Biodiesel production from high FFA tree born non-edible Ceiba Pentandra seed oil

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Abstract -   **In the present study, high free fatty acid (14.71%) Ceiba Pentandra seed oil was used as a resource for biodiesel production. A two-step transesterification process is developed to change the high FFA oils to its mono-esters. The primary step reduces the acid value of the oil to less than 2mg KOH/g of oil using the acid catalyst (H_2SO_4) and methanol. In the subsequent step, alkaline catalyzed transesterification process converts the products of the first step to its mono-esters and glycerol. The reaction parameters such as catalyst concentration, molar ratio, reaction time and reaction temperature were optimized for production of ceiba pentandra oil methyl ester are analyzed. The two-step esterification procedure converts of crude ceiba pentandra oil to its methyl esters. The yield of methyl esters from ceiba pentandra oil under the optimal condition was 92-93%. The viscosity of biodiesel oil is nearer to that of diesel and the calorific value is less than that of diesel because of their oxygen content. The important properties of biodiesel such as density, flash point, fire point and cetane number are found out and compared with that of conventional diesel fuel. This study supports the biodiesel production from non-edible Ceiba Pentandra seed oil as a feasible alternative to the diesel fuel.**

Keywords - Biodiesel, Ceiba Pentandra seed oil, Transesterification, FFA.

1. INTRODUCTION

Diesel fuel is largely utilized in the transport, agriculture, commercial, domestic, and industrial sectors for the generation of power / mechanical energy. From the point of view of protecting the global environment and anxiety for long term supplies of conventional diesel fuels, it becomes essential to develop alternative comparable with conventional fuels. Of the alternative fuels, vegetable oils shows potential alternative to diesel fuels because they are renewable in nature and can be produced locally and eco-friendly as well [1]. The substitution of even a small fraction of total consumption by alternative fuels will have a significant impact on the economy and the environment. Government of India has formulated a bio fuel policy in which it is anticipated to use 20% of biodiesel at the end of 2017 and this will require a total of 13.38MMT of biodiesel [2]. Biodiesel can be produced from both edible and non edible oils as well animal fats. However, in India, which is not self sufficient in edible oil production, the non edible oils will be the only source of feedstock for biodiesel production. Among the available non edible oils Mahua, Karanja and Jatropha have been successfully proven as potential tree born oil for biodiesel production in India, but their availability is in specific region. Therefore, it is not possible to have sufficient amount of oil at one place to produce biodiesel to cope the exponentially increasing demand for energy in terms of diesel consumption. Hence, it is needed to carry out research on different tree born non edible oils, so that we can able to fulfill the biodiesel requirement of our country without depending on the specific oil and its availability.

Several researchers [3-8] have been made systematic efforts in the recent years to use the various vegetable oils as fuel in compression ignition engines. The viscosity of vegetable oils is about 11-17 times higher than that of diesel. However, their use in direct injection diesel engines is restricted by some unfavorable physical properties, particularly their viscosity. The use of vegetable oil cause poor fuel atomization, incomplete combustion and carbon deposition on the injector and valve seats resulting in serious engine fouling. This necessitates the reduction in viscosity of the vegetable oils for use as fuel in CI engines. The commonly employed methods to reduce the viscosity of vegetable oils are blending with diesel, microemulsion, pyrolysis and transesterification [9]. Among the several methods for reducing the viscosity, transesterification is an extensive, commercial and most promising method of converting vegetable oil into biodiesel that can be used directly or as blends with diesel in diesel engines and also the byproduct (glycerol) has commercial value [10].

At present ceiba pentandra seed oil does not find any major applications and hence even the natural production of seeds itself remains unidentified. In this study, typically non-edible, high FFA content, ceiba pentandra seed oil is considered as a potential feed stock for biodiesel production.

2. CHARACTERISATION OF CEIBA PETANTRA OIL

Ceiba pentandra tree yields about 300 to 1,000 seed pods per year. Pods are ellipsoid capsule of 10-25cm long, and 3-6cm diameter. Capsules split open into 5 valves, having a cotton-like woolly floss, yellowish grey and lustrous fiber in which 120-175 seeds are embedded. Seeds are round and black in colour. The oil seed yield was producing on average 1280kg/ha. It is cultivated for two purposes, first one its fibre is short natured, traditionally it is used as an filling materials for mattresses, pillows, cushions, and stuffed toys and second is its seeds produce pale yellow, bitter, non-drying, non-edible oil used locally in soap, illuminating oil and oil cake can be used as cattle feed and fertilizer. The oil extraction was carried out with mechanical expeller having high pressure continuous screw press and containing a stainless steel helical screw. The extracted oil was kept at atmospheric temperature for few hours in order for solids to settle down. The extracted crude ceiba pentandra oil was filtered and heated to remove unwanted particles in the oil. After filtration, to remove any water content in the oil, the crude ceiba pentandra oil was heated to 120^oC.

Table 1. Physical and chemical properties of in crude ceiba pentandra oil

| Property	Value
Density	916 kg/m^3
Viscosity@40°C	30.42 mm^2/s
Acid value	29.42mg KOH/g
Water content	0.04 wt.%
FFA	14.71% as oleic acid
Flash point	297°C
Saponification value	197
Iodine value	100.6

3. BIO-DIESEL PRODUCTION PROCESS

Transesterification is the chemical reaction between triglycerides and short chain alcohol in the presence of catalyst to produce mono-ester. The long and branched-chain triglyceride molecules are transformed to mono-esters and glycerin [11].

A two-step transesterification process is developed to convert the high FFA oils to its esters. The process consists of two steps namely, acid esterification and alkali esterification.

(a) Acid esterification : The first step (acid catalyzed transesterification) reduces the FFA content of the ceiba pentandra oil to less than 2% using acid catalyst.
(b) Alkaline esterification : After removing the impurities from the first step, the alkaline catalyst transesterification process converts the low FFA ceiba pentandra oil to its mono-esters and glycerol.The parameters affecting the process such as alcohol to oil molar ratio, catalyst amount, reaction temperature and duration are analyzed.

The transesterification reaction was carried out in a laboratory scale reactor as shown in Fig.1. The apparatus used for the experiment consists of 1000 ml three necked flat bottom glass flask and electrical heater with magnetic stirrer arrangement to achieve a perfect contact among the reactants. One side neck of the reactor is plugged with air tight rubber stopper which holds the thermometer used to measure the reaction temperature. The other side neck is used to draw the sample oil and alcohol catalyst mixture. The water cooled condenser was inserted through the main neck of the reactor to recover the escaping methanol which has a boiling point of 65^oC and vaporizes at the elevated temperature during the reaction. The condenser also helps in maintaining atmospheric pressure inside the reactor.
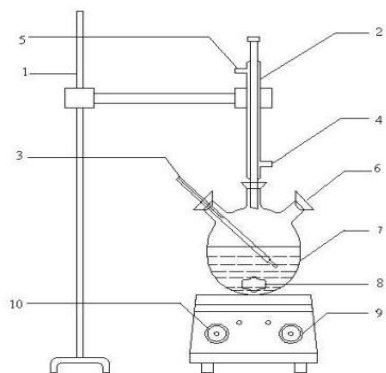
1. Iron Stand
2. Condenser
3. Thermometer
4. Coolant in
5. Coolant out
6. Closed Neck
7. Three Neck Flask
8. Magnetic Stirrer
9. Magnetic Stirrer Controller
10.Temperature Controller

Fig 1.Schematic diagram of reaction setup

4. ACID ESTERIFICATION

The crude ceiba pentandra oil had an initial acid value of 29.42 mg KOH/gm, corresponding to a FFA level of 14.71 %, which is for above the 1 % limit for satisfactory transesterification reaction using alkaline catalyst. The process of transesterification is complicated, if oil contains large amount of FFA content that will form soap with alkaline catalyst. The soap can prevent the separation of the biodiesel from the glycerine fraction[12]. Therefore FFAs were first converted to esters in a pretreatment process using a acid catalyst (H_2SO_4) to reduce the acid value of ceiba pentandra oil to below 2mg KOH/gm and completed transesterification with an alkaline catalyst to produce biodiesel [13].   A known quantity of ceiba pentandra oil was poured into the reaction flask and heated to the desired temperature. The methanol and sulphuric acid (H_2SO_4) was added with the preheated ceiba pentandra oil and maintained at the temperature of 60^oC. During the reaction, the mixture was stirred constantly using a magnetic stirrer at a speed of 500-600 rpm. The product was poured into a separating funnel and left for 2 hours. The excess methanol with sulphuric acid and impurities moved to the top surface and was removed. The lower layer was low free fatty acid oil content. The oil sample was heated to 70^oC to remove the extra methanol and washed with distilled water in a separating funnel. Finally the acid value of the product separated at the bottom was determined. After each parameter's optimum value was attained, this value was kept to be constant during the optimization of the next parameter was determined.

4.1 Influence of molar ratio on reduction of acid value

The acid value reduction at different molar ratios is shown in Fig. 2. It was found that the acid catalyst esterification rate increases with increasing in methanol value. The acid value reduced quickly during the initial phase and after that it reduced slowly. This might be due to the effect of water formation during the esterification of FFAs, which prevented further reaction [14]. The methanol to oil ratio 9:1 was the lowest ratio which gives the acid value of oil less than 2mg KOH/g oil, so it was selected as the optimum methanol to oil ratio.
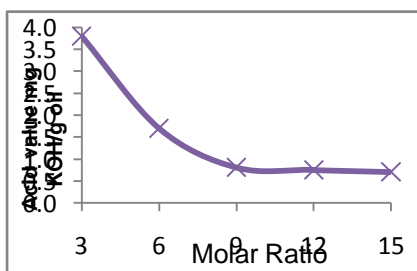

Fig.2. Molar ratio on reduction of acid value.
amount on reduction of acid value
Catalyst amount 0.75% v/v, reaction temperature 60^oC,
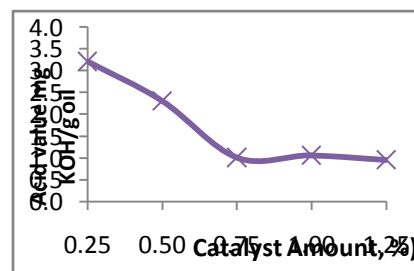reaction time 45 min.
time 45 min.

Fig.3. Acid catalyst

Molar ratio 9:1, reaction temperature 60^oC,
reaction

4.2 Influence of acid catalyst amount on acid value

The catalyst amount is varied in the range of 0.25–1.25% for five different values (0.25, 0.5, 0.75, 1.0 and 1.25% v/v of sulphuric acid). The effect of the acid catalyst amount on the acid value reduction is shown in Fig.3. At lower catalyst concentration acid value could not be reduced below 2mg KOH/g oil. In accordance with the results of other researchers [15,16] the ester formation rate increased with increasing catalyst concentration. However, 0.75% v/v of oil was selected as the optimum catalyst concentration because it was the lowest catalyst concentration which provides the acid value less than 2mg KOH/g oil. It is noted that during the present experiments, that excess addition of H_2SO_4, darken the color of the product and lower amount of addition affects

the yield of the subsequent step.

4.3 Influence of reaction temperature on acid value

The acid value of oil versus reaction temperature was plotted as shown in Fig.4. Studies were carried out at different temperatures (30, 40, 50, 60 and 70°C) while methanol to oil ratio and catalyst concentration were 9:1 and 0.75% v/v of oil respectively. The result shows that the reaction temperature had an important role in the acid catalyzed esterification. The rate of reaction is increased by increasing the reaction temperature. This result was in accordance with the outcome obtained from earlier reports (17). However, it was observed that the acid catalyzed esterification could occur at room temperature but the acid value of oil could not be reduced to less than 2mg KOH/g oil. The highest reaction rate was obtained at 60°C and the acid value reduced from 29.42 to 1.05mg KOH/g oil within 60 min. Hence the reaction temperature 60°C was considered to be the optimum temperature for this reaction.
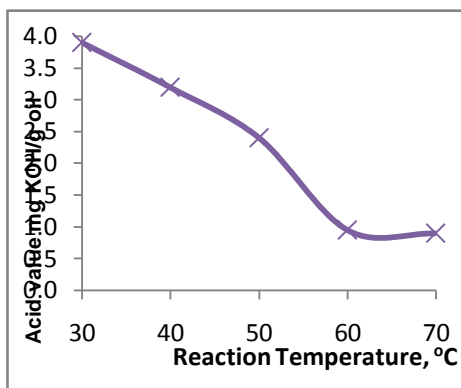

Fig.4. Reaction temperature on reduction of acid value esterification.
    Molar ratio 9:1, catalyst amount 0.75% v/v,
    reaction time 45 min.
reaction temperature 60°C.
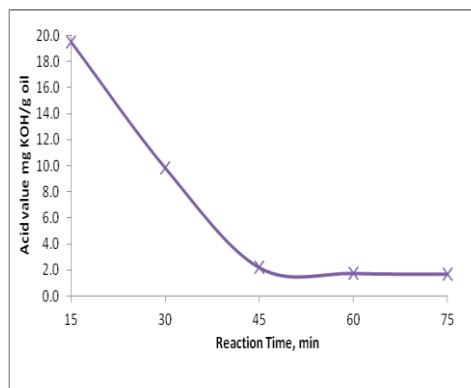

Fig. 5. Reaction time on acid catalyst

    Molar ratio 9:1, catalyst amount 0.75% v/v,

4.4 Influence of reaction time on acid value

Influence of reaction time on acid catalyst esterification is shown in Fig.5. From the figure it was very clearly evident that the pretreatment stage considerably reduced the acid value from 29.42 to below 2mg KOH/g. The rate of reaction was fast in the first 45min, for which the acid value dropped down from 29.42 to 3.85 (86.91%). The reaction slows down after 45min up to 60min, acid value reduction is from 3.85 to 1.76 (94.01%). The esterification reached the equilibrium in the stationary stage after 60min. For economical reasons, the best process is the one that reaches the acid value less than 2mg KOH/g oil in the shortest period of time.

5. ALKALINE ESTERIFICATION

In this process, the low free fatty acid content ceiba pentandra oil was poured into the reaction flask were kept on the electrical magnetic stirrer. The potassium hydroxide-methanol solution was prepared freshly. When the temperature reached 60°C in the reactor, the recently prepared potassium methoxide was added to ceiba pentandra oil in reaction flask rapidly under stirred condition and the measurement of time was started at this point. Then the final mixture was agitated for 45 min at 60°C.After the esterification process, the product was transferred to separating funnel and allowed to settle under gravity for overnight to enhance the separation at room temperature. Two distinct liquid phases were formed during the separation with the methyl ester at the top layer and the glycerol was settled down at the bottom layer. The separated methyl ester was mixed with some warm water by using a sprinkler which slowly sprinkled water. After the mixture had got settled down the water was drained out and washed repeatedly to remove any traces of glycerol at room temperature until the water became clear. After the final washing, the excess methanol and water in the ester phase was then removed by heating the product to 110°C and maintain this temperature for a

while for some water bubbles. Then it is allowed to cool at room temperature.

5.1 Influence of molar ratio on biodiesel conversion efficiency

The variation of the biodiesel conversion efficiency for molar ratio of 3,6,9,12 and 15 was studied. The conversion efficiency of initial step in relation with molar ratio obtained during the present study is shown in Fig. 6. The maximum conversion efficiency is achieved very close to the molar ratio of 6:1, further increase in the molar ratio should be avoided because the reduction in acid value was insignificant. When glycerin remains in the solution, it helps drive the equilibrium back to the left side of equilibrium, resulting in the lower yield of esters [18].
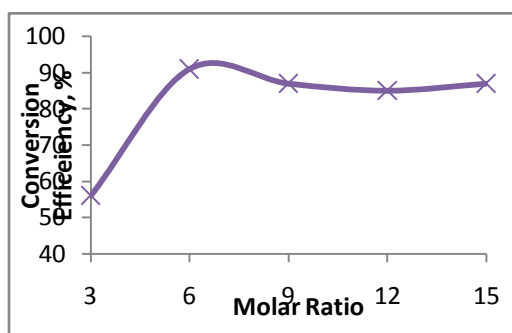

Fig.6. Molar ratio on conversion efficiency.
Catalyst amount 1% w/w, reaction temperature 60°C,
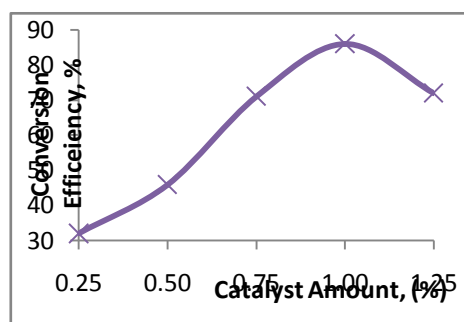reaction time 45 min.

Fig. 7. Acid catalyst amount on conversion efficiency.
Molar ratio 6:1, reaction temperature 60°C,
reaction time 45 min.

5.2 Influence of alkali catalyst on biodiesel conversion efficiency

The amount of alkali catalyst that should be added to the reactor varies from 0.5% to 1% w/w (weight of KOH/ weight of oil). The conversion efficiency at different catalyst amount used in this experiment was shown in Fig. 7. The result shows that the reaction was highly dependent on the catalyst amount. The effect was most evident in relation to the initial reaction rate. The maximum conversion efficiency is achieved at 1.0% of KOH. With further increase in catalyst quantity, there was a decrease in the conversion efficiency. Addition of excess amount of catalyst, gave rise to the formation of soap and glycerol phase. Esterification does not take place effectively for insufficient amount of KOH addition.

5.3 Influence of reaction temperature on biodiesel conversion efficiency

Studies were carried out at different temperature such as 30,40,50,60 and 70°C with 1% KOH as catalyst and molar ratio of 6:1 at a stirring speed of 500-600rpm. The yield of ceiba pentandra oil methyl ester versus time was plotted at different reaction temperature is shown in Fig. 8. It was observed that temperature had positive influence on methanolysis of ceiba pentandra oil. The reaction temperature above boiling point of alcohol is avoided since at high temperature it tends to accelerate the saponification of glycerides by the alkaline catalyst before completion of the alcoholysis [19].
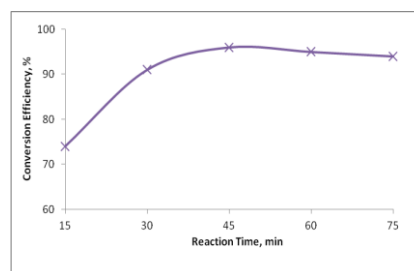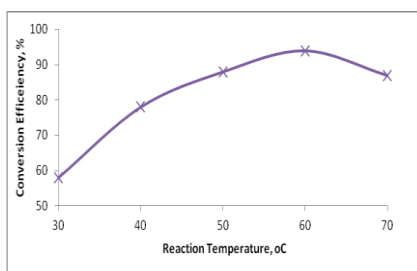
Fig. 8. Reaction temperature on conversion efficiency.   Fig. 9. Reaction time on conversion
efficiency
Molar ratio 6:1, Catalyst amount 1% w/w,   Molar ratio 6:1, catalyst
amount 1% w/w,
reaction time 45 min.
reaction temperature 60°C,

5.4 Influence of reaction time on biodiesel conversion efficiency

In order to optimize the reaction time, the different reaction duration selected for this study were 15, 30, 45, 60 and 75 min. Fig.9. shows the influence of reaction time on biodiesel conversion. The results clearly signify that the biodiesel yield increased with reaction time. The biodiesel yield was found to be more or less same at   45-75 min of reaction time. Results obtained from the present experiments reveal that, about 45 min of reaction is sufficient for the completion of the esterification.

6.   PROPERTIES OF METHYL ESTERS OF CEIBA PENTANDRA SEED OIL

The fuel properties of ceiba pentandra oil methyl ester in comparison with that of diesel is shown in Table 2. The comparison of these properties with diesel shows that the methyl ester has a relatively closer fuel property values to that of diesel [20]. The viscosity value of vegetable oil decreases sharply after two step transesterification. The viscosity of biodiesel is closer to that of dieselThe calorific values of methyl ester are lower than that of diesel because of their oxygen content. The flash point of ceiba pentandra seed oil is lowered by transesterification but it is still higher than that of diesel. A small percentage addition of biodiesel with diesel increases the flash point of diesel. Hence, it is safer to store biodiesel– diesel blends as compared to diesel alone. The properties of biodiesel are compared with ASTM biodiesel standards.

Table 2. Fuel properties of ceiba pentandra oil, ceiba pentandra oil methyl ester and diesel

Properties	Crude ceiba pentandra oil	Ceiba pentandramethyl ester	Diesel	Biodiesel standards ASTMD 6751-02
Density (kg/m^3)	916	885.2	854	880
Kinematic viscosity at 40°C (mm^2/s)	30.42	4.36	2.60	1.9-6.0
Flash point (^{o}C)	297	158	52	>130°C
Fire point(^{o}C)	315	169	64	-
Cetane index	49	49	52	41 min
Gross calorific value (MJ/Kg)	41.62	41.79	44.72	-

7.   CONCLUSION

The high FFA ceiba pentandra feed stock has been investigated as a low-cost biodiesel production in the present study. It is found that the feedstock with high FFAs could not be transesterified with the commercial alkaline catalyst transesterification process due to the formation of soap that prevents the separation of glycerin and ester. A two stage transesterification process was selected to convert the high FFA oil to its methyl ester. The first stage was acid pretreatment process. The high FFA (14.71%) crude ceiba pentandra oil can be reduced to less than 1% in acid esterification, using acid catalyst (1% v/v H$_2$SO$_4$) reacting with methanol oil ratio of 9:1 at 60°C and 45min reaction time. Excess addition of sulphuric acid darkens the product. The first stage product having acid value less than 2mg KOH/g is used for the second stage alkali catalyzed (1% w/w KOH) transesterification reaction, molar ratio of 6:1 favors the completion of alkaline catalyzed esterification process in 45min. The maximum ester conversion is achieved at the reaction temperature of 60°C. The process gives a yield of 92.35% ceiba pentandra biodiesel, which has comparable fuel properties with that of diesel. The viscosity of biodiesel is nearer to that diesel. The flash point

of biodiesel is greater than that of diesel and the calorific value is slightly lower than that of diesel. The present experimental study reveals that biodiesel from ceiba pentandra seed oil is quite suitable as an alternative to conventional diesel fuel.

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