THERMOKINETIC CHARACTERIZATION OF BIOMASS PYROLYSIS BY DIFFERENTIAL SCANNING CALORIMETRY

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Introduction

Detailed knowledge of thermal conversion processes becomes increasingly important in order to formulate mathematical models for the design and optimization of chemical reactors employed in energy and chemicals recovery from biomass. Since heat of reaction has an important influence on the course of thermal conversion, the corresponding kinetic models should be coupled with heat transfer equations as an approach to the characterization of the whole phenomena. Although a substantial amount of information about thermal properties of some biomass, like wood, can be traced in the literature, few values have been reported for the heat of reaction of specific lignocellulosic materials[1-2] (e. g. energy crops) and most of the thermal measurements have been affected by experimental conditions such as sample weight and presence of secondary reactions, or autocatalytic effects due to impurities.

In this work the heats of pyrolysis of an energy crop (thistle) and some classical wood samples (pine and beech) are investigated and compared by simultaneous thermogravimetric analysis and differential scanning calorimetry. Samples with different amounts of mineral matter and extractives are tested at several heating regimes, in order to analyze autocatalytic effects due to non-structural components and the influence of heating regimes on the thermal measurement.

Experimental procedure

The experiments are carried out in a Setaram Setsys 12 thermobalance in the TGA/DSC configuration, at heating rates ranged between 5 and 50 K/min, linear and stepwise heating programs, under atmospheric pressure, using 2 mg samples of untreated, washed (with water at 80ºC to eliminate the soluble inorganic matter), and extracted (with ethyl alcohol) thistle, pine and beech. A nitrogen purge flow of 200 ml/min is applied to remove vapor pyrolysis products. The platinum crucible is open at the top with the purpose to minimize the mass transfer limitations and assure kinetic control. The equipment has been calibrated with metal standards under the same heating rate range of the experiments.

Thermokinetic analysis

Thermogravimetric (TGA) and calorimetric (DSC) results are initially compared for each sample. A qualitative analysis is done to recognize the main changes due to devolatilization, which are strongly reflected by local maximums or shoulders on the DSC curves. Once this correspondence is verified and the reliability of the data is guaranteed, results are compared at different experimental conditions, in order to evidence the dependence

of the reaction heat on the biomass composition. Figure 1 shows the decomposition of thistle sample subjected to several treatments for mineral matter and extractives elimination. The heat flow (magenta line) has evidenced the extremely heterogeneous behavior of the energy crop, represented by several peaks along the curve, with both endothermic and exothermic effects. The autocatalytic effects due to non-structural components have been widely recognized on reaction pathways changes and the exothermic production of char[3]. The treated samples exhibit a more clear endothermic (sharpened peak) at the beginning of the thermal devolatilization, where the extractives decomposition range has been identified[4].
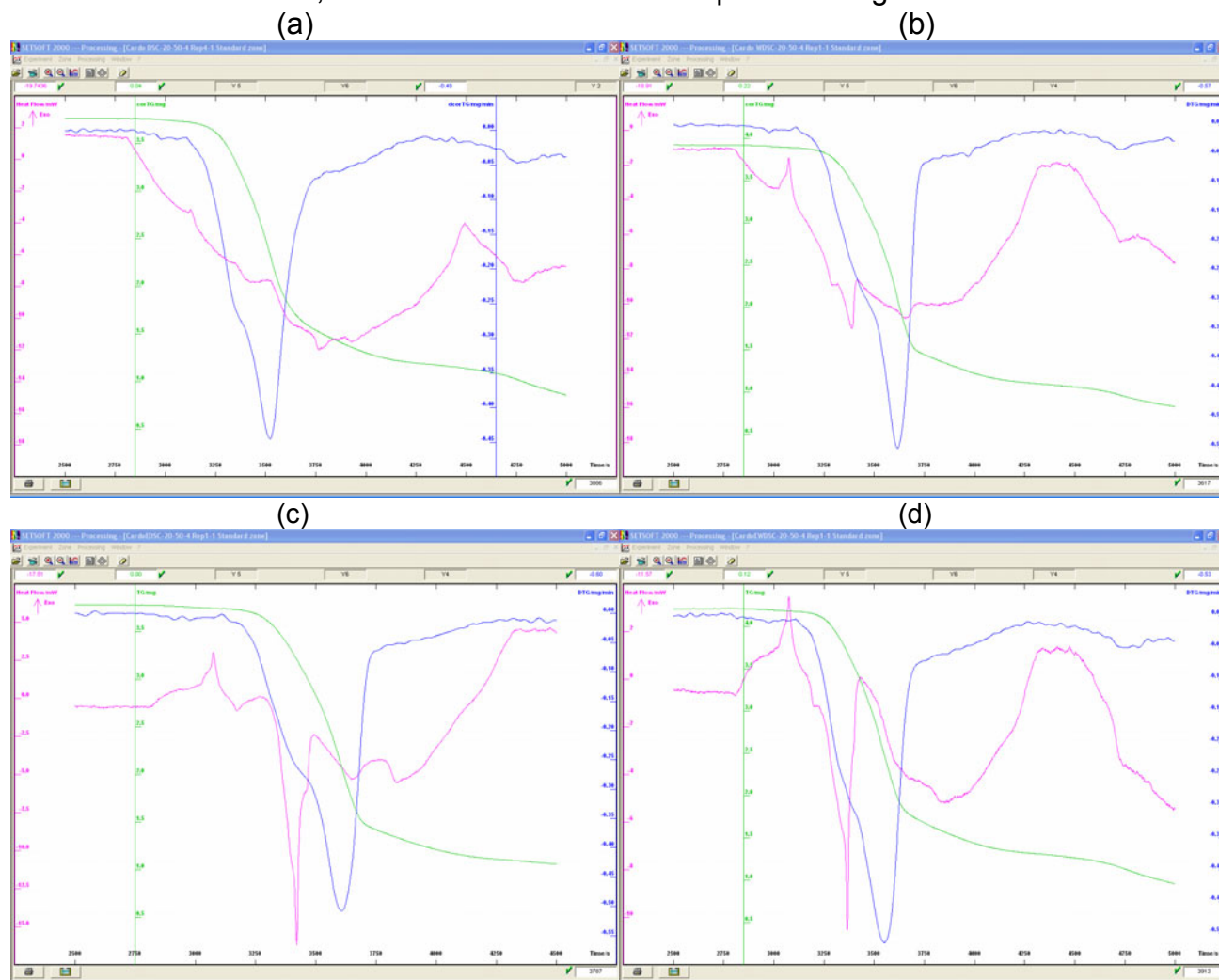
(a)   (b)

(c)   (d)

Figure 1. TG-DSC results for thistle pyrolysis at 20K/min. (a) Untreated thistle, (b) Washed thistle, (c) Extracted thistle and (d) Washed and extracted thistle sample.

Non clear differences have resulted in the reaction heat when different linear heating programs (moderate heating rate) are applied. Higher heating regimes than 20K/min have evidenced more influence of the effect of radiative heat exchange, due to the different emissivity of the sample with respect to the empty crucible in runs without a lid, and the heat flow necessary to heat the sample (see figure 2).
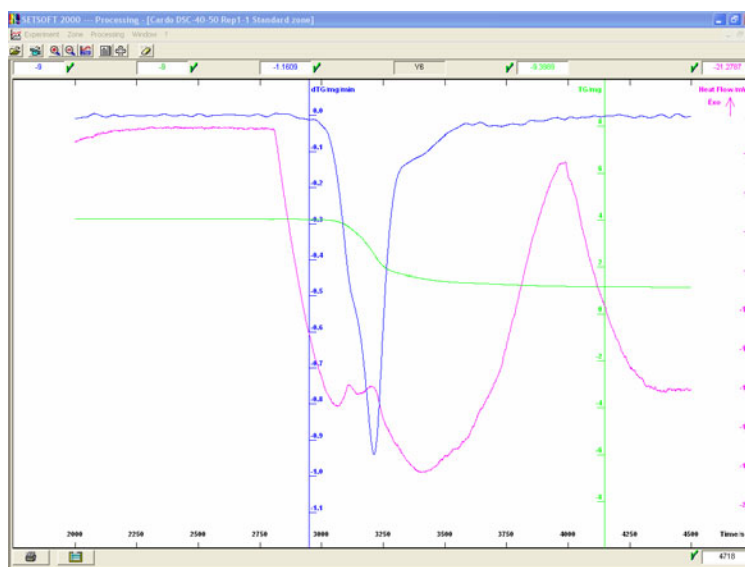
Figure 2. TG-DSC results for untreated thistle pyrolysis at 40K/min.

For the quantification of heat of pyrolysis, heat flow for all the results have been corrected by baselines obtained from blank runs using empty crucibles, and from the calculated radiative effect. Values for wood samples have resulted into the endothermic range reported in the literature for softwood and hardwood[2] (110 – 300 J/g). Thistle sample has evidenced an endothermic reaction heat as well, though the corresponding value presents a decrease, possibly due to the major content in non-structural samples.

Based on calorimetric studies, a model for the TGA/DSC system including heat transfer and pyrolysis kinetics is developed. The model is made assuming heat supply by a combination of convection and radiation. The total weight loss associated to the pyrolysis process is simulated assuming the addition of three independent parallel devolatilization reactions, with the kinetic parameters adjusted for pseudocomponents[3] (fraction of each main component that decomposes at a certain temperature range). Coupling kinetics and heat transfer descriptions allows to show the influence of the reaction heat on the pyrolysis process, determine the level of thermal lag in the system and evaluate the applicability of this type of kinetic model for engineering purposes.

References

[1] Stenseng, M.; Jensen, A.; Dam-Johansen, K. Investigation of biomass pyrolysis by thermogravimetric analysis and differential scanning calorimetry. *J. Anal. Appl. Pyrolysis* **2001**, *58-59*, 765.

[2] Rath, J.; Wolfinger, M.G.; Steiner, G.; Krammer, G.; Barontini, F.; Cozzani, V. Heat of wood pyrolysis. *Fuel* **2003**, *82*, 81

[3] Gómez, C. J.; Manyà, J. J.;Velo, E.; Puigjaner, L. Further applications of a Revisited Summative Model for Kinetics of Biomass Pyrolysis. *Ind. Eng. Chem. Res.* **2004**, *43*, 901.

[4] Mészáros, E.; Várhegyi, G.; Jakab, E. Thermogravimetric and Reaction Kinetic Análisis of Biomass Samples from an Energy Plantation. *Energy & Fuels* **2004**, *18*, 497.