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Research Article

Development of Reaction Kinetics Model for the Production of Synthesis Gas from Dry Methane Reforming

Abrar Inayat[1,2,*], Muhammad A.B. Ahmad[3], Mohsin Raza[4], Chaouki Ghenai[1,2], Salman Raza Naqvi[5], Muhammad Ayoub[3]

[1]Department of Sustainable and Renewable Energy Engineering, University of Sharjah, 27272 Sharjah, United Arab Emirates.
[2]Biomass & Bioenergy Research Group, Center for Sustainable Energy and Power Systems Research, Research Institute of Sciences and Engineering, University of Sharjah, 27272 Sharjah, United Arab Emirates.
[3]Chemical Engineering Department, Universiti Teknologi PETRONAS, Bandar Seri Iskandar, 31750 Tronoh, Perak, Malaysia.
[4]Department of Chemical & Petroleum Engineering, United Arab Emirates University (UAEU), Al-Ain, United Arab Emirates.
[5]School of Chemical & Materials Engineering, National University of Sciences & Technology, 44000, Islamabad, Pakistan.

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Abstract

The energy supply systems dependent on fossils and municipal solid waste (MSW) materials are primarily responsible for releasing greenhouse (GHG) gases and their related environmental hazards. The increasing amount of methane (CH_4) and carbon dioxide (CO_2) is the scientific community's main concern in this context. Reduction in the emission amount of both gases combined with the conversion technologies that would convert these total threat gases (CO_2 and CH_4) into valuable feedstocks will significantly lower their hazardous impact on climate change. The conversion technique known as dry methane reforming (DMR) utilizes CO_2 and CH_4 to produce a combustible gas mixture ($CO+H_2$), popularly known as synthesis gas/or syngas. Therefore, this research study aims to explore and enlighten the characteristics of the DMR mechanism. The conversion behaviour of CO_2 and CH_4 was studied with modelling and simulation of the DMR process using MATLAB. The results showed that inlet gas flow has a significant impact on the reactions. In contrast, the inlet molar composition ratio of the reactions was found to have no substantial effect on the mechanism of DMR.

Keywords: Greenhouse gases; Synthesis gas; Dry Methane Reforming; Reaction Kinetics Modelling

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1. Introduction

Carbon monoxide (CO) and hydrogen (H_2) have high significance as feedstock for various chemical processes in the process and manufacturing industry. These gases ($CO+H_2$) can be produced by multiple commercialized methods like coal/or biomass gasification, partial oxidation of fossil fuel oil, and steam reforming methane. The mixture of gas ($CO+H_2$) is known as syntheses gas or syngas [1,2]. Synthesis gas is

* Corresponding Author.
Email: ainayat@sharjah.ac.ae (A. Inayat);
Tel: +971-5-653972

usually converted into petrochemicals, synthetic fuels, and higher alcohols [3,4]. Carbon monoxide is widely used in the production of paints, plastics, foams, pesticides, and insecticides; meanwhile, hydrogen is used in ammonia synthesis and petroleum refining industries [5].

Methane reforming is the leading method of producing syngas, supplying more than 80% of the world's synthesis gas [6]. The most cost-effective method of synthesis gas production and gas production includes other predominant processes, such as: naphtha reforming, fuel oil partial oxidation, and coal gasification [7]. Useless CO_2 can be converted into the synthesis gas ($CO+H_2$) by the process of dry reforming of methane (DRM) which uses the natural gas for its reaction mechanism [8]. Synthesis gas ($CO+H_2$) can also be produced by the simultaneous transformation of the two significant greenhouses (GHG) gases (CO_2 and CH_4) in a process called catalytic reforming of methane [9].

For the past several decades, hydrogen (H_2) production was produced by the steam methane reforming (SMR) process. The method is preferred for the synthesis of pure H_2 and its production at a large scale in ammonia manufacturing. Fischer-Tropsch conversion processes have facilitated the alteration of carbon-containing gases into the synthesis gas ($CO+H_2$) more efficiently during the recent scientific era [10]. The conversion of methane (CH_4) and carbon dioxide (CO_2) into synthesis gas ($CO+H_2$) took place based on several reactions, including carbon dioxide reduction by methane, reverse water-gas shift (RWGS) equation, methane decomposition, and reverse Boudouard reactions [8,11,12].

The reaction expressed by equation 3 is the main reaction of the dry methane reforming (DMR) process. This reaction is endothermic; therefore, heat will be absorbed in this stage of the process. Methane (CH_4) reacts with carbon dioxide (CO_2) on the active surface of the solid catalyst to form equimolar synthesis gas. The conversion efficiency of the reaction is improved by supplying CO_2 in the excess amount. For this reaction to occur, the right amount of methane (CH_4) must be applied to reduce carbon dioxide (CO_2) convert it into CO and H_2. This reaction typically occurs over Ni-based catalysts at the temperature ranging from 550–1000 ℃ [13].

The reverse water-gas shift reaction (RWGS) converted the CO_2 and produced H_2 into carbon monoxide (CO) and water vapors (H_2O). This reaction is also endothermic and requires heat for its execution and completion. The reversal nature of water-gas shift reaction is essential for its versatility in applications i-e in ammonia production. Most frequently, the reaction is done using a copper or aluminum catalyst [13−15]. Several industries have practiced the RWGS process for converting cheap and invaluable CO_2 into synthetic CO, which is precious gas in the process industry.

Dry methane reforming (DMR) produces less hydrogen (H_2) than the H_2 produced by the steam reforming process (SRM). Therefore, the dry methane process (DMR) has more feasibility for the biogas, which is already a mixture of CH_4 and CO_2 as the final product from the anaerobic digestion (AD) process. There is no additional need for a downstream separation process for CO_2 removal. For dry methane reforming (DMR) there are several kinds of carbon formation on Ni-based catalyst [14−16]. The reactions contribute to carbon deposition on the surface of the catalyst during the complete formation process cycle. The reverse Boudouard reaction represented is limited at high temperatures. However, the methane decomposition reaction described in equation 3 is thermodynamically more favorable at high temperatures. There should be the application of catalysts that can inhibit the carbon formation and its deposition at the reaction condition [17,18].

In this project, a kinetic reaction model was developed to predict the products and investigate the effect of temperature on final product composition using MATLAB. The work is significant towards highlighting the DMR process for producing CO and H_2 from MSW and better understanding its reaction mechanism. It contributes to the utilization of greenhouse gases for energy production. Hydrogen has many applications and is considered the best clean and energy densified fuel. There is not much data available in the literature to perform the kinetic data analysis for DMR.

The work is also important because of the alarming situation of environmental pollution. Global warming resulting from large quantities of greenhouse gases (GHG), mainly CO_2 emitted to the atmosphere, is the most significant environmental hazard. Thus, future research is focusing on developing technologies that enable the utilization of renewable and carbon-neutral resources.

2. Materials and Methods

The study's goal and scope were to develop the reaction kinetics model for the dry reforming of methane (DMR). To perform parametric analysis for the synthesis gas production from

carbon dioxide and methane that was produced from municipal solid waste (MSW) and to calculate all the independent variables such as reaction kinetics constant and activation energy using optimization approach (MATLAB optimization toolbox) [19]. It is available to perform design optimization tasks, including kinetic parameter estimation, selection of components. This tool is very useful for studying the feasibility of processes and finding the optimal solutions. It is a key to efficient energy management and production planning. Few assumptions have been considered during the modeling and optimization approach, including steady-state conditions, reaction proceeds isothermally at constant volume, four main reactions considered for product calculations.

The rate of a chemical reaction can be attributed to its active chemical species' concentration by a relation known as rate law [20]. The active chemical species include reactants, products, and the catalysts involved. Every reaction has its rate of reaction, which is defined by Equation 1-2.

$$r_i = kC_aC_b \quad (1)$$

$$k = A_i \exp^{-\frac{Ea}{RT}} \quad (2)$$

Four main parameters have been identified, including gas flow rate, inlet molar composition, mole percentage and temperature. Process developing and modeling the reaction process was conducted based on four main reactions simulated in MATLAB software as shown in Equations (3)-(6).

Carbon Dioxide reduction by Methane

$$CO_2 + CH_4 \leftrightarrow 2CO + 2H_2 \quad (3)$$

Reverse Water-Gas Shift (RWGS) reaction

$$CO_2 + H_2 \leftrightarrow CO + H_2O \quad (4)$$

Methane decomposition

$$CH_4 \leftrightarrow C + 2H_2 \quad (5)$$

Reverse Boudouard reaction

$$C + CO_2 \leftrightarrow 2CO \quad (6)$$

MATLAB function m-files were developed by writing function codes. The function m-files being developed with the objectives of producing the final guess value of all independent variables such as activation energy (*Ea*) and reaction rate constant (*k*) throughout the optimization process [21]. The MATLAB simulation optimization was carried out using the experimental data taken from literature for studying the reaction kinetics of the dry methane reforming (DMR) process. The flowchart in Figure 1 showed the optimization approach used for reaction kinetics parameters calculations. Reaction kinetics constants were obtained and extended for parametric study. The gas flow conditions at the inlet feed were set constant at 3600 mL/h and 5400 mL/h with an equal molar ratio (CH_4:CO_2 = 1:1).

3. Results and Discussion

Table 1 shows the kinetic parameters calculated from the four reactions considered for re-

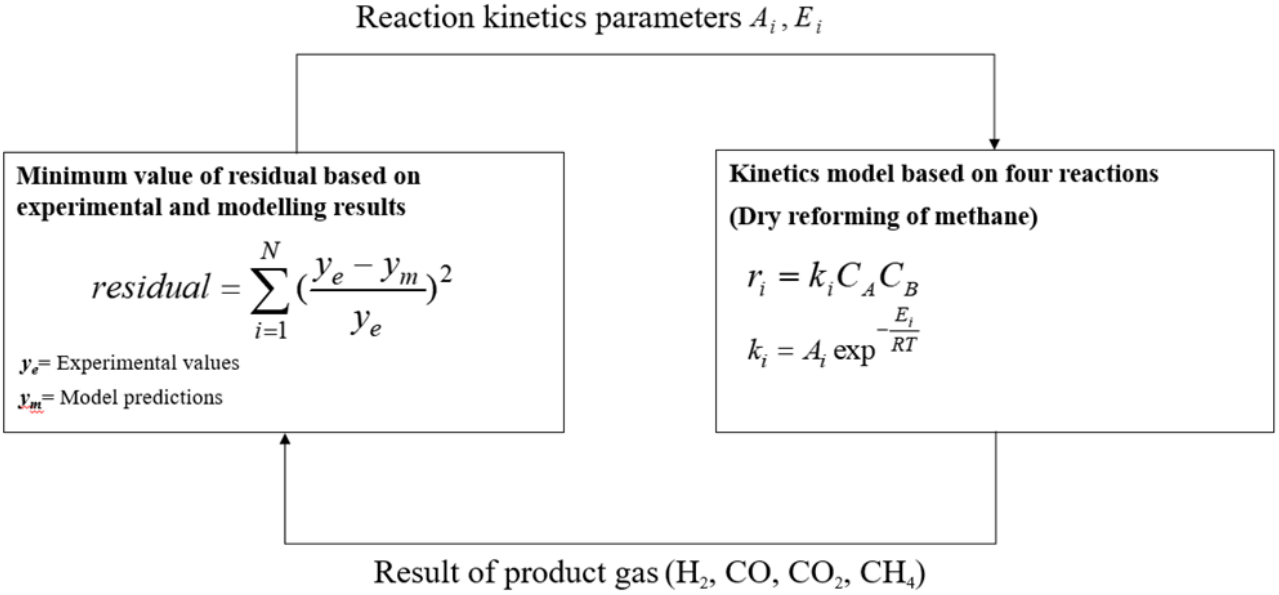

Figure 1. Flowchart for optimization of reaction kinetics parameters of dry methane reforming reactions.

action kinetics modeling of dry methane reforming. Reactions (2) and (3) have the highest values of negative activation energies. Figure 2 showed the product gases CH_4, CO_2, H_2, and CO using 3600 mL/h with a temperature range of 650–850 °C. The mole percentages of all four components were plotted against temperature. It has been observed that as the temperature increases from 650 to 850 °C, there has been a constant increase in the conversion of both CH_4 and CO_2 (decline in mole %) and consequently an increase in the amount (mole %) of H_2 and CO. The decrease in the mol % of CO_2 becomes constant at around 720 °C, but CH_4 mole % shows a decrease until 850 °C. Also, at this molar flow rate, mole % of CO increases significantly up to 750 °C. However, there has been a continuous increase in H_2 mol % up to 850 °C, which shows that higher temperature is favorable for H_2 yields. Also, there has been a more sharp increase in H_2 mole % with an increase in temperature.

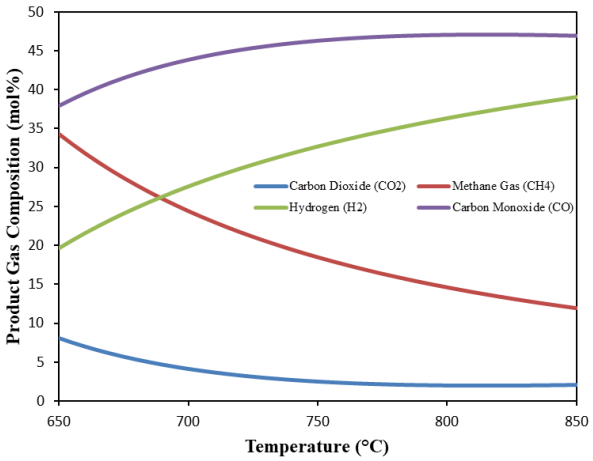

Figure 2. Effect of temperature on product gas composition (mol%) at the gas inlet flow 3600 mL/h.

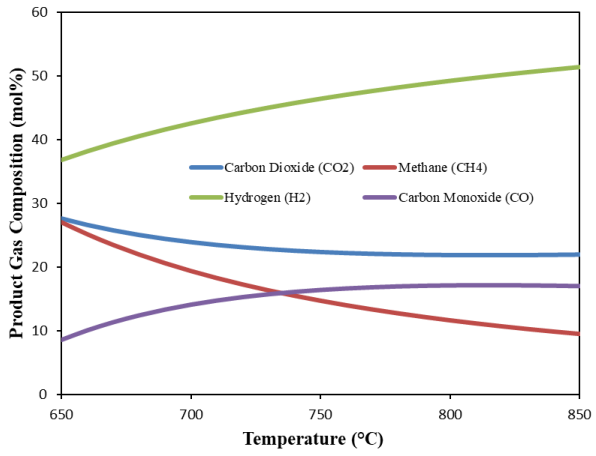

Figure 3. Effect of temperature on product gas composition (mol%) at the gas inlet flow 5400 mL/h.

Similar trends have been observed in the literature by Al-Ali *et al.* [22]. They performed the study in a temperature range of 600–900 °C in a direct contact bubble column. The temperature was found to affect the reaction kinetics mainly. Due to this invention, an optimization strategy was practical to implement and understand the trade-off between high production rates and elevated CO_2 and CH_4 consumption rates in dry methane reforming. The increase in H_2 and CO is mainly caused by the endothermic behavior of reactions involved in the dry methane reforming process.

Furthermore, an increase in the conversion of both reactants (CH_4 and CO_2) was observed due to the reverse water gas shift reaction, methane decomposition, and revers Boudouard reactions. However, different reaction rates for CH_4 and CO_2 were obtained, which was attributed to the undesired formation of water during the reaction. At each point of reaction, the CO_2 conversion is more than CH_4 conversion, and on the product side, the increase in the CO mol% is always more significant than the rise in mol% of H_2.

Figure 3 shows the results obtained from predicted results after optimization at the inlet gas flow of 5400 mL/h. The graph shows when the influence of inlet gas flow is significantly vital as the inlet gas flow increased, the methane and carbon dioxide conversions were both affected. The small carbon monoxide increment in Figure 3 shows that the higher inlet gas flow is not suitable within the range of temperature 650–850 °C. Higher molar flow rate results in higher molar production of H_2. CO molar % decrease with an increase in the gas inlet flow rate. Hence, together with temperature inlet molar flow rate of gas also plays a vital role.

The higher the gas flow, the higher the temperature needed for the reactions. Simultane-

Table 1. Kinetics parameters determined using an optimization approach.

No	Reaction Kinetics	
	Reaction rate constant (*k*)	Activation Energy (*Ea*)
1	0.04	−1285.29
2	0.03	−2747.62
3	1.10	−2714.71
4	−2.31	−716.13

ously, the inlet gas velocity of the syngas production is not produced in maximum value. A trade-off between high production rate and elevated CO_2 and CH_4 consumption rate in dry methane reforming has been observed due to a change in the flowrate. It is also recommended for an additional active optimization attitude to maximize the use of the entire reactant (inlet gas); a suitable inlet gas flow needs to be identified to produce the highest yield of synthesis gas.

4. Conclusion

This study was carried out with the main objective: developing the reaction kinetics model for the dry methane reforming and performing parametric analysis for the hydrogen and carbon monoxide production from greenhouse gases produced from landfills gas. Furthermore, to calculate the reaction kinetics constant using optimization approach (MATLAB optimization toolbox). An operative tool, the dry methane reforming model, was established to assess all the independent variables of activation energy value and reaction kinetics constant value (k). This value indicates how successfully all the independent variables towards producing syngas can be referred to as a general kinetics model for dry methane reforming as future references. The essential features of the reaction mechanism of dry methane reforming were identified via a modeling approach. Gas-phase kinetics has a significant consequence on the production of syngas. The higher the temperature, the better the conversion achieved until a specific limit. Based on the effects of using the same molar composition ratio with increasing inlet gas flow results, it can be concluded that the inlet gas flow in a gas phase reaction is also dominant to the reactions. In addition, it is recommended to perform the full-scale optimization of the process to identify the best optimum operating conditions.

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