

Kinetic Study of Methanol Dehydration to Dimethyl Ether in Catalytic Packed Bed Reactor over Resin

Ghassan J. Hadi¹, Arkan J. Hadi²

¹Technical Institute, Northern Technical University, Adour, Iraq

²College of Engineering, Soran University, Erbil, Iraq

Email: Ghassan.jh@ntu.edu.iq

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Abstract

Dimethyl ether (DME) is considered as a significant fuel alternative with a critical manufacturing process. Only a few authors have presented the kinetic analysis of attractive and alternative catalysts to Al_2O_3 and/or zeolite in DME production, despite the fact that there is a large library of kinetic studies for these commercial catalysts. The purpose of this research was to contribute to this direction by conducting a catalytic test to determine kinetic parameters for methanol dehydration over sulfonic acid catalysts (resin). However, due to the relevance of the mathematical description of this process in the industry was also studied, a study of kinetics parameters and mathematical modeling of methanol dehydration in an atmospheric gas phase in a fixed bed reactor with a temperature range (90°C - 120°C) was examined. The Langmuir-Hinshelwood (L-H) model provides the best fit to experimental data, with an excellent $R^2 = 0.9997$, and the experimental results were compared to those predicted by these models with very small deviations. The kinetic parameters were found to be in good agreement with the Arrhenius equation, with acceptable straight-line graphs. The activation energy E was computed and found to be 27.66 kJ/mole, with an average variation of 0.32 percent between the predicted and calculated results. Simple mathematical continuum models (plug flow reactor PFR) showed an acceptable agreement with the experimental data.

Keywords

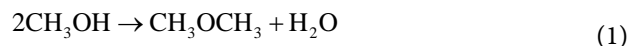
Catalyst, Dimethyl Ether, Fixed Bed Reactor, Dehydration, Modelling

1. Introduction

It became clear that dimethyl ether (DME) is important due to its multi-use in

industry, it represents a fuel alternative with no toxic and no corrosive emissions, raw material in organic synthesis [1] [2] and as a fuel cells hydrogen source by the partial oxidation or reformation of steam [3] are the most important uses of DME, more details about DME utilizing has been mentioned by many researchers [2] [4] [5].

Methanol is considered the main source of DME production over solid phase catalyst according to Equation (1) below:



Alumina and zeolite are most widely used as a solid phase catalyst for methanol to produce DME [6] [7] [8], with the growing demand for DME production and because the conversion of methanol into DME is a catalyzed process, finding the efficient robust catalysts that are commercially attractive have become more and more complicated, ion exchange resin has been used as a catalyst by many researchers [4] [9] [10]. The main advantage of these resins is that the alcohol can be dehydrated at relatively low temperatures (30°C to 150°C) [9] [11] with high selectivity to DME [12] when compared to Alumina and zeolite, this subject has been widely discussed in previous studies [13] [14].

Several catalytic dehydration mechanisms for methanol to DME have been proposed, which include interactions between surface acid and base sites, the reaction of methanol dehydration was reported by both Brønsted and Lewis acid sites [15] [16]. Accordingly, the mechanism of methanol to DME dehydration is still argued, this reaction may be represented by two dissimilar ways called the associative pathway and the dissociative pathway, in the (Langmuir-Hinshelwood) mechanism introduced by Gates and Johnson (1969) [17], (shown in **Figure 1**), it can be assumed that two methanol molecules occupy two adjacent acid sites. On the other hand, in the Eley-Rideal (ER) model proposed by Kiviranta-Paakkonen *et al.* (1998) [18] who proposed that one adsorbed methanol molecule reacts with the other methanol molecule in the bulk fluid (shown in **Figure 2**). One goal of this investigation is to describe the kinetics of catalytic dehydration of methanol over the ion exchange resin.

Mathematical modeling of chemical reactors is very important and extremely useful in the chemical industry [19] [20]. Many models that help the design have a detailed physical basis, however, are simple models of steady-state. Although these models are intended to describe a variety of conditions in detail, normally, the system of the real world consists of linear/non-linear algebraic/differential/partial steady/unsteady state equations [19] [21]. The design of a fixed reactor takes many considerations like (pressure drops, type of heat exchange and catalyst packing mode, etc. The pseudo-homogeneous model is the simplest model in which the fluid phase and solid phase (catalyst) are entirely treated as homogeneous [22]. It should be recognized that when all transport resistances are missing, heterogeneous models reduce to pseudo-homogeneous models [22] as discussed in (Section 3.3) in this investigation. In fact, there is no reason why we

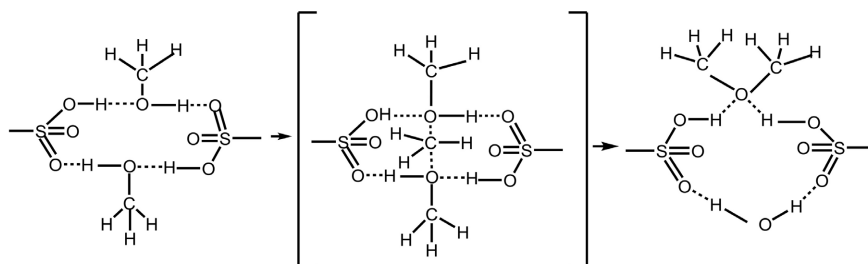


Figure 1. Gates and Johnson *et al.* (1969) mechanism for methanol dehydration reaction.

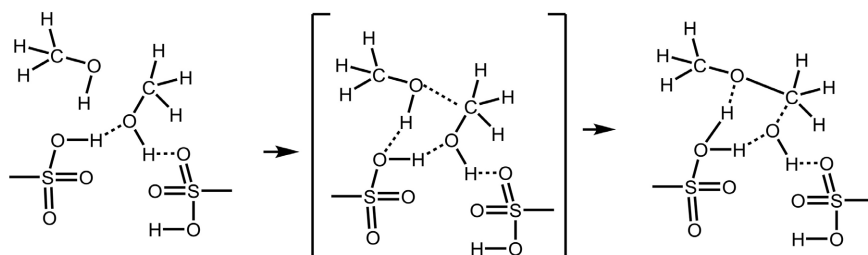


Figure 2. Kiviranta-Paakkonen *et al.* (1998) mechanism for methanol dehydration reaction.

should not use the most simple and easiest fit equation. Indeed, unless the use of the most complicated of two equations is justified, we should choose the simplest one [23]. The second goal of this study is to present a simple mathematical model that describes the system in the conditions used.

2. Materials and Methods

Absolute methanol (Aldrich, 99.99%) as a feedstock was used, nitrogen as a conveyor gas was also used to deplete the gases from the system. **Table 1** lists the physical properties of methanol and nitrogen.

2.1. Catalysts

A commercial sulfonated copolymer of styrene and divinylbenzene in acid form resin (Ionic form: $H^+ R-SO_3^-$) was used with surface area and porosity $96 \text{ m}^2/\text{gm}$ and 0.67 , respectively, mesh size $16 - 50$ ($0.3 - 1.2 \text{ mm}$) and Capacity min. (eq/l) 1.8 .

2.2. Procedure

Catalytic dehydration of methanol in the atmospheric gas phase in a fixed bed reactor has been achieved with the following details:

Dosing pump of maximum and minimum flow rate 2 and 0.02 liter/hr respectively was used to control methanol feeding, QAV tubular reactor with inside diameter 2.54 and 100 m length was used, this reactor is divided into two sections; evaporator and reaction section. The reaction has been conducted with a temperature range ($90^\circ\text{C} - 120^\circ\text{C}$) and 40 gm (*i.e.* 7 cm high) catalysts, methanol flow rates were $0.39 - 1.48$ mole/hr or $W/F = 27 - 100.2$ ($\text{g hr}/\text{gm}$). The vent gases

Table 1. Physical properties of the materials used.

Property	Methanol	Nitrogen
Molecular Formula	CH ₃ OH	N ₂
Molecular Weight	32.04	28.02
Specific Gravity	0.791 g/mL at 25 °C	0.808
Melting Point (°C)	-98 °C	-209.86
Boiling Point (°C)	64.7 °C	-195.8

were condensed with a condenser designed for this purpose, Samples of liquid and vapor were taken for analysis regularly. The apparatus of this examination is showing in **Figure 3**. More details about the experimental work are discussed in the literature [14]. The rate of methanol consumption, ethylene, and ether rate formation was calculated based on material balances.

2.3. Samples Analysis

Data were collected after an appropriate period (usually 1 h) for each set of experimental conditions to enable a steady state to be established. Testing was conducted by using a Gas Chromatography (Shimadzu-9A); an externally (3.17 mm) and 3 m long (Parapak Q)-treated steel section; The GLC segment was linked with warm TCD; hydrogen was used as a carrier gas. Column and TCD temperatures were 250 °C and 200 °C respectively, initial and injection temperatures were 175 °C and 200 °C.

3. Results and Discussions

3.1. Mass Transfer Resistance

In order to confirm that the process is kinetically controlled, the mass transport limitation and the internal diffusion limitation have to be discarded, *i.e.* the diffusion of the reactant from the outer surface of the porous catalyst to the reactive sites, external diffusion, *i.e.* the transport of reactants from the bulk to the outer surface of porous catalyst [5]. To confirm that, the procedure mentioned in the literature [24] has been followed.

3.1.1. Internal Resistance Transport Influence

To evaluate the importance of internal diffusion experimentally, changing particle size is the best solution, if the rate is proof to be independent of particle diameter, it is an indication that intraparticle diffusion is negligible [17] [25]. Range of particle size (0.3 - 1.2 mm) and temperature (90 °C - 120 °C) with constant catalyst weight (40 gm) was used, it was clear that there is no change in the reaction rate, so the internal resistance has been discarded (see **Table 2**).

3.1.2. External Film Resistance Influence

Changing in superficial velocity (with same residence time) gives a good indication of whether the external film is effective or not. Therefore; variable catalysts

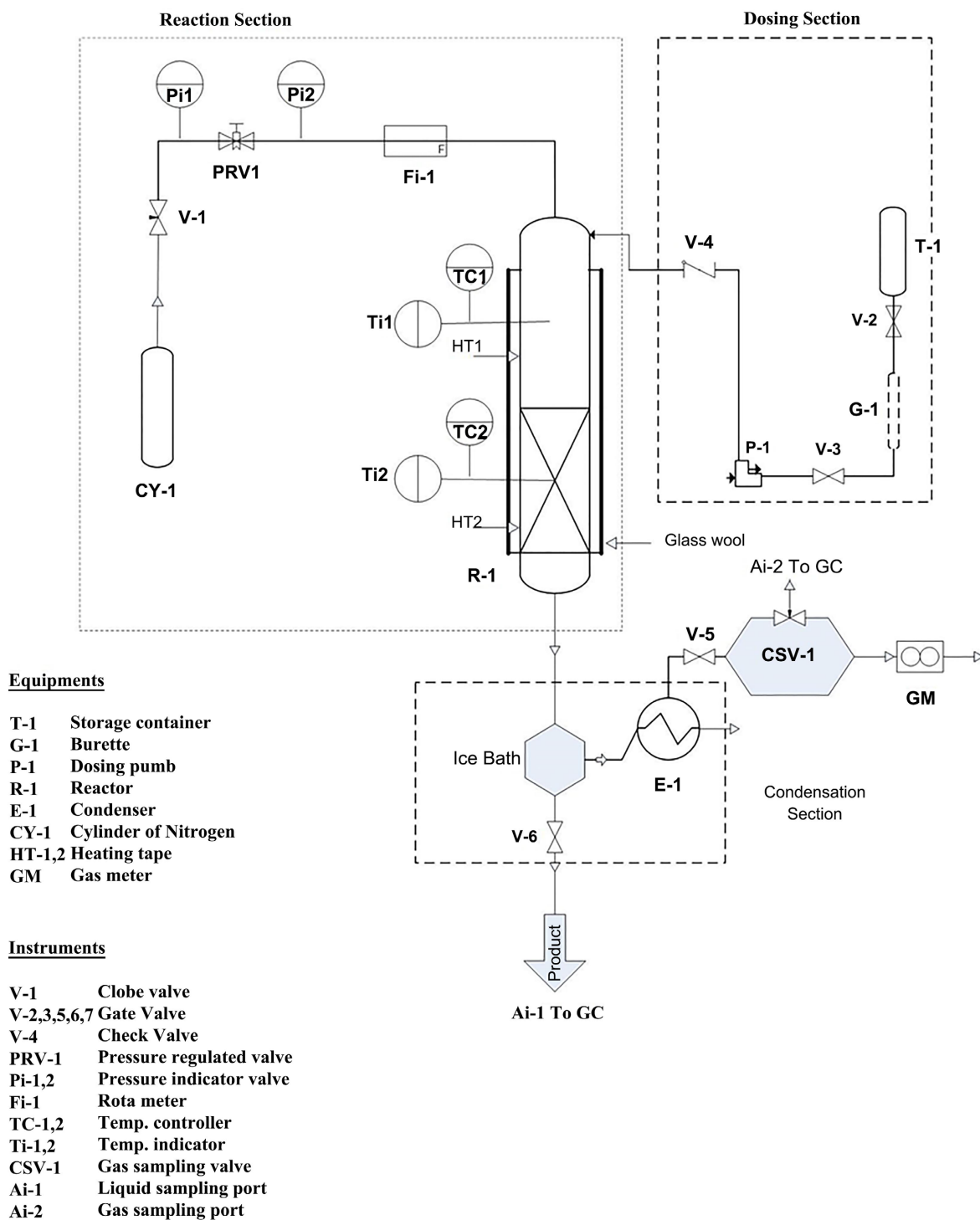


Figure 3. Schematic diagram of the experimental rig.

weight (30 - 40 gm) with feed range (0.37 - 0.495 mole/hr) to keep $W/F = 81$ g cat-hr/g-mole were used, as it is shown in (Table 2) with all range of conditions rate of reaction was fixed, so the external resistance could be neglected. Many researchers used resin as a catalyst [12] [26] found that it is possible to exclude external resistance.

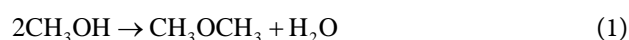
Table 2. Estimation of internal and external resistance.

Internal resistance			
Particle size (mm)	Temperature (°C)	W/F (g cat·hr/g mole)	r_A (g mole/g cat·hr)
0.3	90,110,120	81	0.0002463
0.7	90,110,120	81	0.0002463
1.2	90,110,120	81	0.0002463
External resistance ($T = 120^\circ\text{C}$)			
Weight (gm)	F(feed) (mole/hr)	W/F (g cat·hr/g mole)	r_A (g mole/g cat·hr)
40	0.495	81	0.00099
35	0.433	81	0.00099
30	0.371	81	0.00099

3.2. Surface Kinetic

Several mechanisms for catalytic dehydration of methanol to DME have been suggested by many researchers (some of these are mentioned in literature [27]). Thus, just two possible kinetic models have been evaluated for modeling reaction 1 over resin catalyst as shown below. Each model is based on the surface reaction as the rate-determining step.

L-H Model: assumes that the surface reaction takes place according to the Langmuir-Hinshelwood mechanism in which two chemisorbed adjacent alcohol molecules react to form the chemisorbed products. Sequence equations of the reaction for this model are depicted below:

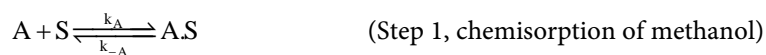


where:

A = Methyl alcohol

E = Ether

W = Water

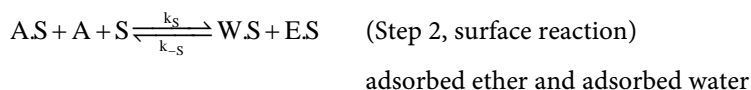
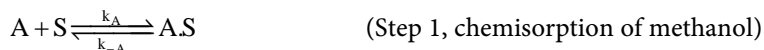


By assuming surface reaction is controlled step will get:

$$r_S = \frac{\kappa K_A^2 (P_A^2 - P_E P_W / K_P)}{(1 + K_A P_A + K_W P_W + K_E P_E + K_I P_I)^2} \quad (3)$$

REM model: It assumes that the surface reaction follows the Rideal-Eley mechanism in which one alcohol molecule in the gas phase reacts directly with

another alcohol chemisorbed molecule in the presence of a vacant site adjacent to the chemisorbed product. The reaction sequence for this model is:



By assuming surface reaction is controlled step will get:

$$r_s = \frac{\kappa K_A (P_A^2 - P_E P_W / K_P)}{(1 + K_A P_A + K_W P_W + K_E P_E + K_I P_I)^2} \quad (4)$$

where r_s is a rate of reaction, κ is the reaction rate constant and K_i is materials adsorption equilibrium constant and P_i is the partial pressure of material where A, E, and W are Alcohol, ether, and water respectively.

As it is clearly shown, the kinetics of this reaction depends on the partial pressure of both products (water and DME), it is known [7] that DME concentration does not affect the reaction rate, most polar components (alcohol and water) are adsorbed considerably more than less polar components (ether), due to the marked difference in dielectric constants Linnekoski *et al.*, 1997 [28]; Zhang and Datta, 1995 [29]. Therefore, ether contribution can be neglected in any kinetic equation, on the other hand, due to the absence of water in feed (*i.e.* pure methanol feed) its contributions can be neglected also [12] [30], therefore, Equations (3) and (4) could be reduced to:

$$r_s = \frac{k K_A^2 P_A^2}{(1 + K_A P_A)^2} \quad (5)$$

$$r_s = \frac{k K_A P_A^2}{(1 + K_A P_A)^2} \quad (6)$$

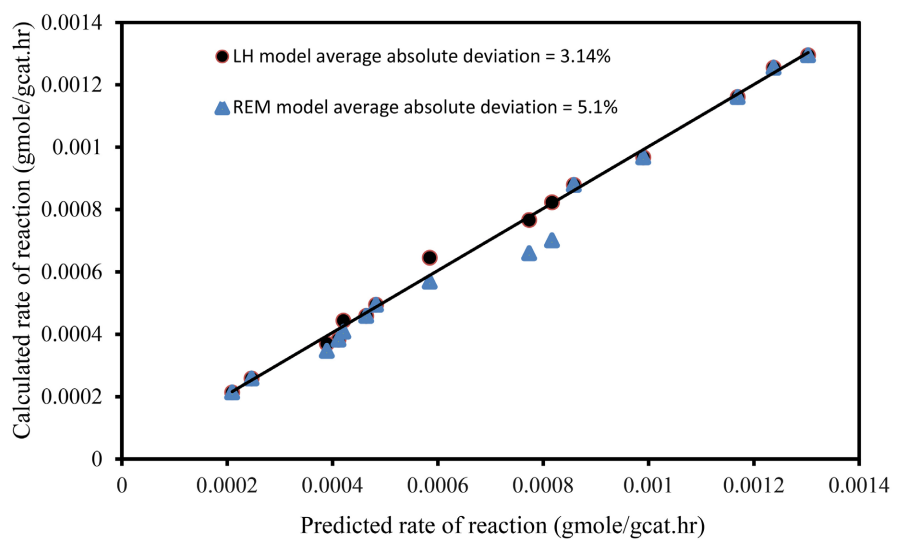
To find which model better represents the kinetics of dehydration of methanol to DME, a series of experiments were done and listed in **Table 3**. Linear regression for the two rate expression Equations (5), (6) to find which one has the best fitting for the data was used. Regression showed that the L-H model (*i.e.* Equation (5)) has best fitting with the experimental data with excellent $R^2 = 0.9997$, the experimental results have been compared with those predicted by these models in **Figure 4** with very well deviation ($AD\% = (\text{Calc.} - \text{Predic.}/\text{Predic.}) * 100$). According to that, kinetic and adsorption parameters are calculated and listed in **Table 4**. The parameters of kinetic and adsorption with temperature dependence are shown in **Figure 5** and **Figure 6**, The kinetic parameters were determined to be compatible with the Arrhenius Equation (7) with good straight-line plots, suggesting that the kinetic data were obtained during surface control and no major deactivation of the catalyst took place (Yue, 1984)

Table 3. Experimental work data over resin catalyst.

Temp. (°C)	W/F (g cat-hr/g mole)	Methanol conv. X_A	Rate of reaction r_A (g mole/g cat-hr)
90	26.93602694	1.3	0.000482625
90	32.32323232	1.5	0.000464063
90	46.17604618	1.9	0.000411469
90	80.80808081	1.99	0.000246263
90	100.2	2.1	0.000209581
110	26.93602694	2.2	0.00081675
110	32.32323232	2.5	0.000773438
110	46.17604618	2.7	0.000584719
110	80.80808081	3.4	0.00042075
110	100.2	3.9	0.000389222
120	26.93602694	3.51	0.001303088
120	32.32323232	4	0.0012375
120	46.17604618	5.4	0.001169438
120	80.80808081	8	0.00099
120	100.2	8.6	0.000858283

Table 4. Kinetic and adsorption parameters.

Temp. (°C)	k (K mole/kg-hr) $\times 10^4$	K_A (atm)
90	7.5	2.3
110	12.2	4.07
120	15.2	8.58

**Figure 4.** Comparison of measured and predicted reaction rate (according to the two models).

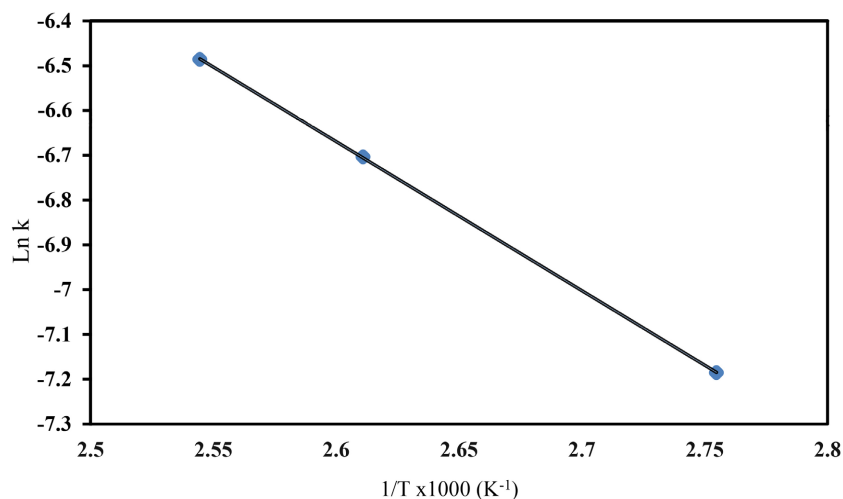


Figure 5. Variation of adsorption equilibrium constant with temperature.

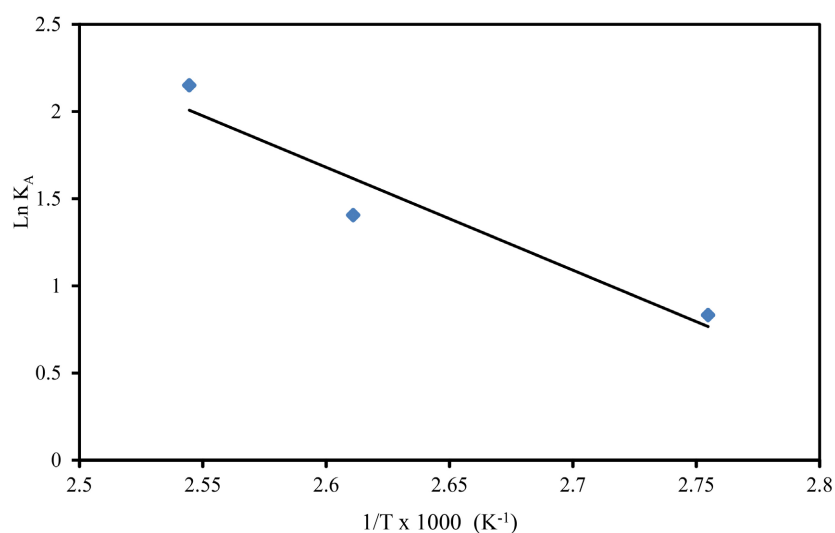


Figure 6. Variation of kinetic parameter with temperature.

[31]. The value of activation energy E and pre-exponential factor A were calculated and it was 27.66 kJ/mole and 7.24 mol/kg.hr respectively. By comparing this value with the literature (Table 5), it was very low and that could be attributed to the $-\text{SO}_3\text{H}$ group network in polystyrene sulfonate which acts in methanol coordination as mentioned by Gates and co-workers [32] [33], Barbarossa [5] has also attributed the low activation energy to the ability of a propyl-sulfonic chain to be re-arranged around the methanol molecule.

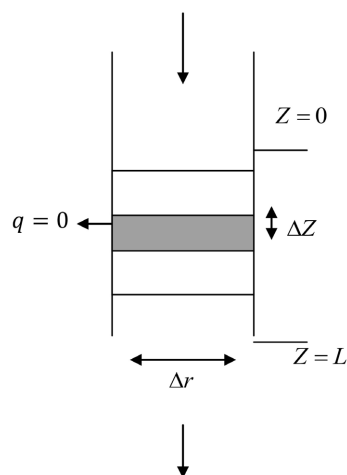
$$k = Ae^{-\frac{E}{RT}} \quad (7)$$

where

- A : Pre exponential factor
- E : Activation energy
- R : Gas constant
- T : Reaction temperature

Table 5. The activation energy of various investigations.

Ref.	This work	[2]	[34]	[18]	[12]	[5]
$E_{\text{kJ/mole}}$	27.66	256	136	95	51.7	44
Catalyst type	Sulfonic resin	Al_2O_3	Al_2O_3	Resin (Ambelyst 16)	Resin (Ambelyst 35)	Sulfonic resin

**Figure 7.** Packed bed reactor.

3.3. Mathematical Modeling

A comprehensive numerical model of the entire reactor is now available with the obtained reaction rate function, According to Bird *et al.* [35] and the Packed Bed Tubler Reactor PBTR geometry shown in (Figure 7). The general mass balance equation can be presented in cylindrical coordination for z components as in (Equation (8)).

$$u_s \frac{\partial C_i}{\partial z} - \frac{D_r}{r} \frac{\partial}{\partial r} \left(r \frac{\partial C_i}{\partial r} \right) - D_z \frac{\partial^2 C_i}{\partial z^2} = -\rho_B Ri(C, T) \quad (8)$$

where D_z and D_r denote the effective diffusivity in axial and radial directions respectively, ρ_B and C_i are catalyst density and material concentration respectively. Many assumptions to simplify this equation were given, according to Berčić [36] an adiabatic reactor can be well described as on dimensional model (*i.e.* no radial dispersion effect). However, this reactor could be assumed PFR (*i.e.* pseudo homogeneous reactor) according to Froment and Bischoff [37] and Rase [38] criteria for packed-bed reactors, these criteria ($L/d_p > 50$ and $d_t/d_p > 10$ where L , d_t and d_p are length of reactor, diameter of reactor tube and diameter of catalyst particle respectively) these confirm that reactor flow conditions are close to plug flow to achieve the isothermal reactor operation. In this investigation $L/d_p = 116.6$ and $d_t/d_p = 42.3$. By these assumptions we discard all transport resistance [22] and Equation (8) will be:

$$u_s \frac{\partial C_i}{\partial z} = -\rho_B Ri(C, T) \quad (9)$$

initial condition:

$$\text{At } z = 0, C_A = C_{A0}$$

Numerical method Runge-Kutta 4th order model in MATLAB software was used to solve the first-order differential equation (Equation (9)) to obtain concentration profile in the reactor as shown in (Figure 8). The exit concentrations based on the solution of the numerical model (Equation (9)) of methanol were compared to those calculated experimentally and listed in (Table 6). The predicted and calculated results are in good agreement with a 0.32% average deviation.

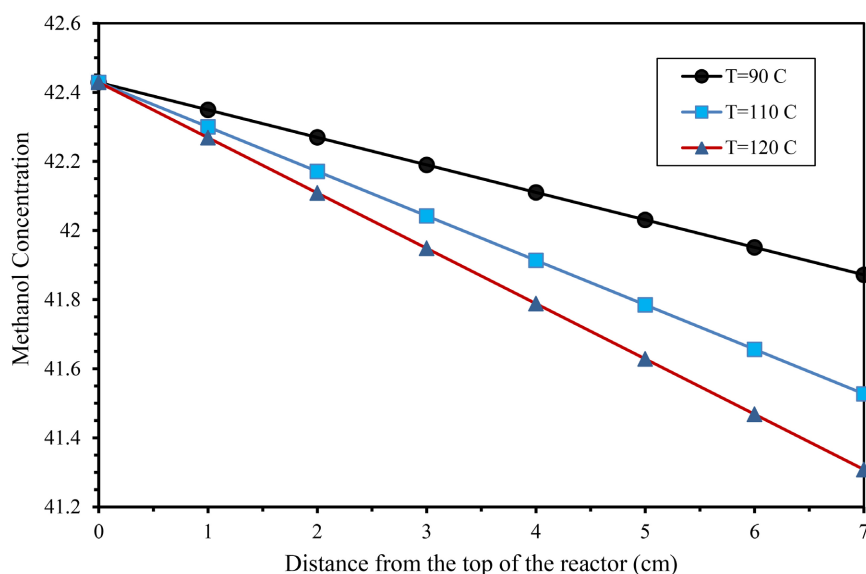


Figure 8. Concentration profiles along the reactor at three feed temperatures and $W/F = 81$ (gcat.hr/gmole).

Table 6. Comparison between calculated and predicted concentration.

Temperature °C	Calculated concentration	Predicted concentration	AD%
90	41.877	41.8716362	0.01281
110	41.49514286	41.52720933	0.07721797
120	40.93932857	41.3080801	0.892686195
Average absolute deviation AAD%			0.327571419

4. Conclusion

The use of resin materials as catalysts in the methanol dehydration reaction to produce DME was proven to be a good technique to obtain active catalysts. The L-H mechanism, in which the surface reaction is the rate-determining step well-fit the experimentally established reaction kinetic data, and the experimental results have been compared to those predicted by this model with little deviation. The kinetic and thermodynamic constant values were found at various temperatures. The apparent activation E energy for this reaction was calculated

to be 27.66 kJ/mole during the experiment. On the other hand, simple mathematical continuum models (PFR) exhibited acceptable agreement with experimental data, with an average variation of 0.32 percent between the expected and the observed results.

Conflicts of Interest

The authors declare no conflicts of interest regarding the publication of this paper.

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