



# Assessment of the Energy Recovery of Aloe Vera Solid Residues by Pyrolysis and Hydrothermal Conversion

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The renewable energy sources are being considered as an alternative to solve energy needs and reduce environmental problems. Compared with other renewable energy, biomass from different production processes are an interesting alternative. In particular, the Aloe Vera waste, because has increased their use in the cosmetic, pharmaceutical and food industry. Biorefining has now been introduced as a new concept that integrates conversion processes that allow sustainable treatment of biomass to be converted into products such as synthesis gas, bio-oils, charcoal and energy. Different thermochemical conversion processes have been used with biomass, in order to guarantee energy recovery and reuse. The four main processes used are pyrolysis, combustion, gasification and liquefaction. When these processes are carried out in the presence of water in sub-critical state, it is called hydrolysis or hydrothermal carbonization (HTC). When are executed at temperatures above 280°C is called hydrothermal liquefaction (HTL). In this research was studied the effect of HTC and HTL in neutral and basic medium. As well as the pyrolysis process, in performance and characteristics of products such as biochar and condensable on Aloe Vera leafs. The highest yield in biochar was observed for pyrolysis with  $31 \pm 3$  %w/w followed by the HTL in neutral medium with  $28 \pm 3$  %w/w. The biochars were characterized by Fourier transform infrared spectroscopy (FTIR), absorption indexes and scanning electron microscopy. The characterization by FTIR showed the presence of functional groups characteristic of aromatic compounds products of condensation processes after applying the thermal treatments. The higher carbon densification was observed for pyrolysis and HTL, while the presence of carbonyl groups is evidenced only for hydroconversion processes. The methylene blue index in the biochars of different thermochemical treatments was 80-100 mg/g, comparable with some commercial activated carbons. For iodine number, the highest value was  $224 \pm 13$  mg/g that was obtained by HTL in a neutral medium. The yield of biofuels in hydrothermal conversion processes was 18 to 26 %w/w; while in the pyrolysis were over 50 %w/w. These were characterized by FTIR and could not identify significant differences in the functional groups existent. The results in the Aloe Vera leaf indicate that the pyrolysis treatment is a low-cost, environmentally friendly management of this biomass, and economic feasibility; with which the highest performance in biochar and condensable fuel is obtained with lower gas production. In addition, biochar obtained can be used for energy purposes due to its densification as well as for amendment in contaminated soil or production of activated carbon, nanostructured materials, and catalysts.

## 1. Introduction

Reducing conventional sources, environmental regulations and increased fuel demand has increased the need to find alternative energy sources to fossil fuels. Renewable plant materials are one promising alternatives for fuels and chemicals production. Biomass conversion into fuels and chemicals can save foreign exchange reserves and improvement economic activity in regions without fossil fuel resources and have abundant biomass such as Malaysia, Thailand and Indonesia. Conversion of waste and biomass would also reduce landfill costs such as municipal waste incineration down to 90% and increase the production of biomass-based fuels or chemicals (Hornung 2014).

The biomass transformation can convert waste into energy resources, thereby reduce their environment impact. These mostly involve the thermal degradation of biomass under presence or absence of oxygen conditions and convert the feed into a wide range of products such as synthesis gas, bio-oils, charcoal and

energy (Srirangan *et al.* 2012). If these processes are performed in the absence of oxygen they are called pyrolysis and in presence of water in a subcritical state, it is often called hydro-pyrolysis or HydroThermal Carbonization (HTC) and if executed at higher temperature ( $\geq 280$  ° C) HydroThermal Liquefaction (HTL). The advantage of hydrothermal conversion processes is that good yields are obtained when applied to materials with a high moisture content; and do not require additional energy consumption for drying, before or during the process. These processes are also capable of producing high quality fuels and materials with different characteristics than their dry counterparts (Libra *et al.* 2011). The main objective of this research is to study the thermal processes of pyrolysis, HTL and HTC applied in Aloe Vera (*Aloe barbadensis Mill*) leaf using batch reactors laboratory scale, evaluating the biochar and biofuel yield and properties. In order to assess the feasibility of applying this technology on the revaluation of these solid waste.

## 2. Experimental Methodology

### 2.1 Selection, pretreatment and conditioning of biomass

The biomass used for this study was Aloe Vera leaf, an agro-industrial waste obtained locally. The biomass was dried at 80 °C for 14 h and was then milled and sieved to a particle size between 1 - 2 mm.

### 2.2 Experimental assembly of batch reactor to thermal conversion processes

The thermal processes were run in one batch reactor of stainless steel PARR model 4652 with a 500 ml capacity. Equipped with a conventional heating furnace PARR model 4923 EB. In pyrolysis, a condensation and trap system of condensable was required. Table 1 shows temperature, pressure and reaction time conditions used in each of heat treatments. In all cases, the tests were performed in triplicate.

Table 1: Product yield in thermal treatment

Process	Temperature, °C	Pressure, Psig	Reaction time, hours
Pyrolysis	500 ± 5	Atmospheric	1
Hydrothermal Carbonization (HTC)	250 ± 5	680 ± 30	4
Hydrothermal Liquefaction (HTL)	280 ± 3	970 ± 30	4

For HTC and HTL weighed 245,0 ± 0,1 g of biomass with 83% w/w moisture. On the other hand, for the basic medium 30,0 ± 0,1 g of dry biomass was weighted and added 220 ± 10 mL of 1% w/v of sodium carbonate. In the pyrolysis treatment, 50,0 ± 0,1 g of biomass were weighted. The system was assembled and initial heating was applied at 100 °C, afterwards it was set to reach 500 ± 10 °C, where the reaction was allowed to proceed for 1 hour.

### 2.3 Product separation

The biochar were washed using a Soxhlet extraction system with 200 ml of dichloromethane p.a. until a clear extract was obtained. The recovered organic phase was added to the extracts from the separation of the condensable fuels. The biochar was brought to constant weight in an oven at 60 ± 2 °C for 48 hours. This weight was recorded for the determination of the biochar yield in the heat treatment. Condensate fractions were also weighed to evaluate the biofuels yield.

### 2.4 Characterization of biochar and biofuel material.

The methylene blue index was determined using 0.2 ± 0.1 g of dry biochar and commercial activated carbon (Scharlau Chemise S.A.) in 50 mL of a methylene blue solution of 350 ppm, stirred for 24 hours. The methylene blue concentration in the supernatant was determined with a spectrophotometer model Zuzi 4430 a 690 nm. Previously a calibration curve of 6 points using methylene blue solutions of concentrations between 2 ppm and 10 ppm was performed. The results were obtained by difference with the blank and were expressed as mg of methylene blue absorbed per gram of sample (Liu *et al.* 2012).

The iodine number or index was carried out by placing 0.5 g of biochar sample and commercial activated carbon in 50 mL of iodine solution of 0.05 N. The solution was stirred for 24 hours. The concentration in supernatant was determined by titration with 0.1 N sodium thiosulfate. The iodine index was obtained by difference with the blank and expressed as mg of iodine adsorbed per gram of biochar.

For the morphological analysis of the raw biomass as well as the pyrolysis and hydrothermal conversion samples use the MEB, all samples were prepared by suspension, requiring you to be subjected to coating with pure gold in an ion cover Brand SAIA, model Sputter SCD-050-12 mA 60 s to generate a layer of 10 Å thick, in order to make the conductive sample. The images obtained from the samples were taken in a scanning electron microscope JEOL brand; model JSM-6380, under program control microscope control.

The biochar and biofuel samples were characterized by Fourier Transform Infrared Spectroscopy (FTIR) using a Thermo Scientific iS5 spectrometer. The total number of scans was 50 with spectral resolution of  $4\text{ cm}^{-1}$ . In the preparation and analysis of solid samples,  $2.0 \pm 0.1$  mg of sample was weighed and filled with KBr (Ir spec. Grade, Scharlau PO0168) to  $80 \pm 2$  mg, the mixture was thoroughly homogenized in an agate mortar and dried in an oven at  $80\text{ }^\circ\text{C}$  prior to analysis. The infrared spectrum was acquired in Fourier transform mode using the KBr pellet technique. Liquid samples were analyzed directly using Attenuated Total Reflection (ATR) with a GeSe glass.

### 3. Results and Discussion

Table 2 presents the results obtained in %w/w of solid (biochar), condensable (biofuel) and non-condensable (biogas) products after application of different thermochemical processes (HTC, HTL and pyrolysis), in neutral and basic medium.

Table 1: Product yield in thermal treatment

Medium	Process	Yield <sup>1 2</sup> % w/w		
		Biochar	Biofuel	Biogas
Neutral	Pyrolysis	$31 \pm 3$ (9,7%)	$29 \pm 5$ (17%)	$40 \pm 5$ (12%)
	Hydrothermal Carbonization (HTC)	$22 \pm 1$ (4,2%)	$26 \pm 0,6$ (2,3%)	$54 \pm 8$ (14,4%)
	Hydrothermal Liquefaction (HTL)	$28 \pm 1$ (2,6%)	$24 \pm 0,5$ (2,2%)	$49 \pm 1$ (2,4%)
Basic	Hydrothermal Carbonization (HTC)	$29 \pm 3$ (10,6%)	$20 \pm 3$ (14,1%)	$56 \pm 5$ (8,3%)
	Hydrothermal Liquefaction (HTL)	$17 \pm 2$ (12,2%)	$17,8 \pm 0,1$ (0,8%)	$61 \pm 6$ (9,4%)

<sup>1</sup>The results correspond to the mean value and standard deviation of the replicates.

<sup>2</sup>The values in brackets correspond to the coefficients of variation (%) for the replicates.

All cases biogas was the major product, between 40-54% w/w for neutral media and 56-61% w/w for basic media. The highest yield was obtained for HTL treatment in basic medium with  $61 \pm 6\%$  w/w. Some authors have reported yields higher than 30% for thermal treatments with reaction times greater than 30 min. Mahinpey et al. (2009) studied the influence of the pressure for the pyrolysis of wheat straw, finding biogas yields between 30-55% at  $500\text{ }^\circ\text{C}$  and 125 min. While Beis et al. (2002) performed slow pyrolysis between  $400\text{-}700\text{ }^\circ\text{C}$  for minimum 30 minutes; reporting biogas yields between 30-40%. Therefore, high yield can be attributed to the high reaction times in different treatments (1 to 4 hours); approving densification mechanisms of biomass and the generation of non-condensable fractions. Figure 1A shows that highest biochar yield was obtained for the pyrolysis treatments, HTC in basic medium and HTL in neutral medium, with values between 28-31% w/w. However, the results obtained do not observe the trend reported by Cha et al (2016); that is, the biochar yield decreases between pyrolysis, HTC and HTL, respectively. In relation to biofuels fraction (Figure 1B), the results were lower than reported in the literature (Cha et al. 2016; Libra et al 2011) attributed to the longer processing time (1 to 4 hours) that increasing carbon densification and fractionation of condensed products.

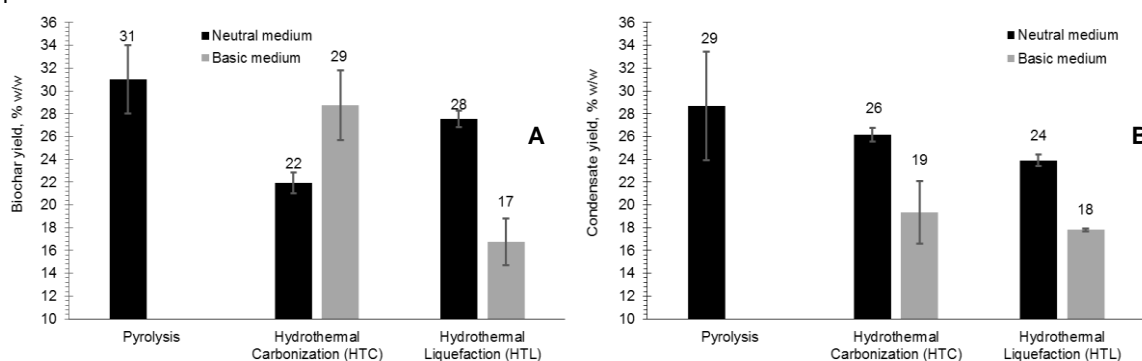


Figure 1: Comparison of biochar (A) and condensate (B) yields for different thermal treatments

The adsorption tests of methylene blue are more suitable for size molecules between 1-25 nm. Figure 2A shows that this adsorptive property was higher in pyrolysis treatments and HTC in basic medium, which coincide with treatments that generate highest yield. In addition, these were in the same order of magnitude as in the reference coal. Therefore, could be affirmed that methylene blue index in the biochar of different treatments are comparable with commercial coals. It is relevant to highlight how the basic medium contributes

to increase absorption rate for HTC treatment. The iodine index can be used to approximate the surface area of carbon particles since it has been shown to correspond to the surface occupied by iodine ions and is a good indicator of the pores with radius < 1 nm or micro pores. Figure 2B show that for each experiment it is possible to obtain a biochar with adsorption capacities higher than 176 mg/g of iodine. The highest value was obtained for HTL in basic medium; where again the basic medium to increasing the adsorptive properties.

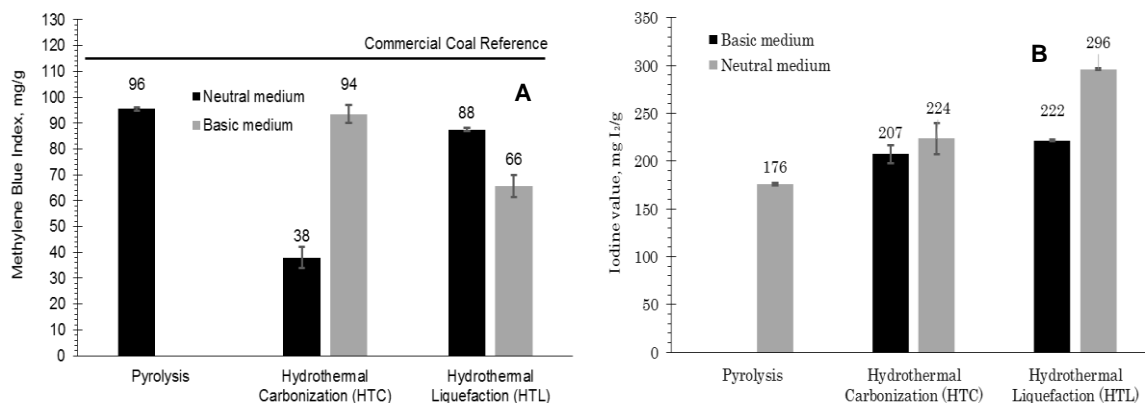


Figure 2: Comparison of the methylene blue index (A) and iodine value (B) of biochar for different thermal treatments

Figure 3 presents the infrared spectra corresponding to the biochar. The frequencies around 3000 and 2850  $\text{cm}^{-1}$  represent the C-H asymmetric and symmetrical elongation vibrations of the terminal methyls; while 2935 and 2845  $\text{cm}^{-1}$  are C-H asymmetric and symmetrical elongation vibrations related to the presence of  $-(\text{CH}_2)_n-$ . It is relevant to note that these signals disappear in the biochar generated by the pyrolysis process, compared to hydrothermal treatments and these in turn with the sample of Aloe Vera, indicating that only the functional groups associated to a hard or highly densified carbon remain in heat treatments at high temperature.

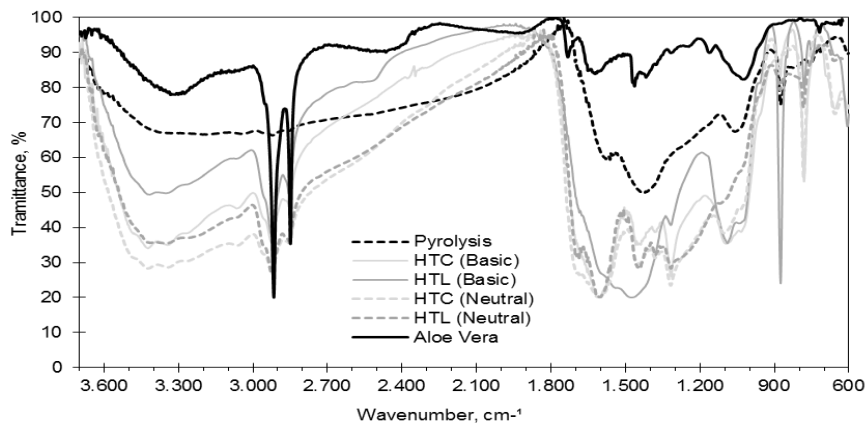


Figure 3: FTIR spectrum of raw biomass and biochar samples obtained from different thermal processes

At lower wave numbers, it can be seen that there are two peaks in the frequency between 1550-1650  $\text{cm}^{-1}$  indicative of aromatic compounds; with greater proportion in the biochar product of hydrothermal treatments; signals equivalent to HTL and HTC are observed. These may be due to the fact that in these treatments conditions are reached that give the water properties that allow it to more easily carry out depolymerization, hydrolysis and decomposition reactions of the biomass (Christensen et al. 2014). Similarly, are evidenced for these treatments peaks between 1600-1820  $\text{cm}^{-1}$ , corresponding to carbonyl groups bonds produced by the reactions mentioned above. As expected, these functional groups are absent in the pyrolysis product biochar; This can be due to the fact that the biomass was completely carbonized, preventing the generation of the characteristic reactions formed by hydrothermal treatments such as hydrolysis, depolymerization and recombination of biomass. The infrared spectra of condensable products of different thermal treatments did not present significant differences between the functional groups.

Micrographs obtained for Aloe Vera before and after pyrolysis, HTC and HTL are discussed below. Figure 4 shows the MEB for the Aloe Vera leaf, taken at x200 and x1500, the original fibrous structure is observed, which indicate the presence of vegetable cuticle formed by granules, tubers, warts and short, almost parallel ribs, the elements of which merge. After the pyrolysis, the micrograph of Figure 5 (A and B) shows the rupture of the fibrous structure of the material, showing rupture of the leaf cuticle and formation of multiform granules < 5  $\mu\text{m}$ . The effect of the high temperature of pyrolysis leads the rupture of the fibrous structure to produce small multiform particles mainly from the cellulose contained in the biomass, which is the main component of the same. Because pyrolysis is performed very quickly and short reaction times, the formation of typical cellulose spheroid particles, which require a longer reaction time for formation, is not observed as in other treatments.

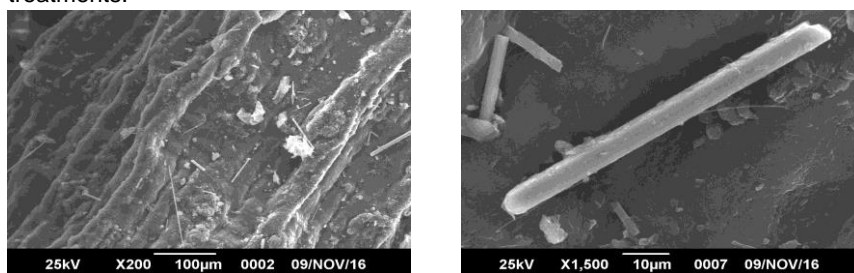


Figure 4: Aloe Vera wastes material raw.

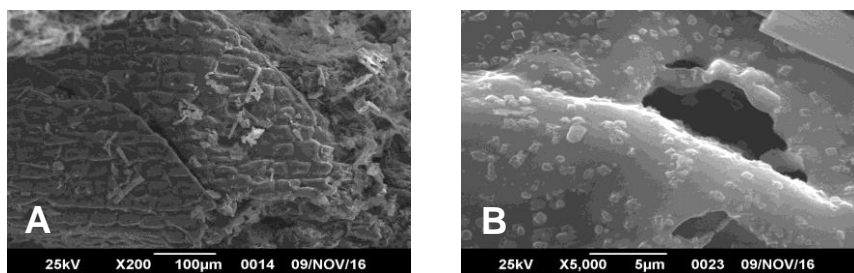


Figure 5: Biochar product of Aloe Vera leaf pyrolysis.

Figure 6 (A and B) and 7 (A and B) show the micrographies of biochar product of Aloe Vera leaf of HTC and HTL. In both treatments, it is possible to appreciate rupture of original fibrous wall. However there is no appreciable formation of spheroid particles coming from cellulose hydrolysis for HTC, whereas for HTL the temperature increase promotes the formation homogeneous particles of sizes <10  $\mu\text{m}$ , which confirms that the temperature induces hydrolysis process that leads the formation of cellulose particles (Titirici 2013). It can be seen that HTC maintains part of the fibrous structure of the starting material, since there are structures arranged with spacing's between them similar to the so-called "short ribs" which remain in the resulting carbon.

Finally, by comparing the obtained micrographs for the heat treatment carbon in the basic medium for HTC and HTL conditions, Figure 8 (A and B) respectively, we can see the fibrous structure with changes produced by hydrolysis in basic media. In the case of HTL, the formation of small particles of well-dispersed homogeneous sizes with sizes <1  $\mu\text{m}$  is observed, which is not seen for the sample treated under HTC conditions. In both cases the activation treatment with basic medium shows a significant change in the roughness of the surface obtained in both materials (Titirici 2013).

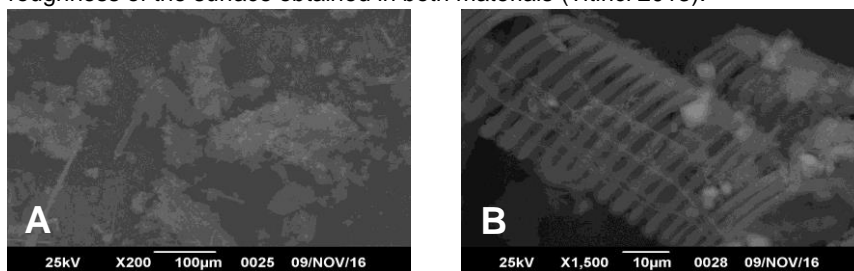


Figure 6: Aloe Vera wastes HTC sample.

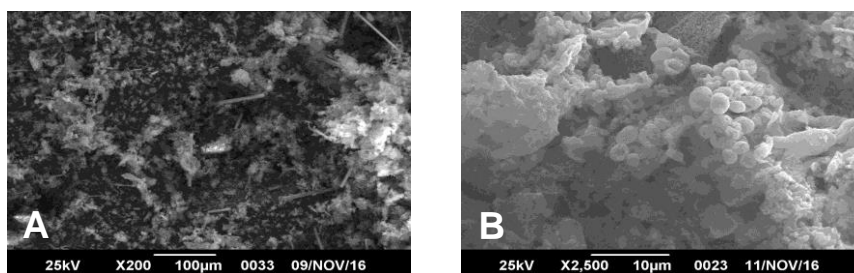


Figure 7: Aloe Vera wastes HTL sample.

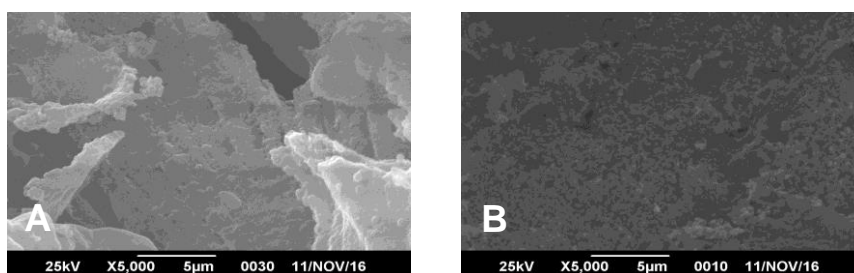


Figure 8: Compares between Aloe Vera wastes HTC and HTL sample basic medium.

#### 4. Conclusions

Residence times greater than 60 minutes increase biogas and biochar products. The yield for non-condensables was greater than 40% w/w. While the biocarbon yield was process dependent; The highest yield was for the pyrolysis treatments, HTC in basic medium and HTL in neutral medium, with values between 28-31%w/w. In the methylene blue index, it was higher in pyrolysis (96 mg/g) and HTC in basic medium (94 mg/g) treatments, supporting the presence of meso and macropores. While for iodine index the highest value was obtained for the treatment of HTL in basic medium. In which it was observed that the basic medium in general favors the increase of adsorptive properties. The biochar obtained by pyrolysis differs from that obtained by HTC and HTL by the presence of aromatic groups; While for hydrotreatments the presence of OH, methyl and C=O groups is identified. The alkyl groups were reduced for the treatment of pyrolysis as for the HTC, demonstrating the densification of the material.

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