Physico-Chemical Properties of the Biodiesel Extracted From Rubber Seed Oil Using Solid Metal Oxide Catalysts

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Abstract

Physicochemical properties of the commercially procured rubber seed oil (RSO) were studied to evaluate its potential as viable feedstock for biodiesel production. The procured rubber seed oil were characterized for acid value, saponification value, free fatty acid, flash point, kinematic viscosity, and refractive indices using standard methods. Results indicate that the procured rubber seed oil is a potential biodiesel feed stocks and it is possible to convert this to biodiesel with a single stage process. The trans-esterification reactions were carried out in the presence of a solid metal oxide catalyst, calcium oxide (CaO) and the yield estimated was around 98%.The quality of the biodiesel produced was comparable with that of the petro diesel which indicates that this can be blended with the commercial petro diesel. The calorific value and cetane number of this biodiesel was higher than that of the petro diesel which indicates that the blending may increase the fuel efficiency as well.

Keywords: Biodiesel, Rubber seed oil, Solid metal oxides, Catalysts

I. Introduction

Competition for fossil fuel reserves and growing concern for the environment have given rise to increased demand for biodiesel research [1-3]. More over biodiesel has gained significant attention as it is a renewable, biodegradable, less pollutant emitting, non-toxic and more environmentally friendly fuel source as compared with the fossil diesel fuel available at present. It is a renewable and biodegradable fuel that consists of fatty acid methyl esters (FAMEs). It is carbon neutral because the carbon content in the exhaust is equal to the amount initially fixed from the atmosphere. Most of the research activities reported so far is about the production of the biodiesel from the edible oils and fats [4-6]. Despite the considerable potential of biodiesel, the production of biodiesel is found to be expensive from edible oils owing to the growing demand for edible oils and the high cost of the feedstock. According to previous reports, the raw materials for biodiesel production account for almost 75% of the total biodiesel cost.

Hence future of the biodiesel is going to be limited unless biodiesel can be extracted from other non edible raw materials. Therefore, a number of research projects have been carried out using non-edible oils such as jatropha oil or fats, and other waste oils, to reduce the raw material cost. Large scale plantations of non edible oil plants were also being thought of. An important constraint of this is its sustainability, as the extension of land required for biodiesel production is considerably larger. Nevertheless, such oils usually contain a high percentage of free fatty acids (FFAs) that severely affect the biodiesel production process. So explorations of alternate options are highly important. In this context the research activities of rubber seed oil has its importance. As far as the availability of the feed stock is concerned Kerala is the leader in rubber production among the states of India. More than 90 percent of the Rubber produced in India is from Kerala. Rubber seeds are being a by product in this plantation which are not being utilized properly at present.

In the trans-esterification process, biodiesel is usually prepared in the presence of a homogeneous base/acid catalyst [7-8]. In this conventional homogeneous process the catalyst removal is a big problem and most of the acid and base catalysts are corrosive in nature. Many studies are being carried out for the replacement of this homogeneous catalyst[9-10]. In this regard solid metal oxide based heterogeneous catalysts were being considered as a promising candidate [11-12]. They are known to be environment friendly with added advantageous like easy catalytic separation, purification etc. In this context the present investigation aims to evaluate the performance of the solid metal oxide catalyst calcium oxide, CaO for the trans-esterification reaction of rubber seed oil. Experimental studies will be conducted to investigate the effects of main parameters, including methanol to rubber seed oil ratio, catalyst to oil weight ratio, reaction temperature, and reaction time to obtain the optimal condition. Various analyses such as acid value, flash point, heating value and cetane number will be applied to the biodiesel product obtained, and then, its quality will be compared with the available standard quality of biodiesel. This research is an effort to find out an efficient, timesaving, economically functional and environmental friendly biodiesel production process at industrial scale having superiority over the classical procedure.

II. Material and methods

Crude rubber seed oil had been selected as a potential feedstock for biodiesel preparation. Oil used is non-edible and is commercially obtained after extraction from rubber seeds. Methanol with a purity of 99.5% and calcium oxide, CaO are purchased from Chemind Chemicals Ltd. Fatty acid composition of crude rubber seed oil has been obtained from GC-MS data taken at CUSAT, Cochin. Physical and chemical properties of crude rubber seed oil had been analysed. Physical properties include density, viscosity, flash & fire point, cloud & pour point and calorific value. Chemical properties include acid value, iodine value and saponification value.

III. Experimental Procedure

3.1 Catalyst preparation

Calcium oxide (24 g) was dipped in 200 ml of ammonium carbonate solution then the mixture was stirred for 30 minutes at room temperature. After filtration and drying at 112 ^{0}C till constant weight, the dried solid was milled and sieved then calcined at 850 ^{0}C for 1.5 hrs. After cooling in a dessicator to room temperature the base CaO is ready to use. High temperature calcinations of CaO improved the performance of the catalyst.

3.2 Biodiesel preparation

A bench scale set-up consisted mainly of a round glass reactor placed in an adjusted temperature bath is used for the trans-esterification reaction. This flask was provided with reflux condenser, magnetic stirrer, and thermometer for temperature follow up and funnel for methanol addition. Measured amount of methanol + calcium oxide (CaO) stirred by a magnetic stirrer for 10 minutes after which it was preheated to about 65 ºC below the boiling point of methanol. Thereafter, 150 ml of RSO was taken and heated to 65 ºC on a temperature water bath before it was poured into a blender. Methanol + CaO were then poured gently into the RSO in the blender. The entire content was allowed to blend for the required reaction time. After the completion of reaction, the product was decanted from the blender & centrifuge at 6000 rpm for 10 minutes, where the CaO catalyst was separated from the reaction product. Then the supernatant product mixture was exposed to open air for 30 minutes to evaporate excess methanol. Thereafter, it was poured into a separating funnel and allowed to settle overnight so as to separate the glycerine from the biodiesel. The lower glycerine layer was drawn off and the upper biodiesel layer was then removed, dried and weighed.

3.3 Physico-chemical properties

An approximate estimation of the molecular weight of the RSO was determined from the estimation of fatty acid composition in the oil from the gas chromatographic analysis. Molecular weight of crude rubber seed oil was also calculated using its measured acid and saponification values using as per equation 3.1. Here AV is the acid value (mg KOH/g oil) and SV is the saponification value (mg KOH/g oil).

$$M = (56.1 * 1000 * 3) / (SV - AV) \quad (3.1)$$

The physical and chemical properties like kinematic viscosity were determined using the ASTM D445 method and flash point using the ASTM D 93 method. Pour point and density of the biodiesel was determined by following ASTM D97 and ASTM D1298 respectively. Cloud point was estimated by ASTM D2500 procedure and calorific value was estimated using ASTM D240.

IV. Results and discussion

The results of the gas chromatographic analysis of the fatty acid composition of the crude rubber seed oil is shown in table 1. From this table it is clear that the rubber seed oil used in this present study mainly consist of linoleic, oleic and stearic acids with minor component of palmitic acid. The ability of biodiesel to meet ASTM D 6751 standard criteria is dependent on the fatty acid composition [13]. Petroleum diesel is largely made of hydrocarbon with carbon chain length of 8 to 10 carbon atoms compared to rubber seed oils that contained fatty acids comprising mainly of 18 carbon atoms. Cetane number which is a prime indicator of fuel quality for diesel engines is increased with increased carbon number [14]. Branched chains and double bonds improve low temperature flow properties [15-16]. So from this analysis it is clear that the biodiesel produced from this rubber seed oil will have a higher cetane number as it contain fatty acids with 18 carbon atoms [17-18].

Table 1 Fatty acid composition of the crude rubber seed oil

Sl No	Component	Structure	Percentage
1	Palmitic acid	C16:0	0.23
2	Linoleic acid	C18:2	52.84
3	Oleic acid	C18:1	12.7
4	Stearic acid	C18:0	35.85

The quality of biodiesel is important for end-users, engine manufacturers and petroleum companies to ensure that it can be used directly or blended with petroleum diesel. So a detailed analysis about the qualities of the bio diesel as well as the feed stock is important. Table 2 presents various physic-chemical properties measured for the crude rubber seed oil as well as that of the biodiesel produced using the present method.

Table 2 Physico-chemical properties measured

Oil/Fuel	**Kinematic Viscosity [mm^2/s]**	**Flash Point [^{0}C]**	**Acid Value [mg KOH/g]**	**Cloud Point [^{0}C]**	**Density [kg/m^3]**	**Calorific Value [MJ/kg]**
Crude RSO	6 ± 0.2	208 ± 0.5	1.68 ± 0.3	-5 ± 0.2	857 ± 0.5	36.1±1.08
Biodiesel from RSO	3.7 ± 0.2	110 ± 0.5	0.22 ± 0.3	-6 ± 0.2	892 ± 0.5	39.78 ± 1.08

As we know the fuel's viscosity is an important factor since it has the effect on pumps and influence on injector systems spray pattern. On comparison of the viscosity of the Bio diesel produced from the rubber seed oil it is clear that the Kinematic viscosity is of the Bio diesel produced is in comparison with that of petro diesel and it is having a moderate value. This is quite interesting because High viscosity will cause poor atomization, and high spray jet penetration. The jet tends to be a solid stream. The fuel spray may impinge upon the cylinder walls, washing away the lube oil film and causing dilution of the crankcase oil. Low viscosity fuel does not penetrate far enough in the combustion chamber. Low viscosity leads to excessive leakage past the injection pump plunger. In either case the results are poor combustion, loss of power, inaccurate metering and increased wear in both the fuel system and engine.

From the data presented in table 2 it can be seen that the measured acid values of the rubber seed oil is not so high in comparison with that of the ASTM standard of 0.8 mgKOH/g for non edible oils This is an interesting result since the acid value measures the presence of corrosive free fatty acids and oxidation products. Which is an important variable in considering the quality of oil because the lower the free fatty acid, the better the quality of oil. The acceptable limit for edible oils is ≤10. Non edible vegetable oils generally contain high free fatty acids and have significant effects on the trans-esterification with methanol using alkaline catalyst. It also interferes with the separation of fatty acid ester and glycerols. This means that these types of oils would be better converted to biodiesel using the two-stage process of esterification and trans-esterification. But the measured acid value of the rubber seed oil shows that it is possible to convert rubber seed oil to bio diesel with a single stage process. Similarly the trans-esterification process brings down the flash point and kinematic viscosity to an acceptable level. This shows that its volatile characteristics had improved and it is also safe to handle.

Table 3 Property comparison of biodiesel produced with commercial petro diesel

Fuel property	**Biodiesel from RSO**	**Petro diesel**
Kinematic Viscosity [mm^2/s]	3.7	2.0-5.5
Flash Point [^{0}C]	110	54
Acid Value [mg KOH/g]	0.22	0.835
Cloud Point [^{0}C]	-6	2max
Calorific Value [MJ/kg]	39.78	43.73
Cetane number	50	45

Similarly the cloud point is relatively low compared to that of petro diesel. The cloud point relates to the tendency of filter plugging at cold temperatures. The cloud point is a guide as to what temperature the fuel may plug filter systems and restrict flow. The higher cloud point indicates a higher precipitation temperature of the fuel. Which indicates the fuel is less suitable for low temperature operation.

The flash points of the obtained bio diesel extract are found to be higher than that of petro diesel. The flash point temperature is the minimum temperature at which the fuel will ignite (flash) on application of an ignition source under specified conditions. Flash point varies inversely with the fuel's volatility. Flash point minimum temperatures are required for proper safety and handling of fuels. Note that the biodiesel component must meet flash point criteria, prior to blending. In general fuels with flash point above 66°C are considered as safe fuels which can be blended with petro diesel. The obtained results shows that the bio diesel extract from rubber seed oil can be safely blended with petro diesel.

Another important parameter which quantify the quality of a fuel oil is its cetane number. Cetane number is a measure of ignition quality of the fuel. A high cetane number indicates shorter ignition delay and improved combustion. For most engines, high cetane number fuels generally cause a shorter ignition delay period and therefore lower rates of pressure rise. This tends to lessen combustion noise, improve control of combustion, and results in increased engine efficiency and power input. The present bio diesel extract has got a cetane number of 50 which shows it will improve the cetane number of petro diesel on blending.

V. Conclusion

In conclusion it can be confirmed that the biodiesel derived from the rubber seed oil is suited for use in diesel engines given that its kinematic viscosity, flash point, cloud point, and calorific value conform to the recommended international standards. This means that CaO can be effectively used as a solid metal oxide catalyst in the trans-esterification reaction of the rubber seed oil for biodiesel production. By the usage of CaO catalyst savings could be made from the expensive refining processes admissible in the case of conventional acid/alkali based trans-esterification reactions. More over rubber seed oil can be converted into biodiesel directly by a single stage trans-esterification process while most of the non edible vegetable oils required two stage trans-esterification reactions for the bio diesel conversion. This is also an added advantage in this process.

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