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Production of Solid Fuel by Pyrolysis Process using Neem De-Oiled Seed Cake

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ABSTRACT: *The Solid fuel biochar is a low-energy value byproduct of biomass pyrolysis with many applications, such as an absorber, catalyst, the synthesis of activated carbon soil amendment, and high value products. Outputs of pyrolysis process are liquid fuel i.e bio-oil, solid fuel i.e biochar and gas i.e syngas. In this paper neem de-oiled seed cake is chosen as feedstock for pyrolysis. The properties of end products mainly depend on feedstock, pyrolysis operating parameters. Bio-oil having advantage of storage and transportation finds application in producing heat, power and also in making chemicals. Biochar finds it applications in agricultural, environmental and industrial. The bio-oil is highly viscous denser and even heating value is less than the petroleum fuels which makes it unsuitable to use in diesel engines. This paper reports the production, characterization and utilization of biochar. The minerals present in biomass are left as ash after pyrolysis. The yield of biochar decreased with increasing temperature. The biomass consisting of 22 fixed carbon is converted to bio-char, having 80.3% fixed carbon. The calorific value of end products increased from 21.84 to 28.52 for bio-oil and 30.4 MJ/kg for biochar.*

KEYWORDS - De-oiled seed cake, Pyrolysis, Bio-char, Bio-oil, TGA

INTRODUCTION

The earth’s fossil fuel supplies are limited, hence in the future biofuels are considered as the most attractive alternative energy sources. Among the other options, biodiesel production is one of the best methods used by all the developing countries as the replacement of fossil fuel. Figure 1 shows utilization of non-edible seeds. Biodiesel mainly uses non edible seeds oil to produce the biodiesel mainly by transesterification process. The end products of biodiesel production, glycerin and de oiled seed cake should be utilized effectively to make the biodiesel program successful in all aspects. The glycerin has a good market as it can be used in making cosmetics, soaps, candles etc. The de-oiled seed cakes composition mainly depends on their seeds quality, condition of growing, oil extraction methods, storage methods etc. Oil cakes are used in production of enzymes, pesticides, antibiotics, antimicrobials, biochemicals and organic fertilisers. Oil cakes also provides alternative to transportation by their utilization in production of environmental friendly bio-fuel [1]. All these application are still not commercial yet, hence there is a need to develop a technology for conversion of the de-oiled seed cakes into the useful products, or else it may lead to problems like waste disposal management, space occupation, smell etc. Our effort in this paper is to use non edible seed cakes in production of liquid fuel (bio-oil) and solid fuel (bio-char) source of energy by pyrolysis process.

Biomass fuels and residues can be converted to more valuable energy forms via a number of processes. Among them the thermochemical conversion processes, pyrolysis is considered to be an emerging technology due its advantages over other products. Biomass can be converted to fuel via pyrolysis process, which refers to the heating of biomass in the absence of oxygen. This process breaks down the structure of the biomass and yields three products: condensable gases (bio-oil), solid char, and non-condensable gases [2].

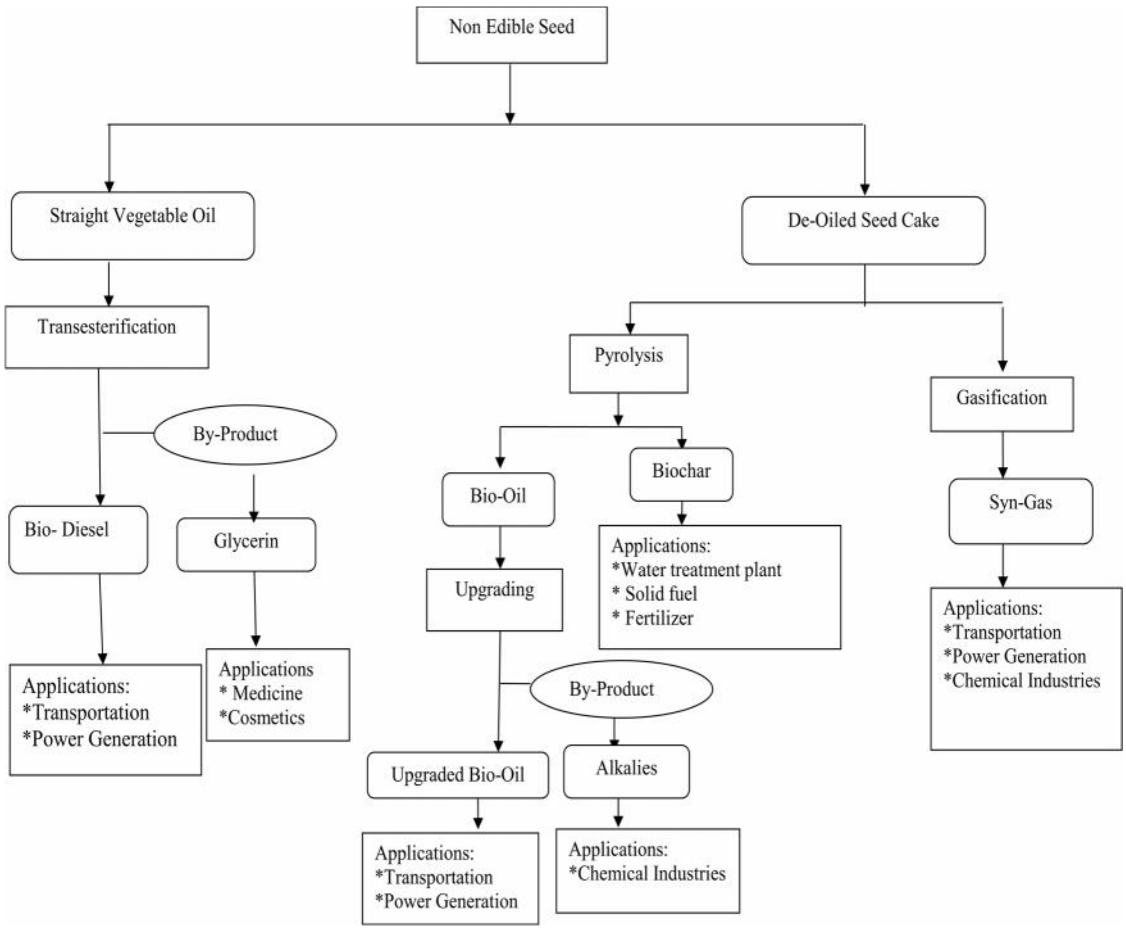

Figure 1: Utilization of non edible seed

Few works were carried out on production of bio-char by pyrolysis process such as switchgrass, forage sorghum and red cedar [3], wheat straw, sawdust, flax straw and poultry litter [4], sugarcane bagasse, casuarina leaves, coconut coir pith, groundnut shell, rice husk, sawdust, and wheat husk, [5] but very less work is carried out on neem de-oiled seed cake; hence it is the motivation to choose it as a feedstock.

MATERIAL AND METHODS

The neem de-oiled cake was bought from "Biodiesel Production Center" Bagalkot- Karnataka, which was left out after extraction of crude oil for producing the biodiesel. The cake was in the form of flakes and is powdered using a household grinder, before carrying out the pyrolysis experiments.

Figure 2 shows the neem de-oiled seed cake, which is characterized by proximate and ultimate analysis in Bangalore Testing Laboratories Pvt Ltd Bangalore. The volatile matter, fixed carbon, moisture and ash content were carried by the test method IS 1350: (P 1), 1350: (P 1), 1448: (P 40) and 1448: (P 4) respectively. Instrument used for determining moisture and volatile matter are hot air oven of make Care. For determining ash content instrument used was muffle furnace of make Sai Electronics. Ultimate analysis was carried out at Indian Institute of Science (IISc) - Bangalore with instrument model Thermo Scientific Flash 2000 Organic Elemental Analyzer using Eager Experience software under CHNS/O analysis mode with reference and carrier gas as helium. Calorific value was determined by IS 1448: (P 6) using a Bomb Calorimeter of MAC make in Bangalore Test House Bangalore.

Figure 2: Photograph of neem de-oiled seed cake

The liquid product was characterised by calorific value, density, viscosity and flash point. The calorific value was found by using bomb calorimeter of make MAC, moisture content by Dean and Stark glass apparatus, viscosity in Ostwald's U tube viscometer & viscosity bath of make Techno instruments, flash point by Pensky martin's of make Techno instruments and carbon residue by Ramsbottom apparatus of Techno instruments make.

For char the calorific value was found by using bomb calorimeter of make MAC, moisture content by Dean & Stark glass apparatus, ash content in muffle furnace of culture instrument make, viscosity in Ostwald's U tube viscometer & viscosity bath of make Techno instruments, flash point by Pensky martin's of make Techno instruments and carbon residue by Ramsbottom apparatus of Techno instruments make. The phosphorus, nitrogen and magnesium were determined by UV visible spectrophotomer of make Shimadzu, kjeldahi nitrogen setup and titration respectively.

PYROLYSIS PROCESS

The pyrolysis process is carried in a reactor where PID controller is used to control the temperature. The reactor is made of mild steel and to minimize heat losses it is insulated with refractory bricks. The length of reactor is 56 cm with the internal and external diameter of 21 and 56 cm respectively. The length of the condenser is 140 cm having inner and outer diameter of pipe is 1.905 and 3.81 cm. The inner pipe is made up of galvanized iron (GI) and outer with copper material. The vapor residence time in the reactor is maintained around 10 seconds. Water is used to condense the vapors coming out of reactor. The nichrome coil having capacity of 3 kW is used to heat the reactor and J type thermocouple having range of -99 to 870 ^{0}C is used to measure the temperature of biomass.

The reactor is filled by known weight de-oiled seed cake, then all the openings are closed and gasket is used to make the reactor leak proof. As pyrolysis process starts, the condensed gases are condensed while passing through condenser and collected in form of liquid, whereas the non-condensable gases are left out to the atmosphere. The liquid fuel collected contains oily viscous water (mainly water) along with liquid fuel, which is separated by density difference. The liquid fuel obtained is known as bio-oil or pyrolytic oil. Figure 3 shows the experimental setup of pyrolysis process. The experiment is conducted at various temperature range of 350 to 600 ^{0}C at a constant heating rate of 20^{0}C/min. After the completion of pyrolysis process, the bio-oil and bio-char are weighed and difference among them gives the gas yield. After each experiment the inner reactor is removed, filled with feedstock and assembled to carry out the experiment.

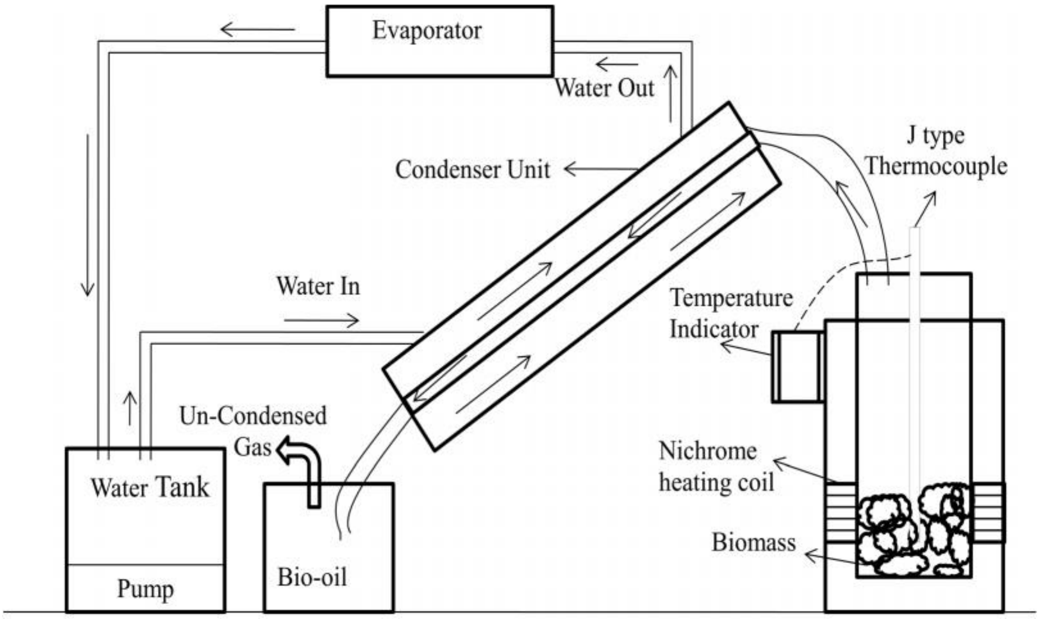

Figure 3: Experimental setup

RESULT AND ANALYSIS

PROXIMATE ANALYSIS OF FEEDSTOCK

Proximate analysis is the quickest and simplest way of investigating the fuel quality of solid materials. The proximate analysis of neem de-oiled seed cake is shown 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 products 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.

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

Sample	Moisture	Volatile matter	Ash	Fixed carbon	Calorific value (MJ/kg)	References
Neem cake	4.7	73.2*	4.8*	22.0*	21.84	Present Study
Jatropha cake	5.0	69	5.0	21	16.86	[6]
Sesame cake	6.57	86.2	4.0	3.23	19.78	[7]
Rice husk	7.7	64.3	18.8	9.2	13.36	[8]

*Results on dry basis.

ANALYSIS OF BIO-OIL

It is observed from the table 1 and 3 that the neem de-oiled seed cake consisting about 73.2 of volatile matter reduces drastically to 8.0% after pyrolysis, which indicates higher conversion of biomass to bio-oil. Figure 4 shows the yield of pyrolysis end products at different temperature of 350 to 600 ^{0}C. As the temperature increases, the liquid product also increases to a maximum of 38.6% at a temperature of 500 ^{0}C and then decreased with further increase in temperature. The char yield decreased with the increase in pyrolysis temperature, char yield was maximum 43.8% at initial temperature of 350 ^{0}C. Initially the gas yield decreased but as the temperature increased gas yield also increased. The bio-oil yield is probably dependent on the sum of cellulose and hemicelluloses content of the biomass. We can conclude that at higher than optimum temperatures, the bio-oil yield decreases due to gasification reactions and secondary cracking reactions and favors the gaseous products. Z Ji-lu [8] and C.H.Biradar [6] observed similar trends for maize stalk and Jatropha curcas de-oiled seed cake respectively.

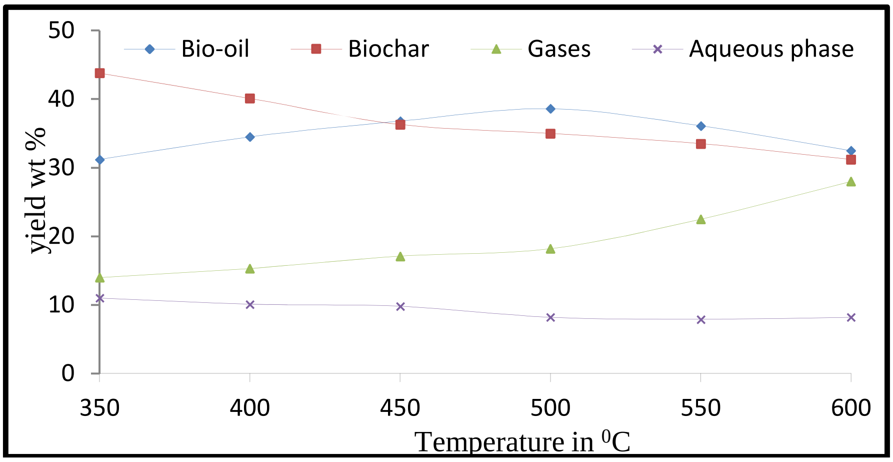

Figure 4: Yield of pyrolysis products at different temperature.

Table 2 shows the physical properties of bio-oil. The calorific value of bio-oil increased from 21.84 to 28.52 MJ/kg. Neem bio-oil is denser, highly viscous and calorific value is less than the commercial fuels. The bio-oil obtained is dark in colour as shown in figure 5, having smoky smell and cannot be mix directly with diesel due to poor miscibility, which makes it unsuitable to use in diesel engines. These problems are mainly due to the physicochemical properties of crude bio-oil which differs significantly from that of base diesel hence need up gradation before using it in diesel engines [9].

Figure 5: Top bio-oil and bottom viscous liquid layers

Table 2. Comparison of physical properties of liquid product with other fuels.

Fuel	Viscosity cSt	Calorific Value MJ/Kg	Density kg/m^3	Flash point ^{0}C	References
Neem cake	10.6	28.52	995	131	Present study
Mustard cake	39.6	25.5	10.29	182	[7]
Diesel	2.58	43.8	854	50	[9]
Biodiesel	5.38	42	875	175	[10]

APPLICATION OF BIO-OIL

Like petroleum products bio-oil can be stored, pumped and transported and finds its application as a renewable liquid fuel in boilers, turbines and diesel engines. Pyrolysis oil is CO_2 neutral, contains no sulfur and therefore does not produce sulfur dioxide emissions during combustion. Bio-oil is combustible but not flammable, ignites and burns readily when properly atomized, and once ignited burns with a stable, self-sustaining flame1. The bio-oil is acidic and corrosive in nature hence the storage vessel and pipes should be made up of corrosive resistance material. Bio-oil is also used in for the production of chemicals, such as phenols used in the resins industry; volatile organic acids in the formation of de-icers; levoglucosan; hydroxyacetaldehyde; and some additives applied in the pharmaceutical, fiber synthesizing, or fertilizing industry; and flavouring agents in food products [11,12,13].

ANALYSIS OF BIO-CHAR

It is observed from the table 1 and 3 that the neem de-oiled seed cake consisting about 22 of fixed carbon increases drastically to 80.3 % after pyrolysis, which indicates higher conversion of biomass to biochar. Figure 4 shows the yield of pyrolysis end products at different temperature of 350 to 600 ^{0}C. The calorific value of neem de-oiled seed cake increased from 21.84 to 30.4 MJ/kg. Similar trend were observed by [14] on hornbeam shell residue. Figure 6 shows photograph of bio-char produced by pyrolysis.

Figure 6: Photograph of bio-char

Table 3. Physical properties of bio-char (wt %).

Properties	Moisture content	Volatile Matter	Ash content	Fixed Carbon	Calorific Value MJ/kg	References
Neem	2.0	8.0	9.7	80.3	30.4	Present study
Karanja	0.0	32	8.9	68.32	25.2	[15]
Linseed	-	23	12	65	24.96	[16]
Mustard	4.8	21	28.1	46.1	29.1	[7]

Lignin is known to be more thermally stable than cellulose and hemicellulose and leads to higher char yields. The biochar yield falls slightly with increasing temperature, the opposite seen for the non-condensable gases, due to the greater primary decomposition of the biomass at higher temperature, or secondary decomposition of the char residue have given rise to some non-condensable gaseous products that contributed to an increasing gas yield with the temperature. Similar trends were seen by Rahul Sinha [16] on linseed.

Table 4. Elemental analysis of bio-char %.

Elements	Nitrogen	Phosphorus	Sulfur	Magnesium	References
Neem char	2.6	0.42	0.65	0.4	Present study
Switchgrass char	-	0.68	0.1	1.05	[4]

APPLICATION OF BIO-CHAR

In today's scenario, depending upon composition and physical properties, biochar can be utilised in agricultural, environmental and industrial applications [4]. From table 3 and 4 the various elements present in bio-char (mainly carbon 73.3%, nitrogen 1.6%, phosphorous 0.48 %) can be considered as nutrient and help plant growth.

Depending upon composition and physical properties, bio-char can be used in various industrial processes such as boilers, producing activated carbon, making carbon nanotubes, waste water treatment, producing hydrogen rich gas, etc [13]. Biochar having high calorific value of 30.4 MJ/kg can be used as an alternative fuel. Apart from industrial use biochar is added to agricultural soils, in which the carbon can be seized safely for hundreds of years. Biochar has positive impact on the climate and environment mainly because of its nutrient retention capacity as it reduces the total fertilizer requirements. Char-amended soils have shown 50 - 80 percent reductions in nitrous oxide emissions and reduced runoff of phosphorus into surface waters and leaching of nitrogen into groundwater. Biochar thus offers the promise of carbon-negative biofuel production sustained by a cycle in which crop production is boosted, emissions lowered, and reliance on synthetic fertilizers reduced [17]. The biochar obtained at higher temperature are much better and more stable than obtained at lower temperature [4].

CONCLUSION

Pyrolysis of neem de-oiled seed cake was carried out in the range of 350 to 600 ^{0}C at a constant heating rate of 20^{0}C/min to obtain biochar, bio-oil and gaseous products. The char yield decreased with the increase in pyrolysis temperature, char yield was maximum 43.8% at initial temperature of 350 ^{0}C. Neem de-oiled seed cake consisting about 22 of fixed carbon increases drastically to 80.3 % after pyrolysis, which indicates higher conversion of biomass to biochar. The volatility decreases from 73.2 to 8.0, which indicates higher conversion of biomass to other valuable products. As the temperature increases, the bio-oil increases to a maximum of 38.6 % at a temperature of 500 ^{0}C and then decreased with further increase in temperature. The calorific value of end products increased from 21.84 to 28.52 for bio-oil and 30.4 MJ/kg for biochar. Bio-oil having advantage of storage and transportation finds application in producing heat, power and also finds its application in making chemicals. Biochar finds it applications in agricultural, environmental and industrial.

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