



COST FP0901 meeting “Current needs in Biorefinery analytics”; Vienna, February 4-5, 2010

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

**Mihai Brebu¹, Carmen-Mihaela Popescu¹, Maria-Cristina Popescu¹,
Cornelia Vasile¹, Stefan Willfor²**

*¹Romanian Academy “P.Poni” Institute of Macromolecular Chemistry,
41A Gr. Ghica Voda Alley, Ro.700487, IASI, Romania*

²Abo Akademi University, Finland

● Despite the abundance of the Eucalyptus species, only recently has a start been made towards its full utilization. In the Iberian region of the European Union, *Eucalyptus globus*, the tree, occupies an increasingly large part of the surface area being over one million hectares which produces more than seven million m³/year of round wood, principally for pulp manufacturing.

Only a few paper are known about thermal characterization of the Eucalyptus wood

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 between samples after various treatments.

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 BS.

Materials

Average contents of total extractives, carbohydrates and lignin in Eucalyptus globulus

Samples	Moisture (wt %)	Extractives* (wt %)	Carbohydrates ** (wt %)	Lignin *** (wt %)	Ash (wt %)
Eucalyptus chips	7.03	1.06 – 2.98	57.1 – 70.6	24.5 – 27.6	0.53
Eucalyptus BSP	5.8	0.14 – 2.16	88.7 – 99.2	1.0 – 1.7	1.32

* total amounts determined by extraction in different solvents [27 S. Willfor, Summary of results of WG3 on the joint analysis effort of eucalypt and spruce samples, Proceedings of the COST E41 meeting, Progress of the “COST Action E41 Joint Analysis effort” on Wood and Fiber Characterisation, 12 – 13 April 2006, Grenoble, France

** total amounts determined by HPAEC-PAD [28 J. Puls, Summary of WG2 results, Proceedings of the COST E41 meeting, Progress of the “COST Action E41 Joint Analysis effort” on Wood and Fiber Characterisation, 12 – 13 April 2006, Grenoble, France]

*** total amounts (ASL+AIL) [29 E de Jong, Compositional characterisation of wood and pulps: Summary WG1, Proceedings of the COST E41 meeting, Progress of the “COST Action E41 Joint Analysis effort” on Wood and Fiber Characterisation, 12 – 13 April 2006, Grenoble, France

Conditioning and drying (Reported to 1g sample, *adsorbed, **desorbed)

Elements in the ash of the studied sample 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

Sample	m** H ₂ O (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

Investigation method

TG/DTG curve was recorded on a Shimadzu Thermogravimetric Analyser under the following operational conditions: heating rates of 1; 2.5; 5 and 10 (or/and 20) °C/min, temperature range 25 – 600 °C, sample mass of ~ 20 mg, platinum crucible, nitrogen flow 100 cm³/min.

Kinetics' analysis: $\beta \, d\alpha / dT = A e^{-E/RT} [\alpha^m (1 - \alpha)^n [-\ln(1 - \alpha)]^p]$ was done by different methods as: Versatile programme for global values, Reich-Levi and Flynn-Wall for dependence of kinetic parameters on conversion degree, DTG curve deconvolution for separation of the components decomposition steps.

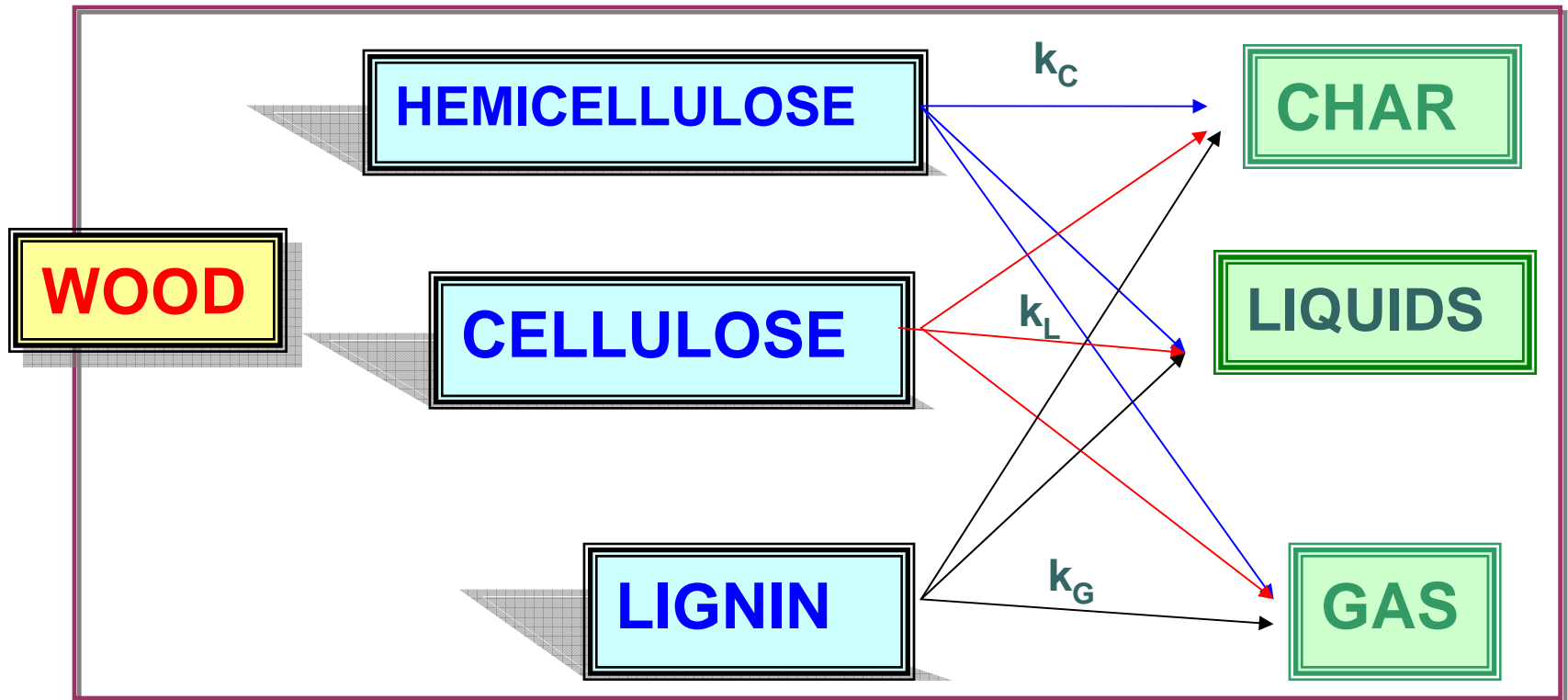
Normal Log Function:

$$y = y_0 + \frac{A}{\sqrt{2\pi}wx} e^{-\frac{\left[\ln\frac{x}{x_c}\right]^2}{2w^2}}$$

y_0 -offset; x_c -x center; w-width; A-amplitude

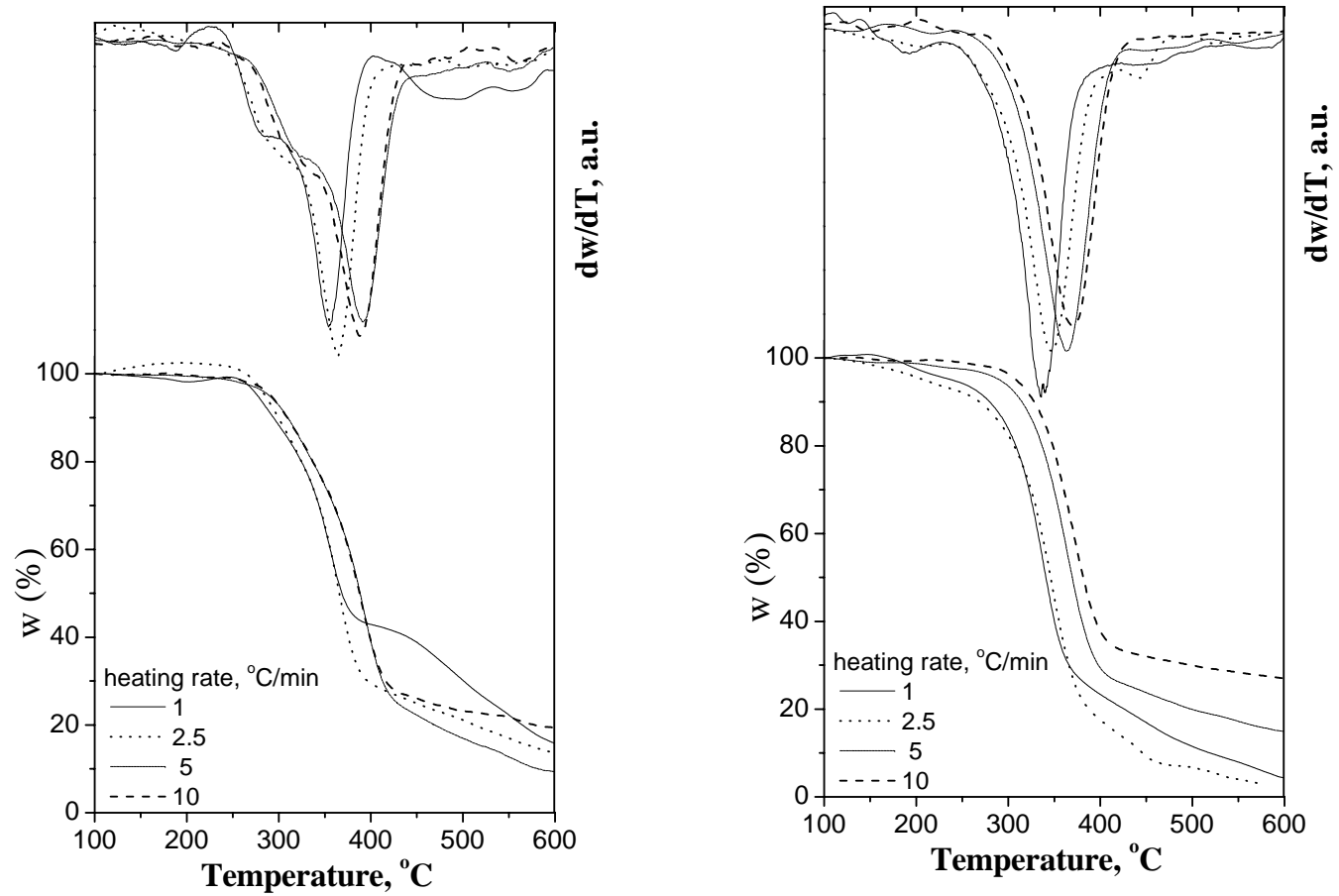
Kinetic model

A mechanism with three parallel reactions for the formation of the main product classes:

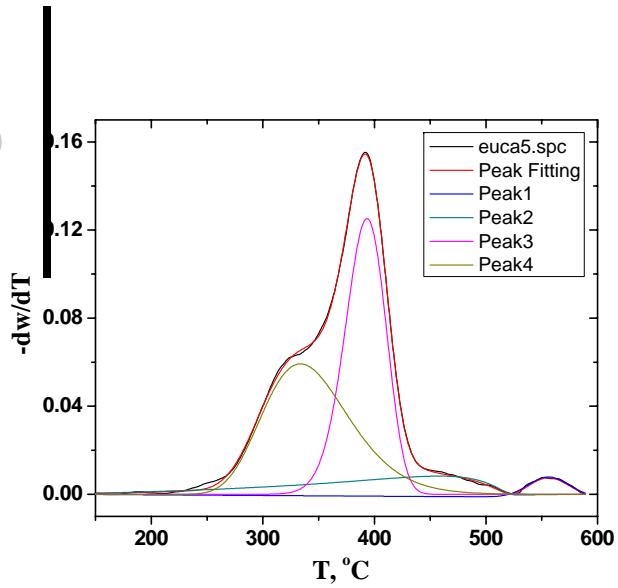


$$k_D = k_{Gi} + k_{Li} + k_{Ci} = A_j \exp E_j/RT \text{ where } j \text{ is gas, liquid or char}$$

Experimental TG/DTG curves

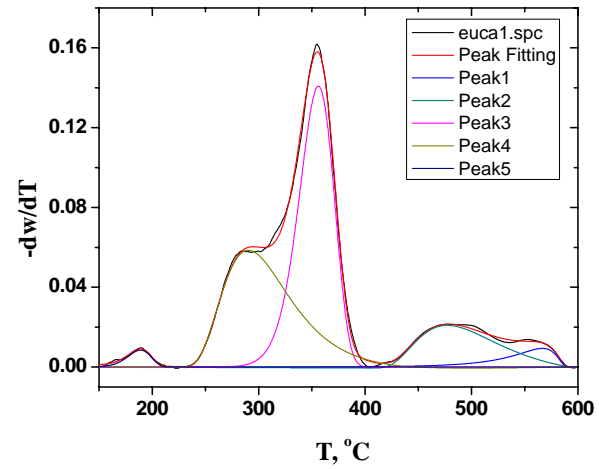


Eucalyptus chips *Eucalyptus BS*

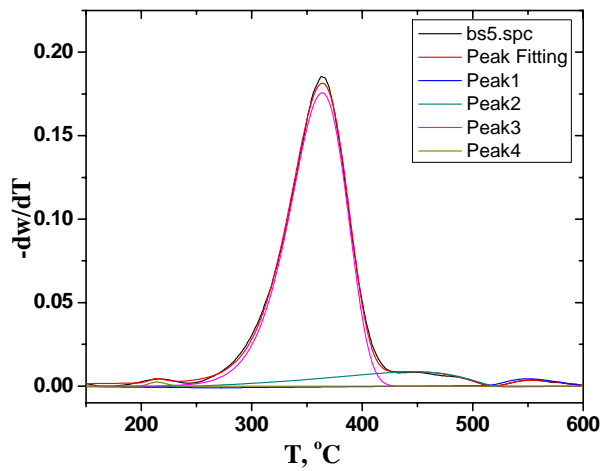


1 °C/min

Eucalyptus chips

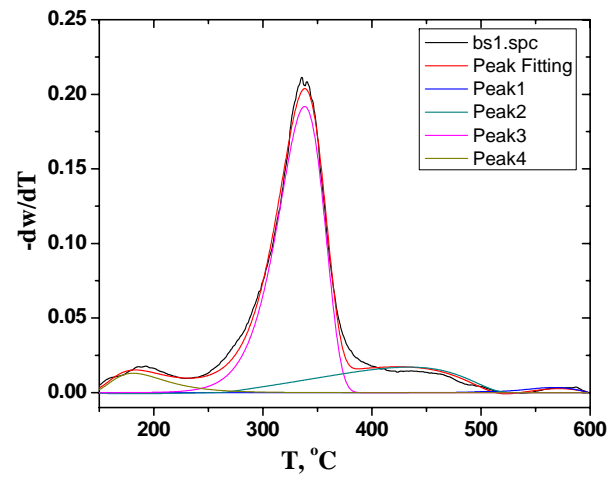


10 °C/min

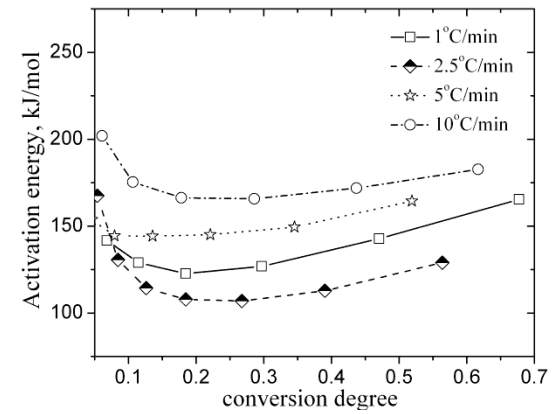
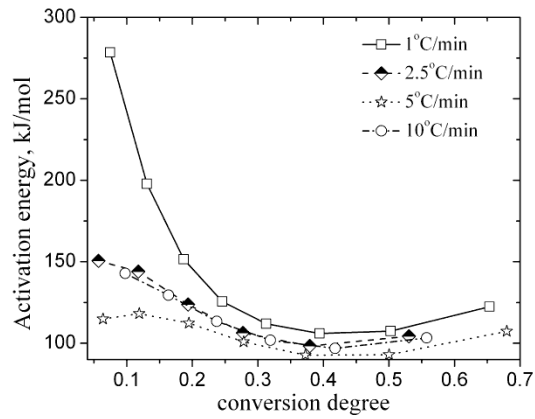
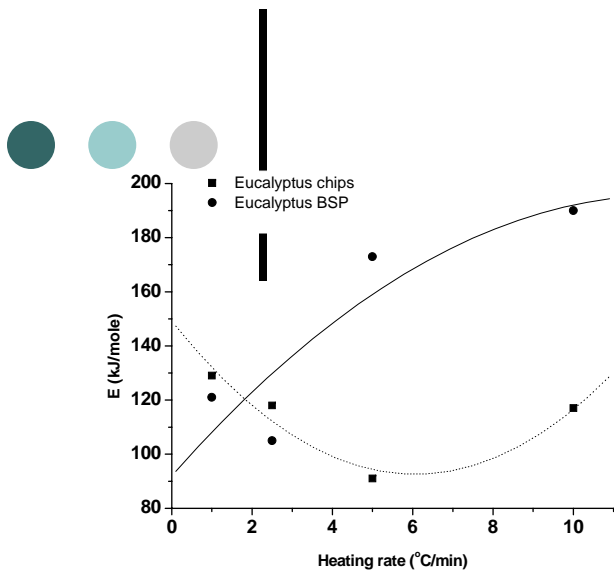


1 °C/min

Eucalyptus BS

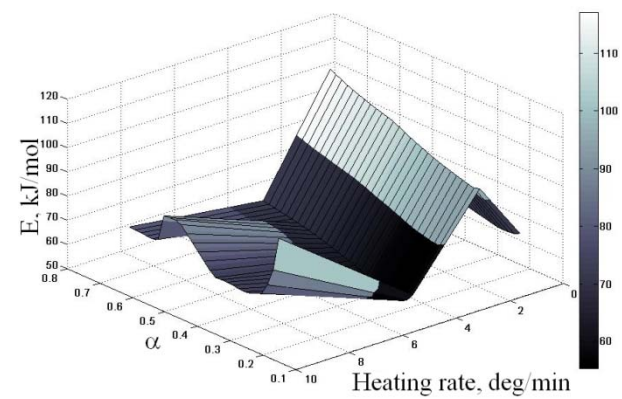
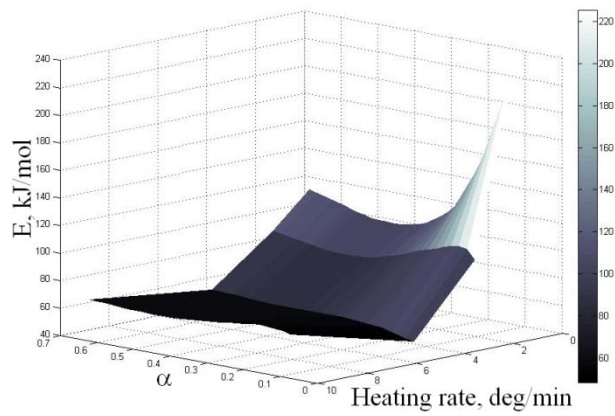


10 °C/min



CHIPS

BS



CHIPS

BS



Conclusion

- Decomposition is a complex process both because the studied samples have many components and each of them decompose in several stages and also the thermal behavior is dependent on operational conditions especially heating rate, final temperature of heating, heat transfer, degradation/decomposition occurs by competitive and/or consecutive reactions.
- As each TG/DTG curve of the Eucalyptus samples seems to be much complex than those described in literature, because wood components in fact decompose by a variety of reactions occurring parallelly or consecutively, a clarification of this aspect is necessary. In this respect the deconvolution of the curves was performed. A complex dependence of the activation energy both on heating rate and conversion degree was found