International Journal of Renewable Energy Resources 1 (2011) 45-49

BIODIESEL PRODUCTION FROM MUTTONTALLOW

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ABSTRACT

The high energy demand in the industrial world as well as in the domestic sector and pollution problems caused due to the widespread use of fossil fuel make it necessary to develop the alternate energy from renewable sources which must be from a fuel which must be technically feasible, economically competitive, environmentally acceptable and readily available. One possible alternative is the use of oils of plant origin, which is termed as Biodiesel which is biodegradable, non-toxic, domestic resource thereby relieving reliance on petroleum fuel imports. It also has more favorable combustion emission profile, such as low emission of CO, particulate matter and unburned Hydrocarbon. Transesterification is a common well established chemical reaction in which linear monohydroxyl alcohols reacts with vegetable oils which are triglycerides of fatty acids, in the presence of a catalyst. Alkali catalyzed transesterification is considered to be the best amongst all methods available for the production of biodiesel from fresh oil. In the present investigation an attempt has been made to use mutton fat as low cost sustainable potential feed stock for biodiesel production. Effect of various process parameters such as amount of catalyst, temperature, amount of methanol and reaction time on biodiesel production was investigated. The optimal conditions for processing 50 g of mutton fat were obtained. Under optimal conditions, the yield of mutton fat methyl esters was 93.2%. The fuel properties were estimated. Mutton fat was found to be highly suitable to produce biodiesel with recommended fuel properties.

Keywords: Mutton fat, Biodiesel, Optimization, Transesterification, Renewable energy

1. INTRODUCTION

Biodiesel is an alternative fuel for diesel engines that is receiving great attention worldwide as it reduces the dependence on petroleum products, the energy crisis, global climate changes and environmental pollution. Biodiesel and its blends can be used in diesel engines without any major modification. It is defined by ASTM that it is a fuel composed of Mono alkyl esters of long-chain fatty acids derived from renewable vegetable oils or animal fats (Ma and Hanna, 1999, Srivastava and Prasad, 2000). Chemical Biodiesel can be produced by transesterification, which is a three step reversible reaction that converts the intial triglycerides into a mixture of Fatty acid Methyl Ester(FAME) and glycerol in the presence of a catalyst usually homogeneous bases such as NaOH, KOH, or their alkoxides (Han et al, 2009). Although Vegetable oil esters have certain advantages such as lower viscosity, lower flask point, higher vapour pressure and easier processing relative to animal fatty acid esters, hence they are non-economical and non-feasible due to the prohibitive cost (Metin et al,2009). Moreover, the use of vegetable oil leads to shortage of food while use of animal fat for human consumption is a health hazard. Drawbacks of using animal fat as a raw material for Biodiesel production is its physical properties which could be eliminated by adding necessary amount of alcohol, catalyst for a required period of time. In the present work, we intent to produce methyl esters from the waste mutton fat and to optimise the reaction variables.

2. METHODOLOGY

2.1. Materials and Methods

The mutton fat was obtained from a slaughter house. The fat was washed, cleaned with deionised water and was free of flesh. The solid fat was melted at around 65°C. This was then filtered, centrifuged and decanted to remover other suspended particles. The processed fat which was homogeneous in nature was stored in air tight opaque plastic jars to prevent oxidation. The free fatty acid (FFA) of the and mutton fat was determined and found to be 12.4 mg of KOH/gm of fat. All the analytical grade reagents were bought from the local chemical supplier.

2.2. Transesterification

Biodiesel production from mutton fat consist of two steps: Acid esterification (Step 1) and alkali transesterification (Step 2) as the acid value of mutton fat is more than 2%.The parameters such as alcohol to oil molar ratio, catalyst amount, reaction temperature and reaction time were analysed. As the mutton fat had an initial acid value of 12.4 mg KOH/g, which is far above the 1% limit for satisfactory transesterification reaction using alkaline catalyst. Therefore, FFA levels were first reduced in a multi-step pretreatment process using acid catalyst (H_2SO_4 1% v/v) to reduce the acid value of Mutton fat below 1%. KOH/g (Encinar et al 2011). Experiments were conducted in a laboratory-scale setup which considered of 250cc glass flasks with air tight caps and a water cooled condenser that returned any vaporized methanol to the reacting mixture. The flasks were kept in an oil bath maintained at 60^{o} C, just below the boiling point of methanol. The mixture was stirred using an agitator at the same rate for all runs. The same setup was also used for the alkaline catalysed transesterification reaction. At various time the progress of the reaction was monitored by measuring the acid value. The fatty acid profile of mutton fat is given in Table 1 and the properties of mutton fat are shown in table2. Its FFA content was determined by the standard titrimetry method.

Table 1 Fatty acid profile of mutton fat

Fatty Acid	Formula	Mutton Weight %
Lauric Acid	C12:0	0.2
Myristic Acid	C14:0	3
Myristoleic Acid	C14:1	-
Palmitic Acid	C16:0	27
Palmitoleic Acid	C16:1	2
Stearic Acid	C18:0	24.1
Oleic Acid	C18:1	40.7
Linoleic Acid	C18:2	2
Linolenic Acid	C18:3	-

Table 2 comparison of properties of mutton fat, mutton fat methyl esters and diesel

Properties	MFME	Diesel	ASTM Standards for Biodiesel
Density at 15 ^{o}C kg/m^{3}	882	840	860-890
Kinematic Viscosityat 40 ^{o}C mm^{2}/s	4.75	2.6	2.5-6
Acid value mg of KOH/gm of oil	0.3	0.35	<0.8
Cloud point, ^{o}C	16	23	-
Iodine value, G I_2/100 gm	40		3.05
Saponification value, mg of KOH/gm	210.5	181	-
Pour point ^{o}C	-5	-30	-
Cetane value	59	50	47 min

2.3. Pretreatment of Melted Mutton Fat

The pretreatment process comprised of two steps. In each step, molar ratios of methanol to oil varied from 3:1 to 7:1 with variations in reaction times (30, 60, 90, 120 min.) were used to investigate their influence of alcohol to oil molar ratios on the acid value of melted mutton fat. After the reaction, the mixture was allowed to settle for 1 hr and the methanol- water fraction that separated at the top was removed in a separating funnel.

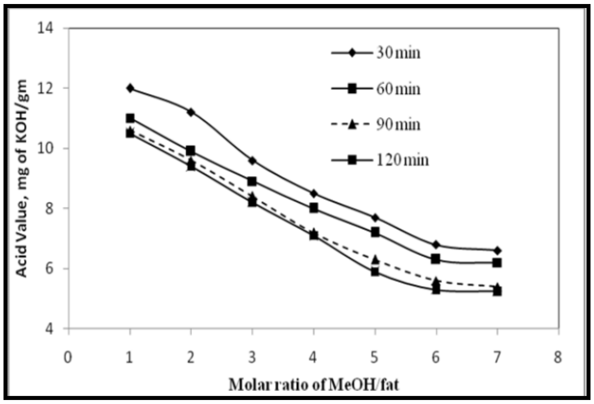

Figure 1 Effect of methanol quantity and reaction time on reduction of acid value of mutton fat during the first step pretreatment for biodiesel production. Initial acid value was 12.3 mg KOH/g of oil

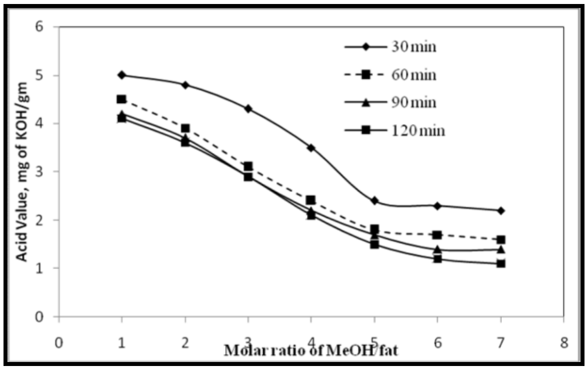

Figure 2 Effect of methanol quantity and reaction time on reduction of acid value of mutton fat during the second step pretreatment for biodiesel production.

The acid value of the product separated at the bottom was determined. The product having low acid value by using lowest quantity of methanol in minimum reaction ime was used as the raw material for the second step. Again the effect of methanol to oil ratio and reaction time on reduction of acid value of this raw material was studied. The final product having acid value less than 2mg KOH/g using lowest methanol amount and reaction time in the second step was used for the main transesterification reaction. The initial acid value from the first stage pretreatment was 5.64mg KOH /g of oil.

2.4. Alkali Transesterification:

In alkali transesterification, treated oil (mutton fat) from pretreatment procedure was allowed to cool at normal temperature. Mean while, calculated amount of KOH was dissolved with the required amount of methanol and was poured into the preheated oil (pretreated Mutton fat) in the flask. The reaction was conducted for various times and at 900rpm speed. After the reaction was completed for melted mutton fat, the reaction mixture was allowed to be separated into two layers. The bottom is the brownish red colour and containing the impurities and crude glycerol was drawn off. The esters along with the catalyst remained in the upper layer were then separated from the reactant Mixtures. The transesterified product (biodiesel) after separation was first distilled to remove the unreacted methanol and then washed 2-3 times with hot water to remove the dissolved glycerol in the biodiesel phase.

3. RESULTS AND DISSCUSSION

3.1. Effect of Methanol Amount and Reaction Time on Acid Value:

The variation in the acid value of the mixture on the first and second step pretreatment is shown in Figure.1 and 2, respectively. It can be seen that the rate of reaction was greatly influenced by both the quantity of methanol and reaction time. The reaction progressed rapidly during the first 90 min showing over 15% reduction in acid values at low-methanol and over 58% for high-methanol ratios. After 90 min, there was no significant reduction in the acid value. This might be due to the effect of water produced during the esterification of FFAs, which prevented further reaction. With 1:1 methanol-to-oil molar ratio, the acid value could not go below 10.5mg KOH/g even after 2hrs reaction during the first stage. Since the increase in the reaction time was not effective after 90min, the methanol quantity was varied. It was found that increasing the methanol to oil molar ratio above 6:1 did not reduce the FFA amount considerably. Hence the combination of 6:1 molar ratio of methanol to oil and 90 min reaction time which reduce the acid value from 12.4 to 5.6 mg KOH/g was selected as optimum for first pretreatment step.

In the second step, the optimized sample was used as the feed, to this 1% sulphuric acid was added and the methanol to oil ratio along with the reaction time was varied. The reaction time showed the same trend as in the case of first step, the methanol-oil ratio of 5:1 was found to be the optimum for the second step reaction to reduce the acid value below 2mg KOH/g in 1 hour reaction time. It was observed that the high amount of methanol is required to bring down the FFA content from 12.4 to 1.8. However the high consumption of methanol was recovered by distillation from the top layer during the pre-esterification step and also from ester phase and glycerol layer.

3.2. Transesterification

Alkaline catalyzed transesterification was run using a pretreated sample that had an acid value of 1.8 mg KOH/g for mutton fat. Following this process, an yield of 94% biodiesel was obtained from mutton fat. The fuel properties of Mutton fat methyl esters (MFME) along with melted mutton fat and diesel are summarized in Table2. It can be seen that MFME biodiesel had comparable fuel properties with those of diesel and were within the limits prescribed in the standards.

3.3 Optimization of Transesterification Process

The percentages of yield of methyl esters are presented as graphs for the different amounts of methanol to oil ratio, reaction temperature, and catalyst amount. The percentage of yield of methyl esters is calculated by using equation (1)

% of yield = (Methyl esters (in ml)
----------------------------- X 100 – (1)
(Vegetable oil (in ml) used in the reaction)

3.3.1. Effect of Catalyst Amount & Reaction Temperature:

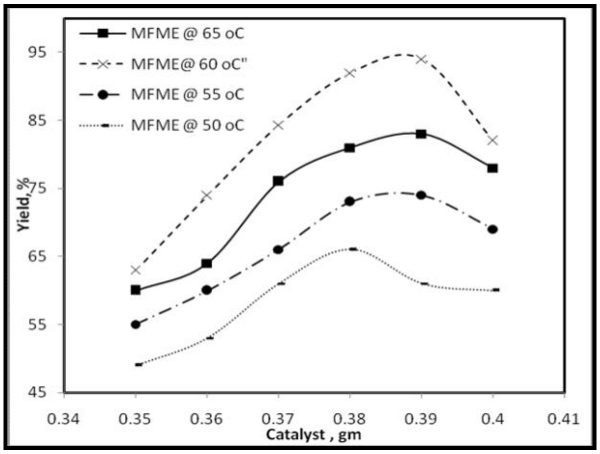

Figure 3 Effect of amount of catalyst and Reactiontemperature on mutton fat (Reaction Time: 90 min, Molar ratio of MeOH:oil : 6:1)

Methanolysis of mutton fat was carried out with KOH as a catalyst at a concentration of 0.35 – 0.4 gms of KOH with MeOH/oil molar ratio of 6:1 at stirring speed of

900 rpm, reaction time 90 min. Figure 3 shows the yield of Mutton fat methyl esters vs. Catalytic concentrations at different reaction temperature. For lower catalytic concentration of 0.35gm of KOH was insignificant to catalyze the reaction to completion. However 0.39 gms of KOH for mutton fat methyl esters in the reaction with a yield of 94% for Mutton fat at 60^{o}C. Increasing the catalyst amount above the optimal value decreased the yield due to the fact that, soap formation occurs at higher amounts of catalyst and also backward reaction was favored at high catalyst concentration. It is also observed that the reaction achieved a maximum yield at 60^{o}C for all amounts of catalyst added. For higher reaction temperature, the yield decreased as the reaction temperature was very close to the boiling point of Methanol where most of the Methanol would be in the vapor phase which actually affects the Mass transfer between the gas and liquid phase and also the higher temperature accelerates the side saponification reaction of triglycerides.

3.3.2. Effect of Methanol/ Oil Ratio:

The alcohol/oil ratio is one of the important factors that affect the reaction. The variation in the yield of methyl esters with different methanol to oil molar ratio for various reaction time is shown in Figure 4. It is also observed that the percentage yield increases with increase in excess amount of MeOH. Transesterification is an equilibrium reaction in which a large excess of MeOH is required to drive the reaction to the right. For maximum conversion to the ester, a molar ratio varying from 3:1 to 7:1 was used.

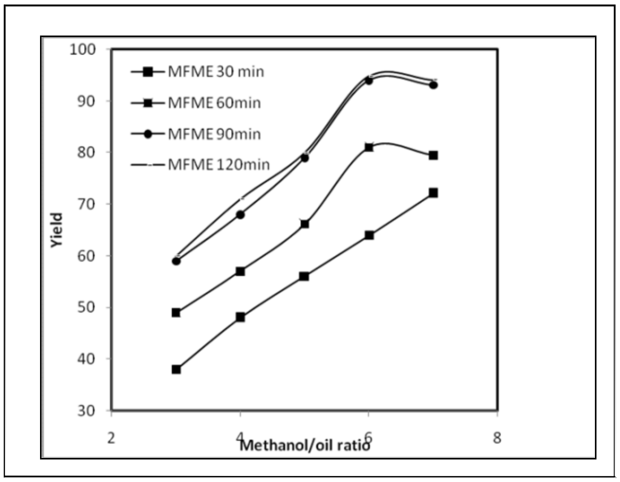

Figure 4 Effect of molar ratio of MeOH/oil and Reaction time on mutton fat (Reaction Time: 90 min, catalyst /oil wt%:0.39 gm of KOH/gm for mutton fat)

The high molar ratio of MeOH to vegetable oil interferes with the separation of glycerin because there is an increase in solubility. When glycerin remains in solution, it helps drive the equilibrium to back to the left, lowering the yield of esters. It is advisable to use molar ratio of methanol/oil ratio of 6:1 since increase in the amount of methanol does not show a significant increase in the yield. However on an industrial scale increasing the amount of methanol would not be a problem since methanol can be recovered from glycerol and methyl esters phase. However increasing the consumption of methanol will inevitably increase its recovery cost. It was also observed that there was significant increase in the yield up to 90min and thereafter it became almost constant for higher reaction time. It was found that for a reaction time of 90min and methanol/oil ratio of 6:1 the yield was optimum.

4. CONCLUSION

The study on the biodiesel productin process optimization of mutton fat showed that the quantity of catalyst, amount of methanol, reaction temperature and reaction time are the main factors affecting the production of methyl esters. The optimal values of these parameters for achieving maximum conversion of oil to esters depended on the chemical and physical properties of these fats.The following conclusions are drawn from the study.

1. Addition of excess catalyst causes more triglycerides participation in the saponification reaction leading to a marked reduction in the ester yield
2. Biodiesel production process is incomplete when the methanol amount is less than the optimal value. Operating the optimal value, the ester yield would not be increased but will result in additional cost for methanol recovery.
3. Sufficient reaction time should be allowed to ensure complete conversion of triglycerides into esters. However, excess reaction time did not promote the conversion but favours the reverse reaction of transesterification which resulted in a reduction of ester yield.
4. The optimal reaction conditions for production of methyl esters from mutton fat are established as follows. The reaction time of 90 min at 60^{o}C, 6:1 molar ratio of methanol to oil and 0.39 gms of KOH/gm of oil for mutton fat for 50ml of mutton fat.
5. Results of present study clearly demonstrated that the use of mutton fats is very suitable as low cost feed stocks for biodiesel production.

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