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Research Article

An In Silico Temperature Sensitivity Study of the Pyrolysis of Beech, Ailanthus and Spruce

Joshua O. Ighalo [1]*, Adewale George Adeniyi [1]**

[1] Department of Chemical Engineering, Faculty of Engineering and Technology, University of Ilorin, Ilorin, P. M. B. 1515, NIGERIA
***Corresponding Author:** oshea.ighalo@yahoo.com
****Corresponding Author:** adeniyi.ag@unilorin.edu.ng

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ABSTRACT

In the current investigation, a temperature sensitivity analysis of hard and softwood pyrolysis was conducted on an *in silico* platform. The selected samples were beech (hardwood), ailanthus (soft hardwood) and spruce (softwood). Upon the successful development of the model on ASPEN Plus v8.8, the results of the model prediction showed that the yield of bio-oil reduced with a rise in process temperature. Beech had the highest bio-oil yield of the feedstock investigated. At 350°C, oil yield was 36.72%, 35.13% and 32.89% for beech, ailanthus and spruce respectively. The syn-gas yield was 39.99%, 38.25% and 35.82% and bio-char yield was 45.44%, 47.58% and 50.77% for beech, ailanthus and spruce respectively (at 650°C). For the entirety of the temperature range studied, a gentle fall in char yield was observed for all feedstock type (though more significant at temperatures above 500°C). The model also predicted the yield of volatiles (bio-oil and syn-gas) to be higher for the hard and soft hardwood than for the softwood and this was vice versa for the char yield.

Keywords: ASPEN Plus, Pyrolysis, Beech, Spruce, Ailanthus

INTRODUCTION

In a bid to combat climate change and foster energy and environmental sustainability, research interests in forest residues as a renewable energy source is on the rise (Abdelouahed *et al.,* 2012; Hosseinpour *et al.,* 2018). The utilisation of fossil fuels has resulted in two-thirds of the global anthropogenic CO_2 emissions (Mohan *et al.,* 2006) while the use of bio-fuels has significantly decreased the emission of green-house gases (Sharma *et al.,* 2015). Many thermochemical processes can be used to recover energy from both natural and derived biomass amongst which are pyrolysis (Arregi *et al.,* 2016; Kan *et al.,* 2016), gasification (Block *et al.,* 2018; Gu *et al.,* 2018), steam reforming (Santamaria *et al.,* 2018; Valle *et al.,* 2018), combustion (Emadi *et al.,* 2017; Gani and Naruse, 2007), hydrogenation and liquefaction (Goyal *et al.,* 2008). Pyrolysis is considered as a popular and important technique for the thermochemical conversion of biomass (Adeniyi and Ighalo, 2020). Several research efforts have been channelled towards different aspects of the pyrolysis of wood.

Process simulation are important because they can be used to study chemical processes on *in silico* (computer-based) (Dabiri Atashbeyk *et al.,* 2018; Moradi *et al.,* 2014) and mathematical (Khadem-Hamedani *et al.,* 2015; Torabi *et al.,* 2016) platforms. The modelling of thermochemical conversion processes can be used to achieve process optimisation (Darvishi *et al.,* 2016). Several simulation models have been prepared for soft and hardwood pyrolysis but none has taken the approach used in the current paper whilst considering the biomass samples in question (Di Blasi, 2008; Sinha *et al.,* 2000).

Onarheim *et al.* (2014) simulated the fast pyrolysis of pinewood on ASPEN (Advanced System for Process Engineering) Plus. Peters *et al.* (2015) conducted a simulation and life cycle assessment of the fast pyrolysis of poplar wood also ASPEN Plus. Peters *et al.* (2013) prepared a predictive model of pinewood on ASPEN Plus using a kinetic approach. Biomass has three major polymeric constituents which are lignin, hemicellulose and cellulose (Qu *et al.,* 2011). These constituents possess very different thermal behaviours (Asmadi *et al.,* 2011; Collard and Blin, 2014). The nature (in terms of ratio) of the composition of these building-blocks in the wood feedstock will influence their overall behaviour in the pyrolytic system and the product distribution and yield.

Using a variety of approaches that takes into cognisance this basis, this research team have examined the pyrolysis of banana residues (Adeniyi *et al.,* 2019c; Ighalo and Adeniyi, 2019), sugarcane bagasse (Adeniyi *et al.,* 2019a) and rice husk (Adeniyi *et al.,* 2019b, 2019e). Within the scope of the authors' exhaustive search, an *in silico* study for the pyrolysis of Beech, Ailanthus and Spruce are unreported except for the recent paper by the research group (Adeniyi and Ighalo, 2019a). This is an important novelty of this paper. The study by Adeniyi and Ighalo (2019a) observed an optimum bio-oil yield of 62.8% for beech wood, 58.3% for Ailanthus

Table 1. Composition Analysis of Beech, Ailanthus and Spruce wood samples (Adeniyi and Ighalo, 2019a; Demirbaş, 1997)

	Beech wood	Ailanthus wood	Spruce wood
Proximate analysis (wt%)			
Fixed Carbon	24.6	24.8	28.3
Volatile Matter	74	73.5	70.2
Ash	0.4	1.7	1.5
Moisture	7.4	8.1	7.6
Ultimate/Elemental analysis (wt% moisture-free)			
Carbon	49.5	49.5	51.9
Hydrogen	6.2	6.2	6.1
Sulphur	-	-	-
Oxygen	41.2	41	40.9
Nitrogen	0.4	0.3	0.3
Ash	1.4	1.7	1.5
Chemical analysis (wt%)			
Cellulose	45.8	46.7	50.8
Hemicelluloses	31.8	26.6	21.2
Lignin	21.9	26.2	27.5
Ash	0.4	0.5	0.5

and 54.2% for spruce wood. However, the temperature sensitivity on the product distribution was not investigated. This is an important aspect of pyrolysis investigation as it determines the theoretical optimum ahead of experimental studies. The distinctive novelty of this paper is to determine the theoretical temperature optimum for the pyrolysis of beech, ailanthus and spruce.

As a sequel to that investigation, this study utilised the validated ASPEN Plus model of Adeniyi *et al.* (2019e) to evaluate the temperature sensitivity of the three biomass feedstock. The samples selected were beech (hardwood), ailanthus (soft hardwood) and spruce (softwood). A key aspect of process systems engineering is investigating the effects of process variables on chemical process systems in both the real and *in silico* domains (Adeniyi and Ighalo, 2020) and this study helps in fulfilling part of this objective. Furthermore, this study is important as it can help gain true insight to the potentials of the feedstock for the production of bio-oil via the pyrolysis thermochemical conversion process free of extraneous factors and it comes at a time when research interest in such renewable energy technologies is on the rise. The reason for the choice of feedstock that is Beech wood is hardwood; Ailanthus wood is a soft hardwood while spruce is a softwood. This gives a good representative for each wood type.

METHODOLOGY

Much details of the underlying thermodynamics theories, simulation component list and accompanying are process integration and description steps are exactly same as discussed elsewhere (Adeniyi *et al.,* 2019e). However, the information on the proximate and ultimate analysis of the biomass is needed to model the feedstock in the simulation. These are presented in **Table 1**. PR-BM (known as Peng-Robinson with Boston-Mathias alpha function equation of state) was implemented as the global calculation method for the process simulation. The method is accurate and is an improvement of the Peng-Robinson equation because there is an alpha function. The alpha function is a temperature-dependent parameter that improves the correlation for the vapour pressure of pure components at very high temperatures. It is suitable for pyrolysis because the process involves relatively high temperatures. It and has been utilised in previous studies (Adeniyi *et al.,* 2019c; Ighalo and Adeniyi, 2020) where pyrolysis simulation was done on ASPEN plus. The overall component list consisted of acetic acid, ethylene glycol, ethanol, phenol, water, propanol, acetaldehyde, acetone, formaldehyde, propionic acid, xylan, methyl acetate, pyrrole, ethyl formate, carbon graphite, propionic acid, formic acid, methanol, hydrogen sulphide, carbon monoxide, methane, ethane and hydrogen and silicon oxide as listed in Adeniyi *et al.* (2019e).

The model on ASPEN Plus v8.8 can be described as a sequential-modular one. The concept of sequencing means that the order of performance of a task is designated in such a way as to assure the best possible use of available inputs (Licker, 2003). It is sequential in the sense that the output values of a module serve as the input values to the next module in the sequence (a block-by-block computation approach). The process flow diagram utilised in a previous study was implemented (Adeniyi *et al.,* 2019e). This is shown in **Figure 1**. The current simulation is one that runs based on the minimisation of Gibbs free energy thermodynamic calculation method (Adeniyi and Ighalo, 2019b; Adeniyi *et al.,* 2019f). The results obtained are discussed in the foregoing section. The model takes into cognisance the differences in the in cellulose, hemicellulose and lignin content of the biomass and the approach is described in Adeniyi *et al.* (2019e). Furthermore, several assumptions were implemented in the process simulation. the particle sizes of the feedstock were not considered in the simulation. All the moisture content of the biomass feedstock was considered as either the water content in the liquid product or as water vapour traces in the initially evolved gaseous product. The char was considered to be composed of a solid stream alone. The process flow sheet and simulation assumptions are the same as those discussed elsewhere (Adeniyi *et al.,* 2019e). The temperature range selected for the study was between 350°C and 650°C because this is the region of the disintegration of biomass constituents (Collard and Blin, 2014).

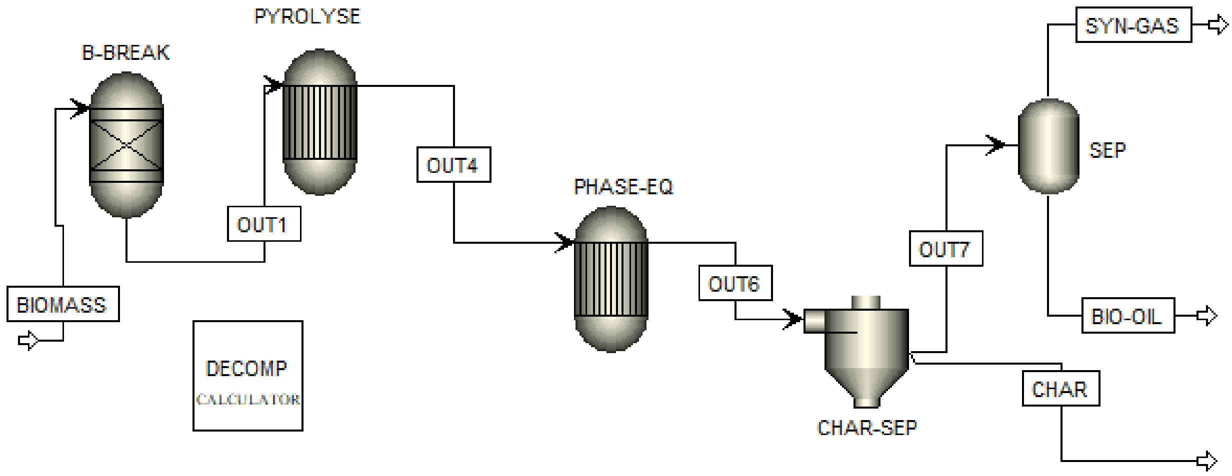

Figure 1. Process flow diagram for the pyrolysis simulation (Adeniyi *et al.,* 2019e)

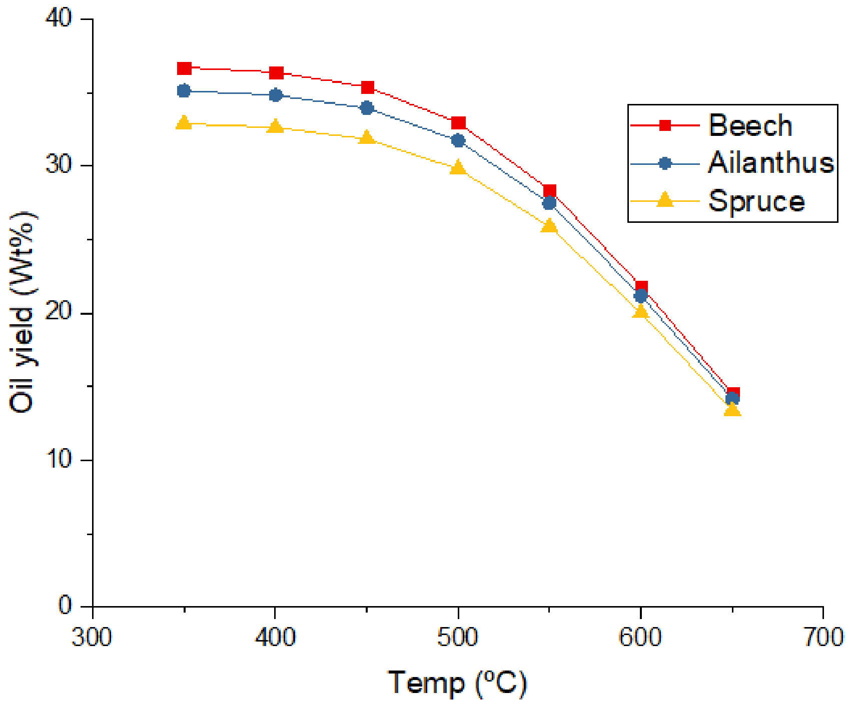

Figure 2. Temperature sensitivity of wood pyrolysis oil yield

RESULTS AND DISCUSSION

The simulation was successfully run on ASPEN Plus v8.8 and there were no errors in computation. This informs that the process integration was done accurately. The temperature sensitivity of different product species was examined. Beech wood is hardwood; Ailanthus wood is a soft hardwood while spruce is a softwood (Adeniyi and Ighalo, 2019a). In the discussion approach, the comparison of the three considered wood types are evaluated as the utilised modelling approach (Adeniyi *et al.,* 2019e) takes into cognisance the differences in cellulose, hemicellulose and lignin content of the biomass. In describing the product streams, their composition is consistent with those of real systems. The bio-oil stream was composed of alcohols, aldehydes, organic acids and pyrolytic water. The gaseous product stream was composed of methane, hydrogen, carbon monoxide and some water vapour while the bio-char stream was composed of carbon and silicon oxide ash.

Bio-oil Yield

Figure 2 shows the sensitivity of bio-oil yield to temperature for the pyrolysis of Beech, Ailanthus and Spruce. It can be observed from the figure that the yield of bio-oil reduces gradually from 350°C to about 450°C and drops drastically beyond that point. This is typical of pyrolysis systems as the increase in temperature leads to the more intense thermal cracking and breakdown of the compounds in the reactor which leads to a lesser proportion of oil-range liquid-phase compounds. Below 350°C is

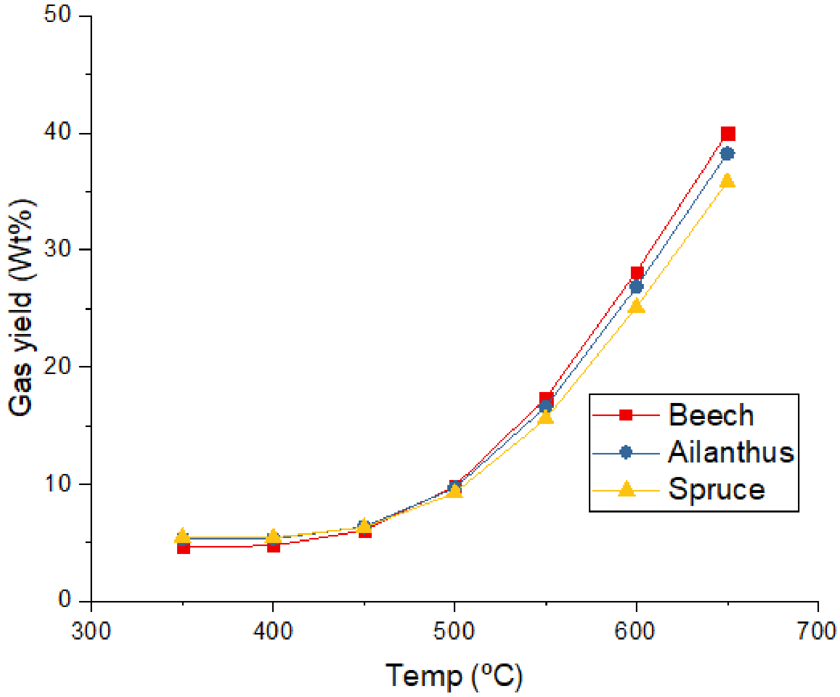

Figure 3. Temperature sensitivity of wood pyrolysis gas yield

characterised by free radical formation, water elimination and depolymerisation (Jahirul *et al.,* 2012), while between 350°C and 450°C is characterised by the breaking of the glycosidic linkages of the tar fraction while above 450°C is characterised by a combination of all above processes. It can also be observed that the oil prediction is higher for beech (hardwood) than for ailanthus (soft hardwood) and then the least is spruce (softwood). The differences are however greater at the lower temperature range. At 350°C, oil yield was 36.72%, 35.13% and 32.89% for beech, ailanthus and spruce respectively while at 650°C, oil yield was 14.55%, 14.17% and 13.39% for the three biomasses respectively. The temperature effect on oil yield is similar to those observed in other studies albeit for banana residues (Ighalo and Adeniyi, 2019), switchgrass (Ighalo and Adeniyi, 2020), and poultry litter (Adeniyi *et al.,* 2019d). Though oil yield was observed to be higher for hardwood than for the others the difference is not quite large. The maximum difference in yield (about 5%) was achieved at the optimum temperature with greater similarity in value being observed at lower oil yield.

Syn-gas Yield

Figure 3 shows the sensitivity syn-gas yield to temperature for the pyrolysis of Beech, Ailanthus and Spruce. A gradual rise in the gas yield was initially observed between 350°C and 450°C and then it becomes drastic beyond that point. As explained in the earlier section, the more intense thermal breakdown and cracking of the compounds in the reactor at higher temperatures lead to a greater portion of lighter gaseous-phase chemical species. There is not much difference in the gas yield between the wood samples at low temperatures but the at 650°C, the gas yield was 39.99%, 38.25% and 35.82% for beech (hardwood), ailanthus (soft hardwood) and spruce (softwood) respectively. The yield of volatiles (bio-oil and syn-gas) is higher for the hard and soft hardwood than for the softwood. The temperature effect on gas yield is in agreement with the observations in other studies albeit for banana residues (Ighalo and Adeniyi, 2019), switchgrass (Ighalo and Adeniyi, 2020), and poultry litter (Adeniyi *et al.,* 2019d).

Bio-char Yield

Figure 4 shows the temperature sensitivity of char yield for Beech, Ailanthus and Spruce. For the entirety of the temperature range studied, a gentle fall in char yield is observed for a wood species (though more significant at temperatures above 500°C). At higher temperatures, the formation of the carbonyl compounds (such as acrolein, glyoxal and acetaldehyde) do occur (Jahirul *et al.,* 2012) which leads to the drop in char yield. It can also be observed from the figure that the yield of char from spruce (softwood) is higher than for ailanthus (soft hardwood) and beech (hardwood). This is the direct opposite of the observed trend for the fluid products but is expected as all yields must sum up to 100%. At 650°C for example, the char yield was 45.44%, 47.58% and 50.77% for beech (hardwood), ailanthus (soft hardwood) and spruce (softwood) respectively. The temperature effect on char yield is similar to those observed in other studies albeit for banana residues (Ighalo and Adeniyi 2019), switchgrass (Ighalo and Adeniyi, 2020), and poultry litter (Adeniyi *et al.,* 2019d).

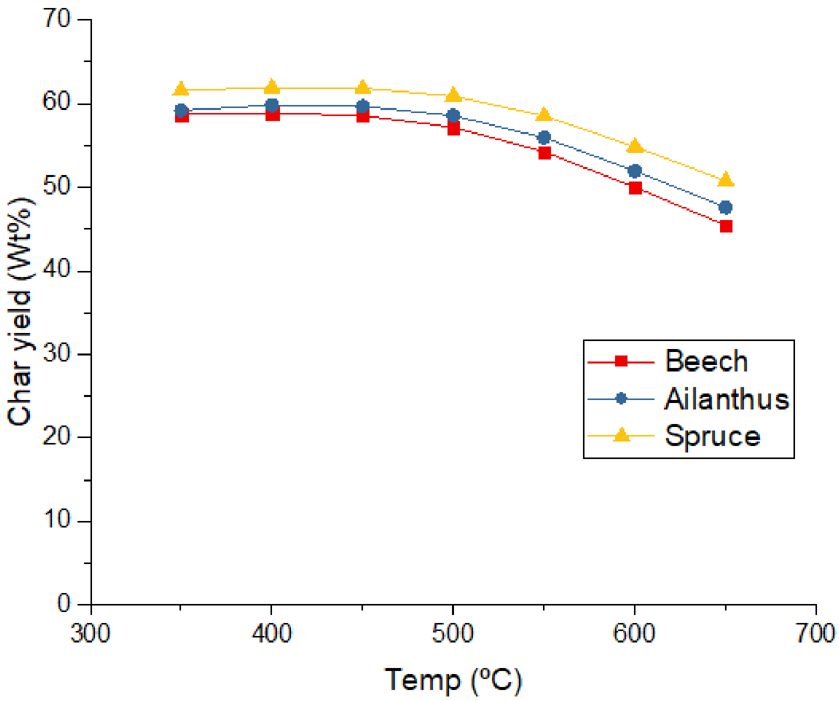

Figure 4. Temperature sensitivity of wood pyrolysis char yield

CONCLUSION

Upon the successful development of the model on ASPEN Plus v8.8, the analysis of temperature sensitivity of different product species in the pyrolysis of beech (hardwood), ailanthus (soft hardwood) and spruce (softwood) was examined. It was observed that oil yield fell with temperature with the Beech having the highest yield over the domain of the temperature range studied. At 350°C, oil yield was 36.72%, 35.13% and 32.89% for beech, ailanthus and spruce respectively while at 650°C, oil yield was 14.55%, 14.17% and 13.39% for the three biomasses respectively. A gradual rise in the gas yield was initially observed between 350°C and 450°C and then it becomes drastic beyond that point. At 650°C, the gas yield was 39.99%, 38.25% and 35.82% for beech (hardwood), ailanthus (soft hardwood) and spruce (softwood) respectively. For the entirety of the temperature range studied, a gentle fall in char yield is observed for a wood species (though more significant at temperatures above 500°C). At 650°C for example, the char yield was 45.44%, 47.58% and 50.77% for beech, ailanthus and spruce respectively. It was observed that the yield of volatiles (bio-oil and syn-gas) is higher for the hard and soft hardwood than for the softwood and this is vice versa for the char yield. This study has helped gain some insight into the process systems engineering of hard and softwood pyrolysis systems.

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