Study in the Changes on the Functional Groups Present in Biomass during Pyrolysis Process

S Suman¹, AM Yadav², T Jain¹, A Ali SK¹

¹Department of Mechanical Engineering, Meerut Institute of Engineering and Technology, Meerut-250005, Uttar Pradesh
²Department of Chemical Engineering, Meerut Institute of Engineering and Technology, Meerut-250005, Uttar Pradesh
Email: swapan.suman@miet.ac.in

Abstract. In this study, investigate the changes occurs on the functional groups of biochar materials. The biomass materials subjected to the pyrolysis, which is a thermochemical conversion process to obtain biochar material. It was produced by slow-pyrolysis method by subjected in different pyrolysis temperatures (400, 600, 800 and 1000°C). Effect of the treatment procedures was determined by the modifications in the functional groups of the obtained bio-char during the pyrolysis treatment was determined with the Fourier transform infrared spectroscopy (FT-IR). FTIR methods deliver fast, low-cost and non-destructive analysis and have shown qualitative and quantitative outcomes. The analysis was applied to some agricultural biomass materials such as saw dust, rice hull, wheat hull, tea wastes, and eucalyptus shell. Results are associated with literature, and species potentially computable by Fourier Transform Infrared Spectroscopy are reviewed. The result showed that the aliphatic, hydroxyl and aromatic groups gradually diminishes by increasing the temperature from 400 to 1000°C.

Keywords: Biomass; Pyrolysis; Biochar; FTIR Spectroscopy
Graphical Abstract

Statement of Novelty

This research demonstrates the optimization and changes in functional groups of selected biomass during pyrolysis process at different pyrolysis temperature. Throughout the pyrolysis method, oxygen and hydrogen contents were reduces and enrich carbon rest remains in form hydroxyl (C–H stretching) and aromatic carbon bonds and aromatic groups are gradually diminishes. During the pyrolysis chemical modification enriches the functional groups of biochar. This study has shown to high potential of biochar to get a deeper understanding of structural relationships with their functional groups.

1. Introduction

Recently, energy needed in the world has increased dramatically. Therefore, it is likely that fossil fuels cannot meet the energy demand in the next some decade. Besides, the fossil fuels and its derivatives have caused significant environmental risks due to the formation of harmful oxides likes nitrogen, carbon, and sulphur. These reasons have moved our attention towards alternative energy source that is renewable and environmentally friendly. Solid bio-waste is one of the demandable source of energy for future energy demand due to its sustainable nature.

Biomass is the leading energy source in the world which comes after fossil fuels and it providing about 14% of the world’s energy demand. Biomass is providing 35% of their energy in developing nations [1].

Biomass has likely to provide energy with almost zero-emissions [2]. Biomass and its application provides an effort to utilize the energy stored in it as an alternate fuel in order to conserve the other energy sources like coal, oil etc.

Pyrolysis is one of the thermo-chemical processes that are conducted at high temperatures (400-1100°C) in the oxygen-less condition. During the pyrolysis process, biomass is converted into solid, liquid and gaseous products based on heating rates and time of pyrolysis [3]. Hence we can say that energy generated from biomass has a high capacity to bridge the global energy shortage gap caused by the depletion of fossil fuel resources while keeping environmental sustainability.
This study includes the influence of temperature on different biomass feedstocks and their physicochemical properties. The different agricultural biomass were characterized by proximate & ultimate analysis, higher heating value (HHV) and field-emission Fourier transform infrared (FTIR) spectroscopy.

2. Materials and Methodology

2.1. Biomass materials

The conditions in which pyrolysis process is accomplished can dramatically change the final properties and composition (solid, liquid and gaseous) of the products obtained from the process. The parameters like feedstock type and heating profile (i.e. pyrolysis temperature) have been frequently recognised as important variables for determining the composition and characteristics of produced biochar [4-7]. Besides, the significance of pyrolysis time during biochar production is less conclusive due to a limited number of studies varying these conditions. Therefore detailed investigations would aid in reaching a definitive conclusion on the importance and preferred value for these variables.

Biomass samples used were mainly woody waste, crop residues and shells, this includes Saw Dust (SD), Rice Hull (RH), Wheat Hull (WH), Tea Wastes (TW), and Eucalyptus Shell (ES). The pyrolysis temperature range studied throughout the experimental work covered a range from 400°C to 1000°C with 600°C and 800°C values serving as intermediate values. This temperature choice covered the main regions of biomass degradation as well as the respective upper and lower limits of temperatures associated with slow pyrolysis at a slow heating rate (15-25ºC/min). A low heating rate was selected to provide longer heating time in an attempt to provide tolerable time for sufficient heat transfer and heat penetration into the biomass particles. Based on realistic times seen in industrial sized units to generate fast conversion of feedstock to biochar, the residence times chosen were therefore 60 minutes.

2.2. Preparation of Biochar

Biochar is a solid and carbonaceous by-product of biomass. To obtain biochar, selected biomass subjected to reactor at different pyrolysis temperature at a low heating rate for characterization [8]. After pyrolysis, products were determined for biochar and yields of product were calculated as a proportion of feedstock weight on a dry weight basis.

2.3. Methodology

2.3.1. Proximate and ultimate analyses and higher heating value (HHV)

“Proximate analysis” was employed on selected and prepared materials for the estimation of physiochemical properties with ensuing standards “(ASTM E871-82, E1755-01, and E872-82)” [9]. And the proximate analysis for obtained biochar from studied samples was evaluated according to “ASTM D1762-84” standard method [10].

“ASTM E777, E778 and E775” standard method was ensued for “ultimate analysis” [11] to calculate the elemental components of the selected samples and their corresponding biochar using “CHNS analyser” (Vario EL III). In the ultimate analysis we determine the Carbon, Hydrogen, Nitrogen and Sulphur in weight percentage.

Higher Heating Value (HHV) of all samples were estimated by “bomb calorimeter” (Model: AC-350 LECO) according to “ASTM D4809” standard [12].

2.3.2. Fourier-transform infrared (FT-IR) spectroscopy

FT-IR spectroscopy has been used as an influential methodical tool for the swift description of different types of biomass. FTIR spectroscopy tracks the existence of ‘molecular vibrations’ that are representative of a chemical compound. This technique has broadly been used for the qualitative and quantitative interpretation of modifications in biomass structure during the process [13].
study, FT-IR spectrometer (Perkin Elmer Spectra 2, USA) was exploited by the ‘pellet method’ by blend with dried bio-char and pulverized KBr in the ratio proportion of 1:200 (Potassium Bromide).

3. Results and Discussion

3.1. Proximate, ultimate analyses and heating values of studied biomass samples

The physicochemical characteristics of the selected biomass samples are tabulated in Table 1. As per the literature, the parametric values in case of a variety of biomass vary in the range: ash (1.45-18.20%), VM (67.38-81.33%), FC (13.11-17.22%), C (39.40-50.11%), O (37.06-41.78%), H (3.59-5.50%), N (0.27-0.75%), and S (0.12-0.18%). These results are verified with literature values [14]. Their ash depends on the sample types and their geographic region. The HHV of selected biomass vary in the range of 14.77-19.61 MJ/Kg. These values are also within the range of literature value [15] and that is comparable with primary and other renewable energy source. Heating value directly affected by ash, its high or less weight percentage depends on the calorific value which shows their heating energy. From above evident, it can be concluded that high ash containing samples makes it less desirable as a ‘fuel’ [16-17].

Table 1. Proximate analysis (dry basis), Ultimate analysis and higher heating value of studied biomass samples

| Samples           | VM%  | ASH% | FC%  | C%      | H%     | N%     | S%     | O%     | HHV(MJ/Kg) |
|-------------------|------|------|------|---------|--------|--------|--------|--------|------------|
| Saw Dust (SD)     | 81.33| 1.45 | 17.22| 51.11   | 5.50   | 0.27   | 0.12   | 41.67  | 19.61      |
| Wheat Hull (WH)   | 71.24| 14.56| 14.20| 40.32   | 5.34   | 0.43   | 0.15   | 39.20  | 15.43      |
| Rice Hull (RH)    | 69.62| 17.27| 13.11| 39.40   | 4.23   | 0.75   | 0.18   | 39.17  | 14.77      |
| Tea Waste (TW)    | 73.33| 11.47| 15.20| 42.35   | 3.59   | 0.67   | 0.14   | 41.78  | 16.11      |
| Eucalyptus Shell  (ES) | 67.38| 18.20| 14.42| 39.46   | 4.84   | 0.31   | 0.13   | 37.06  | 15.68      |

Agricultural biomass contains much more ash-forming components than some woody biomass [18]. In particular, the straw, grasses, and fast growing crops mostly have higher content of both the ash and high mobile elements (like Cl, K, Mg, S, Na, and Si) than wood biomass; and reverse is true for C content [18-19]. The higher HHV of Saw Dust and Coconut Shell is because of lower content of ash i.e. an incombustible component and higher amount of combustible components such as volatile matter, fixed carbon, carbon and hydrogen than in other biomass materials.

3.2. Fourier transforms infrared spectroscopy of studied biomass samples

Figure 1(a)-(e) demonstrate the FTIR spectra plots of selected biomass samples. These graphs are the plot versus wavenumbers (cm\(^{-1}\)) and transmittance %, which shows the aliphatic losses in their functional groups. The all selected biomass have mutual bands i.e., O-H stretching occurs at 3390-3420 cm\(^{-1}\), CH, CH\(_2\) stretching occurs at 2900-2930 cm\(^{-1}\), C=O stretching occurs at 1615-1640 cm\(^{-1}\), benzene ring occurs at 1500-1520 cm\(^{-1}\), aromatic skeletal vibrations occurs at 1405-1465 cm\(^{-1}\), Phenolic OH and aliphatic C-H deformation occurs at 1315-1380 cm\(^{-1}\), C-O-C stretching occurs at 1235-1245 cm\(^{-1}\) in alkyl aromatic, C-O-C asymmetry stretching occurs at 1155-1165 cm\(^{-1}\), C-O stretching occurs at 1030-1060 cm\(^{-1}\). Other peaks seemed at 1720 cm\(^{-1}\) i.e., C=O stretching and at 605cm\(^{-1}\) i.e., OH bending modes in WC [20-21]. In Addition the peak at 440, 805 and 1045-1108 cm\(^{-1}\) seemed in Wheat Hull and Rice Hull, i.e., for SiO\(_2\) [22].
During FTIR analysis (Figure 1(a)-(e)), the covalent bonds of the functional groups absorbed from infrared radiation causing the bonds to be stretched, vibrated, bended, rocked or twisted. The main application of this method is to observe the cellulosic contents which can be clearly observed by the O-H bonds. The O-H bonds after the absorption of energy were stretched resulting in enhancement of the peak’s intensity. The peak intensity is indicated by either the peak’s sharpness or broadness and also the percentage transmittance (%T). The transmittance percentage indicates the how much lights been transmitted through the molecules which means the absorption energy by the O-H bonds is the deduction of the transmittance percentage by hundred per cent.
3.3. Proximate, ultimate analyses and higher heating value of obtained biochars

The ‘proximate’, ‘ultimate analyses’ and ‘HHV’ of the carbonized products of studied biomass samples at different temperature are shown in Figure 2 (a)-(f). Biochar is mainly formed from the thermal breakdown of biomass. During pyrolysis the volatile matter is distorted into the gas and residue left as ashes [23]. From the Figure 2 (a)-(e), it can be seen that volatile matter gradually decreases with rise in temperature from 400 to 1000°C during the pyrolysis process. Biochar derived at low temperature contains high VM because the existence of lignin in the biomass sample. Lignin cannot decompose at low temperature i.e. 400°C [24]. When the temperature increases upto 800°C, a rapid loss seen in volatile matter content [25-26] because volatile organic compounds are breakdown at high temperature in organic cyclic and aromatic molecules. The observations of higher content of ash in WHC, RHC, and ESC than SDC, and TWC are similar to the observations of others [27-28]. Enriched content of silica, K₂O, and other ash forming elements presents the in straw and husk materials, may be this reason of higher content of ash than in woody materials [25, 27]. The content of inorganic salts influences the property of volatiles and reduction in the yield of the formation of biochar [28]. The ‘fixed carbon’ in SDC, WHC, RHC, TWC, and ESC increases with increase in temperature. The related range values have presented in form of figures as we can see.

From ultimate analysis data, it can be observed that the principal components [22] such as, C, H, N, S, and O, differed in both cases (biomass and its corresponding biochars). The higher the content of VM and FC in SDC are reason for the higher the content of C and H in SDC than others. The carbon contents of obtained biochars are 86.57, 59.82, 52.52, 71.82 and 70.05% for SDC, WHC, RHC, TWC, and ESC, respectively. Among all these elements, the contribution of carbon was highest in most of the biochars [23], which was followed by oxygen, then hydrogen and then the rest of the components, although the compositions of nitrogen and sulphur content in biochar materials are low or approximately same. Presence of these C, H and O elements in biomass leads to more char formation as well as to the higher heating value of the product. Among C, H, N, S and O, the contribution of carbon (C) is highest in most of the biochars. Although, nitrogen and sulphur contents are low or approximately same.

![Figure 2](https://example.com/figure2a.png)  
**Figure 2.** Physiochemical analysis of (a) SDC of all studied biochar samples  
![Figure 2](https://example.com/figure2b.png)  
**Figure 2.** Physiochemical analysis of (b) WHC of all studied biochar samples
3.4. Fourier transforms infrared spectroscopy analysis of obtained biochar samples

During the process of biomass carbonization/pyrolysis, many reactions take place in parallel and series as well, including ‘aromatisation’, ‘isomerization’, ‘dehydration’, and ‘charring’ [29-30]. Pyrolysis process comprises an increase in aromatic structures in the obtained biochars structure. Figure 3 (a)-(e) demonstrate the FTIR spectra of biochar derived from different agricultural biomass samples at different temperatures. From Figures, it was seen that with increasing temperature from 400 to 1000ºC, the aliphatic losses occurs at 2944–2845 cm⁻¹ band i.e. aliphatic C–H stretch [31]. The peaks appeared at (753–908 and 3040–3005 cm⁻¹), (1375–1445 cm⁻¹) and (1581–1708 cm⁻¹) for aromatic carbon include C–H stretching, C=C & C–C and C–O Carbonyl stretch respectively [32-33]. This is obviously because during the carbonization process modification takes place in the functional group and with this aliphatic C–H band decreases but aromatic C–H band increases [34].

At 800-1000ºC, the strength of the hydroxyl groups and aromatic groups [31, 35], gradually diminishes, i.e. band occurs at (3204–3411 cm⁻¹) and (1570–1610 and 3045–3005 cm⁻¹) respectively. At lower temperature (300 and 500ºC) the presence of number of bands representing functional groups in biochars but it disappeared in the temperature 800-1000ºC derived bio-chars. The shoulder around 1610 cm⁻¹ in the WHC and RHC bio-chars, allocated to the ‘aromatic compounds’, is still present at 800ºC temperature during the pyrolysis.

At 400ºC, there was greater transmittance at band of 1700 to 1000 cm⁻¹, stretching of the carboxyl group of C=O and the molecular bonds of C=C of the aromatic compounds compared to the biochar produced at higher temperatures.

In general, the presence of organic components with chemical responses and distinct structures is observed in the biochar samples, which affects on the reactivity of these materials. The biochars of
SD, WH, RH, TW and EC are composed of the carboxylic acid, ketone, alcohol, ester and aromatic compounds were identified. The persistence of char in the environment for a long time is due to its polycyclic aromatic structure [36] (GLASER et al., 2001). The stability and recalcitrance of biochar can contribute over the long period to retention of water in the soil [37] (OH et al. 2012). The chemical interactions between biochar and the environment are directly related to its surface structure. The presence of the carboxyl and hydroxyl groups propose that all biochar samples present in this paper could have utilized as a soil amendment for improving of the cation exchange capacity in soil [37] (OH et al. 2012).

Figures 3(a) to 3(e). FTIR analysis of saw dust char, wheat hull char, rice hull char, tea wastes char, and eucalyptus shell char.
4. Conclusion
This study demonstrated the pyrolysis temperature effect on the physical and chemical characteristics of prepared biochars. The influence of the thermal modification on the Saw Dust, Rice Hull, Wheat Hull, Tea Wastes, and Eucalyptus Shell was investigated. With increasing in pyrolysis temperature, the yield%, VM and hydroxyl and aromatic functional groups of biochar significantly decreases. The degree of carbonization for biochars was enhanced with increasing temperature from 400°C to 1000°C. The aromaticity was considerably improved in biochar at high temperatures because a phase transition occurred in studied biomass samples.
FT-IR analyses have shown to high potential to get a deeper understanding of structural relationship with their functional groups.

References
[1] McGowan F 1991. Controlling the greenhouse effect: the role of renewables. Energy Policy, 111–8.
[2] Demirbas A 2005. Potential applications of renewable energy sources, biomass combustion problems in boiler power systems and combustion related environmental issues. Progress in Energy and Combustion Science, 31, 171–192.
[3] Chew JJ and Doshi V 2011. Recent advances in biomass pretreatment—Torrefaction fundamentals and technology. Renewable and Sustainable Energy Reviews, 15, 4212–22.
[4] Williams PT and Besler S 1996. The influence of temperature and heating rate on the slow pyrolysis of biomass, Renewable Energy 1481, 6–7.
[5] Antal MJJ and Grønli M 2003. The Art, Science, and Technology of Charcoal Production, Industrial & Engineering Chemistry Research, 42, 1619–1640.
[6] Downie A and Crosky A 2009. Munroe, P. Physical properties of biochar. In: Biochar for Environmental Management: Science and Technology. 1st edn (eds Lehmman J, Joseph S), Earthscan, London, 13–29.
[7] Angin D 2013. Effect of Pyrolysis Temperature and Heating Rate on Biochar Obtained from Pyrolysis of Safflower Seed Press Cake. Bioresource Technology, 128, 593–597.
[8] Yaman S 2004. Pyrolysis of biomass to produce fuels and chemical feedstock. Energy Conversion and Management, 45 (5), 651-671.
[9] Demirbas A 2004a. Effects of temperature and particle size on bio-char yield from pyrolysis of agricultural residues. J. Ana. and App. Pyro., 72, 243–248.
[10] Demirbas A 2004b. Combustion Characteristics of different biomass fuels. Prog. in En. and Comb. Sci., 30, 219–230.
[11] Mena HLE, Pecora AAB, Beraldo AL 2014. Slow Pyrolysis of Bamboo biomass: Analysis of Biochar properties. Chemical Engineering Transactions, 37, 115-120.
[12] Movasaghi Z, Rehman S, ur Rehman I 2008. Fourier Transform Infrared (FTIR) Spectroscopy of Biological Tissues. Applied Spectroscopy Reviews, 43, 134-179.
[13] Vassilev SV, Baxter D, Andersen LK, Vassileva CG 2010. An overview of the chemical composition of biomass. Fuel, 89, 913–933.
[14] Demirbas A 2002a. Relationships between heating value and lignin, moisture, ash and extractive contents of biomass fuels. Energy Explor. Exploit., 20, 105–11.
[15] Demirbas A 2002b. Fuel characteristics of olive husk and walnut, hazelnut, sunflower and almond shells. Energy Sources, 24, 213–9.
[16] Titiloye JO 2013. Abu Bakar, M.S. Odetoye, T.E. Thermochemical characterstic of agricultural wastes from West Africa. Industrial Crops and Products, 47, 199–203.
[17] Cuiping L, Yanyongjie CW, Haitao H 2004. Chemical elemental characteristics of biomass fuels in China. Biomass Bioenerg., 27, 119–30.
[18] Baxter LL, Miles TR, Jr Miles TR, Jenkins BM, Milne T, Dayton D 1998. The behaviour of inorganic material in biomass-fired power boilers: field and laboratory experiences. Fuel Process Technol., 54, 47–78.
[19] Qian Y, Zuo C, Tan J, He J 2007. Structural analysis of bio-oils from sub and supercritical water liquefaction of woody biomass. Energy, 32, 196-202.
[20] Ghani AWAK 2014. Sawdust-derived Biochar: Characterization and CO2 adsorption/desorption study. J. of App. Sci., 14(13), 1450-1454.
[21] Guo J and Chen B 2014. Insights on the molecular mechanism for the recalcitrance of biochar: interactive effects of carbon and silicon components. Environ. Sci. Technol., 48, 9103–9101.
[22] Sukiran MA, Kheang LS, Bakar NA, May CY 2011. Production and characterization of biochar from the pyrolysis of empty fruit bunches. J. Appl. Sci., 8, 984–988.
[23] Jindo K, Mizumo H, Sawada Y, Sanchez-Monedero MA, Sonoki T 2014. Physical and chemical characterization of biochars derived from different agricultural residues. Biogeosciences, 11, 6613–6621.
[24] Keiluweit M, Nico PS, Johnson MG, Kleber M 2010. Dynamic molecular structure of plant biomass-derived black carbon (Biochar). Environmental Science & Technology, 44, 1247–1253.
[25] Spokas KA 2010. Review of the stability of biochar in soils: predictability of O:C molar ratios. Carbon Manag, 1(2), 289-303.
[26] Bi YY, Guan JP, Wang DL 2008. Comprehensive Utilization Technology of Straw Resources in China (in Chinese), Beijing: China Agricultural Science and Technology Press.
[27] Jensen A, Dam-Johansen K, Wojtowicz MA, Serio MA 1998. TG-FTIR Study of the Influence of Potassium Chloride on Wheat Straw Pyrolysis, Energy & Fuels, 12, 929–938.
[28] Collard FX and Blin J 2014. A review on pyrolysis of biomass constituents: Mechanisms and composition of the products obtained from the conversion of cellulose, hemicelluloses and lignin. Renew. Sustain. Energy Rev., 38, 594–608.
[29] Kan T, Strezov V, Evans TJ 2016. Lignocellulosic biomass pyrolysis: A review of product properties and effects of pyrolysis parameters. Renewable and Sustainable Energy Reviews, 57, 1126-1140.
[30] Haslinawati MM, Matori KA, Wahab ZA, Sidek HAA, Zainal AT 2009. Effects of temperature on the ceramic from rice husk ash. Int. J. Basic Appl. Sci., 9, 111–116.
[31] Wu W, Yang M, Feng Q, McGrouther K, Wang H, Lu H, Chen Y 2012. Chemical characterization of rice straw-derived biochar for soil amendment. Biomass & Bioenergy, 47, 268–276.
[32] Chen B and Chen Z 2009. Sorption of naphthalene and 1-naphthol by biochars of orange peels with different pyrolytic temperatures. Chemosphere, 76, 127-133.
[33] Lee JW 2010. Characterization of of biochars produced from corn-stovers for soil amendment. Environmental Science and Technology, 7970–7974.
[34] Peng X, Ye LL, Wang CH, Zhou H, Sun B 2011. Temperature and duration-depend rice straw-derived biochar: characteristics and its effects on soil properties of an Untisol in southern China. Soil Tillage Res., 112, 159–166.
[35] Yuan JH, Xu RK, Zhang H 2011. The forms of alkalis in the biochar produced from crop residues at different temperatures. Bioresource. Technol., 102, 3488–3497.
[36] GLASER, B. et al. The Terra Preta phenomenon - a model for sustainable agriculture in the humid tropics. Naturwissens chaften. v. 88, p. 37-41, 2001.
[37] Oh TK, Choi BS, Shinogi Y, Chikushi J 2012) Characterization of biochar derived from three types of biomass. J Fac Agric, Kyushu Univ 57(1):61–66.