Kinetic Study of Transesterification of Methyl Acetate with *n*-Butanol Catalyzed by NKC-9

BAOYUN XU, WEIJIANG ZHANG, XUEMEI ZHANG, CUIFANG ZHOU

School of Chemical Engineering and Technology, Tianjin University, Tianjin 300072, People's Republic of China

Received 18 December 2007; revised 10 June 2008, 15 July 2008, 20 July 2008; accepted 20 July 2008

DOI 10.1002/kin.20378

ABSTRACT: The transesterification of methyl acetate and *n*-butanol catalyzed by cation-exchange resin, NKC-9, was studied in this work to obtain the reaction kinetics. The experiments were carried out in a stirred batch reactor at different temperatures (328.15, 333.15, 338.15, 343.15, 345.15 K) under atmospheric pressure. The effects of temperature, molar ratio of reactants, and catalyst loading on the reaction rate were researched under the condition of eliminating the effect of diffusion. The experimental data were correlated with a kinetic model based on the pseudo-homogeneous catalysis. The kinetic equation describing the reaction catalyzed by NKC-9 was developed. © 2008 Wiley Periodicals, Inc. Int J Chem Kinet 41: 101–106, 2009

INTRODUCTION

Methyl acetate is a by-product during the production of PVA (poly(vinyl) alcohol). From 1 ton of PVA, about 1.68 ton of methyl acetate is produced. The industrial application of methyl acetate is low. But as the products of transestrification of methyl acetate with *n*-butyl, methanol is a raw material for PVA production; *n*-butyl acetate is an important solvent in plastics, resins, gums, and coatings, etc.; what is more, it can be used as an extracting agent or intermediate in organic synthesis. Thus the most attractive way will be to convert methyl acetate into methanol and *n*-butyl acetate.

The esterification of acids and alcohols is one of the most important applications of resin catalysis. Like esterification, transesterification can be catalyzed by ion-exchange resin. The advantage of a heterogeneous catalyst is well known, and the use of solid ion-exchange resin as the catalyst has the following inherent advantages: (i) The catalyst can be easily separated from the reaction products by decantation or filtration; (ii) continuous operation in column is possible; (iii) the side reaction can be eliminated and the product purity is high, etc. [1]. The strong acid cation-exchange resin has been used commercially as solid acid catalyst in many areas. Harmer and Sun [2] summarized the recent development on the applications in alkylation, transalkylation, isomerization, esterification, etc. Several papers show that the cation-exchange resin has an excellent catalysis on the reaction.

Correspondence to: Xuemei Zhang; e-mail: zhang-xby@163.com.

Several papers have reported on this transesterification, catalyzed by a heterogeneous catalyst. Bott reported the method that is used to produce acetic acid esters by alkali-transesterification of acetic acid ester with an alcohol. The reaction was carried out in the middle section of a distillation column. The alcohol or the mixture of alcohol and ester is drawn from the top of the column. The higher boiling ester was taken from the lower zone of the column [3]. Jiménez et al. reported the production of *n*-butyl acetate and methanol via reactive and extractive distillation. In this study, Amberlyst 15 was used as a catalyst. The kinetics, mass-transfer, and process modeling were studied [4]. Steinigeweg and Gmehling reported the transesterification process of methyl acetate and *n*-butanol by combination of reactive distillation and pervaporation. The result shows that it is favorable since conversions close to 100% can be obtained with a reasonable size of the reactive section [5]. Bozek-Winkler and Gmehling studied the kinetic behavior of the reaction of methyl acetate and butanol, leading to butyl acetate and methanol catalyzed by Amberlyst 15. Two different kinetic models have been built to describe the reaction kinetics that can be applied to the designing of the reactive distillation process or the membrane reactor [6].

In this paper, the chemical equilibrium and the reaction kinetics of transestrification of methyl acetate with *n*-butanol producing *n*-butyl acetate and methanol were studied. The reaction can be presented as

$$\mathrm{CH_3COOCH_3 + CH_3(CH_2)_3OH \rightleftharpoons CH_3COO(CH_2)_3CH_3 + CH_3OH} \tag{1}$$

A strong acid cationic exchange resin, NKC-9, was used as a heterogeneous catalyst. The forward and reverse reactions were investigated, and the pseudo-homogeneous model was studied in this work.

EXPERIMENTAL

Materials

n-Butanol (99.9% w/w) and methyl acetate (99.9% w/w) were obtained from Ke Wei Co. Ltd., Tianjin, China. The catalyst, i.e., the cationic exchange resin, NKC-9 in the form of H^+, was purchased from Chemical Plant of Nankai University, Tianjin, China. Its appearance is like a camel bead, the particle size was 0.4–0.7 mm, and the volume exchange capacity was 4.7 mmol/g. The catalyst was washed with methanol to remove impurities and dried at 343.15 K.

Apparatus

The experiments were performed in a 500-mL round-bottom glass reactor dipped in the constant-temperature water bath. The reactor was equipped with the temperature indicator (Pt-100) and a speed-monitoring facility. The reflux condenser was used to avoid any possible loss of volatile components.

Procedure

The methyl acetate, *n*-butanol, and catalyst were charged into the separate vessels dipped in the water bath. Once the desired temperature was attained, methyl acetate and catalyst were charged into the *n*-butanol, it was considered as the zero reaction time. One-milliliter samples, which were considered negligible to the total volume of reactants, were withdrawn at specified time intervals.

Samples were analyzed by SP-2100 gas chromatography with a thermal conductivity detector (H_2 as a carrier gas, a stainless-steel column packed with PEG 20 M 3 m × 2 mm, column temperature 140°C, detector temperature 160°C, injector temperature 200°C; retention time: methanol 0.98 min, methyl acetate 1.4 min, *n*-butanol 3.6 min, and *n*-butyl acetate 5.4 min). Chromatography data were collected at a workstation N2000 (Zhejiang University Zhida Information Engineering Co. Ltd.) and processed with the modified area normalization method to determine the product composition.

RESULTS AND DISCUSSION

Calculation of Activities

Nonideality of the liquid phase was corrected by replacing components' concentration with activities. The components' activity coefficients were calculated by the UNIFAC group contribution methods. The splitting of the groups is shown in Table I. The volume and area parameters of the groups and their interaction parameters are quoted from Peisheng Ma [7].

Mass-Transfer Resistance

To evaluate the effect of external mass-transfer resistance on the conversion of methyl acetate, the reaction was carried out at three different stirring speeds, meanwhile the rest of the reaction conditions were similar. As we can see from Fig. 1, the speed of agitation had no effect on the reaction rate at third and fourth gears, which ensured the absence of external mass-transfer resistance. All further experiments were performed at

Table I UNIFAC Group Identification of the Components

	Group Identification					
Molecular	Group Name	Main	Secondary	$v_j^{(i)}$	Volume Parameter, R_j	Area Parameter, Q_j
Methyl acetate	CH_3COO	11	22	1	1.9031	1.728
	CH_3	1	1	1	0.9011	0.848
	CH_3	1	1	1	0.9011	0.848
n-Butanol	CH_2	1	2	3	0.6744	0.54
	OH	5	15	1	1.000	1.200
	CH_3COO	11	22	1	1.9031	1.728
n-Butyl acetate	CH_2	1	2	3	0.6744	0.54
	CH_3	1	1	1	0.9011	0.848
Methanol	CH_3OH	6	16	1	1.4311	1.432

the third gear to ensure that the reaction rate was not restricted by external diffusion.

To evaluate the effect of internal diffusion on the conversion of methyl acetate, the commercial NKC-9 resin was screened into four different sizes. Identical operations were carried out with each of the fractions obtained. The experimental results in Fig. 2 show that the internal mass transfer was to be considered negligible in the particle diameter range used in this work. Because the resin was composed of small microspheres with large internal macropores, mass transfer can be excluded for this reaction. Unsifted resin was used for all further experiments.

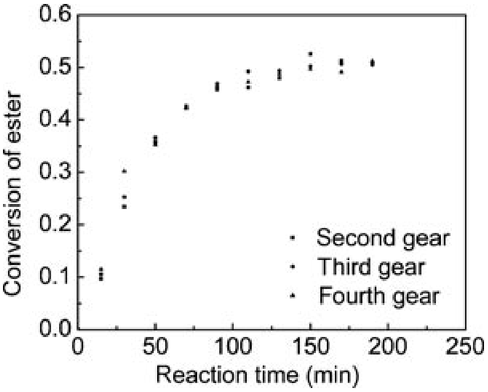

Figure 1 Effect of the stirring rate on the conversion of MeOAc (BuOH/MeOAc = 1, reaction time = 200 min, 343.15 K, catalyst mass concentration = 87.06 g/L).

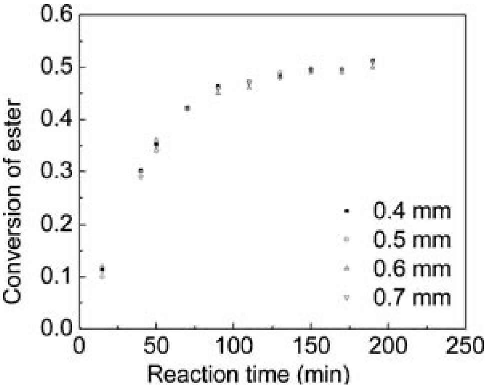

Figure 2 Effect of the internal diffusion on the conversion of MeOAc (BuOH/MeOAc = 1, reaction time = 200 min, 343.15 K, catalyst mass concentration = 87.06 g/L).

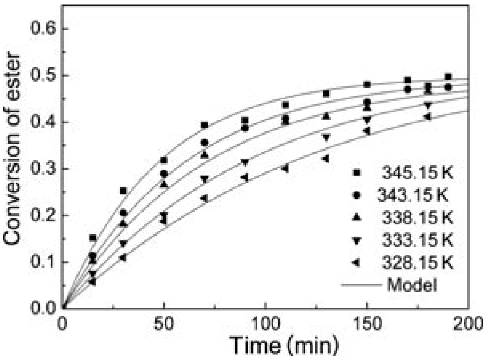

Figure 3 Effect of temperature on the conversion of MeOAc (BuOH/MeOAc = 1, catalyst mass concentration = 87.06 g/L).

Effect of the Reaction Temperature

To investigate the effect of the reaction temperature, operations were carried out at 328.15, 333.15, 338.15, 343.15, and 345.15 K. The initial molar ratio of n-butanol to methyl acetate was 1, and the catalyst mass fraction was 20% (by mass of methyl acetate). The experimental results in Fig. 3 show that the conversion of methyl acetate increased rapidly with the increase of the temperature.

Effect of Catalyst Loading

The effect of catalyst loading on the conversion of MeOAc is depicted in Fig. 4. With the catalyst loading increasing, the reaction rate increased and thus the time

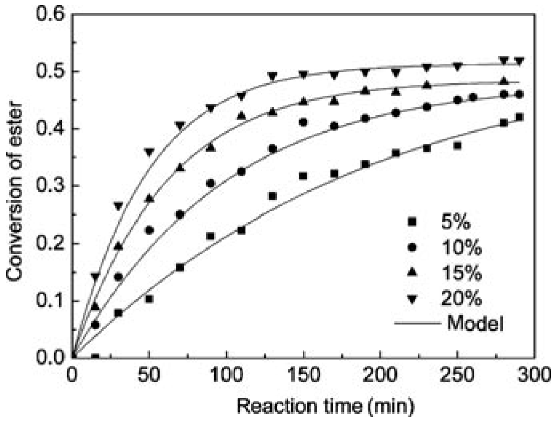

Figure 4 Effect of catalyst loading on the conversion of MeOAc (BuOH/MeOAc = 1,343.15 K).

to reach the reaction equilibrium reduced. The increase of the reaction rate was due to the increase in the total number of acid sites available for the reaction with the increase of catalyst loading. Furthermore, the catalyst loading had no effect on the equilibrium constant.

The effect of catalyst loading on the reaction rate constant is shown in Fig. 5. The forward reaction rate constant increased with the increase of the catalyst loading. The relationship between catalyst loading and rate constant could be expressed as

$$\begin{aligned} k_0 &= k_1 \times m_{\text{cat}} \\ &= 1.95 \times 10^{-4} \times m_{\text{cat}} \end{aligned} \tag{2}$$

Effect of the Molar Ratio of *n*-Butanol to Methyl Acetate

The initial molar ratio of n-butanol to methyl acetate was varied between 1:1 and 1.5:1 during the experiments. Figure 6 shows that the equilibrium conversion of methyl acetate increased with the increase in the molar ratio of n-butanol to methyl acetate.

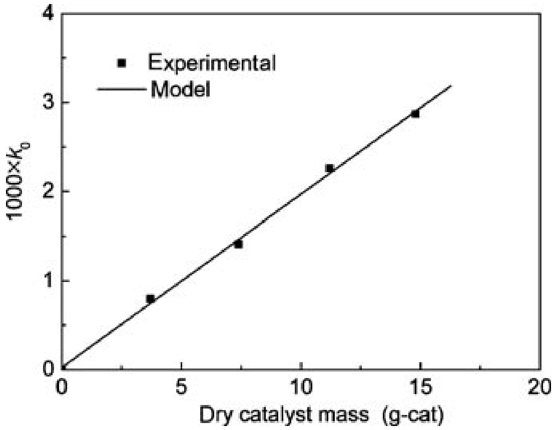

Figure 5 Effect of catalyst loading on the forward reaction rate constant (BuOH/MeOAc = 1,343.15 K).

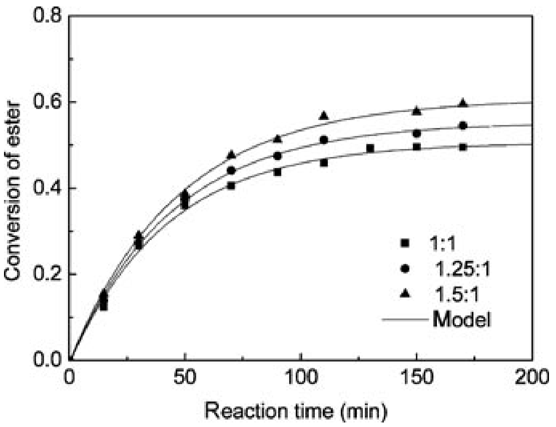

Figure 6 Effect of the molar ratio of reactants on the conversion of MeOAc (343.15 K, catalyst mass concentration = 87.06 g/L).

Kinetic Model

Kinetic Equation. Most resin-catalyzed reactions could be expressed as either quasi-homogeneous or two adsorption-based models, i.e., Langmuir–Hinshelwood (L–H) and Elay–Rideal (E–R) model [6,8–10]. The idealized homogeneous state required complete swelling of the resin and total dissociation of the polymer-bound-SO_3H group. However, the heterogeneous state was characterized by a direct interaction of the substance with the polymer-bound-SO_3H group. A pseudo-homogeneous model could be applied for the system where the mass-transfer resistance was absent. One of the reactants or solvents was high polar; the rate of the reaction could be expressed as a simple pseudo-homogeneous model. The pseudo-homogeneous model was based on the Helfferich approach, which treated catalysis confined within the internal catalyst mass, wherein the reactants, products, and solvents were in distribution equilibrium with the bulk solution. The swelling of the resin particle in the presence of polar solvents led to an easy accessibility of the acid groups for the reaction and free mobility of all components [11].

The transesterification reaction was known to be a reversible second-order reactions. Therefore, the reaction rate could be expressed as a pseudo-homogeneous model:

$$\begin{aligned} r &= \frac{1}{m_{\mathrm{cat}}}\frac{1}{\nu_i}\frac{1}{V}\frac{dn_i}{dt} = \frac{1}{m_{\mathrm{cat}}}\frac{dC_{\mathrm{BuOAc}}}{\mathrm{d}t} \\ &= k_1 C_{\mathrm{BuOH}} C_{\mathrm{MeOAc}} - k_2 C_{\mathrm{MeOH}} C_{\mathrm{BuOAc}} \qquad (3) \\ &= k_1 (a_{\mathrm{MeOAc}} a_{\mathrm{BuOH}} - a_{\mathrm{MeOH}} a_{\mathrm{BuOAc}}/K) \end{aligned}$$

To obtain a general model to produce the reaction kinetics with a set of parameters, the data obtained from the experiment in this work were correlated. Parameters for the models were estimated by minimizing the sum of the residual squares (SRS) between the experimental and calculated mole concentration of n-butyl acetate through the simplex Nelder method.

$$\mathrm{SRS} = \sum_{\mathrm{all..samples}} (r_{\mathrm{exp}} - r_{\mathrm{calc}})^2 \qquad (4)$$

Equilibrium Constant. The equilibrium constant of the reaction in this work could be obtained from the equilibrium composition of the mixture

$$K = \frac{a_{\mathrm{BuOAc,e}} a_{\mathrm{MeOH,e}}}{a_{\mathrm{MeOAc,e}} a_{\mathrm{BuOH,e}}} \qquad (5)$$

Most of the kinetic experiments lasted long enough until the chemical equilibrium was reached. The equilibrium constant K could be calculated from the equilibrium concentration, which was measured in each operation. The reaction equilibrium was reached in 7–23 h based on the reaction temperature and catalyst loading. Figure 7 shows that the equilibrium constant slightly increased with an increase in the reaction temperature.

The dependence of the equilibrium constant on the temperature was obtained by the traditional method as indicated by Eq. (6)

$$\ln K = 0.365 - \frac{276}{T} \qquad (6)$$

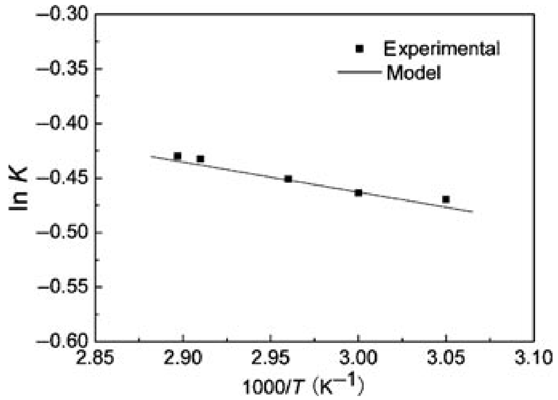

Figure 7 Effect of the reaction temperature on the equilibrium constant (BuOH/MeOAc = 1, catalyst mass concentration 87.06 g/L).

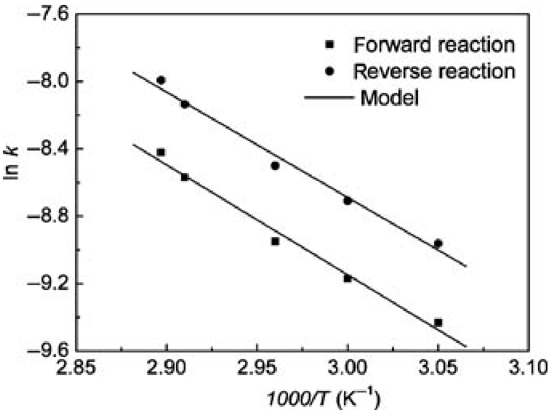

Figure 8 Arrhenius plot for reactions (BuOH/MeOAc = 1, catalyst mass concentration = 87.06 g/L).

The reaction enthalpy could be calculated from the plot of ln$K$ vs. 1/T as indicated by the Van't Hoff equation. The standard enthalpy of this reaction obtained from the experiment was $\Delta H_r^o = 2.29$ kJ/mol, which agrees with the anticipation for an endothermic reaction.

Activation Energy. The Runge–Kutta method was used to integrate the rate equation with the kinetic parameter determined by experiments. As could be seen from Figs. 3–6, a good agreement between calculated curve and the experimental points was observed.

The value of k_1 and k_2 is a function of the temperature and could be expressed as the Arrhenius equation:

$$k_1 = A_1 e^{(-E_{a,1}/RT)} \qquad (7)$$

$$k_2 = A_2 \mathrm{e}^{(-E_{a,2}/RT)} \qquad (8)$$

The kinetic parameters could be obtained from the linear regression of the Arrhenius plot (Fig. 8). The values of A_1, $Ea,_1$, A_2, $Ea,_2$ are given in Table II.

Table II Kinetic Parameter for the Pseudo-homogeneous Model

Reaction	i	A_i (L · mol^{-1} · min^{-1} · g-cat^{-1})	$E_{a,i}$ (J · mol^{-1})
Forward reaction	1	3.45×10^4	54,315
Reverse reaction	−1	2.39×10^4	52,021

CONCLUSION

The kinetic behavior for the synthesis of *n*-butyl acetate catalyzed by the cationic-exchange resin, NKC-9, from methyl acetate and *n*-butanol was carried out in the experiments described in this paper. The reaction was performed in the stirred batch reactor. The effects of temperature, reactants' molar ratio and catalyst loading were studied. The kinetic data were correlated with the pseudo-homogeneous kinetic model, and as a result the experiment agreed with the model very well. Then the kinetic parameters were obtained from the linear regression of the Arrhenius plot and the kinetic equation describing the reaction catalyzed by cationic exchange resin was developed.

NOMENCLATURE

A_1	frequency factor for forward reaction, $\mathrm{L \cdot mol^{-1} \cdot min^{-1} \cdot g\text{-}cat^{-1}}$
A_2	frequency factor for reverse reaction, $\mathrm{L \cdot mol^{-1} \cdot min^{-1} \cdot g\text{-}cat^{-1}}$
a_i	activities of component i, $\mathrm{mol \cdot L^{-1}}$
$a_{i,e}$	equilibrium activities of component i, $\mathrm{mol \cdot L^{-1}}$
C_i	concentration of component i, $\mathrm{mol \cdot L^{-1}}$
$E_{a,1}$	activation energy for forward reaction, $\mathrm{J \cdot mol^{-1}}$
$E_{a,2}$	activation energy for reverse reaction, $\mathrm{J \cdot mol^{-1}}$
K	equilibrium constant
k_0	used in Eq. (2); $\mathrm{L \cdot mol^{-1} \cdot min^{-1}}$
k_1	reaction rate constant of forward reaction, $\mathrm{L \cdot mol^{-1} \cdot min^{-1} \cdot g\text{-}cat^{-1}}$
k_2	reaction rate constant of reverse reaction, $\mathrm{L \cdot mol^{-1} \cdot min^{-1} \cdot g\text{-}cat^{-1}}$
m_{cat}	catalyst mass in reaction mixture, g-cat
n_i	moles of component i in reaction mixture, mol
R	general gas constant, 8.314 $\mathrm{J \cdot mol^{-1} \cdot K^{-1}}$
r	reaction rate, $\mathrm{mol \cdot L^{-1} \cdot min^{-1} \cdot g\text{-}cat^{-1}}$
r_{calc}	calculated value
r_{exp}	experimental value
SRS	residual squares
T	absolute temperature, K
t	time, min
V	volume of reaction mixture, L
ν_i	stoichiometric coefficient of component i

Subscripts

BuOAc	*n*-butyl acetate
BuOH	*n*-butanol
MeOAc	methyl acetate
MeOH	methanol

BIBLIOGRAPHY

1. Roy, R.; Bhatia, S. J. Chem Technol Biotechnol 1987, 37, 1–10.
2. Harmer, M. A.; Sun, Q. Appl Catal A 2000, 221, 45–62.
3. Bott, K.; Kaibel, G.; Hoffmann, H.; Irnich, R.; Schaefer, E. US Patent 4370491, 1983.
4. Jiménez, L.; Garvin, A.; Costa-López, J. Ind Eng Chem Res 2002, 41, 6663–6669.
5. Steinigeweg, S.; Gmehling, J. Chem Eng Process 2004, 43, 447–456.
6. Božek-Winkler, E.; Gmehling, J. Ind Eng Chem Res 2006, 45, 6648–6654.
7. Peisheng, M. Chemical Engineering Thermodynamics; Chemical Industry Press: Beijing, People's Republic of China, 2005.
8. Liu, W. T.; Tan, C. S. Ind Eng Chem Res 2001, 40, 3281–3286.
9. Sanz, M. T.; Murga, R.; Beltran, S.; Cabezas, J. L. Ind Eng Chem Res 2004, 43, 2049–2053.
10. Silva, Viviana V. T. M.; Rodrigues, A. E. Chem Eng Sci 2006, 61, 316–331.
11. Helfferich, F. Ion Exchange; McGraw-Hill: New York, 1962; pp 519–550.