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Contribution of Parent Wood to the Final Properties of the Carbonaceous Skeleton via Pyrolysis

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Abstract- Wood branches of ten hardwood species were pyrolyzed at 450°C with 2.5°C/minutes in a flowing N_2-atmosphere. Physical and chemical properties of wood and its carbonaceous skeleton (CS) were measured. The CS properties were found to be species dependents. The ten species gave good biocarbon in considerable yields (35.82-45.23%) and were suitable for biocarbon production, especially when pyrolyzed at elevated temperatures to enhance their quality properties. *Prosopis juliflora* produced biocarbon with the highest yield, apparent density (0.581g/cm^3), gross heat of combustion of 7673 cal/g and the lowest volumetric shrinkage (35.01 %), ash content of 0.79 %, volatile matter content of 26.5 % and fixed carbon content of 69.23 %.

Keywords- *Wood, Biocarbon, Yield, Apparent density, Gross heat of combustion, Proximate analysis, Shrinkage.*

I. NTRODUCTION

Biomass resources include wood and wood wastes, agricultural crops and their waste byproducts, municipal solid waste, animal wastes, waste from food processing, and aquatic plants and algae. The major organic components of biomass can be classified as cellulose, hemicelluloses, and lignin.

As a fuel, biomass suffers from its bulky, fibrous, high moisture content and low-energy-density nature, leading to key issues including high transport cost and poor biomass grindability [1]. Converting biomass to biochar leads to a substantial increase in fuel mass energy density from ~10 GJ/ton of green biomass to ~28 GJ/ton of biochars prepared from pyrolysis at 320 °C, in comparison to 26 GJ/ton for Collie coal [1].

The methods available for energy production from biomass can be divided into two main categories: thermo-chemical and biological conversion routes. There are several thermo-chemical routes for biomass-based energy production, such as direct combustion, liquefaction, pyrolysis, supercritical water extraction, gasification, air–steam gasification and so on. Bio-oil can be used as a fuel in boilers, diesel engines or gas turbines for heat and electricity generation [2].

Pyrolysis is thermal degradation of biomass by heat in the absence of oxygen, which results in the production of charcoal (solid), bio-oil (liquid), and fuel gas products. Pyrolysis conditions are known to affect the chemical and physical characteristics of biochar [3]. Charcoal produced at high temperature will have lower value of volatile matter than charcoal produced at low temperature. In addition, the high value of volatile charcoal tends to be stronger, heavier, harder and easier for the ignition than low volatile charcoal. Therefore, high volatile charcoal is easier to ignite but may burn with smoky flame while low volatile charcoal is difficult to ignite and burns with less smoke [4].

The charcoal produced from high temperature will be higher in fixed carbon than the charcoal produced at lower temperature. In addition, the charcoal has the high volatile matter is lower in fixed carbon, which low fixed carbon tends to be harder, heavier, stronger and easier to ignite than high fixed carbon charcoal [4].

For high char production, a low temperature, low heating rate process would be chosen [5]. It was found that the char yield decreases and the char structure becomes more deranged with increasing temperature. Further, the volume shrinkage was found to be 45-70% [6].

In addition, the proximate composition of the biochar depends not only on the starting wood, but also the carbonization system [7].

This study was initiated to evaluate the properties of the pyrolytic products produced in the laboratory from ten species of timber and fruit trees grown in Egypt, study relationships between properties of biocarbon and the parent wood.

II. MATERIALS AND METHODS

2.1. *Raw Material*

Branches of ten hardwood species, namely *Casuarina glauca* Sieb., *Casuarina cunninghamiana* Miq., *Eucatyptus camaldulensis* Dehn., *Eucalyptus microtheca* F.V.M., *Prosopis juliflora* D.C., *Acacia ampliceps* MSLN, *Ficus retusa* Linn., *Citrus sinensis* Osbeck, *Malus domestica* Borkh. and *Psidium guajava* Linn. were used. Three trees were selected from each species from the same location. The ages of the selected trees ranged from 11-15 years old. The ages of the chosen branches were nearly similar in all species and varied from 6 to 8 years. The diameter outside bark of the selected trees ranged from 15-45 cm. From each of the selected trees, one of the primary branches was selected. Accordingly, three branches were selected from each species. The diameter outside bark of the selected branches ranged from 8-15 cm. Each of the selected branches was cut at height of 10 cm above its base at about 140-170 cm above ground level for *C. glauca*, *C. cunninghamiana*, and *F. retusa*, and 40-90 cm for the other species. From each isolated branch, one disc of about 20 cm along the grain was cut at height of 10 cm above the branch base that was specified for the determinations of wood properties. Furthermore, the subsequent disc, about 30 cm thick along the grain, was cut and used for pyrolysis process and consequently for the determinations of pyrolytic products properties as well as specific gravity of the original wood before the pyrolysis applying. For the disc specified for wood properties determinations, both the pith and outer- zone wood were discarded. The remainder volume of the disc was converted into meal by frequent crosscut using a disc saw machine. Then, wood meal was screened using different sieves depending on the standard methods for determinations of ash, total extractives and lignin contents of wood. For the disc specified for pyrolysis process, one bolt (about 1.8 cm tangentially and 30 cm long) from heartwood was cut longitudinally. A diametric strip (nominal 1.8 cm tangentially and radially, and 30cm longitudinally) was removed and subsequently crosscut into 12 cubic samples free of visible

2.2. *Pyrolysis Process*

The pyrolysis runs were carried out with a bench scale reactor (Figure. 1)

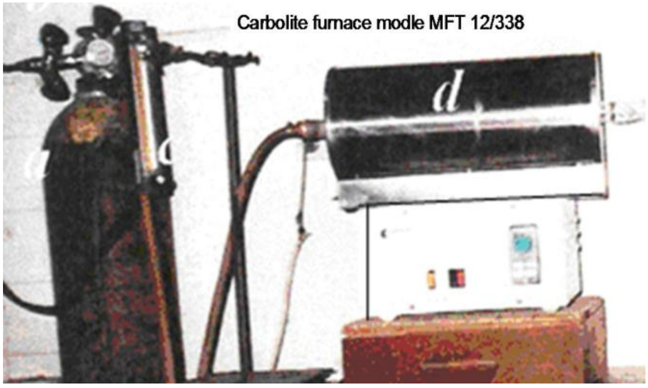

Figure 1. The pyrolytic apparatus: a) N2-cylinder, b) regulator, c) flow- meter and d) electric tube furnace.

The apparatus consists of an electric tube furnace (carbolite furnace modle MTF 12/338) controlled by a microprocessor temperature programmer with an error of ±5°C with an accuracy of 1°C and heating rate of 0.01°C/min., digital thermometer with a chromel alumel thermocouple (type K with an error of ±1°C), nitrogen regulator system consisted of a regulator and a flowmeter with an accuracy of ±2% of the full scale and the reactor body made up of Pyrex glass [8].

2.3. *Determination of wood properties*

The specific gravity (SG), ash content (AC), total extractives (TE) and lignin content (LC) were determined based on [9] & [10] and the ASTM standard methods. The SG was calculated by using Pycnometric displacement of water based on oven-dry weight and saturated volume. The AC was determined according to the [11]. The TE was determined according to the [12]. Furthermore, the LC of wood was determined according to the described by ASTM [13].

2.4. *Determination of biocarbon properties*

The biocarbon properties, namely yield (BY), apparent density (AD) and volumetric shrinkage (VS) were determined according to Hindi [10]. The BY was calculated based on the oven-dry weight of wood. The AD was measured using Pycnometric displacement of water based on oven-dry weight and saturated volume. The VS was determined based on saturated volume of wood. The gross heat of combustion (GHC) of biocarbon was determined using an adiabatic oxygen bomb calorimeter, Parr 1341, according to procedures recommended by Parr instruction manual and in accordance with ASTM [14]. The moisture, volatile matter, ash, and fixed carbon contents were determined according to the ASTM [15] for proximate analysis of wood charcoal.

III. RESULTS AND DISCUSSION

Wood properties, namely specific gravity (SG), ash content (AC), total extractives (TE) and lignin content were examined (Table 1). It is clear that each of the four wood properties are species dependent.

Table 1. Mean values[1,2] for specific gravity (SG), ash, total extractives (TE), and lignin contents of wood samples

Species	SG	AC (%)	TE (%)	LC (%)
Casuarina glauca	0.619^{BCD}	1.19^{CDE}	12.2^{DE}	27.7^{AB}
Casuarina cunninghamiana	0.505^{E}	1.01^{DEF}	13.8^{BCD}	25.6^{B}
Eucalyptus camaldulensis	0.563^{CDE}	0.78^{FG}	16.9^{BC}	28.9^{A}
Eucalyptus microtheca	0.792^{A}	0.89^{EFG}	17.6^{B}	27.8^{AB}
Prosopis juliflora	0.861^{A}	0.62^{G}	26.8^{A}	26.9^{AB}
Acacia ampliceps	0.633^{BC}	1.591^{B}	13.3^{CDE}	21.8^{C}
Ficus retusa	0.542^{CDE}	2.66^{A}	14.7^{BCD}	29.5^{A}
Citrus sinensis	0.683^{B}	1.35^{BC}	10.9^{DE}	22.2^{C}
Malus domestica	0.585^{BCDE}	0.61^{G}	9.1^{E}	21.5^{C}
Psidium guajava	0.531^{BE}	1.21^{CD}	12.6^{DE}	27.1^{AB}

[1] Means with the same letter are not differed significantly at 5% Level.

The main pyrolytic products, namely biocarbon, produced from the ten wood species was found to be species dependent (Figure 2).

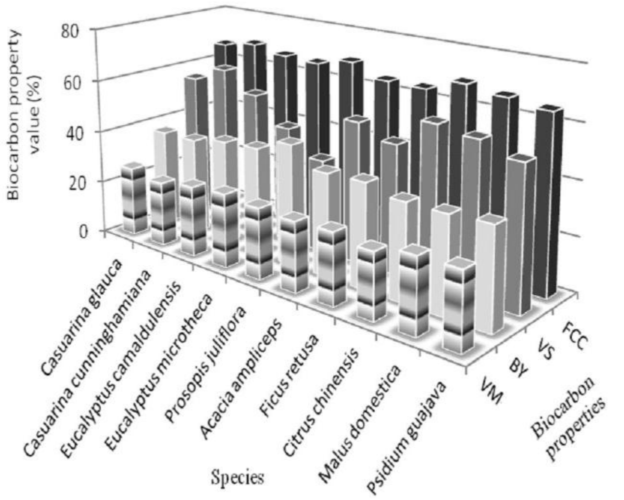

Figure 2. Volatiles content (VS), biocarbon yield (BY), volumetric shrinkage (VS) and fixed carbon content (FCC) of biocarbon made from the ten hardwood species.

Furthermore, the highest biocarbon yield (BY) was obtained from *P.juliflora* (45.23 %) while *C.sinensis* and *M.domestica* gave the lowest BY (35.83 and 35.87 %, respectively). However, the species other than *Prosopis juliflora* produced good BY ranged from 35.83 to 40.36%. The BY was directly related to TE and inversely to volumetric shrinkage (VS) as shown in Table 2 (equations no. 1 and 2).

The VS of biocarbon ranged from 35.01 to 61.52 % for *P.juliflora* and *C.cunninghamiana*, respectively. These woods shrinkaged higher than that expected except for *P.juliflora*. The VS of biochar was inversely related to each of the SG and TE (Table 2). Further, the *C.sinensis* and *C.cunninghamiana* had the lowest volatiles (VM) content of biocarbon of 24.16 and 24.23%, respectively. The other species had the highest VM of biocarbon (26.30-27.61%) except for *A.ampliceps* whereby it had a VM statistically equal to the other species. Also, the higher FCC of biocarbon was obtained from *P.juliflora*, *C.cunninghamiana* and *C.sinensis* (69.23, 68.98 and 68.69 %, respectively). Contrarily, *F.retusa*, *A.ampliceps* and *P.guajava* contained the lower FC of biocarbon (64.48, 64.63 and 65.17%, respectively).

Table 2. Regression equations between biocarbon and wood properties.

Simple regression	SEE	R^2
$BY^1 = 29.73+0.58\ TE^2$.	2.22	0.796^{**}
$BY^1 = 55.71-0.33\ VS^3$.	2.43	0.750^{**}
$AD^4 = 0.14+0.52\ SG^5$.	0.04	0.859^{**}
$VS^3 = 82.95- 49.26\ SG^5$.	5.54	0.738^{**}
$VS^3 = 71.47-1.31\ TE^2$.	4.88	0.805^{**}
$AC_1{}^6 = 0.316 + 1.74\ AC_2{}^7$.	0.56	0.881^{**}

[1] Biocarbon yield; [2] Total extractives of wood; [3] Volumetric shrinkage of biocarbon; [4] Apparent density of biocarbon; [5] Specific gravity of wood; [6] Ash content of biocarbon; [7] Ash content of wood (at 0.05 significance level).

The higher apparent density (AD) of biocarbon was obtained from *P.juliflora*, *E.microtheca* and *C.sinensis* (0.581, 0.549 and 0.533 g/cm^3, respectively). Whereas, *F.retusa*, *P.guajava* and *E.camaldulensis* gave the lowest values (0.371, 0.385 and 0.429 g/cm^3, respectively) (Fig. 3).

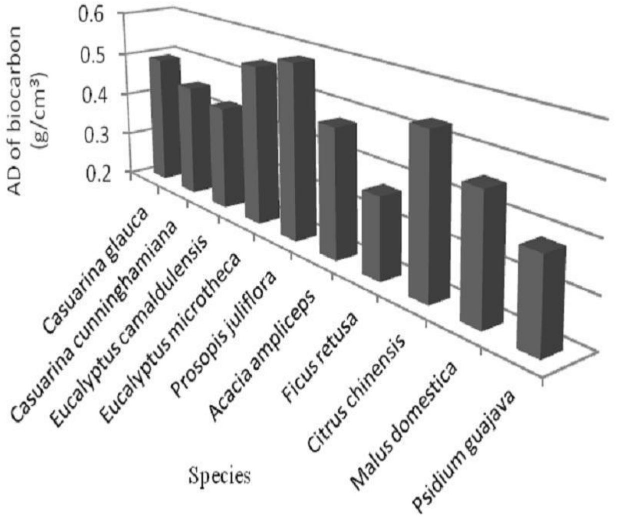

Figure 3. Apparent density (AD) of biocarbon made from the ten hardwood species.

It is clear from Table 2 that the AD and AC of biocarbon was directly related to the SG of the parent wood, respectively [16] & [17].

The higher AC of biocarbons were contained in *F.retusa* and *A.ampliceps* biocarbon (4.52 and 3.50 %, respectively). Whereas, *P.juliflora* and *M.domestica* contained lower AC (0.79 and 1.11 %, respectively) as presented at Fig. 4.

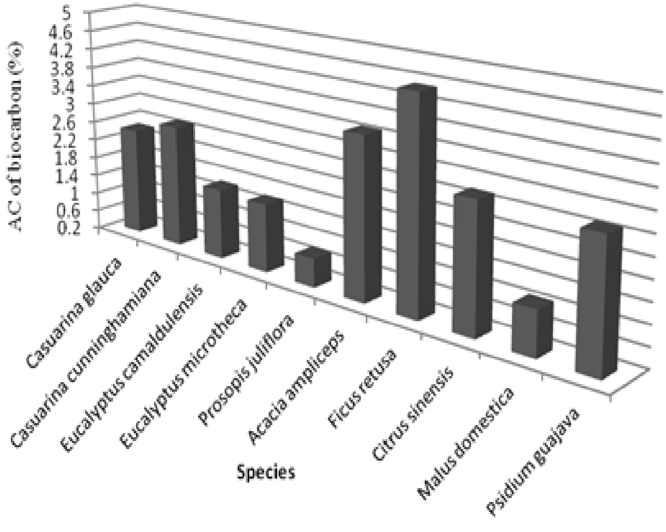

Figure 4. Ash content (AC) of biocarbon made from the ten hardwood species

The higher gross heat of combustion (GHC) of biocarbon was obtained from *P.juliflora* (7673 cal/g) as shown in Fig. 5. Contrarily, *F.retusa* and *A.ampliceps* had the lowest values (6844 and 6844 cal/g, respectively). However, the other species are considered as good fuels.

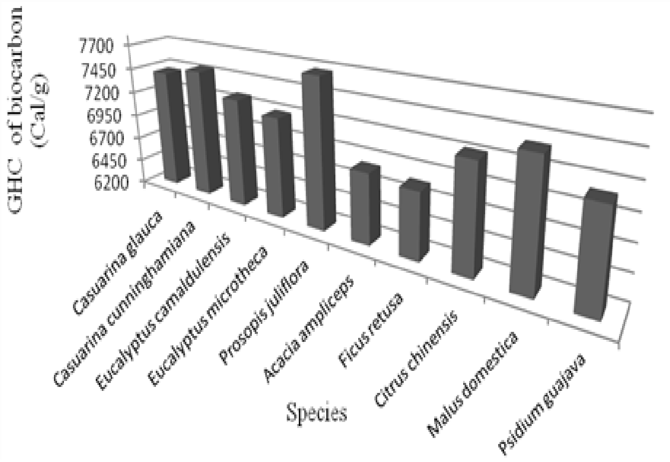

Figure 5. Gross heat of combustion (GHC) of biocarbon made from the ten hardwood species.

The GHC of biocarbon was related directly with fixed carbon (FC) of biocarbon and inversely to ash content (AC) of biocarbon (Table 2).

Under the pyrolysis conditions used, the ten wood species produced good biocarbon for domestic purposes in considerable yields. The resulted biocarbon had relatively high VMC and low FCC that decreased its value as an industrial agent. However, this defect can be readjusted by producing it higher temperatures. *P.juliflora* produced biocarbon with the highest BY, AD, GHC and the lowest VS and AC. If the FCC is readjusted to the accepted level (≥80%), it will be an ideal raw material for production of industrial grade biocarbon.

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