Research Article

Kinetic Behaviour of Esterification of Acetic Acid with Methanol over Solid Acid Catalysts

Mallaiah M and Venkateswarlu Ch*

Department of Chemical Engineering, B.V. Raju Institute of Technology, Narsapur, Telangana, India

*Corresponding author: Ch. Venkateswarlu, Department of Chemical Engineering, B.V. Raju Institute of Technology, Narsapur, Telangana, India

Abstract

Esterification of acetic acid with methanol to form methyl acetate and water in an isothermal well mixed batch reactor is studied. Indion-190 and Amberlyst-16wet ion-exchange resins are used as the heterogeneous catalysts for the reaction. Experimental studies have shown the better performance of Indion-190 for the catalytic conversion of acetic acid. The esterification reaction is carried out using the temperatures in the range of 323 K-353 K and the catalyst loadings in the range of 0.01 g/cc-0.05 g/cc. The influence of reaction temperature and catalyst loading on the reaction rate is investigated. Temperature dependency of equilibrium constant on the reaction is calculated from Van't Hoff equation and the heat of reaction is found to be 12.21 KJ/mol. A second order kinetic rate equation is used to correlate the experimental data. The analysis of the results confirms that the catalyst loading has a strong influence on the rate of reaction.

Keywords: Esterification; Conversion; solid catalyst; kinetic rate equation; heat of reaction

Nomenclature

R: gas constant (J/molK); C: Concentration (mol/lit); X: Conversion; K: Equilibrium constant; k: Reaction rteconstant (lit/molmin); E: Activation energy (J/mol); T: Absolute temperature (K); r: reaction rate (mol/litmin); t: time (min); W: Catalyst loading (g/cc),

Subscripts: A, B, C and D Acetic acid, methanol, methyl acetate and water respectively.

e: Equilibrium; f: Forward; b: Backward; 0: Initial condition; C: Catalyst.

Introduction

Methyl acetate has wide applications in the production of solvents, perfumes, dyes, paints, polyesters, adhesives, photographic films, medicinal and other surface active agents. It is produced by esterification reaction between acetic acid and methanol. In the absence of catalyst, the reaction is very slow requiring longer times to attain equilibrium. The addition of catalyst enhances the rate of reaction facilitating the attainment of faster equilibrium. The reaction for methyl acetate synthesis is performed using homogeneous or heterogeneous catalysts. In the past, several researchers have studied the homogeneous kinetics of esterification of acetic acid with methanol. Agreda et al [1] proposed a second order rate expression for the methyl acetate esterification reaction using sulphuric acid catalyst. The rate expression of this reaction is included as nonlinear dependence on the catalyst concentration. Ronnback et al [2] investigated the kinetics of esterification of acetic acid with methanol using a homogeneous hydrogen iodide catalyst, where the protonation of carboxylic acid was considered as rate-initiating step in the reaction mechanism. Ganesh et al [3] have developed kinetic models for acid-catalysed methyl acetate formation reaction and

studied the effect of catalyst concentration and water inhibition on the rate of reaction.

Heterogeneous catalytic reaction is preferred to homogeneous catalytic reaction due to its advantages such as easy separation of catalyst from the reaction mixture, better selectivity towards desired product, improved product purity due to suppression of side reaction and avoidance of corrosive environment. In heterogeneous catalysis, the forces active at solid surface can distort or even dissociate an absorbed reactant molecule and affect the rate. Many solid catalysed reactions involving new solid acids and bases, ion exchange resins, zeolites and acid clay catalysts have been reported in literature. Among them, ion exchange resins are the most common heterogeneous catalysts used for esterification reaction. These ion exchange resins not only catalyse the reaction but also affect the equilibrium conversion because of their selective adsorption of reactants and swelling nature. Xu and Chuang [4] developed a kinetic model for the solid acid catalysed reaction of acetic acid with methanol to form methyl acetate. Amberlyst 15 was found to be an effective catalyst for this reaction at low reactant concentrations. Popken and Gmehling [5] investigated the reaction kinetics and chemical equilibrium of homogeneously and heterogeneously catalysed acetic acid esterification with methanol. The reaction has been catalysed heterogeneously by an acid exchange resin called Amberlyst 15 for which a pseudo homogeneous kinetic model incorporation and a model based on adsorption information has been developed. Incorporation of adsorption information into the kinetic model is found to provide a better fit to the kinetic model. Yu et al [6] have obtained adsorption equilibrium constants, dispersion coefficients and kinetic model parameters for the liquid phase reversible reaction of methanol with acetic acid catalysed by Amberlyst 15 ion exchange resin. The kinetics was obtained under conditions free of both external and internal mass transfer resistances. The estimated kinetics was found to represent the experimental data closely. More kinetic investigations on solid acid catalysts for
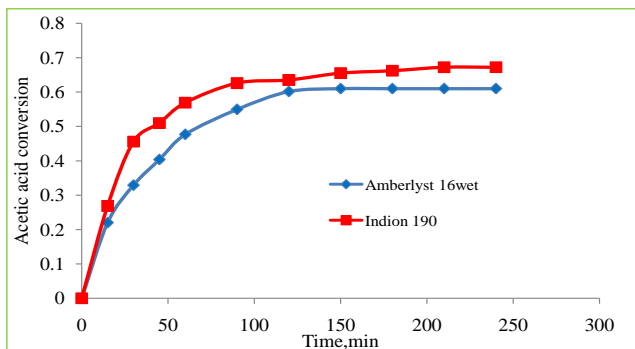
Figure 1: Conversion of acetic acid for different catalyst at 0.025 g/cc catalyst concentration and 343.15 K temperature.
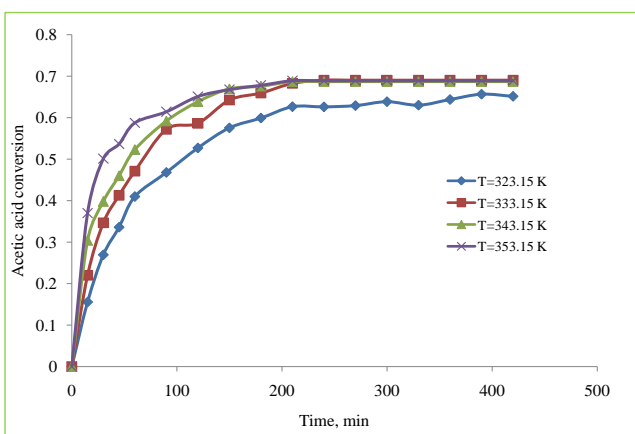

Figure 3: Conversion of acetic acid for different catalyst concentrations at 343.15 K temperature.

Figure 2: Conversion of acetic acid for different catalyst at 0.025 g/cc catalyst concentration at different temperatures.

Figure 4: Effect of catalyst loading on the initial reaction rate.

esterification reactions between acetic acid and methanol can be referred elsewhere [7-10].

In our earlier work, the kinetics of esterification of acetic acid with methanol was carried out in presence of Indion 190 and different kinetic models were developed by accounting the adsorption effects on the catalyst surface [11]. We found that all the kinetic models were agreeing reasonably well with the experimental data. The above study indicated that the effect of adsorption of components on catalyst surface was nominal. The present investigation aims at developing kinetic models for esterification of acetic acid with methanol in the presence of two types of solid acid catalysts, namely, Indion-190 and Amberlyst-16 wet. Experiments are conducted in an isothermal batch reactor at atmospheric pressure and the data is analysed to find the suitability of better catalyst for the esterification reaction. The effect of various parameters such as reaction temperature, reaction time and catalyst loading is studied experimentally on the esterification reaction with the chosen catalyst. Kinetic models are developed and the model predictions are compared with the experimental data.

Materials and Methods

Materials

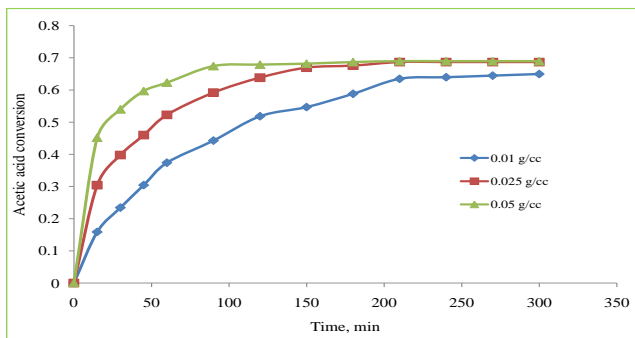Methanol with 99% w/w purity and acetic acid with 99.95% w/w purity procured from SD Fine Chemicals Ltd. (Mumbai, India) are used as such for experimentation without any further purification. The solid acid catalysts Indion-190 and Ambelyst-16 are supplied by Ion-Exchange India Limited, Mumbai and Rohm&Hass, Mumbai, respectively. Indion-190 has cross-linked three-dimensional structures of polymeric material obtained by sulfonation of a copolymer of polystyrene and divinylbenzene (DVB). It is an opaque, faint dark gray coloured solid spherical bead. The resins used in this study are dried for two hours in an oven at temperature 900ºC to remove the moisture content.

Experimental setup

The esterification reaction is carried out in a 500 ml three neck round-bottom flask, which is placed in a heating rota mantle. The rota mantle contains a heating knob and the speed control knob. It is maintained at constant temperature by adjusting the heat control knob. The stirring speed is varied from 0 to 1200 rpm using the speed control knob. A spiral condenser is connected to the reaction flask to condense the vapours and re-circulate the condensate to the reactor. A mercury thermometer is used to measure the reaction mixture temperature inside the flask.

Experimental procedure

The reactants of methanol and acetic acid are weighed and charged to the reactor and heating is put on. When the reaction mixture reaches the desired temperature, the catalyst is added to the reaction mixture. The reaction time is noted from the moment when the catalyst added to the reactor. The samples are withdrawn at regular intervals of time and analyzed for the acetic acid concentration. The
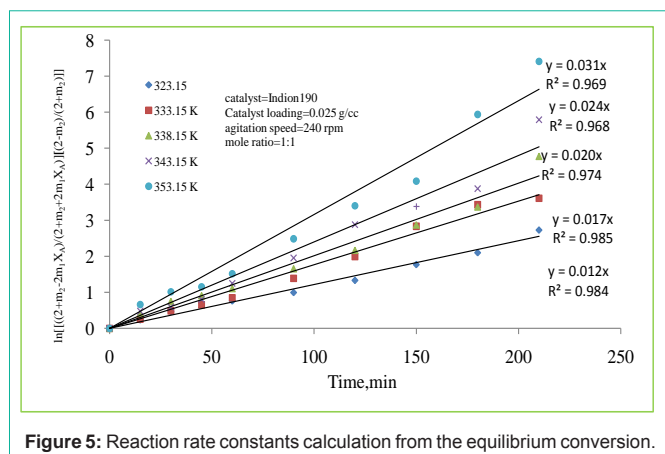
Figure 5: Reaction rate constants calculation from the equilibrium conversion.
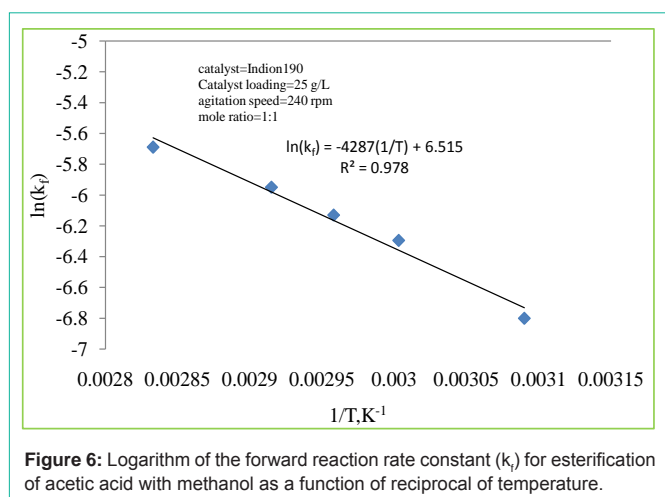

Figure 6: Logarithm of the forward reaction rate constant (k_f) for esterification of acetic acid with methanol as a function of reciprocal of temperature.

operation is continued under isothermal condition until the reaction is completed. After completion of the reaction, the reactor contents are cooled, weighed and analyzed.

Analysis

The standard solution of NaOH is prepared using the water from an ultra-pure water purifier system (Millipore-Synergy UV system) having a resistance of 18.2 MΩ-cm. The acetic acid concentration is determined by titration with standard solution of NaOH using phenolphthalein as the indicator.

Results and Discussion

Experiments are carried out for catalytic esterification of acetic acid using the ion exchange resinsIndion-190 and Amberlyst16-wet catalysts. The selection of the suitable catalyst as well as the effect of different operating parameters on the esterification reaction with the chosen catalyst is investigated.

Selection of catalyst

One of the objectives is to select the suitable catalyst candidate for the esterification of acetic acid with methanol amongst the two resin catalysts, Indion-190 and Amberlyst16wet.The better catalyst is chosen by observing the effectiveness of catalytic conversion of acetic acid as a function of time as plotted in Figure 1. For both the catalytic reactions, the conditions are maintained as: temperature = 343.15 K,

catalyst concentration = 0.025 g/cc, mole ratio of the reactants = 1:1 and agitation speed = 240 rpm. The experimental results in Figure 1 clearly indicate the better performance of Indion-190 over the Amberlyst-16wet. The acetic acid conversion for Indion-190 is 68.7% at 240 min, whereas for Amberlyst-16wet, the acetic acid conversion at the same time is 61.0%. The difference in conversion due to the catalysts can be attributed to variation in the concentration of H+ ion on the surface of the catalyst, pore size distribution and also the initial water content in the resin bead.

Effect of different parameters on reaction rate

The experimental conversion results due to both the catalysts have shown that Indion-190 is the preferred catalyst for the catalytic esterification of acetic acid. The effect of different parameters on the catalytic conversion of acetic acid due to Indion-190 is further assessed.

Effect of reaction temperature

The experimental results obtained for different isothermal temperatures with the fixed catalyst concentration of 0.025 g/cc are shown in Figure 2. From the plot, it is observed that conversion of acetic acid increases with the increase of temperature. This indicates that the reaction is controlled by chemical reaction steps. The system is found to reach equilibrium at all temperatures studied except 323.15 K for which it has taken 270 min to attain equilibrium. The rate of conversion of acetic acid increases with the increase in temperature and the time taken for the system to reach equilibrium is found less when the reaction temperature is high. This further confirms the fact that esterification of acetic acid is controlled by chemical reaction rather than mass transfer rates.

Catalyst loading

Experiments are conducted using the catalyst with different concentrations of 0.01 g/cc, 0.025 g/cc and 0.05 g/cc. The experimental results evaluated for different catalyst concentrations at a fixed temperature are shown in Figure 3. From the results in Figure 3, it is observed that as the catalyst loading increases the conversion of acetic acid increases and equilibrium conversion reaches faster. It can be observed that when the amount of catalyst in the reaction mixture increases, the reaction rate increases as the availability of more H+ ions due to increase in surface area of catalyst. This behaviour can be verified by calculating the initial rate of reaction at different catalyst concentrations.

The initial rate of reaction is calculated by

$$-r_{A0} = \frac{N_{A0}}{W_c}\left(\frac{dX_A}{dt}\right) \tag{1}$$

where, r_{A0} is the initial rate of reaction, N_{A0} is the initial moles of reactant A, W_C is the weight of catalyst and X_A is the conversion of acetic acid at time t. The differential term in the above equation is the slope of the acetic acid conversion versus time evaluated at t=0. Figure 4 shows initial reaction rate as a function of catalyst concentration. From Figure 4, it can be observed that the initial rate of reaction bears a linear relationship with the amount of catalyst and the reaction rate increases as the catalyst load increases. It is also observed that at higher catalyst concentration, the reaction reaches equilibrium at faster rate. The mathematical equation relating the initial reaction

rate to the catalyst loading in Figure 4 is expressed as:-

$$r_{A0} = 5.416 W_C + 0.147 \qquad (2)$$

where W_C is the catalyst loading. The above equation is valid for 343.15 K temperature and 1:1 reactants mole ratio.

Development of kinetic model

Experimental data is generated for the esterification reaction using Indion-190 at different temperatures and catalyst loadings. Mass transfer resistances are assumed negligible as all the reactants are freely moving inside the catalyst particle. The pseudo homogeneous kinetic rate equation considered for the esterification reaction is

$$-r_A = -\frac{dC_A}{dt} = k_f \left(C_A C_B - \frac{C_C C_D}{K_e} \right) \qquad (3)$$

where C_A, C_B, C_C and C_D are the acetic acid, methanol, methyl acetate and water concentrations, respectively, k_f is the rate constant of the reaction, and K_e is the equilibrium constant of the reaction.

The rate equation in Eq (3) is modified and expressed in terms of reactant conversion as

$$-r_A = -C_{A0} \frac{dX_A}{dt} = k_f C_{A0}^2 \left((1-x_A)^2 - \frac{(X_A^2)}{K_e} \right) \qquad (4)$$

The integration of the above equation leads to the following linear relation,

$$ln \left[\left(\frac{2 + m_2 - 2m_1 X_A}{2 - m_2 - 2m_1 X_A} \right) \left(\frac{2 - m_2}{2 + m_2} \right) \right] = m_2 k_f C_{A0} t \qquad (5)$$

where

$$m_1 = \left(1 - \frac{1}{K_{eq}} \right)$$

$$m_2 = 2\sqrt{(1 - m_1)}$$

The temperature dependency of both the reaction rate constants is expressed by the Arrhenius equation,

$$k_f = k_{f0} e^{\left[-\frac{E_f}{RT} \right]} \qquad (6)$$

where k_{f0} is the pre-exponential factor, E_f is the activation energy for reaction, R is the gas constant, and T is the temperature.

The apparent equilibrium constant of the reaction can be found from the equilibrium conversions as

$$k_e = \frac{X_{Ae}^2}{(1 - X_{Ae})^2} \qquad (7)$$

where X_{Ae} is the equilibrium conversion. Calculation of backward reaction rate constant (k_b) is straight from k_f and K_e values. The effect of temperature on the reaction rate is determined by using the fitted values of k_f and k_b in the Arrhenius equation. The slopes of the lines in Figure 5 drawn for Eq (5) give k_f values at different temperatures. Figures 6 and 7 show the Arrhenius plot representing the forward and backward reaction rate constants versus temperature. These plots in Figures 6 and 7 show that the reaction rate constant increases as the temperature increases at fixed catalyst concentration,. The activation energies for both the and backward reactions are found to be 35,642 J/mol and 23,212 J/mol, respectively.

The heat of reaction is calculated from Van't Hoff equation as follows:

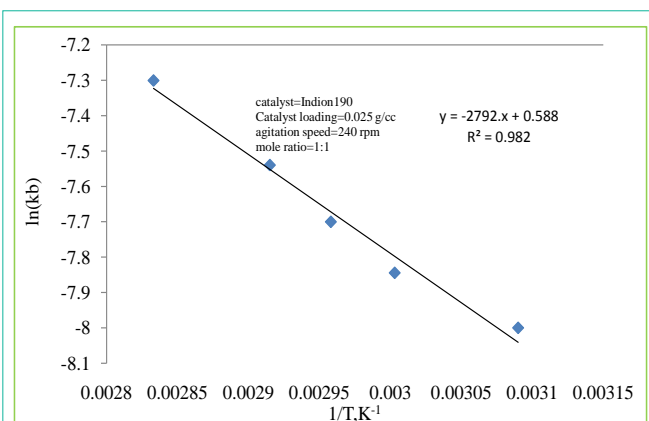$$\frac{d(\ln(k_e))}{dT} = \left(\frac{-\Delta H_R^0}{RT^2} \right) \qquad (8)$$

Figure 7: Logarithm of the backward reaction rate constant (kb) for esterification of acetic acid with methanol as a function of reciprocal of temperature.
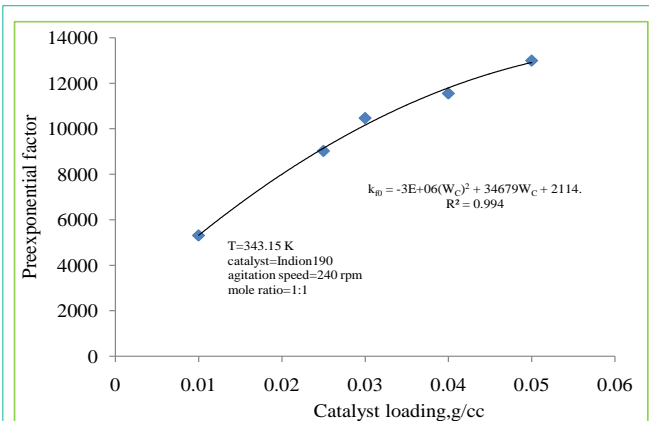

Figure 8: Relation between pre-exponential factor and catalyst concentration.

The above equation is integrated to obtain,

$$\ln(K_e) = \frac{-\Delta G_R^0}{RT} - \frac{-\Delta H_R^0}{R} \left(\frac{1}{T} - \frac{1}{T^0} \right) \qquad (9)$$

where $\Delta G_R^0 = \Delta H_R^0 - T\Delta S_R^0 \qquad (10)$

By substituting the Eq (10) into Eq. (9), we obtain

$$\ln(K_e) = \left(\frac{-\Delta H_R^0}{RT} \right) + \left(\frac{\Delta S_R^0}{R} \right) \qquad (11)$$

Eq. (11) provides information about the temperature dependence of the equilibrium constant. The plot of ln (K_e) versus 1/T gives the heat of reaction and entropy terms which are interpreted as the slope and intercept. The heat of reaction is evaluated as 4.672 KJ/mol indicating the reaction as endothermic. Figure 8 represents the pre-exponential factors versus catalyst loadings drawn at fixed temperature. The relation between pre-exponential factors and catalyst loadings is fitted as a quadratic equation as given by

$$k_{f0} = -3.0 10^6 W_C^2 + 34679 W_C + 2114 \qquad (12)$$

where W_C is the catalyst loading in g/cc of initial reaction mixture. This relation shows the increase in pre-exponential factor with the increase of catalyst loading. The catalyst loading is found to have more influence on the rate of reaction.

Conclusion

Two types of the solid catalysts, Indion-190 and Amberlyst-16 wet, are investigated for the kinetic study of esterification of acetic acid with methanol. The catalytic conversion of acetic acid has shown the better performance of Indion-190 over the Amberlyst-16wet. Further, the kinetic behaviour of acetic acid conversion in the presence of Indion-190 is studied for the temperatures in the range of 323 K-353 K and the catalyst loadings in the range of 0.01 g/cc to 0.05 g/cc. The experimental investigations for the catalytic conversion of acetic acid using Indion-190 have shown the reaction as kinetically controlled. Temperature dependency of equilibrium constant on the reaction is calculated from Van't Hoff equation and the heat of reaction is found to be 12.21 KJ/mol. A complete kinetic model is developed for the acetic acid conversion using Indion-190 as solid acid catalyst.

References

1. Agreda VH, Partin LR, Heiss WH. High purity methyl acetate via reactive distillation. Chem Eng Prog. 1990; 86: 40-46.

2. Ronnback R, Salmi T,Vuori A, Haario H, Lehtonen J, Sundqvist A, Tirronen E. Development of a kinetic model for the esterification of acetic acid with methanol in the presence of a homogeneous catalyst. Chem Eng Sci. 1997; 52: 3369–3381.

3. Ganesh B, Rani KY, Satyavathi B, Venkateswarlu Ch. Development of kinetic models for acid catalyzed methyl acetate formation reaction: Effect of catalyst concentration and water inhibition. Int J Chem Kin. 2011; 43: 263-277.

4. Xu ZP, Chuang KT. Kinetics of acetic acid esterification over ion-exchange catalysts. The Canadian J Chem Eng. 1996; 74: 493-500.

5. Popken T, Gotze L, Gmehling J. Reaction kinetics and chemical equilibrium of homogeneously and heterogeneously catalyzed acetic acid esterification with methanol and methyl acetate hydrolysis. Ind Eng Chem Res. 2000; 39: 2601-2611.

6. Yu W, Hidajat K, Ray AK. Determination of adsorption and kinetic parameters for methyl acetate esterification and hydrolysis reaction catalysed by Abmerlyst 15. Appl Catal A: Gen. 2004; 260: 191-205.

7. Song W, Venimadhavan G, Manning J M, Malone M F, Doherty M F. Measurement of Residue Curve Maps and Heterogeneous Kinetics in Methyl Acetate Synthesis. Ind. Eng. Chem. Res. 1998; 37: 1917-1928.

8. Tsai YT, Lin HM, Lee MJ. Kinetics behavior of esterification of acetic acid with methanol over Amberlyst 36. Chem Eng J. 2011; 171: 1367-1372.

9. Jagadeesh Babu PE, Sandesh K, Saidutta MB. Kinetics of Esterification of Acetic Acid with Methanol in the Presence of Ion Exchange Resin Catalysts. Ind Eng Chem Res. 2011; 50: 7155-7160.

10. Lux S, Winkler T, Berger G, Siebenhofer M. Kinetic study of the heterogeneous catalytic esterification of acetic acid with methanol using Amberlyst 15. Chem Biochem Eng Q. 2015; 29: 549-557.

11. Mekala M, Goli VR. Kinetic study of esterification of acetic acid with methanol over Indion 190 acidic solid catalyst. Kin Catal. 2015; 56: 419-427.