

Kinetics of the Thermal Decomposition of Green Alga *Ulva* by Thermogravimetry

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ABSTRACT: In this article, we present the findings of our study into the thermal decomposition of the alga *Ulva*, which can cause serious problems due to its proliferation in certain seas. Its use as a human foodstuff or other similar applications is limited; however, it could be used as a filling or reinforcement material in the manufacture of composite materials. Since the production processes of such materials usually require heating, the thermal stability of this polymeric material needs to be known, and this is the objective of this work. For this reason, we have studied the thermal decomposition in an air atmosphere using thermogravimetry (TG). On the one hand, we evaluated the thermal sta-

bility temperatures of the seaweed; and on the other, we determined the kinetic parameters of the alga's two main decomposition reactions, using an n -order integral kinetic model. It was, therefore, necessary to calculate the best order of reaction. Finally, we determined a series of characteristic temperatures related to the beginning and the end of each of the thermal decomposition reactions. © 2004 Wiley Periodicals, Inc. *J Appl Polym Sci* 93: 1913–1922, 2004

Key words: alga *Ulva*; thermogravimetry (TG); thermal stability; kinetic model; characteristic temperatures

INTRODUCTION

In recent years, major eutrophication has taken place in the Adriatic Sea, with the consequent growth of alga commonly known as mucilaginous, composed of compatible species, such as: *Ulva armoricana*, *Ulva lactuca*, *Ulva rotundata*, and *Ulva rigida*. The eutrophication caused by the alga *Ulva* is not confined to the Adriatic Sea. In fact, the uncontrolled growth of such seaweed affects coasts worldwide.

Algae collected from harmful proliferations are sometimes incorporated into compost¹ and sometimes into paper.² Conversion to biogas is also feasible.³ Unfortunately, most often it is simply dumped. *Ulva* contains three main polysaccharide components: (a) amorphous cellulose, (b) water soluble anionic polysaccharides containing sulfate groups (named Ulvan), and (c) starch.⁴ The polysaccharides (a) and (b) are located in the cell wall. The Ulvan makes up most of the cellular structure and is involved in controlling osmolar stability and maintaining suitable cellular conditions. The starch is glucose storage. In addition, chlorophylls and several carotenoids, including β -carotene, appear to be present in the alga extract. New applications for the raw algae, as well as for their polysaccharides, can be envisaged. For example, they

may be valuable as reinforcement material in the manufacture of many kinds of composite materials, because their polysaccharides can anchor themselves in a polymeric matrix if suitable coupling agents are employed. In recent years, a great deal of effort has been directed towards investigating the use of lignocellulosic fibers (mainly containing polysaccharides) as reinforcement in thermoplastics.^{5–7} The results of these investigations have demonstrated that it is possible to make composite materials, with good mechanical properties, provided there are suitable coupling agents able to make a bridge between the hydrophobic thermoplastic matrix and the hydrophilic polysaccharide reinforcement. For this reason, we consider that the alga *Ulva* could be used as a reinforcement of filling material in the manufacture of different types of composite materials. To obtain such materials, the different components need to come into very close contact. In most cases, this is made possible by applying heat. Depending on the type of process, temperatures may reach 150–170°C. For this reason, we need to study the thermal stability of the seaweed by submitting it to thermal decomposition in a thermogravimeter. We also need to evaluate the kinetic parameters of the reactions that take place.

Dynamic thermogravimetry (TG) (with a linear increase in heating rate) is widely used as a tool for studying the decomposition of different polymeric materials, to find out the order of reaction and also to estimate other kinetic parameters, such as the activa-

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tion energy, the frequency factor, and the rate of decomposition.⁸ The greater precision of experimental values obtained via thermogravimetric analysis (TGA), compared with differential thermal analysis (DTA) and differential scanning calorimetry (DSC), is attributable to the accuracy in the measurement of mass.⁹

The advantages of determining kinetic parameters by nonisothermal methods rather than by isothermal studies are as follows:

1. The kinetics can be established over an entire temperature range in a continuous manner.
2. It is possible to obtain a lot of information with a single sample, that is, thermal parameters, such as the temperature at maximum decomposition rate, characteristic temperatures, and kinetic parameters.
3. The determination of kinetic and thermal parameters using a single sample removes problems arising from the use of different samples, that is, sample-to-sample errors are avoided.
4. When a sample undergoes considerable reactions as it is heated to the required temperature, the results obtained by isothermal methods are questionable because some decomposition may occur during the preheating period, particularly when the temperature at the onset of reaction is considerably lower than the temperature of the isothermal trials.

It was pointed out that the calculated values of the Arrhenius doublet, that is, activation energy and frequency factor, especially for nonisothermal heterogeneous processes, have only limited validity and cannot be utilized for pinpointing the rate-controlling mechanism solely on the basis of the values evaluated. It is known that the decomposition of a polymer is a very intricate phenomenon, comprising various elementary reactions that are difficult to analyze separately and whose quantitative contribution to the global decomposition process is virtually impossible to evaluate. For these reasons, even if the overall process has no real significance with regard to the reaction mechanism, it is useful as a means of quantifying the rate of reaction and for design purposes. Mathematical modeling of thermal decomposition reactions helps in understanding the processes being studied, in checking the validity of assumptions, and in arriving at quantitative conclusions from them. The latter is essential for the engineering calculations needed to determine the size of reactors required in such operations.

With regard to the activation energy of the reaction, the literature shows that there are large variations for any given polymeric material. These differences are the result of various factors:

1. Method used to prepare the polymer, that is, anionic, thermal, or other type of polymer synthesis, and also lattice defects, weak links, and impurities.¹⁰
2. The molecular weight of the polymer.¹¹⁻¹⁴
3. The experimental techniques and operating conditions of the measurements, that is, sample mass, sample particle size, heating rate, mass flow rate, and type of gas, and thermal contact between sample and sample holder.^{9,15}

The mathematical treatment of kinetic equations makes use of one of the following methods: (a) integral, (b) differential, or (c) approximate or special. It has been found that these methods do not reproduce the values of activation energy and reaction order when the same data are taken for computation.^{16,17}

The goal of this paper is to present a methodology for the study of thermal decomposition kinetics that complies with the requirements listed below. (The mathematical procedure presented in this paper will be applied to the thermal decomposition of green alga *Ulva*.)

1. Use of thermograms to determine the thermal stability of samples (T_5 : temperature at which 5% of the mass is lost; T_{50} : temperature at which 50% of the mass is lost; and T_{95} : temperature at which 95% of the mass is lost).
2. Use of the general analytical solution developed by Carrasco¹⁸ to determine the kinetic parameters (activation energy and pre-exponential factor) of the thermal decomposition reactions.

THEORETICAL CONSIDERATIONS

The rate of weight loss in the process of thermal decomposition depends on weight and temperature according to the following equation:

$$-\frac{dw}{dt} = g(w)k(T)q(w,T) \quad (1)$$

Many heterogeneous decomposition reactions of solids are described by the model of pseudohomogeneous kinetics. Therefore:

$$g(w) = \left(\frac{w - w_r}{w_0 - w_r} \right)^n \quad (2)$$

According to Altofer,¹⁹ some conditions have to be fulfilled to enable an ideal course of reaction as represented by the n -order reaction kinetics, that is, a well-defined, homogeneous sample temperature with no reverse reactions. The latter implies negligible par-

tial pressure of the decomposition gas. Therefore, a continuous flow of gas is recommended to evacuate volatilization products as they are formed.

The variation of the constant rate with the temperature is generally accepted to be of the Arrhenius type, because this relationship dominates physical and chemical phenomena:

$$k(T) = A \exp\left(-\frac{E}{RT}\right) \quad (3)$$

The cross term $q(w, T)$ takes into account the interactions between the weight and the reaction temperature. These interactions arise from different factors: (a) variation of residual weight with operating conditions; (b) variation of kinetic parameters with conversion in the case of competitive reactions; and (c) modifications of the sample physical properties during the decomposition. Because it is very difficult to obtain an equation that considers all these factors, and to facilitate further derivation, the term $q(w, T)$ is generally assumed to be equal to unity.

Dynamic TG is often carried out at a constant heating rate. In such cases:

$$T = T_0 + \beta t \quad (4)$$

Therefore:

$$\beta = \frac{dT}{dt} \quad (5)$$

Taking into account the relationship between mass and conversion, as well as the previous considerations:

$$\int_0^f \frac{df}{(1-f)^n} = \frac{A^*}{\beta} \int_{T_0(f=0)}^T \exp\left(-\frac{E}{RT}\right) dT \quad (6)$$

where:

$$f = \frac{w_0 - w}{w_0 - w_r} \quad (7)$$

$$A^* = Aw_0^{n-1} \quad (8)$$

Several expansions and semiempirical approximations have been suggested²⁰ for the temperature-containing integral: the asymptotic expansion, van Krevelen et al.'s approximation, Doyle's approximation, etc. Other authors have stated that the kinetic analysis of dynamic TG leads inescapably to integral equations which require numerical solution.²¹ Moreover, Coats and Redfern²² reported that the temperature-containing integral has no exact solution. Therefore, they used

an approximation. However, the integral does have a primitive,¹⁸ which is the general analytical solution:

$$-\ln(1-f) = \frac{A^*E}{\beta R} \left[\exp\left(-\frac{E}{RT}\right) \sum_{i=1}^{\infty} (-1)^{i+1} i! \left(\frac{RT}{E}\right)^{i+1} \right] \quad n = 1 \quad (9)$$

$$\frac{1 - (1-f)^{1-n}}{1-n} = \frac{A^*E}{\beta R} \left[\exp\left(-\frac{E}{RT}\right) \sum_{i=1}^{\infty} (-1)^{i+1} i! \left(\frac{RT}{E}\right)^{i+1} \right] \quad n \neq 1 \quad (10)$$

$$f = 1 - \exp\left(-\frac{A^*RT^2}{\beta E} \left[\exp\left(-\frac{E}{RT}\right) \sum_{i=1}^{\infty} (-1)^{i+1} i! \left(\frac{RT}{E}\right)^{i-1} \right] \right) \quad n = 1 \quad (11)$$

$$f = 1 - \left[1 - (1-n) \frac{A^*RT^2}{\beta E} \left[\exp\left(-\frac{E}{RT}\right) \sum_{i=1}^{\infty} (-1)^{i+1} i! \left(\frac{RT}{E}\right)^{i-1} \right]^{1/(1-n)} \right] \quad n \neq 1 \quad (12)$$

When the sum is truncated at the second term ($i = 2$), the kinetic equation developed by Coats and Redfern²² can be found. Their simplification is quite satisfactory when the thermal energy (RT) is significantly less than activation energy. This case is often found for the thermal decomposition of solids. However, if RT tends to E , that is, low activation energy and/or high temperature, it is necessary to take a greater number of terms in the general analytical solution. Because the general analytical solution is an integral method, the values for order of reaction have to be assumed ($n = 0, 1/2, 1, 3/2, 2$). The best order is chosen by means of an analysis of variance (ANOVA).

Conversion can be singled out from Equations 9 and 10, whereas first and second conversion derivatives follow readily from Equation 6.

$$\frac{df}{dT} = \frac{A^*}{\beta} \left[\exp\left(-\frac{E}{RT}\right) \right] (1-f)^n \quad \forall n \quad (13)$$

$$\frac{d^2f}{dT^2} = \frac{df}{dT} \left(\frac{E}{RT^2} - \frac{n}{(1-f) dT} \right) \quad \forall n \quad (14)$$

Because the maximum rate of decomposition is reached when $d^2f/dT^2 = 0$, the activation energy can be evaluated from Equation 15:

$$E = nRT_m^2 \frac{\left(\frac{df}{dT}\right)_m}{(1-f_m)} \quad \forall n \quad (15)$$

However, the values for temperature, conversion, and first conversion derivative at maximum rate of decomposition are not generally known and must be estimated graphically from thermogravimetric (TG) data. Thus, Equation 15 is useful for obtaining an approximate value of the activation energy. This estimate can also serve as the initial value in iterative calculations leading to the determination of activation energy through the general analytical solution.

Two characteristic temperatures (for the two main reactions considered in this study) have been derived from the weight loss curves: The characteristic temperature T_{c0} is obtained from the TG curve as the value of the intercept between the locus of $f = 0$ and the tangent line at the maximum rate of decomposition. On the other hand, the characteristic temperature T_{c1} is obtained from the TG curve as the value of the intercept of the locus $f = 1$ and the tangent line at the maximum rate of decomposition. These temperatures are mathematically expressed as follows:

$$T_{c0} = T_m - \frac{f_m}{\left(\frac{df}{dT}\right)_m} \quad (16)$$

$$T_{c1} = T_m + \frac{(1-f_m)}{\left(\frac{df}{dT}\right)_m} \quad (17)$$

From Equations 16 and 17 it is possible to find out the difference between the characteristic temperatures:

$$\Delta T_c = T_{c1} - T_{c0} = \frac{1}{\left(\frac{df}{dT}\right)_m} \quad (18)$$

By taking into account Equations 15–18 it is possible to eliminate the conversion derivative in the expressions of the characteristic temperatures:

$$T_{c0} = T_m \left(1 - \frac{RT_m f_m}{E(1-f_m)}\right) \quad (19)$$

$$T_{c1} = T_m \left(1 + \frac{RT_m}{E}\right) \quad (20)$$

EXPERIMENTAL

The green algae were collected from the Venetian Lagoon. They were dried at room temperature and later ground. Later, they were sieved through a series of standard sieves to obtain a granulometric distribution between 25 and 500 μm . In its natural state, Ulva contains an average proportion of water of 78%. The mean composition by weight of dried Ulva is as follows²³: Polysaccharides = 42–46%, ash = 13–22% (K = 0.7% and Na = 3.2%), fiber = 4–5%, protein = 15–25%, fat = 0.6–0.7%. The polysaccharides, which constitute the main element of the alga in terms of their use as reinforcement material in the manufacture of composite materials, is made up of 2.5% molar of glucose, 2.8% of galactose, 8.3% of xylose, 51.1% of rhamnose, 20% of glucuronic acid, and 15.5% of iduronic acid, ordered in an essentially linear sequence with some ramifications. These polysaccharides are found as sulfates.

The thermal decomposition of the algae samples was carried out in a thermal analyzer, Linseis Apparatus Model L81+DTA, and the ISO/DIS 9225–1 method was applied. The operating conditions were as follows: heating rate = 5, 10, and 20 K/min, and sample weight = 20–30 mg (organic content = 11–16 mg). Decompositions were conducted at atmospheric pressure and gases produced by decomposition were swept out by a continuous flow of air.

RESULTS AND DISCUSSION

The granulometric distribution of the alga sample (see Fig. 1) shows that the size of the particles is between 50 and 400 μm , the most predominant diameter being 200 μm . The algae used in this study contain sand and seawater, which, after drying, leave deposits of mineral salts. This is why the ashes that are obtained after the thermal decomposition correspond not only to the alga's own mineral substances, but also to the sand and mineral compounds from the alga's habitat. Using TGA, we found that the humidity of the alga dust is between 3 and 4% and the residual minerals between 47 and 48%. Since the clean alga has an average proportion of inorganic substances of 20%, this means that the sand content and marine salt content in the alga used in this study is 27%. It must be noted that, by using the alga exactly as it was collected in the Venetian Lagoon, we avoided cleaning operations and their consequent cost. In addition, both the sand and the marine salts can also exert a filling/reinforcement effect when making composite materials.

Considering the initial mass of the sample, the water mass, and the inorganic residue mass, the degree of conversion of the thermal decomposition reactions can be calculated using Equation 7. Figure 2 shows the

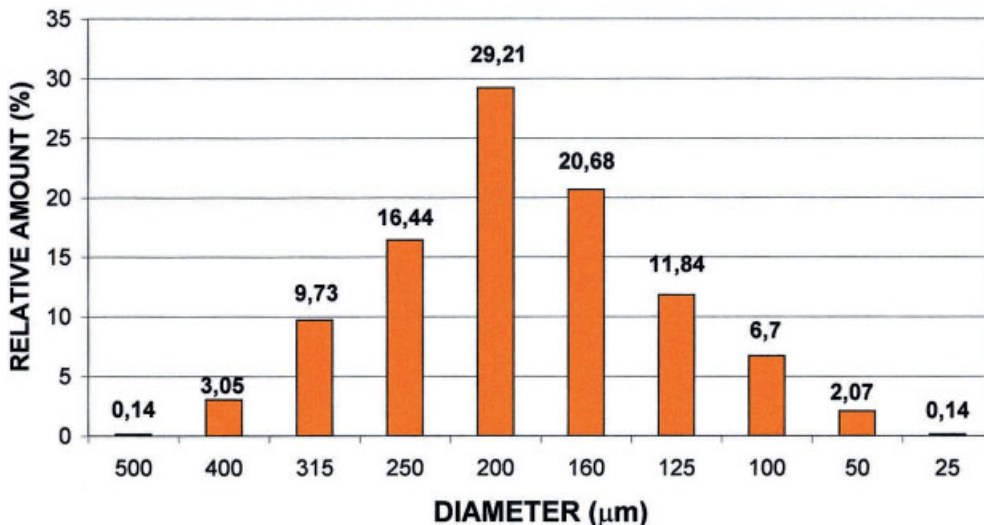


Figure 1 Granulometric distribution of the alga Ulva.

variation of the degree of conversion with the temperature at different heating rates (5, 10, and 20 K/min). There is a preliminary zone of decomposition between 100 and 220°C, corresponding to degrees of conversion of less than 10%. At these temperatures, compounds of low thermal stability decompose, but the global thermal stability of the alga is not jeopardized. The main zones of decomposition occur at higher temperatures. Two clearly differentiated reactions of decomposition can be seen: the first takes place at temperatures between 220 and 450°C and the second, between 450 and 560°C. In the interval of temperatures close to the maximum rate of decomposition, the curves of both zones are in sigma form, which is why the reactions of thermal decomposition adjusted well to a kinetic model of *n*-order reactions. The three

heating rates produce similar curves, although the slopes are different; therefore, so will the kinetic parameters and the thermal stability temperatures. Figure 2 shows clearly that in the first zone of decomposition, conversion is fairly similar for the three heating rates, whereas in the second zone of decomposition, there is a clear difference in the conversion values when the heating rate is 20 K/min. It should be remembered that, above all at high temperatures, the real temperature of the sample and the temperature given by the thermocouple may be quite different at fast heating rates. This is because of the problem of heat transmission (i.e., the sample is not able to warm itself at the same speed as indicated by the temperature programming, due to the conduction of heat within itself).

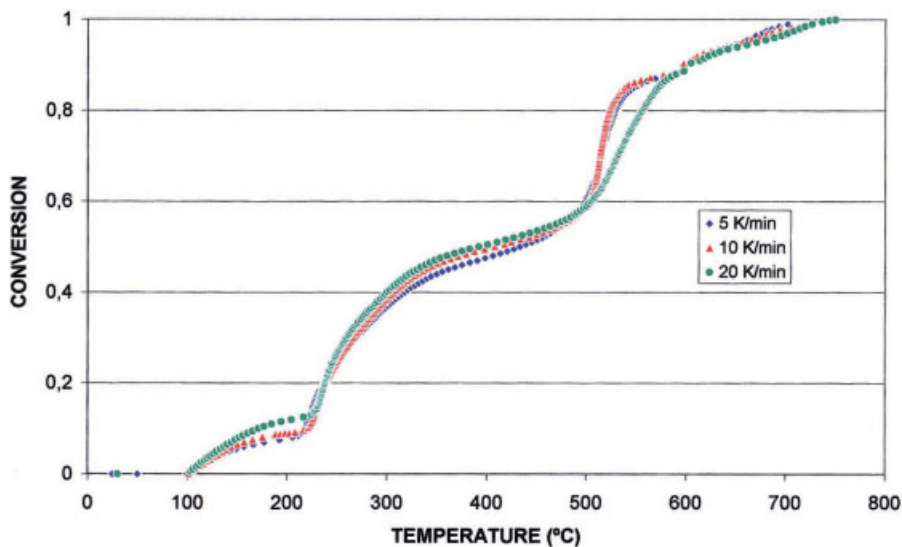


Figure 2 Variation in the degree of conversion of the thermal decomposition reaction, according to temperature.

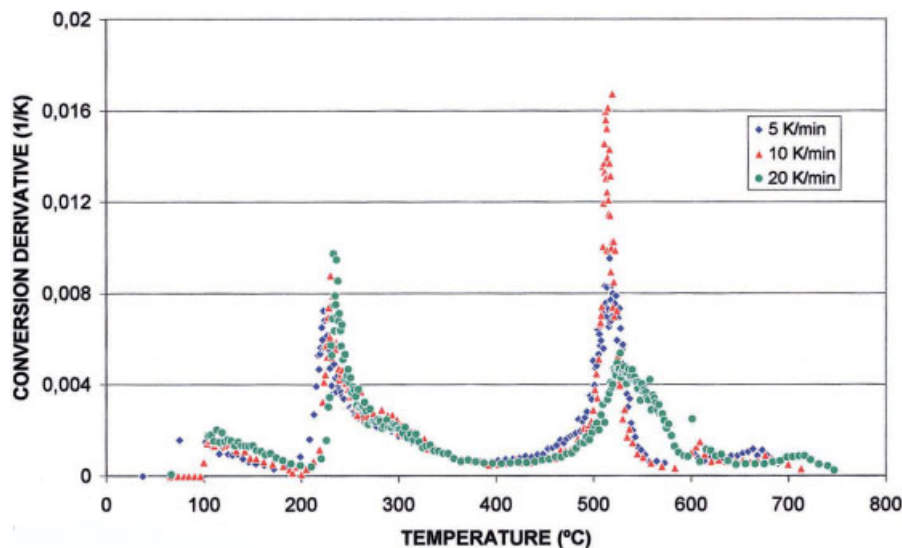


Figure 3 Variation of the degree of conversion derivative of the thermal decomposition reaction, according to temperature.

From the conversion curves, a series of temperatures related to the thermal stability of the alga can be determined: T_5 : temperature at which 5% of the mass is volatilized; T_{50} : temperature at which 50% of the mass is volatilized; and T_{95} : temperature at which 95% of the mass is volatilized. In fact, the T_5 temperature provides a good idea of the thermal stability of the alga. The T_5 for *Ulva* was between 129 and 143°C, depending on the heating rate. The lower the heating rate is, the lower the T_5 temperature. On the other hand, the T_{95} temperature represents the temperature at which almost all of the organic matter is destroyed. The T_{95} for *Ulva* was between 656 and 670°C, depending on the heating rate. Since the decomposition at a high heating rate (20 K/min) may lead to temperature differences between the thermocouple and the sample (due to limitations in heat transmission), we considered only those experiments carried out at 5 and 10 K/min when calculating an average of the temperatures. Hence, $T_5 = 140^\circ\text{C}$ (error = 2.5%) and $T_{95} = 655^\circ\text{C}$ (error = 0.3%).

Using the conversion versus temperature data, it is possible to calculate the derivative of the conversion with the temperature using finite differences (i.e., $df/dT \approx \Delta f/\Delta T$) between two consecutive conversions. In this way, it is possible to calculate the temperature, the conversion, and the conversion derivative at the maximum rate of decomposition, all of which are highly interesting parameters. Figure 3 illustrates the variation of the rate of decomposition with increasing temperature (in terms of the conversion derivative with respect to the temperature) for the three heating rates. The two peaks corroborate the two zones of decomposition mentioned previously. This type of graph is highly useful because the temperature at the maximum rate of decomposition can be deter-

mined with a good degree of precision. Table II shows the values of the temperature, the conversion, and the conversion derivative in conditions of maximum rate of decomposition. In the first peak, the temperature is between 224 and 233°C and conversion is at 13–16%, with slight variations depending on the heating rate. In the second peak, the temperature is between 517 and 527°C with conversion at 71–77%, also with slight variations depending on the heating rate. The values for the activation energy were calculated with Equation 15 using the conditions existing in the peak (i.e., maximum rate of decomposition). The first reaction has an activation energy of between 17 and 25 kJ/mol, whereas in the second, the values we obtained ranged from 90 to 377 kJ/mol, depending on the heating rate. These values are subject to error because the derivative was calculated using finite differences, which introduces a significant imprecision since, in the environs of the point of maximum rate of decomposition, conversion varies very quickly. In any case, these values will serve to initialize the iterative process required for the calculation of the activation energy as we shall explain later.

With the aim of determining the kinetic parameters of the decomposition reactions, we used Equations 9 and 10. Since the order of reaction is not known, we

TABLE I
Temperatures of Thermal Stability at Different Heating Rates

β (K/min)	T_5 (°C)	T_{50} (°C)	T_{95} (°C)
5	142.6	433.4	655.9
10	135.6	408.1	652.3
20	129.4	392.0	670.2

TABLE II
Experimental Values of the Temperature, Conversion, and Conversion Derivative at the Maximum Decomposition Rate, for Different Heating Rates

β (K/min)	1 st decomposition reaction				2 nd decomposition reaction			
	T_m (°C)	f_m (%)	$(df/dT)_m$ (K ⁻¹)	E (kJ/mol)	T_m (°C)	f_m (%)	$(df/dT)_m$ (K ⁻¹)	E (kJ/mol)
5	223.7	13.3	7.24×10^{-3}	17.1	516.9°C	70.8	9.53×10^{-3}	169.2
10	230.0	14.9	8.79×10^{-3}	21.7	519.0°C	76.9	16.74×10^{-3}	377.8
20	233.1	16.3	9.74×10^{-3}	24.8	527.3°C	68.2	5.38×10^{-3}	90.2

performed an analysis of variance (ANOVA) of the regression. The results obtained for the F-value indicate that the best order of reaction corresponds to first order as well as second order kinetics. However, since the first order model is simpler, this model was the one we adopted. It should be borne in mind that the adjustment to Equation 9 requires an iterative procedure due to the presence of $(1-2RT/E)$ term. Hence, the iteration was begun with the value for the activation energy previously calculated by an approximate procedure (see Table II). The value for the activation energy evaluated from the slope is then used in the following iteration until convergence takes place. Equation 10 contains a summation with an infinite number of terms. In any case, it has been verified that taking just two terms ($i = 2$), the errors occurring are less than 1%. Hence, we adopted this number of terms in all the calculations since this simplified the mathematical procedure a great deal. This simplification is quite satisfactory when the thermal energy (RT) is significantly less than the activation energy, which is often the case for the thermal decomposition of solids. Thus, the kinetic parameters (pre-exponential factor and activation energy) obtained by adjusting the experimental points of a first order kinetics and the summation, shortened to two terms, are shown in Table III. The adjustments are relatively good for the first decomposition reaction and excellent for the second decomposition reaction, as we deduced from the regression coefficient values. This can be verified visually in Figures 4 (first reaction) and 5 (second reaction), in which we compare the experimental values of the conversion and the corresponding theoretical values obtained from the kinetics model, when the heat-

ing rate was 10 k/min. The results are similar for experiments carried out at other heating rates. The first decomposition reaction has a relatively low activation energy, 27–34 kJ/mol, and it can be considered independent of the heating rate since any variation is relatively small. However, the activation energy of the second decomposition reaction, which occurs at much higher temperatures, does vary with the heating rate. As we have already mentioned, a heating rate of 20 K/min can cause problems of heat transmission within the sample, which is why we will analyze the behavior of the sample at lower heating rates. At 5 K/min an activation energy of 84 kJ/mol is obtained while at 10 K/min, the value is 156 kJ/mol. This large difference between the activation energies can be attributed to several factors:

1. The type of reaction or reaction mechanism will vary as the temperature-time sequence varies. (This obviously depends on the heating rate).
2. There is a compensation factor between pre-exponential factor and the activation energy, which arises as a result of the mathematical adjustment of the experimental points. A greater activation energy is compensated by a smaller frequency factor.
3. As the heating rate goes from 5 to 10 K/min, there may appear limitations of heat and mass transfer.

It should be noted that when thermal decomposition takes place, the diffusion of heat and/or the gases of decomposition has to be considered as a process that is taking place simultaneously with the chemical

TABLE III
Kinetic Parameters (calculated by linear regression) of the Thermal Decomposition Reactions at Different Heating Rates

β (K/min)	1 st decomposition reaction			2 nd decomposition reaction		
	A (s ⁻¹)	E (kJ/mol)	R ²	A (s ⁻¹)	E (kJ/mol)	R ²
5	0.2008	27.6	0.865	7.0810×10^2	84.0	0.992
10	2,2922	34.4	0.890	1.6391×10^8	156.5	0.994
20	1,3972	29.3	0.870	9,2202	50.1	0.993

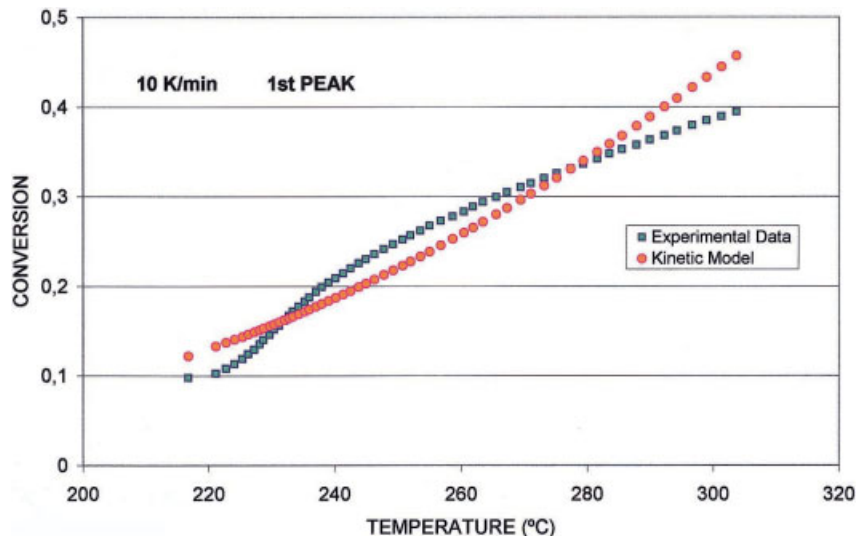


Figure 4 Comparison of the experimental values of the conversion and the values obtained by adjustment of the kinetic model for the first thermal decomposition reaction, carried out at a heating rate of 10 K/min.

reaction. The endothermal/exothermal reaction induces an inhomogeneous temperature distribution. On the other hand, although the constancy of the heating rate in TG is generally assumed when using a linear heating program, this constancy is slightly affected as the reaction takes place. Smaller samples and lower heating rates (i.e., ideal conditions) reduce this influence.

The calculation of the characteristic temperatures of the decomposition reactions was carried out using Equations 19 and 20. The values for the conversion and the conversion derivative were calculated using Equations 11 and 13 using kinetic parameters estimated by linear regression adjustment. As shown in

Table IV, the conversion in the first peak has values between 14 and 18%, which are quite close to the experimental values of 13–16% (Table II). The conversion in the second peak has values of between 69 and 76%, also very similar to the experimental ones of 68–77%. As we have already said, this is not the case with the values for the conversion derivative, because the experimental values are subject to error, since they were calculated by means of finite differences. In contrast, the values obtained from the adjustment of the kinetic model offer greater guarantees, especially in the area close to the peaks, where the rate of conversion changes very quickly. Returning to the characteristic temperatures, the characteristic mean tempera-

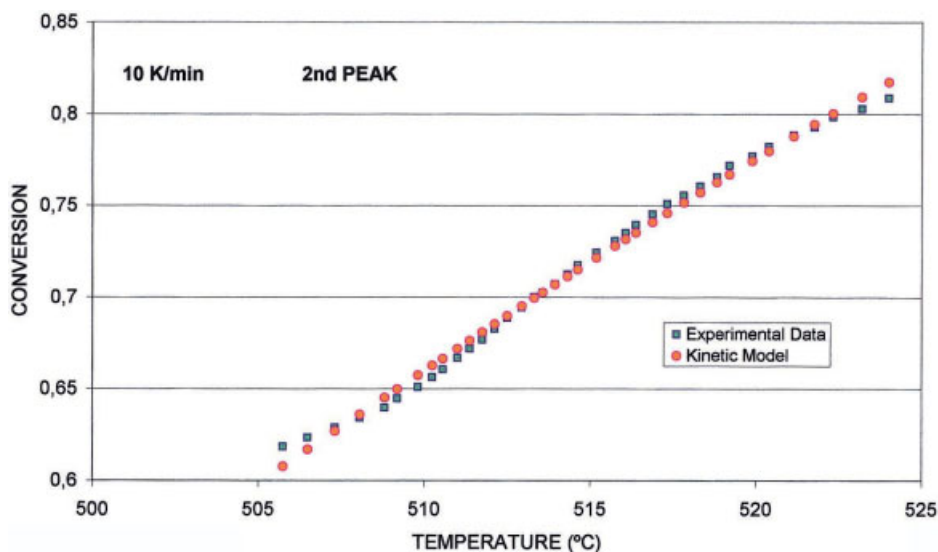


Figure 5 Comparison of the experimental values of the conversion and the values obtained by adjustment of the kinetic model for the second thermal decomposition reaction, carried out at a heating rate of 10 K/min.

TABLE IV
Calculated Values of the Conversion and Conversion Derivative at the Maximum Decomposition Rate and Characteristic Temperatures at Different Heating Rates

β (K/min)	1 st decomposition reaction				2 nd decomposition reaction			
	f_m (%)	$(df/dT)_m$ (K ⁻¹)	T_{c0} (°C)	T_{c1} (°C)	f_m (%)	$(df/dT)_m$ (K ⁻¹)	T_{c0} (°C)	T_{c1} (°C)
5	14.5	2.57×10^{-3}	211.2	298.1	71.0	6.89×10^{-3}	365.5	578.7
10	15.7	3.11×10^{-3}	218.7	291.2	76.5	11.4×10^{-3}	410.2	552.4
20	18.5	3.22×10^{-3}	216.6	305.8	68.7	4.66×10^{-3}	293.7	633.7

tures of the first decomposition reaction are $T_{c0} = 215^\circ\text{C}$ and $T_{c1} = 295^\circ\text{C}$, with relative errors of the order of 1 to 2% (the values at the 20 K/min heating rate were not considered because of the potential problems of heat transfer that we mentioned earlier). It means that the alga *Ulva* is thermally stable up to 215°C (with a loss of only a small quantity of volatile molecules). The characteristic mean temperatures of the second decomposition reaction are $T_{c0} = 388^\circ\text{C}$ and $T_{c1} = 566^\circ\text{C}$, with relative errors of the order of 2–6%. Note that these characteristic mean temperatures represent the temperatures at which the thermal decomposition reaction begins and ends. In addition, since they are calculated using values obtained from the kinetic model that considers the set of experimental points, they offer a great deal of precision.

CONCLUSION

Dynamic TG, with linear temperature increase, is a useful tool for studying the thermal decomposition of solids, for finding out the reaction order, for evaluating the kinetic parameters (frequency factor and activation energy), and also for estimating their thermal stability. Even if the overall process has no real significance with regard to the reaction mechanism, the Arrhenius doublet (A and E) is useful as a means of quantifying the rate of reaction and for design purposes.

The thermal stability of the alga can be established from the T_5 temperature (i.e., loss of 5% organic content) and, although it varies with the heating rate, it has a mean value of 140°C . On the other hand, the almost total destruction of the alga can be defined from the temperature T_{95} (i.e., loss of 95% organic content) and this, although it also varies with the heating rate, has an average value of 655°C .

When the samples of *Ulva* were subjected to TG, two decomposition reactions were clearly differentiated: the first takes place at temperatures of between 220 and 450°C and the second between 450 and 560°C . In the interval of temperatures close to the maximum rate of decomposition, both zones have sigma curves, and so the thermal decomposition reactions have fit nicely into a kinetic model of n -order reactions. Using an analysis of variance (ANOVA), we determined that

best kinetic model corresponds to first order reactions. In addition, we verified that the summation of an infinite number of terms can be cut down to just two terms, with a very small error (1%). The adjustments of the model are relatively good for the first decomposition reaction ($R^2 = 0.88$) and excellent for the second ($R^2 = 0.99$). The first decomposition reaction has a relatively low activation energy (27–34 kJ/mol), which can be considered independent of the heating rate since the variation is relatively small. Nevertheless, the activation energy of the second decomposition reaction, which occurs at higher temperatures, does vary depending on the heating rate. At 5 K/min an activation energy of 84 kJ/mol is obtained while at 10 K/min, the value is 156 kJ/mol. This large difference between the activation energies can be attributed to several factors:

1. The type of reaction or reaction mechanism will vary as the temperature–time sequence varies. (This obviously depends on the heating rate).
2. There is a compensation factor between pre-exponential factor and the activation energy, which arises as a result of the mathematical adjustment of the experimental points. A greater activation energy is compensated by a smaller factor of frequencies.
3. As the heating rate goes from 5 to 10 K/min, there may appear limitations of heat and mass transfer.

For the first reaction, in conditions of maximum rate of decomposition, the temperature is between 224 and 233°C and conversion is at 13–16%, with slight variations depending on the heating rate. For the second reaction, the temperature is between 517 and 527°C with conversion at 71–77%, also with slight variations depending on the heating rate.

The characteristic temperatures represent the temperatures at which the reaction begins and ends (for the two main reactions considered in this study). The advantage they have is that they are calculated using values obtained from the kinetic model, which considers the set of experimental points, and therefore, they offer a great deal of precision. The characteristic mean temperatures of the first decomposition reaction for

this alga are $T_{c0} = 215^{\circ}\text{C}$ and $T_{c1} = 295^{\circ}\text{C}$, with relative errors of the order of 1–2%. It means that the alga *Ulva* is thermally stable up to 215°C (with a loss of only a small quantity of volatile molecules). The characteristic mean temperatures of the second decomposition reaction are $T_{c0} = 388^{\circ}\text{C}$ and $T_{c1} = 566^{\circ}\text{C}$, with relative errors of the order of 2–6%.

NOMENCLATURE

A	pre-exponential factor
E	activation energy
f	degree of conversion
i	iteration number
k	kinetic constant
n	reaction order
R	gas constant
t	time
T	temperature
T_{c0}	characteristic temperature at $f = 0$
T_{c1}	characteristic temperature at $f = 1$
T_5	temperature at which 5% of the organic mass is volatilized
T_{50}	temperature at which 50% of the organic mass is volatilized
T_{95}	temperature at which 95% of the organic mass is volatilized
w	weight of solids at time t
w_0	initial weight of solids
w_r	residual weight of solids (i.e., residue remaining at the end of thermal decomposition)

Greek letters

β linear heating rate

Subindex

m conditions at maximum rate of decomposition

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