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The Effect of Water Sorbent on Lipase-Catalysed Esterification of Fatty Acid

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Abstract High conversions in lipase-catalysed production of fatty acid esters from fatty acids and alcohols require efficient removal of water preferentially. A lipase-catalysed esterification of oleic acid and dodecanol using adsorbent (zeolite) and absorbent (superabsorber) was investigated. The zeolite and the superabsorber were used to shift the equilibrium toward fatty acid ester production by preferential elimination of the water by- product during the esterification reaction. Improved products of fatty acid esters with lower acid values were obtained for both the zeolite and superabsorber systems. The superabsorber exhibited better water removal property in shifting the equilibrium toward the desired product compared to the zeolite.

Keywords Esterification, Fatty acid ester, Lipase, Zeolite, Superabsorber

1. Introduction

The products from chemical and process industries have been an indispensable commodity in modern day life. These industries are, however grappling with the need to improve upon these products as well as handling the industrial wastes that are generated. Industries are therefore highly demanded to develop products and processes that are sustainable. Raw materials and advanced methods must be carefully selected to achieve high conversion rates and efficient use of energy. Therefore, the existing and future design processes must exceed those achieved by using the toolbox of conventional process units to overcome these challenges [1]. This necessitated the introduction of process intensification [2-4] in recent years, which Lutze et al., [4] described as a tool for the targeted improvement of phenomena that occur at different scales to achieve a targeted benefit. The ultimate aim at the reaction stage is to attain the highest production efficiency and yield of the desired product in a safe operation as well as the highest recovery and purity of products at the separation steps in order to maximize profit. [5].

Esters are one of the most useful classes of organic compounds in the chemical and process industries. Esters, are produced when carboxylic acids are heated with alcohols in the presence of an acid catalyst.

$$R_1 - COOH + R_2 - OH \Leftrightarrow R_1 - COO - R_2 + H_2O \quad (1)$$

In esterification, water is formed as a by-product. This produced water, affects the rate of the reaction negatively by initiating a decreasing effect on the activity of the catalyst (poisoning the acid site) and also limiting the maximum obtainable conversion, [6] since the esterification reaction is a reversible, and also equilibrium limited. In chemical processes, a combination of the reaction and the separation presents a range of opportunities for higher efficiency of the processes. The separation and purification steps are often among the most capital intensive steps in chemical processes. This is particularly true for reversible esterification reactions [7], where thermodynamic equilibrium limitations make it often difficult (if not impossible) to attain high conversions [8]. Several of such state-of-the-art processes which combine the reaction and the separation steps [9, 10] are familiar options to conventional processes with sequential reaction and separation steps. Reactive distillation is one of such process, but has a notable drawback in the formation of non-ideal aqueous- organic mixtures in several cases, which tend to form azeotropic mixtures. Such a disadvantage can be surmounted by introducing pervaporation and vapour permeation membrane separations processes which tend to be very selective and not vapour-liquid equilibrium bounded [11]. Hence a hybrid process made up of membrane-assisted reactive distillation serves a sustainable process improvement. Lipinski et al, [10], reviewed a number of hybrid processes combining pervaporation with one or more other separation technologies. Kreis and G´orak, [12] describe the analysis of hybrid separation processes combining membrane separation with conventional distillation. Von Scala et al., [13] also present an industrially operated hybrid process for the continuous production of fatty acid esters by reactive distillation and pervaporation. A study of another reaction technique in which the water is

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removed by a counter-current operation using a flow through the reactor is also reported [14]. Vapour permeation and pervaporation are most widely used membrane technology. One of the hybrid pervaporation membrane reactor system integrates the pervaporation step through a membrane with adsorption in the permeate side. The development of one such hybrid process which uses only water sorbents to remove water from esterification reaction is described in this paper. Apart from being less energy intensive and more temperature favourable to the biochemicals and fine chemicals, is also less cost-productive. The application is illustrated by esterification of oleic acid (fatty acid) and dodecanol using lipase biocatalyst.

2. Experimental Methods

2.1. Chemicals

Oleic acid was bought from Merck KGaA (Darmstadt, Germany, 65-88%). For the esterification, dodecanol (Merck Schuchardt OHG, Hohenbrunn, Germany, 98%) and biocatalyst (lipase), Novozyme 435 (Novo, Denmark) were used. The zeolite and the superabsorber were obtained from Stockhausen GmbH, (Krefeld, Germany). Differential thermogravimetry (DTG) and differential thermal analysis (DTA) were carried on the zeolite. The analysis (Figure 2) shows that, it is able to withstand a maximum temperature of about 300℃. The zeolite was activated in a drying oven overnight at 250℃ prior to use.

2.2. Procedure

The experimental set-up used for the esterification reaction (3) is schematically shown in Figure 1. The 250- ml three-neck round bottom flask was placed in a thermostatic water bath and a thermocouple was used to regulate its temperature. The esterification reactions were carried out in a fixed-bed reactor. The reactor was filled with the bio-catalyst together with glass beads in a ratio of enzyme to glass beads (vo/vo) of about, 1: 3. The reaction temperature of 50℃ was maintained by circulating heated water. A filter tube was filled with zeolite (and superabsorber in a separate experiment) and inserted into the neck of the flask through which the reaction mixture returns to the flask. The zeolite and the superabsorber were used primarily to adsorb and absorb water respectively. An equimolar ratio of oleic acid and dodecanol was used in the experimental. Oleic acid was put in the flask and heated up to the reaction temperature. Dodecanol was heated separately to the reaction temperature and then added to the flask. The reaction mixture was simultaneously pumped continuously through the reactor unit at the rate of 1.43ml/s. The total volume of the reaction mixture was 350- ml. Samples were withdrawn periodically to determine the acid values based on AOCS Cd 3d-63 procedure [15]. The acid value was calculated using the formula in (1). The esterification of oleic acid with dodecanol, without removing water was also carried out.

Both the zeolite and the superabsorber were regenerated for reuse. The zeolite after freshly used was washed several times with methanol to remove the organic ester from the surface and then repeatedly washed again with distilled water get rid of the methanol. It was then dried in an oven at a temperature of 250℃ overnight. The superabsorber also after freshly used was dried in an oven overnight at a temperature of 150℃. They were both used to repeat the experiment.

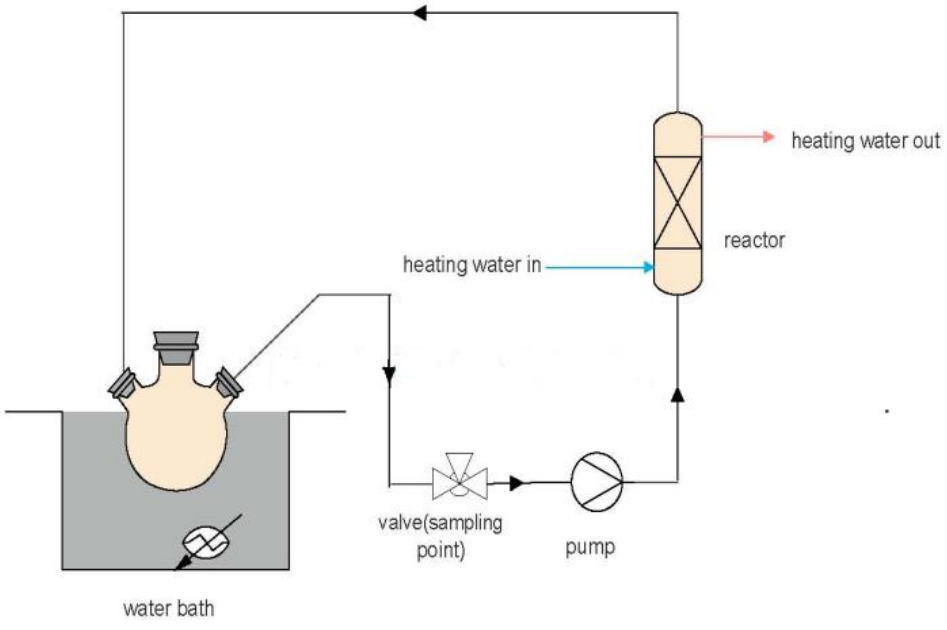

Figure 1. Process flow diagram of liapse-catalysed esterification of and oleic acid dodecanol

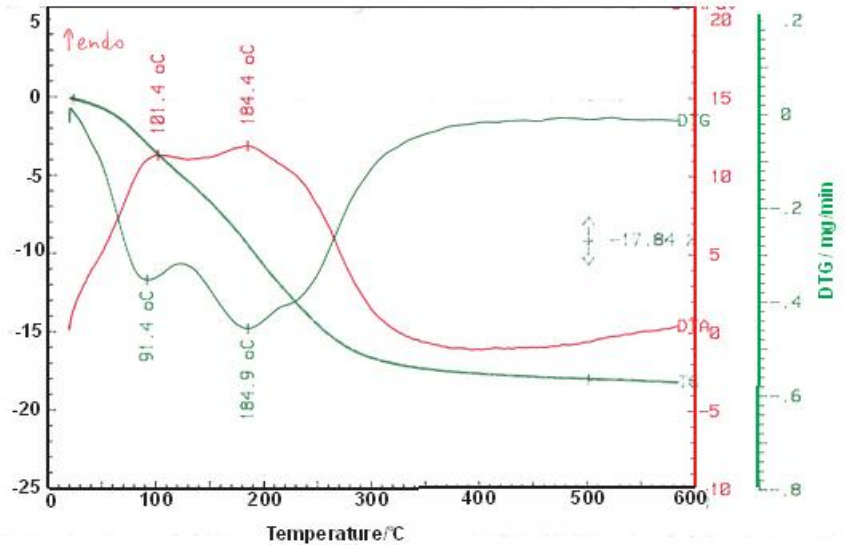

Figure 2. DTA and DTG analysis of zeolite

$$\text{Acid value in mg KOH/g of sample} = \frac{56.1 \times N \times V}{W} \quad (2)$$

where N = normality of KOH solution
V = volume(ml) of KOH used
W = weight of sample in grams(g)

$$CH_3(CH_2)_7(CH)_2(CH_2)_7COOH \quad + \quad CH_3(CH_2)_{11}OH \quad \Leftrightarrow$$

(oleic acid) (dodecanol)

$$CH_3(CH_2)_7(CH)_2(CH_2)_7COOCH_2(CH_2)_{10}CH_3 \; + \; H_2O \quad (3)$$

(fatty acid ester) (water)

3. Results and Discussion

The acid values obtained in the reactions are presented in Figure 3. The results indicate that both the zeolite (adsorbent) and the superabsorber (absorbent) were effective in preferentially removing water during the esterification to yield fatty acid esters with lower acid value. A uniform reference initial acid value for all the esterification reactions was calculated to be 122.4 mgKOH/g. The esterification of oleic acid and dodecanol without removing the water by-product resulted in a higher acid value of the ester 15.70 after 210min of reaction. The introduction of the adsorbent and the absorbent into the reaction system significantly reduced the acid value from 15.70 mgKOH/g to 2.24 mgKOH/g and 1.68 mgKOH/g respectively. However, the results show that the superabsorber yielded a substantial lower acid value than zeolite at the same reaction time (210min) indicating the superabsorber was a better water remover compared to the zeolite. These results were obtained at a reaction temperature of 50℃ and an equimolar ratio of fatty acid to dodecanol.

It can be seen from Figure 3 that, the reaction rate decreased rapidly after an initial high reaction rate within the first 5-30min. The trend could suggest some form of heat and mass transport limitation in the reaction system but the reaction was carried under thorough mixing and continuous pumping at the rate of 1.43ml/s. By the law of mass action, the initial reaction rate was caused by the high initial concentration of reactants resulting in faster early consumption of reactants. However, after the initial fast reduction of reactants there is a significant decrease in reactants effective concentration which results in a fall of the reaction rate. The observed decrease in the reaction rate is also indicative of the reaction approaching equilibrium conditions. Initially, the fatty acid phase is virtually free from dodecanol and water, thus a direct reaction occurs mainly at fatty acid-alcohol interface.

As reaction progresses and fatty acid ester is formed, the fatty acid phase will contain fatty acid, fatty acid esters, dodecanol and water. However, dodecanol and water are partially soluble in fatty acid esters, thus further reducing the reaction rate. This conforms to previous observation by Lucena et al. [16]. The reaction rate for the superabsorber system was extremely faster than that of the zeolite. The

superabsorber system comes to a completion just after 90min whiles that of zeolite is achieved after 210min. This observation was attributed to the faster rate of water removal in the superabsorber system as compared to that of zeolite to shift the equilibrium towards the desired product. This could be due to the molecular structural difference between the two water sorbents. The superabsorber, is a cross linked polymer that form a gel when it absorbs fluid. This trapped liquid is not released even under extreme pressure whereas the zeolite has symmetrically stacked alumina and silica tetrahedral which forms an open and stable three-dimensional honey-comb structure. Indicating that superabsorber possessed superior water removal capacity and enhanced a faster reaction compared to the zeolite. Our results (Figure 4) from the regeneration of both the zeolite and superabsorber showed that the superabsorber could be regenerated for reuse whereas the zeolite lost its effectiveness after primary the initial application. The regenerated superabsorber produced an acid value similar to that of the fresh one (1.68 mgKOH/g). However, the reaction rate for the regenerated superabsorber system was comparatively slower than that of the flesh one. The regenerated zeolite system could only produce results (15.4 mgKOH/g) similar to a conventional reaction with no preferential removal of water indicating the regeneration was ineffective.

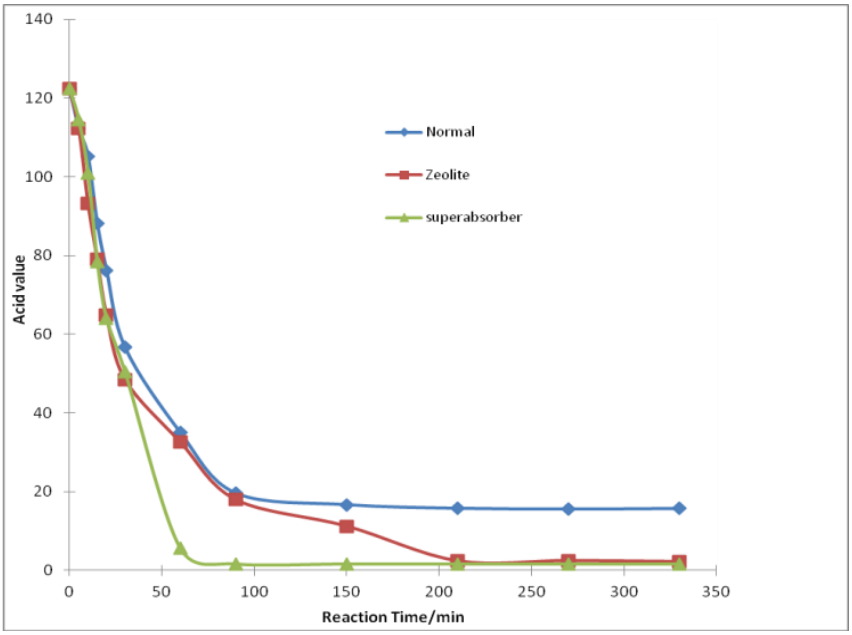

Figure 3. Effect of time on Acid value for esterification of oleic acid and dodecanol for (♦) normal reaction without water removal and water removal (■) with zeolite and (▲) with superabsorber

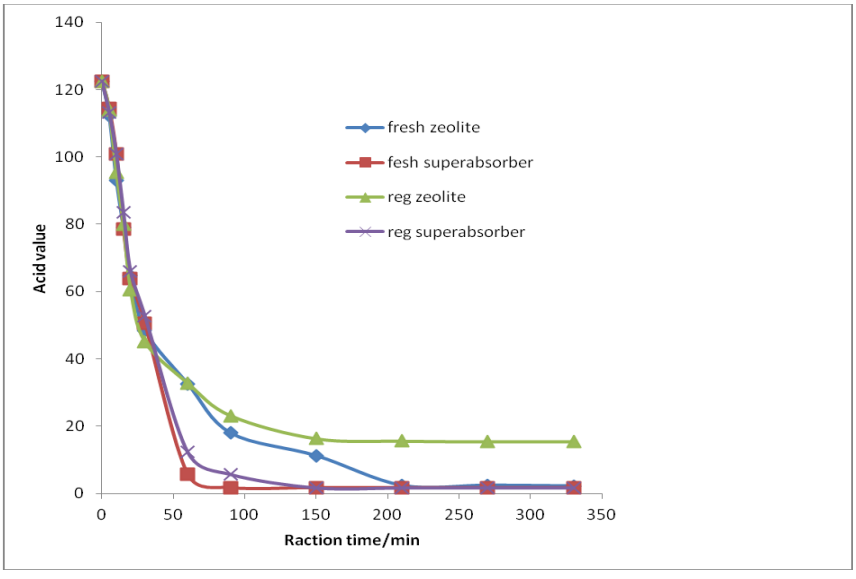

Figure 4. Effect of time on Acid value for esterification of oleic acid and dodecanol for reaction with water removal, (♦) with fresh zeolite (■) with fresh superabsorber (▲) with regenerated zeolite (x) regenerated superabsorber

4. Conclusions

A lipase-catalysed esterification of oleic acid with dodecanol was successfully carried out with equimolar amount of the acid and the alcohol at a temperature of 50℃. Zeolite adsorbent and absorbent were used to selectively remove water during the reaction to displace the equilibrium towards the products. Both the adsorbent and the absorbent system yielded substantially low acid value of 2.24 and 1.68 respectively after 210min of reaction time. However, the superabsorber exhibited superior water removal property compared to the zeolite. The superabsorber could be regenerated for reuse whilst the zeolite could not.

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