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Production of Solid Fuel Biochar from De-Oiled Seed Cake by Pyrolysis

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Abstract: *Solid fuel biochar is a low-value byproduct of biomass gasification and pyrolysis with many potential applications, such as soil amendment, the synthesis of activated carbon and high value products. Considering its high-value applications, char could provide economic benefits to a biorefinery utilizing gasification or pyrolysis process. Outputs of pyrolysis process are liquid fuel, solid char and gas. In this paper pyrolysis process and mahua de-oiled seed cake is chosen as feedstock. The properties of char depend heavily on biomass feedstock, pyrolysis design and operating conditions. This paper reports the production, characterization and utilization of biochar. The yield of biochar decreased with increasing temperature. The biomass consisting of 18.9 fixed carbon is converted to bio-char having 73.3 fixed carbon.*
Keywords: *De-oiled seed cake, biochar, pyrolysis*

I. Introduction

Bio-char which is formed from mainly carbon is gaining more attention because of its various applications in soil amendment, removal of toxic materials and production of value-added products. From agricultural point of view, bio-char has a great potential to improve the soil productivity. Soils amended with the char have very beneficial effects on crop growth. The enhanced nutrient retention capacity of biochar-amended soil not only reduces the total fertilizer requirements but also the climate and environmental impact of croplands. Biochar could also enhance soil conservation. Another potential application of char is in the synthesis of activated carbon. Activated carbon is a form of carbon with a high surface area and a high degree of microporosity, which make it suitable for chemical catalysis or physical absorption, e.g., purification of waste water. Char was even used as an energy resource for heating and cooking in households and for heating in the iron industry because of reduced smoke release and high temperatures reached during its combustion [1]. Activated carbon is widely used as an effective adsorbent in many applications such as air separation and purification, vehicle exhaust emission control, solvent recovery and catalyst support because of its high specific pore surface area, adequate pore size distribution and relatively high mechanical strength [2]. Based on the applications of char, it may be sold or used internally to provide heat for the process [3].

Biochar is typically produced from the conventional carbonization, pyrolysis or gasification of biomass. Pyrolysis is used to convert biomass feedstock into liquid, where as gasification is used to convert biomass feedstock into gas as the main end product. Pyrolysis has been employed to convert biomass feedstock into bio-fuels with high energy density and generates three product streams: liquid (bio-oil), gas and solid product (biochar). The distributions and properties of these product streams are strongly dependent on pyrolysis conditions. The pyrolysis products are mainly generated between 300°C and 600°C, their composition being highly dependent on the temperature.

Compared to liquid and gaseous products, only a few studies have been carried out with the aim of producing solid fuel biochars from waste biomass. In contrast, limited studies are available for the biochars derived from most abundant agricultural wastes. Few works has been carried out on pyrolysis with wood as a feedstock.

The main aim of this paper is to utilize the de-oiled seed cake which is the end product of biodiesel production. The biodiesel program can run successfully, when the waste de-oiled seed cake is converted into other valuable energy products. Hence there is an need to develop a method for conversion of the de-oiled seed cake into the other useful products, or else it may lead to many problems like waste disposal management, space occupation etc. Madhuca indica, commonly known as mahua, is mainly cultivated in central and southern parts of India. The annual production of seed in India is around 0.50 million tons. After the extraction of oil, the cake finds application in dye removal, low quality cattle feed and fertilizer. Due to the presence of bitter saponins in seed cake it can be used as a bio-pesticide and insecticide [4]. Hence that was the motivation to choose, de-oiled seed cake-mahua as a feedstock for producing bio-oil and bio-char by pyrolysis process.

The aim of the present work is production of bio-char by pyrolysis and to study the influence of temperature on the distribution and physico-chemical characteristics of the products obtained from the thermolysis of mahua de-oiled seed cake.

II. Materials And Methods

3.1 Feedstock's Preparation

The mahua de-oiled cake was bought from "Biodiesel Production Centre" Kalaburagi- Karnataka, India, which was left out after extraction of crude oil for producing the biodiesel. The cake was in the form of flakes and was powdered using a household grinder. The particle sizes of feed materials used in the study was around 1-2 mm. The de-oiled seed cake were dried and then used in reactor for pyrolysis.

3.2 Pyrolysis process

The experiment was conducted in a reactor furnace, in which the furnace temperature was maintained constant using a PID controller. Experiment was conducted in the range of 400- 600 ^{0}C. The reactor is 48cm long with inside diameter of 21cm attached with 3kw heater. At the outlet of reactor, a condenser is attached to condense the vapours coming out of it. The gasket is used in between to make it leak proof. The condensed liquid was collected in a collecting jar at the end of condenser.

The mahua de-oiled seed cake is filled in a reactor, as the reaction starts, vapours coming out of reactor through the provided outlet are condensed in a condenser. Water is circulated in counter flow as cooling medium in the condenser via a pump. The water is cooled before it is circulated again in the evaporator. The condensed vapours are collected in a container as the liquid product whereas there is some amount of non-condensable gases which are simply left out. The liquid product collected contains oily water and liquid product. Oily viscous water is basically water with some dissolved hydrocarbons. Oily-water and liquid product is further separated by difference in their density. The black residue left after the pyrolysis process in the reactor furnace is bio-char. Figure 1 shows the experimental setup for pyrolysis.

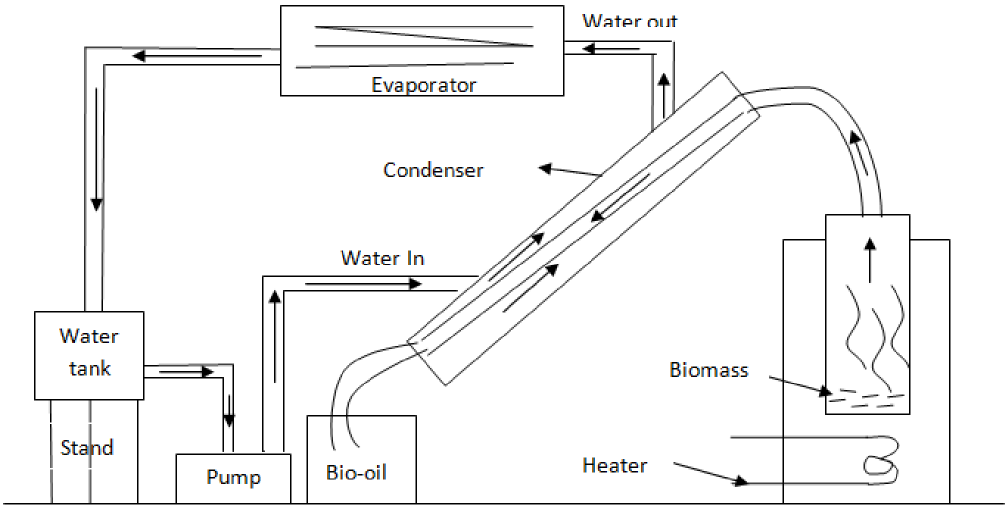

Fig. 1: Experimental setup

3.3 Property Analysis of Biomass, bio-oil and Char

The liquid product or pyrolytic oil also known as bio-oil 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.

Characterization of mahua de-oiled seed cake is done by proximate analysis, calorific value. The proximate analysis and Calorific value was carried out in Bangalore Testing Laboratories Pvt Ltd Bangalore. 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.

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.

III. Results And Discussion

3.1 Analysis of bio-oil

The bio-oil obtained was dark in colour with a smoky smell and has a clear phase separation when stored in bottle as shown in figure 2. Bio-oil is separated and filtered from viscous liquid by density difference. Bio-oil finds its applications in boilers, turbines, furnaces and engines [5,6], production of chemicals [7], in agriculture etc.

Fig. 2: Top bio-oil and bottom viscous liquid layers

Table 1 shows the physical properties of bio-oil. Mahua bio-oil is denser, highly viscous and calorific value is less than the commercial fuels. Bio-oil cannot be made to 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 [8]. There are many substances that can be extracted from bio-oil, 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, fibre synthesizing, or fertilizing industry; and flavouring agents in food products [7].

Table 1. 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
Mahua cake bio-oil	10.2	30.9	980	116	Present study
Diesel	2.58	43.8	854	50	[8]
Biodiesel	5.38	42	875	175	[9]
Wood	25.3	20.5	869	98	[8]

3.1 Analysis of biomass and bio-char

Figure 3 and 4 shows the mahua de-oiled seed cake and bio-char respectively. As shown in table 2 and 3 the biomass consisting of 18.9 fixed carbon is converted to bio-char, having 73.3 fixed carbon. The volatility decreases from 74.9 to 8.2, which indicates higher conversion of biomass to other valuable products. The calorific value of mahua de-oiled seed cake increased from 19.97 to 26.43 MJ/kg. Similar trend were observed by Ugur Morali [10] on hornbeam shell residue.

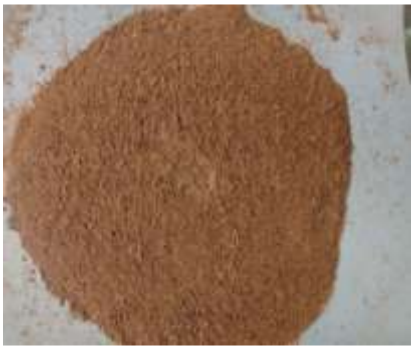

Fig 3: Photograph of Mahua de-seed cake

Fig 4: Photograph of bio-char

Table 2. Proximate analysis of different biomass

Sample	Fixed carbon wt. (%)	Volatile matter wt. (%)	Moisture wt. (%)	Ash wt. (%)	Calorific value (MJ/kg)	References
Mahua de-oiled cake	18.9*	74.9*	6.5	6.2*	19.97	Present Study
Hornbeam shell	9.37	78.83	2.28	9.52	-	[10]

Karanja seed	52.79	73.8	15.2	3.9	22.3	[11]
Groundnut de-oiled cake	6.6	83	5.6	4.8	-	[12]
Eucalyptus wood	5.2	89	5	0.8	14.5	[13]

*Results on dry basis and fixed carbon by calculation.

Table 3. Physical properties of bio-char.

Properties	Fixed Carbon Wt %	Volatile Matter Wt %	Moisture content %	Ash content %	Calorific Value MJ/kg	References
Mahua	73.3	8.2	2.1	16.4	26.43	Present study
Karanja	68.32	32	0.0	8.9	25.2	[11]
Linseed	65	23	-	12	24.96	[14]
Mustard	46.1	21	4.8	28.1	29.1	[15]

The biochar yield fell 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 thermolysis temperature. Similar trend is seen by [2, 13, 14]. The bio-char yield also increased with increasing particle size of the sample. Similar results were obtained by [2, 13, 14]

Table 4. Elemental analysis of bio-char.

Elements	Nitrogen	Phosphorus	Sulphur	Magnesium
Mahua char	1.6	0.48	0.75	0.2

3.2 Application of bio-char

Physical and chemical properties of bio-char depend on the type of feedstock and operating conditions used for pyrolysis. Now a days, agricultural, environmental and industrial applications of bio-char have attracted the attention of scientific community [16]. 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 utilized in various industrial processes such as: solid fuel in boilers, producing activated carbon, making carbon nanotubes, producing hydrogen rich gas, etc [17]. Apart from industrial use biochar is added to agricultural soils, in which the carbon can be seized safely for hundreds of years. The nutrient retention capacity of biochar-amended soil not only reduces the total fertilizer requirements but also impacts positive on the climate and environmental. 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. As a soil amendment, biochar significantly increases the efficiency of and reduces the need for chemical fertilizers. 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 [18].

At different high temperatures bio-chars is better than that for their corresponding biomass precursors. The range of mass loss for bio-chars is much less than that for their parent biomass. In addition, the stability for bio-chars increased with an increase in the pyrolysis temperature [16]. Biochar with high pH may correct the soil acidity problem and therefore, may be used as a liming agent.

IV. Conclusion

Solid (char), bio-oil, and gaseous products were obtained from mauha de-oiled seed cake. Pyrolysis was carried out in the range of 400- 600 ^{0}C. The biochar yield fell slightly with increasing temperature. The bio-char yield also increased with increasing particle size of the sample. The biomass consisting of 18.9 fixed carbon is converted to bio-char, having 73.3 fixed carbon. The volatility decreases from 74.9 to 8.2, which indicates higher conversion of biomass to other valuable products.

Bio-char can be utilized in various industrial processes such as: solid fuel in boilers, producing activated carbon, making carbon nanotubes, producing hydrogen rich gas etc. Now a days, agricultural, environmental and industrial applications of bio-char have attracted the attention. The presence of carbon 73.3%, nitrogen 1.6%, and phosphorous 0.48 % is considered as nutrient and help plant growth. Biochar is added to agricultural soils, in which the carbon can be seized safely for hundreds of years. It high pH nature corrects the soil acidity problem.

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