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Kinetics of esterification of methanol and acetic acid with mineral homogeneous acid catalyst

Mallaiah Mekala *, Venkat Reddy Goli

Department of Chemical Engineering, National Institute of Technology, Warangal 506004, India

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ABSTRACT

In this work, esterification of acetic acid and methanol to synthesize methyl acetate in a batch stirred reactor is studied in the temperature range of 305.15–333.15 K. Sulfuric acid is used as the homogeneous catalyst with concentrations ranging from 0.0633 $\mathrm{mol \cdot L^{-1}}$ to 0.3268 $\mathrm{mol \cdot L^{-1}}$. The feed molar ratio of acetic acid to methanol is varied from 1:1 to 1:4. The influences of temperature, catalyst concentration and reactant concentration on the reaction rate are investigated. A second order kinetic rate equation is used to correlate the experimental data. The forward and backward reaction rate constants and activation energies are determined from the Arrhenius plot. The developed kinetic model is compared with the models in literature. The developed kinetic equation is useful for the simulation of reactive distillation column for the synthesis of methyl acetate.

1. Introduction

Carboxylic acid esters constitute major components of numerous natural products and synthetic compounds. They are widely used as softeners, emulsifiers, dispersants, detergents, surfactants, solvents and biodiesel fuels. Several synthetic routes are available to obtain carboxylic acid esters. A comprehensive review of ester synthesis route is available [1].

The kinetics of esterification reaction between acetic acid and methanol in alcoholic and non-hydroxylic media was investigated earlier by Rolfe and Hinsshelwood [2]. They proposed a kinetic model based on the theory of molecular statistics of esterification reaction by using hydrochloric acid as the catalyst. The kinetics of esterification of acetic acid with methanol using a homogeneous hydrogen iodide catalyst was investigated by Ronnback *et al.* [3], where the protonation of carboxylic acid was considered as the rate-initiating step in the reaction mechanism. They observed that hydrogen iodide was esterified by methanol and produced methyl iodide as a by-product. Hilton and Smith [4] found that the kinetics of acid catalyzed esterification of *n*-aliphatic acid with methanol is influenced by the length of carbon chains with different buffer solutions.

Agreda *et al.* [5] proposed a rate expression for esterification reaction using homogeneous sulfuric acid as a catalyst while carrying out the reaction in a reactive distillation unit. The kinetic model shows nonlinear dependence on the catalyst concentration without the kinetic parameters reported. Engell and Fernholz [6] and Kruel *et al.* [7] modified the kinetic model proposed by Agreda *et al.* [5] for the esterification reaction using heterogeneous sulfonic ion exchange resin as the catalyst. Liu *et al.* [8] developed a rate expression for the esterification reaction of methanol with acetic acid using homogeneous sulfuric acid catalyst, presenting a linear kinetics on catalyst concentration. Elgue *et al.* [9] also proposed a linear kinetics on catalyst concentration and applied it for intensification of methyl acetate production in a continuous reactor. The catalytic esterification reaction between methanol and acetic acid for the synthesis of methyl acetate with Amberlyst-15 (dry) as heterogeneous catalyst was studied by Ismail *et al.* [10] in the temperature range of 318–338 K. The similarities and differences between heterogeneous and homogeneous catalyzed esterification reactions of acetic acid with methanol were described by Liu *et al.* [11]. They presented the kinetics using a commercial nafion/silica nano composite catalyst (SAC-13) and H_2SO_4 separately, reported that heterogeneous and homogeneous catalysts show similar reaction inhibition by water formation, and suggested a common reaction mode based on Bronsted acid sites.

The kinetics of reversible liquid-phase esterification of acetic acid with methanol using sulfuric acid catalyst in an isothermal batch reactor was investigated by Ganesh *et al.* [12]. They observed that the rate constant is influenced by the concentration of catalyst and the reaction rate increases with the catalyst concentration. They also observed that the catalyst activity is slightly inhibited by the formation of water in the reaction mixture. The reaction kinetics and chemical equilibrium of the reversible catalytic esterification of acetic acid with methanol were investigated by Popken *et al.* [13]. The reaction was catalyzed homogeneously by acetic acid itself and heterogeneously by an acidic ion-exchange resin.

Without catalyst it requires very long time to reach equilibrium [13]. Although acetic acid itself may act as a catalyst, its activity for reaction is

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* Corresponding author.
E-mail address: mmyadav2001@gmail.com (M. Mekala).

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very low due to its weak acidic nature. The addition of catalyst improves the acidic nature of the reaction mixture by providing more H^+ ions for the reaction. Homogeneous catalysts such as hydrochloric acid, hydrogen iodide, hydrogen bromide and sulfuric acid have been used for the esterification reaction between acetic acid and methanol. It is reported that sulfuric acid is a better catalyst due to its greater density of acid sites per gram and it can prevent the side reactions [11]. It is more effective than the heterogeneous catalyst for the esterification reaction, so it is selected for the present study.

Although a large number of studies are available in literature, some uncertainties remain in the reported kinetic models. In the present paper, the esterification reaction of acetic acid with methanol to produce methyl acetate using homogeneous sulfuric acid catalyst is studied at different temperatures, catalyst concentrations and feed molar ratios. The kinetic models based on concentration as well as activity are developed and the model predictions are compared with experimental data. The model predictions are also compared with the models in literature.

2. Experimental

2.1. Chemicals

Acetic acid (99.95%, by mass), methanol (99%, by mass), and sulfuric acid (98%, by mass) were purchased from SD Fine Chemicals Ltd. (Mumbai, India) and used without any further purification.

2.2. Experimental setup

The esterification reaction was carried out in a 500 ml three neck round-bottom flask placed in a heating rota mantle, which contains a heating knob and a speed control knob. The rota-mantle was maintained at constant temperature by adjusting the heating knob. The minimum stirring speed was maintained at 240rpm for uniform mixing of catalyst in the reaction mixture using the speed control knob. A glass thermometer inserted into the reactor was used to measure the reaction mixture temperature inside the flask. A spiral condenser was connected vertically to the reaction flask to reduce the vapor losses from the reactor.

2.3. Experimental procedure

In the experiment, equimolar quantities of methanol (32 g) and acetic acid (60 g) were charged to the reactor. The desired amount or concentration of sulfuric acid was added to initiate the reaction. When the reaction mixture reached the desired reaction temperature, the time was noted. The samples were withdrawn at regular intervals of time and analyzed for the acetic acid concentration. The reaction was carried out for sufficient time to reach equilibrium conversion or without further decrease in acetic acid concentration.

2.4. Analysis

The acetic acid concentration was determined by titration of reaction mixture sample with standard solution of NaOH using phenolphthalein as the indicator. To prepare the standard solution of NaOH, pure water was obtained from an ultra-pure water purifier system (Millipore-Synergy UV system) with a resistance of 18.2 MΩ.

3. Results and Discussion

The present esterification reaction with homogeneous catalyst is investigated at 1:1 mole ratio of acetic acid to methanol, with the temperature varied from 305.15 to 333.15 K and the catalyst concentration varied from 0.0633 $\mathrm{mol\cdot L^{-1}}$ to 0.3268 $\mathrm{mol\cdot L^{-1}}$.

3.1. Effect of different factors on the reaction

3.1.1. Effect of temperature

The experimental results for conversion of acetic acid at different temperatures with fixed catalyst concentration (0.1288 $\mathrm{mol\cdot L^{-1}}$) are shown in Fig. 1. The rate of conversion of acetic acid increases with temperature. At the lowest temperature (305.15 K), the reaction reaches equilibrium after 400 min and at higher temperature, and the time required for the reaction to reach equilibrium reduces drastically. At 333.15 K the time needed is only 100 min. The higher the reaction temperature, the shorter the time required to reach equilibrium. At equilibrium, the acetic conversion is 0.69 or 69%.

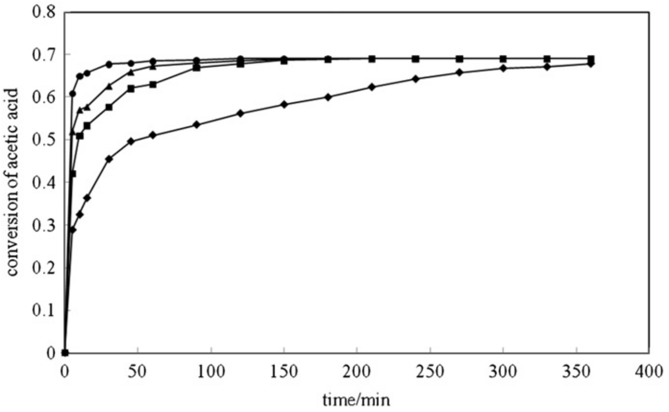

Fig. 1. Effect of temperature on reaction kinetics at 0.1288 $\mathrm{mol\cdot L^{-1}}$ catalyst concentration. ♦ 305.15 K; ■ 313.15 K; ▲ 323.15 K; ● 333.15 K.

3.1.2. Effect of catalyst concentration

Fig. 2 shows the effect of catalyst concentration on the conversion of acetic acid at a fixed temperature of 323.15 K. As the catalyst concentration increases the reaction reaches equilibrium faster. At 0.3268 $\mathrm{mol\cdot L^{-1}}$ catalyst concentration the reaction takes about 70 min to reach equilibrium whereas at 0.0633 $\mathrm{mol\cdot L^{-1}}$ it only takes about 150 min. The effect of catalyst concentration on the acetic acid conversion is similar to that of the effect of temperature.

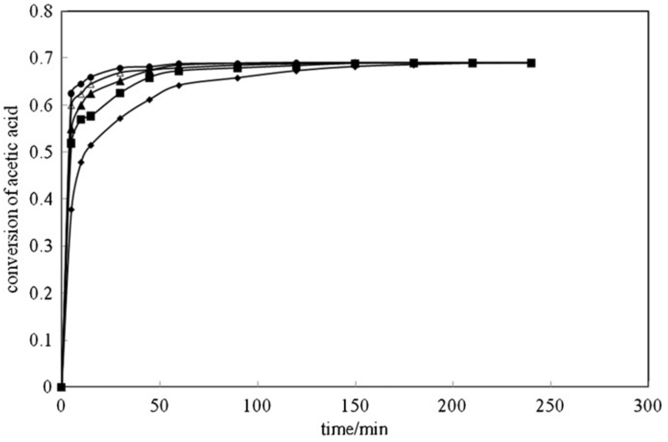

Fig. 2. Effect of catalyst concentration on reaction kinetics at 323.15 K. ♦ 0.0633 $\mathrm{mol\cdot L^{-1}}$; ■ 0.1288 $\mathrm{mol\cdot L^{-1}}$; ▲ 0.1923 $\mathrm{mol\cdot L^{-1}}$; △ 0.2576 $\mathrm{mol\cdot L^{-1}}$; ● 0.3268 $\mathrm{mol\cdot L^{-1}}$.

3.1.3. Effect of initial reactant mole ratio

Fig. 3 shows the effect of initial molar ratio of acetic acid to methanol on the acetic acid conversion at fixed catalyst concentration of 0.1288 $\mathrm{mol\cdot L^{-1}}$ and reaction temperature of 333.15 K. The equilibrium conversion of acetic acid increases with mole ratio due to the availability of excess methanol. With an increase in mole ratio of acetic acid to methanol from 1:1 to 1:4, the equilibrium conversion of acetic acid increases from 69% to 91.7%.

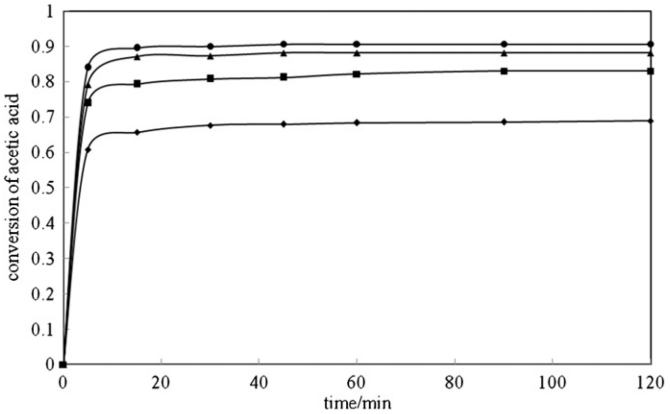

Fig. 3. Effect of reactant initial mole ratio on the acetic acid conversion at 0.1288 mol·L^{-1} catalyst concentration and reaction temperature 333.15 K. ◆ 1:1; ■ 1:2; ▲ 1:3; ● 1:4.

3.2. The kinetic model

3.2.1. Concentration based model

A second-order elementary kinetic model is assumed since the reaction is carried out with a molar ratio of 1:1 of acetic acid to methanol. The reaction rate expression for the homogeneous reaction [14] is

$$-r_\mathrm{A} = -\frac{\mathrm{d}C_\mathrm{A}}{\mathrm{d}t} = k_\mathrm{f}C_\mathrm{A}C_\mathrm{B} - k_\mathrm{b}C_\mathrm{C}C_\mathrm{D} = k_\mathrm{f}\left(C_\mathrm{A}C_\mathrm{B} - \frac{C_\mathrm{C}C_\mathrm{D}}{K_\mathrm{eq}}\right) \tag{1}$$

where C_A, C_B, C_C and C_D are the acetic acid, methanol, methyl acetate and water concentrations, respectively, k_f and k_b are the forward and backward reaction rate constants, respectively, and K_eq is the equilibrium constant of the reaction. It is assumed that products water and methyl acetate are not present at the beginning of the reaction. The reaction volume during the reaction remains constant. Eq. (1) is rearranged in terms of acetic acid conversion, $X_\mathrm{A} = 1 - C_\mathrm{A} / C_\mathrm{A0}$. The rate equation is modified as

$$-r_\mathrm{A} = -C_\mathrm{A0}\frac{\mathrm{d}X_\mathrm{A}}{\mathrm{d}t} = k_\mathrm{f}C_\mathrm{A0}^2\left((1-X_\mathrm{A})^2 - \frac{X_\mathrm{A}^2}{K_\mathrm{eq}}\right). \tag{2}$$

Eq. (2) is integrated and re-arranged to a linear form to find the forward reaction rate constant. The equation is

$$\ln\left[\left(\frac{2+m_2-2m_1X_\mathrm{A}}{2-m_2-2m_1X_\mathrm{A}}\right)\left(\frac{2-m_2}{2+m_2}\right)\right] = m_2k_\mathrm{f}C_\mathrm{A0}t \tag{3}$$

where $m_1 = \left(1-\frac{1}{K_\mathrm{eq}}\right)$ and $m_2 = 2\sqrt{(1-m_1)}$.

From Eq. (3), the forward reaction rate constants at different temperatures and at 0.1288 mol·L^{-1} catalyst concentration are calculated. The temperature dependency of the reaction rate constants is expressed by the Arrhenius equation.

$$k_\mathrm{f} = k_\mathrm{f0}\exp\left(\frac{-E_\mathrm{f}}{RT}\right) \tag{4a}$$

$$k_b = k_{b0}\exp\left(\frac{-E_b}{RT}\right) \tag{4b}$$

where k_f0 and k_b0 are the pre-exponential factors, E_f and E_b are the activation energies for forward and backward reactions, respectively, R is the gas constant, and T is the temperature.

The influence of temperature on the reaction rate constant is determined by fitting k_f and k_b to the Arrhenius Eqs. (4a) and (4b). Fig. 4 shows the Arrhenius plot of lnk_f *vs.* 1/T and lnk_b *vs.* 1/T. The forward and backward activation energies are found to be 62,721 and 62,670 J·mol^{-1}, respectively. Because the two activation energies are nearly equal, it can be concluded that the equilibrium constant (K_eq) for this reaction is nearly independent of temperature [5], and is approximately equal to 5.07. The equilibrium constant can be determined experimentally from the equilibrium conversion X_Ae of acetic acid as follows

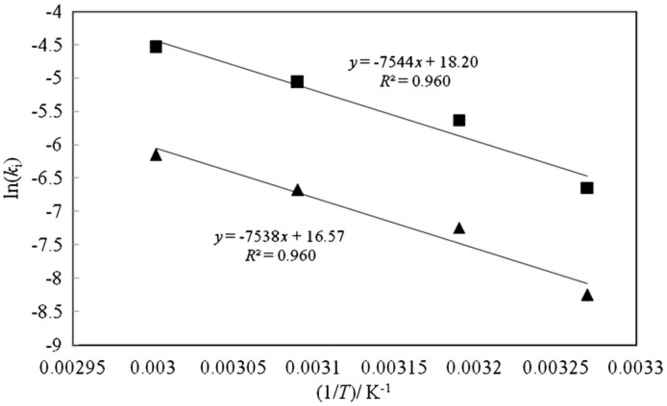

Fig. 4. Arrhenius diagram for reaction rate constants.

$$K_\mathrm{eq} = \frac{(X_\mathrm{Ae})^2}{(1-X_\mathrm{Ae})^2}. \tag{5}$$

Fig. 2 shows the effect of catalyst concentration on the reaction kinetics for five different catalyst concentrations at fixed temperature of 323.15 K. With similar experiments conducted for various catalyst concentrations at different temperatures to the rate constant k_f, and the pre-exponential factor k_f0 are determined. The pre-exponential factor (k_f0) is plotted as a function of catalyst concentration as shown in Fig. 5. A mathematical expression is proposed from the linear fitting of data,

$$k_{f0} = 3.0\times10^8(W_\mathrm{C}) + 8\times10^7 \tag{6}$$

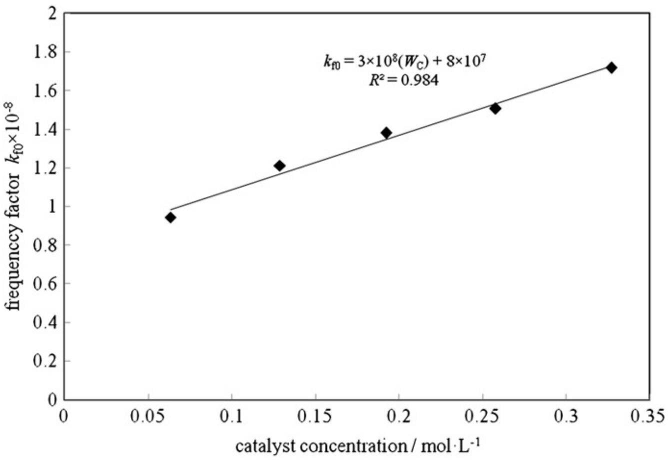

Fig. 5. Relation between pre-exponential factor and catalyst concentration.

where W_C is the concentration of catalyst ($\mathrm{mol \cdot L^{-1}}$) in the initial reaction mixture.

Fig. 6 shows the comparison of acetic acid conversion from experimental results with that from the concentration based model for different catalyst concentrations at 323.15 K. As the catalyst concentration increases, the conversion of acetic acid increases. At lower catalyst concentrations, the model predictions are in close agreement with experimental results. The predictions are a little lower than experimental values at the early stages but as the time proceeds they are in good agreement. At higher catalyst concentration the predictions are lower in magnitude in the initial stage then they tend to approach the experimental results closely. One of the reasons for the mismatch is the formation of water, which may inhibit the rate of reaction until reaching the equilibrium.

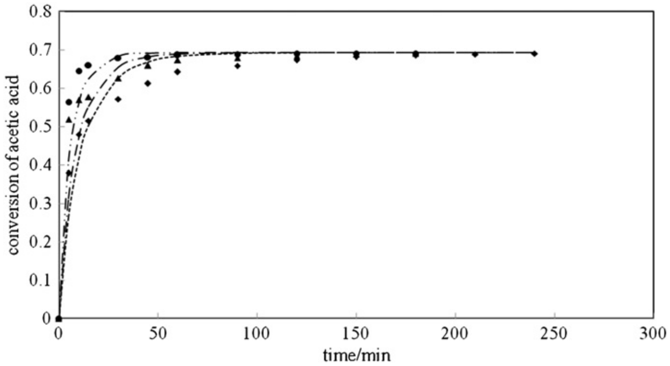

Fig. 6. Comparison of experimental results with concentration based model results for the conversion of acetic acid at different catalyst concentrations at 323.15 K. ◆ 0.0635 $\mathrm{mol \cdot L^{-1}}$; ▲0. 1288 $\mathrm{mol \cdot L^{-1}}$; ● 0.3268 $\mathrm{mol \cdot L^{-1}}$; ······· 0.0635 $\mathrm{mol \cdot L^{-1}}$; –·–· 0.1288 $\mathrm{mol \cdot L^{-1}}$; –··– 0.3268 $\mathrm{mol \cdot L^{-1}}$ (symbols represent experimental data and lines represents concentration based model results).

3.2.2. Activity model

The activity model accounts for the non-ideality of the solution. It can be developed from the concentration-based model by defining the activity as

$$a_i = \gamma_i x_i = \gamma_i C_i / C_t. \tag{7}$$

The reaction rate equation in terms of the activities is given by

$$-r_A = k_{\mathrm{fact}}\left(a_A a_B - \frac{a_C a_D}{K_{\mathrm{act}}^{\mathrm{eq}}}\right) \tag{8}$$

with

$$K_{\mathrm{act}}^{\mathrm{eq}} = \frac{x_C^{\mathrm{eq}} x_D^{\mathrm{eq}} \gamma_C^{\mathrm{eq}} \gamma_D^{\mathrm{eq}}}{x_A^{\mathrm{eq}} x_B^{\mathrm{eq}} \gamma_A^{\mathrm{eq}} \gamma_B^{\mathrm{eq}}}. \tag{9}$$

Based on the equilibrium conversion, the activities and mole fractions are computed and substituted into Eq. (9) to find the equilibrium constant based on activity. k_{fact} is related to the temperature through an Arrhenius relation

$$k_{\mathrm{fact}} = k_{\mathrm{fact0}} \exp\left(-\frac{E_f}{RT}\right) \tag{10}$$

with

$$k_{\mathrm{fact0}} = \frac{k_{f0} C_t^2}{\gamma_A^{\mathrm{eq}} \gamma_B^{\mathrm{eq}}} \tag{11}$$

where k_{f0} is calculated from the concentration-based model. The non-ideality of the reaction mixture is calculated by the UNIQUAC equation. The UNIQUAC r_i and q_i values and the interaction parameters are given in Tables 1 and 2, respectively [12].

Table 1
UNIQUAC r_i and q_i values

Component	r_i	q_i
Acetic acid	2.2024	2.0720
Methanol	1.4311	1.4320
Methyl acetate	2.8042	2.5760
Water	0.9200	1.4000

Table 2
UNIQUAC interaction parameters

i	j	a_{ij}	b_{ij}	c_{ij}
Acetic acid	Methanol	390.26	0.97039	-3.0613×10^{-3}
Methanol	Acetic acid	65.245	−2.0346	3.1570×10^{-3}
Acetic acid	Methyl acetate	−62.186	−0.43637	2.7235×10^{-4}
Methyl acetate	Acetic acid	81.848	1.1162	-1.3309×10^{-3}
Acetic acid	Water	422.38	−0.051007	-2.4019×10^{-4}
Water	Acetic acid	−98.120	−0.29355	-7.6741×10^{-5}
Methanol	Methyl acetate	62.972	−0.71011	1.1670×10^{-3}
Methyl acetate	Methanol	326.20	0.72476	-2.3547×10^{-3}
Methanol	Water	−575.68	3.1453	-6.0713×10^{-3}
Water	Methanol	219.04	−2.0585	7.0149×10^{-3}
Methyl acetate	Water	593.70	0.010143	-2.1609×10^{-3}
Water	Methyl acetate	−265.83	0.96295	2.0113×10^{-4}

Fig. 7 shows the comparison for the conversion of acetic acid from experimental results with that predicted from the activity based model at different catalyst concentrations at 323.15 K. The deviation is little between the experimental and predicted results, except at lower catalyst concentrations.

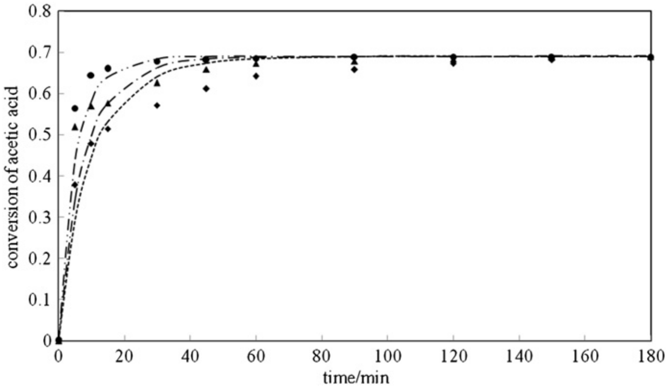

Fig. 7. Comparison of experimental results with activity-based model results for the conversion of acetic acid at different catalyst concentrations at 323.15 K. ◆ 0.0635 $\mathrm{mol \cdot L^{-1}}$; ▲ 0.1288 $\mathrm{mol \cdot L^{-1}}$; ● 0.3268 $\mathrm{mol \cdot L^{-1}}$; ······· 0.0635 $\mathrm{mol \cdot L^{-1}}$; –·–· 0.1288 $\mathrm{mol \cdot L^{-1}}$; –··– 0.3268 $\mathrm{mol \cdot L^{-1}}$ (symbols represent experimental data and lines represents activity based model results).

The experimental results and the activity-based model predicted values are plotted for acetic acid conversion with constant catalyst concentration of 0.1288 $\mathrm{mol \cdot L^{-1}}$ and different reaction temperatures as shown Fig. 8. The predicted and experimental values match well except at lower temperature. As the temperature increases the reaction rate also increases, which may be due to the increase in the kinetic energies resulting in more inter-molecular collisions.

Fig. 9 compares the experimental conversion of acetic acid with that predicted by the concentration based model and activity based model at a fixed catalyst concentration of 0.1288 $\mathrm{mol \cdot L^{-1}}$ and different temperatures. Both models are in good agreement with the experimental data.

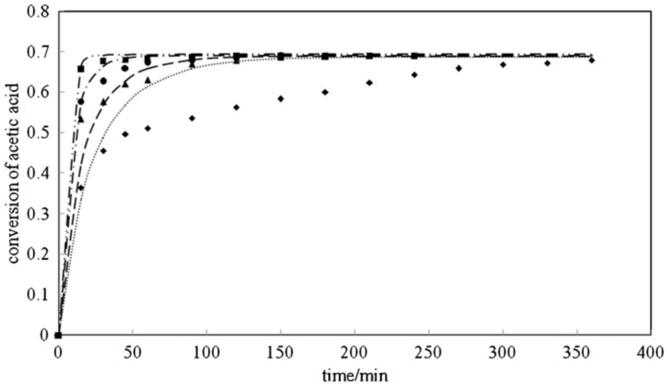

Fig. 8. Comparison of experimental results with activity- based model results for the conversion of acetic acid at different reaction temperatures at 0.1288 mol·L^{-1} catalyst concentration. ◆ 305.15 K; ▲ 313.15 K; ● 323.15 K; ▪ 333.15 K; ······· 305.15 K; ——— 313.15 K; –·– 323.15 K; –··– 333.15 K (symbols represent experimental data lines represents activity based model results).

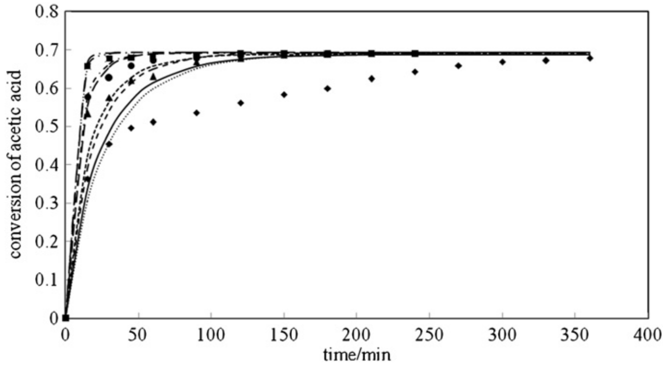

Fig. 9. Comparison of experimental results with respect to concentration and activity-based model results for the conversion of acetic acid at different reaction temperatures at 0.1288 mol·L^{-1} catalyst concentration. ◆ 305.15 K; ▲ 313.15 K; ● 323.15 K; ▪ 333.15 K (symbols represent experimental data); —— 305.15 K; ------ 313.15 K; –·– 323.15 K; –·– 333.15 K (activity based model); ······· 305.15 K; --·--·-- 313.15 K; — 323.15 K; –··– 333.15 K (concentration based model).

3.2.3. Comparison with models in literature

The kinetic models proposed for the esterification of acetic acid with methanol are given in Table 3. Our experimental data and model predictions are compared with these literature models as shown in Figs. 10–12.

Fig. 10 shows the conversions of acetic acid from the concentration and activity based models and the existing kinetic models in literature at temperature 313.15 K and catalyst concentration of 0.3268 mol·L^{-1}.

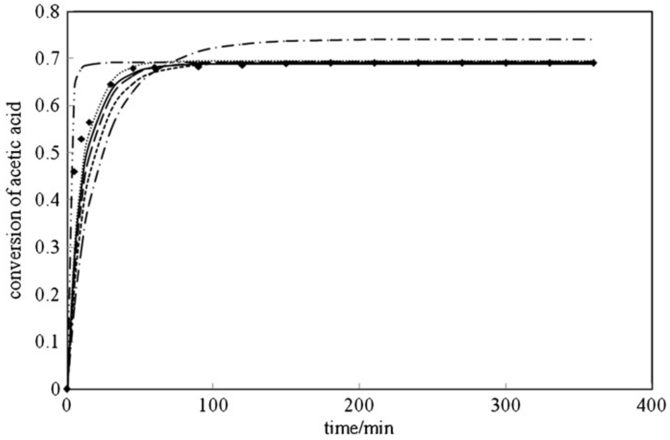

Fig. 10. Comparison of different kinetic models at 313.15 K and 0.3268 mol·L^{-1} catalyst concentration. ◆ experimental; — — — concentration based; —— activity based; –··· Liu *et al.* [8]; –·– Elugu *et al.* [9]; ------ Bonnaillie *et al.* [15]; ······· Agreda *et al.* [5].

The experimental results are quite accurately predicted by our models as well as Agreda *et al.*'s model [5]. The accuracy of the predictions decreases in the following order: activity-based model, concentration based model, Agreda *et al.*'s model [5], Bonnaillie *et al.*'s model [15], Elgue *et al.*'s model [9], and Liu *et al.*'s model [8].

Fig. 11 shows the comparison of the experimental results against kinetic models at temperature of 323.15 K and catalyst concentration of 0.3268 mol·L^{-1}. The experimental results are predicted fairly accurately by the activity-based, concentration-based and Agreda *et al.*'s models. The activity-based model provides a slightly better fit than

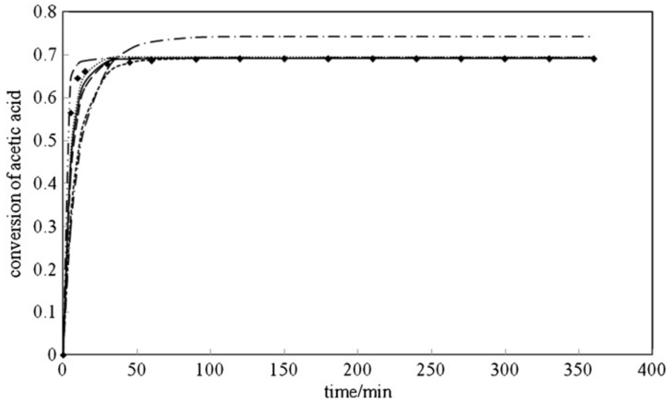

Fig. 11. Comparison of different kinetic models at 323.15 K and 0.3268 mol·L^{-1} catalyst concentration. ◆ experimental; — — — concentration based; —— activity based; –··· Liu *et al.* [8]; –·– Elugu *et al.* [9]; ------ Bonnaillie *et al.* [15]; ······· Agreda *et al.* [5].

Table 3
Kinetic models and parameters in literature

No	Kinetic model	Parameters	Reference
1	$-r_A = k_f \exp\left(\frac{-E_f}{RT}\right)\left(C_A C_B - \frac{C_C C_D}{K_{eq}}\right)$ $k_f = k_1 (W_C)^2 + k_2 W_C$ for $W_C \le 0.004$ $k_f = k_3 - k_4 \exp\left(\frac{k_5}{W_C - 0.004}\right)$ for $W_C > 0.004$	$K_{eq} = 5.2$	[5]
2	$-r_A = W_C\left(\frac{0.38}{C_D}\right)\left(C_A C_B - \frac{C_C C_D}{K_{eq}}\right)$	$K_{eq} = 6.22$ at 333.15 K	[8]
3	$-r_A = W_C\left[k_f \exp\left(\frac{-E_f}{RT}\right) C_A C_B - k_b \exp\left(\frac{-E_b}{RT}\right) C_C C_D\right]$	$k_f = 4.21$ $k_b = 0.322$ $E_f = 53{,}800$ $E_b = 52{,}580$	[9]
4	$-r_A = W_C\left[k_f \exp\left(\frac{-E_f}{RT}\right) C_A C_B - k_b \exp\left(\frac{-E_b}{RT}\right) C_C C_D\right]$	$k_f = 0.0055$ $k_b = 0.011$ $E_f = 41{,}800$ $E_b = 41{,}800$	[15]

Note: the units of k_f and k_b are L·mol^{-1}·min^{-1}; E_1 and E_2 are J·mol^{-1}.

the concentration-based model. Comparing Fig. 11 with Fig. 10, we can conclude that even at higher temperatures, while maintaining the catalyst concentration constant, activity-based and concentration-based models predict the results with reasonable accuracy.

Fig. 12 compares the available kinetic models [5,8,9,15], our models and the experimental data at temperature of 323.15 K and catalyst concentration of 0.1288 $\text{mol}\cdot\text{L}^{-1}$. The models proposed in the present study, concentration-based and activity-based models, are better than the models available in the literature. Our models provide better fit to the experimental data.

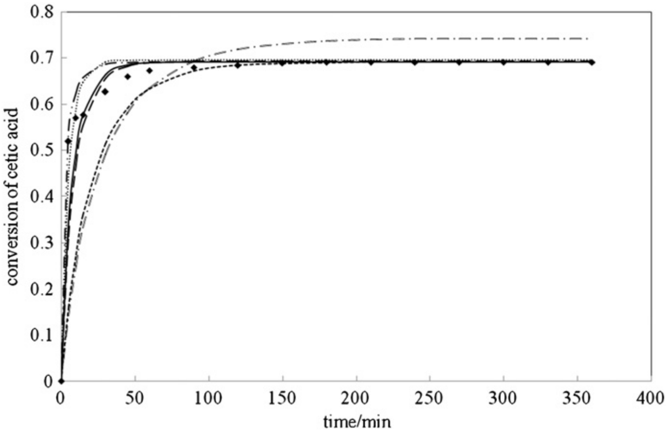

Fig. 12. Comparison of different kinetic models at 323.15 K and 0.1288 $\text{mol}\cdot\text{L}^{-1}$ catalyst concentration. ♦ experimental; — — — concentration based; —— activity based; –··· Liu *et al.* [8]; –·–· Elugu *et al.* [9]; ------ Bonnaillie *et al.* [15]; ······ Agreda *et al.* [5].

4. Conclusions

The esterification reaction between methanol and acetic is conducted in a batch stirred reactor with sulfuric acid as a catalyst. The experimental results show that as the temperature and catalyst concentration increase the reaction rate increases. The experimental data is expressed with a reversible second order reaction rate equation. The activation energies for forward and backward reactions are obtained using the Arrhenius equation. A mathematical equation is developed to describe the relation between the catalyst concentration and the frequency factor. The kinetic models are developed for the concentration-based and activity-based and compared with literature models. The developed kinetic equation predicts the results accurately.

Nomenclature

a_i	activity of component *i*
C_A	acetic acid concentration, $\text{mol}\cdot\text{L}^{-1}$
C_{A0}	initial acetic acid concentration, $\text{mol}\cdot\text{L}^{-1}$
C_B	methanol concentration, $\text{mol}\cdot\text{L}^{-1}$
C_C	methyl acetate concentration, $\text{mol}\cdot\text{L}^{-1}$
C_D	water concentration, $\text{mol}\cdot\text{L}^{-1}$
C_{Ae}, C_{Be}, C_{Ce} and C_{De}	equilibrium concentration of acetic acid, methanol, methyl acetate and water, $\text{mol}\cdot\text{L}^{-1}$
E_b	backward activation energy, $\text{J}\cdot\text{mol}^{-1}$
E_f	forward activation energy, $\text{J}\cdot\text{mol}^{-1}$
K_{eq}	equilibrium constant
k_b	backward reaction rate constant, $\text{L}\cdot\text{mol}^{-1}\cdot\text{min}^{-1}$
k_{b0}	backward frequency factor, $\text{L}\cdot\text{mol}^{-1}\cdot\text{min}^{-1}$
k_f	forward reaction rate constant, $\text{L}\cdot\text{mol}^{-1}\cdot\text{min}^{-1}$
k_{f0}	forward frequency factor, $\text{L}\cdot\text{mol}^{-1}\cdot\text{min}^{-1}$
r_A	reaction rate of acetic acid, $\text{mol}\cdot\text{L}^{-1}\cdot\text{min}^{-1}$
R	gas constant, $\text{J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$
T	absolute temperature, K
t	time, min
W_C	catalyst concentration, $\text{mol}\cdot\text{L}^{-1}$
X_A	acetic acid conversion
X_{Ae}	acetic acid equilibrium conversion
γ_i	activity coefficient of component *i*

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