



ISSN 2278 – 0211 (Online)

## Kinetic Models Evaluation in Methanol Production for Improved Process Design

**Minister E. Obonukut**

Research Student, Department of Chemical and Petroleum Engineering, University of Uyo, Uyo, Nigeria

**Etim N. Bassey**

Professor, Department of Chemical/Petrochemical Engineering, Akwa Ibom State University, Ikot Akpaden, Nigeria

**Benjamin R. Etuk**

Associate Professor, Department of Chemical and Petroleum Engineering, University of Uyo, Uyo, Nigeria

### **Abstract:**

The work aimed to evaluate kinetic models of methanol synthesis for improved design of the process. Graaf's and Kubota's models were chosen based on their goodness of fit to the respective kinetic data. Polymath was used to fit published experimental data to these kinetic models and evaluate kinetic parameters. The statistical results from Polymath show that Graaf's model fits to the data well when the partial pressure of CO<sub>2</sub> in the feed was low and to a reasonable extent when it was high with  $R^2 \approx 0.83$  and 0.52 respectively, with scattered residuals. Kubota's model fits to the data well only when the partial pressure of CO<sub>2</sub> was high with  $R^2 \approx 0.59$  with scattered residuals but poorly fits when it was low with  $R^2 \approx 0.106$  (far from unity). The combined model was the best fit model and it described methanol synthesis kinetics most appropriately with  $R^2 \approx 0.88$  irrespective of CO<sub>2</sub> partial pressure range.

**Keywords:** Methanol, Kinetic Models, Graaf's Model, Kubota's Model

### **1. Introduction**

Kinetic modeling is an important tool in the design and optimization of chemical synthesis processes. Kinetic studies aid in reactor design and are important means to gain a better insight of the overall process so that it can be modified for optimum operating conditions and better yields. A detailed knowledge of the reaction scheme can often lead to betterment of the production process resulting in appreciable profits (Schack, *et al.*, 1989). Synthesis of methanol is one such industrially important process that deserves attention. Methanol is one of the prime candidates for providing liquid fuel and a feedstock in chemical industries from natural gas.

Methanol can be made from a wide array of feedstocks, making it one of the most flexible chemical commodities and energy sources available today. This includes biomass, coal, natural gas, agricultural and timber waste, solid municipal waste, and a number of other feedstocks. Natural gas can be converted directly or indirectly to methanol. While natural gas is most often used in the global economy, methanol has the distinct advantage of 'polygeneration' - whereby methanol can be made from any resource that can be converted first into synthesis gas.

Methanol synthesis occurs via three reactions namely: hydrogenation of carbon monoxide, hydrogenation of carbon dioxide and water gas shift reactions. There had been a number of studies on methanol synthesis kinetics involving Cu-based catalysts for decades but controversies still remain regarding the reaction mechanism. One of the major concerns had been the role of CO<sub>2</sub> in methanol production. Initial kinetic studies on methanol synthesis by Natta, (1955) and Leonov, *et al.* (1973) considered only CO and H<sub>2</sub> as the main reactants and neglected any contribution from CO<sub>2</sub> (Bussche and Froment, 1996). Since then a number of kinetic models had been proposed in the literature and kinetic parameters had been evaluated, each based on a different set of assumptions regarding the reaction pathway and reaction conditions. Leonov *et al.* (1973) were the first to present a kinetic model for methanol synthesis over a Cu/ZnO/Al<sub>2</sub>O<sub>3</sub> catalyst. However, they did not consider the effect of CO<sub>2</sub> in the feed. Later Klier *et al.* (1982) and Villa *et al.* (1985) proposed models which included the CO<sub>2</sub> terms but did not treat CO<sub>2</sub> as the main reactant. The model proposed by Villa *et al.* (1985) was developed based on the scheme that methanol was produced from only CO and a CO<sub>2</sub> adsorption term was included since CO<sub>2</sub> adsorbs strongly at high concentrations.

Takagawa and Ohsugi (1987) derived empirical rate expressions for the three methanol synthesis reactions under a wide range of experimental conditions. Graaf *et al.* (1990) derived a kinetic model taking into account both CO and CO<sub>2</sub> hydrogenation and the water

gas shift reaction. They derived 48 reaction schemes by assuming different elementary steps to be rate limiting and then selected the best possible kinetic model using statistical discrimination. McNeil *et al* (1989) developed a carbon dioxide hydrogenation rate expression based on mechanistic information reported in literature in contrast to the earlier models based on empirical expressions. Skrzypek, *et al*(1991) derived their kinetic model based on the reactions:  $CO_2 + 3H_2 \rightleftharpoons CH_3OH + H_2O$  and  $CO + H_2O \rightleftharpoons CO_2 + H_2$  and they have shown through their experiments that methanol synthesis prefers  $CO_2$  in spite of  $CO$  as a carbon source.

A kinetic model for methanol synthesis was presented by Askgaard, *et al.* (1995) and the kinetic parameters were evaluated using gas phase thermodynamics and surface science studies. They found that the calculated rates when extrapolated to actual working conditions compared well with the measured rates. Froment and Buschhe (1996) conducted experiments and developed a steady state kinetic model based on a detailed reaction scheme assuming  $CO_2$  to be the main source of carbon in methanol. Their model described the effects of temperature, pressure, and gas phase composition on methanol production rates even beyond their own experimental conditions. In another kinetic study by Kubota, *et al.* (2001), kinetic equations for methanol synthesis were developed assuming  $CO_2$  hydrogenation to be the predominant reaction. The authors found their equations to be reasonably accurate since the yield values obtained from their equations and those from experiments conducted in a test plant compared well.

Setinc and Levec (2001) proposed a kinetic model for liquid phase methanol synthesis and showed that methanol production is proportional to the  $CO_2$  concentration and not to the  $CO$  concentration. Rozovskii and Lin (2003) proposed two reaction schemes to build the theoretical kinetic models which could fit the experimental data well. They used two different gas phase compositions, one enriched with  $CO_2$  and the other with  $CO$  to test the applicability of their models. They found that both the schemes proved to be effective when dealing with a  $CO_2$  enriched mixture, but, the kinetic model based on scheme I did not match with the experimental data well when using a  $CO$  enriched mixture. Lim *et al.* (2009) developed a comprehensive kinetic model consisting of 48 reaction rates based on different possible rate determining steps. They showed through parameter estimation that, among the 48 rates, surface reaction of a methoxy species was the rate determining step for  $CO$  hydrogenation, hydrogenation of a formate intermediate was the rate determining step for  $CO_2$  hydrogenation and formation of a formate intermediate was the rate determining step for the water-gas shift reaction. However they used a  $Cu/ZnO/Al_2O_3/Zr_2O_3$  catalyst. Grabow and Mavrikakis (2011) had developed a comprehensive micro kinetic model using density functional theory calculations to deal with the uncertainties regarding the reaction mechanism and nature of active sites. Table 1, summarizes the various kinetic models, proposed in the literature along with the experimental reaction conditions and authors.

Operating Condition	Kinetic Model	Author, Year
500-550K; 20-30MPa	$r_{CH_3OH} = \frac{f_{CO}f_{H_2}^2 - f_{CH_3OH}/K_2^1}{(A + Bf_{CO} + Cf_{H_2} + Df_{CH_3OH})^3}$	Natta, (1955)
N/A	$r_{CH_3OH} = \frac{Ae^{-\frac{E}{RT}}[P_{CO}^m P_{H_2}^n (1 - P_{CH_3OH}/P_{CO} P_{H_2}^2 K_2^1)]}{1 + De^{-\frac{E}{RT}} P_{CO_2}/P_{H_2}}$	Bakemeier, <i>et al.</i> , (1970)
493-533K; 40-55atm	$r_{CH_3OH} = k \left( \frac{P_{CO}^{0.5} P_{H_2}}{P_{CH_3OH}^{0.66}} - \frac{P_{CH_3OH}^{0.34}}{P_{CO}^{0.5} P_{H_2} K_2^*} \right)$	Leonov, <i>et al.</i> , (1973)
498-523K; 75 atm	$r_{CH_3OH} = \text{const.} \frac{K^3 \text{redox}(P_{CO_2}/P_{CO})^3 (P_{CO} P_{H_2}^2 - P_{CH_3OH}/K_2^*)}{[1 + K_{\text{redox}}(P_{CO_2}/P_{CO})]^3 (F + K_{CO_2} P_{CO_2})^n + K^1 (P_{CO_2} - (1/K_1^*)) (P_{CH_3OH} P_{H_2O}/P_{H_2}^3)}$	Klier, <i>et al.</i> , (1982)
N/A	$r_{CH_3OH} = \frac{f_{CO}f_{H_2}^2 - f_{CH_3OH}/K_2^*}{(A+Bf_{CO}+Cf_{H_2}+Gf_{CO_2})^3}, r_{RWGS} = \frac{f_{CO_2}f_{H_2} - f_{CO}f_{H_2O}K_3^*}{M^2}$	Villa, <i>et al.</i> , (1985)
483-518K; 15-50 bar	$r_{CH_3OH} = \frac{f_{CO}f_{H_2}^2 - f_{CH_3OH}/K_2^*}{(A + Bf_{CO} + Cf_{H_2} + Gf_{CO_2})^3}, r_{RWGS} = \frac{f_{CO_2}f_{H_2} - f_{CO}f_{H_2O}K_3^*}{M^2}$ $r_{CH_3OH}^* = \frac{k_3 K_{CO_2} (C_{CO_2} C_{H_2}^{3/2} - C_{CH_3OH} C_{H_2O} / C_{H_2}^{3/2} K_{eq3})}{(1 + K_{CO} C_{CO} + K_{CO_2} C_{CO_2}) (C_{H_2}^{1/2} + (K_{H_2O} / K_{H_2}^{1/2})) C_{H_2O}}$	Graaf, <i>et al.</i> , (1988)

483-513K; 2.89-4.38MPa	$r = \frac{K_f^1 K_{CH_3OH} K_{H_2}^2 K_{H_2O}^2 K_{CO} (P_{CO} P_{H_2}^2 - P_{CH_3OH} / K_{eq})}{K_{CH_3OH} K_{H_2}^3 K_{H_2O}^3 K_{CO} P_{CO} P_{H_2}^3 + K_{CO_2} P_{CO_2} + K_{H_2}^1 P_{H_2}}$ $+ \frac{K_f^1 K_{H_2} K_{H_2O} K_{CO_2} K_{CH_3OH} [P_{CO_2} P_{H_2} - P_{CH_3OH} P_{H_2O} / (K_{eq}^1 P_{H_2}^2)]}{K_{H_2}^{1/2} K_{H_2O}^{1/2} K_{CO_2} K_{CH_3OH} P_{CO_2} P_{H_2}^{1/2} + K_{CO_2}^1 P_{CO_2}^2 + K_{H_2O}^1 P_{H_2O}^3}$	McNeil, <i>et al.</i> , (1989)
<b>Operating Condition</b>	<b>Kinetic Model</b>	<b>Author, Year</b>
460-550K; 30-90 bar	$r_1 = k_1 K_{H_2}^2 K_{CO_2} \left[ \frac{P_{H_2}^2 P_{CO_2} - (P_{CH_3OH} P_{H_2O} / K_{eq1} P_{H_2})}{(1 + K_{H_2} P_{H_2} + K_{CO_2} P_{CO_2} + K_{CH_3OH} P_{CH_3OH} + K_{CO} P_{CO})^3} \right]^3$ $r_2 = k_2 K_{H_2} K_{CO_2} \left[ \frac{P_{H_2} P_{CO_2} - (P_{CO} P_{H_2O} / K_{eq1} P_{H_2O})}{(1 + K_{H_2} P_{H_2} + K_{CO_2} P_{CO_2} + K_{CH_3OH} P_{CH_3OH} + K_{CO} P_{CO})^2} \right]^2$	Skrzypek <i>et al.</i> , (1991)
483-563K; 1-4 bar	$r_+ = k_{-11} K_5^{-3/2} K_8^{-1} K_9 K_{10} K_{11} \left( \frac{P_{H_2}}{P_0} \right)^{3/2} \left( \frac{P_{CO_2}}{P_0} \right) \theta_*^2$ $r_- = k_{-11} K_5^{-3/2} K_8^{-1} K_9 K_{10} K_{11} \frac{1}{K_G} \frac{P_{CH_3OH} P_{H_2O}}{P_{H_2}^{3/2} P_0^{1/2}} \theta_*^2$	Askgaard <i>et al.</i> , (1995)
453-553K; 15-51 bar	$r_{CH_3OH} = \frac{k_{5a}^1 K_2^1 K_3 K_4 K_{H_2} P_{CO_2} P_{H_2} \left[ 1 - \left( \frac{1}{K^*} \right) (P_{H_2O} P_{CH_3OH} / P_{H_2}^3 P_{CO_2}) \right]}{\left[ 1 + (K_{H_2O} / K_8 K_9 K_{H_2}) (P_{H_2O} / P_{H_2}) + \sqrt{K_{H_2} P_{H_2} + K_{H_2O} P_{H_2O}} \right]}$ $r_{RWGS} = \frac{k_1^1 P_{CO_2} \left[ 1 - K_3^* (P_{H_2O} P_{CO} / P_{CO_2} P_{H_2}) \right]}{\left[ 1 + (K_{H_2O} / K_8 K_9 K_{H_2}) (P_{H_2O} / P_{H_2}) + \sqrt{K_{H_2} P_{H_2} + K_{H_2O} P_{H_2O}} \right]}$	Bussche and Froment (1996)
473-548K; 4.9MPa	$R_M = \frac{K_M [P_{CO_2} P_{H_2} - P_{CH_3OH} P_{H_2O} / K_M P_{H_2}^2]}{\left[ 1 + K_{CO_2} P_{CO_2} + K_{H_2O} P_{H_2O} \right]^2}$ $R_R = \frac{K_R [P_{CO_2} - P_{CO} P_{H_2O} / K_R P_{H_2}]}{1 + K_{CO_2} P_{CO_2} + K_{H_2O} P_{H_2O}}$	Kubota, <i>et al.</i> , (2001)
473-513K; 34-41 bar	$r_{Me} = A_{Me} e^{\left( \frac{-E_{Me}}{RT} \right)} \frac{C_{CO_2} (C_{H_2} - C_{H_2,eq})}{\left( 1 + A_W e^{\left( \frac{E_W}{RT} \right)} C_{H_2O} \right)^2}$ $r_{H_2O} = A_{H_2O} e^{\left( \frac{-E_{H_2O}}{RT} \right)} \frac{(C_{H_2} - C_{H_2,eq})}{\left( 1 + A_W e^{\left( \frac{E_W}{RT} \right)} C_{H_2O} \right)}$	Setinc and Levec, (2001)
513K; 5.2MPa	$r = \frac{k_3 P_{H_2} \left( 1 - \frac{P_M P_{H_2O}}{K_{P(M)} P_{H_2}^3 P_{CO_2}} \right)}{1 + K_{-2} P_{H_2O} + (K_{-2} P_{H_2O} / K_1 P_{CO_2})}$	Rozovskii and Lin, (2003)
523-553K; 5MPa	$r_A = \frac{k_A K_{CO} K_{H_2}^2 K_{CH_3OH} (P_{CO} P_{H_2}^2 - P_{CH_3OH} / K_{PA})}{(1 + K_{CO} P_{CO}) (1 + K_{H_2}^{0.5} P_{H_2}^{0.5} + K_{H_2O} P_{H_2O}) + (1 + K_{CO_2} P_{CO_2})}$ $r_B = \frac{k_B K_{CO_2} K_{H_2}^{0.5} (P_{CO_2} P_{H_2} - P_{CO} P_{H_2O} / K_{PB}) / P_{H_2O}}{(1 + K_{CO} P_{CO}) (1 + K_{H_2}^{0.5} P_{H_2}^{0.5} + K_{H_2O} P_{H_2O}) + (1 + K_{CO_2} P_{CO_2})}$ $r_C = \frac{k_C K_{CO_2} K_{H_2} K_{CH_3OH} (P_{CO_2} P_{H_2}^3 - P_{CH_3OH} P_{H_2O} / K_{PC}) / P_{H_2O}}{(1 + K_{CO} P_{CO}) (1 + K_{H_2}^{0.5} P_{H_2}^{0.5} + K_{H_2O} P_{H_2O}) + (1 + K_{CO_2} P_{CO_2})}$	Lim, <i>et al.</i> , (2009)

Table 1: Summary of Kinetic Models Proposed in Literature for Methanol Synthesis

## 2. Methodology

Kinetic models proposed by researchers were selected based on their efficacy in describing methanol synthesis kinetics. The validity and effectiveness of the models were tested by determining how well they fit the experimental data compared to other proposed models. Two models were evaluated. The first (Graaf's) Model based on the reaction scheme which considers CO to be the primary reactant in methanol synthesis. The second (Kubota's) Model based on the fact that methanol was formed from only carbon dioxide and not carbon monoxide. An extensive set of rate versus partial pressure data for a reaction carried out using Cu/ZnO/Cr<sub>2</sub>O<sub>3</sub> catalyst at relevant temperature and pressure was used for testing the goodness of fit of these models. In this study, experimental data reported by Calverley (1989) were used.

Multiple non-linear regression techniques in Polymath were used to fit the models to the experimental data in order to determine the kinetic parameters and the goodness of fit of the models. The goodness of fit of the kinetic models was then evaluated by comparing the rates obtained from the model with those reported by Calverley. The statistical information and plots reported in the Polymath results were used to judge the quality of the developed model. While testing and comparing the models, the following points (sourced from Polymath Help Documentation) were used as guidelines in determining the goodness of fit of the developed kinetic model:

- $R^2$  and  $R^2_{adj}$ :  $R^2$  and  $R^2_{adj}$  are the correlation coefficients which determine if the model represents the experimental data precisely or not. A correlation coefficient close to unity indicates an adequate regression model. They can also be used for comparing various models representing the same dependent variable.
- Variance and Root-mean-square-deviation (Rmsd): A small Variance (< 0.01) and Rmsd usually indicate a good model. These parameters can be used for comparing various models representing the same dependent variable.
- Graph: If a plot of the calculated and measured values of the dependent variable shows different trends, it signifies an inadequate model.
- Residual plot: The residual plot showing the difference between the calculated and experimental values of the dependent variable as function of the experimental values were used as a measure of goodness of fit of the model. A randomly distributed residual plot is an indication of goodness of fit of a model. If the residuals show a clear trend, it is indicative of an inappropriate model.
- Confidence Intervals: The 95% confidence intervals should be smaller and should have the same sign as the respective parameter values for a statistically good model.

The statistical results from Polymath form the basis for comparison of the kinetic models. Four main comparisons were used in this study. They include:

- Graaf's model vs. Kubota's model for low CO<sub>2</sub> partial pressure data
- Graaf's model vs. Kubota's model for high CO<sub>2</sub> partial pressure data
- Combined model vs. Graaf's model for entire range of data
- Combined model vs. Kubota's model for entire range of data

This comparative study was used to select the model that fits the experimental data best and describes methanol synthesis kinetics most appropriately.

## 3. Results and Discussion

A wide range of data including both low and high CO<sub>2</sub> inlet partial pressures was chosen for regression so that the applicability of the kinetic models could be validated properly. The statistical features obtained by fitting Graaf's model to low inlet CO<sub>2</sub> partial pressure data and Kubota's model to high inlet CO<sub>2</sub> partial pressure data are presented in Figures 1a and 2a respectively. The values of the methanol production rate obtained experimentally were found to be very close using the two models. Figure 1a shows that the model proposed by Graaf which was based on CO being the primary reactant, fit to the data well where CO<sub>2</sub> feed partial pressures was very low. The experimental and estimated rates matched each other quite closely. Furthermore, the residual plots which show the deviation between the experimental values and the corresponding values calculated from the models were examined. For a good fit, the residuals should be randomly distributed and not follow a clear trend around the line of err = 0. The residual plots generated as a result of fitting Graaf's and Kubota's models to the kinetic data are shown in Figures 1b and 2b respectively. Figure 1b shows scattered residuals thereby confirming the hypothesis that CO and not CO<sub>2</sub> is the primary reactant for methanol synthesis. Figure 2a shows a comparison of experimental and calculated values of rate for Kubota's model at high CO<sub>2</sub> partial pressure data.

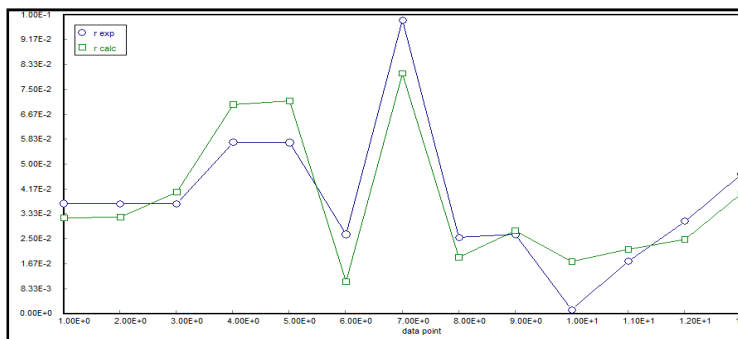


Figure 1a: Experimental and Predicted (by Graaf's model) Methanol Production Rate

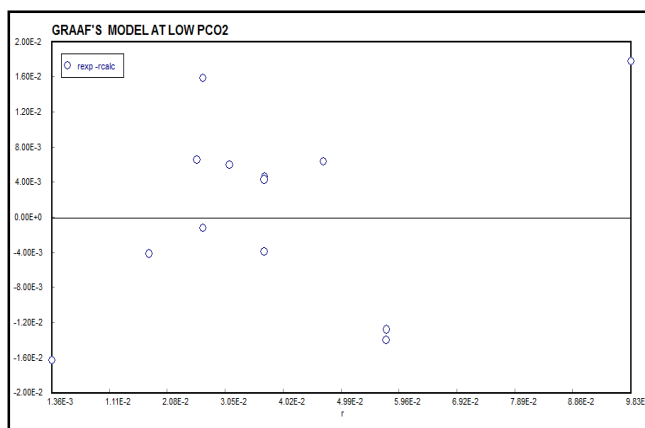


Figure 1b: Residual Plot Generated by Fitting Graaf's Model to Low CO<sub>2</sub> Inlet Partial Pressure

For CO<sub>2</sub> enriched feed, Kubota's model that was derived assuming CO<sub>2</sub> to be the main reactant, provided an effective kinetic description of the methanol synthesis process. As shown in Figure 2a, the rates estimated from Kubota's model are in good agreement with the experimental rate values. Figure 2b shows scattered residuals thereby confirming the hypothesis that CO<sub>2</sub> and not CO is the primary reactant for methanol synthesis.

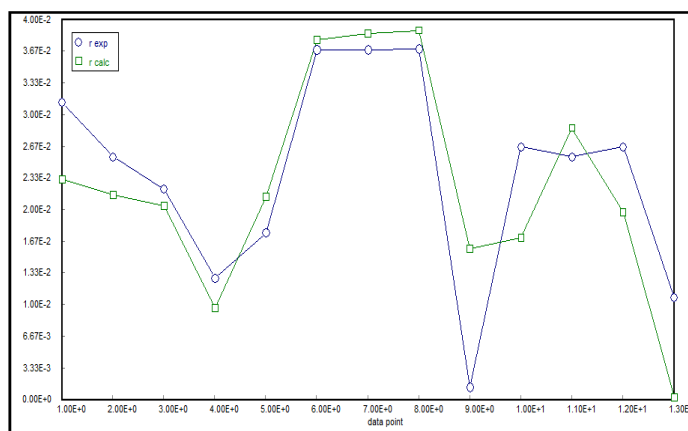


Figure 2a: Experimental and Predicted (by Kubota's model) Methanol Production Rate

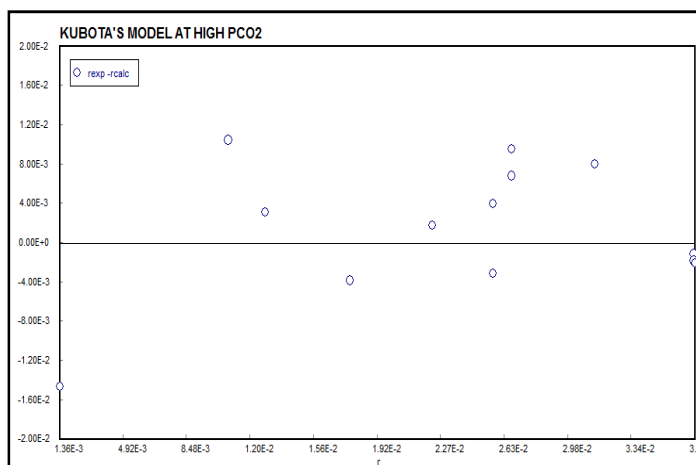


Figure 2b: Residual Plot Generated by Fitting Kubota's Model to High CO<sub>2</sub> Inlet Partial Pressures

As shown in the Figures 1b and 2b, the residuals are distributed in a random manner around the line of  $err = 0$  and did not follow a clear trend indicating the goodness of fit of the two models. In order to compare the effectiveness of each model for the given range of data (i.e., interchanging the data), the two models were fitted to low and high inlet CO<sub>2</sub> partial pressure data and the residuals are presented in Figure 3 for Kubota's model at high inlet pressure and Figure 4 for Graaf's model at low inlet pressure.

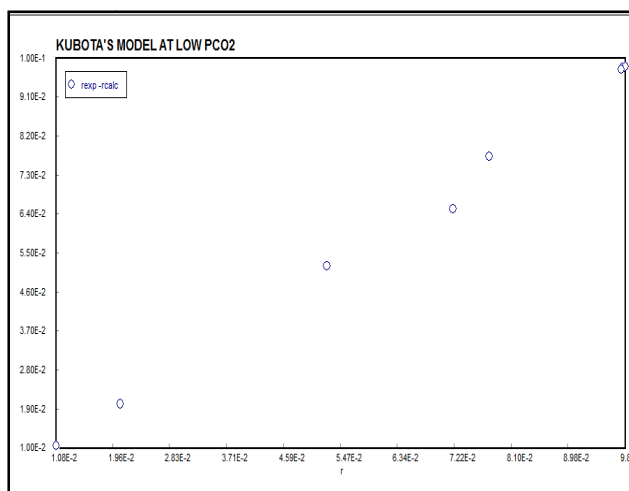


Figure 3: Residual plot generated by fitting Kubota's model to low CO<sub>2</sub> inlet partial pressure

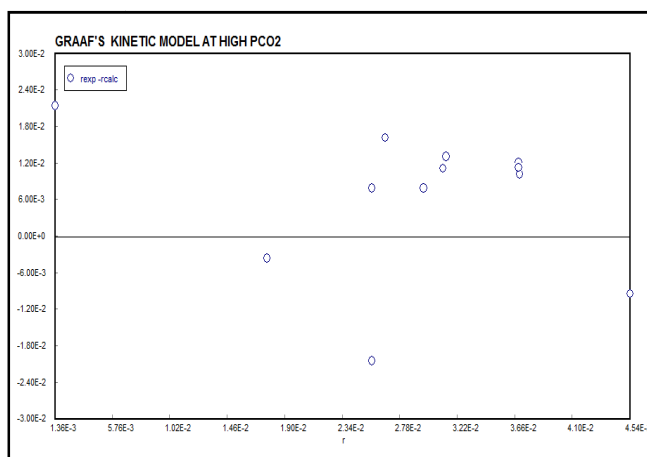


Figure 4: Residual Plot Generated by Fitting Graaf's Model to High CO<sub>2</sub> Inlet Partial Pressure

Figure 5 (Line column chart) shows a comparison of experimental values of rate and those calculated by Graaf's model and Kubota's model when CO<sub>2</sub> partial pressures were negligibly small in the feed. Line column charts have been used to represent the data since it is easier to read the data with these plots. The trend in Figure 5 shows that Graaf's model fits better to the experimental data than Kubota's model when CO<sub>2</sub> is in negligible amounts in the feed indicating that CO is the primary reactant in methanol synthesis than CO<sub>2</sub> when the partial pressure of CO<sub>2</sub> in the feed is low. Thus, the rates calculated by Graaf's model followed the experimental data points very closely leaving the rates calculated by Kubota's model far behind.

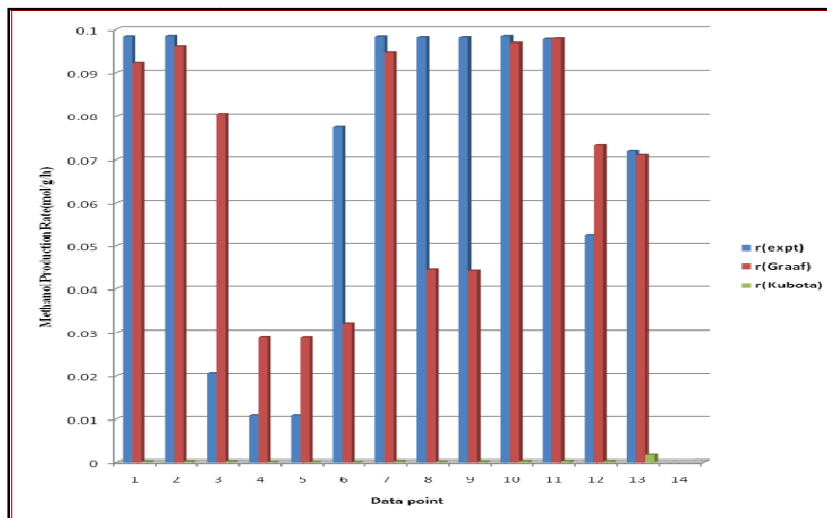


Figure 5: Experimental and Predicted Methanol Production Rate at Low CO<sub>2</sub> Inlet Partial Pressure.

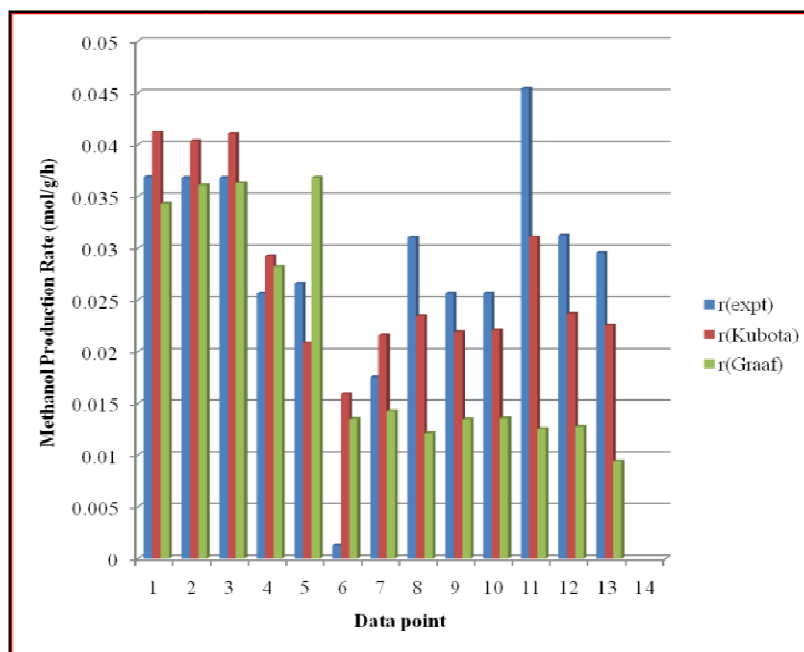


Figure 6: Experimental and Predicted Methanol Production Rate at High CO<sub>2</sub> Inlet Partial Pressure.

Figure 6 shows a comparison of experimental rate values and rate values estimated from Graaf’s and Kubota’s models when the CO<sub>2</sub> partial pressures were high in the feed. It can be observed that in this case, Kubota’s model provides a better kinetic description of the process. Kubota’s model that was based on treating CO<sub>2</sub> as the primary reactant does not match the low CO<sub>2</sub> content data at all (see Figure 5)

However, when CO<sub>2</sub> content in the feed is high, both Graaf’s and Kubota’s models fit to the experimental data satisfactorily. The rates calculated by Graaf also followed the experimental data points closely, though not as close as the rates estimated by Kubota’s model. This feature was also observed by Kubota in his study. The Kubota’s model fits to the experimental results better when CO<sub>2</sub> amounts were higher in the feed. In order to observe the combined effect of CO and CO<sub>2</sub> in methanol synthesis irrespective of CO<sub>2</sub> partial pressure in the feed, the authors proposed a model (combined model) and investigated it using the regression software. The combined model is simply the combined rate expression obtained by summing Graaf’s and Kubota’s Equations (see table 1) to get equation 1

$$r = \frac{k_M \{ P_{CO_2} P_{H_2} - P_{CH_3OH} P_{H_2O} / (K_M P_{H_2}^2) \}}{\{ 1 + K_{CO_2} P_{CO_2} + K_{H_2O} P_{H_2O} \}^2} + \frac{k K_{CO} [ f_{CO} f_{H_2}^{3/2} - f_{CH_3OH} / (f_{H_2}^{1/2} K_{eq}) ]}{(1 + K_{CO} f_{CO} + K_{CO_2} f_{CO_2}) [ f_{H_2}^{1/2} + (K_{H_2O} / K_{H_2}^{1/2}) f_{H_2O} ]} \dots \dots \dots 1$$

The parameters in equation 1 were fitted to the entire range of experimental data including low as well as high CO<sub>2</sub> inlet partial pressures. Figure 7a shows a comparison of experimental values of rate and rates estimated from the combined model. The graph shows a good agreement between the experimental and predicted data and the residuals plot (Figure 7b) shows no trend indicating that the model fits the experimental data.

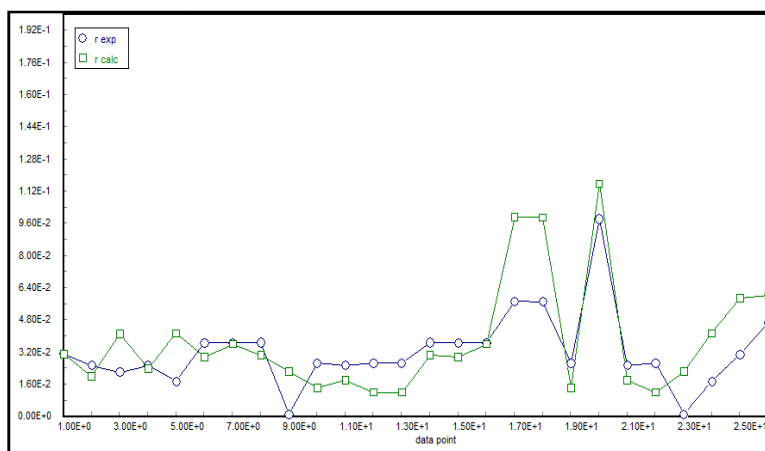


Figure 7a: Experimental and Predicted (by Combine d’s model) Methanol Production Rate

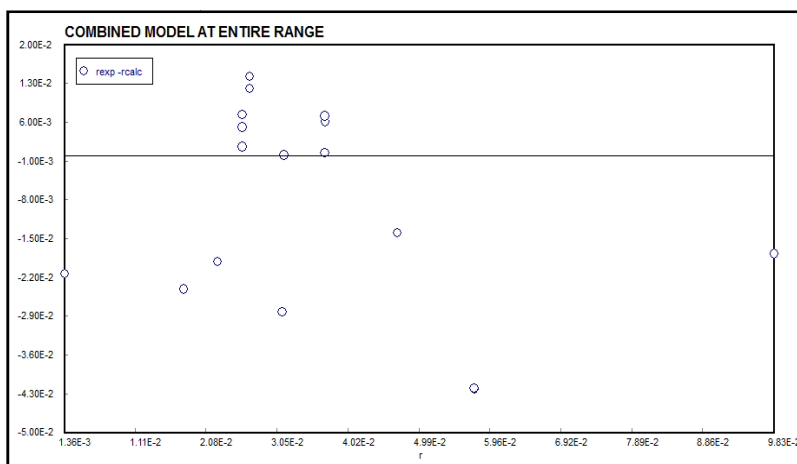


Figure 7b: Residual Plot Generated by Fitting Combined Model to the Entire CO<sub>2</sub> Inlet Partial Pressure

Four main comparisons were carried out in this study. The data set used for fitting to the combined model was also fitted to Graaf's and Kubota's model separately. The comparison of the experimental rate values and those estimated from the combined kinetic rate expression as well as from Graaf's and Kubota's models is shown in Figure 8.

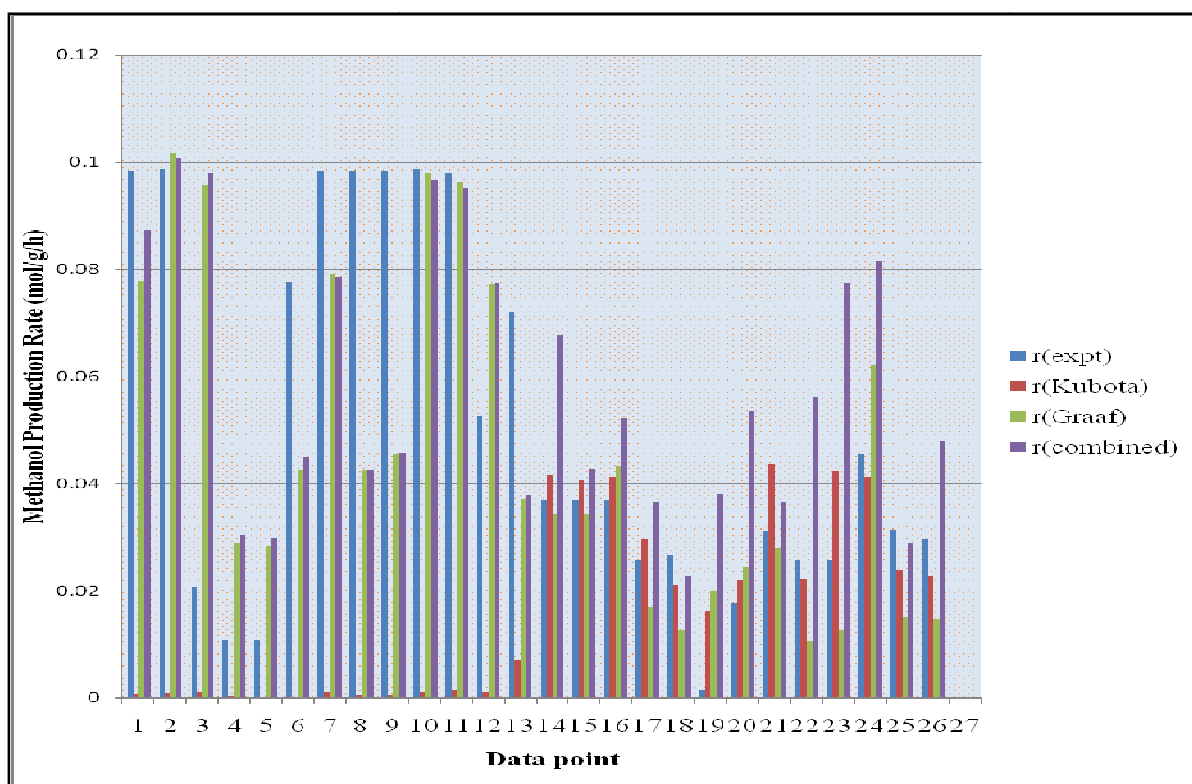


Figure 8: Comparison of Experimental Methanol Production Rate and those Estimated from the Combine d's, Graaf's and Kubota's models

Having seen how the results of each model fitted with the experimental data, the authors intend to present how the kinetic parameters were evaluated along with the methanol production rates presented earlier with the help of Polymath.

**Kinetic Parameter Evaluation:** The statistical features obtained by fitting Graaf's model to low inlet CO<sub>2</sub> partial pressure data and Kubota's model to high inlet CO<sub>2</sub> partial pressure data are summarized in Table 3.

MODEL	PARAMETERS					
	R <sup>2</sup>	R <sup>2</sup> adj	Variance	Rmsd	Residuals	95% Confidence Intervals
Graaf	0.79	0.72	1.5*10 <sup>-4</sup>	0.00286	scattered	positive, smaller
Kubota	0.59	0.55	5.3*10 <sup>-5</sup>	0.00187	scattered	positive, smaller

Table 3: Polymath Results of Fitting Graaf's and Kubota's Model



The statistical features listed in Table 4 are used as indicators of the quality of the regression models. They are explained as follows:

- $R^2$  and  $R^2_{adj}$  which are close to unity suggest that the models satisfactorily represent the kinetic data
- Variance and Rmsd which are sufficiently small indicate that both the models represent the data accurately
- Residuals as shown in Figure 1b and 2b which are randomly distributed, did not follow a particular trend signifying the models are statistically appropriate
- Confidence intervals are small but positive for both the models. The models are statistically stable since the confidence intervals are much smaller than the respective absolute values of the parameters.

The equilibrium constants for CO and CO<sub>2</sub> hydrogenation reactions at the reaction temperature were calculated by Rahman using the THERMOSOLVER software (Rahman, 2012). They were found to be  $3.88 \times 10^{-4} \text{ atm.h}^{-1}$  for CO hydrogenation and  $7.7 \times 10^{-5} \text{ atm.h}^{-1}$  for CO<sub>2</sub> hydrogenation reaction. The parameter values obtained from the fitting procedure are shown in Table 4.

Model	
Graaf	
Parameter	Value
$k \text{ ((atm.h)}^{-1})$	0.0111
$K_{CO} \text{ (atm}^{-1})$	0.0086
$K_{CO_2} \text{ (atm}^{-1})$	0.0533
$K_{wh}$	7.449
Kubota	
Parameter	Value
$K_{CO_2} \text{ ((atm)}^{-1})$	0.036
$K_{H_2O} \text{ (atm}^{-1})$	1.727

Table 4: Kinetic Parameters for Graaf's and Kubota's Model

NOTE:  $K_{wh} = K_{H_2O}/K_{H_2}$

The results of fitting the four comparisons are tabulated in Table 6. The statistical parameters listed in Table 6 as well as the trend in Figure 9 indicate that the combined model is the best fit model.

Low CO <sub>2</sub> Partial Pressure						
Parameter	R <sup>2</sup>	R <sup>2</sup> <sub>adj</sub>	Variance	Rmsd	Residuals	95% Confidence Intervals
Model						
Graaf	0.83	0.75	$1.9 \times 10^{-4}$	0.00286	scattered	positive, smaller
Kubota	0.106	-0.67	$8.5 \times 10^{-4}$	0.0071	follow a trend	positive, smaller
High CO <sub>2</sub> Partial Pressure						
Parameter	R <sup>2</sup>	R <sup>2</sup> <sub>adj</sub>	Variance	Rmsd	Residuals	95% Confidence Intervals
Model						
Graaf	0.52	0.50	$1.5 \times 10^{-4}$	0.00274	scattered	positive, smaller
Kubota	0.59	0.55	$5.3 \times 10^{-5}$	0.00187	scattered	positive, smaller
Entire CO <sub>2</sub> Partial Pressure Range						
Parameter	R <sup>2</sup>	R <sup>2</sup> <sub>adj</sub>	Variance	Rmsd	Residuals	95% Confidence Intervals
Model						
Combined	0.87	0.82	$1.5 \times 10^{-4}$	0.0022	Scattered	Positive, Smaller
Kubota	0.61	0.54	$2.6 \times 10^{-4}$	0.0033	scattered	Positive, Smaller
Entire CO <sub>2</sub> Partial Pressure Range						
Parameter	R <sup>2</sup>	R <sup>2</sup> <sub>adj</sub>	Variance	Rmsd	Residuals	95% Confidence Intervals
Model						
Combined	0.8769	0.82587	$8.58 \times 10^{-4}$	0.005038	scattered	Positive, Smaller
Graaf	0.6814	0.2971	$8.135 \times 10^{-4}$	0.003814	scattered	Positive, Smaller

Table 7: Kinetic Parameter obtained from fitting the Combined Model

Based on the results (Table 7), it can be concluded that the combined rate expression which includes both CO and CO<sub>2</sub> hydrogenation rate terms describes methanol synthesis kinetics in the best possible manner. It was also attempted to fit the combined model separately to low and high inlet CO<sub>2</sub> partial pressure data, however, there were not enough data points in the two ranges to achieve proper regression results.

#### 4. Conclusion

The work involved evaluation of various kinetic models proposed in literature for methanol synthesis and selecting the most appropriate model using regression techniques. Polymath software was the non-linear regression tool used in fitting different models to published experimental data collected at a temperature of 558 K and pressures of 50 and 100 atm over a Cu/ZnO/Cr<sub>2</sub>O<sub>3</sub> catalyst. The result of fitting reveals that the combined model including both CO and CO<sub>2</sub> hydrogenation rate terms is the best fit model. Such a modified kinetic model that can describe methanol synthesis kinetics satisfactorily should prove to be very useful in kinetic studies of methanol leading to a better understanding of the process for improvements in yields and profits.

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