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Development and fabrication of intermediate pyrolysis reactor and characterization of extracted neem oil

Jaysingh Gaharwar
Mechanical department , Bhilai Institute of Technology, Durg, India
Arun Arora
Mechanical department, Bhilai Institute of Technology, Durg, India
Santosh Kumar Sar
Deartment of Applied Chemistry, Bhilai Institute of Technology , Durg, India

Abstract— Intermediate pyrolysis of neem seeds was carried out. Proximate analysis of the seeds gives details of the moisture, volatile, ash and carbon content present in it. The highest yield of bio-oil 45% was obtained at 475^{0}C. Analysis in the variation of bio-oil yield for different particle was done. The maximum bio-oil yield was obtained for the particle size of 2 mm. The calorific value of neem bio char was calculated as 19.365 MJ/Kg. TGA analysis helps in determining the active pyrolysis zone. FTIR study of oil gives information about the chemical compounds present. Chromatogram of GCMS of extracted oil shows the presence of many hydrocarbons that are reported to show medicinal properties. Bio-oil contains compounds that can be used as medicine for curing skin problems, infection etc. The bio-oil also has potential to be used as bio fuel.

Keywords— Intermediate pyrolysis reactor, neem oil, bio-oil, TGA, FTIR, GCMS, proximate analysis.

I. INTRODUCTION

Global warming and declining oil reservoirs and sources of fossil fuels have increased the interest in developing alternate sources of energy such as biomass. Biomass as an energy source has gained so much popularity because of its widespread availability, production of clean energy. Biomass such as non-edible seeds and other parts of plants such as stems, leaves etc. can be used as feedstock for the production of biofuel. Biomass energy can be used in three different ways - thermal, biochemical and thermochemical methods. Process of energy conversion of thermochemical biomass is preferred here over other biochemical processes as the production of fuel to feed ratio is high. [1]. This method converts the biomass into biogas, bio liquid (bio-oil) and biochar. In Pyrolysis, inert atmosphere is used for thermal disintegration of biomass. Liquid, solid and gas products obtained in this process have potential application to be used in boilers, engines etc. The bio-oil get through the pyrolysis of parts of medicinal plants such as neem, mahua, Karanja etc. shows healing properties and can be used in the treatment of various diseases. Fast pyrolysis, intermediate pyrolysis and slow pyrolysis are the three different kinds of methods based on the different heating rate used. Intermediate pyrolysis is used in this work for extraction of bio-oil. This process has been recognized gradually over past few years as a result of the technology development and significant work that were carried out at Aston University. Working conditions used for intermediate pyrolysis doesn't allow the development of high molecular tars. Dry char and brittle char obtained through this method finds suitable application in fertilization or combustion. Intermediate pyrolysis is used to extract oil, char and gas from neem seeds. Properties of the seeds as well as the extracted oil are studied in present work. Fabrication of machine that is used to carry out the pyrolysis has also been done. [1-4].

II. EXPERIMENTAL SET-UP

Intermediate pyrolysis reactor uses a cylindrical shell, heating element such as coil, screw driving unit, two coaxial conveyor screws, temperature controlling unit and condenser. Biomass is fed to the reactor through hopper. The movement of biomass from proximal ends to distal end and vice versa is done using screw conveyor. Coupling at both ends finds use in driving screws and the ball bearings helps in rotation of screws. The topside of pyrolyzer (hopper) is kept closed by a covering plate tightly secured to the flanged opening. Thus, the entry of atmospheric air is prevented during the process of pyrolysis takes place. The gases that are obtained as a result of pyrolysis reach the condenser through the exit pipe. A measuring cylinder is placed at the other end of the condenser to collect the condensed gas in the form of bio-oil. Electrical resistance heating causes the thermal decomposition of biomass. Speed of screw can be changed using a variable rpm motor. This can control the residence time of the solid feed inside the reactor.

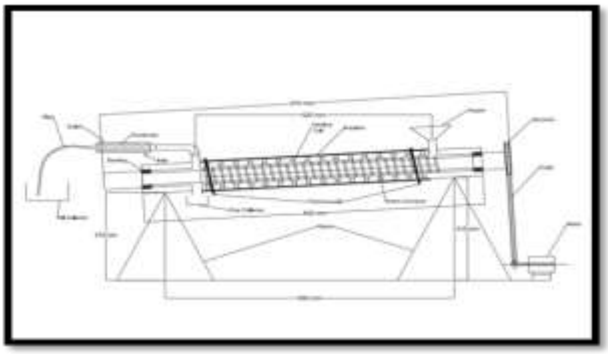

Fig. 1. Intermediate pyrolysis reactor

Chain transmission system drives the screws with two separate motors. Thermocouple (temperature measuring unit) measures the temperature inside the pyrolyzer. Specifications of machine used for intermediate pyrolysis are – total length of shaft is 910 mm, outer and inner diameter of shaft is 90 mm and 45 mm respectively, length of the screw is 830 mm and pitch of screw is 39 mm.

III. MATERIALS AND METHODS

In the process of extraction of bio-oil, neem seeds undergo a series of unit operations. Neem seeds were collected from Bastar area in Chhattisgarh. The seeds were sun dried for 5-6 days to remove moisture. The dried seeds will be crushed to different particle size and then subjected to thermal degradation. The seed sample will be inserted into the heating chamber. When the pyrolysis reactor attains the desired temperature, the reaction will start. The vapours will get condensed in the condenser and then get collected in the measuring jar. Three different product such as condensed liquid (bio-oil), non-condensed liquid (bio-gas) and bio-char will be obtained in the pyrolysis of the crushed neem seeds. Crushed seeds of neem were taken in alumina crucible and heated in the temperature range of 25^0C to 700^0C. Nitrogen gas with the flow rate of 70.0 ml/min was used as an inert purge gas to take the place of air in the pyrolysis zone for keep away from undesired oxidation of the sample. TGA curve is plotted with weight (in mg) in Y axis and temperature (in ^{0}C) in X axis. DTG curve is plotted between weight loss per unit temperature Vs. temperature. For TGA analysis approximately 4.770 mg of crushed seeds of neem were taken. The crushed seeds were placed in alumina crucible and heated up to 700^0C with the rate of heating is 10.0 K/min and TGA and DTG profile were recorded with the help of METTLER TOLEDO TGA 1 MODULE.

Presence of different functional groups inside the sample was determined using FTIR (Fourier Transform Infra-Red) spectroscopy. Range of wavenumber is 600 – 4000 cm-1. FTIR study was carried on with the help of ALPHA ATR-ZnSe Model, Bruker. PerkinElmer Clarus 680 GC equipped with a MS600C was used to identify the composition of neem bio-oil through gas chromatography (GC). The eluting components was fed to a mass spectrometer (MS) based detector. For GC-MS 1 µl of dissolved sample was injected into the column. Initial temperature of column is maintained at 40 ^{0}C for 4 minutes. It is then ensuing raised to 280 ^{0}C and maintained for 15 minutes (at the rate of 50 ^{0}C/min). The temperature of the MS detector and the injection port are maintained at 270 ^{0}C. Helium gas plays the role of carrier gas with the flowrate of 1ml/min. MS detector was employed in the full scan mode from M/Z 45 to 400. The collected data was processed using GC-MS software. Investigation of un-condensed gases was done using Gas chromatography (PerkinElmer Clarus 590 GC equipped with a TCD). The Shin Carbon was utilized. Initially the temperature of oven was kept at 50 ^{0}C for 2 min and then it was raised up to 100 ^{0}C at the rate of 10 ^{0}C/min and was later kept constant at 200 ^{0}C. 30 ml/min nitrogen gas was used as the carrier gas.

Proximate analysis is one of the initial characterizations that is performed before using the biomass as fuel. This analysis gives the idea about the content of moisture, volatile matter, ash and the fixed carbon present in the sample. The quantity of water present per unit mass of dry solid is referred to as the moisture content of the sample. One gram of seed is heated in an electric hot air oven for 1 hour at 105 -1100C. The sample is then placed in the desiccator for cooling and then weighed. The loss of weight in sample gives information about the moisture content present in the seeds. This moisture free sample is then put down in silica crucible with lid and kept inside the muffle furnace. Temperature is maintained at 925 ± 200C for 7 minutes. Crucible is then taken out of the furnace and cooled. The sample is then weighed again. Loss in weight of sample represents the amount of volatile matter present in the seeds. The sample is then heated without lid in oven at temperature 700 ± 200C for 30 minutes. The amount of sample left is the ash content present in the seed. Fixed carbon content in seeds is given by the formula

Fixed carbon content (%) = 100 – % of (moisture + volatile matter + ash)

Toshniwal bomb calorimeter (IS1350-1, India) was used to measure the calorific value of neem char.

IV. RESULTS AND DISCUSSION

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A. Proximate Analysis

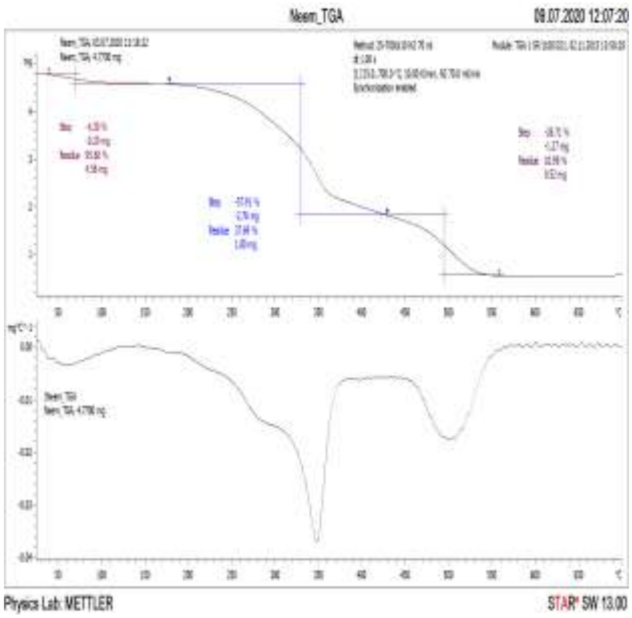
Proximate analysis helps in finding out the content of moisture, volatile matter, ash cand fixed carbon present in the seeds. This study helps in the estimation of quality of biofuel. Table 1 represents the proximate analysis of Neem seeds. High moisture content of biomass decreases its heating value. Analysis shows low moisture content and presence of more than 80% volatile matter in neem seeds. High amount of volatile matter and the presence of fixed carbon content adds to the quality of biomass as they increase the heating value of biomass. Presence of high value of volatile matter content helps in easy ignition of fuel. Fixed carbon content performs the function of main heat generator when the biomass is burnt. The residue obtained after burning is ash which acts as heat sink. High value of ash content lowers the calorific value of biomass. [3,5]

TABLE I. PROXIMATE ANALYSIS OF NEEM SEEDS

Seeds	Moisture content (%)	Volatile matter (%)	Ash content (%)	Fixed carbon content (%)
Neem	7.23	87	1.47	4.3

B. TGA

Pyrolysis is the process of heating the material (sample) in absence of air at a temperature. TGA of neem seeds is carried out to determine the temperature for effective pyrolysis. Thermo-gravimetric weight loss in the sample with increasing temperature was plotted. This graph helps in determining the temperature range where maximum thermal degradation takes place.



TGA and DTG plot of neem seeds.

Moisture and other volatile content present in the Neem seeds gets removed on heating the sample till 150^{0}C due to which loss in initial weight of the sample can be seen. Around 4.30% weight of the sample is lost in this stage of thermal degradation. The next degradation stage starts nearly at 200^{0}C and ends around 420^{0}C in Neem seeds. Maximum weight loss (57.91%) can be observed in this stage. This stage can be considered as active pyrolysis zone. The degradation of hemicellulose followed by degradation of cellulose takes place in this stage. Third stage of degradation can be seen in the temperature range of 430^{0}C to 560^{0}C and can be called as passive pyrolysis zone [6-8]. Decomposition of lignin takes place at this stage. Lignin degrades at high temperature due its high thermal stability which is because of the presence of aromatic hydroxyl group in it. Ash is obtained at the end in the form of residue which is 10.98% of the weight of sample taken. Presence of high ash content and high moisture lowers the combustion efficiency. Amount of ash in the substance depends on the soil where it develops. It is the organic matter being in the biomass.

Low lignin content and higher content of hemicellulose and cellulose indicates that the amount of char formation will be low whereas the yield of liquid fuel will be high. [6]

C. FTIR

Fourier Transform Infrared Spectroscopy study is used to identify the functional group present in the sample. FTIR spectrum of Neem seeds is shown in figure 3. Table 2 shows the details of the identified functional groups in the bio-oil. The broad peak observed in the spectrum from 3500 cm^{-1} to 3300 cm^{-1} represents the presence of moisture, phenols and carboxylic acid in the seeds and is caused due to O-H stretching. It shows the presence of fiber in the seeds. The absorption peak at 2930-2850 cm^{-1} represents the presence of alkanes and can be attributed to the axial deformation of C-H group. Another major peak arising in the range of 1750 -1710 cm^{-1} represents the presence of carbonyl group which provides evidence for the presence of hemicelluloses in the seeds. Presence of alkenes and aromatic compounds can be seen in the range of 1640-1500 cm^{-1} which can be attributed to the C=C stretching vibration. Peaks in the range 1480-1330 cm^{-1} is due to C≡C stretching which shows the presence of alkynes. Peaks in 1290 – 980 cm^{-1} range are due to C-O stretching and designate ester and ether present in the seeds. Peak at 1155.84 cm^{-1} can be associated with the asymmetric deformation of C-O-C of the cellulose and hemicellulose. Absorption peak seen in the range 890-610 cm^{-1} is due to O-H bending and shows the presence of mono and polycyclic substituted aromatics groups. Study shows the presence of aliphatic group in abundance accompanied by the presence of few aromatic groups in the seeds. It clearly suggests the presence of cellulose, hemicellulose and lignin in Neem seeds. [3,5]

TABLE II. FTIR ANALYSIS FOR DETERMINATION OF FUNCTIONAL GROUPS PRESENT IN THE NEEM SEEDS

Wavelength (in cm^{-1})	Functional group	Type of vibration
3500-3250	Carboxylic acid, phenol, water impurities	O-H stretching
2930-2850	Alkane	C-H stretching
1750-1710	Ketone	C=O stretching
1640-1500	Alkene, Aromatic	C=C stretching
1480-1330	Alkyne	C≡C stretching
1290-980	Ester and Ether	C-O stretching
890-610	Mono and polycyclic substituted aromatics groups	O-H bending

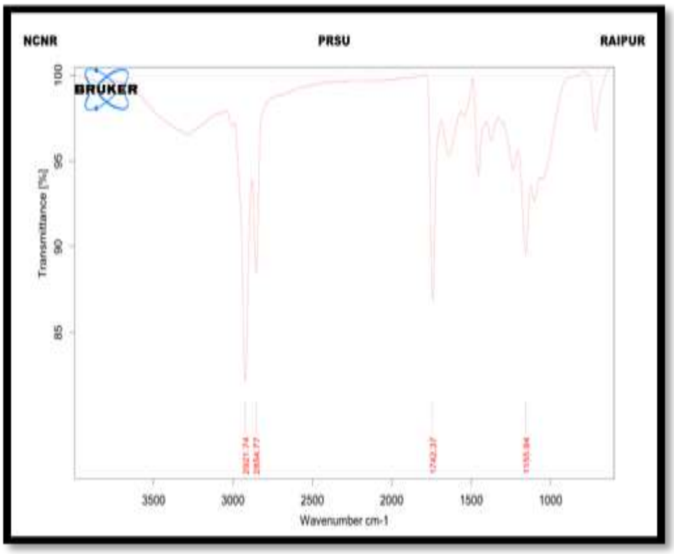


Fig. 2. FTIR spetrum of neem seed

D. GCMS

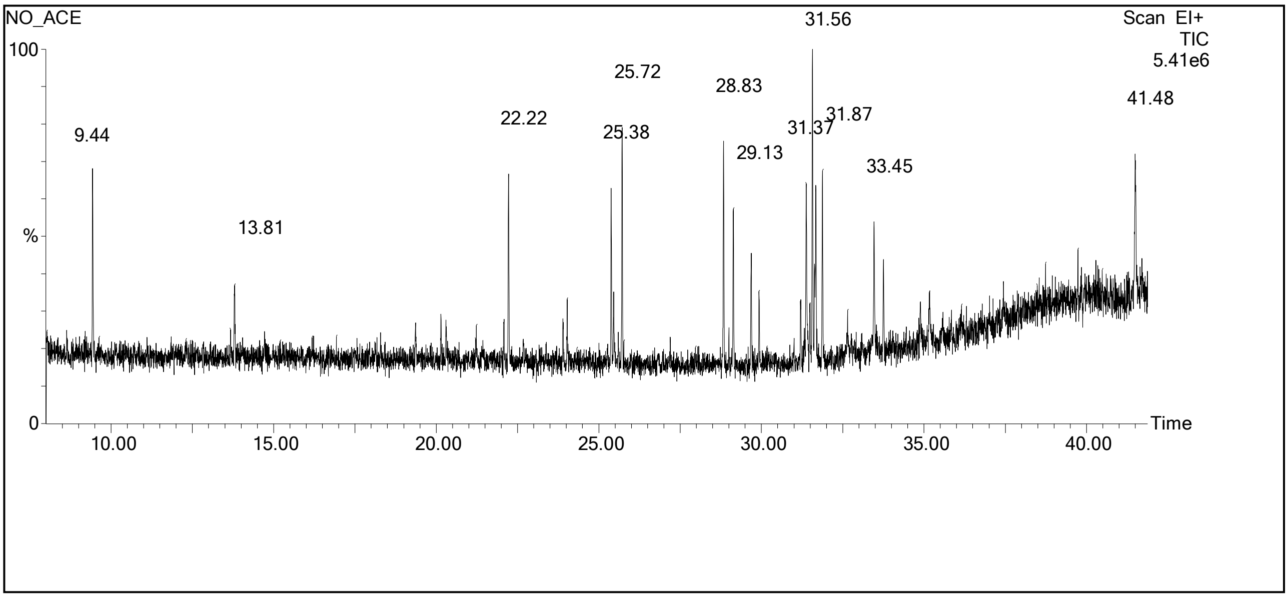


Fig. 3. Gcms spectrum of neem oil

Figure 4 shows the chromatogram of oil extracted from neem seeds through intermediate pyrolysis. In GCMS analysis identification of several components present in bio-oil is done through the peaks shown in chromatogram. Table 3 shows the list of components identified with their retention time. Succinic acid finds use in pharmaceutical industry. It can also be used as a surfactant/ detergent extender/ foaming agent, as an iron chelator where it is used in electroplating to prevent iron from getting corroded. Tridecane is used in the manufacture of paraffin products. It is also used in rubber industry, paper processing industry. It is also used as a solvent and distillation chaser [9]. Thiolane or THT (tetrahydrothiophene) or thiophane is an organo sulphur compound. This has been used as an odorant in LPG and natural gases with some mixtures [10]. Decanoic acid acts as an antibacterial agent and anti-inflammatory agent [11]. Hentriacontane is reported to show antitumor activity and antifungal properties against fungal spore germination. It also acts as antioxidant and antibacterial. [12]

No.	**Retention time**	**Area%**	**Norm %**	**Name**
1	9.439	1.085	74.53	Succinic acid, but-3-yn-2-yl 2-methoxyethyl ester
2	22.224	1.046	71.91	Tridecane, 2,2,4,10,12,12-hexamethyl-7-(3,5,5-trimethylhexyl)-
3	25.375	0.826	56.78	3-n-hexylthiolane, s,s-dioxide
4	25.716	1.247	85.73	Hentriacontane
5	28.832	1.132	77.79	2-pentacosanone
6	29.132	0.808	55.55	Tetradecanoic acid, 10,13-dimethyl-, methyl ester
7	31.373	1.402	96.35	1-undecene, 11-nitro-
8	31.563	1.455	100.00	13-methyltetradec-9-enoic acid methyl ester
9	33.454	0.925	63.59	2-ethylthiolane, s,s-dioxide

TABLE III. GCMS ANALYSIS OF COMPOUNDS PRESENT IN THE NEEM BIO-OIL

E. Calorific value of bio-char

Bomb calorimeter was used to measure the calorific value of neem char obtained after intermediate pyrolysis of neem seeds. The calorific value of neem bio char is found to be 19.365 MJ/Kg.

F. Influence of temperature on yield

Table 4 shows the details of yield obtained as result of extraction through biomass at different temperatures. As the pyrolysis temperature increased, then the gas yield increased and char yield decreased. This indicates that the pyrolysis proceeded further at higher temperature. Bio-oil yield did not show appreciable changes within the temperature range tested. At 475 0C maximum bio-oil yield was observed. TGA results can be used for explaining the decrease in yield after 475 0C. At higher temperature the decomposition of cellulose and hemicellulose gets completed and only the decomposition of lignin takes place that yields bio char. Rate of cracking of condensable molecules into non-condensable gases exceeds the production rates of condensable molecules by decomposition of lignin, thus bio-oil yield decreases with increase in pyrolysis temperature for higher temperature range [1]. Figure 5 shows the graph plotted between yields (biogas, bio-oil and char) and different temperature.

TABLE IV. BIO-OIL YIELD EXTRACTED AT DIFFERENT TEMPERATURE RANGES

Temperature (^{0}C)	bio-oil (%yield)	bio-char (%yield)	bio-gas (%yield)
450	37	25	28
475	45	20	31
500	41	18	33
525	39	15	35
550	37	14	34

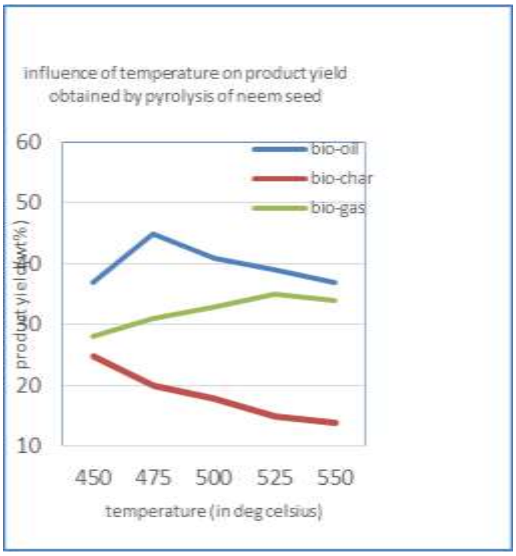


Fig. 4. variation of bio-oil yield for different temperature

G. *Effect of particle size on bio-oil yield*

Particle size of biomass controls the heat transfer rate to the input biomass. Thus, it is also one of the factors that effects the yield in intermediate pyrolysis. Table 5 shows the variation in bio-oil, biogas and char yield obtained as result of extraction for different particle size of biomass. Higher particle size slow down the rapid flow of heat from hot to cold end as the distance between the aid biomass and its core increases. The process of thermal cracking in biomass leads to the formation of vapors. As the particle size is increased these vapors have to travel longer distance through the char which leads to more secondary reactions and hence more char formation. [2] Figure 6 shows the graph plotted between yields (biogas, bio-oil and char) and different particle size of biomass.

TABLE V. BIO-OIL YIELD FOR DIFFERENT PARTICLE SIZES OF BIOMASS

Particle size (mm)	Bio oil (%yield)	Bio char (%yield)	Bio gas (%yield)
0.15	38	17	45
0.30	40	18	42
2	45	20	35
4	42	28	30

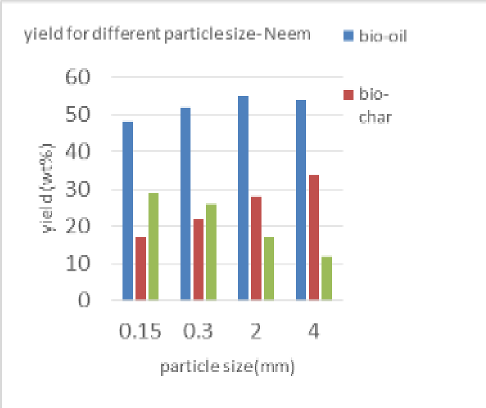


Fig. 5. variation of bio-oil yield for different particle size of biomass

V. CONCLUSION

Bio-oil is extracted from neem seeds using intermediate pyrolysis reactor developed at lab. Proximate analysis represents the volatile content present in the seeds is quite high (87%). Moisture, ash and carbon content are found to be low. TGA shows maximum weight loss between 200- 420 0C temperature range thus it acts as the active pyrolysis zone. Lignin content indicates low char formation. FTIR indicates the presence of various compound of hydrocarbon present in the extracted neem oil such as alkanes, alkenes, aliphatic and aromatic compounds, carboxylic acid, esters etc. The chromatogram obtained from the GCMS of bio-oil verifies the presence of different compounds that show curative properties for skin, hair etc. Antibacterial, antibacterial properties are observed for some of the compounds such as Decanoic acid and Hentriacontane. Different components present in the oil shows wide range of other applications. Calorific value of neem bio-char was measured as 19.365 MJ/Kg. Study on the variation of bio-oil yield for different temperature shows maximum yield at 475 0C. Particle size of biomass is a very important factor that effects the bio-oil yields. Maximum yield was obtained when the particle size of 2 mm was used for extraction. Different medicinal properties are shown by the extracted neem oil. High calorific value, low moisture and ash content and less amount of char formation makes it a potential candidate to be used as biofuel.

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