



# A summative model for the pyrolysis reaction heats of beech wood

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## ABSTRACT

Kinetic models of beech wood decomposition, based on the three main pseudo-components, hemicellulose (one or two steps), cellulose (one step) and lignin (one or two steps), are applied for the first time to predict differential thermogravimetric (DTG) and differential scanning calorimeter (DSC) curves available from the literature. For the conditions that minimize the activity of secondary reactions, it is found that while the DTG curves are already well predicted by the extensively used three-step model, at least an additional step is required for the pseudo-lignin decomposition for a good prediction of the DSC data. The pseudo-cellulose decomposition is a globally endothermic process with the corresponding heat varying from about 601–528 J/g (of volatile evolved), as the number of reaction steps is increased from three to five. Pseudo-hemicellulose decomposition also takes place endothermally with reaction heats of 245 J/g (one step) or 321 and 226 J/g (two steps). Instead pseudo-lignin decomposition occurs with remarkable exothermicity corresponding to –923 J/g (one step) or –728 and –635 J/g (two steps).

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## 1. Introduction

The reactions of biomass torrefaction and pyrolysis to be activated require, for the initial stage, the supply of external heat to bring the temperature at a sufficiently high level. Then the heat requirements are soon modified by the onset of reaction heat effects which, for practical applications, may lead to rather large deviations with respect to the external heating temperature [1–12]. In reality the endothermic or exothermic character of biomass pyrolysis is a topic examined in a significant number of studies but the results are often different even from the qualitative point of view. It is generally acknowledged that the main reason for the observed discrepancies is attributable to modifications in the activity of secondary reactions. Already in the early seventies Roberts [13] postulated that if wood is heated to temperatures in excess of 593 K, the reaction heat is approximately constant at –160 to –240 J/g of products evolved. It is estimated that 65% of this heat generation is due to the primary pyrolysis of lignin and 35% to the primary pyrolysis of cellulose, given a negligible activity of secondary degradation caused by structural failure and rapid escape of volatile products. For heating temperatures below 593 K, it is observed that the reaction heat is highly dependent on the exper-

imental conditions and may rise to –1600 J/g. This is attributed to the activity of secondary reactions that are favored by the prolonged residence of tar vapors inside the degrading sample with a possible extra contribution, with respect to primary reactions, of –1200 J/g. Increasing the pressure during pyrolysis causes a reduction in the reaction endothermicity or a shift to an exothermic behavior with an increase in the yields of char [14,15] again consequent to the enhancement of secondary exothermic reactions. The presence of a lid over the crucible of the thermogravimetric systems also produces the same qualitative effects [14–21]. For instance, in the absence of significant resistance to volatile product flow, DSC analysis of wood [17] shows an endothermic peak followed, at higher temperatures, by an exothermic zone. However, when the activity of secondary reactions is favored with the presence of a lid, the first zone becomes less endothermic or even exothermic. Moreover, the extent of secondary reaction activity is also highly dependent on the microstructure of the material and thus on the sample particle size. For instance, it has been observed that fixed-bed pyrolysis of hazelnut shells, once these are subjected to milling, loses the strong exothermic character leading to pyrolytic runaway [11]. Thus, even for extensively investigated materials, such as wood and the related commercial chemical components, widely variable global pyrolysis heats are reported [14–28].

Quantitative estimates of the pyrolysis reaction heats are needed for the development of predictive models of both pyrolysis and gasification/combustion plants. However, apart from the

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already mentioned difficulty in the selection of the proper global value as provided by previous literature, estimates of the reaction heats are actually needed for the multi-step kinetic models, that are coupled with the description of transport phenomena. Pseudo-components hemicellulose, cellulose and lignin [29] are introduced owing to the difficulty, by means of in-situ analysis of DTG data, to exactly identify and separate the decomposition rates of the various components. Nevertheless the use of pseudo-components is fully justified as the predominant role for the various zones of the main chemical components is generally evident. The reaction heats for these multi-step models have never been estimated, though in a couple of cases they have been used as guessed or adjustable parameters when simulating the pyrolysis of thick wood particles/blocks [7,30].

In this study we propose, for the first time, estimates based on DSC measurements of the heats of the reactions constituting multi-step devolatilization mechanisms of beech wood. The first part re-examines differential thermo-gravimetric measurements [31], already used by Branca et al. [32] for the formulation of a three-step devolatilization model for the main pseudo-components of beech and water-washed beech wood, with the scope of improving the accuracy of the predictions with the introduction of one or two additional steps (four-step and five-step model, respectively). As the model validity is strengthened by increasing the number of experiments evaluated, the two sets of data are again re-examined here. However, the emphasis is on untreated beech wood, as the second part of the analysis is concerned with the analysis of DTG and DSC curves for this material provided by Gomez et al. [18], aimed at the evaluation of the reaction heats for the various multi-step models. It is worth observing that the specific features of the three-step model developed by Branca et al. [32], that is the evaluation of experiments carried out over a wide range of heating rates and the evolution of the pseudo-component lignin localized only at the high-temperature tail zone, once incorporated into CFD models [33,34], are apt to provide quantitative predictions of practical systems. These, on the other hand, are missed by models with the pseudo-component lignin decomposing over wide temperature intervals such as, for instance, by the extensively used models [35,36].

## 2. Materials and methods

The reaction kinetics considered here consists of devolatilization models, assuming that volatiles are released according to a set of parallel reactions from the three pseudo-components [29,35–39]. Then, the overall mass loss rate is a linear superposition of the contributions from the various steps. As anticipated, three-step (one step for each main pseudo-components), four-step (one step for pseudo-hemicellulose and pseudo-cellulose and two steps for pseudo-lignin) and five-step models (two steps for pseudo-hemicellulose and pseudo-lignin and one step for pseudo cellulose) are examined. The reactions 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 dependence on the evolved volatile mass fraction. For the mass conservation equations, the sample temperature,  $T$ , is a known function of time and the mathematical model consists of  $n$  ( $n = 3, 4$  or  $5$ , on dependence of the reaction steps) ordinary differential equations for the mass fractions,  $Y_i$ , of the volatile fractions:

$$\frac{dY_i}{dt} = -A_i \exp\left(-\frac{E_i}{RT}\right) Y_i, Y_i(0) = v_i, i = 1, \dots, n \quad (\text{a1-an})$$

where  $v_i$ , indicated in the following as stoichiometric coefficients, are the initial mass fractions of the lumped classes of volatiles gen-

erated. The evaluation of the reaction heat is straightforward and makes use on the following equations:

$$Q_i = -\Delta H_i A_i \exp\left(-\frac{E_i}{RT}\right) Y_i, i = 1, \dots, n \quad (\text{b1-bn})$$

The parameters are estimated through the numerical solution (implicit Euler method) of the mass conservation equations and the application of a direct method for the minimization of the objective function, which considers the DTG and DSC data for the various heating rates, following the method already described [40].

It is generally accepted that cellulose decomposition can be well described by a single reaction step with high activation energy [29,35–39], but the decomposition of the other two main components is more complex. Two-step mechanisms have been proposed for hemicellulose decomposition [22,41–43] whereas the wide temperature range where lignin decomposes would require multi-step mechanisms [35,36]. These aspects should be taken into account when the heats associated with the occurrence of the various reactions should be estimated. Indeed, as shown in the following, it may happen that, even though a kinetic model gives good or acceptable predictions of the mass loss curves, when applied to estimate the reaction heats by means of the DSC curves, the corresponding accuracy is significantly worsened. Thus the first part of the analysis is motivated by the need to achieve a better description of the thermogravimetric curves. In this regard, the mass loss curves of beech wood devolatilization (heating rates of 5–80 K/min) and water-washed beech wood (heating rates 3–108 K/min) [31], are in the first place used for a more accurate evaluation of the three-step mechanism [32]. Indeed, in this case, the estimation procedure was applied requiring invariant activation energies with the pretreatment. This restriction is removed from the present evaluation. Moreover models are developed with an additional step for pseudo-lignin decomposition (four-step mechanism) and for both pseudo-hemicellulose and pseudo-lignin decomposition (five-step mechanism).

For the evaluation of the reaction heats, the DTG and DSC curves provided by Gomez et al. [18] for beech wood (heating rate 20 K/min) are evaluated. More specifically the experiments made with open crucibles are considered, so as to limit the effects of secondary decomposition and to obtain parameter values essentially representative of primary reaction heats.

## 3. Results

The three-step model [32] has been re-examined and the results compared with those of the newly formulated four- and five-step models. The small modifications are also discussed, that should be introduced to take into account the differences in the sample properties, for the experiments available for both DTG and DSC curves. Finally estimates of the reaction heats are provided for the various kinetic models.

### 3.1. Reaction kinetics

The results obtained for the kinetic parameters of the three-step, four-step and five-step models are listed in Tables 1 and 2 (kinetic parameters and stoichiometric coefficients), obtained from the evaluation of the beech wood and water-extracted beech wood curves [31], already used [32]. These tables also list (in brackets) the kinetic parameters for beech wood when using the data by Gomez et al. [18] (sample of the same wood species but of different origin) with the optimization focused on the DSC curve. It should be noticed that the evaluations made for the three-step model [32] were carried out by requiring the same activation energies for the two data sets, independently from the pretreatment, while a separate evaluation has been made here. The improvements introduced

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