Kinetics Study of Propyl Acetate Synthesis Reaction Catalyzed by Amberlyst 15

YUAN-SHENG HUANG,^{1,2} KAI SUNDMACHER^{1,2}

¹Max-Planck-Institute for Dynamics of Complex Technical Systems, Sandtorstrasse 1, D-39106 Magdeburg, Germany
 ²Otto-von-Guericke-University Magdeburg, Process Systems Engineering, Universitätsplatz 2,
 D-39106 Magdeburg, Germany

Received 6 November 2005; revised 2 November 2006; accepted 1 December 2006

DOI 10.1002/kin.20236 Published online in Wiley InterScience (www.interscience.wiley.com).

> ABSTRACT: The reaction kinetics of esterification of acetic acid with n-propanol was investigated. The reaction was catalyzed by the commercial cation-exchange resin Amberlyst 15, and the kinetic data were obtained in a batch reactor within the temperature range 338–368 K. The chemical equilibrium constant, K eq, was first determined experimentally; the result shows that Keg is about 20 and slightly temperature dependent. Altogether 14 sets of kinetic data were then measured. The influences of operating parameters such as temperatures, initial molar ratios, and catalyst concentrations were checked. The pseudo-homogeneous (PH), Rideal-Eley (RE), and Langmuir-Hinshelwood-Hougen-Watson (LHHW) kinetic models were developed to interpret the obtained kinetic data. The parameters of the kinetic models were identified by the software DIVA, and the confidence interval of each parameter was also estimated. Both the chemical equilibrium constant and kinetic models were formulated in terms of the liquid phase activity, which was described by the nonrandom two-liquid (NRTL) model. The LHHW model gives the best fitting result, followed by the RE model and the PH model, whereas the confidence intervals rank in the reverse order. In addition, an effective solution was proposed to overcome a convergence problem occurring in the LHHW model parameter identification, which has been reported several times in the literature. © 2007 Wiley Periodicals, Inc. Int J Chem Kinet 39: 245-253, 2007

INTRODUCTION

Propyl acetate is often used as a solvent for cellulose nitrate and other cellulose derivatives in industry [1]. It is commonly synthesized by the esterification reaction of acetic acid with n-propanol. This type of esterification reaction is usually equilibrium limited, and the reaction rate can be efficiently catalyzed either homogeneously (e.g., mineral acids) or heterogeneously (e.g., ion-exchangers). The commercial cation-exchange resin, Amberlyst 15, has emerged as a widely used catalyst for esterifications recently since it holds the following advantages: (a) it can be easily removed from the liquid mixture after the reaction, (b) it is not corrosive to the equipment, and (c) the side reactions of etherification and dehydration can be almost completely suppressed.

In recent years, quite a few researchers have investigated different esterification reactions catalyzed by Amberlyst 15. For instance, Song et al. [2] and Pöken et al. [3] studied the esterification of methyl acetate, and Gangadwala et al. [4] investigated the



Correspondence to: Kai Sundmacher; e-mail: sundmacher@ mpi-magdeburg.mpg.de.

^{© 2007} Wiley Periodicals, Inc.

reaction system of butyl acetate. On the other hand, the heterogeneous kinetics of propyl acetate synthesis reaction was less studied; the available two publications [5,6] both reported the reaction kinetics using Dowex-50W as the catalyst. Krishnaiah and Rao [5] reported that the Langmuir–Hinshelwood–Hougen– Watson (LHHW) model was selected to correlate the experimental data in their work. However, the adsorption terms of ester and water were then lumped together in the denominator of the kinetic model, which was in fact the Rideal–Eley (RE) model. Bart et al. [6] determined the kinetic model by selecting the one that gave the best fitting result. Consequently, the RE model, wherein the adsorption of acetic acid is the rate-determining step, was selected.

The kinetics of propyl acetate synthesis reaction catalyzed by Amberlyst 15 has never been reported before; moreover, the equilibrium constant extrapolated from [5,6] did not result in a good prediction for the residue curve map measurement (cf. [7]). Therefore in this work, we investigated the kinetics of this reaction experimentally, using Amberlyst 15 as the catalyst. The reaction scheme reads as

Acetic acid (AcAc) + Propanol (PrOH) $\stackrel{\text{H}^+}{\longleftrightarrow}$ Propyl acetate (AcAc) + Water (H₂O) (1)

The chemical equilibrium constant was first determined by long-time experiments. A total of 14 sets of kinetic data were then measured with different conditions. Three typical kinetic models: the pseudohomogeneous (PH), Rideal–Eley (RE), and Langmuir-Hinshelwood-Hougen-Watson (LHHW) kinetic models were employed to interpret the experimental data. The parameter identification was carried out with help of the in-house software DIVA [8].

For parameter identification problems, the confidence interval is also of primary importance because it provides a measure to judge the accuracy of parameter estimates. For the nonlinear reaction kinetic models, the confidence interval can be obtained by the linearization approximation [9]. In this work, the confidence interval of each parameter was also estimated.

In addition, a convergence problem was encountered when performing the parameter identification for the LHHW model. Such a convergence problem has been reported several times in the literature, in particular for the esterification reactions (e.g., [2,4,10]). Previously, the parameters of the LHHW model for esterification reactions could only be discriminated either with help of extra nonreactive adsorption experiments [2,3], or with the presumption of negligible parameters [5,11]. In this work, an effective solution has been

Table I The Specification of Amberlyst 15 Catalyst

Appearance	Beige, gray-brown spherules
Particle size (mm)	0.355-1.18 (>90%)
Average pore diameter (nm)	30-80
Density (g/cm ³)	0.6
Surface area (m^2/g)	50
Proton concentration	4.7 (dry)
$(meq H^+/g)$	
Degree of cross-linking	20
(wt%)	
Porosity	0.36
Temperature tolerance	$< 120^{\circ}C$

proposed to overcome the convergence problem and to realize the parameters identification for the LHHW model directly from the kinetic data.

EXPERIMENTAL

Materials

Acetic acid (99–100%, Merck, Germany), *n*-propanol (>99%, Merck, Germany), and propyl acetate (>98%, Merck, Germany) were used as reactants; the commercial cation-exchange resin, Amberlyst[®] 15, was used to catalyze the reaction. The specification of Amberlyst 15 catalyst is listed in Table I; the particle size and pore diameter are confirmed by SEM as shown in Fig. 1.

Apparatus

To minimize the liquid composition change due to evaporation, the experiments were carried out in a sealed, steel-jacketed reactor of 1.57 L volume (10 cm inner diameter \times 20 cm height). It was operated isothermally in the batch mode and magnetically stirred. The reactor was equipped with temperature and pressure sensors and a blow-off safety valve. The set temperature was regulated by the thermostat (Julabo, Germany, F30-C). Samples were taken via the sampling hole, which was sealed with the silicone pad; the syringe capped with the 30-cm-long needle (Rettberg, Germany) pierced through the pad to take samples from the reacting liquid phase.

Analysis of Liquid Phase Composition

The samples were analyzed by a gas chromatography (Hewlett-Packard, HP6890 series) where the mixtures were separated in a cross-linked polyethylene glycol column (HP-INNOWAX, part no. 19091N-133). The column temperature was programmed with a 2-min initial hold at 50° C, followed by a 50° C/min ramp up to



Figure 1 SEM image of Amberlyst 15: (a) particle size and (b) pore diameter.

 130° C, and held for 2.5 min. Both the thermal conductivity detector (TCD) and the flame ionization detector (FID) were used for peak detection. Because propanol and water have an inseparable peak time in the column, the water amount was calculated by subtraction of the TCD and FID signals. To guarantee a controlled error of such a subtraction method, the GC was recalibrated when the compositions calculated by TCD and FID differed from each other for more than 1.5%.

Procedure

Mixtures of 3 mol were prepared with different initial molar ratios, and then poured into the reactor. The reactor was then closed and heated. When the liquid mixture was heated to the set temperature, the catalyst was added into the reactor through a peephole on the lid, which was then sealed, and this moment was considered as the starting time. Samples of approximately 1 mL were taken every 5–10 min for the first hour, and 20–40 min for the next 3–4 h. A total of 14 runs, as listed in Table II, were performed and used to discriminate the kinetic models.

RESULTS AND DISCUSSION

Exclusion of External Mass Transfer Influence

The reactor of 10-cm inner diameter was stirred by an 8-cm-long triangular magnetic bar. To confirm the exclusion of solid–liquid interphase mass transfer effect on the kinetics, three stirring speeds (150, 250, and 300 rpm) were tested preliminarily. There was no appreciable difference among these agitation conditions. The magnetic stirrer was operated at the speed of 300 rpm in the subsequent experiments.

Table II Experimental Conditions of the Reaction Kinetic Study (n = 3.0 mol)

Run No.	Temperature (K)	Catalyst (g)	x _{AcAc,0}	<i>x</i> PrOHc,0	x _{PrAc,0}
1	353	5.0	0.5	0.5	0
2	338	5.0	0.2	0.8	0
3	368	3.5	0.2	0.8	0
4	368	2.0	0.2	0.8	0
5	368	5.0	0.2	0.8	0
6	353	3.5	0.8	0.2	0
7	368	5.0	0.5	0.5	0
8	338	3.5	0.8	0.2	0
9	338	5.0	0.5	0.5	0
10	368	2.0	0.8	0.2	0
11	353	2.0	0.8	0.2	0
12	338	3.5	0.5	0.5	0
13	368	2.0	0.5	0.5	0
14	353	5.0	0.35	0.35	0.3

Chemical Equilibrium Constant

In principle, the chemical equilibrium constant can be determined either by the thermodynamic data (the enthalpies and free energies of formation of all components, $\Delta_f H$ and $\Delta_f G$) or by long-time experiments. However, the estimation based on the thermodynamic data is usually much less reliable because a small deviation in $\Delta_f H$ and $\Delta_f G$ can lead to a relatively large error in the reaction enthalpy $\Delta_r H$ and the reaction free energy $\Delta_r G$, and thus the equilibrium constant K_{eq} . Moreover, for the considered reaction system, the necessary thermodynamic data of propyl acetate are not available; therefore, the equilibrium constant is determined experimentally.

Long-time experiments were performed independently to determine the equilibrium constant K_{eq} . The procedure was similar as described previously, but fewer samples were taken. Each run lasted for longer time (≥ 10 h), and the equilibrium was judged to be reached when no measurable concentration changes were observed. The results are listed in Table III. The equilibrium constants were formulated in terms of the liquid phase activity (Eq. (2)), while the activity coefficients (γ_i) were calculated by the nonrandom twoliquid (NRTL) equation [12].

$$K_{\rm eq} = \frac{a_{\rm Pr\,Ac}a_{\rm H_2O}}{a_{\rm AcAc}a_{\rm Pr\,OH}} = \frac{x_{\rm Pr\,Ac}x_{\rm H_2O}}{x_{\rm AcAc}x_{\rm Pr\,OH}} \cdot \frac{\gamma_{\rm Pr\,Ac}\gamma_{\rm H_2O}}{\gamma_{\rm AcAc}\gamma_{\rm Pr\,OH}}$$
(2)

It can be seen from Table III that the equilibrium constant is slightly temperature dependent within the range 338–368 K. The temperature dependence of K_{eq} can be found by the linear regression of all data points in the plot of ln K_{eq} versus the reciprocal temperature (1/T) as shown in Fig. 2:

$$\ln K_{\rm eq} = \frac{-475.42}{T} + 4.3223 \tag{3}$$

Table IIIEquilibrium Constants at DifferentConditions

Temperature (K)	xAcAc,0:xPrOH,0	Keq
338	1:1	18.706
353	1:1	19.643
353	1:4	21.409
353	4:1	17.474
368	1:1	20.971
368	1:4	22.382
368	4:1	19.202



Reaction Enthalpy, Entropy, and Free Energy

If a constant reaction enthalpy is assumed within the operating temperature range, the reaction enthalpy $(\Delta_r H)$ and entropy $(\Delta_r S)$ can be estimated by setting the experimental values of Eq. (3) into Eq. (4):

$$\ln K_{\rm eq} = \frac{-\Delta_r H}{RT} + \frac{\Delta_r S}{R} \tag{4}$$

Consequently, the reaction enthalpy $\Delta_r H$ and reaction entropy $\Delta_r S$ are found to be 3952.6 J/mol and 35.9356 J/mol·K, respectively. Furthermore, the liquid phase reaction free energy change can be calculated to be

$$\Delta_r G = \Delta_r H - T \Delta_r S = 3952.6 - 298 \times 35.9356$$

= -6756.2 (J / mol) (5)

Effect of Catalyst Amount

The concentration profile is plotted for different catalyst amounts in Fig. 3a. For the same conditions of temperature and initial molar fraction, the reaction rate increases in proportion to the catalyst amount added. It can be seen from Fig. 3b that the increase in catalyst amount results in equal acceleration of the initial reaction rate $R_{i(t\to 0)}$. Thus, it is reasonable to presume the proportionality of reaction rate R_i and M_{cat} .



Figure 3 Effect of catalyst loading ($T = 368 \ K$, $n = 3.0 \ mol$, $x_{AcAc,0}/x_{PrOH,0} = 1:4$). (a) Mole fraction profiles of different M_{cat} ; (b) initial reaction rate vs. M_{cat} .

Effect of Temperature

The influence of the temperature on the reaction rate is illustrated in Fig. 4. As expected, the reaction rate increases with temperature. The temperature dependency of the forward rate constant k_f is assumed to obey the Arrhenius equation, and the activation energy will be estimated from the kinetic data as shown later.

Effect of Initial Molar Fraction

The concentration profile of propyl acetate is plotted for different initial molar ratios between acetic acid



Figure 4 Effect of temperature $(n = 3.0 \text{ mol}, x_{AcAc,0}/x_{PrOH,0} = 1:1, M_{cat} = 5.0 \text{ g}).$

and propanol in Fig. 5. Qualitatively speaking, equal initial molar ratios lead to the highest equilibrium composition of propyl acetate, while for asymmetric initial molar ratios, the run with higher acetic acid content ($x_{ACAC,0}$: $x_{PrOH,0} = 4$:1) shows a higher reaction rate than with an excess of propanol (1:4).



Figure 5 Effect of initial molar ratio of acetic acid and propanol (T = 368 K, n = 3.0 mol, $M_{cat} = 2.0$ g).

Mathematical Description of Kinetic Models

In this work, three typical kinetic models were selected to interpret the obtained kinetic data, that is, the PH, RE, and LHHW models. The PH rate equation for the esterification reads as

$$R_{i} \equiv n \frac{\mathrm{d}x_{i}}{\mathrm{d}t} = M_{\mathrm{cat}}r_{i}$$
$$= M_{\mathrm{cat}}\nu_{i}k_{\mathrm{f}}\left(a_{\mathrm{AcAc}}a_{\mathrm{Pr}\,\mathrm{OH}} - \frac{1}{K_{\mathrm{eq}}}a_{\mathrm{Pr}\,\mathrm{Ac}}a_{\mathrm{H}_{2}\mathrm{O}}\right) \quad (6)$$

where R_i is the apparent reaction rate, defined as the increasing (or decreasing) amount of component *i* per unit time; r_i is the intensive reaction rate, defined as R_i divided by the catalyst amount; *n* is total number of moles; v_i is the stoichiometric coefficient of component *i*; M_{cat} is the catalyst amount; k_f is the forward rate constant; $a_i = x_i \gamma_i$ is the activity of component *i*; and K_{eq} is the equilibrium constant.

The heterogeneous LHHW model represents a mechanism wherein all components can be adsorbed on the catalyst surface, and the chemical reaction occurs between the adsorbed molecules. Assuming that the surface reaction in the adsorbed phase is the rate-determining step, the LHHW rate equation can be derived as

equation:

$$k_{\rm f} = k_{\rm f0} \exp(-E_{\rm f}/RT) \tag{9}$$

where the preexponential term $k_{\rm f0}$ represents the frequency factor and $E_{\rm f}$ the activation energy.

Parameter Identification and Confidence Interval Estimation

The kinetic data were obtained to discriminate the parameters of the above kinetic models. Since the equilibrium constant is determined by Eq. (3), the adjustable parameters in Eqs. (6)–(8) include the frequency factor k_{f0} , the activation energy E_f , and the adsorption constants $K_{S,i}$. Thus, the numbers of parameters to be identified in PH, LHHW and RE models are 2, 6, and 5, respectively.

The objective of the data-fitting procedure is to minimize the quadratic sum (QS) of the deviation between the experimental data and the model prediction.

$$QS = \sum_{\text{all samples}} (x_{PrAc,exp} - x_{PrAc,model})^2$$
(10)

The parameter identification was realized by the in-house software DIVA (Dynamic SImulator für Verfahrenstechnische Anlagen) [8]. For the nonlinear

$$R_{i} \equiv n \frac{\mathrm{d}x_{i}}{\mathrm{d}t} = M_{\mathrm{cat}}r_{i} = M_{\mathrm{cat}}v_{i}k_{\mathrm{f}}\frac{\left(a_{\mathrm{AcAc}}a_{\mathrm{Pr}\mathrm{OH}} - \frac{1}{K_{\mathrm{eq}}}a_{\mathrm{PrAc}}a_{\mathrm{H_{2}O}}\right)}{\left(1 + K_{\mathrm{S},\mathrm{AcAc}}a_{\mathrm{AcAc}} + K_{\mathrm{S},\mathrm{PrOH}}a_{\mathrm{PrOH}} + K_{\mathrm{S},\mathrm{PrAc}}a_{\mathrm{PrAc}} + K_{\mathrm{S},\mathrm{H_{2}O}}a_{\mathrm{H_{2}O}}\right)^{2}}$$
(7)

Comparing with the PH model, the extra parameters in Eq. (7) are the adsorption constants $(K_{S,i})$, which are considered temperature independent within the experimental range.

In contrast to the LHHW model, the RE model assumes that one (or some) of the components is not adsorbed by the catalyst. If propyl acetate is considered nonadsorbable on the catalyst, the RE rate equation can be written as

$$R_{i} \equiv n \frac{\mathrm{d}x_{i}}{\mathrm{d}t} = M_{\mathrm{cat}}r_{i} = M_{\mathrm{cat}}v_{i}k_{\mathrm{f}}$$

$$\times \frac{\left(a_{\mathrm{AcAc}}a_{\mathrm{PrOH}} - \frac{1}{K_{\mathrm{eq}}}a_{\mathrm{PrAc}}a_{\mathrm{H}_{2}\mathrm{O}}\right)}{\left(1 + K_{\mathrm{S,AcAc}}a_{\mathrm{AcAc}} + K_{\mathrm{S,PrOH}}a_{\mathrm{PrOH}} + K_{\mathrm{S,H}_{2}\mathrm{O}}a_{\mathrm{H}_{2}\mathrm{O}}\right)^{2}}$$
(8)

The temperature dependency of forward rate constant k_f in Eqs. (6)–(8) is assumed to obey the Arrhenius rate equations, (6)–(8), the confidence interval of each parameter was estimated with the linearization approximation (e.g., [9]). The fitting results and the confidence intervals are given in Table IV.

According to the quadratic sum of deviation, QS, the heterogeneous (LHHW and RE) models fit the experimental data significantly better than the PH model. The obtained adsorption constants show that water is the most adsorbable on the catalyst, followed by propanol, acetic acid, and then propyl acetate. The comparison of predicted curves and the experimental data is illustrated in Fig. 6. Moreover, upon the results of LHHW and RE models, the activation energy $E_{\rm f}$ is estimated to be 54.828 \pm 0.256 kJ/mol.

Generally speaking, the confidence intervals of estimated parameters are satisfactorily small in Table IV. Nevertheless, two evident characteristics can be seen from the result. First, in all three models the confidence interval of activation energy E_f is much smaller than the

Model	$k_{\rm f0} \ ({\rm mol/g.s})$	$E_{\rm f}$ (J/mol)	K _{S,AcAc}	K _{S,PrOH}	K _{S,PrAc}	K_{S,H_2O}	QS
PH	$\begin{array}{c} 1.2556 \times 10^{4} \\ \pm \ 0.044\% \end{array}$	$5.0791 imes 10^4 \\ \pm 0.002\%$	_	_	_	_	0.418
LHHW	$2.7163 imes 10^6 \\ \pm 1.498\%$	$\begin{array}{c} 5.4572 \times 10^{4} \\ \pm \ 0.002\% \end{array}$	$4.5383 \pm 0.910\%$	$7.9183 \pm 0.834\%$	$1.4662 \pm 1.134\%$	$8.7032 \pm 0.774\%$	0.100
RE	$\begin{array}{c} 2.7414 \times 10^{6} \\ \pm \ 0.248\% \end{array}$	$\begin{array}{c} 5.5084 \times 10^{4} \\ \pm \ 0.002\% \end{array}$	$4.1074 \pm 0.150\%$	$7.1982 \\ \pm 0.136\%$	_	$8.9547 \pm 0.132\%$	0.104

Table IV Results of Parameter Identification and Confidence Interval Estimation for Kinetic Models

other parameters, because it is the unique parameter that reflects the temperature dependency and thus can be easily discriminated. Second, the confidence intervals of parameters in the PH model are most satisfactory, followed by the RE model, while the confidence intervals are relatively large in the LHHW model. This is because the frequency factor k_{f0} is correlated with the adsorption constants $K_{S,i}$ in the heterogeneous kinetic models.

Influence of Internal Mass Transfer

To access the activation sites inside the catalyst particle, the reactants have to diffuse into the particle, be adsorbed and react; then the products have to be desorbed and diffuse out of the particle. To set up a model for describing the internal mass transfer effect (e.g., [13]) is not the focus of this work. Instead, the major interest is to study the macroscopic reaction kinetics using the catalyst in its commercially available form. Nevertheless, the influence of the internal mass transfer within the catalyst particle can be discussed qualitatively as follows.



Figure 6 Comparison of experimental data and model prediction for three different kinetic models.

Taking the PH rate equation (6) as an example, a correction factor, fn(intra - diff), is inserted to represent the internal mass transfer effect as Eq. (6a)

$$R_{i} \equiv n \frac{\mathrm{d}x_{i}}{\mathrm{d}t} = M_{\mathrm{cat}}r_{i} = M_{\mathrm{cat}}fn(intra - diff)v_{i}k_{\mathrm{f}}$$
$$\times \left(a_{\mathrm{AcAc}}a_{\mathrm{PrOH}} - \frac{1}{K_{\mathrm{eq}}}a_{\mathrm{PrAc}}a_{\mathrm{H}_{2}\mathrm{O}}\right) \tag{6a}$$

When the internal mass transfer resistance is very large, only the activation sites on the catalyst surface are accessible and effective to catalyze the reaction. In such a case, the internal mass transfer has no effect on the reaction rate, i.e., fn(intra - diff) = 1.

On the other hand, when the intraparticle mass transfer resistance is not so large, the activation sites within the catalyst particle are partially accessible and effective, which will contribute to the chemical reaction rate; thus fn(intra - diff) > 1.

Qualitatively speaking, $fn(intra - diff) \ge 1$, which means the activation energy in Eq. (6) might be underestimated. Nevertheless, for the considered reaction system, the reactants and the ester are quite bulky molecules. The internal mass transfer effects can thus be well omitted.

LHHW Model Parameter Identification Issue

In a previous work of the same reaction system [6], the authors reported that an RE model, wherein the adsorption of acetic acid is the rate-determining step, gave the best fitting results among the 13 mechanisms of consideration. However, from the mathematical point of view, the RE models can be regarded as a subset of the LHHW models when one or some of the components are not adsorbable on the catalyst (e.g., $K_{S,PrAc} = 0$); therefore, it is unreasonable that RE models could give better fitting results than the LHHW models, unless the fitting procedures are not treated equally well for both models. It is believed that, similar as reported elsewhere [2,4,10], the authors of [6] either encountered

a convergence problem or got the negative adsorption constant values for LHHW model, which they did not point out.

This convergence problem of identifying the LHHW model parameters has been reported several times in the literature, especially for the esterification reactions. Previously, to apply LHHW models to the esterification reactions, researchers either predetermined the adsorption constants by separate non-reactive adsorption experiments, or presumed some of them negligible. In fact, such a convergence difficulty was also encountered in this work at first, but this could be easily solved by the incorporation of an additional experiment 14 (cf. Table II), wherein the molar concentrations of ester and water were kept different.

Mathematically speaking, this convergence problem is because the adsorption effects of the ester and water are "coupled" to each other. As a convention of kinetics study of esterification reactions, the experiments are often conducted with the initial compositions of the acid and the alcohol; consequently, the mole fractions of ester and water are always the same through the whole experiment because of the reaction stoichiometry. The adsorption constants of ester and water can be "decoupled" by applying the initial molar ratio that bears significant difference between the concentrations of ester and water, for example, run 14 in this work.

CONCLUSION

The reaction kinetics of esterification of acetic acid with propanol was studied. The reaction was catalyzed by the cation-exchange resin Amberlyst 15. The kinetic data were obtained in a batch reactor within the temperature range 338-368 K. The equilibrium constant was determined experimentally and found to be slightly temperature dependent. The standard reaction enthalpy and free energy were estimated to be $\Delta_r H = 3952.6$ J/mol and $\Delta_r G = -6756.2$ J/mol, respectively. Three kinetic models (PH, RE, and LHHW) were then developed to interpret the kinetic data. Parameters of the kinetic models and the confidence interval of each parameter were estimated from the obtained kinetic data. The LHHW model gives the best fitting result, followed by the RE model, and then the PH model, whereas the confidence interval of estimated parameters ranks in the reverse order. The activation energy was estimated from the heterogeneous kinetic models as 54.828 ± 0.256 kJ/mol. An additional run of kinetic measurements, wherein the initial concentration of propyl acetate and water was different, was incorporated to solve the convergence problem of parameter identification in the LHHW model.

The authors thank Mr. Samuel Tulashie for laboratory assistance, and Mr. Jignesh Gangadwala for fruitful discussion.

NOMENCLATURE

a_i	Liquid phase activity of component <i>I</i>		
$E_{ m f}$	Activation energy, J/mol		
$k_{ m f}$	Forward reaction rate constant, mol/g·s		
$k_{ m f0}$	Frequency factor of $k_{\rm f}$, mol/g·s		
K _{eq}	Chemical equilibrium constant		
$K_{\mathrm{S},i}$	Absorption constant of component I		
LHHW	Langmuir-Hinshelwood-Hougen-Watson		
	model		
$M_{\rm cat}$	Mass of catalyst, g		
п	Total number of moles, mol		
PH	Pseudo-homogeneous model		
QS	Quadratic sum of deviation, Eq. (10)		
r_i	Reaction rate per unit catalyst mass,		
	mol/g·s		
R	Universal gas constant, 8.314 J/(mol·K)		
R_i	Apparent reaction rate, mol/s		
RE	Rideal–Eley model		
t	Time, s		
Т	Temperature, K		
x_i	Liquid phase mole fraction of component <i>i</i>		
$x_{i,0}$	Initial mole fraction at $t = 0$		
γi	Activity coefficient of component <i>i</i>		
$\Delta_{ m f} G$	Free energy of formation, J/mol		
$\Delta_r G$	Reaction free energy change, J/mol		
$\Delta_{ m f} H$	Enthalpy of formation, J/mol		
$\Delta_r H$	Reaction enthalpy, J/mol		
$\Delta_r S$	Reaction entropy, J/mol·K		
v_i	Stoichiometric coefficient of component <i>i</i>		

BIBLIOGRAPHY

- Industrial Organic Chemicals: Starting Materials and Intermediates; Wiley-VCH: Weinheim, Germany, 1999; Vol. 4, Ch. 5.
- Song, W.; Venimadhavan, G.; Manning, J. M.; Malone, M. F.; Doherty, M. F. Ind Eng Chem Res 1998, 37, 1917.
- Pöpken, T.; Götze, L.; Gmehling, J. Ind Eng Chem Res 2000, 39, 2601.
- Gangadwala, J.; Mankar, S.; Mahajani, S.; Kienle, A.; Stein, E. Ind Eng Chem Res 2003, 42, 2146.
- Krishnaiah, D.; Rao, M. B. Indian J Technol 1984, 22, 268–271.

- Bart, H. J.; Kaltenbrunner, W.; Landschützer, H. Int J Chem Kinet 1996, 28, 649.
- 7. Huang, Y.-S.; Sundmacher, K.; Tulashie, S.; Schlünder, E.-U. Chem Eng Sci 2005, 60, 3363.
- 8. Majer, C. Ph.D. Thesis, University of Stuttgart, Stuttgart, Germany, 1998.
- Marsili-Libelli, S.; Guerrizio, S.; Checchi, N. Ecol Model 2003, 165, 127.
- Parra, D.; Tejero, J.; Cunill, F.; Iborra, M.; Izquierdo, J. F. Chem Eng Sci 1994, 49, 4563.
- 11. Silva, V. M. T. M.; Rodrigues, A. E. Chem Eng Sci 2001, 56, 1255.
- Gmehling, J.; Onken, U. Vapour-liquid equilibrium data collection, chemistry data series; Frankfurt am Main, DECHEMA, 1977.
- 13. Rehfinger, A.; Hoffmann, U. Chem Eng Sci 1990, 45, 1619.