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Characterization Of Biocoal From Hydrothermal Carbonization Of Pine Needles And Palm Leaves

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***Abstract*—This work describes preparation of biocoal Pn-HTC and Pl-HTC by hydrothermal carbonization HTC of pine needles and palm leaves respectively. The biomass samples were treated with hot deionized water at a temperature range 180-250 °Cunder saturated pressure and inert atmosphere for six hours.The obtained coal-like residues was well-characterized. They had a porous structure and showed very interesting energetic properties comparedto many biomass with derived energy such as bamboo, paper and food. The recovery of high energy conversion efficiency for Pn-HTC and Pl-HTC are78.4% and 88.7 respectively are recorded at the maximum reactor temperature 225ºC. Calorific values were evaluated at 25.2 and 24.8 Mj/Kg for Pn-HTC and Pl-HTC respectively and showed 21 % increase in energy content compared to that of raw biomass. Palm leaves presented higher coal and fixed carbon yields and lower mass of volatile matter. The analysis of processed water showed good fertilizing property rich of nutrients, especially nitrogen, phosphorus, and potassium. The results of this study demonstrated that hydrothermal carbonization is a viable option for the production of biocoal thru energy recovery from pine needles and palm leaves biomass.**

***Keywords*—biocoal, biomass, hydrothermal carbonization, Renewable energy**

1. Introduction

The economy of the world is outgrowing the natural capacity of the earth, and thus there is a need for deep review in energy policy. Our global footprint now exceeded the world capacity to the point where we need to transform our lifestyles from ecological deficit to ecological credit. The application of biomass-derived energy is gaining much importance due to the decreased supply of fossil energy and growing environmental concerns. Among biomass-to-energy conversion methods, direct combustion and co-combustion with low rank coals are widely investigated, as these methods have less risk, are less expensive, and have the highest potential among short term options for realizing biomass energy utilization. Several reviews on biomass combustion for heat generation concluded that direct combustion is not a satisfying option owing to inherent properties of biomass feedstocks such as high moisture and oxygen contents, and high alkaline earth metal content [1-3]. To overcome these problems, it is necessary to pre-treat, homogenizeor modify the biomass feedstock prior to combustion into a form similar to coal in order to accommodate existing coal-fired plants.

One method in the right track could be hydrothermal carbonization (HTC) of abundant biomass. HTC is a process similar to peat or coal formation [3,4] with time scale decreasing from millions of years to few days. In such process, sugars and carbohydrates are transformed into black soil, peat, brown coal or other carbonaceous materials [5]. Hydrothermal treatment offers significant advantages for biomass conversion compared to other thermal methods including the lack of an energy-extensive drying process, high efficient conversion and relatively low operation temperature in a one-step process.

HTC process is relatively simple, requiring mainly a closed vessel that contains the wet biomass and heating to temperatures between 180 and 250°C over a period ranging from a few hours to a day [6,7, 10]. The process of hydrothermal carbonization includes several reaction mechanisms, such as hydrolysis, dehydration, decarboxylation, polymerization and aromatization. The detailed reactions have been only well characterized for a few types of biomass, such as cellulose [11- 13]. The process takes place effectively only in water and is exothermic. The raw material used for hydrothermal carbonization is preferably plant biomass with high content of lignin, cellulose and hemicellulose, e.g. crop waste or wood material [10]. The products of HTC are distributed in a solid phase “Biocoal”, a liquid phase “processed water” and a gas phase (small amount) [6, 7, 12, 13].

In this work, pine needles and palm leaves were selected as biomass-derived energy. Pines (Pinus genus) are one of the most recognizable trees on the planet. Individual needles range in length from 2-3 to up to 6-20 cm. The needles typically grow in clusters and are traditionally dark green in color [8].Date palm tree (genus Phoenix) is among the most important of Sahara desert plants and it is spread in all Arabic country for use as a staple date food. The leaves are 3–6 m long, with spines on the petiole, and pinnate, with about 150 leaflets. The leaflets are 30 cm long and 2 cm wide. The full span of the crown ranges from 6 to 10 m [9]. Pine needles and palm leaves as biomass have water content values about 50-60 % at harvest which makes them suitable materials for HTC. The characteristics of biocoal as well as the water process from pine needles and palm leaves residues by hydrothermal carbonization are examined, and the feasibility for solid fuel recovery are evaluated.

2. Methodology

2.1 HTC reactor and Test Procedure

Experimental runs of HTC of pine needles and palm leaves were performed in a batch Teflon-lined autoclave reactor. The HTC reactor is a stainless steel cylinder 11.5 cm high, 5.5 cm inside diameter and 150 ml capacity. A 1.7-kW electric furnace is used for heating. The reactor is fitted with temperature and pressure sensors, as well as pressure relieve valve (fig. 1).

Prior to the test, pre-weighed batches (approximately 10 g) of small fragmented pieces of pine needles or palm leaves and pellets of citric acid (10 mg) used as catalyst were dispersed in deionized water (100 mL) [6]. After closing, the nitrogen gas is injected to purge the air outside the reactor [6, 15, and 16], heated at different temperatures during six hours [14] within the 25-800˚C temperature range. The temperature and pressure are recorded at a regular interval of 5 min for the first 90 min and later at a regular interval of 30 min. At the end of each experiment, the biocoal is filtered, and dried in an oven at 105 ºC for 4 h and then weighed to estimate the yield. The processed water is collected also, and weighed to determine the mass balance

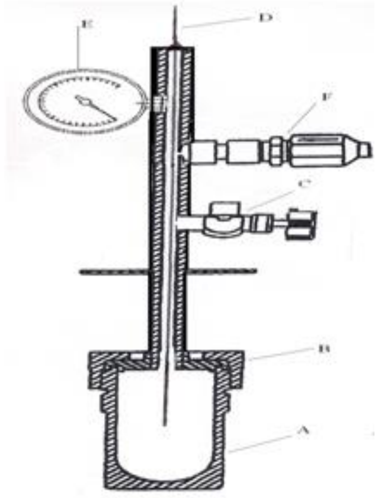


Figure 1. Schematic drawing of HTC cylinder: A: vessel, B: pressure vessel closure, C: valve, D: thermocouple (T_R), E: pressure gauge, F: relieve valve

2.2 Analytical methods

High resolution imaging was performed using a transmission electron microscope operating at 300 kV (Titan Cryo Twin, FEI Company, Hillsboro, OR). Thermogravimetric – differential scanning calorimetric (TG-DTA) curves were recorded on SETARAM LABSYS Thermal analyzer.

Ash and Volatile Matter were determined according to ASTM D 3174 and ASTM D 3175 methods respectively (Samples were run dry). Heating Values of the dried pine needles and palm leaves, and the resulting coal were determined using a bomb calorimeter (Leco AC-500). They were reported as gross heat combustion at constant volume (HHV).% C of coal was analyzed using Elemental Analyzer (Leco SC-144DR). Atomic absorption analysis was used in order to determine the nutrient content in the processed water with Unicam Corporation AA analyst 929 instrument. Total nitrogen was analyzed by Kjeldahl method for the quantitative determination of nitrogen in processed water. Phosphorus content was analyzed using Merck Spectroquant Multycolorimeter according to method 1.00798 (the method is analogous to EPA 365.2+3 and DIN EN ISO 6878).

3. Results and Discussions

3.1 Raw materials

Pine needles “Pinuspinea” and palm leaves “Phoenix dactylifera” are collected from local gardens. The raw material was cut into small particle sizes and was further used without any dehydration. Their physical and chemical properties are shown in Table 1.

Property[db] [%]	Raw Biomass	
	Pine needle (Pn)	Palm leaves (PL)
Moisture	62.5	57.6
Volatile Matter	81.9	75.9
Fixed carbon	14.9	20.1
Ash	2.5	4.0
Carbon content (C)	45.5	42.5
Sulfur content (S)	0.095	0.169
Higher heating value [MJ/kg]	20.1	19.2

Table 1. Chemical analysis of Pine needles and Palm leaves

3.2 Hydrothermal carbonization process conditions

Batch of Pine needles or Palm leaves were run at 500°C furnace temperature with a heating rate of 3˚C/min, and the actual maximum reactor temperature is designated Tmax.

The examination of the variation of the recorded temperature versus time (Figure 3), showed that the heating arrangement is able to reach quickly around Tmax 225 °C in less than 60 min and then remained approximately constant. The reason for measuring the experimental HTC reactor temperature designated (T_R) was to observe the exothermic onsets of the reactions throughout the test run.

In parallel, the variation of the reaction pressure versus time are examined (Figure 3) showing a quick increase during the first hour to reach 140 psi and then became stable approximately for Palm leaves but continue to increase slowly for Pine needles. The pressure increase is explained by the formation of gases from the dehydration and decomposition of raw biomass while the difference in behavior is due to their intrinsic composition.

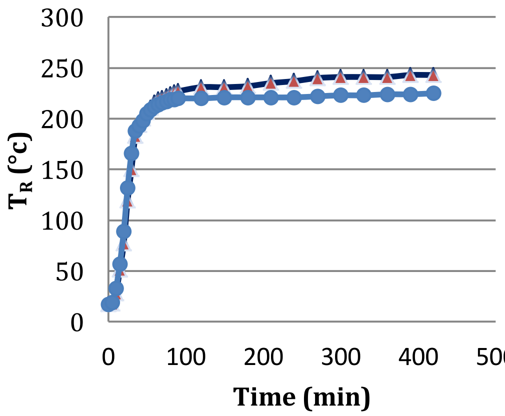


Figure 2. Variation of reaction temperature with time for Pine needles ( ) and Palm leaves ( )

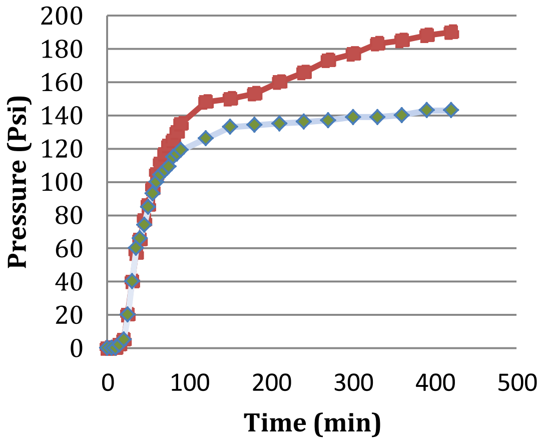
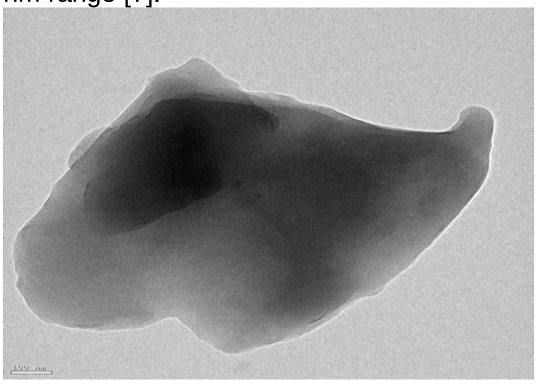


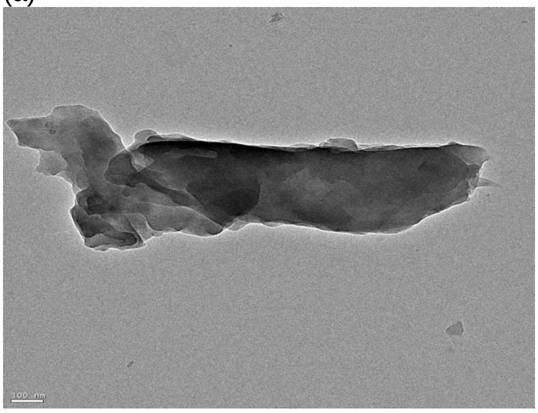
Figure 3. Variation of reaction pressure with time for Pine needles ( ) and Palm leaves ( )

3.3. Characteristics of Biocoal

The analysis of TEM pictures of HTC-treated pine needles and palm leaves local structure (fig 4), indicates a complete change towards a mesoporous sponge-like with cubic nanostructures. This nanostructure is characterized by a highly functional surface, ideal for water sorption, ion binding, or as a catalyst support, with structural elements in the 20–50 nm range [7].



(a)



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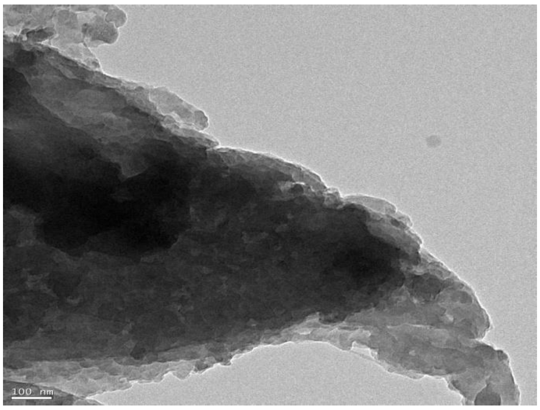
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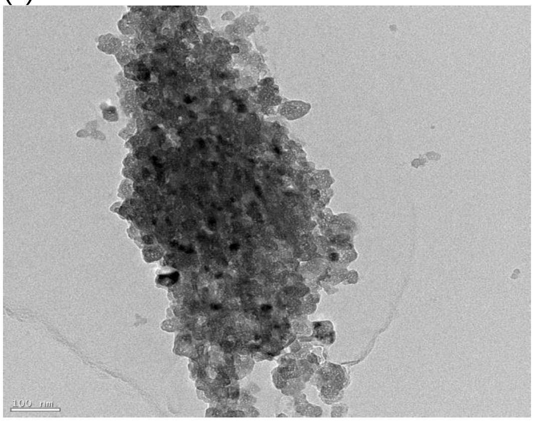
(d)

Figure 4. HRTEM images of (a) raw pine needles (b) raw palm leaves (c) Pn-HTC and (d) Pl-HTC

Analysis, percentages and yields for raw pine needles and palm leaves and biocoal produced by HTC are summarized in table 2.

Parameters	**Biomass**	
	Pine needle	Palm leaves
Carbonization Tmax°C	225	243
Time (hours)	6	6
Volatile Matter (%)	82.1	73.5
Fixed Carbon (%)	16.1	24.5
Fixed Carbon yield(%)	10.3	17.5
Coal yield (%)	62.6	68.8
Carbon (%)	52.6	50.9
Ash (%)	1.8	2
Coal heating value (Mragejoules/kilograms	25.2	24.8
Energy conversion efficiency (%)	78.4	88.7

Table 2: Characteristics of Biocoal

HTC of pine needles and palm leaves leads to the formation of biocoal characterized by high coal heating values (CHV), high efficiency of hydrothermal energy conversion and low rate of ash. But, the comparison of analysis shows a higher coal and fixed carbon yields and lower mass of volatile matter for palm leaves.

The comparison of analysis results of raw materials reported in table 1 and those of biocoal reported in table 2 shows a significant changes. In fact, there are an increase in % C of about 15% for pine needles and about 20 % for palm leaves in going from raw to biocoal materials. The examination of coal heating values (CHV) indicates also an increase of 25 % in comparison with their corresponding raw materials.
In addition, the ash contents formed during combustion of biocoal are smaller than those formed during combustion of the starting raw materials. Th eash content decreases for about 50% for both pine needles and palm leaves. The lower ash content of biocoal is attributed to the fact that most inorganic compounds contained in the raw material are dissolved in the water under hydrothermal conditions [16].
The characteristics of various biomass materials (bamboo, paper, and food) are reported in table 3 [14;17]. The comparison with those of pine needles and palm leaves shows a significant differences, attributed to the difference in the composition of raw biomass. The biocoal obtained by HTC from pine needles and palm leaves have higher Energy conversion efficiency, Coal heating value and lower ash content. These results presents pine needles and palm leaves as an interesting biomass for the production of biocoal as energy carrier.

Parameters	**Biomass**		
	Bamboo [14]	Paper [17]	Food[17]
Carbonization Tmax°C	220	250	250
Time (hours)	20	20	20
Volatile Matter (%)	NR	52.8	53.4
Fixed Carbon (%)	NR	19.8	29.7
Fixed Carbon yield(%)	NR	8.5	15.8
Coal yield (%)	45	29.2	43.8
Carbon (%)	NR	57.4	67.6
Ash (%)	NR	24.2	11.2
Coal heating value (Megajoules/kilogram)	NR	8.5	15.8
Energy conversion efficiency (%)	76.90	49.8	70.3

Table 3: Characteristics of biomass materials

Thermal analysis plays an important role in studying the structure and properties of materials. In TGA, the percent weight losses of pine needles and the palm leaves samples are recorded under heating at a uniform rate in inert (nitrogen, N_2) gas flows. The TGA and DTA curves are obtained as % mass loss versus temperature as shown in (fig. 5). The temperature ranges and the percentage mass losses of the decomposition reaction are given in Table (4) together with the associated enthalpy (heat).

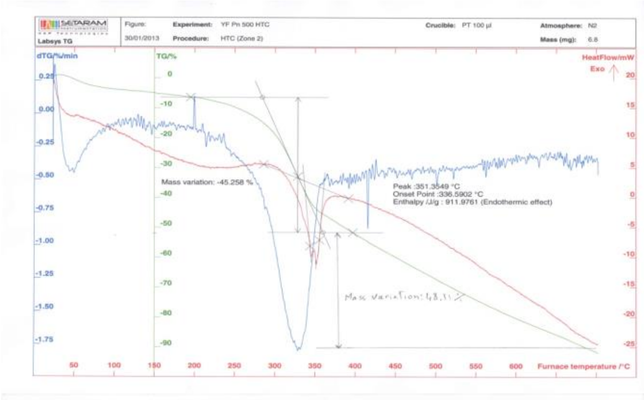

Figure 5. Thermal analysis of Pn-HTC

The analysis of curves shows an increase of the temperature from room temperature to almost 700 °C. The weight loss that occurs when the samples are heated to around 100 °C came from the evaporation of moisture. That one occurred between 150 and 450 °C is due to organic materials decomposition and volatilization. Further weight losses came from coke formation in the absence of air. The total percentage weight loss during heating represents the loss of different gases that are produced during the coke formation.

The pine needles and the palm leaves samples showed a large parental weight losses when the temperature has increased to around 350 °C, which is due to coking of the carbon materials and loss of significant amounts of gases. The comparison of weight losses showed a higher loss for pine needles.

Compound	Biomass Properties		
	% Experimental mass loss	T (^{0}C)	ΔH (J/g)
Pn-HTC	45.26	351.35	911.98
	48.11	400-700	
Pl-HTC	35.8	280.3 345.0	-165.5
	21.0	415.8 509.5	-173.7 51.5

Table 4. Thermal Analysis of Pn-HTC and Pl-HTC

3.3 Nutrients in process water

It is generally known that water plays a significant role as a solvent and reactant in the HTC process. The liquid phase is expected to contain a high load of organics and inorganics compounds (table 5) [14].In fact, a drop in pH of aqueous phase is observed after HTC reaction. The initial pH was 4.15 while the final pH was 3.3-3.5. This is explained by the formation of a variety of organic acids that typically occur during HTC process (Table 5) [11].

Atomic absorption analysis of the processed water collected from Pine needles or palm leaves hydrothermal carbonization was carried out. Analysis of potassium was performed by AAS on filtered samples. Total Nitrogen was measured by Kjeldalh method. The liquid phase was found to contain moderate values of potassium and relatively high amount of phosphorus and a valuable amount of nitrogen is observed.

Therefore the water phase may contain lots of valuable nutrients and can be regarded as a soil amendment. The analysis results of processed water collected after HTC of bamboo, as well as other biomass material, at similar conditions are reported in table 5 [14]. The comparison indicates that the processed water from HTC of pine needles and palm leaves is rich in nutrients and can be a useful fertilizer**.**

Parameters	Biomass		
	pine needles	palm leaves	Bamboo [14]
Carbonization temp. (^{o}C)	225	244	220
Time (h)	6	6	6
Mass of sample (g)	10	10	10
Volume of water added (ml)	100	100	300
Potassium (mg/L)	443	780	1642
Process water total nitrogen (mg/L)	779	90.7	100
Phosphorus (mg/L)	44	18.9	52
pH	3.3	3.5	3.4

Table 5. Comparison of processed water from HTC of pine needles and palm leaves with that of bamboo.

4. Conclusion

Under HTC conditions, physical and chemical properties of pine needles and palm leaves are altered. Under heating and pressure, we can observe the formation of brown coal-like with porous structure. The maximum reactor temperature reached around 225 ^{0}C after a short time. Biocoal obtained by HTC from pine needles and palm leaves are characterized by high efficiency energy conversion, a higher calorific values and lower rates of ash. When compared to those from other biomass such as bamboo, paper and food, these characteristics make them better energy carrier.

Weight losses are observed by TGA. The pine needles and the palm leaves samples present large parental weight losses when the temperature has increased to around 300 °C, caused by significant loss of gases and coking of carbon material. The comparison of weight losses shows a higher rate loss with pine needles.

The analysis of processed water from HTC of pine needles and palm leaves show a solution rich in nutrients such as potassium and a high nitrogen content. Thus the processed water can be a useful fertilizer.

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