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

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Abstract: In our previous papers, thermogravimetric analysis (TGA), differential scanning calorimetry (DSC) and pyrolysis coupled with gas chromatography-mass spectroscopy (Py-GC-MS) techniques were used to investigate the thermochemical conversion of the agricultural biomass, namely the of oilseed rape (*Brassica napus L.*) and of the Spanish broom (*Spartium junceum*) fibres.

1. Introduction

The widespread availability of biomass, the third among primary energy resources after coal and oil, which is also renewable and potentially neutral in relation to global warming motivated the extensive research undertaken in the past decade for the industrial development of thermochemical conversion plants. [1,2] Despite the abundance of the Eucalyptus species only recently has a start been made towards its full utilization. [3] In the Iberian region of the European Union, *Eucalyptus globulus*, occupies an increasingly large part of the surface area, [4] being over one million hectares which produces more than seven million m^3/year of round wood, mainly for pulp manufacturing [5]. Only few papers are known about thermal characterization of the Eucalyptus wood.[6] This paper deals with thermogravimetric study of the Eucalyptus wood, in order to elucidate the dependence of the thermal characteristics and kinetic parameters of each thermogravimetric step on different parameters and also to establish the differences found between samples after various treatments.

2. Materials and methods

The unfractionated samples of wood chips of *Eucalyptus globulus* from the same batch as the pulp, unbleached Kraft pulp brown stock of Eucalyptus globulus (sampled after

washing stages) were provided by Abö Akademi University, Laboratory of Wood and Paper Chemistry, Turku, Finland. All samples are from the COST E41 joint analysis effort. The selected samples for study have very different content in extractives, carbohydrates and lignins (average composition presented in Tab.1). Eucalyptus BSP has ~ 20 wt% more carbohydrates, while lignin content is very small of 1-1.7 wt%.[7]

Tab. 1 Average content of total extractives, carbohydrates and lignin
in Eucalyptus globulus chips and pulp samples.

Samples	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

TG/DTG curves were recorded on a Shimadzu Thermogravimetric Analyser under the following operational conditions: heating rates of: 1, 2.5, 5 and 10 ºC/min, temperature range of 25-600 ºC, sample mass of about 20 mg, platinum crucible, nitrogen flow of 100 cm³/min.

3. Results and discussions

Kinetic of wood pyrolysis is needed for the design of chemical reactors applied for recovering energy and chemicals. The kinetic analysis is complicated by the composite nature of wood, constituted by a mixture of hemicellulose, cellulose, lignin and extractives, with proportion, chemistry, and reactivity affected by variety. Widely different kinetic parameters have been published in the literature because of the greatly different experimental conditions, various experimental problems and the occasional use of unsuitable evaluation methods. The related kinetic mechanisms, usually obtained by the use of a single experiment (heating rate), are based either on a one step reaction or on several parallel reactions. [8] These mechanisms, properly coupled with the description of transport phenomena, have been applied for fixed-bed reactors, where the coarse particles and/or the significant external heat transfer limitations establish 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. Results of kinetic modeling of wood pyrolysis obtained for fast heating rates or isothermal conditions are needed for the development of fast pyrolysis technologies and, in some cases, for the devolatilization stage of gasifiers and combustors. Furthermore, the kinetic constants, estimated by means of different literature sources and used by Chan et al.[9] to model large particle pyrolysis, are also of interest being capable of predicting at least qualitatively the correct behavior of wood pyrolysis. The present study is focused on the influence of the heating rate and conversion degree on kinetics of decomposition of Eucalyptus wood samples.

TG/DTG curves of the Eucalyptus wood samples at different heating rates – Fig. 1 – are shifted to higher temperatures with increasing heating rate; the composition of the decomposition products depend on heating conditions, as can be observed from the residue quantity which decreases with increasing the heating rate -Tab. 2.
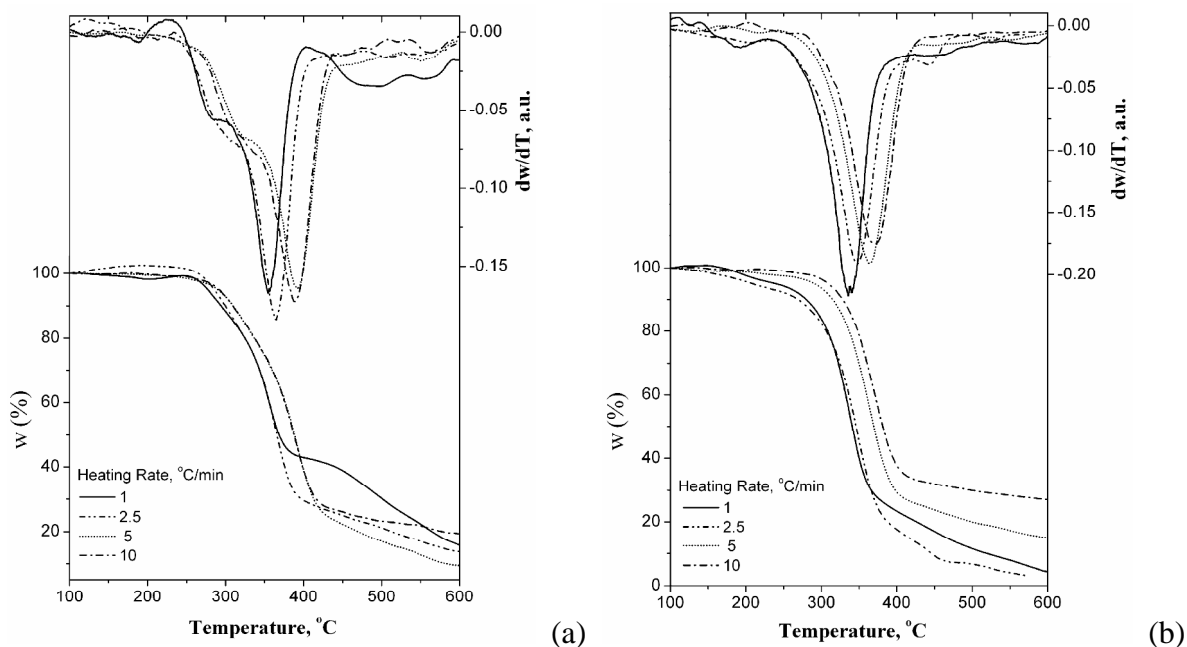

Fig. 1 The TG/DTG curves of the Eucalyptus chips (a) and Eucalyptus BSP (b).

The first thermogravimetric step corresponding mainly to the loss of the physically absorbed water and some of low molecular weight compounds is evident only at high heating rates of 5 – 10 ^{o}C.

Tab. 2 Temperature interval (T_i-T_m-T_f) and mass loss (wt %)
of the second thermogravimetric step

Heating rate (°C/min)	Eucalyptus chips				Eucalyptus BSP			
	Ti (^{o}C)	Tm (^{o}C)	Tf (^{o}C)	wt (%)	Ti (^{o}C)	Tm (^{o}C)	Tf (^{o}C)	wt (%)
1	227.1	354.5	405.7	63	229.4	337.3	417.2	79
2.5	228.4	363.5	421.3	73	236.0	346.5	419.4	86
5	230.4	391.3	447.1	78	238.4	363.7	436.4	80
10	233.2	390.4	449.0	75	268.3	372.0	441.1	77

The differences between Eucalyptus samples appear in the second thermogravimetric step. All characteristic temperatures increase at high heating rates. The onset temperatures are lower for Eucalyptus chips, while the T_m are higher than those of the Eucalyptus BSP. Mass

losses are higher for Eucalyptus BSP. Decomposition is a complex process both because the studied samples have many components and each of them decomposes in several stages and because the thermal behavior is determined by operational conditions especially heating rate, final temperature of heating, heat transfer, degradation/decomposition occurs by competitive and/or consecutive reactions.

The kinetic parameters evaluation was done with a commercial program which give overall kinetic parameters values by using at least 7 intergral [10-12] and differential [13-16] methods – Fig. 2,3. The Reich – Levi method was also employed in evaluation of variation of the kinetic parameters with conversion degree. The global kinetic parameter values, used for comparative purposes, have been evaluated in the same conditions for all studied samples. The obtained values for all kinetic parameters lay in the limits found for other wood species, but of course the Eucalyptus samples have some particularities related to the variation of the kinetic parameters with samples characteristics and operational parameters. Some discrepancy was found in respect with values of cellulose decomposition for the second thermogravimetric step and this can be justified from the possible interference of the lignin decomposition.
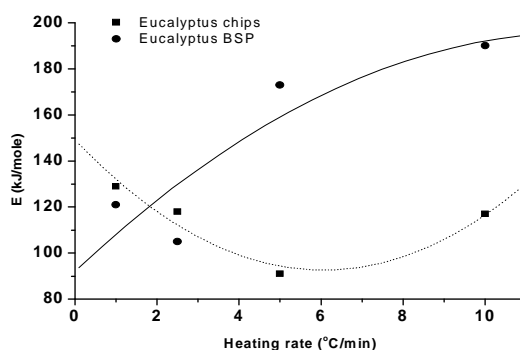

Fig. 2 Variation of the global activation energy vs. heating rate evaluated by Coats- Redfern method
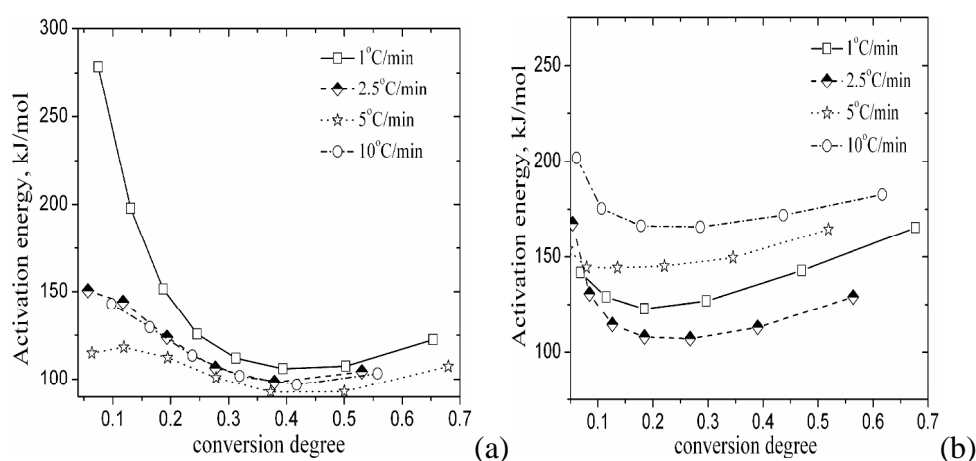

Fig. 3 Reich Levi graphs for variation of the activation energy with conversion degree for Eucalyptus chips (a) and Eucalyptus BSP (b) samples

At low heating rates the values of the activation energy E of both Eucalyptus samples are almost similar. At medium heating rate of 4 - 6 $^{\circ}$C/min a minimum is observed in the case of Eucalyptus chips and then the activation energy increases, while that of Eucalyptus BSP increases with increasing heating rate. The same variation of the activation energy with heating rate is observed from the Reich-Levi graphs for the whole range of the conversion degree studied ($\alpha < 0.6$). Pre-exponential factor A shows the same variation with heating rate as activation energy. 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. Concerning the variation of the activation energy with conversion degree – Fig.3 – it is seems that a small decrease appears at low conversion degree ($\alpha < 0.15$) and than the values are almost constant for a certain heating rate. The Flynn-Wall graphs (not shown) are much complicated for Eucalyptus chips than for Eucalyptus BSP. The discontinuities of the lines for the entire conversion degree region are a proof for a complex reaction mechanism. Decomposition of Eucalyptus BSP sample seems to be much simpler in the conversion degree interval $0.33 < \alpha < 0.74$ where the line are almost parallel.
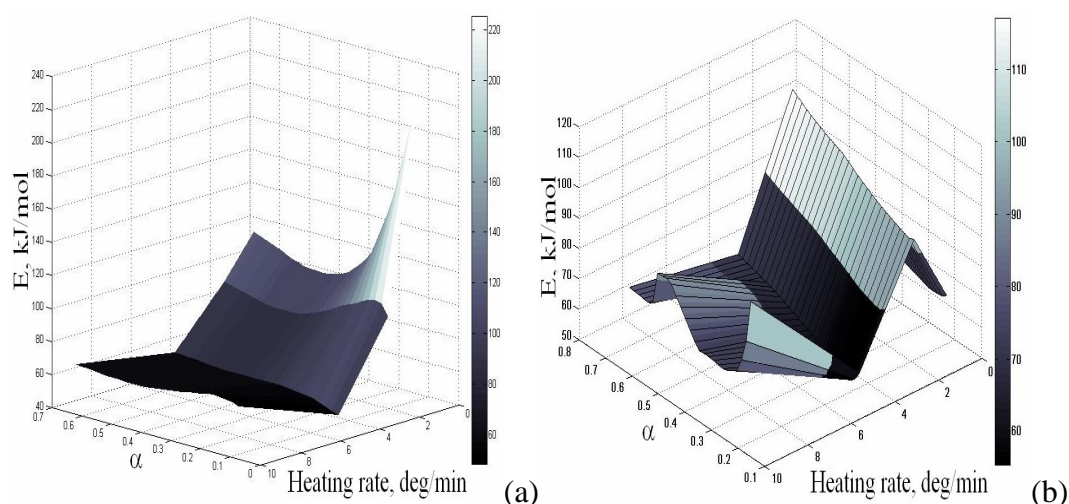

Fig. 4 The dependence of the activation energy on the heating rate and conversion degree for Eucalyptus chips (a) and Eucalyptus BSP (b) samples

It can be concluded that both heating rate, temperature interval or conversion degree significantly influence the kinetic parameters values, therefore the complex dependence of the activation energy both on heating rate and conversion degree should be known – Fig. 4.

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