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Isolation, Spectral Characterization, Thermal Efficiency and Microbial Evaluation Studies on Indian Rubber (Hevea Brasiliensis) Seed Oil

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Abstract: ***Hevea brasiliensis rubber seeds were collected and were extracted by using n-hexane as the solvent in the Soxhlet Extractor. The extracted semi drying oil was characterized by various physio-chemical and thermal properties. Fatty acid composition of the lipid was investigated using gas chromatography techniques. Vibrational studies of the oil show that the characteristic strong absorption at 1741 and 1644cm^{-1} for –C=O and –C=C– groups respectively. Both the ^{1}H NMR and ^{13}C NMR spectral studies indicate that the presences of triacylglycerol groups were saturated as well as unsaturated in nature. Photo pyroelectric technique (PPE) was used for thermal characterization of the extracted oil. The effect of the fuels on engine components and exhaust gas emissions such as total hydrocarbon, carbon monoxide, and smoke and brake specific fuel consumption were also investigated. Antimicrobial activity was compared with the standard control drug of chloramphenicol at a concentration of 10 µg/ml at 30, 37 and 42 ºC.***

Index Terms: ***Hevea brasiliensis rubber seeds, Photo pyroelectric technique, Spectral Studies, Thermal emissions, Microbial screening.***

I. INTRODUCTION

Fossil fuels have been the major store of energy for direction-finding infrastructural and economic developments both in the developing and the developed countries [1]. Fossil fuels emit greenhouse gases that cause wide harm to the environment and human health. The search for alternative fuels is rising and biodiesel is a gifted option, as it is biodegradable, less pollutant, and derives from natural and renewable feed stock [2]. There are different methods for biodiesel production from vegetable oil or animal fat. The most used one is transesterification, which consists of the reaction between triglycerides and alcohol, generally methanol or ethanol, producing esters and glycerin [3]. It is tremendously essential to have information on physicochemical properties of these samples. The photothermal technique can be used for this motive. And its applications engage different systems and comprise solids, liquids, and gases, such as semiconductors, ceramics, polymers, organic materials, and foodstuffs [4]. The use of biodiesels as alternative fuels has been extensively investigated with the objective of ensuring energy security and reducing the environmental impacts of diesel emissions Rubber Seed Oil (RSO) contains 17 – 20 % saturated fatty acids (Myristic, Palmitic, Stearic, Arachidic, Behenic, etc.,) and 77 – 82 % unsaturated fatty acids (Palmitoleic, Monohydric alcohols, etc.,).

Rubber seeds are composed of about 43 % oil. This RSO oil is a semi-dried substance that does not contain any unusual fatty acids, but is a rich source of polyunsaturated fatty acids $C_{18:2}$ and $C_{18:3}$ that make up 54 % of its total fatty acid composition [5] as well as in the production of biodiesel and for use in fuel compression ignition engines. Lower concentrations of biodiesel blends improved thermal efficiency. At higher concentrations of biodiesel in the blend, there was a reduction of smoke density in exhaust gas [6]. In this paper, we studied the rubber seed oil and their methyl ester derivates derived from *Hevea brasiliensis* rubber seeds are desirable as an alternative diesel fuel. Also a conventional diesel (CD) using an endurance test was carried out to enable evaluation of the impact of blended fuels on critical components of a direct injection (DI) diesel engine. Performance and emission parameters were also measured, analyzed. In this paper, we studied the physico-chemical properties, including fatty acids, thermal properties solid fat content and microbial susceptibility characters of rubber seed oil (RSO) were also evaluated. Further, to investigate the potential of alternative hosts for oil production, we screened 8 different microorganisms for their tolerance to this bio fuel.

II. EXPERIMENTAL METHOD

A. Materials and Methods

Rubber seeds were obtained from the Rubber Research Institute, Kottayam from Kerala. All chemicals used in this study were AnalaR grade and used without further purification. Acid value, Percentage free fatty acids (FFAs), Iodine value, Saponification value, unsaponifiable matter of the RSO were determined according to AOCS 5a-40 (1989), British standard BS 684:

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section 2.13:1976 & 2.6:1977 and AOCS Ca 6a-40 (1989) methods respectively. Fatty acid composition of the semi oil was determined using gas chromatography techniques were performed on Shimadzu gas chromatograph equipped with flame ionization detector and capillary column (30 m × 0.25 mm × 0.25 µm films). The detector temperature was programmed for 280 °C with flow rate of 0.3 ml / min and the injector temperature was set at 250 °C. N_2 gas was used as the carrier gas. FTIR of the product was recorded on a JASCO FT/IR- 410 spectrophotometer in the range 400-4000 cm^{-1} using KBr disk. Both ^1H and ^{13}C NMR of the ROS oil was recorded on Perkin ElmeR-32 spectrometer analysis using the solvent $CDCl_3$. Thermal properties, particularly melting temperature and crystallization temperature, were determined by differential scanning calorimeter analysis. The pyroelectric signal was measured by a SR830 lock-in analyzer, using the current mode detection.

B. Extraction of oil from seeds

Damaged seeds were cleaned, shelled and dried at 108 °C for 26 min. The seed and its kernel contain about 638 and 749 mg HCN per Kg. It is reported that storage at room temperature for a minimum period of 2 months is effective in reducing [7] the HCN content. The heating of decorticated seeds to a temperature of 123 °C over an hour for about 48hr may destroy the fat splitting enzyme Seeds were ground using a grinder prior to oil extraction. The kernels were milled using attrition mill and the proximate analysis carried out according to the method of the Association of Official Analytical Chemists (AOAC 1980). Oil was extracted from the milled kernels with the solvent n-hexane (40–60 °C) by using Soxlet extractor. It was dried over anhydrous sodium sulphate and the solvent removed by evaporation.

C. Thermal characterization using PPE techniques

Both for SPPE and IPPE configurations, the sensor used was a PZT (lead – titanium – zirconate) ceramic, 305 µm thick. For the SPPE configuration the samples were held by a copper cylinder, glued to the sensor with silicone. An aluminum mask provides both the superficial absorption (30 µm Al foil on the bottom) and the sample's thickness control, by means of an attached micrometer. The radiation source was a 120 mW argon laser (514 nm), chopped by an acoustic-optical modulator. Measurements were performed at a fixed frequency (2.5 Hz), scanning the sample's thickness from 500 to 200 µm, with a 20 µm step. For the IPPE configuration, the sensor was a black-inked surface to absorb the laser beam. The sample is held as in SPPE, but in this case having around 5 mm thickness, comfortably fulfilling the sample's thermally thick condition. The radiation source was a 15 mW diode laser, electronically modulated. The frequency range used was 1 to 70 Hz. The pyroelectric response $S(t)$ of the detector [8] – [10] due to a periodic (frequency; f) temperature variation is given as:

$$S(t) = A(f)\,\Gamma(f)\,e^{i2\pi f t} \qquad (1)$$

where $A(f)$ is considered as a transfer function; $\Gamma(f)$ is a dimensionless response factor containing relevant information about the thermal properties and thickness of the different layers, among which is the sample layer of interest.

For the SPPE configuration, the 1-D heat diffusion is considered in a four-layer system, constituted of air (g), the sample (s), the pyroelectric sensor (p) and the backing (b). Knowing the sensor's thermal effusivity, e_p, one can obtain the sample's thermal effusivity [2], the e_s is obtained from the following equation as:

$$e_s = \frac{(1 + R_S\, p)}{(1 + R_S\, p).e_p} \qquad (2)$$

III. RESULTS AND DISCUSSION

The refractive index and specific gravity of RSO were measured at 30 °C and 40°C, respectively. The kinematic viscosity was determined using a Ferrantic portable viscometer at 20 °C. Heats of combustion were measured using bomb calorimetry.

A. Physico-chemical characterization

Extracted oils were characterized using suitable physical and chemical techniques. Fuel properties of the oil, their methyl ester and commercial diesel were also characterized by AOCS procedures and compared it.

B. Spectral studies

Vibrational (FTIR)spectroscopy viewing the major peaks and their functional groups of the RSO showed characteristic strong absorption bands at 1741 cm^{-1} for the ester carbonyl (C=O) functional groups. From proton NMR spectrum show the following principal signal assignments of RSO as: 0.73-0.77ppm of terminal (-CH_3), 1.11-1.16ppm of methylene protons (-CH_2-), 1.86-1.91ppm for the protons α to the carbonyl groups (-CH_2-C-), 2.61-2.69ppm for diallylic methylene (-C=C-CH_2-C=C-), and 4.17 ppm of protons in α and β position in glyceryl. ^{13}C NMR, also viewing the main signal assignments of the RSO indicates the presence of allylic carbon atoms at 26.9 ppm, methylene carbon atoms at 26.9-29.9 ppm, glyceryl carbon atoms at 61.9-68.8 ppm, olefinic carbon atoms at128-129.6 ppm), and carbonyl carbon atoms at 172.31-177 ppm [11]. In addition, results showed a tendency of the biodiesel values of thermal properties to be lower than those of the corresponding precursor oils.

Table 1. Thermal properties of RSO with references

Samples	α ($10^{-7}m^2s^{-1}$)	e ($Ws^{1/2}m^{-2}K^{-1}$)	k ($W\,m^{-1}\,K^{-1}$)
Water	1.45 ± 0.04	1597 ± 30	--
Ethylene glycol	0.94 ±0.02[a]	811[a]	--
RSO	0.86 ± 0.02	543 ± 4	0.145 ± 0.002

[a] [Ref. 14 & 16]

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C. *Thermal characterization using PPE techniques*

Thermal-effusivity purpose depends on a reference material by a known thermal effusivity. In this study, we chose ethylene glycol, assuming an averaged value [12], as shown in Table 1. By using the thickness of the sensor, we obtain its thermal diffusivity, i.e., $\alpha_p = (4.82 \pm 0.08)\times10^{-7} m^2\ s^{-1}$, in agreement with the expected value for PZT sensors [15] such a value was used to calculate R_{sp} in eqn 2. Employing ethylene glycol as a reference sample (e = 810 W · s $^{1/2}$ · m^{-2} · K^{-1}), taken from [2] [13], the thermal effusivity could be obtained for the sensor and afterward for the other samples (Table 1), we are able to conclude the thermal diffusivity, whose values were found to be (0.80 ± 0.01) and (0.81 ± 0.01) × $10^{-7} m^2\ s^{-1}$ for the amplitude and phase respectively.

D. *Engine oil Analysis*

The higher Brake specific fuel consumption (BSFC) value of the biodiesel fuels can be attributed to lower heating value and higher viscosity. The fact that diesel has 11% higher caloric value, lower viscosity and better volatility than biodiesel ensures better fuel atomization and results in better combustion of the fuel as it is injected into the combustion chamber. Thus, less biodiesel fuel is needed to provide an equivalent amount of energy. Thermal efficiency is often referred to as the inverse of brake-specific energy consumption. A significant drop in efficiency was found with pure biodiesel when compared with diesel. This may be attributed to the poorer combustion characteristics of methyl esters due to higher viscosity. After the endurance test, the thermal efficiency of all test fuels decreased.

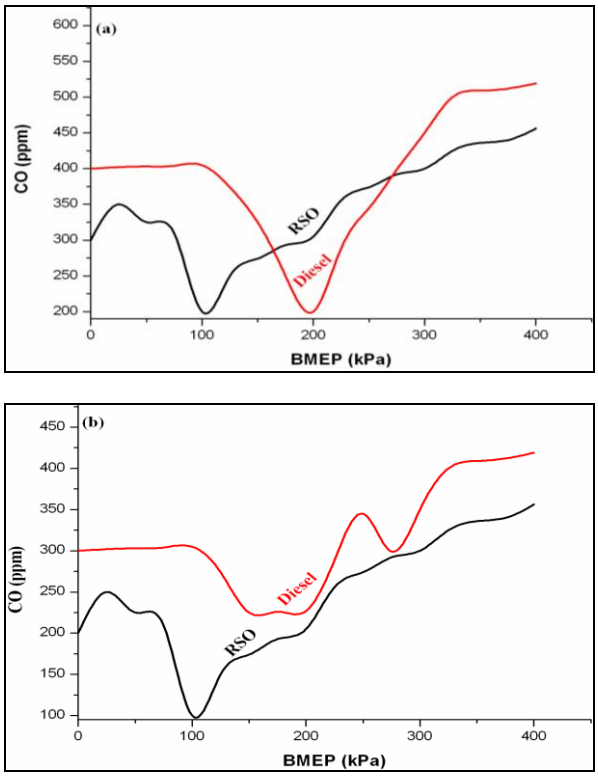

Fig.1.Total Hydrocarbon Emission (a) before and (b) after endurance test at 1500 rpm.

Viscosity is one of the most important properties of engine oils. Viscosity of engine oil was determined at 100 C being close to the average oil temperature during engine operation. This decrease in viscosity was probably due to dilution of the engine oil by the fuel [6]. The higher viscosity and density of bio-diesel compared to diesel fuel may result in passage of bio-diesel through piston rings to the cylinder liner and hence to the crankcase. The biodiesel diluting the lubricating oil may result in a reduction in viscosity. Un-burnt biodiesel passing to the crankcase may reduce lubricant viscosity over time, reducing lubricant film thickness and ultimately increasing component wear.

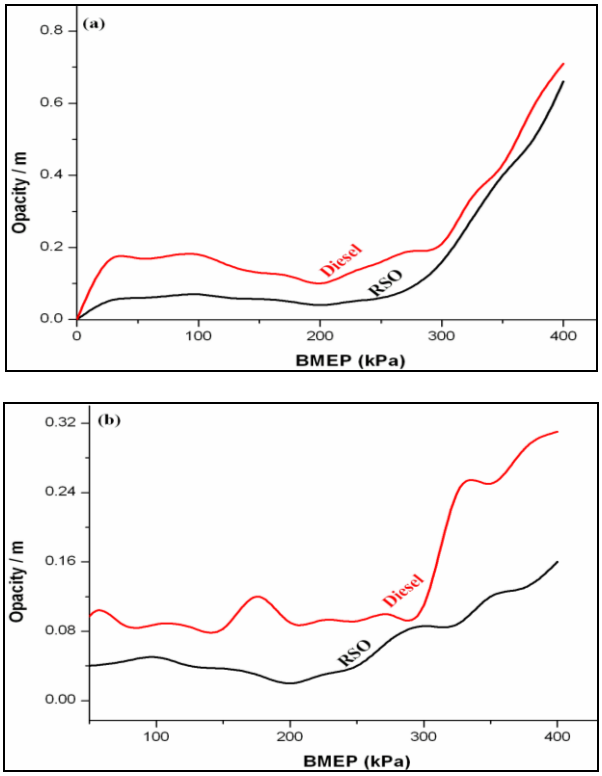

Fig.2. CO and smoke emission (a) before and (b) after endurance test at 1500 rpm.

E. *Engine Exhaust gas emissions:*

Biodiesel fuel produced lower total hydrocarbon (THC) emission than diesel fuel. This is probably due to the effect of the internal oxygen content of biodiesel fuel in the RSO oil blend tending to improve combustion [14]. After the endurance test, the percentage differences of THC, CO and smoke is somewhat high (Fig. 1 and Fig. 2). Increase of hydrocarbon was due to insufficient combustion, caused by deposits and injector clogging.

F. *Microbial activity:*

Interestingly, lots of the lipid extracts had antimicrobial activities. Microbial activity of RSO was studied by disc diffusion method on agar against various microorganisms. These assays are based on the use of discs as reservoirs containing solutions of the substances to be examined.

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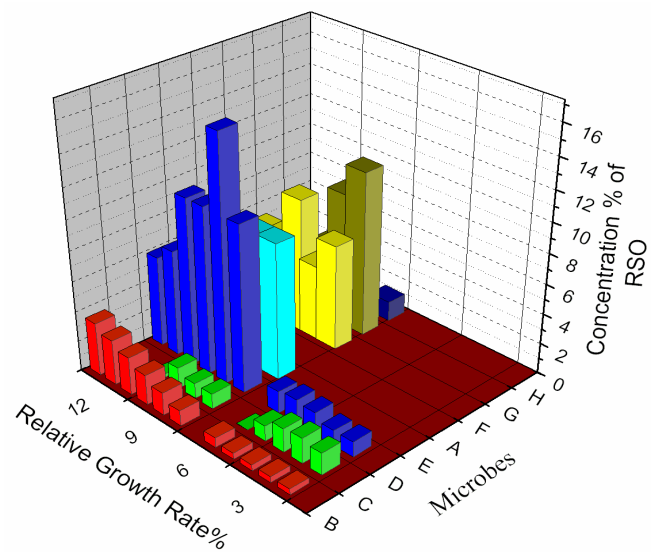
In the case of solutions with a low activity, yet, a large concentration or volume is desirable. Because of the limited capacity of discs, holes or cylinders are rather used [15]. RSO showed a broad spectrum of activity against all the bacterial strains in Chloramphenicol (10 µg / ml / disc) was used as a positive control. The study pointed out that the methanol extracts of RSO inhibit the growth of a few of the tested microorganisms to various temperatures like 30, 37 and 42 °C. The RSO at a concentration of 500 µg/ml and 750 µg/ml exhibited noteworthy ($p < 0.05$) antimicrobial effect against all the tested microorganisms. The extract showed sturdy antibacterial activity against *Escherichia Coli*, *Lactobacillus brevis, Zymomonas mobilis, Pseudomonas aeruginosa, Pichia guilliremondii, Saccharomyces cerevisiae, Aspergillus niger* and *Candida albicans*. Though, their activity against *Pichia guilliremondii* was found to be extensively ($p > 0.09$) less than the control. The antimicrobial activity was compared with the standard Chloramphenicol at a concentration of 10 µg / ml (Fig. 3). All treatments were performed in triplicate and each data point in the results is the mean of two or three replicate tests.



A = *Pseudomonas aeruginosa*, B = *Escherichia coli*, C = *Lactobacillus brevis*, D = *Pichia guilliremondii*, E = *Zymomonas mobilis*, F = *Saccharomyces cerevisiae*, G = *Aspergillus niger* and H = *Candida albicans*

Fig.3. Microbial activities of RSO in different microorganisms at 42 °C.

IV. CONCLUSION

For the most part the results point out that Rubber Seed biodiesel can be used as a limited substitute for diesel fuel. A 5 % blend of RSO with diesel fuel can be used to fuel DI diesel engines providing similar performance, condensed emissions, wear fall of engine components and neutral effect on lubricating oil. The BSFC was significantly higher (22.88%) than for diesel fuel. Brake thermal efficiency of was better but still less than diesel, due to the lower calorific value of RSO blend than diesel. No noteworthy engine modifications are required. The properties of RSO blend get together both ASTM and SNI standards for biodiesel. According to results of CO and smoke emissions, it appears that the most favorable working condition of this fuel at 200 kPa and 1500 rpm due to reduction of those emissions. Enhanced health, socioeconomic position and the by and large improved quality of life for a nation's masses should be the chief objectives for use of such a mass collective technologies.

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