Production and Characterization of Biodiesel from *Hevea Brasiliensis* and Diesel like Fuel from Waste Engine Oil

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Shreya Subedi[1], M Anand[2], Gokul Raghavendra S[3], Ranjitha J[3]*
[1]Department of Mechanical Engineering, School of Mechanical Engineering, Vellore Institute of Technology, Vellore-14
[2]Department of Science and Humanities, Kingston Engineering College, Vellore-59
[3]CO_2 Research and Green Technologies Centre, Vellore Institute of Technology, Vellore-14

*E-mail: ranjitha.j@vit.ac.in

Abstract. In today's application, it is essential to formulate the use of diesel and biodiesel in an environmentally generous manner. In this experimental study, an attempt was made to increase the performance and reduce the exhaust emission by blending biodiesel with diesel extracted from waste engine oil on their performance and emission characteristics. The bio-oil is extracted from the seeds of *Hevea Brasiliensis* using soxhlet extraction process. The crude bio-oil was converted into biodiesel using transesterification process. The percentage yield obtained was high, in the case of heterogeneous base catalyst CaO compared with homogenous base catalyst. Further, the trans-esterification reaction was optimized using the following condition reaction like temperature at 60°C, reaction time ~1.5 h, molar ratio 9:1 (oil: methanol) and 3% catalyst (w/w). The waste engine oil was distilled using fractional distillation process to produce fuels which is used in engines using inert silica granules. The bio-oil, bio-diesel and diesel samples were characterized using FT-IR and GC-MS spectroscopic techniques. Based on the spectral data, fatty acids, fatty acid methyl ester and hydrocarbon derivatives were identified. Similarly, physical properties were analysed for the produced fuel and biodiesel such as density, viscosity, flash and fire point and calorific value and the results are comparable with ASTM standards. Based on the fuel properties, biodiesel and diesel like fuel obtained from waste engine oil will be used in future to study their engine characteristics.

Keywords: *Hevea Brasiliensis*, waste engine oil, biodiesel, and GC-MS spectral analysis.

1. Introduction

As the world fossil fuel reserve is at a diminishing stage it is inevitable to find an alternative fuel, to obtain a proper solution for this impending problem researchers are forced to depend on self-sustaining energy resources. Among the globally available fuels, biodiesel has proved to be a remarkable fuel in the mark of history which was devised by Rudolf Diesel in 1990's to make his diesel engine work with the help of vegetable oil. Biodiesel has been acclaimed as an important substitute for conventional petroleum derived fuels, as concerned to its environmental impact and sustainability. Biodiesel is prepared by direct transesterification process of vegetable oil, animal fat or non-edible plant seed oils in which triglycerides reacts with the small molecules of alcohol such as methanol on behalf of catalyst. Relating to biodiesel production, the feedstock is of great importance that if they are grouped according to their degrees of purity, predominantly concerned to the level of free fatty acid. . Biodiesel is found to be a promising alternative fuel source as it has low content of Sox and Cox, organic as well as inorganic pollutants[1,2]. There are several methods adopted by researchers to convert bio-oil into biodiesel, which includes micro-emulsion, pyrolysis, transesterification etc. [3]. Transesterification is found to be the most effective method concerned to a main aspect that is biodiesel produced via this method is fully miscible with diesel in all kinds of proportion [4]. Recent studies has found that biodiesel produced from *Hevea brasiliensis* seed is a promising non edible plant seed which is widely available in the regions of south east Asia [5]. The average percentage weight of oil found in each kernel is about 40-50%[6] Homogeneous catalyst is usually adopted for biodiesel production in the case of vegetable oils, but the main disadvantages of using this type of

catalyst includes high amount of soap formation ,large quantity of waste water production and also it results in corrosion of the reactor [7]. Numerous attempts has been made by researchers for the utilization of waste materials such as egg shells, animal bones, leaf extract, sea shells as the source of heterogeneous catalyst [8,9,10,11,12]. Lime stone based catalyst has shown efficient conversion of about 96.9% in the case of very high FFA *Hevea brasiliensis* seed oil into biodiesel [13]. Biodiesel produced from rubber seed oil in the presence of sodium metasilicate, calcium oxide based waste coral fragments has shown high amount of biodiesel yield in a single step transesterification reaction [14]. Several methods has been adopted in the previous studies for the extraction of rubber seed oil, includes solvent extraction and mechanical extraction methods(Santaso et.al) recent studies prevails that hydraulic press method is also efficient for oil extraction [15]. The hevea brasiliensis seed oil transesterification with the aid of homogeneous catalysts such as H_2SO_4, KOH has shown a yield of about 31-99% methyl esters depending on various conditions [16, 17]. In a study methyl propyl sulphonic acid – functionalized MCM-41 catalysts was used, which showed 96% of FAME yield [18]. Biodiesel produced from crude rubber seed oil via enzymatic transesterification using lipase immobilized on spherical silica aerogel under optimal condition yields about 93% of FAME [19]. The waste automotive engine oil produced throughout the world is concentrated to 24 million tons per year, the waste is hazardous hence it is a threat to the human society. A recent study has been conducted for the performance and emission characteristics in a diesel engine, biodiesel feedstock for this study was *moringa oleifra* and palm seed oil and this study reveals that the average emission of carbon monoxide for B5, B10 (13.7%, 17.3%) blend of biodiesel from palm oil was higher when compared to that of *moringa oleifra* (5.37%, 10.6%) [20]. The study conducted on cotton seed oil as the feedstock for biodiesel and the exhaust emission results obtained shows that there was a considerable reduction for particulate matter, carbon monoxide and as well as smoke emission [21]. The emission characteristics study conducted in a single cylinder diesel engine with Kapok oil biodiesel as the fuel can be compared to diesel for lower blends of B25 [22]. This paper focusses on Biodiesel production from Heavea brasiliensis seed and waste engine oil, and its performance emission characteristics on a four stroke diesel engine. The catalysts used for this research study is a CaO based heterogeneous catalysts named as Mytilus emulous.

2. Materials and Methods

2.1 The chemicals and reagents used for the extraction of biodiesel from the seeds of *Hevea Brasilinesis* are methanol, n-hexane, sulphuric acid.

2.2 Collection of seeds: *Hevea* brasiliensis seed were collected from Ernakulum district located in Kerala. The rubber shell was removed by manually and the seeds were cleaned. Approximately, 500 grams of rubber seeds were heated in an oven at 110°C for about 5 hours to remove moisture content for soxhlet extraction process. The rubber shell was removed by manually and the seeds were cleaned.

2.3 Extraction of bio-oil using Soxhlet Process: For this study, *Hevea* brasiliensis were taken and it was finely powdered. The equipment consist of a soxhlet extractor equipped with a round bottom flask with a capacity of 500 ml. About 250 g of finely powdered *hevea* seeds were taken ad it was weighed, and then it was transferred into a tea bag which functions as a filter media. After transferring the weighed powdered seed in the tea bag it was tightly tied to ensure that powder should not expel from it. Similarly, three bags were made and it was carefully placed in the soxhlet extraction tube. Then the cylindrical soxhlet extractor was taken carefully and was placed in the flask containing n- hexane as an organic solvent. Top of the soxhlet extraction tube is attached to a LB condenser, which operates on the circulation of water. The solvent n-hexane was heated to reflux the whole reaction mixture. When heated the solvent vapour passes up through the LB condenser and it falls into the chamber. The condenser setup ensures that it has zero loss of solvent vapour. The n-hexane solvent vapour gets cools and excluded back to the chamber. When the soxhlet extraction chamber gets fully filled, the chamber is emptied by symphonic action. After 8-10 hours of the reaction process and finally crude rubber seed oil was obtained.

2.4 Acid pre-treatment process: In this step one litre of crude rubber seed oil was taken, it requires 200ml of methanol to carry out acid treatment process. The crude rubber seed oil was carefully transferred into the conical flask and heated at a temperature of 50°c. After this step, methanol was added to the preheated rubber seed oil and it was carefully stirred for a few minutes. About 0.5% of sulphuric acid was added to the mixture, continuous heating and stirring was carried for 20-30 mints at atmospheric pressure. After completion of the reaction, and the product was poured into a separating funnel to separate the excess alcohol. The excess alcohol along with sulphuric acid and impurities get settled at the top layer and it was removed. The bottom layer was separated for alkaline transesterification.

2.5 Biodiesel transesterification: In this process, the lower layer separated during the acid pre-treatment process was taken in a conical flask and heated at a temperature of 55°c. Meanwhile, 3.5 % weight of prepared CaO based catalyst was dissolved in 300 ml methanol, mixed and it was poured into the flask. The mixture was heated and stirred about 30 mins, reaction was stopped and the mixture was allowed to separate into two layers. The bottom layer contained glycerol, then it was drawn off. The esters was formed in the upper layer, hot distilled water was sprayed over this layer and it was stirred gently.

2.6 Extraction of Waste Engine oil: The used waste engine oil was obtained and collected from an automobile Industry (Hyundai motors and services) located in Trivandrum district of Kerala. 5 litres of used automobile engine oil was collected .The oil was blackish in colour, the viscosity was very high and the obtained engine oil was used for refining process [23, 24].

3 Refining of waste engine oil

3.1. Removal of moisture content: Initially the crude waste automobile engine oil was taken in a cylindrical vessel and it was heated up to 100°C for a particular period of time in order to remove the moisture content.

3.2. Desulphurization: In order to remove the impurities, carbon content, and sulphur content in the moisture free waste engine oil, 8% of concentrated sulphuric acid was added and it was stirred well. This mixture was kept for 40 hours.

3.3. Fractional Distillation: A known amount of chemically treated crude oil was taken in a round bottom flask along with a few quantity of inert silica granules as shown in fig. The distillation column was set up, provided with a heat source at the end of the still pot. The chemically treated crude oil was heated to a temperature of 250-400°C. The condensate was cooled down using a graham condenser. When the desired distillation temperature was reached, the distillate was collected in a collection jar.

4. Results and Discussion

4.1 FT-IR spectra for bio-oil: The infrared spectra of the bio-oil sample shown in the figure 1. According to Figure 1, wave numbers of substantial functional groups in bio-oil were between 3288.99, 2976.92 and 2930.07 cm-1 as well as between 1690.32 cm-1, which indicated the existence of C =O bonds, C =C bonds, C–O bonds, and C–H bonds, etc. in bio-oil.

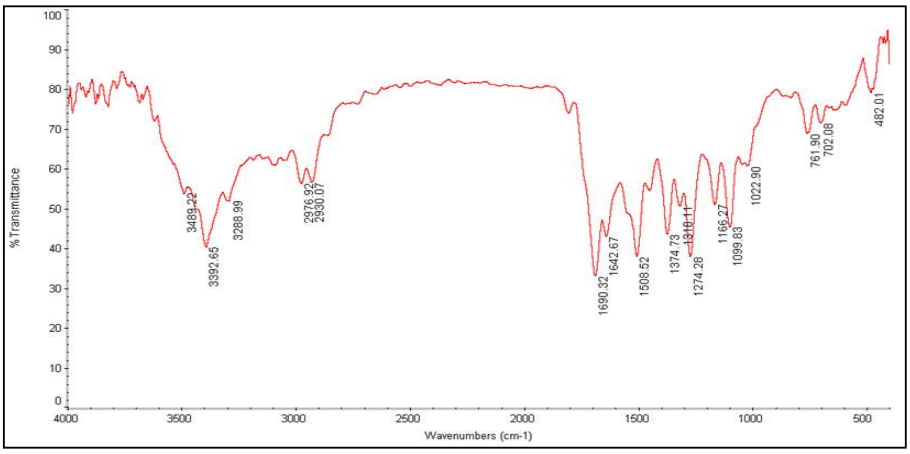

Figure 1: FT-IR for rubber seed oil

4.2 FT-IR spectra for waste engine oil: The infrared spectra of the bio-diesel sample shown in the figure 2. IR spectra clearly confirm the presence of functional groups in waste engine oils were –CH stretching of hydrocarbons in the region of 2975.64 and 2880.03 cm^{-1}. Similarly, on the side –CH bending of hydrocarbon derivatives were given peaks in the area of 1534.99 and 1410.93 cm^{-1}. Based on the FTIR results, clearly confirm the presence of hydrocarbon derivatives in the waste outboard engine oil.

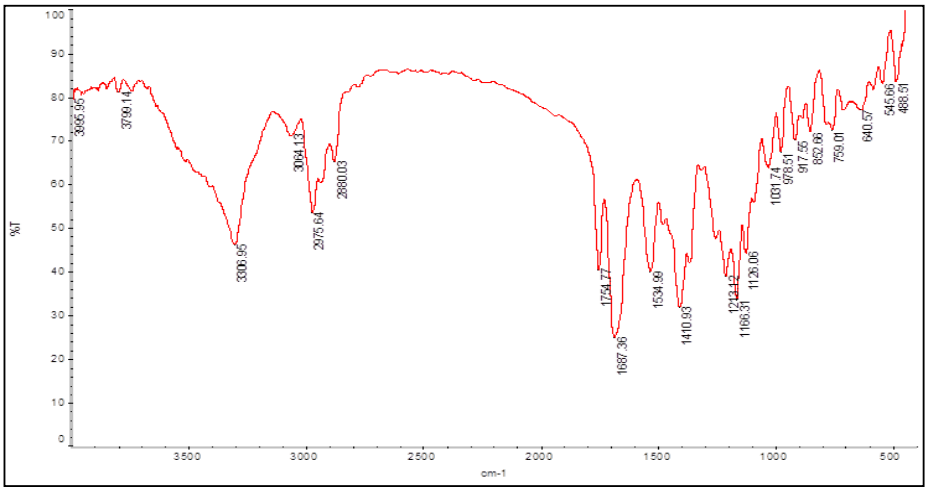

Figure 2: FT-IR for waste engine oil

4.3 Mass spectrometry library search: Identification of the components of the purified compound was matching their recorded spectra with the data bank mass spectra of NIST library V 11 provided by the instruments software. The rubber seed oil was analysed, and the composition of fatty acids identified. The individual peaks of the gas chromatogram were analysed, and the fatty acid components identified using MS database.

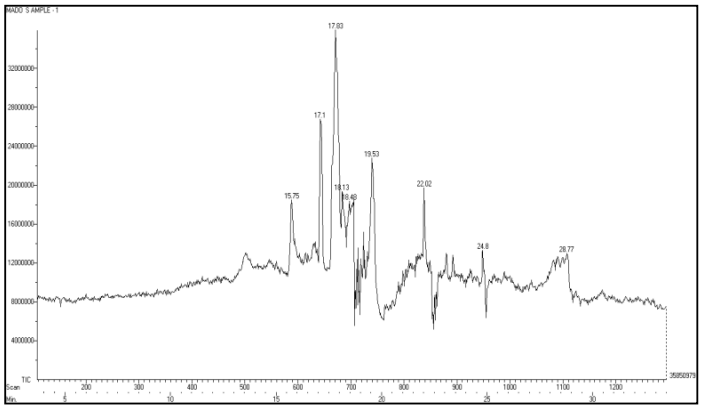

Figure 3: GC-MS for rubber seed oil

The relative percentage of fatty acid esters calculated from total ion chromatography by computerized integrator and results are presented in the Table 1. Totally five fatty acids were identified in the rubber seed oil. These fatty acids are only responsible for the production of bio-diesel using trans-esterification reaction. The fatty acids like Tetradecanoic acid, Pentadecanoic acid, n-hexadecanoic acid, 9-octadecanoic acid and hexadecanoic acid were identified using GC-MS NIST as shown in the figure 3.

Table 1: GC-MS Spectra for rubber seed oil

Peak No.	RT (Min.)	Compound Name
1	15.75	Tetradecanoic acid
2	17.10	Pentadecanoic acid
3	17.83	n-hexadecanoic acid
4	18.13	hexadecanoic acid
5	18.48	Heptanoic acid

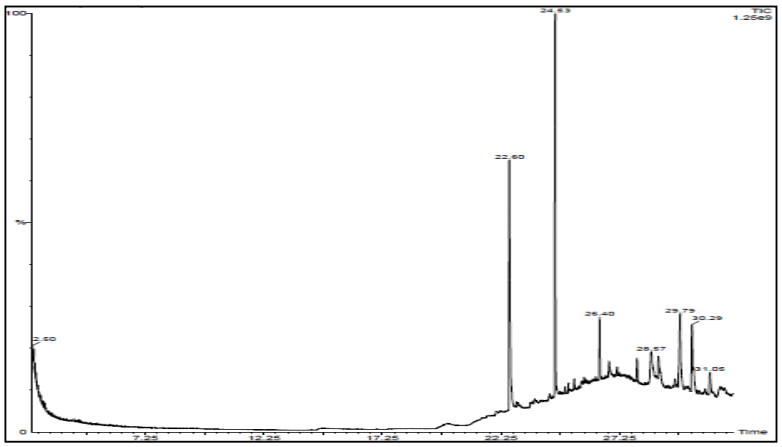

Figure 4: GC-MS for diesel like fuel

Table 2: GC-MS Spectra for diesel like fuel

Peak No.	RT (Min.)	Compound Name
1	22.60	Tetradecanoic acid methyl ester
2	24.53	Pentadecanoic acid methyl ester
3	26.40	n-hexadecanoic acid methyl ester
4	28.57	hexadecanoic acid methyl ester
5	30.29	Heptanoic acid methyl acid

The samples were analysed, and the composition of fatty acid methyl esters identified. The individual peaks of the gas chromatogram were analysed, and the fatty acid methyl ester components identified using MS database. The relative percentage of fatty acid esters calculated from total ion chromatography by computerized integrator and results are presented in the table 2. The biodiesel consists of Tetradecanoic acid methyl ester, Pentadecanoic acid methyl ester, n-hexadecanoic acid methyl ester, 9-octadecanoic acid methyl ester and hexadecanoic acid methyl ester were identified using GC-MS NIST as shown in the figure 4. The GC-MS scan also indicated that the concentration of fatty acid ethyl ester in the biodiesel is 98% due to the usage of heterogeneous catalyst in the transesterification. XRD patterns of synthesized CaO nanoparticles is shown in the Figure 5.

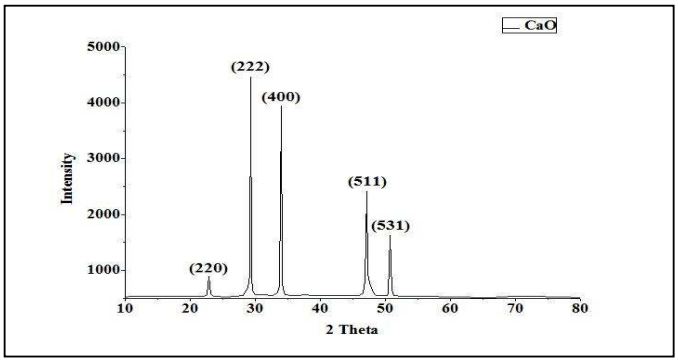

Figure 5: XRD spectrum of catalyst

XRD pattern shows that five different peaks were obtained at different 2 theta values. The strong peaks at 22.95, 29.31, 34.01, 47.10 and 50.78 are corresponded to the planes of CaO (2 2 0), (2 2 2), (4 0 0), (5 1 1) and (5 3 1), respectively (JCPDS card, 01-1160). These peaks corresponds to the standard peaks for CaO nanoparticles as mentioned in JCPDS card no 17-0912 and 01-1160.

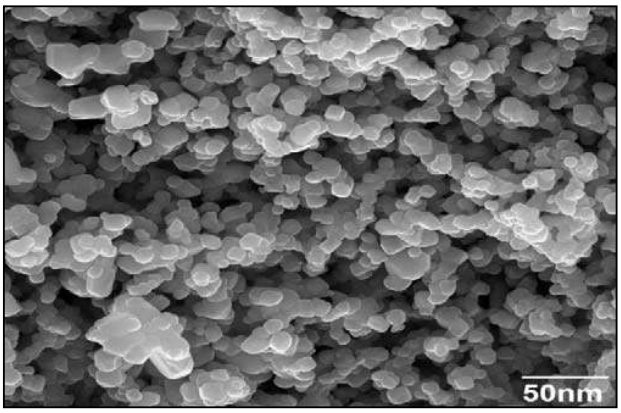

Figure 6: SEM image of catalyst

The SEM result shows that synthesized CaO is crystalline in nature. The peak starts at 10 and ends at 50 nm values confirming the results of SEM analysis. The narrow peak indicates that the size range is not wider and all particles are similar in its dimension as shown in the figure 6.

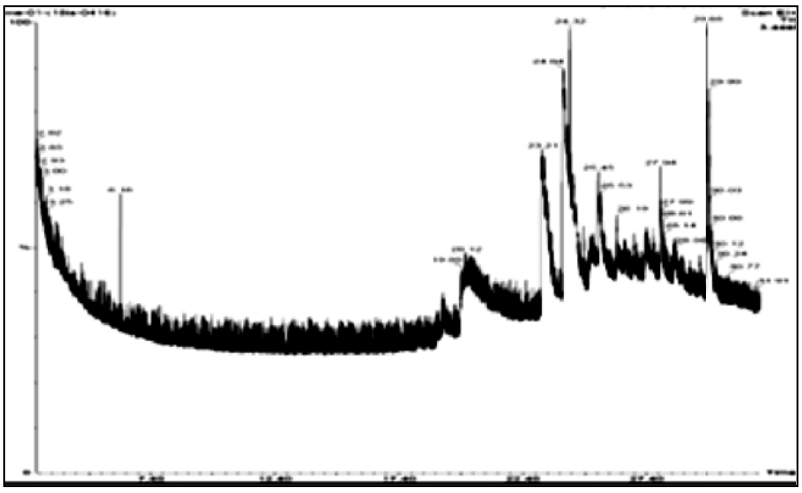

Figure 7: GC-MS Spectra of diesel like fuel

Waste is lubricating oil and distilled diesel samples were analysed using Perkin Elmer GC-MS in total scan mode to identify the hydrocarbon derivatives composition with the help of NIST library as shown in figure 7. The samples were analysed, and the composition of hydrocarbon derivatives identified. The individual peaks of the gas chromatogram were analysed, and the hydrocarbon derivative components identified using MS database. The relative percentage of hydrocarbons calculated from total ion chromatography by computerized integrator and results are presented in the Table 3.

Table 3: List of hydrocarbon compounds present in diesel like fuel

S.No	Retention Time	Hydrocarbon compounds
1	3.619	Nonene
2	4.519	Decene
3	6.010	Cyclopropane
4	6.730	Tetradecene
5	8.281	Hexadecane
6	8.441	Undecane
7	12.322	Pentadecane
8	13.503	Hexadecane
9	15.694	Octacosane
10	16.714	Tridecane

5. Conclusion

To provide sustainability and energy security, the renewable biodiesel was produced from the bio-oil of rubber seeds using heterogeneous catalyst. The synthesized calcium oxide (heterogeneous base catalyst) from Mytilus Emilious (CaO) showed effective conversion of crude bio-oil into biodiesel and enhanced the percentage yield of produced biodiesel 98%. The characterization studies revealed that the presence of FAME in the produced biodiesel from the rubber seed oil and diesel compounds lies in between the range of C9-C17 fatty acid composition. Physical properties for biodiesel from rubber seed and extracted diesel are within the ASTM standards limits. Diesel extracted from waste engine oil was found to have higher calorific value when compared to biodiesel. Based on the fuel properties, biodiesel and diesel like fuel obtained from waste engine oil will be used in future to study their engine characteristics.

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