

Article

The Impact of a Mild Sub-Critical Hydrothermal Carbonization Pretreatment on *Umbila* Wood. A Mass and Energy Balance Perspective

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Abstract: Over the last years, the pretreatment of biomass as a source of energy has become one of the most important steps of biomass conversion. In this work the effect of a mild subcritical hydrothermal carbonization of a tropical woody biomass was studied. Results indicate considerable change in carbon content from 52.78% to 65.1%, reduction of oxygen content from 41.14% to 28.72% and ash slagging and fouling potential. Even though decarboxylation, decarbonylation and dehydration reactions take place, dehydration is the one that prevails. The mass and energy balance was affected by the treatment conditions than the severity of the treatment.

Keywords: hydrothermal carbonisation; pre-treatment; biomass; solid bio fuels

1. Introduction

The World faces an energy crisis and increasing environmental pressures as a result of the development of global industrialization and extensive use of fossil resources. Due to its abundance and renewability, biomass has become one of the most important sustainable energy resource alternatives. As the demand for this kind of energy is growing, the utilisation of solid wood as Fuel has changed from its traditional role as a locally utilized form of energy into an internationally traded energy commodity. This has led to trade flows not only within Europe, but also in other parts of the World, including Mozambique.

Mozambique is an African country with vast forestry resources, including 120 tropical wood species [1], some of them with internationally recognized high commercial value. Thus, exportation of timber is a commercial option of considerable value for the country. However, evidences of the selective logging practices can be found. According to Marzoli [2], only three wood species (*Azelia quanzensis* Welwn, *Milletia stuhlmannii* Taub, and *Pterocarpus angolensis* DC), locally known respectively as chanFuta, jambire and umbila, represented 78% of the total wood exploited in Mozambique in 2004. Moreover, a considerable biomass material such as bagasse, rice husks, sawdust, coconut husks and shells, cashew nut shell and lump charcoal waste is available in the country as residues. The potential biomass residues from forest logging and timber processing were estimated at about 2.7 PJ [3]; however, its utilization as a Fuel is marginal. In this context, an integral and efficient use of timber including residues would contribute to reduce the depletion of this species and therefore contribute to a certain extend to the protection of the forest.

Although biomass is an attractive renewable source of energy, in general it is difficult to handle, transport, store and use [4–6], due to low homogeneity, energy density, and presence of non-combustible inorganic constituents which leads to different problems in energy conversion units like deposition, sintering, agglomeration, fouling and corrosion [7]. It is important to the production of an affordable Fuel alternative which satisfies requirements for biochemical or thermochemical conversion processes, such as fermentation, combustion, gasification, pyrolysis *etc.* requires physical and/or chemical pretreatment.

The hydrothermal carbonization also known as wet torrefaction or wet pyrolysis process is a spontaneous, exothermal and relatively low temperature (175–350 °C) process which, under pressures and subcritical water converts lignocellulosic biomass in order to obtain a carbon-rich solid fraction, so called biochar, biocoal, hydrochar or HTC-char [8–11]. It has shown that hemicellulose, which is the most susceptible to thermal decomposition of three main components of the lignocellulosic biomass [12,13], is decomposed first, while most of the cellulose is retained and lignin fraction, produces apart from char, non-condensable gases such as H₂, CO, CO₂, CH₄ and a large variety of water-soluble organic compounds. However, due to the formation of a multitude of Furan-type dehydrated intermediates from carbohydrates and the complexity of the chemistry, the formation process and the final material structures are rather complicated and a clear scheme has not been reported [14].

Even though, the chemistry of the process for converting biomass into biochar is not yet completely understood [15], it is known that the HTC-coal formation results from hydrolysis, dehydration, decarboxylation, polymerization and aromatization reactions, which in essence are respectively cleavage of ester and ether bonds, removal of biomass water, elimination of carboxyl groups and condensation [9,15].

The main advantage of this process is that it can convert wet input materials, which include animal manures, human waste, sewage sludge, as well as aquaculture and algal residues into carbonaceous solids at relatively high yields without the need for an energy-intensive drying before or during the process [16].

Research on HTC has been carried out over the last few years by several researchers [8–11,17], mainly focusing on the effect of HTC of woody and herbaceous biomass feedstock. In spite of its importance, it is noteworthy that there is only a small amount of research published on the subject of mass and energy balance of HTC process specifically for longer treatment time with or without the use of catalysts. In the present study, a hydrothermal carbonization process was conducted to pretreat umbilica. The objective of this work was not only to investigate the impact of a mild subcritical HTC on pretreatment of biomass but also the mass and energy balance of the process by characterizing and quantifying the solid, liquid and gaseous products.

2. Results and Discussion

2.1. Effect of Pretreatment on Elemental Composition and Ash Characteristics

The Table 1 displays considerable changes in elemental composition due to the effect of the treatment and its severity. As a result of carbonization, the volatile content in the solid decreased substantially, especially in the acid treatment, while the fixed carbon increased from 19.65% wt to 41.4% wt and it was greatly influenced by process conditions. Ash content varied incoherently with treatments and the severity index. It was observed reduction from 0.77 for untreated biomass to 0.3% wt d.b. for water treatment and increment on diluted acid treatments.

Table 1. Proximate and ultimate analysis of untreated and HTC biomass.

	U0	UW1	UW2	UA1	UA2
<i>Proximate analysis (% wt d.b.)</i>					
Fixed Carbon	20	25	27	40	42
Volatile Matter	80	75	73	60	57
Ash	0.8	0.3	0.3	0.8	1
<i>Ultimate analysis (% wt d.b.)</i>					
Carbon (C)	53	54	56	63	65
Hydrogen (H)	6	6	6	5	5
Nitrogen (N)	0.1	0.2	0.3	0.4	0.4
Oxygen (O) *	41	40	38	31	29
Chlorine (Cl)	<0.01	<0.01	<0.01	<0.01	<0.01
Sulphur (S)	<0.01	<0.01	<0.01	1	0.7

* Determined as difference between 100 and the sum of C and H.

The concentration of Cl, which during combustion play an important role as alkaline carrier and also well known to accelerate corrosion rate through the flue gases did not change and it was below the detection limits, while concentrations of nitrogen (N) showed a very slight change in all treatments. On other hand, a considerable change in the concentrations of sulphur (S) was observed, due to the use

of H₂SO₄ as catalyst (Table 1). Ash related problems such as slagging and fouling in different kind of combustion boilers continue to be the most important reason for unscheduled stops of boilers.

The ash fouling potential of treated biomass was reduced from high tendency to levels of low risk of fouling potential, below 0.6, while the slagging potential even with a considerable reduction in all treatments it still at level of severe potential (Table 2).

Table 2. Ash composition and evaluation of slagging and fouling tendency based on different indexes.

Ash composition	Unit	U0	UW1	UW2	UA1	UA2
SiO ₂	% wt d.b.	0.014	0.022	0.010	0.023	0.018
Al ₂ O ₃	% wt d.b.	0.003	0.002	0.002	0.067	0.039
CaO	% wt d.b.	0.252	0.019	0.011	0.067	0.042
Fe ₂ O ₃	% wt d.b.	0.027	0.014	0.012	0.194	0.113
K ₂ O	% wt d.b.	0.451	0.010	0.007	0.008	0.008
MgO	% wt d.b.	0.095	0.044	0.014	0.021	0.012
MnO	% wt d.b.	0.002	0.002	0.000	0.000	0.003
Na ₂ O	% wt d.b.	0.003	0.002	0.001	0.001	0.001
P ₂ O ₅	% wt d.b.	0.020	0.005	0.001	0.004	0.003
TiO ₂	% wt d.b.	0.004	0.000	0.002	0.000	0.000
B/A + P	--	41.525	3.802	3.459	3.287	3.151
Fu	% wt d.b.	18.430	0.040	0.025	0.031	0.028

2.1.1. Ash Fusibility Characteristics

One of the key properties of Fuel ash materials is the Fusion behaviour. The ash Fusibility test is one of the most widely used methods of assessing its behavior.

In general increments of ST, DF, HT and FT were observed (Table 3), which shows an improvement of ash quality, however not sufficient to reduce ash slagging potential, which remains at a severe level, index $\left(\frac{B}{A} + P\right)$ higher than 1.75 in all treatments. It must, however be stressed that the Fuel composition cannot alone justify the ash behaviour, because slagging and fouling also depend on boiler design and operation conditions.

Table 3. Ash Fusion characteristics for untreated and treated biomass, and potential fouling.

Fusion state (°C)	U0	UW1	UW2	UA1	UA2
Shrinkage temperature, ST	830	860	1000	950	950
Deformation temperature, DF	1400	1170	1385	>1500	>1500
Hemisphere temperature, HT	1450	1190	1400	>1500	>1500
Flow temperature, FT	1460	1220	1410	>1500	>1500

2.1.2. Heavy Metals

Even though that biomass has low heavy metal content, however trace amounts of such compounds can be problematic in biomass utilization for thermal energy, causing environmental pollution. Reduction of Pb and other heavy metals were observed in all treatments; however increment in Cr, Cu, Ni, Mo and Co concentrations were observed after UA1 and UA2 pretreatments (Figure 1). One of the

reasons for such increment is the solid mass decreases combined with the biochar adsorption capacity of heavy metals, especially Zn, Cr, Cd, Cu, Ni and Co. According to Al-Asheh *et al.* [18], this is due to biomass carbohydrates and phenolic compounds which have metal-binding Functional groups such as carboxyl, hydroxyl, sulfate, phosphate and amino groups, and not less important its pores formed during the HTC process.

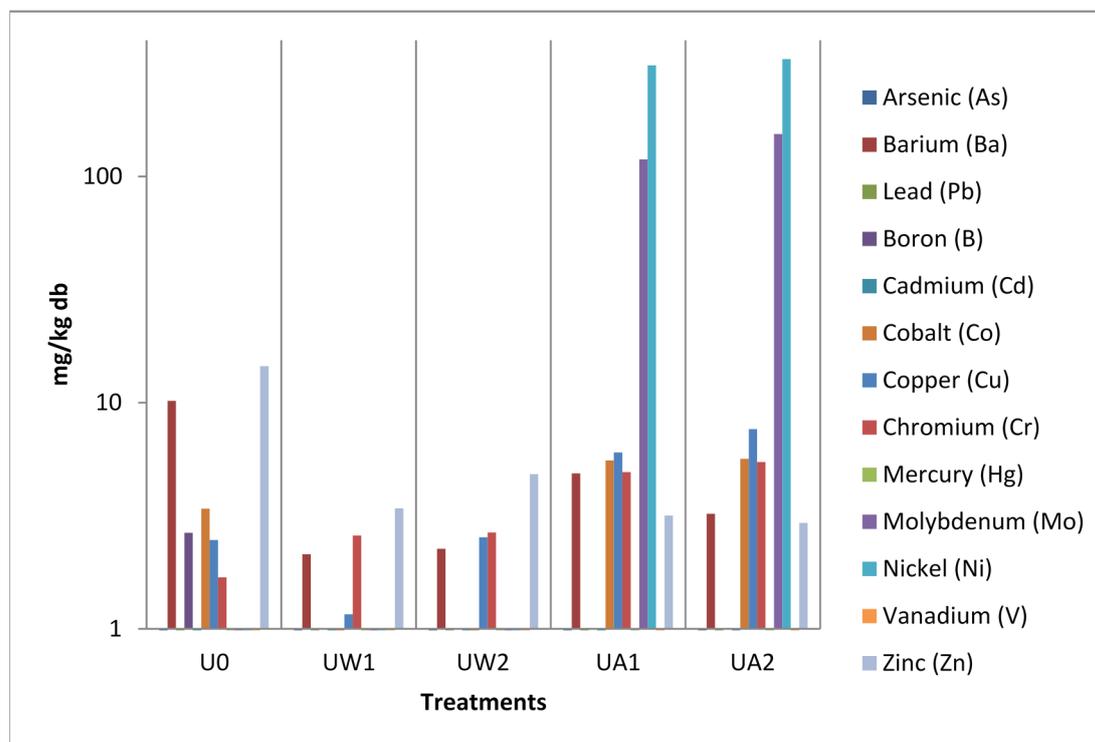


Figure 1. Concentration of heavy metals of untreated and pre-treated biomass.

2.1.3. Van Krevelen Diagram

The alteration of biomass composition can be reflected on a Van Krevelen diagram (Figure 2). It shows decrease of atomic ratio reduction in all treatments, with major reduction for acid treatment. Such decrease is mainly due to the significant reduction of carboxyl groups, from extractives, hemicellulose and cellulose. In general, both the H/C and O/C ratios decreased with time and utilization of acid catalyst. From the van Krevelen diagram, it can also be observed that despite the fact that three processes occur simultaneously (dehydration, decarboxylation and decarbonylation); the prevailing reaction is dehydration, which is in essence, as mentioned before, involves the removal of the hydroxyl groups. Even though according to Chen *et al.* [19], carboxyl and carbonyl groups start to degrade rapidly at around 150 °C, resulting in CO₂ and CO, respectively.

2.2. Mass Balance

The operating conditions employed, the treatment appears to have a stronger effect than the reaction time the on mass yield. Higher mass yield was recovered on water treatment, 87% wt and 82% wt for 150 and 350 min respectively, while for acid treatment the mass yield dropped considerable, consequently producing higher yield of CO₂ and other water soluble compounds (Table 4).

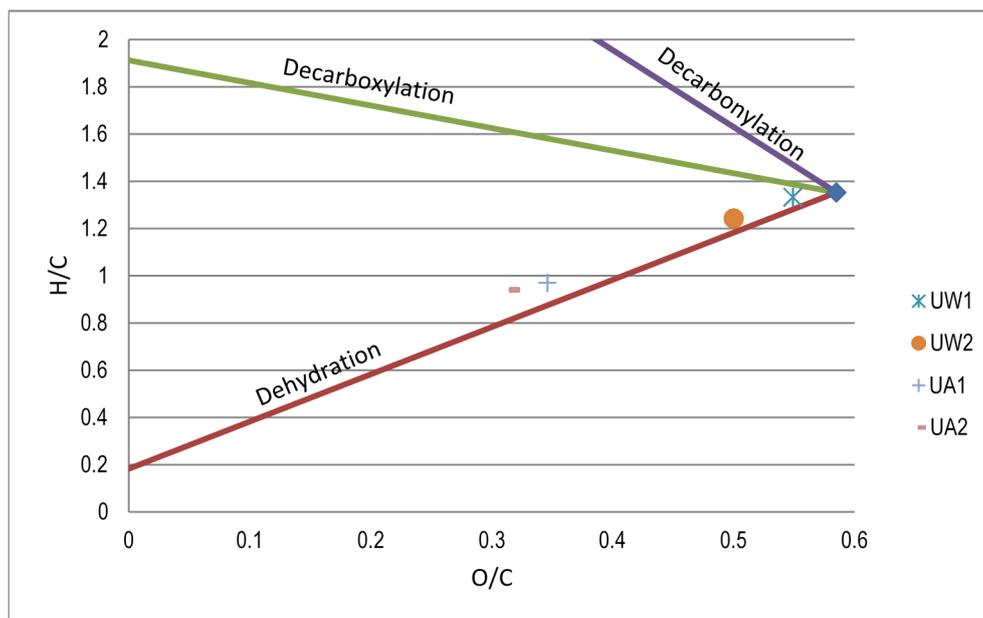


Figure 2. Van Krevelen diagram for untreated and pretreated biomass.

Table 4. Mass of reactants and products in HTC without and with diluted acid.

Treatment	Mass in (g)			Mass out (g)				
	Wood	Water	Acid	Pretreated wood	Acetic acid	Precipitates	Water	Gas
UW1	1.00	16.13	--	0.87	0.00	0.04	16.13	0.09
UW2	1.00	16.13	--	0.82	0.00	0.06	16.14	0.11
UA1	1.00	--	16.94	0.64	0.02	0.03	16.92	0.32
UA2	1.00	--	16.94	0.62	0.06	0.01	16.91	0.33

2.3. Energy Balance

The Table 5 presents the changes of the empirical chemical formulas due to carbonization process, including the respective enthalpies of combustion and formation of raw biomass to new feedstock. At the same time, the energy density was increased by 10%, 13%, 30%, and 35% respectively for UW1, UW2, UA1, and UA2. The process releases energy, leading to a positive energy balance, becoming eventually partially self-sufficient (Table 6).

The addition of acid accelerated the depolymerisation process leading to a quantitative difference on heat released during the reaction process, which was also clearly affected by the severity of the treatment. It is difficult however, to make direct comparisons between reaction process behavior reported in the literature and those observed in the current study, as several factors can influence the process such as type of biomass, severity of treatment, temperature, pressure, amongst others. Even though, it is worth to point it out that once, as mentioned before that the hydrothermal treatment is a slow process, it is important to give time to the treatment to change from endothermic to exothermic reaction process. Yan *et al.* [20], reported an endothermic reaction process after a 5 min treatment, despite higher temperatures (200 to 260 °C).

Table 5. Chemical formula, enthalpy of combustion and enthalpy of formation in HTC without and with diluted acid.

Treatment	Empirical chemical formula	Enthalpy of combustion (kJ·Jg ⁻¹)	Enthalpy of formation (kJ·Jg ⁻¹)
U0	CH _{1.353} O _{0.585}	-17.846	-0.183
UW1	CH _{1.296} O _{0.556}	-19.700	-2.055
UW2	CH _{1.243} O _{0.507}	-20.088	-2.797
UA1	CH _{0.971} O _{0.364}	-23.127	-7.659
UA2	CH _{0.940} O _{0.331}	-24.097	-8.839

Table 6. Enthalpy and heat of reaction in HTC without and with diluted acid.

Treatment	Enthalpy in (kJ·Jg ⁻¹)			Enthalpy out (kJ·Jg ⁻¹)						Heat of reaction
	Wood	Water	Acid	Pretreated wood	Acetic acid	Precipitates	Water	Acid	Gas	
UW1	-0.183	-256.14	--	-1.79	0.0	-0.11	-256.14	--	-0.81	-2.53
UW2	-0.183	-256.14	--	-2.29	0.0	-0.17	-256.30	--	-1.03	-3.47
UA1	-0.183	--	-157.00	-4.92	-0.16	-0.08	--	-156.85	-3.01	-7.84
UA2	-0.183	--	-157.00	-5.51	-0.48	-0.03	--	-156.76	-3.10	-8.69

3. Experimental Section

3.1. Sites and Sampling

Five *Pterocarpus angolensis* (umbila) trees were obtained from an open dry forest subjected to frequent fires set by local people as a result of shift cultivation and traditional hunting routines in each sampling stand. The stands were chosen in the northern and central parts of Mozambique, namely in the provinces of Cabo Delgado, Nampula and Sofala. From each tree a disc, about 3–5 cm thick, was taken at breast height (130 cm).

3.2. Sample Preparation and Analysis

The woody biomass material was prepared, carbonized and analyzed as described in [17]. An electrically heated and rotative 1000 mL autoclave was used to carbonise 80 gr biomass (2–10 mm) in 800 mL 0.1 M H₂SO₄ solution or water at 180 ± 2 °C with a heating rate of 10 °C/min. Four sets of pretreatment conditions were considered in this study (Table 7). Several analyses such as proximate and ultimate analysis were performed according to the respective standards and norms.

Table 7. Treatment conditions considered.

Treatment designation	Treatment agent	Treatment time (min)	R ₀
UW1	Water	150	4.53
UW2	Water	350	4.90
UA1	H ₂ SO ₄ (0.1 M)	150	4.53
UA2	H ₂ SO ₄ (0.1 M)	350	4.90

3.3. Fouling and Slagging Tendency

Ash behaviour has been described by its composition, deformation temperature (DT), shrinkage temperature (ST), hemisphere temperature (HT) and flow temperature (FT). These characteristics are combined through several ratios and indexes developed to predict the risk of ash slagging and/or fouling during the combustion of coal and/or biomass. Such risk is substantially influenced by concentration of potassium, sodium, chlorine and sulphur [21–23]. In this study only the Fouling and slagging are determined as follows:

- Fouling index (Fu)

$$Fu = \frac{Fe_2O_3 + CaO + MgO + Na_2O + K_2O}{SiO_2 + TiO_2 + Al_2O_3} \times (Na_2O + K_2O) \quad (1)$$

According to Pronobis [24], fouling Potential ≤ 0.6 is low, $0.6 < Fu \leq 1.6$ is medium, $1.6 < Fu \leq 40$ is high and $Fu > 40$ severe.

- Slagging index (basic to acid compounds)—B/A + P

$$B/A = \frac{Fe_2O_3 + CaO + MgO + Na_2O + K_2O + P_2O_5}{SiO_2 + TiO_2 + Al_2O_3} \quad (2)$$

The slagging potential is low when $B/A < 0.5$, is medium $0.5 < B/A < 1.0$, is high $1.0 \leq B/A < 1.75$ and severe when $B/A \geq 1.75$ [25].

3.4. Mass and Energy Balance

Mass and energy balance calculations are important criteria widely used to evaluate the feasibility of the process from the raw material to the final product.

3.4.1. Mass Balance

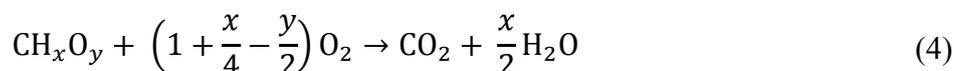
The general mathematical statement can be written as the total mass entering the unit equal the total mass of products leaving the unit:

$$\sum m_{in} = \sum m_{out} \quad (3)$$

3.4.2. Energy Balance

To calculate the energy balance, was applied the method suggested and well described by Yan *et al.* [20] previously, where:

Enthalpy of formation for biomass—is determined using the enthalpy change due to combustion (ΔH_c) of the biomass solids, Equation (4):



where CH_xO_y is the chemical formula of the biomass, with the x and y values determined from the ultimate analysis of the biomass.

ΔH_C —was obtained through combustion in a bomb calorimeter (Parr 6300) and mathematically can be obtained as follows:

$$\Delta H_C = \Delta H_{f(\text{products})} - \Delta H_{f(\text{reactants})} \quad (5)$$

consequently:

$$\Delta H_{f(\text{reactants})} = \Delta H_{f(\text{products})} - \Delta H_C \quad (6)$$

Heat of reaction - to estimate the heat of reaction of the HTC process, several assumptions were made, such as:

- The gas consist only of CO₂ since it accounts for over 90% in the gas product [20];
- glucose represents all precipitates formed at 180 °C;
- acetic acid represents volatile acids; and
- The reference condition for the enthalpy calculations was 25 °C.

The heat of reaction was determined by the difference of the enthalpies of formation of the products and reactants in all treatment conditions considered in this study.

4. Conclusions

The effects of different HTC conditions/severity of treatments were studied. Experimental results indicate that for process conditions employed the mass and energy balance of the HTC is considerable affected by the treatment than the severity of the treatment. The chemical composition of the biochar produced is significantly different than the feedstock. The use of diluted acid as catalyst improves the biochar quality, namely in terms of energy density and ash characteristics; however the increased S content in the final product should be considered for market acceptance (since the Fuels have a maximum S concentration allowance). Moreover waste water treatment of this process is also more demanding.

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Author Contributions

Carlos Cuvilas and Weihong Yung conceived and designed the experiments; Carlos Cuvilas performed the experiments; Carlos Cuvilas analyzed the data; Carlos Cuvilas and Efthymios Kantarelis wrote the paper.

Conflicts of Interest

The authors declare no conflict of interest.

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