Double Distribution Activation Energy Model for microalgae pyrolysis

P. DE FILIPPIS, B. DE CAPRARIIS, M.SCARSELLA, N. VERDONE Department of Chemical Engineering Sapienza University of Rome Via Eudossiana 18, 00184 Rome ITALY Paolo.defilippis@uniroma1.it

Abstract: - Pyrolysis is a fundamental step in thermochemical processes of biomass materials, so a suitable kinetic model is an essential tool to predict the evolution of the resulting products of reaction. However, many difficulties arise in modelling this process step due to the very high number of the involved reactions. In this work, a new double Gaussians distributed activation energy model was applied in fitting the experimental data of olive residue pyrolysis obtained by thermogravimetric analysis. 2-DAEM formulation considers two sets of parallel reactions occurring and sharing the same pre-exponential factor, but showing different distributions of the activation energy, described by two separate Gaussian distributions which, in turn, grasp the two pyrolysis steps with a high accuracy. Since it is well known that in fitting all the kinetic parameters the pre-exponential factor results high correlated with the activation energy, the former parameter was fixed.

Key-Words: Pyrolysis; Distributed activation energy model; Pyrolysis kinetics; Biomass; Thermogravimetric analysis; microalgae

1 Introduction

The environmental impact of fossil fuel exploitation is promoting the development of energetic conversion processes of renewable energy sources such as biomass. The use of biomass helps to reduce the dependence from fossil fuels as well as the carbon dioxide emissions responsible for the greenhouse effect, due to its CO_2 neutrality [1]. Microalgae have been identified as one of the most promising biomass source of energy [2]. In comparison with traditional terrestrial crops, microalgae do not require arable lands and can be produced all year round at high growth rate with a reduced use of fertilizers, pesticides and water [3]. In particular, microalgae have been appointed as ideal biodiesel feedstock in virtue of their high lipids content up to 80% of dry biomass mass [4]. Microalgae biomass can be converted into energy by means of thermochemical processes such as pyrolysis, gasification and combustion. Pyrolysis represents one of the most important steps in all these processes, so understanding and modeling its mechanism are a fundamental prerequisite to predict the behavior of the biomass during the whole process and thus to design a suitable reactor. During pyrolysis, biomass is decomposed into volatiles, which constitute the larger part of the pyrolysis products, and into a solid residue, the char. Volatiles consist of light gaseous (CH₄, CO₂, CO, C₂H₄ and others) and condensable species (tar, with no predictable composition). Moreover, pyrolysis is a complex process whose kinetic parameters are difficult to obtain through models due to by the high number of products, not easily identifiable in experiments. Pyrolysis can be generally described as a two-step process [5]: a primary step occurring in a lower temperature range, where light gas and tar are released, and a secondary one, at higher temperatures, where the release of light gas continues and the aromatization of the biomass macromolecules leads to char production. A large number of kinetic models were proposed in the literature [6,7]. Pyrolysis can be modeled with a detailed kinetic model that takes into account the evolution of a selected number of species or, as in this work, with a global kinetic mechanism that considers the evolution of a unique species, defined as $C_x H_y O_z$, representing all the volatiles.

In this work, the distributed activation energy model (DAEM) is used to model the pyrolysis of the microalgae *Chlorella vulgaris*. The DAEM assumes that a series of first-order parallel reactions occurs, sharing the same pre-exponential factor and characterized by a continuous distribution of the activation energies; in the literature different forms of activation energy distribution can be found: Gaussian [8], Weibull [9] or Gamma [10] distributions; in this study the Gaussian one was adopted.

The DAE model has been extensively applied for modeling algae pyrolysis with good results as reported in literature [11,12].

However, one of the major problems arising in the DAE model application is the interpretation of pyrolysis as a single step process, because its classical formulation is not able to distinguish between the different pyrolysis steps. To circumvent such a limitation, in a previous work focused on coal pyrolysis, the authors proposed an extended model able to catch the kinetic parameters of both the steps by including a second Gaussian distribution [13]. This multi-Gaussian approach was also used by Zhang et al. [14] to model biomass pyrolysis and gasification considering different distribution of activation energy for each class of reactions that share the same pre-exponential factor. In this paper the multi-Gaussian model is applied to predict the behavior of Chlorella vulgaris microalgae and the results are compared with those obtained with the single DAE model. Both the models were used in interpreting the experimental data obtained by thermogravimetric analysis (TGA).

2 Mathematical model

The equation that represents the total volatile yield as a function of time/temperature for the original DAE model is:

$$\int_{0}^{\infty} \exp\left(-\frac{k_0}{\alpha}\int_{0}^{T} \exp\left(-\frac{E}{RT}\right)dT\right)f(E)dE$$
 (1)
where *v* and *v** are the volatile yield and the total
amount of volatiles, respectively, k_0 is the pre-
exponential factor, α the heating rate and *T* the
temperature. $f(E)$ is the distribution curve of the
activation energy *E* which satisfies the condition:

$$\int_{0}^{\infty} f(E)dE = 1 \tag{2}$$

In this work, as already said, the f(E) function is modeled as Gaussian distribution:

$$f(E) = \frac{1}{\sigma_E \sqrt{2\pi}} exp\left(\frac{-(E-E_0)^2}{2\sigma_E^2}\right)$$
(3)

where E_0 is the mean activation energy and σ_E the corresponding standard deviation. The focus of the analysis is to estimate E_0 , σ_E and k_0 from recorded experimental data. However, as already noticed in literature [15], regression algorithms show a strong correlation between k_0 and E_0 leading to a non-uniqueness of kinetic parameters that is called compensation effect [16]. So to overcome this drawback, one choice is to fix k_0 at a defined value, that must be consistent with the transition-state theory which indicates values in the range $10^{11} - 10^{16} \text{ s}^{-1}$ [14]. A value of 10^{13} s^{-1} was chosen for this kind of biomass [12].

In the multi-Gaussian model two distributions of activation energy, sharing the same pre-exponential

factor are considered, so the classical DAEM equation becomes:

$$1 - \frac{v}{v^*} = \int_0^\infty \exp\left(-\frac{k_0}{\alpha}\int_0^T \exp\left(-\frac{E}{RT}\right)dT\right)\left(wf_1(E) + (1 - w)f_2(E)\right)dE$$
(4)

where $f_i(E)$ are Gaussian functions related to the two considered pyrolysis steps, defined in the form:

$$f(E) = \frac{1}{\sigma_{Ei}\sqrt{2\pi}} exp\left(\frac{-(E-E_{0i})^2}{2\sigma_{Ei}^2}\right)$$
(5)

and *w* is a parameter ranging between 0 and 1 which weights the occurrence of the two reaction classes. This parameter describes how many volatiles are released during the primary and the secondary pyrolysis step. The value of *w* would be 0 if all the volatiles were produced during the secondary phase of pyrolysis and 1 if they were totally released during the primary one. In this model, the parameters to be estimated are 5: two mean activation energies E_{01} and E_{02} coupled with two standard deviations σ_{E1} and σ_{E2} , each couple of these parameters characterizing the single Gaussian distribution, and the weighting parameter *w*.

To fit the experimental data, a C++ program was written and run into the ROOT environment [17], an object-oriented data analysis program, using the routine MINUIT for the minimization of the function selected for the fitting:

$$\chi^{2} = \sum_{i=1}^{N} \left(y_{i}^{s} - y(T_{i}) \right)^{2}$$
(6)

where *N* is the number of data points, and y_i^s and $y(T_i)$ are the experimental and the calculated data, respectively. In each step of the minimization, the DAE equation is integrated numerically with the method of Gaussian quadrature.

3 Experimental section

Chlorella vulgaris cultures were grown in BG-11 medium (NaNO₃: 1.50 g L⁻¹, K₂HPO₄: 0.04 g L⁻¹, MgSO₄·7H₂O: 75.0 mg L⁻¹, CaCl₂·2H₂O: 36.0 mg L⁻¹, citric acid (C₆H₈O₇·1H₂O): 6.0 mg L⁻¹, ferric ammonium citrate (C₁₂H₂₂FeN₃O₁₄): 6.0 mg L⁻¹, Na₂CO₃: 20.0 mg L⁻¹, Na-EDTA: 1.0 mg L⁻¹, H₃BO₃: 2.86 mg L⁻¹, MnCl₂·4H₂O: 1.81 mg L⁻¹, ZnSO₄·7H₂O: 0.22 mg L⁻¹, Na₂MoO₄·2H₂O: 0.39 mg L⁻¹, CuSO₄·5H₂O: 79.0 µg L⁻¹, Co(NO₃)₂·6H₂O: 49.4 µg L⁻¹). All the cultures were conducted in 5.0 L flat-plate photobioreactors maintained at 25 ± 1 °C and exposed to a light intensity of 150 mmol photons m⁻² s⁻¹ provided by phytostimulant fluorescent tubes, with a light\dark photoperiod of 12:12 h. In Table 1 and Table 2 the properties of the *Chlorella vulgaris* biomass are reported. The proximate analysis was performed by TG analysis according to the ASTM D5142/02 method. The elemental composition was carried out using a EA3000 (Eurovector) elemental analyzer. To measure the biochemical composition of the biomass, the lipids were extracted according to the protocol described by Bligh and Dyer [18] and the lipids content was determined gravimetrically by evaporating the solvents under vacuum and drying the extract for 4 h at 80°C. Protein content was approximated by multiplying elemental nitrogen concentrations by a factor of 6.25 [19].

Table 1: Chemical and physical properties of *Chlorella vulgaris* biomass.

Proximate analysis (%wt)	
Volatiles(%dry)	73.4
Fixed carbon (%dry)	21.9
Ashes (%dry)	4.7
Ultimate analysis (%wt daf)	
С	41.1
Н	6.4
Ν	7.3
S	0
O (diff)	40.5

Table 2: Biochemical composition of *Chlorella vulgaris* biomass.

Proximate analysis (%wt)	
Lipids (%dry)	16.2
Proteins (%dry)	45.6
Carbohydrates (%dry diff)	38.2

The pyrolysis experimental tests were performed with a thermogravimetric analyzer SDT Q600 (TA Instruments). Before the TG analysis, the biomass was dried, grounded and sieved to select the particles with diameter ranging from 50-100 μ m, in order to avoid diffusional intraparticle effects. Small samples, approximately 7 mg, were used to ensure uniform heating and to minimize the transport phenomena resistance through the sample bed in the crucible. For each experimental tests, the samples were heated in a N₂ inert atmosphere, with a N₂ flux of 100 ml/min, at 10, 20 and 40 K/min up to a temperature of 1223 K and then maintained at this temperature for 10 min.

4 Results and discussion

In Fig. 1 and in Fig. 2 the TG and DTG curves of the microalgae pyrolysis are reported for the three heating rates.



Fig. 1: TG curves of the microalgae Chlorella vlgaris varying the heating rate.



Fig. 2: DTG curves of the microalgae Chlorella vulgaris varying the heating rate.

From the DTG curves the two steps of the pyrolysis are clearly visible, the first occurring at lower temperatures (450-700 K) and the second at higher ones (500-850 K). The first step refers to the primary pyrolysis, where the majority of the volatiles are released, the second step corresponding to the secondary pyrolysis. In the latter case, the repolymerization of the residue solid macromolecule, to form char, occurs with a further but lower release of volatiles.

To show the improvement obtained using the double DAEM, the results obtained with this model were compared with those of the original DAE model.

As shown in Fig. 3, the 1-DAEM represents well the main step of the pyrolysis process, that in the

present case is the primary one and also the predominant part of the *Chlorella vulgaris* pyrolysis, as it can be seen from the DTG curves. However, the single DAEM is not able to catch the second step. The fitting curve, indeed, does not represent well the experimental data.



Fig. 3: Comparison between the biomass experimental data (red points) and the 1-DAEM fitting (black line) data at 20 K min⁻¹.

Looking at the Fig. 4, where the result of the fitting performed with the double DAE model is reported, a great improvement on the agreement with experimental data is obtained. In this case the model is able to grasp the two steps of the biomass pyrolysis.



Fig. 4: Comparison between the biomass experimental data (red points) and the 2-DAEM fitting (black line) data at 20 K min⁻¹.

From the comparison of the numerical value of the kinetic parameters (Table 3), it is clear that the 1-DAEM returns approximately an average value of the activation energy and of the standard deviation of the process.

For what concerns the 1-DAEM, the numerical results confirm the hypothesis made looking only at the plot of Fig. 3. The value of the activation energy is included in the interval of the E_{01} and E_{02} given

by the 2-DAEM even if it is almost similar to the E_{01} confirming that the 1-DAEM grasps only the predominant step.

In the 2-DAEM, the *w* parameter assumes particular importance explaining how many volatiles are released during the primary and the secondary pyrolysis step. In the present case, the value is quite high (w = 0.78) indicating that, as expected, the primary step is the predominant mechanism. Furthermore, the 2-DAEM limits the first step of pyrolysis in a narrow interval of activation energy ($\sigma_{EI} = 17.3$ kJ mol⁻¹), meaning that the process is faster and confined in a narrower temperature interval.

The value of E_{02} is considerably higher than that of E_{01} . This behavior can be explained considering that *Chlorella vulgaris* is constituted mainly by carbohydrates and proteins, which start undergoing thermal cracking at temperature about 250 °C [20] with the breakage of the weakest chemical bonds. The thermal degradation of the residual molecules continues at higher temperatures in the second pyrolysis step, when the repolymerization of carbonaceous substrates forms char with a further volatiles production (secondary pyrolysis) [21]. This step requires the rupture of stronger bonds to extract the hydrogen from the hydroaromatic and aliphatic groups increasing the aromatic carbon content of the solid residue.

Table 3: Kinetic parameters obtained with the 1-DAEM and 2-DAEM at 20 K min⁻¹.

	1-DAEM	2-DAEM
$k_0 [s^{-1}]$ fixed	10^{13}	10^{13}
E_{01} [kJ mol ⁻¹]	184.0	174.5
$\sigma_{E1}[kJ mol^{-1}]$	30.0	17.3
E_{02} [kJ mol ⁻¹]	-	258.5
σ_{E2} [kJ mol ⁻¹]	-	63.5
w	-	0.78

In Fig. 5 the f(E) functions for the 1-DAEM and the 2-DAEM are reported. As already discussed, the single Gaussian model is able to give an average representation of the process focusing on the predominant mechanism. The f(E) function of the double Gaussian model shows that the two pyrolysis steps superimposed. are partly since the repolymerization reactions begin to occur when the reactions of the primary pyrolysis are still ongoing. This behavior was expected, considering that the value of σ_{E2} (63.5 kJ mol⁻¹) is higher than the value of σ_{EL} The first pyrolysis, represented by the first peak of the f(E) curve, is faster and dominates the whole process as pointed out also from the estimation of the *w* parameter.



Fig. 5: Comparison between the f(E) functions carried out with the 1-DAEM (red line) and the 2-DAEM (black line).

Finally a simultaneous fit was performed in order to evaluate the independence of the kinetic parameters from the heating rate. The simultaneous fit gives good results for the three heating rates (Fig. 6) and the values reported in Table 4 show that the obtained kinetic parameters can be considered consistent in the range of the heating rates tested being almost the same of those obtained in the single fit.

Table 4: Kinetic parameters obtained with the simultaneous fit.

	2-DAEM
$k_0 [s^{-1}]$ fixed	10^{13}
E_{01} [kJ mol ⁻¹]	175.0
$\sigma_{E1}[kJ mol^{-1}]$	17.9
E ₀₂ [kJ mol ⁻¹]	263.0
σ_{E2} [kJ mol ⁻¹]	65.1
W	0.79

The improvement in the representation of the pyrolysis process using the 2-DAEM is evident. Table 5 gives the residual sum of squares for the two models and the relative improvement of the 2-DAEM. The 2-DAEM leads to an improvement in the pyrolysis modeling of about 30 times.

Table 5: Summary for the Residual Sums of Squares for the two models.

1-DAEM	0.067
2-DAEM	0.002
χ^2 (1-DAEM)/ χ^2 (2-DAEM)	33



Fig. 6: Comparison between experimental data taken at different heating rate (red points) and 2-DAEM simultaneous fit.

5 Conclusions

The pyrolysis of *Chlorella vulgaris* microalgae was modeled with a double Gaussians activation energy model to catch the kinetics of the two pyrolysis steps. The model estimates two different distributions of activation energies sharing the same pre-exponential factor. The results of the fitting show that the first pyrolysis is the predominant mechanism in biomass pyrolysis process, occurring at lower activation energy in a narrow interval (σ_{E2} =17.3 [kJ mol⁻¹]). The two steps are partially overlapped due to the wide temperature interval of the secondary pyrolysis. The double Gaussian model was compared with the traditional DAEM showing a great improvement. Furthermore the introduction of the w parameter, estimated from the fit, gives important information on the weight of the two pyrolysis steps identified in the process.

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