BIODIESEL DEVELOPMENT FROM HIGH FREE FATTY ACID MAROTTI OIL

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ABSTRACT

Marotti oil, one of the non edible oils available in India, was esterified to produce biodiesel. The optimized procedure for biodiesel development from marotti oil involves a two stage process. The free fatty acid content of the selected oil is 4.5% which necessitates the two stage process. The free fatty acid content is reduced to less than 3% by the acid esterification process and biodiesel is produced in the alkaline transesterification process. The optimum conditions of the biodiesel production were established by studying the effects of various parameters like methanol to oil ratio, catalyst concentration, reaction temperature and reaction time. A conversion efficiency of 92% was attained and the different properties are found to be in the limits specified by biodiesel standards.

1. INTRODUCTION

The world is in search of alternative fuel sources to overcome the expected scarcity of petroleum fuel. Many researchers are successful in developing such alternatives which extend from biofuels to solar energy. In fact the number of sources found out and developed is quite high, but the economical factors and ease of use, limit the possibilities of some of them. These factors are met satisfactorily to a great extent in the case of biodiesel. Biodiesel, as is well known, can be easily produced from any vegetable oil. Most of the oils, especially edible oils, can be converted using the conventional transesterification procedures. But in a country like India which is not self reliant in the production of edible oils, it is not advisable to use edible oils for biodiesel production. This situation emphasizes the importance of attempts with non edible oils. India is a country which is greeted with a variety of non edible oil plants and the different states of India have different species of plants growing.

Researches are carried out successfully in developing biodiesel from different non edible oils like jatropha, rubber seed oil, pongamia, karanja etc. The oil from marotti, punnakka etc. are some of the oils found suitable for biodiesel production in the state of Kerala. In dealing with non edible oils the major factor which influences the biodiesel production method is the presence of free fatty acids (FFA) in the oil. Transesterification using alkaline catalyst is the commonly adopted method of biodiesel production. In the presence of alkaline catalyst the methanol converts the triglycerides of the oil to methyl esters. But the FFA in the oil prevents this reaction by forming soap. This necessitates the conversion of FFA into esters before going for transesterification. Therefore a two stage

esterification procedure is adopted in cases of oils with high amount of FFA content. In fact while producing biodiesel from non edible oils the FFA content affects the value of different parameters in the production procedure. Hence the biodiesel production procedure will be different for the same oil with different FFA contents.

The present paper investigates the possibilities of biodiesel production from Marotti oil with an FFA content of 4.5%. Marotti is a tree available in plenty in the state of Kerala. The oil has been used as fuel in the olden days and is also famous for its medicinal applications. Experiments are conducted for biodiesel production from Marotti oil with various combinations of influencing parameters. Optimum parameter values are determined by analyzing the results.

2. ABOUT THE OIL

The tree called Marotti in the regional language of Kerala, bears the botanical name Hydnocarpus Laurifolia and belongs to the family Flacourtiaceae. The tree is known in different Indian languages as Chaulmoogra (Hindi), Adi-badame (Telugu), Maravatti (Tamil) and Toatti (Kannada). The brown coloured fruit is having the seeds inside containing about 62% oil in it. The oil can be extracted by steam distillation. The oil is having medicinal applications also. Important fatty acids present in the oil, called cyclopentene fatty acids, are hydnocarpic acid, gorlic acid and chaulmoogric acid having carbon chains from C16 to C18. The approximate percentages are 48%, 12% and 37% respectively. The FFA content varies from about 2% to 6%. The oil is highly viscous which prevents its use as a direct fuel in CI engines. The oil used in the present study is having a FFA content of 4.5 % (acid value 9 mg KOH/g of oil). For oils with FFA less than 3%, alkaline transesterification is adopted for biodiesel production. Since the present oil is having FFA content of 4.5% two stage esterification is required. Also the optimum parameters values are to be established by studying the results of experiments with varying combinations of parameters.

Table 1 Fatty Acid Profile of Marotti Oil

Fatty Acid	Acronym	Molecular Weight	Weight % in the oil
Palmitic Acid	16:0	256.43	1.8
Hydnocarpic Acid	16:1	254.47	48.7
Chaulmoogric Acid	18:1	282.47	37.3
Gorlic Acid	18:2	280.45	12.2

3. TWO STAGE TRANSESTERIFICATION

The first stage is acid esterification where concentrated sulfuric acid is used as catalyst. This reaction converts the free fatty acids in the oil to esters thus reducing the FFA content. The FFA content of the oil should be less than 3% so as to facilitate alkaline esterification. The second stage is alkaline esterification which converts the product from first stage in to biodiesel. KOH is used as catalyst in this stage which is dissolved in methanol and mixed with the product from first stage. In both stages the process consists of preheating, mixing of methanol and catalyst, heating with continuous stirring and keeping for settling.

The set up used in both the cases consists of a flat bottom flask to carry out the reaction, a magnetic stirrer with heating coil for continuous heating and stirring. The mixture after reaction is transferred to a separating funnel for settling. Marotti oil is taken in the flask and heated to temperature between 50-55^{o}C. Methanol is added to the

preheated oil and concentrated sulfuric acid is added as catalyst. The quantity of methanol is to be in excess of the stoichiometric ratio since the reaction is reversible. Excess methanol is required to drive the forward reaction to complete. The mixture is heated and stirred continuously for the required time. Reaction temperature is an important parameter affecting the speed of reaction and efficiency of FFA reduction. The mixture after the reaction is transferred to a separating funnel and allowed to settle. The excess methanol, acid and other impurities will form a separate layer in the top. This is removed and the bottom layer is used for the second stage esterification.

The product from the acid esterification stage is measured and taken in the flask. It is heated to temperature between 55-60^{o}C. The methanol quantity is decided based on the quantity of product from the first stage. The required quantity of potassium hydroxide (KOH) as catalyst is dissolved in methanol to avoid problems of moisture absorption by the catalyst. The potassium methoxide solution formed is added to the preheated first stage product. The reaction is carried out with continuous heating and stirring for the specified time. The mixture after reaction is transferred to the separating funnel and allowed to settle. The biodiesel forms the top layer on settling and the glycerin and any impurities form the bottom layer. The bottom layer is drained and the top layer is taken and is subjected to purification processes to remove excess methanol, traces of soap etc.

4. OPTIMIZATION PROCEDURE

The important parameters that influence the process output quantity and quality are methanol to oil ratio, catalyst concentration, reaction temperature, reaction time and settling time. Experiments are conducted with different sets of parameter values and optimum conditions are established for maximum efficiency of the process. For first stage various parameters experimented are methanol to oil ratio, reaction temperature and reaction time. The catalyst concentration is taken as 0.75% v/v of oil in all cases. The FFA content of resulting product in each experiment is determined by standard chemical titration procedure using 0.1 normal KOH solution and phenolphthalein indicator.

For the second stage, product from the first stage carried out with determined optimum parameter values, is used. Here the parameters varied for optimization are methanol to oil ratio, catalyst concentration and reaction time. The reaction temperature used in all cases is 60. The biodiesel separated and purified is measured and the conversion efficiency in each case is determined.

5. INFLUENCE OF PARAMETERS AND OPTIMIZED VALUES

5. 1. Acid esterification

The methanol to oil ratio is varied and the FFA reduction is analyzed. With methanol to oil ratio of 0.4 and 0.45 v/v the reaction was not complete, as indicated by the black layer forming at the bottom instead of forming at the top. Methanol at the ratio of 0.5 is found to be sufficient to complete the reaction. The FFA content is reduced to below 2% at this condition. Further increase in methanol did not result into significant reduction of FFA content. Also this will increase the cost of the production. Hence the ratio of 0.5 is taken as the optimum ratio. The results are shown in Figure 1.

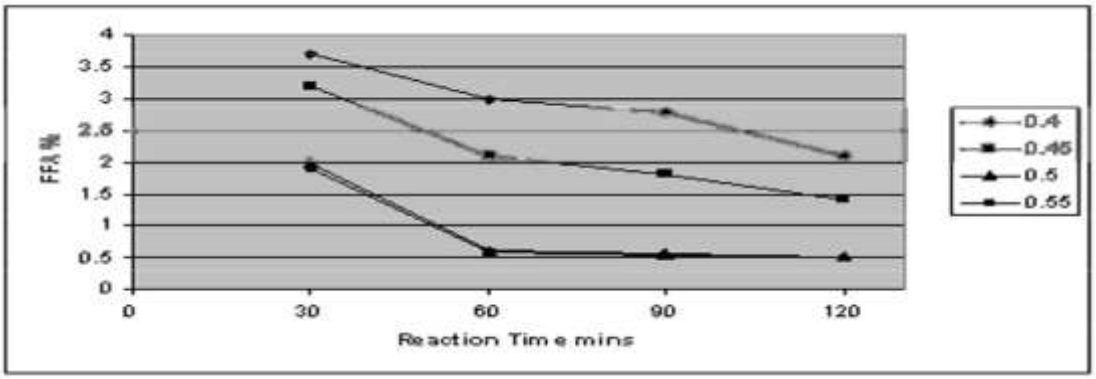

Figure 1 Effect of methanol-to-oil ratio and the reaction time on reduction of free fatty acid content of marotti oil (catalyst concentration of 0.75% v/v of oil, reaction temperature of 60^{o}C).

Heating of the oil increases the speed of the reaction. Preheating of oil is done to temperatures between 50–55^{o}C. Reaction temperatures of 40^{o}C, 50^{o}C and 60^{o}C are used and FFA content of products in each case is measured. The methanol to oil ratio of 0.5, found out as optimum earlier, is used in all cases. The FFA content is reduced to lower values as the reaction temperature is increased. FFA content of less than 2% was obtained at 60^{o}C as shown in Figure 2. Further increase in temperature may cause more reduction in FFA content but is not preferred since there is chance of methanol loss due to vaporization at high temperatures thus affecting the reaction efficiency.

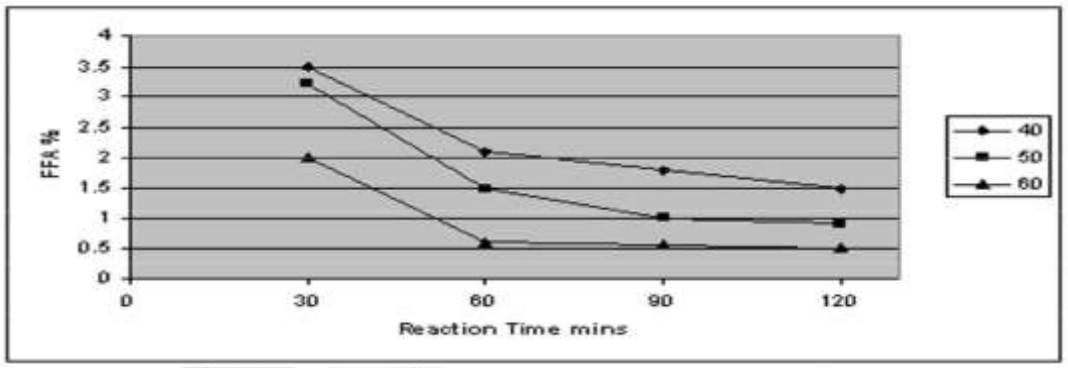

Figure 2 Effect of reaction temperature and reaction time on the reduction of free fatty acid content of marotti oil (methanol-to-oil ratio of 0.50 v/v, catalyst concentration of 0.75% v/v of oil).

Keeping the methanol to oil and reaction temperature at the optimum values experiments were conducted with various values of reaction time. The experiments show that reaction for 60 minutes is sufficient to complete the reaction with required reduction in FFA content of the oil. Further increase in reaction time causes slight increase in FFA content reduction but is not much beneficial as more reaction time needs more heat energy input.

The mixture after completion of reaction is allowed to settle when the excess methanol, acid and other impurities separate as top layer. It is seen that the layer separation starts after 30 minutes settling time. But allowing the mixture to settle for 90 minutes is found as required for complete separation. More settling time does not benefit significantly. Optimum conditions are established based on the observations with varying conditions which lead to reduction in the FFA content to minimum. The established optimum conditions are methanol to oil ratio of 0.5 v/v,

acid catalyst concentration of 0.75% v/v of oil, reaction temperature of 60^{o}C, reaction time of 60 minutes and settling time of 90 minutes.

5.2. Alkaline esterification

The methanol to oil ratio is taken more than the stoichiometric ratio so as to drive the reaction to complete since the reaction is reversible. Experiments are conducted with three different methanol to oil ratios (0.1, 0.2 and 0.3 v/v) at different reaction temperatures and catalyst concentrations. The plot of conversion efficiency to methanol oil ratio is given in Figure 3. It is seen that the conversion efficiency is low when a methanol to oil ratio of 0.1 v/v is used. The efficiency is found high with methanol to oil ratio 0.2 v/v. Further increase in methanol quantity does not produce significant increase in the conversion efficiency. Hence 0.2 v/v is selected as an optimum value for the methanol to oil ratio.

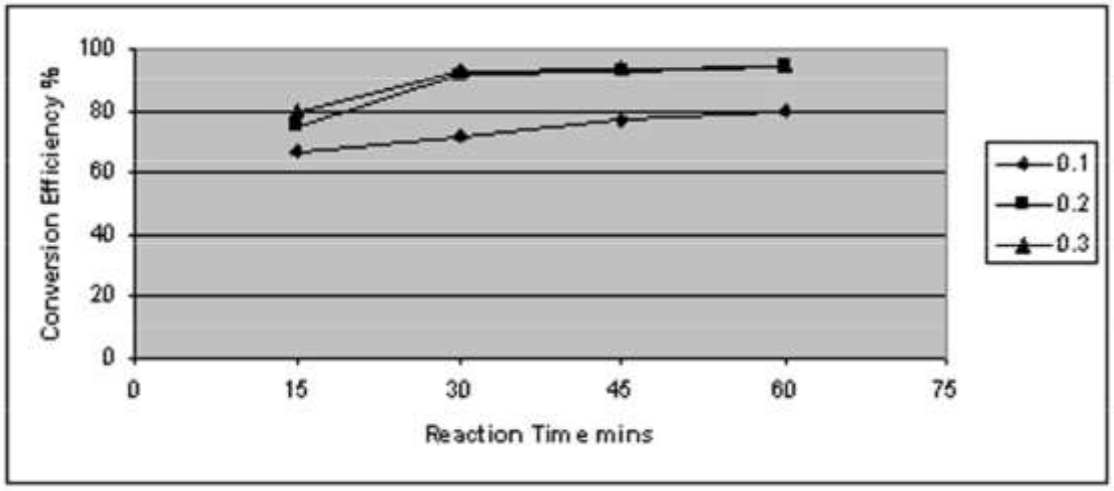

Figure 3 Effect of methanol-to-oil ratio and reaction time on conversion efficiency (catalyst concentration of 1% w/v of oil, reaction temperature of 60^{o}C).

The transesterification is carried out in the presence of an alkaline catalyst. The presence of catalyst is very essential to carry out the transesterification successfully. KOH is used as catalyst in this case. Experiments are conducted with three different catalyst concentrations (0.75, 1.0, and 1.5 w/v of oil) to find out the optimum concentration amount. The conversion efficiency increases with increasing catalyst concentration and maximum efficiency occurs at catalyst concentration of 1.0 as shown in Figure 4 Further increase in catalyst concentration reduces the conversion efficiency due to the gel formation which increases viscosity.

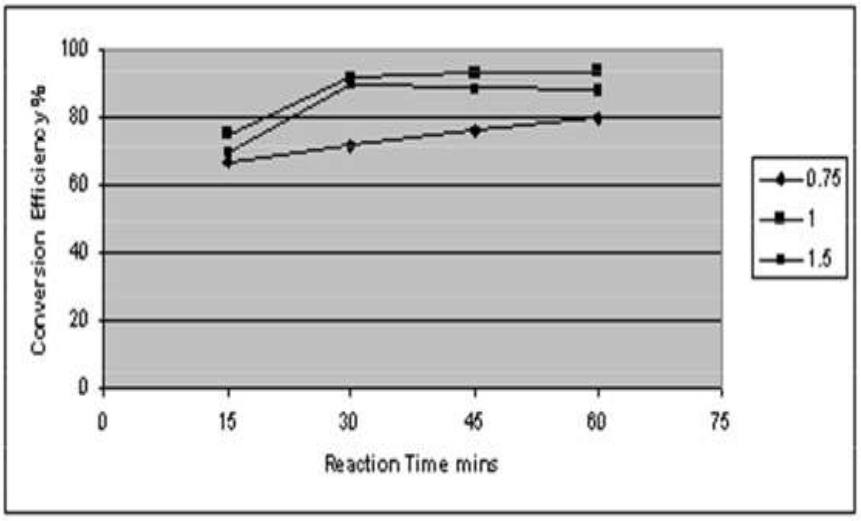

Figure 4 Effect of catalyst concentration and reaction time on conversion efficiency (methanol-to-oil ratio of 0.2 v/v, reaction temperature of 60^{o}C).

The conversion efficiency is found out with different reaction time. The biodiesel starts to form as top layer with 15 minutes of reaction itself. But the conversion efficiency is very low at this stage. The conversion efficiency increases as the reaction time is increased. Optimum conversion efficiency is reached after 30 minutes of reaction time. Further increase in reaction time does not result in significant increase of conversion efficiency. Also more reaction time needs more energy input due to extended heating of the mixture. Settling time of 60 minutes is found to be sufficient for the separation of biodiesel as the bottom layer.

The optimum values of the selected parameters are thus determined based on the conversion efficiency. The obtained optimum parameter conditions are methanol to oil ratio of 0.2 v/v, alkaline catalyst concentration of 1.0% v/w of oil, reaction temperature of 60^{o}C, reaction time of 30 minutes and settling time of 60 minutes.

6. PROPERTIES OF MAROTTI BIODIESEL

Properties of the marotti biodiesel like specific gravity, calorific value, flash point, and FFA content are determined. Standards used for measurement of properties, standards specified for biodiesel by ASTM 6751-02, standard values for petroleum diesel and the property values of marotti biodiesel are listed in Table2. The values are comparable with the standards set for biodiesel and also with those for petroleum diesel. Approximate percentages of carbon, hydrogen and oxygen composition are 77.50% carbon, 11% hydrogen and 11.5% oxygen. The transesterification process reduces the viscosity of the marotti oil from 89.5 mm^2/s to 5.5 mm^2/s, which is in the limits specified for biodiesel. The calorific value of the marotti biodiesel is 35,300kJ/kg and the flash point is 162^{o}C.

Table 2 Comparison of Properties

Property	Testing procedure	Biodiesel standard ASTM 6751-02	Marotti biodiesel	Petroleum diesel

Specific Gravity	ASTM D4052	0.87-0.9	0.870	0.860
Calorific value MJ/kg	ASTM D240	-	35.3	44.22
Viscosity mm^2/s at 40 ^0C	ASTM D445	1.9-6.0	5.5	2.87
Flash point (^0C)	ASTM D93	min. 130	162	76
Acid value mg KOH/g oil	ASTM D974	0.8	0.6	-

7. CONCLUSION

A two stage esterification procedure to produce biodiesel from marotti oil is presented. The oil contains free fatty acids of 4.5% and the main constituent fatty acids are hydnocarpic acid, gorlic acid and chaulmoogric acid. The first stage consists of esterification using concentrated sulfuric acid as the catalyst. The acid catalyst is used to convert the free fatty acids in the oil to methyl esters and thus reduce the free fatty acid content of the oil. The resulting product from this stage is subjected to transesterification in the second stage using potassium hydroxide as catalyst. The biodiesel has properties in agreement with the biodiesel standards and closely matching with those of petroleum diesel. The observations of the analysis are as follows:

Acid esterification reduced the free fatty acid content from 4.5% to 0.61%. The optimum conditions for the reaction are methanol to oil ratio of 0.5 v/v, catalyst concentration of 0.75% v/v of oil, reaction temperature of 60^oC, reaction time of 60 min and settling time of 90 min. The optimum conditions for the second stage transesterification are methanol to oil ratio of o.2 v/v, catalyst concentration of 1.0% w/v of oil, reaction temperature of 60^oC, reaction time of 30 min and settling time of 60 min.

The optimum values are selected based on the reduction in free fatty acid content and the biodiesel conversion efficiency. Even though further increases in some parameters may cause an improvement in the desired results, it is discarded on economic aspects due to increased input energy. The results are direct indicatives of the suitability of the marotti oil for biodiesel production.

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