

# Analysis and modelling of wood pyrolysis

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## ABSTRACT

In many industrial processes wood is treated as big fragments or pellets. In such conditions kinetics and yields are different with respect to the case of particles with few mg weight. However most of published kinetic models were based on experimental data obtained with very small samples. In this work pyrolysis of wood pellets was investigated by using a special experimental device which allowed to determine kinetics of total weight loss, gas and tar production. Two different heating rates, 0.05 and 1 K/s, were employed to determine kinetic parameters. Dynamic and isothermal pyrolysis tests were carried out on beech and pine wood previously dried in an oven. A simple but realistic kinetic scheme was proposed able to take into account the phenomena that happen in big wood particles. The numerical parameters were determined from the results of experimentation on beech wood. The proposed kinetic model takes into account the presence of two different stages during pyrolysis: a first one involving only unreacted wood and a second one where the products not yet escaped from the solid matrix react further. This kinetic model allowed to fit the experimental data quite well. The model was successfully validated with tests performed at an elevated heating rate (approximately 60–100 K/s) of the external surface of the pellets. In these conditions, the pellets showed a marked gradient of temperature inside, which was suitably considered.

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## 1. Introduction

Wood is considered as one of the most important renewable energy sources. Feedstock arise both from specific crops, from forest wastes or from separate collection of woody Municipal Solid Waste (MSW) (Orfao et al., 1999). Direct energy recovery from wood – either electrical or thermal energy – is obtained by combustion, but other thermal processes like pyrolysis or gasification allow to convert woody biomasses in more valuable gaseous or liquid combustibles (Janse et al., 2000).

Pyrolysis is the first stage in any thermal treatment of biomass (Rajeswara Rao and Sharma, 1998) and its kinetics and products have a crucial influence on gasification and incineration. It consists in a decomposition of the wood polymeric chains (cellulose, lignine, etc.); the products of this decomposition can be roughly subdivided into gas, tar and char. Gaseous products are mainly constituted by CO, H<sub>2</sub>, CO<sub>2</sub>, CH<sub>4</sub> and other light hydrocarbons (Fagbemi et al., 2001; Sharypov et al., 2002; Boroson et al., 1989; Williams and Besler, 1996). Tar is made by hydrocarbons of higher C content and other organic compounds which are volatile at the temperature of pyrolysis and condense at low temperature; generally tar is considered as constituted by compounds with a

condensing temperature higher than benzene. Char is the solid residual after pyrolysis; it consists of carbonaceous solid compounds with a high C/H ratio.

Many kinetic models for wood pyrolysis have been reported in the literature; a good review is given by Di Blasi (2008). The simplest models were based on a single decomposition reaction, and they do not allow to predict the influence of pyrolysis conditions on the amount of products (Di Blasi, 1998). Other models assume some parallel reactions to predict the production kinetics of gas tar and char (Turner and Mann, 1981; Chan et al., 1985; Font et al., 1990). More complex reaction schemes were also adopted, involving a further decomposition of tar in the gas phase (Liden et al., 1988; Di Blasi, 1993) or an intermediate product deriving from primary decomposition of biomass, giving rise to gas, tar char (Koufopoulos et al., 1989; Shafizadeh and Bradbury, 1979; Bradbury et al., 1979; Park et al., 2010). Distributed activation energy model (DAEM) approach was also applied to biomass pyrolysis (Rostami et al., 2004; Wojtowicz et al., 2003).

Most of these models were developed on the basis of experimental results obtained by pyrolysis of few mg of biomass in powder, often with a very high increase of temperature.

Actually, the biomass is often treated in the form of pellets or fragment of a certain size. This implies that gradients of temperature exist in the biomass and that the temperature variation is generally slower inside (Babu and Chaurasia, 2004); furthermore, the products generated by decomposition of biomass polymers must diffuse into

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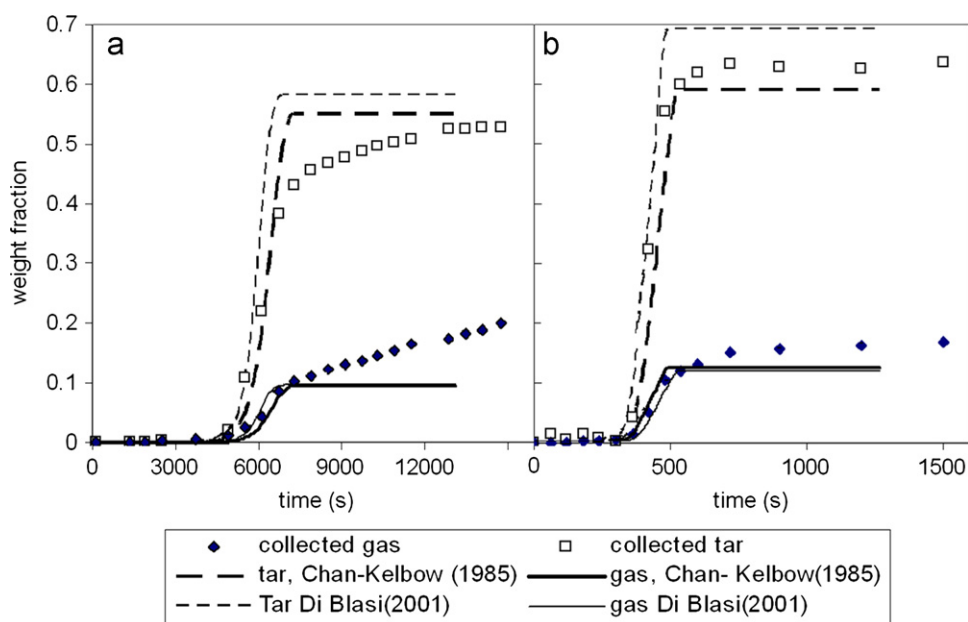


Fig. 1. Gas and tar production, comparison with the results of some well-known literature models; heating rate 0.05 K/s (a) and 1 K/s (b).

the mass of matter. Some literature results have in fact shown an influence of the sample size on the amount of tar and gas yields both for cellulose (Di Blasi and Branca, 2001) and wood (Chan et al., 1985).

However it is quite common to couple kinetic models developed from very small samples to energy, mass and sometimes momentum balances in order to simulate the behaviour of large particles, according to the hypothesis that secondary reactions can be considered negligible or take places only in gas phase (Helsen and Van der Bulck, 2001). Normally very low heating rates are neglected also in complex models for single large particle (Gronli and Melaaen, 2000) and much of the efforts were concentrated on fast heating rates (Di Blasi, 2002). On the other hand, it is well known that characteristic times of heat exchange have often the same order of magnitude of pyrolysis reaction times (Gronli and Melaaen, 2000). As a consequence of this, kinetic phenomena, especially those ones connected with secondary pyrolysis, are often hidden by heat transport effects.

For this reason in this work a kinetic model was developed by using experimental data obtained on large particles at very low heating rate. These tests allowed to highlight the importance of secondary pyrolysis within solid particles. Such reactions with higher heating rates become negligible or simply hidden in the global kinetic of product release.

Fig. 1 shows some results of pyrolysis obtained with 12-mm pellets, compared with the results calculated with two kinetic models (Di Blasi and Branca, 2001; Chan et al., 1985): as can be seen, the agreement is initially good, but the models fail in the final part of pyrolysis in particular when temperature rise is very low.

Aim of this work is to analyze pyrolysis of wood in the form of pellet in different conditions of heating and to propose a model to interpret the phenomenon by taking into account the effect of the secondary reaction within solid, heat transfer in the solid was taken into account too.

## 2. Experimental

### 2.1. Pyrolysis apparatus and procedures

The experimental setup is schematically drawn in Fig. 2. The wood samples were placed in a stainless steel capsule, previously

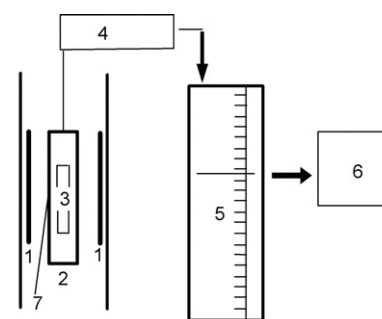


Fig. 2. Organization of the experimental apparatus.

filled by  $N_2$ . The capsule was placed in an oven and heated up. The capsule is 22 mm i.d. and 120 mm length. Through the upper part of the capsule two thermocouples with 1 mm OD were introduced (T1 and T2): the first one was used to measure the temperature at the surface of the sample (T1) and the second one was placed in the centre of the sample (T2). The thermocouple T1 was connected to a temperature programmer in order to impose well-defined rising rates to the sample surface temperature. The heat transfer between biomass and thermocouples could be a critical aspect. In order to reduce this problem, thin thermocouples (1 mm O.D.) were used. The temperature profiles both in the centre and at the surface were highly reproducible, for this reason the errors related to the temperature measurements were considered acceptable. Different procedures were adopted for kinetic analysis and model validation.

#### 2.1.1. Kinetic analysis

The empty oven can reach a maximum heating rate of 5 K/s but in order to obtain a precise control of temperature the maximum temperature rise velocity was limited to 1 K/s.

Each run consisted of two separate tests:

In the first one, the capsule was suspended to an electronic balance and the pyrolysis kinetics (decrease of mass sample with time) was measured; a simultaneous recording of the weight and

the temperatures was realized by a PC. The device composed by balance and suspended capsule can appreciate variation of 0.01 g. The gas and tar produced during pyrolysis escaped from the capsule through a tube in the upper part of the device and were sent in the hood ventilation system.

In the second test, the gas tube was sent first to a tar condenser and finally to a collecting device. The condenser consists in a short aluminium tube kept at about 293 K and filled with ceramic wool: tar condenses on the wool and on the aluminium wall. At the end of each test the condenser was cleaned and the ceramic wool was replaced. The amount of tar produced in each test was determined by the variation of the weight of the condenser after each run. The capsule, the condenser and the tube were flushed with nitrogen before each run. Tar production rate was obtained from the total weight loss rate by subtracting the gas production rate.

Non-condensable gases are collected in a glass reservoir initially filled with water. The variation of the water level allowed the determination of the volume of gas produced as a function of time. A micro GC Varian 4900 and a GC Varian 3400 were used to determine the gas composition required to convert volume increase rate to mass production rate. The collected gas contained an amount of nitrogen, the one held in the tubes and the condenser before starting heating (the amount of nitrogen present in the biomass was negligibly low). This amount was taken into consideration in order to determine the gas composition.

This double test procedure was adopted to avoid an influence on the weight measure of the connection between the capsule and the condenser.

Two heating rates were adopted, 0.05 and 1 K/s; various isothermal pyrolysis tests were also performed on beech wood at a temperature ranging between 523 and 648 K.

#### 2.1.2. Fast heating

Pellets were introduced suddenly in the oven previously heated up to a temperature ranging between 950 and 1250 K and continuously vented by nitrogen in order to avoid firing. Two thermocouples had been inserted into the pellet: one on the external surface, measuring the real heating up of the surface, and the other in the centre of the sample. The weight of the sample and the rise of temperatures were simultaneously recorded.

#### 2.2. Materials

Beech and pine woods have been considered. Beech is a hard wood and pine is a soft wood, densities being, respectively, equal to 730 and 510 kg/m<sup>3</sup>. Pellets of about 13–11 mm diam. and 6 cm length were tested. In order to provide a satisfactory constancy of wood characteristics all the samples were obtained from two cylindrical bars 2 m long. The samples were dried for about 48 h at 383 K and then held in a silica gel dryer for some days. In order to reduce the effects of the borders, the samples always had a length/diameter ratio bigger than 4, according to Alves and Figueiredo (1989).

### 3. Experimental results

Figs. 3 and 4 show examples of the obtained results at two different heating rates, respectively, 0.05 and 1 K/s.

Two different phases can be identified in the whole phenomenon: in the first one a rapid decomposition of wood is observed, with a large and rapid production of tar; the rate of production of gas is not large but fast too. The second phase shows a slow tar and gas production and seems to end at 950–1000 K, where the production rate of tar and gas stops.

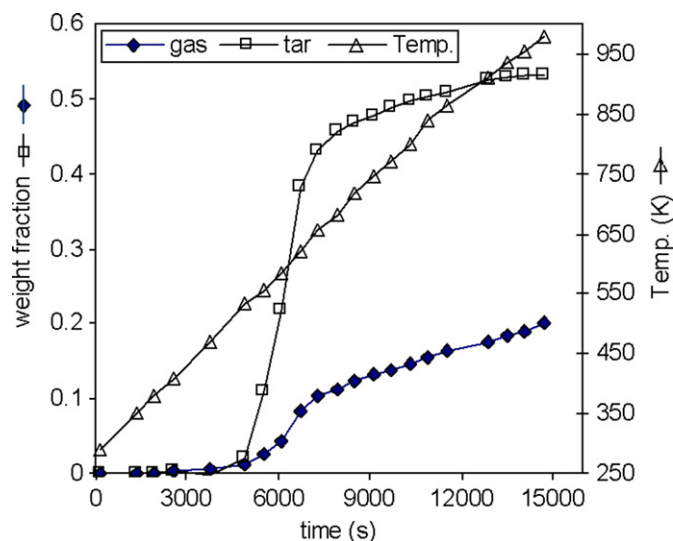


Fig. 3. Tar and gas production during pyrolysis at 0.05 K/s heating rate, beech wood.

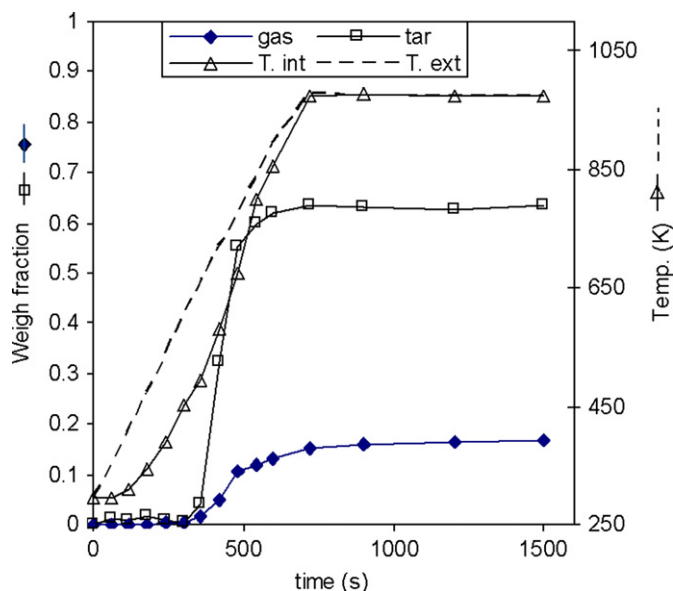


Fig. 4. Tar and gas production during pyrolysis at 1 K/s heating rate, beech wood.

Table 1

Pyrolysis products, mass percentages of the sample initial weight.

	1 K/s		0.05 K/s	
	Beech	Pine	Beech	Pine
Gas	17%	18%	21%	20%
Tar	62%	61%	53%	54%
Char	21%	21%	27%	27%
error	–1.1%	–1.1%	–1.1%	–1.3%

The amount of each pyrolysis product obtained at 1 and 0.05 K/s heating rate are reported in Table 1. In order to check the experimental results the mass balance was verified by means of the difference between the weight of the products and the initial weight of the sample; this difference was expressed as a percentage

of the initial sample weight and reported in Table 1. The composition of light gas is shown in Table 2. Both for products (tar, gas, char) and for gas composition the differences between pine and beech are negligible; on the other hand, an important effect of heating rate was found: at lower heating rate, gas and char increase and tar decreases, this behaviour agrees with many previous studies (Williams and Besler, 1996; Strezov et al., 2003).

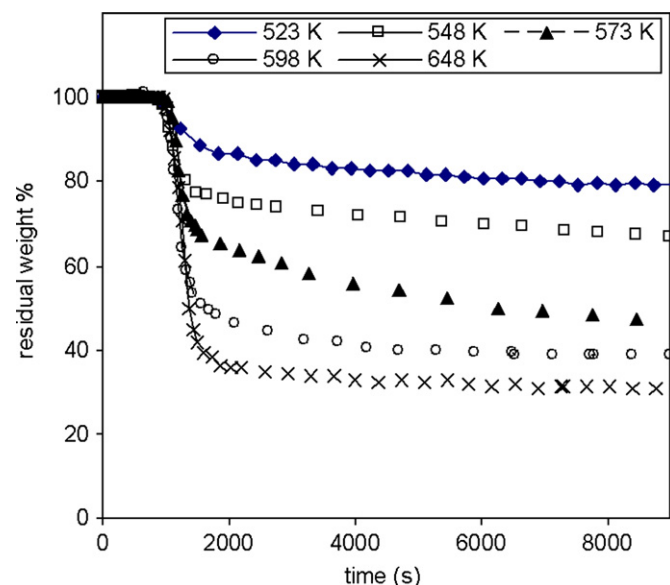
In order to provide other data useful for a kinetic model, some “isothermal” pyrolysis tests were performed. The procedure adopted is the following: the samples were heated at 0.25 K/s until the required reaction temperature is obtained and then maintained for a long time at a constant temperature. The weight loss curves are shown in Fig. 5. The amount of residual solid obtained in isothermal conditions is higher than in the dynamic tests; the main reason of this behaviour being that isothermal tests were performed at quite low temperature and the residual solid contains compounds that evaporate at higher temperatures.

At 0.05 K/s, no radial gradient of temperature exists in the pellet, the maximum difference of temperature between the surface and the centre being less than 5 K. At 1 K/s temperature gradient becomes already apparent. When the pellet was suddenly put into the oven at 1150 K, the difference between surface and centre temperature becomes very important, as can be seen in Fig. 6. Here is also shown the temperature curve in the centre calculated by using literature values of thermal conductivity and also taking into account the heat effects of pyrolysis (see below).

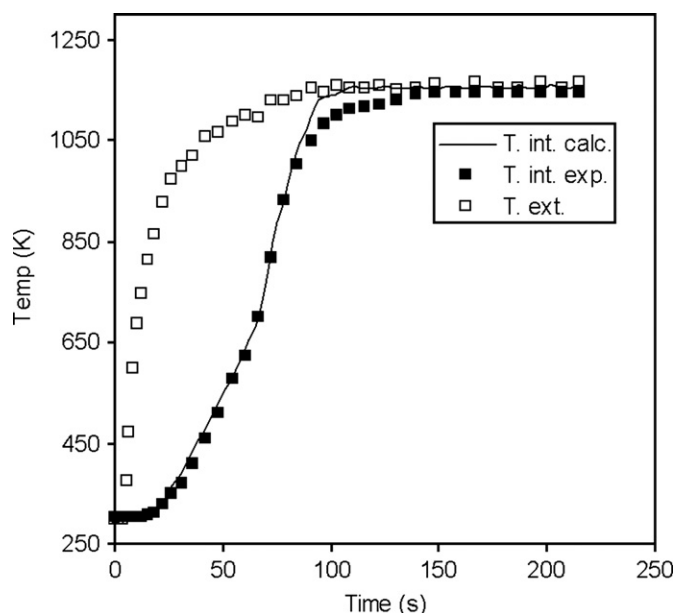
**Table 2**

Pyrolysis products, composition of the light gases (% vol.) for beech and pine wood.

	Beech wood 1 K/s	Beech wood 0.05 K/s	Pine wood 1 K/s	Pine wood 0.05 K/s
CO <sub>2</sub>	38.2	40.1	37.6	36.5
Ethylene	0.4	0.3	0.6	0.4
Ethane	0.8	1.0	1.0	1.2
Propylene	0.2	0.2	0.3	0.3
Propane	0.1	0.2	0.2	0.2
Hydrogen	9.3	10.3	8.8	11.7
Methane	15.4	18.9	15.5	19.8
CO	35.5	28.9	36.1	29.9



**Fig. 5.** Weight of the samples (%) during isothermal pyrolysis tests.



**Fig. 6.** External and internal temperature with fast heating (oven at 1150 K).

## 4. Modelling

### 4.1. Kinetic scheme proposed

The following considerations are based on the results obtained with beech wood at 0.05 and 1 K/s; pine wood results have been considered as a first validation test of the model.

The proposed kinetic scheme is similar to that adopted sometimes for coal pyrolysis (Fig. 7): due to the increase in temperature, polymeric chains of solids first break leading to various kind of products: light gases, and a variety of compounds with a very wide distribution of molecular weight (Niksa and Kerstein, 1991; Solomon et al., 1988; Grant et al., 1989). In the present model these compounds are lumped into three classes: Tar1 (low molecular weight), Tar2 (average molecular weight) and Tar3 (high molecular weight). Tar1 is supposed to leave the sample only for evaporation; Tar2 undergoes evaporation and simultaneously reacts giving rise to gaseous compounds and heavier compounds (Tar3) and Tar3, on its turn, undergoes a cross-linking reaction with formation of gases and char (Bradbury et al., 1979; Ahuja et al., 1996). As a consequence of this mechanism the final amount of tar and gas released by the sample results from primary pyrolysis and from the secondary reactions within solid (secondary pyrolysis).

It can be clearly observed from Figs. 3 and 4 that the emission rate of gaseous products from the sample (gas+Tar1+part of Tar2) is initially quite fast (primary pyrolysis) and then slow but still existing.

According to the adopted reaction scheme, the mathematical model consists in a set of material balance equations—one for each “component”. The reactions were all considered as first-order reactions of Arrhenius type.

This kinetic scheme, and, most of all, the use of first-order Arrhenius type reactions is a simplified representation that does not take into account that pyrolysis is much more complex, as shown for example by Ranzi et al. (2008). This was done because our goal was to have a practical tool to interpret the evolution of pyrolysis together with other physical phenomena as heat transfer for example. The same reason suggested to lump the several reactions with several intermediate products into a limited number of reactions and products.

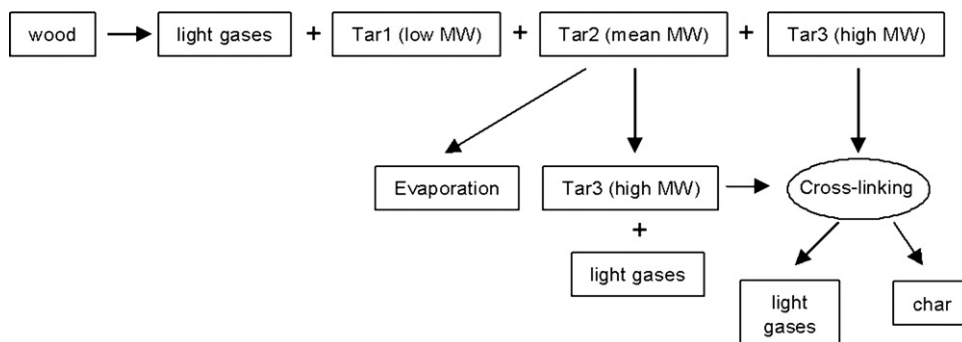


Fig. 7. Proposed kinetic scheme.

## (a) “Wood” component

$$\frac{dm_w}{dt} = -(R_{g1} + R_1 + R_2 + R_3) = -m_w A_w \exp\left(\frac{-E_0}{RT}\right) \quad (1)$$

where  $R_{g1}$ ,  $R_1$ ,  $R_2$  and  $R_3$  are the reaction rates of formation of gas, Tar1, Tar2 and Tar3, respectively. We assumed a constant proportion between these reaction rates

$$\begin{aligned} R_{g1} &= -A \frac{dm_w}{dt} \\ R_1 &= -B \frac{dm_w}{dt} \\ R_2 &= -C \frac{dm_w}{dt} \\ R_3 &= -D \frac{dm_w}{dt} \end{aligned} \quad (2)$$

where  $A$ ,  $B$ ,  $C$  and  $D$  are constants.

## (b) “Gas” component

$$(R_{g1} + R_{g2} + R_{g3}) = \dot{m}_g \quad (3)$$

where  $R_{g2}$  and  $R_{g3}$  are the gas production rate from transformation of Tar2 and Tar3, and  $\dot{m}_g$  is the instantaneous gas flow rate leaving the pellet.

## (c) “Tar1” component

$$R_1 = \dot{m}_1 \quad (4)$$

Tar1 is produced only in the primary pyrolysis of wood and does not transform into any other product.

## (d) “Tar2” component

The mass balance of this component is the most complicated one, as can be seen from Fig. 7

$$(R_2 - R_{23} - R_{g2}) = \dot{m}_{2,ev} + \frac{dm_2}{dt} \quad (5)$$

First member of Eq. (5) represents the net generation rate of Tar2; the second one is the sum of the evaporation flow rate and the accumulation rate in the solid volume (assumed constant in the process).  $R_{23}$  and  $R_{g2}$  are the transformation rates of Tar2 into Tar3 and gas, respectively.

## (e) “Tar3” component

This component is formed by the pyrolysis of wood and further transformation of Tar2; in its turn, it transforms into gas and char

$$(R_3 + R_{23} - R_4 - R_{g3}) = \frac{dm_3}{dt} \quad (6)$$

## (f) “Char” component

$$R_4 = \frac{dm_4}{dt} \quad (7)$$

## 4.2. Determination of the kinetic parameters from primary pyrolysis

The identification of the kinetic parameters of such a complex model was made partly by direct evaluation from experimental results and partly by fitting. They were determined from beech wood results.

First of all, we assumed that till a certain temperature value, the measured decrease of weight of the pellet is due to the formation of primary gas and Tar1

$$\frac{dm_s}{dt} = -(R_{g1} + R_1) = -(A + B)m_w A_w \exp\left(\frac{-E_0}{RT}\right) \quad (8)$$

The value of  $\frac{dm_s}{dt}$  was determined from 0.05 K/s runs, when the temperatures at the centre of the pellet and at the surface coincided. From Eq. (2)

$$\frac{dm_s}{dt} = -(A + B) \frac{dm_w}{dt} \quad (9)$$

By integration from this equation one obtains

$$m_w = m_s \left(1 + \frac{C + D}{A + B}\right) - m_{s0} \frac{C + D}{A + B} \quad (10)$$

From experimental curves it is possible, at a given temperature, determine  $\frac{dm_s}{dt}$  and  $m_s$ , and hence, if  $A$ ,  $B$ ,  $C$  and  $D$  are known,  $\frac{dm_w}{dt}$  and  $m_w$ .

The coefficient  $A$  and  $B$  can be easily determined as they correspond to the amount of gas and tar (referred to the initial mass of the sample) collected during primary pyrolysis; from the experimental data their values are

$$A = 0.10 \quad B = 0.41$$

In Fig. 8 the values of  $\ln(dm_w/dt)/m_w$  are reported as a function of  $1/T$ ; the experimental points fit well a straight line;  $A_w$  and  $E_0$  were found to be, respectively,  $103\,500\text{ s}^{-1}$  and  $87\,500\text{ J/(mol)}$ .

During the pyrolysis test at low heating rate, the temperature increase is low and hence it is reasonable to assume that part of Tar2 reacts before leaving the pellet by evaporation. In the test at higher heating rate, instead, the increase of temperature is so fast that the time for reaction is very short (1/20 of that one available in the other case); therefore, one can assume reasonably that the total amount of tar collected in such experiments correspond to Tar1 + Tar2 formed in primary pyrolysis. Hence

$$Tot_{tar}/m_{s0} = B + C \quad (11)$$

Moreover, from Table 1 and Eq. (11) it is possible to calculate the value of  $C$ , and hence, as the sum of four coefficient is 1, also the value of  $D$ . Actually the values of  $C$  and  $D$  were refined by fitting of beech and pine results, at 0.05 and 1 K/s. The values are listed in Table 3.



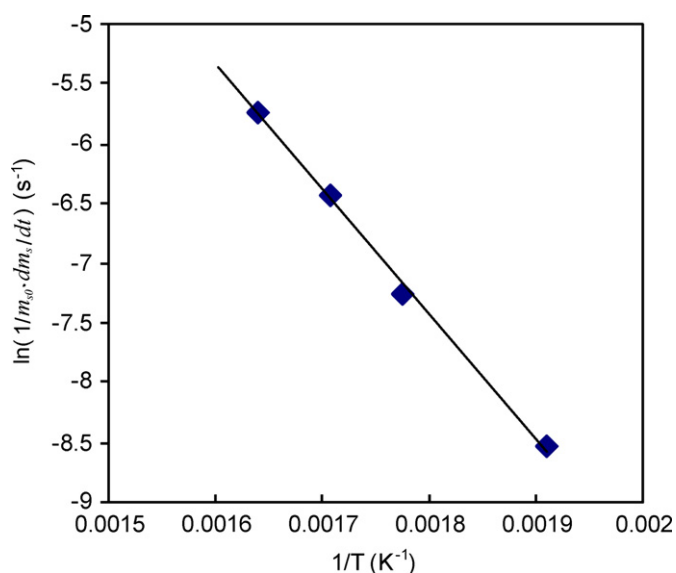


Fig. 8. Reaction rate of wood obtained from isothermal tests as a function of temperature.

**Table 3**  
Numerical parameters of the kinetic model.

Primary pyrolysis (Eqs. (1) and (2))	$A_0 = 103\,500\text{ s}^{-1}$ $E_0 = 87\,500\text{ J/(mol)}$ $A = 0.10\ B = 0.41\ C = 0.22\ D = 0.27$
Secondary reactions Tar2 reaction (eq. 17 and 20)	$A_2 = 1.18\text{ s}^{-1}$ $E_2 = 45\,000\text{ J/(mol)}$ $E = 0.5,\ F = 0.5$
Cross-linking (Eq. (21))	$A_{34} = 2.00 \times 10^{11}\text{ s}^{-1}$ $E_{34} = 251 \times 000\text{ J/(mol)}$ $A_{3g} = 3.00 \times 10^{13}\text{ s}^{-1}$ $E_{3g} = 301\,500\text{ J/(mol)}$

#### 4.3. Secondary pyrolysis

As the temperature increases, Tar2 undergoes transformation, as indicated before, into gas and Tar3, but partially evaporates also. Both phenomena occur simultaneously, but evaporation is much faster than thermal cracking.

Tar2 consists of a series of compounds with different molecular weight and different vapour pressure. Many expressions (empirical or semi-empirical) have been proposed in the literature (Genetti et al., 1999; Niksa, 1988) for the evaluation of vapour pressure of coal tar. Among them, we adopted the following semi-empirical one (Genetti et al., 1999)

$$P^0(T, M_w) = 87060 \exp\left(-299 \frac{(10^3 M_w)^{0.59}}{T}\right) \quad (12)$$

where  $P^0$  is expressed in atmospheres and  $M_w$  in kg/mol.

Evaporation takes place when  $P^0 \geq P_{atm}$ . We assumed that the pressure drop of the vapour flow through the pellet is negligible, so that the pressure of evaporation is the atmospheric pressure. As a consequence, a relationship between the molecular weight and the temperature is obtained from Eq. (12)

$$M_w = 10^{-3} \left( \frac{\ln 87060}{299} T \right)^{1/0.59} \quad (13)$$

Eq. (13) allows to calculate the molecular weight of the compounds being evaporated at a given temperature.

Tar2 is a fraction of the products generated by wood thermal cracking defined in a certain range of molecular weight, between a minimum ( $M_{w,min}$ ) and a maximum ( $M_{w,max}$ ) value.

From experiments it can be observed that the production of tar stops at a temperature of about 973 K. We assumed this temperature as corresponding to the boiling point of the heaviest compound of Tar2, that according to Eq. (13) is characterized by a  $M_{w,max}$  of 0.45 kg/mol. It was also observed that primary pyrolysis ends at around 350 °C and that at temperatures lower than 523 °C only a limited weight loss occurs.  $M_{w,min}$  was determined by fitting in this range of temperatures and the best value was 0.17 kg/mol, corresponding to a boiling point of 543 °C.

Between  $M_{w,min}$  and  $M_{w,max}$  a continuous distribution of molecular weights was assumed and a distribution function  $E_w(M_w)$  was introduced, so that

$$E_w(M_w) dM_w = dm_2 \quad (14)$$

where  $dm_2$  is the mass of Tar2 having a molecular weight between  $M_w$  and  $M_w + dM_w$ . No idea about the function  $E_w$ : for the sake of simplicity a uniform distribution was adopted, i.e.

$$E_w = \frac{m_{02}}{M_{w,max} - M_{w,min}} \quad (15)$$

where  $m_{02}$  is the amount of Tar2 globally produced by primary pyrolysis and it corresponds to  $m_{s0} \cdot C$ .

If the transformation reaction of Tar2 into gas and Tar3 were negligible, the evaporation rate of Tar2 would be

$$\dot{m}_{2,ev,0} = \frac{m_{2,0}}{10^3 (M_{w,max} - M_{w,min})} \frac{(\ln 87.060/299)^{1/0.59}}{0.59} T^{(1/0.59-1)} \frac{dT}{dt} \quad (16)$$

But in parallel Tar2 is transformed also into gas and Tar3, although slowly, according to the following equation:

$$R_{23} + R_{g2} = -m_2 A_2 \exp\left(\frac{-E_2}{RT}\right) \quad (17)$$

As the pyrolysis time increases, evaporation will concern a smaller and smaller fraction  $f_2$  of the original mass of Tar2

$$f_2 = \frac{m_{20} - \int_0^t (R_{23} + R_{g2}) dt}{m_{20}} \quad (18)$$

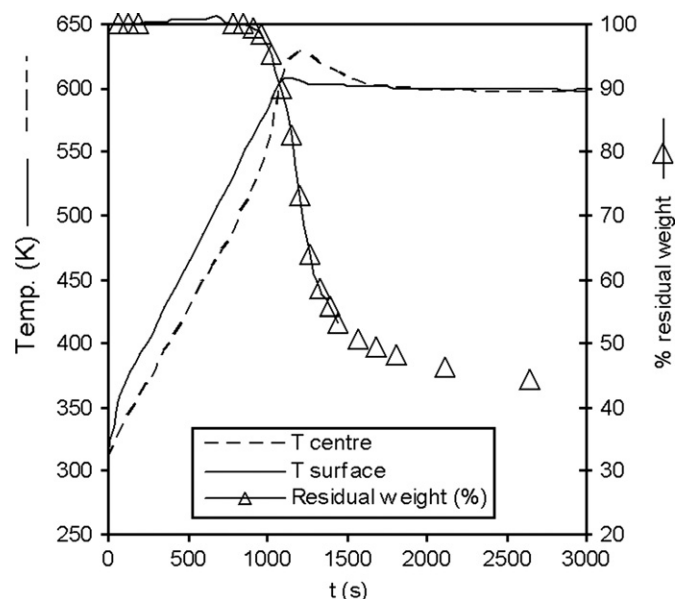


Fig. 9. Isothermal pyrolysis at 598 K.

so that the mass balance of Tar2 is as follows:

$$\frac{dm_2}{dt} = -f_2 \dot{m}_{2, \text{ev}, 0} - (R_{23} + R_{g2}) \quad (19)$$

Gas and Tar3 produced by the secondary reaction of Tar2 can be calculated as follows:

$$\begin{aligned} R_{g2} &= E m_2 A_2 \exp\left(\frac{-E_2}{RT}\right) \\ R_{23} &= F m_2 A_2 \exp\left(\frac{-E_2}{RT}\right) \end{aligned} \quad (20)$$

$E$  and  $F$  are, respectively, the mass fractions of Tar2 converted by this reaction in gas and Tar3; these coefficients are considered constant with temperature.

At high temperature Tar3 evolves towards graphitic structures according to a cross-linking reaction. This reaction can lead to a further production of a moderate amount of gas (Solomon et al., 1988). Cross-linking reactions can be modelled by means of the following expressions, where the rate constants obey the

Arrhenius law:

$$\begin{aligned} \frac{dm_4}{dt} &= m_3 A_{34} \exp\left(\frac{-E_{34}}{RT}\right) \\ R_{g3} &= m_3 A_{3g} \exp\left(\frac{-E_{3g}}{RT}\right) \end{aligned} \quad (21)$$

In the literature various values of activation energy for cross-linking reactions of coal pyrolysis are reported, ranging between 210 000 and 290 000 J/mol (Niksa and Kerstein, 1991; Solomon et al., 1988). It was necessary to use different activation energies to predict with enough accuracy the amount of gas and char found experimentally both with 1 and 0.05 K/s heating rate. This would mean that the transformation of Tar3 to char and formation of gas were independent reactions. For char production a literature value (Solomon et al., 1988) used was equal to 251 000 J/mol, for gas production  $E_{3g}$  was set to 301 500 J/mol. The frequency factors were determined from fitting.

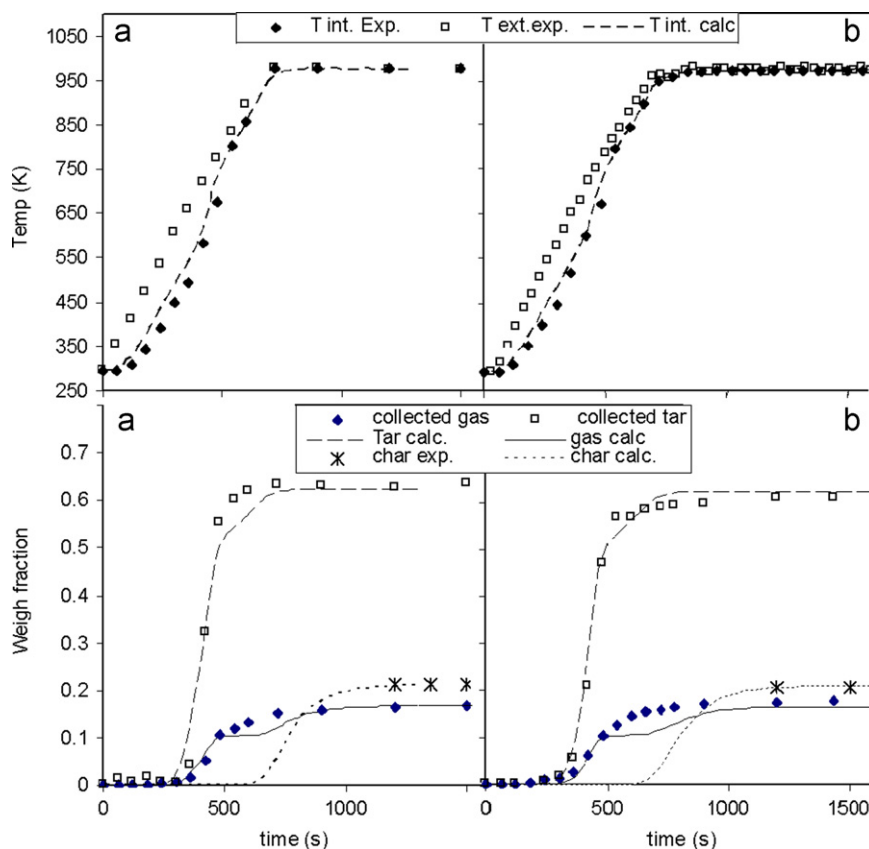
The numerical kinetic parameters employed in simulation are listed in Table 3.

#### 4.4. Modelling of large particles pyrolysis

The kinetic data used to find the parameters of the pyrolysis model arise in particular from the tests performed in isothermal conditions or with low heating rate, where no thermal gradients inside particles were found. With higher heating rates thermal gradients cannot be neglected. In order to apply the kinetic model developed in the previous paragraph to higher heating rate runs, a detailed model for the cylindrical particles was built taking also into consideration the transport of heat and the variation of temperature in the sample. The behaviour of the sample can be described by means of material and

**Table 4**  
Numerical parameters used for modelling of samples heating.

Parameter	Ref.
$C_{p, \text{wood}}$	$1112.0 + 4.85(T - 273.15)$ (J kg <sup>-1</sup> K <sup>-1</sup> ) Babu and Chaurasia (2004)
$C_{p, \text{char}}$	$0.36T + 1390$ (J kg <sup>-1</sup> K <sup>-1</sup> ) Ragland et al. (1991)
$k_{\text{wood}}$	$\rho_w 0.1941 + 0.0186$ (W m <sup>-1</sup> K <sup>-1</sup> ) Ragland et al. (1991)
$k_{\text{char}}$	0.105 (W m <sup>-1</sup> K <sup>-1</sup> ) Bryden et al. (2002)
$\Delta H_{\text{pir}}$	-125 000 (J kg <sup>-1</sup> ) Koufopoulos et al. (1991)



**Fig. 10.** Tar and gas production during pyrolysis at 1 K/s heating rate, internal and external temperature, comparison between model and experimental results, (a) beech wood and (b) pine wood.

energy balance coupled with the kinetic equations. The energy balance inside the sample is the following:

$$\hat{c}_{ps} \frac{\partial T}{\partial t} = \frac{k_s}{\rho_s} \frac{1}{r} \frac{\partial}{\partial r} \left( r \frac{\partial T}{\partial r} \right) - \frac{\hat{c}_{pg}}{2\pi\rho_s} \frac{\partial(\dot{m}_g T)}{\partial r} - \frac{R_{pyr}}{\rho_s} \Delta H_{pyr} \quad (22)$$

where  $R_{pyr}$  is the sum of ( $R_{g1} + R_1 + R_2 + R_3$ ) referred to the pellet volume.

The reaction heat of pyrolysis,  $\Delta H_{pyr}$ , is weak but not negligible. Fig. 9 shows that in the centre the temperature rises above the surface temperature due to  $\Delta H_{pyr}$ . The same value of  $\Delta H_{pyr}$  was assumed for all the reactions. The values of  $\Delta H_{pyr}$  reported in the literature lie in a very wide range (Rath et al., 2003). A reasonable value seem to be between  $-250$  and  $-100$  kJ/kg (Chan et al., 1985; Koufopoulos et al., 1989; Babu and Chaurasia, 2004). According to a parametric analysis of this parameter its influence on the profile of temperature and on kinetics was the same in the range  $-50 > \Delta H_{pyr} > -250$  kJ/kg. As a consequence a value of  $-125$  kJ/kg is fully acceptable.

The values of  $\hat{c}_{ps}$  and  $k_s$  were changed during calculations to take into account of the transformation of the solid structure. Table 4 shows the extreme values (for wood and char) of  $\hat{c}_{ps}$  and  $k_s$ ; the actual value employed in calculation was a local average between char and wood values according their mass fractions.

## 5. Model results

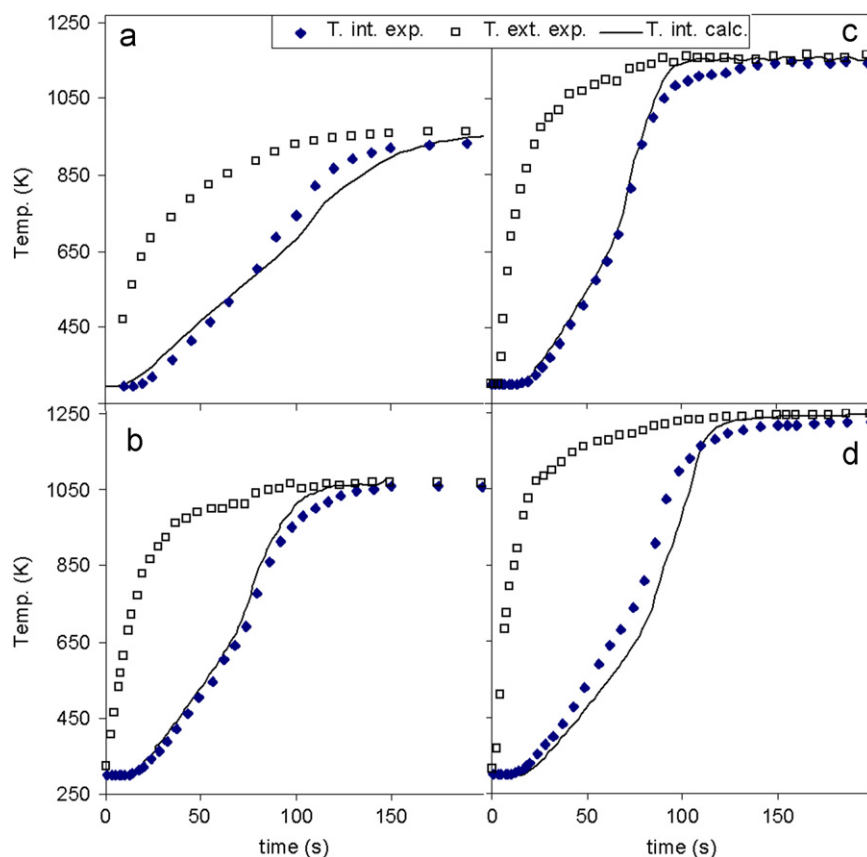
The prediction of the model compares satisfactorily with the experimental tests on beech and pine wood; as an example, fig. 10 shows this comparison at 1 K/s.

The model was validated with pyrolysis data at elevated heating rate, as those obtained by suddenly putting the pellet in a previously heated oven (700–960 °C). The initial temperature rise

of the pellet surface was around 60–100 K/s; in the centre of the sample the temperature rise was around 10 K/s. During these runs, only the mass loss and the solid residual were determined, due to the short duration of time of the run. Figs. 11 and 12 show an example of experimental temperature rise and mass loss in such runs; the experimental values are compared with the values calculated with the proposed model and the kinetic parameters previously determined. At each time, the distribution of temperature inside the pellet was calculated and the kinetics determined according to the temperature value. The final values of the residual mass are in agreement with the experimental ones as can be observed in Table 5. As regards the decrease of mass due to emission of gas and tar from pellet, there is an apparent difference of slope between experimental and calculated values: kinetics of pyrolysis at these elevated temperature rise is higher than that calculated by the model. To this regard, it must be pointed out that the kinetic data were mainly determined with a temperature rise of 0.05 K/s, while the high heating rate runs were carried out at about 60–100 K/s that means 3 order of magnitude higher. Probably the problem is in a too slow cross-linking reaction; indeed, this reaction is very complicated and its interpretation as a first-order reaction connected with a hypothetical reactant identified as Tar3 is a too strong simplification. In spite of this delay, from Table 5 it can be seen that the calculated residual mass is in a very good agreement with the experimental one in all the experiments.

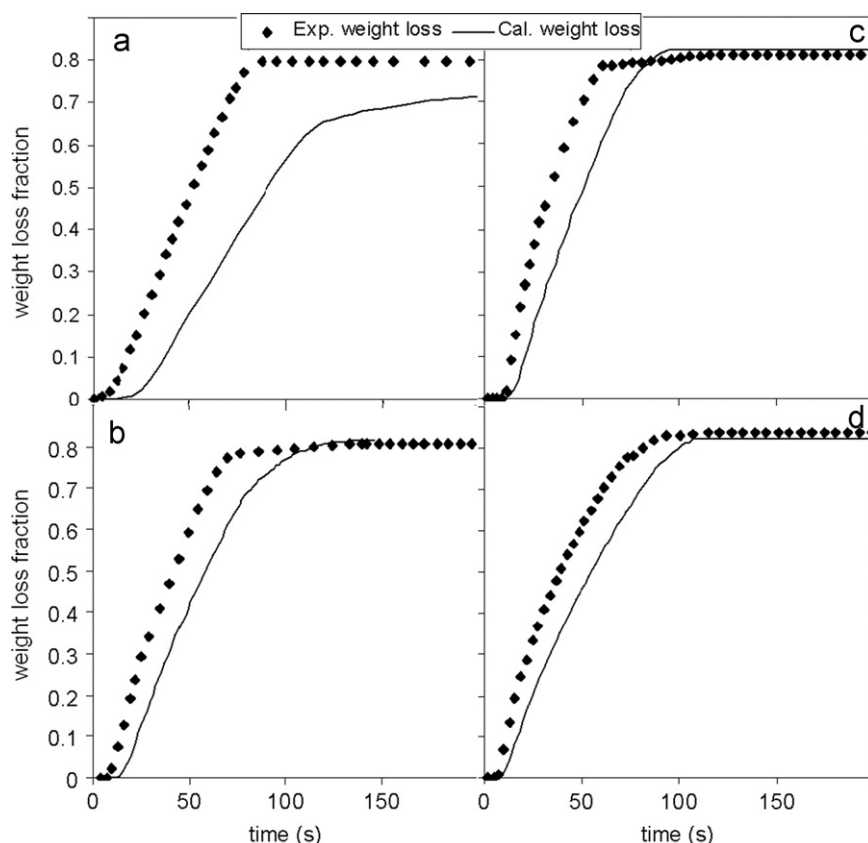
## 6. Conclusions

Pyrolysis of wood very often occurs in the form of pellets or big fragments with heating rates between 0.5 and 50 K/s. In such



**Fig. 11.** Temperatures at the surface and in the centre during fast heating; (a) beech wood, 11.5 mm diam, oven at 950 K; (b) beech wood, 11.5 mm diam, oven at 1050 K; (c) beech wood, 11.5 mm diam, oven at 1150 K and (d) pine wood, 13.5 mm diam, oven at 1250 K.





**Fig. 12.** Mass loss during fast heating; (a) beech wood, 11.5 mm diam, oven at 950 K; (b) beech wood, 11.5 mm diam, oven at 1050 K; (c) beech wood, 11.5 mm diam, oven at 1150 K and (d) pine wood, 13.5 mm diam, oven at 1250 K.

**Table 5**  
Comparison between experimental and calculated amount of residual.

Wood	Sample diameter (mm)	heating	Max external temp. (K)	Residual mass fraction, exp.	Residual mass fraction, calc.
Beech	13.5	Controlled, 1 K/s	973	0.211	0.210
Pine	13.5	Controlled, 1 K/s	973	0.208	0.210
Beech	13.5	Controlled, 0.05 K/s	973	0.267	0.261
Pine	13.5	Controlled, 0.05 K/s	973	0.265	0.261
Beech	11.5	Radiation in a 850 K oven	850	0.237	0.246
Beech	11.5	Radiation in a 900 K oven	900	0.245	0.238
Beech	11.5	Radiation in a 963 K oven	950	0.208	0.214
Pine	13.5	Radiation in a 973 K oven	965	0.212	0.214
Beech	11.5	Radiation in a 1050 K oven	1050	0.191	0.187
Beech	11.5	Radiation in a 1150 K oven	1150	0.188	0.177
Pine	13.5	Radiation in a 1150 K oven	1150	0.187	0.180
Pine	13.5	Radiation in a 1230 K oven	1230	0.162	0.176

conditions the kinetics and yields are not the same as in processes involving powders. The reason is related in particular to the effects of secondary reactions involving solid and gaseous products as showed in Fig. 1. Within big particles such reactions are strongly favoured. However most of the kinetic models published in the literature were based on experimental tests on very small samples with a weight of some mg.

In this work, dynamic pyrolysis tests on beech and pine wood were carried out. A new mechanistic kinetic model was proposed and the kinetic parameters were determined by tests on wood pellets 13–11 mm diameter and 60 mm long. Decrease of the pellet mass, rate of production of gases and tar were measured, together with

temperature at the surface and in the centre of the sample. The experimental results obtained either at low heating rate (0.05–1 K/s) and at elevated heating rate (surface of the sample: till 100 K/s; centre of the sample approximately 10 K/s) were compared successfully with the results calculated by the model. A peculiarity of the experiments at elevated heating rate is the considerable difference of temperature between the surface of the sample and the centre, which was very well interpreted by the model.

The agreement between experimental and calculated data of pyrolysis is excellent at low heating rate, satisfactorily at high heating rate; in any case, the model seems give better results than literature models that forecast primary pyrolysis only. The experimental and

calculated pyrolysis curves as a function of time have different slopes, but the residual mass was very well calculated by the model.

## Nomenclature

$A$	fraction of wood converted in gas as a results of primary pyrolysis
$A_2$	pre-exponential constant of reaction of Tar2, $s^{-1}$
$A_{34}$	pre-exponential constant of reaction of cross-linking (char production), $s^{-1}$
$A_{3g}$	pre-exponential constant of reaction of cross-linking (gas production), $s^{-1}$
$A_w$	pre-exponential constant of the primary pyrolysis reaction, $s^{-1}$
$B$	fraction of wood converted in Tar1 as a result of primary pyrolysis
$C$	fraction of wood converted in Tar2 as a result of primary pyrolysis
$\hat{C}_{ps}$	solid specific heat, $J\ kg^{-1}\ K^{-1}$
$D$	fraction of wood converted in Tar3 as a result of primary pyrolysis
$E$	mass fraction of Tar2 converted in gas as a result of secondary pyrolysis
$E_0$	activation energy of the primary pyrolysis reaction, $J\ mol^{-1}$
$E_2$	Activation energy of the reaction of Tar2, $J\ mol^{-1}$
$E_{34}$	activation energy of the reaction of cross-linking (char production), $J\ mol^{-1}$
$E_{3g}$	activation energy of the reaction of cross-linking (gas production), $J\ mol^{-1}$
$E_w$	distribution function of the molecular weights of Tar2
$F$	mass fraction of Tar2 converted in Tar3 as a result of secondary pyrolysis
$k_s$	solid thermal conductivity, $W\ m^{-1}\ K^{-1}$
$m_2$	mass of Tar2 in the sample, kg
$m_3$	mass of Tar3 in the sample, kg
$m_4$	mass of char in the sample, kg
$m_s$	mass of the sample, kg
$m_{s0}$	initial mass of the sample, kg
$m_w$	mass of wood in the sample, kg
$M_w$	molecular weight, kg/mol
$\dot{m}_1$	production rate of Tar1, kg/s
$\dot{m}_{2,ev}$	evaporation rate of Tar2, kg/s
$\dot{m}_g$	global production rate of light gas, kg/s
$r$	radius of the sample, m
$R_1$	transformation rate of wood in Tar1, kg/s
$R_2$	transformation rate of wood in Tar2, kg/s
$R_3$	transformation rate of wood in Tar3, kg/s
$R_{23}$	transformation rate of Tar2 in Tar3, kg/s
$R_4$	transformation rate of Tar3 in char, kg/s
$R_{g1}$	production rate of light gas from primary pyrolysis, kg/s
$R_{g2}$	transformation rate of Tar2 in gas, kg/s
$R_{g3}$	transformation rate of Tar3 in gas, kg/s
$T$	temperature, K
$\Delta H$	pyrolysis enthalpy, J/kg
$\rho_s$	density of the sample, $kg\ m^{-3}$

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## References

- Ahuja, P., Kumar, S., Singh, P.C., 1996. A model for primary and heterogeneous secondary reactions of wood pyrolysis. *Chemical Engineering and Technology* 19, 272–282.
- Alves, S.S., Figueiredo, J.L., 1989. A model for pyrolysis of wet wood. *Chemical Engineering Science* 44 (n. 12), 2861–2869.
- Babu, B.V., Chaurasia, A.S., 2004. Heat transfer and kinetics in the pyrolysis of shrinking biomass particle. *Chemical Engineering Science* 59, 1999–2012.
- Borson, M.L., Howard, J.B., Longwell, J.P., Peters, W.A., 1989. Products yields and kinetics from the vapour phase cracking of wood pyrolysis tars. *AIChE Journal* 35 (n.1), 120–128.
- Bradbury, A.G., Sakal, Y., Shafizadeh, F., 1979. Kinetic model for pyrolysis of cellulose. *Journal of Applied Polymer Science* 23, 3271–3280.
- Bryden, K.M., Ragland, K.W., Rutland, C.J., 2002. Modelling thermally thick pyrolysis of wood. *Biomass and Bioenergy* 22, 41–53.
- Chan, W.R., Kelbon, M., Krieger, B.B., 1985. Modelling and experimental verification of physical and chemical processes during pyrolysis of a large biomass particle. *Fuel* 64, 1505–1513.
- Di Blasi, C., 1993. Analysis of convection and secondary reaction effects within porous solid fuels undergoing pyrolysis. *Combustion Science and Technology* 90, 315–340.
- Di Blasi, C., 1998. Comparison of semi-global mechanisms for primary pyrolysis of lignocellulosic fuels. *Journal of Analytical and Applied Pyrolysis* 47, 43–64.
- Di Blasi, C., Branca, C., 2001. Kinetics of primary product formation from wood pyrolysis. *Industrial and Engineering Chemistry Research* 40, 5547–5556.
- Di Blasi, C., 2002. Modeling intra- and extra-particle processes of wood fast pyrolysis. *AIChE Journal* 48, 2386–2397.
- Di Blasi, C., 2008. Modeling chemical and physical processes of wood and biomass pyrolysis. *Progress in Energy and Combustion Science* 34 (n. 1), 47–90.
- Fagbemi, L., Khezami, L., Carpat, L., 2001. Pyrolysis products from different biomasses: application to the thermal cracking of tar. *Applied Energy* 69, 293–306.
- Font, R., Marcilla, A., Verdu, E., Devesa, J., 1990. Kinetics of the pyrolysis of almond shells and almond shells impregnated with  $CoCl_2$  in a fluidized bed reactor and in a Pyroprobe 100. *Industrial and Engineering Chemistry Research* 29, 1846–1855.
- Genetti, D., Fletcher, T.H., Pugmire, R.J., 1999. Development and application of a correlation of  $^{13}C$  NMR chemical structural analyses of coal based on elemental composition and volatile matter content. *Energy & Fuels* 13 (n. 1), 60–68.
- Grant, D.M., Pugmire, R.J., Fletcher, T.H., Kerstein, A.R., 1989. Chemical model of coal devolatilization using percolation lattice statistics. *Energy and Fuels* 3 (n. 2), 175–186.
- Gronli, M.G., Melaaen, M.C., 2000. Mathematical model for wood pyrolysis—comparison of experimental measurement with model predictions. *Energy and Fuels* 14, 791–800.
- Helsen, L.M., Van der Bulck, E.V.M., 2001. Study of a new macro-particle model for the low temperature pyrolysis of dried wood chips. *Heat and Mass Transfer* 38, 165–181.
- Janse, A.M.C., Westerhout, R.W.J., Prins, W., 2000. Modelling of flash pyrolysis of a single wood particle. *Chemical Engineering and Processing* 39, 239–252.
- Koufopoulos, C.A., Maschio, G., Lucchesi, A., 1989. Kinetic modelling of the pyrolysis of biomass and biomass components. *Canadian Journal of Chemical Engineering* 67, 75–84.
- Koufopoulos, C.A., Papayannkos, N., Maschio, G., Lucchesi, A., 1991. Modelling of the pyrolysis of biomass particles, studies on kinetics, thermal and heat transfer effects. *The Canadian Journal of Chemical Engineering* 69, 907–915.
- Liden, A.G., Berruti, F., Scott, D.S., 1988. A kinetic model for the production of liquids from the flash pyrolysis of biomass. *Chemical Engineering Communications* 65, 207–221.
- Niksa, S., 1988. Rapid coal devolatilization as an equilibrium flash distillation. *AIChE Journal* 34 (n.5), 790–802.
- Niksa, S., Kerstein, A.R., 1991. FLASHCHAIN theory for rapid coal devolatilization kinetics. 1. Formulation. *Energy & Fuels* 5 (n. 5), 647–665.
- Orfao, J.J.M., Antunes, F.J.A., Figueiredo, J.L., 1999. Pyrolysis kinetics of lignocellulosic materials—three independent reaction model. *Fuel* 78, 349–358.
- Park, W.C., Atreya, A., Baum, H.R., 2010. Experimental and theoretical investigation of heat and mass transfer processes during wood pyrolysis. *Combustion and Flame* 157, 481–494.
- Ragland, K.W., Aerts, D.J., Baker, A.J., 1991. Properties of wood for combustion analysis. *Bioresource Technology* 37, 161–168.
- Rajeswara Rao, T., Sharma, A., 1998. Pyrolysis rate of biomass materials. *Energy* 23 (n. 11), 973–978.
- Ranzi, E., Cuoci, A., Faravelli, T., Frassoldati, A., Migliavacca, G., Pierucci, S., Sommariva, S., 2008. Chemical kinetics of biomass pyrolysis. *Energy and Fuels* 22 (n. 6), 4292–4300.
- Rath, J., Wolfinger, M.G., Steiner, G., Krammer, G., Barontini, F., Cozzani, V., 2003. Heat of wood pyrolysis. *Fuel* 82, 81–91.
- Rostami, A.A., Hajaligol, M.R., Wrenn, S.E., 2004. A biomass pyrolysis sub-model for CFD applications. *Fuel* 83, 1519–1525.
- Shafizadeh, F., Bradbury, A.G., 1979. Thermal degradation of cellulose in air and nitrogen at low temperatures. *Journal of Applied Polymer Science* 23 (5), 1431–1442.
- Sharypov, V.I., Marin, N., Beregovtsova, N.G., Baryshnikov, S.V., Kuznetsov, B.N., Cebolla, V.N., Weber, J.W., 2002. Co-pyrolysis of wood biomass and synthetic

- polymer mixtures. Part I influence of the experimental conditions on the evolution of solids, liquids and gases. *Journal of Analytical and Applied Pyrolysis* 64, 15–28.
- Solomon, P.R., Hamblen, D.G., Carangelo, R.M., Serio, M.A., Deshpande, G.V., 1988. General model of coal devolatilization. *Energy & Fuels* 2 (4), 405–422.
- Strezov, V., Moghtaderi, B., Lucas, J.A., 2003. Thermal study of decomposition of selected biomass samples. *Journal of Thermal Analysis and Calorimetry* 72, 1041–1048.
- Turner, F., Mann, U., 1981. Kinetic investigation of wood pyrolysis. *Industrial and Engineering Chemistry Process Design and Development* 20, 482–488.
- Williams, P.T., Besler, S., 1996. Influence of temperature and heating rate on the slow pyrolysis of biomass. *Renewable Energy* 7 (3), 233–250.
- Wojtowicz, M.A., Bassilakis, R., Smith, W., Chen, Y., Carangelo, R.M., 2003. Modeling the evolution of volatile species during tobacco pyrolysis. *Journal of Analytical and Applied Pyrolysis* 66 (1), 235–261.