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Effect of Temperature on Products Compositions of Beech Wood Pyrolysis

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Abstract
This study investigated the effect of temperature on compositions of gaseous and liquid products of beech wood pyrolysis through model development and simulation using Aspen Plus simulation package. The model was developed based on pyrolysis product yield, proximate and ultimate analysis of the wood specie. In the model development, RYield which is a non-stoichiometric reactor was used to represent pyrolysis reactor which decomposes the wood into various conventional compounds. The model was simulated to give the components compositions in both gaseous and liquid products. The model was first simulated at pyrolysis temperature of 450 °C, particle size ranges of 1.6-2.0 mm at a pressure of 1 atmosphere, and then 5 simulation runs were carried by varying the temperature. Effect of pyrolysis temperature on compositions of liquid and gaseous products was also studied. The results show that production of methanol increases with temperature but decreases at temperatures beyond 550 °C. Carbon dioxide yield decreases with increase in temperature while that of carbon monoxide and methane get higher.
Keywords: Pyrolysis, Beech Wood, RYIELD, Aspen Plus, Composition.

1.0 Introduction

Pyrolysis is a process which thermally breaks down higher molecular carbonaceous compound to produce lower molecular compounds in an oxygen-devoid environment at considerably high temperature. The high temperature is needed for the disintegration of the feedstock molecules into smaller molecular compounds. The products of pyrolysis are condensable gases known as bio-oil or pyrolytic oil, bio-char and non-condensable gases (Mohammed *et al.*, 2015). A carbonaceous material disintegrates into vapor and bio-char on application of heat (Gulzad, 2011). The vapor consists of condensable gases that transform into liquid (bio-oil) after condensation while the non-condensable are collected or vented as gases. High generation of biomass and its potential in production of bio-oil makes it a promising source of renewable energy (Hossain and Islam, 2014).
Wood is an important forest product and residue. About 11.3% of Nigerian total land is made up of forests which are classified under riparian forest, savanna woodland forest, montane forest, lowland rain forest, mangrove forest and freshwater swamp forest found in twenty-eight (28) states of the country (Nigeria) (Simonyan and Fasina, 2013). Forest provides renewable source of wood and residue due to its ability to replenish itself. Wood is used as raw solid fuel in form of fire wood and feedstock for thermochemical processing into various kinds of products.

Modeling and Simulation of pyrolysis process is gaining attention because of the growing interest in pyrolysis of forest residues and agricultural waste for production of liquid and gaseous chemicals.

Temperature is one of the key factors in pyrolysis. It plays significant role in determining product yield in pyrolysis. Selvarajoo and Hanson, (2014) studied the effect of temperature together with heating rate and holding time on bio-char yield from Pyrolysis of Pineapple Peel. Pyrolysis experiments were conducted at temperatures ranging from 300 to 700 ^{0}C. Abdul Rahman *et al*., (2014) studied the effect of temperature on the characterization of pyrolysis products from oil palm fronds and reported increase in yield of gases. Distribution of pyrolysis yield at different temperatures was studied to find the optimum temperature for bio-char yield. Natarajan and Ganapathy (2009) studied the effect of temperature on products yield from pyrolysis of rice husk in a fixed bed reactor and recorded decline in the yield of bio-char with increase in temperature. Mohammed *et al*., (2014) carried out pyrolysis of castor shell to produce bio-oil. They studied the effect of temperature on the products yields by conducting the pyrolysis under varying temperatures while maintaining constant particle size and heating rate respectively and found out that bi-oil yield decreased with increase in temperature.

Temperature effect on yields of liquid, gas and solid products of biomass pyrolysis was studied extensively but no literature to the best of knowledge that reported the effect of temperature on the products compositions of beech wood pyrolysis. The objective of this study is to investigate the effect of temperature on the products compositions of beech wood pyrolysis.

2.0 Materials and Method

Beech wood composition obtained from proximate and ultimate analysis, presented in Table 1 (Rabaçal *et al*., 2014) was used in this work. The components of the product stream are substances on the right hand side of equation 1. Development of the process model was carried out using Aspen Plus Software, Version 8.4. Aspen Plus has no in-built pyrolysis reactor, so the reactor was modelled with RYield which is a non-stoichiometric reactor based on known yield distribution decomposed the wood into various products.

Table 1: Beech Wood Composition

Ultimate analysis(%wt)		**Proximate analysis (% wt)**	
Carbon	49.2	Volatile matter	85.3
Hydrogen	6	Fixed carbon	14.3
Oxygen	44.1	Moisture	0
Nitrogen	0.5	Ash	0.4
Sulphur	0.2		

Source: Rabaçal *et al*., 2014

$$Wood \xrightarrow[heat]{} Char\ (carbon)_{solid} + (C_6H_6, CH_3OH, CH_3COOH, \dots)_{liquid} + (CO_2, CO, CH_4, C_2H_6, \dots)_{gas} \qquad 1$$

Model Assumptions

- Steady state operation was considered
- The temperature in each block was considered uniform with negligible heat losses
- The wood chips are of variable particle sizes and spherical in shape
- The char is virtually made up of carbon

The model represents the decomposition of beech wood into various products as depicted in equation 1. Development of the process model was carried out using Aspen Plus Software, Version 8.4. Beech wood does not exist in the software's library, so it was defined hypothetically using its proximate and ultimate analysis, presented in Table 1 while the rest of the components were defined as conventional compounds from the software's library. In choosing the property package, ideal equation of state was adopted due to high temperatures involved in the process. RYield was used to represents the pyrolysis reactor (PYRO-RE) which allows the decomposition of non-conventional solid into conventional material. RYield is a non-stoichiometric reactor based on known yield distribution, hence suitable for the representation of pyrolysis which involves non-stoichiometric reactions. Table 2 presented the operating parameters of the heart of the process, which was pyrolysis reactor (PYRO-RE). Pyrolysis product separator was represented by CYCLONE to separate the pyrolysis product from the reactor into volatiles and char. The choice of cyclone for the task reflected recommendation of the software's help. Cooler was used to represents CONDENSER which quenches the volatiles into liquid (bio-oil) and non-condensable gases. The complete pyrolysis model built in the simulation environment is depicted in Figure 1.

Table 2: PYRO-RE Inputs

Operating Conditions	
Feed flow rate	10 kg/h.
Feed particle size	1.6-2.0 mm
Pyrolysis temperature	450 ^{o}C
Pyrolysis Pressure	1 atm
Nitrogen gas flow rate	0.2 kg/min

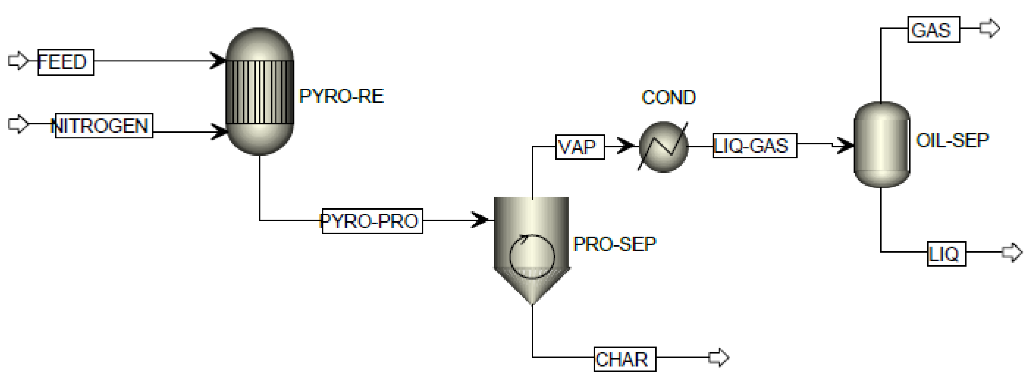

Fig. 1: Flowsheet of the Beech Wood Pyrolysis

3.0 Results and Discussion

The results obtained from the model simulation give the compositions of the products in both gaseous and liquid products. The effects of pyrolysis temperature on the products compositions were discussed in section 3.1.

3.1 Effect of pyrolysis temperature on products compositions

Temperature is one of the key factors affecting product distribution in pyrolysis of biomass. To study the effect of pyrolysis temperature, simulations were performed by varying temperatures from 400 to 600 ^oC. Distribution of components by percentage weight in the gaseous stream at different temperatures was depicted in Figure 2. Most notable species of gases from beech wood pyrolysis are CO_2, CO and methane. The results show that CO_2 decreases with temperature increase. Yield of CO decreased slightly as temperature increased from 400-450 ^oC and continue to increase with further increase in temperature. This might be as the result of decomposition of CO_2 to form more CO (Prins and Jensen, 2006). These led to the depletion of the CO_2 as it was formed. The variation in CO_2 and CO composition with temperature in this model is also in agreement with that presented by Paviet *et al* (2009) in their study of temperature effect on biomass thermochemical treatment. Methane which was the third most abundant component in the gas stream increased with increased in temperature and this is interesting because of its usefulness as source of fuel.

Bio-oil which formed the liquid stream contained many species. Most of the species compositions decrease with temperature increase due to instability which subsequently led to further breakdown into lighter gaseous components. Figure 3 shows the influence of temperature on some major liquid products.

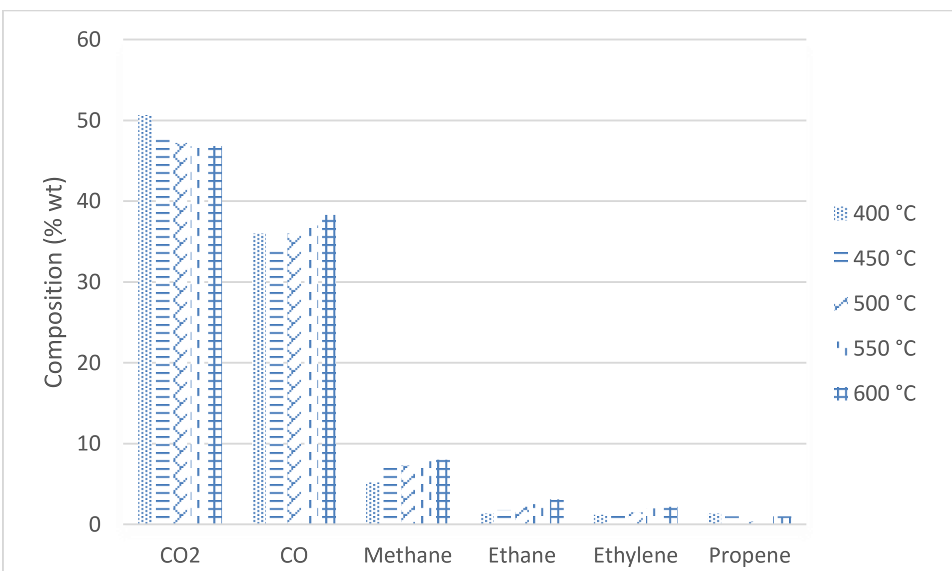

Fig. 2: Variation of products composition with temperatures

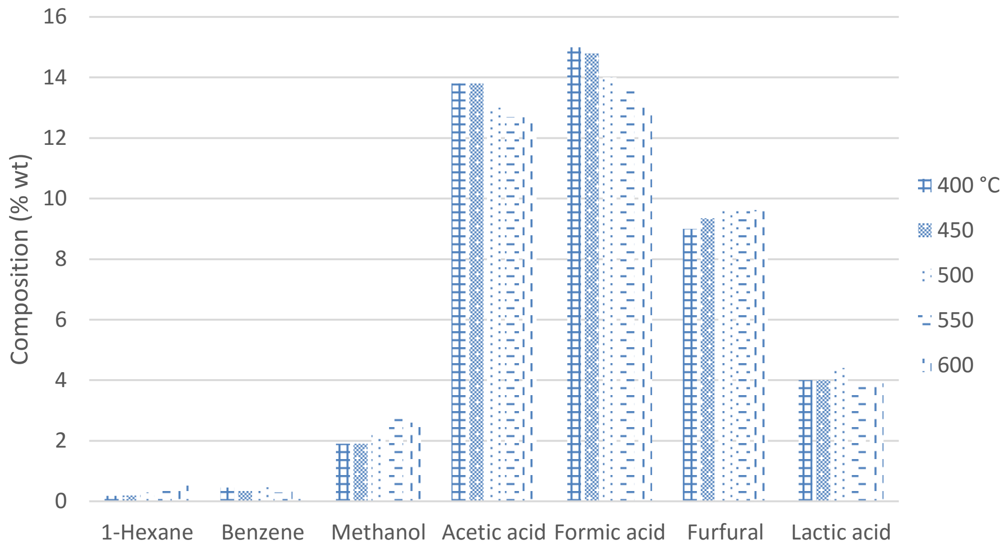

Fig. 3: Plot of bio-oil compositions at different temperatures

Bio-oil is usually acidic due to high composition in acids content. Acetic acid composition was not affected by temperature increase from 400 to 450 °C, the effect becomes more pronounced when the temperature reached 500 °C. Formic acid followed the same trend but sharp decrease in composition with temperature increased from 550 °C to 600 °C was recorded as compared to that of acetic acid. Temperature increase shows significant reduction in the gross compositions of acetic, formic and lactic acids respectively. This might have been resulted from decarboxylation of acids groups present in wood to form CO_2 at high temperatures. This led to increase in CO due to reaction of CO_2, steam and porous char. Furfural was the third most considerable components after acetic acid, formic acid and lactic acid in terms of composition. Temperature increase was accompanied by slight increase in furfural formation up till 500 °C before it started decreasing. High composition of the furfural was achieved at 500 °C, beyond which its production was not favored. Further temperature increase did not favor the production of the product.

Temperature shows no significant change in the composition of methanol as with benzene which was in trace amount. 1-Hexene composition was not affected much with temperature change. Production of methanol composition increases with temperature increase up to 550 °C. At higher temperature of 550 °C, methanol composition dropped. Benzene composition decreases with increasing pyrolysis temperatures.
The decrease in the overall bio-oil contents at higher temperatures may be emanated from secondary reaction which cracked some of the liquid components into non-condensable gases.

4.0 Conclusion

Model of pyrolysis process of beech wood was developed and simulated. Effects of pyrolysis conditions on products compositions were studied. It was found that pyrolysis temperature plays significant impact in determining products compositions. Carbon dioxide and carbon monoxide formed the highest part of the gaseous product followed by methane, ethane and ethylene. Temperature range of 450-600 °C suggested good yield of methane (6-9 %) and ethane (2-5 %) respectively. The liquid fuel yields were also favoured around this temperature range but the fuel tends to be acidic due to higher concentration of formic, acetic and lactic acids. However, at higher temperatures of 500 to 600 °C the acidic groups undergo secondary reactions to form more CO_2 which breaks into CO by secondary reaction as well.

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