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KINETICS OF THE ESTERIFICATION OF PROPIONIC ACID WITH ISOBUTYL ALCOHOL OVER AMBERLYST 36 AND AMBERLYST 70

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Abstract: The esterification of propionic acid with isobutyl alcohol has been studied in a batch reactor in the presence of Amberlyst 36 and Amberlyst 70 catalysts. Reaction parameters applied in this study are speed of agitation (500-1000 rpm), particle size of catalyst (400-600 μm, 600+ μm), temperature (318-348 K) and catalyst loading (4-12 g-dry resin/L). A pseudo-homogeneous kinetic model was derived and all thermodynamic and kinetic parameters were calculated. Forward reaction rate constant for Amberlyst 36 and Amberlyst 70 determined as follows:

$k_1 = 160171 \exp\left(\frac{-56689}{RT}\right)$ (L mol^{-1} min^{-1})
$k_1 = 293314 \exp\left(\frac{-57292}{RT}\right)$ (L mol^{-1} min^{-1})

In a comparison of the two catalysts used in this study, experimental results showed that Amberlyst 70 is more effective than Amberlyst 36.

Keywords: Esterification, pseudohomogeneous kinetics, Amberlyst 36, Amberlyst 70, Heterogeneous catalysis

Propiyonik Asitin İsobütil Alkol ile Amberlyst 36 ve Amberlyst 70 Katalizörleri varlığında Esterleşme Kinetiği

Öz: Propiyonik asidin izobütil alkol ile esterleşme tepkimesi, Amberlyst 36 ve Amberlyst 70 katalizörlerinin varlığında kesikli bir reaktörde çalışılmıştır. Bu çalışmada; karıştırma hızı (500-1000 rpm), katalizör tanecik boyutu (400-600 μm, 600+ μm), sıcaklık (318-348 K) ve katalizör miktarı (4-12 g kuru reçine / L) reaksiyon parametreleridir. Bir yalancı-homojen kinetik model türetilmiş ve tüm termodinamik ve kinetik parametreler hesaplanmıştır. Amberlyst 36 ve Amberlyst 70 için ileri reaksiyon hızı sabiti aşağıdaki gibi belirlenmiştir:

$k_1 = 160171 \exp\left(\frac{-56689}{RT}\right)$ (L mol^{-1} min^{-1})
$k_1 = 293314 \exp\left(\frac{-57292}{RT}\right)$ (L mol^{-1} min^{-1})

Bu çalışmada kullanılan iki katalizörün karşılaştırmasında deneysel sonuçlar Amberlyst 70'in Amberlyst 36'dan daha etkili olduğunu göstermiştir.

Anahtar Kelimeler: Esterleşme, yalancı homojen kinetik model, Amberlyst 36, Amberlyst 70, Heterojen kataliz

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1. INTRODUCTION

Esterification is a condensation reaction between a carboxylic acid and an alcohol to produce ester and water. Esters, the desired products of esterification reaction, are important chemicals and use in many chemical industries as solvents, plasticizers, flavors, fragrance and biofuel components (Ju et. al. 2011;Pappu et. al. 2013)

Esterification reaction can take place in the absence of catalyst due to the autoprotolysis of the carboxylic acid. In this case, esterification reaction proceeds too slowly. An acid catalyst is employed to accelerate the rate of esterification reaction (Park et. al. 1999; Sharma et. al. 2012). These catalysts are divided into two categories: homogeneous catalysts such as mineral acids (i.e. sulphuric and hydrochloric acid) and heterogeneous catalysts like ion exchange resins, zeolites, heteropoly acids and metal oxides. In last decades, heterogeneous catalysts have been commonly used because of their some advantages such as easily separation from liquid reaction mixture, reusability, high selectivity and environment-friendly (Mitran et. al. 2012; Merchant et. al. 2013).

In the literature, there are various studies related to the esterification reactions of a carboxylic acid with an alcohol in the presence of ion exchange resins such as Amberlite IR-120 (Altıokka and Çıtak, 2003), Amberlyst-15 (Chin et. al. 2015), Dowex 50Wx2 (Çıtak and Bodur, 2007) and Amberlyst 39 (Komon et. al. 2013). Ion exchange resins, most important industrial catalysts nowadays, are synthesized from styrene and divinylbenzene monomers by copolymerization and then they are linked to catalytic functional groups, for example $–SO_3H$ (Rezende et. al. 2008). When compared to other solid acid catalysts, although, ion exchange resins show poor thermal stability, their high concentrations of acid sites have advantages (Siril et. al. 2008).

Amberlyst 36 and Amberlyst 70 catalysts were developed as thermally stable ion exchange resins up to 423K and 493K, respectively. They also have more acid sites. Several studies were reported for organic reactions in the presence of Amberlyst 36 (Tsai et. al. 2011; Schmid et. al. 2008; Akbay and Altıokka 2011; Aguiar et. al. 2017) and Amberlyst 70 (Chandak et. al. 2011; Bringue et. al. 2011; Guilera et. al. 2015; Casas et. al. 2017). On the other hand, Amberlyst 36 and Amberlyst 70 were compared in liquid phase dehydration of 1-pentanol to di-n-pentyl-ether (Bringue et. al. 2006). Though Amberlyst-70 has lower acidity than that of Amberlyst 36, it has been reported that Amberlyst 70 shows higher 1-pentanol conversion and yield of di-n-pentyl-ether. In another study, several solid acid catalysts including Amberlyst 36 and Amberlyst 70 were used in the reaction of methanol dehydration to dimethyl ether. Amberlyst 36 showed more activity than Amberlyst 70 for methanol conversion and the amount of the dimethyl ether formation (Hosseininejad et. al. 2012).

Isobutyl propionate has rum-like fruity odor and is used in the food industry for artificial flavor and fragrances. Esterification of propionic acid with isobutyl alcohol gives isobutyl propionate and water:

$$C_2H_5COOH + C_4H_9OH \longleftrightarrow C_2H_5COOC_4H_9 + H_2O \quad (1)$$

Propionic acid (PA)
Isobutyl alcohol (IBA)
Isobutyl propionate (IBP)
Water (W)

The aim of this study is to investigate the esterification reaction of propionic acid with isobutyl alcohol in the presence of Amberlyst 36 and Amberlyst 70 catalysts. The effects of the speed of agitation, particle size of catalyst, temperature and catalyst loading on the reaction were studied over both catalysts. In the light of the results of these parameters, overall reaction control step was determined and discussed. Thermodynamics and reaction kinetics of esterification of propionic acid with isobutyl alcohol were also studied.

2. EXPERIMENTAL

2.1. Materials

Propionic acid (98%, Merck) and isobutyl alcohol (98.5%, Merck) were used as reactants and 1,4-dioxan (99.8%, Carlo Erba) was used as solvent. Moreover, Amberlyst 36 and Amberlyst 70 were used as catalysts in the experiments. The properties of the catalysts are listed in Table 1. Amberlyst 36 and Amberlyst 70 were washed with methanol and water until obtaining a colorless liquid. Catalysts were dried in a vacuum oven at 348 K. They were sieved and kept in a desiccant after water content removed completely.

Table 1.Physical and chemical properties of Amberlyst 36 and Amberlyst 70

Resin	Amberlyst 36	Amberlyst 70
Matrix	Styrene Divinylbenzene medium cross-linking degree [a]	Styrene Divinylbenzene low cross-linking degree[a]
Cation exchange capacity	5.38[b]	2.7 [b]
Maximum operating	423 [b]	463 [b]
Surface area (m^2 g^{-1})	33 [b]	36 [b]
Average pore diameter (Å)	240 [b]	220 [b]
Mean size (mm)	0.6-0.85 [b]	0.5 [b]
Pore volume (mL g^{-1})	0.2 [b]	NA [b]

a data taken from (Bringue et. al. 2006), b data taken from (Hosseininejad et. al. 2012), c data taken from (Golets et. al. 2012)

2.2. Apparatus

A magnetically stirred batch reactor was employed in this study. The 400 mL reactor vessel was equipped with a jacket and a reflux condenser. The inside temperature of the reactor was controlled by circulating water throughout the jacket from a water bath.

2.3. Methods

Experimental procedure employed in this study is as follows. Initially, the catalyst, isobutyl alcohol and 1,4-dioxan were charged into the reactor. The inside temperature of the reactor was raised to the desired temperature. The reaction was started by the addition of propionic acid into reactor. Samples were collected at definite time intervals. All experiments were conducted at three temperatures (318.15, 333.15, 348.15 K), three stirring speeds (500, 700, 1000 rpm) and two catalyst particle sizes (400–600 µm, 600+µm).

2.4. Analysis

The amounts of isobutyl alcohol, propionic acid and isobutyl propionate in the samples were determined by quantitatively using a gas chromatograph (HP 6890) with Flame Ionization Detector. In order to separate the content of reaction mixture, DB-WAX column with dimensions of 30 m ×0.53 mm × 0.25 µm was used. m-xylene was used as internal standart for quantitative calculation of reactant and products. All quantitative results from gas chromatography were obtained by using Chemstation. Isobutyl alcohol conversion was computed as follows:

$$X_{IBA} = \frac{Initial\ mole\ of\ IBA - mole\ of\ IBA\ at\ time\ t}{Initial\ mole\ of\ IBA} \qquad (1)$$

3. RESULTS AND DISCUSSIONS

3.1. Effect of speed of agitation

The effect of speed of agitation was studied at 500, 700 and 1000 rpm under catalyst loading of 8 g-dry resin/L, reactant molar ratio of 1:1 which means that there are 1 molar propionic acid and 1molar isobutyl alcohol in reactor, and temperature of 348 K reaction conditions. The results obtained on Amberlyst 36 and Amberlyst 70 catalysts are shown in Fig. 1.

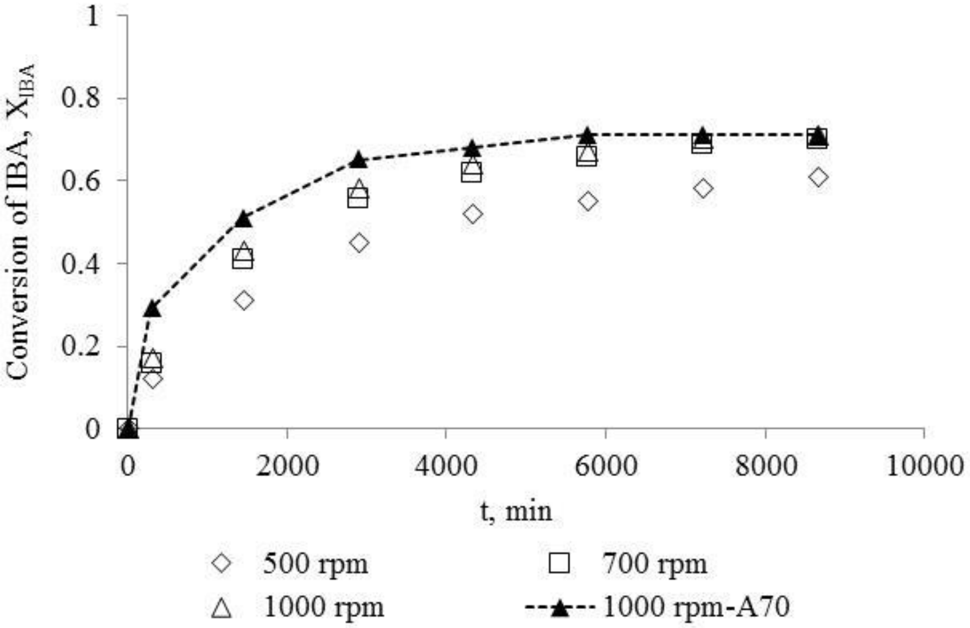

Figure 1:
Effect of speed of agitation, 8 g-dry resin/L, 1:1 reactant molar ratio, 348 K, 600+ µm particle size.

With an increase of agitation speed from 500 rpm to 700 rpm, conversion of isobutyl alcohol was significantly increased for Amberlyst 36 as shown in Fig 1. However, with an increase of agitation speed from 700 to 1000 rpm, there was no change on the conversion of isobutyl alcohol which means that the external diffusion limitation is negligible at stirrer speeds of 700 rpm and above. This trend is also valid for Amberlyst 70 (500 rpm and 700 rpm are not shown in Fig. 1). At 1000 rpm of speed of agitation, Amberlyst 70 reaches equilibrium more rapidly than Amberlyst 36. Therefore, the effect of other experimental parameters were studied by carrying out the experiments at stirrer speed of 1000 rpm to ensure that the measured reaction rate was free from external diffusion effects.

3.2. Effect of catalyst particle size

To investigate the internal diffusion effect on the reaction rate, the effect of particle size on conversion of isobutyl alcohol was studied by using Amberlyst 36 and Amberlyst 70 catalysts with two different particle size ranges as 400-600 µm and 600 µm above. The other reaction conditions were speed of agitation of 1000 rpm, catalyst loading of 8 g-dry resin/L, reactant molar ratio of 1:1, and temperature of 348 K. It can be clearly seen in Fig. 2 for Amberlyst 36 and Amberlyst 70 that the isobutyl alcohol conversion was not changed by using two different particle sizes.

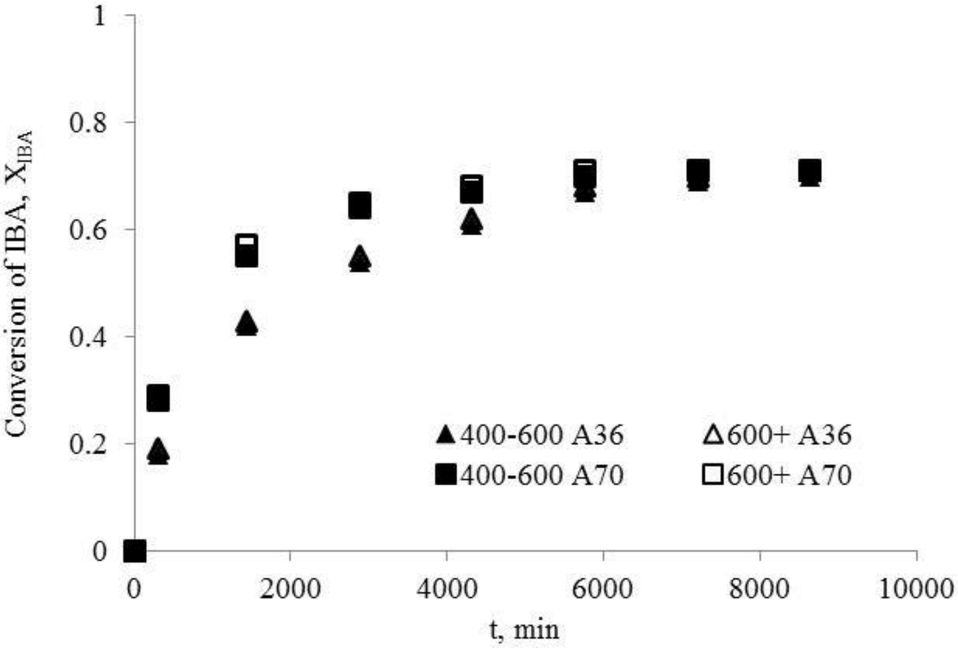

Figure 2:
Effect of catalyst particle size, 8 g-dry resin/L, 1:1 reactant molar ratio, 1000 rpm, 348K

This result indicates that the internal diffusion effect is negligible at the range of catalyst particle sizes used in this study for Amberlyst 36 and Amberlyst 70. All further experiments were done with 600 above particle size for Amberlyst 36 and Amberlyst 70 in order to eliminate the internal diffusion effect. Catalyst activity of Amberlyst 36 and Amberlyst 70 was also compared. Accordingly, Amberlyst 70 was found slightly active than Amberlyst 36.

3.3. Effect of catalyst loading

The effect of catalyst loading was checked at 348 K temperature, 1000 rpm agitation speed and reactant molar ratio of 1:1 with Amberlyst 36 and Amberlyst 70. The catalyst amount was varied from 4 to 12 g-dry resin/L based on the total volume of the reactants. After 2880 minutes, Amberlyst 36 resin achieved the iso-butyl alcohol conversion of 50%, 58% and 61%, while Amberlyst 70 achieved 55%, 65% and 68% for 4, 8 and 12 g-dry resin/L, respectively.

As can be seen in Fig. 3, the conversion of isobutyl alcohol increased with increasing catalyst amount in the studied range. This is explained by that the more catalyst amount was provides more active sites. Thus, reaction rate has increased with increasing the catalyst loading. It has already been mentioned before that the equilibrium conversion is 71% at this temperature and increasing the catalyst amount also reduced the time of achieving the equilibrium conversion.

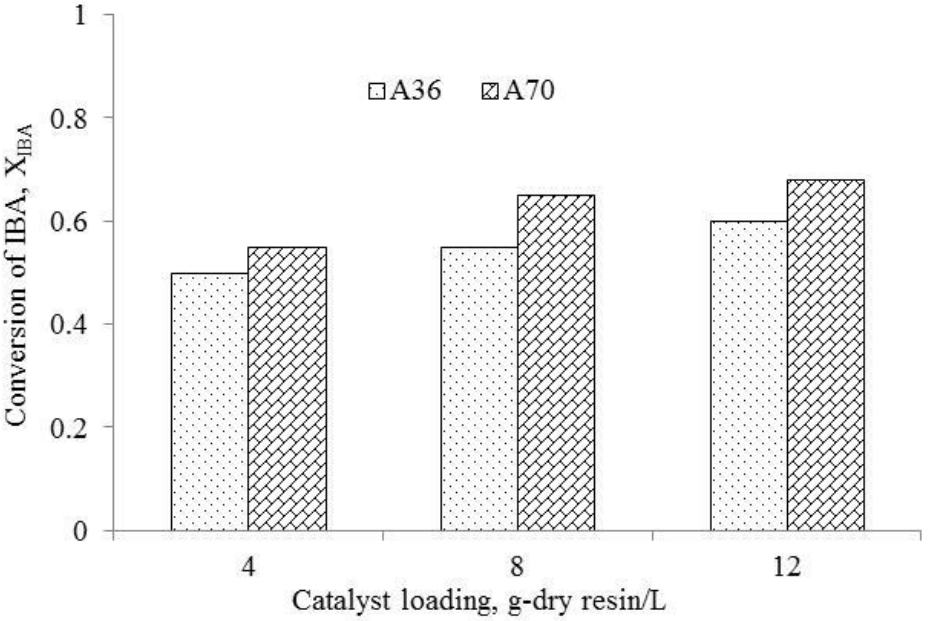

Figure 3:
Effect of catalyst loading, 1:1 reactant molar ratio, 1000 rpm, 348 K, 600+ μm particle size.

3.4. Thermodynamic and kinetic studies

The thermodynamic and kinetic parameters of the esterification of propionic acid with isobutyl alcohol were determined by using equilibrium data at different temperatures. Experiments were preceded until equilibrium is achieved. When the last two conversion data values remains constant, it is accepted as equilibrium conversion. Calculations of thermodynamic parameters were done by using Amberlyst 70 equilibrium data since the equilibrium constant only depends on temperature.

Fig. 4 shows the variation of conversion of isobutyl alcohol at 318K, 333K and 348 K temperatures under Amberlyst 70 catalyst loading of 8 g-dry resin/L, reactant molar ratio of 1:1 and 1000 rpm stirring speed conditions.

For the reaction (1), pseudo-homogeneous kinetic model reaction rate equation can be written as

$$w = -\frac{dC_{IBA}}{dt} = k_1 C_{PA} C_{IBA} - k_2 C_W C_{IBP} \tag{2}$$

Eq.2 with the restrictions that C_{PA0}=C_{IBA0} and C_{IBP0}=C_{W0}=0, can be written to give the following equation in terms of the conversion of the isobutyl alcohol.

$$w = C_{IBA0}\frac{dX_{IBA}}{dt} = k_1 C_{IBA0}^2 (1 - X_{IBA})^2 - k_2 (C_{IBA0} X_{IBA})^2 \tag{3}$$

At the equilibrium, $w=0$. Hence from the above equations, we find the fractional conversion of IBA at equilibrium conditions to be

$$K = \frac{C_{IBPe} C_{We}}{C_{IBAe} C_{PAe}} = \frac{X_{IBAe}^2}{(1-X_{IBAe})^2} \tag{4}$$

where K is equilibrium constant and $K=k_1/k_2$. The reaction enthalpy (ΔH) and the reaction entropy (ΔS) were calculated by plotting ln K versus 1/T (Fig. 5) according to van't Hoff equation:

$$lnK = \frac{-\Delta H}{RT} + \frac{\Delta S}{R} \tag{5}$$

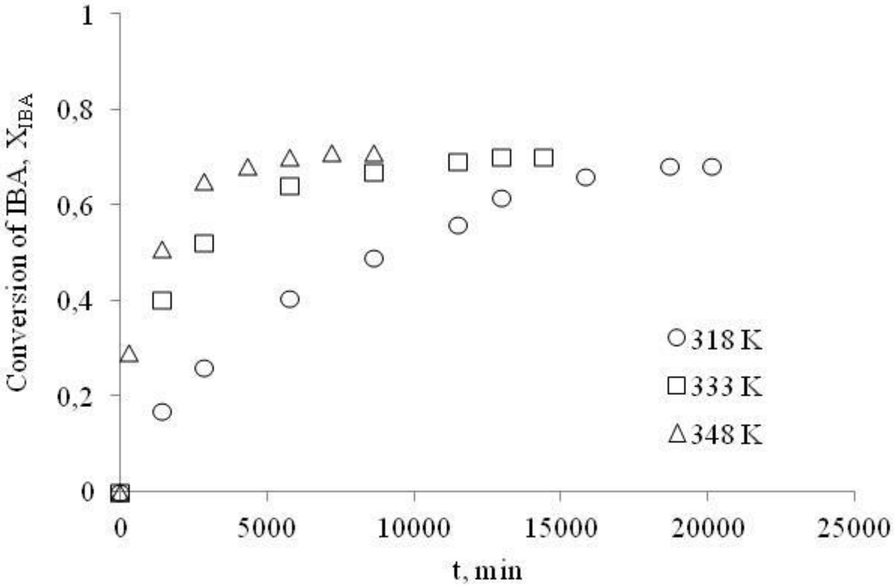

Figure 4:
Effect of reaction temperature for Amberlyst 70 catalyst, 8 g-dry resin/L, 1:1 reactant molar ratio, 1000 rpm, 600+ µm particle size.

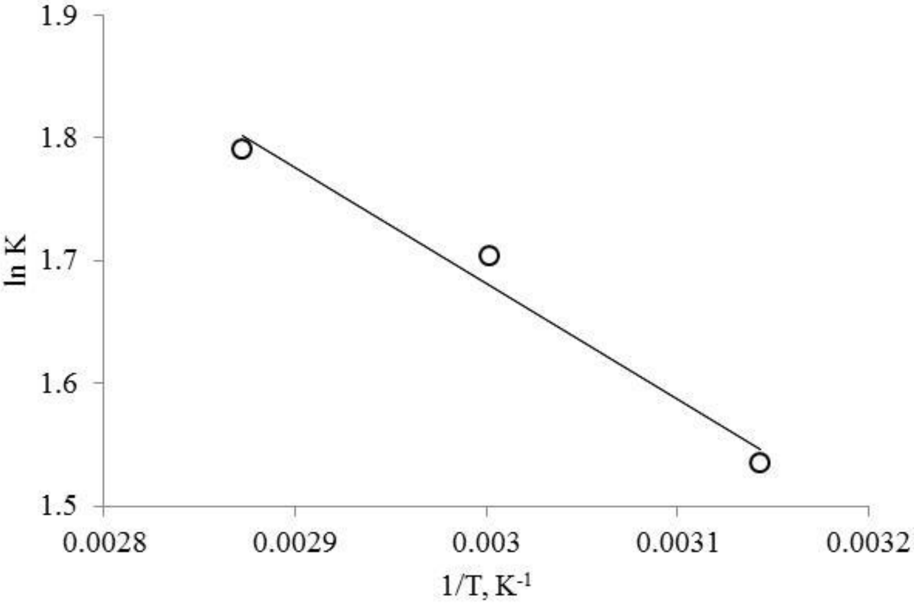

Figure 5:
van't Hoff plot for calculating the reaction enthalpy and entropy

Then, the reaction free energy change was calculated by this equation:

$$\Delta G=\Delta H-T\Delta S \tag{6}$$

Assuming independent of temperature in studied temperature range, from Fig. 5 and Eqs. 4-5, the reaction enthalpy (ΔH) and the reaction entropy (ΔS) are found to be 7871.19 J mol^{-1} and 37.59 J mol^{-1} K^{-1}, respectively. The values of equilibrium constant and the reaction free energy change (ΔG) at studied temperatures are given in Table 2.

Table 2.The values of equilibrium constant and the reaction free energy change (ΔG) at studied temperatures.

T (K)	X_{IBAe}	K	ΔG (J mol^{-1})
318	0,683	4.64	-4088.6
333	0,701	5.49	-4652.5
348	0,710	5.99	-5216.4

On the other hand, modification of Eq.3 with K=k_1/k_2 and integration gives

$$ln\left[\frac{X_{IBAe}-(2X_{IBAe}-1)X_{IBA}}{X_{IBAe}-X_{IBA}}\right]=2k_1\left(\frac{1}{X_{IBAe}}-1\right)C_{IBA0}t \tag{7}$$

The plot of left hand side (L.H.S.) of Eq. (7) versus time has a straight line passing through origin, the slope of which used the calculation of the value of k_1. The values of forward reaction rate constants for Amberlyst 36 and Amberlyst 70 in the studied temperatures were tabulated in Table 3.

Table 3.The values of forward reaction rate constant for Amberlyst 36 and Amberlyst 70 at studied temperatures.

T (K)	k_1(L mol^{-1} min^{-1})	
	Amberlyst 36	Amberlyst 70
318	7.7 ×10^{-5}	11.0 ×10^{-5}
333	21.8 ×10^{-5}	33.2 ×10^{-5}
348	48.7 ×10^{-5}	71.1 ×10^{-5}

The temperature dependency of the forward reaction kinetic constants k is modelled with Arrhenius' law

$$k_1=A\exp\left(\frac{-E_A}{RT}\right) \tag{8}$$

where R is universal gas constant (J mol^{-1} K^{-1}), T is the absolute temperature (K). The kinetic model described by Eq. (8) has two parameters, the pre-exponential factor A (L mol^{-1} min^{-1}) and activation energy E (J mol^{-1}) of the forward reaction. Activation energy of the forward reaction both Amberlyst 36 and Amberlyst 70 were determined by plotting lnk_1 versus 1/T.

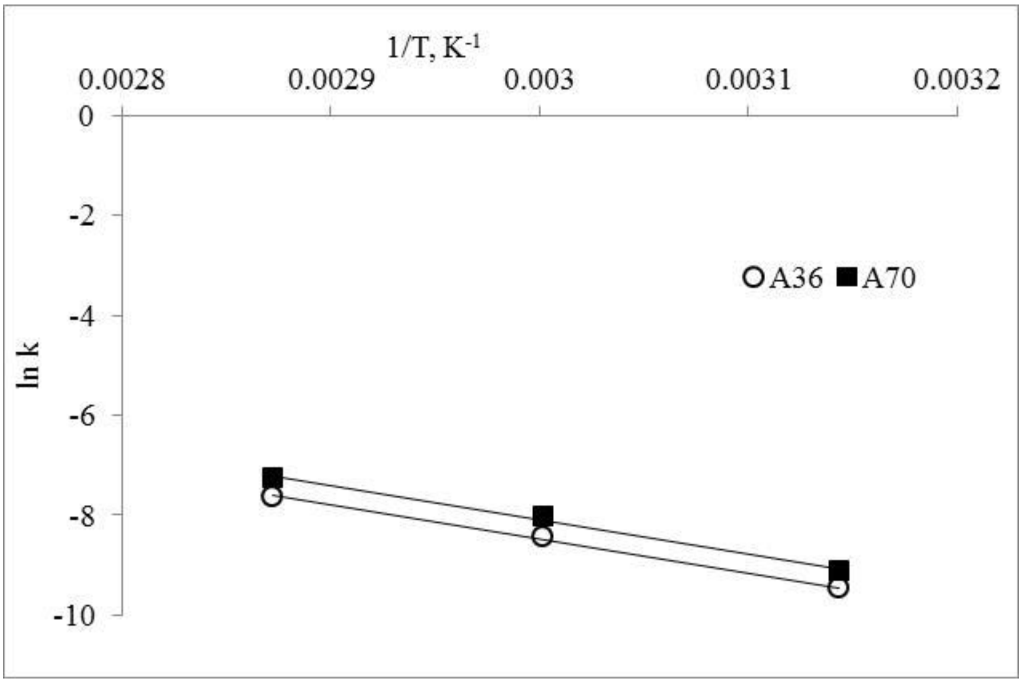

Figure 6:
Arrhenius plot for determining the activation energies both Amberlyst 36 and Amberlyst 70 catalysts

From Fig. 6, the temperature dependency of rate constants was calculated as follows:

$k_1 = 160171 \exp\left(\frac{-56689}{RT}\right)$ (L mol^{-1} min^{-1}) for Amberlyst 36 (9)

and

$k_1 = 293314 \exp\left(\frac{-57292}{RT}\right)$ (L mol^{-1} min^{-1}) for Amberlyst 70 (10)

Amberlyst 36 and Amberlyst 70 are macroreticular resins which have –SO_3H as functional groups. In spite of its low sulfonation and cross-linking degree, Amberlyst 70 is more active catalyst than Amberlyst 36. It can be explained by swelling in polar medium of Amberlyst 70.

4. CONCLUSIONS

The esterification of propionic acid with isobutyl alcohol to isobutyl propionate was studied over Amberlyst 36 and Amberlyst 70 catalyst in a batch reactor. The results demonstrated that the reaction was controlled by kinetically and internal and external mass transfer limitations could be ignored. The kinetic expression was derived on the basis of the pseudo-homogeneous model. The forward reaction rate constant was determined as a function of temperature in Eqs. (9-10). Also, the thermodynamic parameters of the reaction such as equilibrium constant (K), the reaction enthalpy (ΔH), the reaction entropy (ΔS) and the reaction free energy change (ΔG) were calculated. As a result, Amberlyst 70 is more effective catalyst than Amberlyst 36 according to the experimental results.

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