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## Pyrolysis of Forest Residue for Production of Bio Fuel (September 2006)

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**Abstract** - Bio oil, activated charcoal and bio gas were produced using woody forest residue biomass by pyrolysis using simple technique. Biomass was pretreated in different techniques to compare products yield. Heating rate and pyrolysis temperature influence the pyrolysis products. Bio oil has very high heating value comparable to diesel oil and good physical properties for use as alternative to fossil fuels. Besides it contains many valuable chemicals for further processing of it. By products—charcoal and bio gas are also useful fuels and reducing agents. India generates millions tons of biomass as forest and agriculture waste, which can be used in rural sector to trap huge amount of non conventional energy.

### 1. INTRODUCTION

Biomass and other renewable energy sources are receiving worldwide attention for several reasons. These include the increasing concern about potential global climate change and other environmental consequences of the growing consumption of fossil fuels, the desire to develop sustainable energy sources, decreasing dependence on foreign source of oil, improving balance of payment, and decreasing the rate of depletion of the fossil fuel reserves. Biomass fuels constitute the major fraction of domestic energy requirement in most of the developing countries. In India itself, these fuels fulfill about 75% of the domestic energy-requirements [1]. Biomass fuels are generally used in primitive combustion devices, which are reported to be highly energy inefficient, and release vast amounts of pollutants into the environment. Renewable biomass is an attractive alternative to fossil feedstock. Agriculture wastes generate huge amount of woody biomass. India produces annually about several million tons of forest residues. A rough estimate indicates that even if 30% of the agricultural residue is available, there exists a potential to generate about 30,000 MW of power at 36% overall efficiency. Direct combustion of biomass produces heat energy with low efficiency and gives rise gaseous pollutants. Pyrolysis of biomass is very attractive. It converts biomass to bio oil, gaseous fuels and activated charcoal. While the formers are good renewable energy source, the later is also very useful in form of excellent reducing agent, gas absorbent and catalyst.

Biomass is a mix of three basic components, lignin, cellulose and hemicellulose. Lignin serves as a sort of 'glue' giving the biomass fibers its structural strength, while hemicellulose and cellulose polymers are the basic building blocks of the fibers. It generally consists of about 25 to 30% lignin, 25 to 30% hemicellulose, and 30 to 45% cellulose [2]. Cellulose is a straight and stiff molecule with a polymerization degree of approximately 10,000 glucose

units (C6 sugar) in the cellulose chain, the glucose units are in 6-membered rings, called pyranoses [3]. Hemicellulose is polymers built C5, C6 sugars with a polymerization degree of about 200 sugar units. Lignin is a three dimensional branched polymer composed phenolic units. Both cellulose and hemicellulose can be converted to vapour and Lignin contributes to major fraction of char formation. In addition, biomass often contains varying amounts of species called "extractives", which are soluble in polar or no polar solvents, consist of terpenes, fatty acids, aromatic compounds and volatile oil.

Pyrolysis of biomass had been studied extensively worldwide to produce bio oil and gaseous products. Investigations have been carried out with different types of biomass viz. Ground-nut shell, Wood, Rice-husk, Bagasse etc. Works have also been carried out to find the effect of various reaction parameters on product yields and kinetic of the reaction. Biomass in the form of cashew nut shell represents a renewable and abundant source of energy in India. Das et. al [4] pyrolysis Cashew nut shell in a 1xed bed pyrolysis reactor under vacuum produced dark brown oil and on heating up to 175.C. Mario Lanzetta and Colomba Di Blasi [5] investigated pyrolysis of wheat and corn straw. They confirmed two-stage mechanisms, which takes into account the formation of a solid intermediate and volatiles, followed by further degradation of the intermediate to char and volatiles. For all temperatures, the first stage, where most part of volatiles is released, is about 10 times faster than the second. For high reaction rate and more yield of bio oil, pyrolysis of biomass are carried out in fluid bed reactors at extremely high heating rate which involve high equipments making process costly and uneconomical. Studies of woody biomass pyrolysis have been carried out by many workers [6-10] by single step or two steps models. Two-step models include a primary stage, during which wood thermally decomposes to produce light gases, tars, and chars, and a secondary stage, during which tars undergo additional cracking to produce gases. Much more sophisticated devolatilization models exist [11, 12], including some under development by this research group [13]. R Ball, A C McIntosh and J Brindley [14] in their recent studies of pyrolysis of biomass found activation energy involved for char formation is low while that for bio oil is

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high. Mok *et al.* [15], observed during pyrolysis that either a high concentration of vapour products or added water increased char yield and decreased the temperature of onset of decomposition. Subsequent analysis of these data [16] led to the suggestion that the water produced in thermal dehydration reactions feeds back to hydrolyze the unreacted cellulose. Evidence was also presented from pyrolysis experiments [17,18], that product water accelerated the formation of char. Even with so much works, bio oil produced lack of standards and inconsistent quality. Better process technologies are needed for competing with fossil fuels. In the present investigation woody forest of rural front was pretreated and pyrolysed to obtain bio oil and biogas.

**2. EXPERIMENTAL**

Biomass of woody forest residue (twigs) was collected from rural front. They were cut in sizes and were dried by heating in the furnace at 150 °C temperature for one hour to remove physically absorbed moisture. It was sieved and separated to have uniform size of 5 to 6 mm. The sample was analyzed and percentage compositions of cellulose, hemi cellulose and lignin are depicted in Table 1. The sample was pretreated as follows.

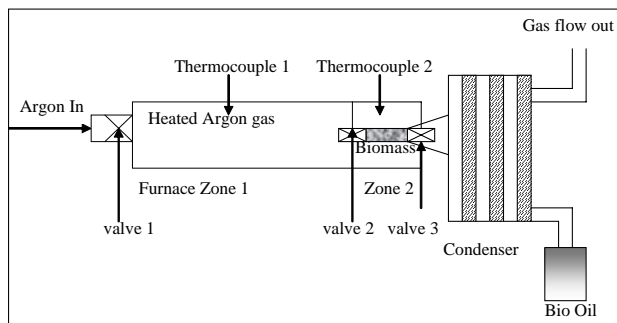
Type	Pretreatment process
1st	Wood dust which is prepared by only passive drying.
2nd	Wood dust which is prepared by passive drying & subsequently heating in the furnace about 150°C for one hour.
3rd	By mixing wood dust in 0.25-wt % nitric acid for one hour to dissolved alkali metal. Demineralization and subsequently heating in the furnace at about 150°C for one hour.

**Table 1. Composition of Biomass**

Cellulose %	Hemicellulose %	Lignin %	Others %
41.71	24.66	28.29	5.34

The preheated and pretreated sample was put into the zone 2 and argon gas was purged into the zone 1 of the furnace as shown in the schematic diagram Fig. 1. All the valves 1,2 and 3 are opened and argon gas is purged through the system. The valves are closed and the zone 1 of the furnace was heated to the required pyrolysis temperature. When the temperature indicated by thermocouple 1 has reached, heating in zone 2 is started with fixed rate of heating, controlled by PID controller and the hot argon gas is immediately allowed to flow through the sample in zone 2 by opening the valve 2. The rate of heating in the zone 2 that is pyrolysis zone is obtained from the readings of the thermocouple 2 with time and final temperature is also recorded. Thus, the rate of heating can be controlled by manipulating the temperature of the hot argon gas in zone 1 along with rate of heating in zone 2 just before

allowing the gas to pass to zone 2. After a predetermined residence time, the valve3 is opened and products of pyrolysis were cooled in condenser. The solid product left inside the furnace is weighed to find percentage charcoal formation, the vapour condensing to liquid is bio oil, which is collected and weighed to find its percentage and the remaining mass from the initial weight of sample taken is the contribution of gaseous fuel formed. The physical properties of bio oil were determined using standard instruments and calorific value in calorimetry. The major chemical constituents of the oil were analyzed.



**Fig. 1. Schematic diagram of experimental setup of pyrolysis of woody biomass and production of bio oil.**

**3. RESULTS AND DISCUSSIONS**

Figure 2 and 3 illustrate DTA and TGA analysis of wood floor at a heating rate of 25 and 40 °C per minute respectively. It is clearly seen that around 100 °C, 5% weight loss occurred due to vaporization of physically absorbed moisture in the wood sample. The major weight loss occurs between 250 °C to 500 °C and it continues till 700 °C, due to decomposition of biomass and formation of gaseous and liquid bio product (Fig. 2) and with higher heating rate the weight loss curve shift to the right hand side and Pyrolysis continues till 800 °C (Fig. 3). In our experiment heating rate was normally chosen at 30 °C per minute so maximum weight loss expected to be in between 700 °C and 800 °C likely 750 °C. So experiments were performed between 500 °C to 750 °C to obtain maximum amount of liquid yield. All the three products of pyrolysis are industrially important. The gaseous product can be used as gaseous fuel, the charcoal obtained being highly porous has a good application as a reducing agent, gas absorbent & catalyst and the bio-oil has wide application as partial substitute for petrol and diesel in automobiles.

Effect of temperature of pyrolysis on weight % of various products has been illustrated in the Figs. 4 to 6 and their result have been tabulated in Tables 2 to 4. It is percentage of gaseous fuels is always much more than those of liquid fuel bio oil and solid fuel activated charcoal. It is seen that increasing pyrolysis temperature produce an increasing in yield of bio-oil till the temperature of about 650 °C to 700 °C depending on the type of sample taken. These confirm pyrolysis temperature to be maintained between 650 °C to 700 °C for maximum bio-oil recovery. For charcoal the weight % yields goes down with increasing

temperature and more or less remains fixed from 650 °C to 700 °C. The weight % of gaseous fuel becomes minimum around 700 °C for first and second type of pretreated wood sample, whereas for the third type, it does not vary much. It is very clearly indicated that third type of pretreated wood sample gave maximum bio-oil yield and the gas yield is minimum. Thus, third type of pretreated wood was recommended for more proportionate of bio-oil & less gas evolution. As far as effect of pretreated wood sample on charcoal yield is concerned, It is seen that first type of pretreated wood gives higher charcoal yield followed by second and third type of pretreated wood sample. Fig. 7 illustrates effect of variation of residence time on percentage yield of various products. It is interesting to see that lower the residence time more is the percentage of bio oil, while char formation is higher with longer duration of residence time, and gas percentage is maximum when the residence time is neither very low nor very high.

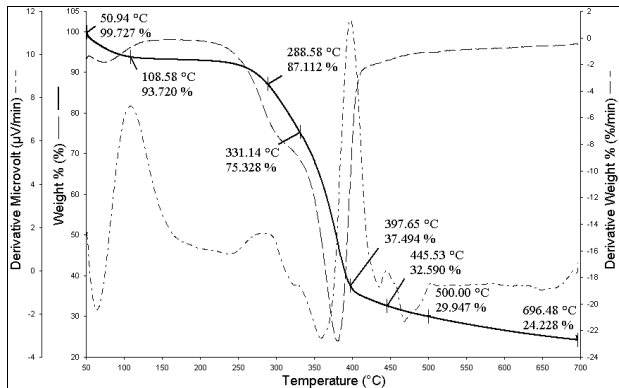


Fig. 2. DTA and TGA analysis of woody biomass, Heating Rate 25°C/min.

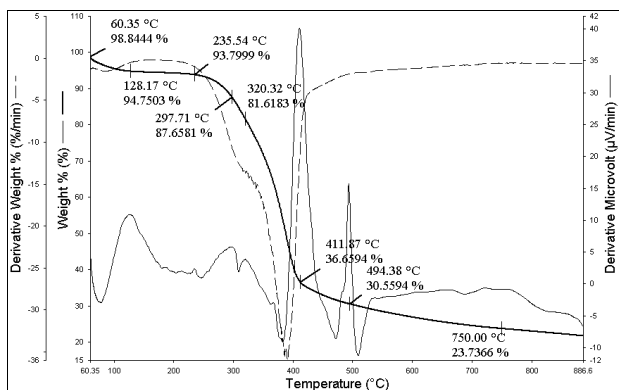


Fig. 3. DTA and TGA analysis of woody biomass, Heating Rate 40°C/min.

The heating rate has a strong influence on proportionate of pyrolysis products as depicted in Fig. 8. It is seen, faster is the rate of heating to the pyrolysis temperature of 700 °C more is the proportionate amount of bio-oil while at lower rate both gas and char formation are more favorable.

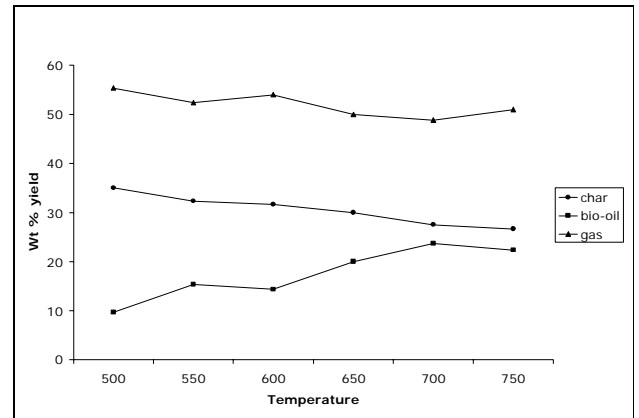


Fig. 4. wt% yield of charcoal, bio-oil & gas Vs Pyrolysis temperature (for first Type of wood sample).

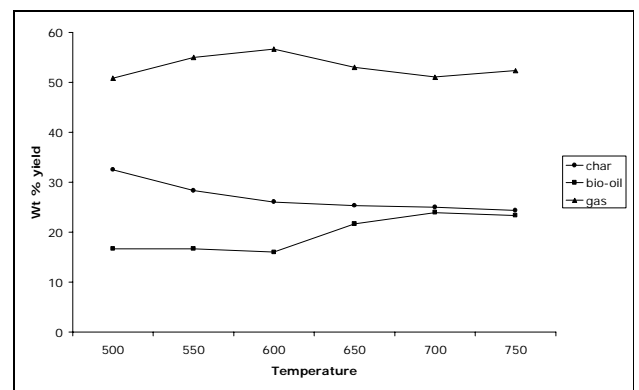


Fig. 5. wt% yield of charcoal, bio-oil & gas Vs pyrolysis temperature (for second type of wood sample).

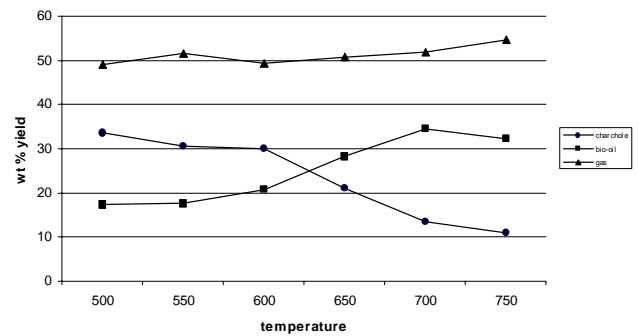


Fig. 6. wt% yield of charcoal, bio-oil & gas Vs pyrolysis temperature (for third type of wood sample).

From the foregoing results and discussion, it is seen that using third type of pretreated woody forest residue and a simple two chambers electrically heated furnace, a sufficiently high heating rate has been achieved to have a good yield of bio-oil. Productions of bio oil out of biomass by fast pyrolysis as performed by many workers [1,4,7-9], occur with very high heating rate so that the required pyrolysis temperature can be achieved within few seconds. This necessities sophisticated types of fluid bed and flow reactors, such as Entrained Flow Reactor, Circulating Fluid

Bed Reactor, Vacuum Furnace Reactor, Vortex reactor, Rotation cone reactor etc. Faster the heating rate, more costly is the infrastructure and higher is the yield of bio-oil out of a given weight of biomass. But in this proposed process, using a simple design and less expensive equipments, bio-oil can be obtained using lot of forest woody residue generated in the rural front. The products of pyrolysis are liquid bio-oil, gaseous fuels and solid porous charcoal. The gaseous fuels can be utilized to generate heat for drying of biomass or in the furnace itself instead of argon gas as used in the present model and porous activated char is a byproduct. So the process can be rural friendly.

**Table 2. Yield of Different Types of Product during Pyrolysis of First Type of Wood Sample at Different Reaction Chamber Temperature**

Sample weight (gm)	Temp (°C)	Bio-oil yield		Char yield		Gas yield	
		(gm)	(%)	(gm)	(%)	(gm)	(%)
30	500	2.89	9.66	10.5	35.00	16.61	55.36
30	550	4.60	15.33	9.67	32.33	15.73	52.43
30	600	4.30	14.33	9.50	31.66	16.20	54.00
30	650	6.00	20.00	9.00	30.00	15.00	50.00
30	700	7.10	23.66	8.25	27.50	14.65	48.83
30	750	6.70	22.33	8.00	26.66	15.30	51.00

**Table 3. Yield of Different Types of Product during Pyrolysis of Second Type of Wood Sample at Different Reaction Chamber Temperature**

Sample weight (gm)	Temp (°C)	Bio-oil yield		Char yield		Gas yield	
		(gm)	(%)	(gm)	(%)	(gm)	(%)
30	500	5.00	16.66	9.75	32.50	15.25	50.83
30	550	5.00	16.66	8.50	28.33	16.50	55.00
30	600	4.80	16.00	8.20	26.06	17.00	56.66
30	650	6.50	21.66	7.60	25.33	15.90	53.00
30	700	7.18	23.93	7.50	25.00	15.32	51.06
30	750	7.00	23.33	7.30	24.33	15.70	52.33

**Table 4. Yield of Different Types of Product during Pyrolysis of Third Type of Wood Sample at Different Reaction Chamber Temperature**

Sample weight (gm)	Temp (°C)	Bio-oil yield		Char yield		Gas yield	
		(gm)	(%)	(gm)	(%)	(gm)	(%)
30	500	5.2	17.33	10.10	33.66	14.70	49.10
30	550	5.3	17.66	9.20	30.66	15.50	51.66
30	600	6.2	20.66	9.00	30.00	14.80	49.33
30	650	6.6	28.22	8.20	21.13	15.20	50.66
30	700	7.5	34.50	6.94	13.53	15.56	51.86
30	750	6.7	32.33	7.50	11.00	15.80	54.66

Bio oil obtained was almost red-brown to dark red-brown color (Fig. 9), with density of 1040 to 1200 kg/m<sup>3</sup>, which are higher than of fuel oil, and significantly higher than of the original biomass (Table 5). The degradation products from the biomass constituents include organic acids (like formic and acetic acid), giving the oil its low pH of about 2.8 to almost 4. There is no such influence of pH due to pyrolysis temperature. The pH indicates that the bio-oil is acidic so it attacks mild steel, and storage of the

oils should be in acid proof materials like stainless steel or poly-olefins. Conductivity of bio-oil ranges 2.8 to 3.6 ms from the Table 5. It is clearly seen that the conductivity of bio-oil is relatively high with third type of pretreated wood sample. The bio-oil produced shows also high heating value (Table 5). Compared to diesel oil, it has energy content of 45 to 55% of diesel oil.

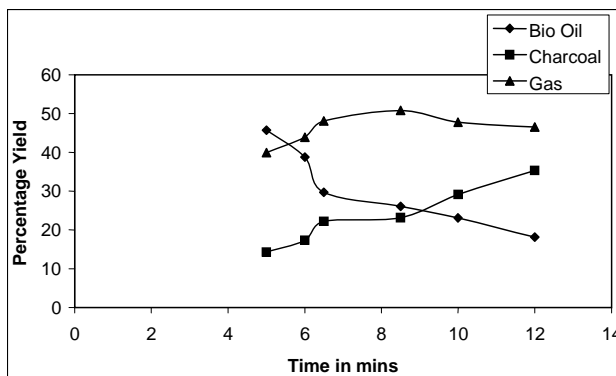


Fig. 7. Effect of residence time on different product yields.

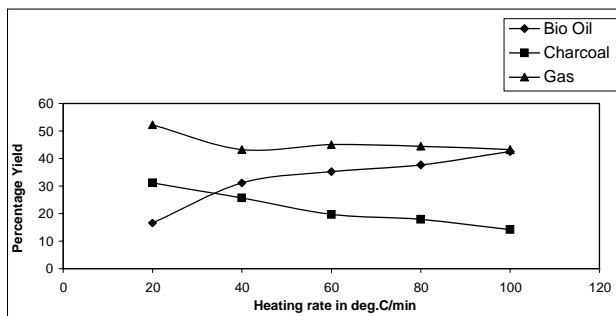


Fig. 8. Effect of heating rate on percentage yields of pyrolysis products.



Fig. 9. Displaying different bio oil samples under several pyrolysis conditions.

Bio oil is a mixture-oxygenated compound of hundreds of chemicals with wide range of molecular weight distribution. An analysis of major constituents have been carried out for only third type of pretreated sample and is given in Table 6. It is found it contains a good proportion of water, pyrolytic lignin and organic acids. Because of so much water, it is non viscous and can be easily transported and stored. Besides its high heating value for its application as source of non-conventional energy, bio-oil can be further converted to many useful organic chemicals [19]. Bio-oil

could be successfully converted to alcohols by fermentation with some microorganisms and algae in our next investigation [20] and the alcohol was used to develop a bio electrochemical fuel cell.

**Table 5. Physical Properties of Bio Oil**

Pretreatment	Color	Density Kg/m <sup>3</sup>	pH	Conductivity ms	Calorific value kj/kg
Type -I	Brown	1040	3.1	2.8	16000
Type -II	Brown	1060	3.0	3.0	17500
Type -III	Dark Brown	1200	2.5	3.6	19000

**Table 6. Chemical Analysis of Bio Oil with Type III Pretreatment**

Constituents	Percentage
Water	20.8
Lignin	23.5
Hydroxyacetaldehyde	10.2
Glyoxal	2.2
Levoglucosan	3.0
Formaldehyde	3.4
Formic acid	5.7
Acetic acid	6.6
Formic acid	5.7
Acetal	5.8
Others	18.8

#### 4. SUMMARY

Pretreated biomass as forest waste under controlled heating rate and cooling to preselected pyrolysis temperature could give more than 30% of bio-oil using simple less costly equipments. The bio-oil is of high heating value and other properties for its use as source of renewable energy.

#### ACKNOWLEDGEMENT

The authors would like express deep gratitude to Sudeshna Paul for valuable advices in the experiments. Chemical analysis of organic constituents were carried in Biotechnology center CSIR laboratory, Jadavpur Kolkata.

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- [20] Thesis of Prakash Mondal Under guidance of S Paul entitled " Production of Bio Fuel by Retreatment and Processing of Woody Biomass and Subsequent Fabrication of Biofuel Cell" Department of Metallurgical and Material Engineering, Faculty of Engineering and Technology, Jadavpur University, Kolkata-700032.