Study on characteristics of acacia wood by ftir and thermogrametric analysis

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Abstract

Renewable energy is very important for future development of society. Biomass is a type of energy that can be renewable. In this study, characterization of acacia wood is focused and discussed. The functional groups, crosslinking in the biomass structures and thermal decomposition were mentioned. In that, functional groups, crosslinking of acacia wood are analyzed by Fourier transform infrared spectroscopy and thermal decomposition is investigated with thermogravimetric equipment. Acacia wood has typical group of wood from FT-IR such as O-H, C-H, C-O, C-O-C of cellulose and lignin. The structure of cellulose is also very easy to be broken by thermal factor. In the inert atmosphere, cellulose decomposed dramatically in the temperature range of 280 to 550 °C and degradation of lignin occurred in the temperature range of 100 to 800 °C. Acacia wood decomposed in the temperature range of 200 to 580 °C with three distinct weight loss stages. The first stage is water removal of biomass and it completes below 120 °C. The second stage is in the range of 200-350 °C that is the initial decomposition of biomass and directly related to the formation of volatile substances from decomposition of hemicellulose and cellulose. The last stage is the continuous decomposition of lignin at higher temperature up to 580 °C. For cellulose, the thermal degradation in air atmosphere has decomposition temperature higher than that in the nitrogen atmosphere but the ending temperature is lower. On the other hand, the thermal decomposition of lignin just occurred from 150 to 560 °C. The reaction for acacia wood demonstrated three stages. The water evaporated at lower than 120 °C in the first stage. The second stage is the devolatilization of biomass (214-322 °C) and the third one (322-420 °C) is the combustion of char.

Keywords. Biomass, acacia wood, cellulose and lignin, FT-IR, characterization of biomass

1. INTRODUCTION

The demand for energy sources to satisfy human energy consumption continues to increase. Currently, the main energy source in the world is fossil fuels. Although it is not known how much fossil fuel is still available, it is generally accepted that it is being depleted and is non-renewable. Other consequences associated with fossil fuel use include the release of the trapped carbon in the fossil fuels to the atmosphere in the form of carbon dioxide which has led to increased concerns about global warming [1]. Given these circumstances, searching for other renewable forms of energy sources is reasonable. Biomass is one of our most important renewable energy. However, the efficient use of biomass for energy production required a detailed knowledge of its physical and chemical properties. These properties are also essential for modeling and analysis of energy conversion processes [2, 3]. On the other hand, the investigation of chemical elemental characteristics of biomass fuels would help them find not only suitable and appropriate energy conversion technologies, but also different existing conversion technologies to effectively use biomass feedstock. Extensive research to determine the physical and chemical properties of the indigenous available biomass resources has been conducted in several countries and international networks [3, 4].

Wood is also biomass that consists of an orderly arrangement of cells with walls composed of varying amounts of cellulose, hemicellulose and lignin. The great diversity of woody plants is reflected in their varied morphology and chemical composition. FTIR spectroscopy using the traditional transmission technique in KBr-pellets has increasingly been used in wood chemistry to characterize cellulose and lignin both qualitatively and quantitatively [5]. Thermogravimetric study is also one of the precious

analysis for studying the combustion, pyrolysis or gasification of biomass. Thermogravimetric analysis of biomass in the inert environment with three values of heating rate 3.5 and 10 ^{o}C/min was reported by Viet et al. [6].

The present research is aimed to perform a basic characteristization as functional groups, linking of acacia wood and thermal behaviors of acacia wood, cellulose and lignin were also mentioned. The experimental technique used was the thermogravimetric analysis (TGA), which is one of the most commonly used techniques to study the primary reactions of thermal decomposition of the solid. On the other hand, Fourier transform infrared (FT-IR) was also performed to help identify functional groups, linking of acacia woodchip. Obtained data could serve to prepare a database of national biomass fuel of acacia wood that very helpful in understanding about biomass pyrolysis, gasification or combustion process.

2. MATERIALS AND METHODS

The acacia woodchip was collected from the factory in Thai Nguyen province, Vietnam and dried for a period of 2-3 weeks. Cellulose and lignin were provided by the School of Chemical Engineering, Hanoi University of Science and Technology. The samples were kept in closed polyethylene bags to avoid contamination prior to the tests. The samples were milled to powder and sieved to a particle size less than 1 mm before the tests. Thermogravimetric analysis (TG/DTG) with PerkinElmer PYRIS Diamond model was used for pyrolysis analysis. 10 mg sample was loaded into an alumina crucible and heated at programmed temperature by the rates of 10°C/min in air environment [6]. FT-IR spectra were obtained by Nicolet 6700 M spectrometer equipment. The method for preparation the samples by dispersing of powder sample in a matrix of KBr, followed by compression at 160 MPa to compact the pellet. Reduced absorbance values were used in order to avoid the spectral differences arising from

the preparation of KBr pellets. In order to normalize the infrared spectra obtained, we used the 4000 cm^{-1} band and was measured at Laboratory of the Petrochemical Refinery and Catalytic Materials, Hanoi University of Science and Technology.

3. RESULTS AND DISCUSSION

Wood is a biomass consisting of cellulose, hemicellulose and lignin, along with smaller quantities of extractives. Cellulose is a linear polymer of glucose units which can form intrachain and interchain bonds yielding a crystalline macromolecule with higher molecular weight that of the other wood components. Hemicelluloses comprise a group of polysaccharides composed of a combination of 5 and 6 carbon ring sugars and have a more irregular structure with side groups, substituent groups, and sugars present along the length of the chain (figure 1). Cellulose is an optically anisotropic system made up of poly(1→4)–b–D-glucose (polysaccharides) chains (figure 2). At first sight, the molecular structure gives the impression of being very simple, but in fact the structural characteristics of the molecule have not yet been fully resolved [7]. The cellulose molecule chain itself is not very stiff, but rather semi-flexible. It is generally known and accepted that the hydrogen bonds play an important role in the conformational and mechanical properties of cellulosic materials [7]. Lignin is a randomized condensed polymer with many aromatic groups and is much more hydrophobic than cellulose or hemicellulose (figure 3). According to Dien et al., [8], cellulose and lignin in acacia woodchip sawdust in Vietnam are 39-42% and 24-25 %, respectively.

The FT-IR spectra of cellulose and lignin were recorded. The results informed the functional groups of cellulose, lignin in region between 4000–2500 cm^{-1} and 2000-500 cm^{-1} and they supported the comparison of functional groups vibrations that were existed in acacia wood.
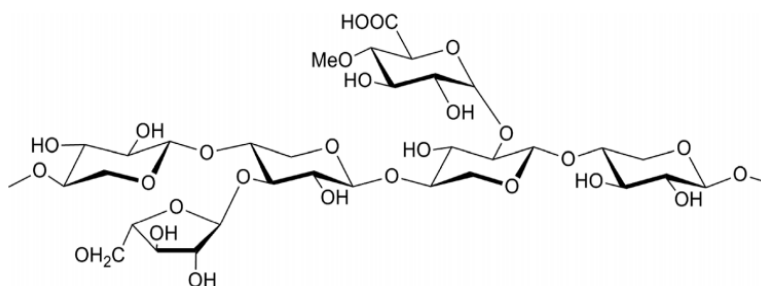

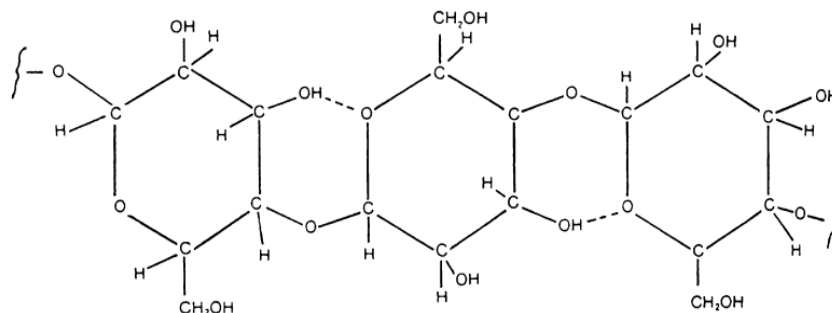*Figure 1:* Molecular structure of hemicellulose [19]

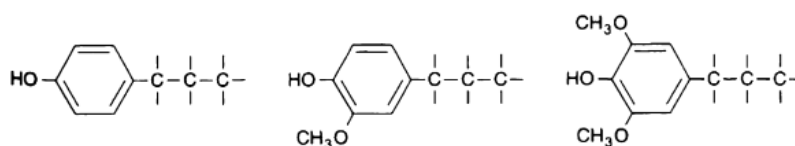*Figure 2*: Molecular structure of cellulose [20]

Figure 3: Some structural units of lignin [20]

The results were also showed in figures 4 and 5. In figure 4, cellulose has the absorbance around at 3420 cm^{-1} in strong spectrum that is attributed to the stretching of O–H in the structure. In lignin's spectrum has also the high and wide peak around at 3420 cm^{-1}; two clear peaks around at 2917 and 2850 cm^{-1} are C–H stretching in aromatic methoxyl groups. The relative intensity of absorption band around at 3420 cm^{-1} of lignin is higher and wider than cellulose. This results are the same as of Popescu et al. [7] who studied characteristics of eucalyptus wood. According to Popescu et al. [7] the absorbance at 2938-2920 cm^{-1} is symmetric C–H stretching and 2840-2835 cm^{-1} is asymmetric C–H stretching in aromatic methoxyl groups. In the spectra the range 2500-2000 cm^{-1} just has the vibration of CO_2 in the measuring environment and all the samples have this vibration, so that we don't show this in the result. In the "fingerprint" region, the spectra contain several bands assigned to the main wood components, as can be seen in figure 5. The absorption bands of cellulose just displayed at 1639, 1382, 1164 and 897 cm^{-1} clearly in figure 5. The aromatic skeletal vibration at 1639 cm^{-1} was so clear and it revealed that the content of aromatic compounds in acacia wood cell walls was almost of cellulose.

The absorption bands at 1375-1365 cm^{-1} is C–H bending in cellulose and hemicellulose [9]. The absorption bands at 1164 cm^{-1} in cellulose is C–O–C asymmetric stretching in cellulose, hemicellulose [1]. The small sharp band at 897 cm^{-1} is originated from the β-glucosidic linkages between the sugar units (polysaccharides) in cellulose. The absorbance bands of lignin are different with cellulose. The
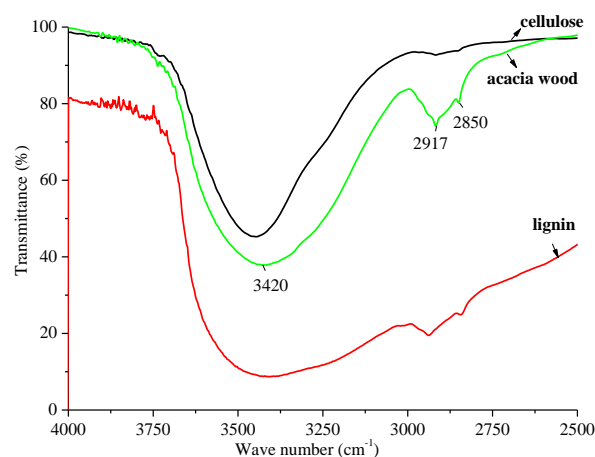
Figure 4: FT-IR spectra of acacia wood, cellulose and lignin in region between 4000-2500 cm^{-1}
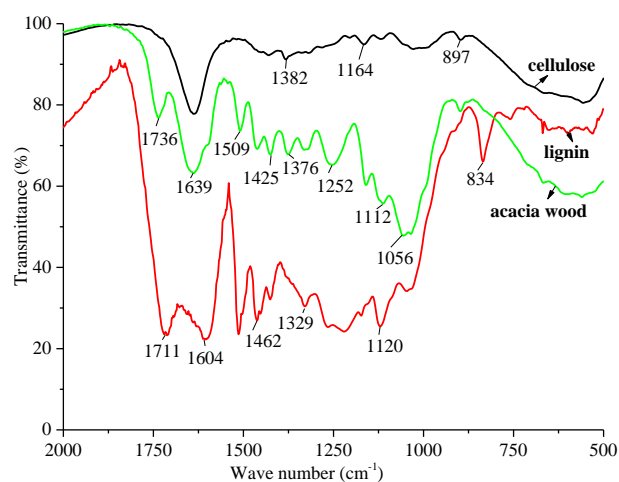
Figure 5: FT-IR spectra of acacia wood, cellulose, lignin in region between 2000-500 cm^{-1}

absorbance of lignin at 1711, 1604, 1513, 1462, 1426, 1329, 1221, 1120 and 1034 cm^{-1} were seen in the spectrum. The bands at 1604, 1509 cm^{-1} are assigned to C=C, C–O stretching or bending vibrations of different groups present in lignin. The bands at 1462, 1426, 1329, 1221, 1120 cm^{-1} are characteristic of C–H, C–O deformation, bending or stretching vibrations of many groups in lignin and carbohydrates. The strong band around 1034 cm^{-1} is assigned to C–O stretching. FT-IR spectra of acacia wood forming tissue display significant difference between cellulose and lignin in "fingerprint" region between 2000-500 cm^{-1}.

On the other hand, FT-IR spectrum of the acacia wood is also shown in figures 4 and 5 for the regions 4000–2500 cm^{-1} and 2000-500 cm^{-1}, respectively. Sixteen peaks are clearly defined at: 3420 cm^{-1} for O–H strectching, 2917 and 2850 cm^{-1} for symmetric and asymmetric C–H stretching in aromatic methoxy groups. In addition, acacia wood has also three peaks with the same FT-IR spectrum of lignin but the peaks at 2920 and 2850 cm^{-1} are a little higher than lignin. The results aslo agree with the previous publication of Yang et al. [10] who reported hemicellulose appeared more C=O contained organics compounds, while higher contents of OH and C–O was found with cellulose. The band at 1736 cm^{-1} for unconjugated C=O in hemicellulose [9] and did not observation for cellulose and lignin. The band at 1639 cm^{-1} assigned for aromatic skeletal vibration and this showed clearly in cellulose and acacia wood samples. Vibration at 1604 cm^{-1} and 1509 cm^{-1} assigned for aromatic skeletal in lignin that we can see in the FT-IR spectrum of lignin, 1462 cm^{-1} and 1425 cm^{-1} for C–H deformation, 1376 cm^{-1} for C–H deformation in polysaccharides [7], 1252 cm^{-1} for O–H in plane in polysaccharides, 1164 cm^{-1} for C–O–C vibration in polysaccharides, 1112 cm^{-1} for aromatic skeletal and C–O stretch, 1056 cm^{-1} for C–O stretch in polysaccharides and 897 cm^{-1} for C–H deformation in cellulose [11] that was seen clearly in the FT-IR spectrum of cellulose. The result is the same as the previous research of Popescu et al [7] about eucalyptus wood.

According to Bodîrlău et al. [12] the spectrum of hardwood shows the same basic structure as all wood samples and it is also true for acacia wood. A group of complex FT-IR absorbance of lignin was found there, indicating that lignin might be rich of methoxy–O–CH$_3$, C–O–C and C=C (aromatic ring) containing compounds.

Thermal degradation of cellulose, lignin and acacia wood in nitrogen atmosphere and air atmosphere were also investigated. TG graphics of acacia wood, cellulose and lignin in nitrogen
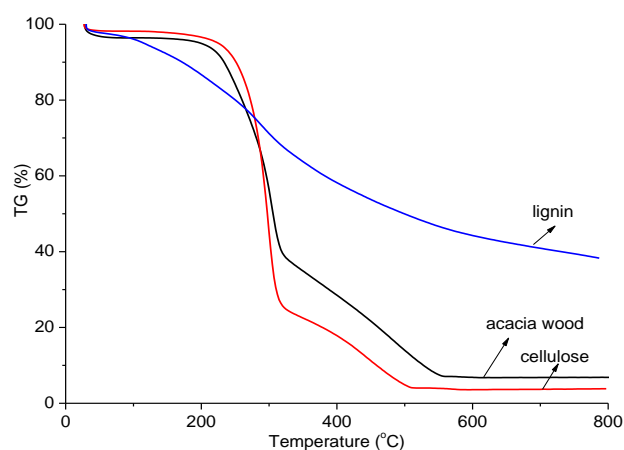

Figure 6: TGA graphics of acacia wood, cellulose and lignin in nitrogen atmosphere

atmosphere at heating rate 10 ^{o}C/min was show in Figure 6. It could be said that the thermal behavior of acacia wood and lignin was nearly different and the thermal behavior of acacia wood and cellulose was nearly similar. Cellulose decomposed dramatically in the temperature range of 280 °C to 550 °C. Degradation of lignin occurred at a slower rate over a much wide temperature range from 100 °C to 800 °C. The cellulose chemically decomposes at high decomposition rate within narrow temperature range. While, decomposition rate of the lignin becomes slower than that of the cellulose. Similar results of lignin degradation at temperature ranges were presented in the literatures [10] Ligninic polymers are highly branched, substituted, mononuclear aromatic polymers forming a lignocellulosic complex in the biomass and this amorphous structure of lignin accounts for 16 % to 33 % of the mass of woody biomass [13]. On the other hand, according to Jin et al., the thermal decomposition of lignin occurs at 280 to 500 °C yielding phenol via cleavage of ether and carbon-carbon linkages [14]. Lignin is composed of aromatic rings with multiple branches, whose degradation occurs in a broad temperature range. Different thermal degradation behavior of hemicellulose, cellulose and lignin are attributed to their individual chemical natures of biomass [15]. Cellulose, which has only glucose in its chain structure, hemicellulose contains heteropolysaccharide and thermally degrades in the temperature range of 130-194 °C [13]. In contrast, cellulose is a linear polymer of glucose (5000-10000 glucose units). The cellulose degrades at 240-350 °C producing anhydrocellulose and levoglucosan [13]. Cellulose consists of long unbranched glucose polymers, which have an ordered and strong

structure and high thermal stability. According to Yang., [10], organics compounds (C=O, C–O–C, etc.) in hemicellulose and cellulose were mainly released out at low temperatures, i.e., 200-400 ^{o}C and 300-450 ^{o}C. Hemicellulose is degraded at low temperatures because it consists of several saccharides, which are amorphous structures rich in branching and easy to be removed. Acacia wood decomposed in the temperature range of 30 to 584 °C with three distinct weight loss stages. The first stage is water removal of biomass and it completes below 120 ^{o}C [6]. The second stage is between 205 ^{o}C and 385 ^{o}C with the total content loss about 65 % in the dry ash free and it is the initial decomposition of biomass or called active pyrolysis and directly related to the formation of volatile substances from hemicellulose, cellulose and lignin decomposition. The last stage is the continuous decomposition of lignin at higher temperature to 584 ^{o}C with the total content loss about 37 % in the dry ash free and at higher temperature it almost does not have dramatical change.
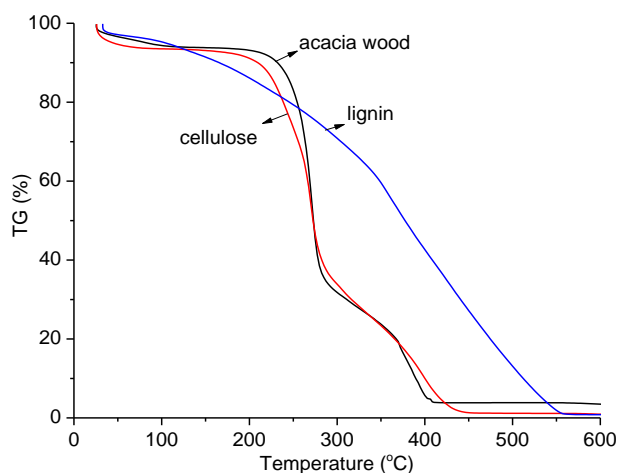

Figure 7: TGA graphics of acacia wood, cellulose and lignin in air atmosphere

The behavior decomposion of acacia wood, cellulose and lignin in air atmosphere is also investigated. The experiment of thermal degradation of acacia wood, cellulose and lignin was conducted from 30 °C to 800 °C at the heating rate of 10 °C/min and the results were shown in figure 7. The TGA curves show the percentage weight remaining over the temperature range. Beside the demoisturization at lower than 120 ^{o}C, it is clearly observed that there were two distinct stages presented. The first stage was the devolatilization of biomass (214-322 ^{o}C) and the second one (322-420 ^{o}C) was the combustion of char. The results showed that for the first stage, the cellulose component of acacia wood was decomposed and generated volatile

substances [16]. The functional groups and linking in cellulose such as C-O, C-O-C broke and reacted with oxygen generating CO, CO_2 [10]. The decomposition reaction rate of the samples became faster than the pyrolysis reaction in this stage. It is also observed that as cellulose, the starting and end point temperature lower than acacia wood may be due to that cellulose has light volatile matter in higher content. On the other hand, lignin just has one weight loss region from 150 ^{o}C to 560 ^{o}C and may be lignin has aromatic hydrocarbon compositions. These results are the same as earlier publications [17, 18]. The thermal degradation in air atmosphere has decomposition temperature higher than one in the nitrogen atmosphere but the end temperature is lower. This may be due to the reactivity of oxygen [21-22].

4. CONCLUSIONS

Characterization of acacia wood was evaluated by FT-IR and TGA methods. The characterization of the main compositions of acacia wood as cellulose and lignin was also investigated for comparision and making clearly about characterization of wood. The cellulose spectrum has aromatic skeletal vibration at 1639 cm^{-1}, C-H bending at 1382 cm^{-1}, C-O-C asymmetric stretching at 1164 cm^{-1} and β-glucosic linkages at 897 cm^{-1}. Lignin component of acacia wood included many complexly functional groups that is also shown in the fingerprint regions. The bands of C=C, C–O stretching or bending vibrations of different groups appeared around at 1604 and1509 cm^{-1}. The bands of C–H, C–O deformation, bending or stretching vibrations of many groups are assigned at 1462, 1426, 1329, 1221, 1120 cm^{-1}. The strong band at 1034 cm^{-1} is assigned to C–O stretching. The thermal decomposition of cellulose was almost complete around 450 ^{o}C (in the air atmosphere) and 549 ^{o}C (in the inert atmosphere). Lignin is thermally stable in both inert environment and air atmosphere. Thus, in the combustion process to burn complete lignin needs high temperature to 555 ^{o}C with the residues 1.1 % at that temperature. In pyrolysis and gasification process in the hypoxic atmosphere, the changes of lignin were very complex and lignin decomposed between 100 ^{o}C and 800 ^{o}C with residues 38.6 % at 800 ^{o}C. Lignin may generate tar in the biomass gasification or pyrolysis process that causes many problems for application of these processes. The conclustion is the thermal decomposition of acacia wood from 200 to 450 ^{o}C that is the thermal decomposition of hemicellulose, cellulose and lignin and at higher temperature almost does not have dramatical change. In the air

atmosphere, the decomposition of cellulose, lignin and acacia wood starts later and ends sooner than in the inert atmosphere

REFERENCES

1. P. McKendry. *Energy production from biomass (part 1): overview of biomass*, Bioresour. Technol., **83**, 37-46 (2002).
2. A. Nordin. *Chemical elemental characteristics of biomass fuels*, Biomass and Bioenergy, **6(5)**, 339-347 (1994).
3. S. Garivait, U. Chaiyo, S. Patumsawad, and J. Deakhuntod. *Physical and Chemical Properties of Thai Biomass Fuels from Agricultural Residues*, 2nd Jt. Int. Conf. Sustainable Energy Environ, **48**, 1-5 (2006).
4. L. Cuiping, W. Chuangzhi, Yanyongjie, and H. Haitao. *Chemical elemental characteristics of biomass fuels in China*, Biomass and Bioenergy, **27(2)**, 119-130 (2004).
5. M. Schwanninger, J. C. Rodrigues, H. Pereira, and B. Hinterstoisser. *Effects of short-time vibratory ball milling on the shape of FT-IR spectra of wood and cellulose*, Vib. Spectrosc., **36(1)**, 23-40 (2004).
6. D. Q. Viet, N. Van Vinh, and V. D. S. Tho. *Thermogravimetric analysis and Kinetic study of acacia wood pyrolysis*, Vietnam J. Chem., **53(6e4)**, 185-191 (2015).
7. C. M. Popescu, M. C. Popescu, G. Singurel, C. Vasile, D. S. Argyropoulos, and S. Willfor. *Spectral characterization of eucalyptus wood*, Appl. Spectrosc., **61(11)**, 1168-1177 (2007).
8. L. Q. Dien, N. T. M. Nguyet, P. H. Hoang, and T. D. Cuong. *Properties of lignocellulosic biomass and aspects of their biochemical refineries in Vietnam: a review of recent*, in Workshop Proceedings of Vietnam Forestry University - International Academy of wood science cooperation for development, 56-63 (2015).
9. C. M. Popescu, G. Singurel, M. C. Popescu, C. Vasile, D. S. Argyropoulos, and S. Willfir. *Vibrational spectroscopy and X-ray diffraction methods to establish the differences between hardwood and softwood*, Carbohydr. Polym., **77(4)**,

851-857 (2009).
10. H. Yang, R. Yan, H. Chen, D. H. Lee, and C. Zheng. *Characteristics of hemicellulose, cellulose and lignin pyrolysis*, Fuel, **86(12-13)**, 1781-1788 (2007).
11. O. Faix. *Classification of Lignins from Different Botanical Origins by FT-IR Spectroscopy*, Holzforschung, **45(1)**, 21-28 (1991).
12. R. Bodîrlău and C. A. Teacă. *Fourier transform infrared spectroscopy and thermal analysis of lignocellulose fillers treated with organic anhydrides*, Rom. Reports Phys., **54(1-2)**, 93-104 (2009).
13. D. Mohan, C. U. Pittman, and P. H. Steele. *Pyrolysis of Wood/Biomass for Bio-oil: A Critical Review*, Energy Fuels, **20(3)**, 848-889 (2006
14. W. Jin, K. Singh, and J. Zondlo. *Pyrolysis Kinetics of Physical Components of Wood and Wood-Polymers Using Isoconversion Method*, Agriculture, **3**, 12-32 (2013).
15. H. Yang, R. Yan, H. Chen and C. Zheng. *Influence of mineral matter on pyrolysis of palm oil wastes*, Combustion Flame, **146**, 605-611 (2006).
16. D. Q. Viet, N. Van Vinh, P. H. Luong, and V. D. S. Tho. *Thermogravimetric Study on Rice, Corn and Sugar Cane Crop Residue*, J. Sustain. Energy Environment, **6**, 87-91 (2015).
17. K. G. Mansaray and A. E. Ghaly. *Determination of kinetic parameters of rice husks in oxygen using thermogravimetric analysis*, Energy Sources, **21**, 899-911 (1999).
18. D. Lv, M. Xu, X. Liu, Z. Zhan, Z. Li and H. Yao. *Effect of cellulose, lignin, alkali and alkaline earth metallic species on biomass pyrolysis and gasification*, Fuel Process. Technol., **91(8)**, 903-909 (2010).
19. W. Chen, L.-X. Zhong, X.-W. Peng, K. Wang, Z.-F. Chen, and R.-C. Sun. *Xylan-type hemicellulose supported palladium nanoparticles: a highly efficient and reusable catalyst for the carbon–carbon coupling reactions*, Catal. Sci. Technol., **4**, 1426-1435 (2014).
20. P. Basu, *Biomass Gasification and Pyrolysis Handbook*, Elsevier (2010).
21. M. A. Saffe, M. E. Echegaray, G. D. Mazza, and R. A. Rodriguez. *Thermo gravimetric analysis of peach pits under inert and air atmosphere*, Int. J. Eng. Sci. Innov. Technol., **3(6)**, 21-30 (2014).
22. A. Rastrogi, M. K. Jha, and A. K. Sarma. *Environmental Effects A comparative study of kinetics for combustion versus pyrolysis of Mesua ferrea husk, soya husk and Jatropha curcas husk using thermogravimmetry and different methods*, Energy Sources Part A Recover. Util. Environ. Eff., **38(10)**, 1355-1363 (2016).

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