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Thermogravimetric analysis and kinetics modeling of isothermal carbonization of olive wood in inert atmosphere

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Abstract

The kinetics of olive wood carbonization is investigated by means of isothermal thermogravimetric analysis method. Measurements were carried out in a thermobalance for different fixed temperatures between 498 and 648 K. A two-stage semi-global kinetic model consisting of four sequential steps was proposed to derive kinetic parameters. The olive wood is classified in three pseudo-components. For the first two, similar thermal degradation mechanisms take place in a single reaction step. For the third, the thermal degradation takes place in two consecutive steps. The isothermal conditions allow the kinetic constants (activation energy and pre-exponential factors) to be estimated by means of the analytical solution of the mass conservation equations. An overall good agreement was obtained with activation energy values available in the literature.

Keywords: Carbonization; Olive wood; Kinetic parameters; TGA; Modeling

1. Introduction

Biomass, especially wood, has traditionally been an important source of energy particularly attractive nowadays because of its inherent nature of being environmentally friendly and renewable. Wood has also been considered as a potential feedstock for gasification to produce a mixture of H_2 and CO (syngas). In this process, the wood is converted into char as an intermediate product which is subsequently or simultaneously gasified. The wood carbonization in which the high yield charcoal is the principal product is effectively an initial stage in any gasification process. It is characterized by a slow heating rate, a relatively low temperature (600–700 K) and a long residence time. Indeed, the mechanism of wood carbonization shows the presence of several decomposition phases when the temperature increases. A wood drying phase with elimination of some volatile compounds takes place at temperatures lower than 473 K. For temperature range of 473–553 K, hemicelluloses are converted essentially into gases and acetic acid. This step corresponds to the wood roasting. Above 553 K, the lignin and cellulose decompose to give three products: gas, tar and char. Therefore, the knowledge of the kinetic schemes of the wood carbonization is essential. Particularly, kinetic analyses of wood carbonization, also called low temperature pyrolysis, under isothermal conditions have been carried out by several authors to represent the kinetic schemes of this process [1–8]. The simplest treatment describes the process by means of a one-step global reaction for degradation in which the activation energies vary toughly between 60 and 170 kJ mol^{-1} [1–4]. These models are not applicable for simulating wood carbonization because they assume a constant ratio of the charcoal to volatiles yield [9]. A one-step multi-reaction kinetic mechanism of beech wood was described by [5] as a two-stage temperature process in the range of 523–673 K. Two sets of kinetic parameters (activation energies of 17–115 kJ mol^{-1}) were needed depending on a limit temperature of 603 K. This kinetic scheme cannot be extended to systems different from the one on which it is based [9]. Multistage, semi-global models are developed to describe the kinetic of isothermal wood degra-

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Table 1
Elementary composition of Tunisian olive wood

Elementary composition	Mass fraction (%)
Carbon	45.08
Hydrogen	6.21
Nitrogen	0.4
Oxygen	45.39
Sulphur	Inferior to 0.3

dation [6–8]. For carbonization techniques where the product gases energy is recycled in the process [10], models of this type can be successfully applied to simulate thermal conversion since they include the description of the primary degradation of the virgin wood and the secondary degradation of the primary pyrolysis products. The large differences between reaction schemes and kinetic constant values proposed by previous authors show that further analysis is needed to study the multi-stage thermal degradation kinetics of wood under isothermal conditions.

The main objective of this study is to propose a two-stage, semi-global kinetic model of olive wood carbonization. Isothermal weight loss curves of olive wood, measured in an inert atmosphere for a temperature range of 498–623 K, are used to elaborate a reaction mechanisms scheme. A comparison is also made between the estimated activation energy values and those available in the literature corresponding to isothermal carbonization conditions.

2. Experimental study

2.1. Material specification

A hard olive wood, from Sfax in Tunisia, is used as raw material in all experiments. It was crushed by a robot and the obtained powder was sieved through two sieves. The particle size of the sieved powder was between 0.5 and 1 mm. Table 1 shows the obtained results of the olive wood elementary analysis realized in the Analysis Central Service of CNRS in France. By neglecting the sulphur and nitrogen fractions in the above analysis data, the empirical formula of the used wood can be represented by: $CH_{1.67}O_{0.75}$.

2.2. Apparatus description

A Setaram thermobalance apparatus is used for the thermogravimetric analysis. This apparatus records the different data concerning the evolution of the temperature and the mass loss. The thermobalance consists of three main parts:

- a controller which allows the transfer of the experimental data (mass, temperature) to a computer which records and treats them by Setsys software (e.g. DTG),
- an oven composed of an electrical resistance in graphite and a double envelope cooled by a circulation of water in order to control the heat flow and then the temperature. A PDI regulator allows to vary the rate of temperature change between 0.2 and 50 K min^{-1},
- a micro-balance, based on a compensation permitting to measure the mass of the sample placed in a basket of 5 cm^3 volume, continuously balanced and thus maintained at a fixed position during the experiment. This allows to avoid eventual intra-particle temperature gradients in isothermal conditions in the oven. The maximal mass variation is 200 mg and the mass measurement precision is 0.4 μg. The oven temperature is adjustable with a precision of 0.1 K and can reach a maximum of 1473 K. In order to establish an inert atmosphere during all experiments, a controlled argon flow fixed to 7.2 l h^{-1} at 273 K and 1 atm, sweeps the measurement cell that is purged for 20 min before starting the heating program.

2.3. Experimental methodology

The initial mass of olive wood powder in the basket is about 170 mg. The experiments start with a drying phase during which the temperature is raised from room temperature to 423 K at a heating rate of 20 K min^{-1} with a holding time of 20 min. Then, the same heating rate is applied to the oven until reaching the fixed studied temperature (pre-heated phase). This methodology is followed to reach the isothermal stage in the pre-heated wooden powder without any intra-particle gradients and in order to shorten the first thermal dynamic stage [6]. The subsequent thermal decomposition is carried out in isothermal conditions during 5 h. The same experiment is repeated for seven fixed temperatures (T = 498, 523, 548, 573, 598, 623 and 648 K). Measurements of the mass of the wooden powder are taken in a fixed position during 5 h at each temperature level. In these conditions, the diffusion time is always inferior than the reaction time. Indeed, for a wood particle of $e = 0.5$ mm thickness and a diffusion coefficient D between 10^{-7} and 10^{-8} $m^2 s^{-1}$, the diffusion time $\tau = e^2/D$ is respectively equal to 2.5 and 25 s. This time is always very small compared to the reaction time which exceeds 500 s in all the studied cases. The temperature and the concentration gradients are consequently negligible in the basket which can be assumed to have a uniform temperature and concentration.

2.4. Measurements

The residual weight curves of the olive wood, for the seven studied temperatures T = 498, 523, 548, 573, 598, 623 and 648 K, are plotted in Fig. 1. In all the experiments, the values of the total mass used are those which correspond to the fixed temperatures. In fact, to separate the mass loss during the dynamic stage (non-isothermal) of decomposition from that of the isothermal stage, particularly for higher temperatures (598, 623 and 648 K), the relative values of total mass before reaching the fixed temperature are not taken into account in the estimation of the kinetic parameters. Only the start time at the beginning of the transformation is obtained by extrapolation of the mass values corresponding to the fixed temperature. This time of origin is estimated with a rather good accuracy for the majority of the studied temperatures by an exponential extrapolation at the beginning of the experimental curves.