

ESTERIFICATION OF PROPANOIC ACID IN THE PRESENCE OF A HOMOGENEOUS CATALYST

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ABSTRACT. Esters are organic compounds that are widely used even on an industrial scale, so their production has been extensively investigated. The aim of this work is to carry out the optimization process of esterification of propionic acid with lower monohydric alcohols. The influence of the amount of catalyst (H₂SO₄), the size and structure of the alcohol, the influence of the α -substituent, the molar acid/alcohol ratio and temperature on the esterification process were investigated. The descending order of reactivity tested alcohol is: 1-butanol > 1-propanol > ethanol > 2-propanol. As the acid/alcohol molar ratio increases, the rate and yield of the esterification reaction increase. The maximum yield of n-propyl propanoate in our experiments was 96.9%, achieved at a molar ratio of propanoic acid/1-propanol/catalyst 1/10/0.20 and a temperature of 65°C for 210 minutes of reaction.

Keywords: esters, esterification, propanoic acid, propyl propanoate.

INTRODUCTION

Esterification is a frequently used reaction in the chemical industry due to its great importance and practical application of esters. Esters are suitable intermediates in the synthesis of different compounds; have great application as solvents, plasticizers, pesticides, emulsifiers and monomers; they are used in the food, cosmetics, chemical and pharmaceutical industries (ALI *et al.*, 2007; NEJI *et al.*, 2009; JU *et al.*, 2011; MEKALA and GOLI, 2015). Due to the widespread use of esters in the chemical and related industries, there are currently about 500 commercial esters (SAHU and PANDIT, 2019).

The advantage of esters for their practical application is that they do not accumulate to any great extent in the Humans, do not pollute the environment, pose a low chemical risk, provide maximum safety during use and most are generally biodegradable.

In the esterification reaction, acids (mostly organic) and alcohol give esters and water. The reaction is reversible, slow and without the use of catalysts lasts an infinitely long time and with low yield (JYOTI *et al.*, 2016; KESHAV *et al.*, 2018; SAHU and PANDIT, 2019). Therefore, the rate of the esterification reaction is increased in the presence of a catalyst. In an

acid-catalyzed esterification reaction, the first step is the protonation of the carbonyl group of carboxylic acid. The rate-determining step is the nucleophilic addition in the reaction mechanism. In order to suppress the reversibility of the reaction, the process is carried out in excess of alcohol or water drained from the system. The presence of water as a by-product and undesirable product reduces the reaction rate due to the hydrolysis of the resulting ester into acid and alcohol. Water can be removed from the reaction mixture by distillation, using molecular sieves for water absorption, or some other separation technique (AL-JENDEEL *et al.*, 2010; KONG *et al.*, 2011).

The production of esters is not an efficient process. Conventional production requires energy consumption, the use of a catalyst, and a significantly greater amount of alcohol than stoichiometric. The process is often expensive with unnecessary energy loss, impure compounds are obtained as by-products, with inconsistent quality of the final product. Many researchers examine the esterification reaction to obtain a waste-free process, with the lowest possible energy consumption, higher yield and shorter duration of the esterification process.

The main factors influencing the esterification reaction are the type and amount of catalyst, the size and structure of the alcohol and acid, the molar ratio of acid/alcohol and the reaction temperature. The study of the influence of the main factors on the esterification process shows that they are interrelated and might have ambivalent effects (CHOLAKOV *et al.*, 2013).

Mineral acids as catalysts have many disadvantages such as corrosivity, difficulty in separating from the reaction mixture, polluting the environment and often giving side reactions. The advantages of mineral acids as a catalyst are low cost and high solubility, which gives a large number of reactive sites and thus higher efficiency. Of the mineral acids, sulfuric acid is mostly used due to its high acid strength and significant dehydrating ability.

A comparative study of homogeneous or heterogeneous catalyzed esterification reactions can be found in the literature (SAHU and PANDIT, 2019). In general, the use of homogeneous catalysts (liquid-liquid phase) leads to a higher reaction rate compared to heterogeneous catalysts (liquid-solid phase). In heterogeneous catalysis, steric hindrance occurs due to competition of binding to the solid phase and decreased availability of free protons (SAHU and PANDIT, 2019).

There are many papers in the literature on the topic of esterification of propanoic acid with sulfuric acid as a catalyst (RATHOD *et al.*, 2014; SALMAHAMINATI and JUMINA, 2017). In recent decades, heterogeneous catalysts have been used due to easy separation from the liquid phase, reusability, high selectivity and environmental friendliness. The researchers used heterogeneous catalysts to esterify propanoic acid: fibrous polymer Smopex 101 (LILJA *et al.*, 2005), various enzymes (VARMA and MADRAS, 2010), activated Nigerian clay (DIM *et al.*, 2013), Amberlyst and Dowex resins (CHANDANE *et al.*, 2017), sulfonated rice cumin (TIWARI *et al.*, 2017).

The aim of this work is to carry out the optimization process of esterification of propionic acid with lower monohydric alcohols. It is also intended to examine the influence of the amount of catalyst (H_2SO_4), the size and structure of the alcohol, the influence of increasing the length of the acid chain by one C-atom and the presence of substituents in the side chain, the molar acid/alcohol ratio and temperature on the esterification process.

MATERIALS AND METHODS

In the experimental part of this work, esterification reactions of propanoic acid with lower monohydroxy alcohols were carried out using sulfuric acid as a catalyst. The influence of the size and structure of alcohol and a carboxylic acid, acid/alcohol molar ratio, catalyst amount and reaction temperature on the esterification reaction was investigated.

The reactions were performed according to the procedure given in the work of KASTRATOVIĆ and BIGOVIĆ (2018). Propanoic acid esterification reactions were performed with alcohols: ethanol, 1-propanol, 2-propanol and 1-butanol. The alcohols used were both reactants and solvents. To test the introduction of the side chain in the structure of propanoic acid, lactic acid (α -hydroxypropanoic) and α -methylpropanoic acid were tested. In order to examine the effect of excess alcohol on the yield of the obtained ester, the following molar acid/alcohol/catalyst ratios were used: 1/2.5/0.20 (propanoic acid 13.61 g, 182.8 mmol / 1-propanol, 99.5 wt%, density 0.803 g/cm³ 34.4 cm³, 457 mmol / sulfuric acid, 98 wt%, density 1.83 g/cm³ 2.00 cm³, 36.6 mmol); 1/5.0/0.20 (propanoic acid 6.804 g, 1-propanol 34.4 cm³, sulfuric acid 1.00 cm³) and 1/10.0/0.20 (propanoic acid 3.402 g, 1-propanol 34.4 cm³, sulfuric acid 0.50 cm³). The effect of the amount of catalyst on the reaction rate was investigated at molar ratios acid/alcohol/catalyst: 1/10/0.06; 1/10/0.11; 1/10/0.15 and 1/10/0.20. The selected temperatures were: 35, 45, 55 and 65°C.

The degree of conversion of the propanoic acid into propyl propanoate is calculated with the formula:

$$\% \text{ conversion} = 100 \cdot \frac{c_o - c_t}{c_o} \quad (1)$$

where c_o is the propanoic acid concentration at the beginning of the esterification process and c_t – propanoic acid concentration at the point of time t .

Propanoic acid concentrations were calculated based on expressions (2) and (3):

$$c_o = \frac{c_{NaOH} \cdot V_{initial}}{V_{aliquot}} \quad (2)$$

$$c_t = \frac{c_{NaOH} \cdot (V_t - V_o + V_{initial})}{V_{aliquot}} \quad (3)$$

where c_{NaOH} is the concentration (± 0.0001 mol/dm³) of the standard solution of NaOH; $V_{initial}$ – consumption of NaOH (cm³) for the titration of carboxylic acid at the beginning of esterification; V_o – consumption of NaOH (cm³) for titration of carboxylic and sulfuric acid at the beginning of esterification; V_t – consumption of NaOH for carboxylic and sulfuric acid in the reaction mixture at the point of time t ; $V_{aliquot}$ – volume (cm³) of reaction mixture taken for analysis.

RESULTS AND DISCUSSION

Alcohol reactivity

The influence of alcohol size and structure was investigated in the reaction with propanoic acid in the presence of sulfuric acid as a catalyst (Fig. 1).

In Figure 1. it can be concluded that the conversion of propanoic acid into ester, after a fixed time (210 min) increases with the increasing number of C-atoms in the chain because in this way the nucleophilicity of alcoholic oxygen also increases. The yield of the esterification reaction also depends on the physical properties of the alcohol. 1-Butanol, which has the highest boiling point of used alcohols (117.5°C), i.e. has the highest content in the reaction mixture at given temperatures. With branching, alcohol decreases in reactivity due to steric hindrance. Other authors (LILJA *et al.*, 2005; BRAGA *et al.*, 2008; NEJI *et al.*, 2009; KASTRATOVIĆ and BIGOVIĆ, 2018) also find a decreasing series of reaction rates in relation to

the type of alcohol: primary > secondary > tertiary, during esterification of carboxylic acids, at similar molar ratios acid/alcohol/catalyst and temperatures. In contrast, some authors (ALI, 2009; CARDOSO *et al.*, 2009; SAHU and PANDIT, 2019) find that increasing the length of the alcohol chain has a negative effect on the conversion of propanoic and other carboxylic acids to esters due to steric interference in the presence of heterogeneous catalysts. By using heterogeneous catalysts, larger alcohols interfere with the binding of acids to the active site.

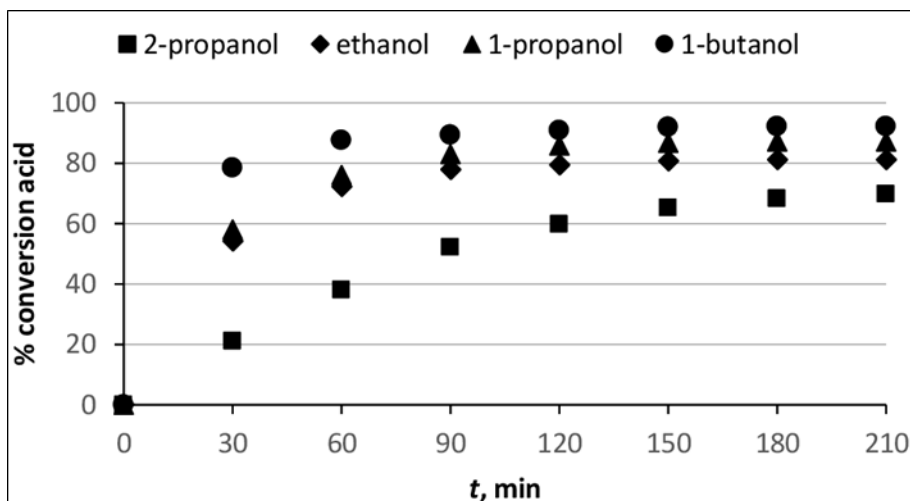


Figure 1. Influence of the chain length and structure of the alcohol on esterification of propanoic acid. Conditions: acid/alcohol/catalyst (H_2SO_4) molar ratios: 1/10/0.20; temperature 45°C.

Influence of acid

Figure 2 shows the results of the investigation of the influence of the acid structure on the rate and yield of the esterification reaction. The influence of the length of the alkyl chain and the presence of substituents in the side chain were investigated. The esterification reaction of propanoic, butanoic, α -hydroxypropanoic and α -methylpropanoic acid with 1-propanol in the presence of sulfuric acid at 45°C was investigated. The molar ratio of acid/alcohol/catalyst was 1/10/0.20.

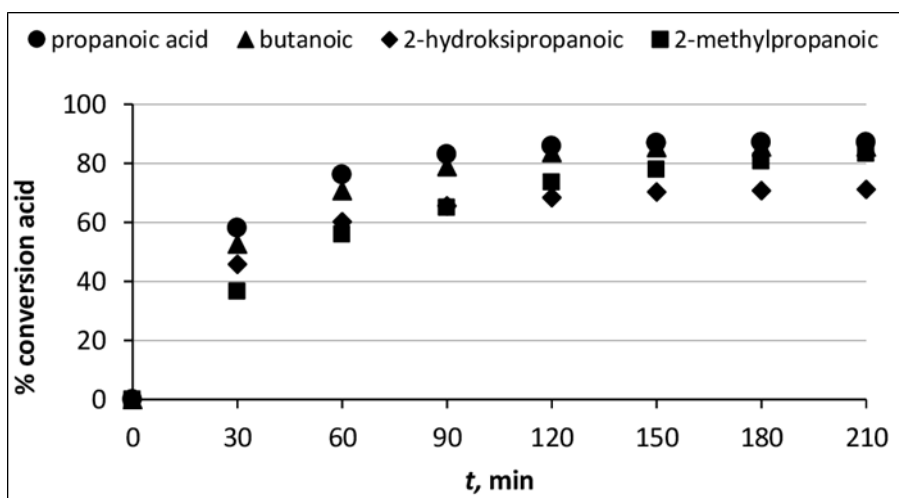


Figure 2. Influence of the length of the alkyl line and substituent in acid side chain on the rate and yield of esterification reaction with 1-propanol. Conditions: molar ratios: acid/alcohol/catalyst (H_2SO_4) was 1/10/ 0.20; temperature 45°C.

For the reactivity of carboxylic acids in esterification reactions, both the steric and electronic factors are important in homogeneous catalysis, while in heterogeneous steric are of higher importance. In the work of LIU *et al.* (2006) it has been found that for small acids, from acetic to butanoic, the reaction rate decreases with an increasing number of C-atoms. For larger acids, a small additional effect on the rate and yield of the reaction was observed with a further increase in the number of C-atoms. Increasing the number of C-atoms in the linear saturated acid chain slightly reduces the rate of the esterification reaction. A slightly larger difference is observed in heterogeneous catalysis (CAETANO *et al.*, 2009; NEJI *et al.*, 2009; SRILATHA *et al.*, 2009; FERREIRA *et al.*, 2012) due to the inhibitory effect of longer chain acids, which are more difficult to adsorb on the surface of the solid catalyst.

The presence of a substituent in the side chain of propanoic acid reduces the rate and yield of acid conversion to the ester. Comparing the reaction of α -hydroxy- and α -methylpropanoic acid, a higher reactivity of lactic acid is noticed in the first 90 minutes of the reaction. Probably the electronic effects of hydroxy and methyl groups have an advantage over the steric effects of the substituent. As the reaction progresses, α -methylpropanoic acid shows a higher conversion to the corresponding ester and approaches the yield of unbranched acids. We assume that the reason for this is significantly less hydrolysis of α -methylpropanoic acid ester in an acidic medium, due to significantly less solubility of the acid in the aqueous medium created during the reaction.

Acid/alcohol molar ratio

Figure 3 shows the results of investigating the effect of the acid/alcohol molar ratio on the rate and yield of the esterification reaction of propanoic acid with 1-propanol.

The molar ratio of acid/alcohol is one of the most important variables that can affect the degree of conversion of acid to an ester (KASTRATOVIĆ and BIGOVIĆ, 2018). As the acid/alcohol molar ratio increases from 1/2.5 to 1/10, the rate and yield of the esterification reaction increase. In the first 30 min, the difference in ester yield is small while with the continuation of the process it increases and after 120 min it reaches a mainly constant difference in ester yield.

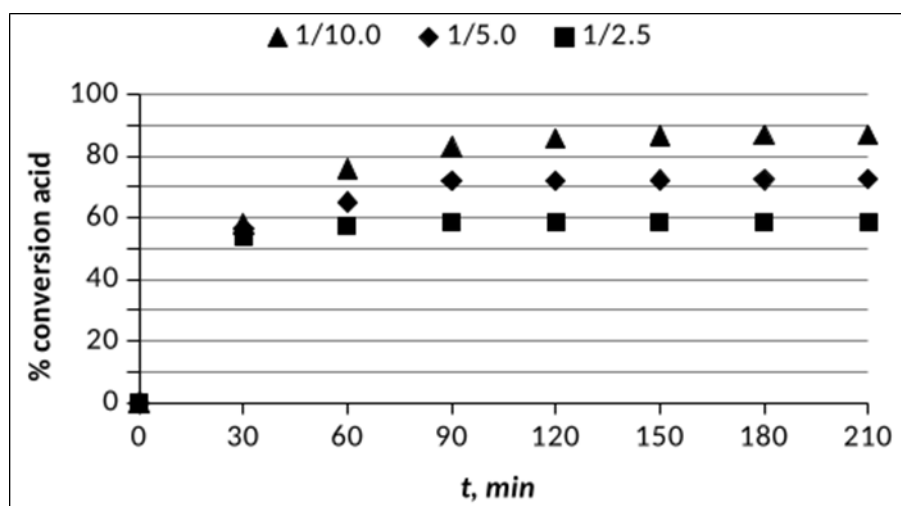


Figure 3. Effect of acid/alcohol molar ratio (1/10; 1/5 and 1/2.5) on the rate of esterification of propanoic acid with 1-propanol. Conditions: molar ratio of acids/catalyst (H_2SO_4) 1/0.20; temperature 45°C.

TSAI *et al.* (2011) performed experiments with molar ratios of methanol and propanoic acid from 1/1 to 5/1. CHANDANE *et al.* (2017) performed esterification of propanoic acid with

2-propanol at molar ratios of alcohol and acid of 1/1 to 3/1. The results of these works show that the equilibrium conversion of propanoic acid to ester increases with an increasing molar ratio. In several papers (CARDOSO *et al.*, 2009; JYOTI *et al.*, 2016; KASTRATOVIĆ and BIGOVIĆ, 2018; SAHU and PANDIT, 2019) higher molar ratios of alcohol/acid (15/1, 20/1 and more) do not lead to an increase in the yield of the formed ester, but only shorten the required time to reach equilibrium concentrations.

Due to the dilution of the reaction mixture with alcohol, the changes in the acid concentration are smaller.

Influence of catalyst quantity

Figure 4 shows the results of testing the effect of the amount of catalyst on the reaction of esterification of propanoic acid with 1-propanol in the presence of sulfuric acid as a catalyst at a temperature of 45°C. The acid/alcohol/catalyst molar ratios were 1/10/0.06; 1/10/0.11; 1/10/0.15 and 1/10/0.20.

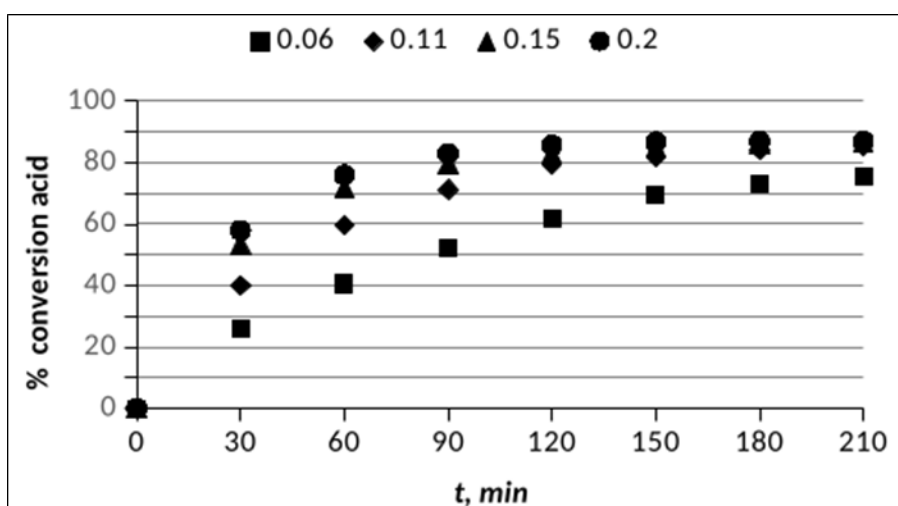


Figure 4. Influence of the catalyst (H_2SO_4) amount on the kinetics of esterification of propanoic acid with 1-propanol. Conditions: acid/alcohol molar ratio 1/10; temperature 45°C; acid/catalyst molar ratios: 1/0.06; 1/0.11; 1/0.15 and 1/0.20.

Catalyst concentration may be an alternative way to speed up the esterification reaction. Increasing the molar ratio of catalyst/acid from 0.06/1 to 0.20/1 results in an increase in the reaction rate. The difference in ester yield at the beginning of the reaction is significant ($\Delta = 31.9\%$), while the difference is reduced later. By the end of the experiment (210 min), the conversion of propanoic acid to propyl propanoate was similar ($\Delta = 1.7\%$) in the range of catalyst/acid molar ratios from 0.11/1 to 0.20/1. This slight increase in ester yield with increasing catalyst concentration (H_2SO_4) is explained by the occurrence of dehydration of alcohol to an alkene in the presence of an excess acid catalyst.

SAHU and PANDIT (2019) examine the influence of the concentration of a homogeneous catalyst (H_2SO_4) on the esterification reaction of a series of lower alicyclic acids with lower monohydroxylic alcohols. With increasing concentration of the catalyst increases the yield of the reaction when its amount is up to 3% wt. In the range of 3.0-5.0 wt.% with increasing catalyst concentration, there is a small decrease in the yield of the obtained ester, with the same other reaction parameters.

ALTIC (2010) investigated the influence of sulfuric acid concentration as a catalyst on the esterification reaction of free fatty acids with methanol. The rate and yield of the reaction are significantly increased within the range of sulfuric acid concentrations from 0.3 wt.% to

1.0 wt.% in relation to the oil used. Outside this range, further addition of sulfuric acid does not lead to significant further transformation of acids into esters.

DIM *et al.* (2013) investigated the influence concentration of clay, in the range of 1-3 wt.%, as a catalyst for the reaction between propanoic acid and 1-propanol. It has been observed that the degree of acid conversion increases with the amount of catalyst. On the other hand, the conversion decreases by the same amount of catalyst when the molar ratio of alcohol versus acid increases. This is explained by the increase in the number of alcohol molecules at the active sites of the catalyst, which interferes with the adsorption of the acid and therefore has a lower rate and yield of the reaction.

Influence of temperature

Data on the influence of temperature on the reaction rate help us to calculate the reaction rate constant and the activation energy. Conversion and reaction rate increase with increasing temperature due to a larger number of successful collisions with enough energy to break the bonds leading to product formation (KONG *et al.*, 2011; SAHU and PANDIT, 2019).

In this work, the effect of the reaction temperature on the reaction of esterification of propanoic acid with 1-propanol was investigated. Esterification reactions were performed at 35°C, 45°C, 55°C and 65°C, and with an acid/alcohol/catalyst molar ratio of 1/10/0.20. The results are shown in Figure 5. As the temperature increases, the rate of formation and the yield of propyl propanoate increase. After 30 min of reaction appears the greatest difference in the conversion of acid (ω) of the ester, 0.423 and 0.856 at 35°C to 65°C. The further duration of the process, up to 210 min, reduce the difference in ester yield: 0.837 and 0.969 at 35°C to 65°C.

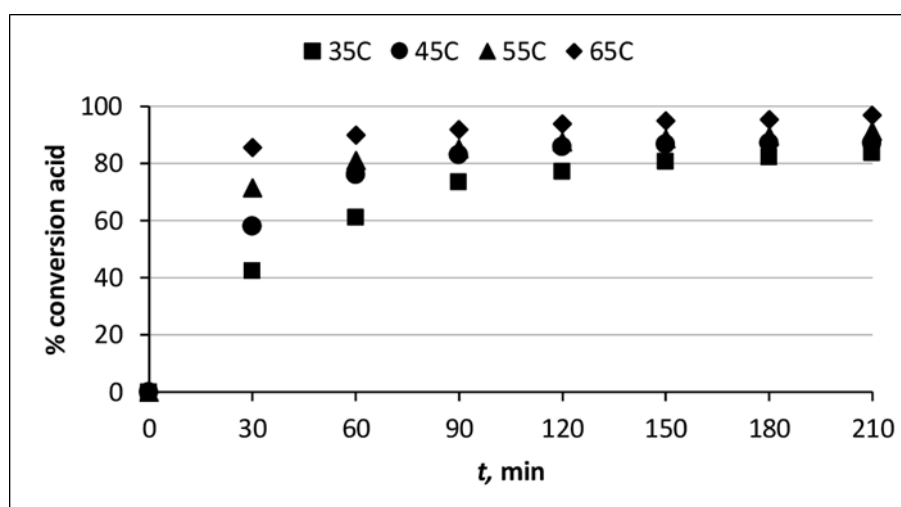


Figure 5. Influence of temperature on the conversion of propanoic acid into propyl propanoate. Conditions: acid/ alcohol/catalyst (H_2SO_4) molar ratio 1/10/0.20.

Reaction rate constant and activation energy

Literature data show that most reactions of esterification of monocarboxylic acids with a large excess of monohydroxyl alcohols are first-order reactions (SAHU and PANDIT, 2019; CARDOSO *et al.*, 2009). Therefore, the following equation can be used to describe changes in substrate concentration over time:

$$\ln[\text{propanoic acid}]_t = -kt + \ln[\text{propanoic acid}]_0 \quad (4)$$

where $[\text{propanoic acid}]_0$ - propanoic acid concentration at the beginning of esterification process, and $[\text{propanoic acid}]_t$ - propanoic acid concentration at the point of time t .

Table 1 shows the values of the rate constant (k) of the esterification reaction obtained for each tested temperature (Figure 5). As expected, an increase in the reaction temperature leads to an increase in the reaction rate.

Table 1. Values of rate constant, k , as the slopes of the linear equation (4) and linear correlation coefficient (R^2) for the H_2SO_4 catalyzed propanoic acid esterification with 1-propanol.

Temperature (K)	$\ln [\text{propanoic acid}]_t = -kt + \ln [\text{propanoic acid}]_0$ $k \text{ (min}^{-1}\text{)}$	R^2
308	$y = -0,252x + 0,150$	0,910
318	$y = -0,263x - 0,135$	0,769
328	$y = -0,283x - 0,188$	0,772
338	$y = -0,384x - 0,397$	0,768

The Arrhenius equation is applied to consider the effect of reaction temperature on the forward rate constant:

$$k = A \cdot e^{-E_a/RT} \quad (5)$$

where A is the pre-exponential factor, E_a is the activation energy, R is the ideal gas constant, and T is the reaction temperature.

This equation can be rearranged as follows:

$$\ln k = \ln A - \frac{E_a}{R} \cdot \frac{1}{T} \quad (6)$$

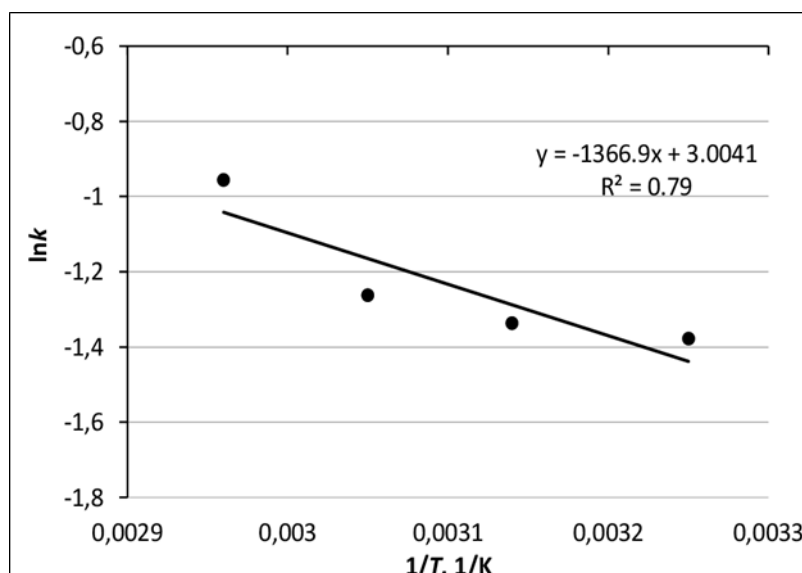


Figure 6. Linear plot of $\ln k$ versus $1/T$ resulting from H_2SO_4 catalyzed esterification of propanoic acid with 1-propanol.

Figure 6 shows the linear dependence of $\ln k$ vs. $1/T$. The activation energies of the reaction are calculated from the slope of the line ($-E_a/R$). The activation energy of the esterification reaction of propanoic acid with 1-propanol is 11.36 kJ/mol. This value is generally lower than the values found in the literature (LILJA *et al.*, 2005; TSAI *et al.*, 2011; JYOTI *et al.*, 2016; SAHU and PANDIT, 2019) for the activation energy of the formation of similar esters. However, it is often difficult to compare the calculated values of the activation

energies of the esterification process due to different reaction conditions, primarily due to the type and amount of catalyst used, different acid/alcohol molar ratios, reaction temperatures and process techniques.

CONCLUSIONS

As the number of C-atoms increases, the reactivity of alcohol in the esterification reaction with propanoic acid increases. The descending series of reactivities of the tested alcohols is: 1-butanol > 1-propanol > ethanol > 2-propanol. In addition to the physical properties of alcohol due to the length of the chain, the esterification process is also influenced by the structure of the alcohol. Due to the steric factor, faster esterification of primary alcohols is observed compared to secondary alcohols.

The longer length of the alkyl chain in carboxylic acid slightly reduces the rate and yield of esterification. There is a small difference in reactivity between butanoic and propanoic acid in contrast to α -substituted acids in which the difference in ester yield is higher. Interesting is the behavior of α -methylpropanoic acid, which in the first 90 minutes of the reaction shows less conversion to an ester than α -hydroxypropanoic (lactic) acid. With the further duration of the esterification process, α -methylpropanoic acid reacts faster and approaches the yield of the reaction given by the unsubstituted acid. Probably the reason is the suppressed hydrolysis of the formed ester, due to the low solubility of α -methylpropanoic acid in water.

As the acid/alcohol molar ratio increases from 1/2.5 to 1/10, the rate and yield of the esterification reaction increase. In the first 30 min, the difference in ester yield is small while with the continuation of the process it increases and after 120 min it reaches a constant difference in ester yield.

As the temperature increases, the rate of formation and the yield of the obtained esters increase. After 30 min of reaction, the largest difference in the conversion of propanoic acid (ω) to n-propyl propanoate occurs, 0.423 at 35°C and 0.856 at 65°C. The further duration of the process, up to 210, reduces the difference in ester yield: 0.837 and 0.969 at 35°C to 65°C.

The maximum yield of ester (n-propyl propanoate) in our experiments was 96.9%, at a molar ratio of propanoic acid/1-propanol/catalyst (H_2SO_4) of 1/10/0.20 and a temperature of 65°C for 210 min of reaction.

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