

## Bio-oil production by pyrolysis of hibiscus cannabinus (Deccan Hemp) and pongamia pinnata (Karanja) seed cake and its characterization

Shivakumar A Patil<sup>1\*</sup> and Omprakash D Hebbal<sup>2</sup> and S R Hotti<sup>3</sup>

Research Scholar, Department of Mechanical Engineering, Poojya Doddappa Appa College of Engineering, Kalaburagi, Karnataka, India<sup>1</sup>

Professor (Emeritus), Department of Mechanical Engineering, Poojya Doddappa Appa College of Engineering, Kalaburagi, Karnataka, India<sup>2</sup>

Professor, Department of Automobile Engineering, Poojya Doddappa Appa College of Engineering, Kalaburagi, Karnataka, India<sup>3</sup>

Received: 14-June-2022; Revised: 08-January-2023; Accepted: 12-January-2023

©2023 Shivakumar A Patil et al. This is an open access article distributed under the Creative Commons Attribution (CC BY) License, which permits unrestricted use, distribution, and reproduction in any medium, provided the original work is properly cited.

### Abstract

*The problems associated with the rising fuel demand constitute a severe challenge to globalisation. To overcome this problem biofuels are being promoted using a variety of strategies. Non-edible oil seeds are utilized as feedstock for generating straight vegetable oils and used for generation of biodiesel. The leftover seed cake after oil removal is converted to usable energy by pyrolysis process. The primary aim of this exploration is, to analyse and characterize bio-oil elicited out of de-oiled seed cakes of Deccan hemp and Karanja by pyrolysis, and employ a simple cost-effective methodology for utilisation in diesel engines. The maximal output of bio-oil was 49.5% with a particle-size of 1.5 mm at an optimal temperature of 450°C and heating rate of 5°C per minute. Density, viscosity, flash-point, pour-point, cloud-point and calorific value were employed to characterize the improved bio-oil as specified by American society for testing and materials (ASTM) standards. The density (ASTM D1298) being 978 kg/m<sup>3</sup> and 960 kg/m<sup>3</sup>, viscosity (ASTM D445) 86.41 centistokes (cSt) and 58.11 cSt, flash-point (ASTM D93) 50°C and 58°C, pour-point (ASTM D97) 6°C and 6°C, cloud-point (ASTM D2500) 10°C and 12°C and calorific value (ASTM D4868) 22.44 MJ/kg and 32.57 MJ/kg for bio-oil obtained through de-oiled Deccan hemp seed cake (DHSC) and Karanja seed cake (KSC) respectively. The analysis found that, bio-oil brought out by the pyrolysis method is inept for use directly in diesel engines as fuel so it is upgraded, blended with diesel and consequently used as an alternative energy source.*

### Keywords

*Non edible seeds, Bio diesel, Seed cake, Bio-oil, Separation, Characterization, Upgradation.*

### 1.Introduction

Global economic development has a direct link to energy usage. The growth in energy usage implies a rise in gross domestic product (GDP). Crude oil will account for 31.23 percent of global energy consumption in 2020, compared to 6.83 percent for hydroelectricity, 4.30 percent for nuclear, 27.18 percent for coal, and 24.70 percent for natural gas. Crude oil prices climbed sharply and fluctuated in an unpredictable manner, causing the rate of economic growth to fluctuate. In a typical scenario, oil reserves will disappear over the next 40-50 years [1]. In any case, renewable energy is making strenuous efforts to replace fossil fuels and close the energy deficit.

Bio-fuels are one of the most promising renewable energy alternatives that are achieving popularity, since it can provide fuel that is on par with fossil oil [2].

Developing countries like India are experimenting with using non-edible seeds for producing biodiesel. In addition to biodiesel, other valuable products can be produced from seed cake which is left over after oil extraction, making the biodiesel program successful. In light of this, there is a need to develop a method for converting seed cakes into other useful products otherwise we may face problems like waste disposal and space utilisation.

Thermo-chemical, biological, and biochemical approaches are all utilized to extract energy out of

\* Author for correspondence

biomass [3, 4]. Regularly adopted thermo-chemical methods for generating energy from bio-mass are pyrolysis, combustion, gasification and hydrogenation. Pyrolysis is a popular approach for immediately converting bio-mass to valuable output such as liquid, gaseous, and solid bio-char [5].

Pyrolysis is a type of heat decomposition that transpires in inert or oxygen-free conditions. Water and oxygenated aliphatic and aromatic compounds make up the liquid phase of bio-oil or pyrolysis oil [6]. Bio-oils across a wide range of compositions, yet they all share the same characteristics. The moisture level ranges from 15 to 30 percent by weight, whereas the oxygen concentration is between 35 and 40 percent by weight. Bio-oil contains alcohols, esters, aldehydes, ketones, phenols and sugars as basic components [6, 7].

The eventual privilege is the transformation of biomass to a transportable liquid (bio-oil) using pyrolysis, which can be used as an alternate fuel. In spite of the advantages, challenges encountered in efficient utilization of bio-oils are poor fuel characteristics (presence of excess oxygen), chemical complexity and instability. The marketability of pyrolysis bio-oils could be articulated by upgrading bio-oil quality and stability. Extensive exploration is concentrated on the augmentation of catalytic hydrogenation to upgrade the bio-oil, but main deterrent is cost of hydrogen. Consequently, lean hydrogen or hydrogen free approach to upgrade the bio-oil is adorable [8, 9].

### 1.1 Motivation for the current investigation

The main motivation for this exploration is, since long more studies were focussed on utilizing the biomass into some useful alternate energy sources like converting it biomass into biodiesel or converting the same into biogas or direct use of biomass. Very few studies have been conducted on seed cake pyrolysis which is used for generation of bio-oil till date. Investigations on bio-oil as an alternate fuel by blending with available fossil fuel have yielded positive outcomes [10, 11].

### 1.2 Objective of current investigation

The elementary objective of the present investigation is to validate the suitability of bio-oil collected out of pyrolysis of Deccan hemp seed cake (DHSC) and Karanja seed cake (KSC) as a potential alternate fuel. To accomplish the objective, the physico-chemical characterization of bio-oil was accomplished in accordance with American society for testing and

materials (ASTM) standards to determine the viability of bio-oil as a diesel engine fuel since very little work is carried out using DHSC and KSC pyrolysis oil.

Karanja is a leguminous plant native to India, China, Japan, Malaysia, and Australia. The potential yield of Karanja is 900-9000 kg. According to published data, Karanja oil has a potential annual production of 135000 million tonnes, of which only 6% is consumed. During the extraction of oil from these seeds, approximately 70% of seed cake and 25% of oil is obtained, with a 5% loss [12].

Deccan hemp is a hibiscus family plant that grows in southern Asia. It's a 1.5–3.5 m tall herbaceous plants with a woody base that grows annually or biennially. The fruit is a two-centimetre-diameter capsule with several seeds within. The cake is widely accessible, especially in Maharashtra and Marathwada in western India [13]. Since there is huge potential for both DHSC and KSC is selected to extract bio-oil for the present work.

### 1.3 Overview of current investigation

Section 1 of the study highlights the backdrop, challenges encountered, motivating factors, and intent of the current investigation. Section 2 contains a comprehensive literature survey of related exploration on extraction and characterization of bio-oil. The precise physico-chemical characteristics of bio-oil collected through seed cake pyrolysis are disclosed in section 3. Section 4 presents the physico-chemical properties of bio-oil. It also offers in-depth insights on how bio-oil potentially be employed as an energy alternative. A brief description of the entire study is covered in section 5. Section 6 reflects the eventual outcome and scope of the present work.

## 2. Literature review

The study done by various researchers on extraction of bio-oil amongst different seed cakes, the characterization of extracted bio-oil and its use as a viable energy source is reviewed in the following literature survey.

“In order to produce bio-oil, Mulimani and Navindgi [14] experimented on the pyrolysis of madhuca indica (mahua) de-oiled seed cake. Particle-sizes ranging from 0.224mm to over 1.8mm have been pyrolyzed at temperatures between 350°C and 600°C. At 450°C and particle-sizes amidst 0.85mm and 1.25 mm, the highest output of bio-oil was 38.6 wt%. The raw bio-oil was found to have a high viscosity,

density, and moisture content. De-oiled seed cake mostly composed of aliphatic, aromatic and alcohol compounds, may act as a suitable choice for an energy source, according to the Fourier transformation infrared spectroscopy (FTIR) results. The emulsifier is employed to improve miscibility because the bio-oil is non miscible with petroleum products. Mahua bio-oil perhaps is utilized to power diesel engines since its physical qualities are comparable to those of diesel.

As a part of their study David and Kopac [15] employed fixed bed reactor to bring out bio-oil from rape seed and the investigation was brought out to work out the effects of pyrolysis temperatures through 400°C and 700°C, in periods of 50°C, at a heating rate of 20°C/min, with particle-size until 2mm (0.5mm; 0.5mm, 1.0-1.5mm; until 2mm and nitrogen (N<sub>2</sub>) gas discharge rates amidst 100 and 400 ml/min. At 500°C pyrolysis temperature, N<sub>2</sub> gas flow rate of 100 ml/min, at a heating rate of 20°C, employing particle-size of up to 0.5 mm the utmost yield of liquid fraction and bio-oil (44.5 wt% and 34.6 wt %, respectively) were recorded. Bio-oil brought about at 500°C has a gross calorific value of 33.13MJ/kg that is comparable to coal. Finally concluded that, bio-oil extracted may be used as fuel and is comparable to fuel of transportation grade.

Using a fixed-bed batch type reactor, Rajamohan and Kasimani [16] explored the pyrolysis about calophyllum inophyllum (CI) de-oiled seed cake to bring out bio-oil. Two samples of bio-oil were investigated one being crude (CI) bio-oil, and another crude bio-oil mixed with 10% methanol (CI-M). The findings of the compositional study made it significantly evident that CI-M oil had lower carbon and higher oxygen than bio-oil from 'CI' cake. Additionally, it appeared that neither bio-oil sample had any sulphur. On addition of methanol, the kinematic viscosity and density were lowered from 12.2 to 3.6 Cst, 1.17 to 1.08 gm/cm<sup>3</sup>. Finally, it was culminated that CI-M bio-oil is more thermally stable than CI bio-oil.

Alagu and Sundaram [17] investigated catalytic along with thermal pyrolysis of neem seed in a slow fixed-bed pyrolysis reactor to obtain bio-oil. Highest yield of oil attained was 55wt% and by catalytic pyrolysis 60 wt% using both Al<sub>2</sub>O<sub>3</sub> and K<sub>2</sub>CO<sub>3</sub> catalysts. Higher calorific and pH values of 23.837 MJ/kg and 5.96 respectively were perceived in pyrolytic oil accomplished by catalytic pyrolysis employing Al<sub>2</sub>O<sub>3</sub>

catalyst. Finally, it was concluded that 'neem-seed pyrolytic oil' is a possible alternate energy source.

Catalytic fast pyrolysis of pongamia residual-cake (PRC) was studied by Masawat et al. [18] and discovered that PRC suffered significant heat deterioration between 150 and 550°C. They performed this to investigate the kinetics of PRC pyrolysis from thermo gravimetric analysis in the stretch of 30°C–900°C at various heating amount in an environment of N<sub>2</sub>. The best method for converting O-compounds to hydrocarbon (HC) was to use 5 wt% 'Ni/AC' at a 1:5PRC: catalyst weight proportion. Nearly all O-compounds were reduced in comparison to the non-catalytic pyrolysis, and under these circumstances, HC yields increased noticeably. These findings suggest that it is feasible to utilize a sizable proportion of PRC waste from biodiesel production as a substitute energy source.

Reshad et al. [19] investigated the preparation of bio-fuels utilizing a semi-batch reactor to thermally pyrolyze rubber-seed cake (RSC) and waste polystyrene (WPS). The thermo gravimetric analysis contour of the RSC specimen demonstrated that the effective pyrolysis of RSC transpired between 200°C and 620°C. It was noticed that as heating amount increased from 10°C/min to 20°C/min, at the beginning the output of liquid product boosted through 47.8wt % to 48.25wt%, but subsequently declined to 45.47wt% at heating amount of 40°C/min. Analysis of the calorific values of RSC bio-oil samples collected under various pyrolysis settings revealed that the calorific value was higher than 32.72MJ/kg at increased pyrolysis temperatures of 500°C, in comparison to transportation fuel. In RSC pyrolytic bio-oil, phenolic, aromatic, and N<sub>2</sub> comprising component concentrations were found to be relatively higher.

Thermo-chemical conversion of Aegle marmelos (AM) de-oiled cake was explored by Paramasivam [20] in a fixed-bed pyrolysis reactor at a temperature of 600°C and a heating amount of 30°C/min. The transit of bio-oil is safe since, diesel's flash point (64°C) and AM seedcake oil's (69°C) were close to one another. The calorific value of AM seed cake was found to be 41.35 MJ/kg, comparable to diesel's calorific value of 45.4 MJ/kg. It was investigated that the high viscosity of bio-oil has an impact on fuel spray and atomization attributes during combustion, which could be rectified through bio-oil up-gradation. Bio-oil made from AM seed cake can be upgraded

after extraction and can be used as an alternate energy source.

Dhanavath et al. [21] explored slow pyrolysis of neem press seed cake (NPSC) using fixed-bed batch reactor. The ideal circumstances were used to conduct the slow pyrolysis of NPSC: 512.5°C, a confinement time of 60 min, and a discharge rate of 0.5 liters per minute (LPM) of N<sub>2</sub>. It was discovered that the pyrolysis temperature, confinement period, and N<sub>2</sub> flow rate all had a considerable impact on the output of liquid and char. With retention duration of 60 minutes and a N<sub>2</sub> flow rate of 0.5 LPM, the highest liquid yield of 52.1% was achieved at 512.5°C. At 450°C, a confinement period of 30 minutes, with N<sub>2</sub> outflow rate of 0.3l/min, highest char output of 42.92 % was achieved. The number of O-H, C-H, C=O, -C-H and C-O groups shown by the FTIR data illustrates that bio-oil can be suitably made use as a source of energy.

Potentiality of de-oiled seed cakes of silk cotton (SC) and African star apple (ASA) as origin of bio-oil was examined by Sokoto et al. [22] employing slow-pyrolysis. The trial was conducted in a N<sub>2</sub> environment at temperatures between 300°C and 450°C with a heating amount of 10°C per minute. SC (33.1%) and ASA (48.3%) both produced highest amounts of bio-oil at 400°C. Bio-char output for ASA seed cake fell from 300°C to 450°C (38 - 28 %), possibly due to more extensive primary decomposition of the biomass samples. With a least 'bio-char' production of 32% at 450°C, SC seed cake also showed a similar trend. SC seed cake bio-oil displayed a larger amplitude FTIR absorption point of 1660 cm<sup>-1</sup> (C = N stretching). At 400°C 72% of SC seed cake feed-stock transformed on-to bio-oil and gaseous products, compared to 68% at same temperature. Finally, it was concluded that bio-oils generated have the potential to be up-graded to synthetic fuel and used as a source of bio-based compounds.

Singh et al. [23] explored the possibility of thermal cracking of Karanja seed (de-oiled) cake utilising electrically heated fluidized bed type pyrolysis reactor. For pyrolysis N<sub>2</sub> gas of analytical reagent (AR) grade was employed along with dehydrating agent's zeolite and sodium sulphate. Temperature ranged from 450°C to 550°C with a 50°C difference, with an 8 LPM sweep gas velocity, the particle size intervals between 0.5 and 0.99mm for the analysis. Under optimal conditions, bio-oil output was 65.56wt% at 500°C, with particles amidst 0.5 and 99

mm in size, and gas flow rate of 8 LPM. As the N<sub>2</sub> flow rate was increased from 6 to 8 LPM the bio-oil output attained a maximum of 48 wt%. The bio-oil output is significantly altered by particle size. The output rose from 59.4 to 65.46 wt% for particle sizes of 0.5mm to 0.99mm. Finally, it was concluded that with up-gradation, bio-oil may be deemed fit for modern engines.

In order to produce liquid oil by co-pyrolysis, Raguraman et al. [24] studied the usage of neem de-oiled cake (NDC) along with WPS in 1:2 proportions adopting a lab-scale fixed-bed reactor for co-pyrolysis. Temperature of 550°C was maintained in the reactor. When employing a feed proportion of 1:2 (NDC: WPS) at a 550°C reactor temperature, it was found that the maximal pyrolysis oil production was 73.4 wt%. Performance analysis was done by blending with diesel. Finally, it was concluded that, liquid oil made from WPS and NDC may be employed as a viable fossil fuel additive.

According to Stas et al. [25] catalytic pyrolysis can greatly improve the composition of bio-oil. To improve the pyrolysis vapour prior to the condensing, the catalyst can be used either directly in a reactor with a fluidized bed or in a secondary reactor with a fixed bed. Enhancing bio-oil through a hydro treatment procedure enables double-bound saturation and better hydro oxygenation for advanced bio-oil usage. Hydro treatment is possible at up to 20 MPa of hydrogen pressure and temperatures as high as 400°C. Noble metals, transition metals, or sulphide transition metals are the commonly used catalysts. The hydro-treated bio-oil products will also be referred to as hydro treated bio-oils (HBOs)".

CI (Beauty leaf tree) oil seed press cake was researched by Ashwath et al. [26] in order to optimize the pyrolysis conditions that would optimize energy recovery. The conduct of pyrolysis products at different temperatures and residence durations was studied using response surface methodology (RSM). According to RSM models, the energy content of bio-char is best at a pyrolysis temperature of 425°C and a 75-minute exposure period with a heating value of 2.5 MJ/kg, which is practically on par with coal. 56.6% of the energy can now be recovered from bio-char, and 20.6% from bio-oil. Finally, this investigation arrived at the conclusion that the waste press cake still contained 61.7% of the energy of the entire seed. In order to increase the quantity of bio-diesel, the press cake's remaining energy should be recovered by the pyrolysis process.

Using a fixed bed reactor, Shah et al. [27] investigated the properties of pyrolytic bio-oil made from walnut shells. Different temperatures, particle sizes, heating rates, and gas flow rates were used in the pyrolysis experiments. It was established that the highest amounts of bio-oil, bio-char, and gas, measured in weight percent, were produced at temperatures of 550°C, 375°C, and 750°C, respectively, at a heating rate of 0.33K/s and particle size 0.5-1.5 mm. The chemical analysis of bio-oils found that oxygenated molecules predominate in the bio-oil content. Based on the above-mentioned conclusions, it was revealed that bio-oil can be treated as a potential fuel and may replace petroleum fuels. It was further emphasized that in order to replace fossil fuels with renewable fuels, bio-refinery techniques and catalytic upgrading should be effectively established.

Madhu et al. [28] looked at individual and co-pyrolysis for the generation, of high-grade liquid oil using waste thermocol (WT) and pressed neem oil cake (NOC) by employing a stainless-steel tubular reactor for pyrolysis process. The active pyrolysis temperature span for NOC was 350°C-550°C, for temperature intervals of 50°C. The maximum oil output, 46.6 wt%, was seen at 500°C. As the heating percentage was raised from 10 to 40°C/min, the NOC results revealed a decrease in bio-char output from 31.9wt% to 28.4wt%. The output of liquid oil rises from 48.1 to 49.3 wt% as the heating amount is increased from 10 to 20°C/min. The WT pyrolysis oil has a heating value that is quite comparable to diesel fuel (42.0 MJ/kg). Maximum hydrocarbon content indicates that the liquid oil may be used as a feedstock for industrial-chemicals and as a fuel additive.

De-oiled seed cakes are being investigated more extensively for the generation of bio-oil and bio-char; according to Rajpoot et al. [29] the examination of de-oiled seed cakes' proximate, ultimate, biochemical, and calorific values was summarized. Researchers have finally come to the conclusion that it is still difficult to optimize the process parameters for pyrolysis of de-oiled seed cakes. The study confirmed that the generation of bio-oil and bio-char was significantly impacted by the heterogeneity of de-oiled seed cakes made from edible and non-edible oil seeds. It was found that the majority of investigators employed fixed-bed and semi-batch reactors. Reactors with plasma and microwave beds have a lot of potential and need to be investigated.

The bio char obtained by pyrolysis of de-oiled seed cakes can be explored for energy storage.

The production of bio-oil from biomass derived from non-edible jojoba seed was studied by Singh et al. [30] using thermo-gravimetric analysis (TGA), proximal and ultimate analysis, gas chromatography-mass spectroscopy (GCMS), and FTIR methods, the generated bio-oil was characterized, and its viability as fuel option was evaluated. According to the investigation, a reactor temperature of 200–350°C resulted in the maximum bio-oil production of 22 percent and had a 48 percent yield of bio-char. The temperature range of the biomass pyrolytic zone was determined to be 200–520 °C. Bio-oil with lower oxygen content tends to have higher heating values. The bio-oils had greater hydrogen to carbon (H/C) ratio (1.85), smaller oxygen to carbon (O/C) ratio (0.38) therefore they could be used in engine applications in lieu of petroleum products. The average bio-oil output was approximately 13 percent due to increased losses in the optimal transfer of heat from the reactor, a shortage of catalysts, and a reduced dispersion of solar radiation. It was reported that the temperature range for biomass deterioration was between 212 and 511 °C. By using FTIR and GCMS, it was found that functional groups based on ester, alkane, alkyne, and alkene were available. The output of bio-oil can be enhanced with a superior reactor mechanism and less heat loss.

The greenhouse vegetable output that generates significant amounts of garbage was the subject of research by Laouge et al. [31] in which the effects of pyrolysis temperature, catalyst type, and catalyst quantity on the quality of bio-oil produced by fast pyrolysis were investigated. Cerium oxide, zinc oxide, zirconium oxide, and Lewis's acid catalysts were used in fast pyrolysis trials in a drop-tube reactor system at pyrolysis temperatures of 450, 500 and 550°C. It was observed that the bio-char yield increased at low pyrolysis temperature, whereas gas yield increased with temperature and amount of catalyst and bio-oil yield varied with type of catalyst. The investigation came to the conclusion that the yield of bio-oil improved with temperature up to the optimal temperature before falling with rising temperature. The blend of bio-oil made from greenhouse vegetable wastes is beneficial in the development of chemicals and potentially viable fuel. Adelawon et al. [32] used a fixed-bed reactor to compare the products generated by fast, slow, and flash pyrolysis of waste maize-cob biomass. By analyzing the individual and combined impacts of

pyrolysis temperature, biomass particle size, and residence time on the yield of product, the research sought to identify the optimal pyrolysis variables that would yield the best possible yield of products from maize cob. Slow, fast, and flash pyrolysis delivered 34.10, 43.13, and 46.25 percent bio-oil, respectively, at a particle size of 0.5mm and a temperature of 600°C. With fast and flash pyrolysis, the bio-oil output rose by 26.5 and 35.6 percent in contrast to slow pyrolysis. The physical properties of the bio-fuel produced from maize cobs met ASTM's basic standards. It is clear from this that maize-cob biomass waste has higher potential as a biomass feedstock for the production of bio-energy.”

Based on the extensive literature review on catalytic pyrolysis, non-catalytic pyrolysis and various pyrolysis reactors, a fixed bed pyrolysis reactor has been selected to carry out the pyrolysis of biomass. The locally accessible biomass, KSC and DHSC were chosen since they have received very little attention. Gravity separation is used to separate the pyrolytic bio-oil into heavier and lighter bio-oil. The lighter oil is upgraded by heating to remove moisture and studied to identify its feasibility as an alternate source of energy in diesel engines.

### 3. Materials and methods

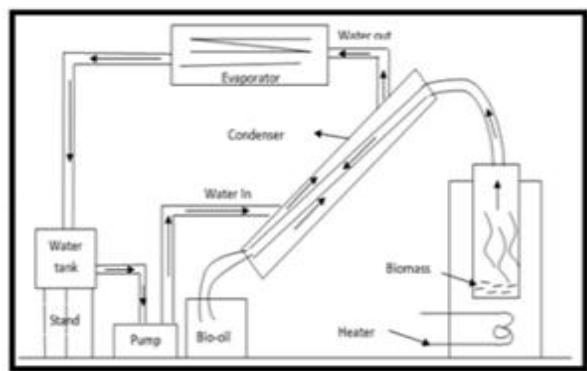
#### 3.1 Characterization of seed cake

The feedstock of non-edible seeds of Deccan hemp and Karanja were bought from the local market. The seeds were cleaned and oil was extracted from the seed and the leftover seed cake samples were collected. The seed cake was in chips and granular shaped. This seed cake was sun dried and was powdered using a household mixer. Ultimate, proximate investigation and calorific value of DHSC and KSC were ascertained as per ASTM standards.

#### 3.2 Extraction of oil using batch type reactor

There are many types of pyrolysis plants, but they can be broadly divided into three types, continuous, semi-continuous and batch type plant. Raw materials are given from one side and carbon is extracted from the other in continuous type. It is extremely expensive for modest investors. The feedstock is fed into the reactor and treated in semi-continuous method. Carbon is removed without being cooled in this process. These are high-volume reactors with a daily processing capacity of 2 to 4 tonnes. Large-scale reactors haven't proven very successful in recent years. Raw material is put into a batch type reactor, and the pyrolysis operation is accomplished, with the carbon removed only after cooling. These reactors are both inexpensive and easy to use. Because there are fewer parts, there is less power consumption and less maintenance. These machines are both cost-effective and friendly to the environment. The batch type reactor is used in this study since it offers various advantages [33].

For pyrolysis of seed cake samples, a batch type reactor present in the laboratory has been considered. *Figure 1 (a)* depicts a diagrammatic flow diagram of the reactor, whereas *Figure 1 (b)* depicts a picture of a pyrolytic reactor in operation. The pyrolysis operation is brought out using a reactor with a proportional-integral-derivative (PID) controller for temperature regulation. The reactor is made of mild steel, insulated with refractory to reduce heat loss. The reactor is 56cm long with an internal diameter of 21cm and 56cm external diameter. The condenser is 140 cm long, with an inside pipe diameter of 1.905cm and outside pipe diameter of 3.81cm. Inner pipe is constructed from galvanized iron (GI), while the outer one is made of copper.



(a)



(b)

**Figure 1** a) Flow diagram of batch type reactor, b) Photographic view of test setup



Two kilograms of ground, dried seed cake with a specific particle-size was ingested into the reactor in the course of experimentation and the reactor was securely closed using gasket to ascertain that the system was leakproof. A 3-kW nichrome coil is employed to heat the reactor, and a J-type thermocouple, with a range of  $-99^{\circ}\text{C}$  to  $870^{\circ}\text{C}$  is used to compute feedstock temperature. Reaction period is till the temperature hits  $450^{\circ}\text{C}$ , which is the ideal temperature for maximizing bio-oil output (as got from TGA analysis of seed cake). The condenser, in which water is pumped by a pump, continually condenses the reaction's vapours. In a liquid collection flask that is a part of the experimental setup, the condensed liquid, which is bio-oil, is continuously gathered. To extract the highest production of bio-oil, it is heated for an additional 30 minutes after reaching  $450^{\circ}\text{C}$ . The furnace's electricity is then turned off, and the experimental setup is given time to cool. The reactor setup is opened once it has cooled to gather the bio-char. The same methodology is adopted to examine the output of bio-oil and bio-char for varied particle-sizes. The yield of bio-oil and bio-char is computed on a weight basis corresponding to weight of biomass fed; and the output of non-condensing gas is got by difference.

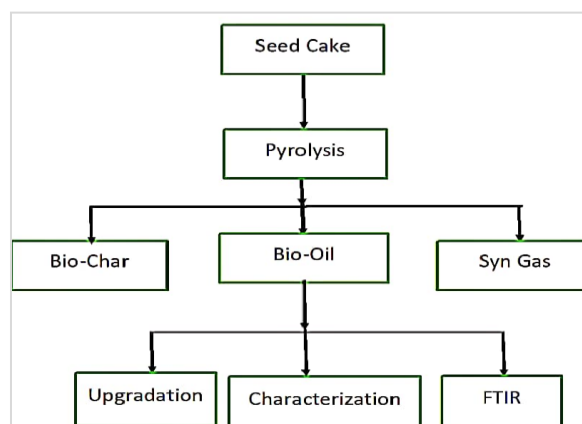
The bio-mass feedstock as well as the operating condition influences the output and proportion of bio-oil [34, 35]. Bio-oil output varies with reaction temperature and biomass feed size parameters [36, –38]. Primary and secondary reactions occur in the biomass, and the biomass's key constituents (cellulose, hemicellulose, and lignin) are broken down in accordance with the main reactions, giving primary and intermediate chemicals. The intermediate products undergo subsequent reactions depending upon the operational status and biomass composition [39, 40].

### 3.3 Test conditions

The pyrolysis of DHSC and KSC were put through at various temperatures of 400, 425, 450, 475 and  $500^{\circ}\text{C}$  to analyze temperature consequence on product dissemination. Further pyrolysis conclusions were established at optimum temperature for three distinct particle sizes 0.6, 1.5 and 2.36 mm to review the effect of particle- size.

### 3.4 Up-gradation, characterization and FTIR of bio-oil

The flow chart for the pyrolysis of seed cake is shown in *Figure 2*. Following the oil extraction process from the Deccan hemp and Karanja seeds, the seed cake samples of DHSC and KSC were collected. This cake was sun dried before being ground and sieved to figure out the desired particle-size. A specific particle-size of ground seed cake was fed into the pyrolysis reactor, and the pyrolysis process was carried out at a predetermined temperature. The amount of collected bio-oil and bio-char is measured after the trial was completed. The bio-oil is also upgraded, and characterized in accordance with standards.



**Figure 2** Flow chart of pyrolysis process of seed cake

#### 3.4.1 Up-gradation of bio-oil

The untreated bio-oil collected from a reactor is separated by gravity separation into two layers due to the difference in density. The fuel layer is an upper dense layer, whereas the aqueous layer is a lowest heavy layer. Perhaps the upper layer may be utilised as a fuel substitute, whereas the base layer contains a blend of water and a bit of organic liquid components, typically 'carbohydrate'-derived compounds. After gravity separation, upper dense layer was heated at temperatures varying from 100 to  $110^{\circ}\text{C}$  to remove any leftover moisture in bio-oil.

#### 3.4.2 Characterization of bio-oil

Up-graded bio-oil was assessed for physical parameters like density, viscosity, flash-point, pour-point, cloud-point, and calorific values, as well as ultimate and FTIR analysis of DHSC and KSC bio-oils using ASTM methods [41, 42].

##### 3.4.2.1 Fuel properties

**Density (ASTM D1298)**

The density is the mass of the fluid to its volume. The density is measured using a hydrometer. Five replicates were collected, and the results are averaged out.

**Viscosity (ASTM D445)**

Fluid viscosity is the amount of its resistance to flow. The viscosity is measured by the Brookfield viscometer model, version 1.0 with cylindrical spindle at steady speed of 60rpm.

**Flash point (ASTM D93)**

The lowest temperature at which, fluid vapours will make the combustible mixture with air is termed as flash point. Pensky-Martens closed cup apparatus was utilized for evaluating the flash point of bio-oil. The test cup fitted with a cover is filled with bio-oil. Bio-oil is heated; agitated and a flame is directed toward the cup at periodic time besides concurrent disruption of agitation till a flash propagates across an inner portion of the cup. This temperature is the flash point of bio-oil.

**Pour point (ASTM D97)**

The sample of bio-oil is enclosed in the test-jar in cold bath which is at 9°C and for each ensuing 3°C the

test-jar is taken out and lopsided to examine for surface motion. If sample does not flow when lopsided, then the jar is kept horizontal for 5 seconds. Further, if oil fails to flow, 3°C is added to the measured temperature and temperature recorded is oil pour point.

**Cloud point (ASTM D2500)**

Bio-oil sample is put in the test-jar filled around halfway. The jar is enclosed with a cork that holds the test thermometer. The thermometer bulb is located at the jar bottom. The whole test setup is later positioned in a cooling bath maintained at constant temperature. The sample is moved out and examined for cloud and then swiftly reinstated at every 1°C. The temperature at which the wax crystals show up is taken as the cloud point

**Calorific value (ASTM D4868)**

The calorific value, also known as heating value is total energy content in the form of heat when a substance is burned completely with air or oxygen. The bio-oil calorific value is found by employing bomb calorimeter. Comparison of fuel qualities of DHSC and KSC bio-oils to those of different biomass bio-oils is shown in *Table 1*.

**Table 1** Comparison of properties of pyrolytic bio-oil of DHSC and KSC with other pyrolytic oils

Properties	DHSC bio-oil (Present work)	KSC bio-oil (Present work)	AM bio-oil [20]	Almond shell bio-oil [43]	CI bio-oil [44]	Paper walnut shell bio-oil [27]
Density (kg/m <sup>3</sup> )	1030	1025	1055	1100	1190	1025
Flash point (°C)	50	58	69	110	96	121
Pour point (°C)	6	6	2.4	-15	10.7	20
Viscosity (cSt)	86.41	58.11	4.82	1.68	1.86	1.27
Water content(wt%)	45.10	20.80	23.60	22.30	21.70	28.50

The pyrolysis bio-oil produced by DHSC and KSC is blackish brown in colour and has a pungent smoky odour. Although somewhat heavier compared to water, density is greater than fossil fuel. The pyrolysis oil's high-water content and heavy molecule contamination are the causes of its high density. Because of its increased density, bio-oil has a high oxygen content [45]. DHSC and KSC bio-oils have lower flash points than other bio-oils, as seen in the *Table 1*, at 50 and 58°C, respectively. High vapour pressure and boiling point of volatile matter are the reasons for lower flash point [46]. For the majority of applications, the pour point represents the least temperature where upon it is useful. The DHSC and KSC bio-oil no longer flows below 6°C because it has either crystallised or become more viscous.

DHSC and KSC bio-oils have high viscosities compared to other bio-oils with 86.41 and 58.11 centistokes (cSt) at 40°C, respectively. Poor atomization, partial combustion, and fouling of

lubricating oil with unburned fuel are all caused by high viscosity. Therefore, using straight bio-oil in diesel engines is not recommended. It might be used by blending bio-oil with diesel which lowers the viscosity. The water content for DHSC and KSC bio-oil is 45.10 and 20.80 wt%. KSC bio-oil has comparable moisture content to other bio-oils. Owing to the absorptive character of biomass and the dissolvability of bio-oil with water, presence of water in bio-oil is ought to be present. Water reduces the heating value while potentially causing phase separation.

**3.4.3FTIR analysis of bio-oil**

For determining organic composition, polymer and inorganic materials FTIR analysis is used. This technology scans test materials and the chemical characteristics are examined using infrared light.

The FTIR method can be used to detect if a material contains functional groups. FTIR can identify the components in a mixture and assess the sample's quality. Chemical bonds, regardless of the structure



of the remaining molecules, expand, contract, and assimilate infrared radiations in a precise wavelength stretch in response to infrared light interactions [47].

Computation of the seed cake's functional group composition was established employing Perkin Elmer Model FTIR C 108079 Fourier transform infrared spectroscopy. The sample's infrared spectrum was measured thru 400 and 4000  $\text{cm}^{-1}$ .

## 4.Results

### 4.1Characterization of seed cake

Moisture, volatile matter and ash contents of seed cakes were obtained as per ASTM D3172 ASTM standard and the fixed carbon content was obtained by difference. The ultimate analysis of seed cakes was carried using ASTM D3176 ASTM standard to know weight percentages of carbon, hydrogen,  $\text{N}_2$ , sulphur as well as oxygen. Calorific value of seed cake was found using ASTM D5865 ASTM standard. In order to select a range of pyrolysis temperature,

the TGA of seed cakes was accomplished. The start and end temperatures were set at 20°C to 620°C at a heating rate of 20°C per minute.

*Table 2* compares the outcomes of proximate analysis of DHSC and KSC. As compared to other biomass sources, the volatile matter content is higher for both DHSC and KSC. High volatile matter existed in biomass makes it a perfect choice for use as a fuel.

*Table 3* compares the outcomes of ultimate analysis of DHSC and KSC. The sulphur concentration of the DHSC and KSC samples is lower; the final product derived from the low-sulphur feedstock is intended to be utilized as high-quality fuel for adoption in internal combustion (IC) engines.

*Table 4* compares the outcomes of calorific value of both DHSC and KSC. The data in the table above shows that seed cake has great potential as a feedstock in the bio-fuel production.

**Table 2** Comparison of results of proximate analysis

Seed cake sample	Moisture -content wt%	Volatile -matter wt%	Ash-content wt%	Fixed-carbon wt%
Deccan hemp	09.41	79.73	04.77	06.09
Karanja	08.65	83.64	02.25	05.46

**Table 3** Comparison of results of ultimate analysis

Seed cake sample	Carbon wt%	Hydrogen wt%	$\text{N}_2$ wt%	Sulphur wt%	Oxygen wt%
Deccan hemp	49.36	03.38	03.66	00.05	28.65
Karanja	51.00	03.69	03.78	00.03	29.42

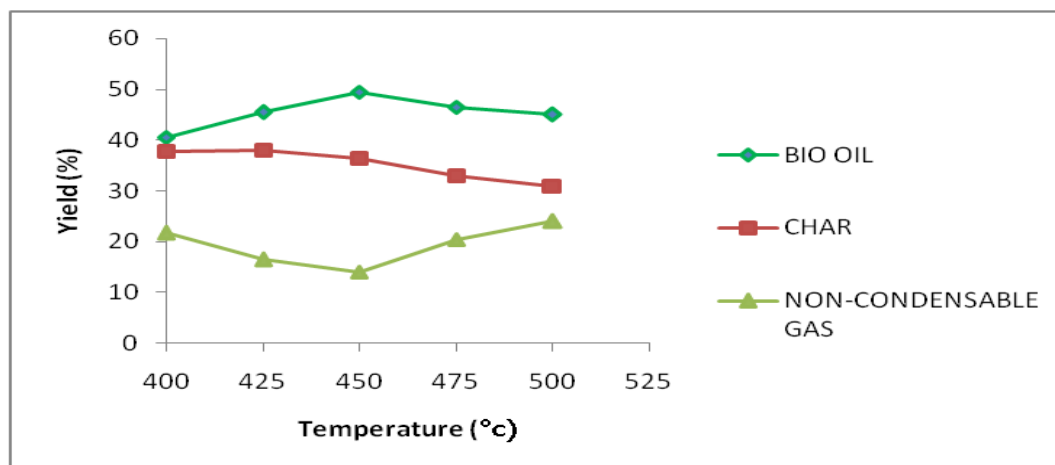
**Table 4** Comparison of calorific value

Seed cake sample	Calorific value (MJ/kg)
Deccan hemp	17.89
Karanja	18.27

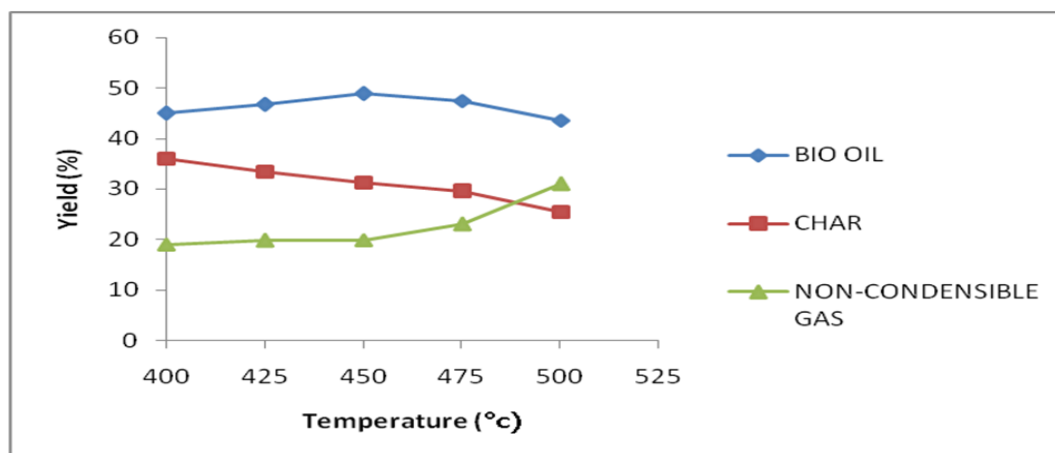
### 4.2Effect of temperature on yield of bio-oil

*Figure 3* manifests the yield of pyrolysis outcomes for various temperatures from 400°C to 500°C for DHSC. With rising temperature, liquid product also increased and peaked at 49.5% at 450°C, later reduced with further advance in temperature. Bio-char output declined while pyrolysis temperature was raised. At above-optimal temperatures, bio-oil output is reduced due to secondary cracking and gasification, yielding gaseous products [48, 49]. Similar patterns were noticed for maize-stalk [50] and de-oiled seed cake of *Jatropha-curcas* [48].

*Figure 4* depicts the output of pyrolysis material for various temperatures from 400°C to 500°C for KSC. With rising temperature, liquid product also increased and peaked at 48.85% at 450°C, later reduced with further advance in temperature. Output of bio-char declined on increasing pyrolysis temperature. It may be culminated that for temperatures greater than the optimal, the bio-oil output plummets because of gasification and secondary crumbling reactions, favoring gaseous substances [48, 49]. Similar patterns were noticed for maize- stalk [50] and de-oiled seed cake of *Jatropha-curcas* [48].



**Figure 3** Yield of pyrolysis products for deccan hemp seed cake at different temperatures

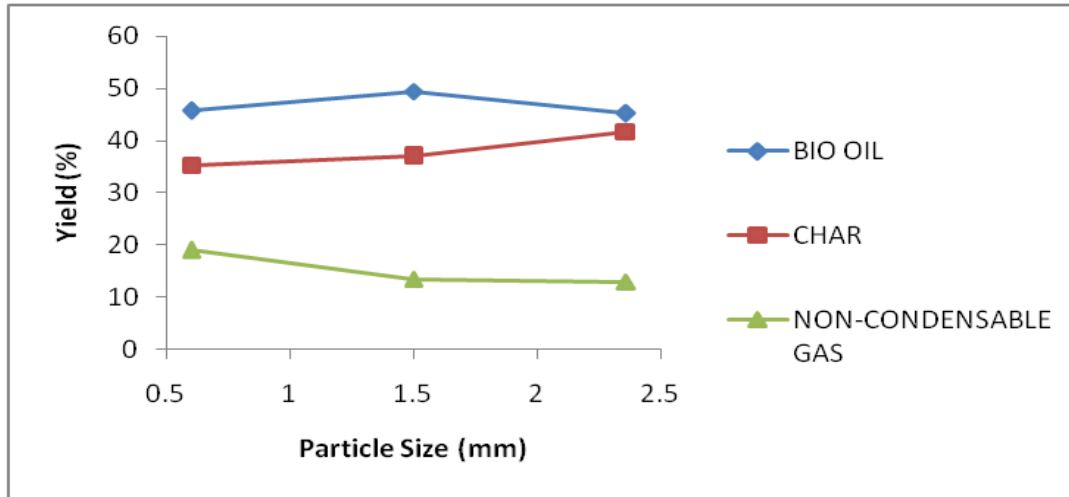


**Figure 4** Yield of pyrolysis products for Karanja seed cake at different temperatures

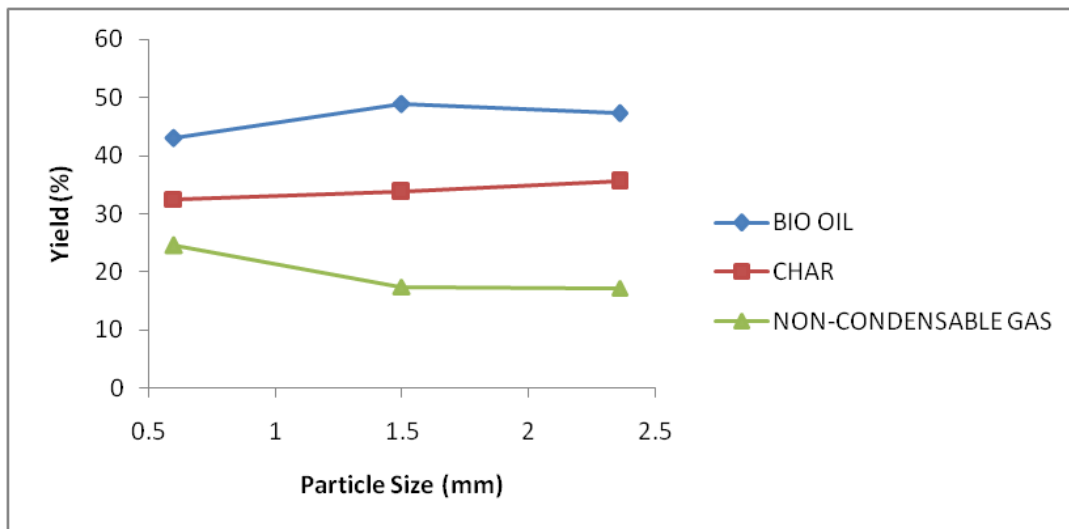
#### 4.3 Effect of particle-size on yield of bio-oil

Distribution of product output is strongly dependent on particle size, which requires a substantially compatible temperature distribution within the reactor. Small bio-mass particle-size was demanded in the pyrolysis process to enable quick heating and effective de-volatilization [51, 52]. *Figure 5* depicts the pyrolysis product yield for various particle sizes varying from 0.6 mm to 2.36 mm for DHSC. The oil yield was up to 49.5 percent for particle size of 1.5mm. As particle size grew, so did the yield of bio-char. Enhanced particle-size initiates a temperature acclivity, that limits the heat-transfer rate, will increase the reaction accomplishment time, favoring secondary reactions, and lowering bio-oil output [53].

These findings were supported by bearings in the literature [54–56] addressing the effect of particle-size in pyrolysis. *Figure 6* depicts the pyrolysis product yield for various particle sizes varying from 0.6 mm to 2.36 mm for KSC. The oil yield was up to 48.85 percent for particles with a particle-size of 1.5mm. As the particle-size grew, so did the yield of bio-char. Enhanced particle-size initiates a temperature gradient, that limits the heat transfer rate, will increase reaction completion time, favoring secondary reactions, and lowering bio-oil output [53]. These findings were supported by bearings in the literature [54–56] addressing the effect of particle-size in pyrolysis.



**Figure 5** Yield of pyrolysis products of Deccan hemp seed cake for different particle size



**Figure 6** Yield of pyrolysis products of Karanja seed cake for different particle size

#### 4.4 Upgradation of bio-oil for utilization as a fuel in diesel engine

Bio-oil recovered appeared blackish brown in the shade with dingy smell. The *Figure 7* depicts the two phases of raw bio-oil. Topmost layer is bio-oil and bottom aqueous phase, separated by gravity separation later. The aqueous phase has not only lower molecular weight aldehydes but also phenolic compounds [57]. Therefore, the pyrolytic oil got by pyrolysis of DHSC and KSC is beneficial from a chemical and fuel point of view.



**Figure 7** Gravity separation: bio-oil and aqueous-phase

#### 4.5 Characterization of the bio-oil for utilization as a fuel in diesel engine

Table 5 depicts the comparison of the fuel attributes for upgraded bio-oil. Physico-chemical attributes of raw bio-oil disagree considerably with base diesel oil. Density of raw bio-oil ( $1030 \text{ kg/m}^3$ ) is significantly greater relative to diesel fuel ( $821 \text{ kg/m}^3$ ). Higher density of fuel exerts grievously on spray-attributes of diesel engines leading to the impoverished mixing of air and fuel. The crude bio-oil contains approximately 40% moisture, which is undesirable for diesel engine applications. The enhanced bio-oil density was reduced to  $978 \text{ kg/m}^3$  for DHSC and  $960 \text{ kg/m}^3$  for KSC. Viscosity of bio-oil seemed to be very high ( $86.41 \text{ cSt}$ ) for DHSC and ( $58.11 \text{ cSt}$ ) for KSC compared to diesel fuel ( $2.6 \text{ cSt}$ ). The most optimal method to reduce the viscosity is intended to mix up bio-oil with diesel. Flash point of bio-oil is ( $50^\circ\text{C}$  for DHSC and  $58^\circ\text{C}$  for KSC) more or less same as compared to diesel ( $55\text{--}66^\circ\text{C}$ ). This quality is critical since it is a safety feature that specifies the minimum temperature when air-vapour concoction can ignite. The pour and cloud point of the bio-oil are

overly high in relation to diesel fuel. Pour point and cloud point depressants can be mixed with bio-oil to improve pour and cloud point. The calorific value of bio-oil was less ( $22.44$  for DHSC and  $32.57 \text{ MJ/Kg}$ ) likened to diesel ( $42.5 \text{ MJ/Kg}$ ).

Table 6 below reveals an ultimate analysis for upgraded bio-oil. Analysis of DHSC bio-oil revealed that it had 65.74 wt% carbon, 9.69 wt% hydrogen, and 4.16 wt%  $\text{N}_2$ , while KSC bio-oil contained 69.98 wt% carbon, 9.74 wt% hydrogen, 4.13 wt %, and the rest was oxygen. Sulphur was not found. When compared to other bio-oils, DHSC has a lower oxygen content of 20.41 wt% and 16.15 wt%. The typical oxygen contentment of bio-oil ranges from 35 to 40 wt% [58]. The higher the percentage of oxygenate, the lower the energy density, which is only half that of traditional fossil fuels [59]. Because bio-oil has no sulphur, it does not now no longer produce sulphur oxides in the surroundings when used as an alternative fuel [60].

**Table 5** Comparison of fuel properties of upgraded bio-oil with diesel

Properties (units)	Diesel (ASTM Standards)	Upgraded DHSC bio-oil	Upgraded KSC bio-oil
Density ( $\text{kg/m}^3$ )	821.5	978	960
Viscosity (cSt)	2.6@40°C	86.41	58.11
Flash- point ( $^\circ\text{C}$ )	55 – 66	50	58
Pour -Point ( $^\circ\text{C}$ )	-18 to -48	6	6
Cloud- Point ( $^\circ\text{C}$ )	-40	10	12
Calorific Value (MJ/kg)	42.5	22.44	32.57

**Table 6** Ultimate analysis of upgraded bio- oil

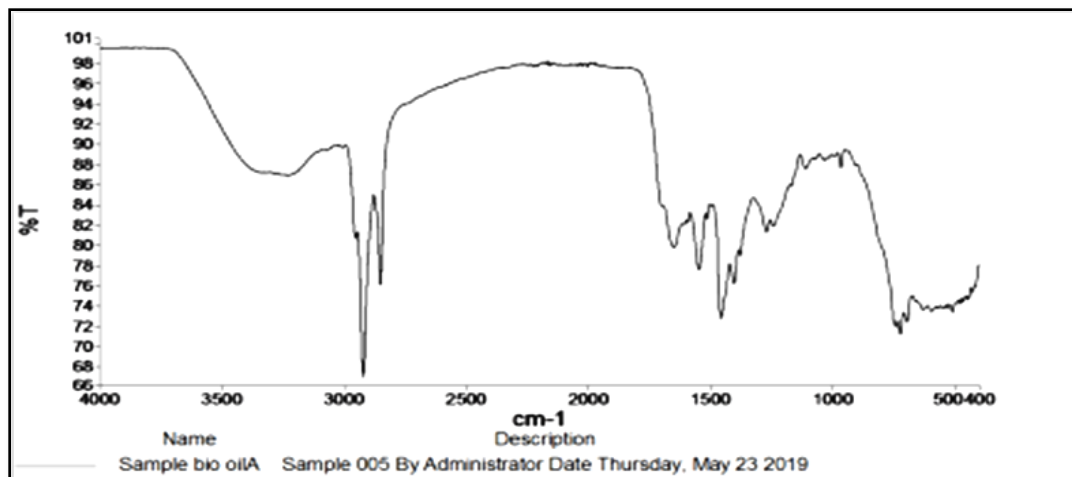
Test Parameters (Unit)	DHSC bio-oil	KSC bio-oil
Carbon (%)	65.74	69.98
Hydrogen (%)	9.69	9.74
$\text{N}_2$ (%)	4.16	4.13
Sulphur (%)	00.00	00.00

#### 4.6 Fourier transformation infrared spectroscopy (FTIR)

##### 4.6.1 Deccan hemp seed cake

Table 7 and Figure 8 depict the findings of FTIR analysis of up-graded bio-oil extracted from DHSC. The FTIR study presents substantial affirmation that the bio-oil extracted from DHSC can well be used as an alternative energy source. Presence of alcoholic and phenolic in bio-oil is perhaps seen in the broad O-H stretching vibrations in the stretch of  $3600\text{--}3300 \text{ cm}^{-1}$ . C-H stretching vibrations in stretch of  $3000\text{--}2800 \text{ cm}^{-1}$  suggest the existence of alkanes. The existence of C=O (carbonyl) aldehyde, ketone, and

carboxylic acids is shown by peaks in the interval of  $1775\text{--}1650 \text{ cm}^{-1}$ . C=C stretching vibration is visible thru  $1680 \text{ cm}^{-1}$  -  $1575 \text{ cm}^{-1}$ , indicating the existence of alkenes. C-O stretching vibrations across the interval of  $1300\text{--}950 \text{ cm}^{-1}$  display the presence of alcohols. Culminations in interval of 900 and  $650 \text{ cm}^{-1}$  suggest the prevalence of aromatic chemicals. FTIR data for rapeseed, lignin and rice stalk powder bio-oils used as fuel have revealed strong similarities with DHSC [61–63].



**Figure 8** FTIR of Deccan hemp seed cake upgraded bio-oil

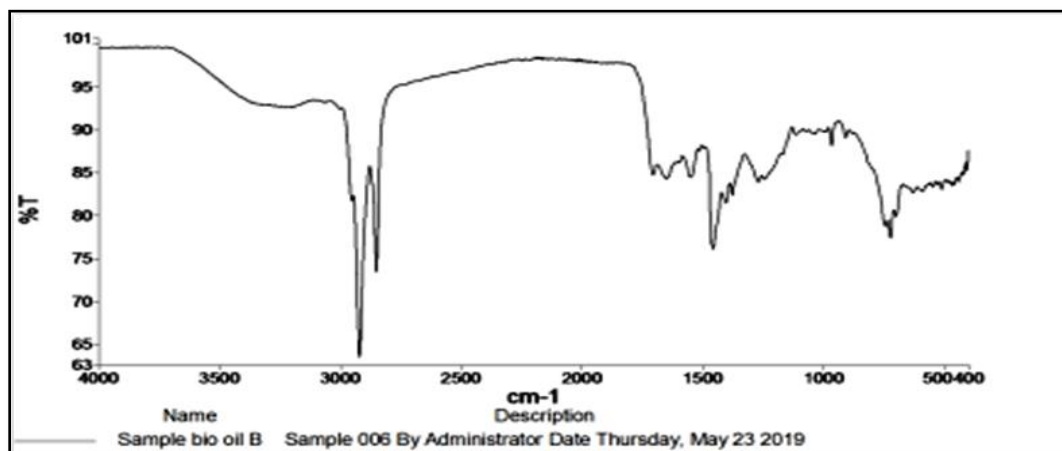
**Table 7** Functional groups for Deccan hemp seed cake up-graded bio-oil

S. No.	Frequency range (cm <sup>-1</sup> )	Groups	Class of compounds
01	3600-3300	O-H stretching	Presence of alcohol and phenols groups
02	3000-2800	C-H stretching	Alkanes
03	1775-1650	C=O stretching	Ketones, aldehydes, carboxylic acids
04	1680-1575	C=C stretching	Alkenes
05	1490-1325	C-H bending	Alkanes
06	1300-950	C-O stretching	Primary, secondary and tertiary alcohols
07	900-650	O-H bending	Aromatic compounds

#### 4.6.2 Karanja seed cake bio-oil

Table 8 and Figure 9 depict the findings of the FTIR investigation for up-graded bio-oil extracted out of KSC. The FTIR study presents substantial affirmation that bio-oil extracted from a Karanja seed cake can be used as an alternative energy source. Presence of 'alcoholic' and 'phenolic' in bio-oil is revealed by broad O-H stretching vibrations in the zone of 3600-3300cm<sup>-1</sup>. C-H stretching vibrations in the stretch of 3000-2800cm<sup>-1</sup> suggested the existence

of alkanes. The existence of alkenes is designated by peak amid 1680cm<sup>-1</sup>-1575cm<sup>-1</sup>, which displays C=C stretching vibration. Existence of alcohols is shown by detection of C-O stretching vibration in the 1300–950cm<sup>-1</sup> range. Peaks in the interval of 900-650cm<sup>-1</sup> indicate the existence of aromatic chemicals. FTIR observations for rapeseed, lignin and rice stalk powder bio-oils used as fuel have revealed strong similarities with KSC [61–63].



**Figure 9** FTIR of Karanja seed cake up-graded bio-oil

**Table 8** Functional groups for Karanja seed cake up-graded bio-oil

S. No.	Frequency range (cm <sup>-1</sup> )	Groups	Class of compounds
01	3600-3300	O-H stretching	Presence of alcohol and phenols groups
02	3000-2800	C-H stretching	Alkanes
03	1680-1575	C=C stretching	Alkenes
04	1490-1325	C-H bending	Alkanes
05	1300-950	C-O stretching	Primary, secondary and tertiary alcohols
06	900-650	O-H bending	Aromatic compounds

## 5. Discussion

In the distribution chain of de-oiled seed cake, availability of seeds continuously is a major issue which involves gathering, storing and transporting. Thorough preparation and proper setup are required to corroborate the amount and regular supply. A methodical repository of de-oiled seed cakes is an additional functional difficulty which is required to be managed for continued supply to pyrolysis reactors [64]. For uninterrupted supply on site storage of seed cake has more benefit for continuous supply as observed by many researchers. But the storage of de-oiled seed cake for prolonged periods causes self-spoilage and generates toxic gases which may be dangerous to the surroundings. Therefore, an effective storage approach needs to consider. Use of mobile pyrolysis reactors is another option wherein we can carry the setup at the feed stock available spot by which storage can be avoided [65].

The literature review disclosed that the pyrolysis of seed cake is a feasible approach, but is restricted to small scale production. The experimental trial and the commercial dimension are lacking in the outlined literature. An experimental trail is decisive in justifying the process prior to its commercial success. Therefore, an attempt in small scale should be carried out to move ahead for progress and commercialize pyrolysis of seed cakes.

Techno-economic study portrays a crucial role in pyrolysis technology, but investigations relating to techno-economic study are missing in the literature. The techno-economic study is a helpful tool that appraises to design a theoretical build up using preliminary lab data [66]. In light of this there should be research to examine the techno-economical study for the pyrolysis of seed cakes that delivers comprehensive resolution to ramp up the task which is lacking in the literature review.

The practical issues in context to generation of bio-oil using de-oiled cakes should be managed,

particularly with regards to enhancing the energy efficiency, environmental and organic impact. Bio-oil derived from de-oiled cakes of Deccan hemp seeds has not been investigated yet and need to be researched. Very few researchers have carried out investigations in bio-oil obtained from KSC and there is a need for further research on its applicability as a substitute fuel in IC engines. Bio-oil characterization is critical in determining whether bio-oil possess favourable qualities analogous to fossil fuels. Since crude bio-oil cannot be utilized directly, it must be upgraded. There is an absence of refining facilities for bio-oil which needs to be addressed. Thermal stability is the major disadvantage associated with bio-oil while it's upgradation. The refining costs of bio-oil are more than fossil fuels as it contains nearly 40% water.

The manufacture of bio-fuel from pyrolytic bio-oil has not yet undergone a commercially viable trial. Refining capability is missing in bio-oil and therefore do not provide deployment for bio-oil upgrading mechanization in plants. Thermal stability is a significant disadvantage not just during upgrading but also during storage and handling. In comparison to fossil fuels refining expenses are very high as the bio-oil contains more than 40% water [67]. Therefore, bio-oil upgradation is carried through stabilization technique for a long-term approach [68]. In order to lower the production, cost the current technologies could be made use for accomplishing desired result. Remodelling and establishing new setups for refining bio-oil and its blends are necessary for long-term investment [69]. Bio-oil perhaps be contemplated as an energy saving fuel that is blended with fossil fuel after separation. The cost economics of producing, separating and bio-oil upgradation was done and affirmed the viability of bio-oil being employed as an alternate source for production of energy [70]. At last, with an inexpensive production price, bio-oil can proceed as an unceasing source of energy with lower CO<sub>2</sub> emission. A complete list of abbreviations is shown in *Appendix I*.



### 5.1 Limitations

The following limitations were observed during the present investigation:

- The bio-oil produced has higher water content since the biomass feedstock comprises moisture.
- The increased viscosity of produced bio-oil may be due to phase separation driven on by the high moisture content.
- Bio-oil has a decreased calorific value since it contains more oxygen and moisture that culminates in fuel of lower quality.
- Due to the presence of hemicelluloses, which causes volatile organics to develop, the bio-oil generated has a smoky smell.

### 6. Conclusion and future work

The following observations were made as a result of the current study:

- This study shows that DHSC and KSC are likely to be raw materials to produce fuel quality bio-oils and beneficial bio-chars. Yields of bio-oil and bio-char are 49.5% and 36.5% wt% and 48.85% and 31.25%, respectively, under optimal pyrolysis operating environment of reactor temperature 450°C and particle-size of 1.5mm.
- Bio-oil calorific value reported was 22.44 MJ/kg for DHSC and 32.57 MJ/kg for KSC, which is remarkably greater compared to other bio-oils. As a result, by blending with diesel oil, bio-oil might be employed as an alternative to fossil fuel.
- Gravity separation and upgrading by heating, the lighter fractions (100-110°C) could moderately enhance the bio-oil to fuel grade like density (978 kg/m<sup>3</sup> (DHSC) and 960 kg/m<sup>3</sup> (KSC)), calorific value (22.44 MJ/kg (DHSC) and 32.57 MJ/kg for KSC). This upgraded bio-oil mixes well with diesel.
- The principal functional groups revealed by FTIR analysis in DHSC and KSC bio-oil indicate that these could be utilized as an energy source.
- Bio-char accomplished as a derivative can be effectively employed to rectify soil acidity in agricultural soils and as a superior material for producing micro-porous activated carbons, in water purification.

Further improvement can be achieved by employing fluidised bed reactor instead of fixed bed reactor. When compared to a fixed bed reactor, the fluidized bed reactor's bio-oil and quality are synonymous. Hydro-cracking, flash co-pyrolysis with poly acetic acid, high pressure thermal treatment, emulsification, and the Hempel distillation process might be made use of to boost the characteristics of crude bio-oil.

Crude bio-oil can be upgraded using a variety of procedures, like esterification, catalytic vapour cracking, and mild cracking, to make it reasonably acceptable as an alternative fuel for diesel engines.

### Acknowledgment

None.

### Conflicts of interest

The authors have no conflicts of interest to declare.

### Author's contribution statement

**Shivakumar A Patil:** Data collection, investigation, data curation and draft manuscript preparation, analysis and interpretation of results. **Dr. Omprakash D Hebbal:** Study conception, conceptualization, supervision, revision of original draft, analysis and interpretation of results. **Dr. S R Hotti:** Study conception, Conceptualization, supervision, Revision of original draft, analysis and interpretation of results.

### References

- [1] <https://www.bp.com/content/dam/bp/business-sites/en/global/corporate/pdfs/energy-economics/statistical-review/bp-stats-review-2021-full-report.pdf>. Accessed 29 May 2022.
- [2] Brown RC. Thermochemical processing of biomass: conversion into fuels, chemicals and power. John Wiley & Sons; 2019.
- [3] Volli V, Singh RK. Production of bio-oil from de-oiled cakes by thermal pyrolysis. *Fuel*. 2012; 96:579-85.
- [4] Demiral I, Eryazıcı A, Şensöz S. Bio-oil production from pyrolysis of corncob (*Zea mays* L). *Biomass and Bioenergy*. 2012; 36:43-9.
- [5] Singh RK, Shadangi KP. Liquid fuel from castor seeds by pyrolysis. *Fuel*. 2011; 90(7):2538-44.
- [6] Yaman S. Pyrolysis of biomass to produce fuels and chemical feedstocks. *Energy Conversion and Management*. 2004; 45(5):651-71.
- [7] García MJF, Cuevas M, Feng CH, Álvarez MP, Torres GM, Sánchez S. Energetic valorisation of olive biomass: olive-tree pruning, olive stones and pomaces. *Processes*. 2020; 8(5):1-38.
- [8] Mettler MS, Vlachos DG, Dauenhauer PJ. Top ten fundamental challenges of biomass pyrolysis for biofuels. *Energy & Environmental Science*. 2012; 5(7):7797-809.
- [9] Jahirul MI, Rasul MG, Schaller D, Khan MM, Hasan MM, Hazrat MA. Transport fuel from waste plastics pyrolysis—a review on technologies, challenges and opportunities. *Energy Conversion and Management*. 2022.
- [10] De BG, Sarmah AK, Sen R. Production and characterization of a value added biochar mix using seaweed, rice husk and pine sawdust: a parametric study. *Journal of Cleaner Production*. 2018; 200:641-56.

- [11] Corton J, Donnison IS, Patel M, Böhle L, Hodgson E, Wachendorf M, et al. Expanding the biomass resource: sustainable oil production via fast pyrolysis of low input high diversity biomass and the potential integration of thermochemical and biological conversion routes. *Applied Energy*. 2016; 177:852-62.
- [12] Chandra R, Vijay VK, Subbarao PM. A study on biogas generation from non-edible oil seed cakes: potential and prospects in India. In the 2nd joint international conference on sustainable energy and environment 2006 (pp. 21-3).
- [13] <https://www.dairyknowledge.in/dkpv759/article/amba-di-cake>. Accessed 26 May 2022.
- [14] Mulimani HV, Navindgi MC. Production and characterization of bio-oil by pyrolysis of Mahua de-oiled seed cake. *ChemistrySelect*. 2018; 3(4):1102-7.
- [15] David E, Kopac J. Pyrolysis of rapeseed oil cake in a fixed bed reactor to produce bio-oil. *Journal of Analytical and Applied Pyrolysis*. 2018; 134:495-502.
- [16] Rajamohan S, Kasimani R. Studies on the effects of storage stability of bio-oil obtained from pyrolysis of calophyllum inophyllum deoiled seed cake on the performance and emission characteristics of a direct-injection diesel engine. *Environmental Science and Pollution Research*. 2018; 25(18):17749-67.
- [17] Alagu RM, Sundaram EG. Preparation and characterization of pyrolytic oil through pyrolysis of neem seed and study of performance, combustion and emission characteristics in CI engine. *Journal of the Energy Institute*. 2018; 91(1):100-9.
- [18] Masawat N, Atong D, Sricharoenchaikul V. Thermo-kinetics and product analysis of the catalytic pyrolysis of Pongamia residual cake. *Journal of Environmental Management*. 2019; 242:238-45.
- [19] Reshad AS, Tiwari P, Goud VV. Thermal and co-pyrolysis of rubber seed cake with waste polystyrene for bio-oil production. *Journal of Analytical and Applied Pyrolysis*. 2019; 139:333-43.
- [20] Paramasivam B. Investigation and improvement on storage stability of pyrolysis oil obtained from Aegle marmelos de-oiled seed cake. *Energy Sources, Part A: Recovery, Utilization, and Environmental Effects*. 2021; 43(8):953-67.
- [21] Dhanavath KN, Bankupalli S, Sugali CS, Perupogu V, Nandury SV, Bhargava S, et al. Optimization of process parameters for slow pyrolysis of neem press seed cake for liquid and char production. *Journal of Environmental Chemical Engineering*. 2019; 7(1):1-12.
- [22] Sokoto MA, Biswas B, Kumar J, Bhaskar T. Slow pyrolysis of defatted seeds cakes of African star apple and silk cotton for production of bio-oil. *Renewable Energy*. 2020; 146:1710-6.
- [23] Singh CS, Kumar N, Gautam R. Thermal cracking of karanja de-oiled seed cake on pyrolysis reactor for producing bio-oil with focus on its application in diesel engine. In IOP conference series: materials science and engineering 2020 (pp. 1-12). IOP Publishing.
- [24] Raguraman D, Kumar A, Prasanna RYS, Patil PY, Samson IJ, Sowmya DC, et al. Performance and emission characteristics of pyrolysis oil obtained from neem de oiled cake and waste polystyrene in a compression ignition engine. *Advances in Materials Science and Engineering*. 2021; 2021:1-10.
- [25] Stas M, Auersvald M, Vozka P. Two-dimensional gas chromatography characterization of pyrolysis bio-oils: a review. *Energy & Fuels*. 2021; 35(10):8541-57.
- [26] Ashwath N, Nam H, Capareda S. Maximizing energy recovery from beauty leaf tree (*Calophyllum inophyllum* L.) oil seed press cake via pyrolysis. *Energies*. 2021; 14(9):1-18.
- [27] Shah MA, Khan NS, Kumar V, Qurashi A. Pyrolysis of walnut shell residues in a fixed bed reactor: effects of process parameters, chemical and functional properties of bio-oil. *Journal of Environmental Chemical Engineering*. 2021; 9(4):1-15.
- [28] Madhu P, Sasireka M, Samikannu R, Vinoth K, Kumar AU, Patil PP, et al. Production and characterization of maximum liquid oil products through individual and copyrolysis of pressed neem oil cake and waste thermocol mixture. *Advances in Polymer Technology*. 2022; 2022:1-11.
- [29] Rajpoot L, Tagade A, Deshpande G, Verma K, Geed SR, Patle DS, et al. An overview of pyrolysis of de-oiled cakes for the production of biochar, bio-oil, and pyro-gas: current status, challenges, and future perspective. *Bioresource Technology Reports*. 2022.
- [30] Singh Y, Singla A, Singh NK, Sharma A. Production and feasibility characterization of bio-oil from jojoba seed-based biomass through solar thermal energy pyrolysis process. *Biomass Conversion and Biorefinery*. 2022; 2022:1-13.
- [31] Laouge ZB, Karademir FS, Merdun H. Production and characterization of bio-oil from catalytic fast pyrolysis of greenhouse vegetables wastes. *Biomass Conversion and Biorefinery*. 2022; 2022:1-12.
- [32] Adelawon BO, Latinwo GK, Eboibi BE, Agbede OO, Agarry SE. Comparison of the slow, fast, and flash pyrolysis of recycled maize-cob biomass waste, box-benhken process optimization and characterization studies for the thermal fast pyrolysis production of bio-energy. *Chemical Engineering Communications*. 2021; 209(9):1246-76.
- [33] <https://pyrolysisplantindia.com/continuous-batch-type-plastic-pyrolysis-plant/>. Accessed 29 May 2022.
- [34] Mohan D, Pittman JCU, Steele PH. Pyrolysis of wood/biomass for bio-oil: a critical review. *Energy & Fuels*. 2006; 20(3):848-89.
- [35] Akhtar J, Amin NA. A review on process conditions for optimum bio-oil yield in hydrothermal liquefaction of biomass. *Renewable and Sustainable Energy Reviews*. 2011; 15(3):1615-24.
- [36] Zabaniotou AA, Roussos AI, Koroneos CJ. A laboratory study of cotton gin waste pyrolysis. *Journal of Analytical and Applied Pyrolysis*. 2000; 56(1):47-59.

- [37] Abdullah N, Bridgwater AV. Pyrolysis liquid derived from oil palm empty fruit bunches. *Journal of Physical Science*. 2006; 17(2):117-29.
- [38] Pütün AE, Özbay N, Apaydın VE, Uzun BB, Ateş F. Rapid and slow pyrolysis of pistachio shell: effect of pyrolysis conditions on the product yields and characterization of the liquid product. *International journal of Energy Research*. 2007; 31(5):506-14.
- [39] Akhtar J, Amin NS. A review on operating parameters for optimum liquid oil yield in biomass pyrolysis. *Renewable and Sustainable Energy Reviews*. 2012; 16(7):5101-9.
- [40] Shafizadeh F. Introduction to pyrolysis of biomass. *Journal of Analytical and Applied Pyrolysis*. 1982; 3(4):283-305.
- [41] Paramasivam B, Kasimani R, Rajamohan S. Characterization of pyrolysis bio-oil derived from intermediate pyrolysis of aegle marmelos de-oiled cake: study on performance and emission characteristics of CI engine fueled with aegle marmelos pyrolysis oil-blends. *Environmental Science and Pollution Research*. 2018; 25(33):33806-19.
- [42] Gharib J, Pang S, Holland D. Synthesis and characterisation of polyurethane made from pyrolysis bio-oil of pine wood. *European Polymer Journal*. 2020; 133:1-37.
- [43] Gupta S, Mondal P, Borugadda VB, Dalai AK. Advances in upgradation of pyrolysis bio-oil and biochar towards improvement in bio-refinery economics: a comprehensive review. *Environmental Technology & Innovation*. 2021; 21:1-36.
- [44] Sakthivel R, Ramesh K, Shameer PM, Purnachandran R. A complete analytical characterization of products obtained from pyrolysis of wood barks of calophyllum inophyllum. *Waste and Biomass Valorization*. 2019; 10(8):2319-33.
- [45] Asadullah M, Rahman MA, Ali MM, Rahman MS, Motin MA, Sultan MB, et al. Production of bio-oil from fixed bed pyrolysis of bagasse. *Fuel*. 2007; 86(16):2514-20.
- [46] Syed-hassan SS, Wang Y, Hu S, Su S, Xiang J. Thermochemical processing of sewage sludge to energy and fuel: fundamentals, challenges and considerations. *Renewable and Sustainable Energy Reviews*. 2017; 80:888-913.
- [47] Nisar J, Ali F, Malana MA, Ali G, Iqbal M, Shah A, et al. Kinetics of the pyrolysis of cobalt-impregnated sesame stalk biomass. *Biomass Conversion and Biorefinery*. 2020; 10(4):1179-87.
- [48] Biradar CH, Subramanian KA, Dastidar MG. Production and fuel quality upgradation of pyrolytic bio-oil from jatropha crcas de-oiled seed cake. *Fuel*. 2014; 119:81-9.
- [49] Demiral I. Pyrolysis of sugar beet bagasse for production of liquid fuels. *Energy Sources, Part A: Recovery, Utilization, and Environmental Effects*. 2014; 36(24):2684-90.
- [50] Zheng JL. Pyrolysis oil from fast pyrolysis of maize stalk. *Journal of Analytical and Applied Pyrolysis*. 2008; 83(2):205-12.
- [51] Bridgwater AV. The production of biofuels and renewable chemicals by fast pyrolysis of biomass. *International Journal of Global Energy Issues*. 2007; 27(2):160-203.
- [52] Huber GW, Iborra S, Corma A. Synthesis of transportation fuels from biomass: chemistry, catalysts, and engineering. *Chemical Reviews*. 2006; 106(9):4044-98.
- [53] Madhu P, Neethi MI, Kanagasabapathy H. Production and upgradation of cotton shell pyrolytic oil for biofuel from flash pyrolysis by fluidized bed reactor. *Proceedings of the National Academy of Sciences, India Section A: Physical Sciences*. 2015; 85(3):457-62.
- [54] Park HJ, Dong JI, Jeon JK, Park YK, Yoo KS, Kim SS, et al. Effects of the operating parameters on the production of bio-oil in the fast pyrolysis of Japanese larch. *Chemical Engineering Journal*. 2008; 143(1-3):124-32.
- [55] Park HJ, Park YK, Kim JS. Influence of reaction conditions and the char separation system on the production of bio-oil from radiata pine sawdust by fast pyrolysis. *Fuel Processing Technology*. 2008; 89(8):797-802.
- [56] Kim SJ, Jung SH, Kim JS. Fast pyrolysis of palm kernel shells: influence of operation parameters on the bio-oil yield and the yield of phenol and phenolic compounds. *Bioresource Technology*. 2010; 101(23):9294-300.
- [57] [http://www.world agriculture.com/agricultural-bioenergy/biomass-fuel-history.php](http://www.worldagriculture.com/agricultural-bioenergy/biomass-fuel-history.php). Accessed 29 May 2022.
- [58] Oasmaa A, Czernik S. Fuel oil quality of biomass pyrolysis oils state of the art for the end users. *Energy & Fuels*. 1999; 13(4):914-21.
- [59] Lødeng R, Bergem H. Stabilisation of pyrolysis oils. In *Direct Thermochemical Liquefaction for Energy Applications 2018* (pp. 193-247). Woodhead Publishing.
- [60] Sukumar V, Senthilkumar R, Manieniyar V. Bio oil from bio waste (Mahua oil cake) using fast pyrolysis process. *International Journal of Innovative Technology and Exploring Engineering*. 2019; 8(10):2525-8.
- [61] Onay O, Koçkar OM. Pyrolysis of rapeseed in a free fall reactor for production of bio-oil. *Fuel*. 2006; 85(12-13):1921-8.
- [62] Gellerstedt G, Li J, Eide I, Kleinert M, Barth T. Chemical structures present in biofuel obtained from lignin. *Energy & Fuels*. 2008; 22(6):4240-4.
- [63] Zhou L, Zong ZM, Tang SR, Zong Y, Xie RL, Ding MJ, et al. FTIR and mass spectral analyses of an upgraded bio-oil. *Energy Sources, Part A: Recovery, Utilization, and Environmental Effects*. 2009; 32(4):370-5.
- [64] Sahoo K, Bilek E, Bergman R, Mani S. Techno-economic analysis of producing solid biofuels and biochar from forest residues using portable systems. *Applied Energy*. 2019; 235:578-90.

- [65] Roy P, Dias G. Prospects for pyrolysis technologies in the bioenergy sector: a review. *Renewable and Sustainable Energy Reviews*. 2017; 77:59-69.
- [66] Scown CD, Baral NR, Yang M, Vora N, Huntington T. Technoeconomic analysis for biofuels and bioproducts. *Current Opinion in Biotechnology*. 2021; 67:58-64.
- [67] Resasco DE, Crossley SP. Implementation of concepts derived from model compound studies in the separation and conversion of bio-oil to fuel. *Catalysis Today*. 2015; 257:185-99.
- [68] Hansen S, Mirkouei A, Diaz LA. A comprehensive state-of-technology review for upgrading bio-oil to renewable or blended hydrocarbon fuels. *Renewable and Sustainable Energy Reviews*. 2020; 118:1-14.
- [69] Valle B, Remiro A, García-gómez N, Gayubo AG, Bilbao J. Recent research progress on bio-oil conversion into bio-fuels and raw chemicals: a review. *Journal of Chemical Technology & Biotechnology*. 2019; 94(3):670-89.
- [70] Hu X, Gholizadeh M. Progress of the applications of bio-oil. *Renewable and Sustainable Energy Reviews*. 2020; 134:1-27.



**Shivakumar A Patil**, hails from Gulbarga (now Kalaburagi) Karnataka born on 05<sup>th</sup> January 1970 has received his Bachelor of Engineering degree in Automobile Engineering in 1991 from Gulbarga University, Gulbarga, Karnataka. Completed his Master's degree in Thermal power Engineering

in 2005 from Visvesvaraya Technological University, Belagavi, Karnataka. He is Member of Indian Society for Technical Education.

Email: bhojupatil40025@gmail.com



**Dr. Omprakash D Hebbal**, hails from Gulbarga (now Kalaburagi), Karnataka born on 17th January 1962, has received Bachelor of Engineering degree in Mechanical Engineering in 1985 from Gulbarga University, Gulbarga, Karnataka. Completed his Master's degree in Thermal Fluid in

1989 from IIT Bombay, Mumbai and PhD in 2007 from Jawaharlal Nehru Technological University, Hyderabad. Got Super annaution from service in February 2022. His research area is Alternate Fuels.

Email: hebbalod@gmail.com



**Dr. S R Hotti**, hails from Gulbarga (now Kalaburagi), Karnataka born 26th January 1970 has received his Bachelors of Engineering degree in Automobile Engineering in 1991 from Gulbarga University, Gulbarga, Karnataka. Completed his Master's degree in Energy Studies in 1999 from IIT Delhi, New Delhi and PhD in 2018 from Visvesvaraya Technological University, Belagavi, Karnataka. His research areas are in the field of Alternate Fuels. He is a member of Indian Society for Technical Education and Institute of Engineers.

Email: hottisr@gmail.com

### Appendix I

S. No.	Abbreviation	Description
1	AM	Aegle Marmelos
2	AR	Analytical Reagent
3	ASA	African Star Apple
4	ASTM	American Society for Testing and Materials
5	cSt	Centistokes
6	CI	Calophyllum Inophyllum
7	CI-M	Calophyllum Inophyllum with 10% Methanol
8	DHSC	Deccan Hemp Seed Cake
9	FTIR	Fourier Transformation Infrared Spectroscopy
10	GCMS	Gas Chromatography- Mass Spectroscopy
11	GDP	Gross Domestic Product
12	GI	Galvanized Iron
13	HBO	Hydro Treated Bio-Oil
14	HC	Hydrocarbon
15	H/C	Hydrogen to Carbon
16	IC engines	Internal Combustion Engines
17	KSC	Karanja Seed Cake
18	LPM	Litres Per Minute
19	N <sub>2</sub>	Nitrogen
20	NDC	Neem De-Oiled Cake
21	NOC	Neem Oil Cake
22	NPSC	Neem Press Seed Cake
23	O/C	Oxygen to Carbon
24	PID	Proportional-Integral-Derivative
25	PRC	Pongamia Residual Cake
26	RSC	Rubber Seed Cake
27	RSM	Response Surface Methodology
28	SC	Silk Cotton
29	TGA	Thermo-Gravimetric Analysis
30	WPS	Waste Polystyrene
31	WT	Waste Thermocol