Estimation of Pyrolysis Model Parameters for Solid Materials Using Thermogravimetric Data

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ABSTRACT

Determination of the material parameters is one of the key challenges of numerical fire simulation attempting to predict, rather than prescribe the heat release rate. In this work, we use common fire simulation software and genetic algorithms to estimate the kinetic reaction parameters for wood components, birch wood, PVC and black PMMA. Parameters are estimated by modelling thermogravimetric experiments and minimizing the error between the experimental and numerical results. The implementation and choice of the parameters for the genetic algorithm as well as the scheme to describe wood pyrolysis are discussed.

KEYWORDS: pyrolysis model, genetic algorithms, fire simulation, thermogravimetry

NOMENCLATURE

$A_{\alpha\beta}$	Frequency factor (s^{-1})	**Greek**	
A_p	Penalty of parameter A	ρ	Mass concentration or density (kg/m^3)
$E_{\alpha\beta}$	Activation energy (kJ/mol)	ω	Weight in fitness function
ΔH	Heat of reaction (kJ/kg)	**subscripts**	
M	Mass fraction (kg/kg)	α	Material index
$\overline{M}$	Average of mass fraction (kg/kg)	β	Reaction index
m	Sample mass (kg)	0	Initial value
N	Number of variables in a model.	i	Index over time series
$n_{\alpha\beta}$	Reaction order	*exp*	Experimental
R	Universal gas constant (8.31431 J/K.mol)	*max*	Upper bound
S_α	Mass production for material α	*min*	Lower bound
T	Temperature (K)	*mod*	Model
fV	Fitness value		

INTRODUCTION

The numerical simulation of fires is used extensively as a tool in performance based design of buildings and ships. Although such a design often relies on the use of prescribed design fires, there is an increasing need for a capability to predict the fire spread. There are several challenges associated with the fire spread simulations, including the difference in scales of close field heat transfer and the largest resolved scales of the geometry, physical and numerical modelling of the mass and heat transfer phenomena within the condensed phase and the definition of the necessary model parameters. During the recent update of the Fire Dynamics Simulator (FDS) to version 5 [1], the treatment of the condensed phase pyrolysis reactions was significantly changed, allowing the definition of a wide range of reactions of varying complexity. Increased complexity has an evident drawback of increased number of model parameters. Quite often, these parameters can not be found directly from literature because the parameters are not material constants by nature. Instead, they are always associated with a specific model of the material, and they should be determined using the exactly same or very similar model.

The reaction parameters for fire models are often estimated by varying the parameters until the model reproduces the measured behaviour in some laboratory experiment. Small scale experiments are typically preferred for the estimation while larger experiments serve as validation tests. It depends on the type of the test, whether it can yield estimates for the thermal parameters or kinetic reaction parameters or both.

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Mathematically, the parameter estimation process can be presented as an optimization problem. In the recent papers of Lautenberger *et al.* [2] and Rein *et al.* [3], Genetic Algorithms (GA) were used for the optimization to estimate the thermal material properties from bench scale experiments [2] and kinetic parameters from thermogravimetric experiments [3]. In this work, we use the ideas of the above mentioned authors to determine the kinetic reaction parameters for the modelling of pyrolysis behaviour of selected solid materials, including wood and its components, polyvinylchloride (PVC) and polymethyl methacrylate (PMMA). The reactions are modelled using FDS and the practical aspects associated with the use of genetic algorithms are studied.

METHODS

Experiments

In this work, the kinetic parameters of selected solid materials were determined using Thermogravimetric Analysis (TGA) [4]. In addition, Differential Scanning Calorimetry (DSC) was used to determine the heat of reaction. In both experiments, just 10-50 mg of sample material is needed. A small furnace is heated at constant heating rate (heating rate typically 2-20 K/min) so that the temperature of the sample is in equilibrium with the environment all the time. The purge gas can be air or nitrogen (N_2). These thermoanalytical experiments were carried out at the Laboratory of Inorganic and Analytical Chemistry, Helsinki University of Technology, using Netzsch STA 449C equipment. The sample materials are listed in Table 1.

TGA measures the sample mass as a function of temperature. In this paper, the results are presented as a fraction of the current mass to the initial mass

$$M = \frac{m}{m_0} \tag{1}$$

The main difference between TGA experiments conducted in air and in N_2 is that in air, direct oxidation reactions may take place parallel or after the pyrolysis reaction. Oxidation decreases the mass of material, so the residual mass is usually smaller in air than in N_2. This is true for all the sample materials discussed in this work. In DSC, temperature of a sample is kept identical with reference sample and the energy needed for that is measured. In DSC data it is possible to see if the reaction is endothermic or exothermic. Sometimes it is even possible to measure the heat of reaction by integrating over the peak in the DSC curve. Nitrogen should be used as a purge gas if the heat of reaction is going to be measured. However, sometimes many parallel reactions take place simultaneously or the measurement is not accurate enough, and the DSC graph does not give the expected results.

Table 1. Sample properties. The moisture-% is wet based.

Material	Description	ρ (kg/m^3)	Moisture-%
Cellulose (Avicel® PH-101)	High purity cellulose powder.	360	4
Lignin (alkali)	Powder, 4 % sulphur, carbon typically 45 % - 65 %	494	8
Xylan from birch wood	Powder, xylose residues ≥90 %	312	7
Birch	-	550	3
PVC	Almost pure PVC pipe material.	1440	0
Black PMMA	ICI, Perspex	1180	0

Kinetic modelling of pyrolysis reactions

The condensed phase materials are modelled as mixtures of material components. In the modelling of condensed phase reactions, the rate of an individual condensed phase reaction β converting material α to something else is expressed as an Arrhenius equation

$$r_{\alpha\beta}(T) = A_{\alpha\beta}\left(\frac{\rho_\alpha}{\rho_{s0}}\right)^{n_{\alpha\beta}} e^{-\frac{E_{\alpha\beta}}{RT}} \tag{2}$$

where ρ_α is the mass concentration of component α and ρ_{s0} the original density of the material. The rate of change for the mass concentration of component α is

$$\frac{\partial}{\partial t}\left(\frac{\rho_\alpha}{\rho_{s0}}\right) = -\sum_\beta r_{\alpha\beta} + S_\alpha \tag{3}$$

where S_α is the production rate of material α. is In words, the mass is consumed by all the reactions converting material α to something else and created by the reactions converting something else to α. If none of the reactions leaves solid residue, the sample volume is reduced correspondingly, thus retaining constant density.

Kinetic parameters A, E and n depend both on the material and the assumed reaction scheme. They must be determined using some sort of experimental data. To estimate the kinetic parameters for Eq. (1), a numerical model of the TGA experiment was created using Fire Dynamic Simulator (FDS) version 5.0.2 [1]. The model is very simple, consisting of only few gas phase control volumes and a single surface element to describe the sample material. A thin layer of sample material is heated by radiation from the surroundings with linearly increased temperature. The layer is thin enough to remain in equilibrium with the surroundings with a tolerance of few Kelvins. Gas phase convection and reactions are neglected and the sample backing is adiabatic.

Correct interpretation of the model output is important when comparing the experimental results and model predictions. TGA results are presented as mass fractions M. The model, in turn, provides us with a sample density ρ which is sum of the individual mass concentrations. Direct comparison between M and ρ/ρ_0 is possible if the sample volume does not change. For non-charring materials, such as PMMA, the sample volume is reduced and the mass fractions leading to ρ/ρ_0 must be based on the initial sample volume.

Parameter estimation

The parameter estimation was performed by minimizing the error between a measured and simulated TGA result using Genetic Algorithm (GA) as a minimization technique. GA was chosen because it is effective for problems with several unknown variables, and can usually find a global minimum instead of converging to some local minimum. Recently, GA has been used for the parameter estimation of condensed phase reactions by Lautenberger *et al*. [2] and Rein *et al*. [3].

Genetic algorithms are based on the idea of evolution and the procedure and the terminology is adapted from references [2], [3] and [5]. The process is iterative, and each iteration round corresponds to one *generation*. The first generation is initialized by generating random numbers for candidate solutions (*individuals*). An individual is a vector with real numbers corresponding to the unknown variables of the model. The individuals of a generation form a *population*. Population can be divided from the beginning into smaller *subpopulations* to keep up the variety of candidate solutions. Each generation goes through several processes. First, the goodness of an individual is tested using a *fitness function* returning a *fitness value*. According the fitness value, the individuals are ranked, and the best of them are selected to produce *offspring*. The offspring are formed by *crossover*, where the chosen individuals are set to pairs and each pair are changing *alleles* (values of variables) according the conditions of crossover. After that occur *mutations*, stochastically according to a predetermined mutation rate. In mutation, one value in an individual is replaced by a new random number. Then fitness values are calculated for the offspring and the best parents and offspring are chosen to the next generation. If population is divided into isolated subpopulations, some individuals *migrate* then between subpopulations bringing new genes and so maintaining variety. After each generation, the best individual is plotted, which enables the user to observe the action of algorithm. The process is repeated until the maximum number of iterations is finished or the user is satisfied with the result and stops the algorithm from outside.

The fitness function compares experimental data to model and returns a metrics of how good is the fit. This is often made by using least mean squares. Based on the numerical experiments, another feature was added to the fitness function: The results of the parameter estimation process are not unambiguous and several well-fitting parameters can be found for the same material. On the other hand, high values of pre-exponential factors A were found to make the FDS simulations more prone for numerical fluctuations. An additional term was thus added to the fitness function to prefer the smaller values of A. The formula for the fitness value is

$$fV = \omega_1 \left(1 - \frac{\sum_i \left(M_{\text{exp}} - \overline{M}_{\text{exp}} \right)^2 - \sum_i \left(M_{\text{exp}} - M_{\text{mod}} \right)^2}{\sum_i \left(M_{\text{exp}} - \overline{M}_{\text{exp}} \right)^2} \right) + \omega_2 A_p \tag{4}$$

where M is mass fraction in TGA experiment and i goes over all the data. ω_1 and ω_2 are the weights of fitness function so that $\omega_1+\omega_2=1$. A_p is the penalty of high parameter A, and has a form

$$A_p = \frac{A - A_{\text{min}}}{A_{\text{max}}} \tag{5}$$

where A is the current value of the pre-exponential factor, A_{min} is its lower bound and A_{max} the upper bound. Weight ω_2 should be in same order of magnitude as the differences in the fitness values of the best solutions. In the tests, these differences were around 15/1000. Too high weight would lead to small pre-exponential factors giving inaccurate predictions.

The population size and the division of one big population into smaller subpopulations are important when fast convergence to a possible local minimum must be avoided. Inside one population, the solution converges quite fast towards the best candidate solution. If there are many independent populations, the probability that one of the solutions is near the global minimum, is much higher. In test simulations, division to subpopulations was found to be even more important than the population size. The populations without separation converged very fast, no matter how big the number of individuals was in the population. On the other hand, when there were at least four subpopulations, each of them could have as few as 20 individuals and the diversity was still maintained well enough. Mutation rate is used to control the maintenance of diversity. It expresses the probability of an individual to mutate during one generation. If the mutation rate is too low, the solution may converge to a local minimum, and if it is too high, good solutions may be lost. A good rule of thumb is to choose a mutation rate close to ratio 1/N, where N is number of variables.

When TGA experiments are available at many different heating rates, the fitness value should be calculated considering all the rates, thus ensuring that the model is good in general, not only with one heating rate. To illustrate this, in Fig. 1 is shown a comparison of measured (solid lines) and simulated (dash lines) TGA results. The simulation used kinetic parameters that provided very good results at 2 K/min heating rate but poor predictions of the residue mass at others.

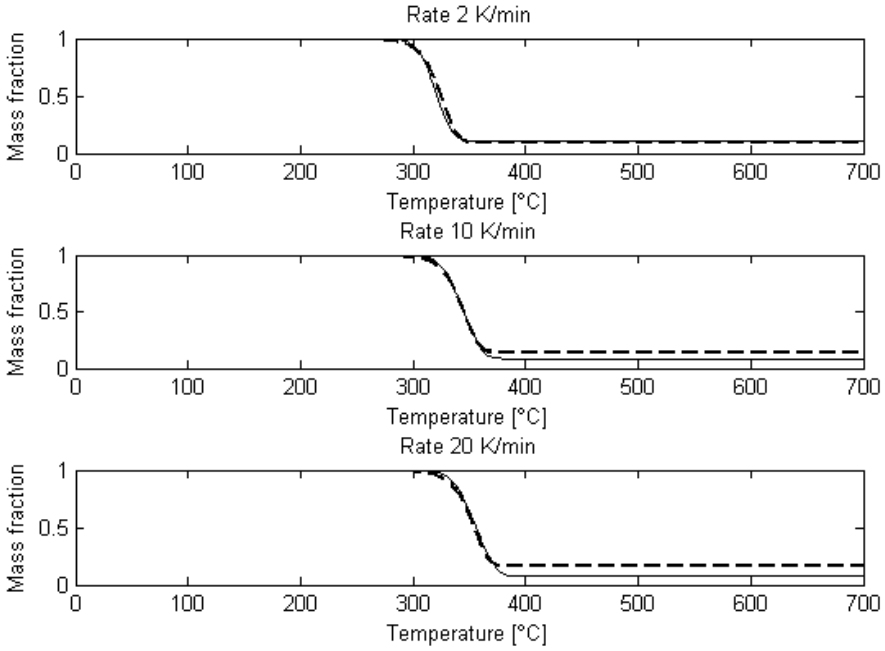

Fig. 1. TGA graphs of same kinetic parameters with different heating rates.

The Genetic Algorithm application was implemented using Genetic Algorithm Toolbox for Matlab, developed by the Department of Automatic Control and Systems Engineering of The University of Sheffield, UK [6]. The toolbox is available for free at http://www.shef.ac.uk/acse/research/ecrg/getgat.html. The parameters used in the estimation are listed in Table 2. Many different combinations were studied and the listed parameters were found to give the best results in estimation of kinetic parameters. The variable and function names are consistent with the Genetic Algorithm toolbox.

Despite the simplicity of the FDS model used for TGA simulation, the computational cost of the parameter estimation was quite high because the model had to be solved for every individual of every generation, and with each heating rate separately. Estimations for this work took from about 10 h to one day to run on a single CPU of a modern workstation.

Table 2. Parameters of Genetic Algorithm application.

Parameter	**Symbol in GA Toolbox**	**Value**
Number of individuals.	NIND	20
Generation gap: The fractional difference between the new and old population sizes.	GGAP	0.8
Crossover rate.	XOVR	0.7
Mutation rate.	MUTR	1/Number of variables
Maximum number of generations.	MAXGEN	1200
Insertion rate: Fraction of offspring reinserted into the population.	INSR	0.9
Number of subpopulations.	SUBPOP	4
Migration rate.	MIGR	0.2
Number of genes per migration.	MIGGEN	20

RESULTS

Heats of reaction were achieved by integrating the reaction peaks of DSC data in nitrogen. Heat of reaction ΔH is the integral divided by consumed mass. Consistent values of ΔH were obtained at all the heating rates only for cellulose and birch. The value for cellulose was -482 kJ/kg and for birch -230 kJ/kg. Negative sign here means endothermic reaction. For comparison, di Blasi [7] has used ΔH = -418 kJ/kg for lignocellulosic fuel, which is relatively close to the value obtained here. However, it is considerably different from our value for birch.

The kinetic parameters of several materials were estimated using genetic algorithm. TGA experiments were made in nitrogen (N_2) because the focus was on the modelling of the pyrolysis (degradation) reactions. For each of the kinetic parameters, a range of possible values was defined, as shown in Table 3. The ranges can be chosen according the literature values, if available, or initial estimates. In the tests, the ranges were set unnecessarily wide on purpose to be able to study the variety of solutions. Unfortunately, the choice of the range may affect the results, as was demonstrated by running two version of the black PMMA with different bounds for the reaction order *n*. Experimental results at four different heating rates (2, 5, 10 and 20 K/min) were used for the estimation. The iterations normally converged during the first 50 generations, but often the iteration process was continued at least up to 100, sometimes even 1000 generations. Most of the materials include some amount of moisture, and the evaporation of water was modelled as a one step reaction with own kinetic parameters. The numerical results are presented in Table 5 and as model behaviour in figures below.

Table 3. Estimation ranges for sample materials.

Material	A (s^{-1})	E (kJ/mol)	n	residue
Cellulose	$[10^{10},10^{20}]$	[100,300]	[0,7]	[0,1]
Lignin (alkali)	$[10^{10},10^{20}]$	[100,300]	[0,7]	[0,1]
Xylan from birch wood	$[10^{10},10^{20}]$	[100,300]	[0,7]	[0,1]
Birch (all reactions)	$[10^{10},10^{20}]$	[100,300]	[0,5]	[0,1]
PVC (all reactions)	$[10^{8},10^{20}]$	[100,300]	[0,4]	[0,1]
Black PMMA –estimation 1	$[10^{2},10^{10}]$	[100,300]	[0,2]	-
Black PMMA –estimation 2	$[10^{2},10^{10}]$	[100,300]	[0,7]	-

Components of wood

The three main components of wood are cellulose, hemicellulose and lignin. Roughly 40-44 % of hardwood is cellulose, 23-40 % hemicellulose and 18-25 % lignin [8]. All the components of wood produce char in combustion but lignin yields most of the char. The sample of hemicellulose was xylan, which is dominant hemicellulose specie in birch wood. The samples of components were in powder form, so the densities and thermal characteristics may differ from real. However, the kinetics' were assumed to be the same. Cellulose was modelled using di Blasi's model [7] and simple one-step model. The di Blasi model was slightly more accurate, but did not differ from the one-step model significantly. For other components, simple one-step reactions were assumed. With lignin and xylan, the experimental TGA data is not the best possible: Unexpected mass losses in the ends of the graphs are seen, which makes it more difficult to decide the residual mass. The results at 2 K/min heating rate are shown in Fig. 2. All the models succeed to predict the total mass loss quite well and the reactions take place in correct temperature range. The dominant shapes of graphs are correct but small errors can be found close to the end of the pyrolysis period. The numeric values of the kinetic parameters are given in Table 5.

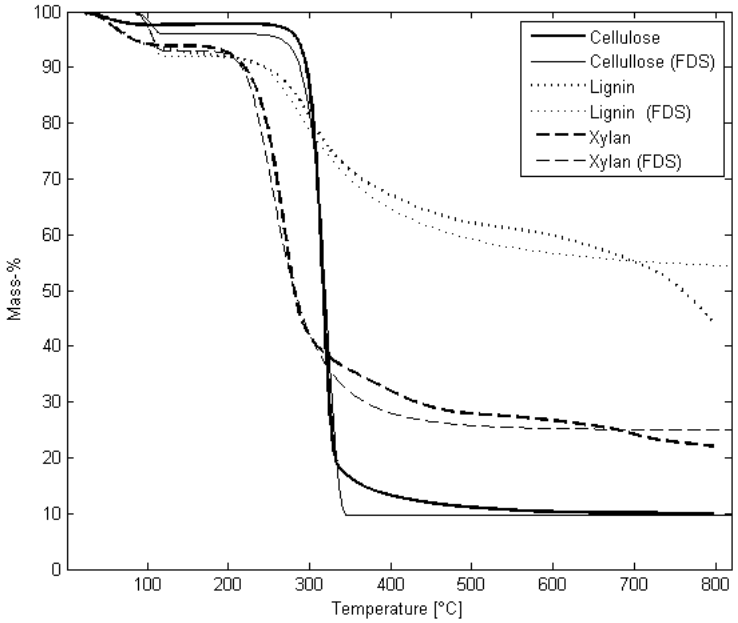

Fig. 2. TGA models of components of wood in N_2. Heating rate is 2 K/min.

Birch

Birch is typical Finnish hardwood specie. When the temperature rises, the moisture of wood evaporates [8]. After this, the fibres start to degrade. The volatiles are now generated, and they consist of a combustible mixture of gases, vapours and tars. A solid carbon char matrix remains, and its volume is smaller than original volume of wood. The sample density was 550 kg/m^3, which is higher than any of the component densities studied above. That is because the powders form of component samples.

For modelling the pyrolysis of birch four different schemes were used: Scheme 1 was a sum of the one-step reactions of components (cellulose, hemicellulose and lignin) yielding independently certain amount of char. Besides of char, fuel gases are released. In this scheme, the mass fractions of the component variables were also estimated using GA, in order to achieve the total density of birch. Scheme 2 was a one-step reaction converting virgin solid to char. Schemes 3 and 4 were presented by Liu *et al*. in Ref. [9]. In Scheme 3, there are two separate pseudo-components, which both produce char and fuel gases in parallel. In Scheme 4, there is only one material that has two consecutive reactions. The reaction formulas are summarized in Fig. 3.

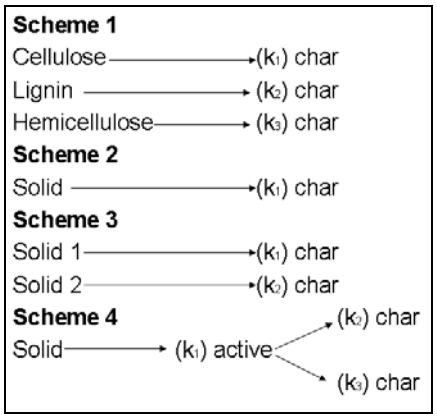

Fig. 3. Reaction schemes for birch.

A comparison of the measured and predicted TGA curves at 2 K/min heating rate is shown in Fig. 4, and the fitness values corresponding to the last iteration are listed in Table 4. In scheme 1, the best model had the composition 44 % cellulose, 18 % lignin and 38 % xylan. Other parameters are listed in Table 5. According to a visual comparison and the fitness values, Scheme 2 gives the best prediction of the TGA curve, which suggests that the components in wood are behaving like a homogenous solid material rather than a mixture of three. Scheme 1 gave the worst results of all the studied schemes, and its fitness value was more than 10 times the fitness value of Scheme 2.

Table 4. Fitness values of TGA results of birch schemes.

Scheme	1	2	3	4
Fitness value	0.0691	0.0069	0.0119	0.0123

PVC

The sample was almost pure polyvinyl chloride (PVC) pipe material. PVC undergoes two reactions: Release of hydrochloric acid between 200 and 300°C and the pyrolysis reaction of the remaining solid at about 400°C. The pyrolysis products are HCl, benzene and toluene [8]. Reactions were modelled by two pseudo-components, of which the first does not yield any tar and the second does.

The mass fraction of volatiles was assumed to be 0.54 (taken directly from the graphs). A comparison of the measured and predicted TGA curves at the end of the parameter estimation is shown in Fig. 5. The solid lines denote the experimental data and the dash lines the model. Good predictions of the PVC pyrolysis are achieved at all heating rates. The numeric values of the kinetic parameters are given in Table 5.

Black PMMA

PMMA (Polymethyl methacrylate) is a non-charring thermoplastic that melts and then burns. The pyrolysis product is 100 % monomer [8] with no significant residue yield. Different from charring materials where the density decreases, in PMMA model the sample thickness decreases instead. This may cause problems when modelling TGA test where the sample is very thin from the beginning. As a result, care must be taken to define a sufficiently high sampling frequency for the numerical results.

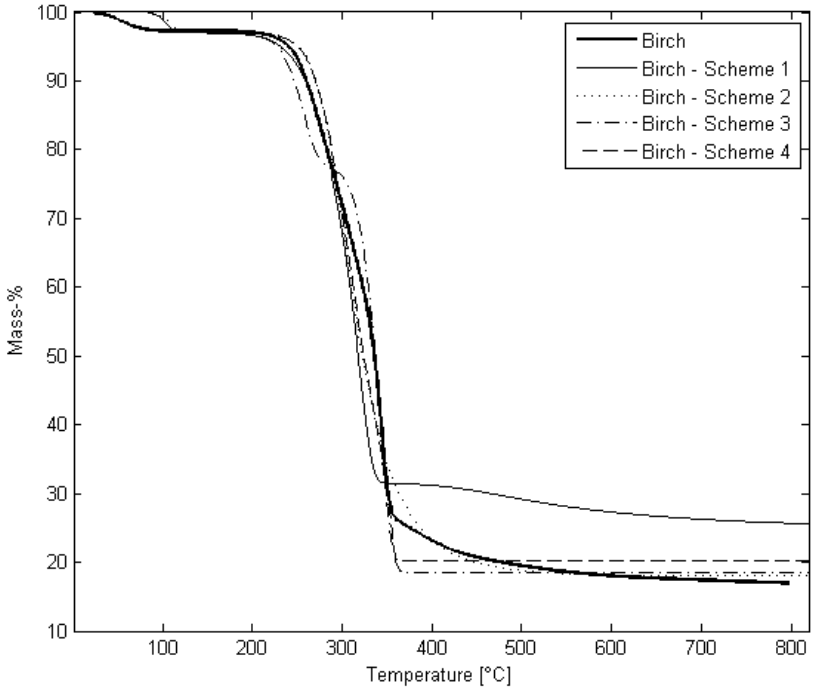

Fig. 4. TGA models of birch in N_2. Heating rate is 2 K/min.

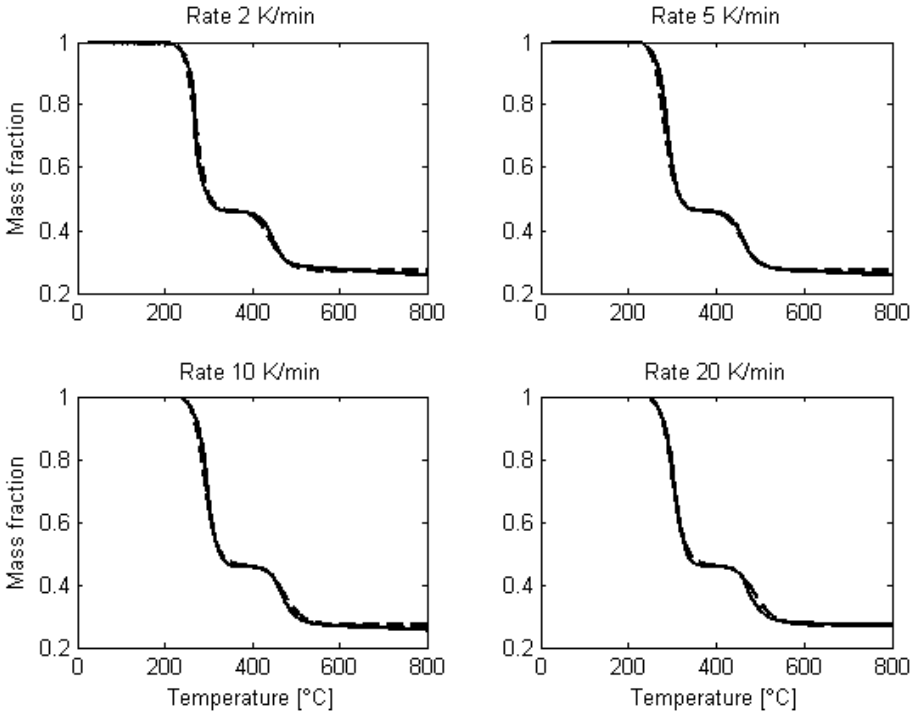

Fig. 5. TGA model of PVC in N_2.

The estimation was made twice using different range for the reaction order parameter *n*. In the first run, the range was [0, 2] and in the second, it was [0, 7]. The result of estimation run 1 is shown in Fig. 6. Again, the solid line denotes the experimental data and the dash line the model. An accurate prediction of the mass loss is achieved at heating rates 5 and 10 K/min, and reasonably well at heating rates 2 and 20 K/min. The results of the estimation run 2 look very much the same and the model is considered as accurate as in estimation run 1. That suggests that the parameter sets can be chosen among various alternatives and the genetic algorithm can find solutions from desired range. The numeric values of the kinetic parameters are given in Table 5.

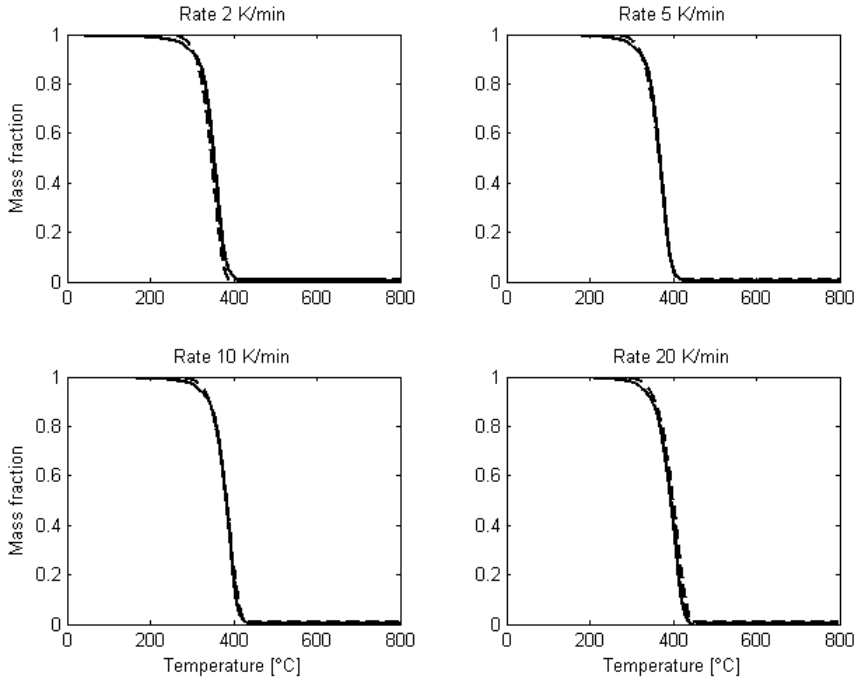

Fig. 6. TGA of black PMMA in N_2.

CONCLUSIONS

Kinetic pyrolysis model parameters were estimated for six different solid materials using FDS fire model and genetic algorithm for the estimation. The estimation parameters, such as variable bounds and time step size, were carefully chosen to minimize the effect of the estimation procedure. The results were promising and indicated that the thermogravimetric experiments and genetic algorithm can successfully be used for the parameter estimation in fire engineering. As the material models were created using the actual fire simulation tool, the results can be directly used in applications. The estimation process is computationally expensive, taking several hours to a day on a single computer, but needs to be performed only once for each material. Validation of the current parameters and estimation of the lacking ones is still needed to build a full parameter set for fire spread computation.

Different reaction schemes were considered for the hardwood charring process. Best results were obtained using a simple one-step reaction for the pyrolysis. From the engineering viewpoint this is a very good result because the model simplicity means smaller number of unknown parameters to estimate and computational savings. Some of the resulting parameter values were quite different from those previously presented in literature. This demonstrates that the kinetic parameters are model dependent and should not be considered as fundamental material properties. The parameters should therefore be used only in models with similar structure. In addition, the estimation results are not unambiguous and there may be many suitable sets of parameters that predict the mass loss accurately.

Table 5. Kinetic parameters of materials, estimated using genetic algorithm.

Material	A (s^{-1})	E (kJ/mol)	n	residue
Moisture	$1 \cdot 10^{20}$	162	1	0
Cellulose	$2.68 \cdot 10^{14}$	195	0.85	0.1
Lignin	$2.18 \cdot 10^{10}$	138	7	0.567
Xylan	$5.78 \cdot 10^{13}$	164	4.166	0.268
Birch – scheme 2	$7.51 \cdot 10^{11}$	161	3.12	0.172
Birch – scheme 3 – k_1	$8.64 \cdot 10^{16}$	230	1	0.19
Birch – scheme 3 – k_2	$1.3 \cdot 10^{12}$	150	1	0.19
Birch – scheme 4 – k_1	$9.26 \cdot 10^{18}$	142	1	1
Birch – scheme 4 – k_2	$3.91 \cdot 10^{10}$	148	1	0.268
Birch – scheme 4 – k_3	$1.05 \cdot 10^{14}$	210	1	0
PVC (chlorides) k_1	$6.12 \cdot 10^{16}$	198	2.18	0
PVC (solid) k_2	$3.63 \cdot 10^{13}$	219	2.08	0.589
Black PMMA – estimation 1	$2.43 \cdot 10^{9}$	146	1.758	0
Black PMMA – estimation 2	$1.35 \cdot 10^{9}$	143	4.01	0

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