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# Thermodynamic sensitivity analysis of CO<sub>2</sub> reforming of methane based on equilibrium predictions

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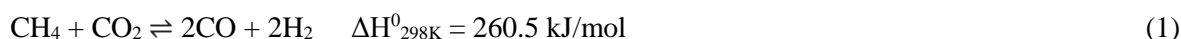
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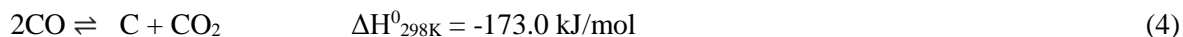
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**Abstract.** Thermodynamic sensitivity analysis was conducted to evaluate the selectivity dry reforming of methane (DRM) with respect to other competing side reactions in terms of Gibbs energy minimization and equilibrium reactor compositions. Spontaneity of each reaction was evaluated by their corresponding changes in Gibbs energy as a function of reactor temperature from 100 – 1000 °C. At temperatures above 700 °C, all reactions considered with the exception of the Boudouard reaction are spontaneous due to their negative deltaG values. Equilibrium compositions were computed for 40 kmol of feed (CO<sub>2</sub> + CH<sub>4</sub>) to determine its sensitivity to occurrence of reverse water-gas-shift (RWGS) reaction and changes in feed CO<sub>2</sub>/CH<sub>4</sub> ratio. The presence of RWGS reaction results to higher reactant conversion accompanied by more severe carbon formation. The H<sub>2</sub>/CO ratio was however not affected by its occurrence. At CO<sub>2</sub>/CH<sub>4</sub> feed ratio of 2, the product ratio was barely affected and at minimal carbon formation while CO<sub>2</sub>/CH<sub>4</sub> ratio value of 0.5 produced a lot of carbon especially at high temperatures due to the prevalence of CH<sub>4</sub> cracking. DRM is thus more preferable at temperatures above 700 °C, devoid of RWGS and high feed CH<sub>4</sub>.

## 1. Introduction

Production of essential long-chain hydrocarbons from synthetic gas via Fischer-Tropsch process has triggered proliferation of world syngas demand [1, 2]. Methane gas is the most widely used for syngas production by reforming with carbon dioxide, steam or partial oxidation because of its widespread availability and renewability potentials [3, 4]. From environmental and economic perspective, syngas generation from catalytic dry reforming of methane (DRM) is the most promising over others. This is due to fact that it produces syngas with a stoichiometric H<sub>2</sub>/CO ratio of 1 (Equation 1) which is a more suitable feedstock for the Fischer-Tropsch synthesis and conversion and converts two gases with green house tendencies to value-added fuels and chemicals [5]. The major challenge of the industrial application of DRM process is the short lifespan of existing catalysts as a result active metal or support sintering and carbon deposition [6]. Carbon deposition occur as a consequence of carbon precipitating side reactions such as methane cracking (Equation 2), reverse water-gas-shift (Equation 3) and Boudouard reaction (Equation 4).





Catalysts from noble metals such as Pt, Pd, Rh and Ru are known for their high resistance to carbon deposition at high activity, but their associated high cost and scarcity hampered their industrial application [7]. Beside noble metals, the potential other metals predominantly Ni, Co and Fe based catalysts have been investigated out of which Ni catalysts produced higher activity emulous to noble metals and thus, commonly used [8 - 11]. Despite its associated performance and economic viability, vulnerability of Ni-based catalysts to sintering and carbon deposition at high reaction temperature is the bottleneck of its DRM applications [12]. From the thermodynamics of DRM, high temperatures are necessary to attain the required syngas yield and reactant conversion, a condition at which carbon deposition is inevitable [13]. Carbon formed during DRM are detrimental to catalyst performance through different media namely: encapsulation of active crystallites phase, pore blockage, collapse of pore structure, clogging of reactor bed and diffusion limitation [14, 15].

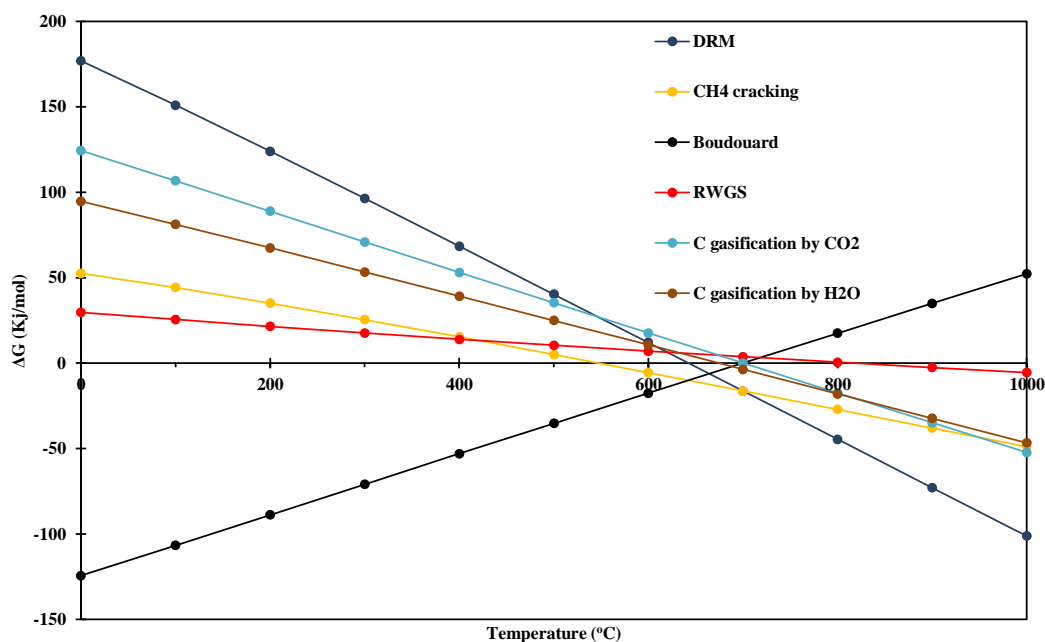
The objective of this paper is to conduct a theoretical thermodynamic studies of DRM reaction alongside competing side reactions such as methane decomposition, reverse water-gas-shift, Boudouard reaction and carbon gasification reactions aided by carbon dioxide or steam. The simulation was conducted using theoretical equilibrium computations and Gibbs free energy minimization on HSC Chemistry 6.0 software.

## 2. Experimental

The thermodynamic analysis was also conducted to investigate the effects of temperature on DRM in the presence of other competitive side reactions at equilibrium conditions. The thermodynamic computations were carried out with the aid of HSC Chemistry 6.0 software, utilizing the reaction equations and equilibrium compositions interface of the software. The effect of reaction temperature on Gibbs free energy ( $\Delta G$ ) minimization for all reactions was also computed to evaluate the spontaneity of DRM in comparison to other side reactions.

## 3. Results and discussions

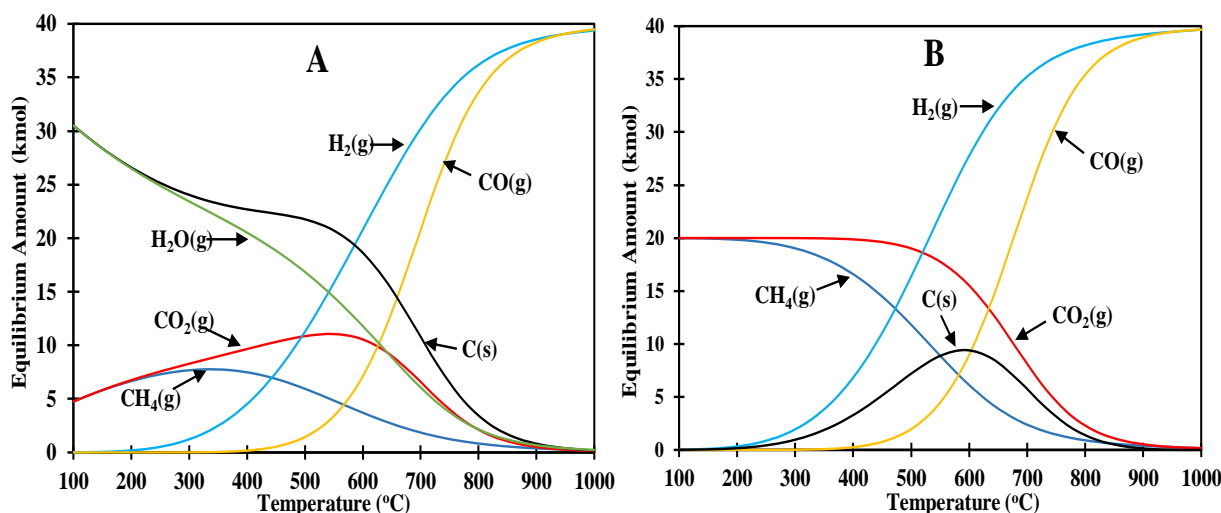
A thermodynamic feasibility studies was conducted using the HSC Chemistry 6.0 software to evaluate the effect of change in Gibbs free energy ( $\Delta G$ ) on the spontaneity of DRM and major competitive side reactions such as methane cracking, RWGS, Boudouard and carbon gasification reactions using carbon dioxide or steam. The effect of temperature on  $\Delta G$  for all chemical reactions from 100 – 1000 °C are depicted in Figure 1. The  $\Delta G$  with negative values implies the spontaneity of the system towards favouring forward reaction while positive values are indicative of non-spontaneous chemical reactions [16]. A zero value of  $\Delta G$  signifies a reaction in the state of equilibrium with no visible conversion. From the figure, it was observed that reaction temperature significantly affects the  $\Delta G$  of each reaction pathway.



**Figure 1.** Thermodynamic analysis to determine spontaneity of DRM and side reactions.

All reactions considered with the exception of the Boudouard reaction are highly endothermic particularly at low temperatures which is attributed to the high stability of their respective reactants. DRM becomes thermodynamically favourable when the reaction temperature is increased to about 700 °C, below which only methane cracking is favourable (~550 °C). It should also be noted that each reaction attains equilibrium at different temperatures, with DRM and methane cracking reaching equilibrium at temperatures approximately 150 °C and 250 °C lower than the equilibrium temperature of RWGS reaction respectively. Boudouard reaction being highly exothermic was spontaneous at low temperatures [17], with equilibrium attained at 700 °C and temperatures above 700 °C are unfavourable for the reaction. The results obtained agrees with the thermodynamic computations conducted by [18]. The DRM above 700 °C is therefore considered the most suitable, with lower feasibility of Boudouard reaction, methane cracking and RWGS. The feasibility of carbon gasification by CO<sub>2</sub> or steam are also greatly enhanced in this temperature range.

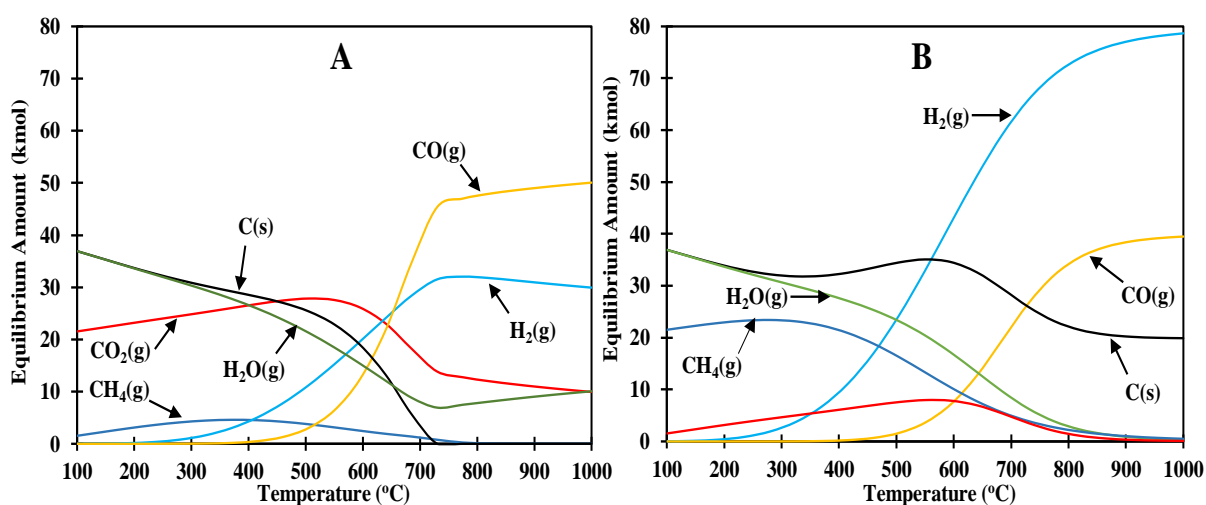
Figure 2 shows the thermodynamics of the equilibrium compositions of all desired and side products at atmospheric pressure as a function of reaction temperature. The molar composition of reactants and products are determined from the Gibbs energy minimisation simulations at equimolar mixture of CO<sub>2</sub>(g) and CH<sub>4</sub>(g), with H<sub>2</sub>(g), CO(g), C(s) and H<sub>2</sub>O(g) taken as components in the equilibrium mixture [19]. Methane cracking and RWGS occur simultaneously alongside the main DRM reaction producing equilibrium stream compositions and H<sub>2</sub>/CO ratios as a function of temperature. The impact of RWGS based on H<sub>2</sub>O produced was investigated by making comparison of equilibrium plot with water (Figure 2A) with that without water formation as obtained in Figure 2B. The presence of RWGS reduces the amount of CO<sub>2</sub> in the system by about 50 % especially at temperatures below 800 °C due to high CO<sub>2</sub> consumption. High CO<sub>2</sub> composition in the RWGS free system produced less carbon deposits (Figure 2B), which is attributed to the superior carbon gasification by CO<sub>2</sub> over gasification using steam produced from RWGS. Methane composition was also higher in the absence of RWGS because of the absence of H<sub>2</sub> consumption which can adjust the equilibrium towards forward reaction for less CH<sub>4</sub> conversion.



**Figure 2.** Thermodynamic plots for  $\text{CH}_4 + \text{CO}_2$  reaction at 1 atm, temperature of 100 – 1000 °C and inlet feed ratio of  $\text{CO}_2:\text{CH}_4 = 1$  with equilibrium reactor product compositions obtained (A) with the presence of RWGS and (B) without RWGS reaction.

For both systems,  $\text{H}_2/\text{CO}$  ratio became constant at a value of 1.0 for temperatures above 750 °C. Below the 750 °C,  $\text{H}_2/\text{CO}$  ratio increases without RWGS as a result of lower CO production. In summary, the occurrence of RWGS was found to significantly affect the equilibrium conversions and composition during DRM. Therefore, tuning this reaction selectivity by the appropriate catalyst development is crucial towards obtaining the desired results.

The effect of variations in the feed ( $\text{CH}_4/\text{CO}_2$ ) composition on the product distribution was investigated by feeding a total of 60 kmol of reactants at a ratio of 1:2 and 2:1 as a function of temperature (Figure 3). From the figure, changing the stoichiometric amount of the reactants thermodynamically affects the product selectivity. Higher amount of  $\text{CO}_2/\text{CH}_4$  in the feed produces syngas with higher CO content than  $\text{H}_2$  (Figure 3A). Similar trend was obtained with higher feed  $\text{CH}_4$  producing more  $\text{H}_2$  (Figure 3B). Carbon deposition is however more prominent on increasing  $\text{CH}_4$  in the feed, especially at temperatures above 700 °C. This is indicative of the carbon deposition predominantly from methane cracking as validated by the rapid increment in  $\text{H}_2/\text{CO}$  ratio. This further confirms that methane cracking contributes the highest amount of carbon deposits compared to the Boudouard reaction [20]. Similar approach was conducted to analyse and compare carbon deposition from different reforming reactions [21] and comparative study of types of carbon deposited during steam and dry reforming [17]. For a high  $\text{CO}_2$  feed, an increase in the amount of  $\text{CO}_2$  was noticed in the system producing larger amount of  $\text{H}_2\text{O}$  at temperatures above 700 °C attributed to more occurrence of RWGS [22]. It can be deduced that beside influencing the product selectivity, altering the stoichiometric feed ratio can also be detrimental to the stability of DRM catalyst. High  $\text{CH}_4$  feed produces more carbon deposits while high  $\text{CO}_2$  feed produces more water that can affect the thermal stability of catalysts [23].



**Figure 3.** Thermodynamic plots for DRM at different inlet feed ratio with equilibrium reactor product compositions obtained (A) with the  $\text{CO}_2:\text{CH}_4 = 2$  and (B) with the  $\text{CO}_2:\text{CH}_4 = 0.5$ .

#### 4. Conclusion

Thermodynamic analysis was conducted for DRM reaction and other side reactions to evaluate and compare the spontaneity of each reaction as a function of reaction temperature. It was observed that dry reforming of methane is most affected by methane cracking and RWGS reaction than it is by Boudouard reaction. This is because the three reactions are spontaneous at high temperatures above 700 °C. Boudouard reaction was however found to be less detrimental due to its spontaneity found to exist only at temperatures lower than reaction temperature. From the thermodynamic sensitivity analysis conducted, it was observed that RWGS reaction does not significantly affect the syngas  $\text{H}_2/\text{CO}$  ratio, but was found to cause more carbon formation. This is attributed to the increased favourability of  $\text{CH}_4$  cracking caused by consumption of  $\text{CO}_2$  and  $\text{H}_2$ . The sensitivity of products composition to changes in  $\text{CO}_2:\text{CH}_4$  ratio in the feed also revealed that syngas  $\text{H}_2/\text{CO}$  ratio is more affected by low  $\text{CO}_2:\text{CH}_4$  and is accompanied by more carbon formation. It can thus be concluded that, for a dynamic upstream feed composition, higher  $\text{CO}_2$  in the feed than the stoichiometric amount has less consequences on the product ratio and catalyst life span. Higher amount of  $\text{CH}_4$  in the feed favours more  $\text{CH}_4$  cracking for increased  $\text{H}_2$  production and carbon deposition.

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