ONLINE ISSN 2069-7430
ISSN-L 1841-4737
PRO LIGNO
www.proligno.ro
Vol. 17 N° 3 2021
pp. 18-25

IMPACT OF TORREFACTION ON THE CHEMICAL COMPONENT OF NIGERIAN GROWN *PINUS CARIBAEA MORELET* WOOD

Francis Akinyele FARUWA*
Research scientist - Department of Forestry and Wildlife Technology, Federal University of Technology
Address: Owerri, Imo State, Nigeria
E-mail: faruwa@gmail.com

Ebenezer Adeyemi IYIOLA
Research scientist - Department of Forestry and Wood Technology Federal University of Technology
Address: Akure, Ondo State, Nigeria
E-mail: eaiyiola@futa.edu.ng

Maureen ANYACHO
Research scientist - Department of Forestry and Wildlife Technology, Federal University of Technology
Address: Owerri, Imo State, Nigeria
E-mail: faruwa@yahoo.com

Anne WEKESA
Tutorial Fellow - Department of Agroforestry, Environmental Studies and Integrated Natural Resource Mangement, University of Kabianga
Address: P.O. Box 2030 -20200, Kericho, Kenya
E-mail: annehabwe@gmail.com

Samuel Oluwafemi AYANLEYE
Research scientist - Department of Wood Science, University of British Columbia, Vancouver, BC, Canada
E-mail: ayanleyeoluwafemi@yahoo.com

Abstract:

Wood is a three-dimensional biopolymer composite; comprising of cellulose, hemicelluloses and lignin with minor amounts of extractives and inorganic. The amount of each of these carbohydrate polymers can be altered or changed by torrefaction. Hence, the impact of toreffaction on the chemistry of selected pine grown in Nigeria was the focus of this study. Torrefied samples of Pinus caribaea used in this study were subjected to different temperatures regimes at 225, 250, 275 and 300°C. Extractives analysis and ash content were determined using gravimetric and proximate analysis respectively. The chemical characterization was carried out using wet chemistry method. The result from this study revealed that, as the torrefied temperature increases from 225 to 300, the volatiles within the torrefied wood samples reduced from 8.00 to 4.47%. The ash content varied between 1.44 and 2.7%. The hemicelluloses were found to range between 21 to 33%, the lignin content from 33- 53% for torrefied sample and this was found to increase with temperature. The cellulose content reduced with increasing temperature from 24% to 13 %. This study evidently showed that the composition of polymers of Pinus caribaea wood was affected by the different temperatures and slightly by different tree parts. The study shows that most of the polymers were evidently degraded between 225 and 250°C and more evidently as the temperature approaches 300°C. The decrease in pine wood component can be attributed not to volatiles loss but also the char formation during torrefaction. The wet chemistry methods used in this study further proven its reproducibility and representative for the analysis of torrefied biomass in developing country. Also, this study gives an insight into chemical alteration that occurred in torrefied Pinus caribaea grown in a typical Nigerian Plantation.

***Key words**: Pinus caribaea Morelet wood; torrefaction, biofuel, energy, wet chemistry.*

INTRODUCTION

Torrefaction of woody biomass is a thermo-chemical process in the temperature range of about 200-300°C under an inert atmosphere (Bourgois & Guyonnet 1988) or low-oxygenated field. The method helps to improve the properties of biomass, which includes resistance to biodegradation, reduction in hydrophilicity, and higher energy density. These features make the storage and handling of biomass and pellet production more convenient. It also enhances the grindability and ignitability are which are beneficial in pulverized fuel combustion (Van der Stelt *et al*. 2011). Torrefaction has been studied extensively and reviewed by several authors (Van der Stelt *et al*. 2011; Chew and Dochi 2011; Chen *et al*. 2015; Madanayake *et al*. 2017).

* *Corresponding author*

The energy crisis and over-use of fossil fuels globally has caused major concerns for environmentalist which led to renewed interest in sustainable biofuels. This core interest in the search for an alternative has led to a search for plant biomass, which is seen as an ideal source of sustainable energy and biobased products because it is renewable and available in high amounts and relatively low cost (Del 2012). Several countries has pioneered change in this regard; for instance, just recently, in the United Kingdom, wood pellets are now being utilized for co-firing and for biomass power plants with the aim of reducing the greenhouse gases emission and increase of renewable energy usage in total energy consumption in order to meet the European Commission's 2020 Climate and Energy Plan (US EIA, 2016), also biomass comprising of wood and waste has been used to generate at least 1.5% of the country total power output in 2016 (US EIA 2017). Therefore, in order to increase domestic biomass utilization, the development of low-cost technologies with utilization of enhanced efficiency is required.

Most plant biomass is lignocellulosic and mainly consists of three biopolymers: cellulose, hemicelluloses, and lignin with minor amounts of extractives, and inorganics which together form a complex and rigid structure (Xu *et al*. 2013, Roger *et al.* 2013). This chemical composition varies with tree species, part (root, stem, or branch), type of wood (i.e. normal and reaction wood), geographic location, climate, and soil conditions. The amount of each of these carbohydrate polymers can be altered or changed by the age, type of species and through a heat treatment (torrefaction). Torrefaction of biomass e.g.; wood, is a mild form of pyrolysis at temperatures between 200° C to 300° C (392 to 608° F). This torrefaction alters the inherent properties (chemical makeup) of the treated material. Several methods have been previously studied to determine the chemical changes during the torrefaction process. The wood polymers (cellulose, hemicelluloses and lignin) degradation at mild heat treatment has also been studied with the utilization of sugar analysis (Bourgois & Guyonnet 1988; Phuong *et al*. 2007). Phuong *et al*. (2007) also observed a decrease in sugar content after heat treatment at 200°C. In addition, different spectroscopic methods have been utilized to study the chemical changes that occurred during torrefaction (Windeisen *et al*. 2007; Rousett *et al*. 2011). For instance, Shang *et al*. (2010) observed a decrease in the concentration of carboxylic groups with FTIR (Fourier….) after torrefaction. Likewise, Khazraie *et al*. (2012) reported decrease in carboxylic group using quantitative wet chemistry.

Since torrefaction affects the organic nature of biomass, it is essential to have determined the level of chemical alteration in the basic wood polymer subjected to this process, hence the purpose of this study. Therefore, the objective of this study was to determine hollocellulose, lignin, ash and extractive content of a torrefied *Pinus caribaea Morelet wood* species grown in Nigeria using the wet chemistry method.

MATERIALS AND METHODS

Sample Preparation and Torrefaction

Sample Preparation

The wood of *Pinus caribaea Morelet* obtained from the the plantation of the Department of Forestry and Wood Technology of Federal University of Technology (FUTA), Nigeria was used in this study. The tree was sectioned into top, middle and base and this is referring to as tree part. The wood samples were dimensioned into chips of 10x10x60mm. The moisture content of each sample was determined using an electrically powered oven with the gravimetric method, dry mass.

Torrefaction

In order to measure the properties modifications due to the heat treatment, the treatment itself is of greatest importance and has to be accurately applied. In the present study we used a device (Fixed bed reactor) specifically designed and developed at Federal University of Technology Akure (FUTA). The dimensioned wood sample was subjected to torrefaction in the fixed bed reactor at a temperature range of 225°C, 250°C, 275°C and 300°C. Upon successful modification, the samples were kept in an air tight chamber too cool and further prepare for various analysis.

Chemical reagent and methods

All chemicals and reagents used for this study were of analytical grade and commercially available. Raw biomass. The study detailed investigations was carried out using gravimetric method for the compositional analysis of lignocellulosic biomass. The choice of this method was hinged on its proven result reproducibility, representative for the analysis of biomass and economically viable gravimetric methods particularly suitable for developing countries

Extractives Analysis and Ash Contents

Wood extractive (WE) were quantified by the procedure as reported by Rabemanolontsoa (2011) and (TAPPI 1988). This procedure was based on gravimetric analysis method to quantify extractives. By acetone extraction, lipophilic wood components, such as fatty acids, resins, fatty alcohol, sterols and

glycerides were extracted. In addition, low molecular phenolic compounds like lagans were also extracted. (Chacha *et al*. 2011). The extractives were expressed as total percentage weight for all extractives. WE was calculated as:

$$WE = \frac{W_0 - W_1}{W_0}[\%] \quad (1)$$

where: WE = Wood Extractive, in %;
W_0=Weight of Wood before extraction, in g;
W_1=Weight of wood after extraction, in g.

The proximate analysis was carried on all the torrefied samples to determine the percentage of percentage of ash content (PAC) following Kurada (2000) procedures.

Determination of Hemicellulose

1g of extracted biomass (W_2, g) was carefully transferred into a 250mL Erlenmeyer flask. 150mL (Mililitre) of 0.5M NaOH was measured out accurately into the Erlenmeyer flask. The mixture was allowed to boil in a water bath for 3.5hrs using distilled water. After boiling, the mixture was left to cool at room temperature. The slurry was filtered through the vacuum filtration and set until the pH of the solution approached the residues were dried to a constant weight of 103 ± 2°C. The difference between the sample weight before and after this treatment is the hemicellulose content (%w/w) of dry biomass (Ayeni *et al.* 2013 and 2015, Blasi *et al*. 1999 and Li *et al*. 2004).

Determination of Lignin Content

The acetone extracted wood samples of 200mg were weighed into small test tubes and 2mL of 72% H_2SO_4, was added to each sample and incubated for 60 minutes at 30^0C with regular stirring to allow for complete hydrolysis. Thereafter, the primary hydrolysates were transferred into Erlenmeyer flask and 56mL of distilled water was added, thereby resulting to the final sulphury acid concentration of 4%. The second step of hydrolysis was made to occur in an autoclave for 30 mins. The slurry was then cooled at room temperature. The pressure cooker was allowed to cool down slowly and then the samples were then removed. The secondary hydrolysates were filtered through vacuum using a filtering crucible. The acid insoluble lignin was determined by drying the residues at 105°C and accounting for ash by incinerating the hydrolyzed samples at 575^0C in a muffle furnace. The acid soluble lignin fraction was determined by measuring the absorbance of the acid hydrolyzed samples at 320nm. The lignin content was calculated as the summation of acid insoluble lignin and acid soluble lignin (Sluiter *et al*. 2008).

$$\%\, KL_{ext,free} = \frac{A}{W} X100 \quad (2)$$

where: A = Extract free wood;
W = Drendy weight.

Determination of cellulose content

Cellulose: The cellulose content (%w/w) was calculated by difference, assuming that extractives, hemicellulose, lignin, ash, and cellulose are the only components of the entire biomass. (Ayeni *et al.* 2013, Blasi *et al*. 1999 and Li *et al*. 2004).

Data Analysis

The experimental design used for this study was Randomized Completely Block Design (RCBD); the different sawdust species parts of the tree (top, middle and base) and different temperature regime. The data obtained was analyzed using Analysis of variance (ANOVA) and descriptive statistics was used to show the results.

RESULTS AND DISCUSSION

The results of Moisture content, Wood Extractive, Ash, Hemicellulose, Lignin and Cellulose of torrefied Nigerian grown *Pinus caribaea Morelet* wood was represented using statistical models such as tables as relevant to the objective of the study. The results of Analysis of variance (ANOVA) for moisture content, extractives, lignin, hemicelluloses and celluloses were presented in Table 1 and their respective mean values were presented in Table 2.

Moisture Content (MC)

The result of ANOVA in Table 1 revealed that, for moisture content, a significant difference was recorded within the different temperatures of the torrefied samples. The moisture content did not vary significantly within the tree parts used in this study. The moisture content (Table 2) revealed that the moisture content reduces with increase in temperature. The reduction in MC was due to continue loss of both free water and bond water present within the cell wall as the temperature progresses. The MC ranged between 2.92% (300°C) 11.48% (un-torrefied samples). The moisture content reported MC in the study were within the 5-10% range reported by Maciejewska *et al*. (2006) and Carl Wilen *et al.* (2013) 2-12% for torrefied samples.

Table 1

ANOVA for Moisture content, Wood Extractive, Ash, Hemicellulose, Lignin and Cellulose of *Pinus caribaea*

	Source	Sum of Squares	Df	Mean Square	F	P value
Moisture Content	Torrefaction temperature	127.10	4	31.77	4.13	0.04*
	Tree parts	3.84	2	1.92	0.25	0.78^{ns}
	Error	61.51	8	7.69		
	Total	192.46	14			
Extractives	Torrefaction temperature	28.89	4	7.22	4.59	0.03*
	Tree parts	10.05	2	5.02	3.19	0.09^{ns}
	Error	12.56	8	1.57		
	Total	51.50	14			
Hemicelluoses	Torrefaction temperature	60.40	4	15.10	3.39	0.07^{ns}
	Tree parts	3.73	2	1.87	0.42	0.67^{ns}
	Error	35.60	8	4.45		
	Total	99.73	14			
Ash Content	Torrefaction temperature	2.879	4	0.720	4.93	0.03*
	Tree parts	0.254	2	0.127	0.87	0.46
	Error	1.168	8	0.146		
	Total	4.301	14			
Lignin	Torrefaction temperature	1009.10	4	252.27	41.00	0.00*
	Tree parts	42.17	2	21.08	3.43	0.08^{ns}
	Error	49.22	8	6.15		
	Total	1100.49	14			
Cellulose	Torrefaction temperature	482.13	4	120.53	5.80	0.01*
	Tree parts	62.17	2	31.09	1.49	0.28^{ns}
	Error	166.18	8	20.77		
	Total	710.48	14			

Table 2

Mean value for Moisture content, extractives, Ash, Hemicelluloses, lignin and Cellulose of *Pinus caribaea*

Treatment	Moisture content	Extractives	Ash	Hemicelluloses	Lignin(klasson)	Cellulose
Raw	11.48^{a}	8.00^{a}	1.44	28.56^{a}	32.48^{c}	29.52^{a}
225 **(°C)**	6.85^{ab}	7.53^{ab}	1.50^{c}	33.00^{a}	33.70^{c}	24.27^{ab}
250 **(°C)**	4.38^{b}	5.20^{bc}	2.33^{ab}	30.67^{a}	42.60^{b}	22.20^{abc}
275 **(°C)**	5.91^{b}	4.47^{c}	2.55^{ab}	25.00^{a}	46.05^{a}	18.48^{bc}
300 **(°C)**	2.92^{b}	7.20^{ab}	2.70^{a}	21.00^{b}	53.49^{a}	13.98^{c}

Means with the superscript are not significantly different from each other.

Extractive content

As shown in Table 1, there is significant difference among the temperature regime, and within the different tree parts, no significant difference was recorded (p-value > 0.05). The extractive contents (Table 2) ranged between 4.47% and 8.00%. This is higher than the reported result of Shebani *et al*. (2008), where the extractive content varies between 2-5% but later stated that it can exceed 15% in some species. The result of this work is similar to the study conducted by Sixta (2006) where the Extractive content ranges between 2-8%.

Ash Content

The ANOVA (Table 1) revealed that there were no significant differences recorded for the different temperatures and different parts of the tree at P-value ≤0.05. Though, there were no significant differences recorded, the result of mean separation revealed that the value increased with increase in temperature i.e., 1.44 to 2.70% for raw and 300 respectively as shown in Table 2. It is evident from this study that as the torrefied temperature increases, the volatiles reduces while the fixed carbon is increased. The result of this work also shows a similar trend with the work of Ho *et al*. (2014) where they reported that in Ash content in Larch wood, increasing the reaction temperature.

Hemicellulose Content

The result of ANOVAs in Table 1 revealed that no significant difference was recorded within the different temperatures. The hemicellulose content was found not to be significantly different within the tree parts was recorded as P value >0.05. Previous studies reported that hemicelluloses are the most thermally sensitive of the biomass components (Wang and Howard 2017) and decreased with increased temperatures (Strandberg *et al*. 2015). Hemicellulose decomposition results mostly in char and formation of extractable matters, but the majority of the decomposition products are volatiles. Volatiles consist of carbon monoxide and carbon dioxide, while condensable fraction includes water, acetic acid, methanol, formic acid, lactic acid, and furfural.

Lignin Content (LC)

Table 1 revealed that torrefaction temperature significantly affects the LC. In the case of tree parts, LC were not significantly affected in this study. The lignin content of pine in Table 2 showed that the raw sample had the lowest value of 32.48% for lignin and temperature 300 has the highest value of 53.49%. This means that lignin content was affected by temperature used. This study is corroborated by the work of Wenjia *et al*. (2013). They reported that the thermal decomposition of lignin occurs at 280 to 500°C yielding phenol via cleavage of ether and carbon-carbon linkages and in accordance with the research of Yang *et al*. (2007) and Wang and Howard (2017). As the temperature increases, the lignin content increases as well and this report is consistent with previous studies (Medic *et al*. 2012; Inari *et al*. 2011 and Windeisin *et al*. 2007). This result is higher than the result reported by Yongfeng Li. (2011) where the lignin content ranges from 25 and 35% but similar to the study conducted by Dardick *et al.* (2010) where the Lignin content ranges from 32-54%. The result of this study also showed similar trend with 32-56.8% reported in the study conducted by Reyes *et al.* (2015).

Cellulose Content (CC)

The ANOVA (Table 1) for cellulose content of Pine revealed that, significant difference were recorded for the different temperatures as P≤0.05 and for different parts of the tree, there was no significant

difference. The result of cellulose content in Table 2 revealed that cellulose reduced with increasing temperature, that is, the raw sample had the highest value of 29.52% and temperature 300 had the lowest value of 13.98%. Cellulose is known to have a crystalline structure which makes it to be stable than other components during mild torrefaction process as supported by the (Strandberg *et al*. 2015). The presence of 1-4-β-glucosidic bonds between glucose units and inter and intramolecular hydrogen bonds are responsible for the crystalline structure in cellulose. Subjection of cellulose to heat treatment during torrefaction leads to depolymerization particularly at 280°C where there is an increase in glucose using the acid methanolysis method (Tooran *et al*. 2014).

This result is lower than the reported result of Sixta (2006) where the cellulose content of wood ranges from 40-44% but similar and within the range of the study conducted by Bhuiyan and Hirai (2005) where the cellulose content ranges from 13-49%. This shows that within the torrefaction temperature used in this work, celluloses degradation was initiated massively.

CONCLUSION

This study evidently showed that the composition of carbohydrate polymers of *Pinus caribaea Morelet* were affected by the different temperatures and slightly by different tree parts. Extractive content, ash and weight of hemicellulose were significantly affected. The cellulose content reduced with increasing temperature while the lignin content increased with increasing temperature which is also consistent with previous reports on torrefaction. The work shows that most of the sugars were evidently degraded between 225 and 250°C and more evidently at the temperature approaches 300°C.The decrease in pine wood component can be attributed not to volatiles production but also the char formation during torrefcation.

Finally, additional work is required to relate the end use properties such as energy value, hydrophilic, grindability and bio-degradability to the chemical changes experienced in the torrefaction regimes and to make a comparison on effect of temperature between soft wood and hard species to allow for improved fuel flexibility.

Competing Interest Declaration

The author(s) declare that they have no competing interests.

Acknowledgements

I acknowledge the moral and academic support of my colleagues throughout the course of this research in person of Mr Iyiola, Mrs Wekesa, Mr. Ayanleye, Mr Anyacho and other people that contributed to the creation of this study. I also appreciate the staff at the wood workshop of the Federal University of Technology, Akure for their contribution to the obtaining of this study.

Authors' Contribution

This work was carried out in collaboration between all authors. Faruwa F.A and Iyiola E.A Performed the experiment and Supervised the study, Mr Anyacho helped in the data analysis, Mrs Wekesa and Mr Ayanleye proof-read the first draft, Mr Iyiola with Ayanleye helped in the literature searches and reviewed the final manuscript. All authors read and approved the final manuscript.

REFERENCES

Agar D, Demartini N, Hupa M (2016) The influence of elevated pressure on the torrefaction of wood. Energy & Fuels, 30, 10.1021/acs.energyfuels.5b01352.

Ayeni OFK, Hymore SN, Mudliar SC, Deskmukh DB, Satpute JA, Omoleye RA, Pandey (2013) Hydrogen peroxide and lime based oxidative pretreatment of wood waste to enhance enzymatic hydrolysis for a biorefinery: process parameters optimization using response surface methodology, Fuel, 106, 2013, 187-194.

Ayeni Augustine O, Opeyemi A, Adeeyo Oyinlola M, OresegunTemitayo E, Oladimeji (2015) Compositional analysis of lignocellulosic materials: Evaluation of an economically viable method suitable for woody and non-woody biomass American Journal of Engineering Research (AJER) Volume 4(4):14-19.

Bhuiyan MT, Hirai, N, Sobue N (2000) Changes of crystallinity in wod cellulose by heat treatment under dried and moist conditions. Journal of Wood Science, 46(6):431-436.

Blasi C, Signorelli DG, Di Russo C, Rea G (1999) Product distribution from pyrolysis of wood and agricultural residues, Industrial Ayeni et alEngineering Chemistry Research, 38(6):2216-2224.

Bourgois J, Guyonnet R (1988) Characterization and analysis of torrefied wood. Wood Science and Technology. 22:143-155. 10.1007/BF00355850.

Chacha N, Toven K, Mtui G, Katima J, Mrema G (2011) Steam pretreatment of Pine (Pinus patula) wood residue for the production of reducing sugar. Cellulose Chemistry Technology, 45(7-8):459-501.

Chen WH, Peng J, Bi XT (2015) A state-of-the-art review of biomass torrefaction, densification and applications. Renewable and Sustainable Energy Reviews, 44:847–866.

Chew JJ, Doshi V (2011) Recent advances in biomass pretreatment - Torrefaction fundamentals and technology.Renewable and Sustainable Energy Reviews, 15:4212–4222

Del Río J, Prinsen P, Rencoret J, Nieto L, Jiménez-Barbero J, Ralph J, Martinez AT, Gutiérrez A (2012) Structural Characterization of the Lignin in the Cortex and Pith of Elephant Grass (Pennisetum purpureum) Stems. Journal of Agricultural and Food Chemistry, 60:3619-34. 10.1021/jf300099g.

Ho Seong Y, Hang Seok C, Hoon Chae P, Jae Gyu H (2014) Torrefaction of woody biomass. A report on Knowledge-based environmental service (Waste to Energy recycling, Ecodesign) Human resource development Project" A National Research Foundation of Korea Grant funded by the Korean Government (NRF)" supported by Korea Ministry of Environment (MOE).

Inari GN, Petrissans M, Gerardin P (2007) Chemical reactivity of heat-treated wood. Wood Science and Technology, 41:157–168. doi: 10.1007/s00226-006-0092-7

Khazraie ST, DeMartini N, Ivaska A, Fardim P, Hupa M (2012) Measuring the Concentration of Carboxylic Acid Groups in Torrefied Spruce Wood. Bioresource Technology, 123:338–343.

Kurada K, Mokuzai B (2000) In: Yoshida H, editor. Mokushitsu kagaku jikken manual, Tokyo: Buneido shuppan; 2000, pp. 87-98.

Li S, Xu S, Liu S, Yang, Lu Q (2004) Fast pyrolysis of biomass in free-fall reactor for hydrogen-rich gas, Fuel Process Technology, 85(8–10):1201-1211

Maciejewska A, Veringa H, Sander J, Pefves SD (2006) Co-firing of biomass with coal: constarin role of biomass pre-treatment: Institute of Energy, European communities.

Madanayake BN, Gan SY, Eastwick C, Ng HK (2017) Biomass as an energy source in coal co-firing and its feasibility enhancement via pre-treatment techniques. Fuel Processing Technology, 159:287–305.

Medic D, Matthew D, Ajay S, Rahn S (2012) The Effects of Particle Size, Different Corn Stover Components, and Gas Residence Time on Torrefaction of Corn Stover. Energies, 5, 10.3390/en5041199.

Phuong LX, Takayama M, Shida S, Matsumoto Y, Aoyagi T (2007) Determination of the accessible hydroxyl groups in heat-treated ***Styrax tonkinensis*** (Pierre) Craib ex Hartwich wood by hydrogen-deuterium exchange and ^{2}H NMR spectroscopy. Holzforschung 61:488–491.

Prins M, Ptasinski K, Janssen FJ (2006) Anal. Appl. Pyrolysis 2006, 77:35−40.

Rabemanolontsoa H, Ayada S, Saka, Shi (2011) Quantitative method applicable for various biomass species to determine their chemical composition. Biomass and Bioenergy, 35(11):4630-46//hdl.handle.net/2433/1518

Reyes-Rivera J, Canché-Escamilla G, Soto-Hernández M, Terrazas T (2015) Wood Chemical Composition in Species of Cactaceae: The Relationship between Lignification and Stem Morphology. PLoS ONE 10(4): e0123919. doi:10.1371/journal.pone.0123919

Roger M, Rowell (2013) The Chemistry of Solid Wood Advances in Chemistry Series 20, Chapter 2, pp. 57-126, Washington, DC: ACS.05-180. https://www.ecn.nl/docs/library/report/2005/rx05180.pdf [Cited 3.4.2015].

Rousset P, Davrieux F, Macedo L, Perre P (2011). Characterisation of the torrefaction of beech wood using NIRS: Combined effects of temperature and duration. Biomass and Bioenergy, 35:1219-1226. 10.1016/j.biombioe.2010.12.012.

Shang L, Ahrenfeldt J, Holm JK, Sanadi AR, Barsberg ST, Thomsen T, Stelte W, Henriksen UB (2012) 'Changes of chemical and mechanical behavior of torrefied wheat straw' Biomass & Bioenergy, 40:63-70. https://doi.org/10.1016/j.biombioe.2012.01.049.

Shebani AN, van Reenen AJ, Meincken M (2008) The effect of wood extractives on the thermal stability of different wood species. Thermochimica Acta, 471:43–50.

Sixta H (2006) Introduction to industrial pulping. Handbook of Pulp.

Sluiter A, Hames B, Ruiz R, Scarlata C, Sluiter J, Templeton D et al. (2008) Determination of structural

carbohydrates and lignin in biomass: laboratory analytical procedure (LAP). Golden, CO: National Renewable Energy Laboratory; April 2008. NREL Report No.: TP-510-42618. Contract No.: DE-AC36-99-G010337. Sponsored by the U.S. Department of Energy

Strandberg M, Olofsson I, Pommer L, Wiklund-Lindström S, Åberg K, Nordin A (2015) Effects of temperature and residence time on continuous torrefaction of spruce wood. Fuel Processing Technology, 134, 10.1016/j.fuproc.2015.02.021.

Tappi Standard T204 om-88: Solvent extractives of wood and pulp. Tappi test methods; 1988.

Tooran KS, Nikolai D, Willför SM, Pranovich A, Smeds A, Virtanen T, Maunu SL, Verhoeff F, Kiel J, Hupa M (2014) Impact of Torrefaction on the Chemical Structure of Birch Wood. Energy & Fuels, 28:3863–3872, 10.1021/ef5004683.

U.S. Energy Information Administration (EIA). International Energy Outlook 2016; DOE/EIA-0484 (2016) U.S. Energy Information Administration: Washington, DC, USA, 2016. Available online: https://www.eia.gov/ outlooks/ieo/ (accessed on 11 May 2017).

U.S. Energy Information Administration (EIA). June 2017 Monthly Energy Review; DOE/EIA 0035(2017/6); U.S. Energy Information Administration: Washington, DC, USA, 2017. Available online: https://www.eia.gov/totalenergy/data/monthly/pdf/mer.pdf (accessed on 11 May 2017).

Van der Stelt MJ, Gerhauser H, Kiel J, Ptasinski K (2011) Biomass Upgrading by Torrefaction for the Production of Biofuels: A Review. Biomass & Bioenergy, 35:3748-3762. 10.1016/j.biombioe.2011.06.023.

Wang P, Howard B (2017) Impact of Thermal Pretreatment Temperatures on Woody Biomass Chemical Composition, Physical Properties and Microstructure, Energies, 10.3390/en11010025.

Wenjia Jin K, John Z (2013) Pyrolysis Kinetics of Physica Components of Wood and Wood-Polymers Using Isoconversion Method. Agriculture, *3*(1):12-32.

Windeisen E, Strobel C, Wegener G (2007) Chemical changes during the production of thermo-treated beech wood. Wood Science and Technology, 41:523-536. 10.1007/s00226-007-0146-5.

Xu F, Yu JM, Tesso T, Dowell F, Wang DH (2013) Qualitative and quantitative analysis of lignocellulosic biomass using infrared techniques: A mini-review. Applied Energy, 104:801–809.

Yang H, Yan R, Chen H, Lee DH, Zheng C (2007) Characteristics of hemicellulose, cellulose and ligninpyrolysis. Fuel, 86:1781–1788.

Yongfeng Li (2011) Wood Polymer composite, Key Laboratory of Bio-based Material Science and Technology of Ministry of Education, Northeast Forestry University, Harbin 150040, P. R. China.