*Korean J. Chem. Eng.*, **30**(5), 1039-1042 (2013)
DOI: 10.1007/s11814-013-0023-x

# Kinetics of transesterification of methyl acetate and *n*-octanol catalyzed by cation exchange resins

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(*Received 3 December 2012 • accepted 11 February 2013*)

**Abstract**−The transesterification kinetics of methyl acetate with *n*-octanol to octyl acetate and methanol were studied using Amberlyst 15 as catalyst in a batch stirred reactor. The influence of the agitation speed, particle size, temperature, catalyst loading, and initial reactants molar ratio was investigated in detail. A pseudo-homogeneous (PH) kinetic model was applied to correlate the experimental data in the temperature range of 313.15 K to 328.15 K. The estimated kinetic parameters made the calculated results in good agreement with the experimental data. A kinetic model describing the transesterification reaction catalyzed by cation exchange resins was developed.

Key words: Transesterification, Octyl Acetate, Kinetics, Cation Exchange Resins

## INTRODUCTION

Methyl acetate (MeOAc) is a by-product in the industrial manufacturing process of poly(vinyl) alcohol (PVA). From 1 ton of PVA, about 1.68 ton of methyl acetate is produced [1]. The by-product methyl acetate is generally hydrolyzed to acetic acid and methanol which can be used as the raw materials of PVA. With the limited application in industry, it is necessary to develop the new applied field of methyl acetate. At present, the transesterification of methyl acetate with *n*-butanol to produce *n*-butyl acetate using the acidic catalysts has been studied [2-8]. However, studies on the transesterification of methyl acetate with *n*-octanol (OcOH) have not been reported in the literature so far.

On the other hand, octyl acetate (OcOAc) is an industrially important chemical with application as solvent and food flavor. It is used in large quantities as food additive with fruity, jasmine-like, and orange-like odor. It may also be used in the coating industry as a solvent for resins and paints. Herein, the more attractive way would be to prepare octyl acetate by transesterification of methyl acetate with *n*-octanol, which may provide a highly profitable method for the application of methyl acetate.

In addition, the study of kinetics is very important to understand the process of transesterification of methyl acetate, and is of great importance in simulation and design of reactive distillation. So the reaction kinetics of he transesterification of methyl acetate with *n*-octanol producing octyl acetate and methanol were studied in this paper. The reaction equation can be written as

$$CH_3COOCH_3 + CH_3(CH_2)_7OH \xleftrightarrow{H^+} CH_3COO(CH_2)_7CH_3 + CH_3OH \quad (1)$$

A strong acid cation exchange resin Amberlyst 15 was used as catalyst in this work. The effect of the agitation speed, particle size, temperature, catalyst loading, and initial reactants molar ratio on the reaction kinetics was studied in detail. A pseudo-homogeneous (PH) kinetic model was presented for the correlation of the experimental data, and corresponding kinetic parameters were estimated.

## EXPERIMENTAL SECTION

### 1. Materials

Methyl acetate and *n*-octanol were purchased from Tianjin Kermel Chemical Reagent Co., Ltd. (China). Octyl acetate was supplied from Westingarea Technology (China) Co., Limited. The commercial cation exchange resin Amberlyst 15 in the form $H^+$ was purchased from Rohm and Haas Company. Its appearance was opaque beads with the particle size of 0.600-0.850 mm, surface area of 53 $m^2/g$ and average pore diameter of 30 nm. The concentration of active sites was 4.7 eq/kg, and temperature stability was 393.15 K. The catalyst was washed with methanol to remove impurities and dried at 343.15 K under vacuum until the mass remained constant.

### 2. Apparatus and Procedure

The transesterification reactions were performed in a stirred glass reactor with a volume of 250 ml. The reactor was equipped with an online measuring device of agitation speed and temperatures. A reflux condenser was used to avoid any possible loss of volatile components. The reactor was placed into a constant temperature water bath (±0.1 K). Methyl acetate and *n*-octanol were charged into the reactor, and the mixture was preheated in the water bath. When the desired temperature was achieved, the catalyst (Amberlyst 15) was then added into the reactor and the agitation speed was adjusted to 500 rpm. The corresponding time was considered as the zero reaction time for the run. Samples were taken out at specific time intervals, were cooled rapidly to about 273.15 K in an ice bath to avoid any further reaction, and were then analyzed by gas chromatography.

Samples were analyzed by gas chromatograph (Shimadzu GC-

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17A) equipped with a capillary column and a hydrogen flame ionization detector (FID). A DB-17 capillary column (30 m×0.544 mm×1.0 μm) was used for the separation of the components and nitrogen was used as a carrier gas. The temperature of the inlet and the detector was set to be 573.15 K.

## RESULTS AND DISCUSSION

### 1. Effect of Mass Transfer Resistances

To ensure that there was no external mass transfer resistance in methyl acetate transesterification, the reactions were performed at three different stirring speeds under the same reaction conditions of 328.15 K, MeOAc to OcOH molar ratio of 1, and catalyst loading of 12% (wt/wt, of MeOAc). The results are shown in Fig. S1 (see Supplementary Information). As seen in Fig. S1, the conversion of MeOAc increased with the increase of the agitation speed from 300 rpm to 500 rpm, and kept unchanged for the agitation speed up to 700 rpm. It showed that the external mass transfer resistance could be neglected when the agitation speed was over 500 rpm. Therefore, all subsequent experiments were performed at constant agitation speed of 500 rpm to ensure that the reaction rate was not restricted by external diffusion.

The effect of particle size of resins on the transesterification reaction was examined using different particle sizes in the range of 0.40-0.85 mm under the same conditions. The experimental results are shown in Fig. S2 (see Supplementary Information). As seen in Fig. S2, the reaction rate was almost independent of particle size. It indicated that the influence of particle size on the conversion of methyl acetate was negligible in this work, implying that the reaction was not controlled by internal mass transfer.

### 2. Effect of Temperature

To investigate the effect of the reaction temperature, kinetic experiments were carried out in the range from 313.15 K to 328.15 K under the constant reaction conditions of MeOAc to OcOH molar ratio of 1, and catalyst loading of 12% (wt/wt, of MeOAc). As seen in Fig. 1, the conversion of methyl acetate increased with the increase of reaction temperature, because the increase of temperature brought more successful collisions. These successful collisions had sufficient energy (activation energy) to break the bonds and form products and thus resulted in higher conversion of methyl acetate.

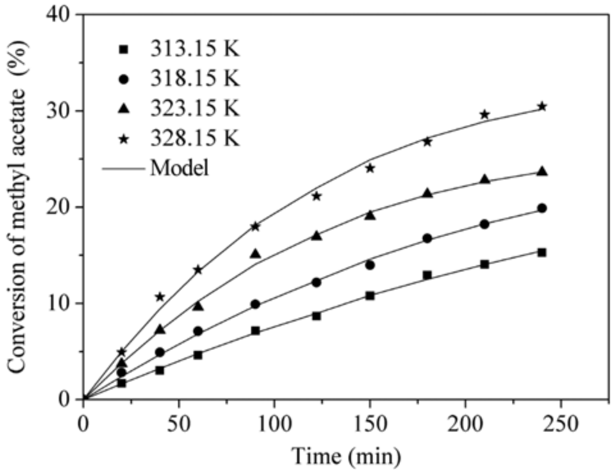

**Fig. 1. Effect of temperature on the conversion of MeOAc at catalyst loading of 12%, and MeOAc to OcOH molar ratio of 1.**

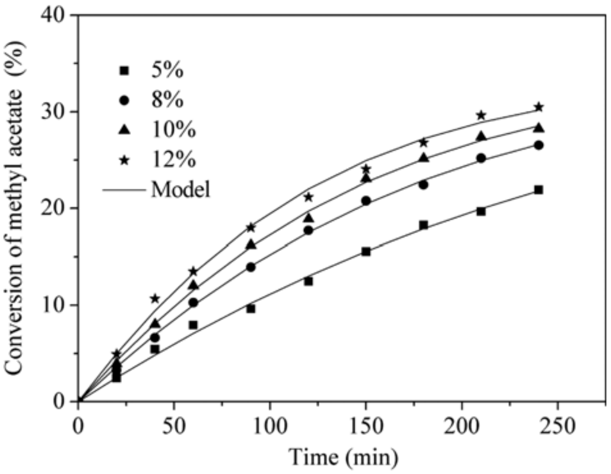

**Fig. 2. Effect of catalyst loading on the conversion of MeOAc at temperature of 328.15 K, and MeOAc to OcOH molar ratio of 1.**

### 3. Effect of Catalyst Loading

The effect of catalyst loading on the conversion of methyl acetate was tested under the same reaction conditions, and the results are shown in Fig. 2. It can be observed that the conversion of methyl acetate increased with the increase of catalyst loading. It was due to the fact that the increase of catalyst loading corresponded to more available active sites for the transesterification reaction, resulting in higher reaction rate. Fig. 3 shows a linear relationship between the initial reaction rate ($r_0$) and the catalyst loading. The initial reaction rate was calculated by using Eq. (3) at the starting point of reaction (t=0). The initial reaction rate increased with the increase of the catalyst loading, which may be because the available active sites for this reaction were proportional to the catalyst loading. The relationship between catalyst loading and the initial reaction rate could be expressed as:

$$-r_0=0.0795C_{cat} \tag{2}$$

where $C_{cat}$ was the catalyst loading, kg $L^{-1}$. This equation was valid

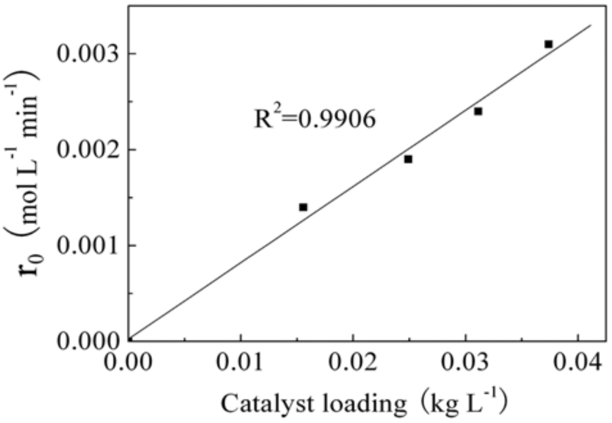

**Fig. 3. Effect of catalyst loading on the initial reaction rate at temperature of 328.15 K, and MeOAc to OcOH molar ratio of 1.**

only at 328.15 K, and MeOAc to OcOH molar ratio of 1 at which the experiments were carried out.

### 4. Effect of Initial Reactants Molar Ratio

The effect of different initial reactant molar ratio of MeOAc to OcOH from 2 : 1 to 1 : 2 was determined at 328.15 K, and loading catalyst of 12% (wt/wt, of MeOAc). The results are shown in Fig. 4. As seen there, the conversion of methyl acetate increased with decreasing the MeOAc to OcOH molar ratio from 2 : 1 to 1 : 2. It may be ascribed to the fact that the reaction equilibrium moved forwards the product side with the increasing concentration of reactant *n*-octanol. However, when the amount of *n*-octanol was further increased (MeOAc : OcOH=1 : 2), the conversion of MeOAc had no remarkable increase. It may be because MeOAc was diluted by increasing *n*-octanol contents, which prevented methyl acetate from adsorbing on the catalyst acid sites.

In addition, the experiment was carried out at 328.15 K, loading catalyst of 12% (wt/wt, of MeOAc), and MeOAc to OcOH molar ratio of 1. The products were analyzed by gas chromatography. During the transesterification of methyl acetate and *n*-octanol, besides the product octyl acetate no other by-product has been found. That is, the selectivity of the product was close to 100%.

## REACTION KINETIC MODEL

Many of the resins-catalyzed reactions could be expressed as a pseudo-homogeneous (PH) model [2,3,5,8-12]. The idealized homogeneous state required complete swelling of the resins and total dissociation of the polymer-bound-$SO_3H$ group. A PH model could be applied for the system where the mass transfer resistance was negligible and one of the reactants or solvents was highly polar. The PH model was based on the Helfferich approach, which treats catalysis confined within the internal catalyst mass, wherein the reactants, products, and solvents are 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 group for the reaction and free mobility of all components [2,5,13,14].

The kinetic equation of the transesterification of methyl acetate with *n*-octanol in the presence of Amberlyst 15 cation exchanger resin as catalyst can be established under conditions of negligible external and internal mass transfer limitation. The transesterification reaction was known to be reversible second-order reactions. Therefore, the PH model can be written as

$$\begin{aligned} r &= \frac{1}{m_{cat}}\frac{1}{v_i}\frac{1}{V}\frac{dn_i}{dt} = \frac{1}{m_{cat}}\frac{dC_{OcOAc}}{dt} \\ &= k_1 C_{OcOH}C_{MeOAc} - k_{-1}C_{MeOH}C_{OcOAc} \end{aligned} \tag{3}$$

Where $m_{cat}$ is the catalyst loading per unit volume, $k_1$ is the forward reaction rate constant, and $k_{-1}$ is the reverse reaction rate constant. In the investigated reaction, the stoichiometric coefficient $v_i$=1.

The kinetic equations were integrated numerically by a fourth-order Runge-Kutta method. The parameters of the kinetics model were estimated by minimizing the sum of residual squares (SRS) between the experimental and calculated conversion of methyl acetate using Eq. (4).

$$SRS = \sum_{samples} (x_{exp} - x_{calc})^2 \tag{4}$$

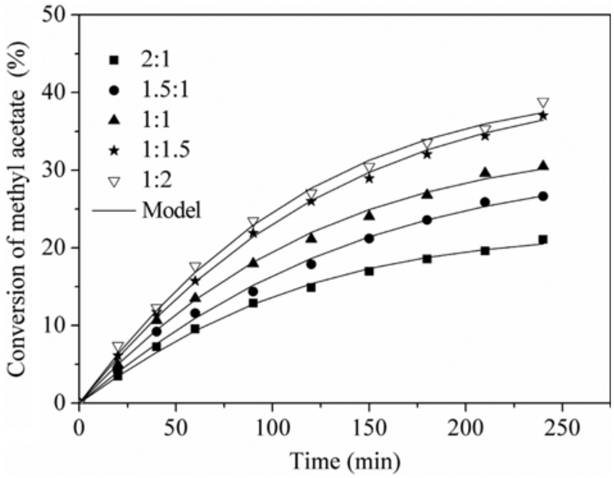

**Fig. 4. Effect of initial reactants molar ratio on the conversion of MeOAc at temperature of 328.15 K, and catalyst loading of 12%.**

where SRS is the minimum sum of residual squares, and x is the conversion of methyl acetate. The subscripts exp and calc denote experimental and calculated values, respectively.

The PH model was applied to describe the experimental kinetic data. From Figs. 1-2 and Fig. 4, the calculated conversion of methyl acetate by the reaction kinetic model was in good agreement with the experimental data. This indicated that the PH model gave a good representation of the kinetic behavior for the transesterification reaction of methyl acetate with *n*-octanol in the presence of Amberlyst

**Table 1. Temperature dependence of the forward and reverse kinetic constants**

| T (K) | $k_1$ (L $mol^{-1}$ $g^{-1}$ $min^{-1}$) | $k_{-1}$ (L $mol^{-1}$ $g^{-1}$ $min^{-1}$) |
|---|---|---|
| 313.15 | $5.36\times10^{-6}$ | $2.63\times10^{-5}$ |
| 318.15 | $7.88\times10^{-6}$ | $3.89\times10^{-5}$ |
| 323.15 | $1.52\times10^{-5}$ | $5.64\times10^{-5}$ |
| 328.15 | $1.68\times10^{-5}$ | $7.21\times10^{-5}$ |

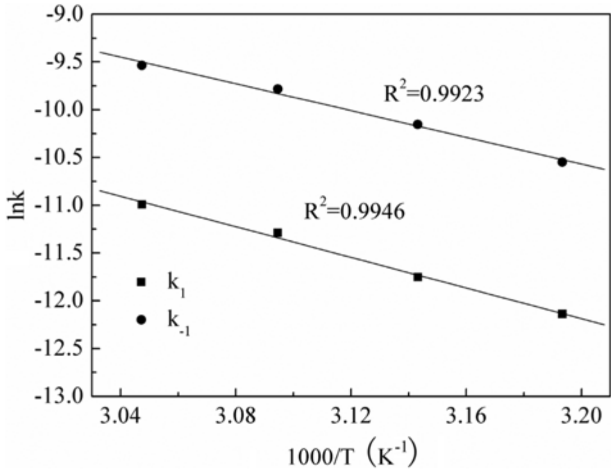

**Fig. 5. Arrhenius plot for transesterification of MeOAc with n-octanol.**

**Table 2. Kinetic parameters for the pseudo-homogeneous model**

| Reaction | Catalyst | $k_{01}$ ($L^2$ $mol^{-1}$ $g^{-1}$ $min^{-1}$) | $k_{02}$ ($L^2$ $mol^{-1}$ $g^{-1}$ $min^{-1}$) | $E_{a1}$ (kJ $mol^{-1}$) | $E_{a2}$ (kJ $mol^{-1}$) | References |
|---|---|---|---|---|---|---|
| MeOAc+OcOH | Amberlyst 15 | $6.85\times10^5$ | $1.39\times10^5$ | 68.48 | 58.23 | This work |
| MeOAc+BuOH | Amberlyst 15 | $2.02\times10^8$ | $2.89\times10^8$ | 71.96 | 72.67 | [3] |
| MeOAc+BuOH | NKC-9 | $3.45\times10^4$ | $2.39\times10^4$ | 54.32 | 52.02 | [5] |

15 as catalyst.

The regressed kinetic parameters for the PH model (Eq. (3)) and the dependence of this parameter on temperature are shown in Table 1. The temperature dependence of the rate constants can be expressed by the Arrhenius law:

$$\ln k = \ln k_0 - \frac{E_a}{RT} \tag{5}$$

The activation energy can be calculated from the slope of $(-E_a/R)$ in the Arrhenius diagram, which is the natural logarithm of the rate constant plotted versus the inverse temperature (as shown in Fig. 5). The value of pre-exponential factor ($k_{01}$, $k_{02}$) and activation energy ($E_{a1}$, $E_{a2}$) are given in Table 2. The calculated activation energy for methyl acetate with *n*-octanol transesterification ($E_{a1}$=68.48 kJ $mol^{-1}$, Table 2) is higher than the value of methyl acetate with *n*-butanol over NKC-9 [5], and is similar to the value reported in literature for methyl acetate with *n*-Butanol using Amerlyst 15 as catalyst [3].

## CONCLUSIONS

The kinetic behavior for the transesterification of methyl acetate with *n*-octanol to produce octyl acetate using Amberlyst 15 cation exchange resin as catalyst has been studied experimentally. The reaction was performed in a bath stirred reactor. The effects of various parameters such as agitation speed, particle size, temperature, catalyst loading, and molar ratio of reactants were studied. There was a linear relationship between the initial reaction rate and the catalyst loading. The kinetic experiment data were correlated with the pseudo-homogeneous kinetic model under the conditions that the external and internal mass transfer limitations were negligible. The calculated results with the estimated kinetic parameters were in excellent agreement with the experimental results.

## SUPPORTING INFORMATION

Additional information as noted in the text. This information is available via the Internet at http://www.springer.com/chemistry/journal/11814.

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