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EXPERIMENTAL INVESTIGATIONS OF SPECIFIC GRAVITY ON TRANSESTERIFIED RUBBER SEED METHYL ESTER

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ABSTRACT - *In the present study, rubber seed oil obtained from rubber seed cotyledons has been considered as a potential feed stock for the production of biodiesel. Physicochemical properties of the oil were analyzed and the production of biodiesel through conventional transesterification technique was well established in this study. The specific objective of the research is to measure the specific gravity of the biodiesel with respect to temperature, molar ratio and alkaline catalyst. Also a comparison between the fuel properties of as-prepared biodiesel and standard biodiesel were made. Results of transesterification of rubber seed oil shows an enhancement in fuel properties and found to meet the ASTM D 6751 standards of biodiesel. Storage of biodiesel leads to degradation of fuel properties and affects the performance of an engine. Hence, an attempt has been made to check the stability of a biodiesel for a period of year. Overall study suggests that rubber seed oil methyl ester can also be used as a substitute to the conventional diesel even after a year.*

Keywords: *rubber seed oil; specific gravity, biodiesel; transesterification; catalyst; FFA.*

I. INTRODUCTION

Technological refinement on the production of biofuels is in progress all over the world and using biodiesel is known for more than 50 years [1, 2]. Biodiesel is a renewable fuel and can be derived from vegetable oils or animal fats or used oils [3]. Further, compared with petroleum based diesel, biodiesel has more favourable combustion emission profile such as low emission of carbon monoxide, particulate matter and unburned hydrocarbons [4,5]. Therefore, researchers and scientific community in worldwide have focused on the development of biodiesel, optimization of the process to meet the standards and specifications needed for the fuel to be used commercially without compromising on the durability of the engine parts.

An ample variety of non edible oil crops are available in nature. The promising non edible oil yielding crops suitable for biodiesel production in India are *Jatropha curcas, Pongamia pinnata, Calophyllum inophyllum and Hevea brasilienisis*. Non edible oil from such crops is currently being used for making low cost soap.

Hevea brasilienisis (Rubber tree) which belongs to the family Euphorbiaceae is being cultivated in India since 1902 for extracting its latex. Seed kernel contains oil to the tune of about 40% by weight. Rubber seed oil is a richer source of essential fatty acids. The oil is used mostly in soap making and observed to be non-toxic. However at a broader sense, rubber seed oil at present has not attracted any major application and therefore the natural production of seeds remains unutilized [6]. Hence, the study selects rubber seed oil as a feedstock for biodiesel production.

When using biodiesel in unmodified diesel engines, one issue that must be noted is that biodiesel have different properties than conventional diesel such as higher viscosity, higher cetane number, higher specific gravity and lower heating value. These fuel properties may affect the engine performance and emissions considering that the engine was originally optimized with petrodiesel. Of all properties, specific gravity is one among the most basic and most important property because some important performance indicators such as cetane number, heating value are correlated with it. It is also a significant parameter in connection with fuel storage and transportation.

One of the major criteria for the quality of a biodiesel is its storage stability. Biodiesel denatures more quickly than fossil fuel due to the vulnerable chemical structure of fatty acid alkyl esters present in it. Due to the fact that vegetable oils possess a significant amount of fatty acids with double bond, oxidative stability was of great concern especially when storing biodiesel over an extended period of time [7]. Industrial experts recommend that biodiesel could be best used within six months of its manufacture to ensure that the quality of the fuel was maintained [8]. Therefore, an attempt is now made to investigate the stability characteristics of the biodiesel thus produced.

II. EXPERIMENTAL METHODS

Different levels of ferric sulphate (1.75, 2, 2.25, 2.5, 2.75 & 3 g/l) with methanol to oil molar ratio of 12:1 were employed to esterify the rubber seed oil at uniform stirring (360 rpm) for 60 min at 60 °C. After a period of time, the catalyst ferric sulphate was recycled and reused [9]. Finally, the acid esterified oil was subjected to transesterification process. Acid esterified oil was heated to 55 °C. Performance of sodium hydroxide as a catalyst was evaluated at various doses of 3.5, 3.6, 3.7, 3.8 and 3.9 g/l of oil under 6:1 molar ratio of alcohol to oil at a reaction temperature of 60 °C for 60 min. Glycerol being the byproduct moved to the lower part and the methyl ester moved to the upper part of the funnel. The product (methyl ester) was washed with distilled water and heated to 110 °C to eliminate the water content if present.

The effect of specific gravity of biodiesel with respect to temperature, molar ratio and catalyst has been studied. Also, the biodiesel thus prepared was then taken for further analysis of fuel properties.

Long term storage tests on biodiesel were conducted for a period of 12 months. Samples were stored in glass containers at room temperature. At regular intervals (every month) the characteristics such as acid value, specific gravity, kinematic viscosity, iodine value and water and accumulation of sediments of the stored biodiesel were also examined.

III. RESULTS AND DISCUSSION

The analytical data obtained indicates that the rubber seed oil is closely equivalent to few edible oils in many respects (Table -1). The specific gravity of most oils and their methyl esters is higher than that of diesel fuel. This is due to the large molecular mass and chemical structures of vegetable oils [10,11]. However, this helps in countering their low heating values in terms of brake specific fuel consumption.

Table 1- Charactersitics of rubber seed oil

Parameters	*Units*	*Rubber seed oil*	*Pongamia oil*	*Waste cooking oil*	*Mahua oil*
Acid number	*mg KOH/g*	*50.30*	*5.40*	*2.64*	*14*
FFA	*%*	*25.15*	*2.7*	*1.32*	*7*
Specific gravity	*g/cm^3*	*0.91*	*0.925*	*0.92*	*0.895*
Kinematic viscosity at 40° C	*cSt*	*41.11*	*40.2*	*36.4*	*41.5*
Iodine value	*(gI_2/100 g)*	*133.20*	*87*	*141.5*	*78*
Saponification value	*(mg KOH/g)*	*182.32*	*184*	*188.2*	*185*
Peroxide value	*meq/kg*	*2.50*	*4.3*	*16.61*	*3.2*
Calorific value	*MJ/kg*	*39.50*	*37*	*41.40*	*36*

3.1 Production Results

The optimized results of biodiesel production from rubber seed oil shows that, it could be produced by using ferric sulphate (2.5 g/l) as an acid catalyst with methanol to oil (12:1) followed by sodium hydroxide (3.7 g/l) as a base catalyst with methanol to oil (6:1) at 60 °C for 60 min. The maximum conversion efficiency attained was 88% [12].

3.2 Fuel Properties of biodiesel

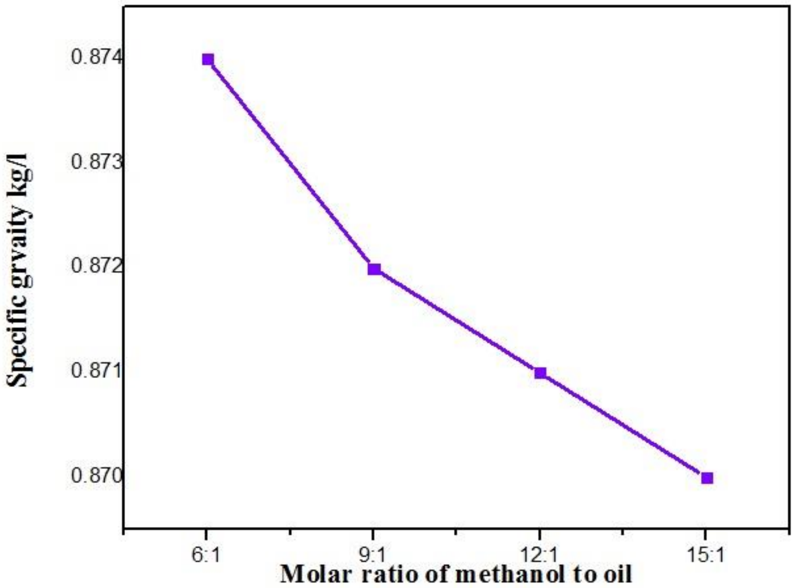

Figure 1. Effect of specific gravity with respect to molar ratio

The specific gravity and viscosity of biodiesel fuels are the key properties in determining the suitability of fuels in diesel engines. The specific gravity of a methyl ester depends on its molecular weight, free fatty acid content, water content and temperature [13]. Specific gravity data is essential in modeling combustion process in internal combustions engines and also in evaluating the thermal efficiency of the fuel. Due to the removal of glycerol from triglycerides, biodiesel are prone to have higher specific gravity than conventional diesel. After the transesterification process in the current case, the specific gravity of biodiesel (0.874 g/cm^3) was found to be lower than that of the rubber seed oil (0.91 g/cm^3) [14] but higher than the conventional diesel (0.85 g/cm^3).

The influence of temperature, catalyst, molar ratio on the specific gravity of the biodiesel was studied by [15]. To investigate the effect of molar ratio, four different molar ratios such as 6:1, 9:1, 12:1& 15:1 were selected. Each reaction was run for 1hr with 3.7% of catalyst at 60 ◦C. It is clear from the fig.1 that specific gravity decreases with increase in molar ratio due to a decrease in residual triglycerides.

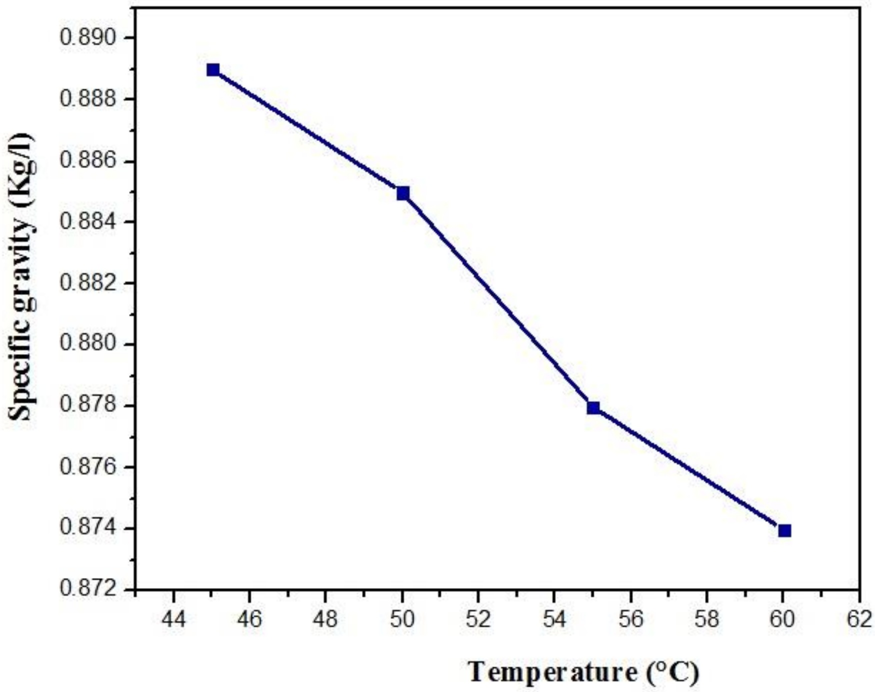

Figure 2. Effect of specific gravity with respect to temperature

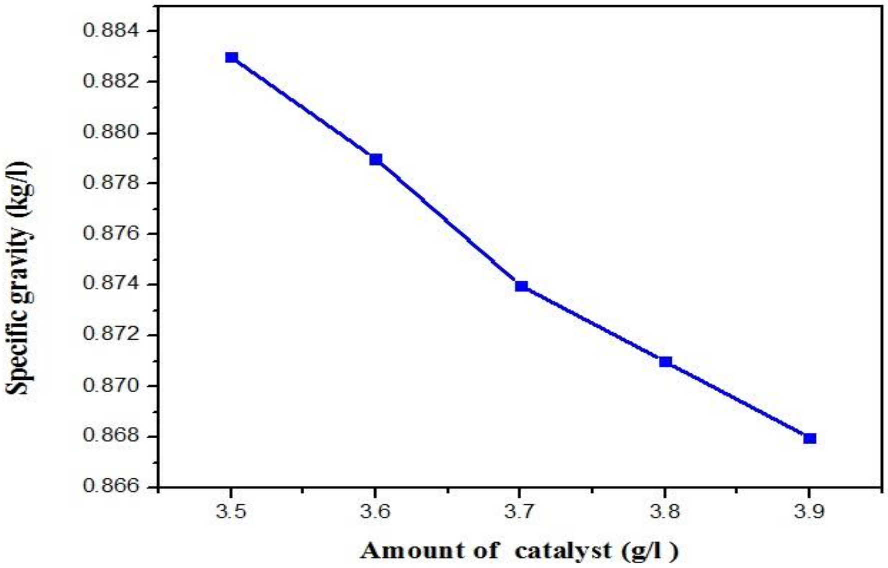

Figure 3. Effect of specific gravity with respect to catalyst.

Another important factor that affects the conversion of vegetable oil to its ester is the reaction temperature. Four various temperatures were chosen to determine the effect of temperature on specific gravity (Fig.2). The specific gravity of the ester decreases with increase in reaction temperature. The relationship between the catalyst amount and specific gravity are shown in Fig.3. The specific gravity of the ester decreases with increase in catalyst.

The quality of biodiesel is most important for engine part of view and various standards have been specified to check the quality. High acid value of biodiesel (above 0.5 mg KOH/g) could damage the injector and also cause deposits in fuel injection system thus seriously impairing the performance of the pumps and filters [16]. Biodiesel thus produced in this study has an acid value of 0.10 mg KOH/g and FFA of 0.05 %.

One of the most important properties of biodiesel and conventional diesel is viscosity, which is also an important property for lubricants [17]. High viscosity leads to poor atomization of the fuel, incomplete combustion, cocking of the fuel injectors and ring carbonization. According to ASTM D 6751 standard, the viscosity of fatty acid alkyl ester should meet 3 – 6 cSt at 40 °C. In the present case, the viscosity of rubber seed methyl ester was 5.80 cSt at 40 °C thus meeting the requirement of ASTM standard. The viscosity of biodiesel is closer to that of ordinary diesel. The rate of change of viscosities of methyl ester and conventional diesel decreases with increase in temperature and are presented in Fig. 4. Thus, it is clearly understood that kinematic viscosity is inversely proportional to temperature.

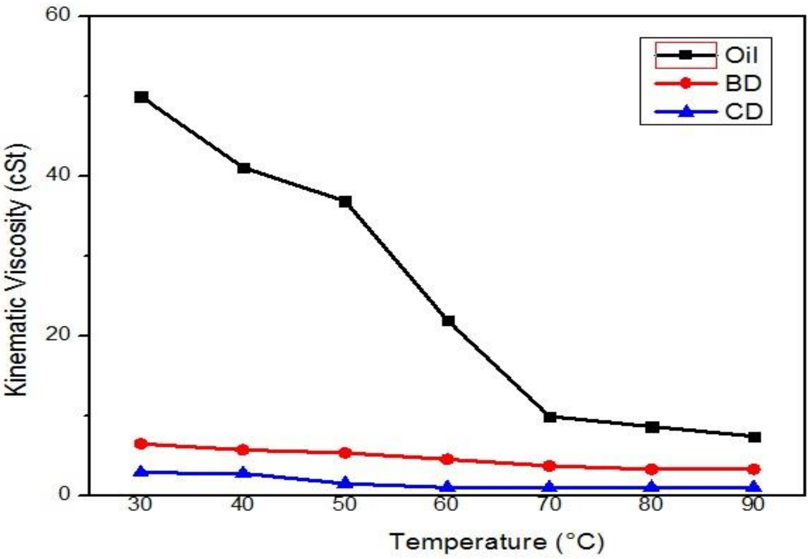

Figure 4. Comparison of kinematic viscosties of rubberseed oil, biodiesel and diesel inrelationship with temperature.

The primary purpose of determining sulphated ash in biodiesel is to ensure whether it contain any contaminants [18]. This test is also an indicator of the quality of residual metals present in the fuel. The sample had sulphated ash of 0.01 % by weight and it implies that, biodiesel thus produced does not have any inorganic contaminants. Water and sediment, if any, in the biodiesel would lessen the effectiveness of the catalyst and fall out in lower efficiency [19]. Enhanced microbial growth could be seen when water is present in biodiesel. Furthermore, it will endorse the corrosion of the fuel tank. The result obtained in this study had water and sediment of about 0.01% which is far below the standard level of ASTM D 6751.

Carbon residue is a deposit of carbon that remains after combustion. In the present case, carbon residue left after burning the biodiesel was observed to be lower (0.021 %) than the maximum limit specified in ASTM D 6751 standard. The flash point of biodiesel produced in this work has 134.8 °C. This feature provides an advantage of biodiesel over conventional diesel since it reduces the risk due to fire and safer for transport purpose.

Thus, the present study suggests that the properties of biodiesel produced from rubber seed oil exhibit better fuel properties and found to meet the requirements of ASTM D 6751 standard (Table-2).

Table 2 - Quality analysis of rubber seed methyl ester

Parameters	*Units*	*Rubber seed methyl ester*	*ASTM D 6751 Limits*	*ASTM D 6751 Methods*	*Diesel*
Acid number	*mg KOH/g*	*0.10*	*0.50 max*	*D 664*	*-*
FFA	*%*	*0.05*	*-*	*-*	*-*
Specific gravity	*g/cm^3*	*0.874*	*0.87 - 0.90*	*D 1250 - 08*	*0.85*
Kinematic viscosity at 40° C	*cSt*	*5.80*	*1.9 - 6*	*D 445*	*2.7*
Peroxide value	*meq/kg*	*0.8*	*-*	*-*	*-*
Calorific value	*MJ/kg*	*35.44*	*-*	*D 240 - 02*	*47*
Sulphated ash	*%*	*0.01*	*0.02*	*D 874*	*0.05*
Water & Sediments	*%*	*0.01*	*0.05*	*D 2709*	*0.05*
Copper corrosion	*-*	*1a*	*No. 3 max*	*D 130*	*No. 3 max*
Carbon residue	*%*	*0.021*	*0.05*	*D 4530*	*0.15*
Flash point	*°C*	*134.8*	*130 min*	*D 93*	*52*

3.4 Storage studies of biodiesel

Biodiesel degrades by 98% biologically within three weeks whereas the conventional diesel will degrade only by 50% within the same period of time [8]. The stability of the biodiesel depends upon the feedstock being used for the biodiesel production. The specific gravity of the product decreases gradually and found to increase after 150 days. It is observed that the specific gravity of the stored methyl ester is found to be in within the limits of ASTM D 6751 standard even after 360 days (Fig.5).

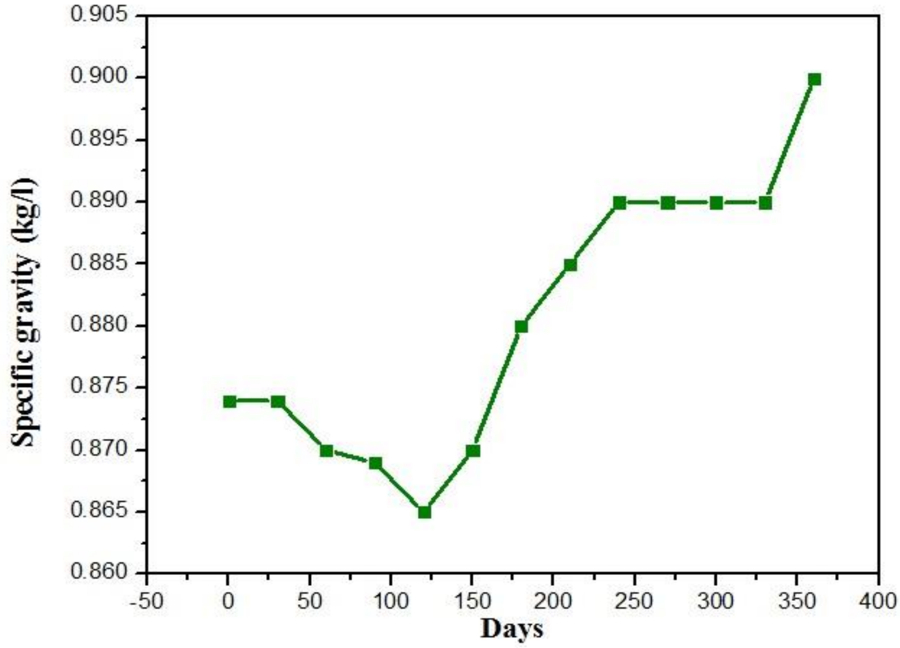

Figure 5. Chenges in specific gravity of biodiesel during storage

Acid value is an indicator of the stability of the fuel and the acid value increases when the fuel is oxidized. Acid value of biodiesel increases with increase in storage days in Fig.6. It is also seen from Fig.6, that the acid value remains relatively stable for a month and then took a significant rise in storage time. Acid value increases slowly and sudden rise in acid value was observed after 210 days. However, the acid value (ASTM D 6751) of the methyl ester sample was within the limits (0.5 mg KOH/g) even after 360 days. Higher the degradation, higher will be its acidity [20].

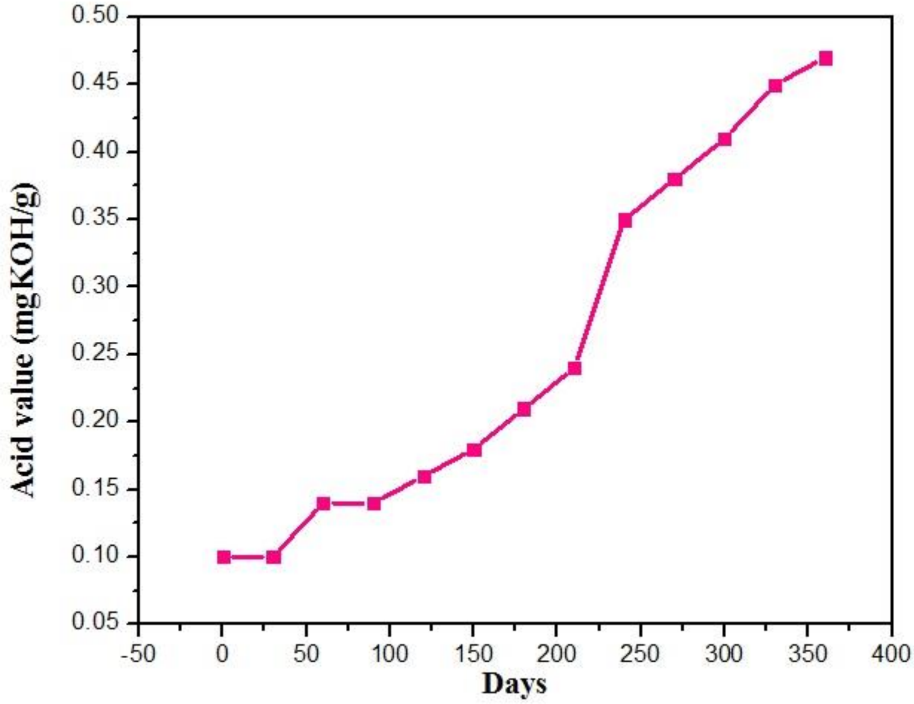

Figure 6. Changes in acid value of biodiesel during storage.

Increasing the storage time in absence of an antioxidant leads to an increase in kinematic viscosity. Increasing the kinematic viscosity of biodiesel was known to increase the storage time as in Fig.7. It was also observed that the sample exhibits slight increase in kinematic viscosity during storage. However, the limit prescribed by ASTM D 6751 was 6.0 cSt at 40 °C which is not exceeded in the present case.

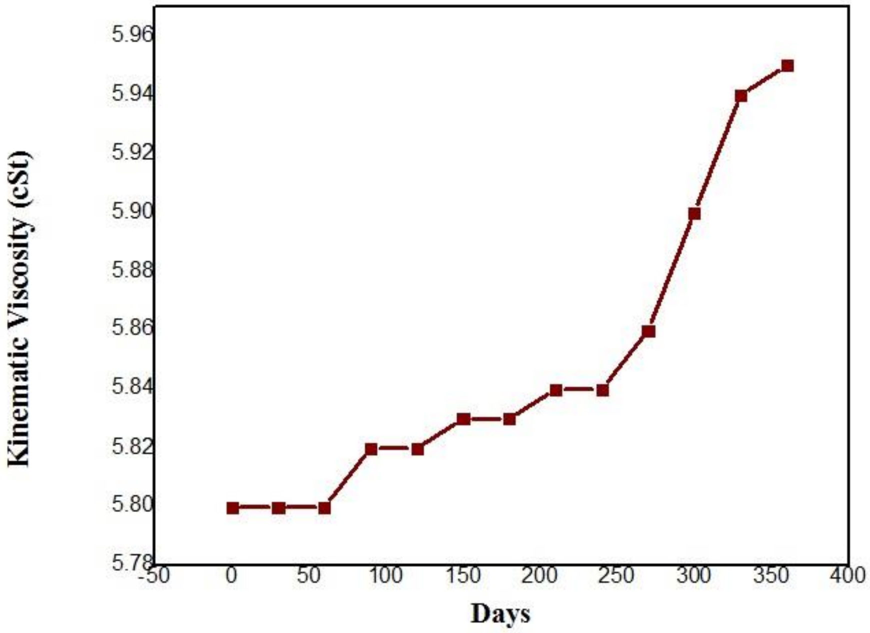

Figure 7. Changes in kinematic viscosity of biodiesel during storage.

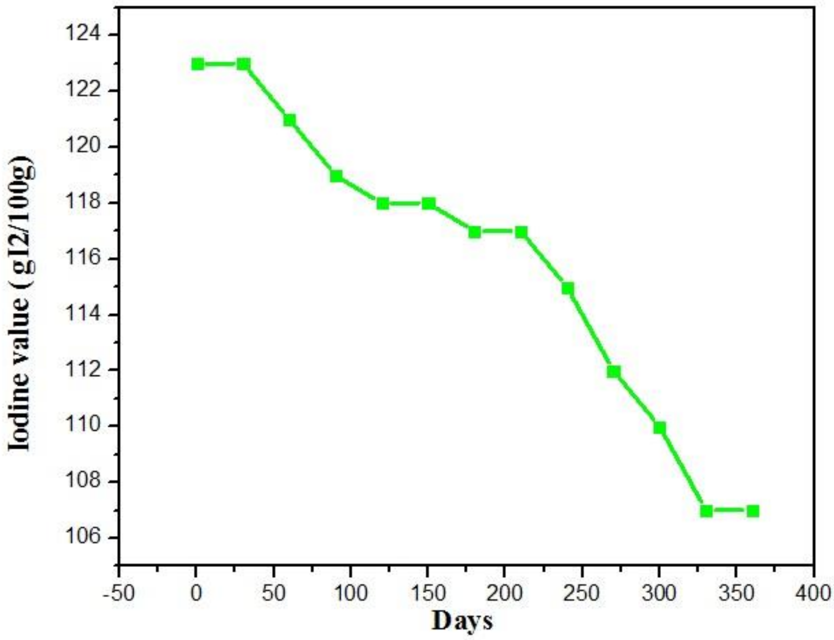

Figure 8. Changes in iodine value of biodiesel during storage.

Iodine value provides information about the degree of unsaturation, which directly affect its stability with regards to oxidation. The auto oxidation of unsaturated fatty compounds depends on the number and position of double bond. The species formed during the oxidation process causes the fuel to eventually deteriorate. Iodine value decreases with the increase in storage days as in Fig.8. The fluctuating values may be due to dehydrogenation and saturation [21]. The decrease in iodine value is an indication of lipid oxidation, since there is a decline in unsaturation during oxidation. Water and sediment is a complicating factor connected with the storage of biodiesel. The presence of water in biodiesel induces hydrolysis of fatty acids leading to the formation of acids and alcohols [19]. It is inferred from Fig.9, that water and sediments did not exceed the ASTM standard of D 6751.

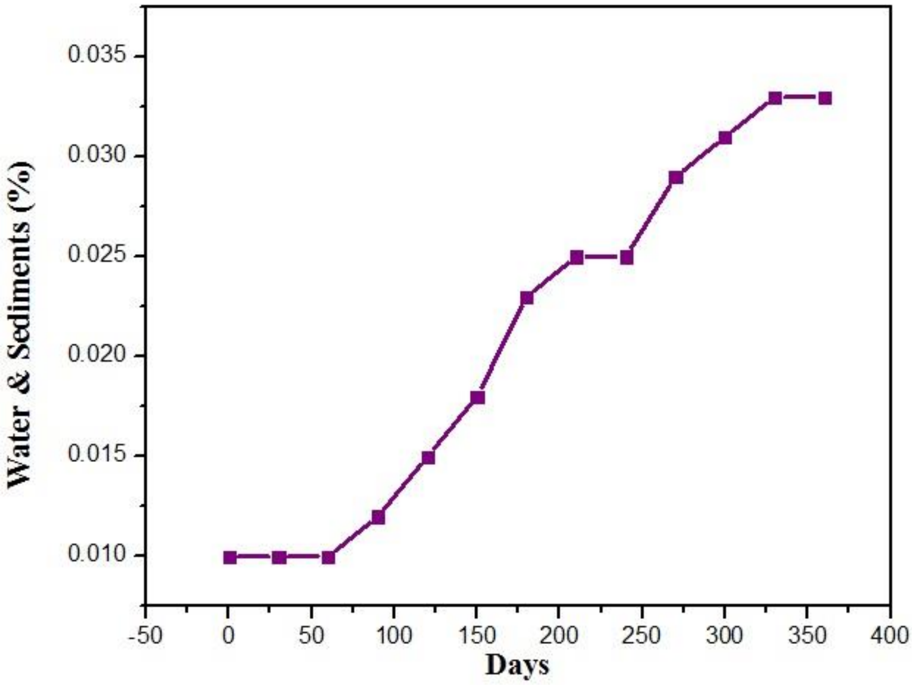

Figure 9. Changes in water & sediments of biodiesel during storage.

IV. CONCLUSION

An attempt was made to investigate the scope of utilizing rubber seed oil as a feedstock for the production of biodiesel. Physical and chemical properties of rubber seed oil were analysed. The effect of specific gravity of the biodiesel with respect to molar ratio, temperature and catalyst were also investigated. Transesterification of rubber seed oil shows an enhancement in fuel properties. During the shelf life of biodiesel for a period of one year, acid value, specific gravity, viscosity, water and sediments were increased, but the iodine value decreased. However, alkyl esters of rubber seed oil meet the ASTMD 6751 standard of biodiesel even after a year. Thus, this study supports the production of biodiesel from rubber seed oil as a viable substitute to the conventional diesel.

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