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AN EXHAUSTIVE STUDY ON THE PERFORMANCE AND QUALITY ASSESSMENT OF BIODIESEL PRODUCED FROM LOW CATALYTIC ACTIVITY CATALYST

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ABSTRACT - *Biodiesel has been receiving a lot of concern throughout the world due to energy needs and environmental awareness. It is an eco- friendly, renewable and alternative diesel fuel. Of late, it is not economically feasible since the cost of biodiesel is high when compared to conventional diesel oil as it is produced from pure vegetable oil. Hence, more attention has been devoted to identify the low-cost feedstock such as animal fat, non edible oil and used cooking oil to produce biodiesel. The present study utilizes mahua oil as a raw material for the production of biodiesel. Production, optimization and characterization of mahua oil methyl ester were well established in the study. The experimental techniques and the product evaluation results show that properties of the produced biodiesel are similar to that of conventional diesel.*

Keywords: *Biodiesel; Mahua oil; viscosity; Free Fatty Acid; catalytic activity.*

I. INTRODUCTION

Biofuels have the exciting potential for mitigating the grave threats of global warming, reducing the world's dependence on imported oil from insecure sources and tumbling the sky rocketing costs of fossil fuels. Biodiesel is a renewable, biodegradable, environmentally benign, energy efficient, substitution fuel which can fulfill energy security needs without sacrificing engines operational performance. Thus, it provides a feasible solution to the twin crisis of fossil fuel depletion and environmental degradation [1]. Depending on climate and soil conditions, different nations are looking into different vegetable oils for diesel fuel substitute. The use of edible vegetable oils and animal fats for biodiesel production has recently been of great concern because they compete with food materials – the food versus fuel dispute [2,3,4&5].

Many researchers have reported that the use of pure vegetable oil in unmodified diesel engines may cause various engine related problems such as severe engine deposits, injector coking and piston ring sticking due to their high viscosity and low volatility [6,7,8&9]. The commonly used methods to reduce the viscosity of vegetable oil are blending with conventional diesel, emulsification, pyrolysis and transesterification [6,7]. Among these, transesterification is the most commonly used method for lessening viscosity in vegetable oil [10,11].

Transesterification is the general term used to describe the important class of organic reactions where an ester is transformed into another through interchange of the alkoxy moiety [12]. Biodiesel may be produced by transesterifying triglycerides such as animal fat or vegetable oil with alcohol in presence of an acid or base catalyst [11]. Selection of a particular process depends on the amount of free fatty acid and water content present in the feedstock.

Mahua oil is an underutilized non-edible vegetable oil which is available plenty in India is chosen for the study. The yield of mahua seeds varies (5 – 200 kg/ tree) depending upon the size and age of the tree [12]. It starts giving seeds after 10 years and goes up to 60 years. Kernel contains 20 – 50 % of oil depending on expelled by ghani or expeller.

In the present study, Mahua oil was experimented as an alternative feedstock for the production of a biodiesel. The scope of the study is to produce, optimize and evaluate biodiesel from mahua oil having high FFA with low catalytic activity catalyst (Lithium hydroxide).

II. EXPERIMENTAL METHODS

Physico-chemical characteristics of the mahua oil such as acid value, FFA, viscosity, iodine value, specific gravity, saponification value were analyzed as per ASTM standard methods.

A. Biodiesel (methyl ester) production methodology

Choice of the acid & alkaline catalyst depends on the amount of FFA content present in the raw oil. If the FFA content is beyond 3%, acid esterification followed by alkaline transesterification process is carried out whereas if the FFA is below 3% only alkaline transesterification process is carried out.

B. Acid – catalysed esterification

This process is carried out to convert FFA into esters. A litre of mahua oil was heated to 110 °C to expel the water if present. It was then allowed to cooling 60 °C. A mixture of solution containing sulphuric acid of various concentrations such as (3, 3.5, 4, 4.5, 5, 5.5 & 6ml) with different molar ratio of methanol (3:1,6:1,9:1,12:1 &15:1) to oil was prepared. The acid mixed in methanol was added to the oil and heated in a magnetic stirrer for 1 hr at 60 °C. It was then transferred to a separating funnel for separation. After 8 h, excess methanol, acid and water mixture ascend to the top whereas the acid esterified oil settles at the bottom of the funnel.

C. Base –catalysed transesterification

The acid esterified oil was then subjected to heating to 55°C. The reaction was carried out using methanol as alcohol and lithium hydroxide as catalyst. Lithium methoxide solution was freshly prepared by dissolving lithium hydroxide in methanol. Performance of the catalyst on the acid esterified oil was evaluated at a doses of 4, 4.5 5, 5.5 6 & 6.5 g/l of oil under different molar ratio of alcohol (3:1,6:1,9:1&12:1) to oil at various temperatures (45, 50, 55, 60 &65 °C) for different duration of time 30, 45, 60 and 75 min.

After the completion of reactions, crude glycerol was separated by gravity. Unreacted catalyst was removed by washing with distilled water. Finally biodiesel was heated to 110 °C to eliminate the water content. Then the yield of methyl ester was calculated. The experiments were run in triplicate: each set of operation conditions was conducted three times and the average was noted.

Qualitative analysis such as acid value, FFA, iodine value, saponification value, peroxide value, specific gravity, kinematic viscosity and calorific value of the produced methyl ester were tested. The quantitative analysis of methyl ester was characterized by Fourier Transform-Infra Red (Perkin Elmer Paragon IR Spectrophotometer).

III. Results and Discussion

Physico-chemical properties of the mahua oil were analysed (Table -1). Mahua seed oil hold an initial acid value of 14 mg KOH/g corresponding to a free fatty acid (FFA) level of 7%. The high value of FFA indicates that the oil is exceedingly acidic. Since high level of FFA in oil (above 3%) is considered to be unfavourable for processing the same to produce biodiesel without pretreatment, it had become necessary to minimize the FFA through esterification process using acid as a catalyst[13].

Table -1 Fuel Properties of oil & biodiesel

Parameters	*Unit*	*Mahua oil*	*Mahua oil methyl ester*
Acid value	*mg KOH/g*	*14*	*0.09*
FFA	*%*	*7*	*0.045*
Iodine value		*78*	*73*
Specific gravity	*g/ml*	*0.895*	*0.865*
Saponification value		*185*	*136*
Kinematic viscosity @ 40 °C	*Cst*	*41.5*	*4.22*
Sulphated Ash	*%*	*---*	*0.01*
Calorific value	*MJ/Kg*	*36*	*38.9*
Flash point	*°C*	*207*	*130*

A. Acid esterification Process
Factors affecting the acid esterification process

A.1 Effect of acid catalyst

The effect of catalyst concentration on esterification was investigated by varying the catalyst amount from 3 to 6 ml/l based on the weight of oil taken. The results are summarized in Figure 1. The reduction of FFA was found to increase with the increase in catalyst concentration. It is noticed that, there was no improvement in reduction of FFA with the amount of catalyst higher than 5ml/l. Quantity of acid beyond the optimum level darkened the product and also retards the reaction. High percentage reduction of FFA (89%) was observed while using 5ml/l (sulphuric acid) with 9:1 ml of methanol at 60 °C for 1h. This reduced the free fatty acid from 7 to 0.045 % respectively.

A.2 Effect of Molar ratio to oil

Short chain alcohols such as methanol, ethanol & butanol are the most commonly employed and methanol was the dominating one in most of the literature reviewed [14,15,16,17&18]. Also, methanol is preferred because, it is commercially available and the downstream recovery of unreacted alcohol is much easier than the other alcohols.

Result in Fig. 2 shows the increasing trend of conversion rate with the methanol/oil molar ratio ranging from 3:1 to 9:1, but afterwards it shows a slight decline in conversion rate with the methanol/oil molar ratio from 9:1 to 15:1. The optimum methanol/oil molar ratio was observed to be at 9:1. Initially, excess addition of methanol increases the solubility of the by-product (glycerol) [19] which may then initiate the reversible reaction and reduce the conversion. Excess methanol can be removed easily by washing with water and its residual may be removed using rotary evaporator.

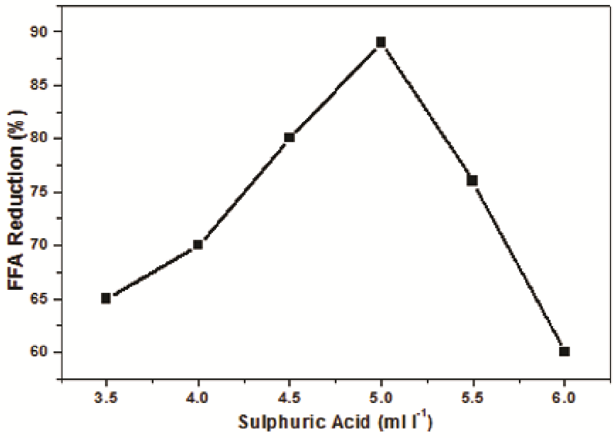

Figure 1. Effect of acid catalyst for the reduction of FFA

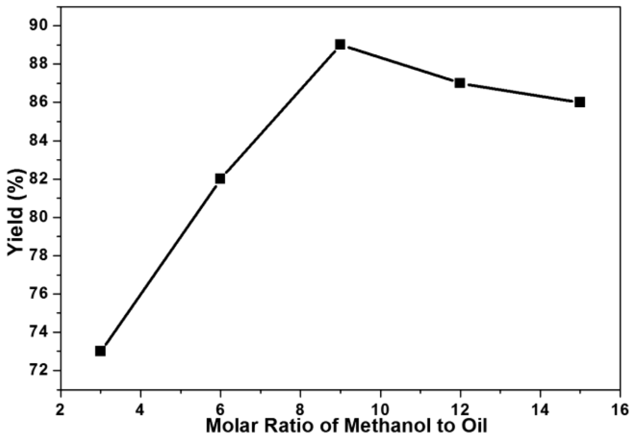

Figure 2. Effect of methanol to oil molar ratio on esterification with respect to their yield

B. Base catalyzed transesterification

B.1 Effect of alkaline catalyst

Biodiesel with the best properties are obtained by using KOH or NaOH as a catalyst in many studies [8,13]. The present study investigates the performance of LiOH as an alkaline catalyst which has low catalytic activity when compared with NaOH & KOH.

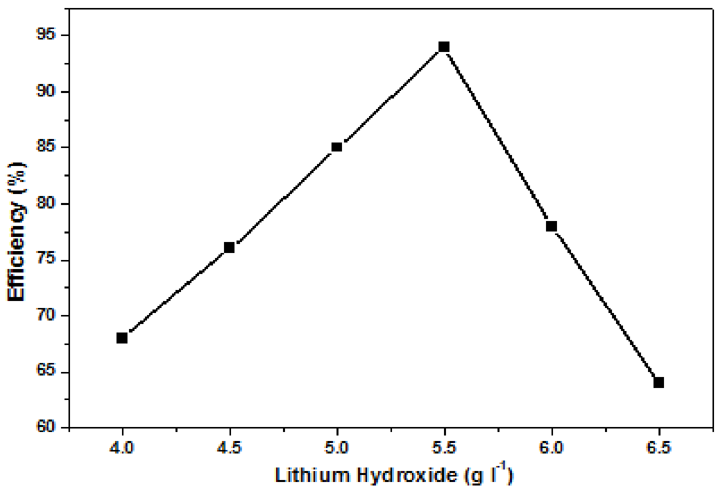

Figure 3. Effect of lithium hydroxide with respect to their efficiency

It was observed from Fig.3, that the highest % of yield (94%) was achieved while using 5.5 g/l of LiOH with 6:1 molar ratio of methanol to oil at 60°C for 1h. Insufficient amount of catalyst results in incomplete formation of an ester. On the other hand, additional amount of catalyst leads to soap formation and also in this study, the catalyst concentration level greater than 5.5 g/l favour the backward reaction. The results suggest that optimum catalyst loading for transesterification is 5.5 g/l with the ester conversion of 94%.

B.2 Effect of molar ratio to oil

One of the most important variables affecting the yield of ester is the molar ratio of alcohol to triglyceride [20]. The stoichiometric ratio for transesterification reaction requires 3 mol of alcohol and 1 mol of triglyceride to yield 3 mol of fatty acid ester and 1 mol of glycerol. Since, transesterification is an equilibrium reaction in which an excess of alcohol is required to drive the reaction to the right side.

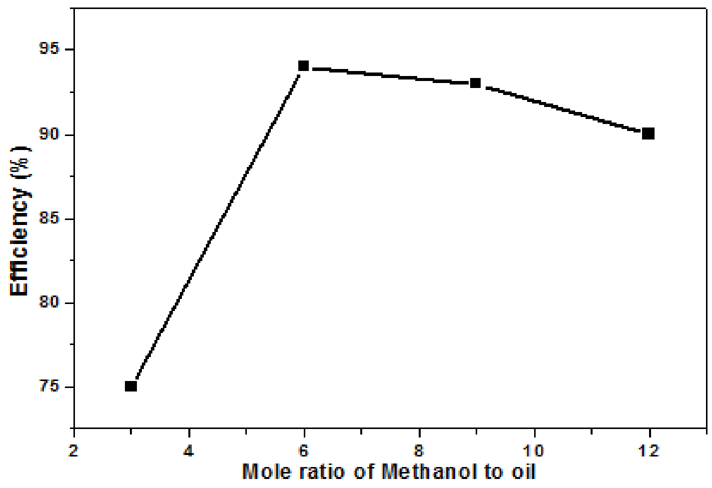

Figure 4. Effect of methanol to oil molar ratio on transesterification with respect to their yield

To evaluate the maximum conversion of the ester, wide range of methanol to oil molar ratio from 3:1 to 12:1 is employed and a molar ratio of 6:1 is acceptable (Fig.4). However, an excessive amount of alcohol makes the recovery of the glycerol difficult so that the ideal alcohol/oil ratio has to be established empirically. With further increase in molar ratio, the conversion efficiency more or less remains the same but the energy required for the recovery of methanol becomes higher.

B.3 Effect on temperature

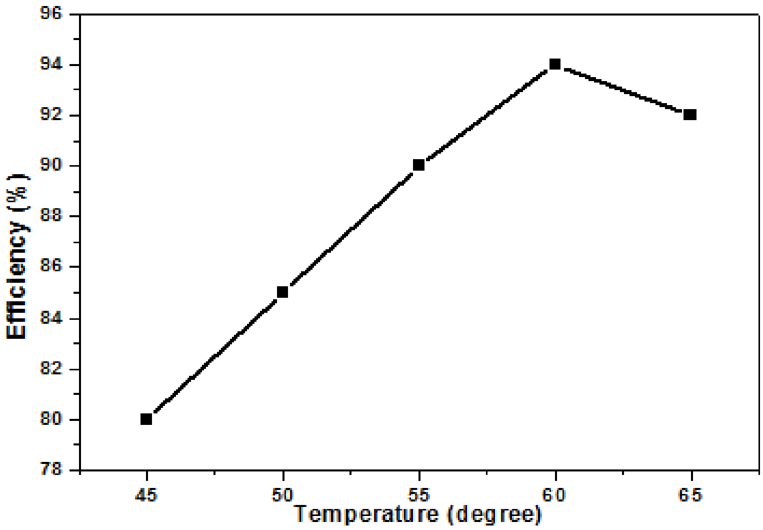

Figure 5. Influence of reaction temperature with respect to their yield of methyl ester

Temperature positively influences the biodiesel yield. The reaction was carried out at 45, 50, 55, 60 and 65°C to experiment the influence of reaction temperature towards ester. Generally, as the reaction temperature increases, the rate of reaction also increases; Fig. 5 shows the conversion increases from 60 to 94 % when the temperature increased from 45°C to 60°C. Higher temperature of 45 – 60°C progress the efficiency of transesterification, which in turn enhances the ester yield.

B.4 Influence of reaction time

The effect of reaction time on fatty acid methyl ester content and it was observed that the conversion rate was dawdling till 45 min and finally reached steady state at 60 min. The conversion rate deprived after 60 min because excess residence time can negatively influence the biodiesel production by favouring the backward reaction (hydrolysis of ester) which results in a reduction of product yield.

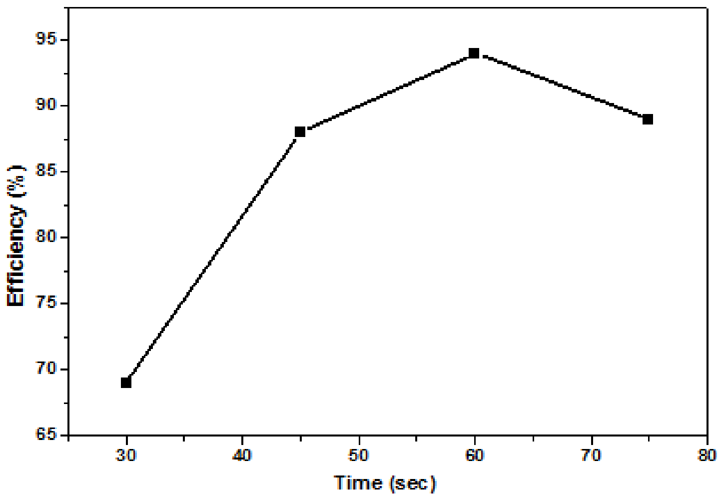

Figure 6. Influence of reaction time with respect to their methyl ester yield

IV. Quality assessment of produced biodiesel

The quality of biodiesel is most important for engine part of view and therefore, the fuel characteristics of the alkyl esters synthesized were studied according to ASTM standard methods.

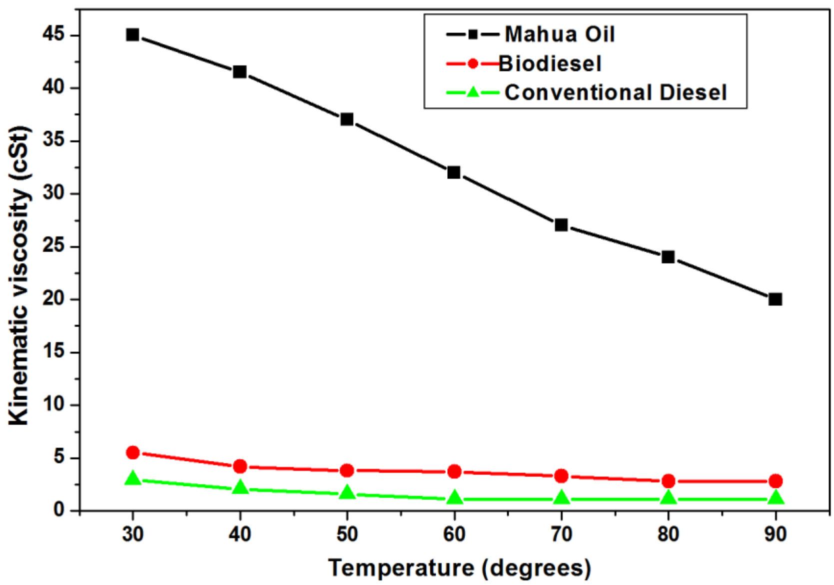

Figure 7. Comparison of kinematic viscosties of mahua oil, biodiesel and diesel in relationship with temperature

The major problem associated with the use of vegetable oils as fuel in diesel engines is caused by viscosity. High viscosity leads to poor atomization of the fuel, incomplete combustion, coking of fuel injectors, ring carbonization and accumulation of fuel in an engine [21]. Hence, it is necessary to check the viscosity of the fuel. Among the general parameters for biodiesel, the viscosity controls the characteristics of the injection from the diesel injector [22]. It is necessary to control it within an acceptable limit to avoid negative impacts on fuel injector system performance. Kinematic viscosity is inversely proportional to temperature. It is clear from Fig.7 that the viscosity of oil is about ten times higher than that of diesel. Transesterification greatly reduced the viscosity. The kinematic viscosity of the biodiesel sample produced in the study was 4.2 cSt at 40°C. It is observed from the Fig.7 that viscosity of biodiesel is closer to that of petro-diesel.

Density is also an important factor mainly in airless combustion system because it influences the efficiency of atomization of the fuel. Biodiesel produced in this study had a density of 0.865 g cm^{-3}.

The flash point of the produced biodiesel was estimated to be 130°C. It is quite high when compared with diesel which is 47°C. Hence, biodiesel is extremely safe to handle than diesel. Calorific value is a measure of energy produced when the fuel is burnt completely. The presence of oxygen in biodiesel helps to have a complete combustion of the fuel in the engine. The calorific value for the mahua biodiesel is 38.9 MJ/Kg.

The primary purpose of determining sulphated ash in biodiesel is to ensure whether it contains any contaminants. The sample contains 0.01% of sulphated ash and confirms that it does not contain any contaminants.

Acid value is an index of aging of the fuel. It reflects the presence of FFA during the production of biodiesel and also degrades biodiesel due to thermal effects. Biodiesel thus produced in the study has an acid value of 0.09 mg KOH/g which satisfies the limit of ASTM D 6751.

Iodine value is also an important measure that allows determination of the unsaturation degree of the fuel. This property greatly influences the fuel oxidation, the type of aging products and the deposits formed in diesel engine injectors. The sample has an iodine value of 73.

All the above parameters were tested and the results show that they are within the limits of ASTM D 6751 standards. Hence, it can be used as a substitute fuel for diesel engine.

A. FT-IR analysis for fatty acid methyl ester

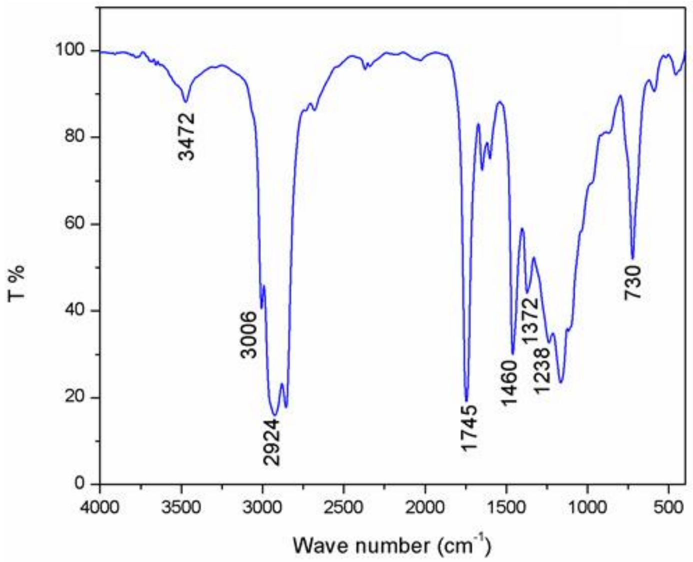

Figure 8. FT-IR spectrum of the optimized Biodiesel

The FT-IR spectra in the mid-infrared region (Fig. 8) have been used to identify functional groups and the bands corresponding to various stretching and bending vibrations in biodiesel. The position of carbonyl group in FT-IR is sensitive to substituent effects and to the structure of the molecule [23]. The methoxy ester carbonyl group in mahua methyl ester was appeared at 1745 cm^{-1} and the band emerged at 3473 cm^{-1} shows the overtone of ester functional group. The C-O stretching vibration in mahua methyl ester shows two asymmetric coupled vibrations and 1172 cm^{-1} is due to C-C(=O)-O and 1020 cm^{-1} is due to O-C-C. From the above analysis the prepared compound has been confirmed as methyl ester.

V. CONCLUSION

In this study, mahua oil methyl ester was produced through conventional techniques. Results of the physico chemical characteristics of the oil show that the oil is exceedingly acidic. Biodiesel from mahua oil could be produced by using sulphuric acid (5ml/l) as an acid catalyst with methanol (9:1) followed by LiOH (5.5 g/l) as a base catalyst with methanol (6:1) at 60°C for 60 min. Fuel properties of methyl esters of mahua oil were found to meet the ASTM D 6751 standard. Functional group vibration of the prepared biodiesel from mahua oil was examined by FT-IR. The overall study suggests that LiOH (whose catalytic activity is low) can also be used as a potential catalyst for the production of biodiesel.

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