A unified mechanism of the combustion reactions of lignocellulosic fuels

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ABSTRACT

Thermogravimetric curves in air, measured for beech and fir wood and three agro-industrial residues (hazelnut shells, olive husks and wheat straw) at different heating rates (5–40 K/min), are subjected to kinetic evaluation. It is shown that a five step mechanism (three reaction for the devolatilization stage and two reactions for the combustion stage) provides good predictions in all cases. Moreover, for the combustion stage (amounts of volatile released between 25 and 40%) the activation energies are the same (113 and 183 kJ/mol). On one side, the devolatilization stage is also very similar for the residues which require activation energies of 125, 170 and 164 kJ/mol for the pseudo-components hemicellulose, cellulose and lignin. On the other, the behavior of the last two pseudo-components is also similar for the beech and fir wood (activation energies of 200 and 176 kJ/mol) whereas the different nature of hemicellulose requires significant changes (activation energies of 147 and 110 kJ/mol, respectively).

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1. Introduction

Thermogravimetry has been extensively applied to investigate weight loss characteristics of biomass fuels. Compared with degradation in inert atmosphere, oxidative degradation has been given considerably less attention. In this case, two main stages are observed representing oxidative degradation of the biomass followed by the oxidation of the charred residue, both associated with peaks in the rates of weight loss curves [1]. The presence of oxygen enhances the degradation of the cellulose component at low temperature, with a sharpening of the peak rate, and the overlapping of the decomposition rates of the chemical components [2–6]. Weight loss measurements are useful to evaluate the feedstock reactivities and, when made under negligible influence of heat and mass transfer effects, can be applied to formulate plausible reaction mechanisms and to estimate the related kinetic parameters. Then kinetic mechanisms can be coupled with the description of transport phenomena to simulate the behavior of practical conversion systems [7–11].

Although commercial thermogravimetric systems have a high precision, the sample temperature is not directly measured or controlled. In the presence of oxygen, given the high exothermicity of the combustion reactions, a thermal runway may occur with the temperature inside the sample becoming considerably higher than that foreseen by the assigned program and the sample being oxidized at high reaction rate. These problems have been extensively discussed in previous literature [1,12–15]. As the highest reaction rate in an experiment is roughly proportional to the sample mass and the heating rate in the kinetic regime, in addition to being obviously dependent on the reactivity of the given sample and on the oxygen partial pressure [15], the sample mass should be adequately reduced until no difference is seen in the normalized weight loss curves. In this way it is also guaranteed that spatial temperature gradients are negligible and oxygen diffusion is not the limiting process. Unfortunately, numerous thermogravimetric measurements reported in literature about biomass combustion show the occurrence of thermal runaway, with the consequent formulation of erroneous reaction mechanisms. Moreover, there are still other aspects that should be taken into account when chemical kinetics is the subject of interest.

A significant number of studies is available where, in addition to the determination of the weight loss characteristics, the examination of the data has led to mechanisms of different complexity with kinetic parameters, in particular the activation energies, dependent on the conversion level and/or the heating rate such, for instance, in Refs. [16–18]. In other cases, only a single heating rate is considered (see, for instance, Refs. [19–22]). These models although based on experimental data apparently not impugned by heat and mass transfer effects, are not truly valid over widely variable conditions. Indeed, only kinetic models capable of explaining the shift in the thermogravimetric curves with the heating rate, without changing the kinetic parameters, can be considered potentially correct [23]. Kinetic models with these features for the oxidation of wood and biomass have also been proposed [6,13,23–34], based on the analysis of several thermogravimetric curves obtained under variable heating conditions, with invariant kinetic parameters. The

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Table 1
Chemical composition of wood and residues.

	Extractives [% wt]	Lignin [% wt]	Holocellulose [% wt]	Ash [% wt]
Beech	2.0	22	78	0.2
Douglas fir	2.6	30	67	0.5
Hazelnut shells	9.2	33	56	1.4
Olive husks	8.7	28	61	2.5
Wheat straw	4.9	23	66	6.2

large majority assumes a mechanism of N reactions with n-order kinetics but a distributed activation energy model (DAEM) for the devolatilization stage has also been proposed [29,33,34]. It is, how-ever, extremely difficult to select the best model because, in the first place, the number of reaction steps has been varied from two (a global reaction for biomass devolatilization and a global reaction for char oxidation) up to nine (devolatilization and/or oxidation of the pseudo-components and oxidation of the related char fractions). Moreover, the estimated kinetic parameters vary over very wide intervals. Although the differences in the nature and properties of the biomass fuels (i.e. chemical composition including content and composition of inorganic matter), the experimental conditions (i.e. actual heating conditions), the mathematical treatment of the data (for instance, use of integral or differential data) and mag-nitude of the deviations between predictions and measurements may explain such a variety of mechanisms and the wide range of variation in the kinetic parameters, the formulation of unified mechanisms valid for a significant number of biomass fuels, with small differences in the kinetic parameters, is highly desirable.

In this study thermogravimetric measurements are made, at several heating rates, for the oxidation of wheat straw, olive husks and hazelnut shells. A peculiar thermogravimetric system is employed which is based on the measurement and control of the sample temperature, thus allowing the reactions to take place under exactly known thermal conditions. Also, the sample mass is accurately determined so as there is no limitation introduced by oxygen diffusion. The weight loss curves, together with two previ-ous sets of data for beech and fir wood, also carefully determined, are applied to understand whether a unified kinetic mechanism can be formulated with activation energies invariant with the lignocel-lulosic material.

2. Materials and methods

2.1. Materials

The materials examined in this study are two wood species, beech (Fagus sylvatica) and Douglas fir, which can be considered representative of the usual standards for the hardwood and soft-wood category, and three agro-industrial residues, hazelnut shells, olive husks (a by-product in the manufacture process of olive oil in mills and consisting of pulp, peel and pits) and wheat straw. The chemical composition is listed in Table 1 [35]. Prior to ther-mogravimetric tests, samples have been milled to powder (particle sizes below 80 μm) and pre-dried for 10 h at 373 K.
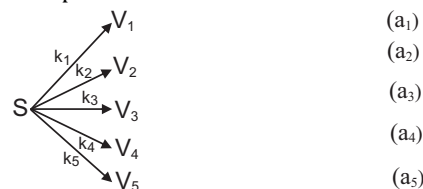
2.2. Experimental details

Solid conversion can be made to occur under known thermal conditions with a proper control of the sample temperature (mea-sured by a close-coupled thin thermocouple), using the intensity of the applied radiative heat flux as the adjustable variable. This principle has been applied in the development of the thermo-gravimetric system used by this research group [12,13,36,37]. The characteristic size of the process is the thickness of the sample layer, whose limit value for a kinetic control depends on the nature of the

solid fuel. For wood and residues, it has been observed that val-ues up to 120 μm allow a good temperature control to be achieved, given maximum heating rates of 40 K/min and a final temperature of 873 K. Also, the weight loss curve is the same as the sample layer thickness is decreased below 120 μm, indicating that conversion is not affected by heat and mass transfer effects. Hence, the tests have been made for sample layers about 110 μm thick (5 mg dis-tributed over a surface 25 mm × 5 mm) using a final temperature of 873 K. The thermogravimetric curves for the two wood species were already available [13] and were obtained with heating rates of 5, 10, 20 and 40 K/min. Those for the residues have been measured for heating rates of 5, 10, 20 and 30 K/min. Each thermogravimet-ric test has been made in triplicate, showing good repeatability. Maximum deviations between the measured weight loss curves are always in the range 0.1–0.3%.

2.3. Kinetic mechanism

As anticipated, lignocellulosic fuel devolatilization, in both pyrolysis and combustion, has been extensively modeled assuming that volatiles are released according to a set of parallel reactions for lumped components [1,6,18,23,28–34,38]. Then, the overall mass loss rate is a linear combination of the single component rates. The mechanism proposed here for the description of the two main reac-tion zones (solid devolatilization and char combustion) consists of five independent parallel reactions as follows:

$$
\begin{aligned}
& S \xrightarrow{k_1} V_1 && (a_1) \\
& \;\;\xrightarrow{k_2} V_2 && (a_2) \\
& \;\;\xrightarrow{k_3} V_3 && (a_3) \\
& \;\;\xrightarrow{k_4} V_4 && (a_4) \\
& \;\;\xrightarrow{k_5} V_5 && (a_5)
\end{aligned}
$$

where S is the solid sample which produces the lumped volatile products V_i ($i=1,5$). From the chemical point of view, reactions a1–a3 are associated with solid fuel devolatilization, in relation to the decomposition of the three pseudo-components hemicellulose, cellulose and lignin, and reactions a4–a5 with char combus-tion, specifically devolatilizion and actual combustion. From the physical point of view solid devolatilization and char combus-tion are sequential processes but the parallel reaction mechanism is more flexible as it can easily guarantee this feature by an appropriate set of parameter values and, at the same time, can describe well the possible overlap between reactions pertinent to either the devolatilization or the combustion stage. The reac-tions rates present the usual Arrhenius dependence (A_i are the pre-exponential factors and E_i the activation energies) on the temperature and a linear (reactions a1–a4) or a power law with exponent n (reactions a5) dependence on the solid mass fraction. The latter treatment takes into account the evolution of the pore surface area during conversion [1]. Since the sample temperature, T, is a known function of time, the mathematical model consists of five ordinary differential equations for the mass fractions, Y_i, of the reacting solid fuel:

$$
\frac{dY_i}{dt} = -A_i \exp\left(-\frac{E_i}{RT}\right) Y_i^{ni}, \ldots, Y_i(0) = v_i, \ i = 1, \ldots, 5 \qquad (1\text{–}5)
$$

where v_i, indicated in the following as stoichiometric coefficients, are the initial mass fractions of the lumped classes of volatiles gen-erated. The kinetic parameters are estimated through the numerical solution (implicit Euler method) of the mass conservation equa-tions and the application of a direct method for the minimization of the objective function, which considers simultaneously both inte-gral (TG) and differential (DTG) data for the various heating rates, following the method already described [39].