

A Process Integration Approach to the Assessment of CO₂ Fixation through Dry Reforming

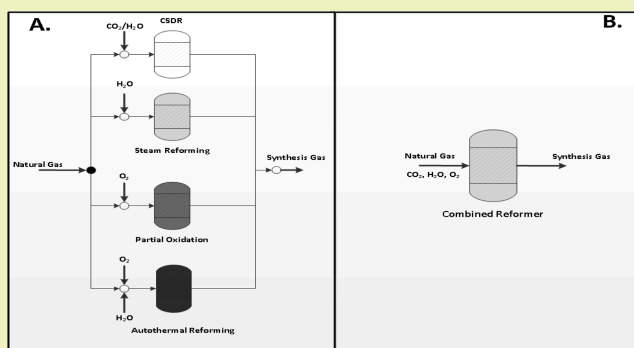
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ABSTRACT: Recently, significant research has been dedicated to the field of mitigating CO₂ emissions. Chemical sequestration (fixation) of CO₂ into value-added products (e.g., methanol, Fischer–Tropsch liquids, propylene) is an emerging option. The fixation of CO₂ via the dry reforming (DR) of natural gas involves the conversion of two greenhouse gases (carbon dioxide and methane) into a useful intermediate (synthesis gas). Synthesis gas can be subsequently converted into various chemicals and fuels. Nevertheless, syngas produced from DR is typically characterized by a H₂:CO ratio lower than that typically required for conversion into high-value hydrocarbons. In addition, DR catalysts continuously deactivate as a result of extensive coke formation. This paper focuses on quantifying the potential for CO₂ fixation using dry reforming and the integration of different reforming technologies. The results highlight the strong inverse relationship between CO₂ chemical fixation and the required syngas H₂:CO ratio. Combined reforming involving DR and steam reforming greatly benefits from the presence of waste heat sources because heat generation is the major source of CO₂ generation. A process case study is presented to illustrate the importance of a process viewpoint with respect to DR.

KEYWORDS: Greenhouse gas emissions, CO₂ capture and sequestration, CO₂ fixation, Dry reforming



INTRODUCTION

In recent years, societies and governments have begun to change their fundamental views on the impact of human development on climate change. Increased fossil fuel use, deforestation, and industrial activity have all contributed to the escalation of greenhouse gas (GHG) emissions. The debate has shifted to focus on the reduction of GHG generation in new systems and the mitigation of existing sources.^{1,2}

Energy use and in particular hydrocarbon fuel combustion represents the largest source of emissions.³ CO₂ emission from fuel combustion is the single largest source of GHG emissions. Together the electricity/heat generation (42%) and industrial (21%) sectors are responsible for nearly two-thirds of the total worldwide CO₂ emissions.³ With increasing population, growing energy demand, and developing economies, the amount of emitted CO₂ is only expected to increase. As a result, significant research effort has been dedicated to mitigating CO₂ through emission reduction, capture and sequestration, and utilization. In terms of reduction, the use of renewable energy (i.e., solar, hydro, biomass, wind, etc.) has steadily increased in recent years.^{4–6} Increased energy efficiency and conservation through improved industrial process design is also expected to lead to reduction in CO₂ emissions.⁷ While a shift in fossil utilization from coal to natural gas also results in lower CO₂ emissions, increased use of natural gas increases the probability of methane leakage and emissions. Given the

potency of methane as a GHG (33 times greater than CO₂ for 20-year horizon), this may present new challenges.⁸

For CO₂ emissions from existing large stationary sources, CO₂ capture and storage (CCS) has received substantial attention.^{9,10} Following capture and storage, the focus shifts to identifying opportunities to physically sequester or chemically convert CO₂. Physical sequestration includes the physical reuse of CO₂ (e.g., enhanced oil recovery, geothermal fluid, beverages). Chemical conversion (fixation) is the chemical conversion of CO₂ into value-added products (e.g., methanol, ethanol, propylene).^{11–13}

Dry reforming (DR) is the chemical reaction between CO₂ and hydrocarbons (primarily methane) to produce synthesis gas (syngas, a mixture of carbon monoxide and hydrogen). The potential to convert two greenhouse gases (carbon dioxide and methane) into a useful intermediate (syngas) makes DR an attractive option for the chemical fixation of CO₂.¹⁴ This syngas can be used to produce a variety of products, including chemicals, synthetic liquid fuels, and polymers.¹⁵ Nonetheless, DR faces a variety of processing and technical challenges that have hindered its commercial application.¹⁶ From an economic perspective, DR needs a concentrated source of CO₂ to supply

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the necessary quantities of CO₂ to justify the capital investment of the reforming system. Catalyst deactivation due to solid carbon deposition is also a major issue that has garnered attention.¹⁷

Typical syngas conversion technologies require a high H₂:CO ratio such as methanol (2:1)¹⁸ and Fischer–Tropsch synthesis (1.7:1 to 2.2:1).¹⁹ Mixed alcohols synthesis is one of the few viable options for syngas with a H₂:CO ratio close to 1:1.²⁰ Otherwise, DR of syngas requires substantial ratio adjustment to meet specifications for other conversion technologies. This ratio adjustment can be conducted by combining DR with other reforming technologies that produce a syngas with a higher H₂:CO ratio. For example, steam reforming (SR) of natural gas can produce syngas with a H₂:CO ratio that typically ranges from 3 to 6. A water–gas-shift (WGS) reactor can also be used to adjust the syngas ratio. To date, the implication of these H₂:CO ratio requirements on CO₂ generation and the prospects of a process that fixates CO₂ using DR have not been thoroughly investigated.

Extensive research has focused on the DR of natural gas from a reaction engineering perspective. Wang et al.¹⁴ investigated the reaction mechanism and appropriate catalyst selection for the production of syngas from the DR of natural gas. Guo et al.²¹ studied the use of different catalyst support for nickel catalysts. Laosiripojana et al.²² studied the doping of CeO₂ on a nickel-based catalyst to improve activity and resistance to carbon formation. Various studies have also proposed combining steam and dry reforming for the mitigation of solid carbon deposition.^{23–26} These studies focus on the reformer performance and in particular catalyst activity, stability, and reaction mechanisms. This work addresses the broader question of whether a process based on the DR of natural gas can be used to chemically fixate CO₂ (by producing less CO₂ than consumed). What is the appropriate reforming technology? What is the quality of the produced syngas? What product is made from such a process? In this paper, initial emphasis is on establishing the CO₂ fixation targets for the various reforming options. First, the amount of CO₂ that can be strictly fixated in DR is investigated. This includes quantifying the impact of reformer operating temperature, pressure, and feed ratios. This is followed by quantification of the energy required for CO₂ fixation and CO₂ emissions associated with energy generation. The findings are subsequently used to investigate possible products that can potentially lead to a sample process that fixates CO₂. Finally, a process is designed based on the chosen products to determine if overall CO₂ fixation using DR can be achieved. This includes the use of mass and heat integration to maximize resource utilization and reduce the external energy requirement.

■ APPROACH

Given the substantial energy and cost associated with the reformer section, particular focus is directed at modeling the different reforming technologies. In most syngas processing routes, the reforming section is operated at relatively high temperatures (800–1400 °C).²⁷ Reformer selection is a complex decision and highly dependent on the downstream application and particular technology provider. In fact, this selection can be different for even the same downstream application. For instance, the world's largest gas-to-liquid (GTL) plants, the Shell Pearl Project and Sasol/Chevron Oryx GTL projects, use partial oxidation (POX) and autothermal reforming (ATR), respectively. Methanol synthesis

can also utilize different reforming approaches (partial oxidation or steam reforming).

Various literature sources indicate that reformer catalysts are typically capable of achieving compositions close to equilibrium,^{27–29} and thus, equilibrium models can be used to give a good estimate of reformer conversion. Equilibrium modeling is not only useful in investigating specific scenarios but also in establishing the impact of certain variables on the reforming system. In this paper, the total Gibbs free energy minimization method is used to model the reforming section. The method of Lagrange undetermined multipliers is used to find a set of molar distribution n_i that minimizes the total Gibbs free energy of the system for a specified temperature and pressure. This can be expressed as¹⁶

$$\sum_{i=1}^N n_i \left(\Delta G_{f_i}^0 + RT \ln \frac{y_i \hat{\phi}_i P}{P^0} + \sum_k \lambda_k a_{ik} \right) = 0 \quad (1)$$

where $\Delta G_{f_i}^0$ is the standard Gibbs of formation for species i , R is the molar gas constant, T the temperature (K), y_i is the mole fraction, $\hat{\phi}_i$ is the fugacity coefficient of species i , P is the pressure, and λ_k the Lagrange multiplier for element k . This is subject to the mass balance constraints described by eq 2, where a_{ik} is the number of atoms of the k^{th} element, and A_k is the total mass of the k^{th} element.

$$\sum_i n_i a_{ik} = A_k \quad (2)$$

Nourelidin et al.¹⁶ details the use of thermodynamic equilibrium modeling to identify the optimal reforming configurations to maximize syngas yield and achieve specific economic objectives. The model is capable of calculating the reformer output composition and corresponding reformer energy balance. The following species were chosen to represent the reforming system: CH₄ (g), CO₂ (g), CO (g), H₂O (g), and H₂ (g). The model is capable of calculating the reformer output composition and corresponding reformer energy balance. Coking is modeled as graphite C_(s), and a multiphase formulation is used, where n_c is the number of moles of carbon, and $\Delta G_{fC(s)}^0$ is the standard Gibbs of formation of graphite (eq 3).

$$\sum_{i=1}^{N-1} n_i \left(\Delta G_{f_i}^0 + RT \ln \frac{y_i \hat{\phi}_i P}{P^0} + \sum_k \lambda_k a_{ik} \right) + (n_c \Delta G_{fC(s)}^0) = 0 \quad (3)$$

The model was implemented in optimization software (LINGO) and in MATLAB to generate plots highlighting thermodynamic trends. The model was used to investigate defined scenarios (set inputs) and to find optimal solutions for defined objectives. In the formulation, the oxidant chosen (CO₂, H₂O, O₂) and reformer output temperature were allowed to vary. The inputs were defined as follows:

$$n_{\text{in}} \text{CH}_4 = 1 \text{ mol} \quad (4)$$

$$n_{\text{in}} \text{CO}_2 = x \times n_{\text{in}} \text{CH}_4 \quad (5)$$

$$n_{\text{in}} \text{H}_2\text{O} = y \times n_{\text{in}} \text{CH}_4 \quad (6)$$

$$n_{\text{in}} \text{O}_2 = z \times n_{\text{in}} \text{CH}_4 \quad (7)$$

where x, y, z are the number of moles of CO₂, H₂O, and O₂ fed per mol of CH₄, respectively.

Table 1. Impact of Pressure on Dry Reforming^a

pressure (bar)	1	5	10	15	20	25
CH ₄ conversion (%)	98.7	94.3	90.1	86.9	84.3	82.2
energy input (MJ/h)	34,912	32,244	29,862	28,105	26,740	25,639
CO ₂ associated with energy generation (kmol/h)	40	37	34	32	30	29
equivalent temperature (K) ^b	1,200	1,440	1,570	1,653	1,717	1,769
CH ₄ for energy generation (kmol/h)	40	37	34	32	30	29
syngas H ₂ :CO ratio	1	1.03	1.05	1.07	1.08	1.09
reformer output mole flow (kmol/h)						
CH ₄	1.3	5.7	9.9	13.1	15.7	17.8
CO ₂	2.0	8.5	14.0	18.0	21.0	23.3
H ₂ O	2.8	11.9	20.2	26.3	31.1	35.0
CO	193.1	171.1	151.8	137.8	127.0	118.3
H ₂	194.5	176.6	160.0	147.5	137.6	129.4
C _(s)	3.5	14.7	24.3	31.2	36.4	40.5
CO ₂ fixated (mol/mol CH ₄ in reformer feed)	0.58	0.55	0.52	0.50	0.49	0.48
CO ₂ fixated (mol/mol CH ₄ total consumption)	0.41	0.40	0.39	0.38	0.38	0.37

^aT = 1200 K, CH₄ = 100 kmol/h, CO₂ = 100 kmol/h. ^bRequired temperature to achieve CH₄ conversion at T = 1200 K and P = 1 bar.

The reformer input temperature was assumed to be 300 K. In addition, the oxidant to methane ratio was bound to ensure a minimum methane input of 20 mol %.

These variables are allowed to vary as follows:

$$500 \leq T_{\text{out}} \text{ (K)} \leq 1500 \quad (8)$$

$$0 \leq x \leq 4 \quad (9)$$

$$0 \leq y \leq 4 \quad (10)$$

$$0 \leq z \leq 2 \quad (11)$$

$$x + y + z \leq 4 \quad (12)$$

The conversion of natural gas to hydrogen and carbon monoxide is suppressed as the pressure increases. In practice, reformers are typically operated at pressures ranging from 20.0 to 40.0 bar.²²

The CO₂ produced by the reforming section includes the reformer CO₂ output and the CO₂ emissions due to external heat generation (e.g., burning of natural gas). According to the U.S. Energy Information Administration (EIA), approximately 117 lbs of CO₂ are emitted per million BTU of energy from natural gas. This is equivalent to approximately 1.14 mol per MJ of energy. This is used to calculate the CO₂ produced during heat generation. The fixation of CO₂ in the reformer section is defined as

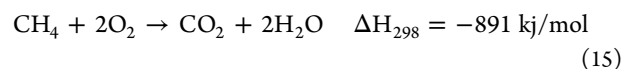
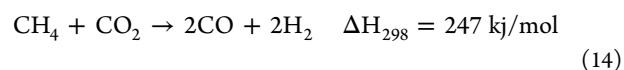
$$M_{\text{CO}_2}^{\text{RS}} = M_{\text{CO}_2}^{\text{RI}} - M_{\text{CO}_2}^{\text{RO}} - M_{\text{CO}_2}^{\text{E}} \quad (13)$$

where $M_{\text{CO}_2}^{\text{RS}}$ is the number of moles of CO₂ chemical fixated by the reforming, $M_{\text{CO}_2}^{\text{RI}}$ is the number of moles of CO₂ fed to the reformer, $M_{\text{CO}_2}^{\text{RO}}$ is the number of moles of CO₂ generated in the reformer, $M_{\text{CO}_2}^{\text{E}}$ is the number of moles of CO₂ produced during external heat generation by combusting methane, and $M_{\text{CO}_2}^{\text{RS}}$, $M_{\text{CO}_2}^{\text{RI}}$, $M_{\text{CO}_2}^{\text{RO}}$, and $M_{\text{CO}_2}^{\text{E}}$ are in relation to one mole of methane fed to the reformer.

The model was solved using the LINGO global solver. The solution times ranged from 10 to 120 s using an Intel i5-2500 CPU @ 3.30 GHz.

RESULTS

Stoichiometric Targets for DR. The DR reaction is an endothermic reaction and requires a considerable amount of heat input. According to reaction 14, one mole of carbon dioxide can be sequestered per mole of methane.



Consideration must also be given to the heat requirement and associated CO₂ generation. Assuming the use of methane as the energy source, approximately 0.28 mol of CO₂ is generated during heat generation for the conversion of one mole of CO₂ into syngas. This requires an equivalent amount of methane (0.28 mol). Thus, from a combined mass and energy perspective, 0.72 mol of CO₂ can be sequestered per 1.28 mol of methane using DR to produce syngas with a H₂:CO ratio of 1:1. This is equivalent to 0.56 mol of CO₂ per mole of methane. This represents a combined mass/energy stoichiometric target for CO₂ fixation using DR.

Equilibrium Targets for Dry Reforming. In a reformer assumed to operate at a CH₄:CO₂ molar feed ratio equal to 1:1, T = 1200 K and P = 2 MPa (typical of SMR operating conditions), the amount of CO₂ that can be sequestered is approximately 0.38 mol of CO₂ per mole of methane. This includes the methane required for energy generation and produces a syngas with a H₂:CO ratio slightly higher than stoichiometric ratio (1.08:1.0). Therefore, roughly 70% of the stoichiometric target can be achieved using a dry reforming reactor while also accounting for the external energy required.

Higher reformer operating pressure has a strong effect on the reformer conversion, syngas ratio, and CO₂ conversion. Higher pressure depresses methane conversion leading to lower H₂ and CO yield while also increasing coke formation (Table 1). To achieve the same CH₄ conversion, a significant temperature increase is required to offset the impact of higher pressures. From a CO₂ fixation perspective, lower pressure results in higher CO₂ fixation. An increase in reformer operating pressure from 1 to 25 bar reduces the achievable CO₂ fixation from 0.41 to 0.37 per mol of methane. This slight reduction in CO₂ fixation indicates that pressure would be set by other

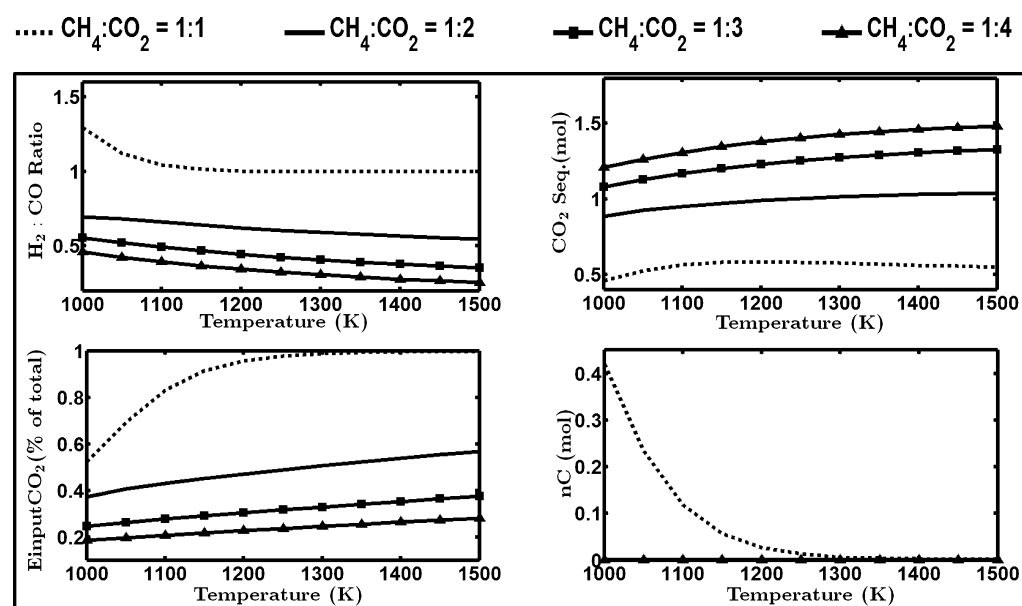


Figure 1. Effect of $\text{CO}_2:\text{CH}_4$ ratio on specific reformer outputs ($P = 1$ bar).

considerations as it has a small impact on the CO_2 fixation. The major benefit of higher pressure is significant reduction in reactor size and the need for compression prior to downstream processing. This becomes a major economic driver to operate reformers at higher pressures. However, this may lead to the recycle of syngas to convert unreacted natural gas.

Figure 1 presents the impact of carbon dioxide to methane feed ratio on CO_2 fixation, syngas $\text{H}_2:\text{CO}$ ratio, and coke formation at a specific pressure ($P = 1$ bar). As the $\text{CO}_2:\text{CH}_4$ ratio increases from 1:1 to 4:1, the amount of CO_2 sequestered increases to more than 1.25 mol per mole of methane. However, the increase in carbon dioxide to methane ratio is also associated with a decrease in the syngas $\text{H}_2:\text{CO}$ ratio. Such a syngas is considered of low value and has limited application. Figure 1 also shows that higher $\text{CO}_2:\text{CH}_4$ ratios reduce the amount of coke formation. This could be attributed to CO_2 serving as an oxidant when present in excess.

For a $\text{CO}_2:\text{CH}_4$ ratio of 1:1, the CO_2 produced during energy generation constitutes the bulk of the CO_2 produced. This shows that with the presence of waste heat sources and/or appropriate heat integration the majority of the CO_2 associated with energy generation can be reduced or avoided. As the CO_2 to CH_4 feed ratio increases, CO_2 generation in the reformer begins to constitute a bigger fraction of the total CO_2 produced.

There is a strong inverse relationship between CO_2 fixation and the produced syngas $\text{H}_2:\text{CO}$ ratio. These DR targets suggest that maximum CO_2 fixation is favored by lower operating pressure, higher $\text{CO}_2:\text{CH}_4$ feed ratios, and lower syngas $\text{H}_2:\text{CO}$ ratios. However, process economics favor higher operating pressure, lower $\text{CO}_2:\text{CH}_4$ feed ratios, and higher $\text{H}_2:\text{CO}$ ratios. Thus, a trade-off exists between the ability to fixate CO_2 using reforming and the quality/value of the syngas produced. This suggests that the commercial viability of DR will require combining DR with other reforming technologies to mitigate coke formation and produce a syngas of sufficient quality for utilization.

Equilibrium Targets for Combined Reforming. Dry reforming of natural gas can be combined with other reforming technology. Steam (steam reforming) and oxygen (partial oxidation) are also used to oxidize natural gas for syngas

production. These oxidants (CO_2 , H_2O , O_2) can be combined in a single reformer (combined reforming). They can also be carried out in individual reformers (parallel reforming) and the outputs combined together. Steam reforming (SR) is the predominant syngas generation technology for hydrogen production. Partial oxidation (POX) is typically used for syngas applications requiring a 2:1 $\text{H}_2:\text{CO}$ ratio.³⁰ Reformer combinations benefit by increasing the advantage and reducing the drawback associated with each technology. For example, autothermal reforming (ATR) combines oxygen and steam. The addition of oxygen helps to balance the endothermic nature of SR leading to a reduction in the external heat requirement. Table 2 presents typical operating conditions and outputs for the various reforming options in comparison to DR.

Typically, POX and ATR operate at lower oxidation ratios compared to steam reforming, which results in a lower rate of CO_2 generation (Table 2). Partial oxidation and ATR also give much higher single-pass methane conversion. The high steam

Table 2. Comparison of Typical Operating Conditions for Reforming Technology³¹

	SR	POX	ATR	DR
operating conditions				
temperature ($^{\circ}\text{C}$)	850	1350	1050	950
pressure (bar)	20	25	25	20
molar input ratios				
CH_4	1	1	1	1
H_2O	3	0	0.6	0
O_2	0	0.7	0.6	0
CO_2	0	0	0	1
outputs (kmol/h)^a				
CH_4	16	0	2	14
CO_2	31	6	16	18
H_2O	184	34	66	27
H_2	284	166	189	145
CO	53	94	82	138
$\text{C}_{(s)}$	0	0	0	31

^a100 kmol/h methane feed basis.

to methane ratio used in steam reforming results in a large quantity of steam in the reformer output. This unreacted steam leads to a higher external heat requirement. However, the hydrogen yield of steam reforming is much greater compared to the other technologies making it advantageous for hydrogen production.

Partial oxidation is exothermic, while ATR can be operated either slightly endothermic or adiabatic depending on the chosen O₂:H₂O feed ratio. Steam reforming requires the most external heating, which increases the generation of CO₂ associated with heat generation (Table 3). The endothermic

Table 3. Comparison of Key Outcomes for Various Reforming Options

key findings ^a	SR	POX	ATR	DR
H ₂ :CO ratio	5.4	1.8	2.3	1.1
syngas yield (mol/mol methane)	3.4	2.6	2.7	2.8
syngas yield (g/g methane)	1.3	1.9	1.7	2.6
energy input (MJ/h)	45,766	-530	5,164	28,296
energy associated CO ₂ (kmol/h)	52	0	6	32
total generated CO ₂ (kmol/h)	83	6	22	50
fixated CO ₂ (mol/mol methane)	-	-	-	0.50
fixated CO ₂ includes methane for heat generation (mol/mol methane)	-	-	-	0.38

^a100 kmol/h methane feed basis.

nature of DR also results in a significant generation of energy-associated CO₂. Of these reforming options, partial oxidation has the lowest total generation of CO₂

These results confirm that each reforming technology offers particular benefits, and the combination of multiple oxidants may result in a more beneficial reforming section. The following sections detail the combination of particular oxidants to dry reforming: steam and oxygen. This is followed by an analysis to determine the optimal oxidant combination and reformer configuration (combined reformer or parallel reforming) to achieve particular syngas H₂:CO ratios.

Combined Dry Reforming and Steam Reforming (CDSR). Dry reforming produces a large amount of coke (Table 4), which means that its commercial success will require the change in operating conditions or the inclusion of an additional oxidant. Changes to operating conditions for DR would require further research to identify catalysts capable of operating at higher temperatures. Combined dry and steam reforming (CDSR) provides an opportunity to mitigate coke formation and increases the H₂:CO ratio. An analysis was conducted to determine the minimum amount of steam necessary to avoid coking while using the operating conditions previously described for DR. Table 4 shows that a CO₂:H₂O input ratio of 1:0.4 is sufficient to thermodynamically hinder coke formation. This steam addition only results in a slight H₂:CO ratio increase but also results in a higher syngas yield due to greater methane conversion. While the additional steam mitigates coke formation, it also leads to an increase in CO₂ production, reducing the amount of CO₂ that could be fixated from 0.38 to 0.27 (mol/mol of methane).

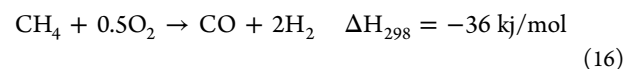
Combined Dry Reforming and Partial Oxidation (CDPOX). Research efforts have also been dedicated to the combination of dry reforming and partial oxidation. In such a configuration, the oxygen in the reformer reacts with methane

Table 4. Impact of Combining DR + SR for Coking Mitigation

	DR	DR + SR
operating conditions		
temperature (°C)	950	950
pressure (bar)	20	20
molar input ratios		
CH ₄	1	1
H ₂ O	0	0.4
O ₂	0	0
CO ₂	1	1
outputs (kmol/h)^a		
CH ₄	14	16
CO ₂	18	22
H ₂ O	27	34
H ₂	145	174
CO	138	162
C _(s)	31	0
H ₂ :CO ratio	1.05	1.07
energy input (MJ/h)	28,296	34,752
energy associated CO ₂ (kmol/h)	32	40
total generated CO ₂ (kmol/h)	50	62
energy associated CH ₄ (kmol/h)	32	40
fixated CO ₂ (mol/mol methane)	0.5	0.38
fixated CO ₂ includes energy associated CH ₄ (mol/mol methane)	0.38	0.27

^a100 kmol/h methane feed basis.

(reaction 16) to produce a syngas with a H₂:CO ratio close to 2:1 while providing heat for dry reforming to occur.



The two reformers can also operate in parallel with the exit streams being combined. It is important to determine which configuration is more appropriate for various objectives. Table 5 presents a comparison between a CDPOX reformer and DR/combustor configuration to generate the required heat. The

Table 5. Comparison of Combined CDPOX and DR/Combustor^a

	DR/combustor	CDPOX
reformer input (mol)		
CH ₄ input	1	1.51
CO ₂ input	2	2
O ₂ input	-	1.03
temperature (K)	1400	1020
reformer output (mol)		
CH ₄ conversion (%)	100	100
H ₂	1.45	1.93
CO	2.55	2.03
CO ₂	0.45	1.47
energy input (kJ)	457	-
combustor input/output (mol)		
CH ₄ combustion	0.51	-
O ₂ combustion	1.03	-
CO ₂ combustion	0.51	-
total CO ₂ generation (mol CO ₂)	0.96	1.47
fixated CO ₂ includes energy associated CH ₄ (mol/mol methane)	0.69	0.35

^aP = 1 bar.

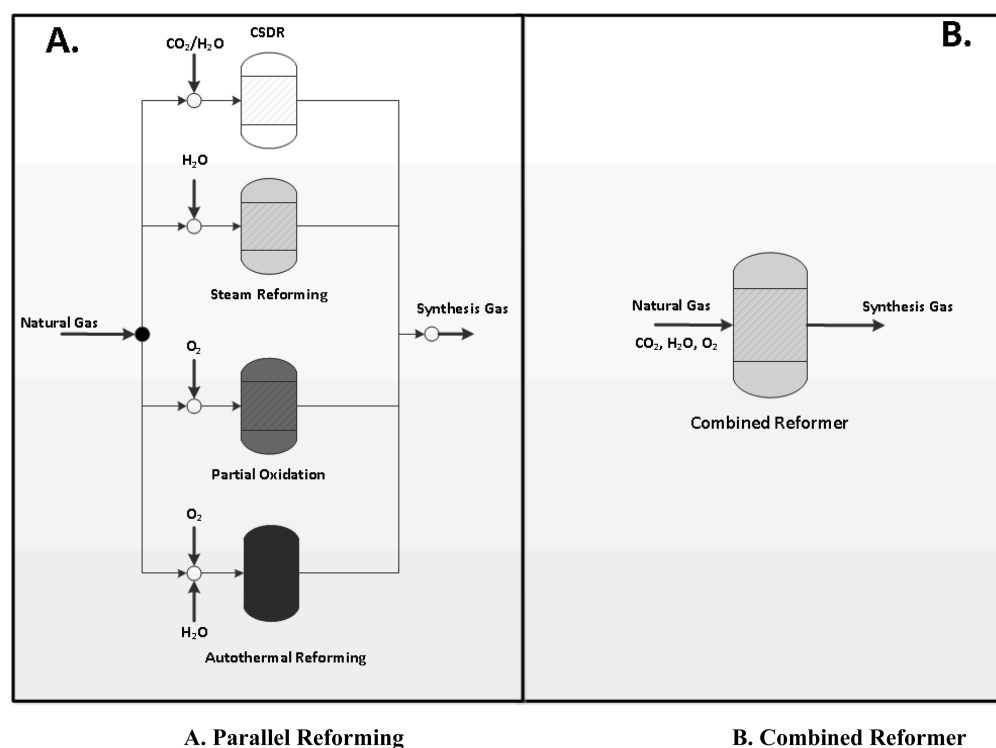


Figure 2. (A) Parallel reforming. (B) Combined reformer.

analysis shows that combining DR and POX produces more CO_2 than simply carrying out DR and using a combustor to produce the required energy. Carbon dioxide is not only produced in the reformer during the combustion of methane but also through the apparent reduction in CO_2 utilization in the reformer. This leads to a higher reformer CO_2 output. The presence of oxygen in the reformer also increases the H_2 :CO ratio.

If the syngas produced by DR is fed to a water–gas shift reactor (WGSR) to achieve the ratio produced by combined DR and POX, the subsequent adjustment would produce additional CO_2 . This additional CO_2 and the amount produced by DR is approximately the same as that produced by CDRPOX. The amount of oxygen required for complete methane combustion (2 mol/mol of methane) is much higher than that required for partial oxidation (0.5 mol/mol of methane). This assessment shows that the major consideration in CO_2 fixation is the required H_2 :CO ratio of the syngas produced and not in particular the number of steps involved in achieving the ratio.

Selection of Optimal Combined Reformer. The combined effect of all the oxidants can lead to synergistic opportunities while allowing for improved heat transfer because the reactions are combined in a single reformer. The use of a single reformer also benefits from economies of scale compared to using separate smaller reformers (Figure 2). However, the use of a single reformer removes the ability to operate at multiple operating conditions.

From a broader perspective, the objective is to identify the configurations best suited to maximize CO_2 fixation while also producing a syngas of use in downstream processing options. Given the trade-off that exists, it is important to quantify the amount of CO_2 that can be fixated while producing syngas with a specific H_2 :CO ratio. For this analysis, the optimization

formulation presented in eqs 8–12 is used to identify the optimal oxidants and operating temperature.

Table 6 presents the combined reformer to maximize CO_2 fixation while achieving a particular H_2 :CO ratio. The optimal

Table 6. Optimal Combined Reformer for Maximum CO_2 Fixation While Achieving a Particular H_2 :CO Ratio^a

H_2 :CO	1.0	1.2	1.4	1.6	1.8
temperature (K)	1176	1165	1148	1127	1102
oxidant input (mol)					
CO_2	1.01	0.82	0.67	0.55	0.45
H_2O	0.02	0.20	0.36	0.49	0.60
O_2	0	0	0	0	0
reformer output (mol)					
CH_4	0.02	0.02	0.03	0.04	0.06
H_2	1.95	2.12	2.25	2.35	2.42
CO	1.95	1.76	1.60	1.47	1.34
CO_2	0.03	0.03	0.03	0.03	0.04
H_2O	0.03	0.04	0.04	0.06	0.07
energy-related CO_2 generation					
heat input (kJ)	350	347	344	339	334
CH_4 for heat generation (mol)	0.39	0.39	0.39	0.38	0.37
CO_2 generation (mol)	0.39	0.39	0.39	0.38	0.37
CO_2 Generation (% of total)	94	94	94	92	90
overall CO_2 fixation ^b	0.42	0.29	0.18	0.10	0.03

^aBasis: 1 mol CH_4 . ^bIncludes methane for heat generation.

inputs for all the scenarios are the addition of carbon dioxide and steam as oxidants (combined dry and steam reforming) and a 1:1 oxidant (x,y,z) to methane ratio. This indicates that the use of excess oxidants only leads to higher CO_2 production in the reformer and during heat generation. Higher temperatures results in a reduction in CO_2 generation in the reformer.

Under these conditions, CO₂ generation is exclusively due to that associated with heat generation.

These findings indicate that, from the perspective of CO₂ fixation, combined dry and steam reforming is favored over the use of tri-reforming, which combines partial oxidation with dry and steam reforming together in one reactor. The results show that without heat recovery CO₂ fixation is not feasible while producing syngas with a 2:1 H₂:CO ratio. This means that technology that requires syngas with such ratios (e.g., methanol synthesis, Fischer–Tropsch synthesis) would not lead to processes that produce less CO₂ than consumed.

Optimal Selection of Parallel Reforming. In order to identify the merits of parallel reforming, a simple linear model was used to choose the optimal combination of individual reformers to maximize CO₂ fixation while achieving particular H₂:CO ratios. The reformer inputs and outputs were fixed based on the values given in Tables 2 and 3. The results show that the optimal combination of parallel reformers to maximize CO₂ fixation while achieving a specific H₂:CO ratio is CDSR and SR (Table 7). As discussed earlier, as the required H₂:CO ratio increases the amount of CO₂ fixation decreases.

Table 7. Optimal Combined Reforming Configurations To Achieve a Particular H₂:CO ratio^a

H ₂ :CO	1.4	1.5	1.6	1.7
methane feed distribution (mol)				
CDSR	587	546	508	473
POX	0	0	0	0
SR	148	184	217	247
ATR	0	0	0	0
heat generation	265	271	275	279
total reforming output (mol)				
CH ₄	118	117	116	115
H ₂	1442	1,472	1500	1525
CO	1030	981	937	897
CO ₂	175	177	179	181
H ₂ O	472	524	572	616
energy-related CO₂ generation				
CO ₂ generation (mol)	265	271	275	279
total CO ₂ generation (% of total)	60	60	61	61
CO₂ generation (mol)				
CDSR	317	295	274	255
SR	123	153	180	205
overall CO₂ balance (mol)				
total CO ₂ generation	440	448	454	460
total CO ₂ feed	587	546	508	473
overall CO ₂ fixation	147	98	53	12
CO ₂ fixation (mol/mol of methane)	0.15	0.10	0.05	0.01

^aBasis: 1000 mol CH₄.

As the required H₂:CO ratio increases from 1.4 to 1.7, the amount of methane fed to SR increases from 15% to 25%. With respect to the CO₂ balance, greater production of CO₂ and a decrease in the amount of CO₂ fixated is a byproduct of the higher H₂:CO ratio requirement. For the different H₂:CO ratios required, the molar yield of syngas (H₂ and CO) produced is constant. Approximately 25 mol % of the feed methane is utilized in heat generation.

Comparing parallel reforming and a combined reformer, the results show that the combined reformer consistently results in higher CO₂ fixation. To achieve the same H₂:CO syngas ratio (1.6:1), the combined reformer results in a slightly higher CO₂

fixation (0.10 mol/mol of methane) compared to combining parallel reformers (0.05 mol/mol of methane). This analysis is an indication that effective CO₂ fixation using DR will require the production of syngas with a relatively low H₂:CO ratios. Given the magnitude of CO₂ produced during external heat generation, it is important to identify how much could potentially be recovered. If significant amounts of energy can be recovered, then it may be possible to produce syngas with higher H₂:CO ratios while fixating CO₂.

Impact of Heat Recovery on Combined Reforming Targets. The syngas leaving the reformer represents a hot stream that serves as an excellent candidate for heat recovery. The heat recovered from these streams replaces heat that would be supplied by the burning of fossil fuels and as such represents a potential CO₂ credit. For the analysis, the recoverable heat is the heat released when the stream is cooled to 100 °C.

Heat recoverable ($Q_{\text{recoverable}}$) given by

$$Q_{\text{recoverable}} = n \times (H(T) - H_{373}) \quad (17)$$

where, n is the number of moles, $H(T)$ is the enthalpy at temperature (T), y_i is the molar composition of species i , and H_{373} is the enthalpy at 100 °C.

$$H(T) = \sum_{i=1}^N y_i \bar{H}_i \quad (18)$$

With the recoverable heat calculated, we use the heat of combustion of methane (890 kJ/mol) to determine the CO₂ credit for the heat recovered.

Table 8 presents the optimal reformer configurations while considering the CO₂ credit due to heat recovery. The optimal combinations of reformers are the same as presented in Table 7. As the H₂:CO ratio increases, the amount of heating associated with CO₂ increases. This leads to greater heat recovery and results in a CO₂ credit. The heat recovery CO₂ credit increases the potential CO₂ fixation from 0.15 to 0.27 (moles CO₂/mol of methane) for syngas with a 1.4:1 H₂:CO ratio. The credit shows that a slightly higher H₂:CO ratio can be achieved while fixating CO₂.

Nonetheless, the amount of CO₂ fixated while producing a syngas that meets most of the conversion technology requirements (H₂:CO > 1.6:1) is not sufficient to justify the processing effort. The amount of CO₂ produced during CO₂ capture can represent 25% of the amount of CO₂ captured.³² This further reduces the amount of CO₂ fixation potential. Combining DR and SR to produce a syngas with a H₂:CO close to 2:1 would only result in minimal CO₂ fixation. External heating is consistently the major source of CO₂ generation in reforming configurations.

Given the CO₂ emissions associated with the CO₂ capture and utilization supply chain (capture, transportation, syngas conversion), a process based on DR would need additional improvements. The use of DR to fixate CO₂ would greatly benefit from the presence of waste heat sources because heat generation is the major source of CO₂ generation.

From this targeting analysis the following conclusions can be made: It is crucial for DR to be combined with another oxidant to mitigate coke formation. Syngas with a high H₂:CO ratio (higher than 2:1) would produce more CO₂ than fixated. Syngas with a low H₂:CO ratio (lower than 1.5:1) may provide an opportunity to fixate CO₂ with the appropriate heat integration to reduce the need for external heat generation.

Table 8. Optimal Configuration To Maximize CO₂ Fixation While Including Heat Recovery (Parallel Reforming)

H ₂ :CO	1.4	1.6	1.8	2.0	2.15
methane feed distribution (mol)					
CSDR	587	508	441	384	347
POX	0	0	0	0	0
SR	148	217	275	324	356
ATR	0	0	0	0	0
heat generation	265	275	284	292	297
oxidant input (mol)					
CO ₂	587	508	441	384	347
H ₂ O	383	420	451	478	495
combined reforming output (mol)					
CH ₄	118	116	115	113	113
H ₂	1442	1500	1548	1589	1616
CO	1030	937	860	795	752
CO ₂	175	179	182	185	187
H ₂ O	472	572	656	727	773
CO₂ generation (mol)					
CSDR	317	274	238	208	188
SR	123	180	228	269	296
energy-related CO₂ generation					
CO ₂ generation (mol)	265	275	284	292	297
total CO ₂ generation (% of total)	60	61	61	61	61
heat recovery CO₂ credit (mol)					
CSDR	82	71	62	54	49
SR	37	54	69	81	89
overall CO₂ balance (mol)					
total CO ₂ generation	440	454	466	477	484
total CO ₂ fixation	587	508	441	384	347
total CO ₂ credit	119	125	131	135	138
overall CO ₂ fixation (mol CO ₂ per mol CH ₄)	0.27	0.18	0.11	0.04	0.01

In the following section, attention is given to conversion technology that can utilize low quality syngas. Mixed alcohol synthesis is used as a case study as a representative of technologies that use low H₂:CO syngas. It can utilize syngas with a 1:1 H₂:CO ratio. This may offer an opportunity to produce a process capable of fixating CO₂ using DR. A process description is presented followed by modeling results including CO₂ balance.

MIXED ALCOHOL SYNTHESIS CASE STUDY

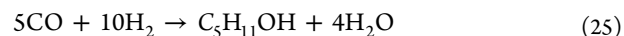
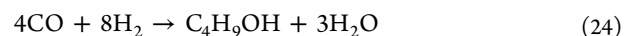
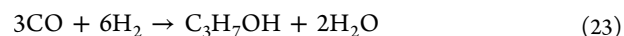
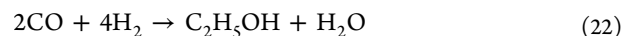
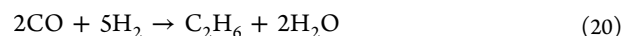
Process Description. The proposed mixed alcohol synthesis (MAS) process can be divided into four sections: synthesis gas production, synthesis gas conditioning, alcohol synthesis, and alcohol product separation. The overall process scheme is shown in Figure 3. The base case was developed and simulated in ASPEN Plus using the Peng–Robinson and NRTL property packages. The process mainly produces ethanol with smaller mixed alcohol coproduct streams. The process capacity was set at 1000 MMgal/yr of ethanol. The following sections describe the process units and reactions.

Combined Dry and Steam Reforming Section. Pipeline-quality natural gas (Table 9) is fed to a compressor where the pressure is increased to the reformer pressure (25 bar). This stream is preheated to 500 °C and fed to the pre-reformer along with high pressure steam and the carbon dioxide. The

carbon dioxide feed at 35 °C and a pressure of 145 bar is assumed to originate from a CO₂ pipeline.⁹ The CH₄:CO₂:H₂O molar feed ratio is 1:1:0.5. The pre-reformer converts the heavy hydrocarbons to synthesis gas to avoid coking in the reformer. The pre-reformer output is further heated to the reformer temperature (900 °C). The reformer produces a syngas with a H₂:CO ratio close to 1:1. The methane single-pass conversion is approximately 70% in the reformer.

Syngas Conditioning. The reformer output is cooled to 60 °C and flashed to remove the water. This also provides an opportunity to recover a significant amount of heat from the syngas following reforming. After water removal, the syngas is compressed in a five-stage compressor to 30 bar for CO₂ removal. An amine-based CO₂ removal system reduces the CO₂ content of the syngas to 5 mol %. Following CO₂ removal, the syngas is compressed in a three-stage compressor to 70 bar and fed to the alcohol synthesis reactor.

Alcohol Synthesis. Alcohol synthesis occurs at 300 °C and 70 bar to convert the syngas to a mixture of alcohols and light paraffins (Table 10).²⁷ The reactions below are used to describe the alcohol synthesis reactor:



The WGS reaction is dominant in the reactor and increases the H₂:CO ratio allowing it to approach the 2:1 ratio required by the alcohol synthesis reactions. The alcohol synthesis reactor requires significant heat removal to maintain the operating temperature at 300 °C.

Following the alcohol synthesis reactor, the output stream is cooled to 45 °C, and a series of flash tanks are used to separate the stream into gas and liquid phases.²⁷ The gas phase (off-gas) consists of the unreacted syngas, CO₂ and light hydrocarbon gases (primarily methane). The utilization of this stream is a major decision variable in the process design. The stream can be recycled to the reformer, alcohol synthesis reactor, or used for any required process heat requirement. This has strong implications on the CO₂ generation and overall CO₂ balance for the process. For the base case, 80% of the off-gas is recycled to the reformer, while the remaining portion is sent to a combustor to generate heat for the process. The remaining tail gas that is not recycled is burned and used for heating.

Alcohol Product Separation. The liquid phase that contains the mixed alcohol stream is sent to a molecular sieve where the remaining water is removed.³⁴ Finally, two distillation towers are used in series to fractionate the mixed alcohol. In the first column, the heavy alcohols (heavier than ethanol) exit in the bottoms stream. The column is a total of 60 stages and operates at a reflux ratio of 2. The ethanol recovery in the overhead is 99%, while the propane recovery in the bottoms is 99%. The overhead is sent to a second column to separate the ethanol (product stream) from methanol and

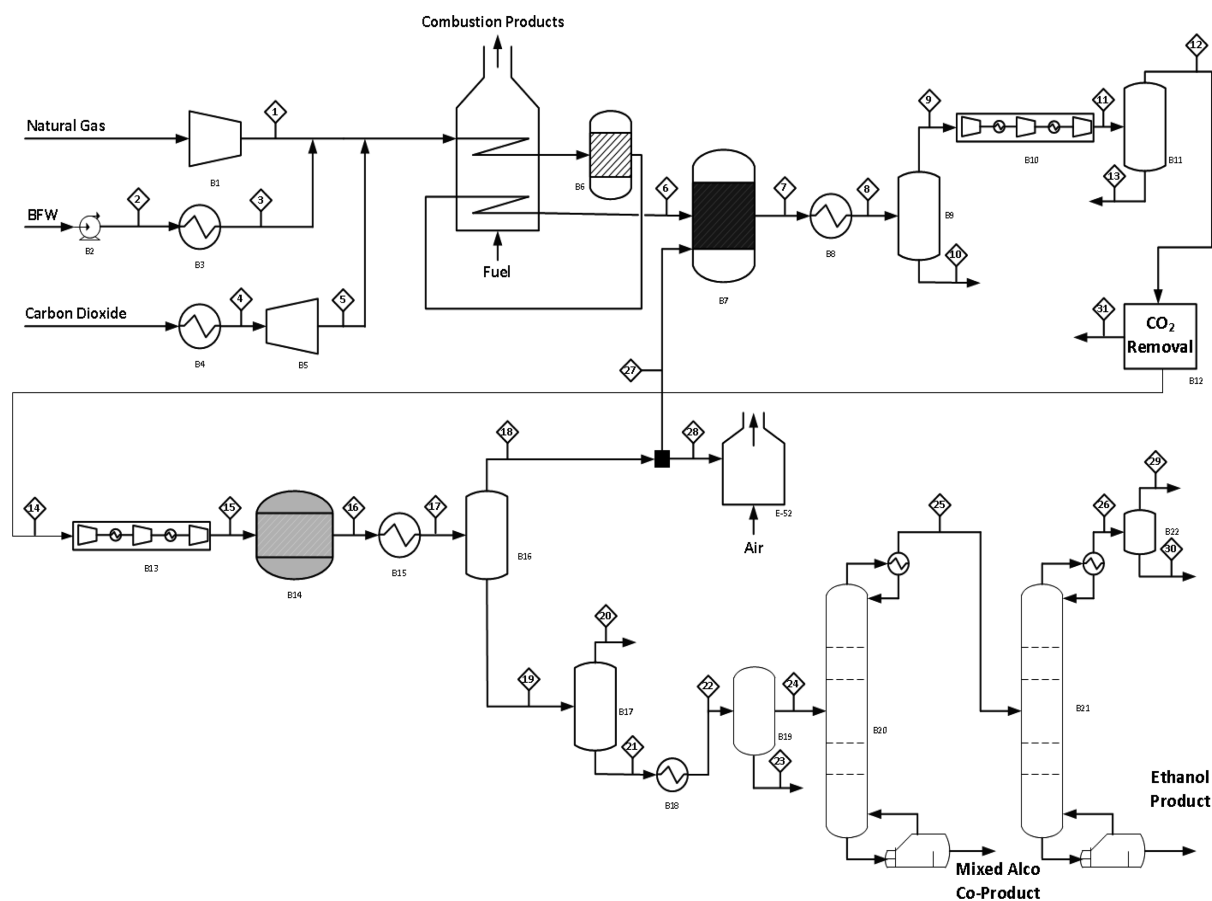


Figure 3. Mixed alcohol synthesis process flow diagram.

Table 9. Natural Gas Feed³³

temperature (°C)	25
pressure (bar)	20
mole fraction	
CH ₄	0.931
C ₂ H ₆	0.032
C ₃ H ₈	0.007
C ₄ H ₁₀	0.004
N ₂	0.016
CO ₂	0.01

Table 10. Alcohol Synthesis Conversion²⁷

chemical species	% conversion CO
CH ₄	3.4
C ₂ H ₆	0.3
CH ₃ OH	0.3
C ₂ H ₅ OH	28.2
C ₃ H ₇ OH	4.6
C ₄ H ₉ OH	0.6
C ₅ H ₁₁ OH	0.1
CO ₂	21.9
total (single pass CO conversion)	59.4

remaining light hydrocarbons. The column has 80 stages to produce an ethanol product stream (96 wt % ethanol).³⁴

Case Study Results. Table 11 summarizes the input–output for the process. Approximately 6500 SCF of natural gas is required per bbl of ethanol product. As mentioned, a portion of the reformer tail gas stream is not recycled to the reformer.

Table 11. Process Input–Output Summary

description	flow rate (kmol/h)	mass flow rate (kg/h)
input		
natural gas feed	25,000	433,188
pipeline CO ₂ feed	25,000	1,100,250
HP steam	12,500	225,191
air	75,000	2,163,780
output		
wastewater	14,926	278,545
flue gas	94,798	2,855,330
CO ₂ removal stream	4827	212,478
CO ₂ tail gas	1721	71,271
mixed alcohol coproduct	459	20,355
ethanol product	9000	413,258
mixed alcohol coproduct	1155	71,201

This tail gas stream, which is mainly unreacted methane, carbon monoxide, and hydrogen, is burned resulting in a significant amount of CO₂ generation (flue gas). If integration opportunities exist with other processes, the burning of the stream may be avoided, but the low H₂:CO ratio (0.8:1) makes it a very low quality syngas.

Tables 12 and 13 summarize the heating and cooling duties for the process. The energy requirement for the process represents another major source of CO₂ generation. As previously mentioned, the syngas generation section constitutes roughly 90% of the heating requirement for the process. This

Table 12. Total Heating Requirement for Mixed Alcohol Synthesis Process

unit no.	description	duty (MJ/h)	duty (MMBTU/h)	% of total
B3	boiler	625,164	592	5
B4	CO ₂ heater	334,223	317	2
B6	pre-reformer	1,393,190	1,319	10
B7	reformer	9,578,137	9,071	72
B17	pre-MS flash	58,077	55	0
B18	MS preheat	555,816	526	4
B20	reboiler	769,762	729	6
B21	reboiler	78,383	74	1
total heating (MMBTU/h)			12,684	100

Table 13. Total Cooling Requirement for Mixed Alcohol Synthesis Process

unit no.	description	duty (MJ/h)	duty (MMBTU/h)	% of total
B8	post-reform heat recovery	-5,684,948	-5384	43
B12	CO ₂ removal	-3518	-3	0
B14	alcohol synthesis reactor	-4,473,510	-4237	34
B15	ACR cooler	-1,635,194	-1549	12
B19	molecular sieve	-12,102	-11	0
B20	condenser	-824,584	-781	6
B21	condenser	-406,959	-385	3
B24	ethanol product cooler	-87,948	-83	1
B26	mixed alcohol product cooler	-20,651	-19	0
B27	cooler	-22,325	-21	0
total cooling (MMBTU/h)			-12,475	100%

includes the reforming section, which accounts for the bulk of the energy required in the syngas generation. The major cooling requirement is for the reformer output and the alcohol synthesis reactor. These streams combine to make up approximately 90% of the cooling requirement in the process.

The opportunity for heat integration and reduction of the heating and cooling requirement is necessary to quantify the amount of CO₂ generated that is associated with energy generation. Focus is on the streams that constitute the bulk of the heating and cooling requirement (Table 14). The top-level heat integration analysis shows that approximately only 25% of the heat required by the reformer input stream (C2) can be provided through heat integration.

Table 14. Major Stream for Heat Integration

stream	stream description	supply <i>T</i> (K)	target <i>T</i> (K)	enthalpy change (MMBTU/h)
H1	reformer output	1123	333	5,384
H2	alcohol synthesis reactor	573	573	4,237
H3	alcohol synthesis reactor output	573	318	1,549
C1	pre-reformer input	413	773	1,319
C2	reformer input	773	1123	9,071

With the remaining heat required from external heating source. This leads to approximately 6500 MMBTU/h of external heating. The portion of the syngas not recycled to the reformer can be combusted to provide approximately 3500 MMBTU/h of heating. This leaves approximately 3000 MMBTU/h of additional external heating. Assuming that this is provided through the combustion of natural gas, this is

equivalent to the generation of an additional 3600 kmol/h of CO₂.

Table 15 summarizes the top-level CO₂ balance for the process. Overall the process produces more CO₂ than

Table 15. CO₂ Balance for Mixed Alcohol Synthesis Process

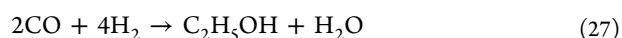
stream	CO ₂ input (kmol/h)	stream description	CO ₂ output (kmol/h)
natural gas feed	250	flue gas	21,081
CO ₂ feed	25,000	CO ₂ separator	4828
		CO ₂ tail gas	1216
		energy associated	3600
total in	25,250	total out	30,726

consumed. While the reformer targeting indicated a potential for CO₂ fixation for low quality syngas (H₂:CO ratio <1.5), the mixed alcohol synthesis process, which is capable of using very low quality syngas (H₂:CO ratio 1:1), still does not result in the overall fixation of CO₂. This can be attributed to the high CO conversion to CO₂ in the synthesis reactor (approximately 22%), the low CO conversion (approximately 50% per single pass), and the combustion of the unrecycled syngas. While these are all sources of process inefficiency (related to the processing pathway) that increase CO₂ generation and energy consumption, the issue at its core remains associated with the overall stoichiometry of the process.

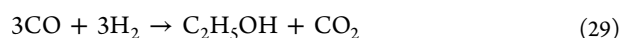
The alcohol synthesis reactions require a H₂:CO ratio of 2:1. The fact that syngas with a 1:1 ratio can be utilized by the catalyst does not change the stoichiometric ratio needed for the reactions and thus the high activity of the water–gas shift reaction in the reactor that converts a significant portion of the

CO into CO₂ for hydrogen generation. Neglecting process inefficiencies, this is equivalent to the use of a reformer to produce a syngas with a 2:1 H₂:CO ratio and thus removes any potential for CO₂ fixation using the mixed alcohol synthesis. This can also be shown from a stoichiometric perspective. If the mixed alcohol product is assumed to be completely ethanol, then the following reaction sequence describes the overall process.

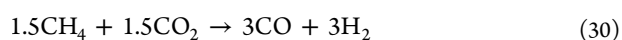
Alcohol synthesis:



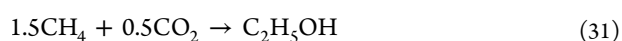
Alcohol synthesis overall:



Reforming



Overall process:



Thus, to fixate 0.5 mol of CO₂ while producing ethanol would require the CH₄:CO₂ feed ratio to be 3:1. Dry reforming uses a CH₄:CO₂ feed ratio of 1:1, and therefore, the excess CO₂ is not fixated in the production of mixed alcohols and thus exits the process. This shows that for CO₂ fixation to be successful (in utilizing more CO₂ than produced), it would require the use of a high CH₄ to CO₂ ratio, the production of highly oxygenated compounds, or in specific situations the utilization of waste energy. The high CH₄ to CO₂ ratio would effectively free up the carbon atoms for conversion to valuable hydrocarbons while making available significant amounts of hydrogen to carry the oxygen in the form of H₂O. Highly oxygenated compounds (high O:C ratio) would allow the CO₂ (in the presence of other C–H–O compounds) to be recombined into useful products. Finally, such scenarios that do not lead to CO₂ fixation due to significant energy requirement may become feasible if waste energy is utilized and a credit is attributed.

CONCLUSIONS

This paper quantifies the potential fixation of CO₂ using dry reforming in a standalone mode as well as via integration with other reforming technologies. Integrated mass and energy effects were included in tracking the net CO₂ fixation. Higher reformer operating temperatures and lower operating pressures result in higher CO₂ fixation. As the carbon dioxide to methane ratio in DR increases from 1:1 to 4:1, the amount of CO₂ fixated increases to more than 1.25 mol per mole of methane. However, the increase in carbon dioxide to methane ratio is also associated with a decrease in the syngas H₂:CO ratio, and such a syngas is considered of low value and limited application. There is an intrinsic inverse relationship between CO₂ fixation and the achieved syngas H₂:CO ratio. A trade-off exists between the ability to sequester CO₂ using reforming and the quality and value of the produced syngas.

For all of the investigated scenarios, the results show that the optimal combination of reformers to maximize CO₂ fixation while achieving a specific H₂:CO ratio is DR and SR. Nonetheless, the use of DR to sequester CO₂ faces many challenges and in particular would greatly benefit by the

presence of waste heat sources because heat generation is the major source of CO₂ generation. The case study highlights that even if low quality syngas (H₂:CO = 1:1) is utilized, the process may still produce more CO₂ than consumed. The success of CO₂ fixation using DR requires the use of a high CH₄ to CO₂ ratio, the production of highly oxygenated compounds, or in specific situations the utilization of waste energy. The high CH₄ to CO₂ ratio frees the carbon atoms for conversion to valuable hydrocarbons while making available significant amounts of hydrogen to carry the oxygen in the form of H₂O. Highly oxygenated compounds (high O:C ratio) provide another opportunity to convert CO₂ (in the presence of other C–H–O compounds) to useful products without leading to significant CO₂ generation.

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Notes

The authors declare no competing financial interest.

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REFERENCES

- (1) Foo, D. C.; El-Halwagi, M. M.; Tan, R. R.; *Recent Advances in Sustainable Process Design and Optimization*; World Scientific: Singapore, 2012.
- (2) Banos, R.; Manzano-Agugliaro, F.; Montoya, F.; Gil, C.; Alcayde, A.; Gómez, J. Optimization methods applied to renewable and sustainable energy: A review. *Renewable Sustainable Energy Rev.* **2011**, *15* (4), 1753–1766.
- (3) *CO₂ Emissions from Fuel Combustion OECD*; International Energy Agency: Paris, 2013.
- (4) *Annual Energy Outlook 2013*; U.S. Energy Information Administration: Washington, DC, 2013.
- (5) Masters, G. M.; *Renewable and Efficient Electric Power Systems*; John Wiley and Sons, Inc.: Hoboken, NJ, 2013.
- (6) Noureldin, M. B.; Bao, B.; Elbashir, N.; El-Halwagi, M. Benchmarking, insights, and potential for improvement of Fischer–Tropsch-based biomass-to-liquid technology. *Clean Technol. Environ. Policy* **2013**, 1–8.
- (7) Pardo, N.; Moya, J. A. Prospective scenarios on energy efficiency and CO₂ emissions in the European iron and steel industry. *Energy* **2013**, *54*, 113–128.
- (8) Howarth, R.; Santoro, R.; Ingraffea, A. Methane and the greenhouse-gas footprint of natural gas from shale formations. *Climatic Change* **2011**, *106* (4), 679–690.
- (9) Metz, B.; Davidson, O.; De Coninck, H.; Loos, M.; Meyer, L. *IPCC Special Report on Carbon Dioxide Capture and Storage*; Working Group III, Intergovernmental Panel on Climate Change (IPCC); Cambridge University Press: Cambridge, U.K., 2005, 4.
- (10) Hasan, M. M. F.; Boukouvala, F.; First, E. L.; Floudas, C. A. Nationwide, regional, and statewide CO₂ capture, utilization, and sequestration supply chain network optimization. *Ind. Eng. Chem. Res.* **2014**, *53* (18), 7489–7506.
- (11) Li, B.; Duan, Y.; Luebke, D.; Morreale, B. Advances in CO₂ capture technology: A patent review. *Appl. Energy* **2013**, *102* (9), 1439–1447.
- (12) Quadrelli, E. A.; Centi, G.; Duplan, J.-L.; Perathoner, S. Carbon dioxide recycling: Emerging large-scale technologies with industrial potential. *ChemSusChem* **2011**, *4* (9), 1194–1215.

- (13) Noureldin, M. M. B.; El-Halwagi, M. M. Synthesis of C–H–O symbiosis networks. *AIChE J.* **2015**, *61*, 1242–1262.
- (14) Wang, S.; Lu, G. Q.; Millar, G. J. Carbon dioxide reforming of methane to produce synthesis gas over metal-supported catalysts: State of the art. *Energy Fuels* **1996**, *10* (4), 896–904.
- (15) Dayton, D. C.; Turk, B.; Gupta, R. Syngas Cleanup, Conditioning, and Utilization. In *Thermochemical Processing of Biomass*; John Wiley and Sons, Inc.: Hoboken, NJ, 2011; pp 78–123.
- (16) Noureldin, M. M. B.; Elbashir, N. O.; El-Halwagi, M. M. Optimization and selection of reforming approaches for syngas generation from natural/shale gas. *Ind. Eng. Chem. Res.* **2013**, *53* (5), 1841–1855.
- (17) Kahle, L. C. S.; Roussière, T.; Maier, L.; Herrera Delgado, K.; Wasserschaff, G.; Schunk, S. A.; Deutschmann, O. Methane dry reforming at high temperature and elevated pressure: Impact of gas-phase reactions. *Ind. Eng. Chem. Res.* **2013**, *52* (34), 11920–11930.
- (18) Ehlinger, V. M.; Gabriel, K. J.; Noureldin, M. M. B.; El-Halwagi, M. M. Process design and integration of shale gas to methanol. *ACS Sustainable Chem. Eng.* **2013**, *2* (1), 30–37.
- (19) Spath, P. L.; Dayton, D. C. *Preliminary Screening -- Technical and Economic Assessment of Synthesis Gas to Fuels and Chemicals with Emphasis on the Potential for Biomass-Derived Syngas*; National Renewable Energy Laboratory: Golden, CO, 2003.
- (20) Phillips, S. D. Technoeconomic analysis of a lignocellulosic biomass indirect gasification process to make ethanol via mixed alcohols synthesis. *Ind. Eng. Chem. Res.* **2007**, *46* (26), 8887–8897.
- (21) Guo, J.; Lou, H.; Zhao, H.; Chai, D.; Zheng, X. Dry reforming of methane over nickel catalysts supported on magnesium aluminate spinels. *Appl. Catal., A* **2004**, *273* (1–2), 5–82.
- (22) Laosiripojana, N.; Sutthisripok, W.; Assabumrungrat, S. Synthesis gas production from dry reforming of methane over CeO₂ doped Ni/Al₂O₃: Influence of the doping ceria on the resistance toward carbon formation. *Chem. Eng. J.* **2005**, *112*(1), 13–22.
- (23) Baek, S.-C.; Bae, J.-W.; Cheon, J.; Jun, K.-W.; Lee, K.-Y. Combined Steam and Carbon Dioxide Reforming of Methane on Ni/MgAl₂O₄: Effect of CeO₂ Promoter to Catalytic Performance. *Catal. Lett.* **2011**, *141* (2), 224–234.
- (24) Roh, H.-S.; Koo, K.; Joshi, U.; Yoon, W. Combined H₂O and CO₂ reforming of methane Over Ni–Ce–ZrO₂ catalysts for gas to liquids (GTL). *Catal. Lett.* **2008**, *125* (3), 283–288.
- (25) Zhou, H.; Cao, Y.; Zhao, H.; Liu, H.; Pan, W.-P. Investigation of H₂O and CO₂ reforming and partial oxidation of methane: Catalytic effects of coal char and coal ash. *Energy Fuels* **2008**, *22* (4), 2341–2345.
- (26) M.E.E, A. Coupling of steam and dry reforming of methane in catalytic fluidized bed membrane reactors. *Int. J. Hydrogen Energy* **2004**, *29* (8), 799–808.
- (27) *Thermochemical Ethanol via Indirect Gasification and Mixed Alcohol Synthesis of Lignocellulosic Biomass*, Vol. 112; National Renewable Energy Laboratory: Golden, CO, 2007.
- (28) Nematollahi, B.; Rezaei, M.; Khajenoori, M. Combined dry reforming and partial oxidation of methane to synthesis gas on noble metal catalysts. *Int. J. Hydrogen Energy* **2011**, *36* (4), 2969–2978.
- (29) Song, C.; Pan, W. Tri-reforming of methane: A novel concept for catalytic production of industrially useful synthesis gas with desired H₂/CO ratios. *Catal. Today* **2004**, *98* (4), 463–484.
- (30) Gabriel, K. J.; Linke, P.; Jiménez-Gutiérrez, A.; Martínez, D. Y.; Noureldin, M.; El-Halwagi, M. M. Targeting of the water-energy nexus in gas-to-liquid processes: A comparison of syngas technologies. *Ind. Eng. Chem. Res.* **2014**, *53* (17), 7087–7102.
- (31) de Klerk, A. *Fischer–Tropsch Refining*; John Wiley and Sons, Inc.: Hoboken, NJ, 2012.
- (32) Kuramochi, T.; Ramírez, A.; Turkenburg, W.; Faaij, A. Comparative assessment of CO₂ capture technologies for carbon-intensive industrial processes. *Prog. Energy Combust. Sci.* **2012**, *38* (1), 87–112.
- (33) Quality Guidelines for Energy System Studies: Specification for Selected Feedstocks, National Energy Technology Laboratory, 2012.
- www.netl.doe.gov/File%20Library/research/energy%20analysis/publications/QGESSec1.pdf (accessed March 2015).
- (34) Dutta, A.; Talmadge, M.; Hensley, J.; Worley, M.; Dudgeon, D.; Barton, D. Techno-economics for conversion of lignocellulosic biomass to ethanol by indirect gasification and mixed alcohol synthesis. *Environ. Prog. Sustainable Energy* **2012**, *31* (2), 182–190.