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Reduction of Free Fatty Acids of Waste Oil by Acid-Catalyzed Esterification

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Abstract

Clean fuels such as biodiesel are used to provide energy in the word, recently. Transesterification of waste oil in the presence of alkali catalyst is used to produce biodiesel. Since free fatty acid (FFA) and water in the waste oil will decrease process efficiency specially in washing step, so concentration of the mentioned component should be reduced to a low value (<1% FFA) using esterification before transesterification process. In this work, silica sulfuric acid is used as heterogeneous catalyst for reduction of FFA in waste cooking oils and effects of variables on the esterification reaction were also studied. To determine FFA decreasing, i.e. esterification reaction conversion, the samples were analyzed by GC and FTIR. As a result of this study, 1.5% wt catalyst, at 60°C, molar ratio methanol to oil 6:1 and 300 rpm are suggested as optimum conditions. Results are shown that conversion of free fatty acids to ester, in terms of waste oil is 90% and FFA concentration is less than1%.

Keywords: Waste cooking oils; Esterification; Silica sulfuric acid; Transesterification; Biodiesel

1. Introduction

Since petroleum reserves are diminished and flue gases have environmental impact, using the biodiesel as a renewable energy is recommended [1]. Biodiesel is a general title that has attributed for the range of oxygen fuels with Ester base that produces from vegetable oils and animal fats [2, 3]. Pyrolysis, emulsification and transesterification processes are used to biodiesel production [4]. Biodiesel could be produced using the high efficient transesterification process not only with simple condition and facilities, but also in the short time [5, 6, and 7]. In this method, oil is converted to methyl ester and glycerin by using alcohol in the presence of acid catalysts:

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$$CH_2OOR1\text{-}CH_2OOR2\text{-}CH_2OOR3+CH3OH \leftrightarrow CH_3OOR2+CH_2OH\text{-}CH_2OH\text{-}CH_2OH$$

Reaction 1- Transesterification reactions of glycerides with methanol

where $CH_2OOR1\text{-}CH_2OOR2\text{-}CH_2OOR3$, CH_3OH, CH_3OOR2 and $CH_2OH\text{-}CH_2OH\text{-}CH_2OH$ are trigelycerid, methanol, methyl ester and glyserin, respectively.

Water in waste oil will hydrolysis and produce extra FFA (*Scheme2*), so acid catalyst shall be used to decrease FFA and water concentration to a low level in order to avoid saponification reaction. In other word, FFA concentration shall be decreased before Transesterification process. [8, 9, 10, 11 and 12]

$$CH_2OOR1\text{-}CH_2OOR2\text{-}CH_2OOR3+H_2O \leftrightarrow R1COOH\text{-}R2COOH\text{-}R3COOH+CH_2OH\text{- }CH_2OH\text{- }CH_2OH$$

Reaction 2- Hydrolysis process leads to the production of Fatty acids and glycerine

where $CH_2OOR1\text{-}CH_2OOR2\text{-}CH_2OOR3$, H_2O, $R1COOH\text{-}R2COOH\text{-}R3COOH$ and $CH_2OH\text{-}CH_2OH\text{-}CH_2OH$ are fat, water, free fatty acids and glyserin, respectively.

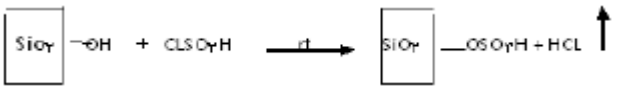
Veljkovié et al studied the biodiesel production from seed oil. They found that 2%wt H_2SO_4 could reduced FFA to less than 2%wt in 25 minutes for the molar ratio of methanol to oil equal to18:1[13]. Thaweesinsopha et al were used acid-catalyzed esterification to reduce FFA in mixed crude palm oil (MCPO). They found FFA in MCPO would be reduced to less than 2%wt in 1 hour at 60°C by using 3%wt H_2SO_4 as a catalyst and 10%wt methanol [14]. They use acid catalyst in homogenous phase that causes problems such as, difficulties in recycling, high temperature, corrosion and serious environmental risks [15] but acidic heterogeneous catalysts such as solid catalysts don't have these problems [16,17]. In this study, waste cooking oils was used as raw material and silica sulfuric acid as heterogeneous acidic catalyst in esterification reaction. Reaction time, catalyst amount, molar ratio of methanol to oil and temperature were studied to determine optimum conditions of reducing FFA process efficiency.

2. Materials and Methods

Waste cooking oils (collected randomly from the Restaurant whose average acid values are 7.1mg KOH/g oil), Silica gel (For thin layer chromatography 60G), Cholosulfonic acid, Methanol (95%), Hexane, potass, Iso propel alcohol and starch was purchased from Merck, were used in this work.

Catalyst preparation

A 500 ml suction flask equipped with a constant-pressure dropping funnel and a gas inlet tube for conducting HCL gas over an adsorbing solution (i.e.water) was used. It was charged with silica gel (60.0 g). Chlorosulfonic acid (23.3 g, 0.2 mol) was added drop wise over a period of 30 min at room temperature. HCL gas evolved from the reaction vessel immediately after the addition was complete the mixture was shaken 30 min. A white solid (silica sulfuric acid) 76.0g was obtained (Scheme 3) [18]. The final catalyst was tested with FT-IR for its structure.



Reaction 3- Reaction produces silica sulfuric acid from silica powder and Chlorosulfonic acid

The preparation waste cooking oil

The waste cooking oil was filtered to remove its waste materials, and then the filtered oil was heated at 65°C for about 15 min to water particles be settled and separate water by using decanter.

Esterification stage

About 50 gr of the prepared oil poured in the 100ml flask and temperature set at 60°C with water bath. Then methanol was added to the flask and mixed completely with oil. Silicasulfuric acid was added to the reaction mixture as the catalyst. Since methanol and oil constitute two immiscible phases, mixing is required to increase the contacting surface between them. The esterification reaction was done and 2ml of

mixture were collected as sample. Reaction condition such as weight percentage of catalyst, molar ratio of methanol to oil and temperature were changed as shown in Table1 to determine the optimum condition for the reaction. In order to stop esterification reaction the samples were placed in bath of cold water at 5°C immediately after sampling until their temperature have reach to ambient temperature, then samples were washed 5 times by warm water to separate esters from impurities. Sample washing have to repeat until the ester phase became transparent. To determine the free fatty acids and methyl ester in samples, the standard method ASTM D 5555 and gas chromatography were used.

Table1- Variable and Fixed parameters used in this study and acid value

variable parameter	fixed parameters
Reaction time (min) ۵ ۲۵ ۳ ۴۵ ۶۰	^ type of alcohol : methanol ^ molar ratio of alcohol to oil : ۶:۱ ^ type of catalyst : silica sulfuric acid) ^ amount of catalyst : ۲% ^ reaction temperature : ۶۰°C ^ mixing intensity : ۳۰۰ rpm
amount of catalyst % ۰.۵ ۱ ۱.۵ ۲ ۲.۵	^ reaction time : ۳۰ min ^ type of alcohol : methanol ^ molar ratio of alcohol to oil : ۶:۱ ^ type of catalyst : silica sulfuric acid ^ reaction temperature : ۶۰ °C ^ mixing intensity : ۳۰۰ rpm
molar ratio of alcohol ۳:۱ ۵:۱ ۶:۱ ۸:۱ ۹:۱	^ amount of catalyst : ۱.۵ % ^ reaction time : ۳۰ min ^ type of alcohol : methanol ^ reaction temperature : ۶۰ °C ^ mixing intensity : ۳۰۰ rpm
reaction temperature ۵۰ ۵۵ ۶۰ ۶۵ ۷۰	^ molar ratio of alcohol to oil : ۶:۱ ^ amount of catalyst : ۱.۵% wt ^ reaction time : ۳۰ min ^ type of alcohol : methanol ^ mixing intensity : ۳۰۰ rpm

Catalyst recycling

Since recycle of catalyst for repeated use due to economical aspects is important, after finishing the esterification reaction silica sulfuric acid catalyst was washed in three stages by using acetone and dried in oven (100°C). This catalyst was used in the esterification reaction for five times.

Analysis of ester conversion percentage

The product of Esterification reaction of oil is methyl ester, which is analyzed by gas chromatography with the following conditions: GC-MSD: GC-7890 AMSD: 5975C, Column: Agilent: 325 °C: 30 m x 250 µm x 0.25 µm, HP-5MS 5% Phenyl Methyl Silox, Oven Program: 100 degrees C for 2 min, then 5 °C/min to 225 degrees C for 6 min, then 10 °C/min to 300 degrees C for 8 min.

3. Results and Discussion

FT- IR spectrum of silica sulfuric acid

The FT-IR spectrum of the catalyst was shown in Fig.2. For silica, the major peaks are broad anti symmetric Si-O-Si stretching from 1200 to 1000$cm^{-1}$and symmetric Si-O-Si stretching near 800cm^{-1}. For sulfuric acid functional group, the FT-IR absorption range of the O=S=O asymmetric and symmetric stretching modes lies in 1120-1230 and 1010-1080cm^{-1}respectively, and that of the S-O stretching mode lies in 600-700cm^{-1}.FT-IR spectrum shows the overlap asymmetric and symmetric stretching bands of

SO2 with Si-O-Si stretching bands in the silica sulfuric acid. The spectrum also shows a broad OH stretching absorption around 3400-3700cm^{-1}. The spectrum shows that the catalyst prepared correctly.

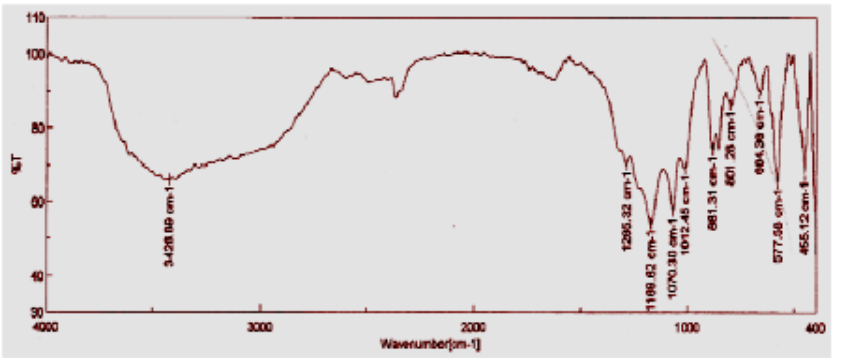


Fig.2. FT-IR spectra of silica sulfuric acid

Effect of retention time on the reaction conversion

Esterification reaction was performed in the presence of 2% wt catalyst, Molar ratio of 6:1 of alcohol to oil and Stirring speed 300 rpm in 60°C. Figure 3 shows that the rate of acid value decreased to less than 1% and the percentage of ester conversion reached about 90% after 30min and then reaction reaches to equality,. After that in 60 and 90min , the percentage of ester conversion decrease and acid value increase because of the reverse equation that takes place because of equilibrium. Therefore the optimum reaction time for highest decrease in FFA in these conditions is 30 min.

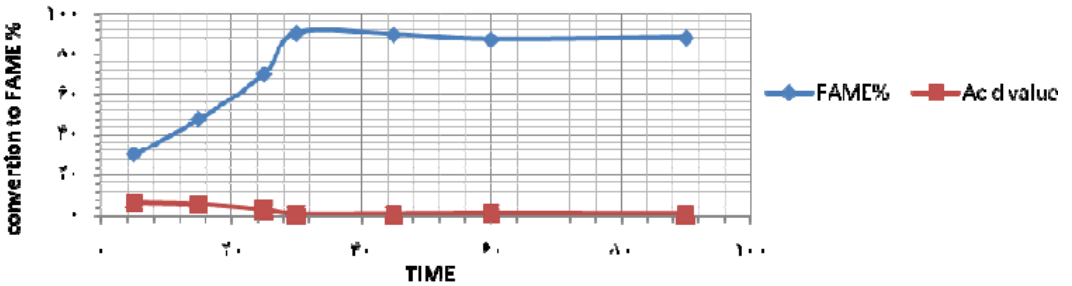
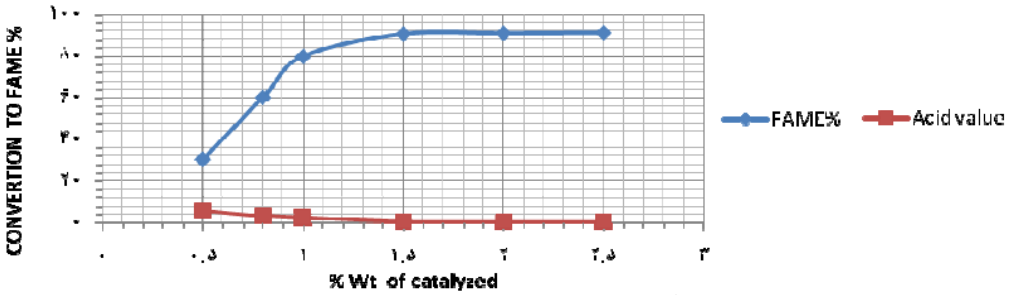


Fig.3- Effect of retention time on reaction conversion and acid value 2%w acid catalyst, methanol to oil molar ratio 6:1, 60°C and 300rpm.

Effect of catalyst concentration

Specific amount of catalyst is needed for the slow esterification reaction. The reaction was done with different catalyst weight percentages. This reaction was performed in 60°C temperature with molar ratio 6:1 methanol to oil and stirrer speed of 300 rpm and 0.5, 0.8, 1, 1.5, 2, 2.5 %w of catalyst. As shown in figure 4 with increasing weight percentage of catalyst from 0.5 to 1.5 %wt, the percentage of free fatty acid conversion to methyl ester increased and the acid value of oil decreased to less than 1%. With increase amount of catalyst to 2 to 2.5 %w no visible change shown in the conversion and acid value. The suitable catalyst concentration is 1.5 %w.



Fige4- Effect of catalyst concentration on reaction (methanol to oil molar ratio 6:1, 60°C and 300 rpm in 30 min)

Effect of molar ratio of methanol to oil

The molar ratio of alcohol to oil in esterification reaction is 3:1 theoretically, but, scientifically because of equivalent reaction, it requires greater amount of alcohol for completing the reaction. In this step, the effect of molar ratio 3:1, 5:1, 6:1, 8:1 and 9:1 of methanol to oil was considered. The reaction takes place in 60 ℃ with 1.5 %wt catalysts, 300 rpm and 30 minutes. The results are shown in Figure 5. At the molar ratio of 6:1 for alcohol to oil shows the highest efficiency for ester production and acid value reduction.

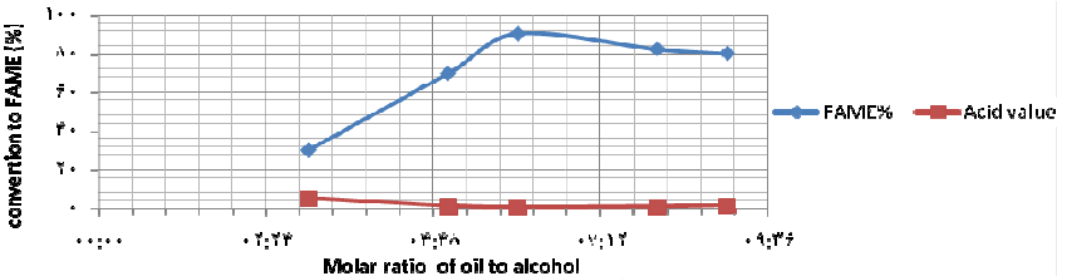


Fig5- Effect of molar ratio of methanol to oil (1.5% wt acid catalyst, 60°C and 300rpm in 30 min)

Effect of temperature

Temperature has significant effect on the rate of reaction. The reaction was performed under the conditions as follow: concentration of catalyst 1.5wt %, molar ratio of 6:1 of methanol to oil and temperatures variables to 55, 60, 65, and 70 ℃ In 30 minutes. As shown in Figure 6 increase of temperature from 50 to 60 shows increasing the percentage of ester conversion and decreased of acid value to less than 1%. Increasing the temperatures higher than 60℃ reduces the efficiency of reaction because increasing temperature more than boiling point of methanol (64℃), reduces amount of methanol in reaction mixture.

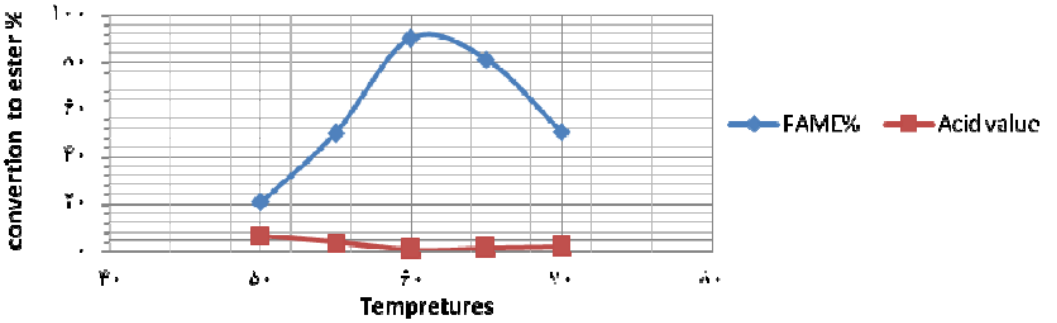


Fig6- Effect of temperature on reaction (1.5% acid catalyst, methanol to oil molar ratio 6:1, and 300rpm in 30 min)

Conversion for main FFA

The analysis of GC-MS of waste cooking oil shows that main FFA of oil are Oleic acid, Palmitic acid and Stearic acid. Figure 7 shows the result of conversion of these acids to methyl ester. The conversion of Oleic acid, Palmitic acid and Stearic acid under optimal conditions: 1.5%wt catalysts, molar ratio of methanol to oil 6:1, 60℃ , 300 rpm respectively was reached to 86, 90 and 98 % after 30 minute. These results confirm the reduction of FFA in oil.

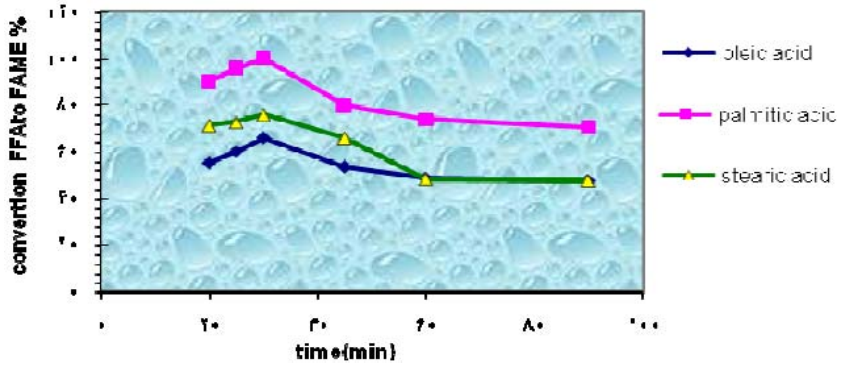


Fig7- Conversion of main FFAs to methyl ester (1.5% by weight acid catalyst, methanol to oil molar ratio 6:1, 60 ℃ and 300rpm)

4.Conclusion

Using waste cooking oil as Feed stock for biodiesel production has economical and bioenvironmental points. But presence of free fatty acids and water in oils produce many problems in process of biodiesel production. So in this study for reduction of free fatty acid in waste cooking oils was performed by method of catalytic esterification in the present of silica sulfuric acid as catalyst to reduce the FFA of oils. The silica sulfuric acid was choose because its stability, lack of solubility in all solvents, recyclability, easier separation from other compounds in the reaction mixture and high purity. The effective parameters optimized and the catalyst was recycled and used repeated times in the same reaction. The FFA in oil with optimal condition (molar ratio methanol to oil 6:1, 60℃ , 1.5 %w of catalysts in 30 minutes) decreased to less than 1% and the conversion of methyl ester production reached 90%. The results show that the used oil could be used for biodiesel production with high efficiency.

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