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Nonisothermal drying kinetics of biomass fuels by thermogravimetric analysis under oxidative and inert atmosphere

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ABSTRACT

In depth investigation of nonisothermal drying kinetic, the first stage of thermal decomposition was conducted using thermogravimetric analysis, to deepen the thermal processes' knowledge. The studied biomass wastes were peach pits, marc, and stalk from the canning, jam, and wine industries, respectively. The experimental data have been obtained under oxidative and inert atmospheres at different heating rate (5, 10, and 15 K/min), to fit to different isoconversional models to describe drying behavior of agro-industrial wastes. These models were evaluated based on different statistical parameters. The best fitting for all experiments were showed by Jander's model. It is assumed that the three-dimensional diffusion is the drying rate controlling step. The calculated activation energy values are between 20.31 and 48.41 kJ/mol for all agro-industrial wastes at different experimental conditions. Calculated kinetic parameters for the nonisothermal drying under nitrogen atmosphere are generally higher than those for this phenomenon under air atmosphere. Different physicochemical phenomena are produced, which cause this variation during the drying under different atmospheres. Heating rates have a slight effect on the activation energy since the kinetic rate of drying phenomenon is controlled by the physical transformation occurrence, which is dependent on temperature and it is not on mass dependent.

Introduction

Biomass, particularly agro-industrial wastes, is a renewable fuel and the fourth largest following coal, oil, and natural gas. If it is compared to these fossil fuels, it has the advantages of being neutral concerning the emissions of the greenhouse gas carbon dioxide, because it participates in biomass growth through the photosynthesis reactions and the reducing pollutant species generation due to the low sulfur and nitrogen contents. Biowastes can create major environmental problems if not properly handled. There are growing interests in worldwide efficient biomass thermal conversion technologies developing to combat climate change and provide the solutions for current energy crisis. Therefore, it is recommended to recycle this material to yield other functional products or green energy. The recent Argentine political are strongly encouraging in the biomass use for energy purposes, mainly owing to three targets economic and social development of countryside, elimination of wastes, and reduction of CO_2 emissions. The most highly developed obtaining energy or fuels from biomass technologies are those based on thermochemical treatments, namely, pyrolysis, gasification, and combustion.

During the pyrolysis, the high yield of bio-oil is obtained, but the high oxygen content and phenolic oligomers presence difficult the biorefinery development.[1] Gasification is considered as a suitable technology for the treatment of lignocellulosic wastes,[2] but tar formation is a problem to be solved to optimize the use of syngas. However, the biomass combustion has comparative advantages into operating conditions and fuel flexibility.

The moisture content of biomass wastes is an important property in the thermal treatment (pyrolysis, gasification and combustion) since the moisture levels may affect its performance and reliability. As is well known, the first step of pyrolysis and combustion corresponds to water evaporation, which requires energy and reduces overall process efficiency. Numerous pyrolysis and combustion studies have used this dry-basis biomass for experimental research and kinetic analysis.[3,4] From the literature point of view, little attention has been given to this stage, because the biomass used in the pyrolysis and combustion studies is not composed of raw materials but of dried materials. However, the moisture content also has an impact on transport and storage of biomass wastes. High moisture content has

a much lower net energy density by mass, owing to the weight of the water, but also by volume due to the energy required to evaporate the water.

The kinetic modeling of the drying stage is crucial for an accurate prediction of the material's behavior under different working conditions. Investigation of this stage kinetics and its parameters contributes to further information of heat and mass transfer.

Drying is a complex process of heat and mass transfer, therefore, in practice; effective models are necessary for mechanism analysis and process prediction. Theoretical models include many assumptions that cause considerable errors, while the empirical models strongly depend on the experimental conditions. Their application is less than the semitheoretical models, which need fewer assumptions and give more information on the drying behaviors. The semitheoretical drying models are the Page and Newton models, derived by analogues with Newton's law of cooling, while the other two models were derived from Fick's second law of diffusion.[5] Chen et al.[6] used the nonisothermal Page model and the activation energy in the drying stage ranged from 10 to 30 kJ/mol. These researchers worked with wheat straw and corn stalk. Chen et al.[7] studied the heat and mass transfer characteristics of biomass in the first pyrolysis stage of rice husk and cotton stalk, which takes place in the range of temperature to 423 K. These researchers found that the Page model describe the nonisothermal drying kinetics. The calculated activation energy was determined to be 9.2 and 15.1 kJ/mol for rice husk and cotton stalk, respectively.

On the other hand, the isoconversional integral and differential models are equations widely used because they are able to estimate the activation energy, which requires only a mathematical approximation for the temperature dependency. However, when the pre-exponential factor and reaction order are to be estimated, it is mandatory to use an approximation for the composition dependency. These methods have the ability to reveal complexity of the process in the form of a functional dependence of the activation energy on the extent of conversion. Application of model-free methods was highly recommended to obtain a reliable kinetic description of the investigated process. The basic assumption of these models is that the reaction rate for a constant extent of conversion depends only on the temperature. These models do not require previous knowledge of the reaction mechanism for biomass thermal degradation. Another advantage of isoconversional approaches is that the systematic error resulting from the kinetic analysis during the estimation of the Arrhenius parameters is eliminated. They can follow either a differential or an integral approach to the treatment of TGA data.

Coats–Redfern, FWO, Vyazovkin, and Kissinger–Akahira–Sunose methods are classified like integral isoconversional methods. Friedman, Sharp, and Friedman–Reich–Levi models are differential methods.

Then, the aim of this work was to study the nonisothermal drying kinetics of marc, stalk, and peach pits from Argentine agro-industry. The isoconversional methods were used to obtain the kinetic parameters (pre-exponential factor and activation energy). Different models were applied, using integral and differential methods.

Materials and methods

Materials

The raw material used in this work was peach pits from canneries and jam factories and marc and stalk from wineries located in the San Juan province, localized in Cuyo Region, Argentine. This material was ground, sieved and the resulting 0.10–0.21 mm size fraction was used for the thermogravimetric tests. ASAE Standard S319.3 was used to determine the size distribution of the ground samples.[8] The weight loss at 378 K, ash and organic matter content were conducted according to ASTM standards.[9,10] Ultimate analyses of the samples were performed using EuroEA3000 model elemental analyzer. The results are shown in Table 1.

To calculate the high heating value (HHV), the correlation proposed by Channiwala and Parikh[11] was used (Table 1):

$$HHV\ (MJ/kg) = 0.3491C + 1.1783H + 0.1005S \\ - 0.1034O - 0.0151N - 0.0211A \tag{1}$$

where C, H, S, O, N, and A are the content of carbon, hydrogen, sulfur, oxygen, nitrogen, and ash in the peach pit, respectively.

The concentration of 28 elements in the peach pit samples were determined using inductively coupled plasma mass spectrometer Shimadzu ICPE 9000. The results are shown in Table 2.

Table 1. Results of proximate and ultimate analyses (dry basis, weight percentage).

	Peach pits	Stalk	Marc
C (%)	53.01	46.14	52.91
H (%)	5.90	5.74	5.93
N (%)	2.32	6.37	5.41
S (%)	1.88	4.21	5.34
O (%)	36.89	37.54	30.41
Ash (%, dry basis)	1.30	10.16	8.81
Volatile matter (%, total weight)	79.10	55.84	68.60
Fixed carbon (%, dry basis)	13.90	23.07	21.98
Weigth loss at 105℃ (%, total weight)	5.70	7.70	8.38
HHV (MJ/kg)	21.39	18.33	20.41

HHV, High heating value.

Table 2. Metals contents in agro-industrial wastes (dry basis).

	Peach pits	Stalk	Marcs
Cu (µg/g)	15.32	17.31	14.86
Al (µg/g)	27.19	28.86	26.97
Si (µg/g)	1.66	4.22	4.04
Na (µg/g)	103.10	149.10	105.90
K (µg/g)	118.50	191.90	160.70
Ca (µg/g)	53.40	276.60	165.40
Mg (µg/g)	26.85	63.72	48.67
Zn (µg/g)	22.42	24.26	22.36
P (µg/g)	15.03	63.64	72.27
Ba (µg/g)	12.71	5.11	5.36
As (µg/g)	3.47	3.65	2.12
Co (µg/g)	3.62	3.57	3.54
In (µg/g)	7.77	8.14	8.27

Thermogravimetric analysis

Thermogravimetric and derivative thermogravimetric (DTG) experiments of the powdered samples of peach pits, marcs, and stalks were performed using a TGA-50 Shimadzu microbalance, under nitrogen and air atmospheres, heated from room temperature to 1173 K. The experiments were performed at three different heating rates of 5, 10, and 15 K/min for each sample. To mitigate the difference of heat and mass transfer, all samples' weight were kept at 12 mg approximately. The inert gas used for pyrolysis was nitrogen with a flow rate of 100 mL/min. For the experiment under oxidative atmosphere, air was used; its flow rate was of 100 mL/min. The reproducibility of the experiments was acceptable.

Nonisothermal drying kinetics

Drying is a complex process of heat and mass transfer; it is difficult to understand in the microscopic level because mathematical descriptions have many deficiencies. Therefore, in practice, effective models are necessary for mechanism analysis and process prediction.

The semitheoretical drying models considering their nonisothermal forms (Henderson and Pabis, Newton, Page and logarithmic models[12]) were also used in this study but the setting between the experimental and predicted data was not satisfactory because the statistical parameters were high, indicating a bad fitting. For this reason, the following procedure was applied. The kinetics of biomass decomposition are routinely based on a single reaction and can be expressed under by the following equation:

$$-\frac{d\alpha}{dt} = Kf(\alpha) \qquad (2)$$

where t, α, $d\alpha/dt$, $f(\alpha)$, and K are time, conversion degree or extent of reaction, the process rate, conversion function, and rate constant, respectively. The conversion function represents the reaction model used and depends on the controlling mechanism. The extent of reaction, α can be defined as the mass fraction of biomass substrate that has decomposed and can be expressed as shown below:

$$\alpha = \frac{W_0 - W}{W_0 - W_f} \qquad (3)$$

where W, W_0, and W_f are the mass present at any time t, the initial mass and final mass of solids remaining after the reaction, respectively.

K is the temperature function. The temperature dependence of the rate constant K for the process is described by the Arrhenius equation:

$$K = Ae^{-E_a/RT} \qquad (4)$$

where A is the pre-exponential factor, T is the absolute temperature, R is the universal gas constant, and E_a is the apparent activation energy of the process. Substituting Eq. (4) in Eq. (2):

$$\frac{d\alpha}{dt} = Ae^{-E_a/RT}f(\alpha) \qquad (5)$$

If the temperature of the sample is changed by a controlled and constant heating rate, $\beta = dT/dt$, the variation in the conversion can be analyzed as a function of temperature, this temperature being dependent on the heating time. This variation can be expressed through a superficial transformation:

$$\frac{d\alpha}{dT} = \frac{d\alpha}{dt}\frac{dt}{dT} \qquad (6)$$

where dt/dT describes the inverse of the heating rate in case of nonisothermal conditions, $1/\beta$, $d\alpha/dt$ represents the isothermal reaction rate, and $d\alpha/dT$ denotes the nonisothermal reaction rate. An expression of the rate law for nonisothermal conditions can be obtained by substituting Eq. (6) in Eq. (5):

$$\beta\frac{d\alpha}{dT} = Ae^{\frac{-E_a}{RT}}f(\alpha) \qquad (7)$$

where A (the pre-exponential factor) and E (the activation energy) are the Arrhenius parameters and R is the gas constant. Arrhenius parameters (A, E), together with the reaction model, $f(\alpha)$ are called the kinetic triplet. By separation of variable and integration, the following equation is obtained:

$$g(\alpha) = \int_0^\alpha \frac{d\alpha}{f(\alpha)} = \frac{A}{\beta}\int_{T_0}^T e^{-\frac{E_a}{RT}}dT \qquad (8)$$

For nonisothermal conditions, there are several relationships used to compute Arrhenius parameters, each of which is based on an approximate form of the temperature integral.[13] Equation (8) can be rewritten

by taking $x = E_a/RT$:

$$g(\alpha) = \int_0^\alpha d\alpha/f(\alpha) = AE/\beta R \int_0^\infty \frac{\exp(-x)}{x^2} \qquad (9)$$
$$dx = AE/\beta R \cdot p(x)$$

where $p(x)$ is the exponential integral. Senum and Yang[14] developed an accurate nonlinear approximation of the temperature integral.

In the literature, several methods, which can be performed kinetic analysis of solid state reactions, are known. Generally, they can be grouped in (a) integral methods: if data used directly in weight loss versus temperature and (b) differential methods: using weight loss rate.

The Coats–Redfern integral method is more used of the first group and they are based in the Arrhenius integral approximation. The Sharp differential method is more used of the second group and they use the reaction rate or its transformed mathematics.

The expression $p(x)$ is expressed using the Coats–Redfern approximation[15]:

$$p(x) = \frac{e^{-x}}{x^2} \qquad (10)$$

Replacing $p(x)$ in the Eq. (9) and applying logarithm to both members:

$$\ln\frac{g(\alpha)}{T^2} = \ln\frac{AR}{E_a\beta} - \frac{E_a}{RT} \qquad (11)$$

Plotting the left-hand side of Eq. (10), which includes $g(\alpha)$ versus $1/T$, gives E_a and A from the slope and intercept, respectively.

Sharp et al. use the logarithms form of the Eq. (2)[16]:

$$\ln f(\alpha) = \frac{E_a}{RT} + \ln\left(\frac{d\alpha/dt}{A}\right) \qquad (12)$$

The kinetic parameters are calculated follows a method similar to the preceding. Some of the more important rate equations used to describe the kinetic behavior of solid-state reactions are listed in Table 3.

Table 3. Expressions for the most common reaction mechanisms in solid-state reactions.

Reaction model	Symbol	f(a)	g(a)
Order zero mechanism	R1	1	a
Order ½ mechanism	R2	$(1-a)^{1/2}$	$2[1-(1-a)^{1/2}]$
Order 2/3 mechanism	R3	$(1-a)^{2/3}$	$3[1-(1-a)^{2/3}]$
One-dimensional diffusion	D1	$1/(2a)$	a^2
Two-dimensional diffusion	D2	$-1/\ln(1-a)$	$(1-a)\ln(1-a)+a$
Three-dimensional diffusion (Jander)	D3	$3(1-a)^{2/3}/2$ $[1-(1-a)^{1/3}]$	$[1-(1-a)^{1/3}]^2$
Three-dimensional diffusion (Ginstling–Brounstein)	D4	$3/2[(1-a)^{-1/3}$ $-1]^{-1}$	$(1-2a/3)-(1-a)^{2/3}$

These expressions are used to solve the Eqs. (11) and (12). The fitting of the experimental data of $g(\alpha)$ and $f(\alpha)$ versus temperature for all proposed models was performed using Data Fit 9.1 software, estimating the E_a and A.

Results and discussion

Characterization

The results of the proximate and ultimate analyses are shown in Table 1. High water content increases the energy requirements to perform the thermal treatment, rises the residence time for drying, and reduces the temperature, resulting in incomplete conversion of the hydrocarbons. These aspects decrease the process efficiency. The marc has the highest moisture content. Regarding the ash content of three agro-industrial wastes, a low percentage of it will minimize the production of fly and the bottom ash and affect positively the HHV.

The ultimate analysis showed higher oxygen concentrations (30.41–37.54%). These concentrations have a negative impact on the HHV because (carbon–oxygen bonds) tends to decrease the calorific value of studied agro-industrial wastes. Demirbas and Arin[17] determined the HHV for 16 different biomass fuels and reported similar values, Quirino et al.[18] reported similar values for wood, too.

Twenty-eight metals are analyzed and Fe, Cr, Pb, Sn, Mo, Ni, Ag, Ti, V, Mn, Cd, and B are not present in the composition of the studied agro-industrial wastes. The chemical composition of the mineral matrix has a great influence on the kinetics of heavy metal vaporization; it determines the bonding strength between the mineral matrix and these elements as well as the time required for diffusion out of the particle. Thus, basic species in the matrix (SiO_2, Al_2O_3, CaO) can react with these metals encapsulating them in the particle center. Velghe et al.[19] studied the municipal sewage sludge pyrolysis and found that the distribution of metal ions toward oils is negligible, most of the metals retain in the pyrolysis reactor: on fixed carbon, as metallic pieces and on sand.

Mayer et al.[20] analyzed the pyrolysis of metal- and ash-enriched wood and the combustion properties of the gained char and concluded that (a) the cellulose can bind more metals than lignin; (b) the metal-binding capacity of wood is stronger in case of heavy metals like Pb and Cd than for alkali earth and alkaline metals; (c) the presence of Ca, Fe, Pb, and Zn ions slightly changed the main degradation peak temperature of cellulose while Na, Mg, and Cd ions did not seem to affect the mass loss rate during pyrolysis; (d) char formation

was influenced mainly by the quantity and not the quality of the metal ions.

Kinetic behavior of drying under inert and oxidative atmospheres

To predict the nonisothermal drying, the first peak of DTG curves was considered in all cases. This peak is produced between 298 and 423 K. Fitting calculations have been performed using the models listed in Table 3. With the purpose of evaluating each model, an estimation of the parameter values is needed. The statistical parameter determined apart from the determination coefficient, R^2, were the reduced χ^2 defined by:

$$\chi^2 = \frac{\sum_1^N \left(X_{\text{exp},i} - X_{\text{pre},i}\right)^2}{N - z} \quad (13)$$

where $X_{\text{exp},i}$ is the experimental moisture ratio, $X_{\text{pre},i}$ is the predicted moisture ratio, N is the number of experimental data points, and z is the number of parameters in the model.

The R^2 values for the models are greater than the acceptable R^2 value of 0.90 for the following models: (a) for marc and stalks: D1, D2, and D3, under both atmospheres; (b) for peach pits: D1, D2, D3, and D4, under nitrogen atmosphere; and (c) for peach pits: D3 and D4, under air atmosphere. However, the highest R^2 values are presented for the model D3, under both atmosphere and for all agro-industrial wastes.

It can be observed that Jander's model has the best fit for nonisothermal drying of all studied agro-industrial wastes under both atmospheres, using differential and integral isoconversional methods. However, the Sharp procedure presented better statistical parameter values since the isoconversional differential methods are more accurate than the integral methods. Furthermore, Li and Tang[21] found that activation energy values are consistently overestimated using integral isoconversional methods versus those evaluated using differential isoconversional method.

Tables 4–6 show the pre-exponential factor and activation energy obtained and the statistical parameter values for different studied agro-industrial wastes. For

Table 5. Pre-exponential factor and activation energy obtained and the statistical parameter values for stalk.

Atmosphere	Heating rate, β (K/min)	E_a (kJ/mol)	Statistical parameter values	
			χ^2	R^2
Oxidative	5	36.56	3.17	0.98
	10	23.12	3.17	0.96
	15	22.72	1.99	0.94
Inert	5	41	1.23	0.99
	10	48.41	9.55	0.97
	15	38.22	5.14	0.98

this model, the R^2 and χ^2 values were between 0.92 and 0.98, 0.55 and 9.55, respectively. These statistical parameter values present greater variation for the studied agro-industrial wastes. The higher values of R^2, and the lower values of χ^2, the better is the goodness of fit. Figures 1–6 show the comparison between the predicted values of $f(\alpha)$ calculated by this model and the experimental data, observing a good correlation. These figures demonstrate that Jander's model fits the drying kinetics of studied agro-industrial under inert and oxidative atmospheres perfectly well. A lightly better fit is obtained for the experimental data under inert atmosphere, except the case of marc, presenting similar values of R^2 (Table 6). However, the χ^2 values not present this tendency, perhaps, due to the curves' noises at the beginning of the drying phenomenon (Figs. 1–6 and Tables 4–6). The Jander's model follows the assumption that the movement of the frontier between the solid in the time t and the original material determines the drying rate. D3 is the equation for diffusion-controlled reaction in a sphere. Masnadi et al.[3] studied the copyrolysis of two types of biomass with widely differing ash compositions, Manitoba switchgrass and beetle-killed BC pine sawdust from British Columbia and fossil fuel. These researchers applied the isoconversional Coats–Redfern method and they concluded for the first pyrolysis stage below 473 K that the Zhuravlev diffusion model gave the best fit implying that it corresponds to the reaction mechanism to evaluate the activation energies of all fresh and mixture samples. Hnini et al.[22] analyzed the drying of red alga under inert atmosphere. They applied the Coats–Redfern method and found that the global phenomenon is controlled by the three-dimensional diffusion according to Jander's law.

Table 4. Pre-exponential factor and activation energy obtained and the statistical parameter values for peach pit.

Atmosphere	Heating rate, β (K/min)	E_a (kJ/mol)	Statistical parameter values	
			χ^2	R^2
Oxidative	5	47.05	2.38	0.92
	10	21.39	0.63	0.96
	15	20.31	1.17	0.95
Inert	5	33.39	1.48	0.97
	10	28.92	0.55	0.97
	15	27.7	0.81	0.96

Table 6. Pre-exponential factor and activation energy obtained and the statistical parameter values for marcs.

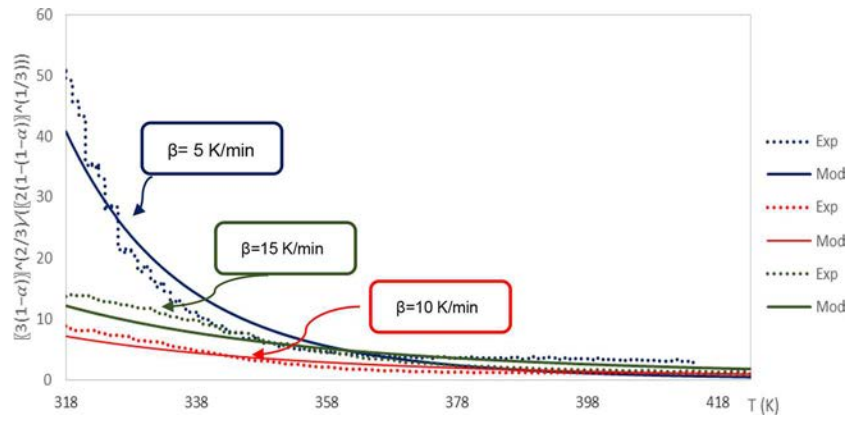| Atmosphere	Heating rate, β (K/min)	E_a (kJ/mol)	Statistical parameters values	
			χ^2	R^2
Oxidative	5	35.35	3.24	0.98
	10	26.31	2.09	0.98
	15	32.57	2.81	0.98
Inert	5	25.32	1.73	0.98
	10	42.51	8.08	0.98
	15	30.81	6.06	0.97

Figure 1. Comparison of experimental and predicted values of f(α) for peach pits drying under air atmosphere at different heating rates.
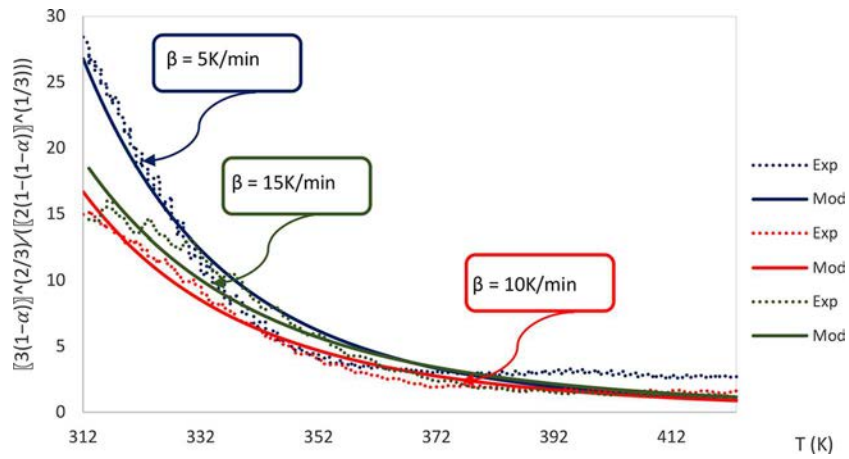

Figure 2. Comparison of experimental and predicted values of f(α) for peach pits drying under nitrogen atmosphere at different heating rates.
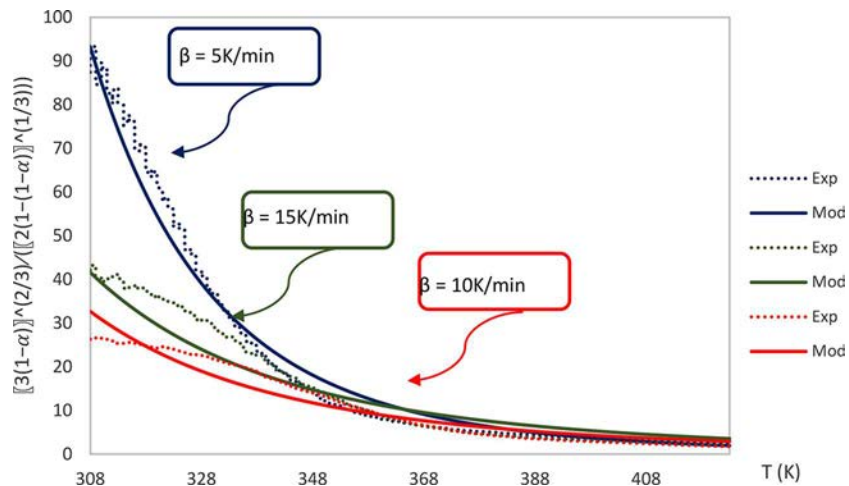

Figure 3. Comparison of experimental and predicted values of f(α) for stalk drying under air atmosphere at different heating rates.
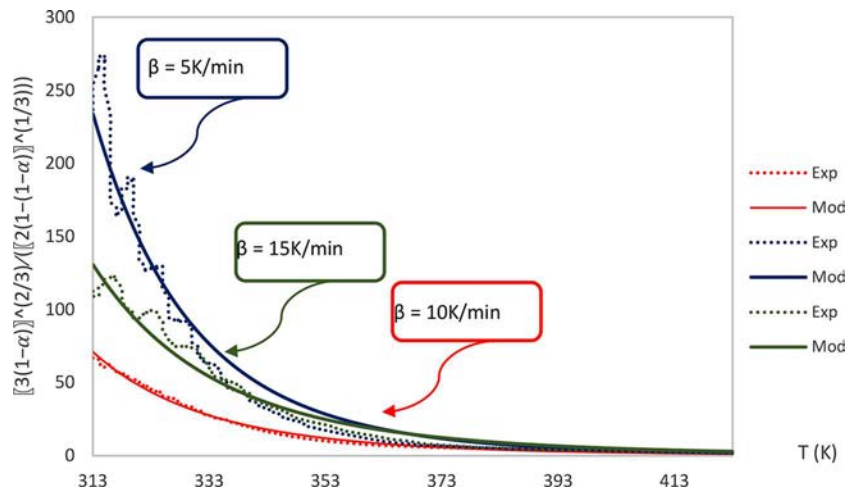
Figure 4. Comparison of experimental and predicted values of $f(a)$ for stalk drying under nitrogen atmosphere at different heating rates.
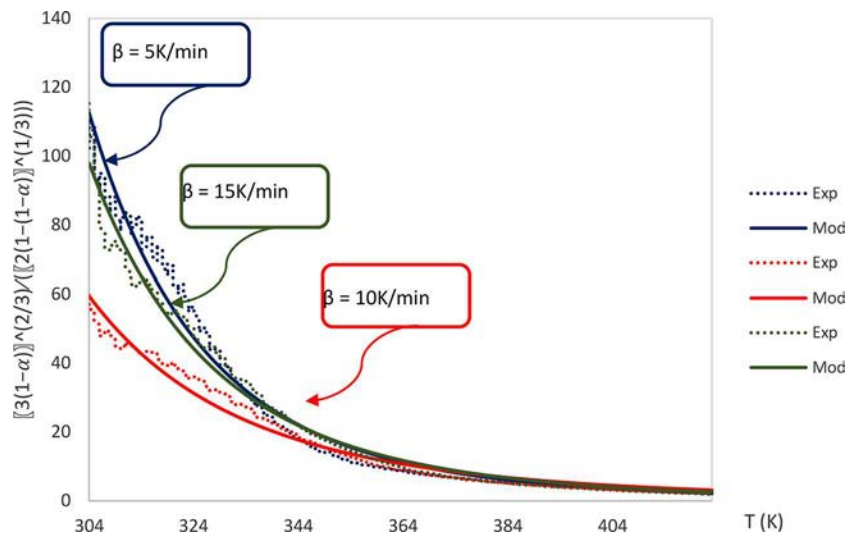

Figure 5. Comparison of experimental and predicted values of $f(a)$ for marc drying under air atmosphere at different heating rates.
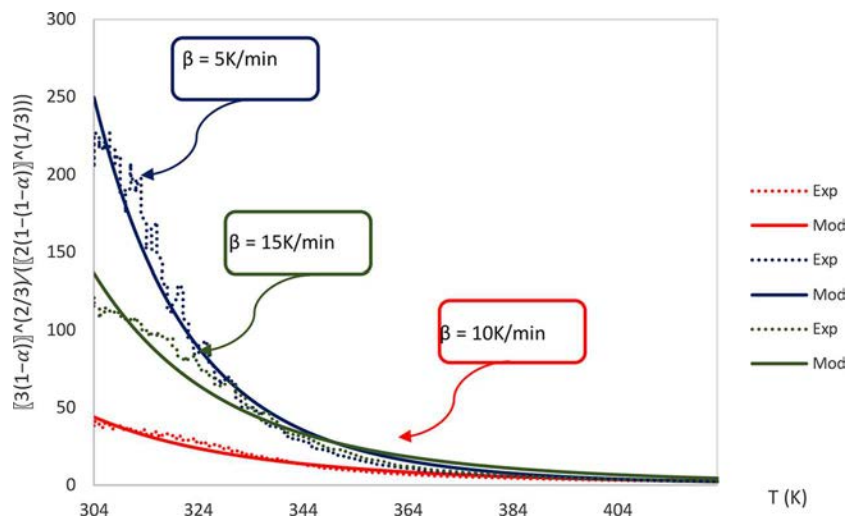

Figure 6. Comparison of experimental and predicted values of $f(a)$ for marcs drying under nitrogen atmosphere at different heating rates.

Optimal E_a values were obtained, generally in the ranges of 20.31 and 48.41 kJ/mol for different studied agro-industrial wastes under both atmospheres. The lowest activation energy value was obtained for the peach pit drying under air atmosphere heating at 15 K/min.

The highest value of this parameter was predicted for stalks under nitrogen atmosphere heating at 10 K/min. The found activation energy values are similar to obtained values by Chen et al.[6], although they are lightly higher, but the values obtained in this work are always higher than those obtained by Chen et al.[7] However, Chen et al.[23] reported values between 143.8 and 152.03 kJ/mol for the drying stage during the pyrolysis process of different lignocellulosic biomass.

Generally, E_a for the drying under nitrogen atmosphere are higher than those for this phenomenon under air atmosphere. This fact suggests that under oxidative atmosphere, the studied agro-industrial wastes need less energy for drying than under inert atmosphere. The recorded weight loss in the region of lower temperatures for inert and oxidant atmospheres could, in both cases, be attributed to the release of moisture or of substances physically absorbed to the surface. Tahmasebi et al.[24] founded that during air drying, the aliphatic hydrogen region was the most active sites regarding to reaction with absorbed oxygen. Therefore, carboxyl and carbonyl groups increased gradually with oxidation temperatures up to 423 K. Carboxylate groups showed a negligible decrease in absorption in this temperature region. However, these researchers concluded that during drying under nitrogen atmosphere, the aliphatic hydrogen absorption remained relatively unchanged up to 473 K, indicating that methylene groups are preferably lost up to 423 K. This is due to a progressive loss of alkyl chains and the conversion of hydroaromatic methylene structure to aromatic rings.[25] These researchers concluded that drying under inert environment up to 523 K can significantly decrease its oxygen content and increase its degree of aromaticity. These described phenomena could explain the variation of E_a values with the drying atmosphere.

These results are consistent with those reported by Madhava et al.[26] These authors applied the ASTM and FWO methods to study the nonisothermal drying of paddy and concluded that the order reaction and activation energy values change with the partial mass loss representing that the drying reaction was of complex type of reaction.

On the other hand, the calculated E_a values vary slightly with the heating rate. The increasing of heating rate leads to a simultaneous decrease in the effect temperature and an increase in the heat effect. Increasing the heating rate signifies that higher temperature is required to set off the drying process. The moisture release can affect the heat transfer in particle. This release leads to the formation of solid which is in poor heat transfer performance and prevents the heat transfer into particle core to some extent. Furthermore, the drying process is endothermic. The endothermic processes result in the heat that transfers along the radial direction is absorbed before transferring to the core.

In this point, it is important to consider that the frequency factor obtained from standard isoconversional techniques is tainted by association with the reaction model that must be assumed to permit its calculation. To disconnect and evaluate the kinetic parameters and $f(\alpha)$, Vyazovkin and Lesnikovich[27] proposed other methodology wherein a linear relation that exists between the Arrhenius parameters is used to extract the frequency factor for a given isoconversional value of E_a. When E_a depends on α, however, it was found that the integral isoconversional methods' use leads to systematic errors. E_a is overestimated, generally, due to error introduced by the truncation of the additional higher order terms in Doyle's approximations.[28] Vyazovkin and Lesnikovich[27] proposed a modification for his isoconversional method that accounts for the variation in apparent activation energy with increasing the conversion. However, this modification is an artifact that in reality conceals the true differential character of the method.

Isoconversional methods are unsuitable for those reaction schemes containing competing reactions, where the net rate of reaction depends on changes in temperature, or concurrent reactions that switch which reaction is rate-limiting over the experimental temperature range. Thereby, in heterogeneous reactions, it is possible that the kinetic rate-controlling event may be the occurrence of the temperature-dependent physical transformation which is not mass dependent, explaining the variation of E_a with the heating rate and according the phenomena described by Tahmasebi et al.[24]

Conclusion

The drying data should better not be ignored because water is the natural component of biomass. For that, nonisothermal drying of three agro-industrial wastes: peach pits (canning industry), marcs, and stalks was studied using thermogravimetric analysis under nitrogen and air atmospheres at different heating rates (5, 10 and 15 K/min) to deepen the thermal processes' knowledge. Different isoconversional models were selected to describe the drying characteristics of these wastes. The goodness of fit was evaluated by different statistical parameters. The Jander's model showed the best fitting for all

experiments, assuming that the three-dimensional diffusion is the controlling step of the drying rate. The kinetic parameters were calculated using this model. The calculated activation energy values are between 20.31 and 48.41 kJ/mol for all agro-industrial wastes at different experimental conditions.

Calculated kinetic parameters for the nonisothermal drying under nitrogen atmosphere are generally higher than those for this phenomenon under air atmosphere, suggesting that these wastes need less energy for drying under oxidative atmosphere. This variation could be explained considering different physicochemical phenomena. During the drying under oxidative atmosphere, carboxyl and carbonyl groups increased gradually with oxidation temperatures up to 423 K. However, during drying under nitrogen atmosphere, the aliphatic hydrogen absorption remained relatively unchanged up to 473 K, indicating that methylene groups are preferably lost up to 423 K, due to a progressive loss of alkyl chains and the conversion of hydroaromatic methylene structure to aromatic rings. This phenomenon would affect adversely the pyrolysis process.

Heating rates have a slight effect on the activation energy. This E_a variation with the heating rate can be due to the kinetic rate of drying phenomenon that is controlled by the occurrence of physical transformation the temperature dependent which is not mass dependent.

Even though a variation of kinetic parameter values with heating rate exists, the isoconversional methods' application to biomass drying is the first step to study this process and to establish the reaction mechanism, i.e., nucleation, geometrical contraction, diffusion, or reaction order.

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