THERMAL ANALYSIS OF BYPRODUCTS FROM FAST-PYROLYSIS OF *EUCALYPTUS* FLOUR

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Abstract

Fast pyrolysis is the thermal decomposition of biomass in the absence of oxygen. This study aims to evaluate thermal analysis of byproducts from fast-pyrolysis of *Eucalyptus* wood fines. The pyrolysis was conducted in a pilot-scale at 500°C and 100 mm H_2O. Charcoal from this process showed high ash content (over than 20%) and incomplete carbonization. Aqueous extract and bio-oil showed similar thermal decomposition events. However, mass percentage decomposed at each temperature was different between these samples.

Keywords: *bio-oil, aqueous extract, charcoal.*

Introduction

In the last decades, demand of energy from renewable materials has increase due to limitation of fossil sources. One of the most promising processes to produce energy is the fast-pyrolysis. Fast-pyrolysis is a thermochemical process in the absence of oxygen with yields higher than 70% [1]. This process presents a controlled reaction temperature of pyrolysis of approximately 500°C, very high heating and heat transfers rates and produces of bio-oil by fast cooling of pyrolysis vapors [2]. Many biomasses have been investigated as renewable source in the fast-pyrolysis reactors, such as *Eucalyptus* bark [3] and switchgrass [4].

Bio-oils, aqueous extract and char are the main byproducts produced in fast-pyrolysis process. Among these byproducts, bio-oil from different biomasses has been extensively investigated [5,3] due to its high potential. This byproduct is an organic liquid with dark brown color, which could be combusted to produce electricity and used in the manufacture of chemicals [6], as wood preservative [7] and for production of hydrogen by gasification methods [8]. Bio-oil from pyrolysis has molecules with different sizes derived from depolymerization and fragmentation reaction of the main lignocellulosic materials compounds (hemicelluloses, cellulose and lignin) and contains large amount of oxygen (45-50 wt) [9].

Thermal analyzes – especially thermogravimetry and differential scanning calorimetry – are interesting tools to characterize byproducts from fast-pyrolysis. These analysis permit identification of thermal events of main compounds of lignocellulosic materials, which is feasible to investigate variation in chemical structure and new applications for these byproducts.

Objective

The objective of this work was to identify the thermal events on byproducts – especially bio-oil – from fast-pyrolysis of *Eucalyptus* wood. Bio-oil, aqueous extract and char collected in a fast-pyrolysis pilot plant were characterized by thermogravimetric and differential scanning calorimetric techniques

Material and Methods

Fast-pyrolysis reactor

Bio-oil, aqueous extract and charcoal were produced in a pilot-scale fast-pyrolysis reactor (brand BIOWARE) from Suzano Papel e Celulose, Limeira-SP unit. The reactor operates in a fluidized bed and continuous process with a nominal supply of 20 kg/hour. For this study, the reactor was set to work at 500°C of temperature and 100 mm H2O of static pressure. Wood fines were used as raw material.

Thermal analysis

Byproducts from fast-pyrolysis were characterized as received. Thermogravimetric analysis (TGA) was performed in a DTG-50 equipment from Shimadzu using an air synthetic atmosphere with gas flow of 150 mL min^{-1}, temperature range between 25 and 650 ºC and heating rate of 10 ºC min^{-1}. Samples weighing 5-8 mg were put inside a platinum pan to perform the tests. Differential scanning calorimetry analysis (DSC) were carried out in a DSC Q200 equipment from TA Instr. (USA) using an inert nitrogen atmosphere (gas flow of 150 mL min^{-1}) at a temperature rate of 20 ºC min^{-1}. Samples - weighing 3-6 mg - were put inside an aluminum pan, cooled from room temperature to - 50 ºC and then immediately heated to 50 ºC.

Results and Discussion

Thermogram of raw material (Figure 1a) was very similar to thermograms of other wood samples [10]. The derivative thermogravimetric curve shows three main steps of thermal decomposition, and an overlapped peak that appears as a shoulder (Figure 1b). Adsorbed water loss occurs around 70 ºC. Overlapped thermal decompositions at 250 ºC and 300 ºC were related to the hemicellulose and amorphous cellulose, at lower temperature, and to the crystalline cellulose, at higher temperature. In oxidant atmosphere, this thermal degradation occurs at lower temperatures when compared with inert atmosphere, as nitrogen [11].

Thermogram of charcoal from fast-pyrolysis shows two important differences related to charcoal produced by conventional methods (slow pyrolysis, and poor oxidation atmosphere). The charcoal from fast-pyrolysis shows a residual content of carbohydrate (Figure 1b) and very high ash content (Figure 1a), which was higher than value observed by Missio et al. [12] in *Eucalyptus* charcoal produced with lower heating heat (1.6 ºC min^{-1}). These authors found ash content less than 1% after carbonization at 550°C.

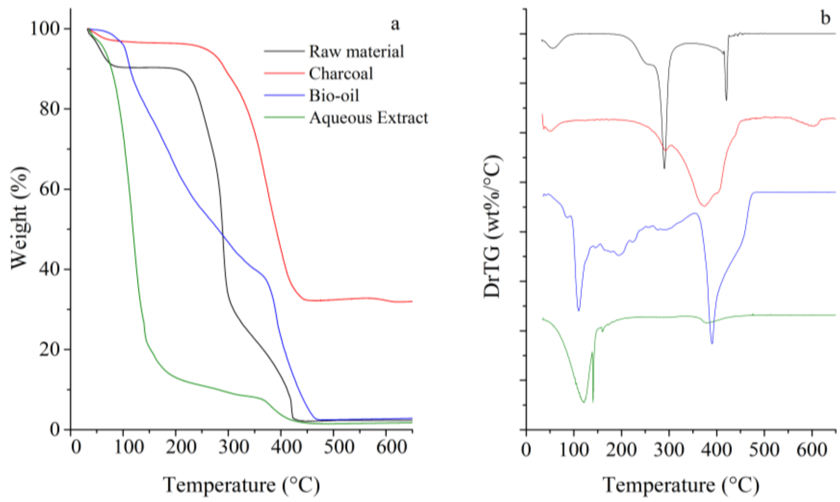

Figure 1. Thermogravimetric curves of byproducts from fast-pyrolysis of *Eucalyptus* flour.

The thermograms of bio-oil and aqueous extract samples showed two main peaks of thermal decomposition. The first peak has high rate of decomposition around 120 ºC and the second at 400 ºC. According to Pimenidou and Dupont [13], - in study with bio-oil from wood - thermal degradation of low boiling point volatiles (as acid acetic, n-propyl acetate, and 2-cyclopenten-1-one) occurs up to 120°C, followed by thermal degradation of monoterpenes, furans and sugars at 150-300ºC. The same authors affirmed thermal decomposition of lignin derived oligomers and cracking products of oligomers occurs at 400ºC.

Thus, aqueous extract from pilot-scale is composed especially by low boiling point volatiles and low percentage of lignin derived oligomers. On the other hand, the aforementioned thermal results suggests the main compounds of bio-oil are lignin derived oligomers, low boiling point volatiles and low percentage of monoterpenes, furans and sugars.

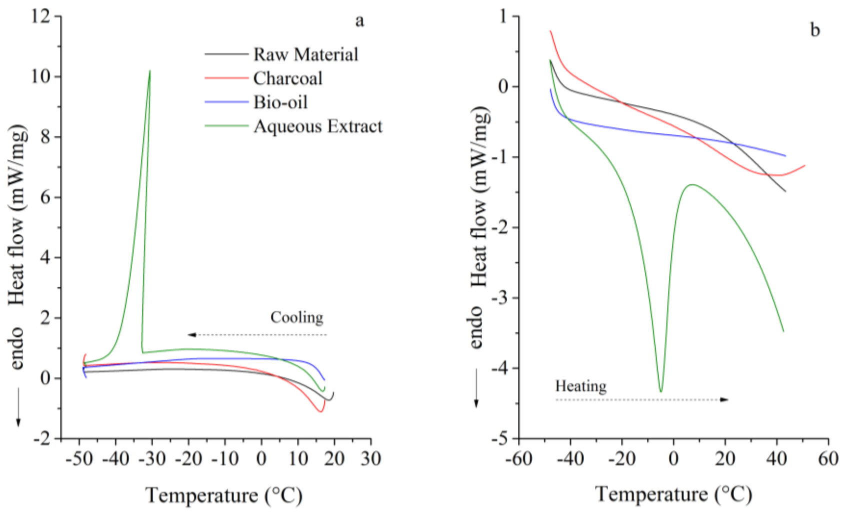

Figure 2. DSC results of byproducts from fast-pyrolysis of *Eucalyptus* flour.

DSC thermogram shows aqueous extract was only byproduct with thermodynamic events at low temperature (Figure 2a, and 2b). Aqueous extract presents a crystallization event around -35ºC (exothermic), and melting temperature around 0ºC (endothermic). According to Garcia-Perez et al. [14], exothermic events below -30ºC are common associated to crystallization of methyl esters of unsaturated fatty acids presents in aqueous phase during the bio-oil production.

Conclusions

Charcoal produced by fast-pyrolysis of *Eucalyptus* wood fines has lower quality when compared with charcoal produced by conventional processes, since present high both ash content and residual carbohydrates, which probably will decrease the heating value. Bio-oil and aqueous extract presented similar composition. Nevertheless, the proportion of these compounds is very different between the samples analyzed.

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