Application of CHL model for estimating biomass pyrolysis yield

FRANCESCO MARRA
Dipartimento di Ingegneria Chimica e Alimentare
Università degli studi di Salerno
via Ponte Don Melillo 84084 Fisciano - SA
ITALY
http://www.dica.unisa.it

Abstract: - The pyrolysis of wood biomass represents a valid technique for recovering "green" fuel from residues of forestry and other activities, in agriculture as in industry, where wood and other plant residues are available. Wood biomass is essentially a composite material, the major constituents being cellulose, hemicellulose, lignin, organic extractives, and inorganic minerals. The weight percent of cellulose, hemicellulose, and lignin varies in different species of wood biomass. In this paper, a model based on cellulose, hemicelluloses and lignin content of investigated materials is proposed, as simple but effective tool for estimating the yield of pyrolysis of various biomasses available as by-product of typical agricultural activities in South of Italy. Results show that hazelnut shells and poplar prunings gives high yield in fuel (gas and tar vapours) between 700 K and 900 K, both for conventional slow pyrlysis and for fast pyrolysis, whereas olive tree prunings and chestnut wood residues give an appreciable yield (higher than 70%) only for temperatures above 900 K, for fast pyrolisis. Sunflowers residues, characterized by higher content of non-CHL compounds, give the lower yield in fuel for all the investigated conditions.

Key-Words: biomass, pyrolysis, CHL model, rate estimation, biogas yield, numerical analysis

1 Introduction

The development of the pyrolysis process for the biomass conversion and the design of required equipments demands the acquaintance of various aspects: the understanding of the mechanisms governing the process; the acquaintance of the most meant parameters to be estimated during the pyrolysis and their effect on the process; the determination of the devolatilization rate.

In many cases, the description of the pyrolysis rate through relatively simple models is extremely useful, from an engineering point of view. In other cases, instead, it is necessary to look at more complex models, characterized by an important number of parameters, leading to higher computational costs. It is the case of models in which the pyrolysis of the wood biomass single components (that are, essentially, cellulose, hemicellulose and lignin) is described: in this case one speaks about models CHL (Cellulose - Hemicellulose - Lignin) model.

The numerous existing studies on the mechanisms of biomass pyrolysis of the biomass and its components ([1], [2], [3], [4], [5]) and on process rate modelling ([6, [7], [8]) have produced various reasonable rate models, all from the analysis of several woody materials and from experiments conducted in a wide range of operating conditions.

The reasons of the different approaches reside in some parameters, which: the particular nature of the processed material; the composition, that influences the rates of biomass pyrolysis; the rate of the devolatilization process, that depends strongly on the operating conditions, in particular temperature, speed of heating and time of residence. In fact, several are the important variables affecting the yield, such as the biomass species, chemical and structural composition of the biomass, particle size, temperature, heating rate, atmosphere, pressure, and reactor configuration. In this paper only the composition of biomass in term of cellulose, hemicellusose and lignin (CHL) was considered in order to estimate the pyrolysis yield in volatile compounds, gas and tar vapours, suitable as fuel.

2 Problem Formulation

The biomass pyrolysis rate was related to wood biomass composition, in order to set-up a model useful for all wood materials.

Defined as x, y and z the percentage of cellulose, hemicellulose and lignin, respectively, and indicating with v_i the thermal degradation rate of each of the considered components with respect of its initial mass, one can write:

$$v_{BIOMASS} = x \cdot v_C + y \cdot v_H + z \cdot v_L \quad (1)$$

and, then, if Y_i is the mass fraction of pyrolysis products with respect to the mass of each component, one can write:

$$Y_{BIOMASS} = x \cdot Y_C + y \cdot Y_H + z \cdot Y_L \quad (2)$$

This assumption considers also that all the possible interactions among biomass components have a negligible effect on the advance of the pyrolysis.

In 1980, Bradbury and Shafizadeh [1] introduced a new model for the description of the rate of wood biomasses pyrolysis (it was developed, in particular, for the cellulose);

other authors ([3], [7]) improved the model and extended it to other biomass components (hemicellulose and lignin):

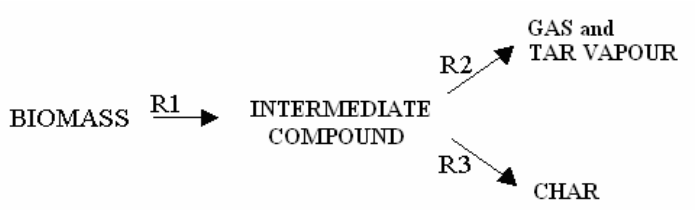

Fig.1 – *Model of pyrolysis mechanism with intermediate compound [1]*

According with figure 1, the model previews an initial reaction (R1), that describes the global result of all reactions happening below 473 K. Below this temperature, one can observe transformation and a preliminary depolymerisation of the starting material, which becomes an active intermediate. This first step is considered as a zero order rates model [4].
The intermediate active compound is then subjected to a further decomposition, following two competitive reactions, leading to gaseous products (gas and tar vapours, as in reaction R2, of order n2) and to char (as in reaction R3, of order n3).
Equations describing the model are the following:

$$\frac{dY_B}{dt} = -k_{0,1}\, e^{-\frac{E_{A,1}}{RT}} \tag{3}$$

$$\frac{dY_{B^+}}{dt} = k_{0,1}\, e^{-\frac{E_{A,1}}{RT}} - k_{0,2}\, e^{-\frac{E_{A,2}}{RT}} (Y_{B^+})^{n_2} - k_{0,3}\, e^{-\frac{E_{A,3}}{RT}} (Y_{B^+})^{n_3} \tag{4}$$

$$\frac{d(Y_G + Y_T)}{dt} = k_{0,2}\, e^{-\frac{E_{A,3}}{RT}} (Y_{B^+})^{n_3} \tag{5}$$

$$\frac{dY_C}{dt} = k_{0,3}\, e^{-\frac{E_{A,3}}{RT}} (Y_{B^+})^{n_3} \tag{6}$$

where Y_B, Y_{B+}, Y_G, Y_T e Y_C are the mass fraction (that is kg of product with respect to kg of fed biomass), respectively, of biomass, intermediate compound, gas, tar vapour and char.
A similar set of equations can be used for each single component: in this way, we do not refer to the whole biomass, but to cellulose, hemicellulose and lignin.
Initial conditions (t=0) are:

$$Y_B = 1 \tag{7}$$ and $$Y_{B^+} = Y_G = Y_T = Y_C = 0 \tag{8}$$

In order to evaluate the theoretical yield of pyrolysis products, the biomass is considered reduced in particles having a size so small that internal profiles of mass or of temperature can be neglected. According with this hypothesis, the linear heating rate of whole biomass is described as follows:

$$T = T_0 + (HR) \cdot t \tag{9}$$

where HR is the heating rate and T_0 is the initial temperature.
When all the biomass is converted (Y_B=0), equation (3) and the first term in the equation (4) are omitted.
In isothermal conditions (T=T_0=*constant*) as well as in non isothermal ones, equations (3)-(6) represent a system of ordinary differential equations, non linear, that can be solved using a Runge – Kutta algorithm.

2.1 Model parameters

Literature [4] states that reactions R2 and R3 are often of order *n2* = *n3* = 1.5. In such case, the fitting of TGA results with results of model for each component allows to calculate the rate parameters (activation energy, $k_{0,i}$, and frequency factor, $E_{A,i}$), as reported in Table 1. These values were used to evaluate the model results, in term of yield of gas, vapour of tar and char.

Component	Reaction	N	$k_{0,i}$ [s^{-1}]	$E_{A,i}$ [kJ/mol]
Cellulose	R1	0	2.2e14	167.5
	R2	1.5	9.4e15	216.6
	R3	1.5	3.1e13	196.0
Hemicellulose	R1	0	3.3e6	72.40
	R2	1.5	1.1e14	174.1
	R3	1.5	2.5e13	172.0
Lignin	R1	0	3.3e12	147.7
	R2	1.5	8.6e8	137.1
	R3	1.5	4.4e7	122.1

Table 1 - *Rate parameters for CHL model in the temperature range 573 K < T < 873 K [4]*

2.2 Materials and methods

As materials to be investigated, biomasses available as by-product of typical agricultural activities in South of Italy were considered.
Materials and their composition are shown in Table 2.
Furthermore, in order to test the hypothesis of an overall reaction order of 1.5, 12 mg samples of beech wood residues (composed by 50.5% cellulose, 29.6% hemicellulose and 12.7% lignin, being the 7.2% non CHL components) went under thermo-gravimetric analysis, between 520 K and 640 K, in a current of nitrogen, using a TA Instruments Q500 TGA. Beech wood residues were used being available as fine dry powder (average dimension less than 0.08 mm), from a local industry.

Material	*Cellulose*	*Hemicel.*	*Lignin*	*Non CHL*
Hazelnut shells	25.9	29.9	42.5	1.7
Poplar prunings	42.3	31.0	16.2	10.5
Olive tree prunings	22.2	21.1	45.0	11.7
Chestnut wood residues	41.1	16.0	22.8	20.1
Sunflowers residues	27	18	27	28

Table 2 – *CHL composition for some common biomasses available as by-product of typical agricultural activities in South of Italy*

3 Results

Thermo-gravimetric analysis on 12 mg samples of fine powder obtained from beech wood residues, at a heating rate of 20 K s^{-1}, in a current of pure nitrogen, gave the results shown in Fig.2.

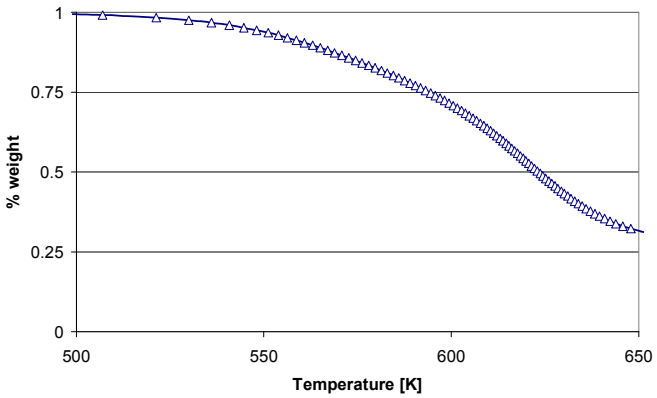

Fig.2 – TGA of beech wood residues, heated at 20 K s^{-1}.

TGA data were used in order to evaluate an overall rate for the pyrolysis reaction.
In fact, for an overall *n*-order rate, the weight decay with the process time is given by the following equation:

$$\frac{dW}{dt} = -k_0 e^{\frac{E_A}{RT}} W^n \qquad (10)$$

where W is the sample weight and the rate constant is expressed according with the Arrhenius law.
The equation (10) can be rearranged in terms of logarithms and it gives the following expression:

$$\ln\left(\frac{-\frac{dW}{dt}}{W^n}\right) = \ln k_0 - \frac{E_A}{RT} \qquad (11)$$

Guessing the value of *n*, using the TGA data, it is possible to plot the first term versus 1/T: the data will lay on a straight line with best correlation factor in correspondence of best value guessed for *n*.
The results of this analysis are reported in Fig.3, where the first term of equation (11) was plotted versus the inverse of temperature. The best correlation is given when n=1.5, according to quoted literature [4].
This overall model cannot give any indication about the yield in term of char and of volatile products one can obtain by the pyrolysis of biomass. For this purpose, the rate model with active intermediate is used.
First of all, theoretical yield of char and of gas and tar vapour was calculated for a hypothetical biomass constituted of only cellulose, of only hemicellulose and of only lignin, respectively.
Results calculated at 700 K are shown in Fig.2. The higher yield in volatile compounds (gas and tar vapour) is given by 100% cellulose biomass, whereas the 100% lignin biomass gives the higher yield in char.

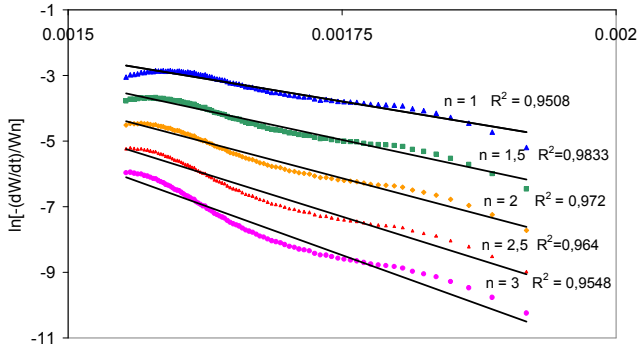

Fig.3 – Elaboration of TGA data for the evaluation of overall reaction rate order of beech wood residues slow pyrolysis.

It is expected that the higher is the content of cellulose with respect to hemicellulose and lignin, the higher will be the yield in volatile products.
For this purpose, the materials listed in Table 2, can be divided into two groups: the first one, composed by poplar prunings and chestnut wood residues, that show the higher cellulose content (42.3% and 41.1% respectively); the second one, composed by hazelnut shells, olive trees prunings and sunflower residues, with a lower content of cellulose (25.9%, 22.2% and 27%).
In the first group, poplar prunings show higher hemicellulose content with respect to the chestnut wood residues one, and also a lower content of non-CHL components. In the second group, hazelnut shells and olive tree prunings show similar content of lignin (42.5% and 45% respectively), but hazelnut shells are characterized by the lowest content of non-CHL components.

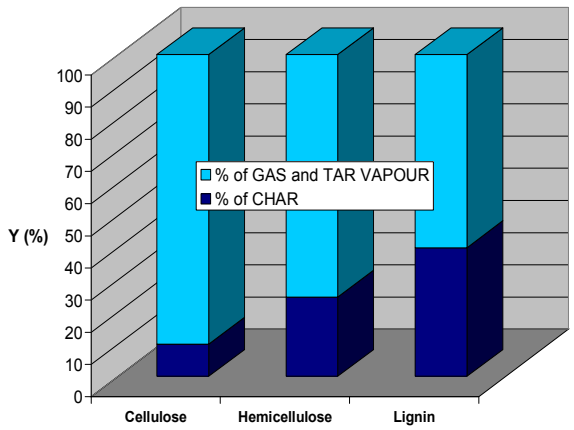

Fig.4 – Theoretical yield of char and of volatile products of cellulose, hemicellulose and lignin, at 700 K

Figs.5 and 6 show the theoretical yield of char and of volatile products of considered biomasses, evaluated by solving the CHL model in isothermal conditions at 700 K and at 900 K, respectively.

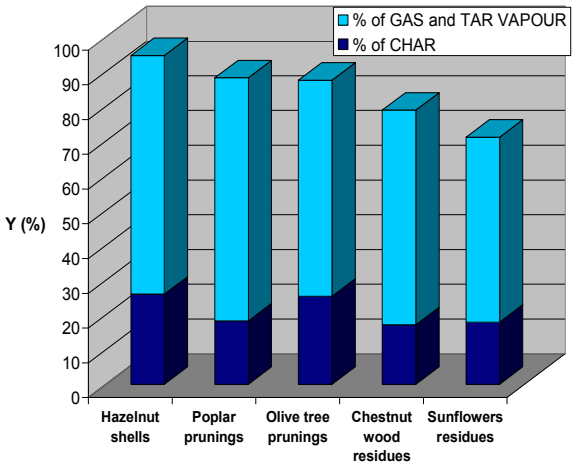

Fig.5 – *Theoretical yield of char and of volatile products of considered biomasses, evaluated by solving the CHL model in isothermal conditions at 700 K*

Higher yields of volatile products are given by hazelnuts shells and by poplar prunings, for both analysed temperatures (69% at 700 K and 75% at 900 K).
Higher yields of char are given by hazelnuts shells and by olive tree prunings, for both analysed temperatures (25% at 700 K and 18% at 900 K).
Hazelnut shells show also the highest overall yield (almost 95%), whereas the lowest is the one referred to sunflower residues (almost 71%). Obviously, the overall yield is lower when the content of non-CHL components is higher.
Fig.7 summarizes the theoretical yields of gas and tar vapours obtained solving the model in non-isothermal conditions. During pyrolysis process, in fact, the material is heated in order to reach temperature values between 800 K (conventional pyrolysis) and 1000 K (fast pyrolysis).

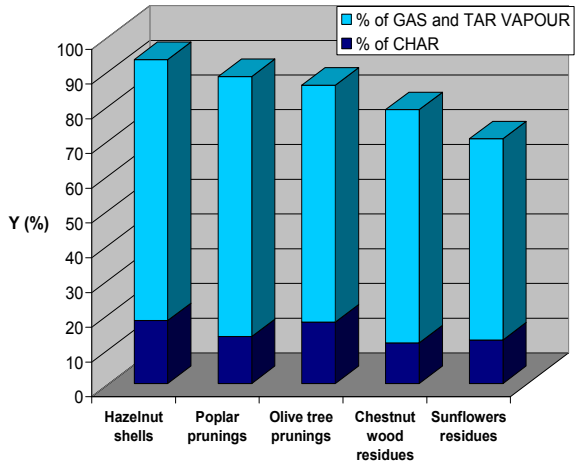

Fig.6 – Theoretical yield of char and of volatile products of considered biomasses, evaluated by solving the CHL model in isothermal conditions at 900 K

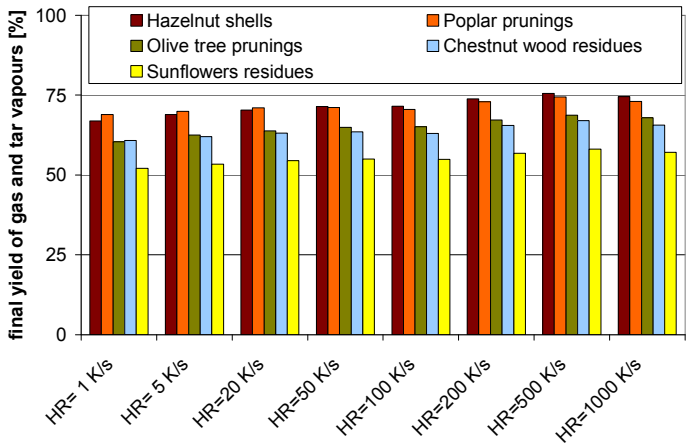

Fig.7 – Theoretical yield of gas and tar vapours of considered biomasses, evaluated by solving the CHL model, as a function of heating rate (HR)

Eight different heating rate (HR) values were considered: four values below 100 K/s, considered as slow or conventional pyrolysis conditions, and four from 100 K/s up to 1000 K/s, considered as fast pyrolysis, with residence time between 0.5 s and 5 s. Results show that hazelnut shells and poplar prunings gives higher yields in gas and tar vapours for all the heating rates investigated; olive tree prunings and chestnut wood residues give an appreciable yield (around 70%) only for temperatures above 900 K, for fast pyrolisis conditions. Sunflowers residues, characterized by higher content of non-CHL compounds, give the lower yield in fuel (always less than 60%) for all the investigated conditions. Almost for all considered materials, there is a maximum of yield for heating rate of 500 K/s.

4 Conclusion

For the estimation of volatile product yield of pyrolysis of wood and plant biomass, a CHL model was presented. Investigation on five biomasses available as by-product of

typical agricultural activities in South of Italy allowed to characterize the role of composition and of heating rate on the final yield. Among the considered biomasses, hazelnut shells and poplar prunings gave high yield in fuel (gas and tar vapours) between 700 K and 900 K, both for conventional slow pyrlysis and for fast pyrolysis, whereas olive tree prunings and chestnut wood residues gave an appreciable yield (higher than 70%) only for temperatures above 900 K, for fast pyrolisis. Sunflowers residues, characterized by higher content of non-CHL compounds, give the lower yield in fuel for all the investigated conditions.

References:

[1] A.G.W. Bradbury, Y. Sakai, and F. Shafizadeh, A kinetic model for pyrolysis of cellulose. *Journal of Applied Polymer Science*, Vol.23, 1979, pp. 3271–3280.

[2] C.A. Koufopanos, G. Maschio, A. Lucchesi, Kinetic Modeling of the Pyrolysis of Biomass and. Biomass Components. *The Canadian Journal of Chemical Engineering,* Vol.67, 1989, pp.75-84.

[3] T. Fisher, M. Hajaligol, B. Waymack, and D. Kellogg, Pyrolysis behavior and kinetics of biomass derived materials. *Journal of analytical and applied pyrolysis*, Vol. 62, 2002, pp. 331–349.

[4] C. Di Blasi, Influences of physical properties on biomass devolatilization characteristics. *Fuel*, Vol.76, N.10, 1997, pp. 957–964.

[5] F. Thurner, and U. Mann, Kinetics investigation of wood pyrolysis, *Ind. Eng. Chem. Res.* 1981, Vol.20, pp. 482-489.

[6] M.J.jr Antal and G. Varhegyi, Cellulose pyrolysis kinetics: The current state of knowledge. *Ind. Eng. Chem. Res*., Vol.34, N.3, 1995, pp. 703–717.

[7] J.A. Caballero, R. Font, A. Marcilla, and J.A. Conesa, New kinetic model for thermal decomposition of heterogeneous materials. *Journal of Applied Polymer Science*, Vol.34, N.3, 1995, pp. 806–812.

[8] X.H. Liang and J.A. Kozinski, Numerical modeling of combustion and pyrolysis of cellulosic biomass in thermogravimetric systems. *Fuel*, Vol.79, 2000, pp. 1477–1486.