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PREPARATION OF BIODIESEL FROM WASTE COOK OIL BY USING DIFFERENT METHODS

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Abstract: *In the present study, biodiesel was prepared from waste cook oil (WCO). The property of WCO was measured by standard methods. Biodiesel was prepared by different methods, such as base catalyzed transesterification, acid catalyzed transesterification and a three-step method where the biodiesel yield was found as 58%, 64% and 79% respectively. In three-step method where in the first step, oil was saponified by aqueous NaOH solutions. The second step the soap was converted to Free Fatty Acid (FFA) by acidification and in the final step the FFA was converted to fatty acid methyl ester (FAME) by acid catalyzed esterification reaction. The reaction parameter for saponification, acidification and esterification reaction was optimized. Silica gel was used in both transesterification and esterification reaction for biodiesel production. The biodiesel properties such as density, viscosity, FFA content, moisture content, pour point, cloud point, Saponification value, iodine value, specific gravity and cetane index were measured by standard methods and compared with the standard biodiesel and diesel properties.*

Key words: Transesterification, Saponification, Acidification, Esterification, Biodiesel.

1. INTRODUCTION

Biodiesel, which is a new, renewable and biological origin alternative diesel fuel, has been receiving more attention all over the world due to the energy needs and environmental consciousness. Biodiesel oil, having the chemical structure of fatty acid alkyl esters (usually methyl esters, FAME), is a clean burning fuel produced from renewable domestic sources such as vegetable oils and animal fat. It is biodegradable, non-inflammable, non-toxic and has a favorable combustion–emission profile [1]. The interest in the use of renewable raw materials for fuel production started during the early 1990's and one significant research has been the utilization of fatty acids esters derived from vegetable oils for biofuel production [1, 2]. The most common oil sources are waste cook oil, sunflower oil, corn oil, canola oil, soybean oil, castor oil, rapeseed oil, soybean soap stock, koroch seed oil, sclerocarya birrea oil (SCO), melon bug oil (MBO), sorghum bug oil (SBO), cardoon (Cynara cardunculus L.), Gum copal (kauri resin), frying oil (a mixture of olive oil and sunflower oil), Karanja (Pongamia pinnata), Jatropha (Jatropha Curcas), Neem (Azadirachta indica), Mahua (Madhuca indica),Simarouba (Simarouba indica), Jojoba (Simmondsia chinensis Link Schneider) etc. Some of these sources are now used for the commercial production of biodiesel. Such as our neighboring country India is producing biodiesel from Jatropha seeds. Isonox bioenergy has started operations at the Ambad area of MIDC. The unit will manufacture biodiesel from jatropha seeds [3]. Fatty acids and glycerol have wide range of applications and fatty acids are used as a feedstock for the production of oleo chemicals such as fatty alcohols, fatty amines and fatty esters. These oleo chemicals

are used as lubricant greases, anti-block agents, plasticizers, emulsifiers and as ingredients in the manufacture of soaps, detergents and animal feed. The high cost of biodiesel is mainly due to the cost of virgin vegetable oil. Therefore, it is not surprising that the biodiesel produced from vegetable oil (for example, pure soybean oil) costs much more than petroleum based diesel. It is necessary to explore ways to reduce production costs of biodiesel. In this sense, methods that permit minimizing the costs of the raw material are of special interest. The use of WCO instead of virgin oil to produce biodiesel is an effective way to reduce the raw material cost because WCO is estimated to be about half of the price of virgin oil. The fact is so far, that only a very small percentage of these oils have been collected and used for soap production. In addition, the utilization of WCO diminishes the problems of contamination because the reusing of these WCO can reduce the burden of the government in disposing of the WCO, maintaining public sewers. The main ingredient for biodiesel preparation from WCO is CH_3OH. Biodiesel can be prepared from the WCO by base catalyzed, acid catalyzed transesterification and three-step methods, which were investigated. At first base catalyzed and acid catalyzed transesterification was conducted but yield was very low that's why we have done three-step method and FFA was prepared from WCO reacting with oil to NaOH solution and HCl. FAME was prepared from FFA by esterification of FFA with methanol. The biodiesel properties were measured and compared with the standard biodiesel and diesel properties.

2. MATERIALS AND METHODS

2.1. Chemicals

Methanol (99-100%), ethanol (99-100%), calcium oxide (CaO)or "dry lime", sodium hydroxide pellets (96%), potassium hydroxide pellets (>84%), phenolphthalein (P^H 8.2-9.8), acetone (99%), diethyl ether , hydrochloric acid (37%), sulfuric acid (98%), iodine , sodium iodide, bromine, carbon tetrachloride, glacial acetic acid, potassium dichromate etc. All the chemicals were used as analytical reagent grade.

2.2. Waste Cook Oil Collection

Waste cook oil (palm oil) was collected from local restaurants located in Sylhet city in Bangladesh. The oil was filtered and its properties are measured.

2.3. Preparation of biodiesel

2.3.1. Base catalyzed transesterification

Biodiesel was prepared from WCO by base catalyzed transesterification reaction as described by Meher et al [4]. Typically, the reaction was carried out in a three-necked 250 mL round bottom flask by taking 50 mL waste cook oil. Required amount of sodium hydroxide pellets (1 wt% of oil) was dissolved in required amount of methanol. Methanol was used 6:1 molar ratio of oil. This sodium-methoxide solution was transferred to the reaction medium and heating under reflux at 60^0C temperature with vigorous stirring. After 2 h the reaction mixture was cooled to room temperature and allow stand for 10-12 h in a separatory funnel for phase separation. The upper layer contains biodiesel, excess methanol and trace amount of catalyst and the lower layer contains glycerin and catalyst. The upper layer was separated and given hot water wash for removing methanol and catalyst. Then washed biodiesel was dried at 100^oC temperature under vaccum.

2.3.2. Acid catalyzed transesterification

Biodiesel was prepared from WCO by acid catalyzed transesterification reaction. The reaction rate of acid catalyzed transesterification was very low and the reaction was completed within 18 h. Acid catalyzed transesterification reaction was carried out in a three-necked 250 mL round bottom flask by taking 50 mL WCO. Required amount of sulfuric acid (2 wt% of oil) was mixed in required amount of methanol. Methanol was used 9:1 molar ratio of oil. This methanesulfonic acid solution was transferred to the reaction medium and heating at 70 ^{0}C temperature under reflux with vigorous stirring [5, 6]. After 18 h the reaction mixture was cooled to room temperature and allow stand for 10-12 h in a separatory funnel for phase separation. The upper layer contains biodiesel, excess methanol and trace amount of catalyst and the lower layer contains glycerin and lye catalyst. The upper layer was separated and given hot water wash for removing methanol and catalyst. Then washed biodiesel was dried at 100^oC temperature under vacuum.

2.3.3. Biodiesel preparation by Three- step method

Biodiesel was prepared from WCO by three-step method [7]. In this method the raw oil was saponified, acidified and esterified sequentially. For saponification process, certain amount of WCO was taken in a three necked flask and mixed with different stoichiometric amount of aqueous sodium hydroxide solution. The mixture was heated with vigorous stirring at 100 ^{0}C temperature for different time intervals. The reaction was stopped by cooling the reaction volume. The reaction time and molar ratio of oil to sodium hydroxide solution in saponification reaction were optimized. After saponification the soap solution was treated with different stoichiometric amount of concentrated hydrochloric acid at 60 -70 ^{0}C temperature with vigorous stirring.

After dissolving the soap, the FFA contents are separated in separatory funnel. After separation, the FFA content was determined by titrametric method. Esterification of FFA was carried out at different molar ratio of FFA to methanol, temperature and catalyst concentration for different times. In esterification reaction silica gel was used to adsorb water produced in reaction hence increase the reaction rate. The molar ratio of FFA to methanol, catalyst concentration, reaction temperature and time were optimized. The biodiesel was washed and dried under vacuum. The yield of biodiesel from raw oil was measured by the following equation:

$$\text{Yield} = \frac{W_{biodiesel}}{W_{oil}} \quad 1$$

where, $W_{biodiesel}$ is the weight of produced biodiesel and W_{oil} is the weight of oil.

2.4. Analytical methods for Oil and Biodiesel

To determine FFA of sample and biodiesel, 1mL oil and biodiesel were weighed in g , then dispersed in 5mL diethyl-ether solution followed by titration against 0.1 M KOH [8]. Saponification value (SV) was determined by method described by Jeffery et al. [8]. To determine SV 2 gm sample was taken in 50 mL alcoholic KOH solution then heated at 65 °C temperature under reflux with vigorous stirring for 30 min and titrated against 0.5 M hydrochloric acid. The iodine value (IV) was determined by titrating the sample with 0.01 N sodium thiosulphate and chemical reagents until the disappearance of blue color [8]. Iodine value was calculated by following equation:

$$IV = (V_1\text{-}V_2) *S*0.1269*100/ W \quad 2$$

V_1 and V_2 are the volume of sodium thiosulphate (in mL) required for titration with sample and blank titration, S is the concentration of $Na_2S_2O_3$ in Normality, W is the weight of oil sample in g. Cetane index (CI) was calculated by following equation [9]:

$$CI = a + \frac{b}{x} + cy \quad 3$$

Where, x is the saponification value, y is iodine value a, b, c are constants. Here, a, b, c was calculated by using the above equation for palm, peanut, soybean fatty acid methyl esters. Physical properties color, moisture content and density of the sample were by the following ASTM D 1500, ASTM D 1744 (Karl fisher method), ASTM D 1480/81 and ASTM D 240. Viscosity, cloud point, pour point were determined by standards ASTM D445 respectively.

3. RESULT AND DISCUSSION

3.1. Characterization of WCO

The properties of WCO such as viscosity, density, moisture content, saponification value, pour point, cloud point etc were measured and presented in Table 1.

Table 1: properties of WCO:

Properties	Experimental Value
Color	Yellowish
Specific gravity, at 25 ^oC	0.902
Kinematic viscosity (mm^2/s), at 40^oC	47.60
Free fatty acid content (%FFA)	1.83
Moisture content (%)	0.40
Saponification value(mg KOH/mg oil)	238
Clod point(^oC)	12
Pour point (^oC)	6

3.2. Preparation of biodiesel from WCO

3.2.1. Preparation of biodiesel by base Catalyzed Transesterification Method

Biodiesel was prepared from WCO by base catalyzed transesterification reaction. The properties of produced biodiesel by base catalyzed transesterification reaction are presented in Table 2. Viscosity and FFA content in the transesterification reaction product similar to the biodiesel standard. This biodiesel can be used in diesel engine but the reaction yield was only 58%.

3.2.2. Preparation biodiesel by acid Catalyzed Transesterification Method

The properties of biodiesel produced by acid catalyzed transesterification reaction are presented in Table 2. Viscosity and FFA content in the transesterification reaction product similar to the biodiesel standard. The reaction yield was 63.5%. The process was time consuming.

3.2.3. Biodiesel Prepared by three step Method

3.2.3.1. FFA Preparation

FFA was prepared from WCO by saponification followed by acidification. Saponification was done by the method described above. After saponification and acidification FFA was produced. Saponification was done with different stoichiometric molar amount of NaOH. The results are present in Figure 1.

Table 2: Properties of base catalyzed and acid catalyzed transesterification products

Property	Biodiesel produced by base catalyzed transesterification	Biodiesel produced by acid catalyzed transesterification
Specific gravity, at 25 ^oC	0.743	0.798
Kinematic viscosity (mm^2/s), at 40^oC	3.52	3.61
FFA (wt%) Free fatty acid content (%FFA)	0.28	0.85
Saponification value	183	191

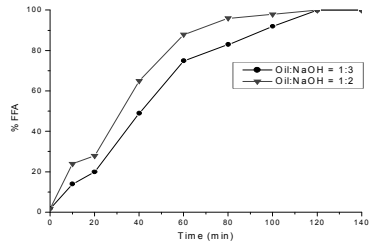

Fig.1: Preparation of FFA from WCO through saponification and acidification by different stoichiometric molar ratio of NaOH to oil in aqueous solution [Reaction temperature = 100 ^0C under reflux with vigorous stirring].

From the Figure 1 it can be seen that, the optimum molar ratio of oil to NaOH was 1:2 and the reaction time was 2.0 h.

3.3. Biodiesel Preparation from FFA

3.3.1. Effect of FFA/ methanol molar ratio

The FFA/methanol molar ratio is one of the important parameter that affecting the FFA conversion to methyl ester. The effect of methanol to FFA molar ratio on conversion of FFA was investigated at fixed temperature and catalyst concentration. The results are shown in Figure 2.

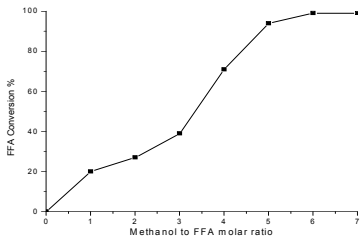

Fig.2: Effect of Methanol/FFA molar ratio on FFA conversion [temperature 60 ^oC, catalyst (HCl) 5 wt% of FFA and time 2 h under reflux with vigorous stirring]

From the Figure 2, it can be seen that the FFA conversion to biodiesel was 99.5% at the molar ratio of FFA to methanol 1:6. With further increase in FFA to methanol molar ratio, conversion does not increase. The optimum molar ratio of FFA to methanol was 1:6.

3.3.2. Effect of catalyst (HCl) concentration on esterification

Catalyst concentration has a significant role on conversion of FFA to biodiesel. Increase of catalyst concentration increases the percentage of FFA conversion. At a certain catalyst concentration the conversion was maximum. The effect of catalyst (HCl) concentration on conversion of FFA was investigated the results are shown in figure 3.

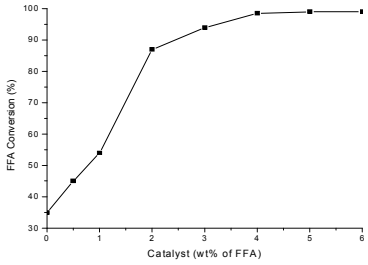

Fig.3: Effect of catalyst concentration on esterification reaction [Reaction temperature 60 ^0C, FFA / methanol ratio 1:6, vigorous stirring and Reaction time 2 h under reflux with vigorous stirring].

From Figure 3, it can be seen that the conversion was 99.5% at the catalyst (HCl) concentration of 5 wt% of FFA. Further increase in catalyst concentration the does not increase the conversion. The optimum catalyst concentration is 5 wt% of HCl to FFA.

3.3.3. Effect of silica gel on esterification reaction

The effect of silica gel was studied in esterification reaction by taking 5 gm silica gel for 50 g FFA. The results are presented in Figure 4. It can be seen that the presence of silica gel enhanced the rate of reaction and the reaction was completed in 40 min, where as without silica gel the same conversion is achieved after 120 min. Silica gel adsorbs the water produced in esterification reaction which facilitates the forward reaction.

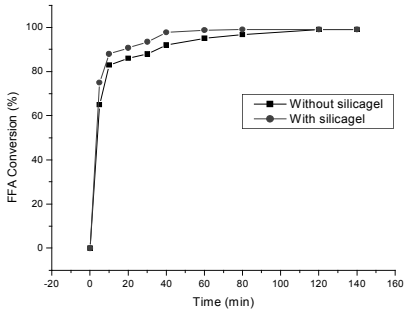

Fig.4: Conversion of FFA to biodiesel at different FFA/ methanol molar ratio of FFA in absence and presence of silica gel [Reaction temperature 60 ^{0}C, Catalyst(HCl) concentration 5.0% wt of FFA and Reaction time 2 h under reflux with vigorous stirring,].

3.3.4. Effect of Temperature

Temperature has a significant effect on conversion of FFA to methyl ester. Increase of temperature increases the %FFA conversion. At a certain temperature the conversion was high. The effect of temperature on conversion of FFA was investigated the results are shown in figure 5.

From Figure 5, it can be seen that the conversion was 99.5% at 60 ^{o}C temperature. Further increase of temperature the percentage FFA conversion remains unchanged. The optimum temperature was 60 ^{o}C for esterification.

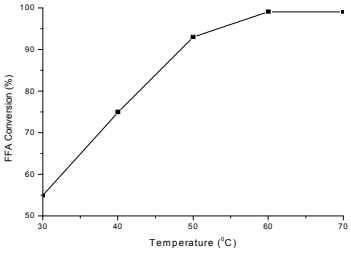

Fig.5: Effect of Temperature on esterification reaction [Catalyst concentration 5 wt% to FFA, FFA / methanol molar ratio 1:6 and time 2 h under reflux with vigorous stirring].

3.4. Properties of biodiesel

Properties of produced biodiesel by three-step method and comparison with biodiesel and conventional diesel standard are given in Table 3. The quality of biodiesel is determined by measuring some properties such as cetane index which indicates ignition characteristic.

Table 3: Properties of biodiesel produced from WCO by three-step method and comparison with standard biodiesel and diesel.

Properties	Produced biodiesel value	Biodiesel Standard [6,10]	Diesel standard [10]
Specific gravity, at 25 ^{o}C	0.792	0.88 (at 15.5^0 C)	0.85(at 15.5^0 C)
Kinematic viscosity (mm^2/s), at 40^{o}C	3.29	1.9–6.0	1.3 – 4.1
FFA content (wt%)	0.94	-	-
Moisture content (%)	0.12	0.05% max.	0.161
Saponification value	194	-	-
Flash point (^{0}C)	150	100 to 170	60 to 80
Iodine value	88	-	-
Cloud point (^{o}C)	0	-3 to 12	-15 to 5
Pour point (^{o}C)	-3	-15 to 10	-35 to -15
Cetane Index	54	-	-

The properties of produced biodiesel such as density, viscosity, FFA content, moisture content, pour point, cloud point, saponification value, iodine value were measured and compared with standard value. The reaction yield was 79.1%.

4. CONCLUSION

Biodiesel has been synthesized from WCO by base catalyzed, acid catalyzed transesterification and three-step method. All properties of biodiesel are desired level through base catalyzed, acid catalyzed transesterification process but yield is very low, that's why we use three-step method for biodiesel preparation. The reaction yield was 79.1% .Three-step method for biodiesel preparation comprises with

saponification to produced soap and acidification of the soap to produce FFA and esterification of FFA to produce biodiesel. Saponification was done by aqueous sodium hydroxide solution at different molar ratio of oil to NaOH and optimized. The optimum molar ratio for saponification by aqueous sodium hydroxide was 1:2 oil to NaOH and reaction time 120 min at 100 ^{0}C. In acidification the molar ratio of soap to hydrochloric acid was 1:1.5 for sodium soap. In Esterification the optimum molar ratio of FFA to methanol was 1:6, the catalyst concentration was 5 wt% of HCl to FFA, the reaction temperature was 60^{0}C and the reaction time was 2 h ,with silica gel reaction time is reduced to 40 min. The properties of biodiesel such as density, viscosity, specific gravity, cloud point, pour point, flash point, cetane index are nearest to the petro-diesel. The present experimental results support that biodiesel can be produced from WCO by three-step method with high yield and it can be successfully used as diesel.

5. REFERENCES

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6. NOMENCLATURE

Symbol	Meaning	Unit
M	Molarity	Mol/L
N	Normality	Equivalent mol/L