Study of The Contribution of Carbon Iv And Carbon II Oxides in Methanol Synthesis With Modified Kinetic Model

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ABSTRACT

The objective of this work was the simulation of methanol production process using a modified kinetic model to study the effect of reaction conditions on the relative contribution of Carbon II and Carbon IV oxides in methanol synthesis. The results showed that Carbon II oxide hydrogenation decreased as percentage of Carbon IV oxide increased and vice-versa. However it was observed that no generalizations could be made regarding the main carbon source in methanol but that the pathway of contribution from CO/CO_2 hydrogenation depends on process/reaction conditions. It is recommended that for improved process design, there is the need to carefully interpret experimental data and extrapolate results from low pressure/low conversion to high pressure/high conversion laboratory conditions.

Keywords: *Methanol, Natural gas, Kinetic Models, Modified Model, Simulation,*

INTRODUCTION

A number of kinetic models for methanol synthesis have been proposed in the literature (Natta, *et al.*, 1955, Bakemeier, *et al.,* 1970, Leonov, *et al.*, 1973, Klier, *et al.*,1982, Villa, *et al.*, 1985, Graaf, *et al.*, 1988, McNeil, *et al.,* 1989, Skrzypek *et al.*, 1991, Askgaard, *et al.,*1995, Bussche, *et al.*, 1996, Kubota, *et al.*, 2001, Setinc and Levec, 2001, Rozovskii and Lin, 2003, Lim, *et al.*, 2009). One of the major concerns has been the role of CO and CO_2 in methanol production. Initial kinetic studies on methanol synthesis by Natta *et al*. (1955) and Leonov, *et al*.(1973) considered only CO and H_2 as the main reactants and neglected any contribution from CO_2. Later, Klier, *et al.* (1982) showed that methanol was mainly formed from CO and H_2 that adsorbed on the catalyst and CO_2 acted only as a promoter and not as a main reactant. They also suggested that methanol production rate was maximum at a CO_2/CO ratio of 2:28 which was governed by a balance between the promoting effect of CO_2 and the retarding effect due to strong adsorption of CO_2. In another study, Liu, *et al*. (1985) conducted initial rate experiments in a batch reactor to determine the effect of feed composition on methanol production rate and obtained conflicting results.

Furthermore, Sahibzada, *et al*.(1998) showed that the intrinsic rate of CO_2 hydrogenation was twenty times faster than CO hydrogenation and at CO_2 greater than 1%, it was the main source of methanol production. They reported that methanol formation rate increased linearly with increase in CO_2 concentration in the absence of products. Establishing the role of CO_2 in methanol production, Ostrovskii, (2002) studied methanol synthesis mechanism on Cu/Zn containing catalyst under a wide range of experimental conditions and showed that CO_2 was the principal source of methanol production.

Lim et al. (2009) conducted a comprehensive study using Cu/ZnO with the view that CO and CO_2 adsorb on different Cu sites while water adsorbs on a ZnO site. They found that CO_2 hydrogenation rate was slower than CO hydrogenation rate which decreased methanol formation rate but since CO_2 decreases Water Gas Shift (WGS) reaction rate, it, therefore decreases the production of Dimethyl Ether, a byproduct from methanol. It was therefore, concluded that methanol production rate can be indirectly enhanced by finding an optimum CO_2 concentration. Lim, et al., (2009) claimed to be the first to report the role of CO_2 in methanol synthesis, suggesting a kinetic mechanism relating CO and CO_2 hydrogenation reactions. In a more recent study by the same authors, they have used the developed kinetic model to evaluate the effect of carbon dioxide fraction on the methanol yield, and have also devised an optimization strategy to maximize methanol production rate taking CO_2 fraction and temperature profile into account (Lim, et al, 2010). However, the controversies regarding the carbon source in methanol and the nature of active sites still remain unsolved.

The simulation of methanol process is based on the model proposed in this work which is considered to adequately describe some features and resolve questions related to methanol synthesis kinetics. An effort, therefore, was reported by the authors in previous work (Obonukut, et al., 2015) of a modified model that can adequately describe some features and resolve questions related to methanol synthesis kinetics. The proposed model is based on the fact that CO and CO_2 hydrogenation both contribute to overall methanol production and when tested it fits better to the experimental data than others. Further, the issue regarding the main source of carbon in methanol was investigated to see its dependence on reaction conditions like conversion, pressure, relative amount of CO and CO_2, as well as hydrogen content in the feed.

In order to observe the contribution of CO and CO_2 in methanol synthesis, the investigation was carried out using Hysys simulation software on the basis of the modified model. The modified model is simply the combined rate expression obtained by adding Graaf's (CO Hydrogenation) model (see equation 1) to Kubota's (CO_2 hydrogenation) model (see equation 2). In equation 1, the authors assumed that CO is the main source of carbon in methanol (Graaf, et al., 1988) whereas in equation 2 the authors assumed that CO_2 is the main source of carbon in methanol (Kubota, et al., 2001).

$$r = \frac{kK_{CO}\left[f_{CO}f_{H_2}^{3/2} - f_{CH3OH}/\left(f_{H_2}^{1/2}K_{eq}\right)\right]}{(1 + K_{CO}f_{CO} + K_{CO_2}f_{CO_2})\left[f_{H_2}^{1/2} + \left(K_{H_2O}/K_{H_2}^{1/2}\right)f_{H_2O}\right]} \quad \ldots\ldots.1$$

where: r = reaction rate; f_i = fugacity of component i; k = reaction rate constant; K_i = constants relative to adsorption equilibrium terms in the model; K_{eq} = equilibrium constant for methanol synthesis reaction

$$r_M = \frac{k_M\left\{P_{CO_2}P_{H_2} - P_{CH3OH}P_{H_2O}/\left(K_M P_{H_2}^2\right)\right\}}{\left\{1 + K_{CO_2}P_{CO_2} + K_{H_2O}P_{H_2O}\right\}^2} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots.2$$

where: r_M = reaction rate, k_M = reaction rate constant, K*i = equilibrium constant of step i; Pi = partial pressure of component i (bar).

The modified model is shown in equation 3.

$$r = \frac{k_M\left\{P_{CO_2}P_{H_2} - P_{CH3OH}P_{H_2O}/\left(K_M P_{H_2}^2\right)\right\}}{\left\{1 + K_{CO_2}P_{CO_2} + K_{H_2O}P_{H_2O}\right\}^2} + \frac{kK_{CO}\left[f_{CO}f_{H_2}^{3/2} - f_{CH3OH}/\left(f_{H_2}^{1/2}K_{eq}\right)\right]}{(1 + K_{CO}f_{CO} + K_{CO_2}f_{CO_2})\left[f_{H_2}^{1/2} + \left(K_{H_2O}/K_{H_2}^{1/2}\right)f_{H_2O}\right]} \quad \ldots\ldots\ldots.3$$

It assumes that CO and CO_2 hydrogenation both contribute to the overall methanol production but that the relative contribution of CO and CO_2 hydrogenation in producing methanol cannot be generalized. Rather it is opined that the main source carbon in methanol could be influenced by reaction conditions like conversion, pressure, relative amount of CO and CO_2, as well as hydrogen content in the feed which postulation was tested with simulation of a methanol production process via steam reforming of natural gas. In carrying the simulation process the modified model was used together with some hypothetical reactors.

METHODOLOGY

The conventional method of producing methanol from steam reforming of natural gas was simulated using Aspen HYSYS version 3.2 and the process flow diagram is as shown in Figure 1.
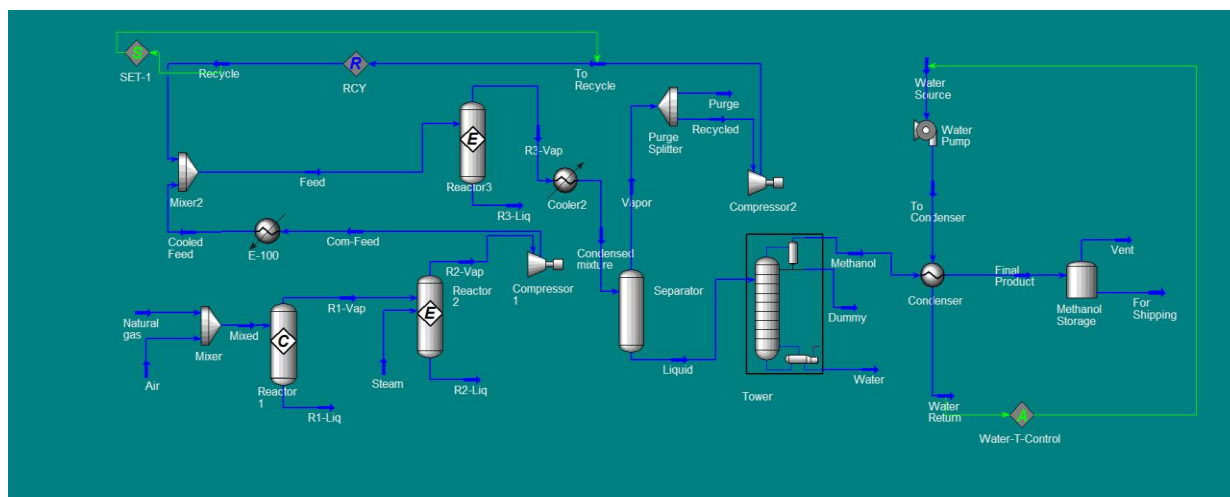

Figure 1: Simulation of Methanol Production Process

The feedstocks, natural gas and air were fed into the Oxidation reactor to produce synthesis gas which in turn is fed together with steam into Reactor E for water-shift reaction to take place. The product from reactor E - during the investigation for CO and CO_2 contribution, the reactor was a stirred tank with modified kinetic parameters as shown in Figure 2 was compressed and heated to the required temperature of 500K for methanol synthesis to take place. The methanol produced is condensed and ejected into a separator where the unreacted feedstocks are separated and the splitter purge the unwanted part and sent the useful part to the compressor which sent it back to the reactor for recycling.
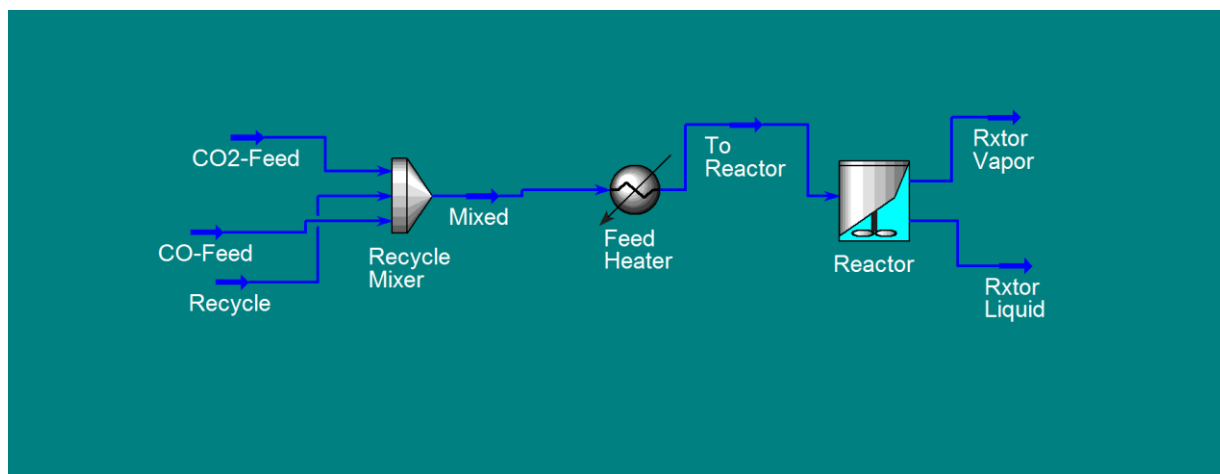

Figure 2: Reactor Simulation of Methanol Production Process using Modified Kinetic Model

Meanwhile, the methanol (Liquid from the separator) is sent to the Tower (distillation column) for purification. The final step in the process is to condense the methanol product and prepare it for storage. Before the condenser is put to use, a source of cooling water is required, hence the need for water source. It will be taken from a storage tank (Water source) and pumped to the required pressure. Initially, the flow rate is set very high (100,000 kg/hr) to ensure that enough cooling water is pump for the heat exchanger to condense the product.

During the heat exchanger design this was reduced to a reasonable value. The cooling water's exit temperature is too low (and need to be adjusted) because of the high flow rate. HYSYS has a unit called an adjust (A for Water-T-Controller). It is something like a process controller in a plant, but it manipulates the model, not the process. It tells us nothing about the dynamics of the process. Like a controller, it changes the value of one parameter in order to bring another parameter to a specified value. In this case, the cooling water flow is manipulated while the outlet water temperature is controlled. Finally, a tank is designed to store the final product which is a two phase mixture containing some vapor (mostly CO_2 and H_2) which has to be vented from the tank and the liquid methanol is stored for shipping.

The results obtained from the simulation were used to analyze the trends and other aspects related to methanol synthesis. The analysis will mainly concentrate on the effect of different reaction conditions on the relative contribution of CO and CO_2 to producing methanol.

RESULTS AND DISCUSSION

The effect of CO_2 and CO hydrogenation on methanol production rate was studied by varying the reaction conditions to see their effect on Methanol production process during the simulation with Aspen Hysys in Figure 1. The modified kinetic model was incorporated into reactor simulation for the methanol production as in Figure 2, which then aided the study of the relative contribution of CO and CO_2 to the hydrogenation process during methanol synthesis.

The results as obtained from the simulation study are discussed under the following conditions: Conversion, Hydrogen content in the feed, Pressure and CO/CO_2 content in the feed

Conversion

Figure 3 shows the Gibb's free energy change of hydrogenation of CO and CO_2 to methanol as a function of temperature. It can be observed that CO_2 hydrogenation has more negative Gibb's free energy change (ΔG) and thus a higher driving force at very low conversions whereas CO hydrogenation is more likely to occur at higher conversions at a temperature of 558 K (Grabow, *et al.*, 2011). These results from thermodynamics prove that conversion levels can affect the extent to which CO and CO_2 hydrogenation will contribute in producing methanol.
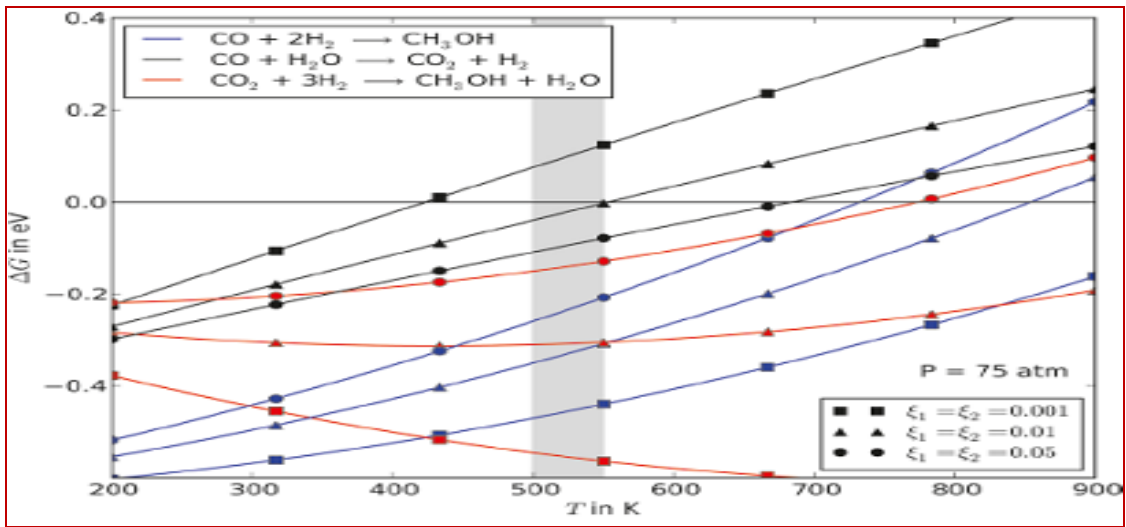
Figure 3: Gibb's free Energy change, ΔG, for CO and CO_2 Hydrogenation to CH_3OH and the WGS reaction at P = 75 atm and three different conversion levels as a function of temperature
Source: Grabow, *et al.*, 2011

The study could not show the same behaviour using our results since not enough data points were available at a constant feed composition and the conversions did not change much in order of magnitude. A similar result was reported by Liu *et al*. (1985) in their study in which they showed that hydrogenation of CO_2 was the primary reaction in producing methanol at low conversion

Hydrogen Content in Feed
Grabow and Mavrikakis have reported that hydrogen content in the feed can have a marked effect on methanol production rates for CO rich feeds (Grabow, *et al*., 2011). Methanol production rate decreases almost linearly with increasing CO_2 content in the feed when the feed is lean in H_2 (< 50 %).
A similar trend was predicted by the model and the simulated result confirmed it as shown in Figure 4. Figure 4 shows a plot of methanol synthesis rate and % CO_2 in the feed under lean H_2 conditions.
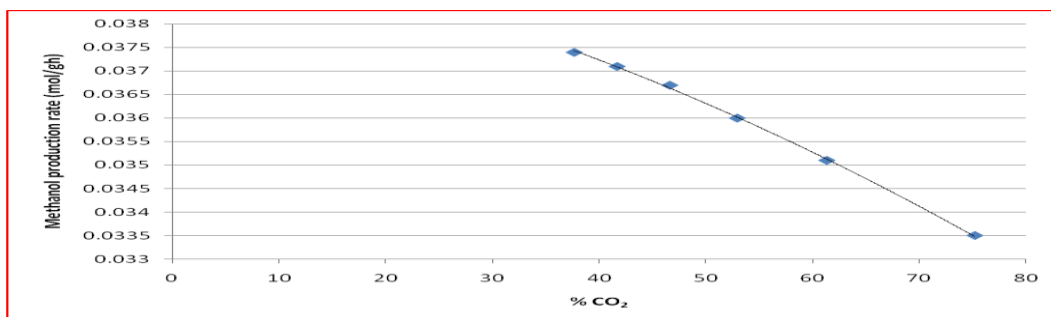

Figure 4: Methanol synthesis rate and % CO_2 in the feed under lean H_2 conditions

It was observed that the rate decreased linearly as CO_2 content in the feed increased. This behaviour can be attributed to the fact that hydrogenation of one mole of CO to methanol needs two moles of H_2 compared to CO_2 which needs three moles of H_2 to form methanol. Therefore, under lean hydrogen conditions, CO hydrogenation activity is increased. However, as percentage of CO_2 in the feed increased, the overall rate decreased since CO hydrogenation was inhibited by increased amounts of CO_2 in the feed. Also, since there was no water in the feed in the beginning, CO_2 participated competitively in methanol synthesis as well as RWGS resulting in lower methanol production. At a pressure of 5066kpa (50 atm), when hydrogen in the

feed was increased slightly, the overall rate showed a maximum value at $CO_2/(CO+CO_2) = 0.046$ (asterisk in Figure 5) as predicted by the model developed in this study.
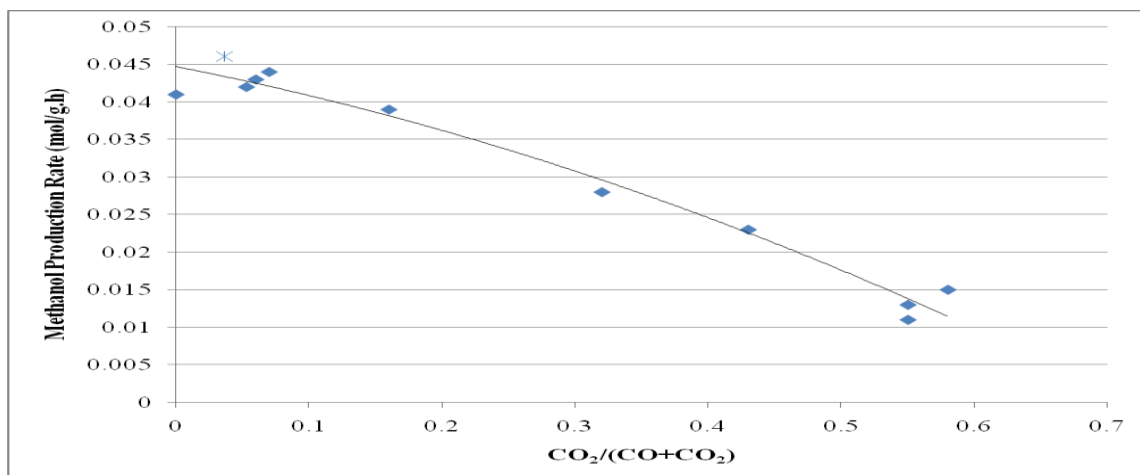

Figure 5: Overall Rate as Function of % CO_2

Calverley reported similar results in their study. However, they observed the maxima when $0.05 < CO_2/(CO+CO_2) < 0.2$ (Calverley, 1989). In this study, hydrogen content in the feed never increased beyond 60%. But at lower pressures (50 atm in our case), less hydrogen may be needed in the feed for the rate to increase with increasing CO_2 amounts. Figure 4.9 shows the overall rate plotted as a function of CO_2 % at a pressure of 50 atm. Therefore, at 50 atm and H_2 content of around 56% in the feed, overall methanol synthesis rate showed an increase in value as % CO_2 increased but it decreased again. This behavior showing maximum rate a particular value of CO_2 % has been reported by other authors as well like Rahman, Klier, *et al.* McNeil, *et al.*, and Lim, *et al.* (Rahman, 2012, Klier, *et al.*,1982, Lim, *et al.,* 2009 and McNeil, *et al.*, 1989).

Pressure

Total pressure also affects the relative contribution from CO and CO_2 in producing methanol. Figure 6 shows the relative contribution of CO and CO_2 at a pressure of 50 atm calculated using the results from the modified model.
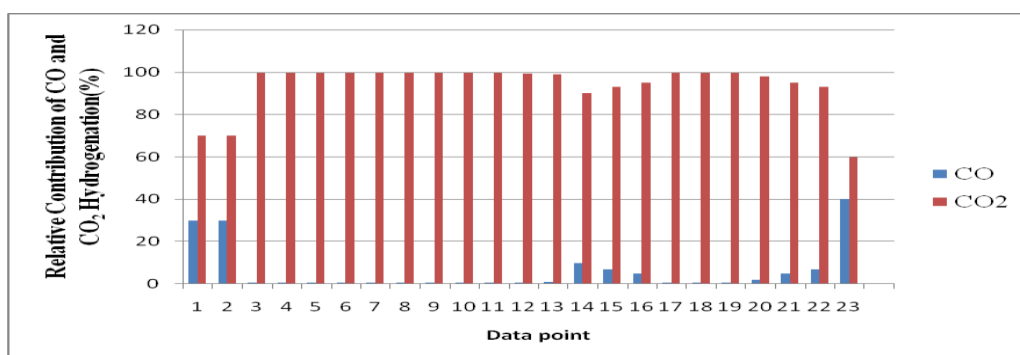

Figure 6:   Relative Contribution of CO and CO_2

The plot clearly shows that CO_2 contributes more than CO to methanol production at a low pressure of 50 atm. The effect of pressure on the relative contribution of CO/CO_2 hydrogenation to methanol synthesis can be explained using Le Chatelier-Braun's principle. This principle states that "whenever stress is imposed on any system (in the form of a change in concentration, temperature, volume or pressure) in a state of equilibrium, the system will always react in a direction which will tend to overcome the imposed stress"

(Onuchukwu, 2004). During CO hydrogenation, three moles of CO react to form one mole of product, whereas, during CO_2 hydrogenation, four moles of CO_2 react to form two moles of product. When the pressure was high, CO hydrogenation was favoured since it is the pathway which results in lower compression.

CO/CO_2 Content in the Feed

Results obtained from the modified model form the basis of studying a few trends related to methanol synthesis kinetics. Figure 7 shows overall rate plotted as a function of % CO in the feed in the absence of CO_2.
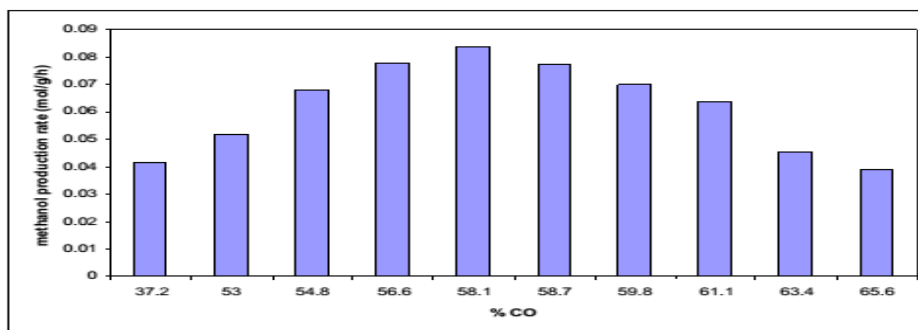
Figure 7: Plot of Overall Methanol Synthesis Rate as a Function of % CO in Feed when % CO_2 in Feed is Low

The rate increased as CO amount in the feed increased, while it decreased when % CO increased beyond 58 %. The increasing trend has also been shown by other authors, for example, McNeil *et al*. (McNeil, *et al*. 1989), as shown in Figure 8. The decreasing trend can be explained by using the fact that in the absence of CO_2, catalyst deactivation occurs via the Boudouard reaction resulting in carbon deposition and, therefore, decreasing methanol synthesis rate. As amount of CO increased, the reaction proceeded in the forward direction at a faster rate leading to more carbon deposition and fouling of the catalyst, and therefore, reducing methanol production rates.
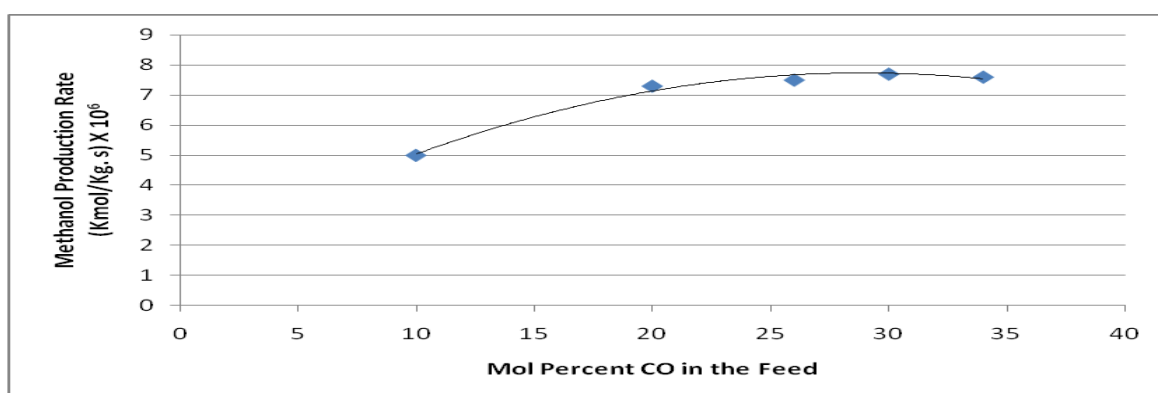
Figure 8: Methanol Production Rate versus Mole Percent Carbon monoxide in the Feed at 513K and 2.89/4.38 MPa

Source: McNeil, *et al*., 1989

The volcanic shape of the plot shown in Figures 7 - 8 has also been reported by Grabow and Mavrikakis (Grabow, *et al*., 2011). They observed a volcano-shaped curve when methanol production was plotted as a function of $CO_2/(CO+CO_2)$ feed ratio for CO- rich feeds.

Another trend predicted by the modified model is that the contribution from CO hydrogenation to forming methanol decreased as % CO_2 increased (see Figure 9).
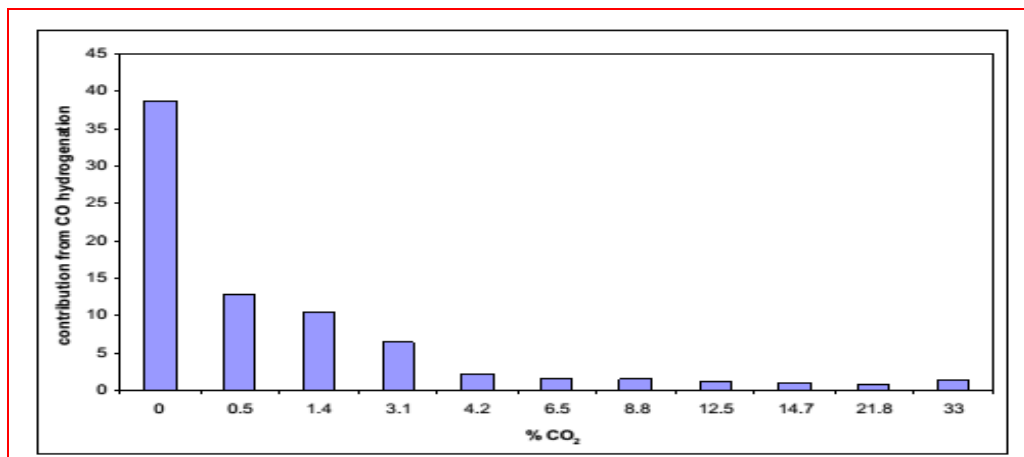

Figure 9: Plot of Relative Contribution of CO Hydrogenation versus %CO_2 in the Feed

The relative contribution from CO hydrogenation in synthesizing methanol plotted as a function of % CO_2 is shown in Figure 10. The plot shows the expected behavior since a high CO_2 content can lead to inhibition of CO hydrogenation due to the strong adsorption of CO_2 on active Cu sites necessary for CO activation. The major fraction of methanol resulted from CO_2 hydrogenation is shown in Figure 10. It is obvious that the intrinsic rate of CO_2 hydrogenation was twenty times faster than CO hydrogenation and at $CO_2 > 1\%$, it was the main source of methanol production. This trend is similar to what Sahibzada, *et al*. reported (Sahibzada, *et al*., 1998).
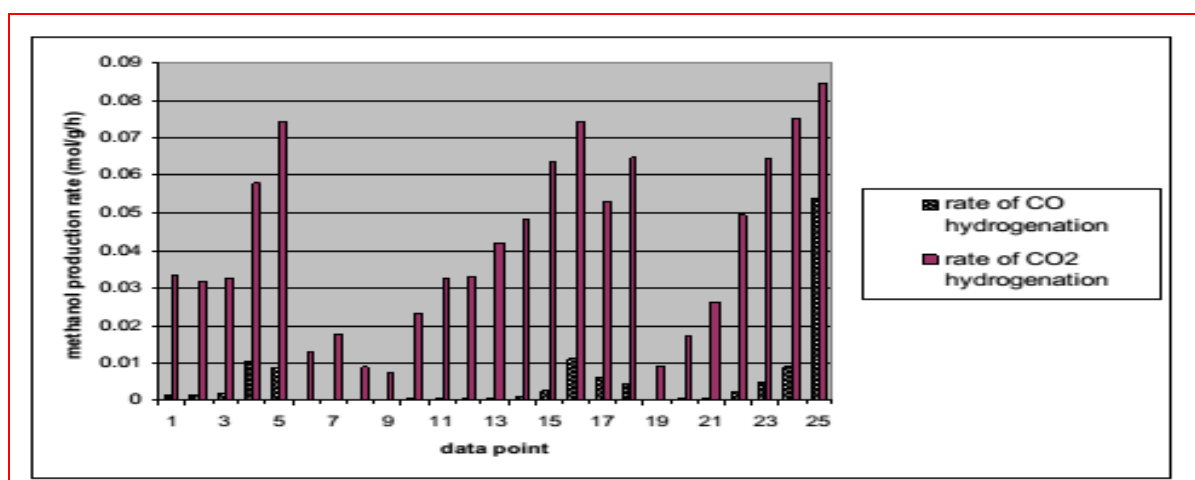

Figure 10: CO versus CO_2 Hydrogenation Rate

This aspect was also studied by Grabow and Mavrikakis who showed that larger fraction of methanol was formed from CO_2. However, they used a different feed composition (Grabow, *et al*., 2011).

CONCLUSIONS

Based on the simulation results, the modified model successfully explains the trends related to methanol synthesis kinetics. The results suggest that no generalization can be made regarding a more dominant reaction pathway. Instead, the contribution from each hydrogenation pathway depends on reaction conditions like conversion, pressure, CO/CO_2, and hydrogen content in the feed. Methanol production can be maximized by optimizing these conditions. Thus for improved process design it is necessary to carefully interpret experimental data and extrapolate results from low pressure/low conversion to high pressure/ high conversion laboratory conditions.

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