

# Esterification of propanoic acid with ethanol, 1-propanol and butanol over a heterogeneous fiber catalyst

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## Abstract

Esterification kinetics of propanoic acid with ethanol, 1-propanol and butanol over a fibrous polymer-supported sulphonic acid catalyst (Smopex-101) was studied. Experiments were carried out in a batch reactor operating isothermally at three different temperatures: 60, 70 and 75 °C (80 °C for butanol) and with different initial molar ratios of propanoic acid and alcohol (1:1, 1:2 and 2:1). The fiber catalyst was active and stable in all the experiments. The experimental results were modeled according to a Langmuir–Hinshelwood model and with an advanced adsorption-based model. The activity coefficients were calculated according to the UNIFAC model. The activation energy of esterification of propanoic acid with ethanol was found to be 52.6 kJ/mol, 49.9 kJ/mol with 1-propanol and 47.3 kJ/mol with butanol. The kinetic model, which includes the adsorption of carboxylic acid and water combined with the activities of the species, explained the experimentally recorded concentrations well.

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**Keywords:** Esterification; Polymer-supported sulphonic acid catalyst; Density; Viscosity; Activity; Kinetic modeling

## 1. Introduction

The best known acid-catalyzed reactions are esterification, etherification, hydration, hydrolysis, alkylation and isomerisation [1]. Esters, which are products of one of these reactions, esterification, are used as solvents of paints, adhesives and organic media instead of aromatic compounds, which usage should be restricted due to their negative environmental impact [2]. Typically esterification reactions are extremely slow; it requires several days to attain the equilibrium in the absence of a catalyst. To accelerate the reaction rate, catalysts are always employed in liquid phase esterification. Despite the strong catalytic effect, the use of homogeneous catalysts, such as sulphuric acid and *p*-toluenesulphonic acid suffers from several drawbacks, such as the existence of side reactions, corrosion of the equipment and the need to deal with acidic wastes [3]. Homogeneous catalysts may also result in sulphur contamination of the final ester product [4]. In this situation, the use of solid catalysts has received increasing attention in the past years [3]. Many

solid-acid catalysts have been used, such as iodine [5], MCM-41 [6], zeolite-T membrane [7], ZSM-5 [8–11], HY zeolite [8,11,12], zeolite beta [8,13], acid treated clays [10], heteropolyacids [10,14–18], copper catalysts [2], sulphated oxides [19] and sulphated zirconia [20]. Ion-exchange resins, however, are the most commonly used solid catalysts and they have been proved to be effective in liquid phase esterification [3,20–33]. There is a strong economic driving force to use solid catalysts instead of liquid ones. By using a solid catalyst, the number of processing options, such as a gas flow reactor and a fixed bed is increased [4].

In previous works of our group [34–36], polyvinylbenzene and polyolefin-supported sulphonic acid catalysts were compared in the esterification of acetic acid with methanol [36], the kinetics of the esterification of propanoic acid with methanol on a polymer-supported sulphonic acid catalyst [34] have been studied and in order to reveal the structural relationships in kinetics a family of carboxylic acids and alcohols were utilized [35].

The goal of this work was to demonstrate the applicability of the polymer-supported sulphonic acid catalyst, Smopex-101 (Smoptech Ltd., A Johnson Matthey Company), in esterification reactions and to study the esterification kinetics. The effect of the reaction temperature and the initial molar ratio of the

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## Nomenclature

A	propanoic acid
A'	reaction intermediate
A' <sub>i</sub>	constant in Andrade equation
A''	constant
a <sub>i</sub>	activity of component <i>i</i>
B	alcohol
B' <sub>i</sub>	constant in Andrade equation
B''	constant
<i>c</i>	concentration, mol/dm <sup>3</sup>
C	ester
D	water
D <sub>e,A</sub>	effective diffusion coefficient, m <sup>2</sup> /s
E' <sub>1</sub>	parameter in Eq. (22), K
E' <sub>2</sub>	parameter in Eq. (22), K
E <sub>1</sub>	E' <sub>1</sub> R = activation energy, kJ/mol
E <sub>2</sub>	E' <sub>2</sub> R = activation energy, kJ/mol
<i>k</i>	rate constant, dm <sup>9</sup> /(mol <sup>2</sup> g min)
<i>K</i>	equilibrium constant
<i>K</i> <sup>T</sup>	activity based equilibrium constant
<i>Q</i>	objective function in parameter estimation (mol/dm <sup>3</sup> ) <sup>2</sup>
<i>r</i>	reaction rate, mol/(g min)
<i>r</i> '	normalized reaction rate
<i>R</i>	gas constant, 8.31 J/(mol K)
<i>R</i> <sup>2</sup>	degree of explanation
<i>t</i>	reaction time, min
<i>T</i>	temperature, K
<i>V</i>	volume, dm <sup>3</sup>

### Greek letters

α	combined parameter in rate equation
β	combined parameter in rate equation
γ <sub><i>i</i></sub>	activity coefficient of species ( <i>i</i> )
ε <sub>p</sub>	porosity
φ*	normalized Thiele modulus
μ	dynamic viscosity, cP
ν	stoichiometric coefficient
ρ <sub>B</sub>	catalyst bulk density, g/dm <sup>3</sup>
τ <sub>p</sub>	tortuosity
ν	kinematic viscosity, cSt

### Subscripts

cat	catalyst
<i>i</i>	component index
<i>c</i>	concentration
L	liquid phase

### Superscripts

^	a value predicted by the model
-	mean value
*	surface concentration

reactants on esterification kinetics were studied and the results were described by an advanced activity based kinetic model. Esterification of propanoic acid with ethanol, 1-propanol and butanol were selected examples.

Specific advantages of fiber catalysts are due to short diffusion paths, which provide high catalyst efficiency and excellent separation abilities. The polymer-supported fiber catalyst could be used in various industrially relevant heterogeneous reactions, such as esterification [34–36], etherification, aldolization and hydrogenation [37–40]. The catalyst is utilized in batch and continuous processes. The polyethylene-based fiber catalyst is modified by grafting different functional groups, such as pyridine, carboxylic acid and sulphonic acid or a combination of them. In this way homogeneous catalysts can be replaced by fiber catalysts.

## 2. Experimental section

Esterification of propanoic acid with ethanol, 1-propanol and butanol over a fibrous polymer-supported sulphonic acid catalyst (Smopex-101) was carried out in an isothermally operating glass reactor. The reactor was equipped with a heating jacket and a reflux condenser, which was placed on top of the reactor to prevent the escape of volatile components. The reaction was commenced by pouring the preheated acid into the reactor. The stirring rate in all the experiments was 550 rpm and temperature was kept within 0.1 °C. Liquid samples (1 cm<sup>3</sup>) were withdrawn and the amount of unreacted acid was analyzed by titration with 0.1 M NaOH with an accuracy of 0.5%. The ratio between the molar mass of propanoic acid and the amount of active sulphonic acid groups on the catalyst was maintained constant, 8.475 × 10<sup>-3</sup>. The liquid volume in all of the experiments was 0.427 dm<sup>3</sup>.

The effects of temperature and initial molar ratio between the acid and alcohol on the esterification of propanoic acid with ethanol, 1-propanol and butanol were studied at three different temperatures (60, 70 and 75 °C (80 °C for butanol)) and with three different initial molar ratios (2:1, 1:1 and 1:2).

The preparation procedure of Smopex-101 (Smoptech Ltd.) has been described in a previous paper [36]. Three different batches of Smopex-101 were used, which had the capacities, 3.0, 3.2 and 3.5 mmol/g determined by acid-base titration and diameter 10 μm.

### 2.1. Density and viscosity measurements

Density measurements of the reaction liquid were carried out with an Anton Paar DMA 512 P densitometer equipped with a mPDS 2000 analyzer. The densitometer had a U-formed thin capillary tube. The capillary tube acts as an oscillator, the frequency of which depends on the injected substance. The densitometer was calibrated with distilled water at the experimental temperatures (60, 70 and 75 °C).

Viscosity measurements were performed with a thermostated Ostwald viscosimeter (Normschliff Gerätebau Wertheim, No. 2, 75–100 s). The viscosity was calculated from the flow time of the liquid in the viscosimeter. The flow time of distilled water,

which has a well-known density and viscosity, was compared to the flow time of the experimental liquid.

### 3. Results

#### 3.1. Physical properties

The temperature dependence of the viscosities of the reactant mixtures followed the Andrade equation:

$$\ln \eta_i(\text{cP}) = \frac{A'_i - B'_i}{T} \quad (1)$$

where  $A'_i$  and  $B'_i$  are constants. Temperature has the unit (K).

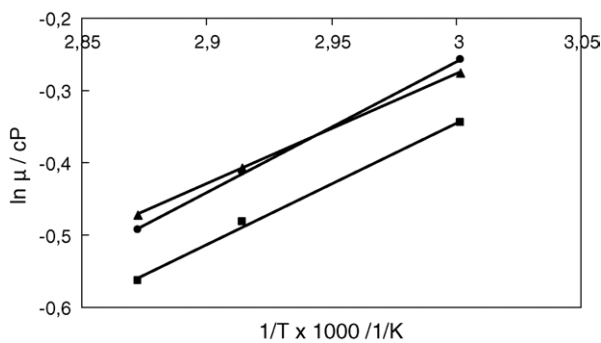


Fig. 1. The effect of temperature on the viscosity of propanoic acid with ethanol at different acid-to-alcohol molar ratio, 1:1 (●), 1:2 (■) and 2:1 (▲).

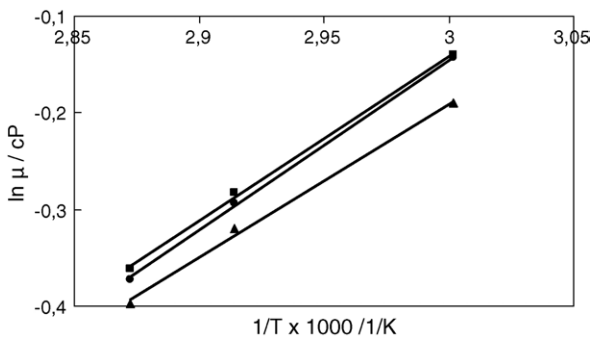


Fig. 2. The effect of temperature on the viscosity of propanoic acid with propanol at different acid-to-alcohol molar ratio, 1:1 (●), 1:2 (■) and 2:1 (▲).

Table 1

Experimentally determined Andrade parameters and density parameters for propanoic acid with ethanol and propanol at different acid-to-alcohol molar ratio

Alcohol	Molar ratio	Andrade parameters		Density parameters	
		$A'_i$	$B'_i$	$A''$	$B''$
Ethanol	1:1	-5.663	1800.7	1.402	-0.0016
	1:2	-5.357	1670.5	1.130	-0.0090
	2:1	-4.836	1519.4	1.225	-0.0010
Propanol	1:1	-5.433	1762.7	1.378	-0.0015
	1:2	-5.235	1698.1	1.124	-0.0090
	2:1	-4.939	1582.7	1.208	-0.0090

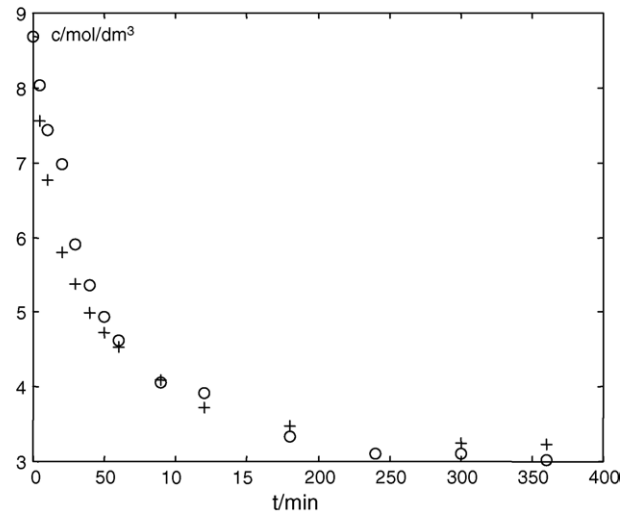


Fig. 3. Esterification of propanoic acid with ethanol (at 60 °C) (○) 0.3 mm long fibers with 50 μm thickness, (+) 4 mm long fibers with 10 and 50 μm thickness.

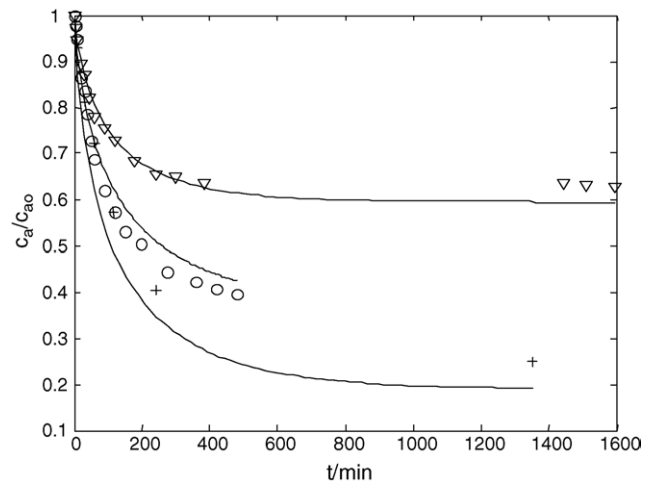


Fig. 4. Esterification of propanoic acid with ethanol (at 60 °C) at acid-to-alcohol molar ratio 2:1 (▽), 1:1 (○) and 1:2 (+). The continuous lines represent the model predictions (Eq. (23)).

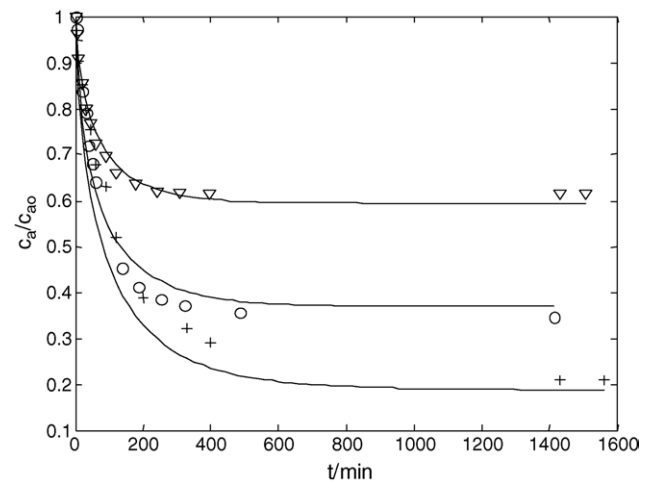


Fig. 5. Esterification of propanoic acid with ethanol (at 70 °C) at acid-to-alcohol molar ratio 2:1 (▽), 1:1 (○) and 1:2 (+). The continuous lines represent the model predictions (Eq. (23)).

Table 2  
Experimentally measured kinematic viscosity and density values as well as calculated dynamic viscosity for reactant mixtures

Acid	Alcohol	$T$ (°C)	Initial molar ratio	$\nu$ (cSt)	$\rho$ (g/cm <sup>3</sup> )	$\mu$ (cP)
Propanoic	Ethanol	60	1:1	0.873	0.8846	0.773
		70	1:1	0.764	0.8666	0.662
		75	1:1	0.710	0.8619	0.612
		60	1:2	0.840	0.8433	0.709
		70	1:2	0.740	0.8347	0.618
		75	1:2	0.686	0.8304	0.570
		60	2:1	0.839	0.9051	0.760
		70	2:1	0.744	0.8955	0.666
		75	2:1	0.700	0.8907	0.624
	1-Propanol	60	1:1	0.989	0.8760	0.867
		70	1:1	0.868	0.8585	0.745
		75	1:1	0.807	0.8540	0.689
		60	1:2	1.070	0.8378	0.896
		70	1:2	0.910	0.8292	0.754
		75	1:2	0.845	0.8249	0.697
		60	2:1	0.922	0.8971	0.827
		70	2:1	0.818	0.8878	0.727
		75	2:1	0.761	0.8831	0.672
	Butanol	60	1:1	1.070	0.8699	0.931

The densities were correlated with temperatures:

$$\rho \left( \frac{\text{g}}{\text{cm}^3} \right) = A'' + B''T \quad (2)$$

where  $A''$  and  $B''$  are constants.

The Andrade parameters were estimated from the slopes of the Figs. 1 and 2 and are listed in Table 1, where also the temperature dependencies of the densities of the reaction mixtures are presented. The experimentally measured kinematic viscosity and density values as well as calculated dynamic viscosity are listed in Table 2.

### 3.2. Modeling of intraparticle diffusion

The accessibility of active sites could be hindered by diffusion in polymers, which could be important especially in case of reaction in the liquid phase with extensive polymer swelling. The modeling of intraparticle diffusion follows our previous article [34].

With the aid of the normalized Thiele modulus the role of internal mass transfer resistance inside the catalyst particles was revealed. The normalized Thiele modulus is defined as:

$$\phi^* = \frac{\phi}{\left[ 2 \int_0^1 r' dy \right]^{1/2}} = \frac{\phi}{\omega} \quad (3)$$

Table 3  
Effective diffusion coefficient, normalized Thiele modulus and effectiveness factor for Smopex-101,  $\varepsilon = 0.25$

Acid	Alcohol	$T$ (°C)	Initial molar ratio	$D_A$ (m <sup>2</sup> /s)	$D_{e,A}$ (m <sup>2</sup> /s)	$\phi^*$	$\eta_e$
Propanoic	Ethanol	60	1:1	$2.24 \times 10^{-9}$	$5.60 \times 10^{-10}$	0.35	>0.99
		70	1:1	$2.68 \times 10^{-9}$	$6.69 \times 10^{-10}$	0.43	>0.99
		75	1:1	$2.94 \times 10^{-9}$	$7.35 \times 10^{-10}$	0.53	>0.99
		60	1:2	$2.28 \times 10^{-9}$	$5.69 \times 10^{-10}$	0.41	>0.99
		70	1:2	$2.69 \times 10^{-9}$	$6.72 \times 10^{-10}$	0.46	>0.99
		75	1:2	$2.96 \times 10^{-9}$	$7.40 \times 10^{-10}$	0.66	0.99
		60	2:1	$2.40 \times 10^{-9}$	$6.00 \times 10^{-10}$	0.34	>0.99
		70	2:1	$2.82 \times 10^{-9}$	$7.04 \times 10^{-10}$	0.42	>0.99
		75	2:1	$3.05 \times 10^{-9}$	$7.63 \times 10^{-10}$	0.56	>0.99
	1-Propanol	60	1:1	$1.95 \times 10^{-9}$	$4.88 \times 10^{-10}$	0.32	>0.99
		70	1:1	$2.33 \times 10^{-9}$	$5.82 \times 10^{-10}$	0.54	>0.99
		75	1:1	$2.55 \times 10^{-9}$	$6.38 \times 10^{-10}$	0.62	0.99
		60	1:2	$1.80 \times 10^{-9}$	$4.49 \times 10^{-10}$	0.40	>0.99
		70	1:2	$2.13 \times 10^{-9}$	$5.33 \times 10^{-10}$	0.55	>0.99
		60	2:1	$2.18 \times 10^{-9}$	$5.44 \times 10^{-10}$	0.16	>0.99
		70	2:1	$2.55 \times 10^{-9}$	$6.38 \times 10^{-10}$	0.37	>0.99
		75	2:1	$2.80 \times 10^{-9}$	$7.00 \times 10^{-10}$	0.38	>0.99
		Butanol	60	1:1	$1.87 \times 10^{-9}$	$4.67 \times 10^{-10}$	0.37

where  $r'$  and  $y$  denote the normalized reaction rate and normalized concentration of the key reactant, respectively. If the carboxylic acid is chosen to be the key reactant,  $y = c_A/c_A^B$ , where  $c_A$  and  $c_A^B$  denote the concentration inside the particle and in the liquid bulk, respectively. The normalized reaction rate ( $r'$ ) is defined  $r' = r(c_A)/r(c_A^B)$ .

The initial rate was used to evaluate the role of mass transfer at the moment when the reaction rate is the fastest. At the beginning of the reaction, no reaction products are present, and the expression for irreversible second-order kinetics can be used,  $r = kc_A c_B$ , where  $c_B = \alpha c_A$ . The expression for  $r$  becomes:  $r = c_A \alpha c_A / (c_A^B (\alpha c_A^B))$ . Thus, the expression for  $r'$  is  $y^2$ . The integral  $(2 \int_0^1 r' dy)^{1/2}$  becomes  $\omega = \sqrt{2/3}$  under the actual circumstances.

The Thiele modulus [42] ( $\phi$ ) for a second-order reaction is defined as:

$$\phi^2 = \frac{r_{y=1} \rho_P}{D_{e,A} c_A^B} R^2 \quad (4)$$

where  $r$  is the experimentally recorded reaction rate,  $D_{e,A}$  the effective diffusion coefficient and  $R$  is the particle radius, i.e. the diffusion distance. The effective diffusion coefficient ( $D_{e,A}$ ) is obtained from the molecular diffusion coefficient ( $D_A$ ) and the particle porosity-to-tortuosity ratio:  $D_{e,A} = (\varepsilon_P/\tau_P) D_A$ . The initial rate is obtained from the experimentally recorded kinetic curves, i.e. from the derivative of the concentration of A at  $t=0$ :  $r = -(dc_A/dt)_{t=0}/\rho_B$ . Thus, the final expression for normalized Thiele modulus at the beginning of the reaction becomes:

$$\phi^{*2} = \frac{-(dc_A/dt)_{t=0} \rho_P R^2}{\omega \rho_B (\varepsilon_P/\tau_P) D_A c_{0A}} \quad (5)$$

The molecular diffusion coefficient ( $D_A$ ) can be evaluated from the Wilke–Chang equation [41] for molecular diffusion coefficients in liquid phase,

$$D_A = \frac{7.4 \times 10^{-12} \sqrt{\Phi' M T}}{(V_A)^{0.6} \mu} \quad (6)$$

where  $\Phi'$  and  $M$  denote the association factor and the molar mass (g/mol) of the solvent,  $V_A$  (cm<sup>3</sup>/mol) the molar volume at normal boiling point and  $\mu$  is the dynamic viscosity of the solution (cP). For solvent-mixtures,  $\sqrt{\Phi' M} = \sqrt{\sum x_j \Phi'_j M_j}$ .

The dynamic viscosity was obtained from laboratory measurements of the kinematic viscosity ( $\nu$ ) and density ( $\rho$ ):  $\mu = \nu \rho$ . The molar volumes of the carboxylic acids at the normal boiling point were calculated from the atomic increments of Le Bas [41].

The physical parameters for propanoic acid and ethanol, 1-propanol and butanol valid for the initial conditions ( $t=0$ ,  $c_A = c_{0A}$ ) are listed in Table 2.

The uncertain factor in the evaluation of the Thiele modulus is the porosity-to-tortuosity ratio. An order of magnitude estimate can be obtained by setting  $\varepsilon_P/\tau_P \in [0.25, \dots, 0.5]$ , which is realistic for most catalysts. The effective diffusion coefficient ( $D_{e,A}$ ) was approximately  $4\text{--}6 \times 10^{-10}$  m<sup>2</sup>/s (Table 3). The values of the effectiveness factors were obtained from the Thiele modulus

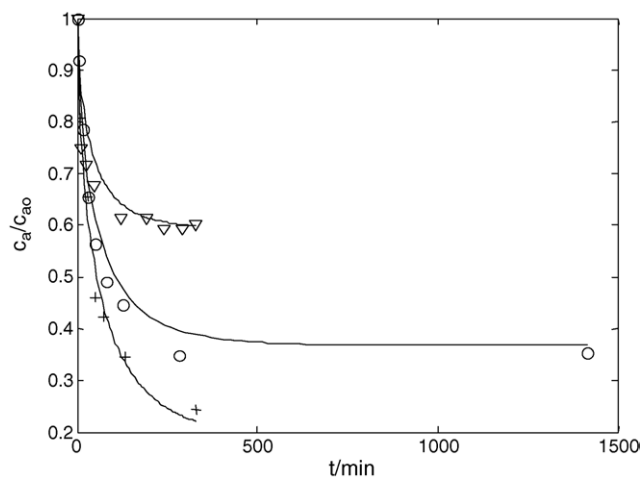


Fig. 6. Esterification of propanoic acid with ethanol (at 75 °C) at acid-to-alcohol molar ratio 2:1 ( $\nabla$ ), 1:1 ( $\circ$ ) and 1:2 ( $+$ ). The continuous lines represent the model predictions (Eq. (23)).

by using the generalized graphs of Aris [42] and are 0.98 and higher (Table 3). Polymers swell in solvents, which affects the interparticle diffusion. The catalyst manufacturer has given the information that Smopex-101 swells seven times by weight in water and five times in methanol. Calculations by mass swelling number with assumption that no elongation of fibers exist gives effectiveness factors, which exceed 0.93. We can thus conclude that the fiber catalyst, Smopex-101 operated practically under diffusion-free conditions. This conclusion is further supported with experiments, where the fiber length and thickness were changed (Fig. 3) resulting in the same values of reaction rates. The further treatment of the experimental data can thus safely be based on the concept of intrinsic kinetics observed in the experiments.

### 3.3. The effect of reactant molar ratio and reaction temperature

The results from the esterification of propanoic acid with ethanol over Smopex-101 at 60 °C with different initial molar ratios are shown in Fig. 4. To facilitate comparison the data relative initial concentrations are used. An increase of alcohol concentration leads to an increase of the final conversion. The same can be noticed in Figs. 5 and 6, where the results from esterification of propanoic acid with ethanol at 70 and 75 °C with different initial molar ratios are presented. The use of excess alcohol is typical in order to shift the equilibrium towards the formation of the ester [15,43,44]. Furthermore, high initial amount of acid has a retarding effect on the esterification kinetics (Figs. 4–6). Altiokka and Çitak [45] have noticed in the esterification of acetic acid with isobutanol over an ion-exchange resin that the initial reaction rate increases linearly with acid concentration and for alcohol, such an increase is linear only at low alcohol concentrations, but is nearly independent of it at high levels.

In Figs. 7–12, the results from esterification of propanoic acid with 1-propanol and butanol at different temperatures (60,

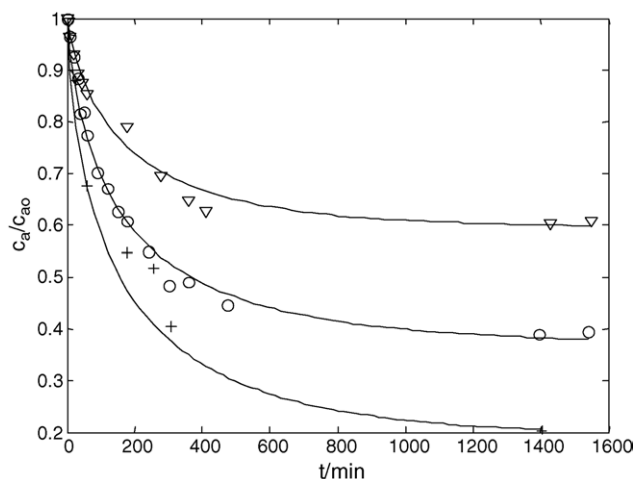


Fig. 7. Esterification of propanoic acid with 1-propanol (at 60 °C) at acid-to-alcohol molar ratio 2:1 ( $\nabla$ ), 1:1 ( $\circ$ ) and 1:2 ( $+$ ). The continuous lines represent the model predictions (Eq. (23)).

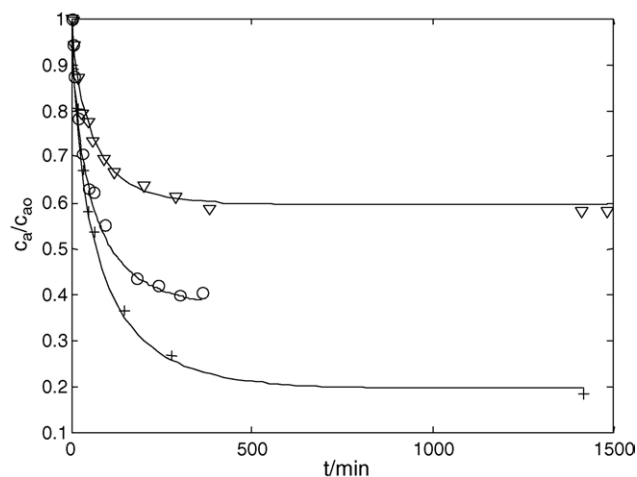


Fig. 9. Esterification of propanoic acid with 1-propanol (at 75 °C) at acid-to-alcohol molar ratio 2:1 ( $\nabla$ ), 1:1 ( $\circ$ ) and 1:2 ( $+$ ). The continuous lines represent the model predictions (Eq. (23)).

70 and 75 °C (80 °C for butanol)) at different acid-to-alcohol molar ratios (1:1, 1:2 and 2:1) are presented. The higher is the excess of alcohol the higher is the final conversion, as with esterification of propanoic acid with ethanol. When comparing the same reactant molar ratios at different temperatures, the final conversion is almost independent of temperature, as can be seen in Figs. 4–12. On the other hand, Yadav and Kulkarni [43] have found in esterification of lactic acid with isopropanol over an ion-exchange resin that the conversion increases with temperature, and Liu and Tan [3] reported, that the conversion is dependent on both the temperature as well as on the catalyst concentration in the esterification of propanoic acid with *n*-butanol over an ion-exchange resin.

The reaction enthalpy was calculated from the experimentally recorded values of equilibrium constants assuming that the reaction is isoentropic. Small positive values were obtained for  $\Delta H$  for both ethanol, 1-propanol and butanol corresponding well with data reported in the literature, showing that esterification is

a reaction without significant changes in enthalpy. Altiokka and Çitak [45] determined that the equilibrium constant has a value of 4 between 30 and 90 °C. In the case of homogeneous catalysis, e.g. esterification of formic acid and methanol with sulphuric acid, Indu et al. [46] found that between 35 and 65 °C the equilibrium constant has an approximate value 8.7. Contradictory results have been given by Petro and Marvec [47] who found in esterification of 1-pentanol with isobutyric acid and benzyl alcohol with acetic acid over sulphuric acid that the equilibrium constant has the tendency to decrease slightly with temperature.

From Figs. 4–12 can also be noticed that the esterification rate increases with increasing temperature, similar to esterification of propanoic acid with methanol [34]. Fig. 13 demonstrates the Arrhenius plot of the second-order forward rate constant in esterification of propanoic acid and ethanol, 1-propanol and butanol recorded at three temperatures. The apparent activation energy estimated from the slope of the Arrhenius plot is in case of ethanol ca. 52.6 kJ/mol, 49.9 kJ/mol for 1-propanol

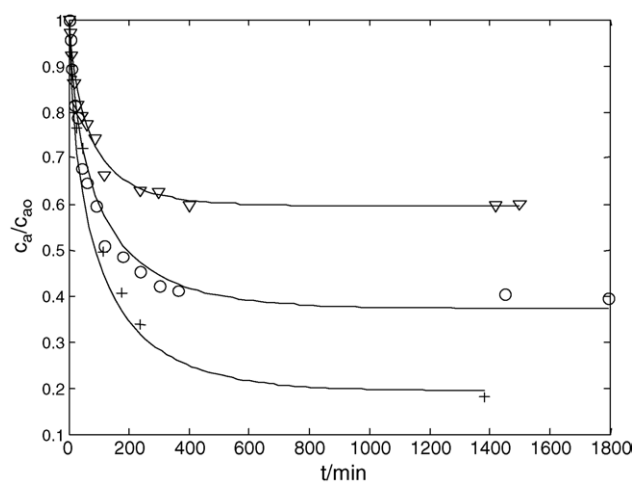


Fig. 8. Esterification of propanoic acid with 1-propanol (at 70 °C) at acid-to-alcohol molar ratio 2:1 ( $\nabla$ ), 1:1 ( $\circ$ ) and 1:2 ( $+$ ). The continuous lines represent the model predictions (Eq. (23)).

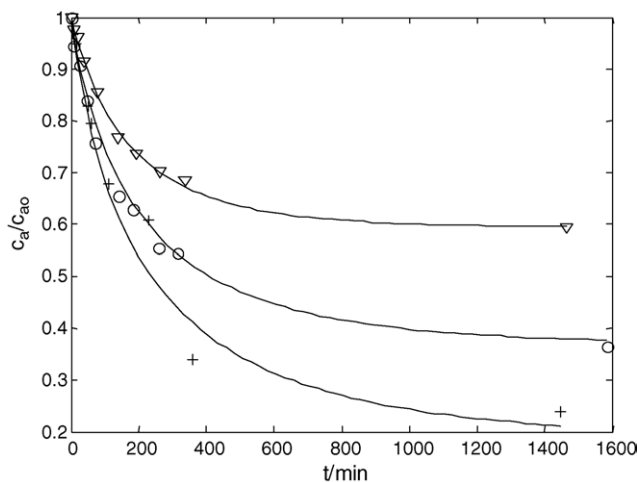


Fig. 10. Esterification of propanoic acid with butanol (at 60 °C) at acid-to-alcohol molar ratio 2:1 ( $\nabla$ ), 1:1 ( $\circ$ ) and 1:2 ( $+$ ). The continuous lines represent the model predictions (Eq. (23)).



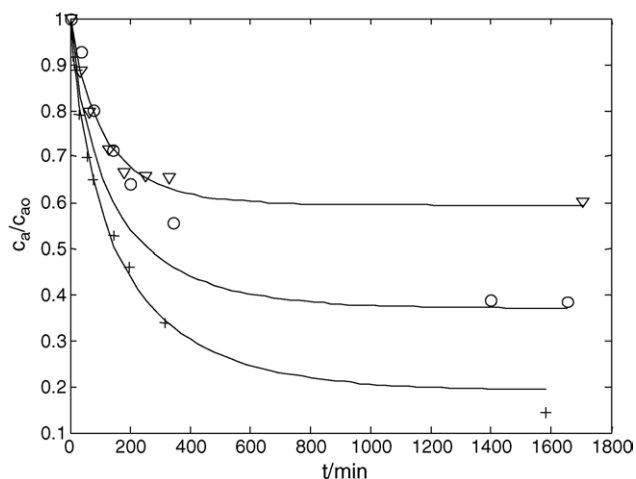


Fig. 11. Esterification of propanoic acid with butanol (at 70 °C) at acid-to-alcohol molar ratio 2:1 ( $\nabla$ ), 1:1 ( $\circ$ ) and 1:2 ( $+$ ). The continuous lines represent the model predictions (Eq. (23)).

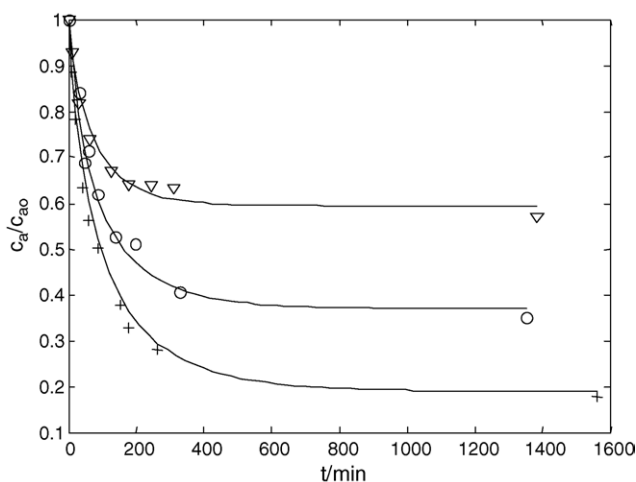


Fig. 12. Esterification of propanoic acid with butanol (at 80 °C) at acid-to-alcohol molar ratio 2:1 ( $\nabla$ ), 1:1 ( $\circ$ ) and 1:2 ( $+$ ). The continuous lines represent the model predictions (Eq. (23)).

and 47.3 kJ/mol for butanol. Even if these values should be taken with care due to narrow temperature interval, they correlate quite well with literature; Liu and Tan [3] have investigated esterification of propionic acid with *n*-butanol over Amberlyst 35 and found out that activation energy is 59 kJ/mol. For the same

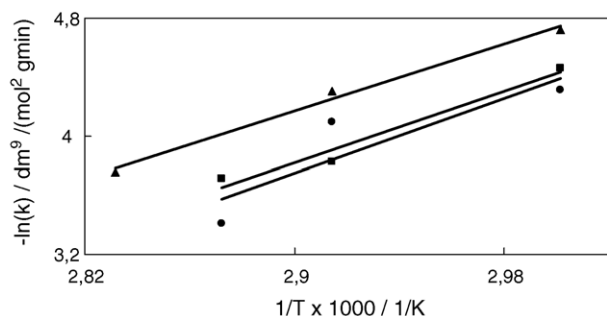


Fig. 13. The effect of temperature on the esterification rate constant of propanoic acid with ethanol ( $\bullet$ ), propanol ( $\blacksquare$ ) and butanol ( $\blacktriangle$ ).

reaction Lee et al. [21] have calculated a bit higher value for activation energy, 63.7 kJ/mol. Lower values have been reported by Aboul-Magd et al. [48], for esterification of propanoic acid with propanol 33.3 kJ/mol and with butanol 34.0 kJ/mol. The same author Aboul-Magd has also given activation energy for esterification of propanoic acid with ethanol in another publication [49].

## 4. Discussion

### 4.1. Mathematical model for esterification kinetics

Modeling of esterification kinetics is traditionally done in a way, which is typical for homogeneous catalysis, i.e. the mechanistic steps are copied from text books of organic chemistry and a rate equation, which includes the catalyst, reactant and product concentrations is proposed. In our previous works [34,35] we have, however, shown that this is not by any means sufficient for heterogeneous catalytic kinetics; the obtained kinetic parameters are dependent on the acid-to-alcohol ratio, which shows that they are not intrinsic parameters. The proper mechanistic approach is then to consider the interactions of the reactant and product molecules with the catalyst surface.

There exist many different approaches about the adsorption strengths of the reaction components. For example, Altiokka and Çitak [45], in esterification of acetic acid with isobutanol in dioxane with Amberlite IR-120 as catalyst, have used a reaction mechanism based on the Eley–Rideal model, that is, the reaction takes place between adsorbed molecules of alcohol and the molecules of acid in the bulk solution. The esterification of propanoic acid with *n*-butanol over Amberlyst 35 was found to follow the Rideal–Eley theory, too [3].

In gas-phase esterification of acetic acid and ethanol over MCM-41 a Langmuir–Hinshelwood type model, involving a protonated acetic acid intermediate has been utilized [6]. Also few other authors have used the Langmuir–Hinshelwood type model, namely Giménez et al. [51] in vapor-phase esterification of acetic acid with ethanol over a macroporous sulphonated styrene-divinylbenzene resin and Pöpken et al. [26] in liquid phase esterification of acetic acid with methanol over ion-exchange resin, Amberlyst 15. González and Fair modified the Langmuir–Hinshelwood model by introducing an empirical exponent to the activity of water in the rate expression [50]. The esterification of propionic acid with *n*-butanol over Amberlyst 35 have been described with the quasi-homogeneous model, the Langmuir–Hinshelwood model [21], the Eley–Rideal model and with a modified Langmuir–Hinshelwood model of González and Fair [50]. The Langmuir–Hinshelwood model yielded the best representation of the kinetic behavior [21].

Initially, the modeling in the present study was based on the Langmuir–Hinshelwood model, which is frequently applied, even if it is known, that the mechanism of esterification reactions is significantly more complex [52,53]:

$$r = \frac{k(c_A c_B - c_C c_D / K)}{(1 + K_A c_A + K_B c_B + K_C c_C + K_D c_D)^2} \quad (7)$$

Scientifically correct way is to apply activities instead of concentrations. Activity based modeling is commonly used in esterification by reactive distillation [4,54–59]. The true activity of a species in the reaction mixture depends not only on the concentration of the species, but also on the conditions in the liquid phase, for example, on the concentrations of other species in the mixture, on the ionic strength of the solution and on temperature. Only in case of ideal solutions, the concentrations can be utilized in the modeling. Eq. (7) is then modified to include activities:

$$r = \frac{k(a_A a_B - a_C a_D / K)}{(1 + K_A a_A + K_B a_B + K_C a_C + K_D a_D)^2} \quad (8)$$

The activity coefficients of the reacting components were estimated with the UNIFAC method [60]. According to UNIFAC, an activity coefficient for a component  $i$  is calculated as follows:

$$\ln \gamma_i = \ln \gamma_i^C + \ln \gamma_i^R \quad (9)$$

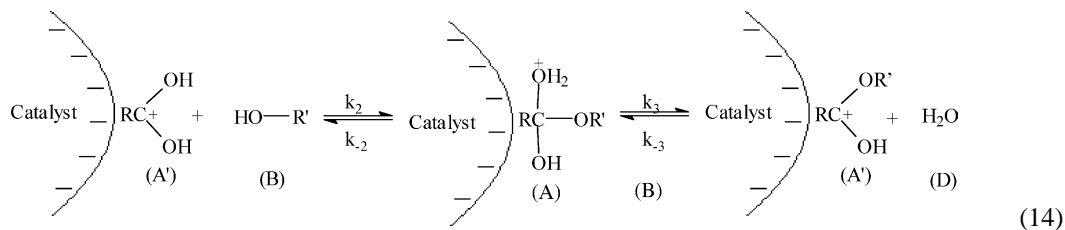
where  $\ln \gamma_i^C$  denotes the combinatorial part, which is defined on the basis of the size and shape differences between the groups and  $\ln \gamma_i^R$  is the residual part describing the energetic interactions between the groups. The parameters  $r$  and  $q$ , the size and shape of the molecules, were not implemented in the modeling. Detailed equations for  $\ln \gamma_i^C$  and  $\ln \gamma_i^R$  are given in the properties of gases and liquids by Aris [42].

The mass balance for an arbitrary component  $i$  in the batch reactor is given by:

$$\frac{dn_i}{dt} = \nu_i r m_{cat} \quad (10)$$

where  $\nu$  is the stoichiometric constant. The amount of substance is related to the concentration and to the liquid volume:  $n_i = c_i V_L$ .

The differential Eq. (10) combined with the rate expression (8) was solved numerically with the backward difference method using the software Odessa [61]. The differential equation solver



operated under a parameter estimation routine, which minimized an objective function, the residual sum of squares:

$$Q = \sum_t (c_A(t) - \hat{c}_A(t))^2 \quad (11)$$

where  $c_A$  and  $\hat{c}_A$  denote the experimental and predicted activities. A hybrid Simflex–Levenberg–Marquardt algorithm was used in the minimization of the objective function. The numerical algorithm was included in the program package MODEST [61].

The quality of the model fit and the model parameters were tested by calculating the standard deviations of the parameters and the degree of explanation of the model. The degree of explanation was defined as follows:

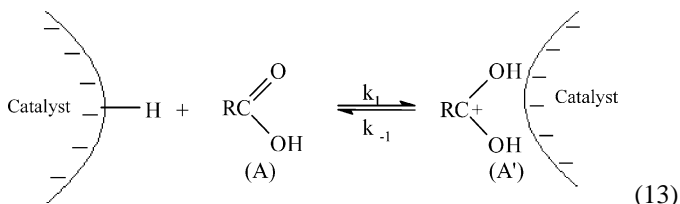
$$R^2 = 1 - \frac{\sum (c_A - \hat{c}_A(t))^2}{\sum (c_A(t) - \bar{c}_A)^2} \quad (12)$$

where  $\bar{c}_A$  is the average value of the experimentally recorded concentrations.

The results of parameter estimation for Langmuir–Hinshelwood model are presented in Fig. 14. As one can see the description was rather bad with poor identifiability of parameters, showing also quite high correlation. Therefore, a more mechanistically sound kinetic model with less parameter was tested and will be described below.

#### 4.2. Kinetic modeling

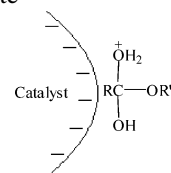
The esterification process starts by a proton donation from the sulphonic acid group to the carboxylic acid (RCOOH). To maintain the charge equilibrium the carboxylic acid remains at the surface of the catalyst as demonstrated below:



The proton is first transferred to the oxygen giving it a positive charge, but then the positive charge is delocalized over the whole of the right-hand end of the ion, with a fair amount of positiveness on the carbon atom.

After the proton transfer the carboxylic acid is susceptible to a nucleophilic attack of the hydroxyl group of the alcohol (R'OH). The subsequent steps can be summarized to

The step (14) is a complex one, and consists of formation of the short living intermediate



which is then losing water.

The positive charge of species A' is actually delocalized all over that end of the ion. In the final reaction step, the sulphonic



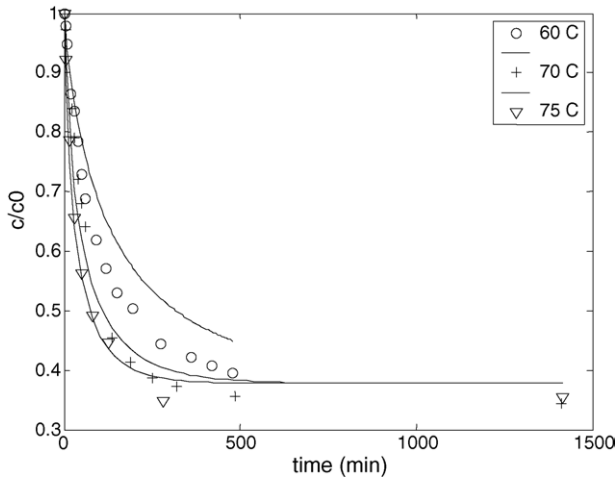
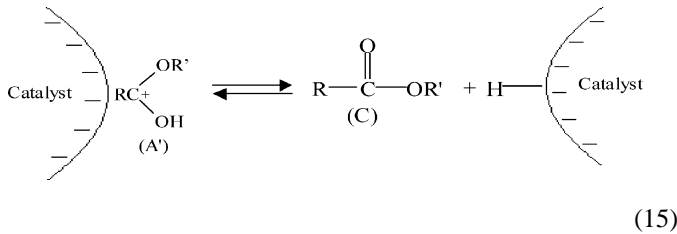
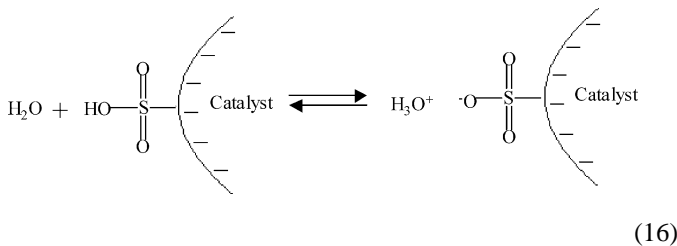


Fig. 14. Esterification of propanoic acid with ethanol with model predictions according to Eq. (8).

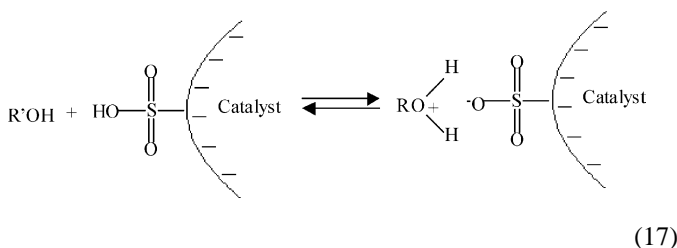
acid group of the catalyst is regenerated:



It is well-known that water molecules interact with sulphonic acid through protolysis equilibria,



Similarly, alcohol molecules can act as weak bases and receive the proton from sulphonic acid:



A step analogous to steps (16) and (17) is improbable for ester molecules; therefore, the interaction of ester with the catalyst surface is discarded.

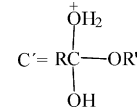
The discussion above indicates that the adsorption of carboxylic acid, alcohol and water are of importance for the reaction. For alcohol, the active form in the catalysis is, however, the dissolved form being present in the liquid bulk as follows from the analysis of structure–activity relationship [35].

A reasonable assumption is that the protolysis equilibria (16) and (17) are rapid. In addition, the nucleophilic attack (14) is equally claimed to be rate determining in esterification. This assumption is used below in evaluating the model against experimental evidences.

The rate of the rate-determining step is thus given by

$$r = k_2\theta_A c_B - k_{-2}\theta_{C'} \tag{18}$$

where



As already mentioned above scientifically correct way is to apply activities instead of concentrations. After applying the quasi-equilibrium hypothesis to the remaining steps and Langmuir’s adsorption isotherm

$$\theta_i = \frac{K_i a_i}{1 + K_i a_i + \sum K_j a_j} \tag{19}$$

where  $i \neq j$  and  $i, j = A, B, C'$  and D, the following rate expression is obtained:

$$r = \frac{k(a_A a_B - a_C a_D / K)}{1 + K_A a_A + K_B a_B + K_D a_D} \tag{20}$$

where  $K$  is the concentration-based equilibrium constant of the overall reaction. It should be remembered that  $k$  is a combined rate constant incorporating not only the intrinsic rate constant but also adsorption equilibrium constants.

In the mechanistic model the adsorption of alcohol is neglected according to our previous considerations, based on structure–activity relationship [34,35]. The number of free sulphonic acid sites ( $-\text{SO}_3\text{H}$ ) might be smaller than the sum of the sites occupied by carboxylic acid and water, i.e.  $1 \ll K_A a_A + K_D a_D$ . After lumping the rate and adsorption equilibrium constants, the following rate expression is formed:

$$r = \frac{a_A a_B - a_C a_D / K}{\alpha a_A + \beta a_D} \tag{21}$$

where  $\alpha = K_A/k$  and  $\beta = K_D/k$ .

By introducing the temperature dependencies,  $\alpha = \alpha_0 e^{(E_1/T)}$  and  $\beta = \beta_0 e^{(E_2/T)}$ , where  $E_i = E/R$ , the Eq. (21) can be written as:

$$r = \frac{a_A a_B - a_C a_D / K}{\alpha_0 e^{+E_1/T} a_A + \beta_0 e^{+E_2/T} a_D} \tag{22}$$

The mass balance for an arbitrary component  $i$  in the batch reactor is given by Eq. (10) leading finally after introducing the activity coefficients,  $a_i = \gamma_i c_i$  to the following equation:

$$\frac{dc_A}{dt} = - \frac{(\gamma_A c_A \gamma_B c_B - \gamma_C c_C \gamma_D c_D / K K_\gamma) c_{\text{cat}} \rho_B}{\bar{\alpha}_0 e^{+E'_1(1/T-1/\bar{T})} \gamma_A c_A + \bar{\beta}_0 e^{+E'_2(1/T-1/\bar{T})} \gamma_D c_D} \tag{23}$$

where  $\bar{T}$  is the average temperature of the experiments and  $\rho_B$  is the catalyst bulk density defined as  $\rho_B = m_{\text{cat}}/V_L$ . The concentration of B, C and D were obtained from stoichiometry.

Table 4

Estimated equilibrium and lumped constants (activity based modeling Eq. (23)) for the esterification of propanoic acid with ethanol, 1-propanol and butanol over Smopex-101

Parameter	Value		
	Ethanol <sup>a</sup>	Propanol <sup>b</sup>	Butanol <sup>c</sup>
$K$	$2.95 \pm 0.36$	$2.86 \pm 0.21$	$2.91 \pm 0.25$
$\alpha_0$ (mol/(g min dm <sup>6</sup> ))	$3.66 \pm 0.63$	$4.72 \pm 0.35$	$9.63 \pm 0.64$
$\beta_0$ (mol/(g min dm <sup>6</sup> ))	$9.14 \pm 0.28$	$8.16 \pm 0.62$	$7.71 \pm 0.88$
$E_1$ (kJ/mol)	$63.6 \pm 2.6$	$40.5 \pm 11.5$	$44.9 \pm 7.7$
$E_2$ (kJ/mol)	$40.0 \pm 1.7$	$61.4 \pm 10.5$	$47.3 \pm 12.6$

<sup>a</sup> Degree of explanation: 97.83%.

<sup>b</sup> Degree of explanation: 99.26%.

<sup>c</sup> Degree of explanation: 99.30%.

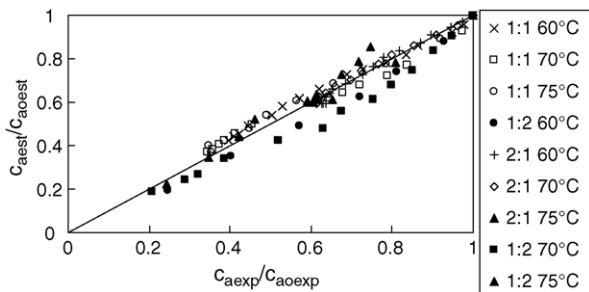


Fig. 15. A parity plot of esterification of propanoic acid with ethanol (Eq. (23)).

The activity based equilibrium constant  $K^T$  is calculated as follows:

$$K^T = K K_\gamma \quad (24)$$

where  $K_\gamma = \gamma_C \gamma_D / \gamma_A \gamma_B$

The estimated equilibrium and lumped constants as well as the degree of explanation for esterification of propanoic acid with ethanol, 1-propanol and butanol over Smopex-101 are pre-

Table 5

Correlation matrix of parameters for the esterification of propanoic acid with ethanol, 1-propanol and butanol over Smopex-101 (Eq. (23))

	$K$	$\bar{\alpha}_0$	$\bar{\beta}_0$	$E_1$	$E_2$
<b>Ethanol</b>					
$K$	1				
$\bar{\alpha}_0$	-0.233	1			
$\bar{\beta}_0$	0.429	-0.794	1		
$E_1$	0.072	-0.460	0.255	1	
$E_2$	-0.032	0.222	-0.114	-0.781	1
<b>1-Propanol</b>					
$K$	1				
$\bar{\alpha}_0$	-0.218	1			
$\bar{\beta}_0$	0.421	-0.783	1		
$E_1$	0.032	0.047	0.049	1	
$E_2$	-0.091	0.059	-0.164	-0.778	1
<b>Butanol</b>					
$K$	1				
$\bar{\alpha}_0$	-0.131	1			
$\bar{\beta}_0$	0.302	-0.808	1		
$E_1$	0.008	-0.049	-0.039	1	
$E_2$	-0.023	-0.040	0.129	-0.815	1

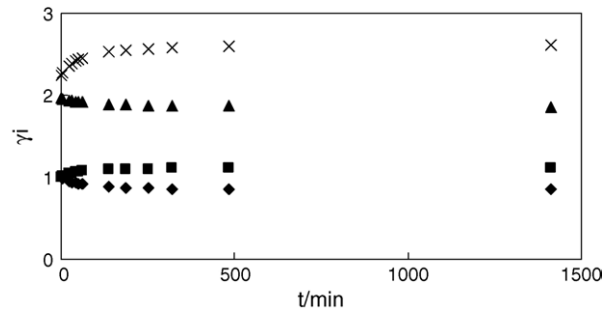


Fig. 16. The activity coefficients, water (x), propanoic acid ethyl ester ( $\blacktriangle$ ), ethanol ( $\blacksquare$ ) and propanoic acid ( $\bullet$ ) of the different species for the esterification of propanoic acid with ethanol at 70 °C with the initial acid-to-alcohol ratio 1:1.

sented in Table 4. The model can explain the experimentally recorded values fairly good, as can be noticed from the degrees of explanation and from the parity plot, Fig. 15. The correlation coefficients (Table 5) of the parameters received acceptably low values, indicating a good identifiability of the parameters.

Table 6

Estimated equilibrium constants (activity based modeling Eq. (23)) for esterification of propanoic acid with ethanol, propanol and butanol at different acid-to-alcohol molar ratio

Alcohol	Molar ratio		
	1:1	1:2	2:1
<b>Ethanol</b>			
60 (°C)			
$K_{\gamma i}$	4.38	5.16	3.87
$K_{\gamma final}$	5.18	6.13	4.44
70 (°C)			
$K_{\gamma i}$	4.42	5.18	3.91
$K_{\gamma final}$	5.16	5.94	4.38
75 (°C)			
$K_{\gamma i}$	4.43	5.18	3.93
$K_{\gamma final}$	5.09	5.81	4.34
<b>Propanol</b>			
60 (°C)			
$K_{\gamma i}$	5.13	6.05	4.50
$K_{\gamma final}$	6.07	6.98	5.13
70 (°C)			
$K_{\gamma i}$	5.17	6.06	4.55
$K_{\gamma final}$	5.92	6.78	5.06
75 (°C)			
$K_{\gamma i}$	5.18	6.05	4.56
$K_{\gamma final}$	5.82	6.66	5.02
<b>Butanol</b>			
60 (°C)			
$K_{\gamma i}$	5.32	6.26	4.64
$K_{\gamma final}$	6.08	6.99	5.11
70 (°C)			
$K_{\gamma i}$	5.35	6.27	4.68
$K_{\gamma final}$	5.93	6.81	5.04
80 (°C)			
$K_{\gamma i}$	5.37	6.26	4.72
$K_{\gamma final}$	5.78	6.61	4.96

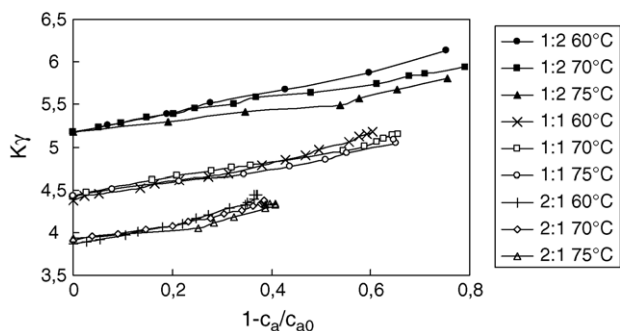


Fig. 17. The equilibrium constant ( $K_\gamma$ ) for esterification of propanoic acid with ethanol at different temperatures and with different acid-to-alcohol molar ratio.

#### 4.3. The effect of the activity coefficients on the modeling

Even though the modeling with the aid of activities is the theoretically correct approach necessity of introducing activity coefficients should be verified. To determine the effect that the activity coefficients have on the outcome, the values of the coefficients should be examined. In Fig. 16, typical values for the activity coefficients for the different species can be seen for the esterification of propanoic acid with ethanol at 70 °C with the initial acid-to-alcohol molar ratio 1:1. The activity coefficients differ from one and are not constant during the reaction. The activity coefficient of water gets the highest value. In Table 6, the values of  $K_\gamma$  in the beginning and at the end of the reaction are presented. The value of the constant changes during the reaction, which indicates that it has an obvious effect on the equilibrium constant, and thus on the modeling of the reaction. Temperature does not have a strong effect on  $K_\gamma$ , Fig. 17. The value  $K_{\gamma\text{final}}$  decreases slightly with increasing temperature.

## 5. Conclusions

The esterification of propanoic acid with ethanol, 1-propanol and butanol has been carried out over a polymer-supported sulfonic acid catalyst, Smopex-101 at different temperatures (60, 70 and 75 °C (80 °C for butanol)), and reactant molar ratios (1:1, 1:2 and 2:1). The increase of temperature increased the reaction rate and the activation energy of esterification of propionic acid with ethanol was found to be 52.6 kJ/mol, 49.9 kJ/mol with 1-propanol and 47.3 kJ/mol with butanol. The higher the excess of alcohol the higher was the final conversion. A small positive value was obtained for reaction enthalpy for ethanol, 1-propanol and butanol showing that esterification is a reaction without significant changes in enthalpy. The experimentally recorded concentrations were modeled according to a model, which included the adsorption of acid and water and incorporated concentration and temperature dependent activity coefficients of the species. Advanced kinetic model explained the reaction kinetics reasonably well.

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