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KINETIC STUDY OF CATALYTIC HYDROLYSIS REACTION OF METHYL ACETATE TO ACETIC ACID AND METHANOL*

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Abstract– The reaction kinetics and chemical equilibrium of the reversible catalytic hydrolysis reaction of a methyl acetate to acetic acid and methanol using a strongly acidic ion exchange resin catalyst named Amberlyst 15 were studied. To investigate the different behavior of Amberlyst 15 in the adsorption of reactants and product species, the equilibrium behavior of binary non-reactive liquid mixtures, consisting of one reactant and one product were studied experimentally. The Langmuir model was used to describe the equilibrium condition, quantitatively. Then the employed model was compared with the more complicated thermodynamic models to describe the equilibrium between the catalytic polymer resin and the liquid phase. The results indicated a good agreement. The effects of temperature, catalyst weight, and feed molar ratios on reaction kinetics were investigated. Results revealed that the reaction rate was strongly temperature dependent. The chemical equilibrium compositions were measured in a wide range of temperatures and feed molar ratios. Finally, pseudo homogeneous and LHHW (Langmuir Hinshelwood Hougen Watson) models were developed to calculate the rate of the reaction. Optimization of the model's parameters indicated that the use of activity instead of mole fraction, and also the use of LHHW rather than a pseudo homogeneous model resulted in much smaller residual errors. Also the equilibrium compositions obtained from the equation of rates were in good agreement with the experimental results.

Keywords– Methyl acetate, kinetics, amberlyst 15, hydrolysis, rate of reaction

1. INTRODUCTION

Hydrolysis of methyl acetate (MeOAc) to acetic acid and methanol is one of the major reactions since a great deal of methyl acetate is produced as by-product during the synthesis of polyvinyl alcohol (PVA) and pure terephthalic acid (PTA). It is estimated that 1.5-1.7 tons of MeOAc is produced per ton of PVA [1, 2].

Methyl acetate can be hydrolyzed into value-added products of methanol and acetic acid which can be recycled on site into the mentioned processes. As well as the industrial application, this system is of major importance as an experimental model reaction for reactive distillation research [2].

Acetic acid (HOAc) and methanol (MeOH) can be made by the liquid-phase reaction of methyl acetate (MeOAc) and water. The MeOAc hydrolysis reaction is reversible and the reaction equilibrium constant, K, is relatively small. Therefore, H+ ion is employed as the catalyst in order to increase the reaction rate [3]. Strong acids such as sulfuric acid and hydrochloric acid can be used to produce an H+ ion and catalyze the reaction [4]. The reaction is

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$$CH_3COOCH_3 + H_2O \xleftrightarrow{H^+} CH_3OH + CH_3COOH \tag{1}$$

Strong acids cause corrosion in the whole process and it is costly to separate and purify the final product [5]. In order to eliminate the mentioned disadvantages, a strongly cation-exchange resin containing a sulfonic acid (SO_3H) is usually used as an acid catalyst for hydrolysis. Conventional sulfonic-acid-type resin is prepared by sulfonation of the styrene (St) -divinylbenzene (DVB) copolymer, where the polystyrene chains were cross-linked with DVB [6] as illustrated in Fig. 1.

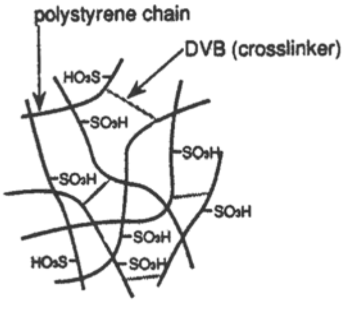

Fig. 1. Schematic of Amberlyst 15 resin structure

The specific structure of ion-exchange resins causes different behavior in various reaction locus [5]. When a dry resin is brought into contact with a liquid, it swells; i.e., a portion of the liquid component is absorbed by the resin up to reaching equilibrium with the liquid phase. In the case where the liquid phase is constituted of a multi-component mixture, in principal all components are absorbed, but each of them to a different extent. The preferential selectivity of the resin toward one of the components of the binary solution has been proved. For instance, the resin exhibits a much higher affinity for water than for other components such as acetic acid and methanol. In particular, if these exhibit different affinities toward the resin, such that one of the reaction products tends to be selectively removed from the reaction locus, then the rate of the inverse reaction is minimized, and it is possible to achieve higher equilibrium conversions than those obtained with a homogeneous catalyst [7].

The selective adsorption of ion-exchange resins have been investigated by many researchers [8-11]. These types of resins have even been used for purification of water-hydrocarbon systems [8, 9, 11]. Nevertheless, a reliable thermodynamic model to predict selective adsorption of components on polymeric resins has not been developed yet. However some simple adsorption models such as Langmuire can be used for representing semi-empirical equations describing this phenomenon.

Methyl acetate hydrolysis and methanol esterification reactions have been studied before by some researchers. Mazzotti *et al*. investigated ethanol esterification with acetic acid in liquid phase. They described the selective swelling in terms of the equilibrium between a multi-component polymeric phase containing all compounds, and a liquid phase which doesn't contain the polymer. The activity of each component in the liquid phase has been evaluated using the UNIFAC method, and the behavior of the polymeric phase described in the framework of the extended Flory-Huggins model [7]. Although the suggested model predicted the reaction rate and selective swelling of the resins, it involved complexity and inconvenience in computation and was just valid through a small range of experimental data.

Song *et al*. [12] studied methanol esterification with acetic acid. A Langmuire-Hinshelwood/Hougen-Watson (LLHW) was developed to represent the reaction kinetics. The reaction rate was expressed in terms of activities which were calculated using a UNIFAC model. To study the importance of side reactions, the reaction kinetics of methanol dehydration was also included in the model. Methanol esterification has been well predicted by the represented model in the range of the experimental data, but it can not be employed reliably for the methyl acetate hydrolysis reaction. In other words, the accuracy of extrapolation was very poor.

Popken *et al*. [3] improved the Song *et al*. model and presented a new model by modifying the LHHW model. They used the Langmuire model to predict selective adsorption of cationic resins and presented many experimental data for both hydrolysis and esterification reactions. They also modeled the reaction kinetics in the absence of a catalyst.

Yu. *et al*. [13] presented methyl acetate hydrolysis and esterfiaction reaction rates considering more simplified assumptions. In contrast to previous research, they used a packed column as a fixed bed reactor instead of the batch one and conducted the experiments continuously. Because of so many simplified assumptions and few experimental data, the obtained reaction rate was valid only under the experimental condition used and the extrapolation accuracy of the proposed mathematical model was poor.

The methyl acetate hydrolysis reaction catalyzed by Amberlyst 15 has been investigated in the present research. The LLHW model has been adopted to describe the reaction rate accurately and quantitatively and the results obtained from the model compared with the previous models represented in the literature, as well as with the experimental results.

2. EXPERIMENTAL SECTION

Chemicals. Methyl acetate (purity > 99.436 wt %), methanol (purity > 99.811 wt %) and acetic acid (purity > 99.746 wt %) were purchased from Merck (as determined by gas chromatography) and water was distilled.

Catalyst. The macro-porous sulfonic ion-exchange acid resin Amberlyst 15, dry, purchased from Merck was chosen as the catalyst in this work. The main characteristics of the Amberlyst ion-exchange resin are listed in Table 1. Amberlyst resins were sufficiently washed with distilled water several times until the supernatant liquid was colorless to remove impurities. Then the catalyst were placed in the oven for one to three days and dried at 80°C until the mass remained constant (usually 2 days). Drying at higher temperatures involves the risk of losing sulfonic acid sites. In all the experiments, the dried catalyst was used.

Table 1. Properties of Amberlyst 15 dry ion-exchange resin

Appearance	Hard, dry, spherical particles
Typical particle size distribution	
16 mesh	2-5%
16-20 mesh	20-30%
20-30 mesh	45-55%
30-40 mesh	15-25%
40-50 mesh	5-10%
Through 50 mesh	1.0
Bulk density (Kg/m^3)	608
Moisture (by weight)	Less than 1%
Hydrogen ion concentration (meq./g dry)	4.7
Surface area (m^2/g)	50
Porosity (ml pore/ml bead)	0.36
Average pore diameter (A^o)	240

Composition Analysis. An HP Agilent Technologies 6890 N, gas chromatograph (GC) equipped with Chemstation software was used to analyze the samples. The sample size for GC was 0.1-0.3 µL. The injection port (thermal conductivity detector) temperature was set to 200 °C and the detection port was set to 220 °C. A CP-WAX 52 CB column was used to separate methyl acetate, methanol, water and acetic acid. The column temperature was programmed to start from an initial value of 70 °C for 3 minutes, followed by a 25 °C/min ramp up to 150 °C. High purity N_2 gas was used as a carrier gas. The flow rate of the carrier gas was 1.8 ml/min (constant flow).

Kinetic experiments procedure and apparatus. A 500 ml, three-neck glass flask was used for kinetic experiments. A schematic of the experimental setup is shown in Fig. 2.

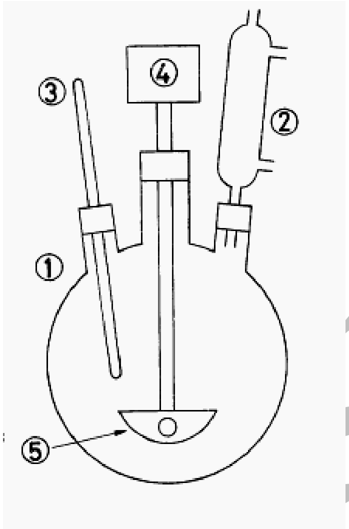

Fig. 2. Experimental setup for the measurement of methyl acetate Hydrolysis reaction kinetics
1-reactor, 2- condenser, 3- thermometer, 4- motor, 5- impeller

One neck was connected to a condenser in order to avoid loss of volatile components such as methyl acetate, methanol and other volatile components, another to a thermometer to measure the reaction temperature with an accuracy of ± 0.5 °C. The third was sealed with a septum cap. To improve mixing, 4 baffles were installed. A plate type, variable speed stirrer made of Teflon was used for stirring the flask mixture. The absence of external mass transfer resistance and catalyst abrasion were ensured by a stirrer speed higher than 180 rpm (to allow a complete suspension of catalyst), plate type shape and Teflon material, respectively. Liquid samples of about 0.5 cc were taken using a syringe.

The reactor was immersed in a bath filled with water as the heating fluid. Catalyst and water were weighed and heated together to the desired reaction temperature. Methyl acetate was heated in a separate vessel. When the liquid in the reactor reached the desired reaction temperature, the second reactant was added to the reactor. The stirrer and the time measurement were started immediately. Approximately 15 samples were taken according to the sampling program concluded from computing the previous models proposed in the literature, until equilibrium time was reached. The liquid samples were poured into a 3-cc glass vial and analyzed with GC after sudden cooling at -20 °C. The experiment conditions are listed in Table. 2. Some obtained results are represented in Figs. 5-7, in the result and discussion section.

Chemical equilibrium experiments. To obtain reliable data about the chemical equilibrium, independent experiments were conducted. The experiments were performed by placing the desired amount of reactants and catalyst (total 2 cc, different compositions) in a 3-cc glass vial, which was then sealed and placed in a bath at a given constant temperature for 1 week. Just before analysis, the vials were cooled rapidly and then analyzed by GC. The experiments were performed at temperatures of 32, 39, 46, 53 and 60 °C and fifteen samples were prepared with different compositions (initial mole ratio of methyl acetate to water) for each temperature. The final results can be seen in Fig. 3.

Table 2.Conditions of kinetic experiments

No	Catalyst (gr)	Feed		Temp. (°C)	Water / MA molar ratio	Experiment duration (hr)
		MA (gr)	Water (gr)			
1	26.50	119.11	30.22	47.0	1.04	5.26
2	30.49	100.30	49.88	47.5	2.04	5.00
3	42.20	87.36	63.89	47.5	3.01	5.01
4	45.71	76.57	74.62	48.0	4.01	5.01
5	45.50	74.94	108.67	48.0	5.96	3.26
6	45.15	50.85	99.80	48.0	8.07	4.05
7	45.04	87.53	64.18	38.0	3.01	5.00
8	45.02	120.00	30.00	38.0	1.03	5.09
9	35.30	87.10	36.00	38.0	1.70	5.26
10	55.80	87.60	63.30	38.0	2.97	4.53
11	35.70	44.30	107.40	54.5	9.97	3.81
12	20.20	43.70	106.50	54.5	10.02	4.50
13	35.30	32.40	118.30	55.0	15.01	3.27
14	55.30	121.90	30.70	32.0	1.04	5.22
15	40.60	120.50	31.20	32.0	1.06	5.01
16	35.30	47.40	106.90	55.5	9.27	2.86
17	45.70	86.90	63.30	44.0	2.99	3.75
18	45.50	87.10	63.70	32.0	3.01	5.84
19	45.20	87.70	63.90	55.5	3.00	2.09
20	45.10	89.00	63.50	35.7	2.93	5.26
21	55.80	27.10	124.80	58.0	18.93	2.07

3. KINETIC MODELS

a) Pseudo-homogeneous model

Pseudo-homogeneous model does not consider catalyst selective adsorption. It is represented as follows:

$$r=\frac{1}{\nu_i}\frac{dn_i}{dt}=m_{cat}\left(k_1 a_{MeOAc}a_{H_2O}-k_2 a_{HOAc}a_{MeOH}\right) \tag{2}$$

$$k_1=k_1^0\exp\left(\frac{-E_1}{RT}\right) \tag{3}$$

$$k_2=k_2^0\exp\left(\frac{-E_2}{RT}\right) \tag{4}$$

where the ion-exchange resin is thought to act as a source of solvated proton. Assuming the ideal liquid phase behavior and substituting activities with mole fractions, the model can be simplified as follows:

$$r=\frac{1}{\nu_i}\frac{dn_i}{dt}=m_{cat}\left(k_1 x_{MeOAc}x_{H_2O}-k_2 x_{HOAc}x_{MeOH}\right) \tag{5}$$

b) LLHW heterogeneous model

Song *et al*. represented the kinetic model considering the following assumptions [12, 14]:

(1) The adsorption sites are uniformly energetic.

(2) Catalyst surface consists of constants active sites.

(3) The site activity is just dependent on temperature and a molecule on site 1 does not influence what attaches onto a nearby site.

(4)The surface reaction is the rate-controlling step. A possible mechanism for the hydrolysis reaction is as follows:

$$MeOAc \cdots S \longleftrightarrow MeOAc + S \tag{6}$$

$$H_2O + S \longleftrightarrow H_2O \cdots S \tag{7}$$

$$H_2O \cdots S + MeOAc \cdots S \longleftrightarrow HOAc \cdots S + MeOH \cdots S \tag{8}$$

$$HOAc \cdots S \longleftrightarrow HOAc + S \tag{9}$$

$$MeOH \cdots S \longleftrightarrow MeOH + S \tag{10}$$

The resulting LLHW model is [14]

$$r = \frac{1}{\nu_i}\frac{dn_i}{dt} = m_{cat}k_1K_{MeOAc}K_{H_2O}\left(\frac{a_{MeOAc}a_{H_2O} - \frac{a_{HOAc}a_{MeOH}}{k_{eq}}}{\left(1+K_{MeOAc}a_{MeOAc}+K_{H_2O}a_{H_2O}+K_{HOAc}a_{HOAc}+K_{MeOH}a_{MeOH}\right)^2}\right) \tag{11}$$

The fifth assumption was confirmed by Popken *et al* [3]. They repeated the Song *et al.* experiments with the same conditions, just varying the catalyst pellet size [12]. No effect of the catalyst pellet size on the reaction kinetics was observed, which is consistent with the fact that pellets of Amberlyst 15 are composed of very small micro spheres which are similar in size, hence it was concluded that catalyst adsorption does not control the reaction rate kinetics [3].

Popken *et al.* [3] indicated that the assumption of a constant mole adsorbed on catalyst was not suitable because there was an order of magnitude difference between the values for methyl acetate and water. A better choice would be the assumption of a constant adsorbed mass, for which the values for the individual compounds were similar. For this reason, the equations given by Song *et al.*, were modified to allow for a constant adsorbed mass [12]. The results of the measurements are shown in Table 3.

Assuming Langmuire-type adsorption based on mass, the following relation for the mass coverage m_i/m can be obtained:

$$\frac{m_i}{m} = \frac{K_i a_i}{1+\sum_j K_j a_j} \tag{12}$$

where m denotes the total adsorbed mass on the catalyst, m_i is the adsorbed mass of component i of the solvent on the catalyst, K_i is the Langmuire adsorption constant of component i, and a_i is the liquid phase activity of component i that is calculated by the UNIQUAC model. The parameters of the proposed model are represented in Table 4.

Binary adsorption parameters are needed for the kinetic model. In order to obtain the experimental amount of K_i, a set of experiments was conducted considering the Popken *et al.* assumption (Fig. 4) [3]. This was done with the four non-reactive sets of binary adsorption data, i.e. water-methanol, water-acetic acid, methyl acetate-methanol and methyl acetate-acetic acid. A mixture of non-reactive binary pairs with specific initial composition (w_1^0 , w_2^0) was contacted with a specified mass of dry catalyst in a sealed vial.

After allowing enough time for the adsorption of the components on the catalyst (about 2 weeks), the new composition of the binary solution contacting with the swelled catalyst (w_1,w_2), was determined by GC.

Table 3. Experimental swelling ratios obtained for the pure components and adsorbed volumes, masses, and mole per gram of dry Amberlyst 15 [3]

Component	Swelling ratio	Adsorbed volume (cm^3/g)	Adsorbed mass (g/g)	Adsorbed amount (mmol/g)
Acetic acid	1.43	0.307	0.319	5.31
Methanol	1.55	0.393	0.309	9.60
Methyl acetate	1.40	0.286	0.265	3.58
Water	1.67	0.479	0.478	26.5

Table 4. UNIQUAC parameters used for the calculation of activity coefficients [15]

Components	a_{ij}				r_i	q_i
	Methyl acetate	Water	Acetic acid	Methanol		
Methyl acetate	-	789.996	806.844	585.482	2.5759	2.8041
Water	117.211	-	-305.452	-10.377	1.3997	0.9200
Acetic acid	-467.125	427.741	-	-51.049	2.0720	2.2023
Methanol	-54.338	95.259	-40.725	-	1.4320	1.4311

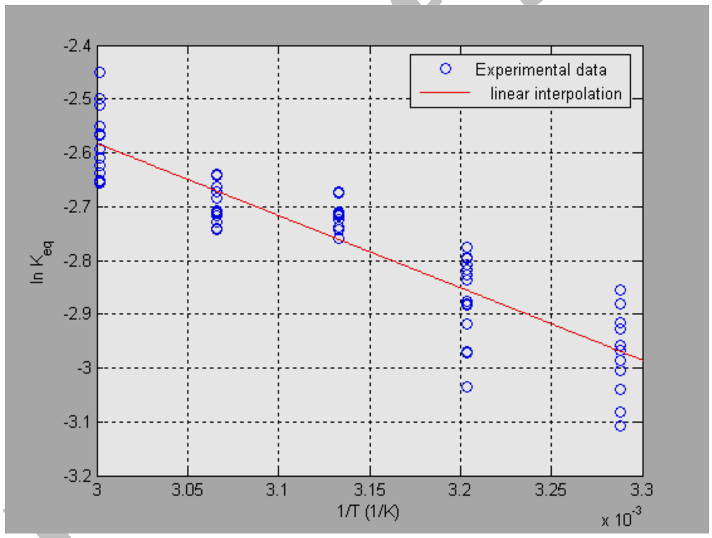

Fig. 3. Chemical equilibrium constants of methyl acetate hydrolysis based on the experimental results

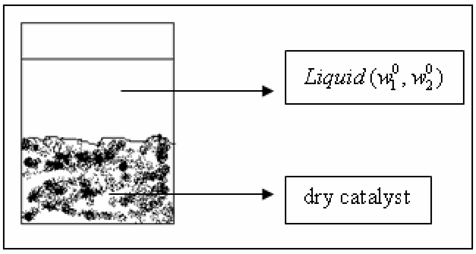

Fig. 4. Adsorption constant experiments

From the overall mass balance of the binary liquid phase adsorption, and considering the Langmuire adsorption model for expressing the equilibrium between liquid and polymer phases, the following equations can be written:

$$m = m_1 + m_2 \tag{13}$$

where m denotes the total adsorbed mass on the catalyst, m_1 is the adsorbed mass of solvent 1, and m_2 is the adsorbed mass of solvent 2. The mass balance equation of component 1 can be written as follows:

$$m_0 w_1^0 = m_1 + w_1 (m_0 - m) \tag{14}$$

Where m_o is the initial total solvent weight, w_1^0 is the overall weight fraction, and w_1 is the equilibrium liquid-phase weight fraction of solvent 1.

Assuming Langmuire-type adsorption based on mass for a binary system, the following relation for the mass coverage m_1/m can be obtained:

$$\frac{m_1}{m} = \frac{K_1 a_1}{1 + K_1 a_1 + K_2 a_2} \tag{15}$$

Mass balance equations can be simplified to the equation below:

$$m_0 (w_1^0 - w_1) = m_1 w_2 - w_1 m_2 \tag{16}$$

Combining Eqs. (15) and (16) for the binary case (substituting m_1 and m_2 using Langmuir equation), the following relation is obtained.

$$\frac{m_0}{m_{cat}}(w_1^0 - w_1) = \frac{m}{m_{cat}} \frac{K_1 a_1 w_2 - K_2 a_2 w_1}{1 + K_1 a_1 + K_2 a_2} \tag{17}$$

The left hand side of the equation can be obtained from experimental data and the right hand side consists of three unknowns K_1, K_2 and m/m_{cat}. This was done with the four non-reactive sets of binary adsorption data (water-methanol, water-acetic acid, methyl acetate-methanol, methyl acetate- acetic acid). Unknown parameters K_1, K_2, K_3, K_4, and the total adsorbed mass m/m_{cat} were optimized using Matlab optimization algorithms in the way that the right hand side of the equation would be consistent with the experimental results (left hand side of the equation).

Including the selective adsorption of the components by the catalyst in the reaction rate, it can be represented by a mole fraction of the components in the adsorbate phase (catalyst)

$$r = \frac{1}{\nu_i}\frac{dn_i}{dt} = m_{cat}\left(k_1 x^s_{MeOAc} x^s_{H_2O} - k_2 x^s_{HOAc} x^s_{MeOH}\right) \tag{18}$$

where x_i^s denotes the mole fraction of component i adsorbed in the catalyst. If x_i^s is expressed in terms of the component activities in the liquid bulk using the Langmuire model, Eq. (19) can be written for the reaction rate

$$r = \frac{1}{\nu_i}\frac{dn_i}{dt} = m_{cat}\left(\frac{k_1 a'_{MeOAc} a'_{H_2O} - k_2 a'_{HOAc} a'_{MeOH}}{\left(a'_{MeOAc} + a'_{H_2O} + a'_{HOAc} + a'_{MeOH}\right)^2}\right) \tag{19}$$

$$a'_i = \frac{K_i a_i}{M_i} \tag{20}$$

$$k_1 = k_1^0 \exp\left(\frac{-E_1}{RT}\right) \tag{21}$$

$$k_2 = k_2^0 \exp\left(\frac{-E_2}{RT}\right) \tag{22}$$

4. OPTIMIZATION OF PARAMETERS

The optimization tool box of Matlab 7 software was used to optimize the parameters of kinetic equations. Thus an objective function was defined as follows:

$$O{\cdot}f{\cdot}\left(k_1^0, k_2^0, E_1, E_2\right) = \sum_{j=1}^{N}\left(\sum_{i=1}^{n}\frac{\left|w_{MeOH,i}^{ex.} - w_{MeOH,i}^{calc.}\right|}{w_{MeOH,i}^{ex.}}\right)_j \tag{23}$$

Where $w_{MeOH}^{ex.}$ represents the experimental methanol weight percent, $w_{MeOH}^{calc.}$ is calculated methanol weight percent using the reaction rate, and N is the number of experiments. The reaction rate, which is a differential equation, was solved using the Runge-Kutta method to obtain $w_{MeOH}^{calc.}$. The parameters of the differential equation are set according to the initial ratio of feed, catalyst mass and temperature at the start of the reaction. It should be noted that while employing the Minimax method, the first summation symbol is omitted from the objective function.

5. RESULT AND DISCUSSION

As mentioned before, the effects of temperature, initial mole ratio of the feed, and catalyst mass on the reaction rate were investigated.

The influence of temperature on the reaction rate is shown in Fig. 5. The reaction rate and equilibrium time were found to be affected considerably by slight changes of temperature. For instance, as the temperature increased from 35.7 ^{o}C to 55.5 ^{o}C the equilibrium time decreased from 4 hours to 1.5 hours.

The effect of catalyst loading on the reaction rate is shown in Fig. 6. An increase in catalyst mass leads to a slight increase in reaction rate. It can be seen from Fig. 6 that the assumption of a linear dependence of the rate on the mass of the catalyst is valid.

The influence of the initial molar ratio of the feed on the reaction rate at 48 ^{o}C is shown in Fig. 7. It is observed that the effects of variations in the molar ratio of water to methyl acetate in the feed can be neglected.

The optimization results of the pseudo-homogeneous model are represented in Table 5. It can be concluded that the use of activity in the kinetic model instead of mole fraction results in a much smaller residual error. Furthermore, the optimization error of the present research is much smaller than the reported values in the literature.

Table 5. The results of optimization of pseudo-homogeneous model parameters

Model	$k_1^0\left(\frac{gmole}{s}\right)$	E_1 $\left(\frac{J}{mole \cdot K}\right)$	$k_2^0\left(\frac{gmole}{s}\right)$	E_2 $\left(\frac{J}{mole \cdot K}\right)$	Mean relative error	Optimization method
This work, Ideal	13325	53340	17.67	30363	14.6	Minimax SQP
Popken, ideal	1.16E+05	58600	1.65E+04	47980	15.61	Simplex nelder mead
This work, activities by UNIQUAC	4688	55316	886115	60709	8.61	Minimax SQP
Popken, activities by UNIQUAC	1348000	69230	29610	49190	13.9	Simplex nelder mead

Table 6 represents the optimization results of the LLHW model. It was found that the results obtained from the first optimization procedure were not consistent with experiments 1, 8, 14 and 15. As all the above mentioned experiments were performed at a high ratio of methyl acetate to water, the high volatility of methyl acetate could lead to great loss and large errors. Omitting the mentioned experimental results, the optimization procedure was repeated and resulted in a good agreement with the proposed model. The comparison between empirical values of experiment No. 2 as typical, with the LLHW model results (results obtained by solving the proposed model) and the Popken model is shown in Fig. 8. The model predictions and experimental data compared in Fig. 8 shows very good fitting.

Table 6. The results of optimization of LLHW model parameters

Model	k_1^0	E_1	k_2^0	E_2	K_1	K_2	K_3	K_4	Mean error
Popken	612700	63730	8497000	60470	4.15	5.24	3.15	5.64	5.64
This work	599983	63916	7999999	60638	3.11	3.548	2.10	3.951	6.81

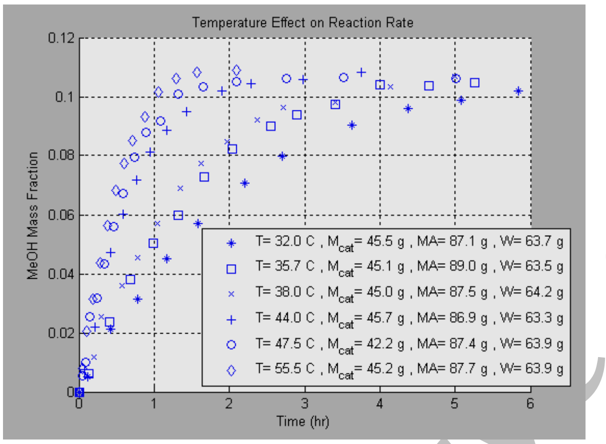

Fig. 5. Effects of temperature on reaction rate

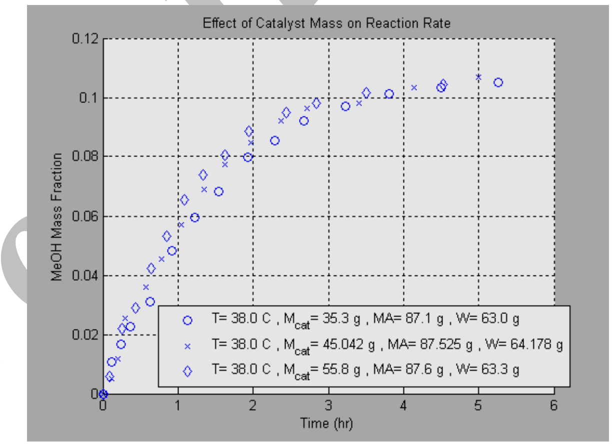

Fig. 6. Effects of catalyst mass on reaction rate

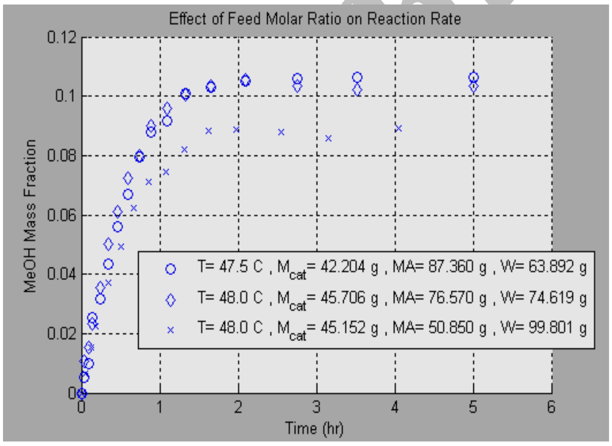

Fig. 7. Effect of feed molar ratio on reaction rate

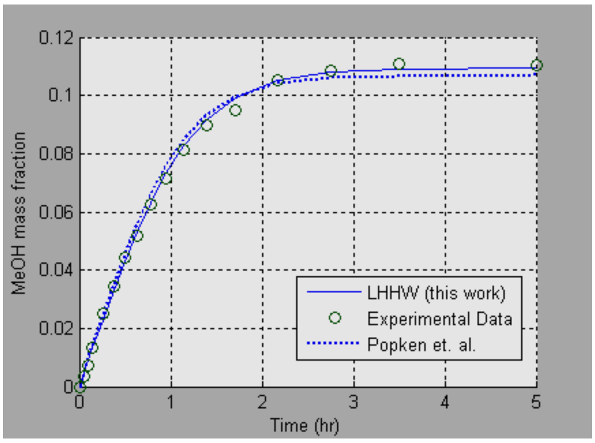

Fig. 8. Comparison between the experimental values, LLHW model results and Popken model for experiment No.2

6. CONCLUSION

In simulation and design of methyl acetate hydrolysis, which is a major process in PVA and PTA plants, an appropriate and simple kinetics is required that can be added to optimization software. Such a model would be based on a data bank of experimental information. The effects of different parameters such as temperature, initial molar ratio of water to methyl acetate in feed and catalyst mass were studied. It was found that the increase of catalyst mass to feed ratio results in a linear increase of the hydrolysis reaction rate. Furthermore, the temperature variation has considerable influence on the reaction rate, but the effect of the molar ratio of the components in the feed on the reaction rate can be neglected. The fitting results of the pseudo-homogeneous model on experimental data indicated that using activity instead of the mole fraction leads to a smaller residual error. Furthermore, using a model based on the selective adsorption of the components such as LLHW can decrease the residual error to the minimum range. Anyway, using a more complicated model than the LLHW may lead to smaller residual errors, but so much data is required and these types of models have not been developed in polymeric systems yet. Thus, it seems that the LLHW model is an appropriate adsorption model for predicting the reaction rate.

NOMENCLATURES

a_i	activity of component i
E_1, E_2	activation energies of forward and backward reactions, $\left(\frac{J}{mole.K}\right)$
k_1	Forward reaction rate (hydrolysis), $\left(\frac{gmole}{s}\right)$
k_2	backward reaction rate (esterification), $\left(\frac{gmole}{s}\right)$
k_1^0, k_2^0	exponential function coefficient of reaction rate, $\left(\frac{gmole}{s}\right)$
K_i	Langmuir adsorption constant of component i
m	the total adsorbed mass on catalyst, (gr)
m_0	the initial total solvent weight, (gr)
m_{cat}	catalyst mass, (gr)
m_i	the adsorbed mass of solvent i, (gr)
M_i	molar mass of component i, $\left(\frac{gr}{gmole}\right)$
n_i	mole number of component i
N	number of experiments
r	reaction rate, $\left(\frac{gmole}{g.s}\right)$
-s	active site of catalyst
v_i	stoichiometric coefficient of component i in the reaction
w_i^0	the overall weight fraction of component i
w_i	the equilibrium liquid-phase weight fraction of solvent i
x_i	mole fraction of component i in the reaction
MeOAc	methyl acetate
HOAc	acetic acid
MeOH	methanol

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