

Termogravimetric Characterization of Biomass Impregnated with Biodegradable Ionic Liquids

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ABSTRACT

Different classes of solvents such as mineral acids and ionic liquids have proved to be capable of disrupting hydrogen bonds among different polysaccharide chains. Recently, a specific family of protic ionic liquids (PILs) has been developed with functionality in various industrial applications, adding to the benefits and advantages of their use, since they are absent of aromatic or halogenated molecular structure, making them structurally free of toxicity. This work aimed to verify the influence of protic ionic liquids 2-HDEAS, 2-HEACi, 2-HEAL impregnated in the *Prosopis juliflora* (mesquite) biomass, through the thermogravimetric analysis of macrocomponents hemicellulose, cellulose and lignin. Tests were performed in a simultaneous thermogravimetric analysis equipment under inert atmosphere, 100 mL/min of nitrogen, and 10 °C/min heating rate. It was verified that all PILs present great potential in the degradation and dissolution of the macrocomponent structure of *Prosopis juliflora*.

Keywords: lignocellulosic, protic ionic liquid, *Prosopis juliflora*.

1. INTRODUCTION AND OBJECTIVES

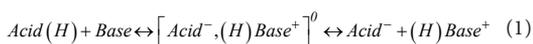
According to the Brazilian Association of Planted Forest Producers (ABRAF, 2017), about 41 million tons of wood residues are annually generated from wood processing and forest harvesting industry, capable of generating energy equivalent to 1.7 GW/year.

Through law project 3.529/2012, as a result of the diversification of the national energy matrix, the Brazilian government instituted the national policy for the generation of electric energy originated from biomass, establishing the mandatory bioenergy contracting in the composition of the national electricity generation. With the enforcement of this law, electricity generation originated from biomass will be unavoidable and the participation of renewable sources will be even higher (ABRAF, 2017).

The inherent properties of raw biomass, such as high moisture content, low energy density, biological degradation and alteration of physicochemical properties during storage and milling difficulty limit its wide use in the industry.

Room Temperature Ionic Liquids - RTILs are organic salts with melting point lower than 100 °C, which has received considerable attention as substitutes for many volatile organic solvents (Ghandi, 2014). However, for some commercially found ILs, there are several aspects considered undesirable for certain applications (Burrell et al., 2010). Such negative aspects include traces of halide impurities from metatheses, toxicological profile in the synthesis of new materials and high cost of ILs in relation to molecular solvents.

A method to overcome these negative aspects is the use of protic ionic liquids - PILs, which are formed by the neutralization reaction of Brønsted acids and bases, according to Equation 1 (Greaves & Drummond, 2008).



Since they are non-flammable, non-volatile and recyclable, they are classified as green solvents, due to their excellent solvation potential, good thermal stability and configurable properties depending on choices of cations and anions (Meine et al., 2010; Ahrens et al., 2009; Welton, 1999).

ILs can also be classified into two broad categories: protic ionic liquids - LIPs and aprotic ionic liquids

- ILAPs. ILPs are produced through the transfer of protons from a Brønsted acid to a Brønsted base (Ghandi, 2014). ILPs generally have higher conductivity and flowability as well as lower melting points when compared to ILAPs. In addition, they have reduced costs and are easy to be prepared, as their synthesis does not involve by-products (Markusson et al., 2007; Greaves & Drummond, 2015).

Thus, protic ionic liquids 2-HDEAS, 2-HEACi, 2-HEAL impregnated in *Prosopis juliflora* biomass were used to identify changes in biomass structure.

2. MATERIAL AND METHODS

2.1. Ultimate, proximate analysis, heating value measurement

Immediate analysis, including moisture, volatiles, ashes and fixed carbon content, was performed in accordance with ASTM E871/13 (ASTM, 1998), E1756-08/08 (ASTM, 2008a), E1755-01/07 (ASTM, 2007) and D5832-98/2008 (ASTM, 2008b). For elemental analysis, ASTM D5291/10 (ASTM, 2010) method was used, allowing the quantification of carbon, hydrogen and nitrogen content using a Perkin Elmer 2400 series ii. The calorific value determined in a IKA C2000 calorimeter pump by checking the thermal energy generated by the sample combustion inside the calorimetric chamber under constant pressure, according to ASTM D-2015/00 (ASTM, 2000).

2.2. Ionic liquids summary

Bases were deposited in the synthesis reactor and the desired acid slowly added under continuous mechanical stirring for 24 hours at room temperature. The amounts of acid and base were stoichiometrically calculated from their chemical structures and molecular masses. After this step, the purification process was performed, in which the synthesized protic ionic liquid was subjected to mild heating (50 °C) to remove the unreacted compound, and moisture was acquired due to its high hygroscopicity.

2.3. Impregnation with ionic liquids

Biomass was passed in a Willye type mill, followed by screen sieving between 40-50 mesh, and then oven dried at 105 °C for 24 hours according to ASTM E871-13

(ASTM, 1998). Then, for impregnation of ionic liquids, 10.0 g of biomass and 200g of ionic liquids (ILs) were used, under constant agitation on a stirring plate at 40 °C for 5 hours. Subsequently, about 15 g of distilled water were added to “biomass + IL” and vacuum filtration with filter paper. Next, biomass was oven dried at 105 °C for 24 hours for complete water removal.

2.4. Thermogravimetry analysis

The thermal decomposition of the main biomass components (cellulose, hemicellulose and lignin) performed in simultaneous thermogravimetric analysis equipment (TG-DTA, Shimadzu DTG-60H) with temperature measurement accuracy of ± 2 °C and microbalance sensitivity of 0.001 mg. Tests were carried out under inert atmosphere, nitrogen flow of 50-100 mL/min, variable heating rate, platinum crucible and sample mass of 7-12 mg.

3. RESULTS AND DISCUSSION

The physical-chemical characteristics is relevant for verification of the alterations caused by impregnation of the biomass with ionic liquid. Table 1 shows the proximate and ultimate analysis of raw biomass.

Figure 1 presents the TG and DrTG curves characteristic of the decomposition of raw *P. juliflora* impregnated with different ionic liquids (2-HDEAS, 2-HEACi, 2-HEAL).

As some decomposition bands of components were overlapped, deconvolution of the derived curves was necessary, Figure 2. The use of this mathematical skill enables performing the relative quantification of macro components by devolatilization, Table 2.

The thermal events of hemicellulose, cellulose and lignin devolatilization are often observed between 220-315 °C, 315-400 °C and 160-850 °C, respectively (Yang et al., 2007).

Table 1. Proximate and ultimate analysis of raw biomass (dry basis^a).

Proximate analysis (%)	MC ^b	0.21	Ultimate analysis (%)	C	46.11
	VM ^b	86.48		H	6.49
	FC ^b	10.44		O	47.36
	Ash	2.87		N	0.06
O/C ratio	1.03				
H/C ratio	0.14				
HHV (MJ/kg) ^c	16.33				

^aProximate and ultimate analyses data were presented as a dry basis. ^bMC = moisture content (% as received); VM = volatile matter; FC = fixed carbon. ^cHHV = Higher Heating Values (dry-basis).

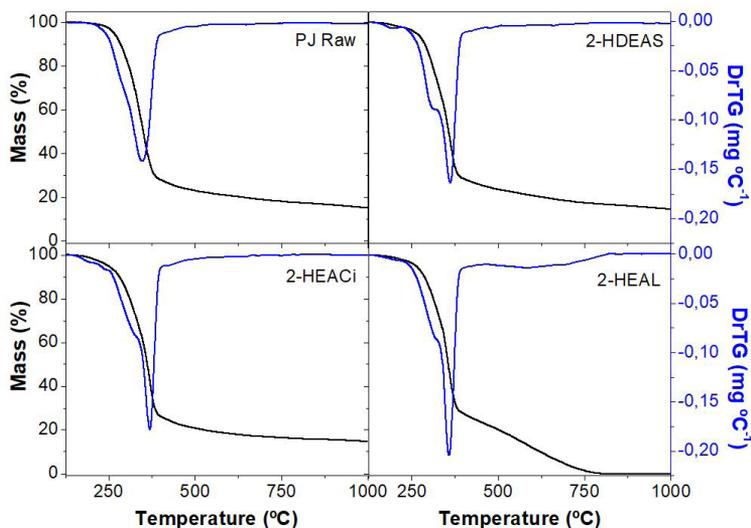


Figure 1. TG and DrTG curves of raw biomass impregnated with LIPs.

Table 2. Contents of hemicellulose, cellulose and lignin (wt.%) for fresh *P. juliflora* (dry basis) impregnated in LIPs.

Sample	Macrocomponent (T_m^a)			Devolatilization ^c (%)
	Hemicellulose ^b (%)	Cellulose ^b (%)	Lignin ^b (%)	
Raw	28.10 (300)	44.72 (345)	9.87 (435)	82.69
2-HDEAS	32.26 (305)	49.76 (362)	1.50 (424)	83.52
2-HEACi	33.95 (311)	49.19 (367)	1.03 (431)	84.17
2-HEAL	31.66 (318)	43.76 (357)	24.58 (607)	100

^aMaximum degradation temperature of each macrocomponent (°C), determined from the deconvolution of the TGA curve derivative.

^bEstimated from volatile matter (m/m %). ^cDetermined from the TGA curves (%).

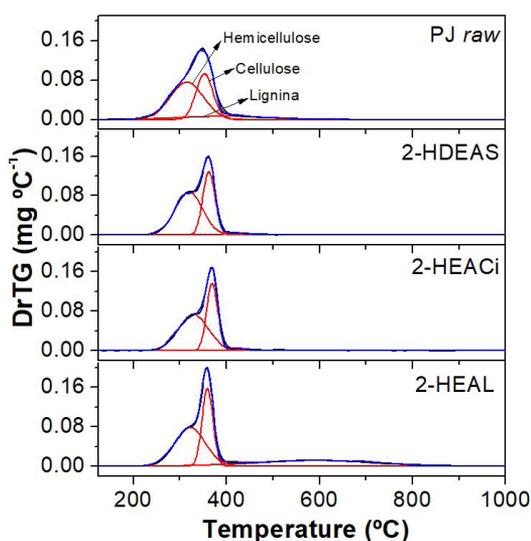


Figure 2. DrTG deconvolution curves of *P. juliflora* samples impregnated with different LIPs. Black line represents the experimental DrTG, blue line represents the calculated DrTG and red lines represent the deconvoluted DrTG.

Figure 2 exhibits at DrTG that the first two most intense peaks refer to hemicellulose and cellulose, with peak temperatures ranging from 300-318 °C to 345-357 °C, respectively. Lignin occurs throughout the decomposition range of the other components, with peaks around 424-607 °C. The quantification of macrocomponents of raw biomass by devolatilization showed 28.10% of hemicellulose, 44.72% of cellulose and 9.87% of lignin.

Ionic liquids 2-HDEAS and 2-HEACi presented increased lignin dissolution capacity under the impregnation conditions adopted. As for hemicellulose and cellulose, a slight increase was observed, which might have been caused by lignin dissolution, since volatile matter did not change significantly in relation to raw biomass.

Table 2 shows that the 2-HEAL ionic liquid used in biomass impregnation favored considerable

devolatilization increase, being able to infer that both inorganic components and macrocomponents were altered. Hemicellulose and cellulose were reduced while lignin increased considerably. Inorganic components underwent total dissolution in the 2-HEAL ionic liquid.

4. CONCLUSION

As previously demonstrated, protic ionic liquids present large potential for alteration of the biomass macrocomponent structure. Based on studies carried out in this work, it was verified that all ionic liquids presented satisfactory results. 2-HDEAS and 2-HEACi liquids directly influenced lignin reduction, while 2-HEAL resulted in the reduction of hemicellulose and cellulose, significant lignin increase and total dissolution of *Prosopis juliflora* inorganic components.

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