



Enhanced removal of Free Fatty Acid from waste oil for Biodiesel production

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ARTICLE INFO

Article history:

Received: 23 June 2011;

Received in revised form:

17 January 2015;

Accepted: 31 January 2015;

Keywords

Biodiesel,
Equilibrium,
Extraction,
Free fatty acid,
Organic solvents.

ABSTRACT

Free Fatty Acid (FFA) was removed from waste oil and favorably employed for the production of high quality biodiesel. FFA extraction minimizes the drawbacks encountered with alkaline catalysts in biodiesel production. Three combinations of reagents (methanol-benzene, methanol-toluene and methanol-xylene) were used for extraction purpose and a rapid extraction of FFA has been obtained. The composition of non-polar solvent (benzene, toluene and xylene) in each of the above mentioned reagents was varied from 1% to 10% by weight. An optimal ratio of (0.8:1) reagent and oil by weight was found to reduce the FFA concentration by 43.3% in single step. Equilibrium study for the extraction of FFA was also carried out. The experimental data obtained were presented on the basis of amount of FFA extracted, with respect to time required for extraction (25 to 300 min) and stirrer speed (50 to 300 rpm). The optimum value for the time required for extraction was obtained at 150 min. the optimum value for the stirrer speed required for the extraction of FFA was obtained at 150 rpm.

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Introduction

The possibility of using vegetable oils as fuel has been documented in the beginning of diesel engines. Biodiesel produced from waste oil by trans-esterification process can be used as a substitute for diesel in internal combustion engines [1]. Biodiesel can be produced by the transesterification of vegetable oils [2] such as soyabean oil, rapeseed oil, sunflower oil etc. [3].

Transesterification is a well known process since 1864. Rochleder described glycerol preparation through the ethanolysis of castor oil [4]. Solvent used for the production of biodiesel affects the process in terms of conversion efficiency [5] and the conversion differs according to oil quality. Transesterification is the general term used to describe the organic reactions where triglyceride is transformed into methyl ester through interchange of the alkoxy moiety. The general equation for a transesterification reaction is shown in Figure 1 [6].

Transesterification of oils can be carried out using either an acid or base catalyst [7]. The use of homogenous acid catalysts for the esterification of oil has several disadvantages such as the catalyst could not be recovered and limited use for continuous process [8]. Acid catalyzed transesterification reaction rate is much slower than alkali.

The ester conversion efficiency is strongly affected by molar ratio of alcohol to oil. In acid catalyzed transesterification a high molar ratio is required than alkali catalyzed. If acid catalyzed reaction takes place at room temperature, the reaction is very slow and poor ester conversion is obtained [9]. Alkaline catalyzed transesterification process is faster than acid catalyzed reaction and also requires less time when compared to acid-catalyzed transesterification. Hence most commercial processes employ homogenous base catalysts for biodiesel production [10].

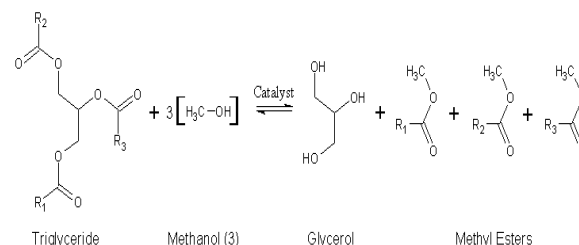
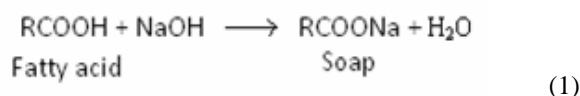


Figure 1. General equation for a transesterification reaction

Many edible and non-edible oil sources are available for transesterification. However these oils cannot be used as a viable source for biodiesel production due to their high FFA content. Hence a suitable solvent system for the removal of high FFA oil is essential to make these sources reliable for base catalyzed transesterification.

The yield of base-catalyzed transesterification decreases when the FFA value of oil is greater than 2%. It has been found that transesterification would not occur if FFA content in the oil is high [11]. The difficulty with FFA content transesterification is that it rapidly reacts with the alkaline catalyst forming soap [12], as shown in reaction equation (1). This soap formation inhibits the separation of ester and glycerol. Increase in acid value of oil reduces the conversion efficiency [13, 14].



The standard deacidification techniques involve high energy consumption (physical refining) [15], saponification, loss of neutral oil (chemical refining) [16] and fouling (ion-exchange resins) [17].

The present study deals with the development of a suitable reagent for liquid-liquid extraction of FFA. This method is based

on the difference of solubility of FFA and triglycerides in a suitable solvent [18]. The reagent prepared consists of low concentration of non-polar solvents (benzene, toluene and para-xylene) in methanol. Oil and methanol form immiscible phases hence the purpose of non-polar solvent addition is to enhance the extraction of FFA into the reagent.

On the basis of solubility data it is observed that methanol is suitable for extraction of FFA up to a carbon number of 16 whereas benzene, toluene and para-xylene are found to be more effective for even higher carbon number of FFA.

The non-polar solvents (benzene, toluene and para-xylene) were used to reduce the polarity of methanol nearly equal to that of FFA. The dissolution of methanol in the FFA was enhanced by the addition of non-polar solvents in the methanol.

Only low concentration of non-polar solvents was used with methanol because at higher concentration the non polar solvents become soluble in oil.

So using higher concentration of non-polar solvent is undesirable. In addition higher concentration of non-polar solvent requires a separate process for the removal solvents from oil which increases the processing cost.

Materials and Methods

Methanol (99.9%), benzene, toluene and p-xylene were purchased from Ranbaxy Laboratories Limited, New Delhi, India. Potassium hydroxide and Phenolphthalein were purchased from Merck, Mumbai, India. All other chemicals used were analytical reagent grade.

The waste oil was obtained from a local oil mill, Chennai, India. It was a mixture of residual oils obtained from various oil seeds. The oil was heated at 105°C until the moisture content reaches below 0.05 wt% .Moisture content was analyzed by Karl Fisher titration. The oil was then cooled to room temperature.

Characterization of Oil

One gram oil was taken in a 250 mL round bottomed flask. The glass neck was fitted with a reflux condenser. 40 mL of anhydrous methanol and 0.2 mL of 60 g L⁻¹ solution of sodium hydroxide in methanol were added.

The mixture was shaken well and heated to the temperature of 65 °C. Heating the mixture was continued till the mixture turns into clear solution. After obtaining the clear solution, the mixture was heated for further 5 more minutes. Methyl orange indicator was added followed by titration with 2 % concentrated sulphuric acid to neutralize excess sodium hydroxide and the mixture was refluxed for 30 minutes.

The flask was cooled under running water and the contents were transferred into a separating funnel. The flask was rinsed with 50 mL of petroleum ether and this was also transferred to the separating funnel.

The two phases (organic phase and aqueous phase) were separated using the separating funnel.

The separated organic phase was allowed to pass through anhydrous sodium sulphate. The petroleum ether layer was evaporated by heating. The organic phase liquid is diluted with acetone and 1µL of this mixture was injected into the chromatograph.

The Gas Chromatograph (GC) consists of CHEMITO GC 8610 with flame ionisation detector and nitrogen as carrier gas. Hydrogen and oxygen were used for ignition purpose.

Column BPX-70 consists of 50 % cyanopropyl and 50 % methylsiloxane. The injector port was at 250 °C and detector port at 260 °C. Oven starting temperature was increased from 160 °C to 240°C at the rate of 7.5 °C per minute. The data were

collected using Winchrom software and compared with standards. The GC results were presented in the Figure 2.

Analysis of FFA

The FFA content of the sample was determined using acid and base titration technique [19]. A standard solution of 0.1N NaOH was used. The iso-propanol solution was brought to boil on a hot plate. Phenolphthalein was added and then neutralized by drop-wise addition of NaOH till a faint pink colour appeared. Thus neutralized iso-propanol was prepared. A specified amount of oil sample was weighed for analysis.

Then the neutralized solvent was added into the sample. The mixture was shaken gently while titrating with standard alkali till pale permanent pink colour appears.

Experimental procedure

Initially the FFA of sample oil was determined using standard FFA determination techniques. The experimental procedure consists of two steps, the first step was the process of extracting FFA from oil using the prepared reagents and the next was the determination of amount of FFA.

The solvent reagents (methanol-benzene, methanol-toluene and methanol-xylene) were prepared by adding non-polar solvents (Benzene, Toluene and Xylene) to methanol to form solutions containing 0 to 10% (by weight). If the concentration of non polar solvent exceeds 10 %, traces of residual solvent will be present along with the oil in the raffinate phase. Hence, a non polar solvent concentration more than 10 % is not employed for extraction.

50 g of oil and 50 mL of reagent were taken in a three necked 250 mL round bottom flask equipped with a 0.25 inch propeller type mechanical stirrer and the whole experimental set up was kept inside a constant temperature bath maintained at required temperature.

To maintain a constant pressure of 1 atm inside the extractor, the third neck was left open to the atmosphere through a reflux condenser [20].

The reflux condenser was employed to minimize the escape of methanol vapors. After the extraction process the mixture was transferred into a separating funnel where complete phase separation was obtained with in 30 minutes [21].

Two distinct phases were formed after separation. The top layer was the extract phase containing methanol, non-polar solvent with FFA. The bottom layer was the raffinate phase containing oil.

In the second step FFA content was determined separately in both raffinate and extract. Even though methanol is insoluble in oil there will be traces of solvent present in the raffinate. Since the raffinate will be used for biodiesel production, the presence of methanol does not cause any hindrance.

The methanol present in the extract phase can be regenerated by simple distillation and recycled for further use [22]. The residue left after distillation contains mainly fatty acid which has some commercial importance in soap, cosmetics manufacturing industries etc. The same experiment was repeated at different stirring speeds and stirring times.

Results and Discussion

Characterization of oil

Based on the chemical analysis of oil by GC (Figure 2), the composition of oil was determined as 47.19 wt% of saturated fatty acids, 51.78 wt% of polyunsaturated fatty acids and 1.03 wt% of undetectable. GC provides accurate fatty acid composition of oil. The fatty acid composition were presented in Table 1.

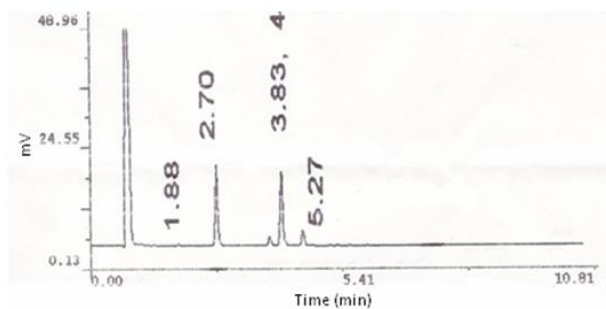


Figure 2. Gas Chromatography analysis of Waste Oil

Physical equilibrium

On the basis of obtained experimental data the physical equilibrium for FFA using (methanol-benzene, methanol-toluene and methanol-xylene) reagents were studied. The maximum amount of FFA present in the extract was obtained as 7.4 mg KOH g⁻¹ oil by using methanol-benzene reagent (Figure 3). The amount of FFA removed by using methanol-toluene reagent was observed as 11.2 mg KOH g⁻¹ oil (Figure 4). The FFA present in the extract was 9.8 mg KOH g⁻¹ oil while using methanol-xylene reagent (Figure 5).

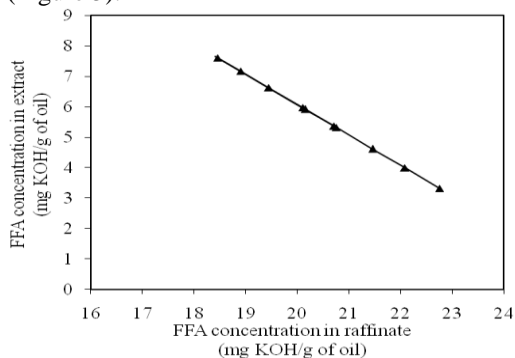


Figure 3. Physical equilibrium for the extraction of free fatty acid using Methanol-Benzene Reagent

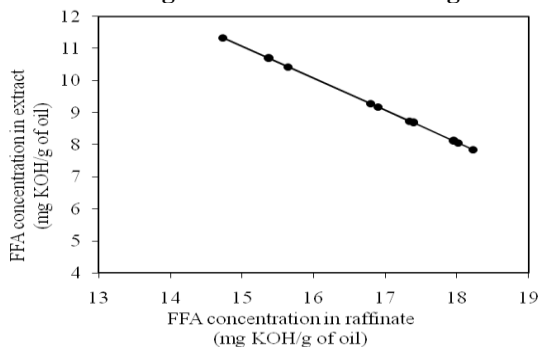


Figure 4. Physical equilibrium for the extraction of free fatty acid using Methanol-Toluene reagent

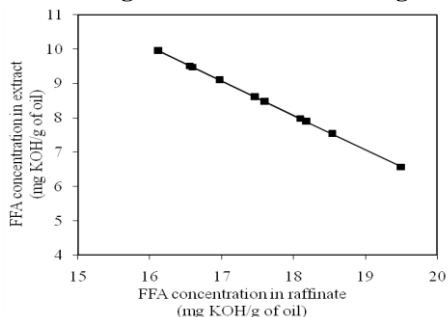


Figure 5. Physical equilibrium for the extraction of free fatty acid using Methanol-Xylene reagent

From the results, it was observed that the recovery of FFA from the oil using methanol-toluene reagent was found to be more when compared to all other reagents studied in the present investigation. The extraction of FFA from the oil using methanol-benzene reagent was found to be less when compared to all other reagents studied.

Effect of non-polar solvent concentration in reagent

The experiments were carried out at fixed condition of 150 rpm stirrer speed and stirring time of 150 minutes. Percentage of FFA in the extract was greater with increasing the non polar solvent concentration up to 4 % of an optimal value. On further increase in non-polar solvent concentration led to a decline in percentage of FFA available in the extract. Lower concentrations of non-polar solvent (1 to 10% by weight) were found to be more favorable when compared to high concentration.

From the Figure 6, it was observed that percentage of FFA extracted was found to be increasing with increase in the composition of benzene in the methanol-benzene reagent up to a value of 6% composition. On further increase in composition of benzene led to decrease in percentage of FFA extracted. The maximum percentage of FFA extracted was observed as 29.2 %.

The percentage of FFA extracted from the oil was found to be increasing with increase in the composition of xylene up to a value of 4 %. The percentage extraction of FFA from oil was found to be 38 %.

The percentage of FFA extracted was found to be maximum as 43.5% in the methanol-toluene reagent with the composition of 4% toluene. The FFA extracted from the oil using toluene was found to be more when compared to all other non-polar solvent used in the present investigation. Methanol-toluene reagent was found to be the most efficient among the three reagents studied in the present work.

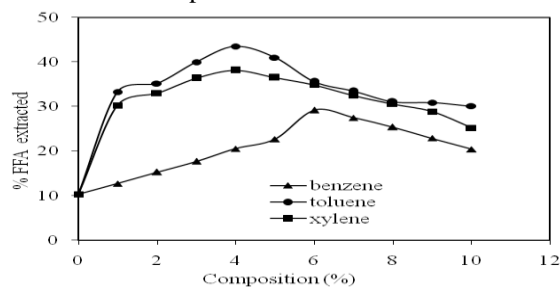


Figure 6. Effect of composition of non-polar solvent on FFA extraction from the oil

Effect of stirring time

The optimal stirring time for the extraction of FFA from the oil using methanol-toluene reagent (4%) was determined at a constant speed of 200 rpm. From the Figure 7, it was observed that the optimal stirring time was found to be 150 minutes. Even if more stirring time was allowed beyond the optimal value, only a negligible increase in percentage extraction was observed. When stirring time was kept less, equilibrium was not achieved and hence desirable extraction could not be obtained.

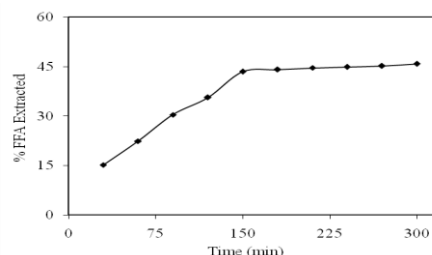


Figure 7. Effect of stirring time for the extraction of FFA from the oil using methanol-toluene reagent

Effect of stirrer speed

For an optimum toluene concentration of 4% in the methanol-toluene reagent with a stirring time of 150 minutes, the experiment was conducted to determine the effect of stirring speed on FFA extraction. Stirring speed of 50 to 300 rpm was studied. From the Figure 7, it was observed that the stirring speed of 150 rpm was found to be an optimum stirred speed. At lower speed below 150 rpm incomplete mixing was observed. Complete mixing was observed at the stirrer speed value of 150 rpm. At high speeds above 150 rpm substantial rise in amount of FFA extracted could not be achieved. Further increase in stirrer speed above 150 rpm led to increase in power consumption

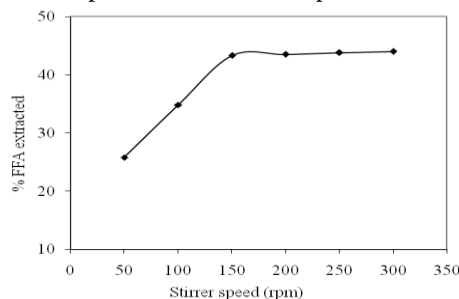


Figure 8. Effect of stirrer speed for the extraction of FFA from the oil using methanol-toluene reagent

Conclusions

Liquid-liquid extraction with the developed reagent was investigated as a pretreatment technique for oil used to enhance the production of biodiesel. The FFA content in the oil was extracted by using various reagents and under different conditions such as the composition of non-polar solvents in reagents, stirrer speed and stirring time. Removal of FFA from the oil was achieved as 43.5% with the use of methanol-toluene reagent and was found to be more effective. The maximum amount of FFA extracted was observed at 150 rpm of stirrer speed and 150 minutes of stirring time using methanol-toluene reagent. Maximum amount of FFA was removed from the oil through extraction and the oil was found to be made more suitable for the synthesis of high quality biodiesel. Single stage extraction was found to be more effective for oils containing FFA ranges from 2 to 4 wt%. For high FFA content oils, multistage liquid-liquid extraction can be carried out to reduce the FFA content to the required amount. The resulted oil was found to be more suitable for the production of biodiesel using basic catalysts.

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Table1. Fatty acid composition of feedstock oil

Fatty acid	Retention Time (min)	Composition in weight, %
Lauric acid C 12 : 0	1.38	0.14
Myristic acid C 14 : 0	1.88	0.72
Palmitic acid C 16 : 0	2.70	41.65
Stearic acid C 18 : 0	3.83	4.54
Oleic acid C 18 : 1	4.11	43.27
Linoleic acid C 18 : 2	4.54	8.51
Arachidic acid C 20 : 0	5.27	0.14

Acid value of the oil = 26 mg KOH per g of oil