Solar Dry Reforming: What is it good for?

Supplementary information

TABLE OF CONTENTS

Thermodynamic Analysis of the Dry Reforming Reaction System						
1.1 Thermodynamics of The Dry Reforming Reaction System	2					
1.1.1 Dry Reforming Reaction Network	2					
1.1.2 Free Energy Analysis of Dry Reforming Reaction Network	2					
1.1.3 Equilibrium Product Compositions	4					
Photocatalytic Dry Reforming Literature Overview						
Process Model Example						
Process Model Example Case Study Results	15 22					

Thermodynamic Analysis of the Dry Reforming Reaction System

1.1 Thermodynamics of The Dry Reforming Reaction System

The thermodynamics of the dry reforming system serve to demonstrate the energy requirements of the reaction, the thermodynamic driving force behind each reaction in the reaction network, the composition of the reaction product mixture at equilibrium, and the maximum possible reactant conversion. The equilibrium product compositions and reactant conversions represent the maximum possible concentrations and conversions and provide no insight into the speed at which these equilibrium compositions are reached, which is under the control of the reaction kinetics governed by the operating conditions and/or a specific catalyst. As a result, the catalyst development work presented later aims to control the kinetics of the dry reforming reaction network presented here such that the optimum and desired product composition is achieved.

Below, the dry reforming reaction network is reviewed, and a free energy analysis of this reaction network is completed to understand the thermodynamic driving force behind each reaction in the reaction network. The compositions of the equilibrium product mixture are then calculated, and the effects of temperature, pressure, and feed mixture composition on carbon deposition, H_2 /CO ratio, and energy content of the product mixtures is commented on.

1.1.1 Dry Reforming Reaction Network

Dry reforming of methane has a complex reaction network, represented by the following set of reactions:

- Equation 1. Dry Reforming of Methane $(CH_4 + CO_2 \rightleftharpoons 2H_2 + 2CO)$
- Equation 2. Reverse Water Gas Shift ($CO_2 + H_2 \rightleftharpoons CO + H_2O$)
- Equation 3. Steam Reforming of Methane $(CH_4 + H_2 O \rightleftharpoons CO + 3H_2)$
- Equation 4. Methane Decomposition ($CH_4 \rightleftharpoons C_{(s)} + 2H_2$)
- Equation 5. Boudouard Reaction ($CO \rightleftharpoons CO_2 + C_{(s)}$)

A system with high selectivity for the desired dry reforming reaction (DRM, Equation 1) would produce an H_2/CO ratio in the product of 1:1, assuming stoichiometric feed and conversion. However, H_2/CO ratios of less than 1 are often observed in product gas mixtures due to the presence of the reverse water gas shift reaction (RWGS, Equation 2) that consumes the H_2 produced by the dry reforming reaction, and itself produces CO and H_2O , increasing the proportion of CO in the product and therefore decreasing the H_2/CO ratio. The water produced by the RWGS reaction can subsequently participate in the steam reforming of methane (SMR, Equation 3), producing more H_2 and CO [1].

Carbon may be deposited on the surface of the catalyst by either methane decomposition or CO disproportionation, also known as the Boudouard Reaction. Solid carbon accumulation on the surface of solid heterogeneous catalysts and subsequent deactivation is a main inhibitor for industrial dry reforming.

1.1.2 Free Energy Analysis of Dry Reforming Reaction Network

The relative free energies of the reactions in the dry reforming reaction network provide insight into the magnitude of the thermodynamic driving force present for each reaction at a certain set of reaction conditions [2] [3].

The free energy of reaction for each reaction at a given temperature was calculated using the heats of formation for the reaction network components obtained from the NIST Chemistry Webbook [4]. These are shown in

Table 1.

Table 1. Heats and Entropies of Formation for DRM Reaction Network Components

	CH₄	CO2	H ₂	со	H₂O	С
ΔH_{f}° (kJ mol ⁻¹)	-74.87	-393.51	0	-110.53	-241.83	0
S_f° (kJ mol ⁻¹)	0.19	0.21	0.13	0.20	0.19	0.01

Free energies of reaction for each reaction were calculated from these values using the relation $\Delta G_{rxn} = \Delta H_{rxn}^{\circ} - T\Delta S_{rxn}^{\circ}$, and using the heats and entropies of formation in

Table 1 to calculate ΔH_{rxn}° and ΔS_{rxn}° . This method assumes that ΔH_{rxn}° and ΔS_{rxn}° do not change with temperature. Further, the calculations take place at atmospheric pressure. The results are shown in Table 2.

	ΔH°_{rxn} (kJ mol ⁻¹)	$\Delta S^{^{\mathrm{o}}}_{rxn}$ (kJ mol ⁻¹)
Dry Reforming of Methane ($CH_4 + CO_2 \rightleftharpoons 2H_2 + 2CO$)	247.32	0.25
Reverse Water Gas Shift $(CO_2 + H_2 \rightleftharpoons CO + H_2O)$	41.15	0.04
Steam Reforming of Methane $(CH_4 + H_2 O \rightleftharpoons CO + 3H_2)$	206.16	0.21
Methane Decomposition $(CH_4 \rightleftharpoons C_{(s)} + 2H_2)$	74.87	0.08
Boudouard Reaction $(CO \rightleftharpoons CO_2 + C_{(s)})$	-172.45	-0.182

Table 2. Standard Heats and Entropies of Reaction for DRM Reaction Network

Table 2 shows that the DRM, SMR, and RWGS reactions are all endothermic, and therefore require high amounts of available energy to react, which is most commonly supplied to the system in the form of heat. Further, the two carbon-producing reactions, methane decomposition and the Boudouard reaction, have opposite temperature dependencies. This means that at low temperatures, the highly exothermic Boudouard reaction will be favored, whereas at high temperatures, methane decomposition is favoured, highlighting the difficulty in operating in a thermodynamically carbon-free regime and the necessity for kinetic inhibition of carbon deposition.

Figure 1 shows how the ΔG_{rxn} for each reaction in Table 2 changes with respect to temperature, and thereby gives an indication of the strength of the thermodynamic driving force behind each reaction at the given conditions.

At temperatures below roughly 700 °C, ΔG_{rxn} for the RWGS reaction is much less than the ΔG_{rxn} for the desired DRM reaction, and is therefore more thermodynamically favored. However, both reactions have ΔG_{rxn} s that are greater than zero, indicating that neither occur spontaneously at temperatures below 700 °C. The driving force for the SMR reaction has a similar profile to that of DRM.

The two main carbon-producing reactions follow the same trends as their exo- or endothermicity suggested above. At temperatures below 700 °C, the Boudourard reaction is highly favoured and is the only reaction with a ΔG_{rxn} below zero at those conditions. Above temperatures of 700 °C, carbon-deposition is thermodynamically favored through CH₄ decomposition. The thermodynamic inescapability

of carbon deposition highlights the necessity for kinetic solutions to catalyst deactivation, which will be discussed later on.



Figure 1. Free energy diagram depicting the free energies of reaction for the reactions in the dry reforming reaction network at varying temperatures. Atmospheric pressure is assumed.

1.1.3 Equilibrium Product Compositions

The composition of the gas mixture at equilibrium represents the maximum possible concentrations of reaction products. It is defined by the thermodynamic state of the system, which in the case of dry reforming are represented by the temperature and pressure at which the reaction is run, as well as the relative concentrations of the reactants [5].

1.1.3.1 Calculation Details: Gibbs Free Energy Minimization Using NASA's CEA Algorithm

The composition of the equilibrium mixture resulting from a dry reforming reaction system is a determined by several simultaneous reactions, representing a complex reaction network where both phase and reaction equilibria are involved. In the literature, this system has been represented from anywhere from 2-17 simultaneous reactions [6].

For complex equilibrium calculations, the method of Gibbs Free Energy Minimization (GFEM) is the most direct method for calculating the composition of the equilibrium mixture, as only the reactive compounds must be specified, rather than a specific set of reactions [7] [8].

(GFEM) is used to calculate the equilibrium product composition for the dry reforming system at hand, which is assumed to take place in a constant volume reactor vessel, therefore allowing its thermodynamic state to be defined by temperature and pressure.

The equilibrium composition is calculated based on the postulate that, at constant temperature and pressure, chemical equilibrium is reached when the change in the Gibbs Free Energy of the system is at a minimum. The total Gibbs Free Energy of the system (ie. the gas mixture) is the sum of the chemical potentials of all of the components, as shown in Equation 6.

Equation 6. $G^{total} = \sum_{i=1}^{N} n_i \mu_i$

Where: n_i is the number of moles of component *i* in the system; μ_i is the chemical potential of component *i*; and *N* is the total number of components in the gas mixture.

In turn, μ_i for each component is calculated using the relationship shown in Equation 7.

Equation 7.
$$\mu_i = \left(\frac{\partial g}{\partial n_i}\right)_{T,P}$$

Mass and energy balances also constrain the problem. The total mass in the system is constrained by:

Equation 8. $\Sigma n_i a_{ik} = A_k$

Where: n_i is the number of moles of component *i*; a_{ik} is the number of atoms of the k^{th} element; A_k is the total mass of the k^{th} element.

The energy balance across the dry reforming process is constrained by the following relationship:

Equation 9.
$$E_{in} = \Sigma n_{i,f} H_{i,f} - \Sigma n_{i,0} H_{i,0}$$

Where: E_{in} is the energy that needs to be put into the system; $n_{i,f}$ is the final number of moles of the component *i* in the product; $H_{i,f}$ is the enthalpy of the product stream; $n_{i,f}$ is the final number of moles of the component *i* in the product; $H_{i,f}$ is the enthalpy of the product stream.

The product composition that has the minimum Gibbs Free Energy is calculated from this constrained system of equations using the method of Lagrange multipliers and a descent Newton-Raphson numerical method.

The shortcoming of this approach to GFEM is that it is limited to gas-phase reactions [7]. In the dry reforming system, the potential for liquid water and solid carbon to form in a dry reforming reaction system necessitates the inclusion of condensed phases in the calculation of equilibrium compositions. Since the above described minimization algorithm is subject to the constraint of mass conservation, and also takes into account only gas phase components, the numerical method will fail to converge on a solution if some of the mass has been removed from the gaseous system as a condensed phase.

A method for calculating equilibrium composition with the inclusion of condensed phases was put forth by Gordon and McBride in the development of NASA's Chemical Equilibrium with Applications (CEA) software, which extends the method of Gibbs free energy minimization for the calculation of chemical equilibrium compositions and properties of complex mixtures [9].

The online version of NASA's CEA software (CEARUN) was used to carry out the calculations for the composition of the equilibrium mixture using the "assigned temperature and pressure" problem type [10]. Feed temperature was set to 50 °C, and ionized species were not considered in the analysis.

The first iteration of the algorithm takes into account only gas-phase species in the feed, After every subsequent convergence, the program automatically tests for the inclusion or elimination of condensed phases. This test is also based on the method of Gibbs' free energy minimization. Specifically, the postulate is made that the presence of a condensed phase will decrease the Gibbs free energy of the system such that the change in Gibbs free energy of the system with respect to the number of moles is

negative as a consequence of the fact that the chemical potential of the condensed phase is less than the chemical potential of the gas and condensed phases together [9]:

Equation 10.
$$\frac{\partial G}{\partial n_i} = \left(\frac{\mu_i}{RT}\right)_c - \sum_{i=1}^l \pi_i a_i < 0$$

This relationship is valid even when the gas phase of the species corresponding to the condensed phase to be tested for is not present. This is particularly advantageous for our dry reforming system which is known to deposit solid carbon on the surface of the catalyst.

If this test is completed and it is found that several condensed species are present, only the species with the largest $-\partial G/n_j$ are included, and the numerical method is repeated to find a new equilibrium product composition. This process is repeated for all *j* species.

The CEA software operates under several important assumptions. Ideal gas/Raoult's Law equations of state are used, and have been shown elsewhere to be valid up to 100 bar [8]. Further, the calculations assume that condensed phases are pure and can also themselves change between condensed phases, allowing for calculations that may occur at a triple point to converge and provide a solution.

A comprehensive list of combinatorially possible product species that can be synthesized from the feed gases are considered in this calculation. Products that were tested for but whose mol fractions were found to be less than 0.000005 (ie. molecular concentration less than 5 ppm) are automatically removed from the product mixture. These include C, CH, CH₂, CH₃, CH₂OH, CH₃O, CH₄, CH₃OH, CH₃OOH, CO, CO₂, COOH, C₂, C₂H, C₂H₂ (acetylene), C₂H₂ (vinylidene), CH₂CO (ketene), O(CH)₂O, HO(CO)₂OH, C₂H₃ (vinyl), CH₃CO (acetyl), C₂H₄, C₂H₄O (ethylene oxide), CH₃CHO (ethanol), CH₃COOH, OHCH₂COOH, C₂H₅, C₂H₆, C₂H₅OH, CH₃OCH₃, CH₃O₂CH₃, C₂O, C₃, C₃H₃ (1-propynl), C₃H₃ (2-propnyl), C₃H₄ (allene), C₃H₄ (propyne), C₃H₄ (cyclo-), C_3H_5 (allyl), C_3H_6 (propylene), C_3H_6 (cyclo-), C_3H_6O (propyl oxide), C_3H_6O (acetone), C_3H_6O , C_3H_7 , C_3H_7 , C₃H₈, C₃H₈O (1-propanol), C₃H₈O (2-propanol), C₃O₂, C₄, C₄H₂ (butadiyne), C₄H₄ (1,3-cyclo-), C₄H₆ (butadiene), C_4H_6 (1-butyne), C_4H_6 (2-butyne), C_4H_6 (cyclo-), C_4H_8 (1-butene), C_4H_8 , C_4H_8 , C_4H_8 (isobutene), C4H₈, (CH₃COOH)₂, C₄H₉, C₄H₉, C₄H₉, C₄H₉ (t-butyl), C₄H₁₀ (n-butane), C₄H₁₀ (isobutane), C₅, C₅H₆ (1,3-cyclo-), C₅H₈ (cyclo-), C₅H₁₀ (1-pentene), C₅H₁₀ (cyclo-), C₅H₁₁, C₅H₁₁ (t-pentyl), C₅H₁₂ (n-pentane), C₅H₁₂ (ipentane), CH₃C(CH₃)₂CH₃, C₆H₂, C₆H₅ (phenyl), C₆H₅O (phenoxy), C₆H₆, C₆H₅OH (phenol), C₆H₁₀ (cyclo-), C₆H₁₂ (1-hexene), C₆H₁₂ (cyclo-), C₆H₁₃ (n-hexyl), C₆H₁₄ (n-hexane), C₇H₇ (benzyl), C₇H₈, C₇H₈O (cresol-mx), C₇H₁₄ (1-heptene), C₇H₁₅ (n-heptyl), C₇H₁₆ (n-heptane), C₇H₁₆ (2-methyl), C₈H₈ (styrene), C₈H₁₀ (ethylbenzene), C₈H₁₆ (1-octene), C₈H₁₇ (n-octyl), C₈H₁₈ (n-octane), C₈H₁₈ (isooctane), C₉H₁₉ (n-nonyl), C₁₀H₈ (naphthalene), C₁₀H₂₁ (n-decyl), C₁₁H₂₁, C₁₂H₉ (o-biphenyl), C₁₂H₁₀ (biphenyl), H, HCO, HCCO, HO₂, H₂, HCHO (formaldehyde), HCOOH, H₂O, H₂O₂, (HCOOH)₂, O, OH, O₂, O₃, C_(gr), CH₃OH_{(L}), C₂H₅OH_{(L}), C6H14_{(L}), C₆H_{6(L)}, $H_2O_{(cr)}$, and $H_2O_{(L)}$.

1.1.3.2 Equilibrium Product Compositions at varying temperatures, pressures, and feed ratios

Figure 2 shows the equilibrium product mixture compositions for varying temperatures, pressures, and feed ratios. Equilibrium product mixture compositions were calculated for temperatures ranging from 0 to 1000 °C and pressures ranging from 1 to 30 atm, as well as feed ratios of 83.3, 75.0, 66.7, 50.0, and 33.3 wt% CH₄, corresponding to CO₂:CH₄ molar ratios of 1.8, 1.1, 0.7, 0.4, and 0.2 respectively. These results can provide an ideal assessment of the product mixtures expected at various operating conditions.

The operating conditions that provide an optimal product mixture for a given application inform the process design surrounding the reactor. For example, while low pressures are preferred from a process safety point of view, in order to facilitate the economic transport of material through a plant, process pressures of 30 to 40 atm are commonly used in reforming reactors. If low pressures are used in the dry

reforming reaction system, compression will be required downstream to transport material to subsequent unit operations.

Further, the goal of the application may be different. For example, if 100% CO₂ consumption is desired to minimize emissions, then the process conditions can be optimized to provide maximum CO₂ consumption.

wt% CH₄ in Feed	Equivalent CO ₂ :CH ₄ Molar Ratio
83	1.8
75	1.1
66	0.7
50	0.4
33	0.2

Table 3. Reactant mixture compositions used in equilibrium product mixture composition calculations.



Figure 2. Equilibrium product mixture compositions for varying temperatures, pressures, and feed ratios.

Table 4. Equilibrium product mixture compositions in mol% corresponding to Figure 2.

						1	.8 mol C	O₂ / mol C	CH4							
Pressure		1	atm			10	atm			20) atm			30	atm	
Temp. (ºC)	0	500	750	1000	0	500	750	1000	0	500	750	1000	0	500	750	1000
CH₄	0.0	3.4	0.5	0.0	0.0	4.8	3.0	0.2	0.0	5.0	3.8	0.6	0.0	5.2	4.2	1.1
со	0.0	3.7	65.3	70.6	0.0	1.1	29.4	70.1	0.0	0.8	20.9	68.8	0.0	0.6	17.1	67.2
CO2	37.6	56.5	25.0	18.1	37.6	54.5	44.3	18.4	37.6	54.1	48.2	19.2	37.6	53.9	49.9	20.2
H₂	0.0	1.1	3.4	3.3	0.0	0.4	2.0	3.2	0.0	0.3	1.5	3.1	0.0	0.2	1.3	3.0
H ₂ O	37.4	19.6	5.7	8.0	37.4	22.9	13.0	8.0	37.4	23.4	15.3	8.2	37.4	23.7	16.4	8.4
Cgr	25.0	15.7	0.0	0.0	25.0	16.3	8.3	0.0	25.0	16.4	10.2	0.0	25.0	16.4	11.1	0.0

						1	.1 mol C	O ₂ / mol (CH₄							
Pressure		1	atm			10	atm			20) atm			30	atm	
Temp (ºC)	0	500	750	1000	0	500	750	1000	0	500	750	1000	0	500	750	1000
CH₄	0.0	8.0	1.5	0.0	0.0	12.0	6.6	1.9	0.0	12.8	8.6	3.3	0.0	13.1	9.8	4.4
со	0.0	2.2	38.6	50.2	0.0	0.7	17.4	49.3	0.0	0.5	12.8	46.0	0.0	0.4	10.6	43.4
CO ₂	2.3	17.5	5.8	0.9	2.3	17.6	13.7	1.8	2.3	17.6	15.3	3.1	2.3	17.6	16.2	4.3
H ₂	0.0	15.9	42.5	47.4	0.0	6.1	26.3	44.3	0.0	4.4	20.8	40.9	0.0	3.7	17.9	38.2
H₂O	48.9	24.7	4.9	1.4	48.9	30.4	15.8	2.6	48.9	31.4	19.2	4.6	48.9	31.8	20.9	6.2
C _{gr}	48.9	31.6	6.8	0.0	48.9	33.1	20.3	0.1	48.9	33.3	23.2	2.1	48.9	33.4	24.6	3.6

						C).7 mol C	O ₂ / mol C	H ₄							
Pressure		1	atm			10) atm			20) atm			30) atm	
Temp (ºC)	0	500	750	1000	0	500	750	1000	0	500	750	1000	0	500	750	1000
CH₄	8.5	11.6	2.0	0.3	8.5	17.8	9.1	2.5	8.5	18.9	12.0	4.4	8.5	19.4	13.6	5.8
со	0.0	1.8	29.1	38.8	0.0	0.6	13.7	36.6	0.0	0.4	10.2	34.5	0.0	0.3	8.5	32.8
CO ₂	0.0	11.3	3.5	0.1	0.0	11.4	8.8	1.1	0.0	11.4	10.0	1.9	0.0	11.4	10.6	2.6
H ₂	0.0	19.0	47.4	53.1	0.0	7.4	30.3	48.9	0.0	5.4	24.2	45.4	0.0	4.5	20.9	42.6
H₂O	45.8	23.9	4.4	0.3	45.8	29.7	14.9	2.4	45.7	30.7	18.3	4.2	45.7	31.1	20.1	5.6
C _{gr}	45.7	32.5	13.5	7.4	45.7	33.2	23.2	8.5	45.7	33.2	25.3	9.6	45.7	33.2	26.3	10.5

						0	.4 mol C	D ₂ / mol C	H4							
Pressure		1	atm			10) atm			20) atm			30	atm	
Temp (ºC)	0	500	750	1000	0	500	750	1000	0	500	750	1000	0	500	750	1000
CH₄	30.4	18.9	2.8	0.4	30.4	30.2	13.7	3.6	30.4	32.3	18.4	6.2	30.4	33.3	21.1	8.3
со	0.0	1.1	17.0	21.6	0.0	0.4	8.6	20.7	0.0	0.3	6.6	19.9	0.0	0.2	5.5	19.2
CO ₂	0.0	4.6	1.3	0.0	0.0	4.7	3.6	0.4	0.0	4.7	4.2	0.7	0.0	4.8	4.5	1.0
H ₂	0.0	24.6	53.9	58.9	0.0	9.9	36.6	54.9	0.0	7.3	29.8	51.4	0.0	6.0	26.0	48.5
H₂O	34.8	19.5	3.2	0.2	34.8	25.0	11.8	1.7	34.8	25.9	14.7	3.0	34.8	26.4	16.3	4.1
Cgr	34.8	31.2	21.7	18.9	34.8	29.8	25.7	18.8	34.8	29.4	26.3	18.8	34.8	29.3	26.5	18.8

						0	.2 mol C	D ₂ / mol C	: H 4							
Pressure		1	atm			10) atm			20) atm			30) atm	
Temp (ºC)	0	500	750	1000	0	500	750	1000	0	500	750	1000	0	500	750	1000
CH₄	52.9	26.3	3.5	0.5	52.9	43.7	17.9	4.4	52.9	47.1	24.5	7.7	52.9	48.7	28.3	10.4
со	0.0	0.7	9.4	11.4	0.0	0.2	5.1	11.2	0.0	0.2	3.9	10.9	0.0	0.1	3.4	10.6
CO ₂	0.0	1.6	0.4	0.0	0.0	1.7	1.3	0.1	0.0	1.7	1.5	0.2	0.0	1.7	1.6	0.3
H ₂	0.0	29.7	58.2	62.4	0.0	12.4	41.6	58.6	0.0	9.2	34.6	55.2	0.0	7.6	30.5	52.5
H₂O	23.6	13.6	2.0	0.1	23.6	17.9	7.9	1.0	23.6	18.7	10.1	1.9	23.6	19.1	11.3	2.6
C _{gr}	23.6	28.1	26.5	25.6	23.6	24.0	26.2	24.7	23.6	23.2	25.4	24.1	23.6	22.8	24.9	23.6

1.1.3.3 Equilibrium Reactant Conversion

The equilibrium reactant conversion represents the maximum possible reactant conversion at the given conditions. The results are shown in Figure 3.



Figure 3. Equilibrium reactant conversions at varying temperatures, pressures, and feed compositions.

Equilibrium conversions of both CH_4 and CO_2 decrease with pressure, a feature commonly ascribed to the increase in the number of moles in the system as the main DRM reaction proceeds to completion.

However, at the right operating conditions, high pressures advantageous to large scale process development may be possible. For example, the feed conversions in a system using a 1.1 mol CO_2 / mol CH_4 feed achieves conversions above 60% for pressures ranging from 1 to 30 atm.

The equilibrium conversion of both CH_4 and CO_2 decreases when its proportion in the feed increases. This can be for two reasons. First, in a system with a high proportion of CH_4 in the feed, there is a limiting amount of CO_2 present in the system to react with CH_4 , and as a result the percentage of CH_4 that will react is limited. The opposite is true for a system with a CO_2 -rich feed.

Which of these cases is optimal depends on the goal of the process design. For example, if the goal of a system is to consume 100% of all CO_2 , this would demand a different set of operating conditions than if the goal of the system was to produce as much H_2 as possible. These different use cases are explored later on.

1.1.3.4 H₂:CO Ratio

Synthesis gas is most commonly characterized by its H_2 :CO ratio, which gives an indication of the downstream processes that grade of syngas may be appropriate for, although H_2 and CO are not necessarily the only two components in the product stream. For example, the syngas produced by SMR generally has an H_2 :CO ratio of 3:1, and is ideal for H_2 production, while H_2 :CO ratios of 2:1 are more ideal for Fischer-Tropsch type gas-to-liquids operations.

The ratios of H_2 :CO in the equilibrium product mixture are shown in Figure 4. The H_2 :CO ratio reaches a maximum at 500 °C for all feed ratios, likely due to the thermodynamic preference for the Boudouard reaction and the water gas shift reaction (ie. the reverse of Equation 2) at that temperature, which both consume CO, and in the case of the water gas shift reaction, produce H_2 in the process. The H_2 :CO ratio in the product increases with an increased proportion of CH_4 in the feed, likely due to the increased concentration of H atoms in the reaction system.





Figure 4. H₂:CO ratio in the equilibrium product mixture under varying conditions.

1.1.3.5 Carbon Deposition

Carbon deposition decreases as the proportion of CO_2 in the feed increases, implying that the thermodynamically favoured origin of carbon is CH_4 decomposition.

Increasing pressure has a negligible effect on the equilibrium mol fraction of carbon that is deposited onto the surface of the catalyst. This can be advantageous as high pressures can be used in a scaled process if a catalyst can be developed that is able to kinetically hinder carbon deposition, knowing that the thermodynamic driving force behind carbon deposition is the same at all pressures.



Figure 5. Solid carbon content of the equilibrium product mixture.

Photocatalytic Dry Reforming Literature Overview

Table 5 summarizes the academic publications demonstrating photocatalytic dry reforming in the last twenty years. Several examples in more recent years have demonstrated production rates in the mmol g_{cat} ⁻¹ h⁻¹ range, which, depending on the catalyst lifetime and cost, can present a commercially viable system. However, these systems invariably make use of precious metals, and the longest stability test present in the literature is 50 h.

 Table 5. Academic publications demonstrating photocatalytic dry reforming from 2000-2020. The surface area (SA), temperature from artificial heating (Temp), the illumination intensity (No. Suns), and the production rates of hydrogen and carbon monoxide are detailed for each.

Year	Reference [No.]		Catalyst	SA (m²/g)	Temp (°C)	No. Suns	r _{H2} (mol/g _{cat} h)	r _{co} (mol/g _{cat} h)
2000	Kohno et al., <i>Phys. Chem.</i> <i>Chem. Phys.</i> (2) pp. 5302- 5307	[11]	ZrO ₂		400	416.67		4.67 x 10 ⁻⁷
2004	Shi et al. <i>Catalysis Today</i> (98) pp. 505-509	[12]	Cu/CdS- TiO2/SiO2	264.0		129.92		
2004	Teramura et al. <i>J. Phys.</i> Chem. B. (108) pp. 346- 354	[13]	MgO	110.0		396.83	3.33 x 10 ⁻⁸	2.40 x 10 ⁻⁶
2008	Yuliati et al., Chemical Physics Letters (452) pp. 178-182	[14]	Ga ₂ O ₃	2.0	200	214.29	4.13 x 10⁻ ⁶	1.80 x 10 ⁻⁶
2013	Mahmodi et al., Solar Energy Materials & Solar Cells (111) pp. 31-40	[15]	ZnO	0.0		6.02		
2013	Mahmodi et al., Solar Energy (97) pp. 186-194	[16]	TiO ₂ /ZnO			3.01		
2013	Yazdanpour et al., Solar Energy Materials & Solar Cells (118) pp. 1-8	[17]	CuPc/TiO ₂	55.0		27.78		
2014	Merajin et al, J. Taiwan Inst. Chem. Eng. (45) pp. 869-879	[18]	TiO ₂	55.0	60			
2015	Han et al. <i>, ACS Catalysis</i> (6) pp. 494-497	[19]	Pt/TiO ₂ -SiO ₂	48.0	650	1.00	1.30 x 10 ⁻²	3.70 x 10 ⁻¹
2016	Delavari et al., <i>J. Cleaner</i> Production (111) pp. 143- 154	[20]	N/TiO ₂	238.1		6.25		
2016	Laszlo et al., <i>App. Cat. B:</i> Env. (199) pp.473-484	[21]	Au/TNT	185.0		1.99	1.04 x 10 ⁻⁴	1.20 x 10 ⁻⁵
2017	Tahir et al., <i>Applied</i> <i>Surface Science</i> (419) pp. 875-885	[22]	$Cu/g-C_3N_4$	11.0		1.00	1.50 x 10 ⁻⁴	2.80 x 10 ⁻⁴
2018	Pan et al., Chem. Cat. Chem. (10) pp. 940-945	[23]	Pt/Si-CeO ₂		180	30.00	9.00 x 10 ⁻²	1.54 x 10 ⁻¹
2018	Wibowo et al., <i>Chem. Lett.</i> (47) pp. 935-937	[24]	SrTiO ₂	15.4	700		1.20 x 10 ⁻⁴	8.40 x 10 ⁻⁴

2018	Tahir et al., Energy Conservation and Management (159) pp. 284-298	[25]	La/TiO ₂	120.0		1.50	7.00 x 10 ⁻⁴	3.50 x 10 ⁻⁴
2018	Mao et al. <i>, Green</i> Chemistry (20) pp. 2857- 2869	[26]	Pt/CeO ₂	123.0	500	1.00	3.42 x 10⁻¹	3.60 x 10⁻¹
2019	Tahir et al., <i>J. Cleaner</i> Production (213) 451-461	[27]	Ni-MMT/TiO ₂	58.0		1.50	7.50 x 10 ⁻⁴	6.00 x 10 ⁻⁴
2019	Tahir et al., Applied Surface Science (493) pp.18-31	[28]	Ag/pg-C ₃ N ₄	12.0	100	1.50	2.53 x 10 ⁻⁴	7.80 x 10 ⁻⁴
2019	Takami et al. <i>, Sustainable</i> <i>Energy & Fuels</i> (3) pp. 2968-2971	[29]	Ni/Al ₂ O ₃		200	2.50	4.00 x 10⁻³	6.67 x 10⁻³
2019	Li et al., Applied Surface Science (498) 143861	[30]	Zn/g-C ₃ N ₄	21.7	80	29.84	1.55 x 10⁻⁴	6.66 x 10 ⁻⁴
2020	Muhammad et al., Applied Surface Science (504) 144177	[31]	La/g-CNT	4.0		0.20	4.60 x 10⁻⁵	4.91 x 10 ⁻⁴
2020	Takeda et al., Global Challenges (4) 1900067	[32]	Ni/TaC	1.0	500		1.30 x 10 ⁻²	1.40 x 10 ⁻²
2020	Tahir et al, <i>J. CO</i> 2 <i>Utilization</i> (38) pp. 99-112	[33]	Ti ₃ AlC ₂ /TiO ₂			1.00	6.40 x 10⁻⁵	7.83 x 10 ⁻⁴
2020	Pan et al. <i>, App. Cat. B: Env.</i> (260) 118189	[34]	MgO/Pt/Zn- CeO ₂		600	30	3.56 x 10 ⁻¹	5.16 x 10 ⁻¹
2020	Tahir et al., Energy Technology 2000106	[35]	La/TiO ₂	120	100	1.50	3.30 x 10 ⁻⁴	1.03 x 10 ⁻⁴
2020	Zhou et al., <i>Nature Energy</i> (5) pp. 61-70	[36]	CuRu/MgO- Al ₂ O ₃			0.02	3.96 x 10 ⁻¹	3.96 x 10⁻¹
2020	Shoji et al. <i>, Nature</i> <i>Catalysis</i> (3) pp. 148-153	[37]	Rh/STO		200	0.06	5.40 x 10 ⁻²	5.40 x 10 ⁻²

Process Model Example

Below are screenshots of the process model developed to study the solar dry reforming reaction.

Process #2 - Synthesis Gas Production

Inputs		
Basis: CO2 feed rate	0.359	kmol/s
Target Syngas Production	87992.24	kg/h
Time on Stream	24	h/day
Time on Stream	8760	h/y
Feedstock Cost	0.83	\$/kg
Utilities		
Electricity Cost	0.1	\$/kWh
Carbon Tax	0	\$/t CO2
Electricity Carbon Intensity	0.031	kg CO2e per kWh
Light Use		
Hours of Sun	0	(zero indicates 100% electrical heating)
Light Use Compensates For	0%	of total reactor duty during sunlight hours
Catalyst Details		
rate	0.03	kg syngas/kg(cat)-h
cost	33	\$/kg (input from cat_cost sheet)
lifetime	3	У
Operating Conditions		
Raw Feed Temperature	25	degC
Target Reaction Temperature	750	degC
Pressure	1	atm
Reactor Feed Composition		
H2	0.0%	mol%
СО	0.0%	mol%
CO2	40.00%	mol%
CH4	60.00%	mol%
H2O	0.0%	mol%
C	0.0%	mol%
Total	100.00%	mol%
Reactor Product Composition		
H2	50.0%	mol%
СО	50.0%	mol%
CO2	0.0%	mol%
CH4	0.0%	mol%
H2O	0.0%	mol%
С	0.0%	mol%

Total Outputs

Total Syngas Produced	kg/h	87992.24
Operating Cost	\$/kg	\$ 0.93
Total Capital Cost		\$ 1,535,155.03

100.0% mol%

	molecular weight	dH (formation)	dH (combustion)	dH (condensation)
	g/mol	kJ/mol	kJ/mol	kJ/mol
H2	2.0	0.0	286.0	
со	28.0	-110.5	283.0	
CO2	44.0	-393.5		
CH4	16.0	-74.9	891.0	
H2O	18.0	-241.8		-44.0
с	12.0	0.0		

8.314

Physical Constants R J/mol-K

Shomate Equation Parameters (from NIST Webbook)										
	hydrogen		carbon monoxide		carbon dioxide		methane	wat	er vapour	
Temperature Range	298-1000K	1000-2500K	298-1300K	1300-6000K	298 1200.	1200 6000.	298 1300.	1300 6000.500	1700.	1700 6000.
A	33.066	18.563	25.568	35.151	24.997	58.166	-0.703	85.812	30.092	41.964
в	-11.363	12.257	6.096	1.300	55.187	2.720	108.477	11.265	6.833	8.622
c	11.433	-2.860	4.055	-0.206	-33.691	-0.492	-42.522	-2.114	6.793	-1.500
D	-2.773	0.268	-2.671	0.014	7.948	0.039	5.863	0.138	-2.534	0.098
E	-0.159	1.978	0.131	-3.283	-0.137	-6.447	0.679	-26.422	0.082	-11.158
F	-9.981	-1.147	-118.009	-127.838	-403.608	-425.919	-76.844	-153.533	-250.881	-272.180
G	172.708	156.288	227.367	231.712	228.243	263.613	158.716	224.414	223.397	219.781
н	0.000	0.000	-110.527	-110.527	-393.522	-393.522	-74.873	-74.873	-241.826	-241.826

Operating Cost Estimates

1. Variable Costs	Relative Cost/Unit	CAD/y
Misc.		
raw materials	-	636000546.5
operating labor	-	\$104,000
direct supervisor or clerical labor	0.18 x operating labor	\$18,720
maintenance or repairs	0.06 x fixed capital	\$ 76,757.75
operating supplies	0.01 x fixed capital	\$ 12,792.96
laboratory charges	0.15 x operating labor	\$ 100,000.00
patents and royalties	0.03 x total operating costs	\$ 20,017,308.43
Utilities	-	
time on stream	h/d	24
time on stream	h/y	8760
preheater power consumption	kW	33909.91
preheater electricity required in 1 year	kWh	297050816.7
condenser power consumption	kW	-34519.00
Condenser electricity 1 yr	kWh	-302386414.08
Reactor	•	
reactor power consumption	kW	35703.62
hours of sun	h/d	0
Light Use Compensates For	of total reactor duty during sunlight	0%
time on stream	h/d	24.00
electricity during cup use	kWb	0.00
electricity during dark hours	kWh	312763696.7
total reactor electricity use	kWh	312763696.74
electricity grid cost	\$/kWh	0.1
total electricity cost	\$/v	\$ 30,742,809,93
Catalyst	÷/ 1	<i> </i>
target syngas production	kg/h	87992.24
rate	kg syngas/kg(cat)-h	0.03
cost	\$/kg (input from cat, cost sheet)	33
lifetime		3
antolyst romacom ont cost	¢ hr	¢ 22 262 910 72
	\$/y	\$ 52,205,819.75
	\$/y	\$719,336,755.31
2. Fixed Costs		
depreciation		-
local taxes and insurance	0.03 x fixed capital	\$ 38,378.88
plant overhead costs	0.6	\$ 119,686.65
Total Fixed Costs	\$/y	Ş 158,065.53
3. General Costs		
administrative costs	0.15	\$ 29,921.66
distribution and marketing costs	0.1 x total operating costs	\$ 66,724,361.43
research and development	0.05 x total operating costs	\$ 33,362,180.72
Total General Costs		\$ 100,116,463.81
Total operating cost less depreciation		\$819,611,284.64
Carbon Tax Savings	<u> </u>	
carbon tax	\$/t CO2	0
annual co2 consumption	kg/y	8306017.194
carbon tax gain		Ş -
Net Operating Costs	\$/kg	\$ 719,494,820.83

 Total operating cost estimation
 D
 \$
 667,243,614.33

 \$
 813,711,724.79
 F
 18.0%

18.0%

Capital Cost Estimation

Purchased Equipment Cost			
Preheater		\$	235,022.07
Reactor		\$	37,850.34
Condenser		\$	21,365.64
Total		\$	294,238.05
Component	% of total	Сс	ost
Purchased Equipment	23%	\$	294,238.05
Purchased Equipment Installation	8%	\$	102,343.67
Instrumentation	9%	\$	115,136.63
Piping	7%	\$	89,550.71
Electrical	5%	\$	63,964.79
Buildings	5%	\$	63,964.79
Yard Improvements	2%	\$	25,585.92
Service Facilities	14%	\$	179,101.42
Engineering and Supervision	7%	\$	89,550.71
Construction Expense	9%	\$	115,136.63
Legal Expense	2%	\$	25,585.92
Contractor's Fee	2%	\$	25,585.92
Contingency	7%	\$	89,550.71
Sanity Check	100%	\$	1,279,295.86
Total Fixed Capital Cost		\$	1,279,295.86
Working Capital		\$	255,859.17
Total Capital Cost		\$	1,535,155.03

Equipment Sizing from US DOE Costs

		Preheater	Reactor	Condenser
		E1	E2	E3
Heat Transfer Coefficient	kW/m2-K	0.17		0.2
Power Consumption	kW	3.39E+04	3.57E+04	-3.45E+04
Area	m2			2.47E+02
Cost		\$ 110,000.00	\$ 37,850.34	\$ 10,000.00
scaling exponent		0.85	0.6	0.65

Preheater Costs

duty	kW	3.39E+04
cost	1998 USD	\$ 110,000.00
CEPCI 1998	-	389.5
CEPCI 2019	-	607.5
cost of preheater	USD	171566.1104
Exchange Rate		1.369863014
Cost of Condenser	CAD	\$ 235,022.07
Reactor Costs	2020	
capacity of pilot	kmol/s CO2	0.000001
shielding	CAD	\$ 2,298.00
frame	CAD	\$ 4,137.00
solar concentrator	CAD	\$ 8,761.00
reactor	CAD	\$ 20,501.00
total	CAD	\$ 35,697.00
cost of reactor	CAD	\$ 37,850.34
Condenser Costs		
area	kW	4.14E+03
cost	1998 USD	\$ 10,000.00
CEPCI 1998	-	389.5
CEPCI 2019	-	607.5
Cost of Condenser	USD	15596.91913
Exchange Rate		1.369863014
Cost of Condenser	CAD	\$ 21,365.64

Inputs (From Dashboard)				
CHANGE VALUES IN DASHBOARD - NOT HERE!				
Basis: CO2 feed rate	0.35907577	kmol/s		
Operating Conditions				
Temperature	750	degC		
Reactor Pressure	1	atm		
Time on Stream	24	h/day		
Light Use Compensates For	0%	of reactor duty		
Feed Composition		o/f ratio =	0.55	by mass
H2	0%	mol%	0.00%	wt%
со	0%	mol%	0.00%	wt%
CO2	40%	mol%	64.65%	wt%
CH4	60%	mol%	35.35%	wt%
H2O	0%	mol%	0.00%	wt%
C (gr)	0%	mol%	0.00%	wt%
Total	100%	mol%	100%	wt%
Product Composition				
H2	50.0%	mol%	6.66%	wt%
СО	50.0%	mol%	93.34%	wt%
CO2	0.0%	mol%	0.00%	wt%
СН4	0.0%	mol%	0.00%	wt%
H2O	0.0%	mol%	0.00%	wt%
C (gr)	0.0%	mol%	0.00%	wt%
Total	100%	mol%	100%	wt%

Stream Table

		Cold Feed	Hot Feed	Wet Product	Dry Product	Water Product
Physical Properties		S1	S2	S3	S4	S5
Temperature	degC	25.00	750.00	750.00	50.00	50.00
Pressure	atm	1.50	1.00	1.00	1.00	1.00
Vapor fraction	-	1.00	1.00	1.00	1.00	0.00
Molar Weight	kg/kmol	27.228	27.228	15.005	#DIV/0!	#DIV/0!
Density	kg/m3	1.6694706	0.3243269	0.178732398	0.1787324	#DIV/0!
Specific Enthalpy	kJ/kg	-0.0165209	1387.3295	1460.731451	48.466057	0
Molar Flow Rates						
H2	kmol/s	0.00	0.00	0.81	0.8145	0
СО	kmol/s	0.00	0.00	0.81	0.8145	0
CO2	kmol/s	0.3590758	0.36	0.00	0.0000	0
CH4	kmol/s	0.54	0.54	0.00	0.0000	0
H2O	kmol/s	0.00	0.00	0.00	0.0000	0.00
C (gr)	kmol/s	0.00	0.00	0.00	0.0000	0
Total (by sum)	kmol/s	0.90	0.90	1.63	1.63	0.00
Total (sanity check)	kmol/s	0.90	0.90	#DIV/0!	1.63	
C atom	kmol/s	0.90	0.90	0.81	0.81	0.00
H atom	kmol/s	2.15	2.15	1.63	1.63	0.00
O atom	kmol/s	0.72	0.72	0.81	0.81	0.00
Mass Flow Rates						
H2	kg/s	0.00	0.00	1.63	1.629	0
СО	kg/s	0.00	0.00	22.81	22.813	0
CO2	kg/s	15.80	15.80	0.00	0.000	0
CH4	kg/s	8.64	8.64	0.00	0.000	0
H2O	kg/s	0.00	0.00	0.00	0.000	0.000
C (gr)	kg/s	0.00	0.00	0.00	0.000	0
Total by conservation	kg/s			24.44	24.4423	0.0000
Total (sanity check by sum)		24.44	24.44	24.44	24.44	
Volumetric Flow Rates						
H2	m3/s	0.00	0.00	68.38	68.38	0.00
СО	m3/s	0.00	0.00	68.38	68.38	0
CO2	m3/s	5.86	30.15	0.00	0.00	0
CH4	m3/s	8.78	45.22	0.00	0.00	0
H2O	m3/s	0.00	0.00	0.00	0.00	0.000
Total	m3/s	1.46E+01	7.54E+01	1.37E+02	1.37E+02	0.00E+00

Energy Flow Rates

Case Study Results

	Petrochemical Scale	Biogas from AD	Landfill Gas (LFG)	Post- Combustion Flue Gas	Direct Air Capture
H_2 Production (kg h ⁻¹)	5 000	640	4	25 000	8300
Cost for use as feedstock (kg ⁻¹)	\$0.01	\$0.82	\$0.02	\$0.05	\$0.15
Target (kg H ₂ -1)	\$1.00	\$1.00	\$1.00	\$1.00	\$1.00
Min. cost achievable	\$1.74	\$1.73	\$1.62	\$1.00	\$1.04
Associated min. cat activity (mol H ₂ /g _{cat} -h)	7.33 x 10 ⁻³	7.99 x 10 ⁻⁴	3.30 x 10 ⁻²	1.28 X 10 ⁻³	1.33 x 10 ⁻²
CO ₂ captured (kg h ⁻¹)	6.87 x 10 ⁴	8.79 x 10 ³	56.43	3.44 x 10 ⁵	1.14 10 ⁵

Table 6. Minimum photocatalyst activities for H2 production from solar dry reforming, using the current cost of fossil produced hydrogen as a target price.

Table 7. Minimum cost of production for methanol from syngas made from a photocatalytic dry reforming process.

	Petrochemical Scale	Biogas from AD	Landfill Gas (LFG)	Post- Combustion Flue Gas	Direct Air Capture
MeOH Production (kg h ⁻¹)	1.56 x 10⁵	5.05 x 10 ⁴	325	4.08 x 10 ⁶	6.55 x 10⁵
Cost for use as feedstock (kg ⁻¹)	\$0.05	\$0.86	\$0.06	\$0.05	\$0.15
Target (kg syngas ¹)	\$0.05	\$0.05	\$0.05	\$0.05	\$0.05
Min. cost achievable	\$0.15	\$0.99	\$0.89	\$0.20	\$0.23
Associated min. cat activity (mol syngas/g _{cat} -h)	1.31 x 10 ⁻²	7.23 x 10 ⁻³	7.89 x 10 ⁻³	7.89 x 10 ⁻³	4.72 x 10 ⁻³
CO ₂ consumed (kg h ⁻¹)	1.31 x 10 ⁴	4.25 x 10 ³	27.3	3.44 x 10 ⁵	1.44 x 10 ⁵

	Petrochemical Scale	Biogas from AD	Landfill Gas (LFG)	Post- Combustion Flue Gas	Direct Air Capture
Butanal Production (kg h ⁻¹)	9.36 x 10 ⁴	2.94 x 10 ⁴	189	1.15 x 10 ⁶	4.81 x 10 ⁵
Cost for use as feedstock (kg ⁻¹)	\$0.01	\$0.82	\$0.02	\$0.05	\$0.15
Target (kg syngas ⁻¹)	\$0.09	\$0.09	\$0.09	\$0.09	\$0.09
Min. cost achievable	\$0.09	\$0.89	\$0.78	\$0.09	\$0.19
Associated min. cat activity (mol syngas /g _{cat} -h)	2.08 x 10⁻³	1.04 x 10 ⁻²	9.03 x 10 ⁻³	1.39 x 10 ⁻²	2.64 x 10 ⁻²
CO₂ consumed (kg/h)	5.61 x 10 ⁴	8.79 x 10 ³	56	3.44 x 10 ⁵	1.44 x 10 ⁵

Table 8. Minimum catalyst activities for the solar dry reforming reaction as applied to the hydroformylation process.

Bibliography

- [1] M. Bradford and M. Vannice, "CO_2 Reforming of CH_4," Catalysis Reviews, vol. 41, pp. 1-42, 1999.
- [2] D. Pakhare and J. Spivey, "A review of dry (CO2) reforming of methane over noble metal catalysts," *Chemical Society Reviews*, vol. 43, pp. 7813-7837, 2014.
- [3] S. Wang and G. Lu, "Carbon dioxide reforming of methane to produce synthesis gas over metal-supported catalysts: State of the art," *Energy and Fuels,* vol. 10, pp. 896-904.
- [4] D. Burgess, Jr., "Thermochemical Data," in *NIST Chemistry WebBook, NIST Standard Reference Database Number 69*, Gaithersburg, National Institute of Standards and Technology, 2020.
- [5] T. Roussiére, Catalytic Reforming of Methane in the Presence of CO2 and H2O at High Pressure, Karlsruher Institut für Technologie Universitätsbereich genehmigte, 2013.
- [6] M. Nikoo and N. Amin, "Thermodynamic analysis of carbon dioxide reforming of methane in view of solid carbon formation," *Fuel Processing Technology*, vol. 92, pp. 678-691, 2011.
- [7] H. van Ness and M. Abbott, "Thermodynamics," in *Perry's Chemical Engineers' Handbook (8th Ed.)*, McGraw-Hill Professional Publishing, 2007.
- [8] J. Gmehling, M. Kleiber, B. Kolbe and J. Rarey, Chemical Thermodynamics for Process Simulation, Verlag: Wiley VCH, 2019.
- [9] S. Gordon and B. McBride, "Computer Program for the Calculation of Complex Chemical Equilibrium Compositions and Applications, 1. Analysis," NASA Reference Publication 1311, 1994.
- [10] S. Gordon and B. McBride, "CEARUN," NASA, [Online]. Available: http://cearun.grc.nasa.gov. [Accessed 2020].
- [11] Y. Kohno, T. Tanaka, T. Funabiki and S. Yoshida, "Reaction mechanism in the photoreduction of CO with CH over 2 4 ZrO 2," *Phys. Chem. Chem. Phys.*, vol. 2, pp. 5302-5307, 2000.
- [12] D. Shi, Y. Feng and S. Zhong, "Photocatalytic conversion of CH4 and CO2 to oxygenated compounds over Cu/CdS–TiO2/SiO2 catalyst," *Catalysis Today*, vol. 98, pp. 505-509, 2004.

- [13] K. Teramura, T. Tanaka, H. Ishikawa, K. Yoshiumi and T. Funabiki, "Photocatalytic Reduction of CO2 to CO in the Presence of H2 or CH4 as a Reductant over MgO," *J. Phys. Chem. B.*, vol. 108, pp. 346-354, 2004.
- [14] L. Yuliati, H. Itoh and H. Yoshida, "Photocatalytic conversion of methane and carbon dioxide over gallium oxide," *Chemical Physics Letters*, pp. 178-182, 2008.
- [15] G. Mahmodi, S. Sharifnia, M. Madani and V. Vatanpour, "Photoreduction of carbon dioxide in the presence of H2,H2O and CH4 over TiO2 and ZnO photocatalysts," *Solar Energy*, vol. 97, pp. 186-194, 2013.
- [16] G. Mahmodi, S. Sharifnia, F. Rahimpour and S. Hosseini, "Photocatalytic conversion of CO2 and CH4 using ZnO coated mesh: Effect of operational parameters and optimization," *Solar Energy Materials & Solar Cells*, vol. 111, pp. 31-40, 2013.
- [17] N. Yazdanpour and S. Sharifnia, "Photocatalytic conversion of greenhouse gases (CO2 and CH4) using copper phthalocyanine modi fied TiO2," *Solar Energy Materials & Solar Cells*, vol. 118, pp. 1-8, 2013.
- [18] M. Merajin, M. Nasiri, E. Abedini and S. Sharifnia, "Performance of WO3 nanoparticles in photocatalytic conversion of greenhouse gases under visible light irradiation," *Indian Journal of Chemical Technology*, vol. 25, pp. 208-215, 2018.
- [19] B. Han, W. Wei, L. Chang, P. Cheng and Y. H. Hu, "Efficient Visible Light Photocatalytic CO2 Reforming of CH4," ACS Catalysis, vol. 6, pp. 494-498, 2016.
- [20] S. Delavari and N. Amin, "Photocatalytic conversion of CO2 and CH4 over immobilized titania nanoparticles coated on mesh: Optimization and kinetic study," *Applied Energy*, vol. 162, pp. 1171-1185, 2016.
- [21] B. László, K. Baán, E. Varga, A. Oszkó and A. Erdöhelyi, "Photo-induced reactions in the CO2-methane system on titanate nanotubes modified with Au and Rh nanoparticles," *Applied Catalysis B: Environmental*, vol. 199, pp. 473-484, 2016.
- [22] B. Tahir and M. Tahir, "Photo-induced CO2 reduction by CH4/H2O to fuels over Cu-modified g-C3N4 nanorods under simulated solar energy," *Applied Surface Science*, vol. 419, pp. 875-885, 2017.
- [23] F. Pan, X. Xiang, W. Deng, H. Zhao, X. Feng and Y. Li, "ANovel Photo-thermochemical Approach for Enhanced Carbon Dioxide Reforming of Methane," *Chem. Cat. Chem.*, vol. 10, pp. 940-945, 2018.

- [24] S. Wibowo, A. Yamaguchi, S. Shoji, T. Fujita, H. Abe and M. Miyauchi, "Photo-ass isted Dry Reforming of Methane over Strontium Titanate," *Chem. Lett.*, vol. 47, pp. 935-937, 2018.
- [25] B. Tahir, M. Tahir and N. Amin, "Tailoring performance of La-modi fied TiO2 nanocatalyst for continuous T photocatalytic CO2 reforming of CH4 to fuels in the presence of H2O," *Energy Conversion and Management*, vol. 159, pp. 284-298, 2018.
- [26] M. Mao, Q. Zhang, Y. Yang, Y. Li, H. Huang, Z. Jiang, Q. Hu and X. Zhao, "Solar-light-driven CO2 reduction by methane on Pt nanocrystals partially embedded in mesoporous Cite this: Green Chem., 2018, 20, 2857 CeO2 nanorods with high light-to-fuel e fficiency," *Green Chemistry*, vol. 20, p. 2857, 2018.
- [27] M. Tahir, B. Tahir, Z. Zakaria and A. Muhammad, "Enhanced photocatalytic carbon dioxide reforming of methane to fuels over nickel and montmorillonite supported TiO2 nanocomposite under UV-light using monolith photoreactor," *Journal of Cleaner Production*, vol. 213, pp. 451-461, 2019.
- [28] B. Tahir, M. Tahir and N. Amin, "Silver loaded protonated graphitic carbon nitride (Ag/pg-C3N4) nanosheets T for stimulating CO2 reduction to fuels via photocatalytic bi-reforming of methane," *Applied Surface Science*, vol. 493, pp. 18-31, 2019.
- [29] D. Takami, Y. Ito, S. Kawaharasaki, A. Yamamoto and H. Yoshida, "Low temperature dry reforming of methane over plasmonic Ni photocatalysts under visible light irradiation," *Sustainable Energy and Fuels*, vol. 3, pp. 2968-2971, 2019.
- [30] N. Li, Y. Li, R. Jiang, J. Zhou and M. Liu, "Photocatalytic coupling of methane and CO2 into C2-hydrocarbons over Zn T doped g-C3N4 catalysts," *Applied Surface Science*, vol. 498, p. 143861, 2019.
- [31] N. Li, R. Jiang, Y. Li, J. Zhou, Q. Ma, S. Shen and M. Liu, "Plasma-Assisted Photocatalysis of CH4 and CO2 into Ethylene," ACS Sustainable Chem. Eng., vol. 7, pp. 11455-11463, 2019.
- [32] K. Takeda, A. Yamaguchi, Y. Cho, O. Anjaneyulu and F. Takeshi, "Metal Carbide as A Light-Harvesting and Anticoking Catalysis Support for Dry Reforming of Methane," *Global Challenges*, vol. 4, p. 1900067, 2020.
- [33] M. Tahir, "Enhanced photocatalytic CO2 reduction to fuels through bireforming of T methane over structured 3D MAX Ti3AlC2/TiO2 heterojunction in a monolith photoreacto," *Journal of CO2 Utilization*, vol. 38, pp. 99-112, 2020.

- [34] F. Pan, X. Xiang, Z. Du, E. Sarnello, T. Li and Y. Li, "Integrating photocatalysis and thermocatalysis to enable efficient CO2 T reforming of methane on Pt supported CeO2 with Zn doping and atomic layer deposited MgO overcoating," *Applied Catalysis B: Environmental*, vol. 260, p. 118189, 2020.
- [35] B. Tahir, M. Tahir and N. Amin, "Photoinduced Dry and Bireforming of Methane to Fuels over La-Modi fied TiO2 in Fixed-Bed and Monolith Reactors," *Energy Technology*, p. 2000106, 2020.
- [36] L. Zhou, J. Martirez and e. al., "Light-driven methane dry reforming with single atomic site antenna-reactor plasmonic photocatalysts," *Nature Energy*, vol. 5, pp. 61-70, 2020.
- [37] S. Shoji, X. Peng and et al., "Photocatalytic uphill conversion of natural gas beyond the limitation of thermal reaction systems," *Nature Catalysis*, vol. 3, pp. 148-153, 2020.