Thermogravimetric Analysis of High-Density Cork Granules Using Isocoversional Methods

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ABSTRACT
In the present work thermogravimetric techniques were used to study the thermal degradation of high-density cork granules. Pyrolysis experiments were carried out for four heating ramps (10, 15, 20 and 25 °C/min), using nitrogen as the carrier gas. From the differential thermogravimetric (DTG) curves it was seen that degradation mainly occurs from 220 °C to 525 °C for the main components of cork (suberin, lignin, cellulose, and hemicellulose). It was also observed that for temperatures higher than 525 °C and up to 900 °C, lignin continued to decompose. Activation energies were calculated using the data obtained and the two isoconversional methods Kissinger-Akahira-Sunose (KAS) and Flynn-Wall-Ozawa (FWO). For the KAS method, and for degrees of conversion between 0.10 and 0.85, the activation energies varied between 232.2 and 353.0 kJ/kg. Using the FWO method and for the same degrees of conversion, the activation energies were in the range of 230.0 to 346.6 kJ/kg. These values agree with data provided by other authors, for different lignocellulosic biomass.

Keywords: cork granule, kinetic analysis, pyrolysis, thermogravimetric analysis

1. INTRODUCTION

At the present time there is increasing concern over the use of fossils fuels, their future reduction in nature, and the environmental problems created by their continuous utilization. For these reasons there is a tendency to introduce renewable energy sources, such as energy from biomass.

Biomass conversation into energy can be achieved by pyrolysis, a thermochemical process where it is heated in the absence of oxygen and decomposes into volatiles and biochar. Several authors investigated the pyrolysis of different types of biomass using thermogravimetric analysis (TGA). Using this technique, the variation of the mass of a fuel sample was tracked against time or temperature, in an inert atmosphere, for a specific heating rate. These data together with kinetic models allowed the calculation of kinetic parameters, including the activation energy (E), pre-exponential factor and the order of reaction [1, 2, 3, 4].

Of the various kinetic models developed to mathematically represent the decomposition of the biomass, isoconversional methods consider that the rate of reaction for a given degree of conversion (α) is only dependent on the temperature (T) [5]. Yuan et al. provided the equations for the Flynn-Wall-Ozawa (FWO) and Kissinger-Akahira-Sunose (KAS) isoconversional models [3].

The objective of this work was to study the thermal degradation of high-density cork granules in an inert atmosphere, using TGA techniques. The experiments were carried out at four heating rates (β = 10, 15, 20 and 25 °C/min), using nitrogen as the carrier gas. Using two kinetic models (FWO and KAS methods), E was calculated for different degrees of biomass conversion.

2. MATERIALS AND METHODS

The high-density cork granules were supplied from a manufacturer located in the North of Portugal. The TGA experiments were performed in a thermal gravimetric analyser type Netzsch STA 449 F3 Jupiter. The runs were carried out using nitrogen as the carrier gas, at a flow rate of 50 mL/min. The temperature was varied from 50 to 900 °C, using heating rates of 10, 15, 20 and 25 °C/min. The data was treated using Proteus software.

3. RESULTS AND DISCUSSION

The differential thermogravimetric (DTG) curves of the decomposition of cork granules, for heating rates of 10, 15, 20 and 25 °C/min, are presented in Fig. 1. Fig. 2 shows the variation of the activation energies calculated *versus* the degree of conversion for the FWO and KAS methods.

The DTG curves show several stages. The first, for temperatures lower than ~200 °C, was mainly due to loss of humidity. The second stage at temperatures up to ~525 °C, was where the components of cork residues (hemicellulose, cellulose, suberin and lignin) suffered pyrolysis with the release of volatiles. From 525 °C and up to 900 °C, lignin continued its slow decomposition.

The data obtained from the TGA were used to calculate the activation energy of pyrolysis for temperatures in the range of 220 °C to 525 °C and for several degrees of conversion. The methods of FWO and KAS were used to treat the data. For the FWO method and for $0.1 < \alpha < 0.7$ the values of E were almost constant, varying from

230.0 to 246.0 kJ.mol^{-1}. For α = 0.8 and α = 0.85, the activation energies were 318.6 and 346.6 kJ.mol^{-1}, respectively. With the KAS method, E remained almost constant up to a degree of conversion of 0.7 (between 232.2 and 250.3 kJ.mol^{-1}) and then increased to 323.9 and 353.0 kJ.mol^{-1} for α = 0.80 and α = 0.85, respectively. The zone of constant activation energy probably corresponds to the decomposition of hemicellulose, cellulose and suberin, which occurs at lower temperatures. For α = 0.80 and α = 0.85, the degradation of lignin becomes predominant, needing a higher activation energy to breakdown its chemical bonds.

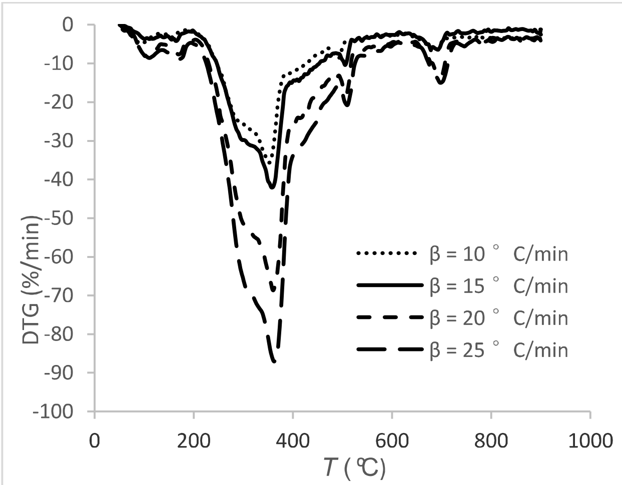

Figure 1 – DTG curves for the degradation of cork granules using nitrogen as carrier gas.

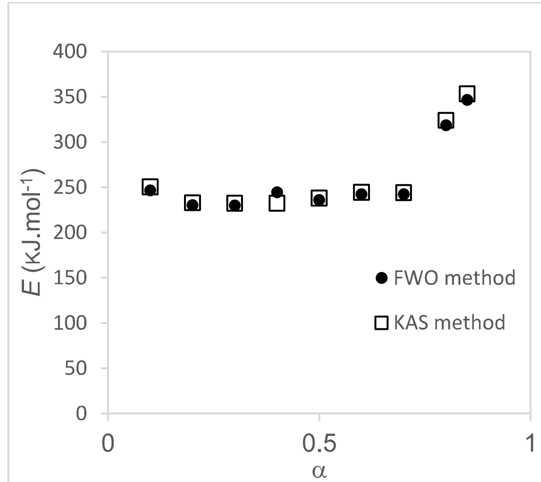

Figure 2 – Variation of E versus α for the FWO and KAS methods

4. CONCLUSION

The TGA results show that the degradation of high density cork granules occurs in several stages, linked to humidity loss and thermal decomposition of hemicellulose, cellulose, suberin and lignin. The energies of activation calculated from kinetic analysis of the data using the FWO and KAS methods are in agreement with results obtained by other authors, for different biomass residues.

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