

Esterification of Lauric Acid with Ethanol Using Zirconium Oxide as Heterogeneous Catalyst

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Abstract

Esters play an important role in everyday life as well chemical industry. Esterification is the common name of chemical reaction in which two reactants free fatty acid and alcohol were reacted to produce ester and water. In this study investigate the influence of parameters on the esterification of lauric acid with ethanol in the presence of zirconium oxide as catalyst to produce ethyl laurate as ester. These parameters were molar ratio of lauric acid to ethanol (1:1-1:6), temperature (25-70°C) and catalyst amount (0-1%wt) at reaction time 120 minute. The conversion was calculated depending on acid value measured by titration. The results show the conversion increases with the increasing time, molar ratio, catalyst amount, and temperature. The maximum conversion was 89% which obtained at lauric acid to ethanol molar ratio 1:6, reaction temperature 70°C and 1%wt catalyst concentration after 120min. From kinetic study, the reaction order was second order and the rate limiting step was surface reaction when both lauric acid and ethanol adsorbed while only ester desorbed.

Keywords: Esterification; Zirconium Oxide; Heterogeneous Catalyst; Ester.

1. Introduction

The wide range of application of esters in chemical process industries has increased the importance of its study. In recent years, the consumption of esters has increased enormously. It constitutes a group of convenient chemical intermediates in the composition of different compounds such as fatty alcohols, amides and sulfonates. These compounds are so employed as reagents in production of polymers, solvents, also as materials in cosmetics, textile, cotton and pharmaceutical industry [1]. The length of the alcohol chain determinates the application of the ester product. Alcohol with short chain and low molecular weights can be used for biodiesel and biofuels production [2]. Long alcohols chain (5 to 12 carbon atoms) in esterification reaction make lubricants [3]. High molecular weight alcohols (C_{16} - C_{30}) gave fatty acid esters that are waxes. Beside the fuel production, they are used in detergents, food and other industries [4].

Esterification of carboxylic acids with alcohols illustrates a familiar category of liquid- phase reactions that is generally present in industry by mean of the great practical consideration of organic ester products [5], they generally, are not stable to perspiration and tend to break down forming carboxylic acids. The biggest issue extremely happened in (trans) esterification technology originates from equilibrium. To direct the equilibrium to the product side, one of the products should be removed conveniently during the reaction and / or one of the reactants should be used in excess [6].

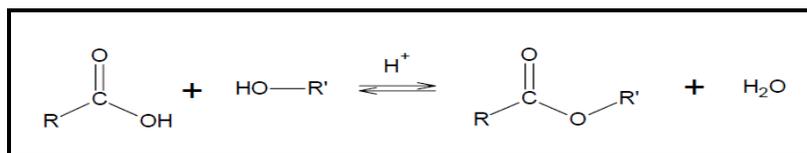


Fig. 1. General mechanism of esterification

The main factors that affect the esterification reaction are: the size and structure of the acid and alcohol, the type and amount of the catalyst, the reaction temperature and molar ratio of acid/alcohol/catalyst [4].

Esterification process can be taken place without a catalyst, even the reactions are, in worst conditions, very slow as a result of depending the rate on autoprotolysis of the carboxylic acid [7], but normally assess days or even months to attain the equilibrium in the absence of a catalyst. To accelerate the reaction rate, homogeneous and heterogeneous catalysts are commonly used [8]. Esterifications are usually catalyzed homogeneously using concentrated sulfuric acid and p-toluene sulfonic acids, which are however cause some problems such as corrosion of equipment, the existence of side reactions, and poor for waste discharge and difficult separation. So as to eliminate problems for separation that denote from the high miscibility of homogeneous catalysis in the reaction medium, such as waste handling and washing, solid acid catalysts are favored, elimination corrosion problems and indicating easy separation of catalysts from the products by filtration [9].

It is known that sulfated zirconia indicates catalytic activity in many reactions such as etherification, esterification, alkylation, etc. because its acid strength is more than other solid acid catalysts and stability which has been exploited in many reactions [10].

The aim of present study esterification of lauric acid with ethanol in presence of sulfated zirconia solid acid catalyst to produce ethyl laurate ester. The study involves the influence of molar ratio of fatty acid to alcohol, catalyst concentration and reaction temperature on the conversion of acid to ester. Also evaluate a general kinetic equation that identify the system.

2. Experimental work

2.1. Materials

The materials used were lauric acid (assay 99.4%), it is also precisely known as dodecanoic acid, is supplied from China. Ethanol alcohol was supplied from Hayman Ltd, East Ways park, UK. Zirconium oxide was prepared by modified method and characterized according to Wadood and Marwa [11] with surface are $125.23\text{m}^2/\text{g}$ and pore volume $0.063\text{cm}^3/\text{g}$ to use in this study. Phenolphthalein and potassium hydroxide used as an indicator and base respectively, for titration.

2.2. Experimental procedure

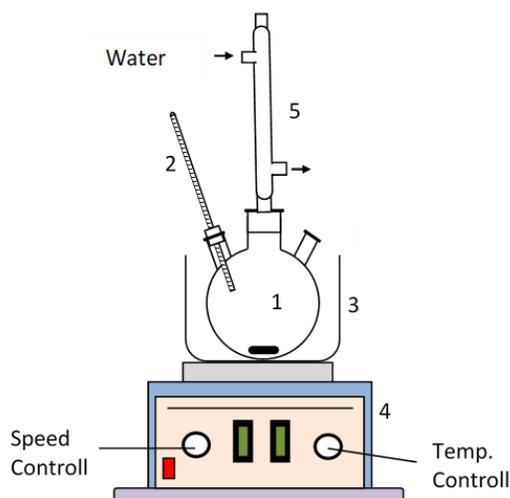


Fig. 2. Diagram of equipment. 1 Neck flask; 2 thermometer; 3 water bath; 4 magnetic stirrer; 5 condenser

Lauric acid was poured into the neck flask and heated to required temperature. Magnetic stirrer was used to change the power of the heating so as to attain the reaction temperature, the heat was supported by water bath as shown in Fig. 2. After achieving the desired temperature, ethanol and zirconium oxide were added. Then agitation was start to have a well mixing of the compounds and to suppress possible problems of mass transfer, this was representing the beginning of the reaction. Reaction was stayed for two hours, throughout this time samples were taken at different periods and centrifuged to separate catalyst from organic compound. The sample was weighted and added 2-3 drops of phenolphthalein as indicator and few ethanol for dilution, then titrate with 0.2M potassium hydroxide to calculate acid value as indicated in Eq. (1) and get free fatty acid conversion to ester as shown in Eq. (2)

$$\text{acid value} = \frac{\text{volume (KOH)} \times \text{molarity (KOH)} \times \text{Molecular weight (KOH)}}{\text{Weight(sample)}} \quad (1)$$

$$X_{\text{conversion}} = \frac{\text{initial acid value} - \text{present acid value}}{\text{initial acid value}} \times 100\% \quad (2)$$

3. Results and discussion

3.1. Effect of time and molar ratio of free fatty acid to alcohol

The molar ratio was varied from 1:1 to 1:6 at time 90 min in order to evaluate the behavior of the excess of one of the reactants on the reaction rate which usually alcohol. Therefore, Fig. 3 demonstrates the conversion of lauric acid with reaction time at various molar ratio of ethanol: lauric acid with constant temperature and catalyst concentration. It can be clearly seen the conversion increased with increasing time for all molar ratio since it increases from 66 to 83% as time increased from 30 to 90 min for ratio 1:6. Also activity profile was shown, when the molar ratio increased from 1 to 3 and 6 the conversion was increased from 46% to 70% and 83% respectively after 90 min reaction time.

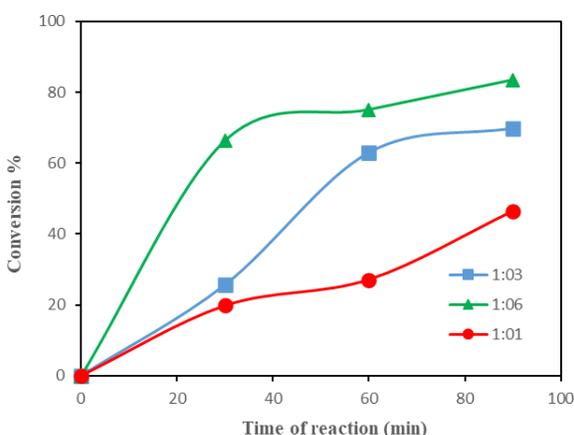


Fig. 3. Effect of molar ratio on conversion at temperature 55°C and zirconium oxide catalyst 1%wt

3.2. Effect of temperature

It is essential in every reaction to realize the temperature reaction that will give optimum conversion. It was determined by varying the reaction temperature at 40°C, 55°C and 70°C and illustrated in Fig. 4.

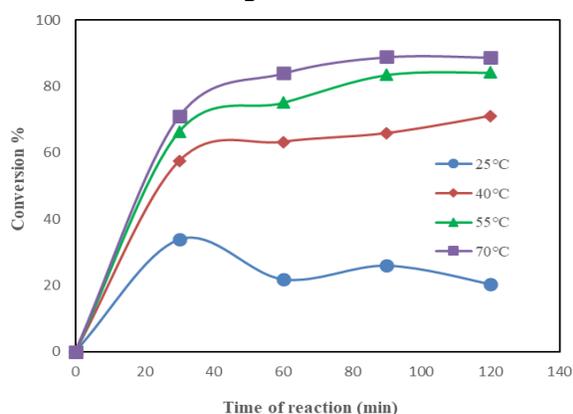


Fig. 4. Effect of reaction temperature on conversion at molar ratio 1:6, zirconium oxide catalyst concentration 1wt%

This increase can be demonstrated by the fact that when the ethanol-to-oil ratio increases, the viscosity of an ethanol/oil mixture decreases and the impact of the diffusion of the reactants towards the catalyst particles decreased and hence improved the interparticle diffusion that inducted to higher conversion [12].

This behavior agrees with Kusmiyati and Sugiharto [13] who showed that esterification of oleic acid with methanol using H_2SO_4 had affected by the molar ratio of alcohol to acid at temperature 150°C, 1wt% catalyst, reaction time 90 min. The conversion increased from 85% to 95% at ratio increase from 1 to 8.

All other parameters were kept fixed i.e. fatty acid to alcohol molar ratio 1:6, catalyst concentration 1wt%. It was observed that as temperature increase the conversion of lauric acid increase also therefore optimum percent conversion was 89% which is obtained at 70°C after time 120min. Also, it can be seen the conversion at 25°C (room temperature) was increased at 30 min (33%) and after that decrease to reach 20% at time 120min this may due to that reaction become reversible.

According to the collision theory [14], which is the famous theory described the chemical reaction, increasing in reaction temperature may causes an increase in molecule activity, which means that more molecules have more energy

to react, and reduction in viscosity of reaction mixture (i.e. remarkable increasing of diffusivity). Thus, increasing of temperature increases the possibility of the molecule to diffuse through the catalyst pores, reach to the active site of catalyst and react.

3.3. Effect of catalyst percent

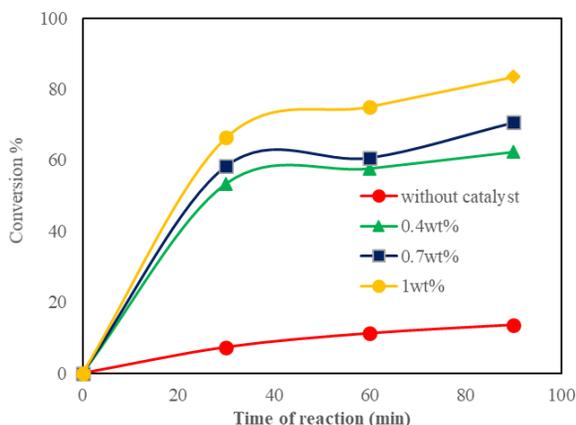


Fig. 5. Effect of Catalyst concentration on conversion at molar ratio 1:6 and temperature 55°C

Fig. 5 shows a gradual increase in the conversion for the different of catalyst concentration 0.4, 0.7 and 1wt% with constant condition of 55°C of temperature and fatty acid to alcohol molar ratio 1:6. The reaction rate of esterification is directly proportional to the amount of a catalyst. As the quantity of the catalyst increased, the rate at which reaction equilibrium was accomplished also increased. The conversion improved from 13%, which that achieved without catalyst after 90min to reach conversion 61% at the reaction catalyzed by 0.4wt% SZ at the same time. While for higher concentration of catalyst (1wt %), the conversion also increased to reach maximum conversion of 84%.

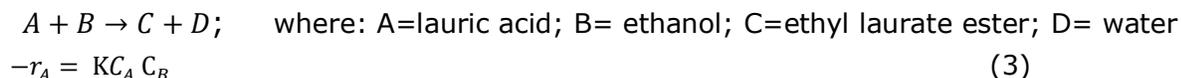
In general, increasing the amount of catalyst will increase the number of active sites ready for the adsorption of the reactants leading to a more immediate increase in the number of active sites of interaction between the reactants [15].

4. Calculation of kinetic model

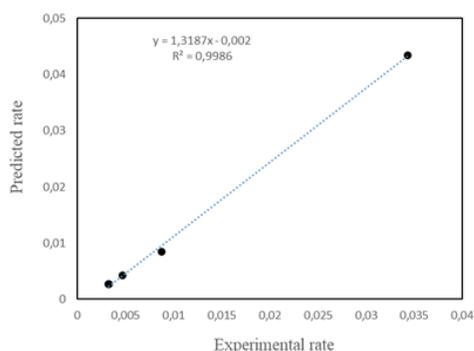
An important step for any kinetic study is a mathematical model capable of predicting rate for giving conversion that close to experimental rate. As was expected the reaction mechanism for heterogeneous catalyst differs from that for homogeneous one and there were many models describing the reaction mechanisms, these were adsorption of reactants, surface reaction and desorption of products [16] and all models tried to reach to true mechanism.

The equation which governs the rate of esterification was determined by trial and error. The rate was calculating at best conditions (molar ratio lauric acid to alcohol 1:6, reaction temperature 70°C and catalyst amount 1%wt). Assuming a non-reversible "second" order reaction.

The actual rate can be calculated from the experimental data by applying the rate of reaction which compared with a theoretical rate using a statistica program. The experimental rate calculated by Eq. (3)



$$C_A=C_{A0} (1-X); \quad C_B= C_{A0} (\theta_b -X) \quad \text{when } \theta_b=C_{B0}/C_{A0} \quad \frac{-dC_A}{dt} = K C_{A0}(1-x) C_{A0}(\theta_b - x)$$



The experimental rate after calculated was compared with predicted rate by statistic program to find which model satisfy the esterification process. The best model was surface reaction when both A and B adsorbed while only C desorbed as shown in Fig. 6.

Fig.6. Predicted vs. experimental rate for lauric acid esterification

5. Conclusions

Increasing the ethanol/lauric acid molar ratio from 1:1 to 6:1 led to increase the conversion of lauric acid. As the amount of zirconium oxide catalyst increased from 0.4 to 1 wt%, conversion of lauric acid increases. As temperature increase the conversion of lauric acid increase. The optimum condition for the esterification of lauric acid by heterogeneous catalyst is 1:6 ratios, 70°C and 1wt% catalyst concentration which gave the highest conversion 89%.

From kinetic study, the reaction order was second order and the rate limiting step was surface reaction when both lauric acid and ethanol adsorbed while only ester desorbed.

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