Product Distribution from Woody Biomass by Fixed-bed Pyrolysis Process

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Abstract:

Conversion of woody biomass to usable energy forms has gained much interest recently due to increase in energy cost as well as greater pressure on the environment by the use of fossil fuel. This paper proposes the quantitative understanding of the thermal decomposition behavior of woody biomass by employing the laboratory-scale batch reactor. Effect of temperature on the yields, the composition and the rate of formation of the products for four different woody biomass materials is studied. The char yield, liquid and total gas, which are relative to the temperature for different samples, are also presented and compared. The result shows that the percentage volatile matter in char decreases with an increase in temperature, while there is an increase in the percentage fixed carbon. Overall, the four investigated woods resemble in their pyrolysis behavior and their yield of pyrolysate, pyrolysis liquids and gas.

Introduction

Since the oil crisis in the early 1970s, awareness to fast depleting fossil fuel resources and need to reduce green house gas and other emission has triggered search for alternative renewable energy source. Biomass is the plant material derived from the reaction between CO_2 in the air, water and sunlight, via photosynthesis in order to produce carbohydrates, which form the building blocks of biomass. Wood is a type of biomass that is considered as one of the most important renewable energy sources. The wood as feedstock for energy production is derived from forestry product or agricultural fast growing tree that abundantly available in the world and can be substituted for fossil fuel source. There are several ways to produce energy by using biomass as a fuel source, from old direct burning to modern gasification and pyrolysis. In developing counties, especially, the use of woody biomass is high interest, since these countries have economies largely based on agriculture and forestry [McKendry, 2002]. Many investigations of the pyrolysis of cellulose, lignin, wood and other form of renewable materials were made previously [Ioannidou et al., 2008; Ioannidou, et al., 2008;

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Park, et al., 2008; Tanoue, 2007]. Nevertheless, there is still a great need for reliable systematic studies of the independent effect of the type of material and commercially interesting reactions such as temperature, product distribution, heating rate and composition of biomass.

Pyrolysis is the thermal decomposition of complex organic matter to simple molecules. It is the first stage in any thermal treatment of biomass in which the absence of Oxygen with a temperature ranging between 200 to 700^{o}C [Saravana Sampath. and Babu, 2005]. The main component of any organic matter is cellulose. Cellulose is again the important constituent that contributes to maximum tar and volatile compounds. The pyrolysis behavior of any biomass is the sum of decomposition characteristics of cellulose, hemi-cellulose, lignin and their interactions. Cellulose is decomposed between temperature 325^{o}C and 400^{o}C, hemi cellulose is decomposed between 250^{o}C and 350^{o}C and lignin start at 200^{o}C continues till 700^{o}C [Besler and Williams, 1996]. Main products of pyrolysis process are char (actived carbon), liquid (tar or pyroligneous acid) and gas. The char can be used as feedstock for gasifier, combustion applications and used as actived carbon. Activated carbons are versatile adsorbents with wide range of applications. One of the largest uses of activated carbons is for water treatment. The carbons are added to remove compounds that effect taste odour of the water. Increasing in use of activated carbons is found also in industrial waste water and gas treatment due to the necessity of environmentally friendly processes and also for material recovery purposes [Zanzi et al., 2001]. The liquid appeared brownish dark with a strong acid smell. It can be used not only as a fuel for direct combustion by upgrading or added to petroleum products but also for several agricultural activities such as improves soil quality, eliminates pests and controls plant growth [FFTC Practical Technology, Rural life PT2005, 2005]. These liquid products contain an aqueous (pyroligneous acid or wood vinegar) and an oil phase (tar or pyrolytic oil). The obtained gas can be directly used for combustion. The amount and nature of end products of pyrolysis process depend on the main parameters that affect to the pyrolysis behavior such as operating temperature, heating rate, solid residence time, volatile residence time, particle size and the composition of the biomass feedstock [Raveendran et al., 1996; Sensoz, 2003].

Under the above mentions, the present study proposes the quantitative understanding of the thermal decomposition behavior of four types of woody biomass; Jatropha Curcas Linn, Acacia auriculaeformis, Eucalyptus camaldulensis and Pine wood. These biomasses are chosen as the renewable energy sources and pyrolyzed under different conditions in a fixed - bed reactor. The aim of this study is to investigate the influence of the pyrolysis temperature on the yields, composition and rates of formation of products in order to provide preliminary data for further investigation.

Materials and Methods

Raw materials

The examined materials in the present study, four ligno-cellulosic materials (woody biomass) i.e. Jatropha Curcas Linn, Acacia auriculaeformis and Eucalyptus camaldulensis were collected from Nongkhai province, Thailand and the Pine wood was collected from local sawmill in Tomsk region, Russia. The woody biomass samples are cut into small pieces in order to minimize heat and mass transport resistances in the boundary layer and within the particles [Parikh et al., 2002] then sun-dry to reduce the moisture content. Their size is 1-5 mm and less than 0.5 mm in thickness. Prior

to the experiments, the samples are oven-dried for 3 hours at 110°C. The proximate analysis is carried out to determine a mineral's thermal stability and it fraction of volatile components by monitoring the weight change at different desired temperatures. All experiments compose of three main different steps: drying, devolatilization in inert atmosphere and combustion in oxygen. The proximate analysis of fresh feed is determined according to American Society for Testing and Materials (ASTM) test methods [ASTM Standards (E872),1986; ASTM Standards (E871),1986; ASTM Standards (D1102),1986]. Table 1 shows the result of proximate and ultimate analysis of the woody biomass samples.

Table1 : Main characteristics of the solid woody biomass (Proximate and Ultimate analysis, % wt. on dry basis)

Samples	Jatropha Curcas Linn.	Acacia auriculaeformis	Eucalyptus camaldulensis	Pine wood
MC	11.48	9.89	13.00	13.76
VM	84.39	81.43	78.53	79.41
FC	12.37	17.36	19.10	19.11
Ash	3.23	1.20	2.37	1.47
C	46.80	47.2	48.1	47.3
H	6.53	3.76	5.27	5.38
O*	41.57	48.4	46.24	45.92
N	4.88	0.61	0.34	1.4
S	0.22	0.03	0.05	N.D.

Remark : * By difference, N.D. (Not Detected)

Experimental set up

A schematic diagram of the experimental apparatus for the fixed-bed pyrolysis unit is shown in Figure.1. This reactor is designed for atmospheric pyrolysis. The apparatus consists of a reactor, condenser and liquid collector, and helium source. The reactor of 40 mm in diameter and 145 mm in length was fabricated by using stainless steel with the heating circuit, which consists of various temperature controllers and time switches. It is heated externally by electric heater. The helium gas is supplied in order to replace the air in the reactor for keeping the inert atmosphere inside the reactor. The maximum loading capacity of reactor vessel is 20g of sample woody biomass. The condenser is fabricated in form of helical coiled tube; water at 10°C is used as coolant. The experiments

are performed at different pyrolysis temperatures (end-operating temperatures) ranging from 250 - 600°C at a constant heating rate of 50°C/min. The temperature within the reactor is measured by employing the K-type thermocouple. The retention time is fixed for 3 hours in order to allow the sample to go to through a complete pyrolysis process and then cool the reactor down to ambient temperature.

A fresh feed of 20 g is taken in the sample boat and then placed in the reactor. Before the experiment, the system is driven off air by allowing helium gas to flow through the system for 5 minutes with the flow rate of 2 liters/min and then helium gas supply is stopped. The feed is then heated up to desired temperature, which is controlled by the temperature controller system. During heating, the system is maintained at slightly above the atmospheric pressure. Experimental conditions carried out for different pyrolysis temperature and raw materials selected. The produced gas is collected in the water container. The volume of water is displaced to determine the gas volume. The liquid product is collected at the liquid collector point. The yields of the different obtained products are determined by weighing; the solid residue (char) and liquid collected and gas evolution by difference. Yields are expressed as a percent by weight of the raw materials as a function of the pyrolysis temperature. In order to test the reproducibility of the experiments, each temperature is tripled.

Conversion of Biomass

The conversion processes of biomass usually involve a reduction of the water content of the

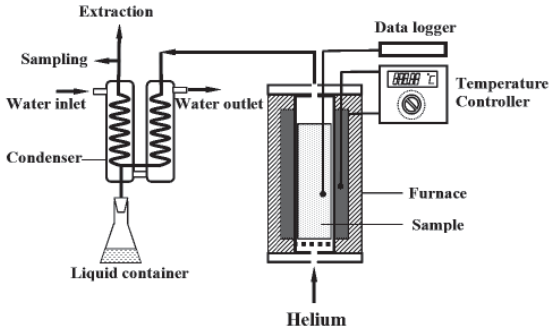

Fig.1 The schematic diagram of the experimental apparatus

materials. The results 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 may be either gas or liquid. Oxygen removing from the biomass in the form of carbon dioxide (and carbon monoxide) will result in products of 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.

Only charring takes place below 260°C, while depolymerization of chemical components generally predominates between 270°C and 400°C. Hemi-cellulose is readily converted into methanol and acetic acid at 200 - 280°C. At temperature range 200 - 500°C, Cellulose that has already undergone some thermal degradation decomposes at an increasing rate, which reaches a maximum at around 320°C, while

lignin decomposes only at the temperatures above 280°C, which is mainly formed as tar and char [Saravana Sampath and Babu., 2005; Peters and Bruch, 2003; Rajvanshi, 1986].

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 is hydrolysis); the rate and amount of destruction can be negligible up to 200°C.After the last traces of water, which requires the temperature about 140°C, are removed, four classes of products are produced by thermal decomposition of wood: 1) Non-condensable gases (CO, CO_2, H_2, CH_4); 2) Pyroligneous products (condensable, contain more than 50 % water); 3) Tar (moisture-free, condensable); 4) Char. Gas are evolved at the temperatures range between 200 - 450°C , which is a maximum at about 350 - 400°C. The rate of production of pyroligneous material passes through a maximum between 250°C and 400°C and virtually ceases at about 500°C. Tar is formed at about 300°C onwards

Results and Discussions

Figure. 2 shows the products of distribution of char, liquid and gas in relation to temperature for different samples. The decomposition of biomass sample just starts and liquid yield is low at the temperature of 250°C,. When the pyrolysis temperature is creased, the liquid yield is also increased up until it reached maximum at 450°C. At the temperature below 400°C, liquid yields are reduced owing to the coking reactions of oil via conversion of the liquid oil to solid products [Parikh et al., 2002; Williams and Ahmad, 1999; Williams and Horne, 1996]. In addition, decrease in liquid yields is observed because of incomplete pyrolysis. In the present study conditions, the maximum liquid yields is found at a temperature range 450 - 600°C with an average heating rate 50°C/min. There is a progressive increase in gas yield at temperature range from 300°C to 500°C.

An increase in gas yield together with a decrease in char yield are observed at temperature range about 550°C to 600°C may be owing to cracking of carbon (char) into gaseous fraction. The decrease in char yield with increasing temperature could either be due to great primary decomposition of the wood sample at higher temperatures or through secondary decomposition of the char residue. The secondary decomposition of the char at higher temperatures may also give non-condensable gaseous products, which would also contribute to increase in gas yield with increasing pyrolysis temperatures [Sukiran et al., 2009]. At temperature is higher than 550°C, there is an increasing in gas yield. At the study temperature conditions range of 250 - 600°C, the gas yield consists of Acacia (8% to 30 %), Eucalyptus (13% to 26.5%), Jatropha (18% to 33.5%) and Pine wood (10.5% to 27%), whereas the liquid yield of all species ranges from (12 % to 49 %).

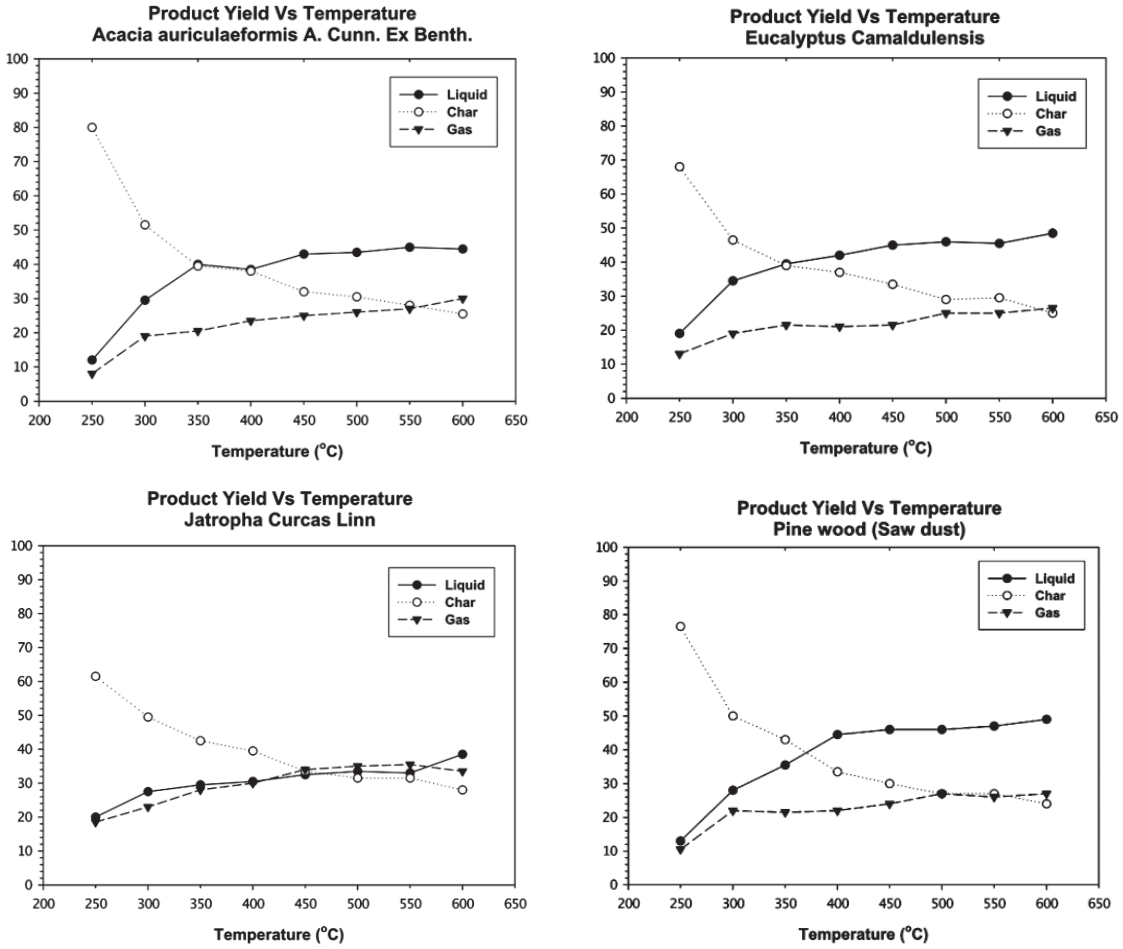

Fig. 2 Relation between the product yield and temperature for different biomass

At the lowest pyrolysis temperature of 250°C, decomposition is significant as char that is the major product. In the temperature range between 250°C to 350°C, there is a very high weight loss from the char, while in the temperature range 450°C to 600°C, the degree of weigh loss is reduced significantly for all species. The higher yield of carbonized material at 250°C, the product results may be limited by thermal decomposition of extractives and hemi-cellulose in wood at temperatures range between 200 to 260°C. Cellulose is thermally degraded at temperatures between 240 to 340°C and lignin starts at 280°C until 700°C [Saravana Sampath. and Babu, 2005]. The lignin is a main source of char yield in biomass fed under conventional pyrolysis conditions while the cellulose and hemi-cellulose are the main sources of volatiles matter. In the present study, the char yields of all species are reduced from 61.5 - 80 % wt. at 250°C to 24 - 28 % wt. at 600°C as resulting from increasing in pyrolysis temperature.

This decrease in the char yield with increasing temperature could be either due to greater primary decomposition of the wood at the higher temperatures or to secondary decomposition of char residue. Figure. 3 shows the comparison of temperature effect on individual product yield for four examined species. The composition of pyrolysis products also varies with temperature [Tanoue, 2007; Raveendran et al., 1996; Tsi et al., 2006; Tsi et al., 2007]. In the present study, the effect of temperature on the obtained solid product is considered. Among the properties characterized with char, the more significant product results

seem to be obtained as volatile matter and fixed carbon content. Whether the char can be regarded as quality product, it 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 future treatment in order to provide more convenient final products such as activated carbon and electrode carbon.

The variation of these three properties with the end-pyrolysis temperature can be deduced from Figure. 4. Char formation processes simultaneously with an intensive development of the volatile products.The percentage volatile matter in char decreases with increasing in pyrolysis temperature, while there is an increase in the percentage fixed carbon. In the initial wood sample, the volatile matter contents are 82.19, 78.48, 84.08, and 81.08 % for Acacia, Eucalyptus, Jatropha and Pine wood, respectively. The initial wood sample gives off 11.2 - 30.5% volatile matter, 55.38 - 61.16 % volatile matter and more than 64.42 % volatile matter of the initial content for all species at temperatures 250°C, 400°C and 500°C, respectively. Obviously, the major evolution is between 250 - 400°C, while 450°C onwards it becomes gradual. The fixed carbon content increases with temperature from 17.81 to 46.93 % for Acacia, 21.51 to 48.52 % for Eucalyptus, 15.91 to 31.01% for Jatropha and 18.92 to 47.63% for Pine wood in the studied temperature range of 250 - 600°C. It is remarkable that the volatile matter of Jatropha is a high significant because its main polymerize structure consists of higher amount of hemi-cellulose than the other types. Naturally, it has more loosely bound fibers.

At a temperature of 600°C, the char 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 portion of ash.

The results indicate that this pyrolyser can produce char suitable for activation. The surface areas may be improved with different methods of the activation. It is given that the pyrolysis process generates large quantities of CO_2 and heat. Furthermore, it is probable that either CO_2 method or steam activation could be used in an industrial scale integrated process.

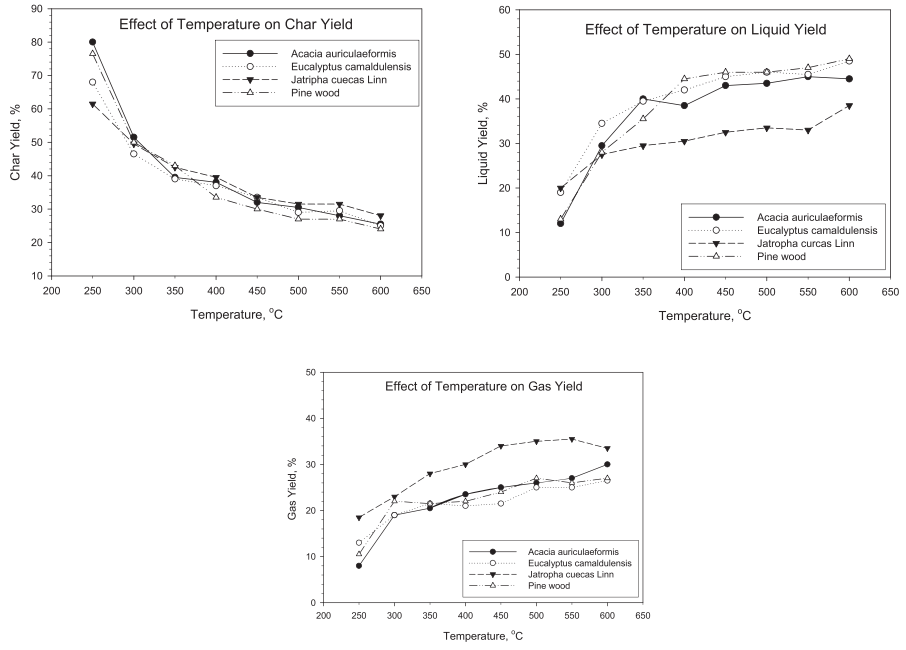

Fig.3 Effect of temperature on individual product yield

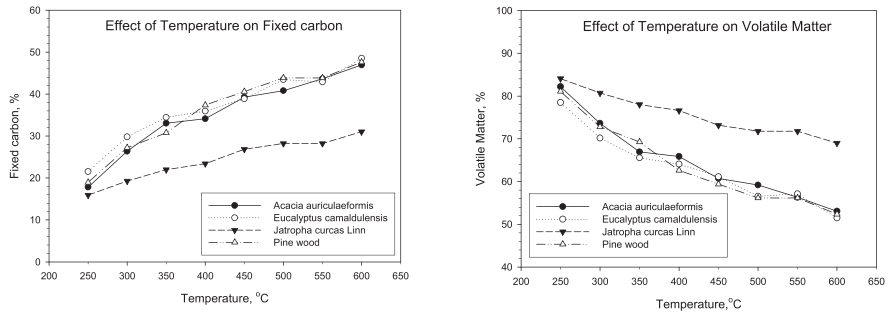

Fig.4 Effect of temperature on composition of char from different biomass

Conclusion

The results indicate 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 takes place between 250 and 450°C. Beyond 450°C, the rate of decomposition becomes gradually stable.

The percentage volatile matter in charcoal decreases with the increase in temperature, while there is an increase in the percentage fixed carbon. The increase is rather large as the final temperature increases from 250 - 400°C, but from 450 - 600°C the increase is gradual. This behavior is observed for all the wood species.

Moreover, the results show 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 a high porous active carbon of renewable energy sources as well as the use of pyrolysate for energytic 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.

Acknowledgements

The authors would like to thank RMUTI Thailand for providing the financial support for the research study.

Symbol	Meaning	Unit
MC	Moisture Content	wt %
VM	Volatile Matter	wt %
FC	Fixed Carbon	wt %
C	Carbon	wt %
H	Hydrogen	wt %
O	Oxygen	wt %
N	Nitrogen	wt %
S	Sulfur	wt %

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