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EXTRACTION OF KARANJA OIL THROUGH PYROLYSIS AND ITS CHARCATERIZATION

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ABSTRACT-

Karanja oil has been used for medical purpose in rural areas for a long time. It was also used to light lamps. This work studies the extraction of oil from karanja seeds through pyrolysis. Proximate analysis shows the content of moisture, and volatile content. The yield of bio-oil, bio-gas and bio-char depends upon the particle size of starting material and also the temperature of pyrolysis. TGA is done to find out the active pyrolysis zone. FTIR study shows the presence of ester, carboxylic acid and aliphatic and aromatic groups in bio oil. GCMS study supports the results obtained. Calorific value is determined using bomb calorimeter. Karanja oil possesses medicinal properties due to its composition as well as shows the potential to be used as bio-fuel.

KEYWORDS- pyrolysis, intermediate pyrolysis, biomass, bio-oil, bio-gas, TGA, FTIR, Proximate analysis, Calorific value

INTRODUCTION-

Energy plays an important role in social and economic development of any country. Energy sources such as fossil fuel are limited and release harmful gases like CO_2, CO etc. resulting in global warming. Biomass has the potential to be used as an energy source to supplement decreasing fossil fuels. It is a renewable clean source of energy and is widely available. Pyrolysis is an efficient thermochemical process to convert biomass into energy as it is simple and energy conversion is also high. This method is used to extract bio-oil, biogas and char from biomass [k1, k4, ot1] . Non-edible seeds such as karanja, jatropha, mahua etc. can be used as biomass. They are available in abundance in Indian forests. Karanja trees can grow well in the tropical climate of India. Karanja belongs to leguminsae family and is found mainly in south-east Asia and Australia. It can be planted in pastures as it is a shady tree and grass grows well in its shade. Also, it can resist drought well and its tolerance towards salinity is quite high. Presence of certain flavones, flavonols and furanodiketones in karanja oil makes it inappropriate for eating[k1]. In this paper we use karanja seeds to extract bio-oil through Intermediate pyrolysis. The residue left after pyrolysis is bio char which finds application in agriculture. The properties of seeds as well as the bio-oil extracted from seeds will be studied to identify its medicinal properties and possibility to be used as biofuel.

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MATERIAL AND METHOD –

Seeds of karanja are collected and dried in sun for 5-6 days. They are then crushed and sieves are used to collect different sized crushed particles. Yield of bio-oil, biogas and bio char is affected by particle size of sample and temperature used as pyrolysis zone. The particle size that shows maximum yield of bio-oil is chosen to study the properties of bio-oil. Proximate analysis of the crushed seeds gives information about the content of moisture, volatile matter, ash and fixed carbon present in it. For TGA curve, the sample is placed in alumina crucible and heated from 25^0C to 700^0C with nitrogen gas flow of 70.0 ml/min. Air in the pyrolysis zone is displaced by this inert purge gas to restrict unwanted oxidation of sample. For plotting the TGA curve weight of sample (Y axis) is measured as the temperature (X axis) is increased from 25 ^{0}C to 700 ^{0}C. Loss in weight per unit temperature is plotted by taking temperature in X axis in DTG curve. For this analysis approximately 7.2450 mg of sample is taken. Heating rate used is 10.0 K/min. METTELER TOLEDO TGA 1 MODULE is used to record the TGA and DTG profile. ALPHA ATR-ZnSc Model, Bruker is used to carry out the FTIR analysis. It provides information about the functional groups present in bio-oil. Wave number range used is 600-4000 cm^{-1}. Calorific value of karanja char is calculated using Toshiwala bomb calorimeter (IS1350-1, India).

RESULT AND DISCUSSION –

1. Proximate analysis

The quality of biofuel is estimated by understanding the amount of moisture, fixed carbon, volatile matter and ash present in it. For this Proximate analysis of the sun dried karanja seeds is done. Moisture content is the amount of water present in unit mass of dry solid. 1gram seeds are heated for 1 hour at 105-110 ^{0}C in hot electric oven. Desiccator is used for cooling the heated sample and it is then weighed to find out the loss in weight of sample. This tells about the moisture present in seeds. Silica crucible with lid is used to heat this moisture free sample in muffle furnace for 7 minutes at temperature range of 925 ± 20 ^{0}C. Crucible is then taken out of the furnace. The cooled sample is weighed. Loss in weight shows the amount of volatile matter of sample. The sample is heated again without using lid in the oven for 30 minutes at temperature range of 700 ± 20 ^{0}C. The sample left is referred to as ash. Fixed carbon content is calculated by subtracting the weight loss percent of moisture, volatile matter and ash from the 100.

Table 1 shows the Proximate analysis of the karanja seeds.

Table 1 Proximate analysis of Karanja seeds

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Moisture content (%)	6.89
Volatile matter (%)	84
Ash content (%)	1.29
Fixed carbon content (%)	7.82

In Karanja seeds content of moisture is low where as that of volatile matter is quite high. Ash content is very low in seeds. Fixed carbon content and low moisture enhances the quality the heating value of biomass. Fixed carbon present in seeds act as main heat generator on burning the biomass. Easy ignition of fuel is supported by high content of volatile matter. The residue left is the ash. It acts as sink. High amount of ash can lower the calorific value. Thus, very low amount of ash adds to the quality of biofuel.

2. Yield at different temperature

Temperature (^{0}C)	bio-oil (%yield)	bio-char (%yield)	bio-gas (%yield)
450	38	30	18
475	42	27	21
500	50	25	22
525	55	22	23
550	48	20	26
575	46	15	27

Table 4 Bio-oil yield extracted at different temperature ranges of Karanja seed

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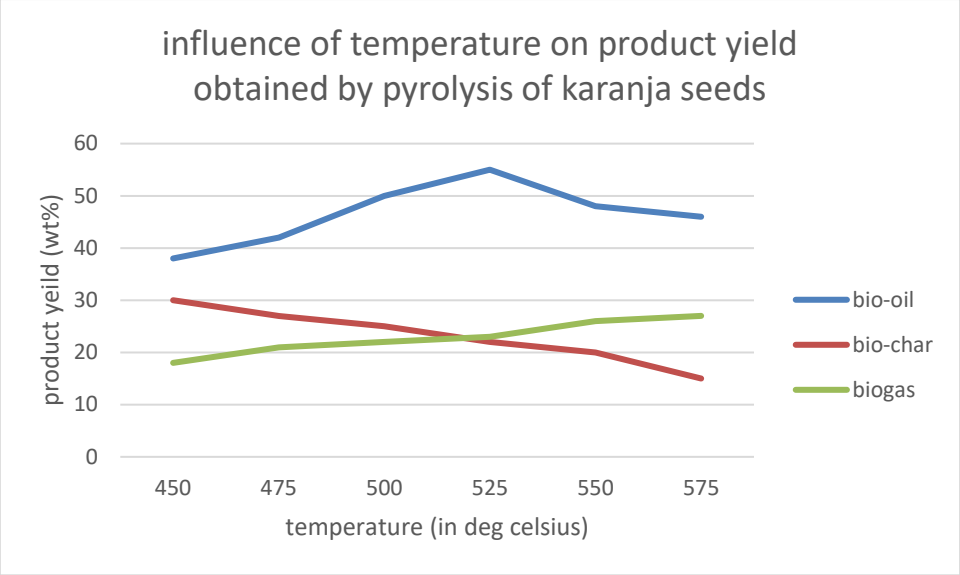

3. Yield for different particle size

In Pyrolysis, thermal degradation of karanja seeds takes place in oxygen free environment. The rate at which heat is transferred to the biomass is controlled by the size of particle. In large particles, the distance between the aid biomass and core increases, which results in slowing down of heat flow from hot to cold end. Vapours are formed when thermal cracking of biomass takes place. In large particles these vapours travel longer distance through the char which results in further secondary reaction and finally results in increased car yield. Thus the yield of biogas, bio-oil and char obtained as a result of pyrolysis depends on the size of particle of biomass.

Table 5 Bio-oil yield for different particle sizes of biomass of Karanja seed

Particle size (mm)	Bio oil (%yield)	Bio char (%yield)	Bio gas (%yield)
0.15	48	17	29
0.30	52	22	26
2	55	28	17
4	54	34	12

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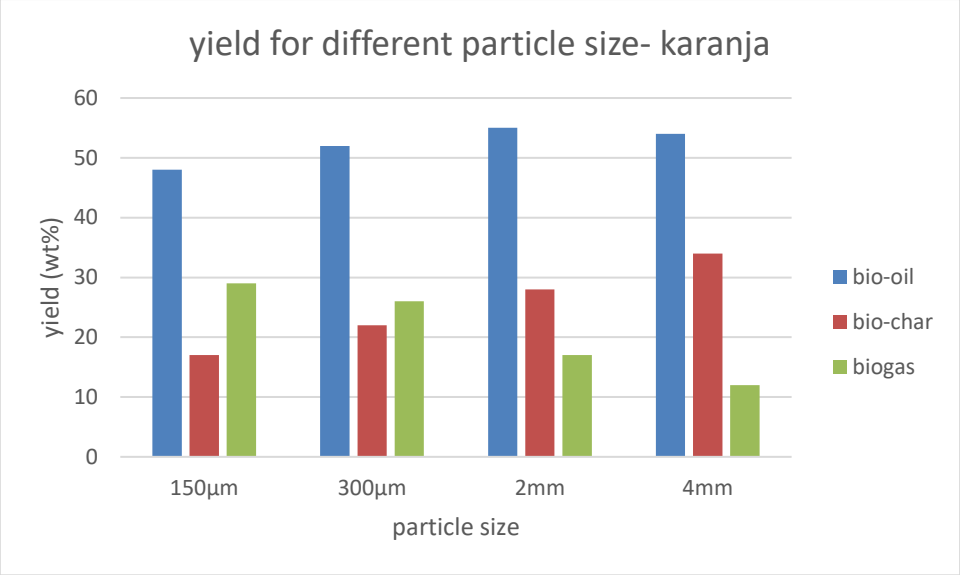

4. Thermal degradation profile for karanja seeds

TGA of sun dried karanja seeds is carried out to determine the temperature for effective pyrolysis i.e., the temperature range where maximum thermal degradation takes place. A graph between Thermo-gravimetric weight loss in the sample with rising temperature is plotted.

Figure 3 shows the TGA curve plotted between weight (in mg) with increasing temperature (in ^{0}C) and DTG curve plotted between weight per unit temperature (in mg/^{0}C) vs. temperature (in ^{0}C) for karanja seeds. Nearly 8.35% loss in weight of karanja seeds can be seen due to thermal degradation till 150^{0}C. This occurs due to loss of moisture and other volatile compounds that are present in the seeds. This is the first stage of degradation for Karanja seeds. The second stage of degradation continues till 500- 510^{0}C where degradation of hemi-cellulose takes place initially till 330^{0}C, followed by the degradation of cellulose. Decomposition of cellulose and hemi-cellulose in this stage results in weight loss of nearly 62.56%. This stage can thus be considered as active pyrolytic zone for karanja seeds where maximum volatilization occurs. The last stage of degradation starts around 510^{0}C and continues till 610^{0}C approx. This stage can be referred to as the passive pyrolysis zone. Lignin or complex high molecular weight compounds present in the karanja seeds degrade thermally into low weight molecular components [7, 8, 9, 10]. At the end, the residue left is bio char which is 0.41 mg (5.62% of initial weight of seeds sample). This can find application as solid fuel, medicinal additive or as bio-adsorbent. Slow and continuous weight loss occurs in the last stage.[9-11]

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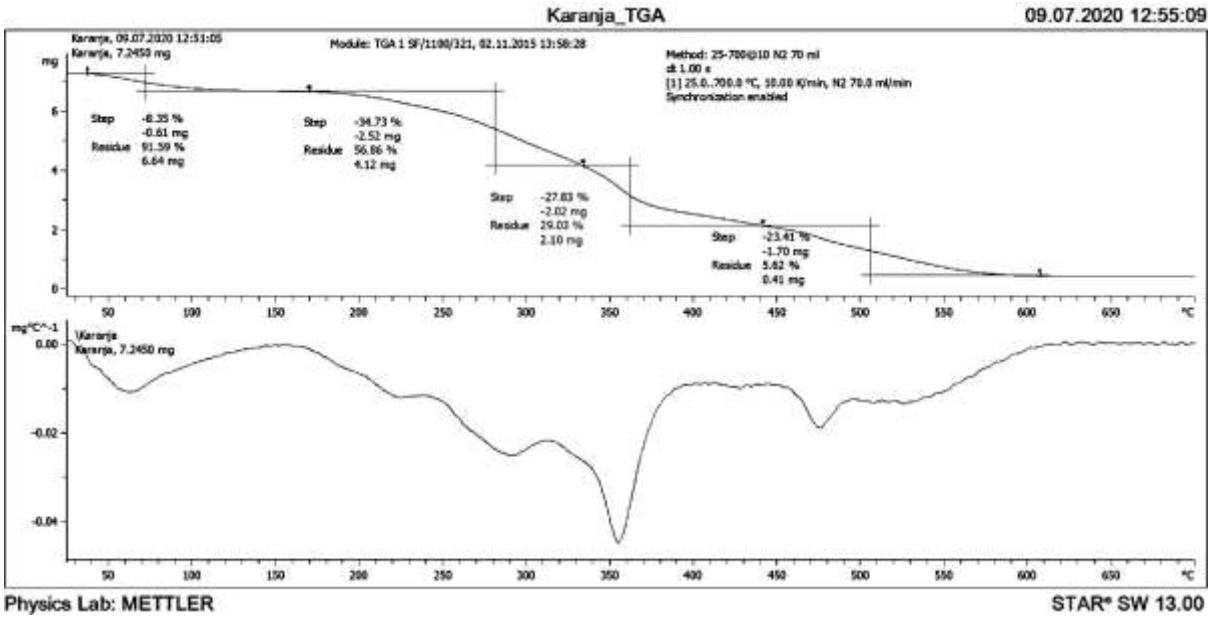

Figure3. TGA and DTG plot of Karanja seeds.

5. Ftir study

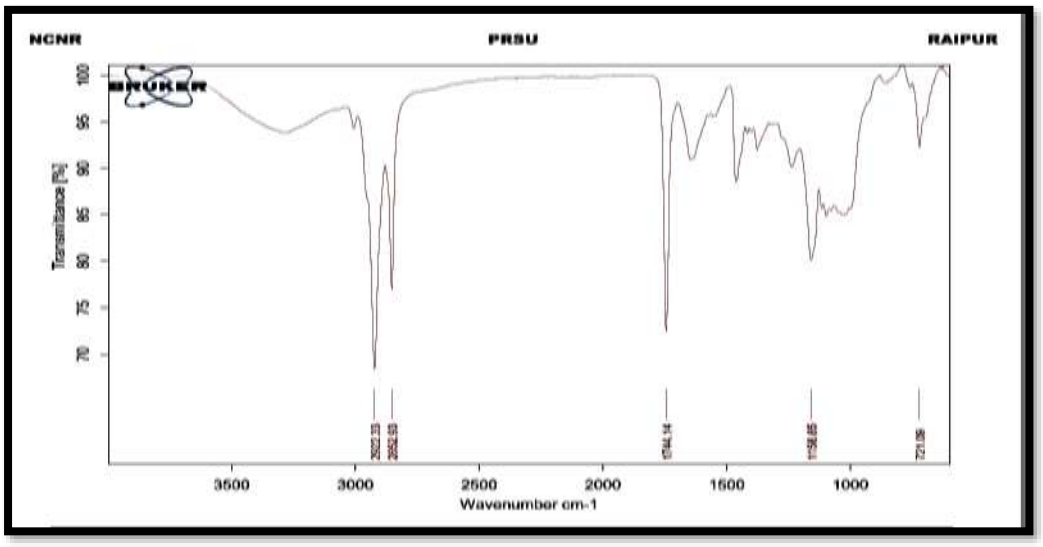

Figure 4 FTIR spectrum of Karanja seeds.

Organic, inorganic and polymeric components present in the sample can be identified through FTIR analysis. FTIR spectrum of karanja oil is in the range of 500 to 4000 cm^{-1} as shown in figure 4. A broad band around 3250 cm^{-1} can be seen in the spectrum because of the bending and stretching vibration of O-H bond which shows oxygenated compounds such as alcohol etc. along with moisture present in the bio oil. C-H stretching can be attributed for the double peak at 2922.33cm^{-1} and 2852.93 cm^{-1} which shows the presence of alkanes and methylene groups. Strong absorption peak at 1744.14 cm^{-1} due to –C=O

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stretching represents free carbonyl groups of hemicellulose and triglycerides [k01]. Peaks around 1600 cm^{-1} were result of C=O stretching and thus attributed to presence of aldehydes, ketones and ester groups and can be associated with lignin bonds. Peaks between 1400 cm^{-1} to 1600 cm^{-1} indicates presence of alkanes and alkenes groups (C-H bending vibrations). Peak at 1158.85 cm^{-1} and nearby peaks represent esters and phenols that show medium vibration C-O-C stretching for esters or carboxylic acids and the peak at 721.09 cm^{-1} can be due to the presence of =C-H group. Peaks around 1000 cm-1 are attributed to alkyl substituted C-O stretching ether. Peaks in the range of 600-900 cm^{-1} show presence of aromatic groups.

6. Calorific value

15.035 MJ/kg

Karanja oil has less calorific value because of the high content of oxygen in bio oil.

Gas chromatography is used to separate the components of a sample and provide a spectral signature for it. The procedure involves injecting the sample into the injection port of the gas chromatography device, which then vaporizes the sample. Post vaporization, the various components can be separated and analyzed as each of them results in a different spectral peak.

Retention time is the time that passes between injection and elusion of a sample component from the column, and this parameter is used to differentiate between the components. Another parameter is the size of the peak, which also gives information on the concentration and type of components of the sample.

Mass spectrometry analyses a sample by electrically charging the molecules of a specimen. These molecules are then accelerated through a magnetic field and broken into charged fragments.

CONCLUSION-

Bio-oil is extracted from karanja seeds using intermediate pyrolysis reactor developed at lab. Proximate analysis represents the volatile content present in the seeds is quite high (84%). 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. . Different components present in the oil shows wide range of other applications. Calorific value of neem bio-char was measured as 15.05 MJ/Kg. Study on the variation of bio-oil yield for different temperature shows maximum yield at 500 0C. Particle size of biomass is a very important factor that effects the bio-oil yields. Maximum yield was obtained when

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the particle size of 2 mm was used for extraction. Different medicinal properties are shown by the extracted karanja 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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