v/v) of a Methanol-Production Process Based on CR[a]

process stream	flow rate[b] (Kmol/h)	composition (vol %)							
		CH_4	CO_2	CO	H_2	H_2O	CH_3OH	N_2	C_2H_6
3	5449	1.6	7.8	25.2	65.4				
4[c]	5993	1.4	7.1	23.0	68.5				
5	22 629	16.5	6.0	7.2	70.3				
6	19 485	19.2	5.1	2.2	63.6	1.9	8.0		
7	17 537	21.3	5.7	2.4	70.6				
8	544	0.0	0.0	0.0	100.0				
9	16 992	22.0	5.8	2.5	69.6				
10	16 635	22.0	5.8	2.5	69.6				
11	357	22.0	5.8	2.5	69.6				
12[d]	390	95.3	0.6	0.0	0.0			1.1	2.0
13	747	60.3	3.1	1.2	33.3			0.6	1.0

[a]The stream identification numbers correspond to Figure 2. [b]On the basis of a feed flow rate (CH_4 + CO_2) of 1886 Kmol/h. [c]R = 2.3. [d]NG necessary as a reformer fuel to close the energy balance.

Table 4. Equilibrium Conversion and Product Distribution for TR[a] (T = 950 °C; P = 20 atm; CO_2/CH_4 = 0.43; H_2O/CH_4 = 2.0; O_2/CH_4 = 0.16; reformer feed = 28% CH_4, 12% CO_2, 55.5% H_2O, 4.5% O_2)

X_{CH4} (%)	X_{CO2} (%)	CH_4 (%)	CO_2 (%)	CO (%)	H_2 (%)	H_2O (%)	H_2/CO	R
95.8	12.9	0.8	7.0	19.0	46.9	26.3	2.5	1.8
(95.2)	(11.9)	(0.9)	(7.1)	(18.9)	(46.8)	(26.3)	(2.5)	(1.8)

[a]The values in parentheses were obtained by using the ASPEN PLUS 11.1 software.

Table 5. Flow Rates and Gas Composition (v/v) of a Methanol Production Process Based on TR[a]

process stream	flow rate[b] (Kmol/h)	composition (vol %)							
		CH_4	CO_2	CO	H_2	H_2O	CH_3OH	N_2	C_2H_6
3	5395	1.2	9.6	25.6	63.5				
4[c]	6400	1.0	8.0	21.6	69.2				
5	24 208	17.3	6.4	7.4	68.9				
6	21 044	19.9	5.0	2.0	63.7	1.9	7.5		
7	19 066	22.0	5.5	2.2	7.03				
8	1005				100				
9	18 061	23.2	5.8	2.3	68.7				
10	17 808	23.2	5.8	2.3	68.7				
11	253	23.2	5.8	2.3	68.7				
12[d]	270	95.3	0.6	0.0	0.0			1.1	2.0
13	523	60.4	3.1	1.1	33.2			0.6	1.0

[a]The stream identification numbers correspond to Figure 1. [b]On the basis of a feed flow rate (CH_4 + CO_2) of 1966 Kmol/h. [c]R = 2.3. [d]NG needed as a reformer fuel to close the energy balance.

Membranes are widely employed in the industry for an economical H_2 recovery from syngas and ammonia purge streams.[42,43] The flow rates and composition of the main gas streams are presented in Table 3.

The per-pass conversion of syngas (H_2 + CO + CO_2) to methanol was 27% and the concentration of CH_3OH in the product stream was ≅8%. These values are in agreement with those mentioned in the literature.[44] Taking into account the flow rate of recycled gas (Figure 2, stream 10) with respect to the flow rate of makeup gas (Figure 2, stream 4), the ratio was 2.7. This relatively low recycle ratio[44] reduces the size of the loop equipment and favors the process economy.

In Table 3, the results also demonstrate that only 4.4% of the H_2 present in the product stream has to be removed to adjust the stoichiometric ratio. The amount of gas purged (Figure 2, stream 11) was ≅2% of the gas remaining in the loop after methanol, H_2O, and H_2 separation. From an environmental point of view, another important result is the low amount of CO_2 present in the purge gas vented to the atmosphere. It represents about 4% of the CO_2 present in the reformer feed mixture. However, the amount of additional NG needed as a reformer fuel (Figure 2, stream 12) to close the energy balance in the reformer is another source of CO_2. It provides 72% of the total energy required, and its flow rate constitutes 52% of the total fuel gas to the reformer (Figure 2, stream 13). From the values in Table 3, it can be estimated that 507 tpd of CO_2 ends up in the flue gas for the CR process.

3.3. Tri-Reforming (TR). Another attempt to obtain a higher H_2/CO ratio was made by the simultaneous addition of H_2O and O_2 to the standard feed mixture. The process scheme is the same as the one shown in Figure 2, with an extra feed of pure O_2 in stream 1. Here again the condition of negligible C formation is pretended, which is satisfied with a slightly lower concentration of H_2O in comparison with CR. This coreactant is partially supplied by the methane-combustion reaction (reaction 7).

The results of the thermodynamic equilibrium analysis for TR of CH_4 are shown in Table 4. Carbon formation is not predicted, and it is assumed that O_2 is completely consumed. The partial combustion of CH_4 and WGS reaction, which are both exothermic reactions, decreases the energy required by the endothermic reforming reactions by 42%. This amount constitutes a significant economic advantage.

The conversion of CH_4 (see Tables 2 and 4) was slightly altered with the participation of reactions 3, 6, and 7. On the other hand, the conversion of CO_2 decreased relatively to the one of CR because this component is produced by CH_4 combustion and it is also formed by the WGS reaction. It is observed that the H_2 production was lower and the CO yield was not altered. Consequently, a slightly lower H_2/CO ratio was predicted. Taking into account the lower conversion of CO_2, the stoichiometric ratio was also lower.

The final adjustment of the gas composition to obtain the $H_2/CO/CO_2$ concentrations required for methanol synthesis was again achieved by using H_2 removed from recycled gas. The flow rates and the composition of the main gas streams for methanol production for the TR case are presented in Table 5. The overall performance of the methanol synthesis loop is quite similar to the one obtained by using CR. The stream compositions were also alike. The ratio of recycled gas to makeup gas was slightly larger for trireforming (2.8 vs 2.7), while the removed amount of H_2 increased by a factor of $\cong$1.8. On the other hand, the amount of gas to be purged and used as a reformer fuel was reduced. As a result, the amount of CO_2 contained in the purge gas was only 2% of the amount fed to the reformer.

In addition, the NG amount needed in order to close the energy balance in the reformer was reduced by a factor of 2, due to the partial autothermal operation. Consequently, CO_2 emissions in the flue gas were reduced to 368 tpd.

Regarding the methanol synthesis section, a low recycle ratio, while the performance and operating conditions of the methanol-loop reactor are kept, constitutes the main result that emerges from the previous analysis based on CR or TR. When syngas for methanol production is obtained by SR of NG, much higher recycle ratios are used ($\cong$3.5−7).[44]

Although most of the CO_2 in the feed mixture (96−98%) is transformed to methanol, it is clear that the NG needed to satisfy the energy balance in the reformer significantly contributes to CO_2 emissions. Consequently, the methanol-plant-wide CO_2 consumption would be 15% and 57% for CR and TR, respectively.

3.4. Steam Reforming (SR).

As mentioned in the Introduction, a syngas-methanol plant based on SR of NG was used for comparative purposes. The selected reformer's operating conditions were T = 880 °C, P = 20 bar, and H_2O/CH_4 = 2.8, which are quite typical values.[44−47] In addition, conditions similar to those selected for CR and TR were chosen for the methanol reactor (T = 255 °C, P = 71 bar) aiming at a production of 400 000 mtpy. The main plant parameters were obtained by using the same methodology for equilibrium analysis and process simulation. In this case, a syngas-composition adjustment section was not included. The main results are presented in Table 6.

As expected, the R and M values are higher than the ideal ones, due to the excessive H_2 production. Consequently, the flow rate of syngas in the methanol reactor and the flow rate of recycled gas are larger than those estimated for CR or TR. The purge-gas flow rate is also higher and contributes significantly to satisfy the energy balance in the reformer.

Table 6. Simulation Parameters for a Methanol Plant Based on SR of NG

reformer	
X_{CH4} (%)	83.5
H_2O/CH_4	2.8
H_2/CO	4.6
NG consumption	1781 (Kmol/h)
reformer fuel (NG)	18.6 (Kmol/h)
methanol reactor	
stoichiometric ratio R	3.24
M module	2.9
recycle ratio	4.0
methanol outlet concentration	5.0 (%)
purge-gas flow rate	1984 (Kmol/h)
purge-gas composition	CH_4 14.1%; CO_2 1.4%; CO 0.95%

As a result, the amount of extra NG needed as reformer fuel (18.6 Kmol/h) is quite low. On the basis of this information and the values shown in Table 6, the total amount of CO_2 emission for SR is 361 tpd. This value is close to the one mentioned above for TR. On the other hand, the CO_2 emissions for CR are much higher.

4. ECONOMIC EVALUATION

At this point it is important to establish the economic and geographical context for the presented proposal. This article is based on the employment of NG with high CO_2 content for the production of higher value derivatives, without needing previous CO_2 separation. The scope of this practical problem is quite ample. Even when the analysis has been focused on NG fields with high CO_2 content placed in Argentina, there are many different locations all around the world where such fields can be found. For example, in Southeast Asia there is one of the biggest reservoirs of NG with high CO_2 content.[48] Besides, there are also fields in Thailand and Malaysia,[49] on the Colorado Plateau and Southern Rocky Mountains,[50] and in Norway.[51] In all cases, the proposed process is equally applicable.

Nowadays, most of the developed methanol projects are designed for capacities ranging from 800 000 mtpy to 1.6 MMmtpy. In this sense, a plant that merely produces 400 000 mtpy is not particularly beneficial on the basis of the economies of scale. Nevertheless, taking into account both the expansion of an existing plant and the present availability of NG in Argentina, the proposal gets more significance. The methanol plant at Plaza Huincul (Argentina) is placed near significant NG fields with high CO_2 content, this location being really advantageous. Regarding the availability of NG with high CO_2 content, it is important to consider that in the vicinity of Plaza Huincul, where the methanol plant is located, there are several fields with this kind of gas. For example, among others, the fields of "Piedra Chenque", "La Calera", and "Sierra Chata" are located in the range of 70−100 km.

For cost analysis, it should be noted that even though there are many NG fields with high CO_2 content all over the world, in many cases they are located too far from industries and conditioning plants. In those cases, the costs for NG transportation are very high due to potential corrosion problems at pipelines. Since there are fields closely located to Plaza Huincul, the transportation costs were considered negligible for the corresponding case study.

The economics of the following reforming schemes were analyzed: (I) CR and (II) TR. Both alternative syngas technologies were considered and compared with the classical SR process. For syngas composition adjustment, the scheme shown in Figure 1 was selected. In all cases, a plant that produces 400 000 mtpy of CH_3OH has been considered for the analysis.

Purchase and installation costs for all the equipment required were estimated by following Ulrich's method.[52] In this method a different bare module cost factor was considered for each piece of equipment, depending on its type, construction material, and operating conditions. In particular, costs for the turbine, flue-gas duct and the oxygen plant were taken from the Sogge et al.,[53] adjusted by its corresponding capacity factor, and updated to 2012. It is important to note that the methanol reactor was not considered at the total investment estimation. In our design, methanol reaction conditions are very similar for both processes (Tables 3 and 5). Besides, since methanol production was fixed, the methanol reactor size was also the same. Therefore, the economic analysis was carried out excluding the reactor unit. Nevertheless, the energy integration between the reformer and the methanol reactor was taken into account.

For the CR plant, the predominant equipment cost in the analysis comes from the reformer, which is a box-type furnace. In contrast, for the TR case the highest capital cost is represented by the air separation unit (ASU). The required ASU is a relatively small-scale plant that produces 170 mtpd of O_2. It may be considered as a small-scale plant because the capacities that correspond to some of the biggest air separation companies are typically larger. Smith and Klosek[54] present a comparison between different air separation technologies and establish an economic range for each of the alternatives. This economic range is the typical production range where the technology currently is economically feasible. For the cryogenic process the lower limit is set at 18 mtpd. The highest capacities range from 4000 to 5000 mtpd.[54,55] Another important company, which is a world-leading supplier of industrial, process, and specialty gases, reports pure oxygen capacities ranging from 450 to 7000 mtpd.[56]

For the adjustment of syngas composition, a hollow-fiber polymeric membrane unit was considered in order to remove H_2. To calculate the required area for the membrane, a modification of Fick's law for diatomic molecules has been employed.[42] The H_2 flux was calculated with eq 8, where PR_{H2} is the H_2 permeation rate (scm/m^2 s Pa), and $p_{H2,l}$ and $p_{H2,0}$ are the measured pressures of H_2 on the product and feedstock side, respectively. J_{H2} is the H_2 flux through the membrane (scm/m^2 s). The value for permeation rate of H_2 through the polysulfone membrane was adopted as 5.75×10^{-6} scm/m^2 s Pa.[43,57] The differential pressure across the membrane was fixed at 5 MPa, by considering pressure operation of the H_2O and methanol separator and pressure from the syngas stream coming out of the reformer.

$$J_{H2} = -PR_{H2}(p_{H2,l} - p_{H2,0}) \tag{8}$$

NG is the most relevant raw material for syngas production. For NG acquisition, a price of 7.5 U.S.$/MMBTU has recently been established[58] by the local government. The main proposal in this study consists in employing NG with high CO_2 content (≈30% v/v) as raw material for the process. This gas is a low-cost feedstock compared to conventional NG (with 95% CH_4). The price of NG with high CO_2 content has been estimated from both its average heating value and the conventional NG price (see Table 7).

Table 7. Relevant Parameters

parameter	value
operating days	330 days/year
CEPCI (2012)	571.65
water price (U.S.$/m^3)	0.06
NG price (U.S.$/m^3)	0.273
high CO_2 content NG price (U.S.$/m^3)	0.189
power price (U.S.$/KWh)	0.095
NG heating value (kcal/m^3)	9200

An overall thermal efficiency of 80% was considered for the reformer, while it was also supposed that 50% of the total heat generated by combustion was supplied to the reaction. Water consumption (T = 20 °C, P = 2.5 bar) costs were calculated by contemplating the steam requirement as reformer feedstock and also assuming water losses of 5%. The electricity cost for the industrial sector was obtained from open sources.[59] For the oxygen plant, which is based on cryogenic distillation, an energy requirement of 0.37 KWh/kg O_2 was considered.[60]

Table 7 summarizes the most important parameters contemplated for the analysis. The chemical engineering plant cost index (CEPCI)[61] was employed in order to update costs from one period to another. Costs for all the equipment were obtained from Ulrich's book[52] for 2004, and then they were updated to 2012.

In Table 8, the total investment costs for each alternative have been summarized. The last row shows total costs relative to the SR process. The highest capital cost among the three alternatives presented is for the SR plant. The capital cost for the CR plant represents 74% from the former; while the one for the TR plant amounts to 71%. The main difference between the SR plant and the proposed alternatives is the lower heat duty for CR and TR. The corresponding values result from the total reformer feedstock flow rate, which is considerably lower (4657 Kmol/h for CR, 4718 Kmol/h for TR vs 6679 Kmol/h for SR) because of the large H_2O/CH_4 ratio at the reformer entrance for the SR plant.

Table 8. Total Investment

total investment (MM U.S.$)			
	SR	CR	TR
battery limit capital cost (BLCC)	151.5	112.8	103.0
outside battery limit capital cost (OBLCC)	23.5	17.37	20.6
grass root capital cost (GRCC)	175.0	130.2	123.6
relative cost	1	0.74	0.71

The pure H_2 recycle, which is generally unemployed at standard SR plants, also contributes to lower the recycle flow to the methanol-loop reactor for CR and TR. In this way, the size of the recycle gas compressor is reduced. Regarding the TR plant, it requires a very expensive ASU that is almost 28% from BLCC. Even when it is an essential item, the total cost is considerably lower than the one for the SR plant because of the reformer's partial autothermal operation. Given the requirement of a cryogenic ASU for the TR process, it should be taken into account that this piece of equipment increases the complexity of the whole process. However, it allows a higher

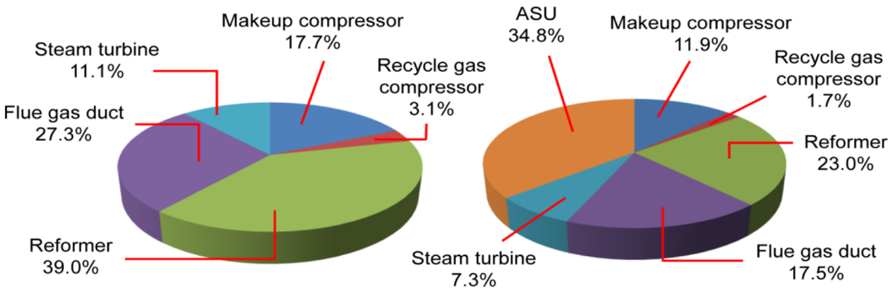

Figure 3. Purchase equipment cost distribution for CR (left) and TR (right) processes.

level of heat integration with economic advantages and prevents the formation of carbon.

For the BLCC calculation, purchase costs for all the equipment, installation costs, construction and supervision, engineering, and contingencies have been considered. Figure 3 shows the purchase equipment costs for CR and TR, as a fraction of the total purchase cost. For CR both the reformer's and flue-gas duct costs represent almost 60% of the total purchase costs. Though the flue-gas duct is expensive, it is essential because it is employed at the same time as a heat exchanger for feed preheating and steam generation. For the TR plant, the ASU represents a great part of the total purchase cost. Cryogenic separation plants are not only expensive plants, but they also contribute to raise syngas plant operation cost because of its high energy consumption.

In Table 9, total operating costs for each alternative have been summarized. The process NG expenditure on the CR and TR alternatives is considerably lower than on the SR process because of the reduced cost of the NG with high CO_2 content. In contrast, the fuel gas expenditure is much higher for CR and TR processes. This fact is due to the lower purge-gas flow rate for both alternatives in comparison to the one for SR. On the other hand, the high heat duty of SR is mainly compensated by the higher purge-gas flow rate. Water consumption is higher for the SR plant, because of the higher steam requirement as feedstock to the reformer. Energy expenditures for TR plant are much higher than the energy budget for the SR and CR processes, because of the high ASU's energy consumption.

Table 9. Operating Costs

	operating costs (MM U.S.$)		
	SR	CR	autothermal reforming
natural gas to process	90.3	63.1	67.2
natural gas as fuel	0.922	18.0	14.6
water cost	0.0455	0.0254	0.0248
total raw material costs	91.2	81.1	81.8
electricity	2.8	2.7	5.2
total operating cost	94.0	83.7	87.0
relative operating cost	1.0	0.89	0.93

On the basis of the results from Tables 8 and 9, CR and TR are convenient alternatives to produce syngas for methanol production by using an available low-cost feed. Capital costs and operating costs for CR and TR are lower compared with SR based on NG. CR has a slightly higher capital cost than TR options, but it has lower operating costs since an ASU is not required.

5. CONCLUSIONS

In this article, the conceptual design for the production of a syngas suitable for methanol production from NG with high CO_2 content is presented. In the first place, different reforming alternatives, such as DR, CR, and TR, were studied through thermodynamic equilibrium analysis to find out convenient operating conditions for the reformer. The DR process did not emerge as a good option since, for stable operation free of carbon formation, the H_2/CO ratio of syngas was too low (≤ 1) for methanol production.

On the other hand, CR became a promising alternative for syngas production since for $H_2O/CH_4 = 2$ no carbon formation was predicted and also the H_2/CO ratio (2.6) was considerably higher than the one for DR. For TR, similar values to the ones exhibited by the CR process were achieved, although a considerably lower CO_2 conversion was obtained for the former process. In both cases, the stoichiometric ratio R was still below the ideal value for methanol production ($R = 2.3$); then, it was necessary to raise the H_2 concentration. For the syngas composition adjustment, the addition of H_2 recovered from the methanol-loop reactor after H_2O removal had been considered a more attractive option than CO_2 removal. In this way, the H_2 excess that appears in SR was avoided.

Second, a simplified model for both of the more proficient reforming alternatives was developed in GAMS. The hypothetical expansion of an existing methanol plant that was operating with SR of NG was chosen as a basis for a comparative study. The objective function was defined as the minimization of the external heating requirement.

In comparison with SR, the only extra piece of process equipment that was introduced was the hydrogen separation unit. In addition, lower recycle ratios were estimated for CR or TR. Moreover, considering the methanol reactor's feed composition and operating conditions, its size remained practically the same.

Both processes proved to be very competitive. The preliminary economic analysis yielded that CR and TR exhibit relatively low operating costs and reduced capital investment in comparison with SR of NG. Even when an ASU is required for TR, the reformer cost is considerably lower than the one for SR and CR. As to operating costs, the TR plant has a lower energy requirement than CR, due to its partial autothermal operation. However, the ASU's energy consumption is very high; therefore, the TR plant shows slightly higher operating costs.

Although most of the CO_2 present in the feed is converted to methanol for both the CR and TR processes, CO_2 emissions to the atmosphere cannot be avoided. This is due to the amount of NG combusted to provide the energy required by the endothermic reactions. However, in this work it is shown that

CO_2 emissions are comparable for SR and TR, while those of CR are higher.

As a result of this study, both alternatives showed very promising values from both technical and economic viewpoints. Nevertheless, the best option should be individualized on the basis of a detailed economic analysis of the global scenario, also including taxes, insurances, operating labor, and methanol prices.

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Notes

The authors declare no competing financial interest.

NOMENCLATURE

ASU = air separation unit
BLCC = battery limit capital cost
CR = combined reforming
DR = dry reforming
GRCC = grass root capital cost
J_{H2} = H_2 flux through membrane (scm/m^2 s)
M = module $(H_2 - CO_2)/(CO + CO_2)$
MMmtpy = million metric tonnes per year
mtpd = metric tonnes per day
mtpy = metric tonnes per year
NG = natural gas
OBLCC = outside battery limit capital cost
$p_{H2,0}$ = H_2 pressure on feedstock side (Pa)
$p_{H2,l}$ = H_2 pressure on the retentate side (Pa)
PR_{H2} = H_2 permeation rate (scm/m^2 s Pa)
R = ratio $H_2/(CO + CO_2)$
scm = standard cubic meter
SR = steam reforming
TR = tri-reforming

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