ICME03-TH-17

PRODUCT DISTRIBUTION FROM WOODY BIOMASS IN A BENCH-SCALE PYROLYZER

Jigisha Parikh¹, S. A. Channiwala² and G. K. Ghosal³

Chemical Engg. Deptt. Sarvajanik College of Engg. & Tech., Surat-395001, India
Mechanical Engg. Deptt. Sardar Vallabhbhai National Inst. of Tech., Surat-395007, India
Chemical. Engg. Deptt .Laxminarayan Inst. of Tech., Nagpur, India

ABSTRACT

Biomass pyrolysis offers promise for producing commercially interesting quantities of high heating value gases, solids and liquids suitable for replacing petroleum-based products. This paper presents quantitative understanding of the thermal decomposition behavior of woody biomass for which laboratory scale batch reactor is employed. Effect of temperature on the yields, composition & rates of formation of products for four different woody biomass materials under an inert nitrogen atmosphere has been studied. The materials considered for detailed investigations were Sawdust, Babul, Gulmahor and Eucalyptus. The yield of char, liquid & total gases in relation to temperature for different samples is presented and compared. The percentage volatile matter in charcoal decreased with an increase in temperature, while there was an increase in the percentage fixed carbon. On the whole, the four investigated woods resemble in their pyrolysis behavior and their yield of pyrolysate, pyrolysis liquids, and gas.

1

Keywords: Woody Biomass, Pyrolysis, Temperature.

INTRODUCTION

Wood and other forms of biomass including energy crops and agricultural and forestry wastes are some of the main renewable energy resources available. These can provide very good source of renewable liquid, gaseous and solid fuels. Biomass is considered as the renewable energy source with the highest potential to contribute to the energy needs of modern society for both the developed and developing economies world-wide and its utilization has increased notably in recent years. Pyrolysis is the basic reaction of all thermal conversions of biomass. Biomass pyrolysis can be described as the direct thermal decomposition of the organic substances in the absence of oxygen to yield an array of useful products – gas, liquid, and solid – a wide range of fuels, solvents, chemicals etc. However, it is extremely complex being the result of many concurrent and consecutive reactions, and hundreds of products and intermediates have been reported [1, 2].

The importance of pyrolysis is still growing up together with development of the pyrolysis systems. From the other side we have increasing amount of biomass, starch and cellulose containing wastes which come from different areas of life (e.g. agriculture, forest, industry, municipal solid waste etc.). The pyrolysis can either join a treatment method for such type of material

or a method for energy and/or material recovery.

There have been many previous investigations of the pyrolysis of cellulose, lignin, wood and other forms of renewable materials [3-10]. However, there still remains a great need for reliable systematic studies of the independent effects of the type of material and commercially interesting reaction conditions such as temperature, heating rate, pressure, gaseous atmosphere, sample dimension, on the yields, compositions and rates of production of pyrolysis gases, liquids & chars. These details are needed to gain better fundamental understanding of biomass thermal conversion pathways and to provide predictive modeling capability for existing and future processes for converting renewable resources to clean fuels & chemical feed stocks. A good knowledge of its mechanisms should improvements in yields and selectivity of the process. The main part of a pyrolysis plant is the reactor. The choice of the reactor type and heating system affects the final product distribution. This choice is strongly affected by the characteristics of the raw materials available and process conditions [4-6].

With respect to above, laboratory scale batch reactor is employed in this work, which is designed to allow total product collection and to minimize secondary (post-pyrolysis) reactions of volatiles evolved from the

decomposing sample. This paper presents quantitative understanding of the thermal decomposition behavior of woody biomass. Effect of temperature on the yields, composition & rates of formation of products for four different woody biomass materials under an inert nitrogen atmosphere has been studied in a bench-scale pyrolyzer developed during the course of this work.

The objective of this work is to investigate and compare the pyrolysis behavior of four non-conventional energy sources.

EXPERIMENTAL SECTIONMaterials

They include four ligno-cellulosic materials (woody biomass) namely Eucalyptus, Gulmahor, Babul & Sawdust. Samples were cut into particles of size less than 1 mm in order to minimize heat and mass transport resistances in the boundary layer and within the particles [4]. Different characteristics (Proximate and ultimate analysis) of samples used in present study are reported in Table 1.

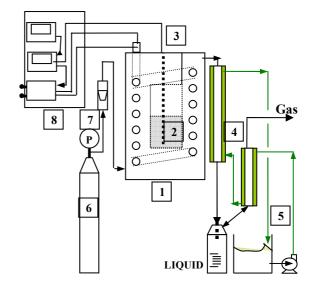
Table 1: Composition of the different woody biomass

Sample	Saw dust	Babul	Gulmahor	Eucalyptus
Ash	1.80	1.27	1.73	1.23
VM	83.20	80.7	82.45	82.62
FC	15.00	18.03	15.82	16.15
С	46.92	45.39	45.99	47.1
Н	6.07	6.12	6.09	6.00
N	0.23	0.33	0.31	0.24

Reactor Description

Laboratory scale batch reactor is employed in this work. A fixed-bed reactor was fabricated to pyrolyse the selected raw material at the desired temperature. It consisted of three main sections: main SS reactor with indirect heating coil, a nitrogen gas supply system and a condensate & gas collection system which is designed to allow total product collection and to minimize secondary (post-pyrolysis) reactions of volatiles evolved from the decomposing sample.

A schematic of this reactor and the product collection equipment is shown in fig. 1. This reactor is designed for atmospheric pyrolysis. It is a cylindrical reactor closed at each end with stainless steel flanges, with electrical furnace, and gas inlet and outlet ports. The sample weighing 50 gm is heated inside a SS mesh basket held on supports mounted within the above vessel. The heating circuit consists of various temperature controller and timer switches. The volatiles generated are immediately passed through condensate collection system and rapidly quenched. The data therefore mainly reflect the primary decomposition behavior of woody biomass with contributions from post-pyrolysis reactions being limited to there occurring within and closely proximate to the sample.



- 1. Reactor
- 2. Sample Basket
- 3. Thermocouple
- 4. Condenser Train
- 5. Cooling System
- 6. N₂ Supply
- 7. Rotameter
- 8. Control Panel

Fig.1. Experimental Set Up

A weighed sample of 50 gm of the feed was taken in the sample boat and then placed in the reactor. The system was purged of oxygen by allowing nitrogen to flow through the system. The feed was then heated up to desired temperature by the temperature controller system. During heating, the system was maintained at atmospheric pressure.

The selected temperature range was 300-500°C. The runs were taken for different temperature & raw materials selected. All the experiments were referred to as a peak temperature (Or zero holding time) run. In all experiments the reactor & remaining solid material cool primarily by radiation and natural convection. All products were collected in each run and presented on mass basis.

Yields of the different products obtained were determined by weighing the solid residue (charcoal) and liquid collected and gas evolution by difference. In order to test the reproducibility of the experiments, we tripled the experiment at each temperature. Yields are expressed as a percent by weight of the raw material as a function of peak temperature.

CONVERSION OF BIOMASS

2

The conversion processes of biomass usually involve a reduction of the water content of the material, resulting in the simultaneous increase in its thermal value and preservation potential and in improving the handling characteristics of the biomass, for example turning it into a fluid, which may be either gas or liquid. Oxygen removal from the biomass in the form of carbon dioxide (and carbon monoxide) will result in products with high hydrogen to carbon (H/C) ratio.

Pyrolytic conversion of wood involves thermal separation of volatile matter from the solid residue. The pyrolytic process is affected by the type of raw material and process parameters, wherein the temperature plays

an important role.

Below 260°C only charring takes place, while depolymerization of chemical components generally predominates between 275 °C and 400 °C- hemicellulose is readily converted into methanol and acetic acid between 200-280 °C, from 280 °C to 500 °C cellulose, which has already undergone some thermal degradation decomposes at an increasing rate which reaches a maximum at around 320°C while lignin decomposes only at temperatures above 280 °C, forming mainly tar and charcoal [3,4,6].

With reference to present work, the general course of pyrolysis of lignocellulosic materials is observed as follows:

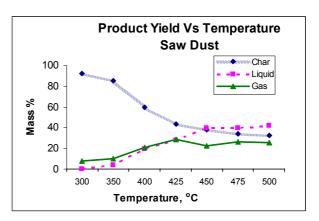
The thermal destruction of lignocellulosic biomass starts at 100 °C (the main process being hydrolysis), the rate and amount of destruction are quite negligible up to 200 °C. After the last traces of water are removed, which requires a temperature of about 140 °C, four classes of products are produced by thermal decomposition (pyrolysis) of wood:

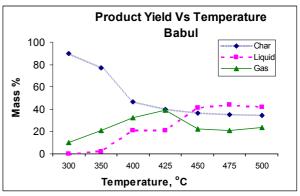
1) Noncondensable gases (carbon monoxide, carbon dioxide, hydrogen, methane) 2) Pyroligneous products (condensable, contain more than 50 % moisture) 3) Tar (moisture-free, condensable) 4) Charcoal.

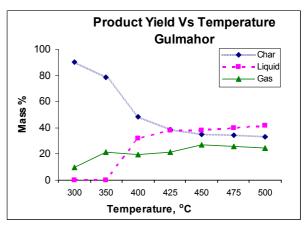
Gases were evolved at temperatures between 200° C and 400° to 450° C, with a maximum at about 350° to 400° C. The rate of production of pyroligneous material passes through a maximum between 250 °C and 400° C and virtually ceases at about 450° C. Tar forms between about 300 °C and 400 °C to 450° C.

RESULTS AND DISCUSSION

Figure 2 shows the yield of char, liquid & total gases in relation to temperature for different samples. At the lowest pyrolysis temperature (300°C) examined, the liquid yield is zero, reflecting incomplete pyrolysis. As the temperature was increased the liquid yield increased until it reached maximum/stable at 475-500°C. At low temperatures, below 425°C, liquid yields are reduced may be because of the coking reactions of oil via conversion of the liquid oil to solid products [4,7,8]. Below about 400°C decrease in liquid yields was observed because of incomplete pyrolysis. There is consequently an optimum temperature where maximum liquid yields are obtained. In the present work, the maximum liquid yield was found for a temperature of 475 °C -500°C at an average heating rate of 10°C/min. There was a progressive increase in gas yield from 300°C to 450°C. A decrease in gas yield coupled with an increase in liquid yield was observed (around 425-475°C) which might be attributed to the presence of condensable chemicals like aldehydes, ketones, organic acids, methanol etc. From 500°C onwards there was an increase in gas yield. Gas yield ranges from 8 % to 25 % for Sawdust, 10 % to 24 % for Babul, 10 % to 25 % for Gulmahor and 5 % to 23 % for Eucalyptus whereas liquid yield ranges from 0.0 % to 40-42 % for all species within the studied temperature range of 300 °C -500 °C.







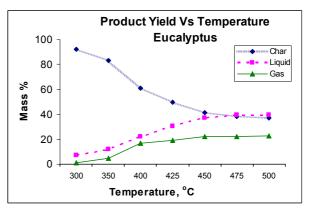
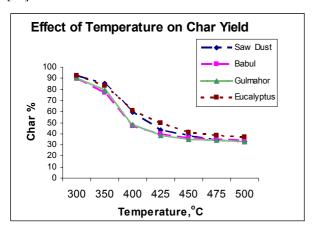
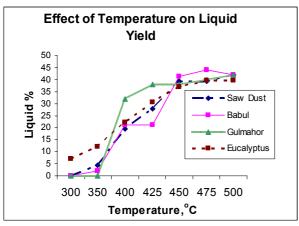


Fig. 2. Product Yield Vs. Temp. for different biomass

The charcoal yield decreased with an increase in pyrolysing temperature for all the species. The higher yield of carbonized material at $300\,^{\circ}\text{C}$ may be due to limited thermal decomposition of extractives and

hemicellulose in wood at temperatures between 190-270 °C. Cellulose, which constitutes about 45% of tropical hardwood, is thermally degraded at temperatures between 270-325 ° C but lignin, which makes up 25-30% of the chemical composition of wood, is thermally stable below 270 °C, while 90% of it is thermally degraded by 400 °C [9,10]. The cellulose and hemicelluloses are the main sources of volatiles in biomass feed stocks, but yield only about 8 to 15% of this weight as charcoal under conventional pyrolysis conditions. The lignins yield nearby 50% of their weight as charcoal under these conditions [11]. It has been also reported, based on experimentation of wood, lignin and hollocellulose that the char yield from the lignin was three times that from the hollocellulose in the temperature range of 400-900 °C [12].





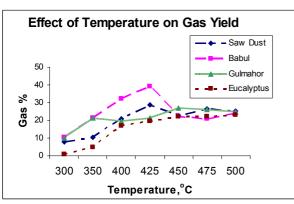


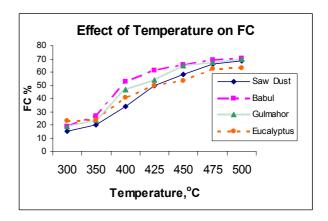
Fig 3. Effect of Temperature on individual product yield

In the present study, the char yield was reduced as the pyrolysis temperature was increased from 90-92 wt% at 300°C to 33-37 wt% at 500°C. This decrease in the char yield with increasing temperature could be either due to greater primary decomposition of the wood at higher temperatures or to secondary decomposition of char residue (latter case may not be significant for the present work). Figure 3 shows the comparison of temperature effect on individual yield for four species studied.

With change in temperature the composition of pyrolysis products also varies [1-3,7,12-15]. Present study has considered the effect of temperature on solid product obtained. Among the properties which characterize charcoal, the more significant seem to be yield, volatile matter and fixed carbon content.

Whether the charcoal can be regarded as quality product, depends on its chemical and physical properties. These are highly related to the raw material and the operating conditions of the pyrolysis process. They will also determine the possibility of the char to undergo further treatment in order to provide more convenient final products such as activated carbon and electrode carbon.

The variation of these three properties with the terminal pyrolysis temperature can be deduced from fig 4. Charcoal formation processes simultaneously with an intensive development of the volatile products.



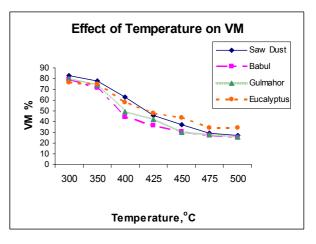


Fig. 4. Effect of Temperature on composition of char from different bio mass

In the original sample the volatile matter content was 83.2, 80.7, 82.45 and 82.62 % for Sawdust, Babul, Gulmahor and Eucalyptus respectively. At 300 °C sample gives off 3-4 %VM while at 400 °C, 25 to 30 % and at 500 °C @50 % of the original content for all the species. It showed that major evolution was between $300\text{-}450\,^{\circ}\text{C}$ while $450\,^{\circ}\text{C}$ onwards it became gradual.

The fixed carbon content increases with temperature from 15 to 68 % for Sawdust, 18 to 70 % for Babul, 16 to 70 % for Gulmahor and 16 to 62 % for Eucalyptus in the studied temperature range of 300 °C -500 °C.

At a temp of 500°C the charcoal yield and fixed carbon content are satisfactory. The composition of the char shows that it is a good material for activated carbon production, due to the high fixed carbon content and the low proportion of ash.

The results of the present work suggest that this Pyrolyser can produce chars suitable for activation. The surface areas may be improved with different methods of activation. Given that the pyrolysis process generates large quantities of CO_2 and heat, it is probable that either the CO_2 method or steam activation could be used in an industrial scale integrated process.

CONCLUSION

It shows that for the above time-temperature history, decomposition of the wood is first observed at about 180°C and becomes rapid from 250°C onwards. Weight loss increases with temperature. Most of the devolatilisation occurs between 300°C and 400°C (@25-30%). Above 400°C the rate of decomposition becomes gradually stable.

The percentage volatile matter in charcoal decreased with an increase in temperature, while there was an increase in the percentage fixed carbon. The increase is rather large as the final temperature increases from 300-450 °C, but from 450-500 °C the increase is gradual. This behavior is observed for all the wood species.

The results shows that the batch fixed-bed pyrolyser described can be used with success on the pilot scale to pyrolyse different biomass residues. Therefore this preliminary study shows that the development of a continuous pyrolysis process is possible. Especially for the production of high porous active carbon of renewable energy sources as well as the use of pyrolysate for energetic purposes wood seems to be an adequate material. On the whole, the four investigated woods resemble in their pyrolysis behaviour and their yield of pyrolysate, pyrolysis liquids, and gas.

REFERENCES

- Bridgewater, A. V., Grassi, G. (Eds.), 1990, "Biomass Pyrolysis liquids upgrading & Utilization", Elsevier Applied Science, London.
- 2. Soltes, J. and Milne, T. A. (Eds.), 1988, "Pyrolysis Oils from Biomass; Producing Analyzing & Upgrading", American Chemical Society, Washington.

- 3. Shafizadeh F., 1985, "Pyrolysis Reactions and Products of Biomass Conversion", Eds. R.P. Overend, T.A. Milne, L.K. Mudge, Elsevier, London, 183.
- Parikh, J. K., Channiwala, S. A. and Ghosal, G. K., 2002, "A Critical Review on Biomass Pyrolysis", Proceedings 12th European Biomass International Conference, The Netherlands.
- 5. Williams, P. T. and Besler, S.,1993, "The Pyrolysis of Rice husks in a TGA and Static Batch Reactor", Fuel, 72: 151 159.
- 6. Hajaligol, M. G. et al., 1982, "Production Composition & Kinetics for Rapid Pyrolysis & Cellulose", Ind. Eng. Chem. Process Design Dev. 21: 457 469.
- 7. Raveendran, K. et al., 1996, "Pyrolysis Characteristics of Biomass & Biomass Components, Fuel, 75: 987 998.
- 8. Williams, P. T. and Ahmad N., 1999, "Influence of Process conditions on the Pyrolysis of Pakistani Oil Shales", Fuel, 78: 653 662.
- 9. Figueiredo, J. L. et al., 1989, "Pyrolysis of Holm oak Wood: Influence of Temperature & Particle size', Fuel, 68: 1012 1016.
- 10. Fuwape J. A., 1996, "Effets of Carbonization Temp. on Charcoal from Some Tropical Trees", Bioresource Tech., 57: 91-94.
- 11. Zaror, C. A. & Pyle, D. L., 1982, Proc. Indian Acad. Sci., (Eng. Sci.), 5(4): 269.
- 12. Sadakata, M. et al., 1987, "Production of Fuel gas and Char from Wood, Lignin and Holocellulose by Carbonization", Fuel, 66: 1667 1671.
- 13. Williams, P. T. and Horne, P. A., 1996, "Influence of Temperature on the Products from the Flash Pyrolysis of Biomass", Fuel, 75: 1051–1059.
- 14. Calahorro, C. V. et al., 1992, "The Use of Waste matter after Olive Grove Pruning for the Preparation of Charcoal", Bioresource Tech., 40: 17-22.
- 15. Sharma, R. K. et al., 2001, "Characterization of Chars from Biomass derived Materials: Pectin Chars', Fuel, 80: 1825 1836.

NOMENCLATURE

Symbol	Meaning	Unit
VM	Volatile Matter	% mass
FC	Fixed Carbon	% mass
С	Carbon	% mass
Н	Hydrogen	% mass
N	Nitrogen	% mass

^{*} author for correspondence.

5