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Thermogravimetric and Kinetic Analysis of Different Agro-Industrial Wastes Under Nitrogen Atmosphere

Echegaray M., Saffe M., Palacios C., Mazza G. and Rodriguez R.
email:rrodri@unsj.edu.ar

Abstract: **In this work, the behavior during thermal treatment processes of marcs, stalk and peach pits, from the wineries, canning and the jam industries was studied.The immediate and elemental analysis are realized.The studied agro-industrial wastes have higher water content than 30%, suggesting that these wastes should be dried before the thermal treatment. The ash contents are smaller than 7%, considering these contents low.The ultimate analysis showed higher oxygen concentrations present in the studied agro-industrial wastes, decreasing the HHV. The trace elements contents in these wastes are determined too. These elements remain in the char/ash fraction of the different pyrolysis products, during thermal treatment under inert atmosphere. Thermal decomposition of the studied wastes was studied in inert nitrogen atmosphere. Their decompositions proceed through three stages of weight loss, dehydration, active pyrolysis and passive pyrolysis. The maximum weight loss took place during the active pyrolysis step. In this stage, the peach pits exhibit the most prominent due to the higher content of hemicellulose. Another reason can be the difference of elements concentrations such us the Ca. This element is present in smaller concentration in the peach pits.Themarcs decomposing at lower temperature compared with the other biomasses. It also has the lowest mass loss. This behavior might be associated with the highest content of extractives in its structure. The higher value of activation energy was obtained for the peach pits, meaning slower reaction. The reaction orders were smaller than 1 for the studied agro-industrial wastes.**

***Keywords*:** **Agro-Industrial Wastes,Inertand Oxidative Atmosphere, Thermal Treatment, Thermogravimetric Analysis.**

I. INTRODUCTION

The need to find alternative raw materials to petroleum, due to the reduction in reserves and a raising demand for energy, has informed the development of technologies for the valorization of biomass. Biomass is considered the most promising alternative to fossil fuels, since its rational use does not contribute to a net rise in the level of CO_2 in the atmosphere. Biomass is one of the promising options as an alternative to fossil fuels because it is clean, renewable and sustainable [1]. The sources of biomass can be divided in two domains. The first consists on the use of the organic fraction of municipal wastes as well as the residual material from forestry to agriculture, such as wood, or straw. The second domain is the growing of energy crops, meaning the cultivationof plants such as whole cereal plants, willows, and fodder grasses specifically to generate electricity or produce biofuel.

On the other hand, one of the most important economic activities in the Cuyo Region, Argentina, is the agro-industry, highlighting the wine and seasonal fruits industries such as peaches.

This sector produces a significant environmental impact in specific geographical areas. In this country, approximately 140000 tons of peaches are processed in the canning and the jam industries, generating an important solid biomass wastes quantity, 37800tn/year. Considering the wine industry, a quantity of marc and stalk equal to 51928.3 tn/year is generated. These wastes have significant amounts of lignocellulosic materials. They are usually disposed in controlled landfills. The large amount of these solid wastes makes it an ideal candidate as the future feedstock for bio-energy production.

In recent years many investigations have been done for the possible use of solid waste biomass for energy obtention, such as combustion, pyrolysis and gasification. In all the thermo-chemical systems, pyrolysis is the first step taking place with consequent occurring of combustion and gasification. A better understanding of the pyrolysis will be of immense help in designing the reactors with better efficiency. The pyrolysis process can be understood thoroughly by knowing the kinetic parameters.

Mathematical modeling to predict the performance of thermal treatment requires the knowledge of reaction kinetics of the volatilization of biomass and subsequent reactions. Thermo gravimetric analysis (TGA) is one of the techniques used for examining the decomposition of solids, and it has been widely used to investigate the thermal decomposition behavior of different types of biomasses [2]. Interpretation of the experimental data can provide information regarding biomass composition, reaction order, and corresponding kinetic constants [3]. For an adequate design of thermal treatment reactor, it is necessary to know the activation energy and the thermal decomposition rate of biomass, which relies on kinetic studies of the concerned biomasses during the heating process.

The present study is focused on understanding the pyrolysis characteristics of agro-industrial wastes, particularly the wine and peaches canning industries.

II. EXPERIMENTAL

A. *Solid biomass wastes characterization:*

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. This material was ground, sieved and the resulting 0.10-0.21 mm size fraction was used for the thermo gravimetric tests. ASAE Standard S319.3 was used to determine the size distribution of the ground samples

[4]. The weight loss at 105ºC, ash and organic matter content were conducted according to ASTM standards (ASTM D3173-87, ASTM D3172-89 (02)). Ultimate analyses of the samples were performed using EuroEA3000 model elemental analyzer. The results are shown in Table 1.

In order to calculate the high heating value, the correlation proposed by Channiwala and Parikh [5] was used (Table 1):

$$HHV\left[{}^{MJ}/_{kg}\right] = 0.3491C + 1.1783H + 0.1005S - 0.1034O - 0.0151N - 0.0211A \qquad (1)$$

Were 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.

B. *Thermogravimetric analysis:*

A series of non-isothermal experiments were conducted for TGA using TGA-50 Shimadzu microbalance under air and nitrogen flows at 100 mL/min. The used heating rate was equal to 10ºC/min; the temperature range was 25-900ºC. Approximately 10 mg of agro-industrial wastes samples were placed in the equipment. The selected particles size avoids diffusion phenomenon, it affects the reactions when the particle size is greater than 2 mm. The experiments were carried out with dried samples. The data were recorded by a data logging system, which provided listings of sample weights and temperatures with time. Figures1 to 3 show thermo gravimetric curves TGA and the DTG curves in air and nitrogen atmospheres, respectively.

C. *Kinetic analysis:*

Parameters of the reaction kinetics were determined using the procedure applied by Karaosmanoglu et al. [6]. Global kinetics of the decomposition reaction can be written as:

$$\frac{dx}{dt} = -kx^n \qquad (2)$$

where x is the sample mass; k, the reaction constant and n, the reaction order.

Table 1: Results of proximate and ultimate analysis (dry basis, weight percentage). High heating value (HHV)

	Peach pits	Stalk	Marc
C (%)	53	46.14	52.91
H (%)	5.90	5.74	5.93
N (%)	0.32	0.37	30.41
S (%)	0.05	0.00	0.03
O (%)	39.14	37.59	30.41
Ash(%)	0.73	6.30	5.08
OrganicMatter(%)	99.27	93.70	94.92
Weigthlossat105ºC (%)	35.57	73.23	55.06
HHV (MJ/kg)	21.39	18.33	20.41

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

The temperature dependence of heterogeneous solid state reactions may be described by the Arrhenius equation (3):

$$\frac{dx}{dt} = -kx^n \qquad (3)$$

Combining Eq. (3) with Eqs. (2), the linear form obtained is Eq. (4):

$$Ln\left[\frac{-1}{w_0 - w_f}\frac{dx}{dt}\right] = Ln(A) - \left(\frac{E}{RT}\right) + nLn\left(\frac{w_i - w_f}{w_o - w_f}\right) \qquad (4)$$

where w_0 (mg) is the initial mass at the start of that stage; wf(mg), the final mass at the end of that stage; w (mg), the mass at any time; dw/dt(mg/s), the ratio of change in mass to change in time; A (s^{-1}), the pre-exponential factor and R, the universal gas constant; E, the activation energy and n, the reaction order. The equation (5) may be written under the linear form:

$$Y = B + Cx + Dz \qquad (5)$$

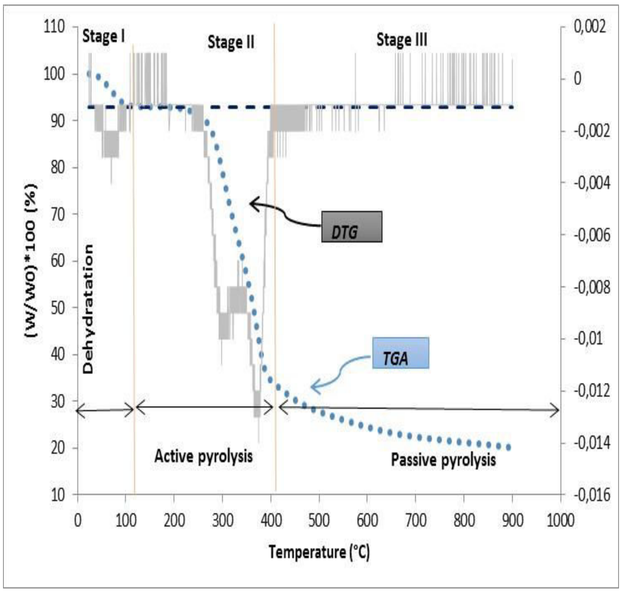

Fig. 1. Temperature ranges and weight loss found in TGA y DTG curves. Experiments under inert atmosphere. Peach pits.

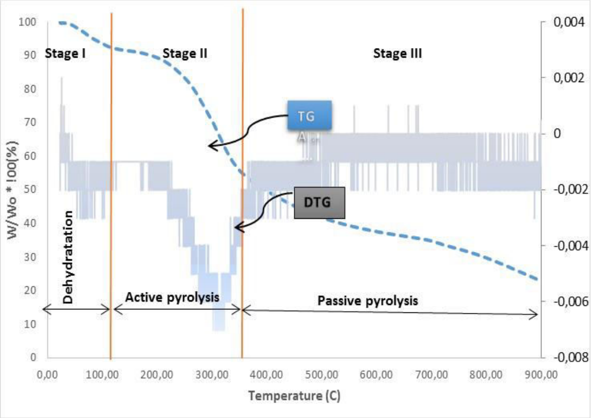

Fig. 2. Temperature ranges and weight loss found in TGA y DTG curves. Experiments under inert atmosphere. Stalk.

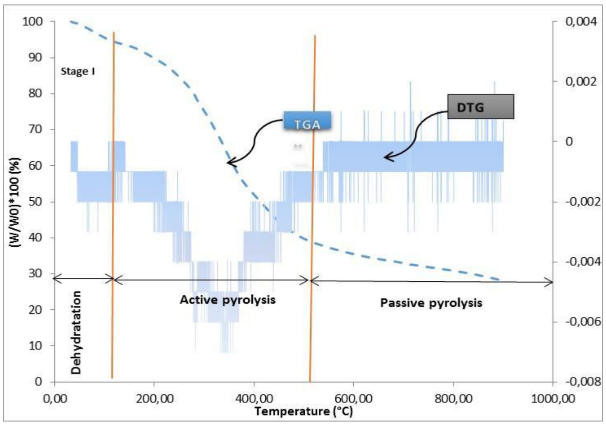

Fig. 3. Temperature ranges and weight loss found in TGA y DTG curves. Experiments under inert atmosphere. Marcs

Where:

$$Y = Ln\left[\frac{-1}{w_0 - w_f}\frac{dx}{dt}\right], x = \frac{1}{T}, z = Ln\left(\frac{w_i - w_f}{w_o - w_f}\right),$$

$$B = Ln(A), C = \left(\frac{-E}{R}\right), D = n \qquad (6)$$

Constants *B, C, D* were estimated by multi-linear regression of TGA data for each stage using Microsoft Excel.

III. RESULTS AND DISCUSSION

A. Characterization:

The results of the proximate and ultimate analyses are shown in Table 1. In the case of a fluidized bed reactor, high moisture biomass causes feeding and fluidization problems. High water content increases the energy requirements to carry out 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. Equilibrium models of the gasification process of peach pits, stalk and grape show similar behavior, the H_2 content in the syngas increases with the moisture content, this increase is not very pronounced, showing a maximum value for a moisture content equal to 30% [7]. According these results, it is necessary a predrying before their reactor inlet.

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 high heating value (HHV) [8]. In general, these solids contain significant amounts of un- reacted carbon and sulfur [9], but the studied agro-industrial wastes contain very small amounts of this last element in their compositions.

The high content of organic matter (93.70-99.27% dry basis) makes these wastes very suitable for thermal treatment [10].

The ultimate analysis showed higher oxygen concentrations (30.41-39.14%). These concentrations have a negative impact on the HHV because (carbon–oxygen bonds) tends to decrease the calorific value of studied agro-industrial wastes [11]. The sulfur and nitrogen content are lower than that reported in the literature for different types of biomass and coal [12], [13]. The ultimate analysis indicates that these agro-industrial wastes are environmental friendly, with only trace amounts of nitrogen and sulfur.

The typical chemical formulas of peach pit, grape marc and grape stalk material, based on a single atom of carbon, are respectively $CH_{1.33}O_{0.55}$, $CH_{1.34}O_{0.43}$ and $CH_{1.49}O_{0.61}$.

The H/C ratios for peach pits, stalk and marc vary between 0.11 and 0.12. The O/C ratios for peach pits, stalk and marc are 0.73, 0.81 and 0.57, respectively. Their HHVs vary between 18.33 and 20.41. Dermibas [8] determined the HHV for 16 different biomass fuel and reported similar values, Quirino et al. [14] reported similar values for wood, too.

28 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. Taking into account the heavy metals partition during thermal treatment in fluidized bed reactor, the turbulence conditions during its operation cause a significant production of fly ash with high concentrations of these elements. The heavy metals partition during heat treatments in fluidized bed is governed by the fluid dynamics, the kinetics of heavy metals diffusion in the ash particles and reaction kinetics between the heavy metals and the ash components.

The chemical composition of the mineral matrix has a great influence on the kinetics of heavy metals 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), present in the composition of studied agro-industrial wastes especially in the stalk, can react with these metals encapsulating them in the particle center [15].

During the thermal treatment under inert atmosphere, heavy metals are enriched in the char/ash fraction of the different pyrolysis products [16]. Velghe et al. [17] studied the municipal sewage sludge pyrolysis, and found that the distribution of metal ions towards oils is negligible, most of metals retain in the pyrolysis reactor: on fixed carbon, as metallic pieces and on sand.

Mayer et al. [18] 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 are 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.

On the other hand, some metals like Ca inhibit the bed material agglomeration, maintaining the fluidization quality and sand mixed with the biomass. Then, Ca improves the fluidization delaying the heavy metals release [19], [20]. The high potassium content negatively affects the melting behavior of ash by decreasing its melting point, causing agglomeration, formation of hard deposit at high temperatures [21]. Moreover, alkali metals, such as potassium, react readily with silica sand, which is a common bed material in thermal process, by breaking the Si–O–Si bond and forming silicates. Stalk presents the maximum concentration of these elements.

If the thermal treatment is carried out into fluidized bed reactor, it is important to consider the biomass tendency to separate from the bed due to its low density, as well as the elutriation tendency of C small particle.

B. Thermal conversion characteristic and kinetic behavior under inert atmosphere:

Figures 1 to 3 show the TGA and DTG curves obtained during the thermogravimetric experiments under nitrogen flow.The derivative plots (DTG) had separate peaks for this zone of weight loss. The first stage of weight loss ranged from 23 ºC to around 144ºC (Table 3) depending on the studied solid agro-industrial waste, which was clearly distinct from the other stages of weight loss. As suggested by Mansaray and Ghaly [22], it may correspond to the loss of water and light volatile compounds in the biomass sample. The weight losses in this stage ranged between 6.53-7.78%.

For second stage, the peach pits decomposition followed the usual shape for lignocellulosic materials [23]. In this sense, it is accepted that the main peak, resulting from the cellulose degradation, is accompanied by a shoulder at low temperature, which is related to hemicellulose degradation, and a tail at high temperature associated to lignin volatilization, is this case, between 402 to 464ºC, and the lignin starts to decompose at 270ºC. This model, denominated as standard pyrolysis model, can be applied to the peach pits, too [24]. The second decomposition step is observed as a shoulder in the 184-409 ºC temperature range and could be attributed to decomposition of hemicelluloses and partially to decomposition of cellulose and lignin. The temperature for the maximum decomposition rate above 370 ºC, can be attributed to the degradation of cellulose, but can be also associated with the pyrolytic degradation of lignin, starting with fragmentation of thei-nter-unit linkages [25].

In the case of stalk and marcs, the second decomposition step is observed as a shoulder in the 121-371 ºC and 141-538ºC temperature ranges, respectively. The temperatures for the maximum decomposition rate above 320 and 350 ºC, for the stalk and marcs correspondingly.

It can be observed that the stalk and marcs start to degrade at lower temperatures compared with the peach pits. This may be due to a higher concentration of low molecular compounds from extractives (oils and resins), which are less stable and start to degrade faster. Another reason by which studied agro-industrial wastes have different temperature ranges for the active pyrolysis can be the difference of elements concentrations such us the Ca. This element is present in smaller concentration in the peach pits, presenting a different behavior during this stage.

The peach pits exhibit the most prominent shoulder while for the stalk and marcs, this shoulder is most weak, mostly due to the lower content of hemicellulose [26].

The temperature for the maximum decomposition rate is also strongly dependent on the biomass type, the marcs decomposing at lower temperature (around 320 ºC) compared with the other biomasses. It also has the lowest mass loss. This behavior might be associated with the highest content of extractives in its structure. Extractives are compounds with low molecular mass, which are removed from samples at lower temperatures due to their higher volatility. The highest temperature (of 370 ºC) was observed for peach pits sample, due to a greater amount of cellulose [27]. The weight losses in this stage ranged between 39.41-59.29%.

A long tail of mass loss was observed above 400 ºC for all biomasses. This stage is called passive pyrolysis, the rate of reaction was minimal, due to advanced charring processes. The weight loss is produced between 409-900ºC, 371-900 ºC and 538-900 ºC for peach pits, stalk and marcs, respectively. During this stage, the lignin continues its decomposition without characteristic peaks [28]-[29]. The lignin decomposition range is wide, from 160 to 900 ºC [30]. Its decomposition passes through the whole temperature range. The weight losses in this stage varied between 9.74-17.06%.

Table 3 shows the temperature range for the main decomposition step of studied biomass samples.

C. Parameters of reaction kinetics:

In order to predict the decomposition of studied agro-industrial wastes particles under inert atmospheres, the kinetic parameters of the overall weight loss were obtained by applying the method introduced in Section II.

Table 3:Temperature ranges of weight loss from TGA and DTG curves.

	Temperature range		
	Stage 1	Stage 2	Stage 3
Peach pits	25.00-125.00 ºC	184.50-409.10 ºC	409.10-900.00 ºC
Weight loss	6.99 %	59.29 %	13.52%

Stalk	25.00-121.26 ºC	121.26-371.40 ºC	371.40-900.00 ºC
Weight loss	7.78%	39,41%	17.06%
Marcs	25.00-141.29 ºC	141.29-537.74 ºC	537.74-900.00 ºC
Weight loss	8.38%	51.68%	9.74%

Under inert atmosphere, for the active pyrolysis stage, the obtained activation energies, order reaction and R^2 value were showed in Table 4 for each studied agro-industrial solid waste. Figures 4, 5 and 6 show the comparison between the experimental data and the model results.

The founded activation energies and reaction orders of the active pyrolysis step were very close in agreement with literature data for other biomasses [31] [32]. The activation energy for marcs and stalk are smaller than this peach pits parameters, however, they are also very close with the value reported by Kumar et al. [33] for the corn stover. Since activation energy is minimum energy requirement to start a reaction, higher values of this parameter mean slower reactions and can also be used for determination of reactivity of a fuel. For all cases, the reaction order n is smaller to 1.

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IV. CONCLUSIONS

The studied agro-industrial wastes have higher water content than 30%, suggesting that these wastes should be dried before the thermal treatment. The ash contents are smaller than 7%, considering these contents low. This aspect will have a significant impact on the obtained amount of fly and bottom ash from the gasification process.

The ultimate analysis showed higher oxygen concentrations present in the studied agro-industrial wastes. These concentrations have a negative impact on the HHV because tends to decrease the calorific value of studied agro-industrial wastes.

28 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. Heavy metals remain in the char/ash fraction of the different pyrolysis products, during thermal treatment under inert atmosphere.

The found Ca concentrations in stalk and marcs are approximately twice the Ca concentration in peach pits.

Thermal decomposition of three agro-industrial wastes was studied in inert nitrogen atmosphere. Under inert atmosphere, from TGA and DTG it was found that decomposition proceeds through three stages of weight loss.

Table 3: Obtained kinetic parameters for active pyrolysis stage.

Active pyrolysis	Reaction order (n)	E (KJ/mol)	R^2
Pich peats	0.64	60.33	0,85
Stalk	0.35	26.55	0,80
Marcs	0.61	19.65	0,70

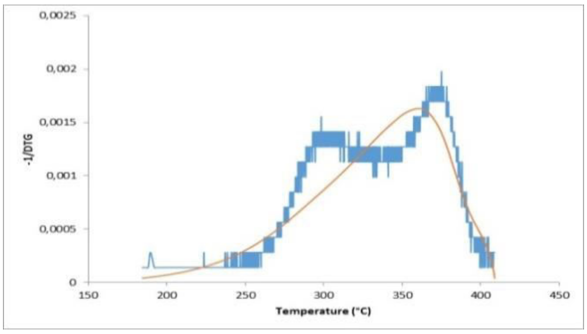

Fig. 4.Comparison between experimental data and model results for the active pyrolysis stage under inert atmosphere. Peach pits.

The first stage is allocated to loss of water and devolatilization of light molecules.

The presence of Ca ions slightly changed the main degradation peak temperature of cellulose, affecting the weight loss during TGA experiments.

For second stage, called passive pyrolysis, the peach pits decomposition followed the usual shape for lignocellulosic materials. In this sense it is accepted that the main peak, resulting from the cellulose degradation, is accompanied by a shoulder at low temperature, which is related to hemicellulose degradation, and a tail at high temperature associated to lignin volatilization. It can be observed that the stalk and marcs start to degrade at lower temperatures compared with the peach pits. This may be due to a higher concentration of low molecular compounds from extractives (oils and resins) and hemicelluloses, which are less stable and start to degrade faster. The peach pits exhibit the most prominent shoulder while for the stalk and marcs, this shoulder is most weak, mostly due to the lower content of hemicellulose.The temperature for the maximum decomposition rate is also strongly dependent on the biomass type, the marcs decomposing at lower temperature compared with the other biomasses.

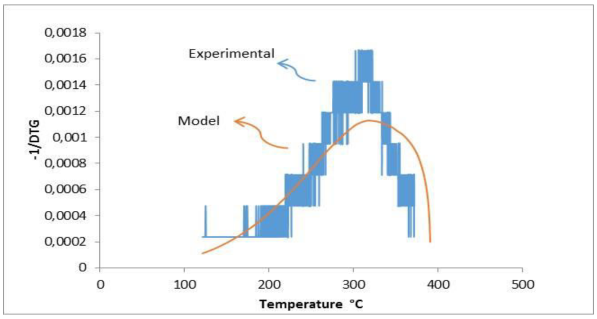

Fig. 5.Comparison between experimental data and model results for the active pyrolysis stage under inert atmosphere. Stalk

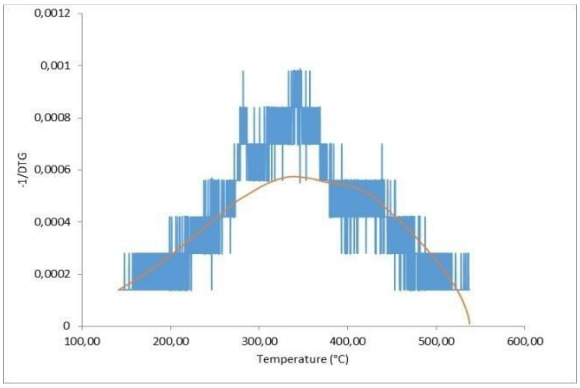

Fig. 6.Comparison between experimental data and model results for the active pyrolysis stage under inert atmosphere. Marcs

It also has the lowest mass loss. This behavior might be associated with the highest content of extractives in its structure.The activation energies obtained were equal to 60.33, 26.55 and 19.65 kJ/mol for the peach pit, stalk and marcs respectively. Higher obtained value of this parameter for the peach pits decomposition in inert atmosphere means slower reaction. The reaction orders were equal to 0.64, 0.35 and 0.61 for the peach pit, stalk and marcs respectively.

The last stage, called passive pyrolysis, the weight loss is produced in the following ranges: 409.1-900ºC, 371.4-900ºC and 537.74-900ºC for the peach pit, stalk and marcs respectively. In this stage, the decomposition rate is very low and the weight loss is almost undetectable. The weight losses in this stage varied between 9.74-17.06%.

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AUTHOR'S PROFILE

Echegaray Marcelo: Argentina, San Juan, 1969

He is professor of San Juan National University. He interested in all field of thermodynamics and thermal treatment. He has several papers in national, international, conference, journals and so on. Here are some of his works:

- Marcelo Echegaray, Rosa Rodríguez, María Rosa Castro. Equilibrium model of the gasification process of agro-industrial wastes for energy production.International Journal of Engineering Science and Innovative Technology.
- Marcelo Echegaray, MarianelaCostante, Alejandra Saffe, Carlos Palacios, Rosa Rodriguez. Behavior of heavy metals during the agro-industrial wastes gasification. Open Journal of Metal.

Saffe Alejandra: Argentina, San Juan, 1989.

She had a CONICET scholarship for obtain the Doctoral Degree in Chemical Engineering, Processes Clean Mention. She interested in all field of thermal treatment. She has several papers in national, international, conference, journals and so on. Here are some of hisworks:

- Rosa Rodriguez, Susana Acosta, Alejandra Saffe, Stella Udaquiola. Predicción de la partición de cd, cr y pb durante la gasificación de residuos agroindustriales. Congreso Internacional de Ciencia y Tecnología Ambiental. ISBN 978-987-28123-1-7.
- Rosa Rodrigue, Alejandra Saffe, Marianela Costante, Carlos Palacios, María Castro, Marcelo Echegaray. Gasificación de residuos agroindustriales: predicción del comportamiento de distintos contaminantes VII Congreso Nacional Ambiental 2012. ISSN 1853-2780.

Mazza Germán: Argentina, San Juan, 1959.

He successfully finished PHD in Engineering at La Plata National University. He is professor of Comahue National University. He interested in all field of thermal treatment. He has several papers in national, international, conference, journals and so on. Here are some of his works:

- D. Asensio, M. Zambon, G. D. Mazza, G. F. Barreto Heterogeneous Two-Region Model for Low-Aspect-Ratio Fixed-Bed Catalytic Reactors. Analysis of Fluid-Convective Contributions. Ind. Eng. Chem. Res.
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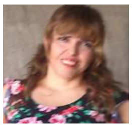

Rodriguez Rosa: Argentina, San Juan, 1968.

She successfully finished PHD in Engineering at La Plata National University and Perpignan University. She is professor of San Juan National University. She interested in all field of thermal treatment. She has several papers in national, international, conference, journals and so on. Here are some of his works:

- Marcelo Echegaray, Rosa Rodríguez, María Rosa Castro. Equilibrium model of the gasification process of agro-industrial wastes for energy production.International Journal of Engineering Science and Innovative Technology.
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