

ARUNDO DONAX SAMPLE PREPARATION, TORREFACTION AND ANALYSES

FINAL REPORT TO THE PORTLAND GENERAL ELECTRIC COMPANY

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1.- Introduction

Portland General Electric (PGE) located in Portland, Oregon, has been utilizing Powder River Basin (PRB) coal in their Boardman Power plant for many years. It is Oregon's only coal-fired plant and is a significant source of air emissions. One of the alternatives under study to reduce the environmental impact of this plant is to blend coal or displace entirely with torrefied *Arundo donax* (Giant Cane). In spite of the importance of blending coal with biomass, the difficulties of grinding the biomass into a powder that can be co-fired with coal is a major hurdle limiting the implementation of this alternative (Bergman et al., 2005). The fibrous structure of biomass is the main cause of the difficulties encountered in grinding lignocellulosic materials with the coal mills operational at the power station.

One of the most promising pretreatment technologies to improve the grindability of lignocellulosic materials and enable higher co-firing rates is torrefaction (Deng et al 2009, Bergman et al., 2005). This thermochemical technology consists of heating the biomass to temperatures between 200 and 320 °C in the absence of oxygen till the fibrous structure of biomass is weakened (Prins et al 2006, Bergman et al 2005). Torrefaction processes can achieve high energy efficiencies, close to 96 % (thermal efficiency) (Bergman et al., 2005). This process results in the production of a material that can be easily ground at coal mills. Furthermore, torrefied biomass presents a low capacity to up-take water and is more resistant to microbial attack due to the removal of OH groups which reduces its capacity to form hydrogen bonds with water.

The coal handling system used by the PGE plant generally works with chunks that are up to 3" to 4" diameter. These chunks require a pretreatment process to pass the ¾" minus mesh before becoming pulverized. Once the material has been pulverized, 75% of it can pass a 200 micron mesh. The co-combustion of biomass with coal requires the reduction of biomass particle size to values comparable to those achieved with the coal. Given the fibrous nature of biomass it is very difficult to achieve these small sizes without major changes in the size reduction system operational at the Boardman Power Plant. The interest at hand is to evaluate a technology able to

produce biomass particles that emulate the physical size of the coal in order to replace a fraction or eventually all of the current coal used at the Boardman Power plant.

The proposed material for the co-combustion studied in this project is *Arundo donax*. *Arundo* is one of the highest cellulosic biomass producing plant species known. It has strands that remain intact through harsh winter conditions, and when harvested, will re-grow in the spring. This plant has been studied for its potential as an appealing source of pulp fiber for the Pacific Northwest paper industry (http://css.wsu.edu/biofuels/progress_report/2008_01/AP_arundo.html). All of these characteristics also make this C_3 plant very appealing for co-combustion with coal in the Pacific Northwest. Our colleagues from WSU Prosser have harvested the *Arundo* used in this study. The collection of the material was done carefully to ensure that the sample material is mostly *Arundo* as opposed to *Arundo* mixed with dirt.

The principles of torrefaction were developed in the 1930's when this technology was evaluated to produce a reducing agent for metallurgical applications; however, up to now no biomass torrefaction plant has been commercialized (Bergman et al., 2005). All the information reported in the literature strongly suggests that developing biomass torrefaction units is critical to implement biomass-coal co-firing in existing power plants. However, the experimental data available on the torrefaction of *Arundo donax* does not provide much information on the relationship between the design and operating parameters of torrefaction reactors and important performance characteristics such as the efficiency of the process, the grindability of the torrefied biomass produced, and the composition of the products of torrefaction (Prins et al 2006, Bergman et al. 2005).

Figure 1 shows a conceptual diagram of a torrefaction plant (Bergman et al., 2005). A typical torrefaction plant consists of a biomass storage area, a dryer, a chopper, screens, a torrefaction reactor, a combustion chamber and a system to cool the torrefied biomass (Bergman et al 2005). The heat released from the combustion of the torrefaction gases will be used to dry the biomass and to heat up the reactor where the torrefaction reactions will occur (Bergman et al 2005). Torrefaction can be energy self sufficient, thus it does not need to be integrated with a power station.

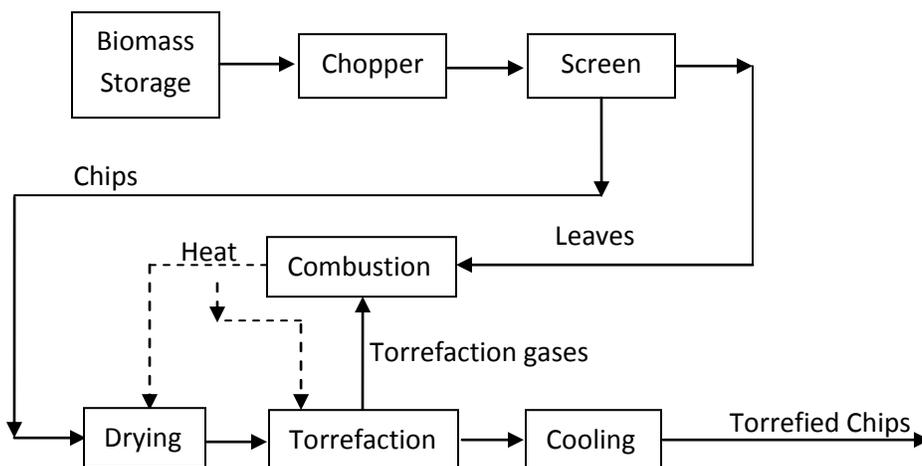


Figure 1.- Conceptual design of the torrefaction process proposed (Bergman et al. 2005).

Thus, this project aims at collecting enough data to conduct a preliminary mass and energy balance of *Arundo donax* torrefaction. This first report focuses on the characterization of the process and the products. The amount of *Arundo* torrefied in each run was enough to collect several pounds of torrefied biomass for proximate and ultimate analyses, as well as for grindability studies with some replications. The liquid products and the gases were then analyzed at Washington State University (WSU). Some tests with the torrefied samples were conducted at WSU while others were performed at the same laboratory where the PGE coal analyses are currently conducted. The goal was to characterize the torrefied *Arundo donax* with the same protocols used for the analysis of PRB coal currently employed by the Boardman Power plant.

In this project we will evaluate the effects of torrefaction conditions (controlled by the temperature and then residence time of the biomass in the torrefaction reactor), on the yield and properties of the resulting torrefied product (calorific value, chemical makeup, and grindability). This data will be used to perform preliminary mass and energy balances. Thus, this report has been divided into four major sections:

- 1.- Sample Preparation and Analyses
- 2.- Differential Scanning Calorimetry (DSC) and Thermogravimetric Analyses (TGA)

- 3.- Torrefaction Studies in the Auger Reactor and Analysis of Products
- 4.- Energy Balances

2.- Sample Preparation and Analyses

2.1.- Materials and Methods

The biomass received from Prosser was chipped using a disk chipper until the fragments were in the range of 1" (approximately 25 mm x 25 mm), it was then dried (105 °C) at the WSU Wood Materials and Engineering Laboratory. The resulting material was screened. The chipper used for breaking down the Arundo did not chip the leaves which tend to be much more flexible than the cane. The yields after a trial chip run and screening were: 8.5 mass % of large leaves, 6.4 mass % of large chipped material consisting of leaves and some small cane fragments, and 85.10 mass % of chips from the cane. Of this, only the chipped stems were to be torrefied (see Figure 2). Developing applications for the leaves, which represent over 15 mass % of the Arundo Donax samples received, warrants further investigation.

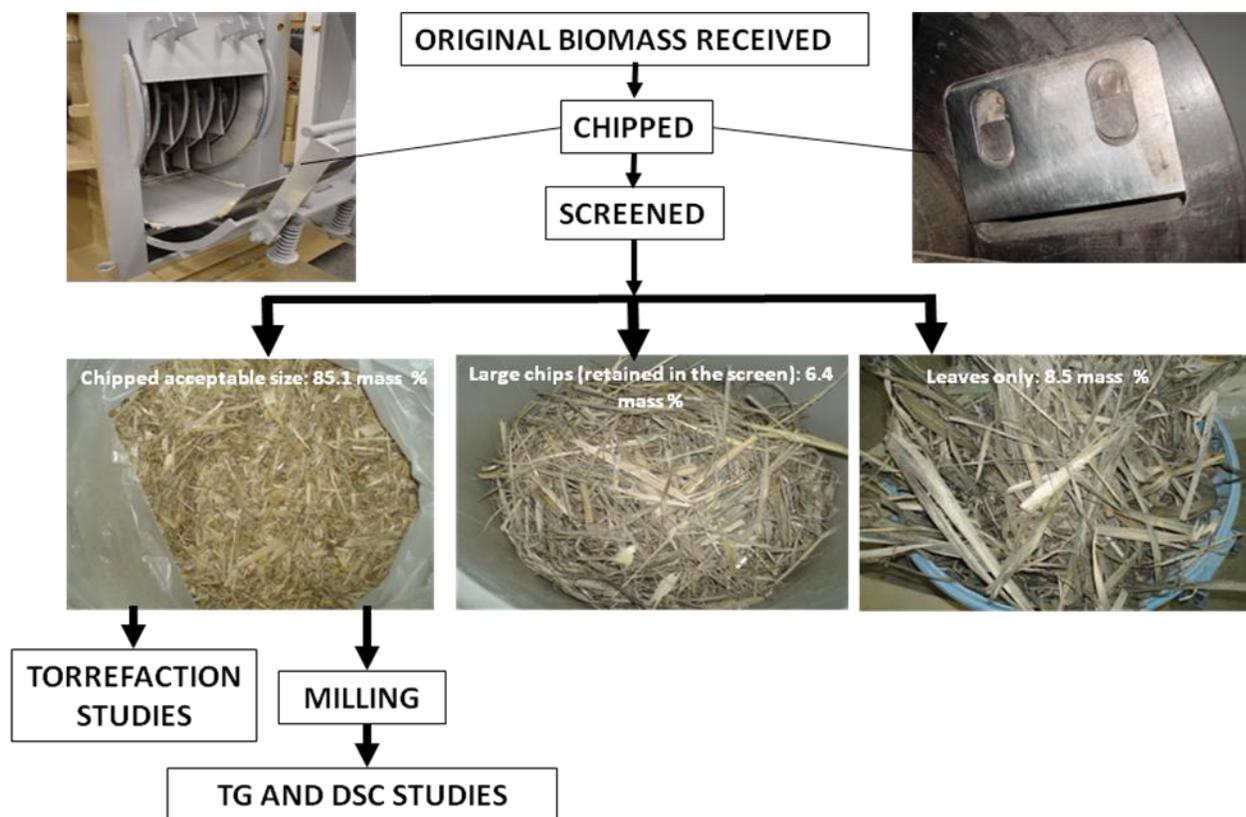


Figure 2.- Sample preparation.

3.- Differential Scanning Calorimetry and Thermogravimetric Analyses

3.1.- Materials and Methods

Thermogravimetric analysis (TGA) and differential scanning calorimetry studies (DSC) were carried out to establish the thermal behavior of the *Arundo donax*.

The TG analyses were done using a Mettler Toledo TGA/SDTA851e TG analyzer with a 70 μL alumina pan. 20 mL/min of Nitrogen was used as carrier gas and to avoid the presence of oxidative agents in contact with the biomass samples. The heating program was set at 25°C as a beginning temperature and was then heated to 600 °C with different heating rates (10, 20, 30, 40, 50, 60 °C/min). The final temperature was held for 20 minutes.

The calorimetric studies were conducted with a DSC Q2000 from TA Instruments. Samples of between 5 and 8 mg were placed into aluminum pans, and then loaded onto the DSC

measurement cell. The DSC tests were conducted varying the heating rates (between 10 and 60 °C/min) and the final torrefaction temperature was between 225 and 325°C. The procedure is as follows: equilibrate at 25°C for 1 min, then ramp at a set heating rate till a final set temperature.

3.2.- Analysis of Results

Thermogravimetric Analyses

Figure 3 shows the weight loss as a function of temperature of the samples heated from 25 °C to a final temperature between 250 and 325 °C at a heating rate of 10 °C/min. The weight losses observed in the first 1000 seconds are associated to the removal of the moisture in the feedstock. Our results indicate that the moisture content of the samples studied, after drying, was 3.18 mass %.

The three main polymers forming woody and herbaceous biomass are: cellulose, hemicelluloses and lignin. The thermal behaviors of each of these bio-polymers as well as their interactions have to be understood to explain the thermal behavior of the lingo-cellulosic materials (Hon et al 2001, Rath et al. 2003, Bergman et al 2005). Hemicellulose is the most reactive of these three bio-polymers and is the one that degrades the most during torrefaction. Although reactions in the solid phase of cellulose and lignin also happen during mild torrefaction conditions (less than 250 °C); these reactions do not lead to important weight losses. At more severe conditions (over 250 °C), hemicellulose extensively decomposes into volatiles while char-like products form from cross linking and polycondensation reactions in the solid phase (Bergman et al 2005).

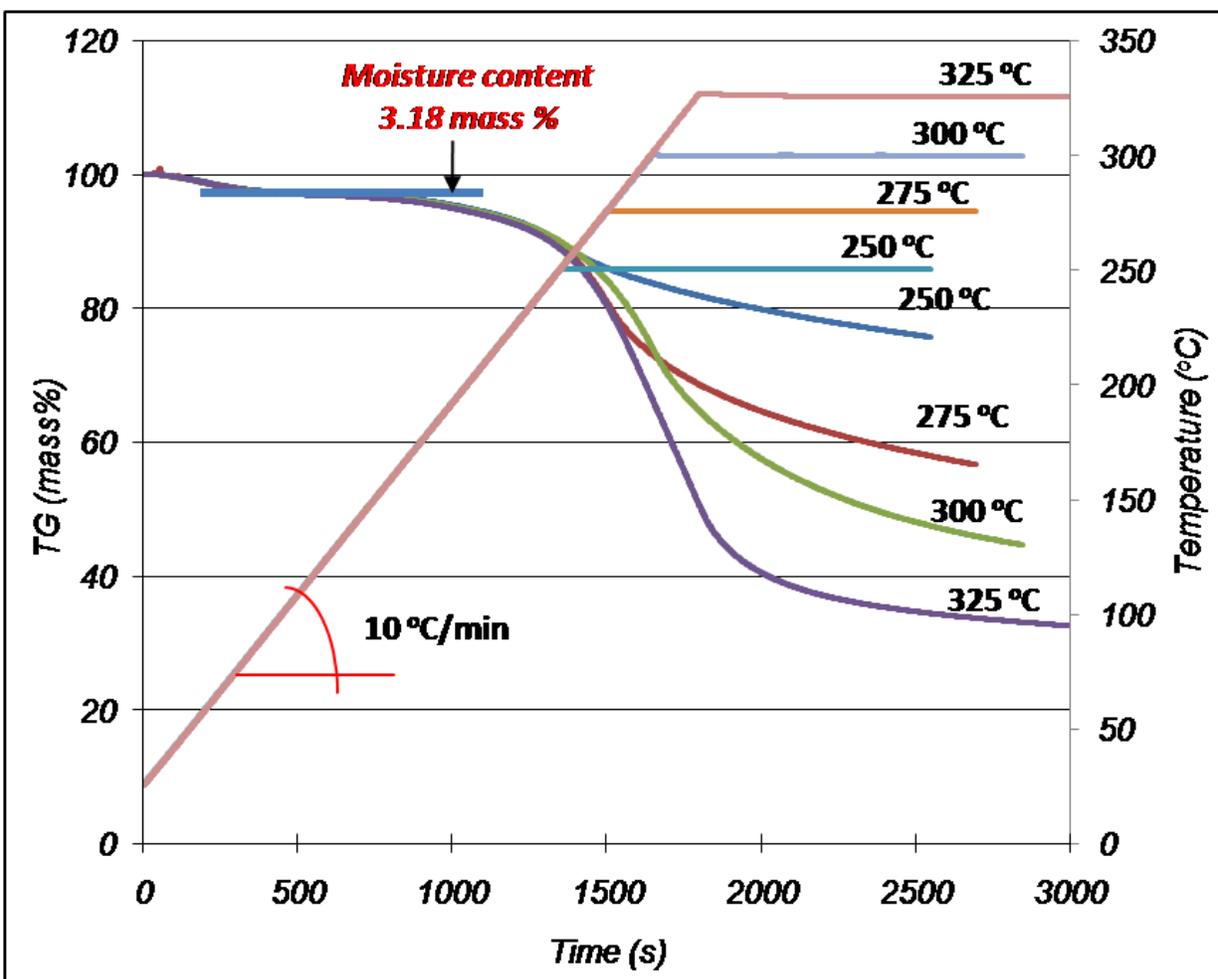


Figure 3.- TG and DTG curve of the samples pretreated with different temperatures.

Figure 4 clearly shows that the yield of torrefied biomass decreases as the torrefaction temperature increases. When plotting the torrefaction final temperature vs. the yield of torrefied biomass obtained, a linear relationship was acquired (see Figure 4). This result suggests that the most important factor controlling the yield of torrefied biomass obtained is the temperature at which the biomass is heated. Similar behaviors, but for other types of biomass, have been reported elsewhere (Prins et al 2006, Bridgeman et al 2008).

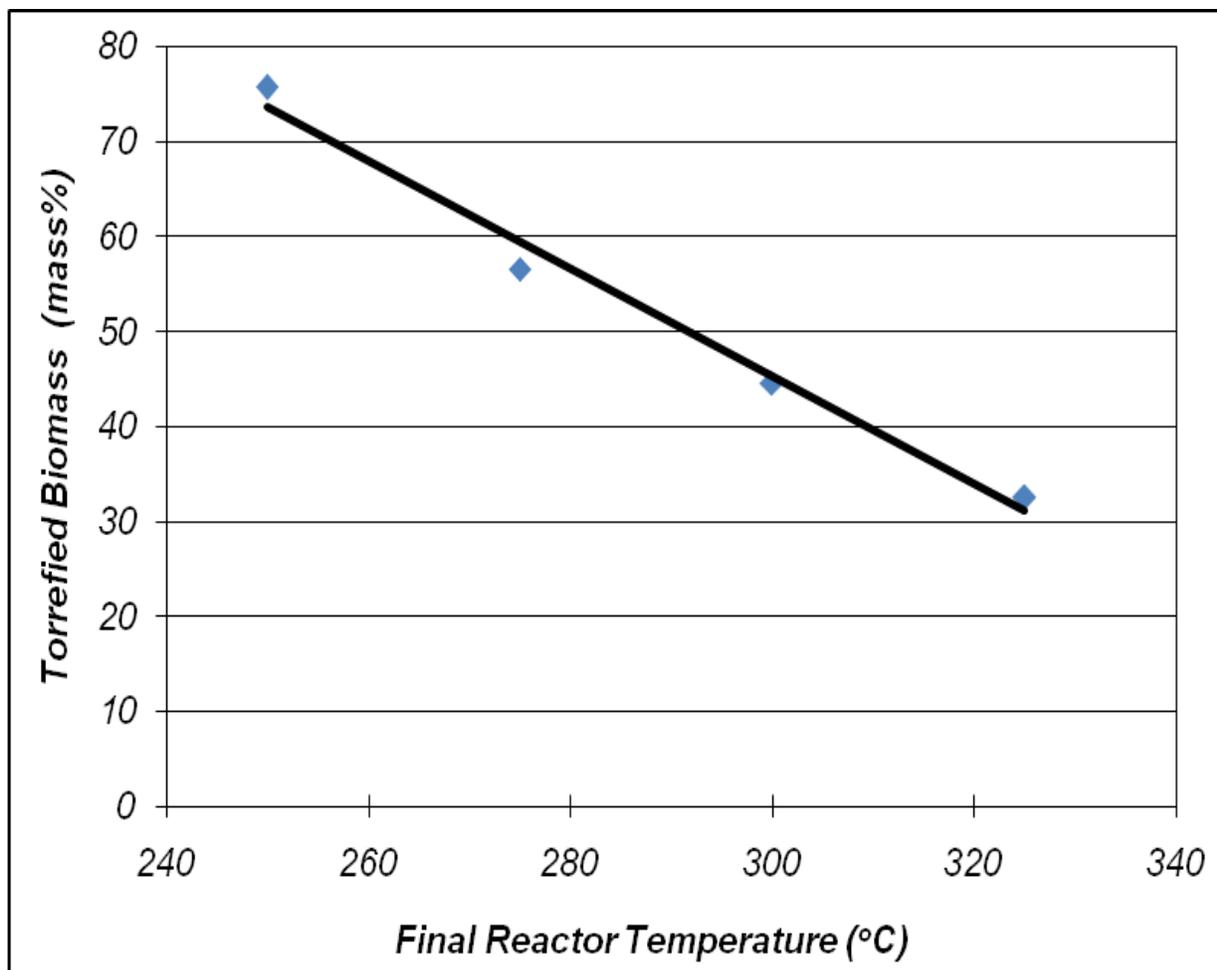


Figure 4.- Effect of final temperature on the yield of torrefied biomass (heating rate 10 °C/min) (Initial moisture content 3.18 mass %).

Figure 5 shows pictures of the crucibles with the torrefied biomass obtained at different final temperatures (250, 275, 300, and 325 °C). The changes in the color observed are a clear indication of modifications in the structure of the biomass studied. These modifications are mainly associated to cross linked reactions of cellulose and hemicelluloses as well as a removal of part of the hemicelluloses.

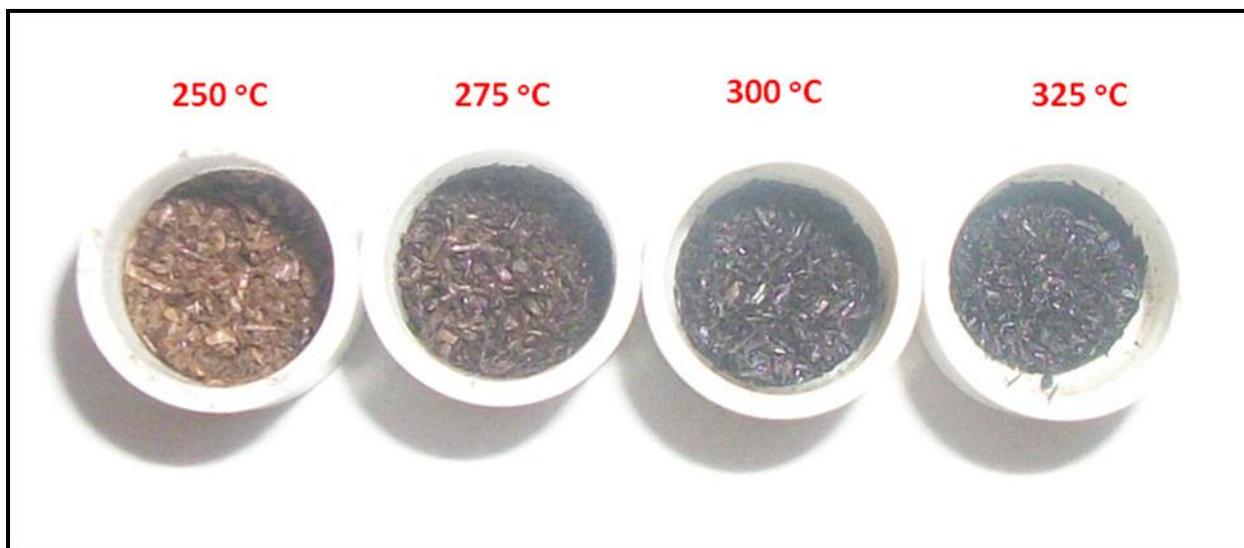


Figure 5.- Effect of the final temperature on the appearance of the torrefied biomass obtained after thermogravimetry.

The effect of biomass heating rate on the yield of torrefied biomass, at the same final temperature is shown in Figure 6. Obviously, the thermal behavior of *Arundo donax* is a function of the heating rate; however the yield of torrefied product does not seem to be affected by the heating rate used (see Figure 7).

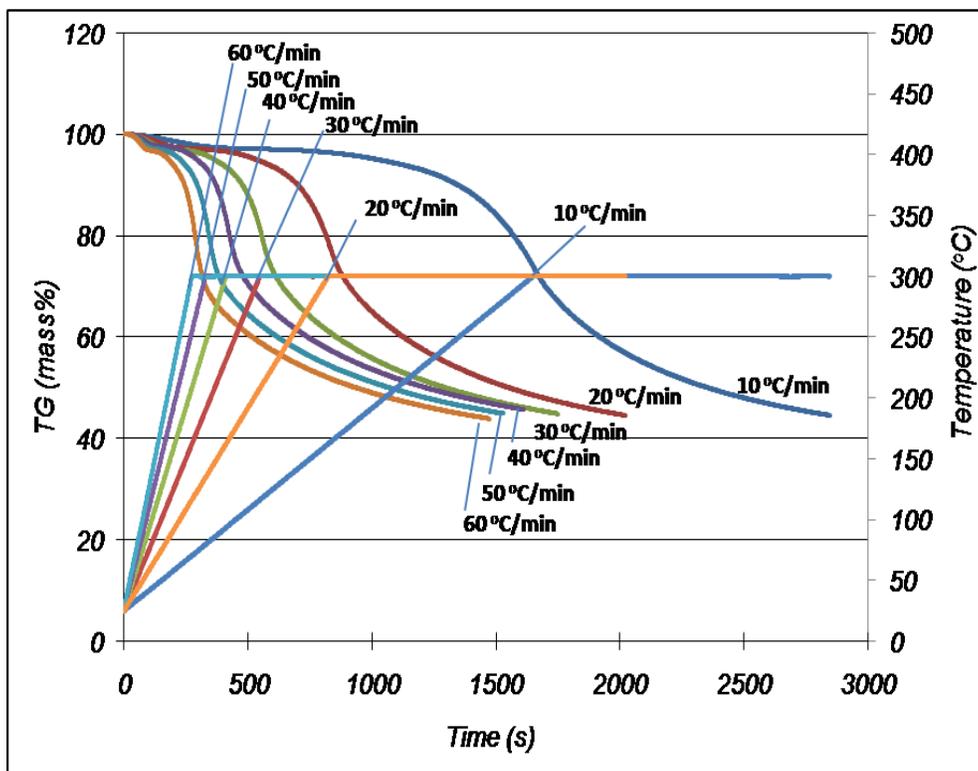


Figure 6.- Effect of heating rate on the yield of torrefied biomass (Final temperature: 300 °C).

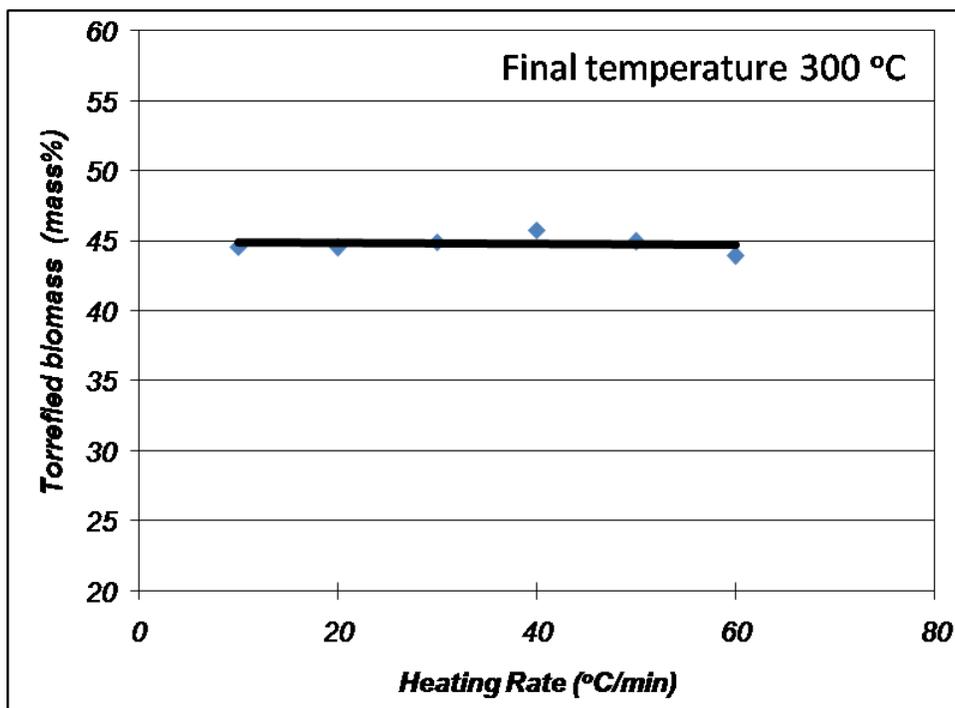


Figure 7.- Effect of heating rate on the yield of torrefied biomass (Final temperature: 300 °C).

Differential Scanning Calorimetric (DSC) Analyses

In spite of the importance of knowing the energy requirements of torrefaction reactions, data relevant to the torrefaction of *Arundo donax* is not available in the existing literature. Torrefaction energy requirements are associated with four main processes: (1) moisture removal, (2) heat required to increase the temperature of the biomass (3) heat associated with torrefaction reactions and (4) heat consumed to increase the temperature of carrier gas (He et al; 2006). Figure 8 shows a typical differential scanning calorimetric curve of *Arundo donax* heated at 10 °C/min under an inert atmosphere (N₂). An important endothermic event was observed from 25 to 150 °C. This event is associated with the heat adsorbed to evaporate the moisture contained in the biomass analyzed. The heat absorbed by this event was approximately 70.8 J/g. Knowing the heat of vaporization of water (2257J/g) it is possible to estimate the moisture content of the samples studied ($70.8 \times 100 / 2257 = 3.13$ mass %). The moisture content estimated by DSC (3.13 mass %) was very close to the moisture content determined by TG (3.18 mass %) (see Figure 2).

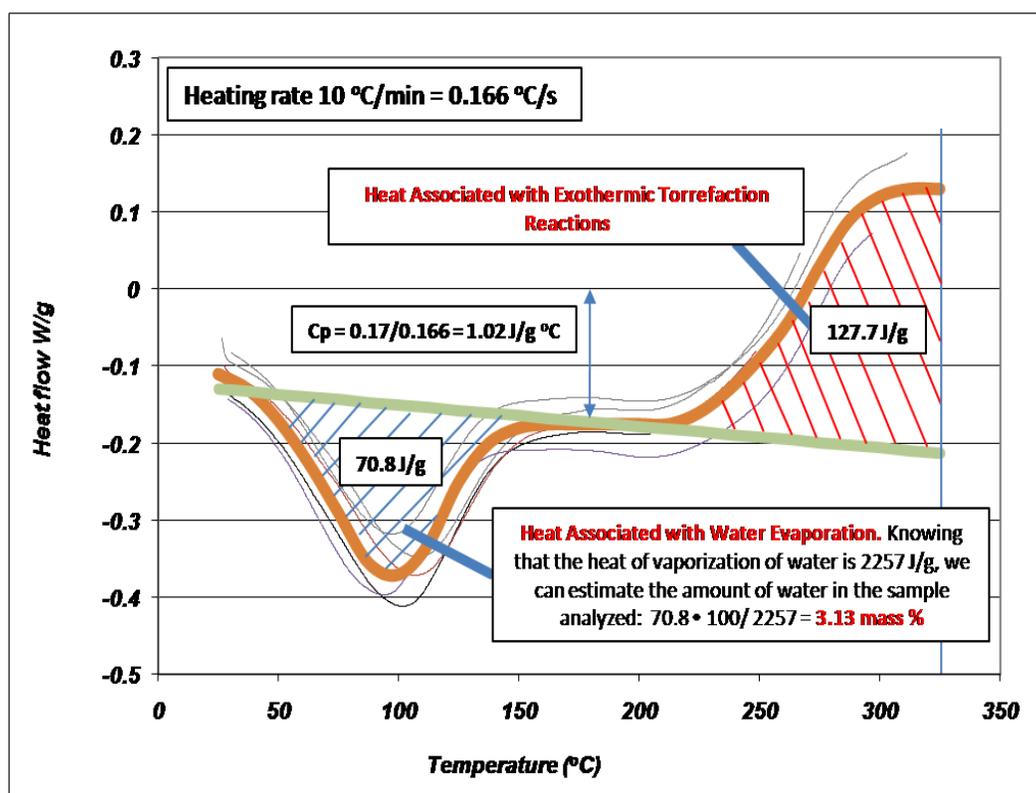


Figure 8.- DSC analysis carried under nitrogen of the samples at a heating rate of 10 °C/min.

The heat flow reaches a plateau at temperatures between 150 and 220 °C. The heat flow in this range of temperatures can be used to estimate the specific heat of the *Arundo donax* samples studied. This is because in this range of temperatures almost all the heat supplied by the DSC machine is used to increase the temperature of the samples. The specific heat (C_p) value estimated (1.02 J/g °C) was calculated by dividing the heat flow by the heating rate (0.17 W/g / 0.166 °C/s). The C_p estimated by the DSC (1.02 J/g °C wet or 1.05 J/g °C dry) is comparable with the C_p estimated, in the same range of temperatures, for other biomasses (between 0.9 and 1.4 J/g °C) (He et al., 2006; Leroy et al., 2006; Leoni et al., 2008; Rath et al., 2003). An important increase in the heat flow was observed for temperatures over 200 °C. This event is a clear indication that exothermic reactions (likely cross linked reactions) occurred in this region. The heat released by the torrefaction reactions (127.7 J/g) in the range of temperatures between 200 and 325 °C was estimated by integrating the DSC curve in this region. It is important to point out that not all lignocellulosic materials exhibit exothermal reactions during torrefaction (He et al., 2006; Leroy et al., 2006; Leoni et al., 2008; Rath et al., 2003). Perhaps the exothermal phenomena observed during the torrefaction of some biomasses can be explained by the nature and the content of the hemicellulose fraction. A large difference exists between the hemicellulose structures of softwood, hardwood and grasses (Bergman et al 2005). Figure 9 demonstrates the existence of a linear relationship between the conversion achieved (as determined by TG) and the heat released by the exothermic torrefaction reactions (determined by DSC).

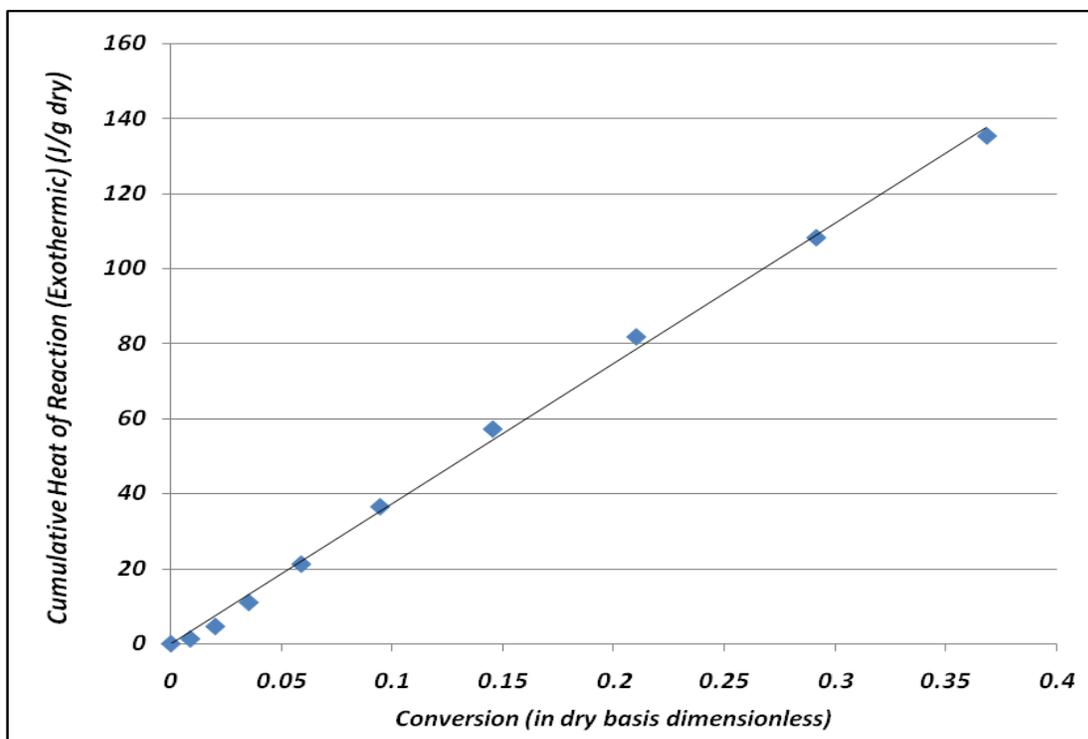


Figure 9.- Relationship between the amount of heat evolved during torrefaction and conversion achieved

Additional DSC studies were conducted to evaluate the thermal behavior of the Arundo samples using a broader range of temperatures (up to 450 °C). Figure 10a shows that the heat released by the exothermic reactions (likely cross linked and polycondensation reactions leading to char formation) is predominate over the endothermic reactions (typically pyrolysis reactions) in the full range of temperatures studied. Figure 10b (on the right side) shows the behavior of the apparent specific heat in the entire range of temperatures studied. At lower temperatures the apparent specific heat is higher than the actual specific heat of the dried Arundo donax (1.05 J/g °C). The reason for the higher value of apparent specific heat is because the extra heat is consumed (without any effect on the increase of the temperature of the sample) to evaporate the moisture. At temperatures over 250 °C a spontaneous increase in sample temperature was observed without heat being supplied from the DSC machine. This effect can be explained by the existence of exothermic reactions. Under these conditions the apparent specific heat can reach negative values.

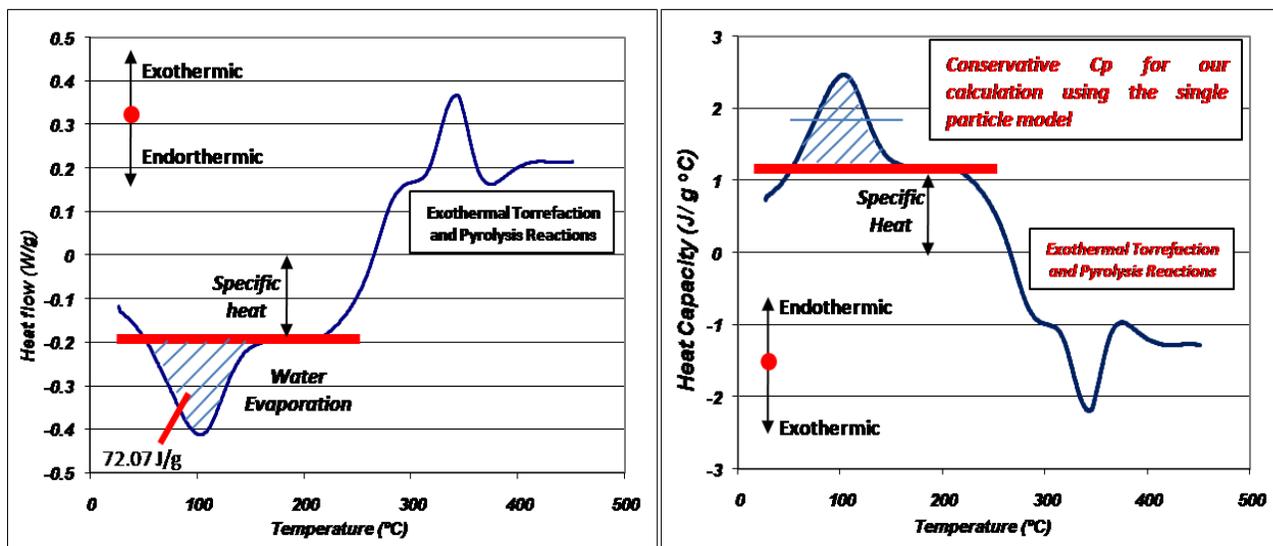


Figure 10.- DSC analysis covering torrefaction and pyrolysis regimes (25 - 450°C)

Figure 11 shows DSC studies at different heating rates. As expected, the heat flow absorbed or released (W/g) by the sample varies with the heating rate. However, no new thermal event was identified when the heating rate of the sample was modified.

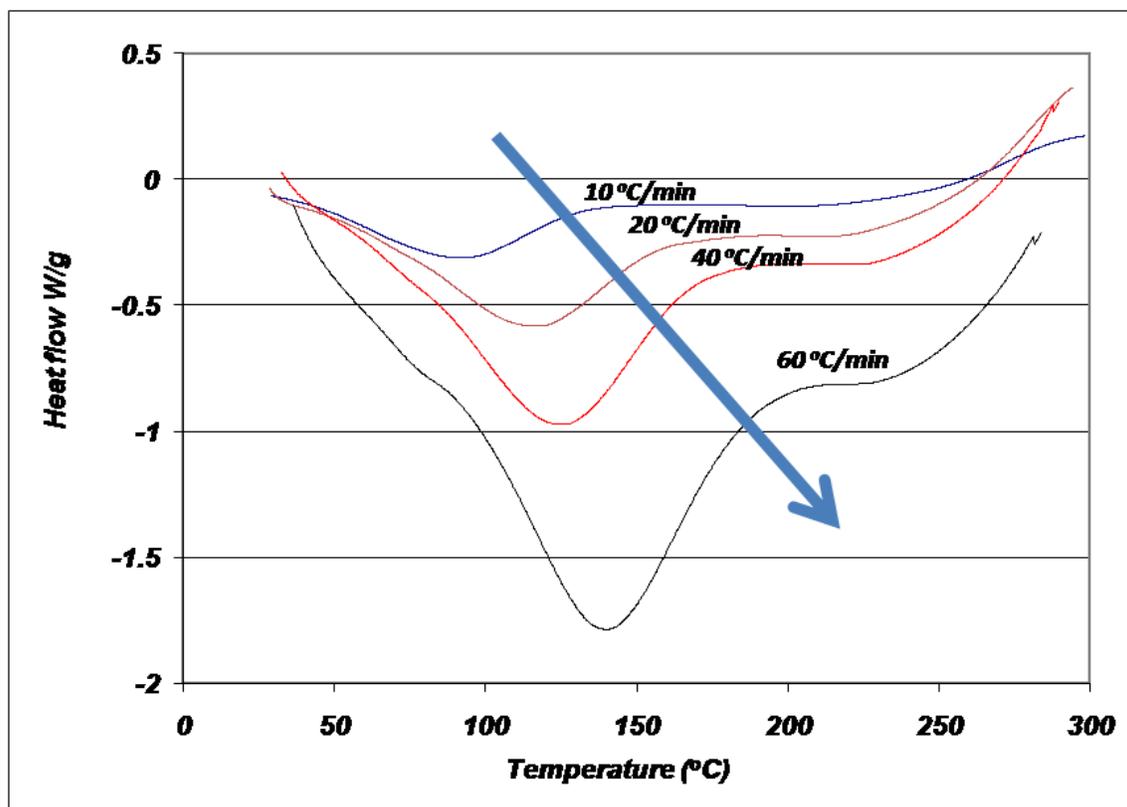


Figure 11.- Effect of heating rate on the thermal behavior of torrefied biomass

4.- Torrefaction Studies in an Auger Reactor and Analysis of Products (torrefied biomass, condensable liquid and gases)

4.1.- Materials and Methods

Arundo donax chips were torrefied in the Auger reactor at wall temperatures of 310 °C and residence times of 3, 5 and 8 minutes (See Figure 12). The reactor consists of 100 mm diameter stainless-steel tube placed in a Linberg/Blue M (model HTF55322A) furnace with an Auger driven by a 1 hp motor (maximum speed 1725 rpm, 10.9 A). The residence time of the biomass inside the reactor can be controlled by varying the speed of the Auger with a manual controller. The torrefied biomass was collected in a stainless-steel container located downstream. A vertical condenser followed by a series of ice-cooled traps was used to condense the torrefaction vapors. The pressure inside the reactor was maintained at a few millimeters of water below atmospheric pressure using a vacuum pump. The flow of nitrogen to the reactor was measured and controlled

with two rotameters (one measuring the flow to the hopper and the other to the Auger Reactor). The furnace was heated to a temperature of 310 °C to promote the thermal degradation of the biomass. The space between the hopper and the furnace was cooled by cold water running through copper tubes. This was done to avoid heating the reactor feed. The auger RPM was maintained to make sure the biomass particles stay inside the torrefaction regime long enough to thermally crack (3, 5 and 8 minutes for the project). The section of system after the end of furnace was heated by heating coils to make sure that the torrefaction gases do not condense before reaching the condenser. A vertical condenser followed by a series of ice chilled condenser pots was placed towards the end of the system to condense the torrefaction vapors. The non condensable gases which pass the condensing system are exited through a smokestack. The carrier gas employed was N₂ under pressure which was fed into the reactor at the entry point of the biomass. The torrefaction process involved heating the *Arundo donax* under an inert environment (2 L/min of Nitrogen). The *Arundo* chips that were larger in size could not be fed through the hopper installed with the reactor as it only permits feeding fine biomass particles. Hence, the *Arundo* chips were fed externally using a zip lock bag attached to the reactor. Approximately 15 g of biomass was fed into the reactor at once. The post-oven temperature was kept at 250 °C to ensure the vapors from the torrefaction step do not condense before reaching the condensers. The pressure inside the reactor was maintained a few millimeters of mercury below atmospheric pressure using a vacuum pump with a valve to control the pressure inside the reactor in order to make sure that the torrefaction vapors travel towards the exit of the system. To control the pressure inside the reactor and collect gases with oxygen content as low as possible, a special loop was built round the vacuum pump.

The condensed liquids collected in the series of condenser pots as well as in the vertical condenser were analyzed. The gases produced during the torrefaction process were collected in gas sample bags and were also analyzed.

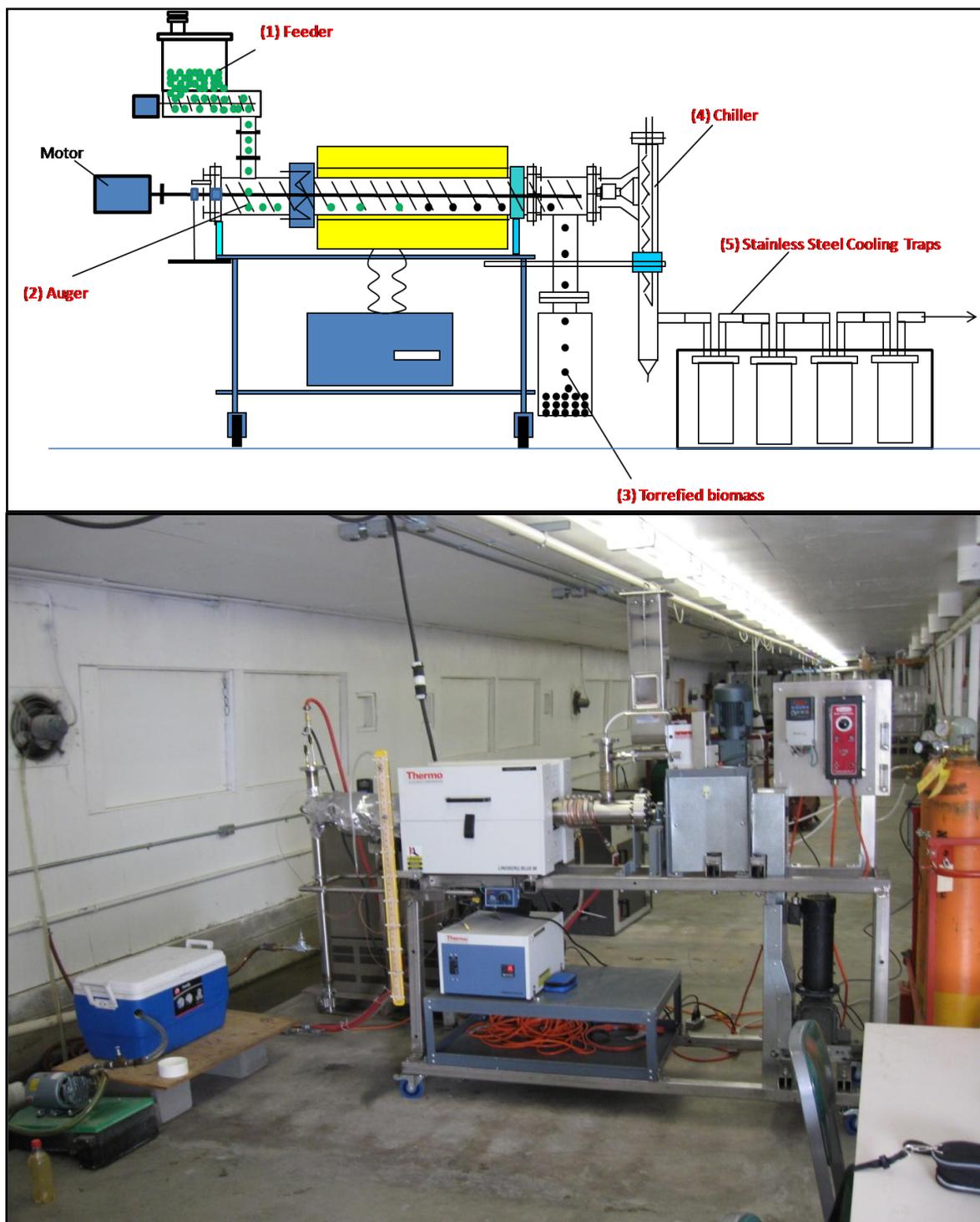


Figure 12.- Auger reactor used for the torrefaction studies (Washington State University)

The content of water in the condensed liquid (product of torrefaction) was determined by Karl Fischer titration; the content of other targeted compounds was determined by GC/MS and

GC/FID. An Agilent 6890N with column HP-5MS (30m×0.250mm, 0.25µm) from an Agilent equipped with a GC 7683B auto sampler was used. The detector was an Agilent 5975B inert XL MSD. The sample used methanol as a solvent and torrefaction liquid was added in a 5 % mass. 0.02 % of phenanthrene which was added as an internal standard. In each experiment, 1 µL of this solution was injected into the system. The GC inlet was set at 250°C and had a split ratio of 1:20. The GC used a constant flow of 1 mL/min. The GC program was set at 40 °C for 1 minute in the beginning. It was then heated to 280 °C with a heating rate of 3 °C/min and held for 10 minutes. All the samples were injected 3 times.

The high heating value was determined using a Parr Bomb calorimeter 6200. Approximately 0.65± 0.1 grams of sample were pelletized using a manual press. A 10 centimeter nickel alloy fuse wire was attached between the ignition terminals of the bomb. The biomass pellet was placed in the bomb, which was sealed and then pressurized with oxygen to 30 atm. The bomb was then submerged in a bucket and filled with 2000 grams of de-ionized (DI) water, which was 3°C – 5°C below the jacket temperature. After the bomb was submerged, the charge was fired. At the end of combustion, the bomb was rinsed with DI water and the remaining length of the fuse wire was measured for fuse correction. Acid titrations of the bomb's washings were used to calculate the acid corrections. The gross heat of combustion was determined after the corrections were applied.

The gas composition was determined by gas chromatography. The analysis of the gases produced by the torrefaction of *Arundo Donax* was carried out using a Varian CP-3800 Gas Chromatograph with a Hayesep-Q 80-100 mesh silcosteel packing 18'x1/8" ID column under a flow of nitrogen at a temperature of 80°C. The detection units used included a thermal conductivity detector (TCD) at 120 °C with a filament temperature of 320 °C using a carrier gas of N₂-Ar, and a flame ionization detector (FID) at a temperature of 225 °C. The gases analyzed consisted of carbon dioxide, carbon monoxide, hydrogen, methane, and oxygen. Methane was analyzed by FID, while all other gases were determined by TCD. All gases, except oxygen, were calibrated using gas standards composed of a 0.1, 1, and 10% concentration of each gas with the remainder as nitrogen. Calibration gases were supplied by ISGAS. Oxygen was calibrated at three points, none present, atmospheric, assumed to be 20.9 %, and 99.5 % from an oxygen canister available in lab.

All gas samples obtained from the torrefaction experiments were tested in triplicate and compared against the calibration standards. High concentrations of oxygen, 14-16%, within the system indicated a gas leak allowing atmosphere into the reactor. The concentration of oxygen determined in the gases was used to estimate the total volume of air present in the gas stream and this value was subtracted prior to determining the gas fractions. Within the torrefaction gases, carbon dioxide was by far the most common accounting for a large majority of the gas, while hydrogen and carbon monoxide added approximately 1 mass % each, and methane accounted for approximately 0.5 mass % of the off gas. No other major gas spikes were observed on the TCD or FID report.

4.2.- Analysis of Results

Table 1 shows the yield of torrefied products from *Arundo donax*: torrefied solid, gases and liquids. These tests were conducted using an *Arundo donax* with a moisture content of 6 mass % subjected to torrefaction at a wall temperature of 310 °C with different residence times. Clearly the yield of torrefied biomass decreases as the residence time of the biomass inside the reactor increases. According to the results shown in Figure 4 when the biomass reaches 300 °C (10 °C less than the wall temperature controlled) the yield of torrefied biomass should be 45 mass %. The fact that the yield of torrefied biomass obtained at 8 minutes was around 50 mass % suggests that the residence time in the reactor was not long enough to ensure that the temperature at the center of the *Arundo Donax* particle reached 300 °C. According to Figure 4, yields of 55.5 mass % are obtained when the average temperature in the particle is 285 °C. Figure 13 shows the yield of products as a function of the residence time of the biomass in the reactor. Higher residence times will result in an increase in the temperature of the particles and consequently in lower yields of torrefied biomass.

Table 1.- Yield of products as a function of the biomass residence time obtained in an Auger reactor when the external wall temperature was 310 °C (moisture content of feedstock 6 mass %).

TORREFACTION TIME (min)	YIELD OF SOLID (TORREFIED MATERIAL) (mass %)	YIELD OF LIQUID (CONDENSABLE) (mass %)	YIELD OF GASES (by difference) (mass %)
3 minutes	86.0	6.7	7.3
3 minutes	87.6	7.9	4.5
5 minutes	59.9	21.8	18.4
5 minutes	64.4	19.4	16.2
8 minutes	55.5	23.3	21.2
8 minutes	54.5	23.3	22.2

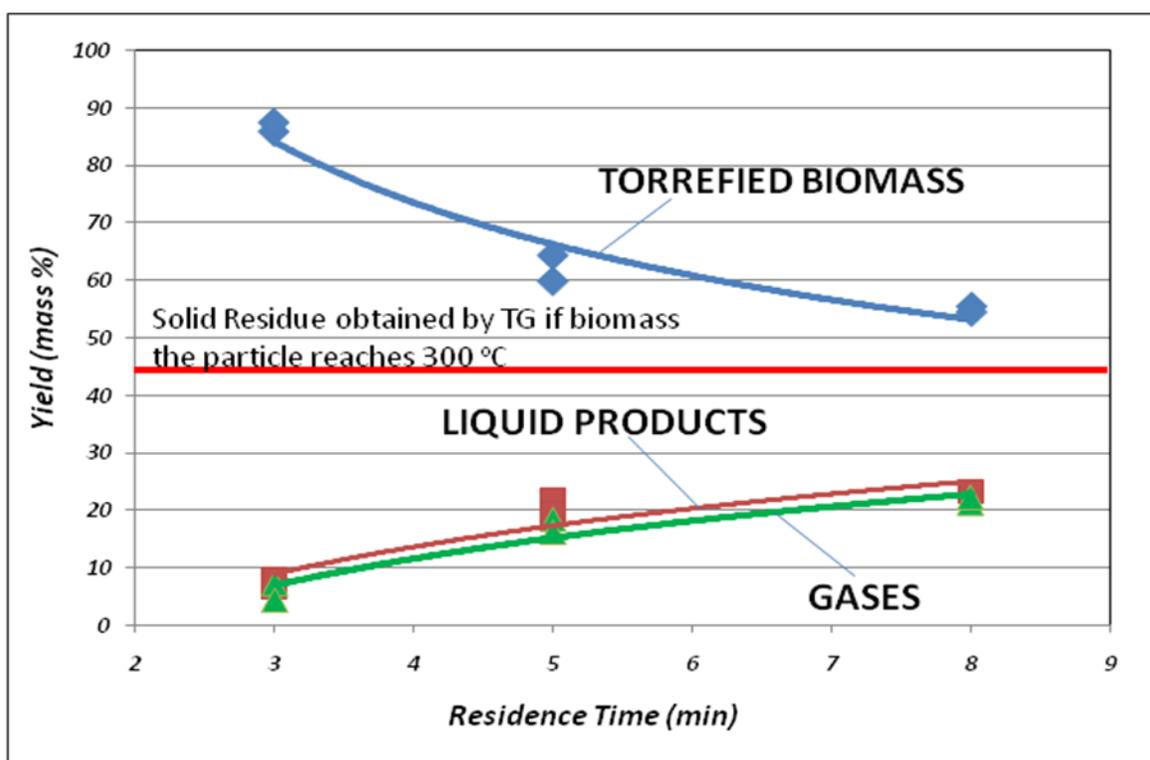


Figure 13.- Yield of products as a function of biomass residence time (external wall temperature: 310 °C, biomass moisture content: 6 mass %).

The heat transfer phenomena happening during torrefaction can be explained by the schematics shown in Figure 14. The heat transferred from the reactor's wall increases the temperature of the bed of particles and each of the particles within the bed starts to heat up. For relatively large particles a reaction front is established. Basically, this model assumes that there is a region outside the reaction front which is completely torrefied and a shrinking core of which is unreacted.

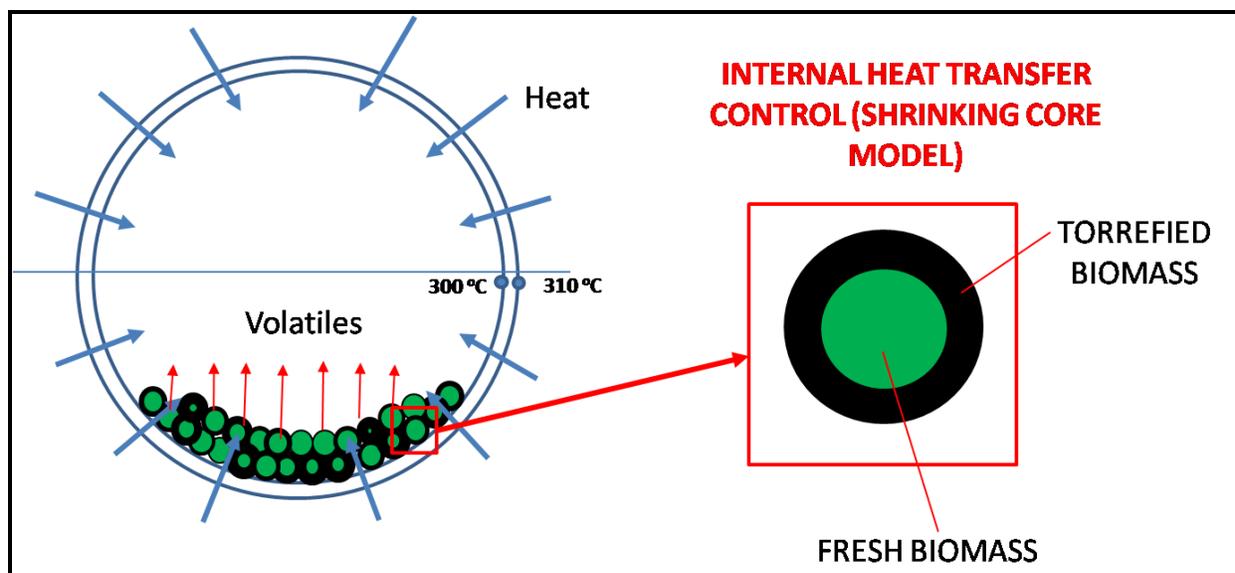


Figure 14.- Schematics describing the torrefaction process inside a Pyrolysis Reactor.

Torrefaction of large particles (chips) is a typical example of a system in which a very slow heat transfer process is accompanied by a much faster rate of reaction (torrefaction reactions) (See Figure 15). If the internal temperature gradient is very large, the reaction zone will be very narrow, and the process can be regarded as a torrefaction front advancing into the virgin solid at a rate determined by the velocity at which the thermal wave propagates into the solid. If torrefaction is assumed complete at a defined temperature $T = T_p$ (say 290 °C), then estimating the rate at which T_p propagates into the particle will be a good way to estimate the rate at which the torrefaction process advances. Estimating the propagation of the reaction front requires the solution of heat transfer equations with appropriate boundary conditions (Bird et al., 2007; Pyle and Zaror, 1984).

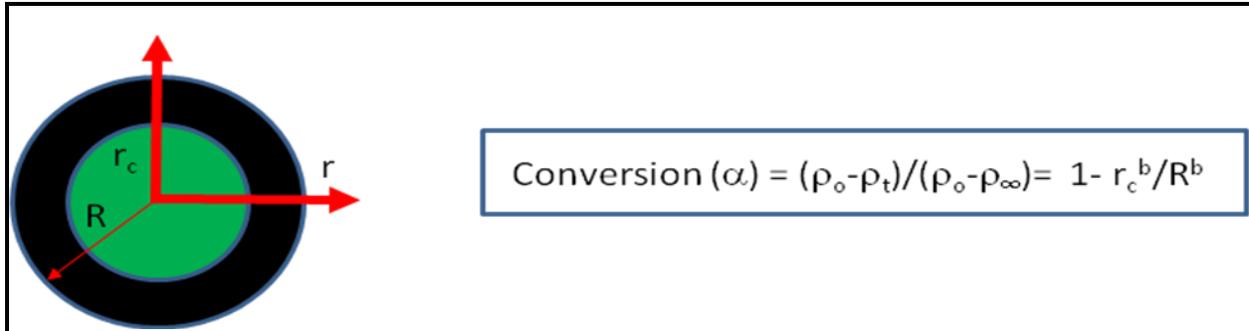


Figure 15.- Representation of the shrinking core model (r_c : Represent the position of the reaction front, i.e, where $T = T_p$, and the time for complete pyrolysis is determined by the time needed for the temperature at the center to reach T_p , which is controlled purely by internal heat transfer)

If the apparent reaction enthalpy is negligible (which is not true for our case but is a good simplification as seen in Figure 9), a number of semi-analytical solutions are available to determine the time required for the temperature in the center of the particle to reach T_p (290°C). For example, if the temperature on the surface of the particle is known (T_f), it is possible to describe the evolution of the temperature inside the particles by solving generalized heat transfer equations. In the case of a cylinder, the solution of the heat transfer equations will result in a temperature profile similar to the one shown in Figure 16 (Bird et al., 2007; Pyle and Zaror, 1984).

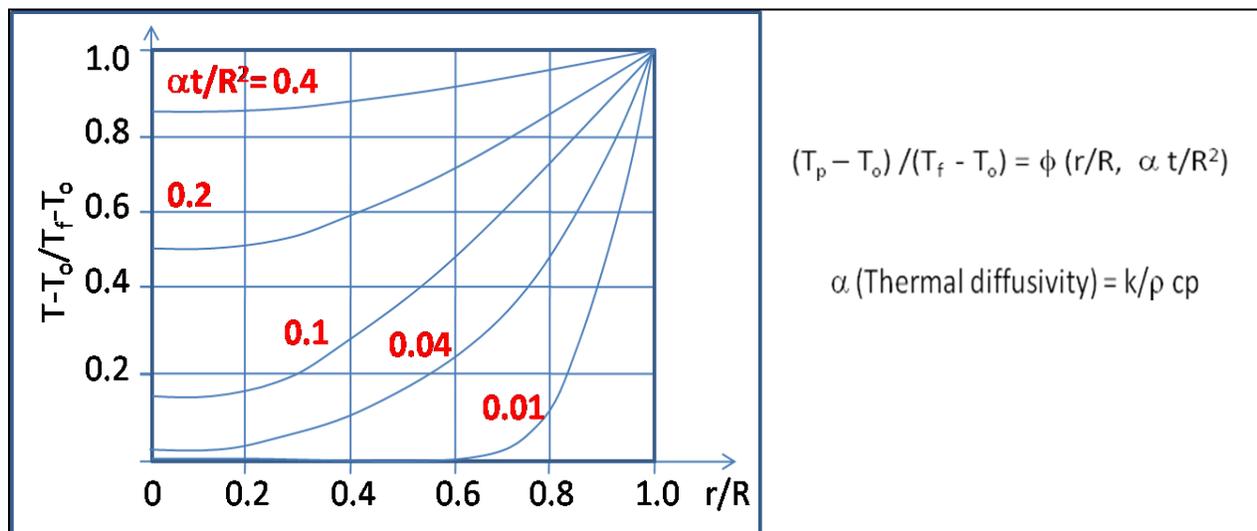


Figure 16.- Temperature profile in a idealized single particle model (Bird et al., 2007).

Using figure 16 it is possible to make a rough estimate of the time at which the particle reaches 95% of its potential conversion (potential yield at 290 °C is 50 mass %, see Figure 4). The temperature at the reaction front was considered 290 °C. According to the shrinking core model, to achieve 95 % of conversion, r/R should be 0.22. For our calculations we assumed that the biomass particle is a long cylinder in which the heat transfer at the edges can be disregarded compared with the heat transferred through the lateral walls. The thermal conductivity of the biomass was considered to be 0.001 J/s cm K and the radius of the particle was considered 1 cm. In order to take into account the heat consumed to vaporize the water, the C_p of the biomass was taken as 1.8 J/g °C (See right side of Figure 10). Other suppositions were: (1) particles were being heated from 25 °C ($T_o = 300$ K) (2) the surrounding temperature was 10 °C below the external wall temperature of the reactor, which means the surrounding temperature used was 300 °C ($T_f = 573$ K).

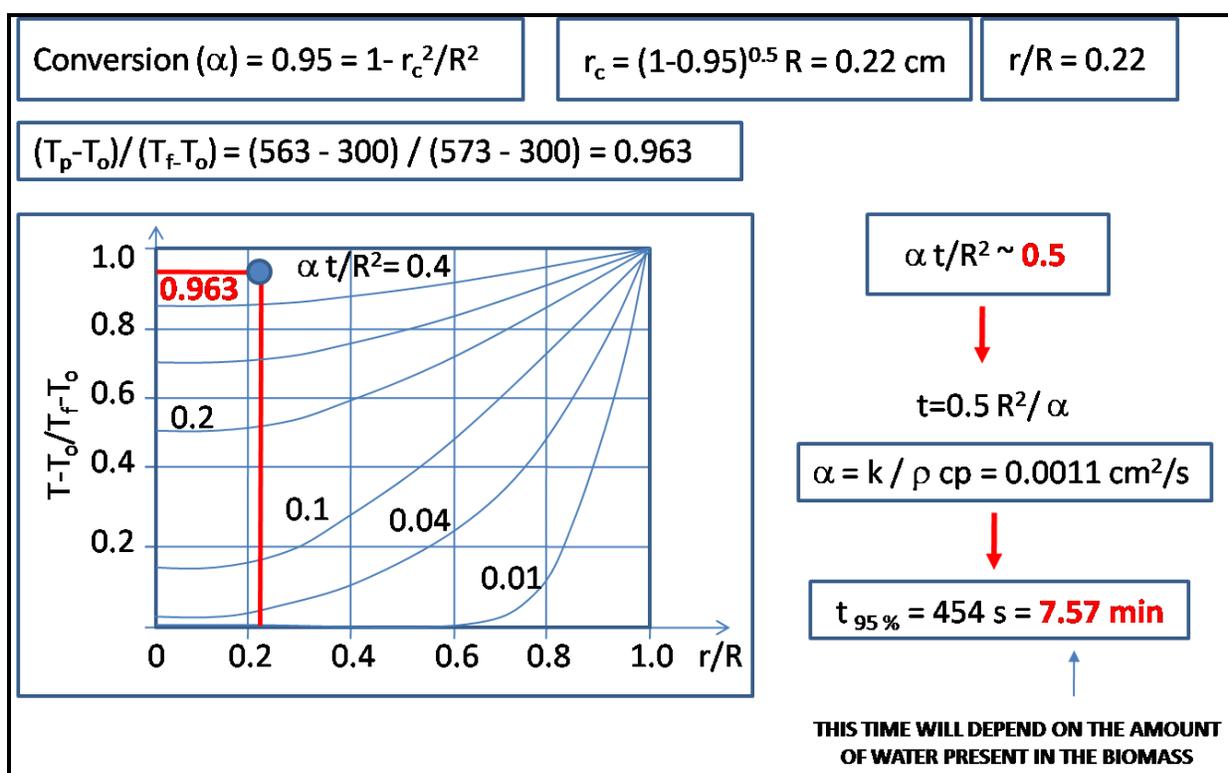


Figure 17.- Rough estimate of the time needed to achieve 95 % of the potential (maximal) conversion achievable at the torrefaction conditions studied.

The rough results obtained suggest that in 7.57 min (almost 8 minutes) the particle is able to reach 95 % of the yield of torrefied biomass achievable if the whole particle is heated at 290 °C. This

result is only an approximation but can be used to understand the importance of particle internal heat transfer on the yield of torrefied biomass achieved.

The nature of the products formed during torrefaction reactions depends on composition of the biomass processed and on the reaction conditions used (temperature and time) (Bergman et al., 2005). During torrefaction, the crosslinking and dehydration reactions happen resulting in the formation of a chaotic structure of the original sugar structures (Bergman et al., 2005).

The main product of torrefaction reactions is the water produced from the thermal decomposition of carbohydrates and from the freely bound water (moisture). The organic products are mainly acetic acid, methanol and 2-furaldehyde. Some products from the evaporation or cracking of biomass extractives are also typically found in the torrefaction condensable fraction (Bergman et al., 2005).

The evolution of water content in the liquid collected (in mass %) as the residence time of the biomass inside the reactor increases (determined by Karl Fischer Titration) is shown in Figure 18. The content of organics was determined by difference. The water collected is produced by two sources: (1) From the biomass moisture and (2) From the cross-linking and condensation reactions. At very low residence times (3 minutes) most of the water collected is derived from feedstock moisture (6 mass %). As the torrefaction process advances more and more water is formed from cross linking and de-hydration reactions.

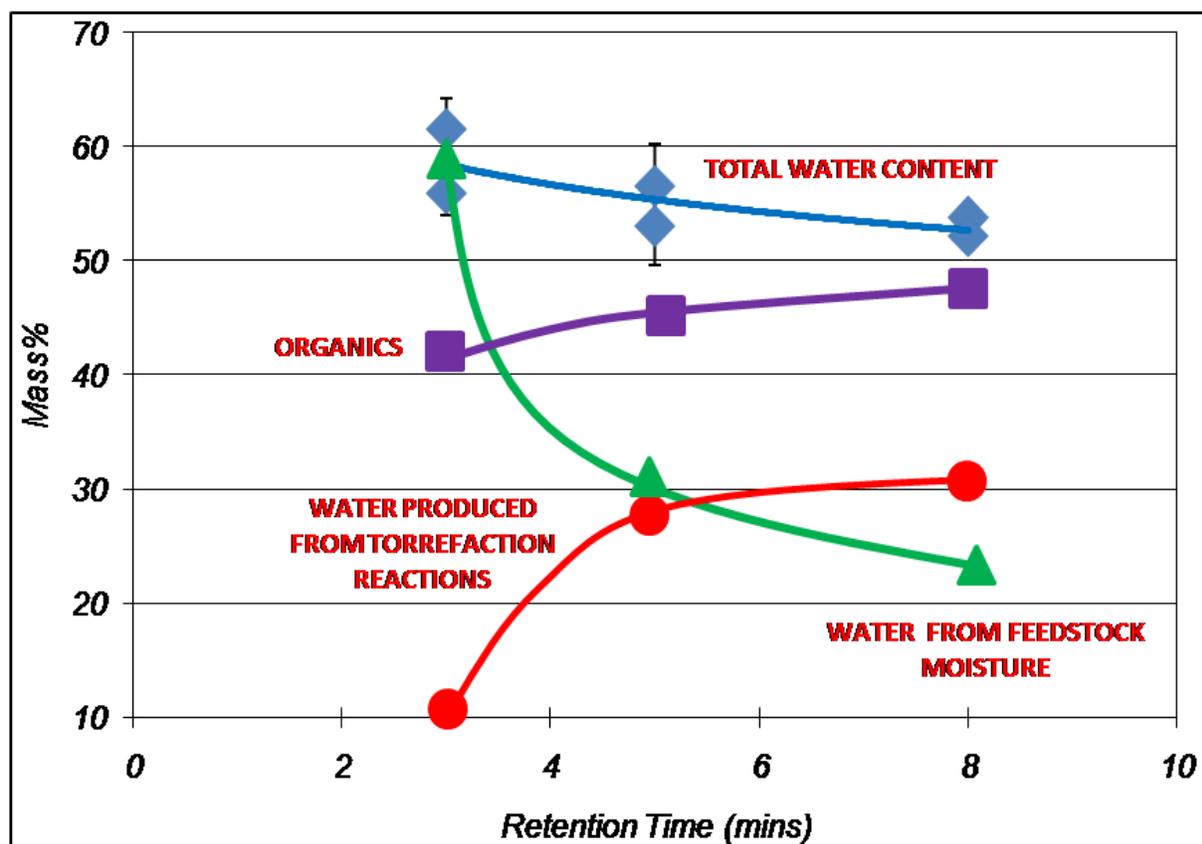


Figure 18.- Composition of condensable fraction in volatiles.

Figure 19 shows the changes in the content of methanol and acetone, determined by GC/FID, in the liquid collected at different residence times (reactor wall temperature: 310 °C). While the content of methanol clearly increases as the residence times augment, no major change was observed in the content of acetone in the liquid collected.

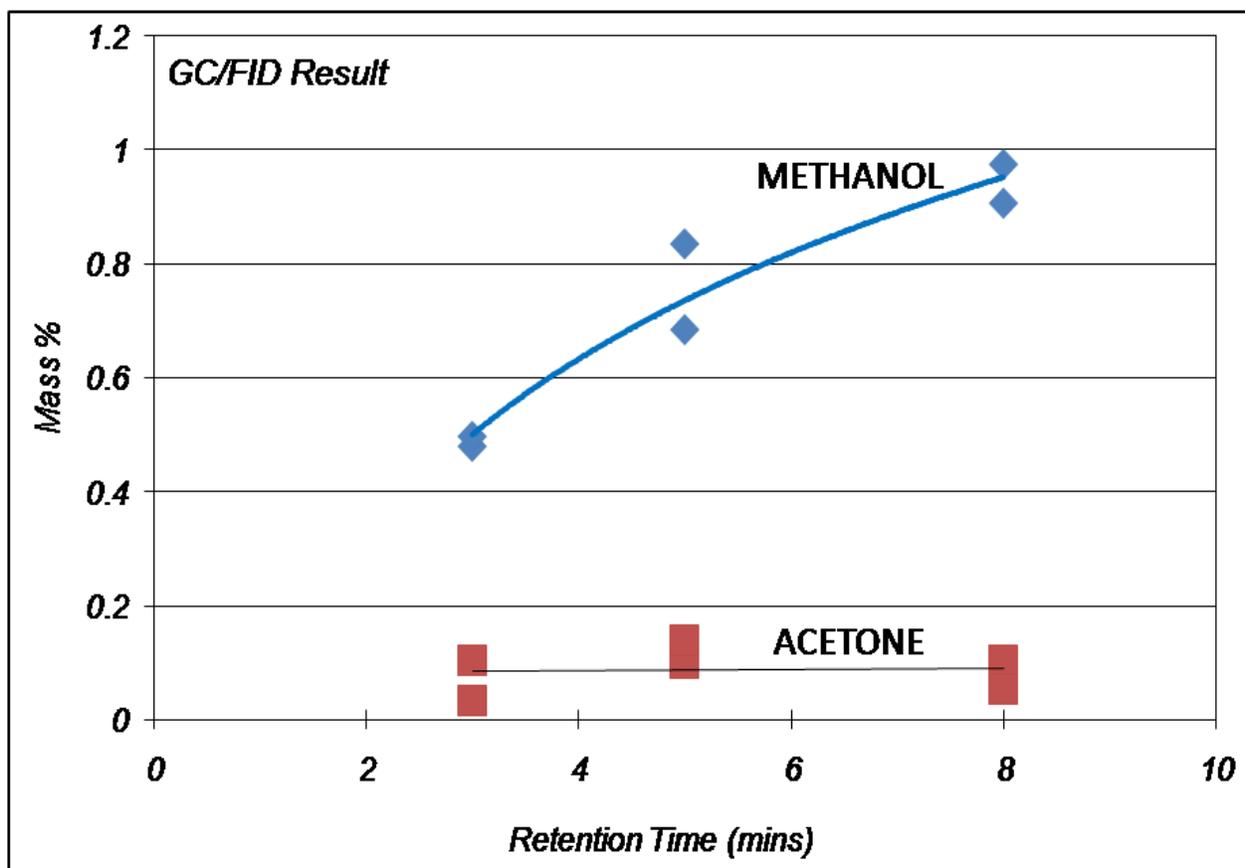


Figure 19.- Content of methanol and acetone in the liquid collected.

The changes in the content of glycoaldehyde, acetic acid, propionic acid and acetol in the liquid condensed, determined by GC/MS, as a function of the residence time of the Arundo donax particle inside the torrefaction reactor, is shown in Figure 20. No major change in the content of these compounds as a function of the residence time in the reactor was observed. It is important to point out that these four compounds account for more than 50 mass % of the organics released during torrefaction. These liquids have very low pH due to the high content of acids, thus, special materials should be used if the vapors are to be condensed and cold regions should be avoided in the combustion chambers if the heat from these streams will be recovered. The recovery and commercialization of the acetic acid contained in the liquid collected should be further investigated.

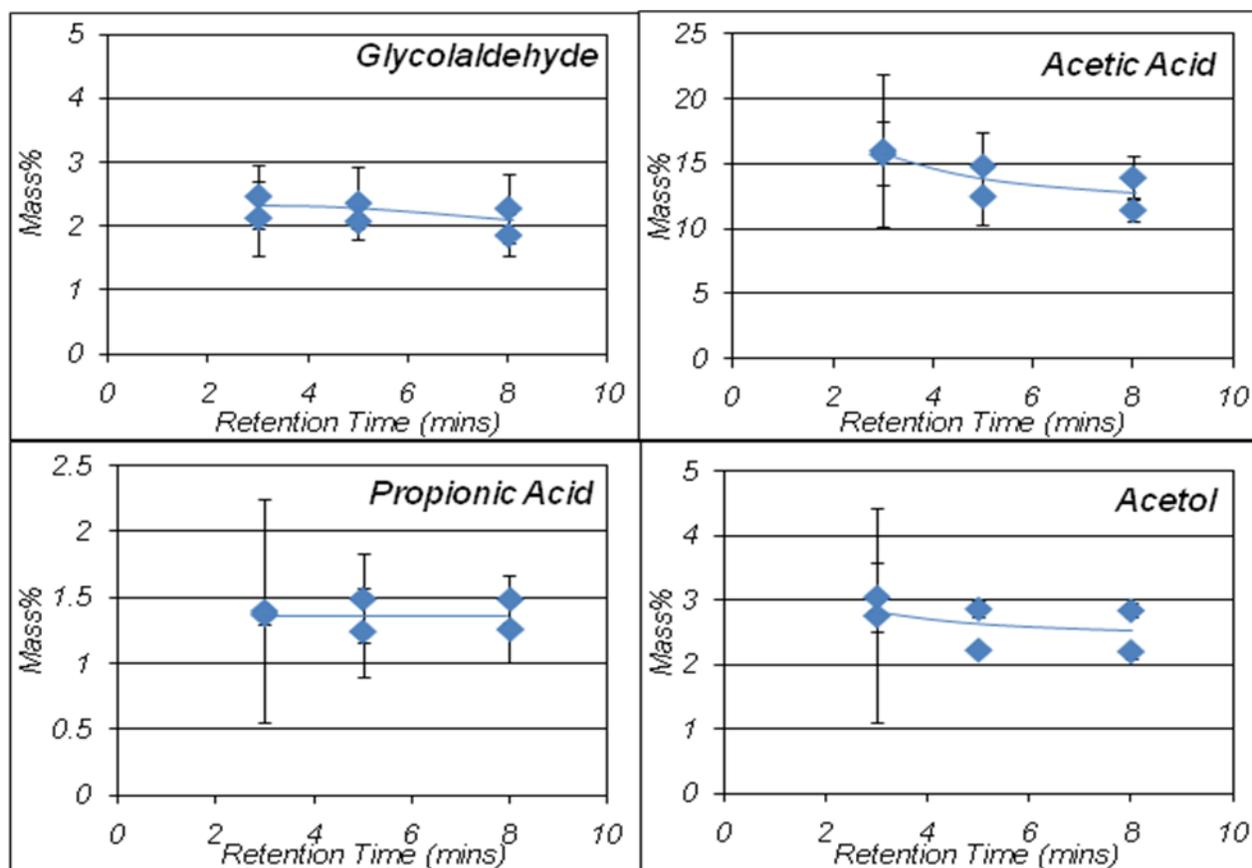


Figure 20.- Content of glycolaldehyde, acetic acid, propionic acid and acetol in the condensable fraction.

The increase in calorific value of the torrefied biomass as opposed to fresh biomass is because during torrefaction the biomass loses more oxygen and hydrogen than carbon. The high heating value of the torrefied materials obtained at different residence times are shown in Figure 21. Clearly the high heating value (HHV) of the biomass increases from 18.4 MJ/kg (for the received samples) to 23.8 MJ/kg for the materials torrefied at 8 minutes. This HHV is very close to those reported in the literature (20-24 MJ/kg) (Bergman et al., 2005).

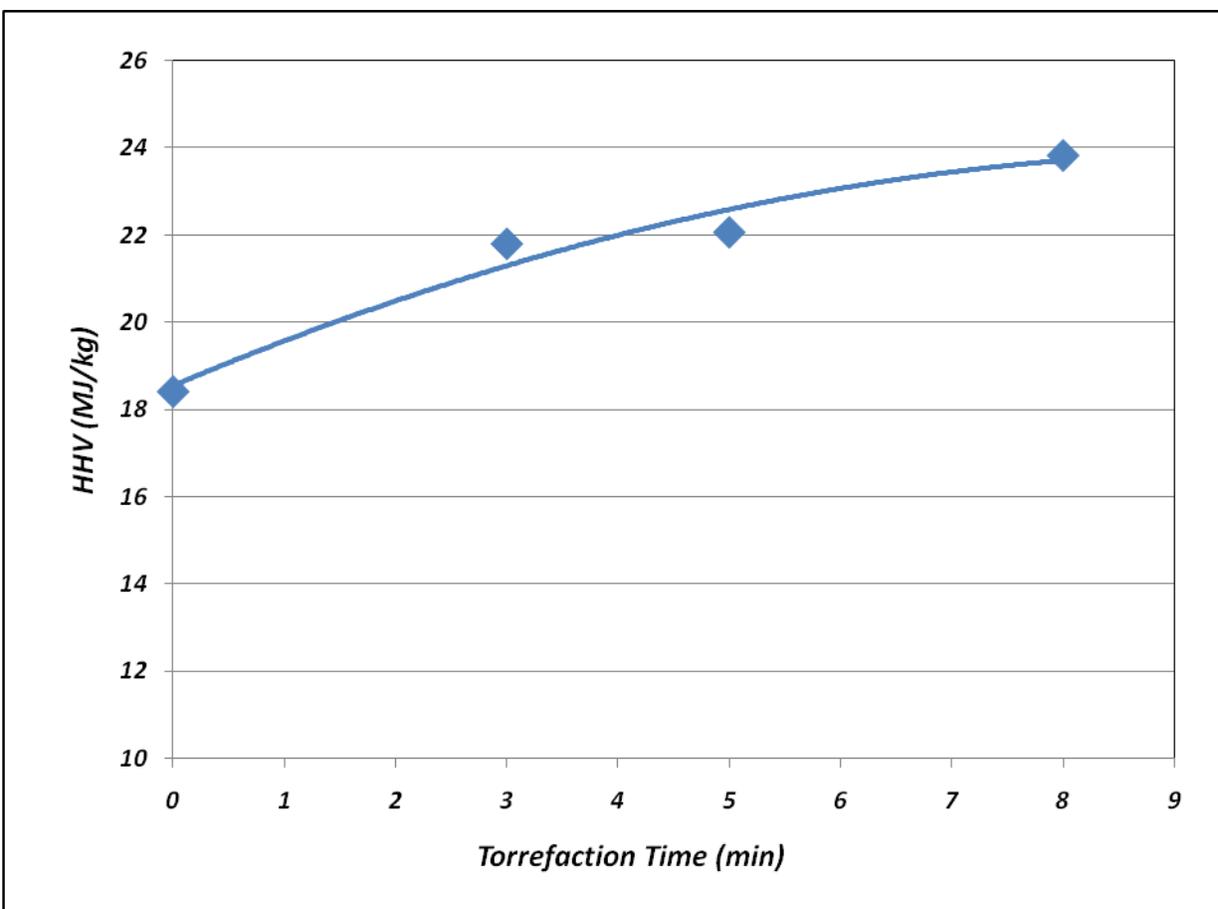


Figure 21.- High heating value of torrefied biomass obtained at different residence times in the reactor (external wall temperature 310 °C).

The composition of the gases released during the torrefaction of *Arundo donax* is shown in Table 2. The composition of these gases does not change much with the torrefaction time. Although the main component is CO₂, small amounts of H₂, CH₄ and CO were also detected (see Table 2). These results are similar to those obtained by Prins et al., (2006) and by Deng et al., (2009). From the distribution of products obtained, we must expect that the torrefaction vapors will have a water content over 25 mass % and a CO₂ content close to 50 mass %. This high content of incombustible molecules creates serious problem when releasing the heat contained in the organic fraction of these vapors. Under these conditions it is very difficult to burn these gases. According to (Bergman et al., 2005), an adiabatic flame temperature of at least 1000 °C is required to combust these gases. This temperature can only be achieved if auxiliary fuels such as the leaves or various other auxiliary fuels are employed in the combustion chamber.

Table 2.- Gas Composition

TORREFACTION TIME (min)	CO₂ (vol. %)	H₂ (vol. %)	CH₄ (vol. %)	CO (vol. %)
3 minutes	96.9	2.2	0.9	ND
3 minutes	98.5	0.9	0.6	ND
5 minutes	97.4	0.9	0.6	1.0
5 minutes	97.7	0.8	0.5	0.9
8 minutes	97.4	1.0	0.6	1.0
8 minutes	97.8	0.7	0.5	1.0

5.- Energy Balance

5.1.- Materials and Methods

The energy balances were carried out knowing the flow rate of biomass, carrier gases, products (solid, liquids and gases) and the calorific value of each of these streams as determined in our studies with the Auger reactor. The heat of torrefaction reactions determined by DSC and the yield of products obtained by the TG were also used to perform the energy balances of a pyrolysis reactor. Two energy balances were conducted. The first one was based on the results obtained by the DSC and TG studies. The second energy balance (an overall balance) used the information of the yield, the composition, and the calorific value of the products obtained in tests conducted with the Auger Reactor.

5.2.- Analysis of Results

First Energy Balance:

Figure 22 shows the basic assumptions used to conduct the energy balance of a torrefaction unit. This first energy balance was conducted using the data obtained by DSC and TG.

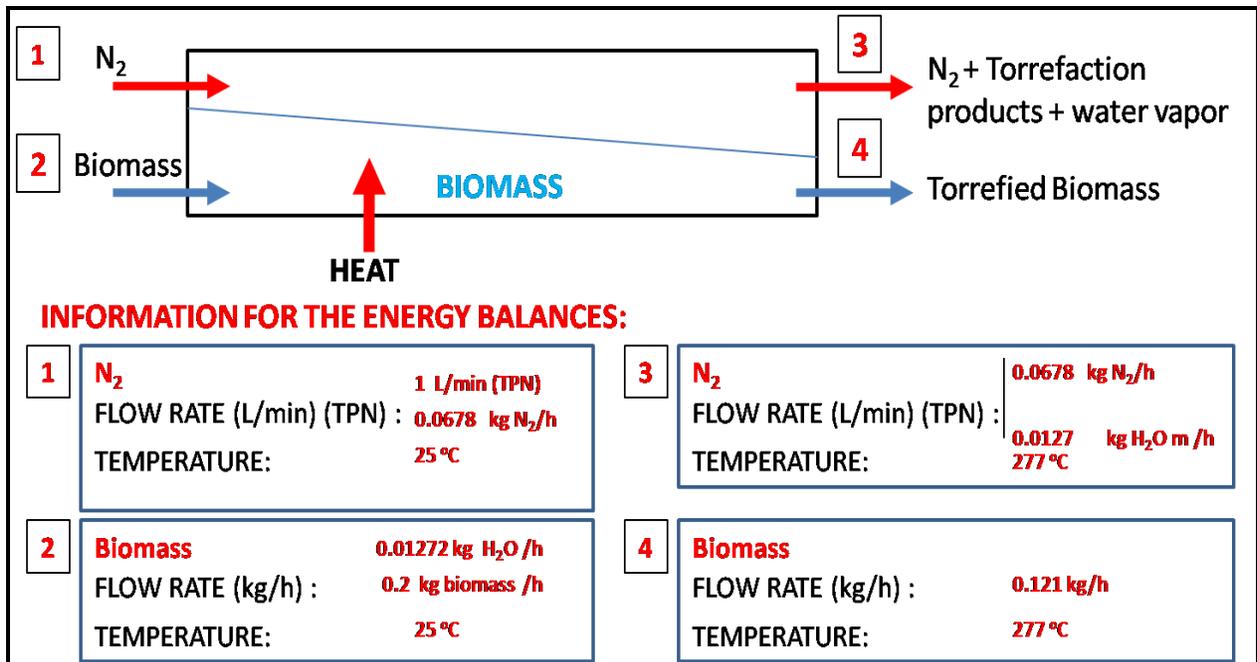


Figure 22.- Energy balance using the data obtained by TG and DSC

The information used to perform the energy balances was the following:

$$\text{Flow of nitrogen (m)} = P \cdot V \cdot M / R \cdot T = (1 \text{ atm} \cdot 1 \text{ (L/min)}) \cdot 28 \text{ (g/mol)} / (8.314 \cdot 10^{-2} \text{ (L atm/K mol)} \cdot (25+273) \text{ K}) = 1.13 \text{ g/min} \leftrightarrow 0.0678 \text{ kg/h}$$

$$C_{p \text{ N}_2 \text{ 25 } 0\text{C}} = 1.04 \text{ kJ/kg K} \quad C_{p \text{ N}_2 \text{ 270 } 0\text{C}} = 1.064 \text{ kJ/kg K} \quad C_{p \text{ average}} = 1.052 \text{ kJ/kg K}$$

$$C_{p \text{ Bio-mass}} = 1.02 \text{ kJ/kg K} \quad \text{Moisture Content initial Bio-mass} = 6 \text{ mass\%} \quad \text{Heat of vaporization of water } 100 \text{ } ^\circ\text{C} = 2257 \text{ kJ/kg}$$

$$\text{Torrefaction Heat}_{\text{Conversion } 0.38} = -150 \text{ kJ/kg biomass} \quad C_{p \text{ H}_2\text{O liquid}} = 4.18 \text{ kJ/kg K} \quad C_{p \text{ H}_2\text{O Vapors (185 } 0\text{C)}} = 2.64 \text{ kJ/kg K}$$

Using this information it was possible to conduct the energy balances of the torrefaction unit.

These balances assumed that the heat that needs to be supplied to the torrefaction unit will be

consumed by three relatively independent processes: (1) heating the carrier gas, (2) heating and evaporating biomass moisture, and (3) heating the biomass to the final temperature and to provide the heat for the torrefaction reactions. In our case the torrefaction reactions are exothermic, so the heat of reaction helps to reduce the heat needed to increase the temperature of the system. The calculations made are as follows:

<p>ENERGY CONSUMED TO HEAT THE CARRIER GAS (NITROGEN) (Q_1)</p> $\dot{Q}_1 = m_1 C_{p_{N_2 \text{ average}}} (T_3 - T_1) = 0.0678 \text{ kg/h} \cdot 1.052 \text{ kJ/kg } ^\circ\text{C} \cdot (277 - 25 \text{ } ^\circ\text{C}) = 17.97 \text{ kJ/h}$ <p>ENERGY CONSUMED TO HEAT AND EVAPORATE THE MOISTURE (Q_2)</p> $\dot{Q}_2 = m_{H_2O_2} \cdot [C_{p_{H_2O \text{ LIQUID}}} (100 - T_2) + \Delta h_{\text{vap } 100 \text{ } ^\circ\text{C}} + C_{p_{H_2O \text{ vapor}}} (T_3 - 100)]$ $\dot{Q}_2 = 0.01272 \text{ kg/h} \cdot [4.18 (100 - 25) \text{ kJ/kg} + 2257 \text{ kJ/kg} + 2.64 (277 - 100) \text{ kJ/kg}]$ $\dot{Q}_2 = 0.01272 \text{ kg/h} \cdot [313.5 \text{ kJ/kg} + 2257 \text{ kJ/kg} + 448.8 \text{ kJ/kg}] = 38.64 \text{ kJ/h}$ <p>ENERGY CONSUMED TO HEAT THE BIOMASS TO THE FINAL TEMPERATURE AND HEAT ASSOCIATED WITH THE TORREFACTION PROCESS (Q_3)</p> $\dot{Q}_3 = m_{\text{BIOMASS } 2} \cdot [C_{p_{\text{BIOMASS}}} (T_4 - T_2) + \Delta h_{\text{TORREFACTION}}]$ $\dot{Q}_3 = 0.2 \text{ kg/h} \cdot [1.02 (277 - 25) \text{ kJ/kg} - 150 \text{ kJ/kg}]$ $\dot{Q}_3 = 21.41 \text{ kJ/h}$ <p>TOTAL HEAT THAT SHOULD BE PROVIDED BY AN EXTERNAL SOURCE OF HEAT: 78.02 kJ/h</p>

These results suggest that the heat required to conduct the torrefaction process was 0.39 MJ/kg. This is barely 2.11 % of the heating value (18.4 MJ/kg) of the biomass processed.

Second Energy Balance:

Figure 23 shows the basic assumptions used to conduct the second energy balance (a global balance) of the torrefaction unit.

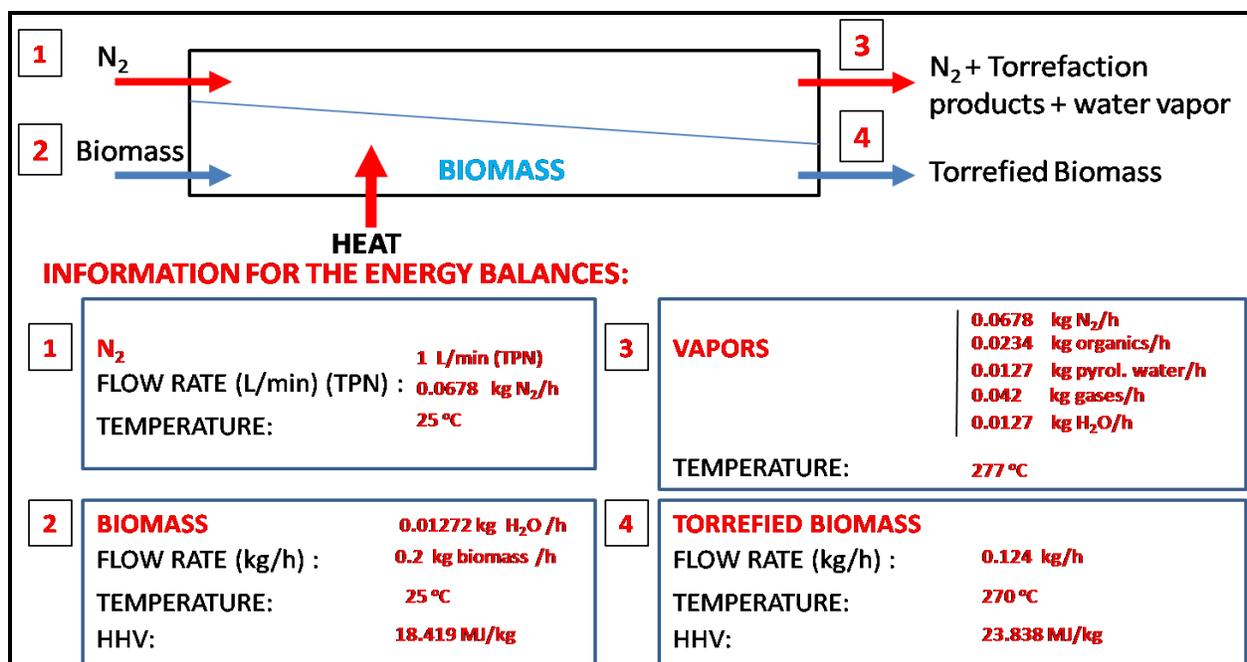


Figure 23.- Overall energy balance of a torrefaction unit

To perform the energy balances the following assumptions were made: (1) the torrefied biomass exits the reactor at an average temperature of 270 °C, (2) the vapors leave the reactor at 277 °C, and (3) the vapors were considered to be formed by the inert carrier gas, by the gases produced from the torrefaction reactions (CO₂, CO, H₂, H₂, CH₄), by the water produced from the torrefaction reactions, from the biomass moisture content, and by condensable organic volatiles (mainly formed by acetic acid and methanol) mostly produced from the torrefaction reactions. The enthalpy of each of these streams used on the energy balances is as follows:

$h_1 = 0$ kJ/kg	$h_{N_2} (277\text{ °C}) = 265.1$ kJ/kg	$h_{H_2} (277\text{ °C}) = 146574$ kJ/kg
$h_2 = 18.419$ MJ/kg (DRY BIOMASS)	$h_{H_2O} (277\text{ °C}) = 3037$ kJ/kg	$h_{CH_4} (277\text{ °C}) = 56302$ kJ/kg
$h_4 = HHV + \Delta H_{25-270\text{ °C}}$	$h_{CO_2} (277\text{ °C}) = 239$ kJ/kg	$h_{ACA} (277\text{ °C}) = 15374$ kJ/kg
	$h_{CO} (277\text{ °C}) = 10514$ kJ/kg	$h_{MeOH} (277\text{ °C}) = 24196$ kJ/kg

In the energy balance it was also assumed that the heat supplied or released from the torrefaction unit will result in enthalpy changes. Thus, the overall energy balances can be expressed as:

ENERGY BALANCE:

$$\dot{Q} = \dot{H}_3 + \dot{H}_4 - \dot{H}_1 - \dot{H}_2$$

$$\dot{H}_1 = 0 \text{ MJ/h}$$

$$\dot{H}_2 = m_{\text{biomass } 2} \cdot h_{\text{biomass } 2} = 0.2 \text{ kg/h} \cdot 18.419 \text{ MJ/kg} = 3683 \text{ kJ/h}$$

$$\dot{H}_3 = m_{\text{N}_2} \cdot h_{\text{N}_2} + m_{\text{CO}_2} \cdot h_{\text{CO}_2} + m_{\text{CO}} \cdot h_{\text{CO}} + m_{\text{CH}_4} \cdot h_{\text{CH}_4} + m_{\text{H}_2} \cdot h_{\text{H}_2} + m_{\text{AcA}} \cdot h_{\text{AcA}} + m_{\text{MeOH}} \cdot h_{\text{MeOH}} + m_{\text{H}_2\text{O}} \cdot h_{\text{H}_2\text{O}}$$

$$\dot{H}_3 = 629.2 \text{ kJ/h}$$

$$\dot{H}_4 = m_{\text{biomass } 4} \cdot [\text{HHV}_4 + C_p \text{ biomass} \cdot (T_3 - 25 \text{ }^\circ\text{C})] = 0.124 \cdot [23.838 + (1.02/1000) \cdot (277 - 25)]$$

$$\dot{H}_4 = 0.1212 \cdot [23.838 + (1.02/1000) \cdot (270 - 25)] = 2922 \text{ kJ/h}$$

$$\dot{Q} = 2922 + 629.2 - 0 - 3683 = -132 \text{ kJ/h} \approx -0.660 \text{ MJ/kg}$$

These results suggest that the enthalpy of the products was smaller than the enthalpy of the reactants. Thus, the system releases heat to the environment. The heat provided by the heater was mostly used to heat up the reactor and to compensate for part of the thermal losses to the environment. It means that at least 3.6 % of the chemical energy contained in the biomass was lost to the environment. This result means that under the conditions studied, the thermal efficiency of the process was 96.4 %. As long as the enthalpy of the vapor products (629.2 kJ/h), which represent 17 % of the energy contained in the biomass, can be released by combustion in order to produce some of the heat needed for the process itself, then these thermal efficiencies can be obtained (Prins et al., 2006; Bergman et al., 2005). These results are similar to the 96 % thermal efficiency reported by Bergman et al. (2005). The moisture content is the most important property that can affect process efficiency, for this reason, only biomass with a water content below 15 mass % should be torrefied.

The differences between the values of the heat that was needed to supply the torrefaction unit obtained using the data acquired by DSC (0.390 MJ/kg) and the values attained when using the enthalpies calculated from the calorific value of reactants and products (-0.66 MJ/kg) can be explained by the magnitude of the errors in our measurements and by the assumptions made in our calculations (approximately 5 % of the heating value of the biomass). These results suggest that although an external source of heat is needed to heat the reactor to the torrefaction temperature, the torrefaction process itself is exothermic. The overall heat requirements for the

process will depend on the design and operation of the installation. It will certainly depend on the heat losses achieved (how well insulated the torrefaction reactor is), the moisture content of the feedstock, the volume of carrier gas used, and the presence of small amounts of oxygen inside the torrefaction reactor. Similar uncertainties on the energy balances, but on wet torrefaction, are commonly reported in the literature (Yan et al. 2010).

6.- Conclusion

Size reduction of *Arundo donax* to produce a powder that can be fed to boilers is one of the major hurdles to co-fire *Arundo donax* and coal at the Boardman Power plant. Torrefaction is an excellent pretreatment approach to improve the grindability of *Arundo donax* and facilitate its size reduction at the pulverizers at the Boardman Power plant. In this project, new experimental data on the torrefaction of *Arundo donax* was collected. This data was used to perform preliminary mass and energy balances of a small torrefaction reactor operational at WSU.

Summarizing the mass and energy balances of the torrefaction of *Arundo donax* under the carbonization conditions studied, it can be said that when *Arundo donax* chips are torrefied at a reactor wall temperature of 310 °C and a residence time inside the reactor of 5 minutes 62 % of the original mass (6 % moisture) was retained as a solid product (torrefied biomass) (66 % *on dry basis*), containing 79% of the energy while 38 % of the mass was converted into torrefaction gases containing 17% of the energy contained in the feedstock. 4 % of the total energy contained in the biomass was lost. If the residence time of the biomass particle inside the reactor increases to 8 minutes the yield of torrefied biomass is reduced to 55 % (as received basis) or 58.5 % *on dry basis*. The energy contained in the gases could be released by combustion and recovered to supply part of the energy needs for the process (drying and compensating the heat losses in the torrefaction reactor).

The results obtained could be used to estimate the yield of torrefied biomass when feedstocks with different moisture contents are processed. If the feedstock has 50 % moisture content and is processed under conditions comparable to those studied in this proposal (similar particle sizes,

reactor temperature: 310 °C, particle residence times between 5 and 8 minutes) then the yield of torrefied solid obtained should be between 29.2 and 33.0 mass % (on biomass as received basis).

Based on our results it can be concluded that the torrefaction of *Arundo donax* can be an efficient technology to produce a material that can grind easily in coal mills operational at existing power plants. Further studies are needed to develop and deploy torrefaction units able to convert *Arundo donax* into a material that can be co-fired with the coal at the Boardman Power plant.

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