



Measurement and Evaluation of Experimental Data for Modelling Thermal Decomposition of Solid Materials

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This paper studies a method of estimating the kinetic parameters for wood thermal decomposition as an input for pyrolysis modelling. Samples of birch and pine wood were firstly examined using Thermogravimetric analysis (TG) both in oxidative (air) and non-oxidative (nitrogen) atmosphere, studying the influence of the heating rate (5, 15, 25 °C·min⁻¹) on the wood mass loss rate.

For a single step thermal degradation reaction in non-oxidative atmosphere activation energy and preexponential factor was determined from experimental data using isoconversional method. The results were used as initial estimates for optimization technique – genetic algorithm (GA). Using GA, three thermal degradation schemes of wood were studied.

GA was proved to be effective tool for estimating kinetic parameters of pyrolysis models. Contrary to isoconversional method GA does not require user's participation during the parameter estimation process and is able to handle several parameters at once.

1. Introduction

Pyrolysis modelling is of interest in many industrial branches. The particular interest of the authors is a CFD based fire modelling of the flame spread and fire growth, which represents an alternative to an expensive and often impossible to perform full scale fire testing (especially in cases of the real world geometries). Pyrolysis model quantify the rate of release of gaseous combustibles from solids when thermally stimulated and thus control ignition and flame spread. It passes information to the coupled gas phase combustion model and gas phase transport phenomena.

Despite of its practical importance, CFD based fire growth models are of the use in the research area only. The main limitation of their usage is in obtaining the pyrolysis input data as there is no standard methodology, how to extract the required data from standard fire tests and laboratory experiments (Lautenberger and Fernandez-Pello, 2011). A mechanism of thermal decomposition has to first described, that can be applied to the pyrolysis modeling. Consequently kinetic parameters for the decomposition scheme have to be evaluated.

TG analysis as a standard experimental technique was used for studying the mechanism of wood thermal degradation. Wood was used as a typical representative of charring material. Experimental results were used to evaluate kinetic parameters using isoconversional method and genetic algorithm (optimization technique).

The main goal of the work was to assess the suitability of the experimental and numerical methods described for obtaining kinetic parameters of charring materials intended for solid pyrolysis modeling.

2. Experimental part

2.1 Materials

Experiments were carried out on pine wood (softwood representative) and beech wood (hardwood representative). Samples were prepared from the small wooden profiles commonly used in construction with no surface modification. Samples contained an average of 7.9 and 6.45 % of moisture for pine and beech wood, respectively. Chemical composition of the wood specimens was not experimentally studied, literature values were used (Matala, 2008).

2.2 Apparatus and experimental conditions

A thermogravimetric instrument Setaram Setsys Evolution for simultaneous TG-DTA measurements was used to perform the thermogravimetric tests. The sample of wood (5 mg) was placed into a platinum crucible and the mass loss was detected using a high precision balance. Three non-isothermal measurements with a heating rate of 5, 15 and 25 °C·min⁻¹ up to 800 °C were performed for both wood specimens. The fire growth and flame spread is a complex issue since the burning of the mass happens at the pyrolysis zone (inert environment), but the flame spread happens in the oxidative environment. All measurements were thus carried out in two ambient atmospheres (pure nitrogen and air) to study the influence of the oxygen presence on the rate of solid decomposition.

3. Numerical part

Thermal decomposition of solids is commonly described using the single step reaction kinetic equation of the form

$$\frac{d\alpha}{dt} = k(T) \cdot f(\alpha), \quad (1)$$

where α denotes wood conversion and is defined as

$$\alpha = \frac{m_0 - m}{m_0 - m_\infty}, \quad (2)$$

where m_0 is an initial sample mass and m_∞ is the sample mass at the end of the TG experiment. Expressing the temperature dependency of the reaction rate (function $k(T)$) using Arrhenius equation and combined with the reaction model $f(\alpha)$ of the form $(1 - \alpha)^n$ Eq. 3 is obtained.

$$\frac{d\alpha}{dt} = A \exp\left(-\frac{E}{RT}\right) \cdot (1 - \alpha)^n \quad (3)$$

A denotes preexponential factor, E activation energy and n is the order of reaction.

3.1 Isoconversional method

Using Eq. 3 to describe the one step thermal degradation of solids three unknown kinetic parameters arises. Isoconversional method (Gašparovič, 2009) is one of the standard methods for evaluating TG analysis data. One of the basic assumptions of the isoconversional method is that A and E are functions of conversion. The result of the isoconversional method is thus the dependency of A and E on conversion, reaction order is not calculated. Using linear isoconversional method, Eq. 3 is rewritten into linear form

$$\ln\left(\frac{d\alpha}{dt}\right) = \ln A + n \cdot \ln(1 - \alpha) - \frac{E}{R T} \quad (4)$$

For the given value of conversion and all values of the heating rate β , $\ln(d\alpha/dt)$ is plotted as a function of $1/T$ and using linear regression isoconversional lines were calculated. Activation energy E is found as a slope of the isoconversional line, preexponential factor A as its intercept. The dependency of A and E on conversion was found using polynomial fit. After obtaining the kinetic parameters, simulation data were calculated using equation 3, which is an ordinary differential

equation. Calculating the kinetic parameters, experimental data were consider only above the temperature of 160 °C to ensure there is no more moisture evaporation to satisfy the simple one step degradation scheme assuming dry wood.

3.2 Genetic Algorithm

Genetic algorithm is based on the Darwinian idea of evolution. It is an optimization technique i.e. it finds parameters that provides the best fit to the experimental data. In the theory of GA unknown parameters are called genes. A group of genes creates an individual and set of individuals create a population. Population evolves with time because individuals that provides the best fit to experimental data are selected for a reproduction and produce offspring for next generation. To maintain the diversity of the population, stochastic mutation takes place. The whole process of selection/reproduction/mutation is repeated every generation and improved population (sets of estimated parameters) is obtained each round. The measure of the parameters fit is evaluated using normalized fitness function of the form

$$R = \omega_1 \left(1 - \frac{\sum (D_{\text{exp}} - \bar{D}_{\text{exp}})^2 - \sum (D_{\text{exp}} - D_{\text{mod}})^2}{\sum (D_{\text{exp}} - \bar{D}_{\text{exp}})^2} \right) - \frac{\omega_2}{I} \sum_{i=1}^I \frac{A_i - A_{i,\text{min}}}{A_{i,\text{max}}}, \quad (5)$$

where D_{exp} denotes experimental data i.e. the TG data, \bar{D}_{exp} is a time average of experimental data and D_{mod} denotes simulated data using model of the form

$$\frac{\partial y}{\partial t} = -(y - y_{\infty})^{n_j} A_j \exp\left(-\frac{E_j}{RT}\right), \quad (6)$$

which is a simplified form of the general equation describing the rate of change of the material density (McGrattan et al., 2009) assuming no volume change of the solid material and that material consists of only one component. The second part of Eq. 5 ensures, that during the selection process, parents with a smaller value of the gene coding for A are preferred. Large values of A often lead to an unstable simulations. I is the number of unknown preexponential factors in the model reaction scheme. ω_1 and ω_2 are weights, summing to one.

Three different reaction schemes were tested. One step reaction scheme (Eq.7) as used in isoconversional evaluation process, two steps reaction scheme where lignin and a pseudo component (holocellulose) decompose independently (Eq.8 and 9), three steps reaction scheme that treats wood as an mixture of its main components (Eq.10-12).



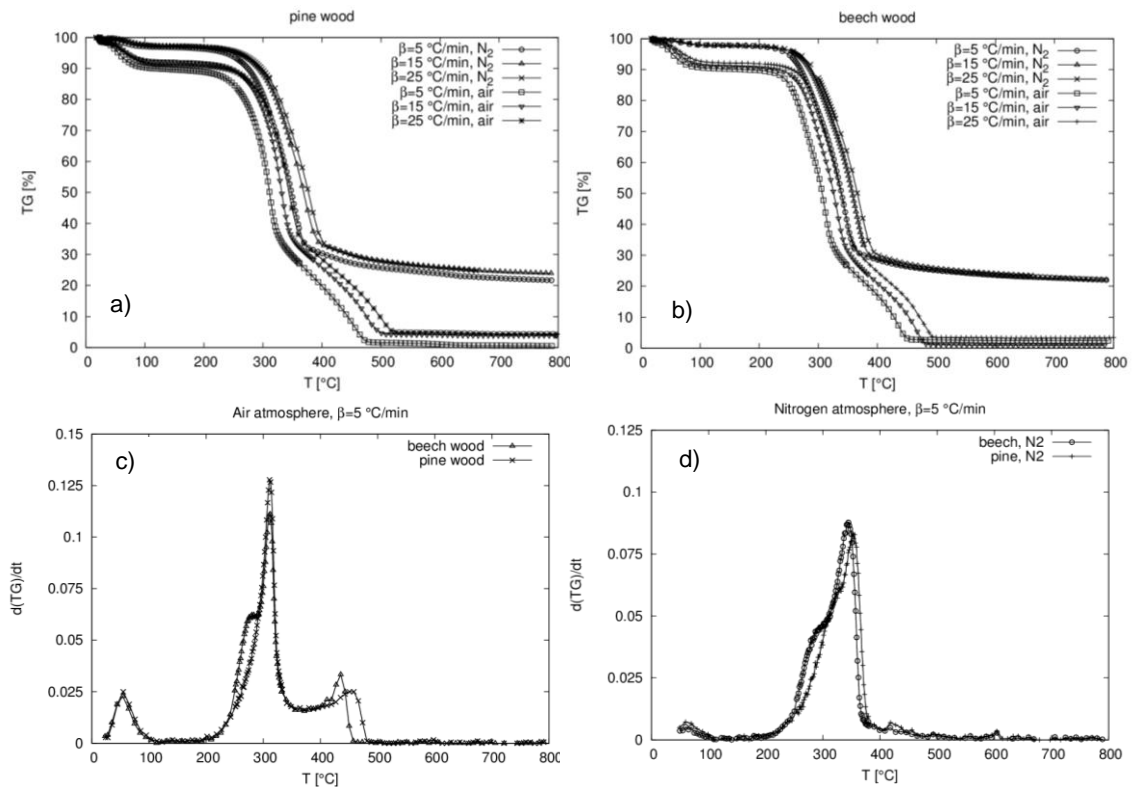


Figure 1: Beach and pine wood mass loss kinetics in air and nitrogen atmosphere as a function of temperature. (a), (b) percentage mass loss of pine and beech wood for three heating rates in both atmospheres; (c), (d) gradient of the percentage mass loss for beech and pine wood for a heating rate $5 \text{ }^{\circ}\text{C}\cdot\text{min}^{-1}$ in air and nitrogen.

GA was implemented using programming language C++ with the use of the C++ GA library (Keijzer et al., 2002). Unknown parameters to estimate are n (reaction order), y_{∞} (the solid mass residue) A , and E for every step in the three decomposition reaction schemes (4, 8 and 12 parameters).

4. Results and discussion

4.1 TGA experimental results

Thermogravimetric results expressed as a percentage mass loss and its gradient are presented in Figure 1. The increasing value of the heating rate does not affect the shape of the TG curve, but there is a shift to higher values on the temperature axis. The residual mass loss for both wood specimens is about 20 % in nitrogen and under 5 % in air for all values of the heating rate. Wood as a charring material undergoes the oxidation reaction in air causing the significant decrease of the residual mass.

The degradation kinetics can be well observed on the gradient of the percentage mass loss curve. First peak corresponds to the evaporation of the wood moisture, which is more significantly observed in air. Second peak corresponds to the degradation of wood. Both in nitrogen and air atmosphere a shoulder on the left side of the peak is observed for a beech wood. Third peak arises only in air atmosphere corresponding to the oxidation reaction of wood char. For both wood specimens, pyrolysis in nitrogen takes place at higher temperature than in air.

Presented results proved the importance of the oxygen presence when dealing with charring materials and the need to involve the oxidation reaction to the overall reaction scheme when modeling the fire spread over charring materials. The results further suggest, that dry beech and pine wood decompose in one step although in case of the beech wood, the shoulder observed on the main peak suggests the

Table 1: Calculated kinetic parameters using isoconversional method for the first order single step kinetic as a function of conversion

α [%]	(n =1)	5	10	20	30	40	50	60	70	80
$E \times 10^3$ [J·mol ⁻¹]	pine	195.550	200.320	201.086	203.604	203.567	207.816	209.012	211.901	214.159
	beech	181.480	184.993	186.680	189.268	186.609	189.342	191.671	193.649	195.724
$A \times 10^{15}$ [s ⁻¹]	pine	2.64	2.79	1.43	1.11	0.68	0.98	1.04	1.44	1.47
	beech	0.20	0.25	0.16	0.12	0.04	0.05	0.07	0.09	0.11

decomposition of the hemicellulose (decomposes at the lowest temperature of all three main wood components) is almost finished when cellulose and lignin are still decomposing.

4.2 Isoconversional method

The comparison of the isoconversional model with the experimental data presented in Figure 2 shows good agreement up to the value of conversion approximately 80 %. As can be seen in Table 1, data were computed only to the maximum value of predefined conversion 80 %, because for higher values, the assumption about the constant E for a given value of conversion and all values of heating rates is not valid anymore. For high temperatures, only a small change in conversion occurs and the isoconversional lines are thus not very precise (Gašparovič et al., 2009). Model data for higher value of conversion than 80 % were obtained using extrapolation.

Isoconversional method as applied requires high user interaction and is user dependant, especially the polynomial fitting process. However it gives a good estimates of the kinetic parameters range, that could be used as reliable initial estimates for GA.

4.3 Genetic Algorithm

The list of kinetic parameters estimated using GA are in Table 2. The parameters presented are the set of parameters from the last generation of GA, that provides the best fit to experimental data. As a nature of GA, not only one set of values is obtained but the number of solutions that corresponds to the initial size of the population (all of them provide a better fit than the previous generation). Estimated kinetic parameters are thus not physical constants with absolute values, but depend strongly on the model.

All three decomposition schemes give very similar results comparing the model with experimental data for both wood specimens. Based on the summed squared deviations of model and experimental data (Table 2), the best fit for the pine wood gives scheme 2, for beech wood scheme 3. However the simple one step decomposition scheme gives good fit as well and is the least demanding. None of the model can correctly fit the initial decrease in mass caused by the evaporation of the moisture, as evaporation reaction is not involved in none of the reaction mechanisms.

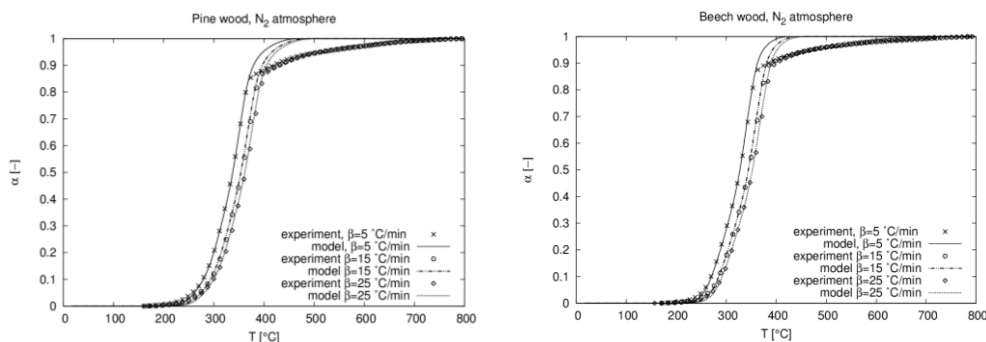


Figure 2: Comparison of the experimental data (lines) and model data (points) computed using isoconversional method; nitrogen atmosphere - three values of heating rate.

Table 2: Calculated kinetic parameters using GA for one step mechanism (scheme 1), two independent step mechanisms (scheme 2) and three independent step mechanism (scheme 3) of beech and pine wood decomposition in nitrogen atmosphere.

	Pine wood			Beech wood		
	Scheme 1	Scheme 2	Scheme 3	Scheme 1	Scheme 2	Scheme 3
A_1 [s^{-1}]	1.527×10^{14}	3.306×10^{10}	1.117×10^{13}	1.724×10^{13}	1.084×10^7	8.144×10^{13}
E_1 [$J \cdot mol^{-1}$]	186.4×10^3	150.0×10^3	158.0×10^3	176.2×10^3	107.5×10^3	136.5×10^3
n_1	3.492	2.101	4.090	2.962	1.805	1.000
$y_{\infty,1}$	0.2361	0.0378	0.0210	0.2276	0.0168	0.0011
A_2 [s^{-1}]	-	5.873×10^{12}	2.417×10^{13}	-	5.912×10^6	5.014×10^7
E_2 [$J \cdot mol^{-1}$]	-	165.3×10^3	188.8×10^3	-	100.0×10^3	100.0×10^3
n_2	-	2.459	1.000	-	1.788	2.743
$y_{\infty,2}$	-	0.2146	0.0010	-	0.2240	0.0023
A_3 [s^{-1}]	-	-	5.598×10^{12}	-	-	4.338×10^6
E_3 [$J \cdot mol^{-1}$]	-	-	175.0×10^3	-	-	111.2×10^3
n_3	-	-	2.271	-	-	2.662
$y_{\infty,3}$	-	-	0.2174	-	-	0.2180
$\sum_{i=1}^3 \sum (D_{exp} - D_{mod})^2$	4.1215	2.8047	2.9022	3.7464	1.6333	1.5861

5. Conclusions

Using TG two and three reactions were observed in nitrogen and air atmosphere respectively. Evaporation of water should be added to the overall reaction scheme as in real cases wood is never oven dried and a significant amount of energy is consumed for the evaporation instead of preheating the virgin material. Beech and pine wood exhibit similar behavior from the point of TG view.

Isoconversional method is a good initial estimate for finding the magnitude of both activation energy and preexponential factor.

GA was found to be efficient and complex tool for estimating all kinetic parameters at once. Even for the most complicated degradation scheme, the computations were fast with a good convergence because of the good initial estimates of the parameters. The disadvantage of GA is that it does not converge to one solution, but provides a set of solutions within the whole initial range of parameters and depends on the initial settings of GA parameters (population size, number of individuals, mutation probability etc.).

One step degradation scheme of wood can be used for modeling of wood pyrolysis.

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