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Kinetic Study of Transesterification of Methyl Acetate with Isobutanol Catalyzed by the Dissociation of Sodium Hydrogen sulphate in Alcoholic Media

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The reaction kinetics of the liquid-phase transesterification of methyl acetate and isobutanol is investigated. The reaction has been catalyzed by sulphuric acid generated by the dissociation of sodium hydrogensulfate in alcoholic media. The experiments are carried out in a stirred batch reactor at different temperatures (50, 70 and 90 ˚C), determining its influence. The experimental results have been modelled assuming a homogeneous model based on the Arrhenius expression. The model fits satisfactorily the experimental data that can be seen from the statistics and errors calculation. A kinetic equation which describes the reaction catalyzed by sodium hydrogen sulfate is provided.

1. Introduction

The Polyvinyl Alcohol (PVA) is a biodegradable polymer and has interesting properties: it is not inflammable and not toxic. PVA is also useful as component for separation membranes (García et al, 2013). However, about 1.68 t of a residual stream is generated for each ton of PVA produced. This residue, called MM80 in the industry, is composed of an azeotropic mixture of methanol (MeOH) and methyl acetate (MeOAc) (80 wt % MeOAc). Methanol is a raw material for the synthesis of PVA, acting as solvent and reactant. Therefore, it should be recirculated to the PVA process. The methyl acetate impurified has a low value. So it is interesting the study the conversion of methyl acetate to a compound with a higher added value. If methyl acetate reacts with an alcohol, then methanol needs for PVA process can be almost entirely satisfied by the methanol generated and recovered. The proposed solution in this study is the equilibrium reaction of transesterification of methyl acetate using isobutanol (IbOH) to methanol and isobutyl acetate (IbOAc) (Eq(1)). Isobutanol can be obtained from renewable sources and isobutyl acetate is a higher value organic solvent than methyl acetate.

$$\mathrm{MeOAc} + \mathrm{IbOH} \Leftrightarrow \mathrm{MeOH} + \mathrm{IbOAc} \qquad (1)$$

There are several studies of transesterification of MeOAc using n-butanol with macroporous acid ion-exchange resins, e.g. Jiménez et al (2002) or Bozek-Winkler and Gmehling (2006). Xianbao et al (2011) proposed the use of ionic liquids as catalyst to avoid the low thermal stability of the ion-exchange resins. The ionic liquid studied had a hydrogensulphate group ([HSO_3-bHim]HSO_4) and a good catalytic activity was reported.

The goal of the present study is to determine the catalyst activity of sodium hydrogensulphate ($NaHSO_4$) in order to elucidate if the catalytic activity observed by Xianbao et al (2011) was promoted by the ionic liquid or the hydrogensulphate group. Moreover, the alcohol media can produce the dissociation of the hydrogensulphate group to sulphuric acid which is a classical homogeneous acid catalyst. The present work is performed using isobutanol instead of butanol in order to complete the several alternative alcohols that can be used for the methyl acetate transesterification, to our knowledge it has not been tested before.

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Several temperatures are studied in order to adjust a kinetic model useful for further process studies. The second order kinetics expression is compared to a Gompertz adjustment, taking into account, in both cases, the effect of the temperature using an Arrhenius-type formulation. The combination between the Gompertz and Arrhenius expressions has been used successfully in literature for some special kinetics, e.g. Gorsek and Zajsek (2010).

2. Experimental

Chemicals**.** Sigma Aldrich supplied the several chemicals required: high-purity methanol (> 99.9 wt%), methyl acetate, isobutyl acetate and isobutanol (> 99 wt%). All purities were checked by gas chromatography.

Catalyst**.** Sodium hydrogen sulphate was manufactured by Fluka (Sigma Aldrich) (> 95 wt%). It was dried at 100 ºC for 24 h.

Apparatus**.** The experiments are conducted in a stainless steel stirred-tank reactor (FC-3 model, 300 mL) manufactured by Pressure Products Industries (Warmister, PA) set up as shown in Figure 1. The unit is equipped with a turbine motor and a digital tachometer speed controller (Dyna/Mag model MM-016-06). The temperature is measured with PT-100 thermometers (accuracy of ±0.1 ºC) and controlled by PID within ±0.2 K with a potentiometer. The pressure indicator is a digital manometer (±0.1 kPa). A filter (45-µm) is used to prevent catalyst form being dragged outside during the sampling.

2.1 Sample Analysis

The analyses are carried out in a Hewlett-Packard (Palo Alto, CA) 5890 Series II Plus gas chromatograph, equipped with a FID detector. It is equipped with a J&W Scientific 123-1364 (DB-624) capillary column manufactured by Agilent Technologies.

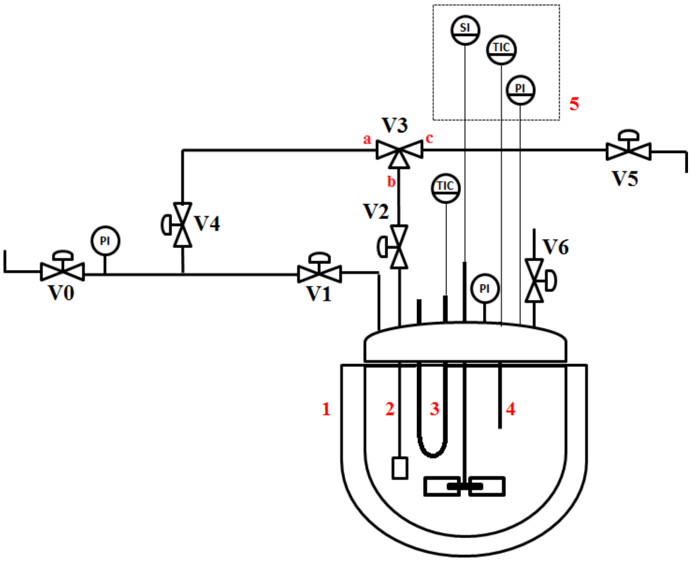


Figure 1: Schematic diagram. 1, heating blanket with electrical resistance; 2, sample point with mesh filter; 3, internal heat exchanger with water; 4, thermometer; 5, control monitor; a, b, c, directions of the V3

Procedure**.** The experiments are performed in a stirred (500 rpm), hermetic and thermostated batch reactor that is pressurized (around 10^6 Pa) with nitrogen to maintain all chemicals in liquid phase. Sodium hydrogen sulphate is charged in a gadget (Figure 2) placed in a pipe that is further pressurized to discharge it and fix the initial time of reaction once the desired temperature set point is reached at the chemicals inside the reactor. The initial composition is equimolar and checked by a first initial analysis. The amount of catalyst used is around 1.2 % wt. Samples around 250 µL are collected each 10 - 15 min. The experiments last for 7 - 8 h. For experiments at lower temperature, e.g. 50 ºC, some samples are taken after 24 h to assure that chemical equilibrium has been attained. Two experiments per temperature and per direction of reaction are carried out. A total of 12 experimental runs are made to evaluate the influence of temperature on the kinetics.

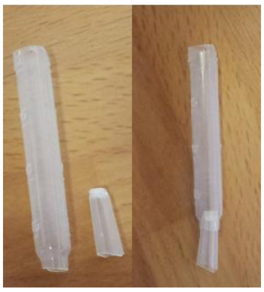


Figure 2: Gadget where sodium hydrogen sulphate is introduced

3. Results and discussion

The experimental results show a good catalyst activity (Figure 3), meaning that the catalyst activity of the ionic liquid used by Xianbao et al (2011) can be attributed mainly to the hydrogen sulphate group. The experimental runs are performed at 323.15 K, 343.15 K and 363.15 K. The reaction rate increases as the temperature increases as expected, but a sigmoid shape becomes evident as the operating temperatures decrease. This initial lag time can be attributed to the dissociation of the sodium hydrogen sulphate to sulphuric acid due to the alcoholic media. At high temperatures, i.e. 363.15 K, a classical kinetic expression can be fitted, but at low temperatures an asymmetric sigmoid function, e.g. Gompertz expression, is required to adjust its behaviour. The results are fitted in two ways, one is obtained by the analytical integration of the kinetic expression without taking into account the lag time and another model is obtained by a numerical adjustment of the kinetic constants taking into account a Gompertz expression. Both models are discussed and compared.

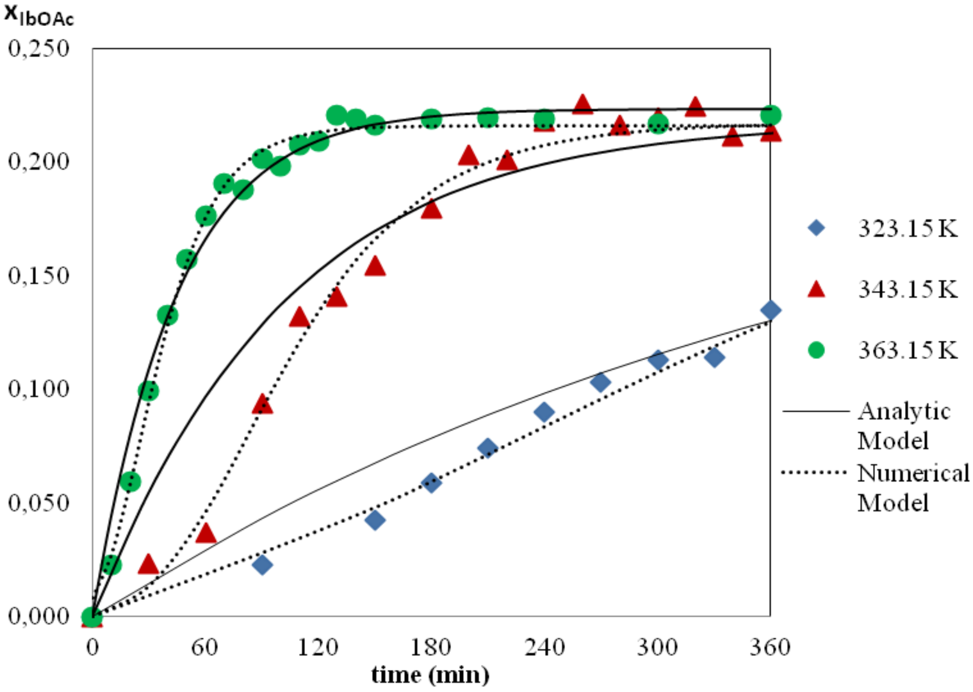


Figure 3: Influence of reaction temperature on IbOAc molar fraction, 1.2% wt of catalyst and initial molar reactant ratio MeOAc/IbOH=1.Solid lines, correlations with Eq (4); dotted lines, correlations with Eq (5)

Assuming that what produces the catalytical activity is the sulphuric acid generated by the hydrogen sulphate dissociation, the reaction rate can be expressed as a homogeneous model - Eq (2). When the stoichiometric coefficients are equal to unity and the initial molar reactant ratio is equal to unity too, the kinetic expression can be solved analytically - Eq (3) (Smith, 2009). This is referred from now on as analytical model. The kinetic parameters (k_i) are fitted at each temperature minimizing the sum of residual squares (SRS) between the experimental and calculated molar fraction of isobutyl acetate. The dependence of the kinetic parameters versus the temperature is fitted to the Arrhenius expression Eq(4). In many cases, the kinetic expression in Eq (2) cannot be solved analytically, and then it is used in the form show in Eq (5) and solved by linear regression. It is expected that the analytical resolution provides a better result than this approximation, but in this case as there is the lag time observed this second way taking into account the sigmoid shape in the calculation of the reaction rate (r) in Eq(5) is also evaluated. This is called from now on as numerical model. The sigmoid shape of the experimental data is taken into account by adjusting the experimental concentrations to a Gompertz expression in Eq(6). Differentiating Eq (6) with respect to time, the expression to calculate the reaction rate at any time is obtained for each temperature. Figure 3 shows that the direct fitting using the Gompertz expression in Eq(6) provides a better adjustment of the experimental points than the expression derived from the homogeneous kinetics in Eq (7). But when the Gompertz is used in Eq (5) to fit to Arrhenius in order to be implemented in a commercial simulator without sigmoid models, then the overall adjustment becomes worst than use directly the non sigmoid analytical model as it is show in the following paragraphs.

$$r = k_1 x_{MeOAc} x_{IbOH} - k_2 x_{MeOH} x_{IbOAc} \tag{2}$$

$$x_A = \frac{\sqrt{k_1 k_2}\left[1 + \exp\left(2x_{A0}\sqrt{k_1 k_2 t}\right)\right]}{\left(k_1 + \sqrt{k_1 k_2}\right)\exp\left(2x_{A0}\sqrt{k_1 k_2 t}\right) - \left(k_1 - \sqrt{k_1 k_2}\right)} x_{A0} \tag{3}$$

$$k_i = A_i \exp\left(-\frac{E_{A,i}}{RT}\right) \tag{4}$$

$$\frac{r}{x_{MeOAc} x_{IbOH}} = k_1 - \frac{x_{IbOAc} x_{MeOH}}{x_{MeOAc} x_{IbOH}} k_2 \tag{5}$$

$$x_i(t) = f(t) = B \cdot \exp\left[-C \cdot \exp(-Dt)\right] \tag{6}$$

Most of the kinetic experiments lasted long enough until the chemical equilibrium was reached. The reaction equilibrium was reached in 6-24 h, based on the reaction temperature. The equilibrium constant of the reaction can be obtained experimentally from the equilibrium composition of the mixture in Eq(7). As reaction of transesterification is only an exchange group reaction, the heat of reaction is very small and the equilibrium constant depends only very slightly on temperature. So it can be assumed that, for the range of temperatures studied, the activation energy of the forward and reverse reaction are equal ($E_{A1}=E_{A2}$) and therefore the chemical equilibrium is constant.

$$K_{eq} = \frac{x_{IbOAc.e} x_{MeOH,e}}{x_{IbOH,e} x_{MeOAc,e}} = \frac{k_1}{k_2} \tag{7}$$

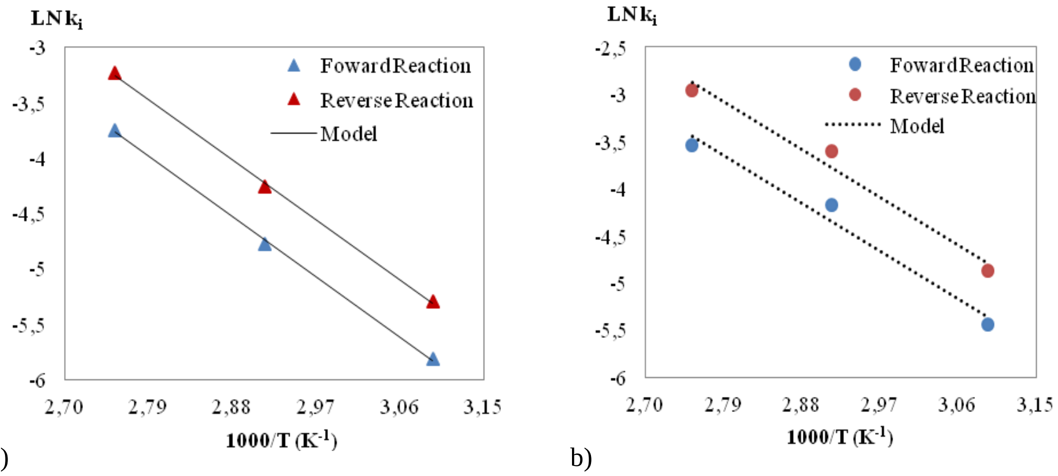
Table 1: Kinetic constants using Eq(2)

Analytical Model			
	Forward reaction	Reverse reaction	Equilibrium
T (K)	k_1 (min^{-1})	k_2 (min^{-1})	K_{eq}
323.15	0.00299 ± 0.00104	0.00501 ± 0,00174	0.5974
343.15	0.00842 ± 0.00105	0.01409 ± 0,00177	0.5974
363.15	0.02352 ± 0.00378	0.03936 ± 0,00565	0.5974

Table 2: Kinetic constants using Eq (5)

	Numerical Model		
	Forward reaction	Reverse reaction	Equilibrium
T (K)	k_1 (min^{-1})	k_2 (min^{-1})	K_{eq}
323.15	0.00432 ± 0.00099	0.00767 ± 0.00175	0.5641
343.15	0.01532 ± 0.00137	0.02716 ± 0.00243	0.5641
363.15	0.02918 ± 0.00104	0.05172 ± 0.00184	0.5641

The kinetic constant values fitted are shown in Table 1 and Table 2. The kinetic constants fitted with the analytical model are smaller than with the numerical model. In some cases are almost half. The errors for the numerical model are in overall smaller than for the analytical model. From these results, the numerical model could be considered advantageous as it takes into account the sigmoid shape. Nevertheless, the analytical method follows well the temperature dependence according to Arrhenius which is not satisfied by the results obtained using the numerical method (Figure 4). Table 3 shows the Arrhenius parameters adjusted for both fittings. Using the Arrhenius fitted parameters to calculate the reaction kinetics; the analytical model reproduces more accurately the experimental data. The errors in Table 4 summarize very well the weak and strong points for both methods. At a fixed temperature, a very good adjustment of the experimental data can be obtained using a Gompertz expression (Figure 3), but it is unable to take into account the temperature influence on the kinetics (Figure 5). Therefore, for the modelling of a single reactor at a fixed temperature, the Gompertz expression works well, but for the design of a reactive distillation column where the temperature change at each stage, the analytical model derived from Eq (3) should be used.



a)

b)

Figure 4: Arrhenius parameter fitting for a) Analytical Model and b) Numerical Model

Table 3: Arrhenius parameters

		Analytical Model		Numerical Model	
Reaction	i	A_i (min^{-1})	$E_{A,i}$ ($kJ \cdot mol^{-1}$)	A_i (min^{-1})	$E_{A,i}$ ($kJ \cdot mol^{-1}$)
Forward	1	388,481.18	50.25	172,301.31	46.81
Reverse	2	650,177.06	50.25	305,590.12	46.81

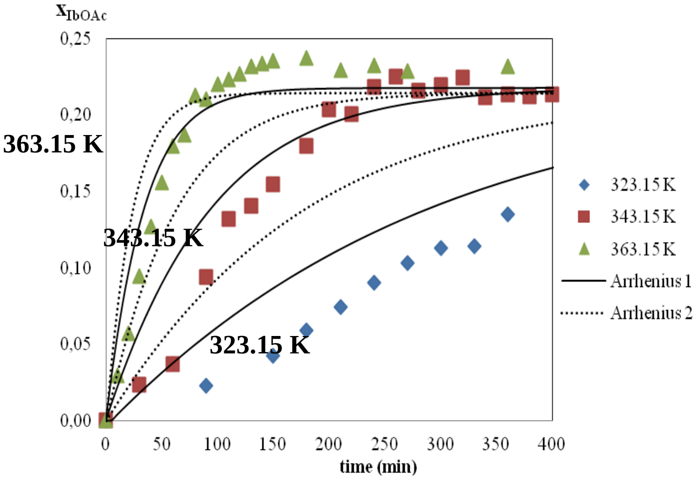


Figure 5: Correlation with Arrhenius parameters. Legend: Arrhenius 1 - Analytical Model; Arrhenius 2 - Numerical Model.

Table 4: Errors in the Estimation of the molar fraction of IbOAc

	Analytical Model		Numerical Model		Arrhenius 1		Arrhenius 2	
T (K)	$\Delta x_{C,med}$ (%)	$\Delta x_{C,max}$ (%)	$\Delta x_{C,med}$ (%)	$\Delta x_{C,max}$ (%)	$\Delta x_{C,med}$ (%)	$\Delta x_{C,max}$ (%)	$\Delta x_{C,med}$ (%)	$\Delta x_{C,max}$ (%)
323.15 K	12.79	24.24	6.68	12.78	14.64	20.89	29.67	53.78
343.15 K	9.70	17.91	3.09	6.77	6.93	10.96	12.43	13.56
363.15 K	7.31	12.68	2.58	3.03	4.78	6.42	8.48	12.61

4. Conclusions

The kinetic study for the synthesis of n-butyl acetate catalyzed by sodium hydrogen sulfate from methyl acetate and isobutanol is carried out. The effect of temperature is studied. The kinetic data are satisfactorily fitted with homogeneous model and the Arrhenius parameters are determined. Unfortunately, at low temperatures the concentration data exhibits a sigmoid shape curve due to the hydrogen sulphate dissociation in alcoholic media. A Gompertz expression fits well the sigmoidal experimental data at constant temperature but it cannot be used in commercial simulation software and does not take into account the temperature dependence.

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