# THERMAL BEHAVIOUR/TREATMENT OF SOME VEGETABLE RESIDUES. IV. THERMAL DECOMPOSITION OF EUCALYPTUS WOOD

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The paper is divided into two parts, as follows: the former includes a short review on the kinetics of wood thermal decomposition, while the latter studies the thermal behaviour of Eucalyptus chips, Eucalyptus brown stock pulp (BSP) and their corresponding lignin samples. The glass transition temperatures of the lignins extracted from Eucalyptus samples have been determined. On the basis of a decomposition model of the wood components, the dependence of the overall kinetic parameters on heating rate and conversion degree has been established.

*Keywords*: Eucalyptus chips, Eucalyptus brown stock pulp, thermal behaviour

## INTRODUCTION

The widespread availability of biomass – the third among the primary energy resources, after coal and oil,[1] also renewable and potentially neutral in relation to global warming[2] – motivated the extensive research undertaken in the past decade for the industrial development of thermo-chemical conversion of plants (see, for instance, two recent reviews[3,4]).

Pyrolysis and other thermo-chemical conversion processes represent important options for biomass and waste utilization. The increasing dependence on imported oil, as well as the urgency to reduce greenhouse emissions, are some of the reasons that justify an energy policy that carefully considers the role of renewable sources as energy carriers. The upsurge of interest in the simulation and optimization of reactors for thermo-chemical processes requires appropriate models that integrate different operational conditions and varied feedstocks and help to achieve a better understanding of the reactions involved in the corresponding processes.

**Kinetics of wood thermal decomposition**

Numerous researchers have intensively investigated the kinetics of cellulose and biomass pyrolysis.[5] The thermal decomposition kinetics has been studied for various kinds of wood, such as: beech wood (*Fagus sylvatica*) – a hardwood with a chemical composition consisting of 20% lignin, 33% hemicelluloses, 45% cellulose, and 2% extractives,[6] pine and beech wood,[7,8] chestnut wood,[9] liquid fractions from (beech and fir) bark, several agricultural residues (straw, olive husks and nut shells), and cellulose.[10] Also, a comparative thermogravimetric study was performed[11] for hardwoods (oak, beech, nut), softwoods (lime, sweet cherry, sycamore maple, aspen and pine), as well as for lime wood of different ages (recent wood ~6 year-old, ~180 year-old and ~250 year-old).

The global devolatilization rates are well-predicted by a mechanism involving three parallel first-order reactions with comparable values of the kinetic parameters. The four partial reactions appropriately described the

global decomposition of most of the samples, while a low-temperature partial reaction was needed for the untreated pine. The three parallel reaction mechanisms for hemicelluloses, cellulose and lignin, with the same activation energies – previously determined for other hardwood species, and proposed by Grønli *et al*.,[12] are still acceptable for engineering applications.

A mechanism for the formation of the main product classes was proposed:

$$\begin{aligned} &\xrightarrow{k_C} CHAR \\ W &\xrightarrow{k_L} LIQUIDS \quad (a_1 + a_3) \\ &\xrightarrow{k_G} GAS \end{aligned}$$

$$k = k_G + k_L + k_C, \quad k_j = A_j e^{-B_j/RT}, \quad j = G, L, C$$
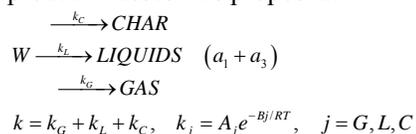
where $k_i$ are rate constants for gas (G), liquid (L) and char (C) formation, $A_j$ is the pre-exponential factor, $B_j$ – activation energy, R – gas constant, T temperature and $a_i$ – stoichiometric coefficients.

The one-step reaction mechanism only describes the central part of the mass loss curves, whose dynamics corresponds to those of the quantitatively higher components.

Mechanisms involving a large set of parameters have also been proposed, based on the component degradation rates.[13] The activation energy of the global reaction presents largely variable values, roughly comprised between 89 and 175 kJ/mol, while the activation energies for the formation of liquids and gases are of 148 ± 17.2 and 152.7 ± 18.2 kJ/mol, respectively. This can be the result of the different heating conditions, different sample characteristics (size and wood variety) and of the mathematical treatment of the experimental data. The following critical points motivate the need for a further, more accurate analysis of the intrinsic kinetics of primary wood degradation: (a) the narrow range of very low (below 593-598 K) temperatures investigated, (b) the inability of most mechanisms to predict the rates of product formation which, together with the conversion time, are needed for the formulation of engineering models for reactor optimization and design, (c) the failure of the most complete mechanisms to predict quantitatively or even qualitatively the correct dependence of the product yields from pyrolysis on the reaction temperature, (d) the use of high temperature (above 750 K) data in the estimation of the kinetic constants, so that the secondary reaction activity is not negligible and, given the extremely fast reaction rates, it is likely that conversion occurs under heat transfer control (apparent kinetics), and (e) the lack of information on the evolution of the sample temperature in all cases, or the use of thick particles/large samples, which again switch the control from the chemical reaction to heat and mass transfer.

Thermogravimetry has proved to be a useful tool in elucidating the decomposition of various biomass materials. The slow heating rates of thermogravimetric analysis (TGA), the specific properties of cellulose and the different measurement systems,[14] among other factors, have been shown to exert a significant influence on the kinetic parameters. The situation is worse for wood for the following reasons: a lower number of studies in this field, its complex structure, and the catalytic role played by inorganic matter in the reaction paths. The total mass loss is associated with the pyrolysis process, assuming the addition of three independent parallel devolatilization reactions,[15] such as: a hemicellulose fraction, which decomposes in the low-temperature range (first peak of the DTG curve); a cellulose fraction, which decomposes in the mid-temperature range (second peak of the DTG curve); the fraction of lignin present plus the extractives and the remaining amounts of holocellulose. The separate formation of different product classes introduced by the reaction mechanism is questionable. Grønli *et al*.[12] examined the thermogravimetric curves of nine wood species with the chemical composition lying within the standard range for hardwoods and softwoods, and established the activation energies for the pseudo-components: hemicelluloses, cellulose and lignin. The decomposition processes were described by global reactions with typical activation energies of 105-111 kJ/mol (hemicelluloses), 195-213 kJ/mol (cellulose) and 35-65 kJ/mol (lignin).[16]

Popescu *et al*.[17] have studied eight wood species, such as: oak, beech and nut wood (hardwood types) and lime, sweet cherry, sycamore maple, aspen and pine wood (softwood types), and found global activation energy values between 72 and 92 kJ/mol for softwood, and between 95 and 122 kJ/mol, respectively, for hardwood species, while Vasile *et al*.[18] have investigated the thermal behaviour of lignin and established the dependence of the kinetic parameters on heating rate, conversion degree and

extraction procedure. On an indicative basis, for a slow rate of heating in thermogravimetry studies,[19,20] primary wood degradation starts at about 500 K, however, at fast rates, it is attained at about 573 K,[21,22] and the process is practically terminated[23] at 700 K. At higher temperatures, secondary reactions of primary tar vapors also become active.[24,25] The reaction products are usually lumped into three main classes (liquids, char and gas),[26] their relative amounts and composition being specifically dependent on the conversion unit (for instance, fixed-bed or fluid-bed reactors), although the heating rate and reaction temperature remain certainly the most important process variables. The mass loss curves of wood, obtained at slow heating rates, show several reaction zones, associated with component decomposition, which attains maximum rates at different temperatures.[27]

Wood pyrolysis kinetics is needed for the design of chemical reactors applied for energy and chemicals recovery. Kinetic analysis is complicated by the composite nature of wood, constituted of a mixture of hemicelluloses, cellulose, lignin and extractives, the ratios, chemistry and reactivity of which are affected by the variety.

Widely different kinetic parameters have been published in the literature, because of the greatly different experimental conditions, various experimental problems and occasional use of unsuitable evaluation methods. The related kinetic mechanisms, usually formulated by the use of a single experiment (heating rate), are based either on a one-step reaction or on several parallel reactions.[20] These mechanisms, properly coupled with the description of transport phenomena, have been applied for fixed-bed reactors,[28] where the coarse particles and/or the significant external heat transfer limitations determine slow heating rates and low conversion temperatures (slow conventional pyrolysis). As a constant ratio between the yields of char and volatiles is assumed, only the conversion time can be predicted. The results of kinetic modeling of wood pyrolysis obtained at fast heating rates or under isothermal conditions are important and necessary for the development of fast pyrolysis technologies[29,30] and, in some cases, for the devolatilization stage of gasifiers and combustors.[31-37]

Furthermore, the kinetic constants, estimated in different literature sources and used by Chan *et al.*[38] to model large-particle pyrolysis, are also of interest, since they are capable of predicting,[39] at least qualitatively, the correct behaviour of wood pyrolysis. Generally, the kinetic constants are based on the assumption of a one-stage process, that is, on a simple devolatilization reaction or on three parallel reactions for the formation of the main above-mentioned product classes, according to the mechanism originally proposed by Shafizadeh and Chin.[40]

Despite the abundance of the Eucalyptus species, only recently has a start been made towards its full utilization.[41] In the Iberian region of the European Union, *Eucalyptus globulus*, covers an increasing part of the surface area,[42] over one million hectares, producing more than seven million m$^3$/year of round wood, mainly for pulp manufacturing.[43]

Only a few papers have been devoted to the thermal characterization of Eucalyptus wood,[44] and no references are known on the kinetics of Eucalyptus wood thermal decomposition.

This study undertakes a thermogravimetric investigation of Eucalyptus wood, for elucidating the dependence of the thermal characteristics and kinetic parameters of each thermogravimetric step on the different experimental parameters, and also for establishing the differences observed among samples after various treatments (Eucalyptus chips with respect to Eucalyptus brown stock pulp).

## EXPERIMENTAL
### Materials

The unfractionated samples of *Eucalyptus globulus* wood chips from the same batch as the pulp and unbleached Kraft pulp brown stock of *Eucalyptus globulus* (sampled after the washing stages) were provided by Abö Akademi University, Laboratory of Wood and Paper Chemistry, Turku, Finland. All samples were characterized by the joint analysis group formed in the framework of COST E41: *Analytical tools with applications for wood and pulping chemistry*. Eucalyptus wood contains tannins extracted by ethanol, but they are normally removed during pulping. *Eucalyptus globulus* pulp does contain some degraded sugars, which can probably form a hydrophilic layer – this could partly explain the dispersion, in gravimetric amounts, of the extractives. It was also evidenced that the pulp did not contain any calcium soaps.

Unbleached Eucalyptus (*Eucalyptus globulus*) Kraft pulp brown stock was sampled after the washing stages but before the $O_2$ bleaching, in a Portuguese mill (never-dried pulp, 27% dryness). The pulp was stored in a freezer.

Working groups of different partner laboratories of the COST Action E41 Project determined the composition of the wood components following different separation procedures.[45-47] The average contents of the components are presented in Table 1. The studied samples have very different contents of extractives, carbohydrates and lignins.

The samples selected for the study have very different contents of extractives, carbohydrates and lignins. Eucalyptus BSP has ~20 wt% more carbohydrates, while the lignin content is very low, of 1-1.7 wt%. Unbleached pulps were studied in a previous paper[48] of ours, devoted to the spectral characterization of Eucalyptus wood. The metal content in ash was determined by absorption spectroscopy (Table 2). It can be remarked that Eucalyptus BSP contains a higher quantity of calcium, but no copper. The other elements occur in approximately the same amounts.

The corresponding lignin samples from these *Eucalyptus globulus* samples have been obtained by mild enzymatic acidolysis, in the Forest Biomaterials Laboratory, College of Natural Resources, North Carolina State University.

*Isolation of mild enzymatic acidolysis lignins (EMALs)* from *Eucalyptus globulus* chips: The wood chips were ground to pass a 20-mesh screen in a Wiley mill and Soxhlet, then extracted with acetone for 48 h. The resulting Wiley-milled wood powder was air-dried and stored in a desiccator under vacuum. The *E. globulus* wood-powder was submitted to alkaline extraction with 0.3% (0.075 mol $L^{-1}$) NaOH for 1 h, to remove the tannins before use.[49] EMALs were isolated from ball-milled wood, according to the procedure described by Wu and Argyropoulos.[50] Caution was taken to avoid contamination in the final product, as previously reported.[51] Residual Kraft lignin was isolated from Eucalyptus Kraft pulp.[52]

**Thermal characterization**

*Conditioning*: to determine the moisture content, the samples were kept for 1 h in a conditioning atmosphere, which may involve exposure of the specimens to circulating air at $50.0 \pm 2.0\%$ and $65.0 \pm 2.0\%$ relative humidity (RH), and $23.0 \pm 1.0$ °C.

*Drying*: moisture was removed by oven-drying the samples for 2 h at $105 \pm 3$ °C, followed by cooling in a dessicator and weighing, the operations being repeated until constant weight.

The quantity of desorbed water is higher than the absorbed one (Table 3), therefore some quantity of water is always present in the initial samples. Whatever the type of water, its amount is higher in Eucalyptus BSP than in Eucalyptus chips.

The DSC curves were recorded on a Mettler DSC 12E instrument with a heating rate of 10 °C/min, in nitrogen atmosphere, sample mass of ~5-8 mg, two scanning runs being applied.

For Tg determination (second run), the samples have been protected against oxidation with inert silicon oil, over the studied temperature range, Tg being taken at the middle of the temperature interval, or at the onset of baseline deviation, for the samples showing degradation at a low temperature.

The TG/DTG curves were recorded on a Shimadzu Thermogravimetric Analyser under the following operational conditions: heating rates – 1, 2.5, 5 and 10 °C/min, temperature range – 25-600 °C, sample mass – ~20 mg, platinum crucible, nitrogen flow – 100 $cm^3$/min.

**RESULTS AND DISCUSSION**
**DSC results. Low temperature range**

In the DSC curves region (Fig. 1), where the loss of water desorption and low molecular weight compounds takes place, an endothermic process is recorded, whose characteristic temperatures and heat of desorption are given in Table 3.

In both samples, the endothermal process occurs over the 20-129 °C temperature range. The samples are differentiated by the heat of desorption, which is much higher for Eucalyptus chips – 204.7 J/g – than for Eucalyptus BSP – 142.4 J/g, which indicates that the material lost in this region is more intensely linked on the substrate in the case of Eucalyptus chips.

Table 1
Average contents of total extractives, carbohydrates and lignin in *Eucalyptus globulus* chips and pulp samples

| Sample | Moisture (%) | Extractives* (%) | Carbohydrates** (%) | Lignin*** (%) | Ash (%) |
|---|---|---|---|---|---|
| Eucalyptus chips | 7.03 | 1.06-2.98 | 57.1-70.6 | 24.5-27.6 | 0.53 |
| Eucalyptus BSP | 5.9 | 0.14-2.16 | 88.7-99.2 | 1.0-1.7 | 1.32 |

*total amounts determined by extraction in different solvents[45]; **total amounts determined by HPAEC-PAD[46]; ***total amounts (ASL+AIL)[47]

Table 2
Elements in the ash of the studied sample evidenced by absorption spectroscopy
(results in mg/100 g ash)

| Sample | Mn | Fe | Ca | Cu | Zn | Mg |
|---|---|---|---|---|---|---|
| Eucalyptus chips | 120.97 | 141.13 | 7987.90 | 52.42 | 116.93 | 2310.48 |
| Eucalyptus BSP | 167.97 | 113.28 | 14515.62 | - | 85.94 | 1898.44 |

Table 3
Conditioning and drying

| Sample | m** $H_2O$ (wt%) | m* I 50% RH (wt%) | m* II 65% RH (wt%) |
|---|---|---|---|
| Eucalyptus chips | 9.33 | 2.93 | 5.51 |
| Eucalyptus BSP | 11.19 | 3.36 | 5.63 |

Related to a 1 g sample; *adsorbed, **desorbed

The decomposition temperature is higher for Eucalyptus BSP than for Eucalyptus chips, the higher thermal stability being possibly explained by the elimination of some instable compounds during processing (the Kraft procedure).

In the second run, this endothermal process does not occur anymore, meaning that, in this range of temperature, no other transitions occur.

*Glass transition of lignins*. The extracted and dried lignins exhibit very clear glass transitions in the DSC curves – Figure 2 – in two consecutive runs. The glass transition temperatures take high values. In run I, for Eucalyptus chips lignin, a single glass transition was found at 158 °C while, for Eucalyptus BSP lignin, two glass transition temperatures were detected, at 124 and 193 °C, respectively. In the second run, the Tg for lignin from Eucalyptus chips is reproducible at 158 °C, while for Kraft residual lignin, glass transition occurred at 141 °C. Degradation starts at 202 °C. Therefore, by protecting the samples against oxidation with silicon oil (see Experimental), the glass transition of lignins can be determined. Thermal history is important, because glass transition is accompanied by decomposition, as both occur at high temperatures. The results agree with those of Hatakeyama[53] and with the values found in our previous study on lignin thermal behaviour.[18]

**TG/DTG results**

The present study is focused on the influence of heating rate and conversion degree on the decomposition kinetics of Eucalyptus wood samples.

As already mentioned,[54] each biomass component decomposes over a certain temperature range. Cellulose decomposes over a narrow temperature range (280-400 °C); hemicelluloses are lost in the 190-380 °C temperature interval, while lignin decomposition starts at very low temperatures – of only 170 °C; the mass loss is low, occurring over a very wide interval, with several large maxima in the DTG curve, extended up to more than 800 °C. This means that, in a complex material as wood, the thermogravimetric processes of all components overlap, that of cellulose being predominant, with a high rate of mass loss within its decomposition interval. Usually, three main zones (or pseudo-components) are introduced, associated with the devolatilization of the main components.[16,20,27,55-59]

The TG/DTG curves of the Eucalyptus wood samples, recorded at different heating rates – Figure 3 – are shifted to higher temperatures, thus increasing the heating rate. For each TG stage, the following thermal characteristics have been determined: onset temperature ($T_i$), temperature corresponding to the maximum mass loss rate ($T_m$), and to the end of the stage ($T_f$), respectively (errors in temperature determination are of ±2 °C), mass loss (Δw, error ±1 wt%) and overall kinetic parameters (errors in activation energy determination ±15-20 kJ/mol). The composition of the decomposition products depends on the heating conditions, as observed from the residue amount, which decreases when increasing the heating rate – Tables 5 and 6.

Table 4
Characteristic temperatures and desorption heat of *Eucalyptus globulus* wood samples*

| Sample | $T_i$ (°C) | $T_m$ (°C) | $T_f$ (°C) | ΔH (J/g) | $T_{dec}$ (°C) |
|---|---|---|---|---|---|
| Eucalyptus chips | 20 | 77 | 121 | 204.7 | 200-253 |
| Eucalyptus BSP | 21 | 77 | 129 | 142.4 | 214-267 |

*$T_i$ – onset temperature, $T_m$ – temperature corresponding to the maximum mass loss rate, and $T_f$ – temperature corresponding to the end of stage, ΔH – desorption heat, $T_{dec}$ – decomposition temperature

Table 5
Characteristic thermogravimetric data for the first thermogravimetric step

| Heating rate (°C/min) | *Eucalyptus* chips | | | | *Eucalyptus* BSP | | | |
|---|---|---|---|---|---|---|---|---|
| | $T_i$ (°C) | $T_m$ (°C) | $T_f$ (°C) | wt% | $T_i$ (°C) | $T_m$ (°C) | $T_f$ (°C) | wt% |
| 5 | 25 | 60 | 121 | 5.59 | 25 | 55 | 115 | 7.27 |
| 10 | 25 | 63 | 132 | 6.44 | 25 | 67 | 123 | 7.91 |
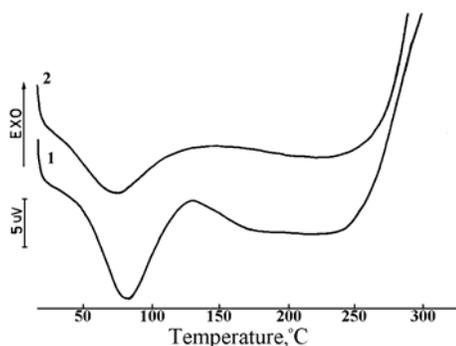


Figure 1: DSC curves in the region of water desorption and low molecular weight compounds loss; 1 – *Eucalyptus* chips; 2 – *Eucalyptus* BSP
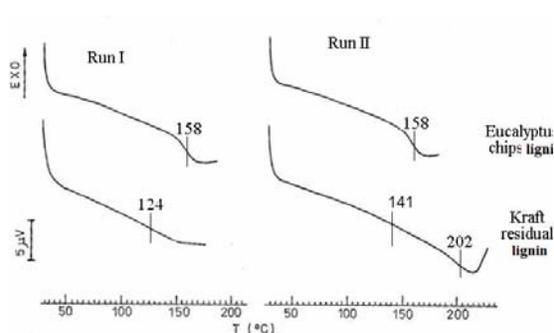


Figure 2: DSC curves of lignins extracted from *Eucalyptus* samples
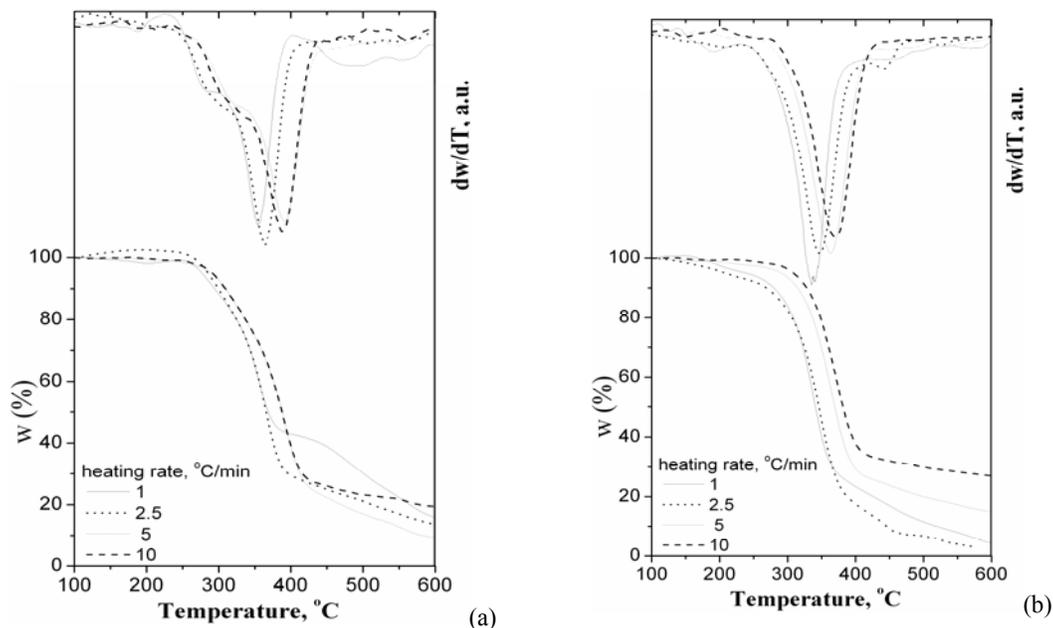


Figure 3: TG/DTG curves of *Eucalyptus* chips (a) and *Eucalyptus* BSP (b), recorded at different heating rates

Table 6
Temperature interval ($T_i$–$T_m$–$T_f$) and mass loss (wt %) of the second thermogravimetric step

| Heating rate | Eucalyptus chips | | | | Eucalyptus BSP | | | |
|---|---|---|---|---|---|---|---|---|
| (°C/min) | Ti (°C) | Tm (°C) | Tf (°C) | wt% | Ti (°C) | Tm (°C) | Tf (°C) | wt% |
| 1 | 226.8 | 354.9 | 405.9 | 58.6 | 230.4 | 337.3 | 420.6 | 75 |
| 2.5 | 228.4 | 363.5 | 421.3 | 74.2 | 233.6 | 347.5 | 419.6 | 67.5 |
| 5 | 230.4 | 391.3 | 447.1 | 72.7 | 238.4 | 364.1 | 432.7 | 66.9 |
| 10 | 233.2 | 390.4 | 449.0 | 70.1 | 268.3 | 369.9 | 441.1 | 61.8 |

**Low temperature region**

The *first thermogravimetric step,* corresponding mainly to the loss of the physically absorbed water and of some low molecular weight compounds, is evident only at high heating rates (of 5 and 10 °C – Table 5). There are no differences among the characteristic temperatures of this step, yet the mass losses are higher in the case of Eucalyptus BSP, because it is less compact and absorbs water more easily.

**High temperature region**

Significant differences among Eucalyptus samples appear in the second thermogravimetric step. All characteristic temperatures increase at high heating rates. For Eucalyptus chips, the onset temperatures are lower, while the $T_m$ values are higher than those for Eucalyptus BSP. The mass losses are lower for Eucalyptus BSP, decomposition at a 1 °C/min heating excepted, because, in this case, lignin decomposition does not interfere. This should mean that the thermally unstable compounds have been removed during Kraft processing, a higher amount of pure cellulose being decomposed in this step. The high mass losses of the Eucalyptus chips could be due to the presence of low molecular mass products (extractives and hemicelluloses), which decompose/volatilize at relatively constant, lower temperatures. Lignin decomposition is better separated at very slow heating rates, with a characteristic peak at temperatures higher than 500 °C, which explains the low mass loss observed in this step, an important mass loss being recorded at high temperatures.

Decomposition is a complex process both because the studied samples have many components, each of them being decomposed in several stages, and because the thermal behaviour is determined by the operational conditions – especially heating rate, final temperature of heating, heat transfer,

degradation/decomposition occurring by competitive and/or consecutive reactions. As each TG/DTG curve of the Eucalyptus samples seems to be more complex than those described in literature, since wood components decompose by a variety of reactions occurring parallelly or consecutively, the elucidation of this aspect is necessary. In this respect, the deconvolution of the curves was performed.

**Deconvoluted DTG curves**

A Grams 32 program, allowing Normal Log fitting of the individual peaks, was employed. The percentage error of the fitted curves to the experimental ones was below 2.5%. Figure 4 shows that the fitting procedure was excellent. The deconvoluted DTG curves recorded at the four heating rates led to the results presented in the Table 7.

The number of deconvoluted peaks depends on sample composition. For a low heating rate, of 1-2 °C/min, deconvolution evidenced four peaks for Eucalyptus chips in the 280-580 °C interval, and two peaks for Eucalyptus BSP, with peak temperatures lower for Eucalyptus BSP chips at the beginning of heating and higher for all other peaks. Peak 4 is present only in the TG/DTG curve of the Eucalyptus chips, because this sample contains a high lignin amount. The separation of the peaks is more evident at low heating rates. These results agree with those found in literature for other kinds of biomass.[54,60,61]

The whole process of biomass pyrolysis can be considered as developing in the following four ranges: <220 °C, moisture evolution; 220-315 °C, predominantly hemicellulose decomposition; 315-400 °C, cellulose decomposition; >400 °C, lignin decomposition. Both cellulose and hemicelluloses have the structural characteristics of polysaccharides, while

lignin has a dissimilar structure. After the removal of the first peaks, corresponding to extractives and soluble minerals, the deconvoluted peaks of the pyrolysis of lignocellulosics show the characteristics of the three main components. Hydrocarbons, aldehydes, ketones, acids, alcohols and others are generated by the primary pyrolysis of hemicelluloses and cellulose in single stages, occurring within the 290-400 °C region. Phenols and alcohols are the dominant volatiles released from lignin pyrolysis in two successive stages, the main one appearing at temperatures over 500 °C. At low heating rates (<100 °C/min), biomass materials decompose in well-described stages of moisture evolution, hemicellulose decomposition and cellulose decomposition, while lignin is decomposed very slowly and at lower levels. No interaction among these three components occurred during the pyrolysis experiments. The overall rate of biomass pyrolysis was considered as the sum of the individual rates of the three components analyzed in previous studies.[17,58,62-66]

The yield of volatiles, gases and char from pyrolysis was found to be proportional to the three components in the virgin biomass. Other studies indicated that the global production of volatile matter corresponds to the summation of the individual contributions from the three main components.

The peak area for peaks 1-3 is approximately constant for Eucalyptus chips, while the area of the fourth peak decreases with increasing the heating rate; therefore, lignin carbonization is reduced at high heating rates. In the case of Eucalyptus BSP, the peak areas vary with the heating rate. An increase of peak 2 area is accompanied by a decrease of peak 3 area. These peaks correspond to cellulose decomposition. Furthermore, studies on cellulose decomposition have shown that, when heated, cellulose undergoes two competitive reactions: depolymerization of the residual cellulose, followed by the volatilization of most of the product, levoglucosan. The yield of levoglucosan may attain 60% or more. In the thermal decomposition of cellulose, hydrolysis, oxidation and dehydration processes are side reactions.[67-69] Therefore, even the step corresponding to cellulose decomposition may be divided into two other steps, depending on the sample's nature and

on the experimental conditions, so that their characteristics may change with the heating rate.

Kinetic analysis of the TG data is based on the equation:

$$\beta \, d\alpha/dT = Ae-E/RT \, [\alpha^m \, (1 - \alpha)^n \, [- \ln(1 - \alpha)]^p]$$

where: $E$ – activation energy, $A$ – pre-exponential factor and $n$ – reaction order. The conversion degree (ratio of weight loss at time "t" and at the end of process) $\alpha = w_t/w_\infty$; $T$ is temperature in K, $A$ is the pre-exponential coefficient, $E$ is the activation energy, $R$ is the gas constant. The differential form of the conversion function is the following:

$$f(\alpha) = [\alpha^m \, (1 - \alpha)^n \, [- \ln(1 - \alpha)]^p$$

From a mathematical point of view, both positive and negative values of $A$, $E$ or of the exponents can sufficiently accurately describe the TG or DTG curves, although not every value has a kinetic significance. The positive values of the kinetic parameters $A$ and $E$ should be used as a selection criterion for "the most probable kinetic parameters". As additional criteria used in our studies, mention should be made of the good reproducibility of the kinetic parameters obtained from different TG data readings, the maximum values of the correlation coefficient or the minimum values of the average square errors for each experimental point of the DTG or TG curves, with respect to the calculated ones, using the obtained kinetic parameters, etc.

The $m$, $n$, $p$ exponents may take different values with respect to the reaction mechanism or physical processes occurring during decomposition, such as diffusion and transport phenomena.

Several semi-empirical methods[70] are available for determining the apparent activation energy of thermal degradation, $Ea$, from non-isothermal thermogravimetic (TG) curves. Among them, the Flynn-Wall method,[71] frequently used to determine the $Ea$ of polymers from the non-isothermal TG curves recorded at different heating rates, represents one of the integral methods that can determine the activation energy, without knowing the reaction order. The goal of the present study, however, was to analyze the Flynn-Wall graphs with respect to the complexity of the degradation mechanism. Thermal degradation of polymers is generally complex, with more than one

operating mechanisms, depending on the degradation temperature.

This is manifested in changes produced in the slope of the TG curves, and in the slope of the line from the Flynn-Wall graphs. The corresponding differential TG (DTG) curves exhibit multiple peaks or asymmetrical peaks with more or less pronounced shoulders.[72] The Flynn-Wall method may be applied to polymers with complex degradation mechanisms, and the values of *E*a may vary with the mass loss.[73]

The evaluation was done with a commercial program providing overall kinetic parameters by using at least 7 integral[74-76] and differential methods;[77-80] also, the Reich-Levi method[81] was employed in evaluating the variation of the kinetic parameters with the conversion degree.

The subscript of the overall kinetic parameters – activation energy (E), pre-exponential factor (A) and reaction order (n) – indicates the evaluation method.

The global kinetic parameter values, used for comparative purposes, have been evaluated under the same conditions for all studied samples (Table 8). The obtained values for all kinetic parameters lie within the limits found for the other above-mentioned wood species, although the Eucalyptus samples have some peculiarities related to the variation of the kinetic parameters with sample characteristics and operational parameters, such as heating rate and conversion degree. The discrepancy with respect to the values of cellulose decomposition for the second thermogravimetric step can be justified from the possible interference of lignin decomposition.

Each evaluation method gives different values of the kinetic parameters, while the variation with the heating rate is similar, as shown in Figure 5, plotting the variation of the global activation energy evaluated by the Coats-Redfern (Fig. 5 – solid symbols) and Flynn-Wall (Fig. 5 – open symbols) methods vs. heating rate.

At low heating rates, the values of the activation energy of both Eucalyptus samples are almost similar. At a medium heating rate of 4-6 °C/min, a minimum is observed for E in the case of Eucalyptus chips, after which the activation energy increases, while that of Eucalyptus BSP decomposition increases with increasing heating rate. The same variation of the activation energy with heating rate is observed from the Reich-Levi graphs over the whole range of the conversion degree studied ($\alpha < 0.6$). The pre-exponential factor A shows the same variation with the heating rate as the activation energy (Table 8). The reaction order n takes values between 0.9 and 1.5 for Eucalyptus chips and varies between 1.0 and 1.8 for Eucalyptus BSP, indicating that the reaction mechanism for cellulose decomposition is controlled by a reaction order law. As to the variation of the activation energy with conversion degree – Figure 6 – it seems that a small decrease appears at a low conversion degree ($\alpha < 0.15$) and also that the values are almost constant for a certain heating rate. It should be noticed that this minimum in Ea versus the mass loss graph corresponds to a slight change in the slope of the TG curves (especially in the curve recorded at a heating rate > 2.5 °C/min), as also evidenced by the deconvoluted curves.

The extrapolated values of the activation energy depend on the evaluation method and vary from 120.3 to 128.4 kJ/mol.

The Flynn-Wall graphs drawn in Figure 7 are more complex for Eucalyptus chips than those for Eucalyptus BSP. The discontinuities of the lines for the entire conversion degree region are a proof of a complex reaction mechanism. The decomposition of the Eucalyptus BSP sample seems to be much simpler over the $0.33 < \alpha < 0.74$ conversion degree interval, where the lines are almost parallel.

Moreover, Figure 7 shows that the Ea value is approximately constant over the 34-70% mass loss range (the 360-320 °C temperature interval corresponding mainly to the cellulose thermal degradation of the first deconvoluted peak) for Eucalyptus BSP, after which it increases steadily during further degradation.

It can be concluded that the heating rate, the temperature interval and the conversion degree significantly influence the kinetic parameters, therefore the complex dependence of the activation energy both on heating rate and conversion degree should be known (Fig. 8).

Eucalyptus chips
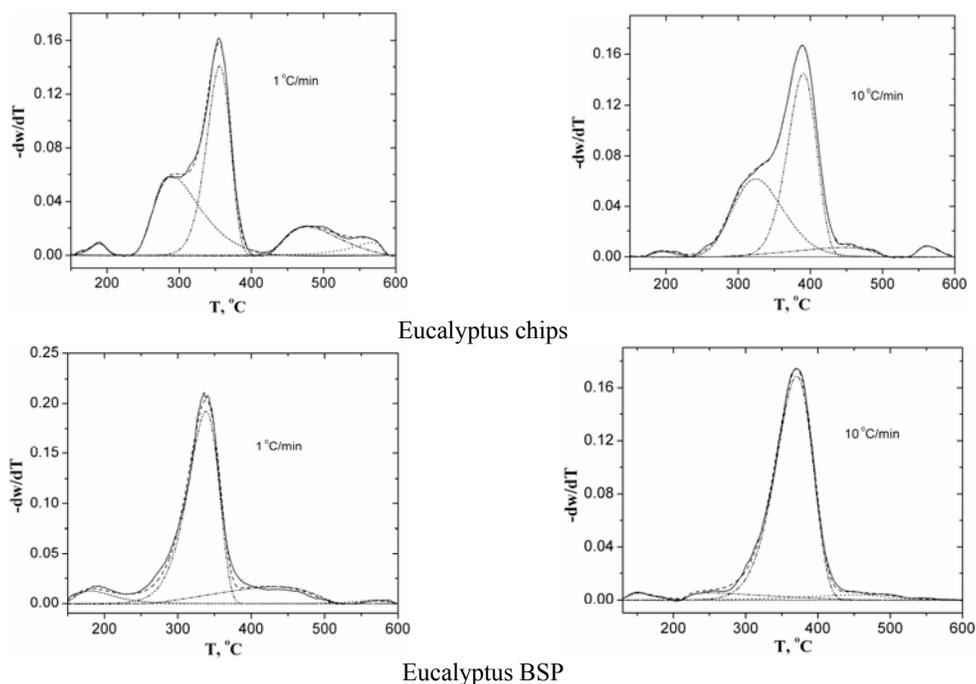


Eucalyptus BSP

Figure 4: Deconvoluted DTG curves recorded at heating rates of 1 °C/min and 10 °C/min for Eucalyptus chips and Eucalyptus BSP samples
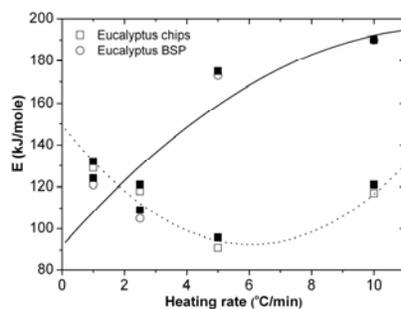


Figure 5: Variation of global activation energy *vs.* heating rate evaluated by Coats-Redfern (solid symbols) and Flynn-Wall (open symbols) methods

Table 7
Characteristics of deconvoluted peaks in region 250-580 °C

| Heating rate, (°C/min) | Nr. of peaks | Peak 1 | | Peak 2 | | Peak 3 | | Peak 4 | |
|---|---|---|---|---|---|---|---|---|---|
| | | T1m, (°C) | area (%) | T2m, (°C) | area (%) | T3m, (°C) | area (%) | T4m, (°C) | area (%) |
| Eucalyptus chips | | | | | | | | | |
| 1 | 4 | 290.2 | 36.87 | 356.1 | 42.21 | 478.4 | 16.16 | 566.6 | 4.06 |
| 2.5 | 4 | 322.4 | 39.65 | 390.5 | 41.98 | 454.1 | 14.39 | 534.6 | 3.98 |
| 5 | 4 | 333.6 | 41.11 | 393.3 | 41.03 | 455.0 | 14.96 | 556.1 | 2.90 |
| 10 | 4 | 324.1 | 41.71 | 395.2 | 40.63 | 444.5 | 15.73 | 560.8 | 1.93 |
| Eucalyptus BSP | | | | | | | | | |
| 1 | 2 | - | - | 338.3 | 70.54 | 421.9 | 29.45 | - | - |
| 2.5 | 2 | - | - | 347.9 | 83.89 | 439.2 | 16.11 | - | - |
| 5 | 2 | - | - | 363.7 | 84.42 | 444.6 | 15.58 | - | - |
| 10 | 2 | - | - | 370.4 | 85.72 | 448.1 | 14.28 | - | - |

Table 8
Global values of kinetic parameters for thermal decomposition of Eucalyptus samples

| Sample/ heating rate | Eucalyptus/ 1 | Eucalyptus/ 2.5 | Eucalyptus/ 5 | Eucalyptus/ 10 | Eucalyptus BSP/1 | Eucalyptus BSP/2.5 | Eucalyptus BSP/5 | Eucalyptus BSP/10 |
|---|---|---|---|---|---|---|---|---|
| $T_i$-$T_f$ (°C) | 249-402 | 202-424 | 217-449 | 233-445 | 230-420 | 235-419 | 252-430 | 270-440 |
| | | | | Coats-Redfern | | | | |
| Ea (kJ/mol) | 129 | 118 | 91.0 | 117 | 121 | 105 | 173 | 190 |
| A (1/sec) | 7.90E07 | 1.36E07 | 4.23E04 | 2.00E07 | 1.49E07 | 1.04E06 | 1.15E12 | 3.35E13 |
| n | 1.3 | 1.4 | 1.1 | 1.3 | 1.5 | 1.3 | 1.6 | 1.6 |
| | | | | Flynn-Wall | | | | |
| Ea (kJ/mol) | 132 | 121 | 95.9 | 121 | 124 | 109 | 175 | 190 |
| A (1/sec) | 1.72E08 | 3.35E07 | 1.83E05 | 5.47E07 | 3.66E07 | 3.37E06 | 1.48E12 | 3.80E13 |
| n | 1.3 | 1.4 | 1.1 | 1.3 | 1.5 | 1.3 | 1.6 | 1.6 |
| | | | | van Krevelen | | | | |
| Ea (kJ/mol) | 159 | 156 | 122 | 150 | 158 | 133 | 220 | 240 |
| A (1/sec) | 2.75E10 | 3.35E07 | 1.82 | 9.37E09 | 2.46E10 | 2.47E08 | 8.91E15 | 4.56E17 |
| n | 1.4 | 1.6 | 1.3 | 1.4 | 1.7 | 1.4 | 1.8 | 1.8 |
| | | | | Urbanovici-Segal | | | | |
| Ea (kJ/mol) | 131 | 119 | 92.1 | 118 | 122 | 106 | 180 | 191 |
| A (1/sec) | 1.10E08 | 1.74E07 | 5.87E04 | 2.73E07 | 1.99E07 | 1.42E06 | 5.03E12 | 4.49E13 |
| n | 1.3 | 1.4 | 1.1 | 1.3 | 1.5 | 1.3 | 1.7 | 1.6 |
| | | | | Achar | | | | |
| Ea (kJ/mol) | 100 | 102 | 79.8 | 108 | 125 | 89 | 138 | 157 |
| A (1/sec) | 1.74E05 | 4.28E05 | 4.41E03 | 3.08E06 | 3.73E07 | 3.85E04 | 7.07E08 | 4.55E10 |
| n | 1 | 1.4 | 0.9 | 1.1 | 1.5 | 1.0 | 1.2 | 1.3 |
| | | | | Piloyan (0.1<α<0.6) | | | | |
| Ea (kJ/mol) | 57.8 | 86.0 | 64.9 | 83.5 | 84.5 | 63.3 | 117.6 | 128.4 |

It appears that the confusing state of things in the literature on global kinetics of biomass pyrolysis may be at least partially attributed to a previously unrecognized shift in the mechanism near 600 K (327 °C). Depending upon the heating rate used to examine the kinetics, different values can easily emerge. Different studies evidence sufficient variability in the wood samples to make the use of any particular global kinetics given in literature highly dangerous, unless a match with the sample of interest is well-established. Only by identifying samples and by characterizing their pyrolysis/ decomposition behaviour for each particular case does it become possible to model more complicated engineering phenomena.



(a)

(b)
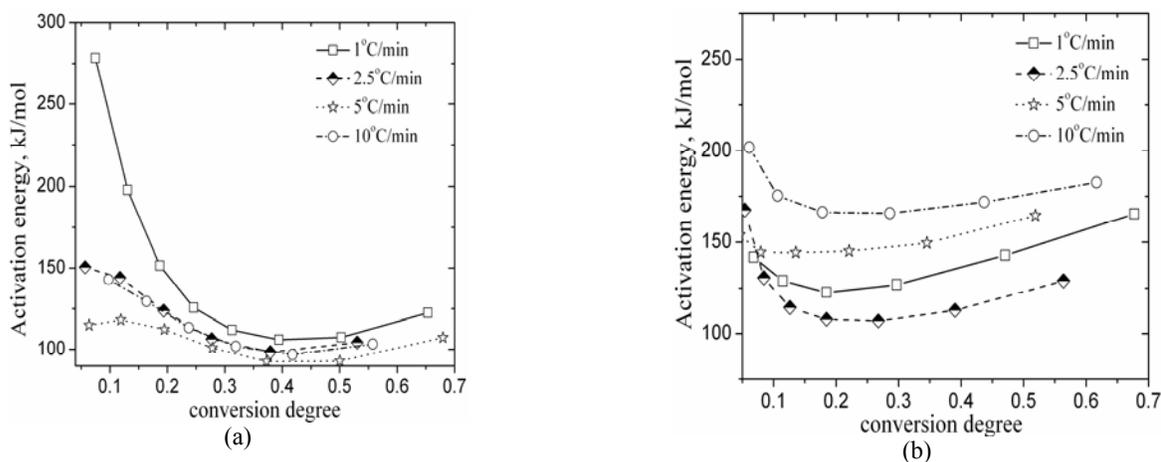
Figure 6: Reich-Levi graphs for variation of activation energy with conversion degree for Eucalyptus chips (a)

(a)

(b)

T 428    382        342        306        274        246
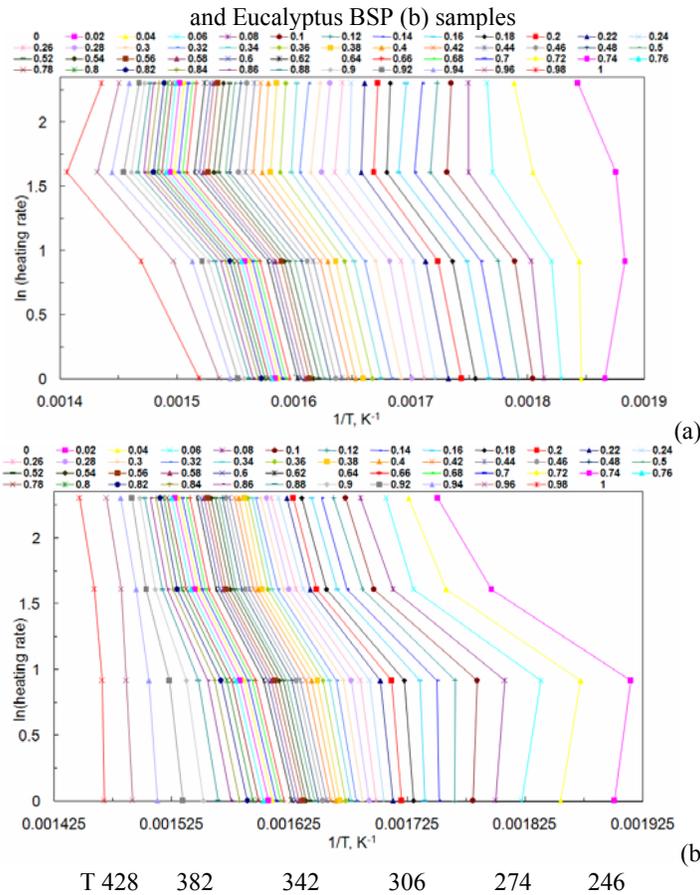
Figure 7: Flynn-Wall graphs corresponding to the second thermogravimetric step for Eucalyptus chips (a) and Eucalyptus BSP (b), at heating rates of 1, 2.5, 5, 10 °C/min
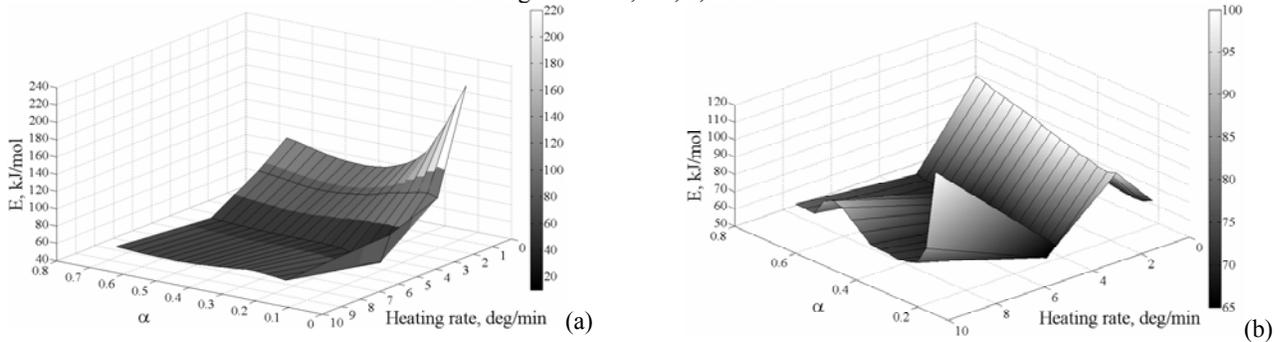


Figure 8: Dependence of activation energy on heating rate and conversion degree for Eucalyptus chips (a) and Eucalyptus BSP (b) samples

**CONCLUSIONS**

A brief review of the kinetic studies on wood thermal decomposition was carried out. The kinetic parameters of Eucalyptus wood decomposition have been evaluated. Differences have been found among the thermal characteristics of the samples, as a function of their composition and of the treatment applied. The complex dependence of the kinetic parameters on the heating rate and conversion degree is characteristic of Eucalyptus chips and Eucalyptus BSP, therefore, in the design of pyrolysis reactors,

the feeding characteristics should play the main role.

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