

Effect of Temperature on Product Yield of Pyrolysis of Seven Selected Wood Species in South West Nigeria

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Abstract—

The effect of temperature variation on the product yield of seven selected woody biomass was investigated. The experiments were carried out in a 17.4 liter capacity batch electronically controlled pyrolysis reactor. It was found that char production was high at low temperature, and decreases with increase in temperature. The liquid yield increased significantly up to 500°C with a product yield of 51 wt%. The char yield decreased rapidly from 62 wt% (at temperature of 200°C) to 44 wt% (at temperature of 400°C). As operating temperature increases from 400°C to 600°C, the char yield decreased sharply from 44 wt% to 28 wt%, and gradually reduced to 20 wt% at 800°C. The gas (includes the loss of fine oil droplets) result showed an opposite trend of solid yield. It showed a progressive increase from 4 wt% (at temperature of 200°C) to 46 wt% (at temperature of 800°C). At an average reactor temperature of 500°C, average char yield was 39.14 %; liquor, 40.29 %; and gas; 20.57 % respectively.

Keywords— Woody biomass, pyrolysis reactor, temperature, char, liquor, batch.

I. INTRODUCTION

Pyrolysis man's oldest and newest thermochemical conversion process: old in the sense of pyrolysis for pine tar, pitch and charcoal fuels; old in the sense of wood destructive distillation processes used at the turn of the century for organic chemicals production; but also new in the sense of some of its promises, [1].

Pyrolysis has been defined as 'the incomplete thermal decomposition of biomass, generally in the production char, condensable liquids (tar oils and acids) and non-condensable gaseous products. In wood pyrolysis, the process is referred to as carbonization if the char is the principal product of interest or wood distillation if the primary product is the liquid. The process is called destructive distillation if the products of interest are the char and the liquid. Generally, it is a well-known method of extracting valuable products from feedstock, especially plant-based biomass,[2], [3], [4].

Pyrolysis (also known as carbonization, destructive distillation, dry distillation, or retorting) is the chemical decomposition induced in organic materials by heat in the absence of oxygen. In practice, it is not possible to achieve a completely oxygen-free atmosphere; pyrolytic systems are operated with less than stoichiometric quantities of oxygen. Because some oxygen will be present in any pyrolytic system, nominal oxidation does occur. If volatile or semi-volatile materials are present, thermal desorption (Changing from an adsorbed state on a surface to a gaseous or liquid state) will also occur. Pyrolysis processes produce an array of solid and liquid derivatives, and fuel gases depending on the process conditions and the organic material content of the feedstock, [5], [6].

Pyrolysis is thermal degradation either in the complete absence of oxidizing agent, or with such a limited supply that gasification does not occur to an appreciable extent or may be described as partial gasification. Relatively low temperatures are employed of 500 to 800 °C, compared to 800 to 1000 °C in gasification. Three products are usually produced: gas, pyrolysis oil and charcoal, the relative proportions of which depend very much on the pyrolysis method, the characteristics of the biomass and the reaction parameters. Fast or flash pyrolysis is used to maximize either gas or liquid products according to the temperature employed, [7].

Pyrolysis is the thermal decomposition of materials in the absence of oxygen or when significantly less oxygen is present than required for complete combustion. It is important to differentiate pyrolysis from gasification. Gasification decomposes biomass to syngas by carefully controlling the amount of oxygen present. Pyrolysis is difficult to precisely define, especially when applied to biomass. The older literature generally equates pyrolysis to carbonization, in which the principal product is a solid char. Today, the term pyrolysis often describes processes in which oils are preferred products. The time frame for pyrolysis is much faster for the latter process, [5]

The general changes that occur during pyrolysis are enumerated below,[8]; (1) Heat transfer from a heat source, to increase the temperature inside the fuel; (2) The initiation of primary pyrolysis reactions at this higher temperature releases volatiles and forms char; (3) The flow of hot volatiles toward cooler solids results in heat transfer between hot volatiles and cooler unpyrolyzed fuel; (4) Condensation of some of the volatiles in the cooler parts of the fuel, followed by secondary reactions, can produce tar; (5) Autocatalytic secondary pyrolysis reactions proceed while primary pyrolytic reactions simultaneously occur in competition; and (6) Further thermal decomposition, reforming, water gas shift reactions, radicals' recombination, and dehydrations can also occur, which are a function of the process's residence time/temperature/pressure profile.

A. Temperature Regimes of Wood Degradation

The products of pyrolysis depend upon temperature, pressure, residence time and heat losses. However, the following general remarks can be made concerning the temperature regimes and the products. Up to the temperature of

200°C only water is driven off. Between 200 to 280°C carbon dioxide, acetic acid and water are given off. The real pyrolysis, which takes place between 280 to 500°C, produces large quantities of tar and gases containing carbon dioxide. Besides light tars, some methyl alcohol is also formed. Between 500 to 700°C the gas production is small and contains hydrogen, [9]. Temperature significantly impacts pyrolysis product yield and composition. High temperatures promote gas production, while lower temperatures promote char and tar formation.

The products from different biomass feedstock are similar at a given temperature, although the gas, liquid, and char yields can be very different depending on the feedstock. Literature data, [1] indicated that gas yield and hydrogen content of the product gas increases with increasing temperature while the gas higher heating value (HHV) remains relatively constant. Increasing temperature also reduces char yield and volatile content.

According to [10], the thermal degradation above 100°C can be broken up into four temperature regimes:

(i) Between 100°C and 200°C, wood becomes dehydrated and generates water vapour and other non-combustible gases and liquids including CO₂, formic acid, acetic acid, and H₂O. With prolonged exposures at higher temperatures, wood can become charred. Exothermic oxidation reactions can occur because ambient air can diffuse into and react with the developing porous char residue.

(ii) From 200 °C to 300 °C, some wood components begin to undergo significant pyrolysis, and in addition to the gases and liquids listed previously, significant amounts of CO and high-boiling-point tar are given off. The hemicelluloses and lignin components are pyrolyzed in the ranges 200-300°C and 225-450 °C, respectively. Much of the acetic acid liberated from wood pyrolysis is attributed to deactivation of hemicellulose. Dehydration reactions around 200°C are primarily responsible for pyrolysis of hemicellulose and lignin and results in a high char yield for wood. Although cellulose remains mostly unpyrolyzed, its thermal degradation can be accelerated in the presence of water, acids, and oxygen. As the temperature increases, the degree of polymerization of cellulose decreases further, free radicals appear, and carbonyl, carboxyl, and hydro-peroxide groups are formed. They assumed tar under-goes cracking to lighter gases and re-polymerization to char while streaming through the hot charred residue. Overall pyrolysis reactions are endothermic due to decreasing dehydration and increasing CO formation from porous char reactions with H₂O and CO₂ with increasing temperature. During this “low-temperature pathway” of pyrolysis, exothermic reactions of ex-posed char and volatiles with atmospheric oxygen are manifested as glowing combustion.

(iii) The third temperature regime is from 300 °C to 450°C because of the vigorous production of flammable volatiles. This begins with significant depolymerization of cellulose in the range 300-350°C. Also, around 300°C aliphatic side chains start splitting off from aromatic rings in the lignin. Finally, the carbon-carbon linkage between lignin structural units is cleaved from 370°C to 400°C. The degradation reaction of lignin is an exothermic reaction, with peaks occurring between 225°C and 450°C. The temperatures and amplitudes of these peaks depend on whether samples were pyrolyzed under nitrogen or air. All wood components end their volatile emissions at around 450°C. The presence of minerals and moisture within the wood tends to smear the separate pyrolysis processes of the major wood components. In this “high-temperature pathway,” pyrolysis of wood results in overall low char residues of around 25% or less of original dry weight. Many fire retardants work by shifting wood degradation to the “low-temperature pathway,” which reduces volatiles available for flaming combustion.

(iv) At > 450°C, the remaining wood residue is char, which undergoes further degradation by being oxidized to CO₂, CO, and H₂O. This is referred to as afterglow.

The aim of this paper therefore is to study the effect of temperature variation on the product yield of seven selected woody biomass from South West Nigeria.

II. MATERIALS AND METHOD

Biomass from seven tropical wood species were retrieved from sawmills across Akure, Nigeria. The wood species were: Obeche (*Triplochiton scleroxylon*); Iroko (*Melicia excelsa*); Danta (*Nesogordonia papaverifera*); Mahogany (*Khaya ivorensis*); Omo (*Cordia platythyrsa*); Mansonia (*Mansonia altissima*); and Afara (*Terminalia superba*). The actual volume converted to planks and the volumes of wastes (sawdust and slabs) were determined from the volume of wood processed in the sawmills.

The woods collected were prepared into 50 x 20 x 20 mm sizes and oven dried to 18% Moisture Content at 100°C for 24 hours per batch. The dried samples were kept in polythene bags to prevent them from excessive humidity, [11].

A thermochemical plant of 17.4 litre capacity was developed. The plant is made up of the Furnace; the Thermal Reactor; The Electronic Control Unit; and the Condensing Unit. It can withstand a temperature of 1,200°C and a pressure of 2.3 MN/m², [7], [12].

The reactor was heated to maintain the inert atmosphere in the reactor and also to drive the pyrolyzed vapour product to the condensing unit. A batch sample of 1000 g was loaded in the reactor vessel for each temperature level.

The temperature range for the reactor was 200 – 800°C. The retention time was left open till it cools down in order to allow the sample to go through a complete pyrolysis process. The liquid product was collected at the liquid collector point. The effect of temperature was analysed by increasing the temperature and fixing the particle size to determine the optimum condition of product yield. The condensable products (liquid) were collected in a series of traps maintained at very low temperature, [7].

III. RESULTS AND DISCUSSION

Results of the products of pyrolysis by weight at different reactor temperatures are detailed in Tables I and II, and presented graphically in Fig. 1.

Table I: Product Yield of Char, Oil and Gas by Weight at Varying Temperatures

Reactor Temperature (°C)	Initial Weight of Wood Sample (g)	Char (g)	Oil (g)	Gas (g)	Volume of Gas (m ³)
200	1000.00	620	340	40	0.06
300	1000.00	560	380	60	0.08
400	1000.00	440	470	90	0.13
500	1000.00	380	490	130	0.18
600	1000.00	280	440	280	0.39
700	1000.00	260	360	380	0.53
800	1000.00	200	340	460	0.64
Average	1000.00	391.43	402.86	205.71	0.29

Table II: Percentage Product Yield of Char, Oil and Gas at Varying Temperatures

Reactor Temperature (°C)	Furnace Temperature (°C)	Char %	Oil %	Gas %
200	300	62	34	4
300	400	56	38	6
400	550	44	47	9
500	650	38	51	13
600	800	28	44	28
700	890	26	36	38
800	1000	20	34	46

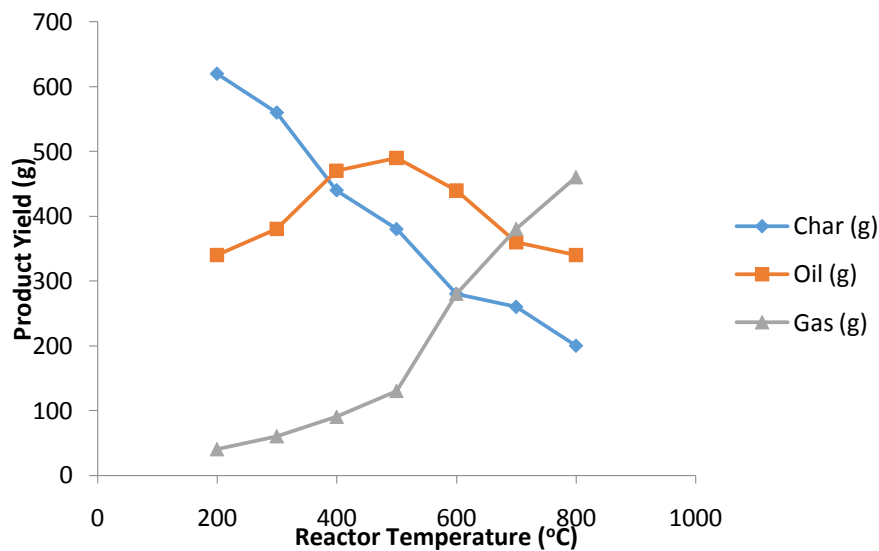


Fig 1: Product Yield of Pyrolysis by Weight

1. Char

The char yields during the pyrolysis of the wood samples are detailed in Table III and graphically presented in Fig. 2.

Table III: Char Yields during Pyrolysis

Experiment No	Reactor Temperature (°C)	Initial Weight of Wood Sample (g)	Weight of Char (g)	Percentage of Char (%)
1	200	1000	620.00	62.00
2	300	1000	560.00	56.00
3	400	1000	440.00	44.00
4	500	1000	380.00	38.00
5	600	1000	280.00	28.00
6	700	1000	260.00	26.00
7	800	1000	200.00	20.00
Average	500	1000	391.43	39.14

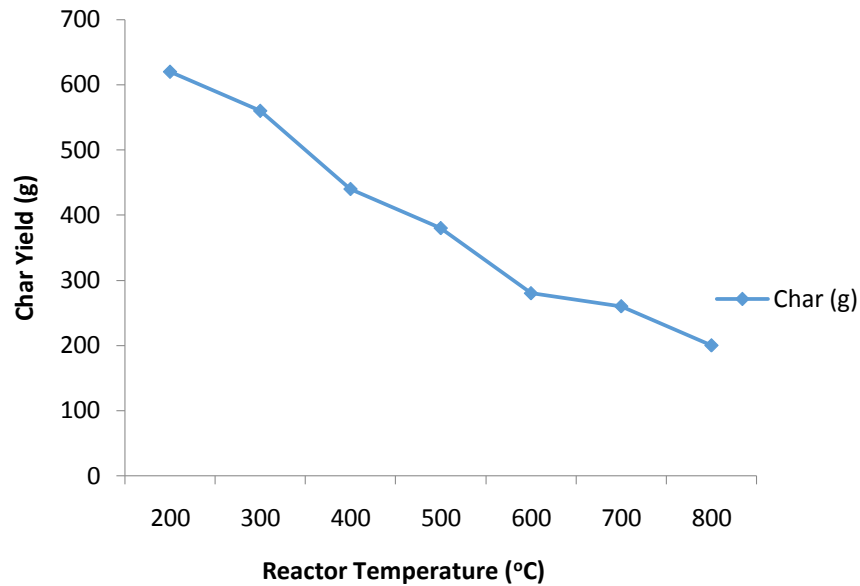


Fig. 2: Char Yield at Varying Temperatures by Weight

The char had a highest yield of 62 % at a pyrolysing temperature of 200 °C. This was expected as little or no disintegration took place at this temperature. It decreased to 56 % at 300 °C, and kept decreasing as the pyrolysing temperature increases. The average char yield was 39.14 % at an average pyrolysing temperature of 500 °C. These results are in agreement with the findings of [13], that when wood is pyrolysed, the char yield decreases as the pyrolysing temperature increases.



Plate 1: a) Feedstock before Charging; b) Produced Char

2. Liquor or Bio-Oil Product

The oil (liquor) yields during pyrolysis are detailed in Table 4, and Fig. 3.

Table IV: Oil Yields during Pyrolysis

Experiment No	Reactor Temperature (°C)	Initial Weight of Wood Sample (g)	Weight of Oil (g)	Percentage of Oil (%)
1	200	1000	340.00	34.00
2	300	1000	380.00	38.00
3	400	1000	470.00	47.00
4	500	1000	490.00	49.00
5	600	1000	440.00	44.00
6	700	1000	360.00	36.00
7	800	1000	340.00	34.00
Average	500	1000	402.86	40.29

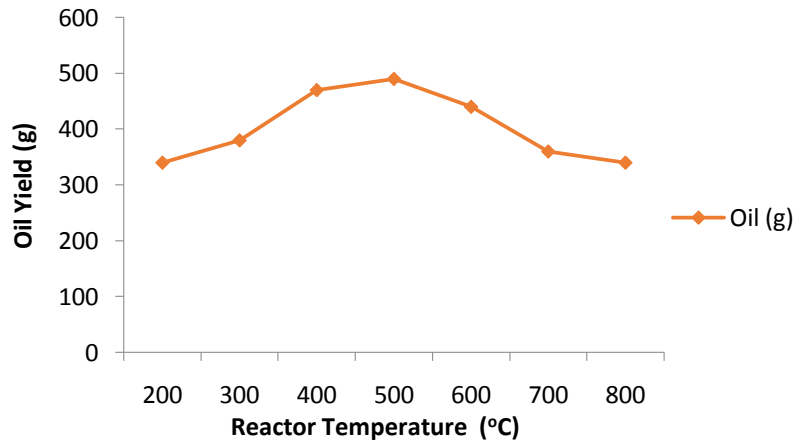


Fig. 3: Oil Yield at Varying Temperatures by Weight

The oil (liquor) yield started increasing with increasing pyrolysing temperature. It increased from 34 % at a reactor temperature of 200 °C. It increased further with increasing pyrolysing temperature up to 49 % at a temperature of 500 °C.

Above this temperature, the liquor yield started to decrease gradually as reactor temperature increased. The average oil (liquor) yield was 40.29 % at an average reactor temperature of 500°C. This result agreed with the result of [4], that liquor yield tended to decrease as pyrolysing temperature increased.

Plates 2 show sample of the oil (liquor) yield collected



Plate 2: The Liquor Product Sample collected

3. Gas

The gas yields during the pyrolysis of the wood samples are detailed in Table 5 and graphically presented in Fig. 4.

Table V: Gas Yields during Pyrolysis

Experiment No	Reactor Temperature (°C)	Initial Weight of Wood Sample (g)	Weight of Gas (g)	Percentage of Gas (%)
1	200	1000	40.00	4.00
2	300	1000	60.00	6.00
3	400	1000	90.00	9.00
4	500	1000	130.00	13.00
5	600	1000	280.00	28.00
6	700	1000	380.00	38.00
7	800	1000	460.00	46.00
Average	500	1000	205.71	20.57

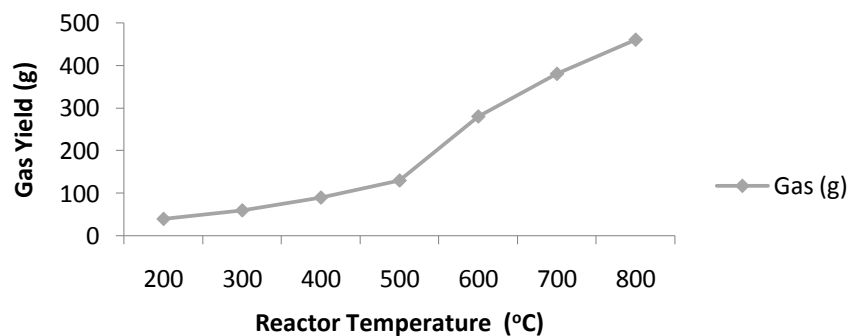


Fig. 4: Gas Yield at Varying Temperatures by Weight

It is seen from the results that the volume of gas produced tended to increase as the pyrolysing temperature increases. At 200 °C, the gas yield was very low. This was expected as the heating at this stage would still be used mainly to reduce the moisture content. The yield was 6 % at 300 °C, 9 % at 400 °C, and the gas yield kept increasing as reactor temperature increases up to 48 % at 800 °C. The average gas yield obtained was 20.57 % at an average pyrolysing temperature of 500 °C. This agrees with the finding of [13], that when biomass is subjected to pyrolysis, the gas produced tended to increase as the pyrolysing temperature increases.

IV. CONCLUSION

The effect of temperature variation on the product yield of pyrolysis was studied. It was seen that bio-oil started to produce at a reactor temperature of 200°C, and furnace temperature of 300°C. This is because at 200°C and below the heat was not high enough for a complete pyrolysis to take place thus yielding less liquid product and very low gas quantity. As the operating temperature increases, the liquid yield increased significantly up to 500°C at a product yield of 51 wt%. The solid (Char) yield decreased rapidly from 62 wt% (at temperature of 200°C) to 44 wt% (at temperature of 400°C). As operating temperature increases from 400°C to 600°C, the char yield decreased sharply from 44 wt% to 28 wt%, and gradually reduced to 20 wt% at 800°C.

The gas (includes the loss of fine oil droplets) result showed an opposite trend of solid yield. It showed a progressive increase from 4 wt% (at temperature of 200°C) to 46 wt% (at temperature of 800°C).

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