Thermo gravimetric analysis of peach pits under inert and air atmosphere

María A. Saffe, Marcelo E. Echegaray, Germán D. Mazza, Rosa A. Rodriguez

Abstract—The aim of this work was to study the peach pits behavior during thermal treatment processes. The immediate and elemental analysis and the determination of trace elements contents are realized. Trace elements remain in the char/ash fraction of the different pyrolysis products, during thermal treatment under inert atmosphere. The different metals presence promote the char combustion under oxidative atmosphere. To determine the kinetic of reactions under inert and oxidative atmospheres, TGA experiments were realized. Under inert atmosphere, the maximum weight loss took place during the active pyrolysis step, the activation energy and reaction order were equal to 60.33kJ/mol and 0.64, respectively. Under oxidative atmosphere, the second stage, called devolatilization, ranging from 205 to 360ºC, with activation energy and order reaction equal to 97.44kJ/mol and 0.94 correspondingly. The third stage, called char combustion is produced at 40-540.1ºC. The obtained activation energy and order reaction were 59.54kJ/mol and 0.44, respectively.

Index Terms— inert and oxidative atmosphere, peach pit, thermal treatment, thermo gravimetric analysis.

I. INTRODUCTION

One of the most important economic activities in the Cuyo Region, Argentina, is the agro-industry, highlighting the seasonal fruits industry 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. These wastes have significant amounts of lignocellulosic materials. They are usually disposed in controlled landfills.

On the other hand, with the depletion of fossil fuels, as well as, their increasing price and undesirable environmental effects, the utilization of residual biomass is getting increased attention as a potential resource of renewable energy. Processes based on the thermo chemical conversion of biomass are nowadays raising importance, since they show higher energy efficiency. The biomass thermal treatment appears as one of the most promising. The most important thermal treatments are combustion, gasification and pyrolysis.

Biomass characteristics such as moisture, ash, volatile matter, inorganic elements, structural constituents, calorific value, particle size, and density are of great importance in understanding the changes that occur in the chemical structure biomass waste, which will affect their performance when exposed to elevated temperatures during thermo chemical conversion [1].

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.

Thermo balance design and low size of sample assure kinetic control, avoiding secondary interactions, under a controlled environment [4]. Occasionally, thermo gravimetric analysis has been used as analytical method under inert [5]-[6]-[7], or oxidative [6]-[8]-[9] atmospheres.
It is important that the use of thermogravimetry analysis as analytical method must fulfill some pre-conditions: (a) use of realistic models that adequately describe samples transformations, and (b) improved fitting of experimental data by using other kinetic models than nth-order equations. In the present study, the chemical, physical, fuel-oriented and thermal characteristics of the peach pits are presented. Additionally, the thermal decomposition behaviors were thermogravimetrically analyzed, determining the kinetic parameters.

II. EXPERIMENTAL SECTION

A. Solid biomass wastes characterization

The raw material used in this work was peach pits from canneries and jam factories 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 [10].

The weight loss at 105ºC, ash and organic matter content were conducted according to ASTM standards and results are given in Table 1 (ASTM D3173-87, ASTM D3172-89 (02)). Ultimate analyses of the samples were performed using EuroEA3000 model elemental analyzer, and results are shown in Table 1. In order to calculate the high heating value, the correlation proposed by Channiwala and Parikh [11] was used:

$$HHV = 0.3491C + 1.1703H + 0.1005S - 0.1034O - 0.0151N - 0.0211A$$  \(1\)

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 ICP. The experimental results are shown in Table II.

<p>| Table I. Results of proximate and ultimate analysis (dry basis, weight percentage). High heating value (HHV) |
|---------------------------------------------------------------|---------------------------------------------------------------|</p>
<table>
<thead>
<tr>
<th>C (%)</th>
<th>H (%)</th>
<th>N (%)</th>
<th>S (%)</th>
<th>O (%)</th>
<th>Ash (%)</th>
<th>Organic Matter (%)</th>
<th>Weight loss at 105ºC (%)</th>
<th>HHV (MJ/kg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>53</td>
<td>5.90</td>
<td>0.32</td>
<td>0.05</td>
<td>39.14</td>
<td>0.73</td>
<td>99.27</td>
<td>35.57</td>
<td>21.39</td>
</tr>
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</table>

<table>
<thead>
<tr>
<th>Table II. Metals contents in the peach pits (dry basis)</th>
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<tbody>
<tr>
<td>Cu (μg/g)</td>
</tr>
<tr>
<td>----------</td>
</tr>
<tr>
<td>15.3</td>
</tr>
</tbody>
</table>

B. TGA experiments

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 5ºC/min; the temperature range was 25-900ºC.

Approximately 10 mg of peach pits 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 peach pits. The data were recorded by a data logging system, which provided listings of sample weights and temperatures with time. Fig.1 and 2 show thermogravimetric curves TGA and the DTG curves in air and nitrogen atmospheres, respectively.
III. PROCEDURE TO DETERMINE PARAMETERS OF REACTION KINETICS

Parameters of the reaction kinetics were determined using the procedure applied by Karaosmanoglu et al. [12]. Global kinetics of the decomposition reaction can be written as:

\[
\frac{dx}{dt} = -kx^n
\]  

(2)

Where \( x \) is the sample mass; \( k \), the reaction constant and \( n \), the reaction order. Applying the Arrhenius Eq. (3) and combining it with Eqs. (2), the linear form obtained is Eq. (4):

Fig.1. Weight vs. temperature (ºC) for a heating rate equal to 5ºC/min in oxidative and inert atmospheres.

Fig.2. dW/dt vs. temperature (ºC) for a heating rate equal to 5ºC/min in oxidative an inert atmospheres.

(2)
where \( w_0 \) (mg) is the initial mass at the start of that stage; \( w_f \) (mg), the final mass at the end of that stage; \( w \) (mg), the mass at any time; \( \frac{dw}{dt} \) (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:

\[
Y = B + Cx + Dz
\]

Where:

\[
Y = \ln \left[ \frac{-1}{w_0 - w_f} \frac{dw}{dt} \right] \quad x = \frac{1}{T} \quad z = \ln \left( \frac{w_l - w_f}{w_0 - w_f} \right) \quad B = \ln (A), \quad C = \left( \frac{E}{R} \right), \quad D = n
\]

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

IV. 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.

Regarding the ash content (0.73% dry basis), a low percentage of it will minimize the production of fly and the bottom ash and affect positively the high heating value (HHV) [13]. In general, these solids contain significant amounts of un-reacted carbon and sulfur [14]. The high content of organic matter (99.27% dry basis) makes peach pits very suitable for thermal treatment [15].

The ultimate analysis showed an oxygen, carbon, hydrogen, nitrogen, and sulfur content of 39.14%, 53%, 5.90%, 0.32% and 0.05%, respectively. A higher oxygen concentration has a negative impact on the HHV because (carbon–oxygen bonds) tends to decrease the calorific value peach pits [16]. The sulfur and nitrogen content are lower than that reported in the literature for different types of biomass and coal [17],[18]. The ultimate analysis indicates that peach pits are environmental friendly, with only trace amounts of nitrogen and sulfur. The typical molecular formula of peach pit, based on a single atom of carbon, is \( \text{CH}_{1.33}\text{O}_{0.55} \).

The H/C and O/C ratios were 0.11 and 0.73, respectively. The peach pit has an HHV of 21.39MJ/kg, a value similar to values reported in the literature for wood [15]-[18].

28 trace elements are analyzed. Fe, Cr, Pb, Sn, Mo, Ni, Ag, Ti, V, Mn, Cd and B are not present in the composition of the peach pits. 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\(_2\)O\(_3\), CaO) can react with these metals.
encapsulating them in the particle center [19]. A high water content of feed waste promotes the heavy metal retention [20].

During the thermal treatment under inert atmosphere, heavy metals are enriched in the char/ash fraction of the different pyrolysis products [21]. Velghe et al. [22] 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. [23] 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 added metal ions; e) Inorganic compounds affected the first step of combustion differently but slightly increased the weight loss rate during the second step of combustion, and f) Metals acted as promoters during char combustion by decreasing the burnout temperature and increased the ignition performance of char.

The conclusions of these researchers are similar to Song et al. [24]; the solid residues of thermal treatment are inert and no involved in chemical equilibrium of the gasification reactions but, it may have a catalytic effect, accelerating the char combustion reaction, especially when the ash contains metal oxides as K₂O, CaO, MgO, P₂O₅, etc.

On the other hand, some metals like Ca inhibit the bed material agglomeration, maintaining the fluidization quality and sand mixed with the biomass to be gasified. Then, Ca improves the fluidization delaying the heavy metals release [25]-[26].

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 [27]. Moreover, alkali metals, such as potassium, react readily with silica sand, which is a common bed material and also used as the bed material in this gasification process, by breaking the Si–O–Si bond and forming silicates.

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

#### Inert Atmosphere

Fig. 1 and 2 shows the TGA and DTG curves obtained during the thermo gravimetric experiments under air and nitrogen flows, respectively. According to these figures, the decomposition during pyrolysis (inert atmosphere) followed the usual shape for lignocellulosic materials [28]. 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 464°C, and the lignin starts to decompose at 270°C. This model, denominated as standard pyrolysis model, can be applied to the peach pits, too [29]. Pyrolysis curve of peach pit took place in three visible stages of weight loss. The first stage ranging from 25 to 125°C corresponded to the loss of water and devolatilization of light molecules [30]. The derivative plot (DTG) had a separate peak for this zone of weight loss. Following the first stage, there was a weight loss in the temperature range of 184.5–409.1°C. In this region, called active pyrolysis, the hemicellulose and cellulose are decomposed, while lignin is decomposed hardly. During the active pyrolysis stage, the decomposition rate reached two maximums, at 298°C and at 375°C. The decomposition process depends on the composition and concentration of the principal components. During this stage the secondary gases evolution is released, leading to the formation of char [31].
The last stage, called passive pyrolysis, the weight loss is produced between 409.1 and 900ºC. During this stage, the lignin continues its decomposition without characteristic peaks [32]-[33]. The lignin decomposition range is wide, from 160 to 900°C [18]. Its decomposition passes through the whole temperature range with a very low rate. Table and Figure 3 show the temperature ranges of each stage and weight loss found in TGA y DTG curves.

| Table III. Temperature ranges and weight loss found in TGA y DTG curves |
|-----------------|-----------------|-----------------|
| Stage 1         | Stage 2         | Stage 3         |
| Temperature range | 25-125 ºC       | 184.5–409.1 ºC  | 409.1–900 ºC   |
| Weight loss     | 1.2 %           | 59.19 %         | 3.52           |

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

**Oxidative Atmosphere**

Under oxidative atmosphere, the different decomposition stages have occurred at lower temperatures than decomposition under inert atmosphere. The first stage of weight loss ranging from 24 to 120ºC (Table 4) corresponds to moisture and light volatile loss, similar to pyrolysis experiments. During the second stage, ranging from 205 to 360 ºC, the pyrolysis and heterogeneous oxidation are produced, and the volatile compounds are released. As shown in Figures 1 and 2, biomass pyrolyzes in a wide temperature range, where the decomposition of the three biomass components overlaps. The greatest weight loss occurs at this stage, 60%, and it is higher than the weight loss under inert atmosphere. Hemicellulose is the component with the lowest thermal stability, and both peaks appear at the lowest temperatures. In this stage, the decomposition rate reached two maximums, at 293 ºC and at 332 ºC. Finally, the third stage begins at 403 ºC and ends to 540.1 ºC. The char combustion was observed during this stage, showing a peak wide and low. Lignin volatilizes in a wide range of temperatures, resulting in a high char yield, which burns at the highest temperature. In this stage, the decomposition rate reached a maximum around 494 ºC. Table and Figure 4 show the temperature ranges and weight loss. During the last stage, called residual combustion, the decomposition rate is very low and the weight loss is almost undetectable.

| Table IV. Temperature ranges and weight loss found in TGA y DTG curves. |
|-----------------|-----------------|-----------------|
| Stage 1         | Stage 2         | Stage 3         |
| Temperature range | 24.2–120 ºC     | 205-360.1 ºC    | 403-540.1 ºC   |
| Weight loss     | 6.51 %          | 53.17 %         | 30.35 %        |
C. Parameters of reaction kinetics

In order to predict the decomposition of peach pit particles under inert and oxidative atmospheres, the kinetic parameters of the overall weight loss were obtained by applying the method introduced in Section 2.1. Under inert atmosphere, for the active pyrolysis stage, the obtained activation energy, order reaction and the pre-exponential factor were 60.33 kJ/mol, 0.64 and 325.58 s⁻¹, respectively. The $r^2$ value was 0.84. Fig. 5 shows the comparison between the experimental data and the model results. The activation energies and reaction orders of the active pyrolysis step under air atmosphere were very close in agreement with literature data for other biomasses [7]-[34].

Under oxidative atmosphere, for the devolatilization stage, the obtained activation energy, order reaction and the pre-exponential factor were 97.44 kJ/mol, 0.94 and 1653301.4 s⁻¹, respectively. The $r^2$ value was equal to 0.94. The parameters values obtained for the active pyrolysis under inert atmosphere are smaller, indicating a minor reaction rate comparing with the volatilization stage under oxidative atmosphere. The obtained activation energy of the devolatilization step under air atmosphere were very similar with literature data for other biomasses like that cotton stalk (Ea = 113 kJ/mol), sugar cane bagasse (Ea = 116 kJ/mol) and shea meal (Ea = 108 kJ/mol) under oxidative atmosphere. The obtained order reaction was bigger than the values found in the literature [35]. Fig. 6 shows the comparison between the experimental data and the model results.
For the char combustion stage, the obtained activation energy, order reaction and the pre-exponential factor were 59.54 kJ/mol, 0.44 and 28.86 s\(^{-1}\), respectively, with \( r^2 \) value equal to 0.86. Fig. 7 shows the comparison between the experimental data and the model results.

During this step, the weight loss rate was lower than the rate of devolatilization stage. The activation energy of the char combustion step was minor that literature data for other biomasses. The obtained order reaction was also minor than the values found in the literature \[36\]-\[37\]-\[38\]. The results may be attributed to a minor oxygen amount in the experiments carried out in this work. Figure 7 shows the comparison between the experimental data and the model results.

Fig. 6. Comparison between experimental data and model results for the devolatilization stage under oxidative atmosphere.

V. CONCLUSION

The studied peach pits have higher water content than 20%, suggesting that these wastes should be dried before the thermal treatment. The ash content is low. This aspect will have a significant impact on the obtained amount of fly and bottom ash from the thermal treatment process.

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 peach pits. Heavy metals remain in the char/ash fraction of the different pyrolysis products, during thermal treatment under inert atmosphere. The presence of different metals affects the weight loss during TGA experiments, promoting the char combustion under oxidative atmosphere.

Thermal decomposition of peach pits was studied in inert nitrogen and oxidative atmospheres. Under inert atmosphere, from TGA and DTG it was found that decomposition proceeds through three stages of weight loss. The first stage is allocated to loss of water and devolatilization of light molecules. In the second step, the mass loss is a consequence of thermal decomposition of peach pits compounds from 184.5 to 409.1°C. The activation energy obtained was equal to 60.33 kJ/mol and the reaction order equal to 0.64. The last stage, called passive pyrolysis, the weight loss is produced between 409.1 and 900°C, the decomposition rate is very low and the weight loss is almost undetectable.

Under oxidative atmosphere, the different decomposition stages have occurred at lower temperatures than decomposition under inert atmosphere. The first stage of weight loss is similar to pyrolysis experiments. The second stage, ranging from 205 to 360 °C, the pyrolysis and heterogeneous oxidation are produced, and the volatile compounds are released. This step is called devolatilization and the obtained activation energy and order reaction was 97.44 kJ/mol and 0.94 respectively. The third stage, called char combustion, begins at 403 °C and ends to 540.1°C. The obtained activation energy and order reaction were 59.54 kJ/mol and 0.44, respectively. During the last stage, the decomposition rate is very low and the weight loss is almost undetectable.
Fig.7. Comparison between experimental data and model results for the char combustion stage under oxidative atmosphere

REFERENCES


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