

Transesterification of Waste Cooking Oil for Biodiesel Production Using Modified Clinoptilolite Zeolite as a Heterogeneous Catalyst

D. Mowla, N. Rasti, P. Keshavarz

Abstract—Reduction of fossil fuels sources, increasing of pollution gases emission, and global warming effects increase the demand of renewable fuels. One of the main candidates of alternative fuels is biodiesel. Biodiesel limits greenhouse gas effects due to the closed CO₂ cycle. Biodiesel has more biodegradability, lower combustion emissions such as CO, SO_x, HC, PM and lower toxicity than petro diesel. However, biodiesel has high production cost due to high price of plant oils as raw material. So, the utilization of waste cooking oils (WCOs) as feedstock, due to their low price and disposal problems reduce biodiesel production cost. In this study, production of biodiesel by transesterification of methanol and WCO using modified sodic potassic (SP) clinoptilolite zeolite and sodic potassic calcic (SPC) clinoptilolite zeolite as heterogeneous catalysts have been investigated. These natural clinoptilolite zeolites were modified by KOH solution to increase the site activity. The optimum biodiesel yields for SP clinoptilolite and SPC clinoptilolite were 95.8% and 94.8%, respectively. Produced biodiesel were analyzed and compared with petro diesel and ASTM limits. The properties of produced biodiesel confirm well with ASTM limits. The density, kinematic viscosity, cetane index, flash point, cloud point, and pour point of produced biodiesel were all higher than petro diesel but its acid value was lower than petro diesel. Finally, the reusability and regeneration of catalysts were investigated. The results indicated that the spent zeolites cannot be reused directly for the transesterification, but they can be regenerated easily and can obtain high activity.

Keywords—Biodiesel, renewable fuel, transesterification, waste cooking oil.

I. INTRODUCTION

THE quickly growing of world population has increased cooking oil and fossil fuel consumptions. The excessive fossil fuel demand has caused reduction of nonrenewable fuel supply, fossil fuel price hike, increasing emission, pollution, and global warming effects. So, it is very necessary to discover other renewable energy sources. One of the main choices of alternative fuels is biodiesel [1], [2]. Biodiesel is fatty acids methyl ester [FAME] and may be produced by transesterification of vegetable oils and animal fats [2]. The most common biodiesel production methodology is transesterification. Transesterification is a catalyzed chemical reaction between vegetable oils or animal fats with a low chain alcohol to yield esters (biodiesel) and glycerin [3], [4]. Biodiesel as compared to petro diesel is nontoxic, more biodegradable, has low emission, decreases greenhouse effect, and so eco-friendlier [5]. However, biodiesel has high

production cost due to the high price of plant oils as raw material [6]. On the other hand, competition of biodiesel feedstock with food supply was a concern [7]. So, the utilization of WCOs or non-edible oils as feedstock, due to their low price and disposal problems reduction is one of the most promising choices for biodiesel raw material [6]. The catalysts used in transesterification process are homogeneous or heterogeneous. Homogeneous catalysts are corrosive, non-reusable, and generate many toxic wastewaters. But, heterogeneous catalysts are less corrosive, reusable, easier to be separated from mixture product, and generate less amount of wastewater [8], [9]. However, heterogeneous catalysts are expensive. To reduce the biodiesel production cost, the chosen catalysts should have low price and be available in large quantity [10].

Zeolites have many applications in chemical industrial such as ion-exchange resins, selective adsorbents and active catalysts [10]. One of the most common zeolites is clinoptilolite with high Na⁺ & K⁺ cations on its sites. There are many natural zeolite resources specially clinoptilolite and mordenite in Iran. Purity of the clinoptilolites is more than 75% and their Si/Al ratio is greater than 4.5 [11].

The aim of this study was production of biodiesel using modified SP clinoptilolite and modified SPC clinoptilolite as heterogeneous base catalysts from WCO. For this purpose, first clinoptilolites were modified by KOH solution. The transesterification conditions effect on biodiesel yield were studied. Produced biodiesel characteristics were analyzed and compared with ASTM standards and petro diesel. Then, the reusability and regeneration of catalysts were investigated.

II. MATERIALS AND METHODS

A. Materials

In this work, natural zeolites were obtained from Afrazand company, Tehran, Iran. The particle size of SP clinoptilolite and SPC clinoptilolite were 6 mesh and 200 mesh, respectively. Purity of natural zeolites was more than 85%.

For transesterification, WCOs were provided from Shiraz university self-service. Methanol with 99.9% purity and potassium hydroxide were purchased from Merck.

B. Catalyst Preparation

A sample of 40 gr of natural zeolite was mixed with 5 molar potassium hydroxide solutions and stirred at 32 °C for 24 h to raise catalyst site activity. Subsequently, KOH solution and

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zeolites were separated by sedimentation. Final, sediment was oven-dried at 120 °C for 24 h and was calcined at 300 °C for 3h in a furnace.

C. Transesterification

WCO usually contains water, free fatty acids (FFA) and solid impurities which characterize the quality of biodiesel. The presence of high FFA and water in WCO causes saponification and biodiesel yield decreases. The solid impurities and water were removed by filtration and decantation funnel, respectively. In order to complete the base catalyzed reaction, FFA value should be lower than 2% [12]. The FFA value of the used WCO was determined by ASTM D974 standard method as 1%.

Transesterification reaction was carried out in a batch reactor with magnetic stirring. First, the catalyst was dispersed in methanol by magnetic stirring. The mixture was heated and 20 gr of warm WCO was added to the reactor. After sufficient time for complete reaction, the reaction mixture was centrifugated and three phases were formed. The upper phase was biodiesel, the middle phase was glycerol, and the lower phase was solid catalyst. The separated biodiesel phase was heated to remove unreacted alcohol, washed with warm deionized water and small amount of dilute sulfuric acid to neutralize and remove possible effects of any catalyst and oil that may be present in the biodiesel. The produced biodiesel yield was determined using (1).

$$\text{Biodiesel yield (\%)} = \frac{\text{mass of produced biodiesel}}{\text{mass of used oil}} \quad (1)$$

The effects of six different parameters, i.e. time, temperature, catalyst concentration, methanol amount, mixing intensity, and water content on biodiesel yield were investigated under the operational conditions as shown in Table I.

In this study, several physical and chemical properties of produced biodiesel such as density, kinematic viscosity, acid number, cetane index, flash, cloud, and pour points were measured and compared with ASTM standards and petro diesel.

TABLE I
DIFFERENT VARIABLES RANGES APPLIED FOR TRANSESTERIFICATION OF WCO

Time (h)	Temperature (°C)	Catalyst to oil mass ratio (wt.%)	Methanol to WCO volumetric ratio (vol.%)	Mixing speed (rpm)	Water to oil mass ratio (wt.%)
0.5-6	60-75	2-8	27-68	500-800	0-2

D. Catalyst Reusability and Stability

The reusability and stability of catalysts are the most important evaluation criteria in the catalyst selection for industrial applications. In this study, the reusability of zeolite catalysts was assessed in five transesterification cycles under optimum conditions. After deactivation, the zeolites can be regenerated by impregnation in 5 molar KOH solutions, again.

III. RESULTS AND DISCUSSION

A. Properties of WCO

Physical and chemical characteristics of WCO were determined and the results are indicated in Table II. After decantation for water removal, the water content of WCO was 0.33 (wt.%).

TABLE II
CHARACTERISTICS OF WCO

Density(kg/m ³)	907
Kinematic viscosity(cSt)	29.8
FFA(mgr KOH/gr Oil)	1
Water content(vol.%)	5%
Cloudy point(°C)	17
Pour point(°C)	2

B. Optimization of Reaction Conditions

1. Reaction Time

The transesterification process is composed of three different reversible reactions to convert triglycerides and alcohol to biodiesel and glycerin. So, it is very important to select the proper reaction time to be sure of reaction completion. The reaction time effect on biodiesel yield for two different catalysts is shown in Fig. 1. As it is shown, at the beginning, the rate of reaction was relatively slow due to the slow dispersion and mixing between three phases of oil, methanol and catalyst. Then, biodiesel yield was enhanced by increasing the reaction time to reach equilibrium after which the yield is decreased due to backward reactions and soap formation.

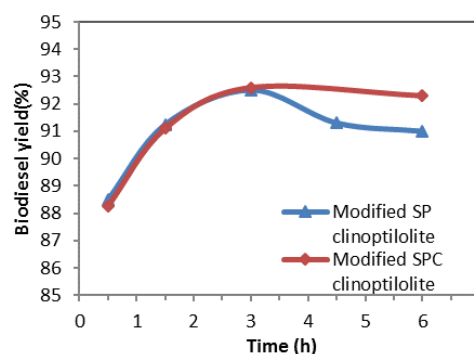


Fig. 1 Variation of biodiesel yield with reaction time

2. Reaction Temperature

The temperature is an important parameter that will influence on transesterification reaction rate. Fig. 2 represents the effect of temperature on biodiesel yield. This figure shows that with increasing of temperature, the biodiesel yield was increased up to about the methanol boiling point due to oil viscosity reduction and increasing of the oil solubility in methanol. However, higher reaction temperatures led to the biodiesel yield reduction due to the increase of saponification rate and methanol vaporization.

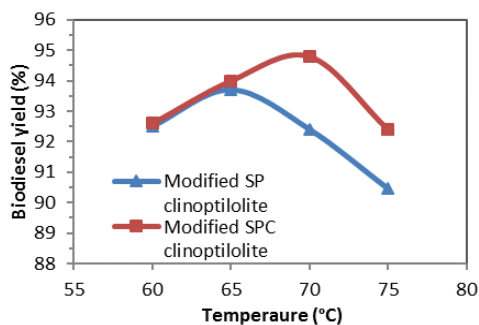


Fig. 2 Variation of biodiesel yield with temperature

3. Catalyst Concentration

Catalyst concentration plays an important role in biodiesel production reaction. The effect of catalyst concentration on biodiesel yield is depicted in Fig. 3. Generally, increasing of catalyst concentration increases the availability of active sites and biodiesel production. But, larger amounts of catalyst led to biodiesel yield reduction, since the excess catalysts react with FFAs and generate soap. On the other hand, it cannot be useful due to increasing catalyst cost, washing cost and wastewater.

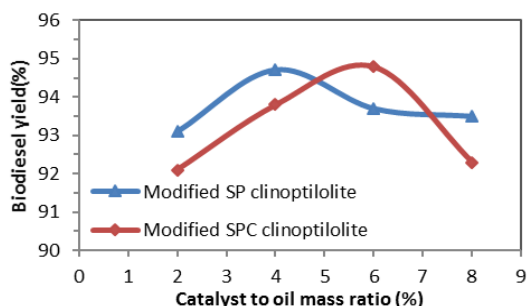


Fig. 3 Variation of biodiesel yield with catalyst concentration

4. Dose of Methanol

In reversible transesterification reaction, stoichiometrically, 1 mol of triglyceride and 3 moles of alcohol generate 3 moles of biodiesel and 1 mol of glycerin. Though excess methanol can shift the equilibrium toward more biodiesel production, but increasing of methanol at the same time can reduce the catalyst concentration and also makes the separation of biodiesel from glycerin more difficult. These effects are shown in Fig. 4.

5. Mixing Intensity

Oil and methanol are immiscible and transesterification reaction of oil and methanol using heterogeneous catalyst form three phases. The reaction can occur slowly in interfacial region between catalyst and liquids. So, mixing is another important parameter for biodiesel production. Experimental results of mixing effect on biodiesel yield are shown in Fig. 5. As it is shown on this figure, the biodiesel yield increases with mixing rate due to reduction of limited mass transfer between three phases. However, higher stirring rate led to biodiesel yield reduction, since it favors saponification reaction.

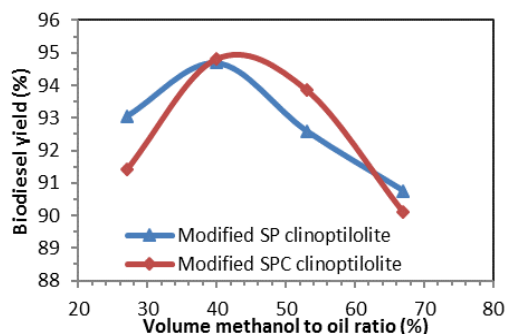


Fig. 4 Variation of biodiesel yield on methanol dose

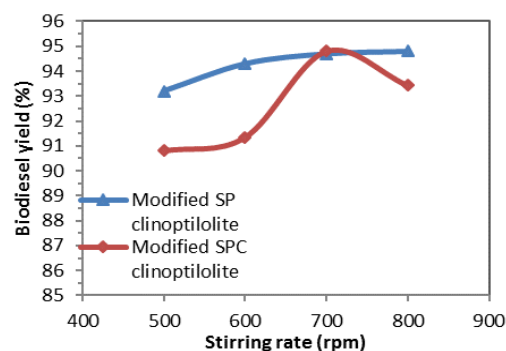


Fig. 5 Variation of biodiesel yield with mixing rate

6. Water Content

The effect of water content on biodiesel yield is depicted on Fig. 6. The presence of water has negative effect on the transesterification reaction, since water can hydrolyze triglycerides and biodiesel to produce FFAs. FFAs react with base catalysts to produce soap and water. So presence of water not only reduces the catalyst effect, but also it inhibits the separation of biodiesel from glycerin due to excess soap formation. So, the presence of water in transesterification reaction reduces biodiesel yield as shown in Fig. 6. This figure shows a maximum point for modified SPC clinoptilolite zeolite. This could be attributed to the creation of more methoxide anion by water in presence Ca of CaO which is stronger base than oxide anions. So, biodiesel yield is increased a little in this case.

C. Catalyst Reusability and Regeneration

The stability and reusability of catalyst are very important in catalyst selection. So, in this work, the reusability of modified clinoptilolite catalysts were assessed for five transesterification reaction cycles. The operation conditions were in optimum point of each catalyst.

Multiple cycle test results of catalyst reusability were shown in Fig. 7. This figure indicates that biodiesel yield was decreased with the run numbers. This is because some of KOH on catalyst active sites were leached or some of active sites were blocked by products and unreacted material during reaction.

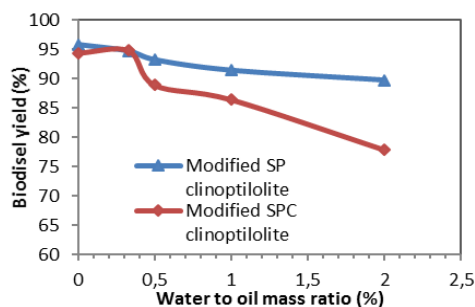


Fig. 6 Variation of biodiesel yield with water content

For catalyst regeneration, the deactivated catalysts were washed with methanol to remove products and unreacted material from active sites. Then, the catalysts were mixed with 5 M KOH solution, filtered and dried at 120 °C for 24 h and calcined at 300 °C for 3 h. Fig. 8 shows the comparison of fresh and regenerated catalysts and indicates that biodiesel yield of fresh and regenerated catalysts are not much different.

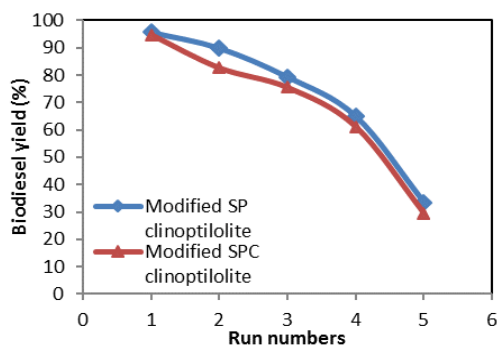


Fig. 7 Variation of biodiesel yield with run numbers

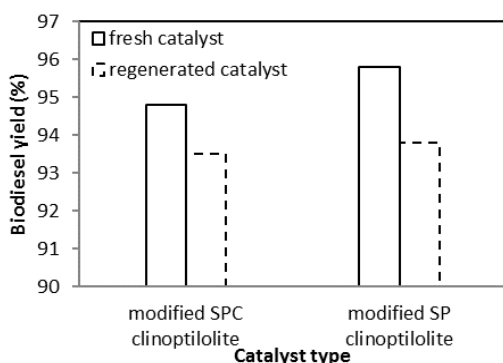


Fig. 8 Comparison of biodiesel yield for fresh and regenerated catalyst

D. Biodiesel Characterization

The physical and chemical properties of the biodiesel produced from WCO were determined and compared with petro diesel (Table III). The results included density, kinematic viscosity, acid number, cetane index, flash, cloud and pour points were found to be within ASTM ranges. The viscosity and density affect injection, lubrication and fuel atomization and high viscosity and density increase engine

deposits. The viscosity and density of produced biodiesel are a little more than petro diesel. Flash point specifies the liquids fire hazard. The produced biodiesel with a higher flash point is safer than petro diesel for storage and handling. Cetane index is an important factor in determining the combustion quality of diesel fuel. Biodiesel has higher cetane index than petro diesel. FFAs are causing corrosion. The acid value of produced biodiesel is lower than petro diesel. The cloud and pour points of produced biodiesel are higher than petro diesel which reduce the possibility of using in cold weather.

TABLE III
PROPERTIES OF BIODIESEL COMPARED WITH ASTM STANDARDS AND PETRO DIESEL

Property	Biodiesel	Petro diesel	Standard limits for biodiesel (ASTM D6751)
Density (kg/m ³ , 15°C)	875	827	860 - 894
Kinematic viscosity (mm ² /s, 40 °C)	3.21	2.8	1.9 - 6
Acid number (mg KOH/g oil)	0.448	1.2	0.5 max
Cetane index	51	48	47 min
Flash point (°C)	163	66	130°C min
Cloud point (°C)	12	2	-3 - 15
Pour point (°C)	5	-17	-5 - 10

IV. CONCLUSIONS

The biodiesel was produced from WCO and methanol in different experimental conditions, and the optimum biodiesel yield was measured. The optimum value of biodiesel yield for modified SP clinoptilolite and modified SPC clinoptilolite as catalyst were 95.8% and 94.8%, respectively which indicate that the reaction procedure had high efficiency. During five cycles of reaction, the spent modified zeolites were deactivated. But, they can be regenerated easily and the regenerated catalysts can obtain activity close to the fresh catalysts. Characterization of the produced biodiesel showed that its properties confirm well with ASTM limits. The properties of produced biodiesel such as cetane index and flash point were higher than petro diesel, which indicates combustibility, transportation and storage of biodiesel are better than petro diesel. But higher cloud point, pour point, viscosity and density of biodiesel are its disadvantages. So, utilization of biodiesel and petro diesel blend is useful and applicable. Due to the environmental problems and low cost of WCO, it is profitable to use WCO as a feedstock for biodiesel production.

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