A combined thermo-kinetic analysis of various methane reforming technologies: Comparison with dry reforming

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ABSTRACT

Dry reforming of methane is one of the few chemical reactions which can effectively convert carbon dioxide (CO$_2$), a major green-house gas, into a valuable chemical precursor, syngas (a mixture of CO and H$_2$), that can be converted into chemicals and fuels via different synthesis routes such as the Fischer Tropsch synthesis. The inherent limitations of dry reforming reaction, for instance, rapid catalyst deactivation by coke deposition and the very high energy requirements, has restricted its use as a commercial technology. This study was performed to evaluate the potential of overcoming the limitations of dry reforming by integrating it with other commercial methane reforming technologies such as steam reforming and partial oxidation reforming in the context of industrial operating conditions. A thermodynamic and kinetic analysis of the combined reforming has been conducted using the software suite MATLAB®. The aim of this complicated assessment is to identify optimized combination of the three reformers and also the corresponding operating conditions that would utilize significant amount of CO$_2$ while ensuring CO$_2$ fixation, minimum carbon formation and optimum energy requirements. The thermodynamic equilibrium product distribution calculations involved the Peng Robinson (PR), Redlich Kwong (RK) and Soave Redlich Kwong (SRK) equations of state (EOS) to identify the best EOS that accounts for the non-ideality associated with the high pressure operation. The study evaluated simultaneous effects of temperature (200 °C–1200 °C), pressure (1–20 bar) and feed mole ratios (of methane, steam, carbon dioxide and oxygen) on the equilibrium product distribution. The addition of oxygen and steam to dry reforming helped in decreasing energy requirements while simultaneously increasing the syngas yield ratio (H$_2$:CO ratio). The numerical evaluation revealed an optimized operating condition of ~750 °C at 1 bar pressure at a feed mole ratio CH$_4$:H$_2$O:O$_2$:CO$_2$ of 1:0.4:0.3:1. For this optimization, the system boundaries were limited only to a reformer block without considering the upstream and dowstream processes. At this optimized condition, the carbon deposition was eliminated and the CO$_2$ conversion was observed to be 47.84% with an energy requirement of 180.26 kJ. The study is further extended to include kinetic analysis of combined dry and steam reforming of methane. The preliminary findings of kinetic evaluation indicated an excellent agreement between combined kinetic model with the thermodynamic equilibrium results.
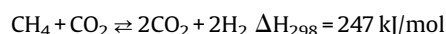
1. Introduction

The need for effective utilization and conversion of the carbon dioxide (CO$_2$) which is a major greenhouse gas (GHG), emphasizes the interest in dry reforming of methane (DRM) reaction. DRM is a process in which CO$_2$ and CH$_4$ (which is a major hydrocarbon feedstock from natural gas) react to form synthesis gas, more commonly known as 'syngas', which is a mixture of carbon monoxide (CO) and Hydrogen (H$_2$).

Dry Reforming of Methane (DRM)

$$CH_4 + CO_2 \rightleftarrows 2CO_2 + 2H_2 \quad \Delta H_{298} = 247 \text{ kJ/mol}$$

Syngas is a valuable precursor for the production of clean fuels via the Fischer-Tropsch Synthesis (FTS) [1–4] and chemicals such as alcohols. Syngas is also attractive in inducing integration among different manufacturing facilities that are located in the same

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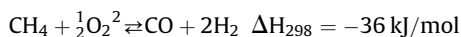*E-mail addresses:* nelbashir@tamu.edu, nimir.elbashir@qatar.tamu.edu (N.O. Elbashir).

industrial city or coupled through an eco-industrial park [5]. In addition to DRM, other natural gas reforming processes include Steam Reforming of Methane (SRM) and Partial Oxidation (POX). The downstream processes in which the produced syngas is to be utilized dictates the appropriate methane reforming technology; for instance, FTS with a cobalt based catalyst requires the synthesis gas yield ratio (H$_2$:CO) of 2:1. Reforming technologies like SRM and DRM are endothermic, while POX is an exothermic process [6,7]:

Steam Reforming of Methane (SRM)

$$CH_4 + H_2O \rightleftharpoons CO + 3H_2 \quad \Delta H_{298} = 206 \, kJ/mol$$
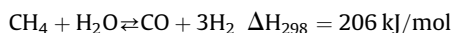
Partial Oxidation of Methane (POX)

$$CH_4 + \tfrac{1}{2}O_2{}^2 \rightleftharpoons CO + 2H_2 \quad \Delta H_{298} = -36 \, kJ/mol$$

Although, in principle, the energy required to drive the SRM and DRM may be provided from various sources including fossil fuels, solar energy, and other renewable sources, fossil fuels are currently most commonly used. Such usage leads to further GHG emissions associated with combustion of fossil fuels. The adoption of DRM presents a very pragmatic route of CO$_2$ utilization for an economy such as the state of Qatar, which has one of the world's largest per capita CO$_2$ emissions rate [8]. Nonetheless, DRM still faces acute issues in the practical implementation because of its inherent process limitations. Among these is the formation of sufficient amounts of carbon that leads to a rapid deactivation of the catalyst [9,10]. This is further complicated by high energy requirements that amount to almost 1.2 times that of the SRM. Another serious consideration for DRM is the problem of low-quality syngas in terms of its hydrogen to carbon monoxide yield ratio (H$_2$:CO ratio of ≤1). Despite the fact that cobalt based FTS requires syngas with an H$_2$:CO ratio of ∼2:1, CO-rich syngas produced from DRM increases the selectivity of long chain hydrocarbons, Dimethyl-Ether(DME) and methanol in direct syngas conversion routes [2,7,11]. Due to these challenges, dry reforming is still a 'gray' area demanding more attention from the scientific community.

In the literature, the issues related to the practical implementations of DRM have been suggested to be addressed by synergistically combining the DRM, SRM and POX reforming into a Combined Reforming of Methane (CRM) process [12–14]. Noureldin et al. [12] reported the comparison between the three reforming techniques in terms of their syngas quality, energy requirements, and operating conditions. They suggested the combined operation of these reforming techniques with their potential benefits in view of CO$_2$ fixation. The same authors in a later study [15] also presented a realistic quantification of the CO$_2$ fixation using DRM process via integration of the conventional reforming technologies. They also highlighted the important tradeoffs associated between the CO$_2$ chemical fixation and its effect on the syngas yield ratio. On a very similar note, Jonas et al. [16] presented a comparative study of a set of five alternative combined reforming routes which compete with DRM process on an annual total cost basis and they demonstrated that DRM/SRM process requires minimum total annual cost. Luyben et al. [17] reported a practical dynamic modeling study highlighting the major tradeoff that could be expected during standalone operation of the DRM process. Özkara-Aydınoğlu et al. [13] analyzed different operating scenarios of the combined SRM/DRM by tuning the reformer feed mole ratio and reported that the activity of methane and H$_2$:CO yield ratio increases considerably upon addition of steam to DRM. Zhang et al. [18] studied the effect of varying the feed mole ratio on the product distribution and proposed an optimum feed ratio (CH$_4$:CO$_2$:H$_2$O:O$_2$ = 1:0.291:0.576:0.088) to maximize H$_2$ yield and CO$_2$ conversion, while maintaining a desired (H$_2$:CO) yield ratio for the downstream methanol synthesis. Chein et al. [19] performed thermodynamic study of

the effect of addition of inert gas on the product distribution of the DRM process and reported that the reactant conversion drops significantly due to the presence of inert gases. They also studied the combined performance of DRM/POX and DRM/SRM bi-reforming processes in view of suppressing carbon formation in single DRM process. Amin et al. [20] reported an optimum feed mole ratio (CO$_2$:CH$_4$:O$_2$ = 1:1:0.1) in view of reducing reforming temperature, while maximizing H$_2$ yield and CO$_2$ conversions. Thermodynamic analysis was also performed by Nematollahi et al. [14] and they reported that pressure has inverse effect on methane conversion in combined POX/DRM reforming of methane. Nikoo et al. [21] carried out similar analysis of carbon formation in a DRM process, and they observed that high pressure operation suppresses the effect of high temperatures on reactant conversions and results in an increased carbon formation. They also carried out a comparison between the experimental and thermodynamically calculated results to study the differences between the real and thermodynamic equilibrium profile in a DRM process.

As seen from the previous studies, the parameters that control the operation of the CRM process are not only temperature and pressure conditions, but also the feed mole ratios [22–25]. In this study, we have taken a base case scenario of CH$_4$:H$_2$O:O$_2$:CO$_2$ feed ratio of 1:0.6:0.1:0.6. This ratio can be approximated to the flue gas composition which can potentially act as a possible feed to the CRM reactor [26].

The challenge related to carbon formation is hypothesised to be addressed in either of the two ways: (a) by introducing either steam, oxygen or both in the feed (i.e., replacing DRM with a CRM process) or, (b) by developing novel catalysts that can either work effectively in coke environment or resist the formation of coke layers on its surface. Recently, through a completely different approach of catalyst formulation, nanoparticle size catalyst were developed by Elham et al. [27]. Their catalyst showed good carbon formation resistance while retaining impressive activity and stability at high temperature conditions. Choudhury et al. [28] reported a rare-earth element Neodymium (Nd)/Cobalt (Co) based catalyst that could prevent itself from carbon deposition. Later, same authors demonstrated the utility of this catalyst for CRM at different process conditions [29]. The effect of addition of oxygen to reduce carbon formation was reported by Song et al. [26], who were amongst the first ones to perform an experimental study on the CRM process, they used flue gas samples as feed to the CRM process and observed that carbon formation occurs in relatively much lower quantities compared to the DRM process. A similar study was also done by Lee et al. [30], the objective of their study being to produce syngas for DME synthesis. They observed that carbon deposition can be suppressed by using coke resistant catalysts and by introduction of oxidant like steam and oxygen in the DRM process. More recently, synthesis gas production for FTS using CRM process has gained immense attention owing to many advantages this process offers compared to the conventional reforming processes.

Much of the research work previously considered the reaction mixture at the reformer operating conditions to be ideal mixture [12,14,19,31]. However, non-ideality could be expected due to high-pressure and high-temperature conditions. In this work, the effect of non-ideality in the reaction mixture has been accounted for by incorporating the fugacity coefficients calculated using Redlich-Kwong(RK), Soave-Redlich-Kwong (SRK) and Peng-Robinson (PR) equations of state (EOS).

One of the major shortcomings of DRM is related to the high energy requirements associated with this process. The energy costs associated with the reforming process directly influences the overall Gas to Liquid (GTL) product cost. Minimizing this cost could present an excellent opportunity to lower the costs of the energy intensive GTL technology. A precise analysis with regards to the