Kinetics and Mechanism of Myristic Acid and Isopropyl Alcohol Esterification Reaction with Homogeneous and Heterogeneous Catalysts

TUNCER YALÇINYUVA,[1] HÜSEYIN DELIGÖZ,[1] İSMAIL BOZ,[2] MEHMET ALI GÜRKAYNAK[2]

[1] *Department of Chemical Engineering, Faculty of Engineering, Chemical Technologies Group, İstanbul University, Avcılar 34320, İstanbul, Turkey*

[2] *Department of Chemical Engineering, Faculty of Engineering, Process and Reactor Design Group, İstanbul University, Avcılar 34320, İstanbul, Turkey*

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ABSTRACT: The reaction of myristic acid (MA) and isopropyl alcohol (IPA) was carried out by using both homogeneous and heterogeneous catalysts. For a homogeneously catalyzed system, the experimental data have been interpreted with a second order, using the power-law kinetic model, and a good agreement between the experimental data and the model has been obtained. In this approach, it was assumed that a protonated carboxylic acid is a possible reaction intermediate. After a mathematical model was proposed, reaction rate constants were computed by the Polymath® program. For a heterogeneously catalyzed system, interestingly, no pore diffusion limitation was detected. The influences of initial molar ratios, catalyst loading and type, temperature, and water amount in the feed have been examined, as well as the effects of catalyst size for heterogeneous catalyst systems. Among used catalysts, *p*-toluene sulfonic acid (*p*-TSA) gave highest reaction rates. Kinetic parameters such as activation energy and frequency factor were determined from model fitting. Experimental K values were found to be 0.54 and 1.49 at 60°C and 80°C, respectively. Furthermore, activation energy and frequency factor at forward were calculated as 54.2 kJ mol^{-1} and 1828 L mol^{-1} s^{-1}, respectively. © 2008 Wiley Periodicals, Inc. Int J Chem Kinet 40: 136–144, 2008

INTRODUCTION

Esterification is an important reaction of alcohols and carboxylic acids [1]. The esterification of carboxylic acids and the acylation of alcohols are fundamental

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Correspondence to: Tuncer Yalçınyuva; e-mail: tuncery@istanbul.edu.tr.

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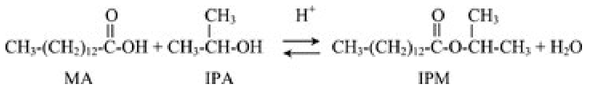
reactions in organic chemistry. Esters, which include a wide category of organic compounds ranging from aliphatic to aromatic, are generally used as plasticizers, solvents, perfume, flavor chemicals, and also precursors for a gamut of pharmaceuticals, agrochemicals, and other fine chemicals [2]. Conversions in esterification reactions are limited by slow reaction rates and low-equilibrium constants. A direct reaction of carboxylic acid with alcohol in equivalent ratios is generally avoided because of the equilibrium that is established between the reactants and the products. This requires the use of an excess amount of one of the reactants or the elimination of water from the reaction mixture to help the completion of the process. Catalysts are always used in liquid phase esterification to accelerate the reaction rate. Despite a strong catalytic effect, the use of homogeneous catalysts such as H_2SO_4 and *p*-toluene sulfonic acid (*p*-PTSA) suffers from the problems of side reactions, corrosions of the equipment, and disposal of environmentally hazardous acid. The use of a heterogeneous catalyst has the following inherent advantages over catalysis effected by dissolved electrolytes: (a) they eliminate the corrosive environment; (b) the catalyst can be easily recycled from the reaction mixture by decantation or filtration; (c) the purity of the products is higher since the side reactions can be completely eliminated or are less significant. There are very few reports on the esterification kinetics of fatty acids for a homogeneous catalyst system [3,4] and a heterogeneous catalyst system [5–9]. Kinetic models and results were reported for the reaction of fatty acids and various types of alcohols with short chain such as methanol in the production of biodiesel fuel [5,6]. When the reaction of oleic acid or fatty acid mixtures with methanol was investigated in the presence of H_2SO_4 and *p*-toluene sulfonic acid, it was found that *p*-TSA is more effective [10].

Kocsisava et al. has reported the esterification of fatty acids with methanol at elevated temperatures above the boiling point of methanol [5]. Furthermore, the kinetics of free fatty acids esterification with methanol was studied [6].

On the other hand, Altıokka and Çıtak have reported that the esterification kinetics of acetic acid with isobutanol in the presence of amberlite catalyst [11]. Kirumakki et al. have investigated the esterification of benzyl alcohol with acetic acid over different types of zeolite catalyst [12]. In addition, an enzymatic esterification reaction of fatty acids (oleic acid and ethanol) has been recently presented [13]. The most recent work has focused on the kinetics of oleic acid esterification with methanol over a heterogeneous catalyst [14]. To the best of our knowledge, no study has been reported on the esterification reaction mechanism of myristic acid as a fatty acid.

Isopropyl myristate (IPM) prepared by the reaction of isopropul alcohol (IPA) and myristic acid (MA) is one of the valuable esters. IPM can be used in the cosmetic industry as an alternative to natural fats, bath oils, cream, sun oil, and lubricants in the formulation of lotions due to excellent distribution properties and good absorbility [15]. The liquid phase esterification of myristic acid in the presence of a suitable acid catalyst yields IPM as the main reaction product. The esterification reaction proceeds by the following stoichiometric equation:



$$\underset{\text{MA}}{CH_3\text{-}(CH_2)_{12}\text{-}\overset{\overset{\displaystyle O}{\|}}{C}\text{-}OH} + \underset{\text{IPA}}{CH_3\text{-}\overset{\overset{\displaystyle CH_3}{|}}{C}H\text{-}OH} \xrightleftharpoons{H^+} \underset{\text{IPM}}{CH_3\text{-}(CH_2)_{12}\text{-}\overset{\overset{\displaystyle O}{\|}}{C}\text{-}O\text{-}\overset{\overset{\displaystyle CH_3}{|}}{C}H\text{-}CH_3} + H_2O$$

Here, we aimed to study the esterification kinetics of myristic acid with isopropyl alcohol with both homogeneously and heterogeneously catalyzed systems. For a homogeneously catalyzed system, catalytic rate equations were derived from the well-known power-law kinetic model and it was assumed that the reaction mechanism follows (1) myristic acid protonated by the catalyst to form a reaction intermediate that cannot be isolated and (2) the esterification reaction proceeds reversibly [3,4]. The influences of initial molar ratios, catalyst loading and type, temperature and water amount in the feed have been examined as have the effects of catalyst size for heterogeneous catalyst systems. In addition, we tried to determine the rate-limiting step for the heterogeneously catalyzed system. Kinetic parameters such as activation energy and frequency factor were also determined from model fitting.

EXPERIMENTAL

Materials

Isopropyl alcohol (purity >99.5), myristic acid (purity >98), and *p*-toluene sulfonic acid (purity >98) were purchased from the Merck Company (Darmstadt, Germany) and used without further purification. Heterogeneous catalysts Amberlyst-15 and Degussa (acidic cation exchange resin) were supported by Merck and Degussa, respectively. Amberlyst-15 was strongly acidic with sulfonic acid functionality (size: 500 μm, surface area: 55 m^2 g^{-1}, porosity %: 36, ion exchange capacity: 4.5 meq g^{-1}). The silica-based Degussa catalyst including sulfonic acid groups was manufactured by Degussa Company. Karl-Fischer solution was supplied from Riedel de Haen, England.

Reaction System and Procedure

Esterification reactions were carried out in a 250-mL round-bottomed, five-necked reactor with a condenser, nitrogen inlet–outlet, magnetic stirrer with 450 rpm speed, and thermometer. First, 80.85 g of myristic acid (0.354 mol) was placed in the reactor and then heated up to reaction temperature. Meanwhile, 42.57 g of IPA (0.708 mol) and 0.82 g of *p*-TSA were mixed in a beaker and subsequently heated up to reaction temperature too. This solution was then added into melted myristic acid by means of a dropping funnel. This time was taken as the beginning of the reaction. Several samples of approximately 1 mL from the reaction medium were collected during the experiment. A sample was drawn off every 5–15 min during the first hour of the reaction. Subsequently, samples were collected every 30 min during the next 2 h and thereafter every hour. These reactions were carried out in the temperature range of 60°C–80°C due to the melting point of MA (58°C) and the boiling point of the IPA (82.4°C). For equilibrium constant determination, reactions were carried out in a glass tube with 5 mL of volume under various reaction conditions for 48 h. In the equilibrium determination experiments, the total amount of reactants charged was nearly 5 mL. The amounts of IPA and MA were 1.79 mL (0.0234 mol) and 3.17 mL (0.0117 mol), respectively.

Analysis

Acid value (AV) analyses were made for the samples collected at different times to follow the esterification reaction (ASTM 1639-70). Preheated pipettes were used to collect samples from the reaction vessel. Gas chromatography (GC) analyses were also performed using the HP 6890 gas chromatography system. The conversion was determined by capillary GC, HP Innowax column, 30 m × 0.32 mm ID. It was also equipped with thermal-conductivity and flame-ionization detectors to determine the amount of all species in the reaction mixtures. In GC analysis, tetrahydrofuran (THF) was used as a solvent and nitrogen was used as a carrying gas with the flowing rate of 0.8 mL $\min^{-1}$. The amount of water in the organic phase was determined by the Karl-Fischer method, and analyses were carried out by the Metrohm 736 GP titrino system. The reproducibility for this system is 0.5%, and methylene chloride was used as the solvent.

RESULTS AND DISCUSSION

Derivation of Catalytic Rate Equation

In this study, a previously reported reaction mechanism for the reaction of alcohol with carboxylic acid protonated by acidic catalysts was utilized [3,4,16]. *p*-TSA is the source of proton in our kinetic study. The reaction mechanism can be written as follows:

$$RCOOH + H^+ \underset{k_{-1}}{\overset{k_1}{\Longleftrightarrow}} RCOOH_2^+ \tag{1}$$

$$\mathrm{A + C \Longleftrightarrow AH}$$

$$RCOOH_2^+ + R'OH \underset{k_{-2}}{\overset{k_2}{\Longleftrightarrow}}$$

$$RCOOR'H^+ + H_2O \tag{2}$$

$$\mathrm{AH + B \Longleftrightarrow EH + W}$$

$$RCOOR'H^+ \underset{k_{-3}}{\overset{k_3}{\Longleftrightarrow}} RCOOR'.. + ..H^+ \tag{3}$$

$$\mathrm{EH \Longleftrightarrow E + C}$$

The rate equation given by Goto et al. [3] is as follows:

$$-\frac{\mathrm{d}C_A}{\mathrm{d}t} = k\left(\frac{C_\mathrm{A}C_\mathrm{B} - C_\mathrm{E}C_\mathrm{W}/K}{C_\mathrm{B} + C_\mathrm{W}K_\mathrm{W}}\right) \tag{4}$$

where $K = k_1k_2k_3/k_{-1}k_{-2}k_{-3}$, $K_W = k_2k_3/k_{-2}k_{-3}$, and $k = k_C C_C$.

The right-hand side of Eq. (4) was assumed to be equal to zero at below 10% conversion of reactants for determination of variables ($C_\mathrm{E}C_\mathrm{W}/K = 0$). This assumption cannot be considered as a coarse approach due to the very small amount of water and nonpresence of IPM at the beginning of the reaction. When the inverse of this shortened Eq. (4a) is taken, then, the reaction rate can be written in the linear form (4b),

$$-\frac{\mathrm{d}C_\mathrm{A}}{\mathrm{d}t} = k_1\left(\frac{C_\mathrm{A}C_\mathrm{B}}{C_\mathrm{B} + C_\mathrm{W}K_\mathrm{W}}\right) \tag{4a}$$

$$\frac{1}{r_{\mathrm{A}-}} = \frac{1}{k_1}\frac{1}{C_\mathrm{A}} + \frac{K_\mathrm{W}}{k_1}\frac{C_\mathrm{W}}{C_\mathrm{A}C_\mathrm{B}} \tag{4b}$$

Using this linear equation, k_1 and K_W can be calculated from experimental results by means of the multiple linear regression method (see Fig. 1). The Polymath program was used to calculate the rate constants.

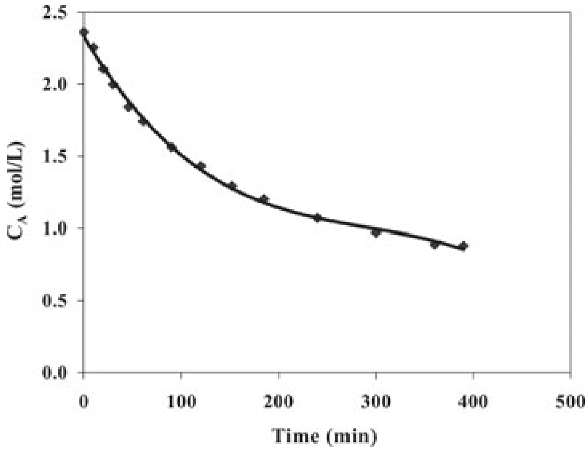


Figure 1 Time dependency of myristic acid concentration changes ($M = 2/1$, $T = 80°C$).

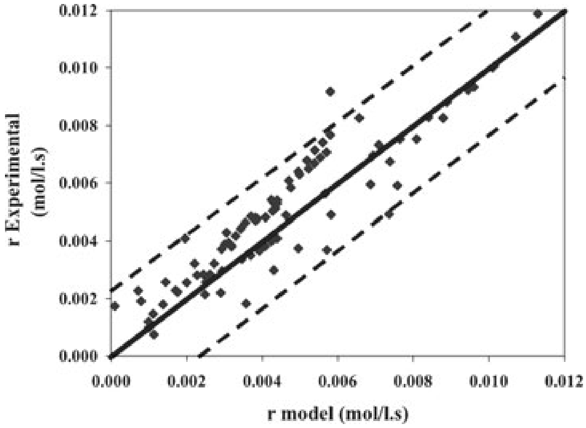


Figure 2 Comparison of experimental and theoretical reaction rates.

C_A (myristic acid concentration) was calculated by means of acid value analysis for the samples that were collected at intervals under different types of reaction conditions. Subsequently, polynomial analysis was applied to a graph that was drawn between C_A and time. Taking derivatives of all corresponding reaction rates, $-dC_A/dt$ values obtained from polinoms for all reactions were determined. On the other hand, reaction rates were calculated by using a derived model for the same obtained data.

Regression results and goodness of fit are shown in Fig. 2. In this case, rates calculated by experimental and derived models are compared. A solid line in Fig. 2 indicates the result of curve fitting for Eq. (4b). All experimental data are in excellent agreement with the calculated results. Dashed lines show confidence intervals and represent 95% confidence level, and they were obtained from four repeat experiments by means of two standard deviation.

Calculation of Equilibrium Constants

Experimentally determined equilibrium constants were calculated using equilibrium conversions with the formula given below:

$$K_{\text{exp}} = \frac{C_{\text{Ee}}C_{\text{We}}}{C_{\text{Ae}}C_{\text{Be}}} = \frac{X_{\text{Ae}}^2}{[(1 - X_{\text{Ae}})(M - X_{\text{Ae}})]} \tag{5}$$

where $M = C_{B0}/C_{A0}$.

Equilibrium constants ($K = k_1/k_2$) of esterification reactions strongly depend on reactant composition and reaction temperature [3,16,17]. In this study, experimental equilibrium constants were calculated while keeping molar ratios of reactants ($M = 2$) constant and catalyst loading (0.0288 mol/L) at four different temperatures (60°C, 70°C, 75°C, 80°C). As seen in Table I, it was observed that equilibrium constants were increased with increasing temperature. K values are in the range of 0.54–1.49. k_1 and k_2 are the rate constants for forward and backward reactions and were found to be 2.083×10^{-5} and 1.401×10^{-5} L mol^{-1} s^{-1}, respectively. Reaction rate constants were calculated by using the above model for the reactions carried out at various temperatures. Furthermore, activation energy was calculated for k_1 and k_2 at different temperatures. The frequency factor was also found by using the linear Arrhenius equation.

$$\ln k_{1,2} = \ln A - \frac{E_a}{R}\left(\frac{1}{T_{\text{ave}}} - \frac{1}{T}\right) \tag{6}$$

where E_a = activation energy, T_{ave} = average temperature (K), and R = gas constant (8.31 J/(mol K)). With linear regression between ln k and $1/T$ (K) data, activation energy and frequency factor at forward were calculated as 54.2 kJ/mol and 1828 L (mol · s)$^{-1}$, respectively.

Table I Temperature Dependency of k_1, k_2, and K

Temperature (°C)	C_C(mol /L^{-1})	M (C_{B0}/C_{A0})	X_{Ae}(%)	k_1(L /mol^{-1} s^{-1})	k_2(L mol^{-1} s^{-1})	K (k_1/k_2)
60	0.0288	2	57.5	0.647×10^{-5}	1.190×10^{-5}	0.54
70	0.0288	2	67.4	0.841×10^{-5}	0.799×10^{-5}	1.05
75	0.0288	2	69.6	1.206×10^{-5}	0.984×10^{-5}	1.22
80	0.0288	2	72.4	2.083×10^{-5}	1.401×10^{-5}	1.49

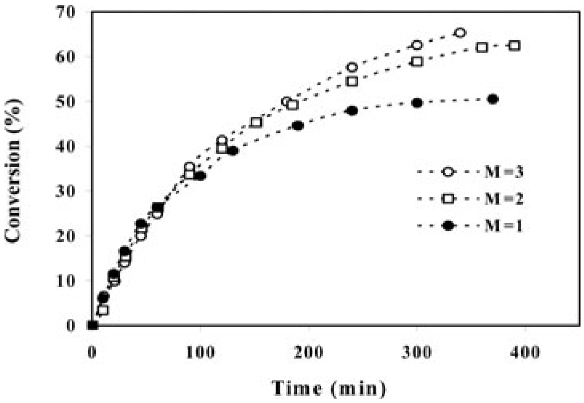


Figure 3 Effect of molar ratio of the reactants on the esterification conversion ($M = C_{B0}/C_{A0}$, isopropyl alcohol to myristic acid).

Effect of Reactant Composition

Esterification of myristic acid with isopropyl alcohol is an equilibrium-limited chemical reaction, and the use of excess isopropyl alcohol increases the utilization of myristic acid. The initial ratio of isopropyl alcohol to myristic acid was varied from 1:1 to 10:1 (2/1, 3/1, 5/1) at a fixed temperature with a loading of 0.0288 mol/L p-TSA to assess its effect on the rate of reaction. Figures 3 and 4 present the effects of ratio of initial concentration of isopropyl alcohol to myristic acid ($M = C_{B0}/C_{A0}$). It was found that as the mole ratio is increased from 1/1 to 3/1, the conversion of the alcohol increases. Beyond a mole ratio of 3/1, conversion becomes independent of the mole ratio.

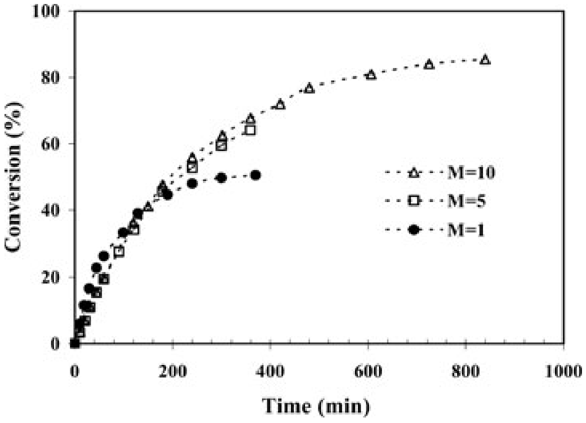


Figure 4 Effect of molar ratio of reactants on the esterification conversion ($T = 80°\text{C}$, $C_C = 0.0288$ mol/L, $M = C_{B0}/C_{A0}$).

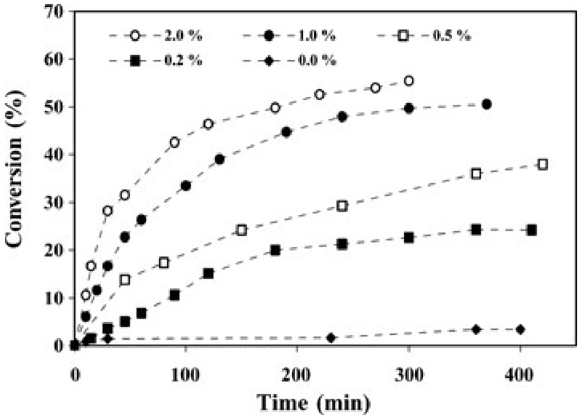
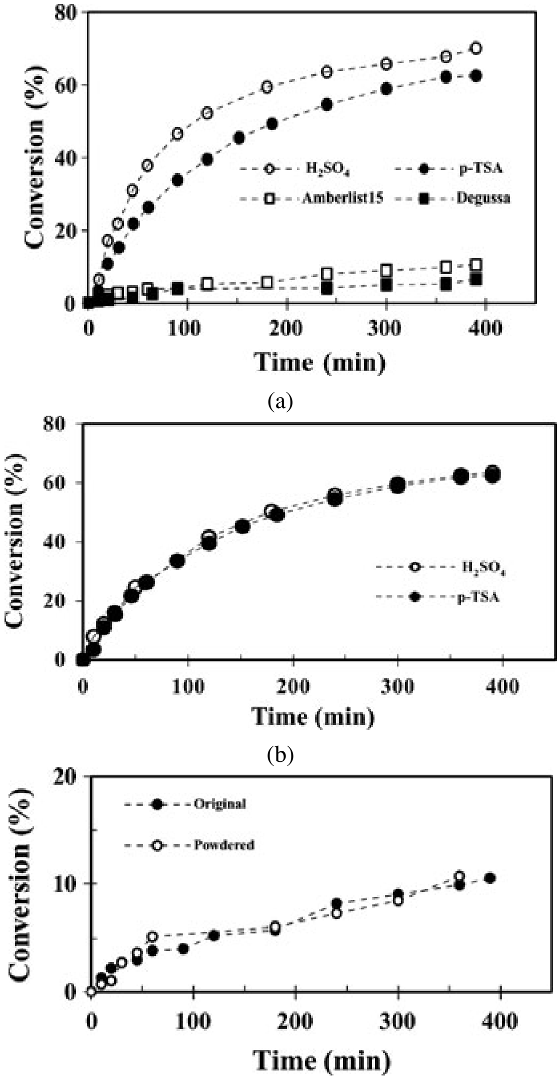


Figure 5 Effect of catalyst (p-TSA) loading on the esterification conversion ($T = 80°\text{C}$, $M = 1$).

Effect of Catalyst

Catalyst Loading. The effect of catalyst loading is shown in Fig. 5. To investigate the influence of catalyst concentration, four different p-TSA concentrations were used while keeping the temperature at 80°C and the molar ratio at 1/1 ($M = 1$). The amount of catalyst was varied from 0.2% to 2% mol up to acid concentration. After a reaction for 6 h, 24.3% and 55.5% yields were obtained for 0.2% and 2% wt catalyst-containing systems, respectively. With increasing amount of catalyst, it was observed that the reaction rate and yield significantly increased. On the other hand, a catalyst-free experiment was performed to follow and compare the esterification reaction rates. In this experiment, it was determined that the reaction was very low and yield reached only 3.4% after 6 h. As proposed in the literature [3,18], the establishment of equilibrium accelerates with the increase of concentration of catalyst. Even in a catalyst-free system, the reaction proceeded, although the reaction rate was very low.

Comparison of Homogeneous and Heterogeneous Catalysts. Both homogeneous (p-TSA and sulfuric acid) and heterogeneous (Amberlist-15 and Degussa) catalysts were used in the preparation of IPM. In a set of experiments, the influences of catalyst type and loadings were studied; they are plotted in Figs. 6a–6c. Concentrated sulfuric acid, Amberlist-15, and silica-based Degussa ion exchange resin were used in our study. From Fig. 6a, one can see the effect of homogeneous and heterogeneous types of catalysts on the reaction rate of the myristic acid esterification reaction. In Fig. 6b, p-TSA, a monobasic organic acid, was used equivalent (mole) to sulfuric acid, and the same effectiveness was nearly observed. If we consider that sulfuric acid releases two times higher H^+ than p-TSA, it can be concluded that p-TSA is a more



(a)

(b)

(c)

Figure 6 (a) Effect of various types of catalyst on the esterification conversion ($T = 80°C$, $M = 2$). (b) Effect of H_2SO_4 and p-toluenesulfonic acid as a catalyst on the esterification conversion comparatively ($T = 80°C$, $M = 2$), (c) Effect of heterogeneous catalyst (Amberlyst-15) size on the esterification conversion. Average sizes are 230 and 80 μm for original and powdered catalyst, respectively.

effective catalyst than sulfuric acid for the esterification reactions. A similar result was reported earlier [3].

On the other hand, surprisingly, heterogeneous catalysts (neither Amberlist 15 nor Degussa) caused poor conversions (5%–10% after 5 h) in the esterification reaction of fatty acid (myristic acid), although some successful results were reported for carboxylic acids with short alkyl chains [11,19]. This phenomenon might be explained by the diffusion problem of myristic acid, which is a long alkyl chain fatty acid, into the pores of catalyst. In general, the rate of a heterogeneously catalyzed reaction is affected by external/internal diffusion, adsorption and desorption, the surface reaction, and the nonideality of the reacting mixture [18].

For this purpose, in another set of experiment, the size of the heterogeneous catalyst was investigated to explain the mechanism properly. Esterification conversion versus time plots for different particle sizes are given in Fig 6c. It was aimed to determine whether the pore diffusion problem is the rate-limiting step for a heterogeneously catalyzed system in the fatty acid esterification reactions. No data are available in the literature for this phenomenon.

To evaluate the effect of internal diffusion on the cation-exchange resins by using the Weisz-pourier criteria, Eq. (7) was used [20]

$$\phi = \frac{r_0^2 k}{9D_\mathrm{e}} \tag{7}$$

where r_0 and D_e denote the radius of catalyst particle and the effective diffusion coefficient, respectively. k is the reaction rate constant, and ϕ is the Thiele modulus. If the calculated value of ϕ was less than 1, the internal diffusion could be neglected. The effective diffusion coefficient was defined as follows:

$$D_\mathrm{e} = \frac{D_\mathrm{A}\varepsilon}{\tau} \tag{8}$$

where D_A is the molecular diffusion coefficient, τ is the particle tortuosity, and ε is the porosity. For most resin catalysts, the values of ε/τ are between 0.25 and 0.50 [20]. In the calculation, the value of ε/τ was taken as 0.5. The molecular diffusion coefficient for liquid phase diffusion can be evaluated from the Wilke–Chang equation.

According to our calculations made by using the Weisz-pourier criteria, interestingly, no pore diffusion limitation was detected. After this result, it can be said that the reaction rate limiting step may be adsorption/desorption of the species. Moreover, it was observed that powdered Amberlist-15 (125–180 μm) exhibited nearly the same effectiveness as the original size.

Effect of Temperature. To investigate the temperature effect on the esterification reaction, the reactions were carried out in the temperature region of 60°C–80°C while keeping the molar ratio of acid to alcohol at 2:1. The conversion versus time graph belongs to experiments that were carried out at 60°C, 70°C, 75°C, and 80°C to determine reaction rates and reaction rate constants and is depicted in Fig. 7. In general, the ester conversion was found to increase with increasing reaction temperature. Increasing the temperature is apparently

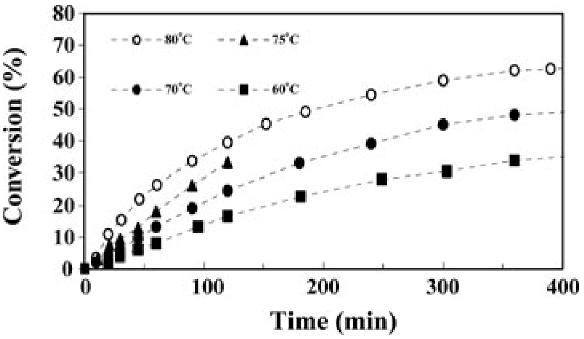


Figure 7 Effect of temperature on the esterification conversion.

favorable for the acceleration of the forward reaction. The conversion value is nearly two times higher for experiment at 80°C than the one for experiment at 60°C.

Effect of Water Content at the Beginning of the Reaction

The effect of water available at the beginning of the reaction is shown in Fig. 8. Two different experiments were carried out by adding 20% and 40% of excess water compared to the initial molar amount of myristic acid to investigate the effect of water presence on the reaction rate and conversion. In these reactions, *p*-TSA was used as a catalyst (C_C = 0.0288 mol L^{-1}, T = 80°C, and $M = 2$).

It was observed that the reaction rate considerably decreased with increasing the amount of water available at the beginning. While water-free system reached 62% conversion after 6 h, 20% and 40% water-containing systems reached 55.7% and 40%, respectively, at the end of the same period of time.

GC Analysis

The time dependency of concentration of products (IPM and water) and reactants (MA and IPA) was investigated by both GC and acid value analysis for a selected experiment for comparison and is depicted in Fig. 9. In this reaction, the molar ratio of the reactants was taken as $M = C_{IPA}/C_{MA} = 2$, and *p*-TSA was used as a catalyst with a concentration of 0.0288 mol L^{-1} at 80°C.

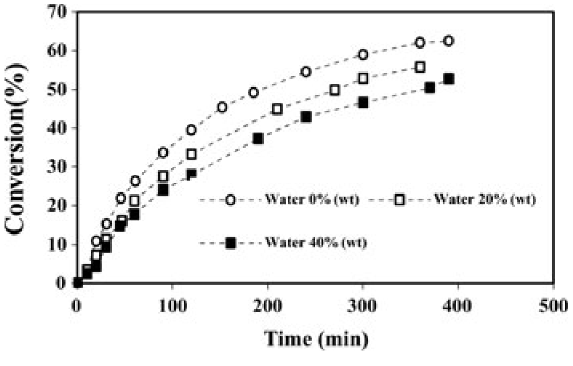


Figure 8 Effect of initial water content on the esterification conversion (C_C = 0.0288 mol/L, T = 80°C, and $M = 2$).

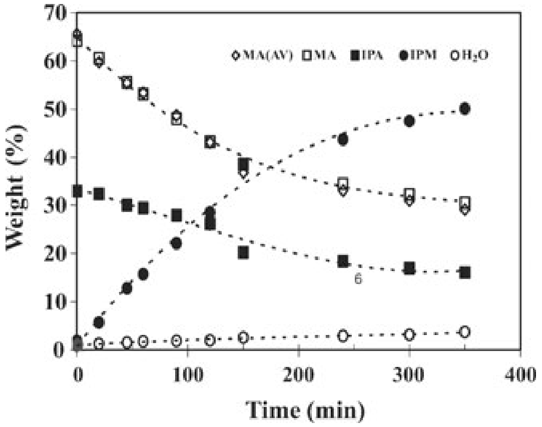


Figure 9 Changes in weight percentage of reactants and products determined by gas chromatography (GC) during reaction time and comparison of myristic acid weight percentages obtained by GC and acid value (AV) methods ($M = 2$, T = 80°C, C_C = 0.0288 mol/L).

One can see from Fig. 9 that 65 wt% myristic acid and 33 wt% isopropyl alcohol (in weight) are available at the beginning of the reaction. After 6 h, there are 50% IPM, 16% IPA, 30% MA, and 3.7% water contents in the reaction medium. On the other hand, the myristic acid concentration of some samples was determined by acid value analysis too. It was found that the results of acid concentrations determined by GC and titration were in good agreement.

Water Determination in Organic Phase

Apart from previously published articles, preliminary studies on both water amount in organic phase and alcohol amount in water phase were performed. As is well known, water evolved during the esterification reaction causes a multiphase reaction medium. During the reaction, myristic acid, isopropyl alcohol, and IPM exist in organic phase, whereas formed water and a small amount of isopropyl alcohol are dissolved in the water-rich phase.

In our experiments, evolved water was dispersed in the reaction medium and there was no observation of a separate water phase in the first few hours of reaction. However, small droplets dispersed in the reaction medium were associated and formed as a different phase with time. This can be explained by the fact that a part of available water dissolves in organic phase whereas the other part forms a water phase in the reaction.

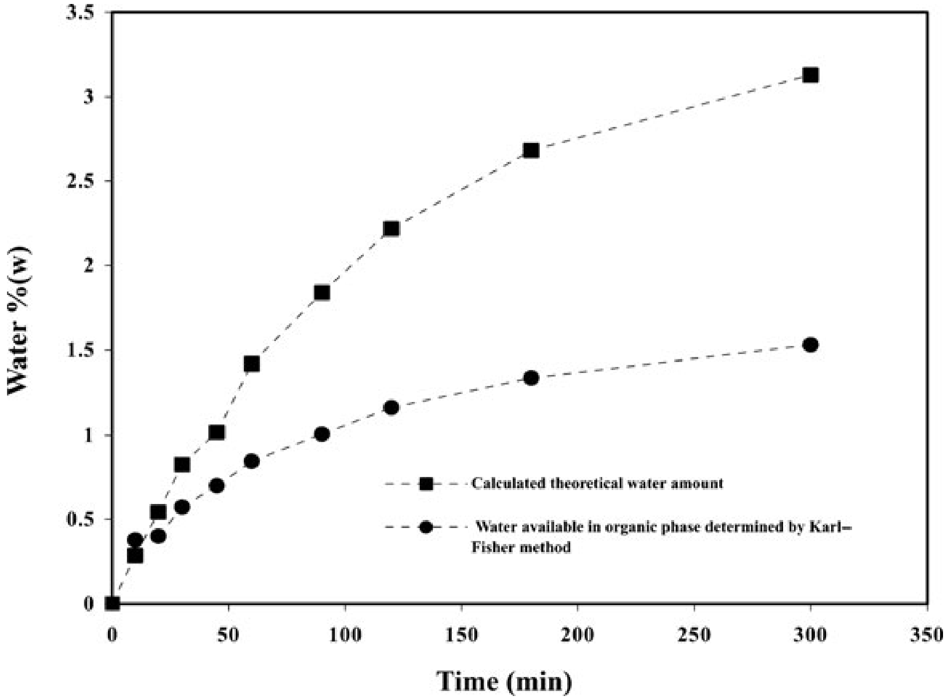


Figure 10 Comparison of dissolved water in organic phase and evolved total water during the reaction. (Isopropyl alcohol, dichloromethane, and THF contain 0.05, 0.02, and 0.17 wt% water, respectively. Required corrections for the calculation were made.)

In general, kinetic studies can be carried out for such a multiphase reaction by assuming all reaction media as a homogeneous phase. In this approach, some correction factors are used. An experiment was carried out, and the water dissolved in the organic phase was determined by the Karl-Fischer method. In Fig. 10, the amount of water determined by the Karl-Fischer method and the amount of theoretical water calculated by the acid value method are given for comparison.

As one can see from the results, the amount of water (wt%) was calculated by using the stochiometric amount as 3.13%, and it was also determined for 1.53 (wt%) of the evolved water dissolved in the organic phase. In other words, after 5 h reaction, roughly 48.9% of the total evolved water dissolved in the organic phase. On the other hand, GC analysis was carried out for the sample collected from bottom of the reactor and it was found that the water phase contains 43.3 (wt%) of IPA. This result confirms that some of the reactant IPA goes through the water phase. In our further studies, it will be tried to create and improve a model for only a homogeneous phase by determination of water in the homogeneous phase.

CONCLUSIONS

The reaction of MA and IPA was carried out by using both homogeneous and heterogeneous catalysts. For the homogeneous catalyst system, catalytic rate equations were derived by the reaction mechanism in which first myristic acid is protonated by the catalyst to form a reaction intermediate and then the esterification reaction proceeds reversibly. It can be concluded that a protonated carboxyl acid is a possible reaction intermediate. The experimental data have been interpreted with a second-order kinetics, and a good agreement between the experimental data and the model has been obtained. For heterogeneously catalyzed reactions, interestingly, no pore diffusion limitation was detected. On the other hand, both powdered and sifted catalysts showed the lowest efficiency, among all the heterogeneous catalysts used.

The influences of initial molar ratios of isopropyl alcohol to myristic acid (1:1 to 10:1), catalyst loading and type, temperature (60°C–80°C), and water amount in the feed have been examined, as well as the effects of catalyst size for heterogeneous catalyst systems. Among used catalysts, *p*-TSA gave the highest reaction rates for the fatty acid esterification reaction. The equilibrium conversion of myristic acid was found to increase slightly with an increase in temperature and also it increased appreciably with an excess of isopropyl alcohol in the reaction system. In addition, it was found that the changes in the reaction rate also depend on the catalyst loading and type.

Experimental K values were found to be 0.54 and 1.49 at 60°C and 80°C, respectively. Kinetic parameters such as activation energy and frequency factor were also determined from model fitting. Activation energy and frequency factor at forward were calculated as 54.2 kJ mol^{-1} and 1828 L mol^{-1} s^{-1}, respectively.

NOMENCLATURE

k_1	rate constant for forward reaction, L mol^{-1} s^{-1}
k_2	rate constant for backward reaction, L mol^{-1} s^{-1}
K	equilibrium constant
K_w	equilibrium constant for water
C_A	outlet concentration of myristic acid, mol L^{-1}
C_B	outlet concentration of isopropyl alcohol, mol L^{-1}
C_E	outlet concentration of isopropyl myristate, mol L^{-1}
C_W	outlet concentration of evolved water, mol L^{-1}
C_C	catalyst concentration, mol L^{-1}
M	ratio of concentration of alcohol to acid
T	temperature, K
$-r_\text{A}$	reaction rate of myristic acid
X_A	conversion of myristic acid
X_Ae	conversion of myristic acid at equilibrium
C_Ae	concentration of myristic acid at equilibrium, mol L^{-1}
C_Be	concentration of isopropyl alcohol at equilibrium, mol L^{-1}
C_Ee	concentration of isopropyl myristate at equilibrium, mol L^{-1}
C_we	concentration of water at equilibrium, mol L^{-1}
R	gas constant, kJ $(\text{mol K})^{-1}$
E_a	activation energy
r_0	radius of catalyst particle effective diffusion coefficient
D_e	effective diffusion coefficient
ϕ	Thiele modulus
D_a	molecular diffusion coefficient
τ	particle tortuosity
ε	porosity

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