IOP Conf. Series: Materials Science and Engineering **923** (2020) 012063 doi:10.1088/1757-899X/923/1/012063

Biodiesel Production from Mixed *Elengi* and *Pongamia* Oil using Calcined Waste Animal Bone as a Novel Heterogeneous Catalyst

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Abstract: Recently, researchers have shown more interest towards biodiesel production from non-edible vegetable oils. The main advantages of biodiesel as a fuel includes biodegradability, non-toxicity, renewability and low emission profiles. In this study, crude mixed oil was used as feedstock for biodiesel production using Heterogeneous Catalyst synthesized from waste animal bone. Initially, mechanical extraction process was used to extract the crude mixed oil from the seeds of Mimusops elengi, and Pongamia pinnata. The crude oil collected from different plant species was characterized using GC-MS spectral data to identify their fatty acid composition. Consequently, the mixed crude oil was converted into biodiesel in the presence of calcinated heterogeneous catalyst obtained from waste animal bone and the catalyst was characterized by SEM, XRD and FTIR spectral data. The effect of variables including methanol to oil molar ratio, catalyst concentration, reaction temperature, reaction time and rate of mixing on the biodiesel yield was evaluated and optimized. The characteristics biodiesel obtained from mixed oil were close to commercial diesel fuel and used as an alternative to diesel in near future.

Keywords: *Mimusops elengi*, *Pongamia pinnata*, Biodiesel, CaO Heterogeneous Catalyst.

1. Introduction

Most of the researchers have gain interest and entered the field of alternative fuel is due to the depletion of fossil fuel resources and the increasing cost of petroleum product. The main reason is greenhouse gas effects and the environmental concerns [1-2]. Some of the hazardous gasses emitted from vehicles are always threats to the human beings. Qiu *et. al.* [3] studied the biodiesel production from the mixed oil of rapeseed and soybean through transesterification reaction in the presence of base and acid catalyst and obtained the optimized conditions as mole to methanol ratio is 5.1:1, reaction time is 2 hours and temperature is 55°C with the maximum biodiesel yield of 94%. In the transesterification of soybean oil - Mg–Al hydrotalcites used as a catalyst along with methanol, resulting in the negative effect of Mg/Al ratio on the basicity and catalytic activity. In addition, the catalyst reuse and the effect of calcinations temperature were addressed [3-5]. The calcium oxide supported on mesoporous silica to enhance the catalytic activity, as determined by the percentage yield and rate of the reaction involved in the transesterification of soybean oil [6]. The advantage of base (alkali) catalyst is requiring a small quantity in catalysis and to increase the activity of KI support catalyst by using mesoporous silica as a supporter [7, 8].

Various catalysts were synthesized in order to study the conditions which give maximum activity for biodiesel production [9-14]. Leevijit *et. al.* [15] investigated the production and utilization of degummed/esterified mixed crude palm oil-diesel blends in turbocharged automotive engine and ound that DgMCPO and EMCPO can be easily produced with cost comparable to diesel. At a speed of 2400 rpm under load range of 5–32.5 kW, the blends (DgMCPO20 and EMCPO30) were able to run the test engine in the same manner as diesel. Their oxygen content promoted easier combustion and resulted in lower emissions of black smoke (−36% and −61%) and carbon monoxide (−25% and −16%) than diesel. Wong *et. al.* [16] evaluated the biodiesel production through transesterification of palm oil using CaO–CeO2 mixed oxide catalysts. The catalysts were synthesized in order to improve the physico-chemical properties, catalytic activity and reusability of the bulk CaO in transesterification of palm oil. CaO–CeO_2 mixed oxide catalysts with diferent CaO compositions were prepared via wet impregnation method. Impacts of different CaO loadings, the relationship between BET surface area and basicity with biodiesel yield were studied. In the present study, *mimusops elengi and Pongamia pinnata* seeds were collected in and around of Vellore City, Tamilnadu and then oil is extracted by the mechanical extraction process. Further, the bio-oil is converted into biodiesel using novel heterogeneous catalyst calcined waste animal bone. The characterization studies were done by SEM, XRD FTIR and GC-MS spectral data.

2. Materials and Methods

2.1. Chemicals

All the chemicals and reagents were purchased from SRL and Sigma Aldrich Chemicals Private Limited., India.

2.2. Collection of the seed materials

The non-edible elengi seed is obtained from the plant nursery located inside the VIT University. The seeds was segregated from unwanted waste and then cleaned thoroughly with water. After washing, the seeds were dried and the kernel present inside the seeds was collected for further processing. The seed kernels are kept in air dryer to remove the moisture content completely. The air-drying process is carried out in the air dryer for about 5 hours. In the similar manner, pongamia seeds were collected from the plant nursery located inside in and around Vellore district. The seeds were removed from the non-edible fruit, after drying in an air dryer. The seed kernel was removed from the seeds by cracking the outer shell. These kernels were washed thoroughly to remove the unwanted foreign bodies (or) dust particles. The rinsed seed was dried in an air dryer for about 5 hours to remove the moisture content.

2.3. Extraction of elengi and pongamia oil

The dried *m. elengi* seeds were then subjected to mechanical oil mill process for the extraction of oil. The 'x' grams of seeds were taken and then grinded using the mechanical oil mill processor. The mill has a central shaft driven by a high-power electric motor; that rotates vertically and crushes the seeds, because of this application of high pressure and constant bruising, the oil starts coming out of the seeds. The extracted oil was then collected in the basin at the bottom of the mill. Finally, the residues in the oil was made to settle down, and then filtered to remove any impurities. In the similar manner, bio-oil is collected from Pongamia seeds.

2.4. Pre-treatment of elengi and pongamia oil

The mixed oil was used for pre-treatment analysis using the following protocol. Initially, mixed oil was treated with potassium hydroxide to maintain alkaline nature, so that, free fatty acid (FFA) value of the mixed oil was neutralized and then purified with water. The resulting mixture was heated up to 100^{o}C to remove all water content present in the oil. The FFA content was analysed by a standard titration method [17].

2.5. Determination of acid value and saponification value
The acid and saponification value of bio-oil was determined according to the standard AOCS methods [18].

2.6. Preparation of Catalyst
The novel heterogeneous catalyst CaO (calcium oxide) used in this study was synthesized from goat bone. The waste animal bones were collected from local meat supplier in Vellore district. The bones were washed with dilute solution of H_2SO_4 to remove the dirty material. The bone was then powdered and treated for hydrothermal process [19]. The powdered material was thermally decomposed in a furnace at 800°C for about 2 hours and then refluxed in distilled water for 24 about hours. The sample was then filtered and dried at 120°C in hot air-oven. Further, the sample was recalcined at 900°C for 2 hours using muffle furnace to produce fine calcium oxide. The synthesized CaO was kept in a vacuum desiccator for further use.

2.7. Catalyst characterization
The XRD analysis was performed on a Siemens D-500 diffractometer equipped – consists of X-ray tube ($CuK\alpha_1$ radiation (λ = 1.54060 Å), power conditions (40 kV / 30 mA)). The source light is germanium monochromatic X-rays collected from linear PSD (opening angle: $2\theta = 6°$). XRD patterns were measured in the range of 20° to 90°, 2θ with the step size of 0.02° and 30 s counting per step at room temperature (25°C). Similarly, SEM analysis was carried out for the synthesized heterogeneous catalyst - JEOL; JSM-6330 LA operated at 20.0 kV and 1.0000 nA.

2.8. Synthesis of Biodiesel
In a 500mL round bottom flask connected with reflux condenser, magnetic stirrer and thermometer added 200 ml of bio-oil and then, 0.5 % w/w CaO, 60 ml CH_3OH was added under stirring condition. After 4 hours, the mixture was cautiously transferred into a separating funnel and allowed to stand 24 hours. The lower layer contains glycerol, methanol and catalysts was decanted. The upper layer contains methyl esters, little amount of methanol, n-hexane and trace amount of the catalyst was washed thoroughly with de-ionized water in order to remove the impurities. The fatty acid methyl ester was washed twice with dilute HCl 0.5 mol/L solution until to get a clear phase. The percentage conversion of biodiesel was calculated by the standard formula; biodiesel conversion yield (%) = (experimental yield)/ (theoretical yield) × 100%. The produced biodiesel was further characterised using GC-MS analytical technique [3, 20].

2.9. Characterization studies for mixed oil and biodiesel
FTIR spectroscopy was carried out using a Nicolet 510 - FTIR instrument equipped with a DTGS detector. Spectra recorded in the 4000-400 cm^{-1} range with a resolution of 2 cm^{-1}. The measurements were made using dried KBr pellets, which were prepared by mixing and pressing 1 mg/ 1ml of the sample with 100 mg KBr.

The qualitative and quantitative analysis of fatty acids was analyzed using GC-MS analytical technique. The detailed protocol used for GC-MS sample analysis is mentioned below; *GC operating condition:* An Agilent 6890 gas chromatograph - straight deactivated 2 mm direct injector liner and a 15m. All tech EC-5 column (250µ I.D., 0.25µ film thickness). The helium carrier gas was set to 2 ml/minute flow rate. *MS operating condition:* JEOL GC mate II bench top double-focusing magnetic sector mass spectrometer operating in electron ionization (EI) mode with TSS-20001 software. The different fatty acid compounds were integrated with the recorded spectra in the data bank mass spectra of NIST library V 11 provided by the GC-MS instrument.

3. Results and Discussion

The acid and saponification value of elengi oil were found to be 0.9248 mg KOH/g and 189.21 mg KOH/g. Similarly, the pongamia oil acid and saponification values were analysed in the range of 1.925 mg KOH/g and 184.45 mg KOH/g, respectively. If the acid value is less than 2.0 mg KOH/g, in the trans-esterification reaction, saponification interface will not significantly affect the mixture oil for biodiesel production and quality standard. Correspondingly, the total free fatty acid composition for the mixed oil was found to be in the level of 13.6%. Based on the above results, the trans-esterification reaction for mixed oil was carried out by using a novel heterogeneous catalyst. Initially, oil/ Methanol molar ratio (1:9) and reaction were conducted at 70°C under constant stirring at 700 rpm for 4 hours. After the reaction, it was transferred into separating funnel allow to settle down for 2 hours to form two layers. The organic layer is collected and concentrated in a simple distillation process to get the product as biodiesel.

FTIR spectra of mixed oil clearly confirm different functional groups present in the bio-oil sample. Based on the IR spectral data, the following functional groups such as –CH stretching bond 3005.17, 2852.72, C=O carbonyl gruop1741.72cm^{-1}. These functional groups represent the presence of aromatic and aliphatic compounds in the bio-oil sample as shown in the Figure 1.

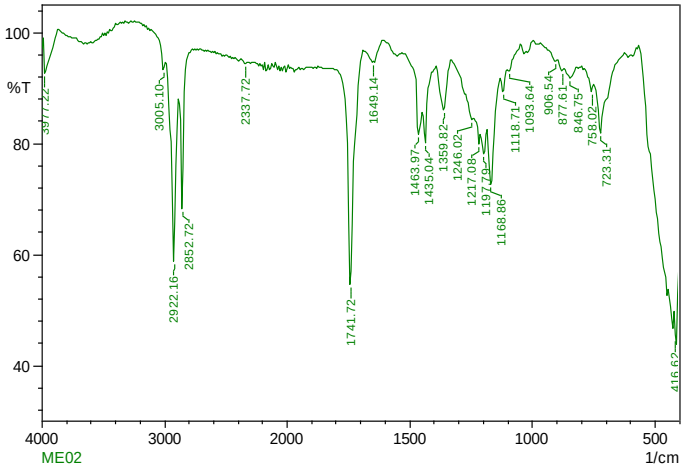

Figure 1. FTIR spectrum of bio-oil

The mixed oil was analysed using Perkin Elmer GC-MS in total scan mode to identify the fatty acid composition. The individual peaks identification was done in GC-MS, based on the NIST inbuilt library search as shown in the Figure 2. The relative percentage of fatty acid esters were calculated from total molecular ion peaks obtained by computerized integrator. Totally nine fatty acid compounds were identified in the mixed oil. These fatty acids are only responsible for the production of bio-diesel using trans-esterification reaction. The fatty acids are caprylic, lauric, arachidic, stearic, palmitic, margaric, nonadecylic, pentadecylic, behenic acids were identified based on the GC-MS spectral data.

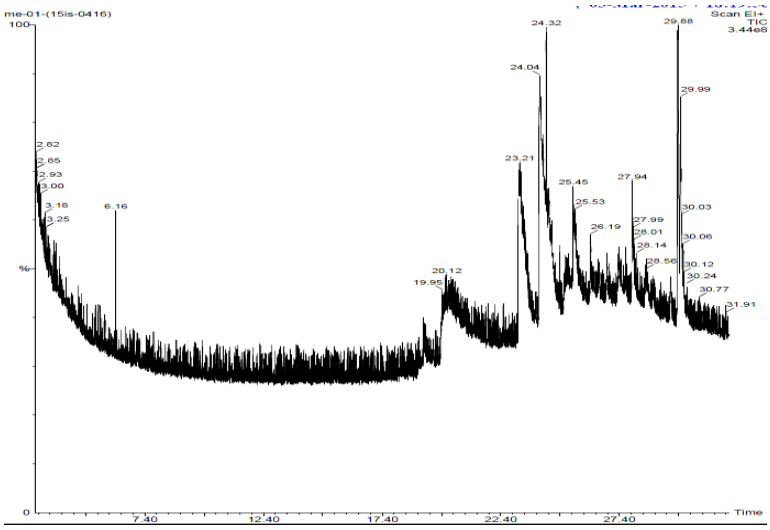

Figure 2. GC-MS Spectrum for mixed oil

The XRD spectrum explains clearly about the initiation of the stable thermal decomposition of $CaCO_3$ into CaO. It can be observed that the spectrum produces a sharp peak beyond 800°C below which the chance of peak formation responsible for CaO was very slim. The peak intensity was at its threshold limit of 1100°C, making it the optimum temperature for thermal decomposition of animal bones as shown in the Figure 3.

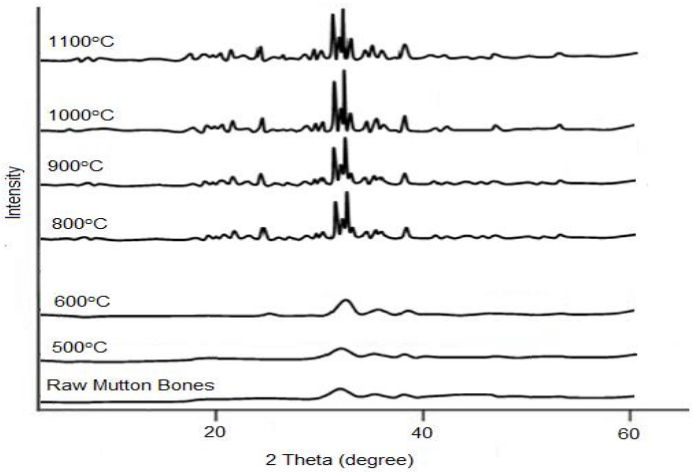

Figure 3. XRD spectrum of CaO Heterogeneous catalyst obtained from animal bone

The microscopic image of the Calcium Oxide was obtained by examining them under the scanning electron microscope (SEM) which displays their porosity behavior. The image of the calcium oxide was recorded at a magnification level of 100 µm which clearly displayed the surface of the calcium oxide. Figure 4 show the SEM image of the calcium oxide respectively. Bio-diesel obtained from mixed oil was analyzed using Perkin Elmer GC-MS in total scan mode to identify the fatty acid methyl esters composition. The individual peaks identification was done in GC-MS, based on the NIST inbuilt library search as shown in the Figure 5. The relative percentage of fatty acid esters were calculated from total molecular ion peaks obtained by computerized integrator and results obtained was compared with standard fatty methyl esters retention time.The biodiesel consists of methyl esters

of caprylic, lauric, arachidic, stearic, palmitic, margaric, nonadecylic, pentadecylic, behenic acids were identified based on the GC-MS spectral data. The GC-MS scan also indicated that the concentration of fatty acid ethyl ester in the biodiesel is 99.98%. Conversion of fatty acids into fatty acid methyl esters were achieved using a novel CaO heterogeneous catalyzed transesterification processs. The best percentage yield given by solid catalyst – calcium oxide 82.3%, compared with acid catalyst sulphuric acid. The comparison of physio-chemical properties of biodiesel with ASTM D0975, ASTM D6751 and EN 14214 standards are given in Table 1.

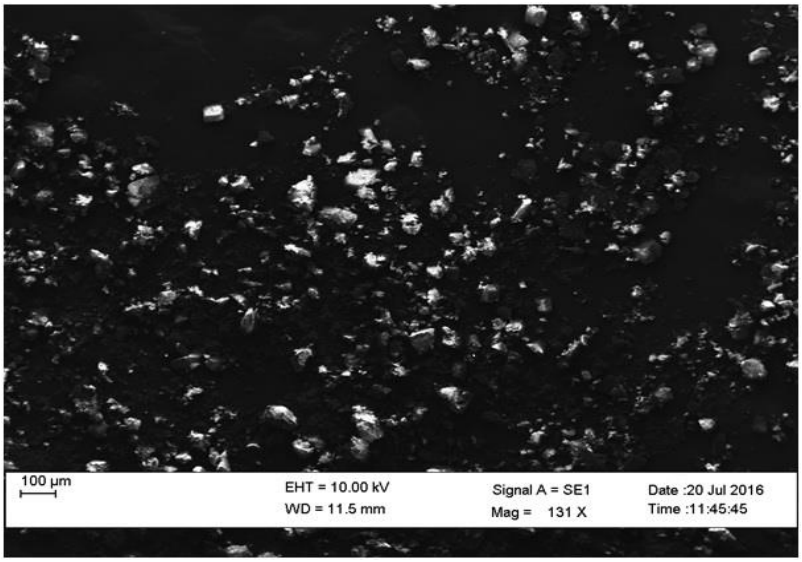

Figure 4. SEM image of calcium oxide synthesized from goat bone

Table 1. Physcio-chemical properties of biodiesel

Properties	Biodiesel	ASTM D0975	ASTM D6751	EN 14214
Density at 30ºC (g/cm^3)	0.88	0.876	0.875-0.90	0.86 to 0.90
Viscosity at 40ºC (mm^2/sec)	3.532	1.9 to 4.1	1.6 to 6	3.5 to 5
Specific gravity	0.815	0.850	0.88	---
Flash point (ºC)	114	60-80	100 to 170	>120
Pour point (ºC)	-11	-35 to -15	-15 to 16	---
Cloud point (ºC)	8	-15 to 5	-3 to 12	---
Cetane number	60	40 to 55	47 to 65	---
Acid value (mg KOH/g)	0.30	0.35	<0.8	<0.5
Iodine value (I_2/g)	86.3	---	---	<120
Ash content (%)	Nil	0.01	<0.02	<0.02
Water content (%)	Nil	0.02	0.03	<0.05

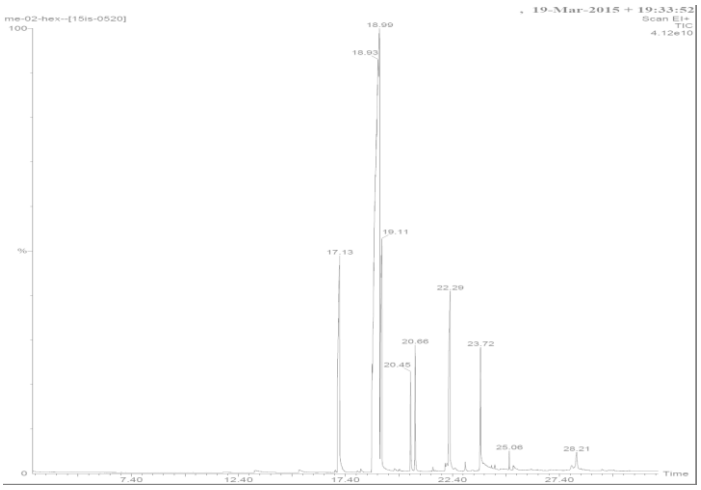

Figure 5. GC-MS Spectrum for biodiesel

4. Conclusion

A higher yield 82.3% was achieved for the production of biodiesel using a novel soil catalyst calcium oxide synthesized from goat bone and the results were compared with acid catalyst H_2SO_4 by monitoring the various parameters like molar ratio, quantity of catalyst, reaction time & methodology and temperature conditions. The synthesis of bio diesel was initiated by carrying out esterification process between oil and methanol in presence of Conc. Sulphuric acid as catalyst in proportional amount under regulated condition of temperature 60ºC. The obtained product was analysed by GC-MS chromatography and found to have a reasonable amount of fatty acid methyl ester, which indicates the formation of bio diesel. The physiochemical properties and performance analysis will be carried to check its characteristics and more improvisation will be enabled in future works.

Acknowledgement

The authors would like to express their deep gratitude to Vellore Institute of Technology, Jyothi Engineering College, Kingston Engineering College for providing the laboratory facilities and Universiti Malaysia Pahang for providing the financial support through research grant RDU190386.

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