EXPERIMENTAL STUDIES ON EXTRACTION OF VALUABLE FUELS FROM KARANJA AND NEEM SEED BY PYROLYSIS

A THESIS SUBMITTED IN THE PARTIAL FULFILLMENT OF THE REQUIRMENT FOR THE DEGREE OF

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Submitted by

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CERTIFICATE

This is to certify that the thesis entitled, **"EXPERIMENTAL STUDIES ON EXTRACTION OF VALUABLE FUELS FROM KARANJA AND NEEM SEED BY PYROLYSIS"** submitted by Mr. Niraj Kumar Nayan (107CH008) in partial fulfillments for the requirements for the award of Bachelor of Technology Degree in Chemical Engineering at National Institute of Technology, Rourkela (Deemed University) is an authentic work carried out by him under my supervision and guidance.

To the best of my knowledge, the matter embodied in the thesis has not been submitted to any other University / Institute for the award of any Degree or Diploma.

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CHEMICAL ENIGEERING

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ABSTRACT

Today we see everywhere that oil has become inherent part of our daily life. Every activity is dependent on the requirement of fuels be it directly or indirectly. The demand of fuels is increasing day by day. Import dependence for oil in India which is about 70 per cent, is likely to increase further. As we all know that the petroleum resources are limited and are non-renewable in nature, we must start to think about the alternatives as we are likely to run out of the petroleum resources in few decades or so. Stress must be given to production of energy from renewable sources as they are biodegradable and non-toxic.

Here an attempt has made to study the feasibility of production of valuable fuels from natural but non edible seeds such as karanja and neem seeds by the method of pyrolysis. Here the production of the fuel can serve purpose of alternative fuels as biomass pyrolysis oil has potential to be used as fuel oil or its substitute.

Keywords: *Biomass, Thermal pyrolysis, TGA, GC-MS, Biofuels*

INTRODUCTION

AND LITRETURE

SURVEY

1.1) INTRODUCTION

The reforms initiated in India since the beginning of the nineties have led to rapid economic progress and better growth rates. In the first decade of this century the growth rates seem to be still better. Studies by several academics and consultants forecast continued high growth rate for the next several decades. Growth in economy is made possible by several inputs, the two most important being energy and human resource. Growth of an economy, with its global competitiveness, hinges on the availability of cost-effective and environmentally benign energy sources, and on the other hand, the level of economic development has been observed to be reliant on the energy demand

For a large country like India with its over one billion population and rapid economic growth rate, no single energy resource or technology constitutes a panacea to address all issues related to availability of fuel supplies, environmental impact, particularly, climate change, and health externalities. Therefore, it is necessary that all non-carbon emitting resources become an integral part of an energy mix – as diversified as possible – to ensure energy security to a country like India during the present century. Available sources are low carbon fossil fuels, renewable and nuclear energy and all these should be subject of increased level of research, development, demonstration and deployment [1].

Below is the table that shows India's fossil fuel reserve and its rate of production and consumption.

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Table 1 Fossil fuel reserve of India (2008) [3]

Resources	Proved reserve	Production	Consumption
Oil	5.8 billion barrels	0.76 million barrels per day	2.88 million barrels per day
Natural gas	1009 billion cubic meters	30.6 billion cubic meters	41.4 billion cubic meters
Coal	58.6 billion ton	512.3 million tons	608.3 million tons

At the end of 2005, India had 0.5 % of the Oil and Gas resources of the world and 15 % of the world's population whereas the reserve to production ratio is 20:7. At the end of 1995 India had the 5.5 thousand million barrels of reserves, grown only 1% till the end of 2005 whereas crude oil consumption has grown more than 10% over the last 5 years. Domestic production of crude oil has been a reason of worry for the Indian economy for some time now. For more than 16 years the total production of crude has stagnated around 32-33 MMT. This has been particularly disturbing given the crude oil consumption in the country implying an increasing dependence on imported crude. At present India's crude dependence is around 78%. According to TERI estimates, by 2030 India's import dependency may shoot up to a disturbing 93%. [20]

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India's Oil Production and Consumption
1990-2009*

Source: U.S. Energy Information Administration

*2008-09 is forecast
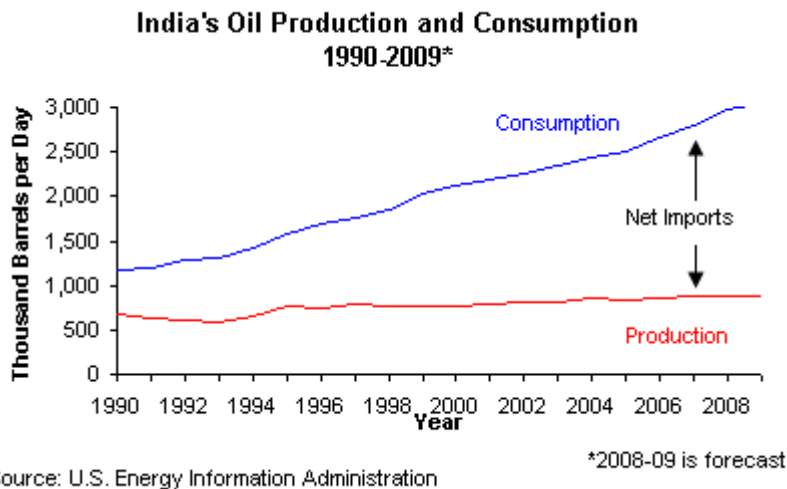
Figure 1 India's oil production and consumption [3]

Seeing the above graph and also observing the rising prices of crude oil and petroleum oil it has become quite necessary that we must start investing in alternative sources of energy. At present, contribution from non-conventional energy sources, such as solar, wind, biomass, small hydro (upto 25 MW capacity), etc. is around 3% of the total installed power generating capacity. The strategy to enhance the grid supply of power from renewable sources of energy or from co-generation has to aim at improving despatchability and cost competitiveness. A suitable policy framework would need to be introduced for providing remunerative returns and encouraging private investments. Development and promotion of this sector, which is environmentally benign, should not be constrained by intrusive regulation. [3]

Also global warming is another aspect in which we have to look into. The emission of the green house gases (GHGs) needs to be controlled. India is the sixth largest greenhouse gas (GHG) emitter in the world, and the fastest-growing one after China. We all know the adverse effect hence the Renewable Energy Plan 2012 calls for achieving a 10 percent share for renewable

energy in incremental power capacity by adding about 10,000 MW of new renewable energy (RE) based generation. [2]
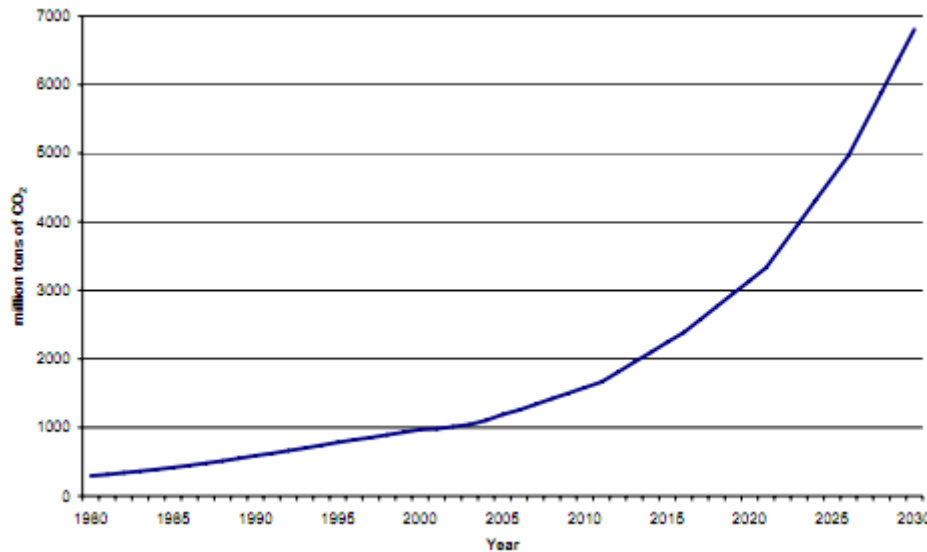
Figure 2 CO$_2$emission from fuel combustion in India [2]

So as to control the emission of GHG the Electricity Act of 2003 has provided a major thrust to RE technologies via its mandate: "To promote cogeneration and generation of electricity through renewable sources of energy by providing suitable measures for connectivity with the grid and sale of electricity to any persons, and also specifying, for purchase of electricity from such sources, a percentage of the total consumption of electricity in the area of a distribution licensee."

Detailed cost-benefit assessments were undertaken for India's energy sector mitigation options in the India country study conducted under the Asia Least Cost Greenhouse Gas Abatement Strategy (ALGAS, ADB, 1998) project. [2]

Table 2 Cost effectiveness of some RE option in India [2]

Technologies	GHGs emission reduction (Kg/KWH)	Investment cost (US$/KW)	Cost effectiveness (US$/ton CO_2)
Small hydro	1.3	1950	88
Wind farms	1.3	1405	257
Biomass	1.6	710	102
Solar thermal	1.3	3730	592
Solar PV	1.6	5952	541

Observing from the table above we can see that the biomass has the maximum potential for GHGs emissions and also the investment cost is lowest than the other RE sources.

Here an attempt is made to study the feasibility of production of valuable fuels from natural but non edible seeds such as karanja and neem seeds by the method of pyrolysis. As the production of the fuel can serve purpose of alternative fuels as biomass pyrolysis oil has potential to be used as fuel oil or its substitute. It can also be used as blend with normal diesel.

Although in European countries and USA the biodiesel are produced from edible oil as their production of edible oil is quite high and surplus but in India we prefer non edible oil seeds as the production of edible oil seeds in India is insufficient and we import it from other countries to fulfill the requirements.

1.2) LITERATURE REVIEW

Krawcyzk (1996) - Biodiesel, an alternative diesel fuel, is made from renewable biological sources such as vegetable oils and animal fats. It is biodegradable and non-toxic. It also has low emission profiles and so is environmentally beneficial. [11]

Importance of biodiesel increases due to [4]:-

1) Rising petroleum prices

2) Limited fossil fuel reserve

3) Environmental benefits of biodiesel

Advantages of biodiesel:-

a) Availability and renewability of biodiesel - Biodiesel is the only alternative fuel with the property that low concentration biofuel–petroleum fuel blends will run well in unmodified conventional engines. It can be stored anywhere petroleum diesel fuel is stored. Biodiesel can be made from domestically produced, renewable oilseed crops such as soybean, rapeseed and sunflower. The risks of handling, transporting and storing biodiesel are much lower than those associated with petroleum diesel. Biodiesel is safe to handle and transport because it is as biodegradable as sugar and has a high flash point compared to petroleum diesel fuel. Biodiesel can be used alone or mixed in any ratio with petroleum diesel fuel.

b) Lower emission from biodiesel - Biodiesel mainly emits carbon monoxide, carbon dioxide, oxides of nitrogen, sulfur oxides and smoke. Combustion of biodiesel alone provides over a 90% reduction in total unburned hydrocarbons (HC) and a 75–90% reduction in polycyclic aromatic

hydrocarbons (PAHs). Biodiesel further provides significant reductions in particulates and carbon monoxide over petroleum diesel fuel. Biodiesel provides a slight increase or decrease in nitrogen oxides depending on engine family and testing procedures. Because biodiesel is made from renewable sources, it presents a convenient way to provide fuel while protecting the environment from unwanted emissions

c) Biodegradability of biodiesel - Biodegradable fuels such as biodiesels have an expanding range of potential applications and are environmentally friendly. Therefore, there is growing interest in degradable diesel fuels that degrade more rapidly than conventional petroleum fuels. Biodiesel is non-toxic and degrades about four times faster than petroleum diesel. Its oxygen content improves the biodegradation process, leading to an increased level of quick biodegradation

Different methods use for production of biodiesel [4]:-

1) **Direct use/blending** - Vegetable oil can be used directly as diesel fuel without any changes in the engine. The very first engine (by Rudolf Diesel) was tested using vegetable oil as fuel. The primary concern with vegetable oil as fuel is its high viscosity (atomization of vegetable oil is difficult) which leads to problem in long run as there is carbon deposits, coking and trumpet formation on injectors, thickening, gelling and oil ring sticking.

2) **Micro emulsions** – It is defined as colloidal dispersion of fluid microstructures (1-150 nm) in solvents forming two immiscible phases. The common solvent used is methanol and ethanol. Micro emulsion is a probable solution to high viscosity of vegetable oil. Their atomization is relatively easy due to lower viscosity.

3) **Pyrolysis** – It is the means of conversion of one substance to another by the application of heat. It is a thermochemical decomposition of organic material at elevated temperatures in the absence of oxygen. Pyrolysis of organic substances produces gas and liquid products and leaves a solid residue richer in carbon content. Catalysts are used to speed up the process. Here the oil yield is due to the fact that cracking of larger hydrocarbons cause them to break into simpler and smaller hydrocarbons by radicalic mechanism which are easily condensable to oil in this case

4) **Trans esterification (alcoholysis)** – It is a kind of organic reaction in which alcohol group in ester is substituted. A catalyst is usually used to improve the reaction rate and yield. Because the reaction is reversible, excess alcohol is used to shift the equilibrium to the products side.

Pyrolysis –

Pyrolysis, strictly defined, is the conversion of one substance into another by means of heat or by heat with the aid of a catalyst (Sonntag, 1979b). It involves heating in the absence of air or oxygen (Sonntag, 1979b) and cleavage of chemical bonds to yield small molecules (Weisz et al., 1979). Chemistry involved in pyrolysis is difficult to characterize because of the variety of reaction paths and the variety of reaction products that may be obtained from the reactions that occur. The pyrolyzed material can be vegetable oil, animal fat, natural fatty acids or methyl esters of fatty acids. The pyrolysis of fats has been investigated for more than 100 years, especially in those areas of the world that lack deposits of petroleum. Many investigators have studied the pyrolysis of triglycerides to obtain products suitable for diesel engines. Thermal decomposition of triglycerides produces alkanes, alkenes, alkadienes, aromatics and carboxylic acids. It is one of the energy recovery processes which have the potential to generate oil, char

and gas products. The process conditions of pyrolysis can be optimized to maximize the production of pyrolytic oil, char or gas, all of which have a potential use as fuels. The process parameters which have the major influence on the products are the pyrolysis temperature, heating rate, particle size and retort atmosphere. The oil produced has a high energy density and may be combusted directly or refined for the recovery of specialty chemicals. The production of liquid product has advantages in that it is easier to handle, store and transport [12]

Pyrolysis can be of two types:-1) Catalytic pyrolysis - Here suitable catalyst is used in addition to the heat which speeds up the reaction by increasing the thermal degradation rate of the substance.

2) Non-catalytic pyrolysis - Here only heat is applied for the thermal degradation of the substance.

Chang and wan (1947) setup a large scale of thermal cracking of tung oil calcium soaps where the oil was first converted to soap with lime and then thermally cracked to yield a crude oil, which was refined to produce diesel fuel and small amounts of gasoline and kerosene. 68 kg of the soap from the saponification of tung oil produced 50 L of crude oil.

Niehaus et al. (1986) (a) and Schwab et al. (1988) (b) studied fuel properties of thermally cracked soybean oil and observed the following data:-

Table 3 Observation for soybeen seed by Niehaus and Schwab [12]

Properties	Soybean oil (a)	Soybean oil (b)	Cracked soyb oil (a)	Cracked soyb oil (b)	Diesel fuel (a)	Diesel fuel (b)
Cetane no.	38	37.9	43	43	51	40
Higher heating value (Mj/kg)	39.3	39.6	40.6	40.3	45.6	45.5
Pour point (°C)	-12.2	-12.2	4.4	7.2	-6.7 max	-6.7 max
Viscosity cst , (37.8°C)	32.6	32.6	7.74	10.2	2.82	1.9-4.1

Ozlem Onay and O. Mete Kockar (2000) investigated fixed bed slow and fast pyrolysis of rapeseed. The influence of final pyrolysis temperature, heating rate, particle size range and sweep gas velocity on the product yields were studied. In addition, the pyrolysis oil at the maximum liquid product yield was investigated, using chromatographic and spectroscopic techniques to determine its possibility of being a potential source of renewable fuel and chemical feedstock. They observed the following pattern.
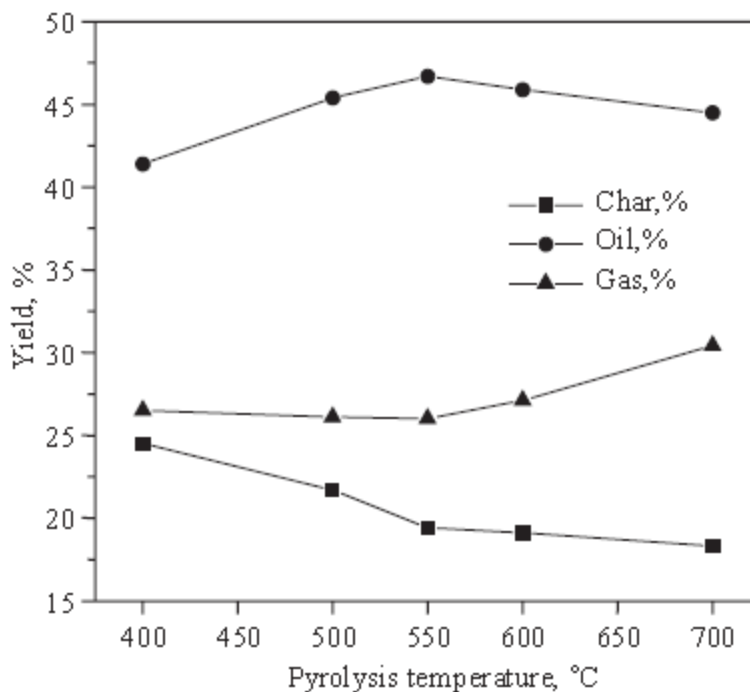
Figure 3 Pyrolysis of rapeseed [7]

They concluded that the oil yield was obtained as 49% from pyrolysis of rapeseed at a final pyrolysis temperature of 550∘C, particle size range of +0:6–1:8 mm with a heating rate of 30∘C min^{-1}. The oil yield only reached 51.7% with the experiments under sweeping gas atmosphere (nitrogen flow rate of 100–200 cm^3 min^{-1}). Employing the higher heating rate of 300∘C min^{-1} breaks heat and mass transfer limitations and the oil yield reach a maximum of 68.0% at the final

pyrolysis temperature of 550∘C, particle size range of +0:6–1:25 mm and sweeping gas flow rate of 100 cm^3 min^{-1} [7].

Ozlem Onay and Ö. Mete Kockar (2003) also studied slow, fast and flash pyrolysis of rapeseed (*Brassica napus*) in particular, the influence of final pyrolysis temperature, heating rate, particle size range and sweep gas velocity. He found out that Employing the higher heating rate of 300 °C min$^-$1 breaks mass transfer limitations and the oil yield reach a maximum of 68%, increasing by 32%, at the final pyrolysis temperature of 550 °C. Furthermore, in flash pyrolysis conditions, the maximum liquid product yield of 73% was obtained at final pyrolysis temperature of 550–600 °C. [5]

S.H. Beis, O. Onay and Ö. M. Kockar (2002) also studied fixed bed pyrolysis of safflower seed and the influence of pyrolytic parameter on product yields. They observed that at a lower heating rate of 5°C min$^-$1, the char yield decreased from 23 to 19% as the final pyrolysis temperature was raised from 400°C to 700°C. For the heating rates of 40 and 80°C min$^-$1 there are no significant changes in yields of the conversion with increasing pyrolysis temperature from 400 to 700°C. However, at the higher heating rates of 40 and 80°C min$^-$1, the overall conversion yields of pyrolysis were approximately 4% higher than that of the lower heating rate of 5°C min$^-$1. In contrast, the oil yields were approximately 3% lower than that of 5°C min$^-$1. Varying the particle size from dp>1.8 to 0.85<dp<1.25 mm at a pyrolysis temperature of 500°C with a heating rate of 5°C min$^-$1 without any sweeping gas atmosphere had a significant effect on the pyrolysis conversion with it increasing from 75 to 80%. Whereas a decreasing particle size from 0.85<dp<1.25 to 0.425<dp<0.85 mm had no effect on pyrolysis conversion, it remaining constant at the level of approximately 80%. [8][9]

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G. Duman, C. Okutucu, S. Ucar, R. Stahl and J. Yanik (2011) studied the slow and fast pyrolysis of cherry seed in fixed bed and fluidized bed reactor at different temperatures. The effects of reactor type and temperature on the yields and composition of products were investigated. In the case of fast pyrolysis, the maximum bio-oil yield was found to be about 44 wt% at pyrolysis temperature of 500°C for both cherry seeds (CWS) and cherry shell seed (CSS), whereas the bio yields were of 21% and 15% by weight, obtained at 500°C from slow pyrolysis of CWS and CSS, respectively. Both temperature and reactor type affected the composition of bio-oils. The results showed that bio-oils obtained from slow pyrolysis of CWS and CSS can be used as a fuel for combustion systems in industry and the bio-oil produced from fast pyrolysis can be evaluated as a chemical feedstock. [11]
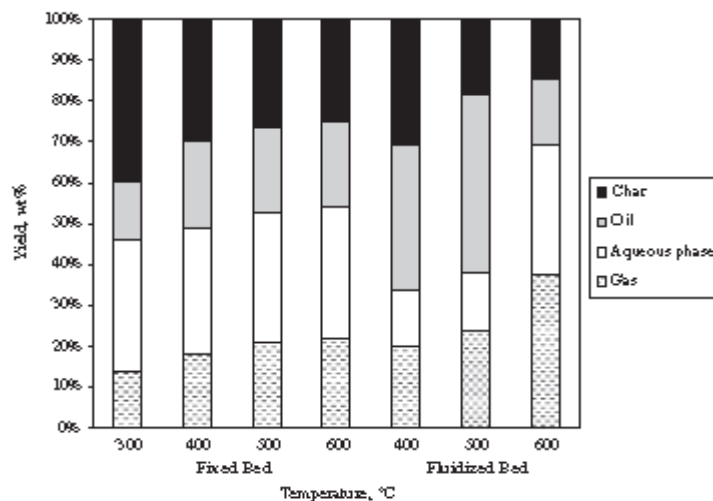

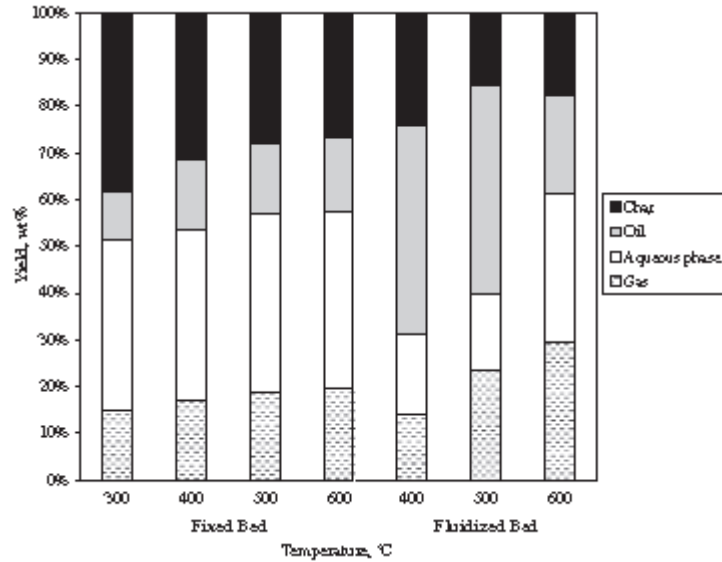**Figure 4 Product distribution from pyrolysis of CWS [11]**

Figure 5 Pyrolysis of CSS [11]

Ozlem Onay (2007) investigated the Influence of pyrolysis temperature and heating rate on the production of bio-oil and char from safflower seed by pyrolysis, using a well-swept fixed-bed reactor. He concluded that high volatile matter content of biomass with low ash and sulfur content is the main criterion for pyrolysis conversion and the high volatile content of safflower seed favors the pyrolysis conversion. He also observed significant decrease in oxygen content of the oil (8.5%) compared to the original feedstock (27.4%) is important, because the high oxygen content is not attractive for the production of transport fuels. As the final pyrolysis temperature was raised from 400 to 700 °C for each heating rate, the char yield significantly decreased. In other words, the pyrolysis conversion increased. The decrease in the char yield with increasing temperature could be due either to greater primary decomposition of the safflower seed at higher temperatures or to secondary decomposition of the char residue. Pyrolysis temperature and heating rate influenced the size and shape of particle through a general increase in size and

proportion of voids and a decrease in cell wall thickness. The fast volatile release during pyrolysis produces substantial internal overpressure and the coalescence a more open structure. Therefore, SEM porosity increased with a pyrolysis temperature and increasing heating rate. The surface area was maximized at pyrolysis temperature of 600 °C and heating rate of 800 °C min−1. Both the hydrogen and oxygen content of char decreased with increase in temperature, indicating an increase in the carbonaceous nature of the char. [9]

R.K.Singh and K.P.Shadangi (2011) investigated Liquid fuel from castor seeds by pyrolysis and concluded that The maximum yield of oil, 64.4% by weight a basis was obtained at a temperature of 550°C. Though the production of oil in volume basis is same from 525°C to 600°C, due to the less completion time and low density oil obtained at 550°C, the optimum temperature for production of oil from castor seed in slow pyrolysis process is 550°C. The functional group present in castor seed pyrolytic oil is similar as compare to other bio oil given in several literatures. The major compounds present in castor seed pyrolytic oil were 10-undecenoic acid, oleic acid, octadecanonic acid, octadec-9-enoic acid, N-hexadecanoic acid, 3-phenyl-5-(pyridin-4-ylmethylidene)-2-thioxoimidazolidin- 4-one, Z-11-pentadecenal, oleanitrile, 9-octadecenamide, (z)-, methy; 12-hydroxy-9-octadecenenoate, 2-pentylnon-2-enal, methy; 12-hydroxy-9-octadecenenoate, 13-hexyl-oxa-cyclotridec- 10-en-2-one with a fewer amounts of ester and alkali compounds. The properties of pyrolytic oil reveal that it can be used as a substitute for fuel. Due to the absence of arsenic compound in the char materials and high calorific value, it can be used as adsorbent as well as solid fuel. [10]

MATERIALS AND METHODS

2.1) Materials

Here two non-edible seeds have been used namely karanja seed (also known as Pongamia glabra) and neem seed (also known as Mellia azadirachta)which was bought from a local fodder shop in Rourkela, Orissa, India. Both the seed were crushed using a household grinder, so that we could feed maximum seed, almost up to the capacity so that there would be minimum void and hence less oxygen for oxidation since pyrolysis is a process of heating substance in absence of oxygen. Below are the figures of karanja and neem seed.

Karanja and neem seed:-

Figure 6 Neem seed

Figure 7 Karanja seed

2.2) Thermo gravimetric analysis

Pyrolysis is heating of a substance in absence of air at a particular temperature. Therefore, the temperature for effective pyrolysis of the karanja and neem seed has to be determined. For this purpose, thermo-gravimetric analysis (TGA) of the sample cake was done using a DTG60 instrument. Around 20-30 milligrams of sample cake was taken and heated up to a final temperature of 800°C and a residence time of 1 minute at 800°C was allowed. TGA was performed in air atmospheres at a heating rate of 10°C/Min. Thermo-gravimetric weight loss curve was plotted against temperature. It provides a range of temperature in which maximum thermal degradation takes place.

2.3) Experimental setup and procedure

The setup consist of a semi-batch reactor in which the seeds are placed and that is then closed very tightly so as to avoid any leakage of gas as the result of pyrolysis. The outlet of the reactor is connected to a condenser (circulating water is the cooling medium) which condenses the gases/vapor coming of the outlet. Just at the other end of the condenser a measuring cylinder is placed where the gases being condensed is collected. The reactor is heated using an electric furnace. The temperature is controlled via PID controller.

The seeds are fed into the reactor and it is closed very tightly using screw and bolt. Once the heating is started and after reaching a suitable temperature the reaction begins and the vapors that are released comes out of the reactor outlet which is connected to the condenser where the vapors are condensed and the collected in the test tube. Most of the non-condensable vapors are simply

released. The product mainly consists of pyrolytic oil and water which then is separated based on density difference.
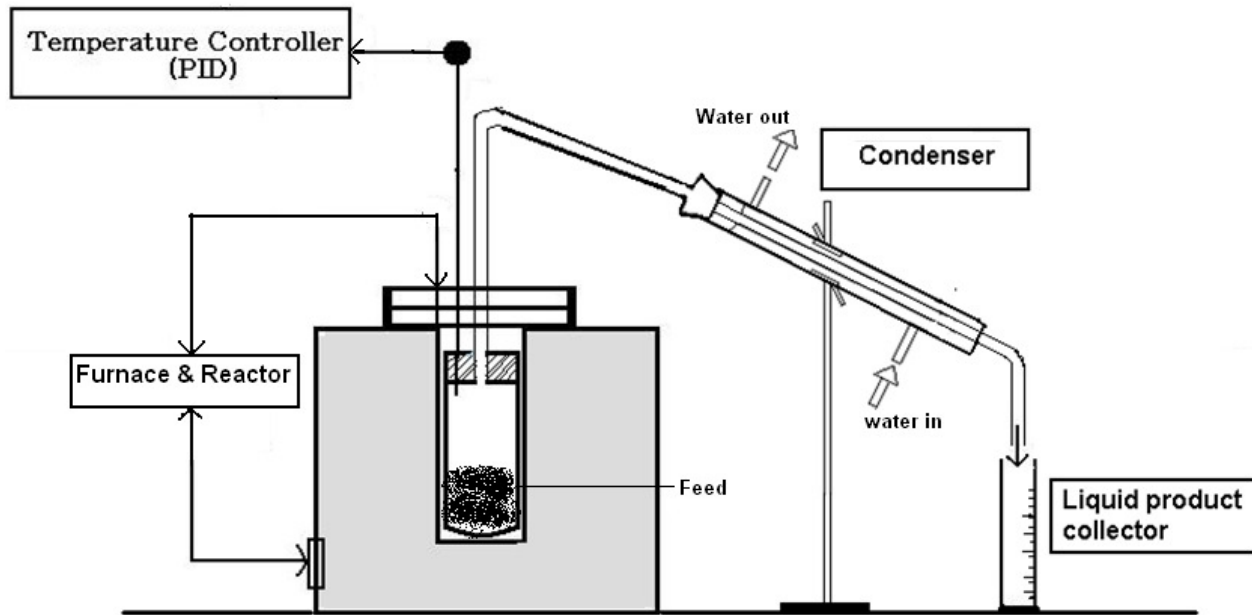
Figure 8 Experimental setup

PROCEDURE

- Firstly approximately 25 gm of sample is taken and fed in the reactor.

- Then the desired temperature is set and the pyrolysis is started.

- Once the reaction begins the reaction time and the yield is noted down.

- This is done for the entire range of temperature with 50°C interval.

- Then the temperature is identified at which there is maximum yield.

- Rest of the extraction is carried out at this temperature.

2.4) Sample pyrolysis run

To determine the temperature at which there is maximum yield in the temperature range obtained by TGA, sample pyrolysis run were done. In the sample pyrolysis run, we took approx. 25 gm of the seed and pyrolysis was done at different temperature in that range at the interval of 50°C, to determine the temperature at which maximum yield of liquid product is obtained. During sample runs various data like reaction time, yield of char, and yield of liquid product were noted down. Variation in yield of char, liquid product and gas (volatiles) with respect to temperature is plotted. Variation in reaction time with temperature was also plotted.

2.5) Characterization of raw material and char

The karanja and neem seed and char of these seeds were analyzed in order to observe the change in the properties of the solid material as a result of pyrolysis.

2.5.1) Proximate analysis

It provides information on moisture content, ash content, volatile matter content and fixed carbon content of the material. It was carried out using ASTM D3172 - 07a method.

2.5.2) Calorific value

Calorific value of a material is the amount of heat liberated when 1Kg of that material is burnt. It was determined for both seed and char using a bomb calorimeter (Model: AC-350, LECO Corporation, USA).

2.5.3) Scanning electron microscopy

The surface of the char obtained was viewed under a Scanning Electron Microscope (Model: JEOL-JSM-6480LV SEM) at different magnification values to have a clear view on pore density and size.

2.6) Physical characterization of bio-oil

Physical properties such as density, specific gravity, viscosity, conradson carbon, flash point, fire point, pour point, cloud point, calorific value, sulphur content, distillation boiling range and cetane index of the bio-oil was determined using the following standard methods:

Table 4 Standard method for physical property analysis

Physical properties	Method
Density	ASTM D1298 - 99
Kinetic viscosity	ASTM D445 - 11
Conradson carbon	ASTM D189 - 06(2010)e1
Flash point	ASTM D6450 - 05(2010)
Fire point	ASTM D1310 - 01(2007)
Pour point	ASTM D5853 - 09
Calorific value	ASTM D5468 - 02(2007)
Distillation boiling range	ASTM D2887 - 08
Cetane index	ASTM D4737 - 10

2.7) Chemical characterization of bio-oil

2.7.1) FT-IR

In order to determine the functional groups present in the pyrolytic oil, Fourier Transform Infrared spectroscopy of the oil was analyzed in a Perkin-Elmer infrared spectrometer.

2.7.2) GC-MS :- Gas Chromatography – Mass Spectrometry of the pyrolytic oil was performed using a GC-MS-OP 2010[SHIMADZU] analyzer in Sargam Laboratory, Chennai to determine the chemical compounds present in the oil.

RESULT AND DISCUSSION

3.1) THERMOGRAVIMETRIC ANALYSIS

Thermo gravimetric analysis (TGA) measures the amount and rate of change in the weight of a material as a function of temperature. TGA is helpful in determining the range of temperature under which the moisture and the volatile content of the substance is driven out which is then condensed and the pyrolysed oil is recovered. Here the TGA is carried in normal atmosphere with the rate of heating being 10°C/minute and the range being room temperature to 800°C.
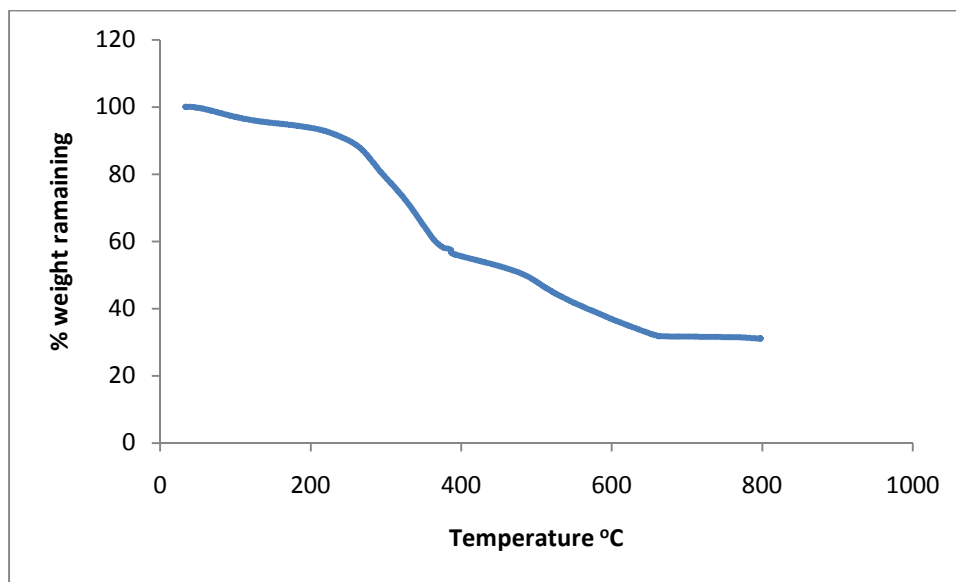
1) NEEM seed

Figure 9 TGA plot for neem seed

The plot shows that maximum thermal degradation took place between ranges of 200°C to 600°C. The initial degradation can be explained by the fact that initially the moisture is driven away as the temperature is increased. Then the removal of volatile matter consisting of relatively

less complex molecules accounts for the further degradation in weight which can be said for the range of 400°C to 550°C. The further degradation can be explained by the fact that much more complex molecules are driven away as the heating progresses.
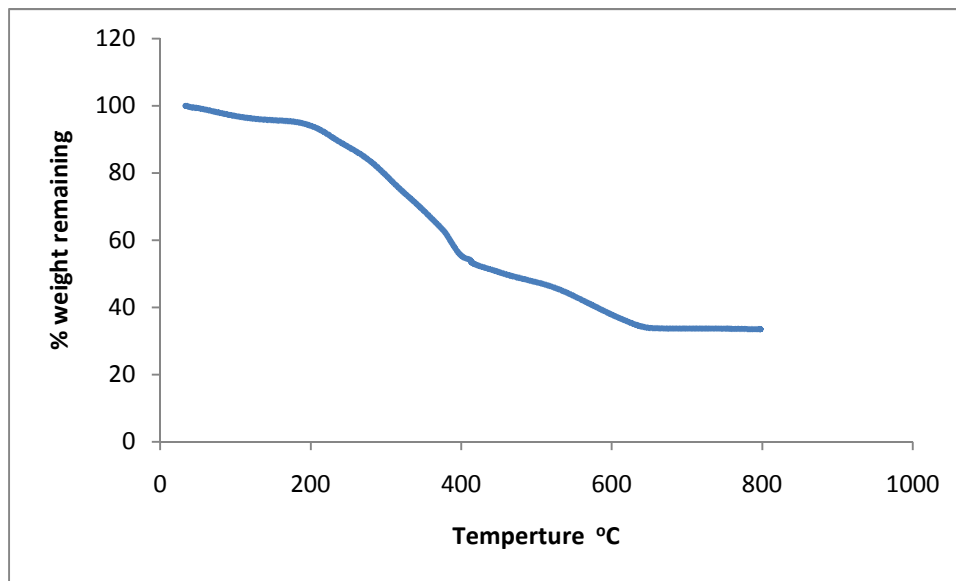
2) KARANJA seed

Figure 10 TGA plot for karanja seed

Here the range in which maximum degradation is taking place is 250°C to 600°C. Here also the moisture is removed by initial heating and then the relatively less complex molecule and then the removal of highly complex molecule.
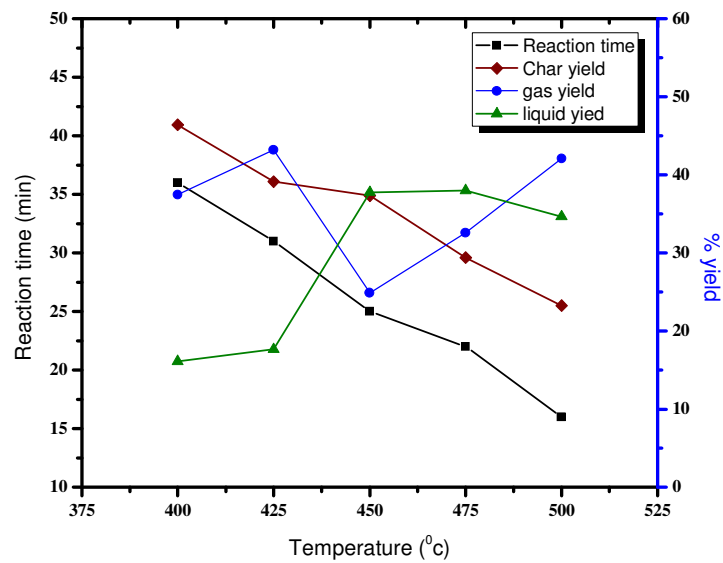
3.2) OBSERVATION

3.2.1) NEEM OIL

Table 5 Observation for neem seed

| Serial no.	Temperature (°C)	Weight of sample (gm)	Reaction time (min)	Weight % of the oil	Density of the oil (kg/L)	Weight % of char	Weight % of volatiles
1	400	25	36	16.12	0.895	46.4	37.48
2	425	25.04	31	17.65	0.884	39.14	43.21
3	450	25.2	25	37.77	0.906	37.34	24.88
4	475	25	22	38	0.863	29.4	32.6
5	500	25.02	16	34.65	0.867	23.26	42.08

a) Graph for above observation

Figure 11 Observational graph for neem pyrolysis

3.2.2) KARANJA SEED

Table 6 Observation for karanja seed

Serial no.	Temperature (°C)	Weight of sample (gm)	Reaction time (min)	Weight % of the oil	Density of the oil (kg/L)	Weight % of char	Weight % of Volatiles
1	450	25	40	49.2	0.911	36.8	14
2	475	25.03	33	50.41	0.902	34.36	15.23
3	500	25.05	24	57.12	0.954	30.01	12.86
4	525	25.04	20	37.02	0.927	27.07	35.90
5	550	25.02	16	24.82	0.887	21.58	53.59

a) Graph for above observation.
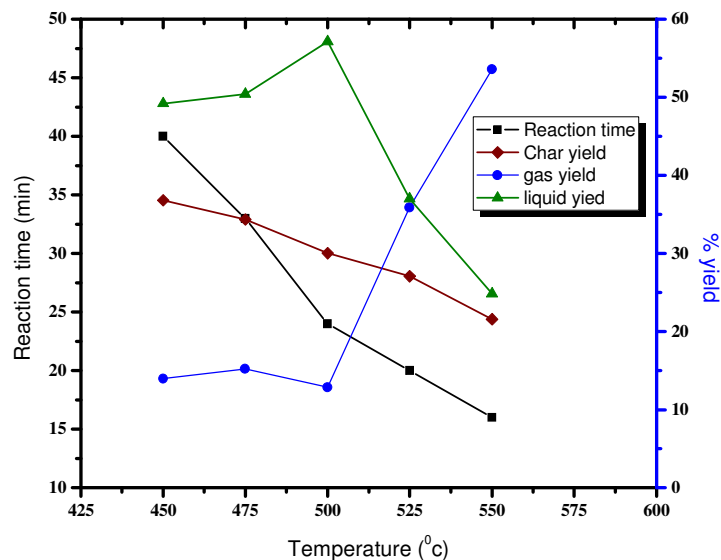
Figure 12 Observational graph for karanja pyrolysis

The plot between yield of liquid, solid and gaseous products vs. temperature clearly shows that in case of neem seed, the yield of liquid product increases with increases in temperature in the range of 400-475°C up to 500°C and then it starts decreasing. Thus maximum yield of liquid product is obtained at 475°C which indicates it as effective pyrolysis temperature for the neem

seed. But in case of karanja seed, the yield of liquid product increases with increase in temperature in the range of 450-500^{0}C up to 500^{0}C and starts decreasing with further increase of temperature. So the maximum yield of liquid product is obtained at 500°C which indicates it as effective pyrolysis temperature for the karanja seed. The reaction time decreases with increase in temperature in both neem seed and karanja seed.

3.3) CHARACTERISATION OF SEED AND CHAR

Proximate analysis is the fastest way of analyzing the quality of the fuel oil. It gives us the information about carbon content, ash content, volatile matter and moisture. Now for instance high moisture content will increase transportation cost, reduce calorific value and most of the energy will be used in removing the moisture. It also affects the conversion efficiency of the biomass and also there is potential to loose energy as a result of decomposition. Whereas high volatile matter means that there would more liquid product due to thermal decomposition as volatile matter is a complex mixture of organic and non-organic compound.

Table 7 Seed and char characterization

Proximate analysis	Karanja seed	Karanja char	Neem seed	Neem char
Moisture %	5	3.9	6	5
Ash content	3.9	8.9	4.95	17.8
Volatile matter	84	32	81	37
Fixed carbon	7.1	55.2	8.05	40.2
Calorific value (kcal/kg)	5350	6050	5500	7100

As can be seen above that the calorific value of the char is quite good and hence it can serve the purpose of alternate source of energy for heating and burning process.

3.4) PHYSICAL PROPERTIES OF THE PYROLYTIC OIL

In the table below are shown some of the physical properties of both the Neem oil and Karanja oil such viscosity index, pour point, fire point, cloud point, gross calorific value, kinematic viscosity, initial and final boiling point, density, appearance, carbon residue, flash point, sulfur content and cetane index.

3.3.1) NEEM oil

Table 8 Physical properties of neem oil

Properties	Neem pyrolytic oil
Appearance	Dark brownish oil
Density at 15°C (kg/m^3)	0.9610
Specific gravity at 15°C/15°C	0.9619
Kinetic viscosity at 40°C in centistoke	22.6
Kinetic viscosity at 100°C in centistoke	3.8
Viscosity index	Plus 11
Conradson carbon residue	5.03%
Pour point	Plus 11°C

Cloud point	22°C
Flash point by Abel method	42°C
Fire point	62°C
Gross calorific value in Kcal/kg	7736
Sulfur content	0.48%
Calculated Cetane index	21
Initial boiling point	98°C
Final boiling point	352°C

3.3.2) KARANJA oil

Table 9 Physical properties of karanja oil

Properties	Neem pyrolytic oil
Appearance	Dark brownish oil
Density at 15°C (kg/m^3)	0.9384
Specific gravity at 15°C/15°C	0.9393
Kinetic viscosity at 40°C in centistoke	27.9
Kinetic viscosity at 100°C in centistoke	4.4
Viscosity index	Plus 34
Conradson carbon residue	4.30%
Pour point	Plus 16°C
Cloud point	28°C
Flash point by Abel method	40°C

Fire point	58°C
Gross calorific value in Kcal/kg	8113
Sulfur content	0.05%
Calculated Cetane index	29
Initial boiling point	96°C
Final boiling point	376°C

Comparison of properties with other commonly used fuels

Table 10 comparison of physical properties with other fuels

Properties Fuel	Specific gravity 15°C/15°C	Kinematic viscosity@ 40°C (Cst)	Flash point (°C)	Pour point (°C)	GCV MJ/kg	IBF (°C)	FBF (°C)	Chemical formula
Neem oil	0.9619	22.6	42	11	32.38	98	352	
Karanja oil	0.9393	27.9	40	16	33.9	96	376	
Gasoline	0.72-0.78	-	-43	-40	42-46	27	225	C_4-C_{12}
Diesel	0.82-0.85	2-5.5	53-80	-40 to -1	42-45	172	350	C_8-C_{25}
Biodiesel	0.88	4-6	100-170	-3 to 19	37-40	315	350	C_{12}-C_{22}
Heavy fuel oil	0.94-0.98	>200	90-180	-	40	-	-	-
Rapeseed pyrolytic oil	0.993	>40	62	6	36-37	-	-	$CH_{1.78}N_{0.04}O_{0.15}$
Sunflower pyrolytic oil	1.02-1.079	50-250	58-76	-16	38-41	92	315	$CH_{1.88}O_{0.15}N_{0.02}$

As can be seen from the above comparison, the kinematic viscosity and density of the neem as well as the karanja oil is greater than the gasoline, biodiesel and diesel oil but is comparatively less than the other three so one can say that the transportation and flow of these oil can be difficult. Hence the pumping and injection of the fuel in the engine will be difficult. Also the pour point is relatively higher than the other fuels so in the area of low temperature the flow and piping of the will be even more difficult. We can see from the above comparison that the gross calorific value is comparable to the other fuel which is almost 75% of gasoline and diesel oil for both neem and karanja oil. Also the flash point is quite high which means it is safe for storage as it will not ignite easily.

As far as the density and viscosity are concerned, we can these fuels as blend with other major fuels as the resulting density and viscosity will be less.

3.5) FOURIER TRANSFORM INFRARED SPECTROSCOPY (FT-IR)

FT-IR is used to determine the different functional group such as alcohol, alkane, alkynes, alkenes and other such groups present in the substance which here is neem oil and karanja pyrolytic oil. Although it has to be confirmed by gas chromatography-mass spectroscopy.
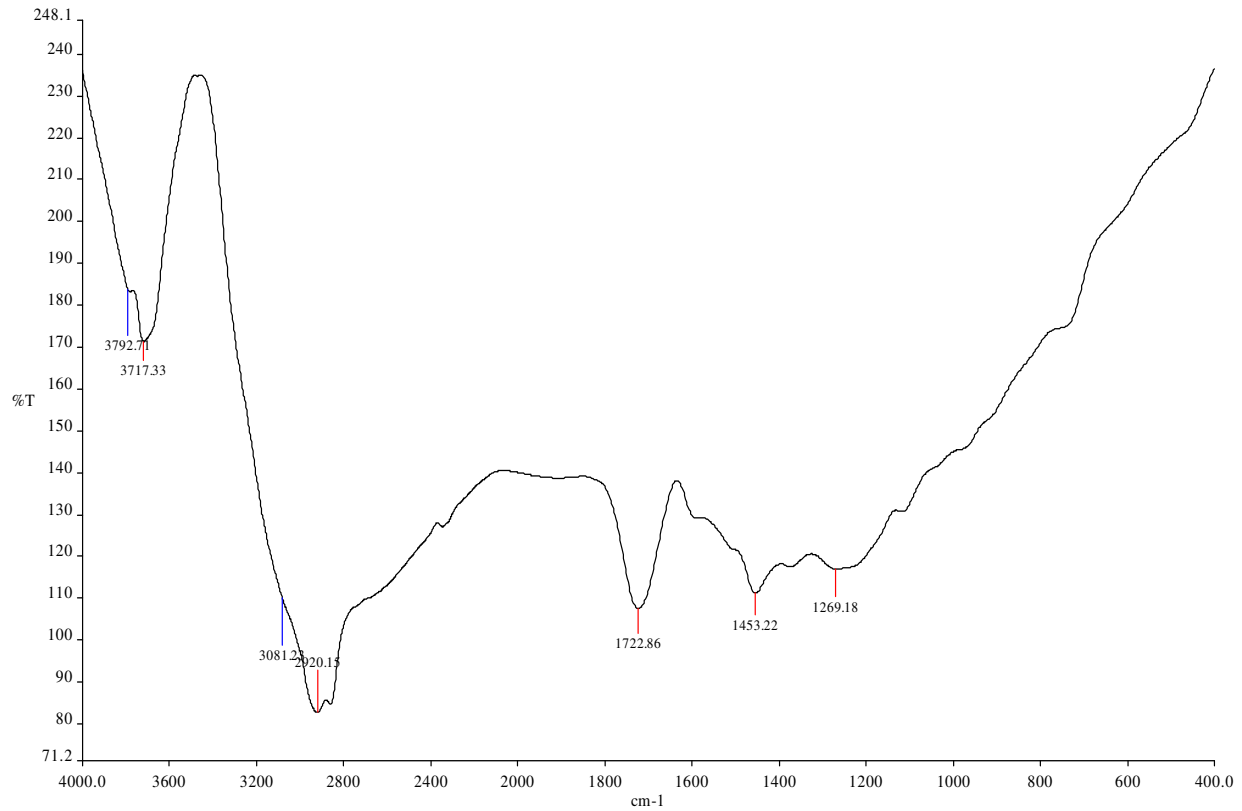
3.5.1) NEEM OIL

Figure 13 FT-IR analysis of neem oil

Table 11 Functional group in neem oil

Frequency	Compound
3717.33	Amide N-H $_{stretch}$
3081.29	$CH_{Stretch}$ of C=C
2920.15	$CH_{Stretch}$
1722.86	C=O
1453.22	C=H
1269	C=H

3.5.2) KARANJA OIL
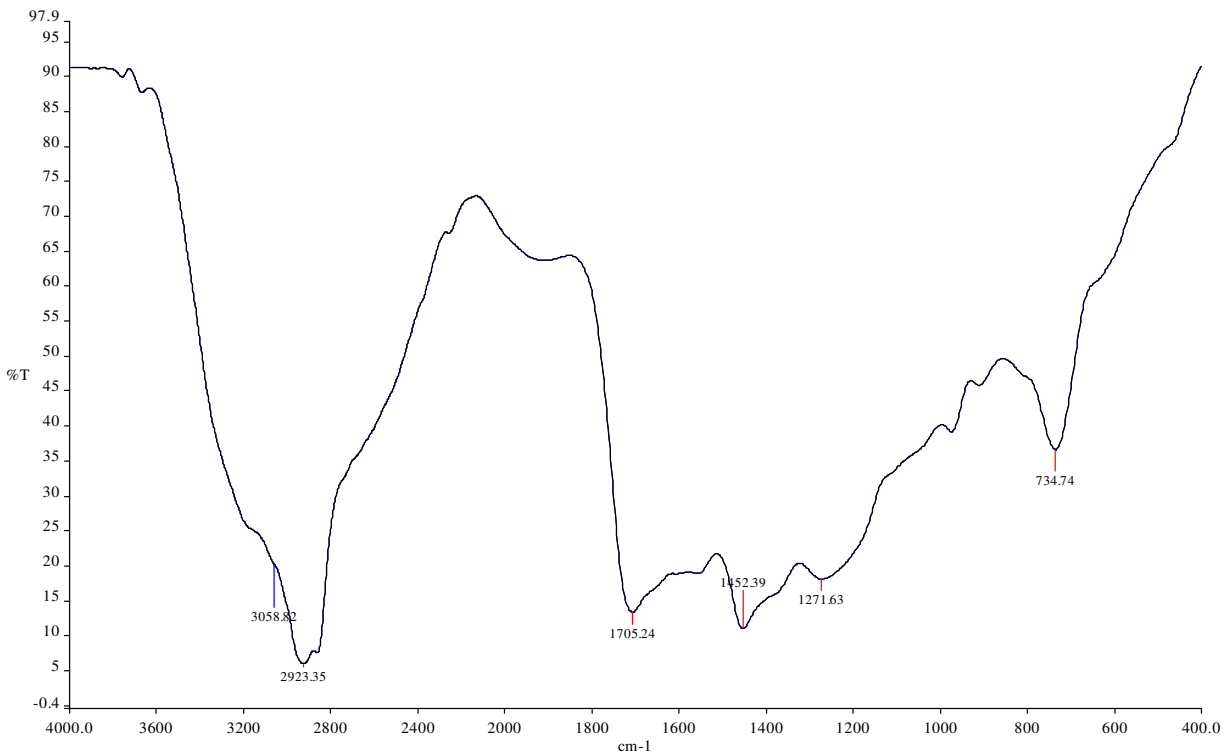
Figure 14 FT-IR analysis of karanja oil

Table 12 Functional group in karanja oil

Frequency	Compound
2923.34	CH $_{Stretch}$
1705.24	C=O
3070.02	CH$_{Stretch}$ of C=C
1452.39	Aromatic CH
1271.63	Aromatic CH

3.6) GAS CHROMATOGRAPHY-MASS SPECTROSCOPY

The chemical composition of the neem oil and the karanja oil was determined using the gas chromatography mass spectroscopy and was found that neem oil consisted of 41 compounds and karanja oil consisted of 21 compounds.
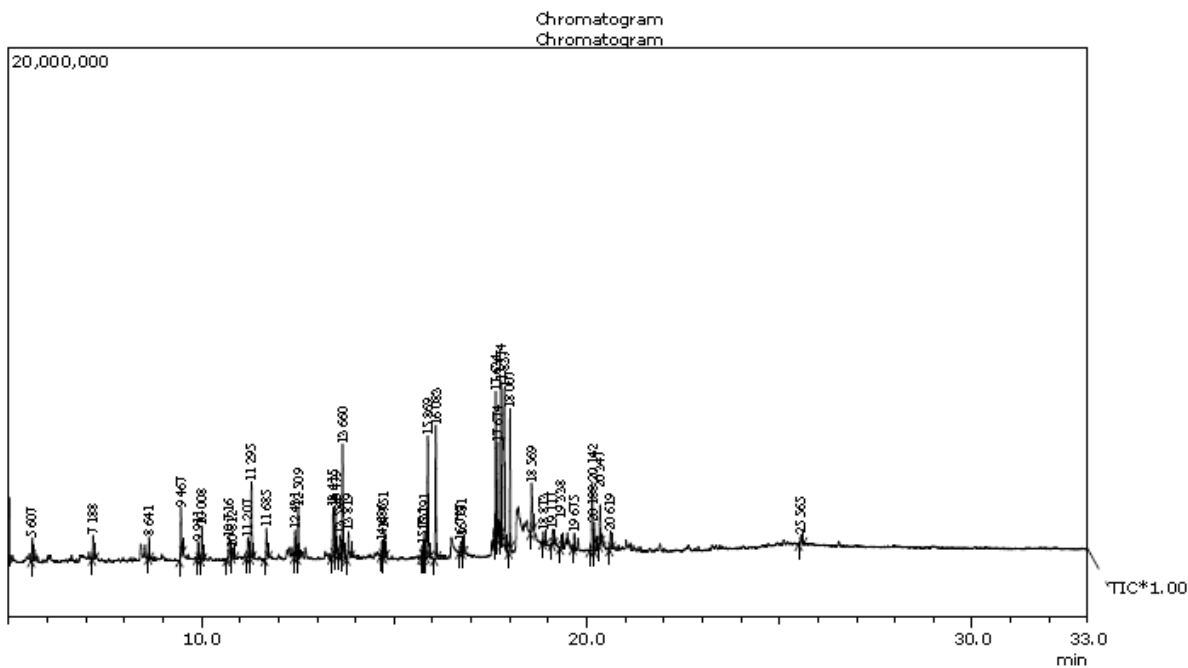
3.6.1) Chemical composition of neem pyrolytic oil

Figure 15 chromatogram of neem oil

Table 13 Compounds present in neem oil

Compound	Area %	Formula
o-Methoxyphenol	1.26	$C_6H_4(OH)(OCH_3)$
1,4-Dimethoxybenzene	1.17	$C_6H_4(OCH_3)_2$
Tridecane	.84	$C_{13}H_{28}$
Pyrogallol 1,3-dimethyl ether	2.23	$C_8H_{10}O_3$
1-Tetradecene	0.75	$CH_2=CH(CH_2)_{11}CH_3$
n-Tetradecane	1.46	$C_{14}H_{30}$
1,2,4-Trimethoxybenzene	1.1	$C_9H_{12}O_3$
(E)-Isoeugenol	0.63	$C_{10}H_{12}O_2$
1-Hexadecene	0.85	$CH_2=CH(CH_2)_{13}CH_3$
Pentadecane	3.44	$C_{15}H_{32}$
Toluene, 3,4,5-trimethoxy-	1.44	$C_{10}H_{14}O_3$
1-Heptadecene	1.19	$C_{17}H_{34}$
Nonadecane	2.23	$C_{19}H_{40}$
3-Heptadecene	2.31	$C_{17}H_{34}$
9-Eicosene	2.55	$C_{20}H_{40}$
1-octadecene	0.93	$CH_2=CH(CH_2)_{15}CH_3$
Heptadecane	5.42	$C_{17}H_{36}$
Phenol,2,6dimethoxy-4-(2-propenyl)	1.71	$C_{11}H_{14}O_3$
1-octadecene	0.58	$CH_2=CH(CH_2)_{15}CH_3$
Heneicosane	1.16	$C_{21}H_{44}$
1-Nonadecene	0.48	$C_{19}H_{38}$
Nonadecane	1.17	$C_{19}H_{40}$
Hexadecanenitrile	6.44	$C_{16}H_{31}N$
Hexadecanoic acid, methyl	6.08	$C_{17}H_{34}O_2$

easter		
1-Nonadecanol	0.50	$CH_3(CH_2)_{18}OH$
eicosane	0.75	$C_{20}H_{42}$
Oleanitrile	7.32	$C_{18}H_{33}N$
E-11-Hexadecenal	4.03	$C_{16}H_{30}O$
9-octadecenoic acid, methyl ester	6.93	$C_{19}H_{36}O_2$
Octadecanenitrile	11.55	$C_{18}H_{35}N$
Stearic acid, methyl ester	6.15	$CH_3(CH_2)_{16}COOCH_3$
Hexadecanamide	2.73	$C_{16}H_{33}NO$
N-methyl hexadecanamide	0.53	$C_{17}H_{35}NO$
4-Fluorophenyl	0.86	C_6H_5F
2-propenyl decanoate	0.60	$C_{13}H_{24}O_2$
Heptadecanenitrile	0.70	$C_{17}H_{33}N$
9-octadecenamide	4.30	$C_{18}H_{35}NO$
13-Docosenamide, (Z)-	1.98	$C_{22}H_{43}NO$
Stearic amide	2.04	$C_{18}H_{37}NO$
N-methyloctadecanamide	0.95	$C_{19}H_{39}NO$
Stigmast-5-en-3-ol, oleate	0.67	$C_{47}H_{82}O_2$

Here we can see that the major component of the neem oil are Octadecanenitrile, Oleanitrile , 9-octadecenoic acid methyl ester, Stearic acid methyl ester, heptadecane, 9-octadecenamide, E-11-Hexadecenal and pentadecane which are 11.55%, 7.32&, 6.93%, 6.15%, 5.42%.4.30%, 4.03% and 3.44% respectively. They almost comprise of 43% of the total mass.

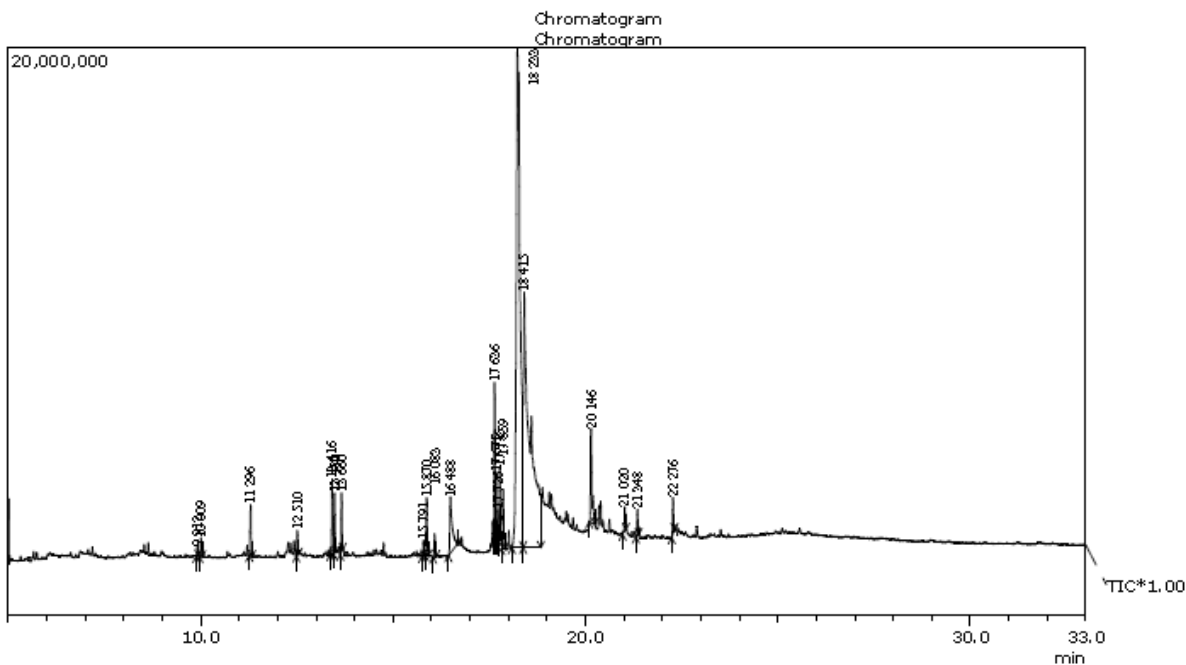### 3.6.2) Chemical composition of Karanja seed pyrolytic oil

Figure 16 Chromatogram for karanja oil

Table 14 Compounds present in karanja oil

Compound	Area %	Formula
1-Tetradecene	0.14	$CH_2=CH(CH_2)_{11}CH_3$
n-Tetradecane	0.32	$C_{14}H_{30}$
Pentadecane	0.91	$C_{15}H_{32}$
Nonadecane	0.43	$C_{19}H_{40}$
3-Heptadecene, (Z)-	1.44	$C_{17}H_{34}$
9-Eicosene, (E)-	1.34	$C_{31}H_{32}N_2O_4$
n-Heptadecane	1.01	$C_{17}H_{36}$
Nonadecane	0.27	$C_{19}H_{40}$
Hexadecanenitrile	1.17	$C_{16}H_{31}N$
Methyl hexadecanoate	0.41	$C_{17}H_{34}O_2$

Palmitic acid	2.97	$CH_3(CH_2)_{14}COOH$
Oleanitrile	3.02	$C_{18}H_{33}N$
E-11-Hexadecenal	1.26	$C_{16}H_{30}O$
n-Heneicosane	0.48	$C_{21}H_{44}$
Methyl elaidate	1.17	$C_{19}H_{36}O_2$
Octadecanenitrile	1.57	$C_{18}H_{35}N$
Oleic acid	44.30	$C_{18}H_{34}O_2$
Stearic acid	33.66	$C_{18}H_{36}O_2$
9-octadecenamide	2.50	$C_{18}H_{35}NO$
9-octadecenal, (Z)-	0.46	$C_{18}H_{34}O$
Nonadecanenitrile	0.43	$C_{19}H_{37}N$
2-phenyl-furo[B]benzopyran-4(4H)-one	0.72	

Here we can see that the main composition of karanja oil is oleic acid, stearic acid oleanitrile and palmitic acid which are 44.30%, 33.66%, 3.02% and 2.97% respectively. These compounds constitute almost 84% of the total mass.

3.7) SCANNING ELECTRON MICROSCOPY

Below are the scanning electron microscopic images of the neem char and that of karanja char. The images are taken at magnification level of 80 and 200 which clearly shows that reasonable amount of pores are present on the surfaces.
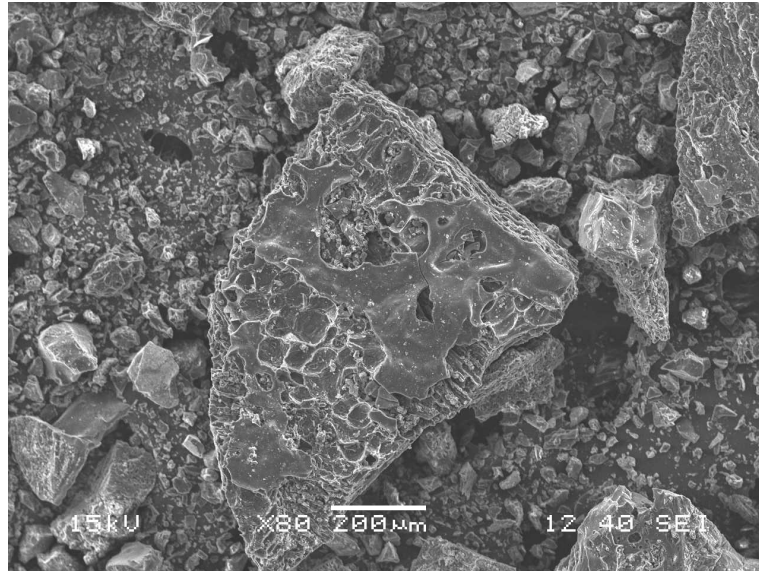
3.7.1) KARANJA char

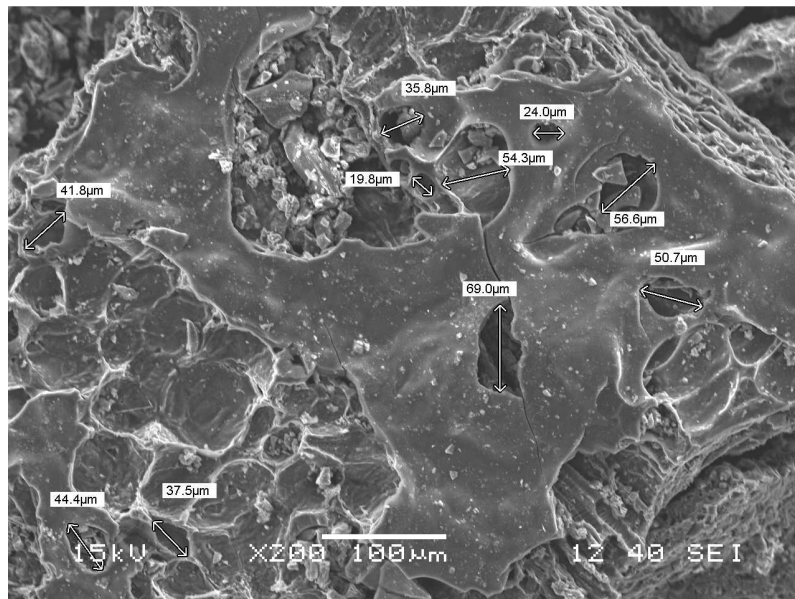**Figure 17 SEM image of karanja char at 80 magnification**

Figure 18 SEM image of karanja char 200 magnification
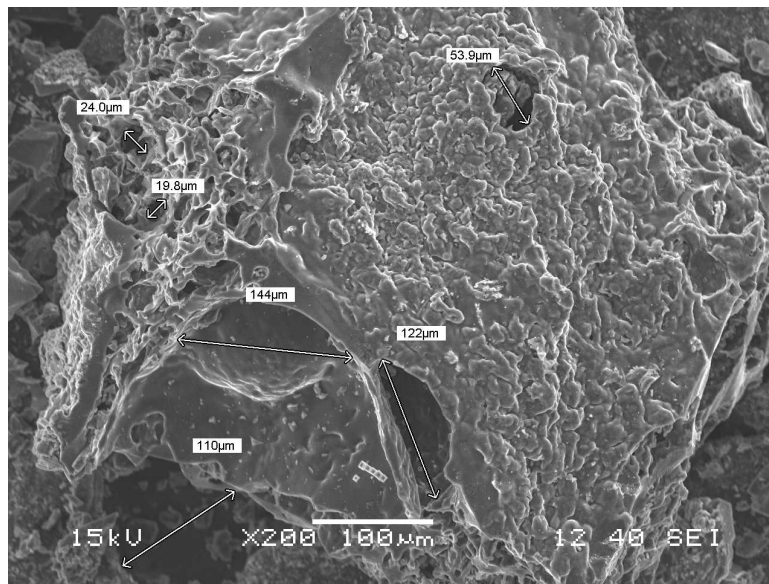
3.7.2) NEEM char

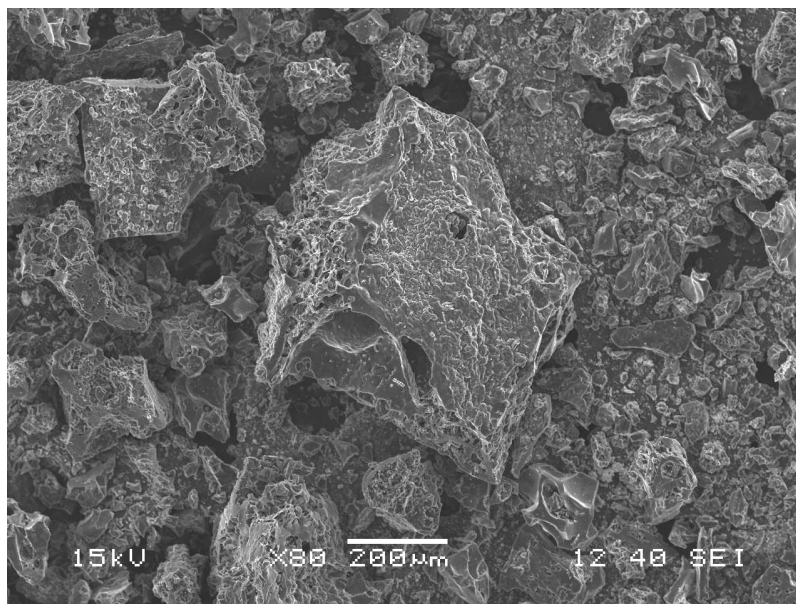**Figure 19 SEM of neem char at 200 magnification**

Figure 20 SEM image of neem char at 80 magnification.

Pyrolysis temperature and heating rate influenced the size and shape of particle through a general increase in size and proportion of voids and a decrease in cell wall thickness. The fast volatile release during pyrolysis produces substantial internal overpressure and the coalescence a more open structure. Therefore, SEM porosity increased with a pyrolysis temperature and increasing heating rate.

CONCLUSION

CONCLUSION

➢ The seeds used here are non-edible and hence they are perfect for biomass. It can also be explained by the fact India do not produce enough edible oils which can be used for this purpose.

➢ Maximum yield of the karanja oil and neem oil are at 500°C and 475°C.

➢ As the heating progresses the oil production increases at first and then after certain extent it start to decrease.

➢ Reaction time decreases as the pyrolysis temperature is increased but char decreases with increase in pyrolysis temperature.

➢ The fixed carbon increases in the char as most of volatile matter is driven away due to pyrolysis. Also the volatile matter in seeds is good which accounts for the production of fuel on pyrolysis.

➢ The oil obtained has comparable calorific value to most of the fuel used in day to daylife but it has comparable higher pour point , density and kinematic viscosity, so one can say that transportation and piping of these fuels can be a tough task especially in cold areas.

➢ Seeing the physical properties one can say that it is moderate grade fuel and can be used as blends with other major fuels.

➢ Neem oil consist of over forty compounds and Karanja oil over twenty compounds functional groups such as alkanes, alkenes, alkynes, alcohols, ketones, aldehydes, aromatics rings, amides, nitriles and nitro compounds.

> ➤ The char of the respective seeds have good calorific value so they can be used as alternate source of energy for heating and other purposes and they also have reasonable amount of pores present on their surface.

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