Thermodynamic Analysis of Dry Reforming of Methane for Valorization of Landfill Gas and Natural Gas

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Dry reforming of methane (DRM) is a promising technology to convert carbon dioxide (CO$_2$) and methane (CH$_4$), two major greenhouse gases into syngas (a mixture of carbon monoxide (CO) and hydrogen (H$_2$)). A thermodynamic equilibrium analysis for DRM with a focus on carbon formation is carried out in Aspen Plus using the Gibbs free energy minimization method. The effects of feed CO$_2$/CH$_4$ ratio (0.5–3), reaction temperature (773–1373 K), and system pressure (0.1–10 atm) on the equilibrium conversion, product distribution, and solid carbon formation are investigated. From the analysis, it was found that the optimal operating conditions of 1 atm, 1123 K, and a feed ratio (CO$_2$:CH$_4$) of 1:1, minimized carbon formation, produced syngas at a H$_2$/CO ratio of 1 (sufficient for downstream Fischer–Tropsch synthesis), while minimizing energy requirements. It is found that adding small amounts of oxygen or water significantly reduced carbon formation, minimized loss in syngas production, and reduced energy requirements. Three application scenarios were simulated to reflect the valorization of vented and flared natural gas and landfill gas (LFG). It was found that using captured CO$_2$ with natural gas and LFG produced favorable results and therefore may be an opportunity for commercial DRM.

1. Introduction

Mitigating greenhouse gas (GHG) emissions while providing access to clean and affordable energy constitutes a major global challenge in the present energy landscape. Dry reforming of methane (DRM, Equation (1)), which is the reaction between the GHGs carbon dioxide (CO$_2$) and methane (CH$_4$), has attracted attention as a means to provide synthesis gas (syngas) as building block to the chemical industry at a lower carbon footprint than conventional methods.$^{[1–4]}$

\[
\text{CO}_2 + \text{CH}_4 \rightarrow 2 \text{CO} + 2 \text{H}_2 \quad \Delta H^\circ_{298K} = 247 \text{ kJ mol}^{-1} \tag{1}
\]

In 2017, CO$_2$ accounted for 81% of US GHG emissions, and methane (CH$_4$) accounted for 10%.$^{[5]}$ Although CH$_4$ is emitted at a smaller scale than CO$_2$, its emissions are deemed to be more detrimental on a mass basis due to their much higher global warming potential (with a 100 year GWP at around 25$^{[6]}$). In remote oil fields, due to a lack of infrastructure to process and transport natural gas, flaring is used for the disposal of 143 billion m$^3$ of natural gas each year (3.5% of global production)$^{[7]}$ If the CO$_2$ content of natural gas in these fields is too high, constituting an incombustible gas, this waste gas is vented. Although the US is the leader in number of flares,$^{[7]}$ in 2018, the UK venting/flaring of natural gas from oil and gas production made up of 1% of the UK GHG emissions.$^{[8]}$ Landfill gas (LFG), which is a result of waste management, can also have a significant impact on emissions. For example, the largest point sources of methane emissions in California, USA, are landfills, accounting for 41.3% of methane emissions in the state.$^{[9]}$ LFG typically contains CO$_2$ and CH$_4$ in quantities that are incombustible and hence released into the atmosphere, accounting globally for 1.9% of GHG emissions.$^{[5]}$

The simultaneous conversion of CO$_2$ and CH$_4$ to high-value liquid products has recently attracted attention as a strategy to utilize the wasted (and emitted) CH$_4$ and CO$_2$ streams from oil and gas, and landfill operation.$^{[10–12]}$ This attention has manifested itself in the form of scientific progress in the electrochemical and thermochemical catalytic processes for natural gas valorization, with emphasis on partial oxidation, dry reforming, and oxidative coupling reactions, among other schemes.$^{[10,13]}$

Traditionally, steam reforming of methane (SRM) is used to produce syngas with a H$_2$/CO ratio of 3. However, this high H$_2$/CO ratio is unsuitable for the Fischer–Tropsch synthesis (FTS) process which is the primary pathway to C–C coupled chemicals production.$^{[14]}$ High ratios of H$_2$/CO favor chain termination in FTS, and increasing the CO content increases chain growth probability.$^{[15]}$ DRM produces syngas with an H$_2$/CO ratio of 1; it is suitable for the direct synthesis of acetic acid or dimethyl ether$^{[16]}$ and can be amenable for downstream FTS for the production of long-chain hydrocarbons.$^{[17]}$ The long-chain hydrocarbons can be used for fuels and as feedstock for plastics, rubber, and petrochemicals.

DRM has attracted significant attention in recent years from catalyst design,$^{[18–27]}$ process development,$^{[28–36]}$ and
optimization\textsuperscript{[37,38]} perspectives. While the net consumption of \( \text{CO}_2 \) in the DRM process itself is questionable due to process energetics and downstream emissions considerations,\textsuperscript{[36]} DRM nonetheless emerges as a technology that can help avoid waste methane and \( \text{CO}_2 \) emissions from vents, flares, and landfills if stable catalysts for DRM and downstream processes are developed.\textsuperscript{[9]}

The largest limitations of DRM are the formation of considerable amounts of carbon that leads to rapid deactivation of the catalyst, in addition to the kinetic barrier that requires significant energy to function. In the literature, the issues related to the industrial applications of DRM have been suggested to be improved by combining DRM, SRM, and/or partial oxidation of methane (POM).\textsuperscript{[39–41]} The positive effect of steam and oxygen on preventing carbon formation during reforming has also been noted in several experimental studies.\textsuperscript{[42–44]} Catalyst developments such as coke resistance and thermal stability are key to ensure feasibility of any proposed process due to the challenging nature of methane activation. However, thermodynamic constraints of operating with real emissions must be accounted for when developing catalysts for waste gas valorization applications. Prior thermodynamic investigations, focus on pure reactant gases (\( \text{CH}_4, \text{CO}_2 \)) representative of laboratory testing environments.\textsuperscript{[39–41,45–47]} Thermodynamic analyses focusing on specific feedstock compositions can enable identification of opportunities and challenges in catalyst development or operation unique to application and some prior research has examined the energetic requirements and \( \text{CO}_2 \) emissions for hydrogen production.\textsuperscript{[48]} In this work, we focus on applying thermodynamic analysis to determine opportunities for DRM in realistic industrial settings, by simulating the reaction equilibrium for reported pipeline gas, vented/ flared natural gas, and LFG compositions. We first establish base case conditions for methane dry reforming, including the stoichiometric reaction of \( \text{CO}_2 \) and \( \text{CH}_4 \) often used for laboratory testing. We identify conditions where coke formation emerges as a significant issue and propose oxygen and water addition as operational modifications to mitigate this issue. We then use this analysis and our thermodynamic model to simulate dry reforming using composition data from pipeline natural gas, vented/ flared natural gas, and LFG to evaluate suitability of this process to generate syngas from both purified and waste \( \text{CO}_2 \) and \( \text{CH}_4 \) streams with a view of identifying opportunities for catalyst development.

2. Results and Discussion

2.1. Effect of Feed \( \text{CO}_2/\text{CH}_4 \) Ratio

The baseline equilibrium methane conversion and extent of coke formation over a range of relevant temperatures for catalysts were calculated using Aspen Plus and are shown in Figure 1 and 2, respectively. The main reactions of \( \text{CO}_2, \text{CH}_4 \), and the products under these conditions are shown in Table 1. \( \text{CH}_4 \) conversion increases with \( \text{CO}_2/\text{CH}_4 \) ratio (Figure 1), suggesting that \( \text{CO}_2 \) acts as a soft oxidant and therefore adding more \( \text{CO}_2 \) to \( \text{CH}_4 \) achieves a higher activity for \( \text{CH}_4 \) and therefore has a positive effect on the conversion of \( \text{CH}_4 \). At lower temperatures (<923 K), the effect of feed ratio on \( \text{CH}_4 \) conversion is greater, for feed ratio >1, this is due to \( \text{CH}_4 \) becoming a limiting reactant and therefore the amount of \( \text{H}_2 \) available for side reactions being reduced.

![Figure 1](https://www.advancedsciencenews.com/)

**Figure 1.** Variation of equilibrium conversion of \( \text{CH}_4 \) with temperature at four different feed ratios (\( \bullet \text{CO}_2/\text{CH}_4 = 0.5, \triangle \text{CO}_2/\text{CH}_4 = 1, \text{CO}_2/\text{CH}_4 = 2, \text{CO}_2/\text{CH}_4 = 3 \)) at a pressure of 1 atm.

![Figure 2](https://www.advancedsciencenews.com/)

**Figure 2.** Variation of equilibrium carbon production with temperature at four different feed ratios (\( \bullet \text{CO}_2/\text{CH}_4 = 0.5, \triangle \text{CO}_2/\text{CH}_4 = 1, \text{CO}_2/\text{CH}_4 = 2, \text{CO}_2/\text{CH}_4 = 3 \)) at a pressure of 1 atm.

| Reaction number [Rxn] | Reaction | \( \Delta H_{298} \) [kJ mol\(^{-1}\)] |
|-----------------------|----------|--------------------------------------|
| 1                     | \( \text{CH}_4 + \text{CO}_2 \leftrightarrow 2\text{CO} + 2\text{H}_2 \) | 247.0 |
| 2                     | \( \text{CO}_2 + \text{H}_2 \leftrightarrow \text{CO} + \text{H}_2\text{O} \) | 41.0 |
| 3                     | \( 2\text{CH}_4 + \text{CO}_2 \leftrightarrow \text{C}_2\text{H}_4 + 2\text{CO} + 2\text{H}_2\text{O} \) | 106.0 |
| 4                     | \( 2\text{CH}_4 + 2\text{CO}_2 \leftrightarrow \text{C}_2\text{H}_4 + 2\text{CO} + 2\text{H}_2\text{O} \) | 284.0 |
| 5                     | \( \text{C}_2\text{H}_4 \leftrightarrow \text{C}_2\text{H}_2 + \text{H}_2 \) | 136.0 |
| 6                     | \( \text{CO} + 2\text{H}_2 \leftrightarrow \text{CH}_4\text{OH} \) | -90.6 |
| 7                     | \( \text{CO}_2 + 3\text{H}_2 \leftrightarrow \text{CH}_4\text{OH} + \text{H}_2\text{O} \) | -49.1 |
| 8                     | \( \text{CH}_4 \leftrightarrow \text{C} + \text{2H}_2 \) | 74.9 |
| 9                     | \( 2\text{CO} \leftrightarrow \text{C} + \text{2CO}_2 \) | -172.4 |
| 10                    | \( \text{CO}_2 + 2\text{H}_2 \leftrightarrow \text{C} + 2\text{H}_2\text{O} \) | -90.0 |
| 11                    | \( \text{CO} + \text{H}_2 \leftrightarrow \text{H}_2\text{O} + \text{C} \) | -131.3 |
| 12                    | \( \text{CO}_2 + 4\text{H}_2 \leftrightarrow \text{CH}_4 + \text{2H}_2\text{O} \) | -165.0 |
| 13                    | \( \text{CO} + 3\text{H}_2 \leftrightarrow \text{CH}_4 + \text{H}_2\text{O} \) | -206.2 |
However, at higher temperatures, the CH$_4$ conversion increases significantly due to methane decomposition (Table 1, Rxn8), becoming more favorable causing also an increase in carbon formation (Figure 2).

Figure 2 shows the production of solid carbon for different feed ratios. Carbon is a solid product that will accumulate in the reactor in a real scenario, which is not accounted for in the steady-state model presented herein. However, the extent of carbon formation provides a baseline for the thermodynamic driving force for coking, which is a major issue that is explored frequently in catalyst development efforts. It can be seen that the carbon formation decreases at higher temperatures and higher CO$_2$/CH$_4$ ratio, in good agreement with prior simulation findings reported in the literature.$^{49,50}$ Furthermore, it can be observed that the carbon distribution (25–34%) at low temperatures (<773 K) is high for all feed ratios. At higher temperatures, carbon formation for CO$_2$/CH$_4$ > 1 approaches zero, whereas for CO$_2$/CH$_4$ = 0.5 ttails off at 14%. From Figure S1, Supporting Information, it can be seen that all four carbon-forming reactions (Rxn8, Rxn9, Rxn10, and Rxn11) are thermodynamically favorable at the lower

Figure 3. Variation of equilibrium conversion of reactants and product distribution with temperature at four different O$_2$ feed ratios at CO$_2$/CH$_4$ = 1 (− CO$_2$:CH$_4$:O$_2$ = 1:1:1.0, ■ CO$_2$:CH$_4$:O$_2$ = 1:1:0.1, ▲ CO$_2$:CH$_4$:O$_2$ = 1:1:0.2, and □ CO$_2$:CH$_4$:O$_2$ = 1:1:0.3) at a pressure of 1 atm. For a) CH$_4$ conversion, b) CO$_2$ conversion, c) H$_2$ distribution, d) CO distribution, e) carbon distribution, and f) H$_2$O distribution.
temperatures. However, at higher temperatures, only Rxn 8 is favorable, resulting in significant carbon formation for CO$_2$/CH$_4$ < 1, as there is an excess of CH$_4$ being converted to carbon. At higher temperatures, Rxn 9–11 become favorable in the reverse direction, causing the surface carbon to be oxidized. For CO$_2$/CH$_4$ > 1, CH$_4$ is a limiting reactant, leading to Rxn 8 being less favorable and the other carbon forming reactions being unfeasible, resulting in a considerable reduction in carbon formation.

From the thermodynamic analysis, it was found that the temperature and reactant ratio have a significant influence on

| Reaction number [Rxn] | Reaction | $\Delta H_{298}$ [kJ mol$^{-1}$] |
|-----------------------|----------|---------------------------------|
| 14                    | CH$_4$ + 1/2O$_2$ ↔ 2CO + 2H$_2$ | -36.0                           |
| 15                    | CH$_4$ + O$_2$ ↔ CO$_2$ + 2H$_2$O | 802.0                           |
| 16                    | C + 1/2O$_2$ ↔ CO | -110.0                          |
| 17                    | CH$_4$ + H$_2$O ↔ CO + 3H$_2$ | 206.3                            |
| 18                    | C + 2H$_2$O ↔ CO$_2$ + 2H$_2$ | 90.0                             |

**Table 2.** Gas phase reactions in oxidative CO$_2$ reforming and steam reforming, equations obtained from the study by Muraza and Galadima.$^{[25]}$

**Figure 4.** Variation of equilibrium conversion of reactants and product distribution with temperature at four different H$_2$O feed ratios at CO$_2$/CH$_4$ = 1 (– CO$_2$:CH$_4$:H$_2$O = 1:1:0, ■ CO$_2$:CH$_4$:H$_2$O = 1:1:0.1, ▲ CO$_2$:CH$_4$:H$_2$O = 1:1:0.2, and △ CO$_2$:CH$_4$:H$_2$O = 1:1:0.3) at a pressure of 1 atm. For a) CH$_4$ conversion, b) CO$_2$ conversion, c) H$_2$ distribution, d) CO distribution, e) carbon distribution, and f) H$_2$O distribution.
the equilibrium of the reactant conversion and product distribution. From the analysis, operating at a higher temperature (1123–1273 K) is thermodynamically optimal in maximizing reactant conversion and reducing coke formation. However, from an energy consumption and catalyst stability perspective, these high temperatures constitute rather harsh conditions. Coke formation decreases at CO$_2$/CH$_4$ ratios above 1, at the expense of H$_2$ production (Figure S4A, Supporting Information). For CO$_2$/CH$_4$ < 1, there is a significant production of H$_2$ (Figure S4A, Supporting Information), accompanied by a large production of solid carbon, indicating that methane cracking products dominate once the feed becomes CH$_4$ rich.

This analysis highlights the fine balance between syngas production and coke formation in DRM. The choice of feed ratio will be dictated by the main aims of a system. For example, operating at higher CO$_2$/CH$_4$ ratios will allow for a reduction in required

![Figure 5](image-url)
temperature, at a cost of conversion and product ratio. In contrast, if the main aim is to maximize H\(_2\) production, operating at lower CO\(_2\)/CH\(_4\) ratios will be preferable, at the cost of higher temperatures and higher carbon formation. For the goal of producing syngas for downstream Fischer–Tropsch reactions, operating at a feed ratio around 1, above 1123 K and at 1 atm is the thermodynamic optimum for the production of both CO and H\(_2\) at a ratio close to 1. This temperature can only be reduced if catalysts suppressing carbon formation can be developed.

### 2.2. Bi- and Tri-reforming Techniques

Dry reforming is an endothermic process which requires high temperatures, as shown by the results in 2.1; at 1 atm and CO\(_2\)/CH\(_4\) = 1, the temperatures greater than 1123 K are required for high reactant conversion, product ratio of 1, and low carbon formation. There will be high energy requirements to achieve significantly high temperatures at an industrial scale, resulting in enormous operational costs. Catalysts can be used to lower the energy demand required for DRM but they must be able to suppress carbon formation and maintain stable performance at high temperature operation. Another option is to adjust the process conditions by adding O\(_2\) or steam to the feed to suppress coking deactivation while tuning H\(_2\)/CO ratio. This option also requires the development of catalysts that will perform well under sintering conditions.

#### 2.2.1. Effect of Co-Feeding O\(_2\)

The effects of adding different amounts of O\(_2\) to the DRM process, with varying temperatures for CH\(_4\) and CO\(_2\) conversions, and the product distribution of H\(_2\), CO, carbon, and H\(_2\)O are shown in Figure 3. Figure 3 shows that the addition of small amounts of O\(_2\) increases the conversion of CH\(_4\). The increases were due to POM (Table 2, Rxn14) and total oxidation of CH\(_4\) (Table 2, Rxn15). An opposite trend was observed for CO conversion from Figure 3b, where the addition of O\(_2\) reduced the CO conversion. The reduction in CO\(_2\) conversion is due to CH\(_4\) becoming the limiting reactant, as it is involved in DRM and POM. Figure 3c,d shows that adding O\(_2\) reduces the selectivity to both H\(_2\) and CO at temperatures above 1073 K, and the differences become larger for H\(_2\) at larger temperatures. This is explained by the considerable increase in H\(_2\)O produced as a side product from Rxn2 (Table 1) and Rxn15 (Table 2), which is shown in Figure 3f.

Figure 3e shows that the addition of O\(_2\) reduces carbon formation. This trend in carbon formation is in agreement with prior work which also showed a similar behavior, as shown here for CO\(_2\) and CH\(_4\) conversions (decreasing and increasing, respectively, with the addition of O\(_2\))\(^{[31]}\). The addition of O\(_2\) at a ratio of CO\(_2\)/CH\(_4\) = 1.1:0.2, lowers the temperature at which coking becomes negligible carbon to 1023 K (compared with 1223 K for the system without O\(_2\)). The main reasons for the decrease in carbon formation are due to Rxn16 (Table 2), the combustion of solid carbon by O\(_2\). Furthermore, the addition of O\(_2\) forces CH\(_4\) to become a limiting reactant and therefore reduces the extent of methane decomposition (Rxn8 in Table 1). The main explanation for this trend is due to the total oxidation of methane (Rxn15 in Table 2) which produces considerable amounts of H\(_2\)O. In addition, Rxn2 is favorable at higher temperatures (>1073 K) and will also contribute to the H\(_2\)O formation.

From the thermodynamic analysis, it was shown that adding small amounts of O\(_2\) can significantly reduce solid carbon formation at lower temperatures and maintain an H\(_2\)/CO ratio of 1, however, there is considerable loss of syngas production and increase in undesired H\(_2\)O. Therefore, it is recommended to operate at 1 atm and 1023 K at a feed ratio of CO\(_2\)/CH\(_4\): O\(_2\) = 1:1:0.1, to reduce carbon formation while minimizing loss of syngas production and water formation.

#### 2.2.2. Effect of Co-Feeding H\(_2\)O

The potential benefits of adding O\(_2\) have been investigated, however, there are financial and safety concerns related to the use of O\(_2\). In addition, if a reforming plant is to be integrated onto an existing plant which is remote, the availability of relatively pure O\(_2\) will be low. Therefore, the effect of adding H\(_2\)O on DRM will be investigated, as it will reduce the safety concerns and is inexpensive compared with O\(_2\). Traditional bireforming requires feed ratios of CH\(_4\):CO\(_2\):H\(_2\)O = 3:1:2, however, this is to produce a product ratio of H\(_2\)/CO = 2. Therefore, only small amounts of H\(_2\)O will be added in our simulation to take advantage of steam’s ability to reduce carbon formation while maximizing syngas production.

The effects of adding different amounts of H\(_2\)O to the DRM process, with varying temperatures for CH\(_4\) and CO\(_2\) conversions, and the product distribution of H\(_2\), CO, carbon, and H\(_2\)O are shown in Figure 4. Figure 4a shows that the addition of H\(_2\)O decreased conversion of CH\(_4\) at temperatures below 1073 K, however, CH\(_4\) conversion increased with the addition of H\(_2\)O above 1073 K. The increase in CH\(_4\) conversion at higher temperatures is attributed to steam reforming (Rxn17, Table 2) which is favorable at higher temperatures. The significant discrepancy between CO and H\(_2\) production is also due to steam reforming (Rxn17, Table 2) producing 3 moles of H\(_2\) and 1 mole of CO.

Similar to the addition of O\(_2\), it was found that adding small amounts of H\(_2\)O decreases the carbon formation at lower temperatures, without significantly affecting the product distribution of syngas. This is in alignment with some prior work that has investigated the effect of cofeeding steam at much higher levels.\(^{[31]}\) The thermodynamic analysis identifies operation at 1123 K at a feed ratio of CO\(_2\)/CH\(_4\)/H\(_2\)O = 1:1:0.1 at atmospheric pressure.

| Table 3. The compositions (in mol%) used for each scenario in the thermodynamic analysis. |
|---|---|---|---|
| Scenario 1 [NatGas/CO\(_2\)] | Scenario 2 [Vented Gas] | Scenario 3 [LFG] |
| CH\(_4\) | 47.26 | 23.82 | 44.00 |
| CO\(_2\) | 50.05 | 51.39 | 50.00 |
| C\(_2\)H\(_6\) | 1.25 | 22.47 | – |
| C\(_3\)H\(_8\) | 0.10 | 1.78 | – |
| n-C\(_4\)H\(_10\) | 0.02 | 0.27 | – |
| iso-C\(_4\)H\(_10\) | 0.02 | 0.27 | – |
| N\(_2\) | 0.80 | – | 5.00 |
| O\(_2\) | 0.05 | – | 1.00 |
2.2.3. Effect of Co-Feeding O\(_2\) and H\(_2\)O

The addition of different amounts of H\(_2\)O and O\(_2\) were investigated to take advantage of trireforming and are shown in Figure 5. It was found that the addition of CO\(_2\):CH\(_4\):H\(_2\)O:O\(_2\) = 1:1:0.05:0.05 was optimum of all feed ratios in reducing carbon formation, while maintaining syngas production.

2.3. Industrial Sources of CO\(_2\) and CH\(_4\) for DRM

2.3.1. Identifying Industrial Feedstocks for DRM

Typical composition ranges reported for pipeline grade natural gas, flared or vented natural gas, and LFG are provided in the Supporting Information with a discussion of how they were adapted to the Aspen Plus simulation. Table 3 shows the compositions of various feedstocks used for this thermodynamic analysis which represent 3 scenarios:

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**Figure 6.** Variation of equilibrium conversion of reactants and product distribution with temperature of using a natural gas/CO\(_2\) mixture as a feed for DRM compared with base case identified in Section 3 (– CO\(_2\):CH\(_4\) = 1:1, ● NatGas/CO\(_2\), ■ NatGas/CO\(_2\)+O\(_2\), and ▲ NatGas/CO\(_2\)+H\(_2\)O) at a pressure of 1 atm. For a) CH\(_4\) conversion, b) CO\(_2\) conversion, c) H\(_2\) distribution, d) CO distribution, e) carbon distribution, and f) H\(_2\)/CO ratio.
1) Scenario 1: The feed is a mixture of pipeline natural gas and captured CO$_2$; 2) Scenario 2: The feed is vented natural gas; 3) Scenario 3: The feed is LFG

2.3.2. Scenario 1: Reforming Pipeline Grade Natural Gas using Captured CO$_2$

The thermodynamic simulation of Scenario 1 compared with the base case and the addition of O$_2$ and H$_2$O, with varying temperatures for CH$_4$ and CO$_2$ conversions, the product distributions of H$_2$, CO, carbon, and the syngas ratio are shown in Figure 6. The natural gas/CO$_2$ mixture performs almost identically to that of the base case, due to the feed ratio (CH$_4$/CO$_2$) being close to 1. Figure 6f shows that scenario 1 reduces the syngas (H$_2$/CO) ratio below 1. However, the addition of O$_2$ restores the syngas ratio to 1 and the addition of H$_2$O increases the ratio above 1. Furthermore, the addition of O$_2$ significantly reduces carbon formation with minimal effect on H$_2$ and CO production.

![Figure 6](image_url)

**Figure 6.** Variation of equilibrium conversion of reactants and product distribution with temperature of using upstream vented gas as a feed for DRM compared with base case identified in Section 3 (– CO$_2$:CH$_4$ = 1:1, ○ vented gas, ■ vented gas + O$_2$, and △ vented gas + H$_2$O) at a pressure of 1 atm. For a) CH$_4$ conversion, b) CO$_2$ conversion, c) H$_2$ distribution, d) CO distribution, e) carbon distribution, f) and H$_2$/CO ratio.
From a thermodynamic perspective, scenario 1 is identified as an opportunity to implement DRM while maintaining excellent control over reaction conditions and hence the resulting syngas composition and extent of catalyst deactivation. The positive results suggest that upstream flared gas from gas processing operations can also be used in the place of natural gas, to utilize the waste natural gas along with CO$_2$ that is typically captured in such a process.

2.3.3. Scenario 2: Vented Gas

The CH$_4$ and CO$_2$ conversions, the product distribution of H$_2$, CO, carbon, and the syngas ratio are for the thermodynamic simulation of Scenario 2 compared with the base case and the addition of O$_2$ and H$_2$O, with varying temperatures shown in Figure 7. Figure 7a shows that the presence of large amounts of C$_2$H$_6$ in the mixture significantly reduces the CH$_4$ conversion,

![Figure 7](image-url)
while having minimal effect on CO₂ conversion (Figure 7b), suggesting that ethane dry reforming is competing with methane dry reforming. Furthermore, Figure 7c,d shows that the product distribution of H₂ and CO is unaffected and the syngas H₂/CO ratio is larger than 1 (Figure 7f), which is favorable, as natural gas streams containing a higher concentration of higher hydrocarbons can still be used for DRM to produce syngas suitable for applications such as Fischer–Tropsch synthesis. Nevertheless, Figure 7e shows that the presence of higher hydrocarbons considerably increases carbon formation, leading to the need for higher-performance catalysts that can suppress coking under these conditions. This analysis highlights the research need to test catalysts under realistic feed conditions and motivates the development for robust catalytic processes that will maintain high performance for the dry reforming of mixed hydrocarbon feeds.

2.3.4. Scenario 3: LFG

The thermodynamic simulation of scenario 3 compared with the base case and the addition of O₂ and H₂O, with varying temperatures for CH₄ and CO₂ conversions, the product distributions of H₂, CO, carbon, and the syngas ratio are shown in Figure 8. It can be observed that LFG exhibits similar results to that of Scenario 1, however, the difference from the base case is larger as the feed ratio CO₂/CH₄ is greater for scenario 3 than scenario 1. Moreover, there is an initial amount of O₂ in the system which is favorable as it results in lower extent of carbon formation. In addition, the higher feed ratio results in a syngas ratio H₂/CO below one. N₂ is an inert gas, and thus will have no effect on the reaction, aside from a dilution effect.

3. Conclusion

The use of upstream natural gas, flared gas, and LFG would be suitable feed sources for implementing DRM to produce syngas for some synthesis applications such as Fischer–Tropsch. It has been shown that DRM is sensitive to the presence of higher hydrocarbons in the feed in terms of carbon formation and therefore, a suitable feed source should contain minimal nonmethane organic compounds. However, more measurements of upstream and downstream flared and vented gas composition are required, as the utilization of these waste streams would significantly reduce GHG emissions of the oil and gas industries. An impactful experimental research direction will be to carry out DRM catalyst testing under such realistic conditions, which will link catalyst performance to opportunities in commercial deployment that will also result in a reduction of GHG emissions. It was found that the addition of small quantities of O₂ reduced the energy demand of DRM and minimized the carbon formation. Similarly, the addition of small amounts of H₂O increased the syngas H₂/CO ratio and reduced the carbon formation. These findings identify LFG and reforming of methane using captured CO₂ as potential scenarios of favorable operation and motivate the search for coking resistant and thermally stable DRM catalysts that can function under these feed streams.

4. Experimental Section

Thermodynamic calculations were conducted using a total Gibbs free energy minimization method with Aspen Plus V9, Aspen Tech. The Gibbs free energy minimization method assumed that the system had reached thermodynamic equilibrium if the total Gibbs free energy was at its minimum value and its applications had been described in previous works to carry out equilibrium calculations for a variety of processes related to energy conversion.[52–57] The total Gibbs free energy of a system (G) was related to the chemical potential of chemical species i (μᵢ), and the number of moles of species i (nᵢ) as follows.

\[ G = \sum nᵢμᵢ \]  

All thermodynamic properties, including chemical potential were calculated using the equation of state which described the relationship between pressure, volume, and temperature of pure components and mixtures. The Soave–Redlich–Kwong (SRK) model was used as the equation of state and is briefly presented in the following paragraph.[58] The SRK model was chosen due to the presence of polar compounds as byproducts.

\[ P = \frac{RT}{(V_m - b)} - \frac{a(T)}{V_m(V_m + b)} \]  

where \( P \) is pressure, \( V_m \) is the molar volume, \( R \) is the ideal gas constant, \( T \) is temperature, \( a(T) \) is a temperature-dependent correction factor for the attraction between molecules, and \( b \) is a correction factor related to volume.

The effects of varying pressure, temperature, and feed ratio on CH₄ and CO₂ conversion, H₂, CO, H₂O, and carbon product distribution were determined using an R-Gibbs reactor (Figure 9), where the feed stream composition was varied to investigate different applications for dry reforming. Various techniques such as bi-reforming, oxy-reforming, and tri-reforming were explored as methods to enhance the DRM process.

Figure 9. Flowsheet used in Aspen Plus simulation to carry out thermodynamic calculations via the Gibbs free energy minimization method.
by reducing carbon formation and to increase CH$_4$ conversion. Therefore, a thermodynamic investigation was conducted to investigate the addition of O$_2$, H$_2$O, and both on the DRM process. The reaction temperature was varied between 773 and 1373 K and pressure was varied between 0.1 and 10 atm to analyze the effect of temperature and pressure on the DRM reaction and its side reactions. These simulations were then used to identify optimal conditions which maximize syngas production and minimizing side reactions, especially coke formation. In addition, the feed ratio (CO$_2$/CH$_4$) was varied between 0.5 and 3.0, to accurately simulate the different waste streams that could be used as a feed source.

The conversion of a chemical species $i$ is defined as

$$\text{Conversion} = \frac{N_{\text{in}} - N_{\text{out}}}{N_{\text{in}}} \quad (4)$$

where $N_{\text{in}}$ and $N_{\text{out}}$ are the molar flow rates of species $i$ at the inlet and outlet of the R-Gibbs reactor, respectively.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

Keywords

Aspen Plus, CO$_2$ utilization, dry reforming, methane valorization, thermodynamic analysis

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