

## Intrinsic reaction rate and the effects of operating conditions in dimethyl ether synthesis from methanol dehydration

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**Abstract**—The kinetic behavior of a commercial  $\gamma\text{-Al}_2\text{O}_3$  catalyst for the methanol to dimethyl ether (DME) dehydration reaction has been investigated using a differential fixed bed reactor at the pressure range 1-16 barg within a temperature range of 260-380 °C. The experimental runs were performed in a wide range of feed to water ratios. The experiments were designed by general full factorial design (GEFD) and a novel rate equation has been developed which exhibited the best fitting with our experimental data. Based on the analysis of variance (ANOVA), the following order of importance for operating conditions was obtained when the objective function is the yield of DME: Temperature > Water % in feed > Pressure. In addition, the optimum operating conditions for the maximum yield of DME, were found at T= 380 °C, P= 16 barg and zero wt% of water in the feed.

Key words: Kinetic, Methanol Dehydration, Dimethyl Ether, Experiment Design

### INTRODUCTION

DME is not only a clean fuel substituting for diesel fuel and liquid petroleum gas, but also an excellent propellant and refrigerant [1-4]. DME is also a feedstock for fuel additives and chemicals, for example, olefins (DTO), methyl acetate, light alkenes and dimethyl sulphate. Furthermore, it may replace methanol as intermediate for obtaining light olefins and fuels from alternative sources to oil (coal, natural gas, and biomass) [5-10]. Due to different new uses of DME, there is a growing demand to produce a larger amount of DME. DME is commercially produced by dehydration of methanol using acidic porous materials such as zeolites, silica-alumina and  $\gamma\text{-Al}_2\text{O}_3$  as the catalysts according to the following stoichiometry:



Among the several solid-acid porous catalysts studied for methanol dehydration reaction,  $\gamma\text{-Al}_2\text{O}_3$  is used to a large extent for this reaction which is due to large surface area, large pore volume, uniform pore size distribution and excellent mechanical properties (attrition, resistance and crush strength) [11-17].

In the open literature for DME synthesis from methanol dehydration, the effects of operational conditions on the yield of DME have not been investigated by a systematic manner to obtain the optimum operational conditions and define the influence of each parameter. The main experimental approach for investigation of the effects of operational conditions and obtaining the optimum conditions is the method of varying one factor at a time when keeping the other factors constant, which may fail to consider any possible interaction between the factors and might miss the real optimum.

Also, in order to provide basic data for designing the reactor for plant or industry, the kinetic study of DME synthesis from methanol dehydration is necessary. Published reaction rates have been derived from the results of experiments with different acidic catalysts and conditions resulting in different reaction rates. Hence, different reaction rate equations must be fitted with experimental data and relative error compared for choosing the suitable kinetic equations [17,18].

In the present work, the experiments have been designed by full factorial method and performed in a differential fixed bed reactor over a well characterized commercial  $\gamma\text{-Al}_2\text{O}_3$  catalyst at different temperatures, pressures and weight percent of water in the feed. The micro reactor results have been used to elucidate the role of each factor in DME yield and the optimum operating conditions. Also, to determine the intrinsic reaction rate of the methanol dehydration for DME synthesis, the results of reaction rates have been fitted with different published equations, and a novel reaction rate equation has been developed which showed the best fitting with our data. Activation energy and heats of methanol and water adsorption on the surface of catalyst have been calculated. The authors believe that investigation the statistical analysis and kinetic of the reactor results simultaneously can be concluded to a more conceptual knowledge of the process.

### EXPERIMENTAL

#### 1. Characterization of Catalyst

The BET surface area, pore volume and pore diameter of catalyst were measured by  $\text{N}_2$  adsorption-desorption isotherm at liquid nitrogen temperature (77 °K) using NOVA 2000 series instrument (Quantachrome, USA). Prior to the analysis, 250 mg of the catalyst was degassed at 250 °C for 16h under flowing nitrogen.

The XRD pattern were recorded on an X-ray diffractometer (PW-

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1800Philips) using Cu K $\alpha$  monochromatized radiation source ( $\lambda=1.5406$  Å) and Ni filter in the range  $2\theta=5^\circ$  to  $90^\circ$ .

Acidity was measured by temperature-programmed desorption of ammonia ( $\text{NH}_3$ -TPD) with a conventional flow apparatus (Micromeritics 2900 TPR/TPD) included an on-line thermal conductivity detector (TCD). In a typical analysis,  $\text{NH}_3$ -TPD was performed using 0.35 g of the catalyst which was degassed at  $600^\circ\text{C}$  in a helium flow, cooled to  $150^\circ\text{C}$  and then saturated with  $\text{NH}_3$  for 15 min. After saturation, the sample was purged with He for 30 min to remove weakly adsorbed  $\text{NH}_3$  on the surface of the catalyst. During this time, a constant TCD level was attained. The temperature of the sample was then raised at a heating rate of  $5^\circ\text{C}/\text{min}$  from  $150$  to  $700^\circ\text{C}$  and the amount of ammonia in effluent was measured via TCD and recorded as a function of temperature.

## 2. Experimental Setup

A schematic view of the bench scale setup is depicted in Fig. 1. In the feed section, nitrogen gas as the internal standard was fed through a mass flow controller and methanol was pumped from a feed tank through a mini-metering pump. The mixture of feed and gases was preheated to the reaction temperature before entering the micro reactor made from stainless steel with an inner diameter of 9 mm. Temperature indicators and controllers (TIC) 1–4 were used for precise temperature control before the feed enters to the catalyst bed (TIC1), at the bed (TIC4) and after leaving the bed (TIC2) and at the exit of reactor (TIC3). TIC4 presents the reaction temperature. The temperature of pre-heater was also set at  $250^\circ\text{C}$  while the temperature of TIC5 was set at  $175^\circ\text{C}$  to avoid the possible condensation of the exit gases before entering to the gas chromatography.

There is a backpressure regulator after the reactor to reduce pressure before exit gases vent or conducted to gas chromatograph.

All experiments for dehydration of methanol to DME were conducted under steady state conditions in a differential fixed-bed reactor (stainless steel, 3/8 inch inside diameter, length 670 mm) at temperatures ranging from  $260$  to  $380^\circ\text{C}$  and a pressure range of 1–16

Barg (gauge pressure) at constant space velocity ( $W/F=1.724$  g/ml·min). The reaction products were sent to a gas chromatograph (HP, Agilent Technologies, Model: HP-6890N) using HP-Plot Q column (connected to FID) for on-line analysis. The whole experiments were performed for 30 h time on-stream (TOS) after steady state was reached so that no significant deactivation was seen for 30 h TOS. Prior to the experiments, the fresh catalysts was crushed and sieved to the mesh size of  $90\text{ }\mu\text{m}$ – $125\text{ }\mu\text{m}$ . The height of catalyst bed was around 0.5 cm.

## 3. Experimental Design

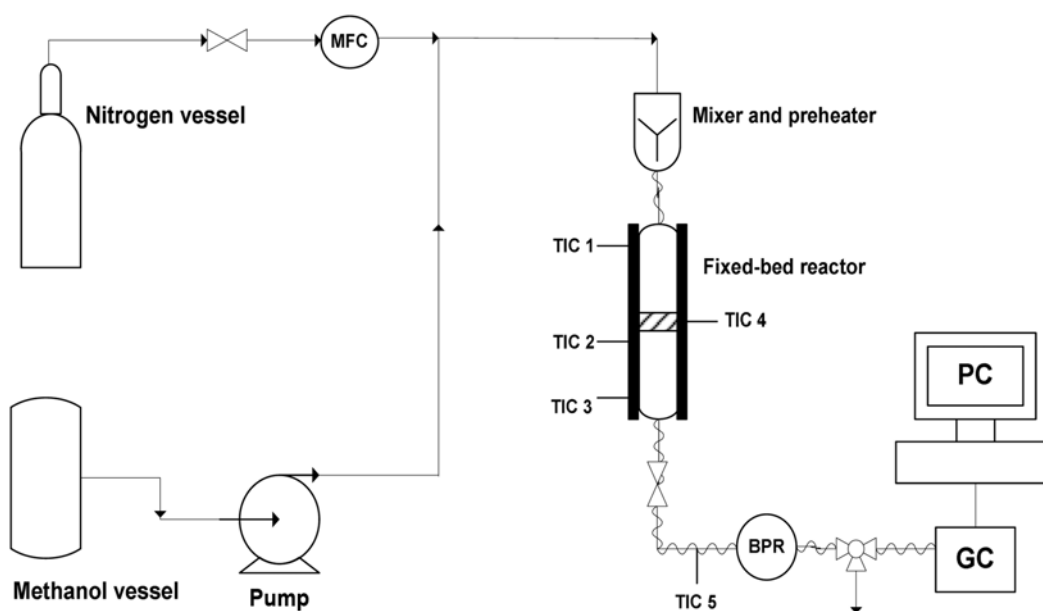
The effects of reaction parameters and their interactions including temperature, pressure and weight percent of water in methanol feed have been investigated on the yield of a commercial  $\gamma\text{-Al}_2\text{O}_3$  catalyst in methanol dehydration process for DME synthesis. In accordance with full factorial design method, for three parameters with three levels, 27 tests must be performed. Table 1 summarizes the levels of three parameters.

## 4. Kinetic Investigation for Methanol Dehydration

To derive reliable intrinsic kinetic data, mass and heat transfer resistances must be eliminated. For this means, the effects of interfaces and intraparticle heat and mass transfer resistance were investigated in separate experiments. Based on the results, no significant effect on methanol conversion was observed by variation of flow rate at constant ratio of catalyst weight to methanol flow rate ( $W/F=1.724$  g/ml·min). At the second stage, performing a series of ex-

**Table 1. The parameters and their levels**

Parameter	Level of parameter		
	–1	0	1
T ( $^\circ\text{C}$ )	260	320	380
P (barg)	1	8.5	16
Wt% of water in feed	0	10	20



**Fig. 1. Schematic view of the bench scale reactor.**

MFC: Mass flow controller; BPR: Back pressure regulator; TIC: Temperature indicator; GC: Gas chromatography; PC: Personal computer

periments with different particle sizes and the constant process parameters showed that at mesh sizes 90-125  $\mu\text{m}$  there is not any intraparticle heat and mass resistance. Consequently, a particle size of 90  $\mu\text{m}$  was selected for the kinetic investigation study. Also, the stability of  $\gamma\text{-Al}_2\text{O}_3$  catalyst was monitored during 180 hr under the same operating condition, and fresh catalysts were loaded in each run in order to ensure of catalyst activation.

To identify an appropriate rate equation for the methanol dehydration on the investigated alumina catalyst, the adequacy of the various published rate expressions was tested to our experimental data. It must be mentioned that, under the conditions used, the values of the kinetic parameters were calculated by fitting the experimental data of the component's partial pressure to the kinetics equations. The kinetic constant of reaction rate ( $k_s$ ) is dependent on temperature according to the Arrhenius relation:

$$k_s = k_{s0} \cdot \exp\left(\frac{-E_a}{RT}\right) \quad (2)$$

Also, the constants for methanol adsorption ( $K_M$ ) and water adsorption ( $K_W$ ) are dependent on the temperature according to the van't Hoff relation:

$$K_{Me} = K_{M0} \cdot \exp\left(\frac{-H_M}{RT}\right) \quad (3)$$

$$K_W = K_{W0} \cdot \exp\left(\frac{-H_W}{RT}\right) \quad (4)$$

where  $E_a$  is the activation energy,  $R$  is the constant of gases,  $T$  is absolute temperature,  $H_M$  is the heat of methanol adsorption on the catalyst surface and  $H_W$  is the heat of water adsorption on the catalyst surface.

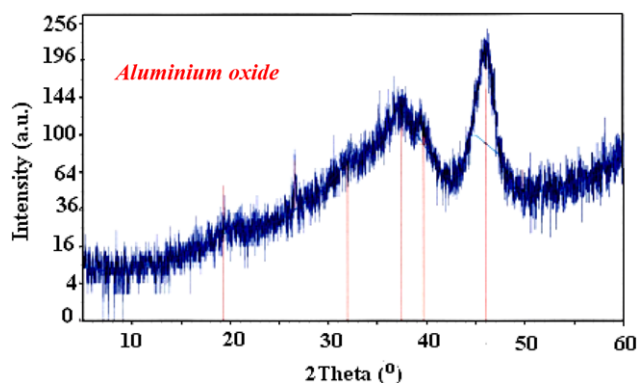
## RESULTS AND DISCUSSION

### 1. Characterization of the Catalyst

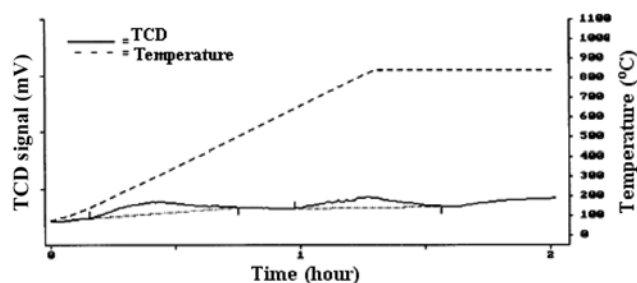
A commercial  $\gamma\text{-Al}_2\text{O}_3$  catalyst produced by Iranian Petrochemical

**Table 2. BET results**

Catalyst name	Multi-point BET ( $\text{m}^2/\text{g}$ )	Single point BET ( $\text{m}^2/\text{g}$ )	Total pore volume ( $\text{ml/g}$ )	Average pore radius ( $^\circ\text{A}$ )
$\gamma\text{-Al}_2\text{O}_3$	108.8431	102.8909	0.0659	12.1044



**Fig. 2. XRD pattern for a commercial  $\gamma\text{-Al}_2\text{O}_3$ .**



**Fig. 3.  $\text{NH}_3$ -TPD profile.**

Research and Technology Company was employed in this research. Table 2 summarizes the specific BET surface area, total pore volume and average pore radius of the fresh catalyst used for experiments. The x-ray powder pattern peaks of the fresh commercial sample are shown in Fig. 2, and the crystalline phase of the catalyst was identified using the JCPDS data bank. The pattern indicates the presence of a crystalline phase, namely cubic  $\gamma\text{-Al}_2\text{O}_3$  (JCPDS No. 79-1558). So it shows that the commercial sample has a  $\gamma\text{-Al}_2\text{O}_3$  crystalline phase on an amorphous background.  $\text{NH}_3$ -TPD measurements were carried out to determine the acid strength and the amounts of acid sites on the dehydration components using ammonia as an adsorbate. It is generally recognized that ammonia is an excellent probe molecule for testing the acidic properties of solid catalysts as its strong basicity and small molecular size allow for detection of acidic sites located also into very narrow pores. In this way, the entire range of acid sites present on the sample, progressing from strong through to weak, could be dosed with ammonia. It is well known that the acidic sites on the surface solid-acid catalysts are two types: Brønsted and Lewis acid sites. It is well known that Brønsted acid sites are able to catalyze the dehydration of alcohols to ethers (such as methanol to DME), being yet not possible to discriminate between Brønsted and Lewis acidity [19,20]. The  $\text{NH}_3$ -TPD spectra of  $\gamma\text{-Al}_2\text{O}_3$  catalyst are shown in Fig. 3. Referring to Fig. 3, there are two maximum peaks at 324 and 829  $^\circ\text{C}$  corresponding to  $\text{NH}_3$  eluted from the medium and strong acid sites, respectively.  $\text{NH}_3$  desorption based on the area under the first peak is 7.1  $\mu\text{mol}/\text{gr-cat}$ . And from the second peak is 5.6  $\mu\text{mol}/\text{gr-cat}$ . Also, the total acid sites density (acidity) is 12.7  $\mu\text{mol}/\text{gr-cat}$ . The results of the reactor test confirmed that the  $\gamma\text{-Al}_2\text{O}_3$  commercial sample has the high conversion. This probability could be due to the amount of medium acid type being high and all the acid sites on the surface catalysts are almost Brønsted type.

### 2. Micro Reactor Results

The rate of methanol dehydration and the yield of DME for all 27 experiments at different operational conditions designed by full factorial method are shown in Table 3. The first three columns of data give the operational conditions including temperature (K), gauge Pressure (barg) and weight percent of water in the methanol feed, and the second three columns give the  $\pm 1$  and 0 coded factor levels for temperature ( $X_T$ ), Pressure ( $X_P$ ), wt% of water in feed ( $X_W$ ) in the dimensionless coordinate. The rate of methanol dehydration and the yield of DME are also given in the last two columns. According to the table, the amount of yield is below 10%, which is due to high space velocity and low conversions of methanol to ensure that the intrinsic rate is the rate-determining step and controls the global

**Table 3. Experimental conditions and reactor results**

Temperature (°C)	Pressure (barg)	Weight% of water in feed	X <sub>T</sub>	X <sub>P</sub>	X <sub>W</sub>	Rate (mol/kg·sec)	DME yield
260	1	0	-1	-1	-1	0.0022	3.12
320	1	0	0	-1	-1	0.0049	5.31
380	1	0	+1	-1	-1	0.0071	7.44
260	8	0	-1	0	-1	0.0027	3.79
320	8	0	0	0	-1	0.0053	5.70
380	8	0	+1	0	-1	0.0073	7.62
260	16	0	-1	+1	-1	0.0034	3.92
320	16	0	0	+1	-1	0.0056	5.94
380	16	0	+1	0	-1	0.0090	9.27
260	1	10	-1	-1	0	0.0013	1.90
320	1	10	0	-1	0	0.0058	6.26
380	1	10	+1	-1	0	0.0076	7.95
260	8	10	-1	0	0	0.0016	2.14
320	8	10	0	0	0	0.0062	6.56
380	8	10	+1	0	0	0.0079	8.17
260	16	10	-1	+1	0	0.0019	2.60
320	16	10	0	+1	0	0.0064	6.83
380	16	10	+1	+1	0	0.0086	8.57
260	1	20	-1	-1	+1	0.0010	1.43
320	1	20	0	-1	+1	0.0038	4.22
380	1	20	+1	-1	+1	0.0065	7.14
260	8	20	-1	0	+1	0.0012	1.68
320	8	20	0	0	+1	0.0042	4.76
380	8	20	+1	0	+1	0.0068	7.30
260	16	20	-1	+1	+1	0.0021	2.92
320	16	20	0	+1	+1	0.0046	4.97
380	16	20	+1	+1	+1	0.0082	8.43

**Table 4. Analysis of variance for yield, using Sequential SS for tests**

Source contribution	DF (%)	Seq SS	Adj SS	Seq MS	F	P	Percentage
T	2	130.6922	130.6922	65.3461	869.95	0.000	91.0
P	2	4.3288	4.3288	2.1644	28.81	0.000	3.0
WT%	2	5.6712	5.6712	2.8356	37.75	0.000	4.0
T*P	4	0.5470	0.5470	0.1367	1.82	0.218	0.2
T*WT%	4	4.9201	4.9201	1.2300	16.38	0.001	1.7
P*WT%	4	0.3036	0.3036	0.0759	1.01	0.456	0.1
Error	8	0.6009	0.6009	0.0751			
Total	26	147.0639					

rate of reaction.

### 3. Analysis of Experimental Data

The ANOVA models are employed to determine whether different variables interact and which factors or factor combinations are most important on the response (yield of DME). Hence, F value, p value (p) and relative percentage contribution among the factors have been computed. It is noted that the F value is the ratio of sum of mean square to sum of mean square of residual. If the calculated F-value is higher than  $F_{\alpha, v_1, v_2}$ -value of the confidence table, where  $\alpha$  is risk,  $v_1$  and  $v_2$  are degrees of freedom associated with numerator and denominator, an effect is considered statistically relevant. Usually, the significant level ( $\alpha$ ) is set to 0.05 [21-23]. The results

of the statistical significance test are shown in Table 4. The F-value of all factors and interaction between temperature and wt% of water in methanol (T\* wt% water) are considerably greater than the extracted F-value of tables with 95% confidence, but two interactions between temperature and pressure (T\*P) and pressure and weight percent of water in feed (P\* wt% water) have F-value less than F-value of tables with 95% confidence. This means that the variance of each factor and one interaction (T\* wt% water) are significant compared with the variance of error and so they have an important effect on the response. Another important statistic parameter in the analysis of variance table is the p-value (P). In other words, the P-values were used as a tool to check the significance of each of the

interactions among the variables, which in turn may indicate the patterns of the interactions among the variables. In general, the smaller the value of  $P$ , the more significant is the corresponding coefficient term [21]. In Table 4, the  $p$ -value for each term has been computed. If the  $p$ -value is less than or equal to the  $\alpha$ -level, then the effect for the term is significant. Two interaction terms between temperature and pressure ( $T^*P$ ) and pressure and weight percent of water in feed ( $P^* \text{ wt\% water}$ ) have  $p$ -value greater than 0.05. So these two interactions can be neglected. Three main factors ( $T$ ,  $P$ ,  $\text{wt\% of water in feed}$ ) and one interaction parameter ( $T^* \text{ wt\% water}$ ) have  $p$ -values less than 0.05 (Table 4), which means that the effects of these factors as well as one interaction effect ( $T^* \text{ wt\% water}$ ) on DME yield as the response parameters, are significant. The experimental results were fitted to a linear model and the following general linear model was obtained:

$$\begin{aligned} \text{Yield} = & 5.41596 + 2.68833X_T + 0.484936X_P \\ & - 0.51445X_W + 0.278333X_TX_W \\ (r^2 = & 0.957) \end{aligned} \quad (5)$$

The above statistical model was obtained from the coded factor levels, and the equation is only valid within the studied experimental range. The predicted yield by Eq. (5) versus experimental yield indicates 4.5% relative error.

The relative contribution percentage of each factor and interactions on DME yield are mentioned in the last column of Table 4, which demonstrates that the temperature of process, with relative percent of contribution equal to 91% of the total effect, is the most significant factor on the yield of DME, while the ( $P^* \text{ WT\%}$ ) has the least contribution on the DME yield. Also, at 260 °C by increasing water content in methanol feed, the yield of DME decreased; however, at 320 °C and 380 °C there is an optimum value for water content at about 10 wt% in methanol feed. This is since  $\gamma\text{-Al}_2\text{O}_3$  tends to absorb water on its surface and thereby loses its activity in the presence of water because of its hydrophilic nature, especially at lower temperatures, while at higher ranges of temperatures an optimum value of water in feed with positive effect in DME yield can be used. In other words,  $\gamma\text{-Al}_2\text{O}_3$  is not a suitable catalyst for dehydration of methanol which contains more than 20% of water at any other operational conditions as it was deduced by the others [19,20]. As can be deduced, higher temperature and higher pressure increase the yield of DME; however, increasing the water wt% in the methanol feed decreases the mean average yield of DME. The highest methanol yield can be obtained in the studied operating range at  $T=380^\circ\text{C}$ ,  $P=16$  barg and zero weight percent of water

in feed.

#### 4. The Results of Kinetics Model

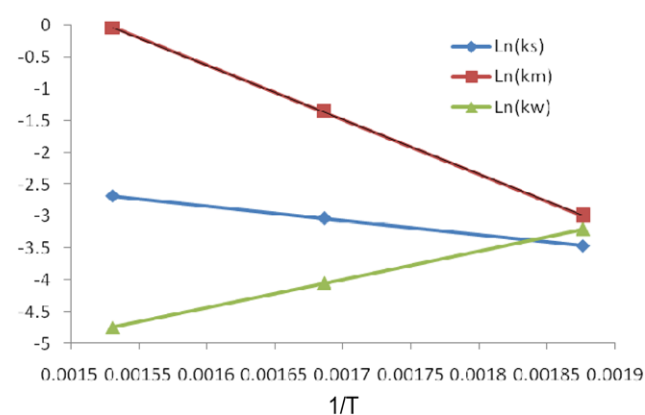
Among the various published rate equations, the three rate equations shown in Table 5 with relative error less than 10%, were the most adequate to our data. Eqs. (1) and (2) in Table 5 were proposed by Sinicyna et al. and Bercic & Levec, respectively [18]. However, Eq. (3) in Table 5 is a novel rate equation which showed the best fitting with our experimental results so that the mean relative error was about 9.2%. The new proposed rate equation is as follows:

$$-r_M = \frac{k_s K_M^2 C_M^2}{(1 + 2(K_M C_M)^{2/3} + K_W C_W)^3} \quad (6)$$

To establish the kinetic parameters as a function of temperature, the Arrhenius and van't Hoff equations (Eqs. (2)-(4)) were used. Then, 27 points of kinetics experiments were used to determine the values of the kinetic parameters with a multivariable non-linear regression method. The whole calculated parameters for three rate equations are given in Table 6. Moreover, Fig. 4 represents the variation

**Table 6. The Fitted Parameters for Eqs. (1)-(3) in Table 5**

Parameter	Units	Eq. (1)		25009.3
		$E_a$ (J/mol)	Eq. (2)	16782.3
$k_s=k_{s0}e^{\frac{-E_s}{RT}}$	mol/kg <sub>cat</sub> ·s	$k_{s0}$	Eq. (3)	18565.4
			Eq. (1)	0.89
			Eq. (2)	3.46
			Eq. (3)	2.07
$K_M=K_{M0}e^{\frac{-H}{RT}}$	m <sup>3</sup> /mol	$H_M$ (J/mol)	Eq. (1)	20773.8
			Eq. (2)	67341.5
			Eq. (3)	71295.2
		$K_{M0}$	Eq. (1)	12.5
			Eq. (2)	230375.04
			Eq. (3)	485462.12
$K_W=K_{W0}e^{\frac{-H_W}{RT}}$	m <sup>3</sup> /mol	$H_W$ (J/mol)	Eq. (1)	−53515.21
			Eq. (2)	−42657.09
			Eq. (3)	−37032.7
		$K_{W0}$	Eq. (1)	8.2614*10 <sup>−7</sup>
			Eq. (2)	1.47*10 <sup>−6</sup>
			Eq. (3)	9.499*10 <sup>−6</sup>



**Fig. 4. Parameters:  $\text{Ln}k_s$ ,  $\text{Ln}k_m$ ,  $\text{Ln}k_w$  vs.  $1/T$  (K) for Eq. (3).**

**Table 5. Rate equations with the better fitting with experimental data**

No.	Equation	Error %	$R^2$
1	$-r_M = \frac{k_s K_M^2 C_M^2}{(1 + K_M C_M + K_W C_W)^2}$	9.865	0.9293
2	$-r_M = \frac{k_s K_M^2 C_M^2}{(1 + 2(K_M C_M)^{1/2} + K_W C_W)^4}$	9.857	0.93
3	$-r_M = \frac{k_s K_M^2 C_M^2}{(1 + 2(K_M C_M)^{2/3} + K_W C_W)^3}$	9.255	0.94

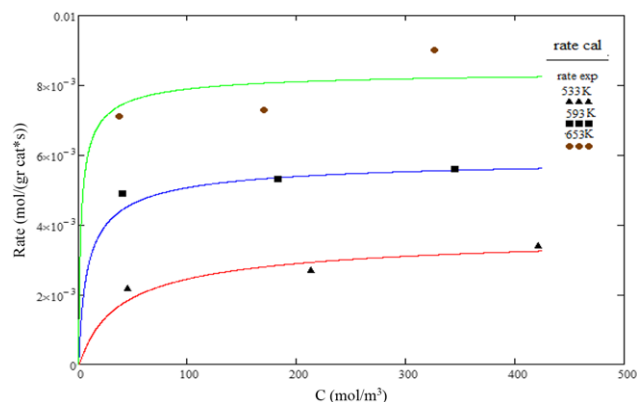


Fig. 5. Rate of methanol consumption vs. concentration of methanol (C) at different temperature, wt% of water in feed=0.

of  $\text{Ln}k_s$ ,  $\text{Ln}k_m$ , and  $\text{Ln}k_w$  for Eq. (3) versus  $1/T$ . The constant values obtained for Eq. (3) agree reasonably with the Arrhenius and van't Hoff equations. A sample plot of the reaction rate behavior versus concentration of methanol in the feed stream at different temperatures is shown in Fig. 5. As seen, the reaction rate is higher for any methanol concentrations at higher temperature, and at low levels of methanol concentration, the reaction rate increases sharply by increasing methanol concentration while it remains nearly unchanged at high levels of methanol concentration.

## CONCLUSIONS

Statistical investigation of the methanol dehydration process can be made in the following order of importance for operational conditions:

Temperature > Water wt% in methanol feed > Pressure

Beside these three factors including temperature, pressure and wt% of water in methanol, the interaction between temperature and wt% of water in feed has shown significant effects on DME yield. The main role corresponds to the temperature with more than 90% effect in DME yield, and by increasing temperature and pressure, the yield of DME increases while wt% of water in feed can have an opposite effect. The optimum operational conditions for maximum DME yield in the studied range are:  $T=380^\circ\text{C}$ ,  $P=16$  barg and zero wt% of water in feed. The statistical model (Eq. (5)) can predict DME yield with average relative error less than 4.5%.

As a result of this study, a novel rate equation was proposed. Although it is based on the same general formula for Bercic & Levec, the modified correlation fits our experimental data better. The statistical comparison shows that new kinetic equation compares favorably well with results from the other two equations included in this study, and the degree of agreement between two sets of data, for steady state condition was about 91%.

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