(Solar) Mixed Reforming of Methane: Potential and Limits in Utilizing CO\textsubscript{2} as Feedstock for Syngas Production—A Thermodynamic Analysis

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Abstract: The reforming of natural gas with steam and CO\textsubscript{2} is commonly referred to as mixed reforming and considered a promising route to utilize CO\textsubscript{2} in the production of synthetic fuels and base chemicals such as methanol. In the present study, the mixed reforming reaction is assessed regarding its potential to effectively utilize CO\textsubscript{2} in such processes based on simple thermodynamic models. Requirements for the mixed reforming reactions based on process considerations are defined. These are the avoidance of carbon formation in the reactor, high conversion of the valuable inlet streams CH\textsubscript{4} and CO\textsubscript{2} as well as a suitable syngas composition for subsequent synthesis. The syngas composition is evaluated based on the module $M = (z_{H_2} - z_{CO_2})/(z_{CO_2} + z_{CO})$, which should assume a value close to 2. A large number of different configurations regarding CO\textsubscript{2}/H\textsubscript{2}O/CH\textsubscript{4} at the reactor inlet, operating pressure and outlet temperature are simulated and evaluated according to the defined requirements. The results show that the actual potential of the mixed reforming reaction to utilize CO\textsubscript{2} as feedstock for fuels and methanol is limited to approximately 0.35 CO\textsubscript{2}/CH\textsubscript{4}, which is significantly lower than suggested in literature. At 900 °C and 7 bar at the reactor outlet, which is seen suitable for solar reforming, a ratio of H\textsubscript{2}O/CH\textsubscript{4} of 1.4 can be set and the resulting value of $M$ is 1.92 (CO\textsubscript{2}/CO/H\textsubscript{2} = 0.07/0.4/1).

Keywords: methane reforming; solar reforming; CO\textsubscript{2} utilization; carbon formation; solar fuels; concentrated solar power (CSP)

1. Introduction

Reforming of natural gas has been a well-established and widely practiced industrial process for the production of synthesis gas (syngas) and hydrogen for several decades now [1–3]. Currently, the reaction is commonly carried out with steam as oxidizing agent, i.e., steam reforming according to Equation (1). The reaction is endothermic; hence heat needs to be provided at a temperature range between 700 °C and 1000 °C. In the conventional steam reforming process, this is done by combustion of natural gas in a chamber surrounding the reactor tubes. Depending on the foreseen application of the syngas, oxygen may also be added to carry out partial oxidation of methane or autothermal reforming to omit the external heating [2]. Accompanying the discussions on the reduction of greenhouse gas emissions, the dry reforming reaction (cf. Equation (2)) has increasingly attracted attention as an option to convert carbon dioxide into a useful product [4,5]:

\[
\text{CH}_4 + \text{H}_2\text{O} \rightarrow 3\text{H}_2 + \text{CO} \\
\Delta H_{R, 298K}^0 = 206 \text{ kJ/mol}
\]
In the published works, carbon formation and the development of catalysts for carbon free operation in dry- or mixed reforming processes is usually the focus of attention. In dry or mixed reforming reactions, the risk of formation of solid carbon is increased due to the lower H/C and O/C ratio. Carbon formation reduces the catalyst activity and reduces its lifetime, hence increases the operational costs [2]. It is commonly known that noble metal catalysts such as Pt-, Ru- or Rh-based ones have a high resistance to carbon formation, but their high cost preclude their application in industrial practice [6]. Nataj, et al. [6] as well as Li, et al. [4] investigated the utilization of non-noble metal catalysts in a dry reforming process. Zhang, et al. [7] investigated catalyst samples with mesoporous structures to reduce the rate of carbon formation. The relevant carbon formation routes for a reforming process are the methane cracking reaction—Equation (3), the Boudouard reaction—Equation (4) and the carbon monoxide reduction—Equation (5).

Methane cracking—Equation (3) is endothermic, i.e., promoted by high temperatures and according to the reaction equation by high CH$_4$ concentration and low H$_2$ concentration. It can therefore be well controlled, as there is commonly low CH$_4$ and high H$_2$ concentration in the hot parts of the reformer. The Boudouard reaction—Equation (4) is exothermic, hence promoted by low temperatures, high CO concentration and low CO$_2$ concentration. It may therefore lead to carbon formation in the cold parts of the reactor if the feed-gas does not contain CO$_2$. The CO-reduction—Equation (5) is exothermic, hence promoted by low temperatures and high CO and H$_2$ concentration and low steam concentration in the reformer. According to Bartholomew and Farrauto [2], the CO-reduction is negligible in reforming reactors. In Table 1, the promoting conditions regarding temperature, pressure and gas composition are listed for the three carbon formation mechanisms. Regarding the gas composition, the “low” column implies that the respective route is promoted by low concentration or absence of the named species. The same is listed for species that promote carbon if present in high concentrations.

$$
CH_4 + CO_2 \rightleftharpoons 2H_2 + 2CO \tag{2}
$$

$$
\Delta H_{R,298K}^0 = 247 \text{ kJ mol}^{-1}
$$

It can be seen from Equations (1) and (2) that the heat of reaction $\Delta H_{R,298K}^0$ is higher for the dry reforming reaction than for the steam reforming reactions. Therefore, the heat demand for the dry reforming reaction is higher than for the steam reforming reaction. Consequently, the aim of reducing greenhouse-gas emissions can only be achieved if a carbon neutral heat source is available. Thus, for processes fueled by combustion of additional natural gas the reasonability of dry reforming is questionable.

A promising way of providing carbon-neutral heat to the reforming reaction is through concentrated solar radiation, which has been investigated for more than two decades by several
research groups [3,8]. In a solar heated reforming process, the concept of solar power tower concept is most suitable to provide concentrated solar radiation at a suitable flux density and scale. In the solar power tower concept, a large number of mirrors are tracked to continuously focus the suns radiation onto a fixed target, which is located atop a tower, typically achieving concentration ratios up to 1000 [9]. Solar heated dry- or mixed reforming of methane is seen as a viable option to effectively reduce greenhouse gas emissions from syngas processes [10].

Another relevant aspect in the assessment of reforming processes, disregarding if it is a steam, dry or mixed reforming process is the product composition. The dry reforming reaction reduces the ratio of hydrogen to carbon monoxide in the product. Hence, utilizing CO₂ in a process for production of pure hydrogen is obstructive. Other typical applications of reforming reactions are the generation of syngas for the methanol or Fischer-Tropsch synthesis [2,11]. Besides outlet temperature, operating pressure of the reforming reactor and approach to equilibrium, the inlet gas composition influences the outlet syngas composition. Therefore, the potential of dry- or mixed reforming can only be assessed when taking into account the requirements of the subsequent syngas processing. This is also done by Blumberg, et al. [12], who come to the conclusion that neither dry- nor steam reforming yields the optimal composition for methanol synthesis, but only a combination of the two, i.e., mixed reforming. Li, et al. [13] assessed the conversion of Methane, Steam and CO₂ and potential carbon formation in a mixed reforming process. However, no conclusions were drawn considering a specific purpose for the product syngas. Zhang, et al. [14] investigated the utilization of CO₂ in a methanol production process and assess feeding the CO₂ into the reforming reactor or directly into the methanol reactor. However, they did not consider in detail the impact of heat supply to the reforming reactor. Hence no conclusion can be drawn regarding the actual reduction in CO₂ emissions. Atashi, et al. [15] carried out an intensive statistical analysis on the conversion, yield and product composition in a dry reforming reaction and propose a value they call “desirability” of the product. They came to the conclusion that a molar ratio of CO₂ to CH₄ of 0.5 at the inlet to the reactor is optimal. It is unclear, how the “desirability” is defined by Atashi, et al. [15] and a sub-stoichiometric input of CO₂, which they propose, leads to incomplete conversion of CH₄, causing a drastic loss of the valuable feedstock CH₄. Therefore, the transferability of their results into practice is questionable. Furthermore, Chein, et al. [16] contradict Atashi, et al. [15] by stating that to their finding a high CO₂ excess enhances the performance of a dry reforming reactor. Choudhary and Mondal [17] investigated mixed reforming of methane over perovskite-type catalysts regarding conversion, selectivity and carbon formation. They showed the carbon free operation of the process and stated that the product composition can be controlled by variation of process conditions such as temperature. However, they do not put the results into context with subsequent syngas utilization. Bradford and Vannice [18] intensively studied dry reforming of methane and state that dry reforming is only suitable when H₂/CO ratios of 1 or lower are desired. Furthermore, they state that H₂/CO ratios of 1 to 3 can be achieved by adjusting the H₂O/CO₂/CH₄ ratio in the reformer. Jang, et al. [19] carried out a thermodynamic equilibrium analysis similar to the one presented here as well as experimental results on mixed reforming of methane. They assessed the conversion of CH₄ and CO₂, as proposed in this work. They find a minimum ratio of (H₂O + CO₂)/CH₄ that is required to avoid carbon formation, which is valuable information for the assessment of this process. Their work is similar to the one presented in this article, however they complement each other, as this work puts the results into the context of the actual syngas utilization which is crucial for the overall process balance. In the context of solar heated reforming, Sun, et al. [20] assessed the risk of carbon formation and outlet composition of syngas for a mixed reforming process for varying conditions in support of their development of a solar heated reforming reactor. They assess the H₂ yield, CH₄ conversion and carbon formation as well as H₂/CO ratio. However, they do not assess conversion of CO₂, which should be a basic requirement to such a process. Furthermore, besides H₂/CO ratio, CO₂ content in the product gas should be assessed, as CO₂ conversion is never complete and CO₂ sequestration from the product expensive. Therefore, it is most reasonable to assess the composition of a product syngas through a module which takes into account H₂, CO and CO₂.
This is common for methanol synthesis and high temperature Fischer-Tropsch synthesis, because both processes can convert CO$_2$. Rostrup-Nielsen, et al. [21] propose the Module $M$, which is defined according to Equation (6), where $z_i$ is the molar ratio of species $i$. For methanol synthesis, DME production and high temperature Fischer-Tropsch synthesis $M$ should assume a value close to 2 [1,12]:

$$M = \frac{z_{H_2} - z_{CO_2}}{z_{CO_2} + z_{CO}} = 2$$  \hspace{1cm} (6)

From the brief literature review above, it becomes clear that a need for more comprehensive understanding of the actual potential of mixed–or dry reforming exists. Therefore, in the present study, the utilization of carbon dioxide in a reforming process for generation of syngas for methanol synthesis and Fischer-Tropsch synthesis is thermodynamically assessed. The results will be put into context with solar heated reforming, for which experience from previous work is taken into account (e.g., [10,22,23]).

2. Materials and Methods

The objective of the present study is to determine the product composition of the dry- or mixed-reforming process as well as to detect possible carbon formation in dependence of inlet gas composition, reaction temperature and pressure. The software FactSage by GTT Technology is a suitable tool to carry out such simulations. However, it is not suitable to be used with automation to carry out a large number of simulations with low effort. For this purpose, the prevalent simulation tool for chemical industry, Aspen Plus is used. In order to ensure validity for the results regarding carbon formation, a validation of the results generated in Aspen with results generated with FactSage is carried out.

The model consists of an RGIBBS reactor-model from the Aspen Plus model library with three inlet streams (CH$_4$, H$_2$O, CO$_2$) and an outlet stream. The operating pressure and temperature are specified. The RGIBBS reactor-model determines the outlet composition for the present conditions based on minimization of Free Gibbs Energy, which is in good agreement with the procedure used by Rodriguez-Olalde, et al. [24]: The Gibbs energy $G$ of a system of $N$ species $i$ is defined as the sum of each species’ chemical potential weighted with its molar amount $n_i$ (cf. (7)). The thermodynamic equilibrium of the multi reaction system is reached where the total Free Gibbs Energy is minimal, i.e., its differential is zero, as described in more detail by Sun, et al. [20]:

$$G = \sum_{i=1}^{N} n_i \cdot \mu_i$$  \hspace{1cm} (7)

Hence the thermodynamic equilibrium is determined, disregarding any potential kinetic limitations. This is considered acceptable, as reforming reactors operated close to chemical equilibrium regarding their primary reactions [1,2]. Carbon formation may be severely limited by kinetics but it is nonetheless advisable to operate the reactor in a regime where carbon formation is not thermodynamically favorable.

The Aspen model is coupled with an MS Excel spreadsheet, through which the input parameters are varied and the results are retrieved automatically. The varied parameters, range and step size or values are given in Table 2. Based on these variations, the total number of combinations to be simulated is 22,176. For each simulation, the molar product composition is retrieved. From this, the conversion of CH$_4$ and CO$_2$, the possibility of carbon formation and $M$ are determined in the spreadsheet. The spreadsheet with all unprocessed results is provided as Supplementary Material.
Table 2. Range and interval for variation of model parameters.

| Parameter       | Range                  | Values/Step Size | Number of Values |
|-----------------|------------------------|------------------|------------------|
| Temperature $T$ | 500–1000 °C            | 50 K             | 11               |
| Pressure $p$    | 1–20 bar               | [1–5,7,10,15,20] | 9                |
| $\text{H}_2\text{O}/\text{CH}_4$ (molar) | 0–3                   | 0.2              | 16               |
| $\text{CO}_2/\text{CH}_4$ (molar)       | 0–2                   | 0.2              | 14               |

The large number of results inhibits a comprehensive presentation and discussion of all data within this article. For this article, a focus is put onto application to solar reforming and to suitable values of $M$. Based on published previous work [10,23], 900 °C is considered as a suitable outlet temperature for a solar reforming reactor. Hence the discussion will focus on this outlet temperature.

2.1. Validation of Reaction Model

The results obtained through the Aspen model are validated with FactSage for selected parameter combinations. These selected combinations are given in Table 3. The total number of validated parameter combination is 120. The results, based on which the model is validated are conversion of $\text{CH}_4$ and $\text{CO}_2$ as well as carbon formation. The entire documentation of the validation is provided in the ESI, in the following only a brief overview is given.

Table 3. Parameter combinations for validation.

| Parameter       | Range                  | Values/Step Size | Number of Values |
|-----------------|------------------------|------------------|------------------|
| Temperature $T$ | 500–1000 °C            | 100 K            | 6                |
| Pressure $p$    | 1–15 bar               | [1,3,5,7,15]     | 5                |
| $\text{H}_2\text{O}/\text{CO}_2/\text{CH}_4$ | 1/0/1; 1/1/1; 0/1/1; 2/0/1 | 4                |

Regarding conversion, the agreement between the Aspen and FactSage results is quantified by the coefficient of determination $R^2$ and the maximum relative deviation between the results. For both the conversion of $\text{CH}_4$ as well as $\text{CO}_2$ a good agreement can be observed. $R^2$ is 0.9994 and 0.9998 the maximum relative deviation is 5.7% and 6.5% for the conversion of $\text{CH}_4$ and $\text{CO}_2$ respectively. For the prediction of carbon formation the procedure is different, as for this aspect not the quantity is of central interest, but if it is predicted (i.e., >0) or not (i.e., =0). In general there is also a good agreement between the results regarding carbon formation: Only four out of the 120 considered parameter combinations show a qualitative deviation. The four parameter combinations, for which deviations occur, are listed in Table 4. In all four cases, carbon formation is predicted by the Aspen model, but not by the FactSage model. The cases for which deviations occur broaden the temperature range, for which a carbon formation is predicted. For instance, in the first row in Table 4 the Aspen model predicts carbon formation from 600 °C to 800 °C for these parameters, while the FactSage model only predicts carbon formation from 700 °C to 800 °C. Hence, the general prediction of carbon formation is correct, but the specific limits may deviate slightly.

Table 4. Parameter combinations for which deviation in prediction of carbon formation is observed between Aspen and FactSage model.

| Temperature (°C) | Pressure in Bar | $\text{H}_2\text{O}/\text{CH}_4$ | $\text{CO}_2/\text{CH}_4$ |
|-----------------|-----------------|-------------------------------|----------------------------|
| 600             | 7               | 1                             | 0                          |
| 700             | 15              | 1                             | 0                          |
| 800             | 15              | 1                             | 0                          |
| 800             | 15              | 1                             | 1                          |

In conclusion, the Aspen model can be considered as sufficiently precise with respect to the results of interest and the purpose of assessing the general potential of mixed reforming. For detailed reactor development, more precise data may have to be used.
2.2. Procedure for Determining Suitable Mixed-Reforming Conditions

The problem of finding an optimal or even suitable process configuration for a mixed reforming process is a challenging task, considering the large number of possibilities due to various options for H₂O/CH₄, CO₂/CH₄ at the inlet, outlet temperature, and reforming pressure that influence the results. Furthermore, as stated above, there are several aspects to be considered in evaluating a mixed reforming process, such as syngas quality, reactant conversion and the possibility of carbon formation.

In order to facilitate the process of finding suitable operating conditions for a mixed reforming process in a Fischer-Tropsch- or methanol-synthesis plant, a procedure based on the present results is proposed in the following.

At first, the requirements to the process need to be defined. In this case these are the avoidance of carbon formation and high conversion of methane and carbon dioxide as necessary conditions. This is especially challenging in the case of CO₂ conversion, as it will assume very low or even negative values when excess steam is added [25], which in turn helps to avoid carbon formation. Even though, unreacted CH₄ and CO₂ could be separated and recycled from the product stream, this is not considered because it is assumed that the gas-gas separation would be neither economically nor energetically viable. In addition to the necessary conditions, a suitable syngas composition is set as sufficient condition. The conditions defined in this work are summarized in Table 5. The numeric values for the requirements on the conversion of inlet species as well as the allowed deviation for M from 2 are debatable and based on experience and previous work on methanol production (cf. [10,22,23,26]). Slightly different values may be defined for other boundary conditions or based on overall process considerations. The general definition of these conditions however should be universally applicable to mixed reforming processes.

| Necessary Conditions | Requirements                  |
|----------------------|-------------------------------|
| Methane conversion   | >85%                          |
| CO₂ conversion       | >50%                          |

| Sufficient Condition | Syngas composition            |
|----------------------|-------------------------------|
| M                    | 2 ± 5%                        |

As the requirements given in Table 5 can be distinguished between necessary and sufficient conditions, we propose the following procedure to determine suitable reaction conditions. For each reactor outlet temperature and pressure, a map is generated to determine suitability for varying H₂O/CH₄ and CO₂/CH₄ ratios at the inlet. This is shown for two examples with reformer outlet temperature of 900 °C in Figure 1 for a pressure of 1 bar (a) and 7 bar (b). The legend given in Table 6 applies. The black, white and grey areas in the maps indicate that one of the necessary conditions is not met. The colors indicate suitability according to syngas composition: Green indicates suitability; orange color indicates a deviation of 5–15% of M from the value 2. Red indicates a deviation >15%. It can be easily seen in the figure that only a narrow range of compositions are suitable for the considered temperature and pressure. These maps are a convenient method to visualize suitable inlet compositions for the reaction. However, as one map is required for each temperature and pressure, 99 maps would be required to display all combinations investigated in this work. As this is not feasible, the data analysis is simplified to determine the maximum CO₂ concentration, for which all conditions are met for each temperature and pressure. This seems to be reasonable, as utilization of as much CO₂ as possible is one of the aims in mixed reforming. Other aims are taken account for in the required conditions. The results for all temperature and pressure levels can then be clearly displayed in a table or color map.
Fig. 1. Exemplary color maps for $M$ in dependence on $\text{H}_2\text{O}/\text{CH}_4$ and $\text{H}_2\text{O}/\text{CO}_2$ ratio. Reformer outlet temperature is 900 ˚C Pressure 1 bar (a) and 7 bar (b). Legend in Table 6 applies.

Table 6. Legend for following contour plots.

| Condition             | Color |
|-----------------------|-------|
| Carbon formation      | Red   |
| low CH$_4$ conversion | Black |
| low CO$_2$ conversion | Yellow|
| Optimum               | Orange|

Based on the available results, reforming pressure and temperature can be determined according to further boundary conditions specific to the application. Regarding the temperature, this may be a material limitation or in the case of solar reforming, it may be limited by the solar components. Regarding the pressure, commonly it is desired to operate at pressures as high as possible. Even though the operating pressure may be limited by construction details of the reformer, it will most probably be limited by the above defined conditions.

When the reforming conditions, i.e., $\text{H}_2\text{O}/\text{CH}_4$ and $\text{CO}_2/\text{CH}_4$ ratio, temperature and pressure are determined based on the above recommendations, it is only ensured that no carbon formation occurs at the outlet of the reactor. As most reforming reactors develop a temperature profile with increasing temperature from inlet to outlet, it needs to be assessed if carbon formation may occur at colder parts of the reactor. For instance, in the above color maps $\text{CO}_2/\text{CH}_4$ ratios up to 0.35 and $\text{H}_2\text{O}/\text{CH}_4$ of 1.2 are identified as suitable combinations for 1 and 7 bar operating pressure. In Figure 2, the carbon formation is shown over temperature in the reactor for these inlet compositions and pressures. It can be seen that over the typical temperature range in a reformer (i.e., 500 to 1000 ˚C), carbon formation may occur up to 750 ˚C for both pressures. To reduce this risk, a promising approach is to only give CH$_4$ and Steam into the reforming reactor at the cold end and add CO$_2$ at a hotter section, where the temperature is high enough to avoid carbon formation. This option is shown in the graph by the dotted lines. It can be seen that this would not solve the problem at 1 bar (which is supported by the results of Jang, et al. [19]), but at 7 bar no carbon formation is predicted when CO$_2$ is added at section where the temperature is above 750 ˚C. The resulting syngas would still have the required composition, but carbon formation is avoided.
3. Results

Based on the above recommendations for determining suitable conditions for a mixed reforming process, the central result to be presented are the maximum values for CO$_2$/CH$_4$, which are possible for each temperature and pressure. These results are presented in Table 7. In the table it can be seen that for outlet temperatures below 750 °C the required conditions cannot be met. Furthermore, it can be seen that for increasing temperature, increasing pressures are possible. When considering the 900 °C, which are assumed as suitable in the case of solar heated reforming, the maximum operating pressure that is feasible is 7 bar. For 1000 °C outlet temperature, up to 20 bar pressure is feasible. It can also be seen that the maximum CO$_2$/CH$_4$ ratio that is possible is 0.35 for all considered data points. At the same time, as can be seen in the data provided in the supplementary material, the corresponding CO$_2$ conversion only marginally exceeds the required minimum of 50%.

| T (°C)  | Reforming Pressure in Bar |
|--------|---------------------------|
|        | 1  | 2  | 3  | 4  | 5  | 7  | 10 | 15 | 20 |
| 500    | 0  | 0  | 0  | 0  | 0  | 0  | 0  | 0  |    |
| 550    | 0  | 0  | 0  | 0  | 0  | 0  | 0  | 0  |    |
| 600    | 0  | 0  | 0  | 0  | 0  | 0  | 0  | 0  |    |
| 650    | 0  | 0  | 0  | 0  | 0  | 0  | 0  | 0  |    |
| 700    | 0  | 0  | 0  | 0  | 0  | 0  | 0  | 0  |    |
| 750    | 0.3| 0.3| 0.3| 0.3| 0.3| 0.3| 0  | 0  |    |
| 800    | 0.35| 0.35| 0.35| 0.35| 0.35| 0.35| 0.35| 0  |    |
| 850    | 0.35| 0.35| 0.35| 0.35| 0.35| 0.35| 0.35| 0.35| 0  |
| 900    | 0.35| 0.35| 0.35| 0.35| 0.35| 0.35| 0.35| 0.35| 0.35|
| 950    | 0.35| 0.35| 0.35| 0.35| 0.35| 0.35| 0.35| 0.35| 0.35|
| 1000   | 0.35| 0.35| 0.35| 0.35| 0.35| 0.35| 0.35| 0.35| 0.35|

Green indicates a maximum CO$_2$/CH$_4$ > 0, red indicates no CO$_2$ possible.

The color map for 900 °C and 7 bar, which were identified as suitable conditions for solar heated reforming was presented above in Figure 1b. In the color map it can be seen that the possible range of H$_2$O/CO values is also very narrow: Between 1.0 and 1.2. A possibility to quantify the range of possible values of H$_2$O/CH$_4$ and CO$_2$/CH$_4$ for the different temperatures and pressures in a comprehensive way is to determine the area of the green field. The area is defined according to Equation (8) and therefore dimensionless:
Area = \Delta \frac{H_2O}{CH_4} \cdot \Delta \frac{CO_2}{CH_4} \quad (8)

In Figure 3, this area is presented in dependence on outlet temperature for different reforming pressures. It can be seen that the area increases with temperature and reduces with pressure. This underlines what was already indicated in Table 7: the higher the reforming temperature, the higher the maximum pressure that is possible while achieving the defined requirements. Furthermore, in Figure 3 it can be seen that when considering 900 °C as maximum outlet temperature, the maximum reforming pressure is 7 bar. When considering 1000 °C as maximum outlet temperature, which is reasonable for conventionally heated reforming, pressures of up to 20 bar are possible. It should be noted that the plateau that can be seen for 1 and 2 bar between 850 °C and 900 °C in Figure 3 is not expected to be an actual physical phenomena but due to the limited resolution of considered CO₂/CH₄ and H₂O/CH₄ values.

For the selected conditions at 900 °C and 1000 °C, the detailed results are summarized in Table 8. It can be seen that the results regarding conversion of CH₄ and CO₂ as well as M do not vary significantly. This indicates that the course of reaction is similar for both cases, the difference in temperature is compensated by the difference in pressure and a comparable syngas product is achieved.

| Reformer Outlet Temperature | 900 °C | 1000 °C |
|----------------------------|--------|---------|
| Reforming Pressure         | 7 bar  | 20 bar  |
| H₂O/CH₄                    | 1.2    | 1.4     |
| CO₂/CH₄                    | 0.35   | 0.35    |
| Conversion CH₄             | 0.928  | 0.936   |
| Conversion CO₂             | 0.546  | 0.520   |
| M                          | 1.90   | 1.91    |

As discussed above, it furthermore has to be assessed, if carbon formation occurs throughout the profile of the reactor. For the 900 °C case, it was shown in Figure 2 that it does and therefore the injection of CO₂ into a hotter part of the reactor is required. Similarly, the carbon formation over temperature is shown for the 1000 °C/20 bar case with and without CO₂. In Figure 4, the carbon
formation is shown over temperature for 20 bar. It can be seen that for the proposed CO$_2$/CH$_4$ ratio of 0.35, carbon formation can occur in the cold parts of the reactor. As for the 900 °C/7 bar case, this is not the case if CO$_2$ injected into a hotter part of the reactor and only CH$_4$ and steam added to the cold inlet.

![Graph showing carbon formation over temperature](image)

**Figure 4.** Carbon formation over temperature without CO$_2$ and with 0.35 CO$_2$/CH$_4$ at the inlet.

**Comparison of Results with Data by Sun, et al. [20]**

As mentioned above, the study by Sun, et al. [20] is the one closest to the present study. Therefore, in order to further assess the validity of the presented results, they are compared to the results by Sun, et al. [20] where possible. The comparison is shown in Figure 5 with respect to the predicted carbon formation. Sun et al. [20] presented results for a ratio of CO$_2$/CH$_4$ of 0.5 while in the presented study only the values of 0.4 and 0.6 were included. Therefore, the range between these two values for CO$_2$/CH$_4$ is presented and compared to the results presented by Sun, et al. [20].

![Graph comparing carbon formation results](image)

**Figure 5.** Comparison of carbon formation results with results presented by Sun, et al. [20]. For H$_2$O/CH$_4$ = 1 at 1 bar (a) and 5 bar (b).

In the figure, a slight deviation in the predicted amount of carbon formation can be seen. However, the regimes in which carbon formation does and does not occur match well. Thus, it can be concluded that the results agree well.
4. Sensitivity Study

The above defined requirements on the reaction, i.e., conversion of reactants and syngas composition are based on experience and not on rigid methodology. Therefore, a variation of the requirements is carried out in order to assess the sensitivity of the results on these changes. The carried out variations are summarized in Table 9. The impact of these variations is presented by the maximum possible CO₂/CH₄ ratio at the inlet of the reactor, as it was shown above that this is the strongly constrained variable. The results are displayed in Table 10 in accordance with Table 7. The reference results from Table 7 are repeated in the top left and bottom right of the table to facilitate comparison of the results.

| Parameter          | Reference Value | Variation   |
|--------------------|-----------------|-------------|
| M                  | 2 ± 5%          | 2 ± 10%     |
| Conversion CO₂     | >50%            | 1. >25%; 2. >75% |
| Conversion CH₄     | >85%            | >95%        |

It can be seen in Table 10 that there is only a minor effect of the variation of required conditions on the results. The maximum possible value of CO₂/CH₄ is only slightly increased by allowing a broader range of values for M (±10%). It is not changed for the variations in required conversion of reactants. A tendency of higher possible operating pressure for a given temperature can be observed when the required CO₂ conversion is reduced to 25%. When increasing the required conversion of CO₂ and CH₄, the opposite effect can be observed.

In conclusion the results of the sensitivity study show that even if other values are defined for the requirements on the syngas, the overall results do not change significantly. Hence the above presented results are valid.

| T (°C) | XCO₂ > 25% | XCO₂ > 75% |
|--------|------------|------------|
|        |            |            |
| 500    | 0          | 0          |
| 550    | 0          | 0          |
| 600    | 0          | 0          |
| 650    | 0          | 0          |
| 700    | 0          | 0          |
| 750    | 0.3        | 0.35       |
| 800    | 0.35       | 0.35       |
| 850    | 0.35       | 0.35       |
| 900    | 0.35       | 0.35       |
| 950    | 0.35       | 0.35       |
| 1000   | 0.35       | 0.35       |

Table 9. Variations in requirements on reaction.

Table 10. Results of sensitivity study, maximum possible CO₂/CH₄ ratio at the reactor inlet.
Table 10. Cont.

| $T$ ($^\circ$C) | $X_{\text{CH}_4} > 95\%$ | Reference |
|---------------|-----------------|-----------|
| 500           | 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 | 0 0 0 0 0 0 0 |
| 550           | 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 | 0 0 0 0 0 0 0 |
| 600           | 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 | 0 0 0 0 0 0 0 |
| 650           | 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 | 0 0 0 0 0 0 0 |
| 700           | 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 | 0 0 0 0 0 0 0 |
| 750           | 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 | 0 0 0 0 0 0 0 |
| 800           | 0.35 0.35 0.35 0.35 0.35 0.35 0.35 0.35 0.35 0.35 0.35 0.35 0.35 0.35 0.35 | 0 0 0 0 0 0 0 |
| 850           | 0.35 0.35 0.35 0.35 0.35 0.35 0.35 0.35 0.35 0.35 0.35 0.35 0.35 0.35 0.35 | 0 0 0 0 0 0 0 |
| 900           | 0.35 0.35 0.35 0.35 0.35 0.35 0.35 0.35 0.35 0.35 0.35 0.35 0.35 0.35 0.35 | 0 0 0 0 0 0 0 |
| 950           | 0.35 0.35 0.35 0.35 0.35 0.35 0.35 0.35 0.35 0.35 0.35 0.35 0.35 0.35 0.35 | 0 0 0 0 0 0 0 |
| 1000          | 0.35 0.35 0.35 0.35 0.35 0.35 0.35 0.35 0.35 0.35 0.35 0.35 0.35 0.35 0.35 | 0 0 0 0 0 0 0 |

Red indicates no CO$_2$ possible.

5. Discussion

The concept of mixed reforming of natural gas, i.e., utilization of steam and CO$_2$ as reactants was investigated with the focus on generating a suitable syngas for subsequent processing. Synthesis reactions such as Fischer-Tropsch or methanol synthesis were identified as the main applications for mixed reforming reactions. Requirements on the process performance regarding the absence of solid carbon formation in the reactor, conversion of valuable reactants as well as product composition where defined. The reaction was simulated with a wide range of inlet compositions as well as reaction pressures and reactor outlet temperatures. Analysis of the results show that CO$_2$ utilization is only possible to a very limited extent of 0.35 CO$_2$/CH$_4$ (molar) in a mixed reforming reaction and the possible reforming pressure is limited by the outlet temperature of the reactor. Furthermore, carbon formation is favored at low temperatures for the relevant inlet compositions. This leads to the proposition not to inject CO$_2$ together with steam and CH$_4$ to the reactor inlet, but to inject it to a hotter part of the reactor.

The definition of the requirements on the conversion of reactants and acceptable range of values for syngas quality (expressed through $M$) was somewhat arbitrarily. However, the sensitivity study showed that a variation of these definitions do not change the results significantly. Therefore, the implications suggested by the results are universally applicable to mixed reforming reactions.

6. Conclusions

In conclusion it can be said that the presented results significantly diminish the potential, which is seen in the mixed reforming reaction to establish a CO$_2$ recycling process. However, the results give a framework to assess the real potential of mixed reforming of natural gas and will support the commercial implementation by allowing estimation of its real potential for the production of synthetic fuels and methanol and generate a relevant CO$_2$ utilization route.

Supplementary Materials: The following are available online at http://www.mdpi.com/1996-1073/11/10/2537/s1, Original Data in .xlsx format.

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