

Heating process characteristics and kinetics of rice straw in different atmospheres

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Abstract

Rice growing engenders large quantities of straw, which is usually burnt in the open field, a practice implying a public health risk. There are, however, several ways of making use of this material, including its conversion into a valuable fuel. The aims of this research are to describe the thermal characteristics of the heating processes of rice straw in different atmospheres of air and nitrogen and to fit the heating profiles to two mathematical models proposed. This research was followed by thermogravimetric analysis, visual observation of the heating profiles revealing three stages in the rice straw heating process: drying, devolatilization and burning. The models described were found to adequately describe the weight loss of rice straw. The approximate integral method (AIM) is less complex than the direct method (DM), but the latter shows the order of reaction. A better fit is obtained for the heating atmospheres with a lesser proportion of oxygen. The presence of oxygen increases the activation energy and decreases the final temperature of each stage considered. © 2003 Elsevier B.V. All rights reserved.

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1. Introduction

Oryza sativa L. (rice) is one of the world's most widespread crops. Annual world production in 2000 amounted to 399.3 million tonnes, as rice is a staple in the daily diet of over half the world's population. A major by-product is rice straw, which is usually treated

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as waste owing to the large amounts generated—it is estimated that a ton of dry rice straw is obtained for every ton of rice grain produced.

In California, USA, where it is one of the most important agricultural waste products in the Sacramento Valley, an average of 1 million tonnes per year is produced, which is usually eliminated by open field burning. Several researchers have studied the effect of the toxic emissions from burning rice straw on air pollution and therefore, on human health [1,2]. Owing to air pollution, the area of rice burned has been phased down by a 1991 law on open field burning passed by the California state legislature (Assembly Bill 1378, Sacramento 1991). Similar legislation has been introduced in other places [3].

Alternative management strategies for this material must be developed. The most widespread one is its re-incorporation into the soil as a source of nutrients for the same wetland rice [4]. Another agricultural option is to make compost to avoid the severe nitrogen immobilization that occurs when fresh straw is incorporated into the soil [5]. Other possibilities include building materials, pulp and paper [6].

All these options mean a significant waste of rice straw's capacity for energy production. The total amount of straw in the state of California represents a potential of 100–200 MWe [1]. Many processes exist for converting rice straw into a valuable fuel, including biological and thermal ones. The former produces ethanol or methane, and the latter heat plus solid, liquid, and gaseous fuels, and a wide variety of by-products [7–9].

Thermal conversions can be classified as combustion (the simplest process), gasification and pyrolysis, which yield, respectively, heat only, combustible gases, and mainly oil and gases.

As the thermochemical conversion of rice straw requires an exhaustive control of the process owing to its high ash content, fouling and low carbon conversion efficiency, a better understanding of the thermal conversion mechanisms at work is necessary before any successful industrial application can be envisaged. In this regard, information on reaction kinetics can be considered a first step. Such information may also be used to describe the mathematical formulation of the reactions and modelling of reactor performance.

Kinetic data for fossil fuels such as coal have been studied by numerous authors [10–12]. In the past, research has also been done into several alternative fuels, especially wood, and their kinetics [13,14] and reports have recently appeared on the kinetic and thermal characteristics of several biomass fuels previously considered as waste [15–17]. However, only a few papers exist on the thermal kinetics of rice straw and information currently available is not sufficient for the comprehensive understanding of the mechanisms involved. Moreover, existing studies deal with kinetics analysed for certain heating rates and pure heating atmospheres [14,18]. For this paper, the heating process was carried out in atmospheres with different proportions of air and nitrogen, which made it possible to ascertain and compare the thermochemical conversion mechanisms at work in combustion, gasification and pyrolysis.

Thermogravimetric analysis (TGA) is a common method for studying the thermal properties of materials [19]. Non-isothermal, or dynamic, TGA is more commonly used than isothermal TGA, as fewer data are needed to determine the reaction kinetics [20].

The objectives of this paper are, therefore, to study the different processes during the heating of rice straw in different atmospheres of nitrogen and air and to fit the heating

profiles to the proposed models, which will allow us to obtain the kinetic parameters of the heating processes.

2. Materials and methods

2.1. Materials

We used rice straw from a commercial variety (M202) collected from Yolo County, in Sacramento Valley, CA, USA.

The sample was knife-milled through a 1-mm screen using a Fritsch Model P-19 mill and stored in an airtight container until the time of use. Before use, samples were ground to pass through 0.2-mm screen for the purpose of feeding to the thermobalance. For the analysis of certain fuel properties, material had to be ground to pass through a 420- μm screen. Representative samples were used in this study.

2.2. Fuel analysis

Before thermogravimetric analysis, rice straw was analysed to determine the main properties that affect to thermal conversion.

Moisture content was determined gravimetrically by the oven drying method. Higher heating value (HHV) at a constant volume was measured by means of an adiabatic oxygen bomb calorimeter. Proximate determinations were made according to modified procedures from ASTM D 3172 to D 3175 (Standard Practice for Proximate Analysis of Coal and Coke), E 870 (Standard Methods for Analysis of Wood Fuels), D 1102 (ash in wood) and E 872 (volatile matter).

For ultimate analysis, straw samples were sent to a commercial laboratory, where standard analytical methods were used. All tests were carried out in triplicate.

2.3. Thermogravimetric analysis

Thermogravimetric analysis was carried out with a TA Instruments DT2960, which is able to provide a continuous measurement of sample weight as a function of time or temperature and, with the appropriate software, produce a DTG signal (rate of weight loss).

Samples weighing 6–9 mg were placed in a pottery crucible and heated at a rate of 15 °C/min from ambient to 923 °C. To simulate the combustion, gasification and pyrolysis processes, samples were heated, in all cases with a flow of 100 ml/min, in seven different atmospheres: 100% air, 80% air/20% nitrogen, 60% air/40% nitrogen, 40% air/60% nitrogen, 20% air/80% nitrogen, 5% air/95% nitrogen and 100% nitrogen, named Atm100, Atm80, Atm60, Atm40, Atm20, Atm5 and Atm0, respectively.

2.4. Kinetic models

Two models were used for studying the kinetic characteristics. The material consists of several components, which presumably decompose independently of one another, so the

best mathematical models for describing overall decomposition consider independent parallel reactions [16].

DTG curves are characterized by the presence of shoulders and/or double peaks due to more than one reaction being involved. The kinetic equations for each single reaction are:

$$\frac{d\omega_i}{dt} = K_i \cdot e^{\frac{-E_i}{RT}} \cdot (1 - \omega_i)^n \quad (1)$$

$$\omega_i = \frac{m_{0i} - m_{ij}}{m_{0i} - m_{fi}} \quad (2)$$

where ω_i is the reacted mass fraction or normalized mass for reaction i at time j ; t is time; R is the gas universal constant; T is the absolute temperature; K_i is the frequency factor; E_i is the activation energy; n is the order of reaction; m_{0i} is the initial mass of the sample i ; m_{ij} is sample mass for the reaction i at time j and m_{fi} is final mass of the sample in that reaction.

2.4.1. Model 1 (approximate integral method—AIM)

In this model, it is assumed that the reaction is a simple first-order one. Therefore, Eq. (1) is modified to obtain the derivative of ω_i with respect to absolute temperature T . For a constant heating rate, the equation can be rewritten as Eq. (3):

$$\frac{d\omega_i}{dT} = \frac{K_i}{q} \cdot e^{\frac{-E_i}{RT}} \cdot (1 - \omega_i) \quad (3)$$

where q is the constant heating rate. The right-hand side of the integral form of Eq. (3) is not directly integrable. Singh [21] shows several approximate solutions to the integral temperature term. The solution given by Agrawal and Sivasubramanian [22] is reported to be the most accurate [20], and can be used to solve the right-hand side of Eq. (3), the resultant solution being Eq. (4):

$$\ln\left(\frac{-\ln(1 - \omega_i)}{T^2}\right) = \ln\left(\frac{k_i}{q} \frac{R}{E_i} \cdot \frac{1 - 2\frac{RT}{E_i}}{1 - 5\left(\frac{RT}{E_i}\right)^2}\right) - \frac{E_i}{RT} \quad (4)$$

The first term on the right tends to be constant over temperature. In this way, a plot of the left-hand side against $1/T$ allows us to determine the activation energy from the slope E_i/R . The frequency factor can be determined from Eq. (4) if E_i is known.

2.4.2. Model 2 (direct method—DM)

It is assumed that the components of the sample decompose independently of one another, so the overall rate of conversion for N reactions can be described by Eq. (5):

$$-\frac{d\omega}{dt} = \sum_{i=1}^n c_i \cdot \frac{d\omega_i}{dt} \quad (5)$$

where c_i is a coefficient that expresses the contribution of each single reaction to the mass global loss.

In this way, Eq. (6) allows us to calculate coefficient c_i after the determination of the frequency factor, activation energy and order of reaction by Eq. (1):

$$\frac{d\omega}{dt} = \sum_{i=1}^N c_i \cdot K_i \cdot e^{\frac{-E_i}{RT}} \cdot (1 - \omega)^n \quad (6)$$

In considering the optimization of the kinetic parameters, we took into account the objective functions proposed by two different research teams: Conesa et al. [23], and Sørum et al. [16]. These objective functions are dependent on the number of points considered in the model. It is not possible to compare the values from them because the authors do not specify the number of points considered. To avoid such dependence when each run has a different number of points to be fitted, a term must be introduced to consider the total number of points. Therefore, these authors' expressions have been divided by the total number of points used for the fitting, which therefore give expressions (7) and (8). Expression (7) is obtained from Conesa's expression and it is described as:

$$\text{OF}_{\text{CC}} = \frac{\sum_i \sum_j \left[\frac{\left(\frac{d\omega}{dt} \right)_{\text{exp } ij} - \left(\frac{d\omega}{dt} \right)_{\text{calc } ij}}{\left(\frac{d\omega}{dt} \right)_{\text{exp } j}^{\text{max}}} \right]^2}{N} \quad (7)$$

where i is the value of the variable at time t for reaction j and N is the number of points considered in the fit. Subscript exp represents the experimental values and subscript calc the calculated values. Finally, superscript max represents the maximum obtained value of the variable.

The other objective function is obtained from Sørum's expression and shown in Eq. (8):

$$\text{OF}_{\text{SC}} = \frac{\sum_{i=1}^N \left[\left(\frac{d\omega}{dt} \right)_i^{\text{exp}} - \left(\frac{d\omega}{dt} \right)_i^{\text{calc}} \right]^2}{N} \quad (8)$$

Subscript j denotes values of the variable at time t , N is the number of points fitted, superscript exp represents the experimental values and calc the calculated values.

Sørum's modified objective function would be similar to the regression variance of the fit. In this way, it shows the dispersion of the experimental values against the calculated values. Conesa's modified objective function gives a value of the dispersion relative to the maximum value of the $d\omega/dt$ because the fit depends on that maximum value. Both have been divided by the total of the points considered.

3. Results and discussion

Table 1 shows the properties of rice straw, literature concerning Californian rice straw giving comparable values [14,18]. However, rice straw ashes from Asia show lower values [24], probably due to management considerations.

Table 1
Rice straw properties

Elemental analysis						Proximate analysis				
C ^a	H ^a	N ^a	S ^a	Cl ^a	O ^a	Moisture ^a	Ash ^a	Volatiles ^a	Fixed carbon ^a	HHV ^b
37.87	4.61	0.63	0.14	1.01	34.87	7.43	19.07	67.95	12.98	14.71

^a In percentage. All values are in dry basis except moisture.

^b HHV: high heating value (MJ/kg).

Rice straw HHV is lower than that of most biomass fuels described in the literature [25–28], although this does not mean that its use as a fuel should be ruled out. Furthermore, it is of considerable interest for power generation because of the large quantities involved.

It will be observed that an elementary analysis rice straw shows a Cl percentage of 1.01 on a dry basis, the combustion of which could lead to dioxin emissions. There are, however, proven environmental benefits, such as a significant reduction of air pollutants and a change from open field burning to controlled heating process [29,30].

On the other hand, it is known that, depending on the amount of excess air, a fixed bed could generate polyaromatic emissions. Although some authors [31,32] have studied the abatement of polycyclic aromatic hydrocarbons from hot gas emissions, further research into this problem will be necessary, but it is not one of the aims of the present paper.

3.1. Thermal analysis of the rice straw heating process

Fig. 1 shows burning profiles for rice straw in the seven different atmospheres tested. Atm0 is representative of a pyrolysis process and Atm100 is representative of a combustion process. Each of the others represents a heating process between pure pyrolysis and pure combustion. Table 2 shows the results of thermogravimetric analysis, such as the initial and final temperature of the reactions taking place, and the maximum DTG value with temperature for each reaction.

A visual observation of the thermograms will reveal three differentiated stages in the rice straw heating process, so three different temperature zones can be interpreted accordingly.

3.1.1. Stage 1: drying

When samples were tested, they contained moisture, owing to the hygroscopic nature of rice straw. The first peak in the burning profiles corresponded to the loss of that moisture and there might also have been some loss of very light volatiles [21]. This first peak was identified as the drying stage, which occurs at temperatures below 125 °C. In most thermogravimetric analyses, authors often neglect this stage because of the very low moisture content of the samples. This stage will not therefore be discussed here.

3.1.2. Stage 2: devolatilization

This stage begins at over 180 °C. Its final temperature depends on the atmosphere tested, increasing as nitrogen content increases. Weight loss in this stage is due to the

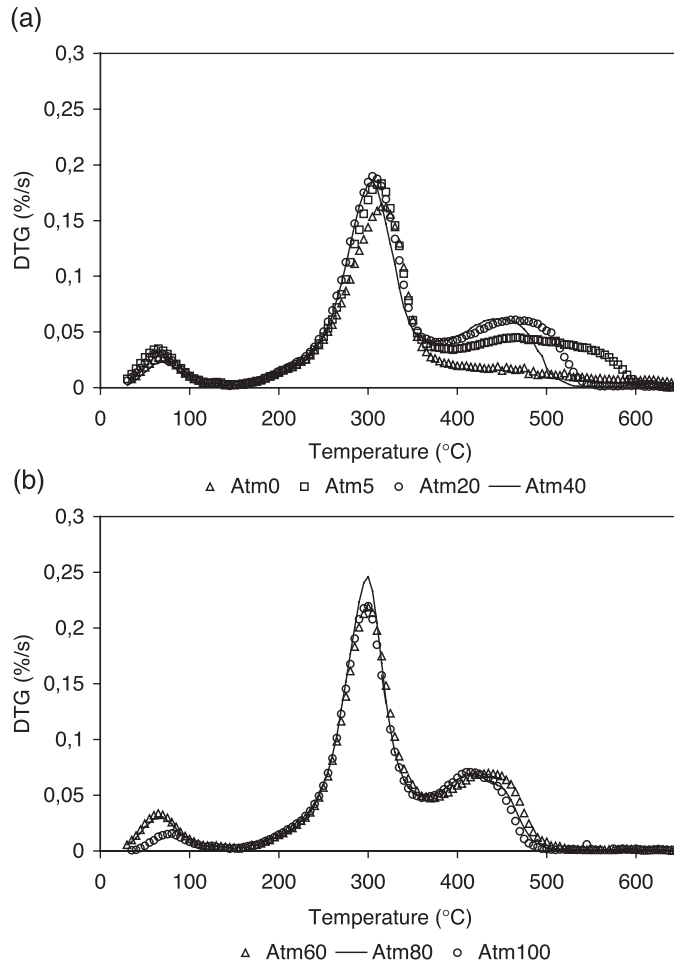


Fig. 1. Rice straw heating profiles. (a) Rice straw heating profiles from Atm0, Atm5, Atm20 and Atm40. (b) Rice straw heating profiles from Atm60, Atm80 and Atm100.

emission of volatiles from cellulose and hemicellulose. Authors [33] have demonstrated that small amounts of volatiles from the lignin component may also be given off in this stage. When there is air in the atmosphere, this stage ends after the next stage starts.

Maximum DTG tends to decrease as the nitrogen content in the heating atmosphere increases, which means that reactions are slower if oxygen content is lower, as the heating atmosphere loses reactivity. So DTG_{max} is 0.22%/s in Atm100 and 0.164%/s in Atm0. These values are lower than those found by Bining and Jenkins [34] due to the different heating rate used. On the other hand, the temperature of maximum DTG increases with nitrogen content, ranging from 299 °C for Atm100 up to 317 °C for Atm0. It may be said that a greater nitrogen content in the heating atmosphere implies a lower reaction speed and the need for a higher temperature for reactions to occur.

Table 2
Results from thermogravimetric analysis for rice straw

	Atm0	Atm5	Atm20	Atm40	Atm60	Atm80	Atm100
<i>Dried</i>							
T_0 (°C)	38	33	37	45	36	38	62
T_f (°C)	100	100	100	98	102	99	95
DTG _{max} (%/s)	0.027	0.035	0.031	0.024	0.032	0.030	0.016
$T_{DTG_{max}}$ (°C)	67	66	64	69	71	66	81
<i>Devolatilization</i>							
T_0 (°C)	190	191	191	191	192	189	189
T_f (°C)	525	405	410	390	385	380	360
DTG _{max} (%/s)	0.164	0.184	0.191	0.186	0.220	0.245	0.220
$T_{DTG_{max}}$ (°C)	317	312	312	302	301	300	299
<i>Combustion</i>							
T_0 (°C)		330	331	320	300	291	290
T_f (°C)		592	535	508	493	491	476
DTG _{max} (%/s)		0.045	0.061	0.062	0.070	0.070	0.070
$T_{DTG_{max}}$ (°C)		458	467	451	438	418	420

T_0 is the initial temperature of the process; T_f is the final temperature of the process; DTG_{max} is the largest value of DTG in the considered process; and $T_{DTG_{max}}$ is the temperature associated to DTG_{max}.

3.1.3. Stage 3: combustion

In 100% air this stage starts at 300 °C, higher temperatures being needed as nitrogen proportion increases. Obviously, this stage cannot take place in 100% nitrogen as there can be no oxidation. Be that as it may, a weight loss takes place due to both devolatilization and reaction between char and volatiles from previous stages [21].

There is combustion of volatiles in the gas phase during this stage. Due to the exothermic nature of this process, the additional heat permits the emission of remaining volatiles as well as a rapid oxidation of the remaining combustible components.

The tendency of DTG_{max} for this stage is the same as for the previous one. It has a value of 0.070%/s for Atm100 decreasing to 0.004%/s for Atm5, while the temperature for DTG_{max} ranges from 420 °C in Atm100 to 458 °C in Atm5.

3.2. Kinetic evaluation

DTG profiles from the thermobalance are obtained considering the difference between the initial and instantaneous mass over time. However, it is not possible to use these values for model kinetic calculations because of the definition of the model equations given in Materials and methods. It is therefore necessary to process the DTG data beforehand.

The two models considered allow for the calculation of the frequency factor (K) and the activation energy (E). The second model also permits the calculation of the order of reaction (n) and the reacting mass. These parameters were calculated for each of the shoulders considered except for the drying stage. The results of kinetic parameters are given in Tables 3 and 4. As an example of the DM method, Fig. 2 shows the kinetic fit of

Table 3
Kinetic parameters of rice straw from AIM and DM

	Atm0	Atm5	Atm20	Atm40	Atm60	Atm80	Atm100
<i>Devolatilization</i>							
AIM	<i>E</i> (kJ/mol)	70	76	78	78	80	83
	<i>K</i> (1/s)	7.32×10^6	2.70×10^6	6.00×10^6	2.46×10^8	2.35×10^6	7.93×10^6
	R^2	0.9988	0.9983	0.9976	0.9966	0.9965	0.9982
DM	<i>E</i> (kJ/mol)	85	90	121	123	109	131
	<i>K</i> (1/s)	2.54×10^5	9.36×10^5	1.15×10^9	5.41×10^6	9.11×10^7	1.43×10^{10}
	<i>n</i>	0.86	1.04	2.39	1.16	1.72	1.78
	<i>c</i>		0.612	0.116	0.716	0.706	0.670
						0.670	0.654
<i>Combustion</i>							
AIM	<i>E</i> (kJ/mol)		76	100	125	126	117
	<i>K</i> (1/s)		5.15×10^2	5.83×10^4	7.42×10^6	1.33×10^7	3.83×10^6
	R^2		0.9933	0.9910	0.9912	0.9945	0.9937
DM	<i>E</i> (kJ/mol)		34	128	123	148	99
	<i>K</i> (1/s)		4.31×10^1	6.21×10^6	1.96×10^9	6.37×10^8	1.63×10^5
	<i>n</i>		0.57	1.3	2.18	1.25	1.08
	<i>c</i>		0.387	0.292	0.284	0.279	0.337
						0.337	0.348

K is the frequency factor; *E* is the activation energy; *n* is the order of reaction; R^2 is the linear regression coefficient; and *c* is the contribution of the single reaction to the mass global lost.

rice straw heated in Atm40. When the AIM method is used, the square of the correlation coefficient is a measure of the linear regression fit between the experimental conversion and the calculated conversion, and is included in Table 3. Modified expressions (7) and (8) serve to determine a measure of fit between experimental and calculated data when DM is used. In this way, it is possible to compare these fits with other experiments as these objective functions are independent of the number of points considered. Sørum's and Conesa's original functions do not allow for that comparison.

In general, for both the devolatilization and combustion stages, the activation energy values obtained with AIM are higher than those obtained with DM. The same may not be said for the factor frequency values, where an unclear tendency is to be noticed.

In the devolatilization stage, the activation energy varies from 83 kJ/mol for Atm100 down to 70 kJ/mol for Atm0 when determined by the approximate integral method (AIM). The corresponding frequency factor values are 6.19×10^{13} and $7.23 \times 10^6 \text{ s}^{-1}$. The activation energy determined by DM varies from 113 kJ/mol for Atm100 to 85 kJ/mol for Atm0, with corresponding frequency factor values of 2.85×10^8 and $2.54 \times 10^5 \text{ s}^{-1}$. The largest activation energy value obtained by DM is for Atm80: 131 kJ/mol with

Table 4
Objective functions values by DM model

	Atm0	Atm5	Atm20	Atm40	Atm60	Atm80	Atm100
OFcc	8.31×10^{-2}	7.70×10^{-2}	2.52×10^{-1}	1.15×10^{-1}	2.09×10^{-1}	1.28×10^{-1}	5.03×10^{-1}
OFsc	6.57×10^{-7}	6.08×10^{-7}	1.99×10^{-6}	9.09×10^{-7}	2.36×10^{-6}	1.01×10^{-6}	3.97×10^{-6}

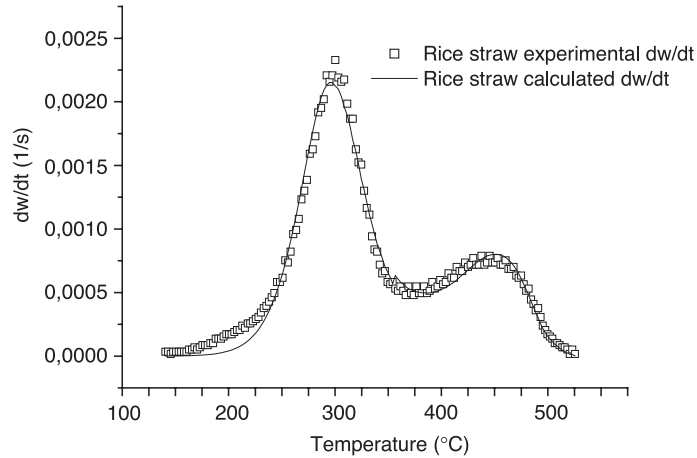


Fig. 2. Kinetic fit by DM model of rice straw when the atmosphere heating is Atm40.

a corresponding frequency factor value of $1.43 \times 10^{10} \text{ s}^{-1}$. Regardless of the model used, the lowest value is always for Atm0. The presence of oxygen means that the activation energy increases, for alongside the pyrolysis reactions, oxidant ones also take place.

In the combustion stage, with AIM the activation energy varies from 126 kJ/mol for Atm100 to 76 kJ/mol for Atm5. The maximum value is again obtained for Atm100 and the lowest for the atmosphere poorest in oxygen, with corresponding frequency factor values of 2.12×10^7 and $5.15 \times 10^2 \text{ s}^{-1}$, respectively. The highest value for the activation energy with DM is for Atm60, 148 kJ/mol, and the lowest again for Atm5, 34 kJ/mol. Obviously, this stage does not take place in Atm0. It will be observed that, in general, the values of activation energy increase with the quantity of oxygen in the atmosphere, perhaps because the number of oxidant reactions is higher and they occur at a lower temperature, that is, the temperature for DTG_{max} is lower. This was borne out when a higher emission of CO_2 was observed in the heating process when there was more oxygen in the atmosphere. Gas emissions associated with the heating processes were monitored with mass spectrometry equipment in line with the thermal analysis apparatus.

The lowest activation energy values, therefore, are always for Atm0 when the devolatilization stage is taken into account, and for Atm5 when the combustion stage is considered.

Other authors, such as Conesa et al. [23] and Sørum et al. [16], present similar activation energy values for other materials, such as municipal solid wastes. Jaber and Probert [35] studied pyrolysis and gasification kinetic processes for oil shales, obtaining activation energy values lower than those found in our study.

AIM is a simple first-order kinetic model while DM offers information about the order of the reaction. It will be observed that the lowest reaction order values are obtained for the atmospheres without oxygen, probably because no oxidation reactions occur. The highest reaction order values are obtained for the atmospheres that simulate the gasification process probably because more complex reactions are taking place.

Both objective functions used show a better fit for Atm5 and Atm0 (the heating atmospheres with least oxygen), as shoulders or double peaks in DTG profiles decrease and the fit is better.

4. Conclusions

The nitrogen content of the heating atmosphere slows the reactions down and necessitates a higher temperature.

The models set out in Materials and methods were found to describe adequately the weight loss of the rice straw. With the approximate integral method model, it is possible to obtain the activation energy and the frequency factor for the differentiated stages in the thermal process. With the direct method model, the order of reaction is also calculated. In this regard, the latter is a more complete model but the former has the advantage of simplicity. In general, for both the devolatilization and combustion stages, the activation energy values obtained with AIM are higher than those obtained with DM. The same may not be said for the factor frequency values, where an unclear tendency may be appreciated. It may be that the presence of oxygen increases the activation energy value and decreases the final temperature of each stage. The values obtained for the kinetic parameters are of the same order as those found by other authors for different material considered biowastes.

A better fit is obtained for the heating atmospheres with less oxygen in their composition. The modified objective functions defined in this paper are independent of the number of points considered in the model, which allows for comparing fits.

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