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Biodiesel from Oleic Acid by Green Catalyst "Catalytic Membrane": a Solution to Global Warming Problems

D. Unlu, F.U. Nigiz and N. Hilmioglu*
Kocaeli University, Chemical Engineering Department, Kocaeli, Turkey

In recent years biodiesel is receiving more attention as a sustainable alternative to fossil fuel. Biodiesel has lower exhaust emissions and toxicity compared to petroleum diesel fuel. In this study, biodiesel is produced from the oleic acid esterification process. We try to develop an efficient heterogeneous catalyst for biodiesel synthesis. A catalytic membrane carboxymethyl cellulose with sulfosuccinic acid has been prepared for using as catalyst. Carboxymethyl cellulose is a natural and biodegradable polymer and it has the advantage of green catalysis. Sulfosuccinic acid is a homogeneous catalyst. To overcome the disadvantages of the homogenous catalyst, sulfosuccinic acid is used together with polymeric membranes. The effects of the ethanol/oleic acid molar ratio, the reaction temperature, the sulfosuccinic acid concentration and the stirring speed were investigated to find out the optimum reaction conditions. The catalytic stability of the catalytic membrane is also studied. The optimum conditions for the reaction were found to be 65 °C, catalytic membrane with 6 mmol of sulfosuccinic acid, 9:1 ethanol to oleic acid molar ratio and 600 rpm stirring speed. The oleic acid conversion using the catalytic membrane was 85% under these conditions after 6 h. Our findings show that carboxymethyl cellulose membrane with sulfosuccinic acid groups is a suitable catalyst for esterification.

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1. Introduction

Global warming poses a fundamental threat to the climate, species and people, in other words all over the world [1]. A major cause of global warming is release of too much carbon dioxide into the atmosphere. As we burn fossil derived fuels like coal, oil, petroleum, natural gas for energy, carbon emission accumulates and overloads our atmosphere [2]. There is no single solution to global warming. The new technologies and approaches are needed to decrease the emissions of these gases. Energy efficiency technologies, green transportation, renewable energy sources such as biofuel are good alternative solutions for clean atmosphere. In recent years biodiesel is receiving more attention as a sustainable alternative to fossil fuel. Biodiesel is manufactured from renewable sources, such as vegetable oils, animal fats or recycled restaurant grease [3]. Biodiesel has lower exhaust emissions and toxicity compared to petroleum diesel fuel. It can be used with conventional diesel as a blend or used on its own without modification [4].

Biodiesel is prepared through the transesterification of triglycerides or the esterification of free fatty acids (FFAs) with low-molecular-weight alcohols. The esterification reactions are mostly carried out by using homogeneous acid catalysts. The homogenous catalysts have high catalytic activity. However, they have some disadvantages, such as corrosion, recovery, reuse and environmental problem. Therefore, homogeneous catalysts should be replaced with heterogeneous catalysts. Recently, catalytic membranes as a form of heterogeneous catalysts have been used in the esterification. Functional catalytic membranes have drawn a great deal of attention in biodiesel production. The catalytic membranes avoid equipment corrosion, separate the catalysts easily from the reaction mixtures and decrease the wastewater effluent [5–7].

In this study, catalytic membrane of carboxymethyl cellulose (CMC) with sulfosuccinic acid was prepared for the esterification of oleic acid. CMC has chemical bonding with sulfonic acid groups (–SO_3H) in the catalytic membranes. Catalytic membrane display good stability and catalytic activity for the reaction. The effects of the ethanol/oleic acid molar ratio, the reaction temperature, the sulfosuccinic acid concentration and the stirring speed were tested and reaction conditions were optimized by experimental studies. 85% conversion value was obtained at 65 °C, 9/1 of ethanol/oleic acid molar ratio, catalytic membrane with 9 mmol SSA and 600 rpm of stirring speed for 6 h.

2. Experimental

2.1. Catalytic membrane preparation

The CMC catalytic membrane was prepared by dissolving in water at room temperature for 24 h. Aqueous 1.5 wt.% CMC polymeric membrane solutions were stirred with the different ratios of sulfosuccinic acid (SSA) for 24 h. The homogeneous polymer solution was cast onto a polymethyl methacrylate (PMMA) plate. The membrane was dried at 60 °C for 24 h. The dried

*corresponding author; e-mail: niluferh@kocaeli.edu.tr

polymeric membrane was heated at 100 °C, during 2 h in order to finish preparing of CMC membrane for using as catalyst in the reaction. Catalytic membrane was characterized by FTIR spectroscopy and by polarized optical microscopy.

2.2. Biodiesel synthesis by oleic acid esterification

The reaction experiments were carried out in a stirred batch reactor, equipped with a condenser and a thermometer. In a typical experiment, the reactor was loaded with the appropriate amounts of ethanol and oleic acid and catalytic membrane cut in small pieces. Samples were taken periodically and analyzed by titration. After the esterification reaction, catalytic membrane was separated from the reaction mixture by filtration.

3. Results and discussion

3.1. Characterization of catalytic membrane

The catalytic sites of the membrane were tested using Fourier transform infrared (FTIR) spectra. Figure 1 shows the FTIR spectra and optic microscope image of catalytic membrane.

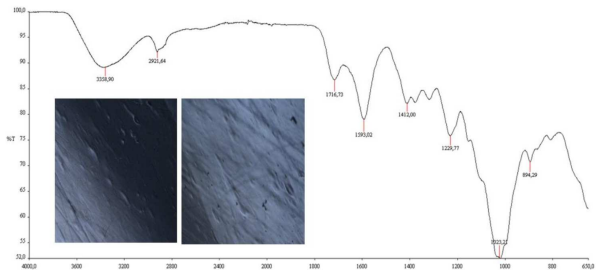

Fig. 1. FTIR spectra and optic microscope image of the catalytic membrane.

The FTIR spectra of the catalytic membrane show that the carboxyl and methyl functional groups are found at 1593.02 cm^{-1} and 2921.64 cm^{-1}, respectively. The band at 3358.90 cm^{-1} is due to the hydroxyl group. The band in the range of 1023.27–1229.77 cm^{-1} is assigned to the ether bonds. The band at 1023.27 cm^{-1} is due to SO_3H groups [8–9].

The surface of CMC was also viewed by the polarized optical microscopy, as shown in Fig. 1. The image of the membrane surface shows that CMC has nonporous-homogeneous surface and SSA catalyst dissolves homogeneously.

3.2. Effect of the ethanol/oleic acid molar ratio

The esterification reaction of ethanol and oleic acid was performed in excess of ethanol to favour the forward reaction, since the esterification reactions of fatty acids with alcohols is reversible. In order to study the effect of molar ratio of oleic acid to ethanol on esterification reaction, different experiments were carried out using 1:3, 1:6 and 1:9 ratios, at 65 °C and 4 mmol SSA loaded catalytic membrane catalyst under the 400 rpm.

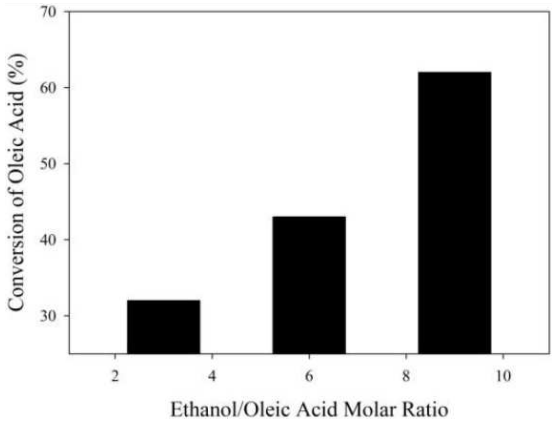

Fig. 2. Effect of the ethanol/oleic acid molar ratio.

Esterification reaction is a reversible reaction. The molar ratio of ethanol to oleic acid is an important parameter that influences the oleic acid conversion. The excess amount of ethanol must be used to change the reaction towards the formation of product. As shown in Fig. 2, the mole ratio of ethanol to oleic acid is changed from 3:1 to 9:1, while keeping the other reaction parameters constant. This shows the relationships between the conversion value and ethanol/oleic acid molar ratios with 4 mmol SSA loaded catalytic membrane catalyst to oleic acid and 65 °C under the 400 rpm stirring conditions. When the molar ratio has increased from 3:1 to 9:1, the conversion of oleic acid has increased, since the excess ethanol shifted the equilibrium to the product side.

Therefore, besides shifting the equilibrium by the excess of the reactant, the higher conversion could be attributed to the availability of the active sites. In addition, high ethanol/oleic acid molar ratio may also result in more water. Water may react with the ethyl oleate and convert it back to oleic acid.

In this study, the usage of polymeric catalytic membrane overcomes these disadvantages due to hydrophilic properties of CMC. CMC has sorbed water and avoided the back conversion of reaction equilibrium. Excess of ethanol molecules may cause flooding of the active sites of the catalyst, but the usage of catalytic membrane hinders the activity loss of active sites. Therefore, 9:1 is found to be the optimal ethanol to oleic acid molar ratio according to conversion results [10, 11].

3.3. Effect of the reaction temperature

Activation energy is required to start the reaction for the esterification of oleic acid and ethanol. For this reason temperature is an important variable, because the reaction rate depends on the reaction temperature. The studied reaction temperature was 45, 55 and 65 °C, with ethanol/oleic acid molar ratio of 9:1 and 4 mmol SSA loaded catalytic membrane catalyst under the 400 rpm stirring conditions. The effect of reaction temperature on oleic acid conversion was investigated and the results are shown in Fig. 3.

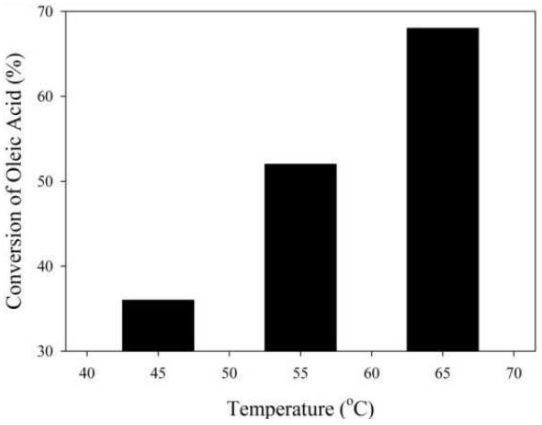

Fig. 3. Effect of the reaction temperature.

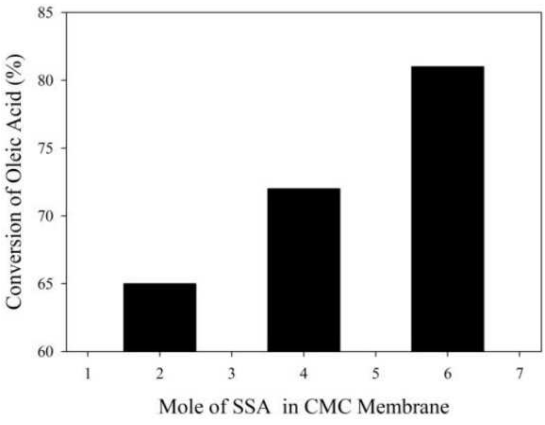

Fig. 4. Effect of the sulfosuccinic acid concentration.

The oleic acid conversion increases with the temperature, because of the characteristic behavior of an endothermic reaction and the increase in the equilibrium constant. The increment of conversion also avoids some mass transfer limitation between reactants and catalyst. In some of the studies in the literature, higher reaction temperature had caused the decrement of the oleic acid conversion. This situation was explained as follows: higher temperature results in the evaporation of reactants, especially of ethanol [9]. In this study, the esterification reaction was carried out at low temperature values (45 °C, 55 °C and 65 °C) compared to the literature data. It can be clearly seen in Fig. 3, that the conversion of oleic acid has reached the maximum conversion value at 65 °C. Hence, an optimum reaction temperature of 65° was selected for esterification of oleic acid. Temperature of 65 °C is lower than temperature values in literature. Low temperature minimizes the use of energy and brings economic benefits [10, 12–13].

3.4. Effect of the sulfosuccinic acid concentration

In order to investigate the effect of sulfosuccinic acid amount on the oleic acid conversion, different catalytic experiments were carried out with 2 mmol, 4 mmol and 6 mmol of sulfosuccinic acid loaded catalytic membrane. The molar ratio of ethanol to oleic acid and temperature were kept constant at 9:1 and 65 °C, respectively. Figure 4 shows the conversion of oleic acid versus sulfosuccinic acid concentration.

The catalyst amount is another important parameter for the esterification reaction of oleic acid and ethanol. The results show that, when the catalyst amount in the catalytic membrane is increased from 2 mmol to 6 mmol, the oleic acid conversion increases from 65% to 81%. When the catalyst amount in the catalytic membrane increases, the conversion of oleic acid is increased, because SSA provides more active sites for the reaction. Low catalyst amount in the catalytic membrane is not supplying enough active sites, thereby conversion value of oleic acid is lower and more catalyst is needed. However, more catalysts could increase the production cost. Therefore, 6 mmol of SSA catalyst loaded catalytic membrane is preferrable. 6 mmol is quite a small amount of catalyst with respect to data from literature. Higher conversion value of oleic acid has resulted in high water concentration. Also, the accumulation of the water on the surface of the catalyst hinders the accessibility of active sites. However the catalytic membrane overcomes this problem of sorption of water because of its hydrophilic character [10–12].

3.5. Effect of the stirring speed

To investigate the effect of stirring on esterification of oleic acid and ethanol, the reaction was carried out at 65 °C using 6 mmol SSA loaded catalytic membrane and 9:1 molar ratio of ethanol to oleic acid. In order to avoid mass transfer resistance, different stirring speeds (400 rpm, 500 rpm and 600 rpm) were tested.

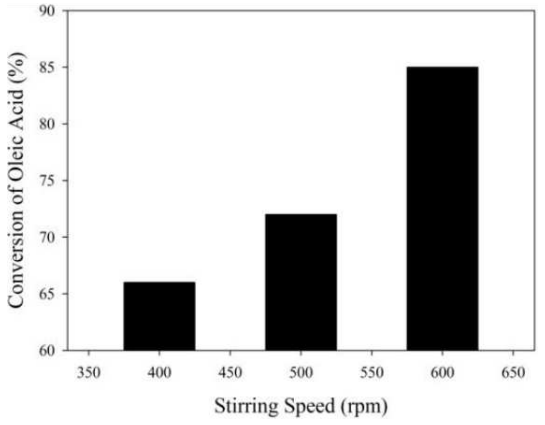

Fig. 5. Effect of the stirring speed.

Figure 5 shows the change of oleic acid conversion at various stirring speeds. At lower stirring speed of 400 rpm, lower conversion value was obtained with respect to that of high stirring speed. While the conversion of oleic acid value was 65% at 400 rpm, 85% conversion value was obtained at 600 rpm. These results indicate

that mass transfer limitations have an important role. In order to overcome this problem, the reaction was carried out at 600 rpm [14, 15].

3.6. Reusability

The catalytic stability of the SSA loaded catalytic membrane was also studied. The experiments were carried out under the same reaction conditions.

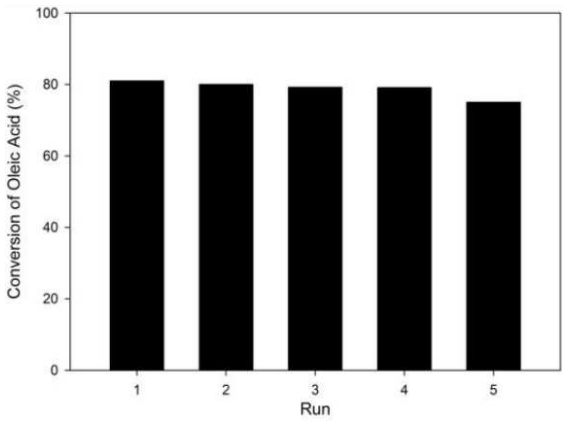

Fig. 6. Reusability experiments.

Reusability of catalytic membrane has an important role in reducing the total cost of the production. The experimental results show that SSA loaded catalytic membrane was reusable with some loss in activity (Fig. 6). The slight decrease of catalytic activity of SSA loaded catalytic membrane may be due to some leaching of sulfosuccinic acid. Figure 6 shows that the catalytic membrane can be used five cycles without significant loss of activity. The reusability experiments show that SSA loaded catalytic membranes are stable and can be used again and again without loss of catalytic activity [10, 13, 16].

4. Conclusions

Carboxymethyl cellulose, functionalised with sulfosuccinic acid, containing sulfonic acid groups, was used as catalytic membrane for the biodiesel synthesis. The effect of reaction parameters, such as the molar ratio of oleic acid to alcohol, reaction temperature, the sulfosuccinic acid concentration and the stirring speed, on the catalytic activity of catalytic CMC/SSA membrane was investigated. The catalytic activity of catalytic membrane has increased with the increase of any of the reaction parameters. Catalytic activity increases with sulfosuccinic acid amount due to the increase in the number of sulfonic acid groups. It was observed that when the sulfosuccinic acid amount increased, the conversion of oleic acid increased from about 65% (2 mmol SSA) to 81% (6 mmol SSA). As the reaction temperature increased from 45 °C to 65 °C, the oleic acid conversion had increased from 36% to 68 %. 62% of oleic acid conversion was obtained when the reaction was carried out with 9:1 of ethanol/oleic acid molar ratio. The optimum reaction conditions were determined as 85% for 65 °C, 6 mmol SSA, 9:1 ethanol/oleic acid molar ratio and 600 rpm stirring speed. The obtained results show that CMS/SSA functional catalytic membrane is an efficient alternative catalyst for the biodiesel synthesis by oleic acid esterification. The potential advantages of the catalytic membranes are reusability and recovery and the large number of catalytic active acid sites, which are properties inherent to a green catalyst.

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