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High Calorific Value Fuel from Pyrolysis of Waste De-Oiled Seed Cakes

H. V. Mulimani and M. C. Navindgi
Department of Mechanical Engineering, PDA Engineering College, Kalaburagi-585102, Karnataka, India

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ABSTRACT

The focus of this paper is to produce high calorific value fuel from mahua and neem de-oiled seed cakes. The proximate and ultimate analysis reveal that the high volatile matter, less sulphur and ash content makes it suitable for producing high calorific fuel. TGA analysis reveals that the operating pyrolysis temperature range is 160-530°C. The maximum yield of bio-oil was 42.6 and 38.6%, at the temperature of 450°C and 500°C, whereas the maximum biochar yield was 40.1% and 43.8% at the temperature of 350°C for mahua and neem de-oiled seed cakes respectively, with the heating rate of 20°C/min. The biochar which is made of mainly carbon also finds many applications in industries, agriculture, etc. The chemical properties of bio-oil were similar to the other bio-oils. The bio-oils find many applications due to its advantages of storage, transportation, etc.

INTRODUCTION

Biodiesel obtained from non edible plants are gaining importance as renewable alternate fuel in all the developing countries. To run biodiesel program fruitfully, the end products of biodiesel production, glycerin and de-oiled seed cake should be utilized effectively. The glycerin can be used directly in making cosmetics, soaps, candles, etc., but there is a need to develop a method for conversion of de-oiled seed cake into other useful products, or else it may lead to problems like waste disposal management, space occupation etc. The de-oiled seed cake having high valuable energy may be converted to high calorific value products by pyrolysis process. In pyrolysis process, biomass is heated in the absence of oxygen, which decomposes to generate mainly a liquid bio-oil, solid biochar and gaseous fuel syngas. Pyrolysis mainly helps in production of liquid fuel compared to gaseous fuel, as the liquid fuel has an added advantage in transportation, storage, safety, etc. Hence, pyrolysis is receiving more attention for producing liquid fuel than other processes in converting biomass and waste residue (Bridgwater 2012, Jahirul 2012).

Bio-oil obtained from biomass by pyrolysis process finds its application in running boilers, furnaces, turbines, etc. and can also act as a commercial fuel (Volli & Singh 2012). Biochar is a solid product from pyrolysis mostly made of carbon, finds its application in soil amendment, removal of toxic materials, as a fuel, and production of other valuable products (Prasad et al. 2014). The pyrolysis was carried out on groundnut de-oiled seed cake of calorific value 15 MJ/kg at a temperature range of 400-500°C to obtain biochar and bio-oil of calorific value 25.6 and 28.91 MJ/kg respectively (Agrawalla et al. 2011).

Mahua (*Madhuca indica*) is commonly cultivated in southern and central parts of India. In India, the annual production of seed is around 0.50 million tons. After the oil extraction, the cake finds its application in fertilizer, cattle feed, dye removal, insecticide and bio-pesticide (Gupta et al. 2013). Neem (*Azadirachta indica*) is grown mostly in all parts of India. It is estimated that the potential availability of neem seeds is about 0.50 million tons/year in India. Neem is a golden tree that has attained importance for its multiple uses such as in cosmetics, pest control, pharmaceuticals, toiletries, animal nutrition and even in organic farming, energy generation (Nayan et al. 2013). Not much work has been carried out on mahua and neem de-oiled seed cake for obtaining the fuel and hence, mahua and neem were used as a feedstock for producing high calorific value fuels by pyrolysis process.

MATERIALS AND METHODS

Raw martial and its characterization: The mahua and neem de-oiled cakes were brought from “Biodiesel Production Centre” in Kalaburagi and Bagolkote district, respectively of Karnataka State, India. The de-oiled seed cake, left out after extraction of crude oil for producing the biodiesel were in the form of flakes. The flakes are powdered and dried before using in reactor furnace for carrying out the pyrolysis process.

Characterization of mahua and neem de-oiled seed cake was done by proximate analysis, ultimate analysis, thermo gravimetric analysis (TGA) and calorific value.

Pyrolysis: The pyrolysis was carried out in a reactor furnace made of mild steel, having a length of 56 cm with the internal and external diameter of 21 and 56 cm respectively, where the temperature is controlled by PID controller. The internal furnace is insulated with refractory bricks to minimise heat losses. Vapour residence time in the reactor is kept around 5 seconds. The condenser was used to condense the vapours coming out of furnace by using water as a cooling medium, which is circulated in counter flow via half hp pump. The inlet and outlet temperature of water is 25°C and 28°C respectively. The condenser length is 140 cm having inner and outer diameter of 1.905cm and 3.81cm pipe. The inner pipe is made up of galvanized iron (GI) and outer with copper material. The reactor furnace is heated with nichrome coil having capacity of 3 kW. The J type thermocouple having range of -99 to 870°C is dipped in the biomass to measure the temperature of biomass.

For pyrolysis experiments, 50 g sample is kept in furnace and all the openings are closed and furnace is made leak proof by using the gasket. As the pyrolysis process starts, the vapours coming out of the furnace through the outlet are condensed and collected in a container as a liquid product and biochar is left in the furnace, whereas the non-condensable gases are left out to the atmosphere. The liquid product collected contains oily viscous water along with liquid fuel, which is separated by density difference. The oily viscous water mainly contains water with hydrocarbons dissolved in it. Fig. 1 shows the experimental setup of pyrolysis process. The experiments were conducted at various temperature range of 350 to 550°C with a constant heating rate of 20°C/min. After the completion of pyrolysis process, the bio-oil and biochar are weighed and the difference among them gives the gas yield. After each experiment the inner furnace is removed, filled with feedstock and assembled to carry out the experiment.

Physical characterization of liquid product and char: The liquid product also known as pyrolytic oil or bio-oil was characterised by calorific value, moisture content, ash content, density, viscosity, flash point and carbon residue. The characterization of char was done by calorific value, fixed carbon, moisture content and ash content using the standard methods.

RESULTS AND DISCUSSION

Proximate and component analysis: Proximate analysis is the quickest and simplest way of investigating the fuel quality. The proximate analysis of mahua and neem de-oiled seed cake is given in Table 1 which indicates that its contents are almost nearer to the values of other biomass materials. During pyrolysis process, the ash and fixed carbon tends to be incorporated into the char. The moisture content affects the pyrolysis process and its end product properties. Due to its high volatile matter, less moisture, less ash content and high calorific value, the de-oiled seed cake can be used as a good source of energy.

Component analysis provides cellulose, hemicelluloses and lignin content as given in Table 2. Scott et al. (1999)

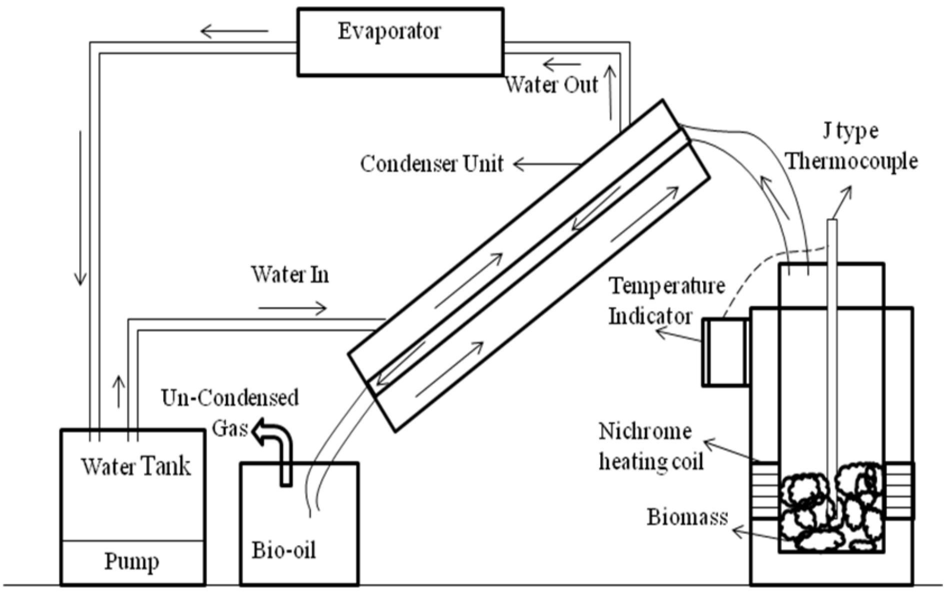

Fig. 1: Experimental setup.

Table 1: Proximate analysis of different seed cakes (wt. %).

Sample	Moisture	Volatile matter	Ash	Fixed carbon	Calorific value (MJ/kg)	Reference
Mahua de-oiled cake	6.5	74.9*	6.2*	18.9*	19.97	Present Study
Neem de-oiled cake	4.7	73.2*	4.8*	22.0*	21.84	Present Study
Jatropha de-oiled cake	5.0	69	5.0	21	16.86	Biradar et al. (2014)
Beech wood	7.6	40.2	0.5	28.3	19.7	Demirbas (2010)
Rice husk	7.7	64.3	18.8	9.2	13.36	Ji-lu (2008)

*Results on dry weight basis.

Table 2: Component analysis of different biomass (wt. %).

Sample	Cellulose	Hemicellulose	Lignin	Reference
Mahua de-oiled cake	59	25	16	Present study
Neem de-oiled cake	45	29	26	Present study
Karanja cake	56.11	17.5	26.39	Parekh et al. (2009)
Wheat straw	28.8	39.4	18.6	Demirbas (2013)

Table 3: Ultimate analysis of different biomass materials (wt. %).

Sample	C	H	N	S	O	Reference
Mahua de-oiled cake	47.28	6.52	2.55	0.32	43.33*	Present study
Neem de-oiled cake	38	8.2	7.4	0.5	45	Present study
Bagasse	44.8	5.4	0.4	0.01	39.6*	Demirbas (2013)
Rice husk	33.1	4.7	0.7	0.0	61.5*	Fukuda (2015)
Wood	52.3	5.2	0.5	-	42.0	Prasad et al. (2014)

***** By difference

observed that the liquid yield is dependent on cellulose and hemicellulose and char yield is dependent on lignin content. The proximate and component analysis suggests that the feedstock can be used for energy production through pyrolysis process.

Ultimate analysis: Ultimate analysis determines the elemental composition of the material, which indicates that the contents of de-oiled seed cakes are almost nearer to the values of the other biomass materials as given in Table 3. The lower sulphur content in de-oiled seed cake indicates that it would be a good quality fuel. The higher oxygen content affects the calorific value. Based on the ultimate analysis, empirical formulas of mahua and neem de-oiled seed cakes are $CH_{1.65}N_{0.04}S_{0.002}O_{0.68}$ and $CH_{2.58}N_{0.166}S_{0.004}O_{0.88}$ respectively.

Thermo gravimetric analysis (TGA): TGA analyses the effective pyrolysis temperature, its fraction of volatile components and materials thermal stability by monitoring the weight change, which occurs as the de-oiled seed cake is heated. The nature of a TGA curve indicates the number of stages of thermal degradation. The degradation temperature depends on the composition of cellulose, hemicellulose and lignin.

Experiments with TGA comprise of three stages of weight loss. The first stage is due to evaporation of moisture present in feedstock. The second stage is treated as active zone due to high decomposition with formation of volatiles, mainly CO and CO_2. During active pyrolysis zone, the weaker chemical bonds and intermolecular associations are destroyed, and small quantities of gaseous molecules are produced. During third stage, the pyrolysis residue is slowly decomposed, and the chemical bonds and the parent molecular skeletons are destroyed (Nayan 2013).

The degradation profile was observed by TGA analysis and are depicted in Fig. 2 for both mahua and neem cakes. The first initial mass loss which is due to moisture occurs from room temperature of 160°C and 180°C, the second mass, corresponds to the degradation of cellulose, hemicellulose and residual oil occurred at the temperature range between 160-500°C and 180-530°C, whereas the third mass loss extended up to 680°C which is related to the degradation of lignin for mahua and neem, respectively. After this temperature, no further mass loss was observed for both the seed cakes.

Similar trend of mass loss was observed for pongamia

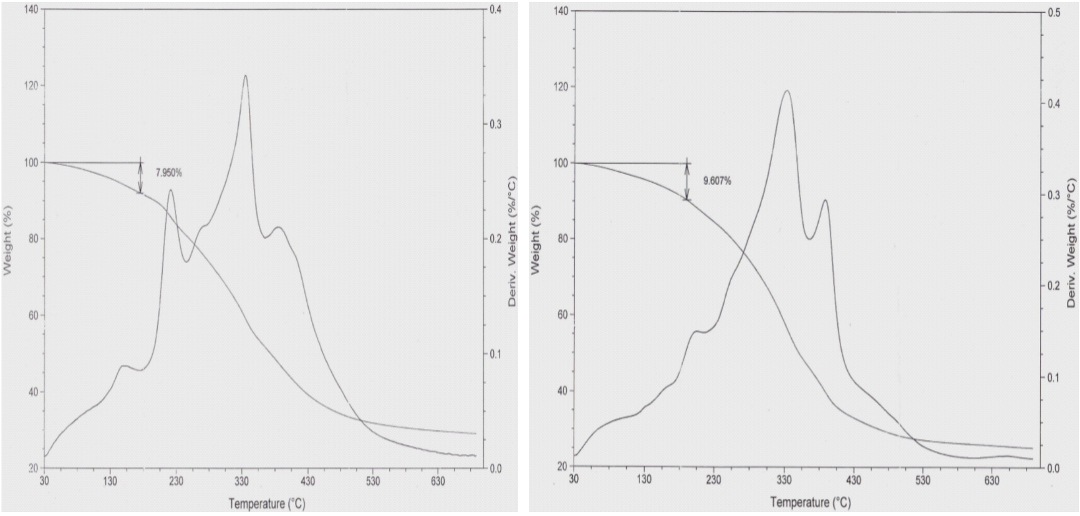

Fig. 2: TGA analysis of mahua and neem de-oiled seed cake.

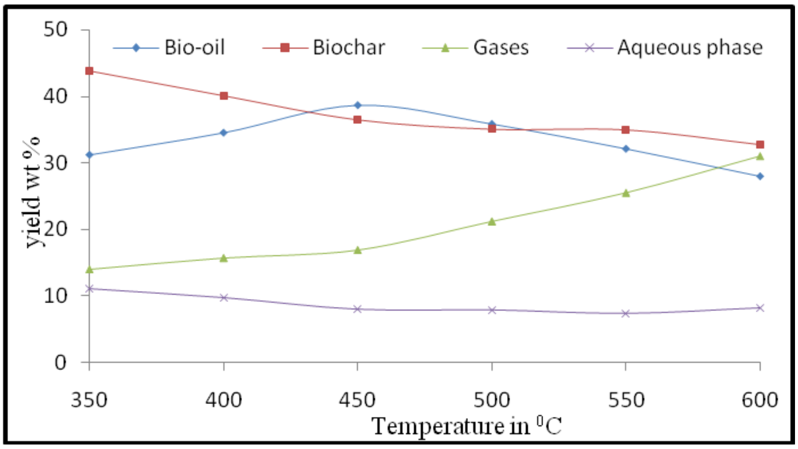

Fig. 3: Yield of mahua de-oiled cake at different temperatures.

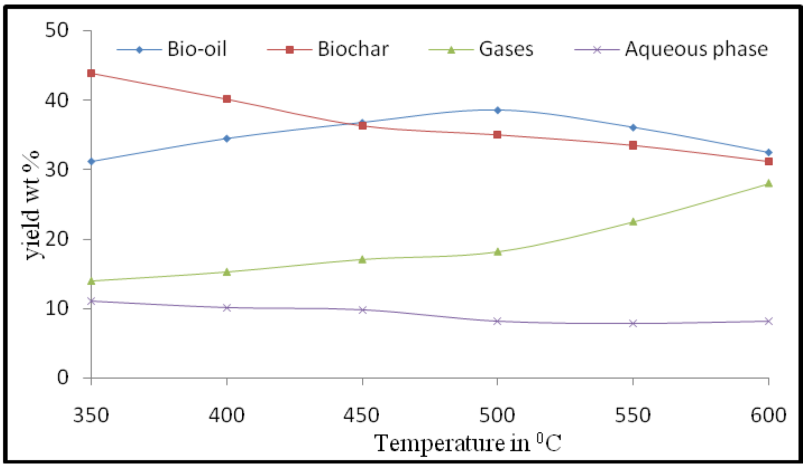

Fig. 4: Yield of neem de-oiled cake at different temperatures.

Table 4: Physical properties of biochar (wt %).

Properties	Moisture content	Volatile matter	Ash content	Fixed carbon	Calorific value MJ/kg	Reference
Mahua	2.1	8.2	16.4	73.3	26.43	Present study
Neem	2	8.0	9.7	80.3	30.4	Present study
Mustard	4.8	21	28.1	46.1	29.1	Volli et al. (2012)

Table 5: Physical properties of bio-oil.

Properties	Mahua bio-oil	Neem bio-oil	Diesel
Appearance	Dark colored liquid	Dark colored liquid	Yellowish
Odor	Smoky smell	Smoky smell	Aromatic
Density at 15°C kg/m^3	980	995	830
pH	3.8	3.6	-
Viscosity at 25°C cSt	10.2	10.6	30.5
Gross calorific value MJ/kg	30.948	28.52	42.0
Moisture content Wt. %	25.0	29	-
Ash Wt. %	0.09	0.1	-
Flash Point °C	116	131	98

Table 6: FTIR functional groups and indicated compounds in mahua bio-oil.

Sl No	Wave number (cm^{-1})	Groups	Class of compounds
1	3398.54, 3209.16	O-H Stretch	Alcohols, Phenols
2	2891.16, 2789.16	C-H Stretch	Alkanes
3	1690.61	C=C Stretching	Alkenes
4	1357.82	C-H Stretch	Alkanes
5	1000.32	C-O Stretch	Alcohol
6	831.82	C-H Bend	Aromatic

Table 7: FTIR functional groups and indicated compounds in neem bio-oil.

Sl No	Wave number (cm^{-1})	Groups	Class of compounds
1	3318.54	O-H Stretch	Alcohols, Phenols
2	2851.16	C-H Stretch	Alkanes
3	1682.61	C=O Stretch	Alkenes
4	1385.41, 951.32, 824.72, 742.41	C-O Stretch	Alcohols

de-oiled seed cake. The first mass loss has occurred approximately between 30°C and 166°C, second mass loss occurred between 166°C and 480°C and third mass loss occurred up to 700°C (Prasad 2014).

Yield of biochar and bio-oil: Figs. 3 and 4 show the yield of pyrolysis end products at different temperatures of 350°C to 550°C. Initially, the bio-oil yield was less, as the temperature increases the yield also increased to a maximum of 42.6% and 38.6% at a temperature of 450°C and 500°C and then decreased with further increase in temperature for mahua and neem respectively. The char yield decreased with the increase in pyrolysis temperature. The maximum char yield was 40.1% and 43.8% at the temperature of 350°C for mahua and neem respectively. Initially, gas yield decreased, but as the temperature increased gas yield also increased. It can be concluded that at higher than optimum temperatures, the bio-oil yield decreases due to gasification reactions and secondary cracking reactions favouring the gaseous products. The composition of cellulose and hemicelluloses is high in mahua than the neem, hence the bio-oil yield was higher in mahua. Yield of biochar was high in neem as its lignin composition was more compared to mahua. The similar trends were observed for maize stalk by Ji-lu (2008), and *Jatropha curcas* de-oiled seed cake by Biradar (2014).

Physical properties of char: The biochar properties obtained were in the range of other biochars as given in Table 4. From

Fig. 5: Photograph of biochar.

Fig. 6: Phase separation: bio-oil and viscous liquid.

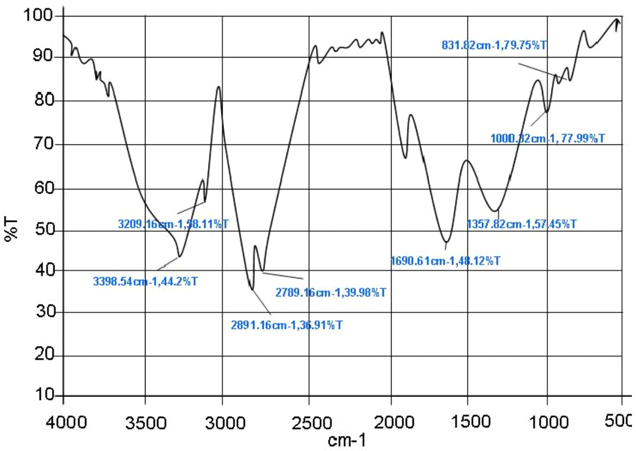

Fig. 7: FTIR analysis of mahua bio-oil.

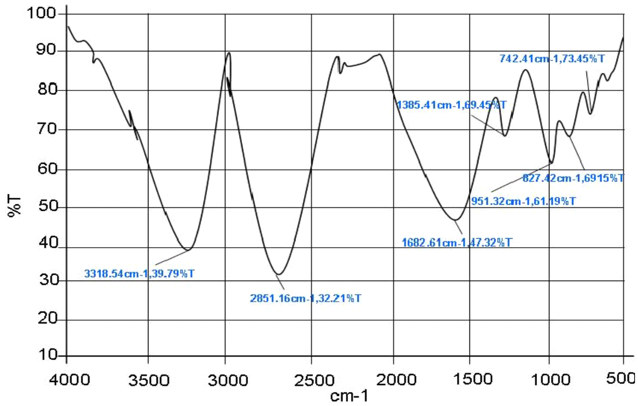

Fig. 8: FTIR analysis of neem bio-oil.

Tables 1 and 4, it is observed that the ash content has increased from 6.2 and 4.8% to 16.4 and 9.7%, which is higher than the initial feedstock due to the presence of non-volatile inorganics within the char particles. The biomass consisting of 18.9 and 22 fixed carbon is converted to biochar, having 73.3% and 80.3% fixed carbon for mahua and neem respectively. The calorific value of feedstock increased from 19.97 and 21.84 MJ/kg to 26.43 and 30.4 MJ/kg in biochar for mahua and neem respectively. The char is used as soil amendment, activated carbons, fertilizer, solid fuels and can be submitted to further processing to produce more value added chemicals (Parthasarathy 2017).

Physical properties of bio-oil: The bio-oil obtained was dark in colour with a smoky smell and has a clear phase separation when stored as shown in Fig. 6. Bio-oil is separated and filtered from viscous liquid by density difference.

Table 5 provides the physical properties of bio-oil and diesel fuel. The density of the crude bio-oil (980 kg/m^3) is higher than diesel (830 kg/m^3). The higher fuel density would severely affect the spray characteristics of diesel engines resulting in poor mixing of fuel with air and also affect the working of pumps (Bridgwater 2012). The bio-oil obtained is corrosive in nature as it is acidic with low pH value of less than 4 for both the seed cakes. The moisture content of the crude bio-oil is about 25%, which lowers the calorific value, but improves the viscosity of bio-oil which is much higher than diesel. Calorific value of feedstock increased from 19.97 and 21.84 MJ/kg to 30.9 and 28.52 MJ/kg in bio-oil for mahua and neem respectively. Bio-oil obtained from both the cakes was denser, highly viscous and calorific value is less than that of the commercial fuels, which affects the direct utilization of crude bio-oil in diesel engines. These problems are mainly due to the physico-chemical properties of crude bio-oil, which differ significantly from base diesel.

FTIR analysis of bio-oil: The FTIR spectra were recorded in transmission mode for bio-oil between 4000 and 500 cm^{-1} are shown in Figs. 7 and 8 for mahua and neem cakes. Tables 6 and 7 give the functional groups identified from FTIR for mahua and neem cakes, respectively.

Both the seed cakes showed the presence of alcohol and aliphatic compounds (alkanes, alkenes and alkynes). The presence of oxygenated functional groups C-O, O-H shows that bio-oil was highly hydro-oxygenated and hence acidic in nature. The presence of oxygenated functional group decreases the calorific value of bio-oil. However, due to the presence of alcohols and hydrocarbon groups C-H indicates that both the seed cakes are a potential feedstock for bio-oil. Previous studies showed the presence of some organics, including alcohols, phenols, aliphatics and acids (Prasad et al. 2014, Biradar et al. 2014).

CONCLUSION

Pyrolysis is one of the best options for producing high calorific value fuel. The high volatile matter, less moisture, ash and sulphur content makes the end product derived from this feedstock a good quality fuel.

Pyrolysis process was carried out in the temperature range of room temperature to 680°C. The maximum yield of bio-oil was 42.6% and 38.6%, at the temperature of 450°C and 500°C, whereas the maximum biochar yield was 40.1 and 43.8% at the temperature of 350°C for mahua and neem de-oiled seed cakes respectively, with the heating rate of 20°C/min. FTIR for both bio-oils reveals that they consist of alcohols and aliphatic compounds and due to the presence of alcohols and hydrocarbon groups C-H indicates that both the seed cakes are a potential feedstock for bio-oil. The calorific value of feedstock increased from 19.97 and 21.84 MJ/kg to 26.43 and 30.4 MJ/kg in biochar for mahua and neem respectively. Calorific value of feedstock increased from 19.97 and 21.84 MJ/kg to 30.9 and 28.52 MJ/kg in bio-oil for mahua and neem, respectively.

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