Periodica Polytechnica Chemical Engineering, 67(2), pp. 271–277, 2023

Developing a Targeting Approach for Syngas Generation from Natural Gas

Bilal Patel[1]*, Bahizire Martin Mukeru[1]

[1] Department of Chemical Engineering, University of South Africa (UNISA), 28 Pioneer Ave, Florida Park, 1709 Roodepoort, South Africa
* Corresponding author, e-mail: patelb@unisa.ac.za

Received: 02 September 2022, Accepted: 19 December 2022, Published online: 06 February 2023

Abstract

The conversion of natural and unconventional gas into syngas is a crucial intermediate step in the production of various important chemicals and liquid fuels. The syngas generation step usually requires the largest capital investment of the process and may also be very energy intensive. Therefore, determining the most efficient method of converting feedstock into syngas of the correct H_2:CO ratio is of significant importance. The aim of this work was to set design and performance targets for different H_2:CO ratios (depending on the downstream requirements) in terms of the carbon efficiency (including CO_2 utilization or emissions), water usage, and energy requirements. It was shown that the overall process for natural gas tri-reforming is limited by the enthalpy change ($\Delta H = 0$) and this process was able to produce work. It was further shown that high syngas ratios not only require significant amounts of natural gas and oxygen but also emit CO_2.

Keywords

design targets, synthesis gas, tri-reforming

1 Introduction

The conversion of natural and unconventional gas (such as shale gas and coal-bed methane) into chemicals and fuel typically requires the intermediate production of synthesis gas (syngas), a mixture of carbon monoxide, hydrogen, and carbon dioxide [1]. The production of syngas is usually associated with high capital cost, accounting for 60–70% of the capital cost of the overall production process [2]. The syngas production section is also responsible for a substantial amount of the energy consumption as well as most of the carbon dioxide emissions of the production process.

Different technologies for syngas generation are utilized including steam methane reforming (SR), partial oxidation (POx), auto thermal reforming (ATR), and carbon dioxide dry reforming (DR) [3]. The choice of a suitable natural gas reforming technology depends on various factors such as syngas ratio (H_2/CO), energy requirements as well as carbon formation (coke deposition). Natural gas steam reforming is considered as the most suitable pathway as it produces higher syngas ratio than partial oxidation and dry reforming. However, this process requires significant amount energy due to its endothermic nature. Natural gas dry reforming is a good candidate for syngas production as it utilizes carbon dioxide in the feed, but high carbon (coke) deposition is a serious issue and leads to catalyst deactivation [4].

Often, there is a mismatch between the ratio of H_2/CO required downstream and the actual ratio produced using these different technologies. In these cases, the ratio would require adjustment using additional unit operations [5]. However, this means further capital and operating costs and also increases the complexity of the process [6]. The direct production of syngas with flexible H_2/CO ratio is therefore an attractive option to reduce the capital cost and possibly the energy requirements and environmental impact of such processes. These techniques can either be based on a single technology or a combination of two technologies (SR + POx, SR + DR) or a combination of all three technologies (tri-reforming) (SR + POx + DR). Tri-reforming is an attractive technology that has the potential to utilize various feedstock (flue gas, coke oven gas, biogas) to develop a less carbon intensive and economical process [7].

Various studies have been carried out in order to address the above-mentioned issues related to natural gas reforming for the production of syngas with a flexible ratio. Process synthesis techniques are regarded as

Cite this article as: Patel, B., Mukeru, B. M. "Developing a Targeting Approach for Syngas Generation from Natural Gas", Periodica Polytechnica Chemical Engineering, 67(2), pp. 271–277, 2023. https://doi.org/10.3311/PPch.21115

one of the most effective ways of addressing these issues. Fox et al. [8] have developed a graphical approach to optimize steam reforming technology for a fixed syngas ratio. Baliban et al. [9] applied a superstructure-based approach optimization for gas-to-liquid (GTL) processes whereas Noureldin et al. [10] used equilibrium and optimization models for the reforming of natural/shale gas. Similarly, Graciano et al. [11] performed an assessment of a process to convert CO_2-rich natural gas to Fischer-Tropsch (FT) liquids via tri-reforming process using Aspen Plus. Jang and Han [12] performed an Aspen Plus optimization approach by combining steam reforming, dry reforming, and partial oxidation in one reformer (tri-reforming process) in order to determine the optimum amount of carbon dioxide, steam, and oxygen required to convert methane for the production of a suitable syngas ratio ($H_2/CO = 2$). Borreguero et al. [4] assessed the economic feasibility of methanol synthesis from natural tri-reforming based syngas. Khademi et al. [13] also applied optimization techniques to investigate the tri-reforming of methane to produce a suitable syngas ratio for the synthesis of methanol and FT fuels with an objective function of minimizing the tri-reformer length. Hernandez and Martin [14] proposed a non-linear programming (NLP) optimization approach for syngas production from biogas by analyzing three syngas ratios (methanol synthesis, $H_2:CO = 2.5:1$, ethanol synthesis, $H_2:CO= 1:1$ and FT fuels, $H_2:CO = 1.7:1$).

Other than theoretical approaches, experimental studies have been conducted to investigate the effect of the feed ratio on the product gas (syngas) composition. Song and Pan [15] performed an experimental investigation of methane tri-reforming using different catalytic configurations. Results showed that it is possible to produce a desirable syngas ratio that can be directly used in downstream processes while at the same time reducing carbon deposition. Majewski and Wood [16] used nickel-silica based catalyst to study methane tri-reforming at different conditions such as feed ratios and temperature. It was found that 1 mol of methane requires 0.5 mol of CO_2, 0.5 mol of H_2O and 0.1 mol of O_2 to produce a syngas ratio of 2 at a temperature of 750 °C. At these conditions, the carbon deposition was significantly reduced. Lino et al. [17] evaluated different nickel catalysts supported on magnesium aluminate at two different temperatures (650 °C and 750 °C). It was observed that 750 °C is the optimal temperature for methane tri-reforming ($H_2/CO = 2$) at a fixed feed ratio. Lino et al. [18] investigated the effect of feed composition and gas hourly space velocity (GHSV) on syngas ratio as well as carbon deposition during the tri-reforming of methane by using nickel supported catalyst. Results indicated that at a fixed GHSV and temperature, an increase in the oxygen to carbon dioxide ratio increased the syngas ratio but significantly decreased the conversion of carbon dioxide. A similar trend was observed when the ratio of steam to carbon dioxide was increased in the feed. Comparing the effect of both O_2/CO_2 and H_2O/CO_2 ratios on carbon deposition, it was shown that the former reduced carbon deposition more than the latter at the same GHSV and temperature. Thus, selection of the correct feed composition is an important consideration in adjusting the H_2/CO ratio [7].

Even though these studies have investigated various aspects regarding the (tri)reforming of methane, theoretical studies focus on the detailed design of the system. Experimental studies have not specified how the feed ratios were selected. Thus, determining systematic- process targets prior to a detailed design can provide valuable insight into the system without detailed calculations. In other words, one can quickly use process synthesis techniques to determine whether the process will produce heat or work at different syngas ratios. One can also determine the effect of feed composition on syngas ratio. These process synthesis techniques will help in determine at which conditions the emission of carbon dioxide as well as the carbon deposition will be dramatically reduced. Knowing these insights will play a crucial role during the development of the process flowsheets and can also guide experimental design. Therefore, the aim of this study is to set design and performance targets for different H_2/CO ratios in terms of the carbon efficiency (including CO_2 utilization or emissions), water usage and energy requirements. The study will also assist in identifying opportunities for combining the various technologies for methane reforming (such as SR, POx, and DR) in order to increase both the carbon and energy efficiency of the syngas generation step. Based on these targets, a conceptual design of the process can be developed. It must be noted that this approach only considers an overall material balance, even though there are various chemical reactions that occur during the process.

2 Approach

The approach used in this study is based on the work of [19–21]. Patel et al. [19] developed a systematic framework and associated tools for the design and analysis of chemical processes, the focus being on reducing the material and energy consumption of these processes as well as reducing the associated carbon dioxide emissions. The framework utilizes fundamental conservation and thermodynamic principles [19, 20] to set targets for processes. The framework takes a macroscopic approach where processes are characterized by inputs and outputs of mass, heat, and work instead of the traditional "unit operations" approach. The flow of mass is usually subjected to the conservation law i.e., a material balance. The species balance will be applied to synthesize a process i.e., the species balances will be used as (equality) constraints in order to determine all process mass balances. When utilized in this way, the mass balance is a powerful tool which provides insight into the efficient utilization of raw materials and helps to determine the minimum waste products that a process should produce and can also give insights into the integration of mass flows.

The flow of energy (heat and work) is constrained by both the first and second law of thermodynamics. Whilst the first law describes the conservation of energy i.e., quantity of energy flow in the form of heat, the second law is used to describe the quality of the energy flows and the magnitude of the irreversibility or "lost work" of the process. Both first and second law of thermodynamic will be used to determine the change in enthalpy ($\Delta H_{\text{process}}$) as well as change in Gibbs energy ($\Delta G_{\text{process}}$) between the product and feed materials. The values of $\Delta H_{\text{process}}$ and $\Delta G_{\text{process}}$ should preferably be equal to or less than zero (i.e., $\Delta H_{\text{process}} \leq 0$), so that the entire process can be feasible. Processes where $\Delta H_{\text{process}} > 0$ would require further energy to convert the feed to the products and usually this energy is supplied by burning a certain amount of the feed material.

Therefore, by evaluating the flows of these three variables (mass, heat, and work) in a process during the conceptual design stage, one can gain tremendous insight into the process before a flowsheet exists and one can also understand the implications of particular design decisions and develop strategies for improving the efficiency of processes.

3 Results and discussion

3.1 Applying elemental balances to syngas production

The overall process for the production of syngas from natural gas (assumed to be methane) can be described as shown in Eq. (1):

$$a\mathrm{CH_4} + b\mathrm{CO_2} + c\mathrm{H_2O} + d\mathrm{O_2} \Rightarrow \mathrm{CO} + x\mathrm{H_2}, \quad (1)$$

where a, b, c, d, and x the respective amount of methane, carbon dioxide, water, oxygen, and hydrogen respectively. It must be noted that methane, water, carbon dioxide, and oxygen are considered as inputs (i.e., positive stoichiometric coefficients (whereas hydrogen and carbon monoxide are considered as products (i.e., negative stoichiometric coefficients).

Solid carbon is not considered as a product. If carbon were included as a component, the formation of carbon would reduce the carbon efficiency of the process, and since the aim of this work is to determine the limit of performance, this would occur when all the methane is converted into carbon monoxide. Further constraint can be applied to the process, for example, oxygen should only occur as a feed and not as a product. Similarly, methane should not occur as a product as the aim would be to achieve a complete conversion of methane. Carbon dioxide and water could be either a feed or a product, but these components could be further constrained, if, for example, one was to consider a process which does not emit any carbon dioxide.

As a basis, carbon monoxide is set to one and hydrogen equal to x. Thus, the H_2/CO ratio is given by the value of x. There are three main elements in the process: carbon, hydrogen, and oxygen. An elemental balance for each element can be written in terms of the quantities of the components required/produced (i.e., a, b, c, d, and x) as shown in Eqs. (2)–(4):

$$\text{Carbon balance: } a + b = 1, \quad (2)$$

$$\text{Hydrogen balance: } 4a + 2c = 2x, \quad (3)$$

$$\text{Oxygen balance: } 2b + c + 2d = 1. \quad (4)$$

It can be noted from the above elemental balances that there are 4 unknown variables and that the species balances only provide 3 equations, allowing the system one degree of freedom.

In order to visualize these balances, consider $x = 2$ i.e., H_2/CO ratio of 2 (preferable ratio for low temperature FT synthesis). Based on Eqs. (2)–(4), the limits of performance from a mass flow perspective can be determined. For example, if oxygen is set to zero ($d = 0$), then the overall mass balance can be represented as shown in Eq. (5):

$$0.75\ \mathrm{CH_4} + 0.25\ \mathrm{CO_2} + 0.5\ \mathrm{H_2O} \Rightarrow \mathrm{CO} + 2\mathrm{H_2}. \quad (5)$$

When the objective of zero carbon dioxide ($b = 0$) is set, the overall mass balance represents partial oxidation of methane as shown in Eq. (6):

$$\mathrm{CH_4} + 0.5\ \mathrm{O_2} \Rightarrow \mathrm{CO} + 2\mathrm{H_2}. \quad (6)$$

Furthermore, one can plot all the possible mass balances within and beyond these limits as shown in Fig. 1.

Fig. 1 can be used to determine the quantity of the various components in and out of the process as the amount of methane fed to the process is varied. When low quantities of methane are fed to the process, CO_2 is required as a feedstock and O_2 is produced. When 0.75 mol of methane has been added, the amount of O_2 produced equals to zero and the overall mass balance is given by Eq. (5). As more methane is added, O_2 switches to a feed material whilst the amount of water and carbon dioxide required decreases. When 1 mol of methane has been introduced, the quantity of both CO_2 and water required is zero, and this mass balance is represented by Eq. (6). Above 1 mol of methane, both CO_2 and H_2O are produced, and increase in quantity as the amount of methane increases. This suggests that the combustion of methane is favored beyond this point ($CH_4 + 2O_2 \Rightarrow CO_2 + H_2O$).

Fig. 1 is useful in assessing all the possible mass balances for the selected components with the objective of producing a H_2/CO ratio of 2. Fig. 1 also provides useful targets such as minimizing the amount of carbon dioxide emissions from the process or minimizing water and/or oxygen requirements.

3.2 Applying the energy and entropy balance to syngas production

The energy balance can be applied to the syngas production process with H_2/CO ratio of 2, assuming streams enter and leave at 25 °C. One can determine the energy requirements for the process as the function of the quantity of methane fed to the process. In doing so, one can determine whether the various mass balances shown in Fig. 1 will require energy or produce energy. This is shown in Fig. 2 (relationship between the amount of CH_4 fed to the process and the energy requirements in terms of the enthalpy change as well as Gibbs energy change). It is apparent from this same figure that both $\Delta H_{\text{process}}$ and $\Delta G_{\text{process}}$ are linearly related to the amount of CH_4 fed to the process.

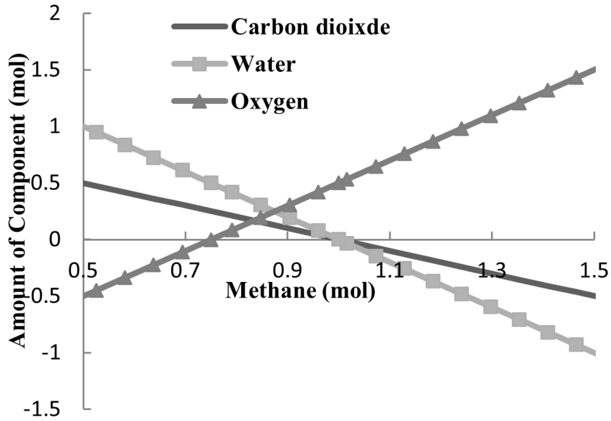

Fig. 1 Attainable mass balances for syngas production with H_2/CO ratio of 2

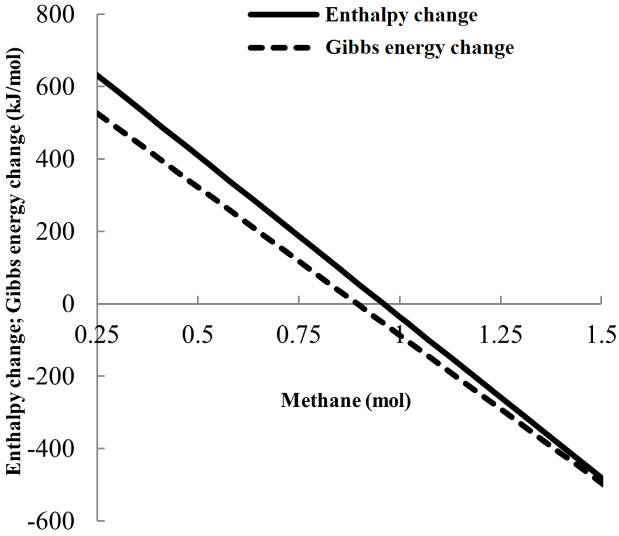

Fig. 2 Enthalpy change and Gibbs energy change for syngas production with H_2/CO ratio of 2

Initially $\Delta H_{\text{process}}$ and $\Delta G_{\text{process}}$ are positive, meaning that the process will require an energy input (heat) and work respectively. It can also be noticed that both $\Delta H_{\text{process}}$ and $\Delta G_{\text{process}}$ are zero when 0.96 and 0.89 mol of methane are fed to the process respectively. As the amount of methane is further increased the process has a negative ΔH (i.e., that energy can be produced or must be rejected from the process) and ΔG (work is produced). As the amount of methane is further increased the more negative ΔH and ΔG become (again, this is indicative of the combustion process, $\Delta H_{\text{combustion}} = -890.36$ kJ/mol and $\Delta G_{\text{combustion}} = -817.83$ kJ/mol). Note that the change in Gibbs energy equals to zero ($\Delta G = 0$) before the change in enthalpy ($\Delta H = 0$). This means that when the change in Gibbs energy is negative the enthalpy change will still be positive (process will still require energy). One can therefore infer that the *process* will be limited by the enthalpy change rather than the change in Gibbs energy. The overall mass balance for the process where $\Delta H = 0$ is given by Eq. (7):

$$\begin{aligned}&0.96\ CH_4 + 0.04\ CO_2 \\ &+0.08\ H_2O + 0.42\ O_2 \Rightarrow CO + 2H_2.\end{aligned} \tag{7}$$

It is clear from the mass balance given by Eq. (7) that small quantities of CO_2 and H_2O as well as O_2 are required as feedstock. This mass balance represents a tri-reforming process [10], where H_2O, O_2, and CO_2 are all utilized to reform methane. The Gibbs energy change for this mass balance (Eq. (7)) is $\Delta G = -53.7$ kJ/mol (showing that the process is thermodynamically possible and can in principle produce work).

In order to determine the viability of the design target, equilibrium modeling can be utilized to determine the composition as a function of the temperature. The equilibrium composition was determined using the Gibbs energy minimization method. In these calculations, carbon was also considered as a component in order to determine under what conditions would carbon formation be an issue. It is clear from Fig. 3 that the reaction temperature significantly affects the equilibrium composition. Both the conversion and formation of carbon is dependent on the temperature. High temperature favors high conversion of methane as well as less carbon formation. Also notice that at high temperatures (> 950 °C), a H_2/CO ratio of 2:1 is achieved as predicted by the mass balance. High temperatures also favor complete methane and oxygen conversion.

3.3 Comparison of limits of performance for various H_2/CO ratios

Design targets for various H_2/CO ratios can be determined in a similar fashion as for the 2:1 ratio (Fig. 4).

It is clear from Fig. 4 that the various component lines are parallel to each other. The CO_2 line remains constant and is therefore not a function of the H_2/CO ratio. In terms of the oxygen requirements, for a fixed amount of methane, the higher the H_2/CO ratio, the less oxygen required. This is the opposite for the water requirements. As for the energy requirements for a fixed methane quantity, the higher the ratio, the more the energy required. For zero energy requirement, the higher the ratio, the more methane is required (see also Fig. 4(d)).

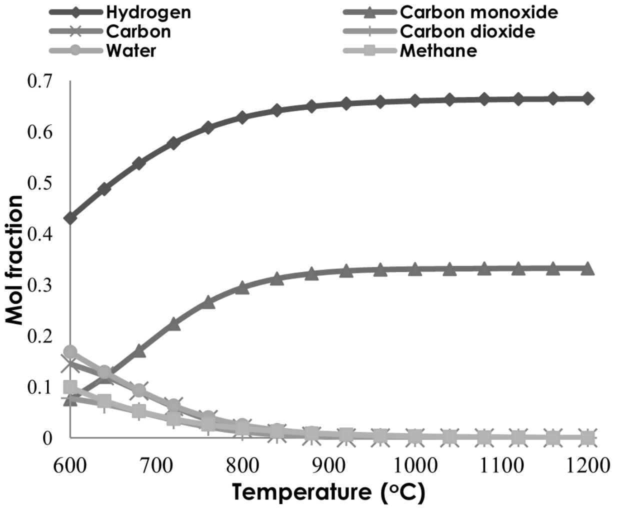

Fig. 3 The effect of temperature on the equilibrium composition of an adiabatic tri-reforming process (1 bar)

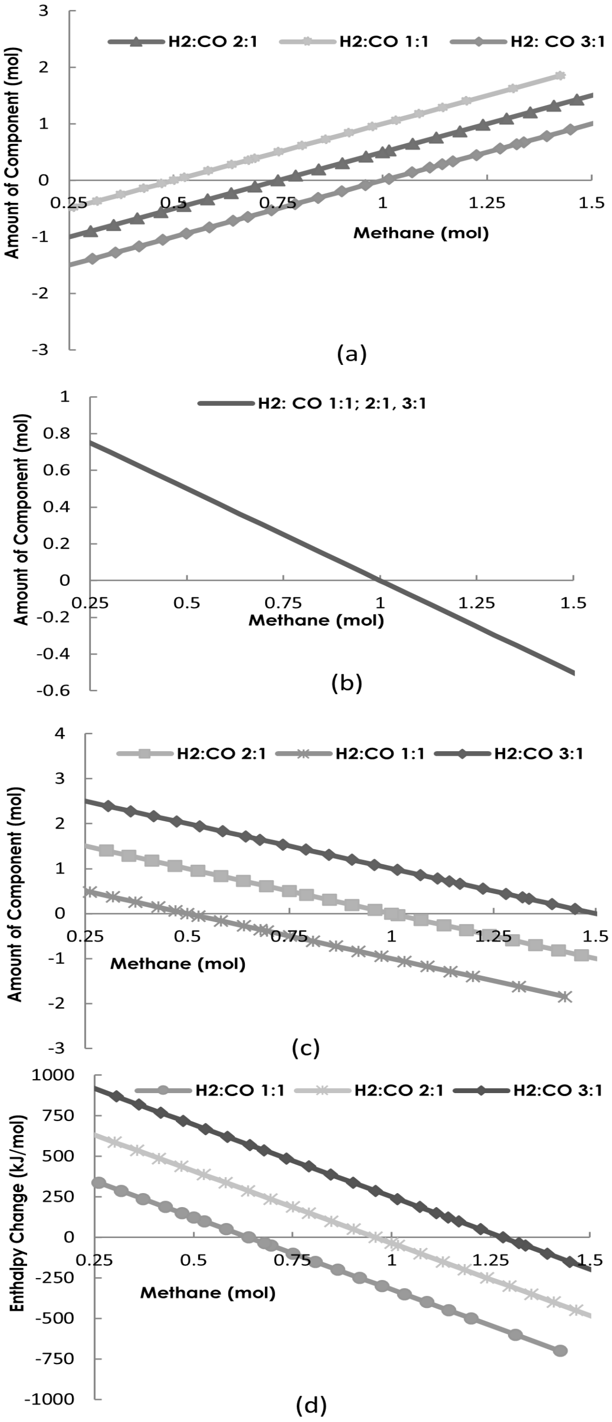

Fig. 4 Design targets for syngas production with different H_2/CO ratios: (a) Oxygen; (b) Carbon dioxide; (c) Water; (d) Energy requirements

It was previously stated that the system is limited by the enthalpy change. The quantity of the various components

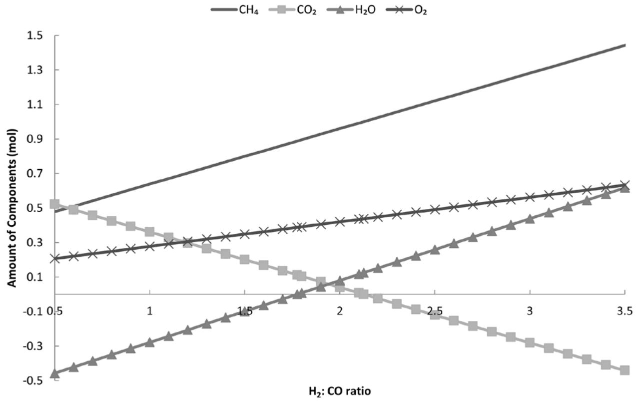

Fig. 5 Attainable mass balances for syngas production with varying H_2/CO ratios

for $\Delta H = 0$ at different H_2/CO ratio can also be determined. Fig. 5 shows the requirements of CH_4, CO_2, H_2O, and O_2 as a function of the H_2/CO ratio. Notice the CO_2 becomes zero at a H_2/CO ratio of approximately 2.13:1 (this is particularly useful for FT synthesis). This would be equivalent to ATR (combination of POx and SMR). Water becomes zero at a ratio of 1.78:1, and this is equivalent to a combination of dry reforming and POx. Between these two limits, there are various tri-reforming mass balances i.e., CO_2, H_2O, and O_2 are utilized without any energy requirements. It is clear that any H_2/CO ratio between 1.78 and 2.13 would require tri-reforming if no further energy is to be utilized.

Higher ratios result in the production of CO_2. As the H_2/CO ratio increases, the amount of CH_4 and O_2 required increases linearly. The equilibrium composition as a function of temperature for these balances can be determined as described in Section 3.2.

4 Conclusions

This manuscript introduces rigorous fundamental and thermodynamic targets for syngas production by considering the impact of producing different H_2/CO ratios. The quantity of water, oxygen, and carbon dioxide as well as the energy requirements were determined for syngas production with varying H_2/CO ratios. It was shown that it is possible to obtain H_2/CO ratios of industrial relevance with no further energy requirements by tri-reforming. Equilibrium composition calculations reveal that at high temperatures carbon deposition should not be an issue. Results further showed that the production of syngas ratios in an approximate range of 1–2.13 does not emit carbon dioxide. These syngas ratios can be directly used for the synthesis of DME, Methanol as well as FT fuels. This study focused on setting targets for syngas generation from natural gas, further studies can use these targets to develop flowsheets for the synthesis of various chemicals.

References

[1] Alipour-Dehkordi, A., Khademi, M. H. "O_2, H_2O or CO_2 side-feeding policy in methane tri-reforming reactor: The role of influencing parameters", International Journal of Hydrogen Energy, 45(30), pp. 15239–15253, 2020.
https://doi.org/10.1016/j.ijhydene.2020.03.239

[2] Aasberg-Petersen, K., Bak Hansen, J.-H., Christensen, T. S., Dybkjaer, I., Christensen, P. S., Stub Nielsen, C., Winter Madsen, S. E. L., Rostrup-Nielsen, J. R. "Technologies for large-scale gas conversion", Applied Catalysis A: General, 221(1–2), pp. 379–387, 2001.
https://doi.org/10.1016/S0926-860X(01)00811-0

[3] Aasberg-Petersen, K., Dybkjær, I., Ovesen, C. V., Schjødt, N. C., Sehested, J., Thomsen, S. G. “Natural gas to synthesis gas – Catalysts and catalytic processes”, Journal of Natural Gas Science and Engineering, 3(2), pp. 423–459, 2011.
https://doi.org/10.1016/j.jngse.2011.03.004

[4] Borreguero, A. M., Dorado, F., Capuchino-Biezma, M., Sánchez-Silva, L., García-Vargas, J. M. "Process simulation and economic feasibility assessment of the methanol production via tri-reforming using experimental kinetic equations", International Journal of Hydrogen Energy, 45(51), pp. 26623–26636, 2020.
https://doi.org/10.1016/j.ijhydene.2020.07.013

[5] Song, X., Guo, Z. "Technologies for direct production of flexible H_2/CO synthesis gas", Energy Conversion and Management, 47(5), pp. 560–569, 2006.
https://doi.org/10.1016/j.enconman.2005.05.012

[6] Raju, A. S. K., Park, C. S., Norbeck, J. M. "Synthesis gas production using steam hydrogasification and steam reforming", Fuel Processing Technology, 90(2), pp. 330–336, 2009.
https://doi.org/10.1016/j.fuproc.2008.09.011

[7] Alli, R. D., de Souza, P. A. L., Mohamedali, M., Virla, L. D., Mahinpey, N. "Tri-reforming of methane for syngas production using Ni catalysts: Current status and future outlook", Catalysis Today, 2022.
https://doi.org/10.1016/j.cattod.2022.02.006

[8] Fox, J. A., Hildebrandt, D., Glasser, D., Patel, B. "A graphical approach to process synthesis and its application to steam reforming", AIChE Journal, 59(10), pp. 3714–3729, 2013.
https://doi.org/10.1002/aic.14116

[9] Baliban, R. C., Elia, J. A., Floudas, C. A. "Novel Natural Gas to Liquids Processes: Process Synthesis and Global Optimization Strategies", AIChE Journal, 59(2), pp. 505–531, 2013.
https://doi.org/10.1002/aic.13996

[10] Noureldin, M. M. B., Elbashir, N. O., El-Halwagi, M. M. "Optimization and Selection of Reforming Approaches for Syngas Generation from Natural/Shale Gas", Industrial & Engineering Chemistry Research, 53(5), pp. 1841–1855, 2014.
https://doi.org/10.1021/ie402382w

[11] Graciano, J. E., Chachuat, B., Alves, R. M. B. (2018) "Conversion of CO_2-rich natural gas to liquid transportation fuels via trireforming and Fischer–Tropsch synthesis: model-based assessment", Industrial & Engineering Chemistry Research, 57(30), pp. 9964–9976.
https://doi.org/10.1021/acs.iecr.8b00135

[12] Jang, J., Han, M. "Tri-reformer with O_2 side-stream distribution for syngas production", International Journal of Hydrogen Energy, 47(15), pp. 9139–9155, 2022.
https://doi.org/10.1016/j.ijhydene.2021.12.266

[13] Khademi, M. H., Alipour-Dehkordi, A., Tabesh, M. "Optimal design of methane tri-reforming reactor to produce proper syngas for Fischer-Tropsch and methanol synthesis processes: A comparative analysis between different side-feeding strategies", International Journal of Hydrogen Energy, 46(27), pp. 14441–14454, 2021.
https://doi.org/10.1016/j.ijhydene.2021.01.215

[14] Hernandez, B., Martin, M. "Optimization for biogas to chemicals via tri-reforming. Analysis of Fischer-Tropsch fuels from biogas", Energy Conversion and Management, 174, pp. 998–1013, 2018.
https://doi.org/10.1016/j.enconman.2018.08.074

[15] Song, C., Pan, W. "Tri-reforming of methane: a novel concept for catalytic production of industrially useful synthesis gas with desired H_2/CO ratios", Catalysis Today, 98(4), pp. 463–484, 2004.
https://doi.org/10.1016/j.cattod.2004.09.054

[16] Majewski, A. J., Wood, J. "Tri-reforming of methane over Ni@ SiO_2 catalyst", International Journal of Hydrogen Energy, 39(24), pp. 12578–12585, 2014.
https://doi.org/10.1016/j.ijhydene.2014.06.071

17] Lino, A. V. P., Colmenares Calderon, Y. N., Mastelaro, V. R., Assaf, E. M., Assaf, J. M. "Syngas for Fischer-Tropsch synthesis by methane tri-reforming using nickel supported on $MgAl_2O_4$ promoted with Zr, Ce and Ce-Zr", Applied Surface Science, 481, pp. 747–760, 2019.
https://doi.org/10.1016/j.apsusc.2019.03.140

[18] Lino, A. V. P., Assaf, E. M., Assaf, J. M. "Adjusting process variables in methane tri-reforming to achieve suitable syngas quality and low coke deposition", Energy & Fuels, 34(12), pp. 16522–16531, 2020.
https://doi.org/10.1021/acs.energyfuels.0c02895

[19] Patel, B., Hildebrandt, D., Glasser, D., Hausberger, B. "Thermodynamics Analysis of Processes. 1. Implications of Work Integration", Industrial & Engineering Chemistry Research, 44(10), pp. 3529–3537, 2005.
https://doi.org/10.1021/ie048787f

[20] Patel, B., Hildebrandt, D., Glasser, D., Hausberger, B. "Synthesis and Integration of Chemical Processes from a Mass, Energy, and Entropy Perspective", Industrial & Engineering Chemistry Research, 46(25), pp. 8756–8766, 2007.
https://doi.org/10.1021/ie061554z

[21] Patel, B., Hildebrandt, D., Glasser, D. "An overall thermodynamic view of processes: Comparison of fuel producing processes", Chemical Engineering Research and Design, 88(7), pp. 844–860, 2010.
https://doi.org/10.1016/j.cherd.2009.11.019