

Ultrasonic pretreatment of soft wood biomass prior to conventional pyrolysis: Scale-up effects and limitations

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ABSTRACT

After finding a successful ultrasonic wood treatment that enhanced bio-oil yield prior to pyrolysis in our laboratory, the next logical step was the scaling up of the process. Hence, this work aims to study the effects and limitations of an ultrasonic wood pretreatment scale-up from the laboratory scale (200 g) to the pilot scale (700 g). Wood chips were characterized by elemental chemical analysis, X-ray Photoelectrons Spectroscopy (XPS), Thermogravimetric Analysis (TGA), and Scanning Electron Microscopy (SEM). XPS and TGA did not show any change in the surface chemical composition. However, the SEM images clearly showed that the treatment in the bath allowed surface cleaning of the wood, thus creating an opening in the wood physical structure and allowing better heat transfer, as seen in the TGA analysis. As often found in such an endeavor, it was shown that these same ultrasonic conditions applied to a larger scale did not lead to the same results. The wood from the pilot scale unit (PSU) exhibited the same characteristics as the untreated wood. Thus, PSU did not allow an opening in the wood structure, as shown in the SEM images, which would have resulted in better heat transfer and thus in a higher bio-oil yield. From our experience with such systems, a hypothesis could be dependent on the greater efficiency of the PSU, especially at high frequencies, which could lead to the opposite effect than what was expected. Further investigations are necessary to overcome this limitation and to truly assess the phenomenon.

1. INTRODUCTION

Over the past 50 years, the world's population has more than tripled, according to the National Institute of Statistics and Economic Studies (INSES), leading to an increasing demand and consumption of energy [1]. Because of this intensive consumption of our resources, problems, notably climatic problems due to pollution, have emerged. Indeed, the climate change that has occurred in recent years is pushing researchers of the scientific

community to find a way to counteract this destructive trend. One of their main concerns is the substitution of fossil fuels, as some forecasts have predicted the depletion of exploitable resources by 2050. However, the ultimate goal is also to replace these polluting, nonrenewable energies with a biosourced, low-polluting and sustainable energy [2].

Due to these considerations, lignocellulosic biomass is a clear point of interest. Promising works on the conversion of corn into ethanol or diesel from soybeans have emerged. However, upon the announcement of the development of these biofuels, the price of these foodstuffs has increased drastically, in addition to pushing farmers to use more of their fields for energy production rather than for food. This situation is not acceptable in a world where global hunger still exists [3]. With that in mind, the focus has now turned to nonfood biomass, such as agricultural residues or wood. There are already many technologies to convert lignocellulosic biomass into energy, especially thermochemical conversion processes. These include gasification, carbonization, liquefaction and pyrolysis [4,5]. The latter appears to be the most promising in terms of fuel production.

The pyrolysis conversion process takes place typically between 400 and 800°C under inert atmosphere. To guarantee the process minimal efficiency, the biomass used must have a moisture content under 10%wt and present a particle size distribution under 10 mm (for best known systems) [6]. However, the process efficiency is still a major obstacle to the development of this technology on a larger scale. Most of the time, the reported bio-oil yields are approximately 50 to 70% only. Now that research has reached the limits of bio-oil systems and the optimization of their conditions, research has turned toward biomass pretreatment, in particular chemical and biological treatment, in order to further improve the process. However, while beneficial for the production yield, these treatments have sometimes proven to be costly, lengthy and/or polluting for the limited efficiency increase [1]. Heterogeneous catalysts [7,8] are now attempting to further expand these studies. Among the conventional catalysts, salts and microwaves, ultrasounds may also be considered as an option.

In this study, the focus was on ultrasounds. By definition, ultrasounds are an energetic acoustic wave, with frequencies ranging from 20 kHz to 1 MHz, which are over the normal human hearing range. Due to this large frequency range, ultrasounds can exhibit mechanical and sonochemical effects at low frequencies (20-60 kHz) and high frequencies (100-1000 kHz) respectively [9, 10, 11]. When passing through liquids, e.g., water, ultrasonic waves move the medium atoms from their mean position, allowing the formation of transient cavitation bubbles (low frequencies) and stable cavitation bubbles (high frequencies). Both types of bubbles grow until implosion, but stable bubbles can oscillate in diameter during several acoustic cycles before breaking down [12]. When a bubble implodes, a violent jet of matter and energy are created, mostly driven toward any interface (solid/liquid in the present case) by surface tension variations. The resulting mechanical shockwave (up to 103 MPa) promotes microconvections, thus increasing both liquid and

solid particles transportation [13]. At this point, extreme conditions (temperature near 500°C and pressure approximately 500 atmospheres) will also lead to water sonolysis. Water sonolysis will in turn lead to the formation of short-life radicals such as H· and OH· [14]. This phenomenon is at its strongest at higher frequencies.

Many studies, dating from the early 20th century, have shown the potential benefits of this technology for the hydrolysis of biomass [13], cleavage of chemical bonds such as the ones found in lignocellulosic biomass [15] or thermal degradation [11,16]. Previous work in our lab [17] has shown that specific ultrasonic biomass pretreatment enables a significant increase in the bio-oil yield (two folds increase) of laboratory-scale pyrolysis. Now, the next logical application step of this promising laboratory research is the industrial scale-up. From the work of Loranger et al. [18], we were able to demonstrate in the past that the use of a large-scale flow through a sonoreactor could provide a superior sonochemical effect than a laboratory unit (ultrasonic bath) under the same ultrasonic conditions.

Therefore, this work will study the scaling of the ultrasonic pretreatment found by Cherpozat et al. [16] in the system presented by Loranger et al. [17]. Benefits or limitations of this technology applied to wood chips as biomass for the pyrolysis will be assessed. To the best of our knowledge, no similar experiment on such a large scale has been conducted or reported. We will study the effect of the two systems on the chemical composition of the wood and also on its physical characteristics through TGA and SEM analyses. The bio-oil yield will also be used to quantify the effectiveness of the treatments.

2. EXPERIMENTAL

2.1. Wood Chips

An Eastern Canadian pulp and paper mill provided the wood chips composed of a softwood medley (spruce, fir, pine and larch). The wood chips were first washed in water, dried at ambient air and, in comparison with their original shape, ground to needle-like shape through a 5 mm by 5 mm grid (at least two dimensions of the wood chips are inferior to 5 mm). Then, they were stored at room temperature in sealed plastic bags to control their humidity. The material was dried at 105°C for 48 h after being treated.

2.2. Ultrasonic equipment

2.2.1. Ultrasonic bath

A 34 liter ultrasonic bath, model BT90 from Ultrasonic Power Corporation (Freeport, Illinois, USA), made of 316 L stainless steel was used (Figure 1). It was equipped with 12 transducers (2 rows of 6, with each row connected to the generator by an individual wire) located underneath the bottom plate of the bath, as described by Loranger et al. [19]. Commercial frequency generators of 40 and 170 kHz were used to produce 1000 W of

nominal ultrasonic energy for the optimal time found in previous research [16]. Using the Vibra-Bar® technology, the piezoelectric bath transducers could generate both frequencies, but only one at a time. The system was calibrated as described by M. Paquin et al. [20] at 40 kHz for the mechanical effect and at 170 kHz for the sonochemical effect according to Koda's methods [21]. For each treatment, wood chips (200 g) were submerged into 4 L of deionized water ($\Omega < 0.8 \mu\text{S}$) and kept at the bottom of the bath with a weighted meshing to ensure that all introduced biomass was being treated by ultrasound. Hence, the ultrasound power was 250 W/L (1000 W / 4 L). To control the temperature, the ultrasonic bath was equipped with a heat-exchange system made from a stainless steel pipe placed at the bottom of the bath that was connected to a thermostatically controlled bath, model 1180A from VWR Scientific.

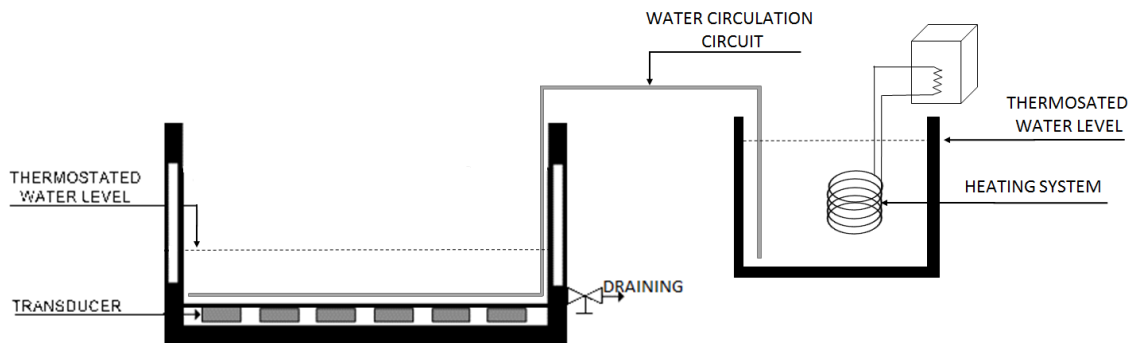


Figure 1: Laboratory scale ultrasonic equipment

2.2.2. Pilot Scale Unit (PSU)

A 45 L flow-through sonoreactor with a nominal input power capacity of 2000 W was used in this study, as described by Loranger et al. [19]. The sonoreactor, which was built with 24 Vibra-Bar® (4 banks of 6 bars, with each bank connected to a generator through single wires, thus needing 2 generators for the whole tube) and a stainless steel pipe (316 L), was supplied by Ultrasonic Power Corporation (Freeport, Illinois, USA). The temperature of the sonoreactor was controlled by a programmable logic controller (PLC) by means of a hot and cold water source. As it was operated in a semi-continuous mode, wood chips were contained in the meshing receptacles to be held away from the pump so that they did not alter its integrity or its operation. As shown in Figure 2, four nets were dropped down in the sonoreactor and used to contain the wood chips: two small nets (S – 40 cm long with 7 cm in diameter) and two large nets (L – 60 cm long with 7 cm diameter). As only the nets in the middle of the reactor were assured to be fully treated, only the wood chips from the large nets (L) were recovered for pyrolysis. Thus, 700 g of wood chips, split between the two large nets, were used for each treatment. The whole apparatus has a volume of 45 L, and the volume of only the tube is 7.62 L. Hence, the ultrasound power is 263 W/L (2000 W / 7.62 L).

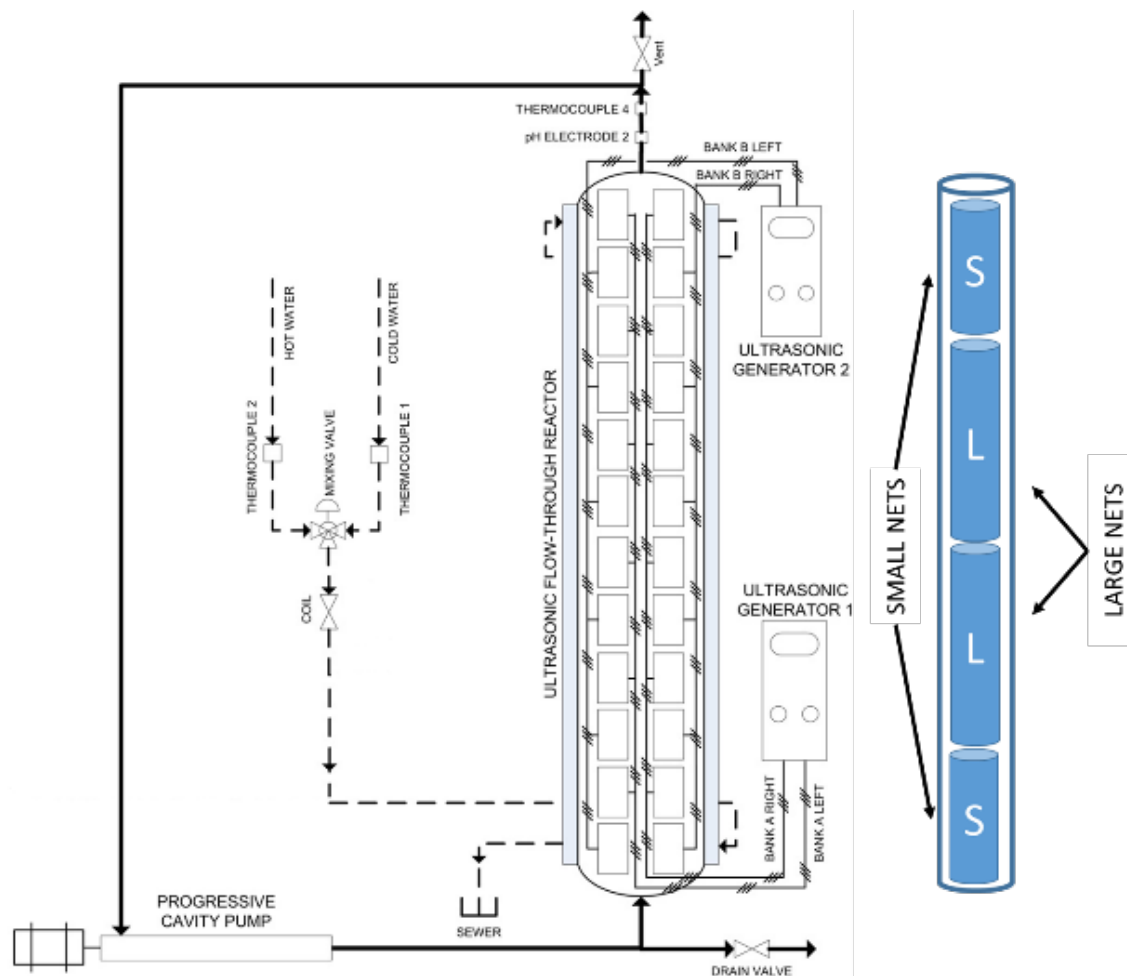


Figure 2: Ultrasonic Pilot Scale Unit (PSU)

2.2.3. Treatments

Ultrasonic treatments in both reactor types were performed in the same conditions: 0.5 h at 170 kHz followed by 1.5 h at 40 kHz with a power of 1000 W and a maximum temperature of $76 \pm 1^\circ\text{C}$. This particular sequence is the result of previous work optimization in our laboratory [16].

2.3. Lab-Scale Pyrolyzer

The pyrolysis was completed with a lab scale pyrolyzer as described by Loranger et al. [18] and shown in Figure 3. The pyrolyzer is composed of a stainless steel cylindrical reactor (36 cm long with an 8 cm inner diameter) that was sealed using a bolted flange and connected to a thermocouple in order to follow the temperature inside the reactor. The produced pyrolytic vapors were recovered with a multiple stage condensing system made of three baths. The first flask was cooled with tap water (15°C), the second with an ice-water mix (0°C) and finally, the third flask was placed into brine (-15°C).

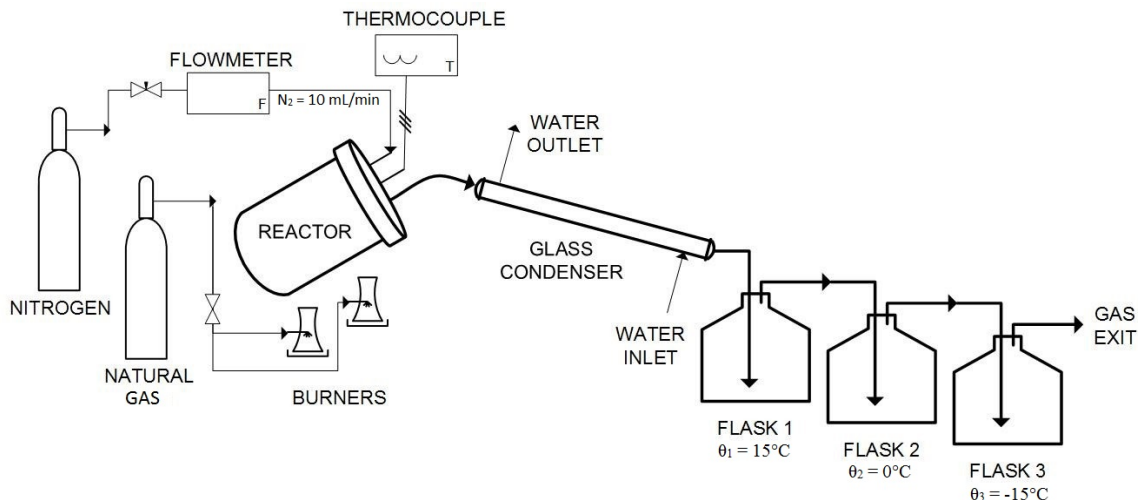


Figure 3: Schematic diagram of the laboratory-scale pyrolyzer

This cooling system allows primary separation of chemical compounds by their molecular weight. In our experiments, flask 1 mainly contained water and a small fraction of oils, flask 2 mainly contained oils, although a small quantity of water was still recovered, and flask 3 only contained a very small amount of oil. The vapors were driven through the system by a nitrogen flow of 10 mL/min, which was used to ensure an inert atmosphere during the thermochemical conversion and also to enable sufficient residence time of the produced vapors. As the gas outlet was composed of various noncondensable chemicals, a flame was ignited at the exit to prevent any potential dangerous accumulation. A heating rate of approximately 16°C/min was accomplished by two natural gas burners. As the necessary time for a complete pyrolysis was approximately 1 hour, our pyrolysis system belongs to the slow pyrolysis category. For each treatment, triplicates were realized with 140 g of wood chips per experiment. The final mean was reported as the value of the experiment.

2.4. Characterizations

All characterizations were conducted at least twice on both the treated and untreated wood chips for the following characteristics.

2.4.1 Bio-oil GC Analysis

Bio-oil chemical composition analysis was conducted with an Agilent 7890B Gas Chromatograph equipped with a flame ionization detector (FID) and a J&W Scientific DB-5.625 column (length: 30 m, internal diameter: 0.25 mm, film thickness: 0.25 μm). For each sample, approximately 1 μL was injected and split to a 50:1 ratio. Samples were carried inside the column to the detector by a helium flow (0.6 mL/min). Two temperature ramps at 3 °C/min from 40 to 200°C and at 6°C/min from 200 to 300°C were applied to the samples. As the bio-oil chemical composition is composed of highly complex

components, they were classified into five categories: lights, acids, alcohols, ketones and phenols. Previously, a 44 component standard with various representatives of each chemical family was injected, measured and classified to obtain the retention time of the different categories. The oils from flask 1 and flask 2 were analyzed separately, and then, the total composition of oil was calculated from these results.

2.4.2. Chemical Composition

Dynamic flash combustion method was used to determine the carbon, hydrogen, nitrogen and sulfur contents in the woods. For each sample, approximately 2 mg of grinded wood was put in a tin cup. The samples were purged with a continuous helium stream before being introduced, one by one, in the combustion reactor (a quartz tube maintained at 1021°C). As this method is based on the total oxidation of the samples, the helium flow was temporarily enriched with oxygen once the sample was placed in the reactor. This technique allows the creation of the perfect condition to oxidize both organic and inorganic substances. The combustion gases are then transported into a chromatographic column to be separated and analyzed by thermal conductivity detectors (TCD). Device calibration was done using certified standards from Isomass Scientific Inc. (Canada) with known quantities of C, H, N and S. All samples were analyzed twice with a precision of +/- 0.3% for N, C, H and +/-1% for S.

2.4.3. X-ray Photoelectron Spectroscopy (XPS)

Precise wood chips chemical bonds analysis was performed with an XPS model Axis ULTRA from Kratos Analytical (UK). The survey scans were performed with an energy of 160 and repeated on three different points of the sample. The oxygen-carbon ratio was determined from these scans.

2.4.4. Thermogravimetric Analysis (TGA)

All samples were heated in open platinum pans under nitrogen atmosphere (200 cc/min) from 50 to 105 °C at a heating rate of 20 °C/min. The temperature was then held for 15 min to eliminate remaining free water in the sample. Then, the sample was heated from 105 to 600 °C at a heating rate of 10 °C/min and held at 600 °C for 15 min. Finally, the samples were heated from 600 to 700 °C under air atmosphere (200 cc/min) at a heating rate of 10 °C/min to finalize the combustion. This study was carried out with a Perkin-Elmer (Pyris Diamond) thermoanalyzer. Analysis was conducted at least twice on each sample.

2.4.5. Scanning Electron Microscopy (SEM)

Scanning electron microscopy (SEM) was used to study the sample morphology. The samples were gold coated using an Instrumental Scientific Instrument PS-2 coating unit

before being placed in the SEM model Si1510 from HITACHI (Japan). At least three wood chips from untreated, bath-treated and PSU-treated groups were analyzed.

2.5. Experimental Process Diagram

Figure 4 summarizes the entire experimental process for easier understanding. After the wood chips are received (50% water content in weight), they are washed with tap water and air dried (10% water content in weight) before grinding. The first set of analysis is conducted after grinding to characterize the raw material. Then, the wood is treated by ultrasounds (PSU or bath) and dried for 48 h at 105°C to ensure minimum moisture content before pyrolysis. After ultrasonic treatment and before pyrolysis, a second characterization is performed on the treated wood so it can be compared to the raw material. After pyrolysis, measurements of the bio-oil, biochar and biogas are conducted for the mass yields and GC analysis (bio-oil only).

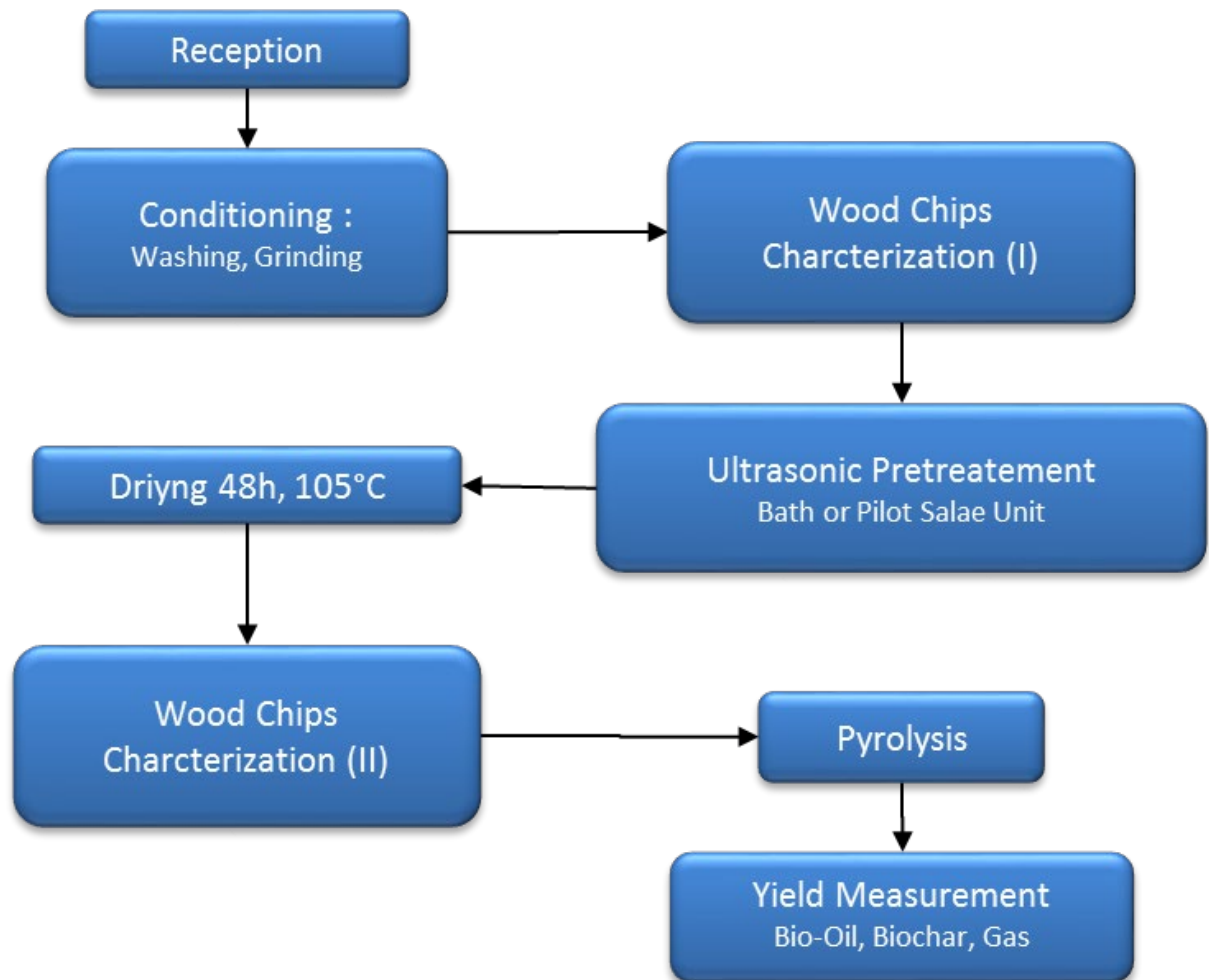


Figure 4: Experimental process diagram.

3. RESULTS AND DISCUSSION

3.1. Bio-oil yield

Figure 5 presents the pyrolysis product yields from the untreated wood (red), the bath-treated wood (green) and the PSU-treated wood (blue). All ultrasonic treatments were conducted at 1000 W. The “Liquids” results are the addition of “Bio-oil” and “Aqueous” weight percentages. Yields were calculated from the recovered products masses in comparison to the introduced wood mass (≈ 140 g). From Figure 5, it can be seen that ultrasonic conditions that allowed a significant increase in the bio-oil yield when using the ultrasonic bath do not correspond to the optimum conditions for a larger scale. Indeed, the treatment carried out in the pilot scale unit (PSU) did not allow a significant yield increase with respect to the standard deviation. However, although the bio-oil yield did not increase when the treatment was done in the PSU, the water content did increase. This particular aspect is discussed in more detail in section 3.2.

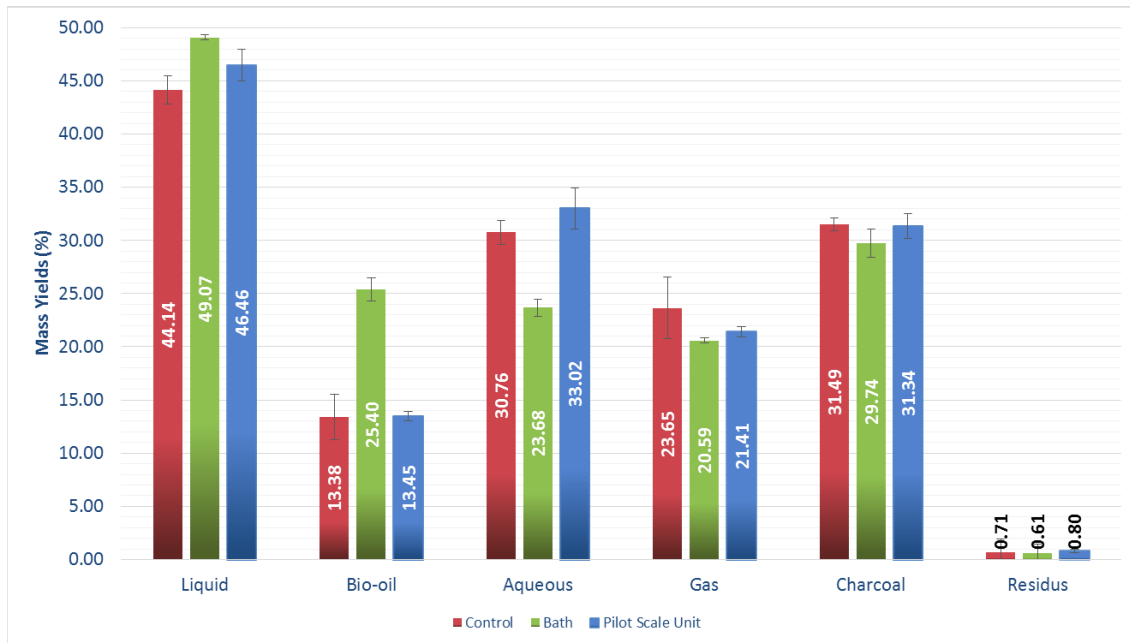


Figure 5: Pyrolysis product yields of the untreated wood, bath-treated wood and Pilot Scale Unit-treated wood (1000 W), from left to right

These results could be explained by the fact that the treated wood quantity more than tripled from one scale to another (from the bath to the PSU), but the power only doubled. According to calculations, we went from an energy of approximately 7.14 W/g of biomass to 1.4 W/g of biomass, respectively. It is therefore likely that the amount of energy delivered as a function of the amount of biomass treated is too low to be able to ensure efficient treatment of biomass when the goal is to increase the bio-oil production. In this case, greater power would be needed to obtain similar results as the ultrasonic bath.

On the other hand, an opposite hypothesis would also be plausible. The PSU system has been shown to be more effective [17] than the ultrasonic bath in regard to the conversion of electrical energy into ultrasonic energy, especially at high frequency. Loranger et al. [17] has demonstrated that experiment conducted in the PSU was 683% better than the one conducted in the bath, in regard to KI oxidation catalysis. Cherpozat et al. [16] also demonstrated, in the bath, that a long exposure at 170 kHz was detrimental to the production of bio-oil. Although the exposure time is suited for the bath, it might be too long for the PSU considering its higher efficiency at a high frequency level. Moreover, an overly high acoustic power could lead to chemical or physical changes that would not occur in the bath. Indeed, Ashokkumar and Mason [10] stated that “for a given ultrasound frequency, an increase in the acoustic power can be expected to increase the number of active cavitation bubbles”, thus a stronger effect can be expected. These changes could then have had an adverse effect on the bio-oil production. Beyond this, it is also possible that the current configuration of the transducers (all used face-to-face) increases the possibility that the ultrasonic waves cancel each other out (they meet at the same moments of the sinusoid).

To investigate these theories, additional tests were carried out in the PSU, namely, a sequence of 30 min at 170 kHz and then 90 min at 40 kHz at a maximum temperature of 76 °C, at nominal powers of 500 W and 1500 W. The results are shown in Figure 6. Thus, although neither of these two additional configurations with the PSU allowed a significant increase in the yield of bio-oil, with respect to the standard deviation, an upward trend is observable with a decrease in nominal power. These results, therefore, seem to confirm the second hypothesis that an increase in the power input leads to a decrease in bio-oil production when in the PSU configuration.

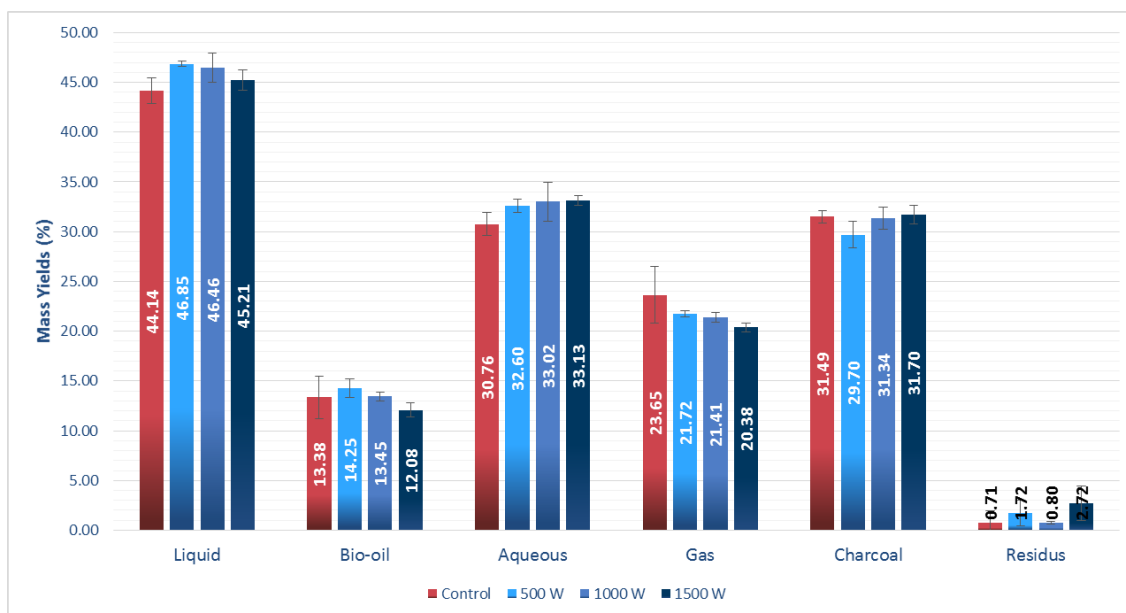


Figure 6: Pyrolysis product yields (from left to right) of the control and the PSU treatment at 500 W, 1000 W and 1500 W

3.2. Bio-oil chemical composition

Figure 7 shows the bio-oil compositions from the control and treated woods. Bio-oils from the three PSU treatments have been grouped under “PSU moy” as their chemical compositions were similar. The bio-oil composition from the bath-treated wood shows a decrease in the light fraction in favor of the phenolic fraction compared to that of the control. In contrast, bio-oils from the PSU-treated wood, although similar to those of the control, show a decrease in the phenolic fraction. This phenomenon can be explained by considering the mass yield from Figure 5 and Figure 6. Indeed, it shows that the bio-oil phase was enlarged to the detriment of the aqueous phase, as confirmed by the overall liquid yield, which did not increase proportionally to the bio-oil increase when compared with that of the bath and PSU treatments. The aqueous phase increase occurs when wood organic molecules undergo secondary cracking, which usually takes place inside the solid wood matrix when the vapor residence time is too long [1]. This reaction will generate smaller, lighter molecules, which can easily remain in the aqueous phase. This is probably what occurred with the PSU-treated wood, which would explain the lower bio-oil yield, in contrast to the bath-treated wood.

As we have demonstrated with SEM analysis, bath treatment allowed structure opening through surface cleaning. Thus, formed vapors were evacuated more quickly and did not sustain secondary cracking, unlike in the PSU treatment. Moreover, biochar yields, being

similar in all cases, show that the same amount of organic compound was extracted from the wood.

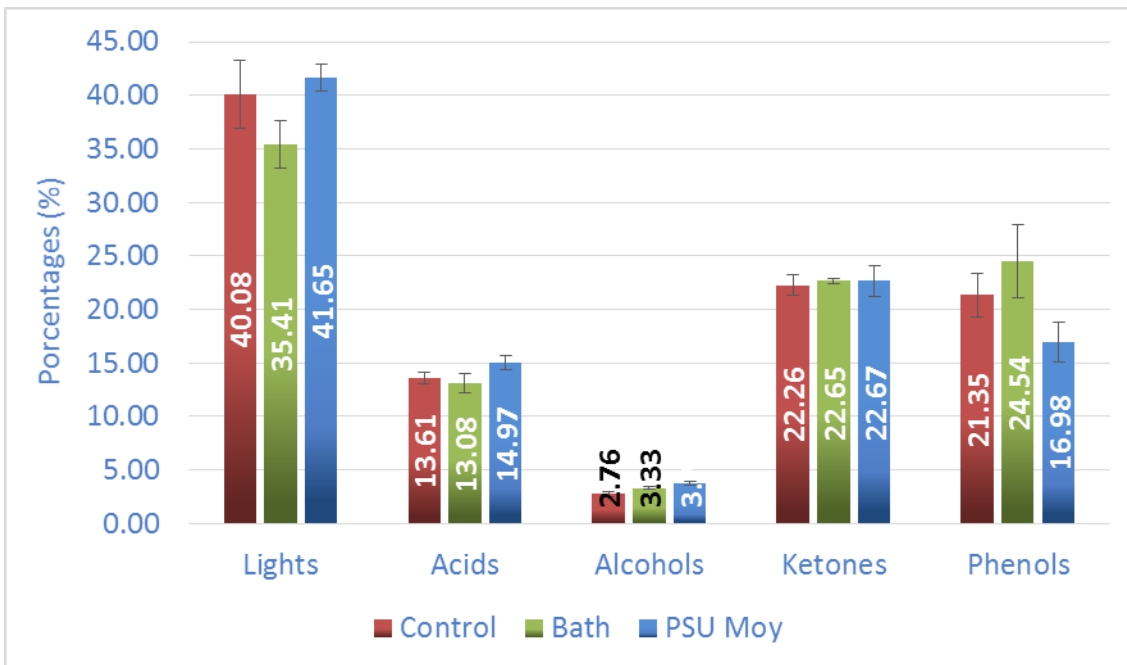


Figure 7: Bio-oil chemical composition

3.3. Wood chemical composition

As the PSU seems to be a more efficient ultrasound transmission system [17], chemical changes could have occurred, unlike in the bath. Thus, elemental analysis of carbon, hydrogen, oxygen, nitrogen and sulfur (Table 1) was performed.

Table 1: Wood chip elemental analysis of carbon (C), hydrogen (H), nitrogen (N) sulfur (S) and others (oxygen, metals,...) on the untreated wood, bath-treated wood and PSU-treated wood.

	% Carbon	% Hydrogen	% Nitrogen	% Sulfur	% Others
Control	46.72 ± 0.04	6.11 ± 0.06	0.00 ± 0.00	0.00±0.00	47.17± 0.01
Bath	47.34 ± 0.08	6.10 ± 0.13	0.00 ± 0.00	0.00 ± 0.00	46.57± 0.21
PSU 500 W	47.00 ± 0.02	6.43 ± 0.06	0.06 ± 0.02	0.00±0.00	46.51± 0.02
PSU 1000 W	48.03 ± 0.12	6.16 ± 0.10	0.00 ± 0.00	0.00 ± 0.00	45.82± 0.22
PSU 1500 W	46.74 ± 0.06	6.35 ± 0.04	0.05 ± 0.01	0.0 ± 0.00	46.86± 0.11

In Table 1, it can be observed that the woods from the bath and from the PSU at 1500 W are quite similar, although the yields results are not similar (Figure 5 and Figure 6). Likewise, the biggest observable differences are between the woods treated in the PSU at different power settings. However, the results in terms of yields are similar. This analysis tells us that the slight difference in elementary composition was not significant enough to impact the yields. As elementary analysis measures both the surface and the bulk composition, XPS analysis (Table 2) was also conducted. As modifications induced by ultrasonic treatment should be mainly found at the surface, any modifications should be observable with XPS analysis, which is specialized for that purpose. The XPS analysis shows no difference regarding the oxygen/carbon ratio when considering the standard deviation. As XPS is a more accurate analytical method, we considered that the changes in the carbon and oxygen content from the elemental analysis results are attributed to the standard deviation of the measurement, combined with the fact that we used a mixture of softwood (see section 2.1.) which is not necessarily homogenous. Thus, no chemical change is observable after the ultrasonic treatment in both bath and pilot scale unit. Thus, the differences in phenolic content in the bio-oils (Figure 7) are not due to any chemical changes in the wood but to the fact that vapors can be evacuated more quickly, allowing the recovery of larger molecules, such as phenols.

Table 2: XPS analysis of the untreated wood, bath-treated wood and PSU-treated wood

	Untreated	Bath	PSU 500 W	PSU 1000 W	PSU 1500 W
% Carbon	74.67 ± 0.00	74.81 ± 2.18	72.33 ± 0.77	74.45 ± 1.09	73.69 ± 0.39
% Oxygen	25.33 ± 0.00	25.19 ± 2.18	27.67 ± 0.77	25.55 ± 1.09	26.31 ± 0.39
Oxygen / Carbon	0.34	0.34	0.38	0.34	0.36

3.4. Thermal Stability

The thermal stability was studied through thermogravimetric analysis, and the results are shown in Figure 8. All curves exhibit the same trend. First, water loss is observed up to 100 °C. It is followed by hemicelluloses degradation starting at 180 °C and up to 300 °C. Then, the cellulose degradation occurs under pyrolytic conditions at temperatures between 350 and 375 °C. Finally, the last product to be degraded is lignins. Their very complex 3D structure gives them a good thermal stability because 450 °C must be reached in order to completely degrade them [1]. This is in accordance with the results of the elementary analysis and XPS, which show that there was no chemical modification because the modifications could have been seen in the degradation pattern if they had occurred.

In the first part of the degradation (up to 375 °C), the curves of all woods are relatively close, and only the control wood seems to degrade a slightly more easily. However, once passing 375 °C, the wood treated in the bath stands out from the others. Indeed, the latter has a mass loss that is 3.6% greater at 600°C than that of the control wood, in contrast to 1% or less that of the woods treated in the pilot-scale unit. The results of these analyses are consistent with the bio-oil yields shown in Figure 5 and Figure 6.

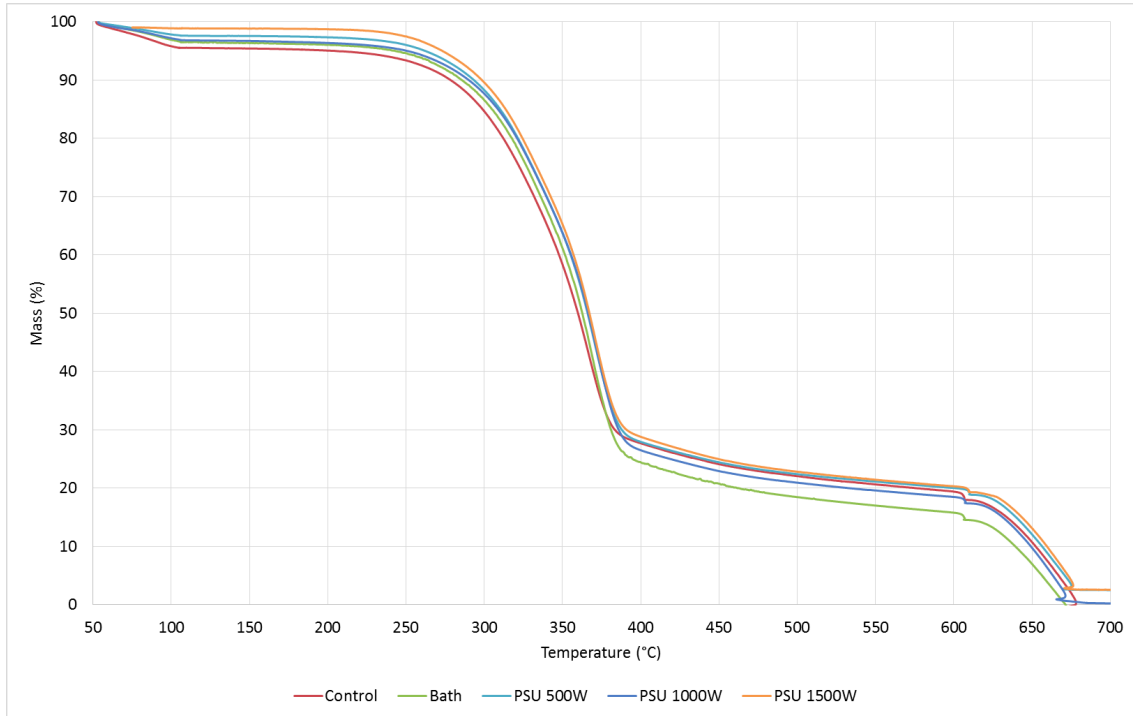


Figure 8: Thermal degradation curves of the different woods

DTG curves (Figure 9) were been drawn for more details and accurate explanations of zones and peaks temperatures. As seen by comparing Figures 8 and 9, the DTG curves are in agreement with the TGA curves.

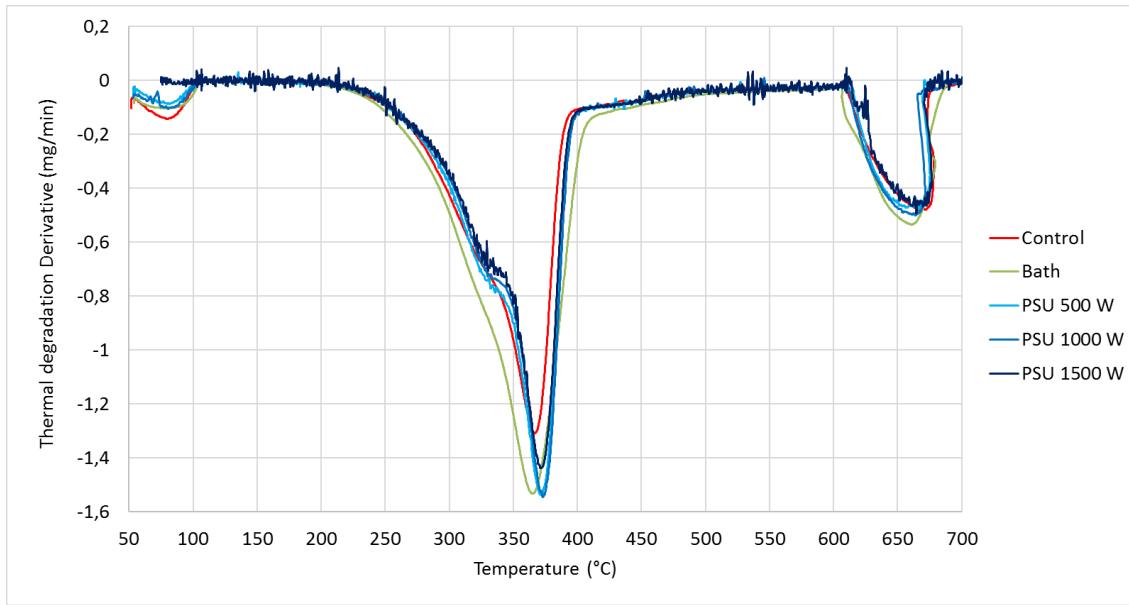


Figure 9: DTG curves of wood from the different treatments

The same wood degradation pattern is observable. First, from 50 to 100°C, water evaporation occurred, and then, lignocellulosic components degradations occurred. However, the DTG curves highlight the differences between the treatments for the major degradation, which are in accordance with the pyrolysis product yields (Figure 5). Indeed, it can be seen that the PSU-treated wood exhibits two steps for the degradation of hemicellulose and then cellulose at approximately 330 °C, unlike the control and bath-treated wood. This demonstrates that ultrasound must have led to a structural modification of lignocellulosic material, as no chemical changes have been noticed so far. In Zumar et al. [22], it is said that cellulose crystallinity is decreased by ultrasound, which depolymerizes it. Therefore, the material is softened (less crystalline so more amorphous) and thus is easier to degrade thermally. Similar results are found at the bath scale, which shows the best bio-oil yield and the biggest peak areas in the DTG curves. Although PSU treatments at 500 and 1000 W tend to be more similar to the bath treatment than the others, it is difficult to say at this point what has truly occurred during treatment. Indeed, the maximum degradation rate temperature is superior to that of the control and bath (373.14°C, 372.34°C, 365.84°C, 365.84°C and 363.75°C for PSU 500, PSU 1000 W, PSU 1500 W, control and bath, respectively). All these observations combined confirm that the treatment occurring in the bath allows easier thermal degradation. It also confirms that an excessive amount of power is unnecessary for the present treatment as wood pretreated in PSU at 1500 W shows less identical curves to the bath treatments.

3.5. Surface morphology

Previous analyses have led us to believe that ultrasound causes physical rather than chemical changes. This hypothesis is also supported by the fact that 75% of the treatment is done under mechanical ultrasonic effects or shock waves. SEM images from all five woods (untreated, bath-treated and three types of PSU-treated woods) are shown in Figure 10.

From these images, it is possible to observe that the untreated wood (Figure 10.a) presents a rather closed structure with multiple fibrils on the surface, giving it a fluffy appearance. In contrast, the wood treated in the ultrasonic bath (Figure 10. b) has a more open structure. Indeed, as can be seen, the treatment has allowed the cleansing of the surface and hence the clearance of tube vessels (1) and “pits” (2) naturally present in the common wood structure. As no significant chemical composition has been noticed so far, this physical modification of wood particulates explains the large increase in the bio-oil yield observed in Figure 5. Indeed, this surface opening allows a greater heat transfer and in any type of pyrolysis, this characteristic is decisive for a maximized bio-oil production. As reported by Bussemaker et al. [19], ultrasonic treatment on wood can improve accessibility and particle surface erosion, which leads to a better heat and mass transfer, thereby contributing to the subsequent process. Therefore, wood thermal degradation observed in TGA curves (Figure 8) is easier after the ultrasonic bath treatment, explaining the good yield.

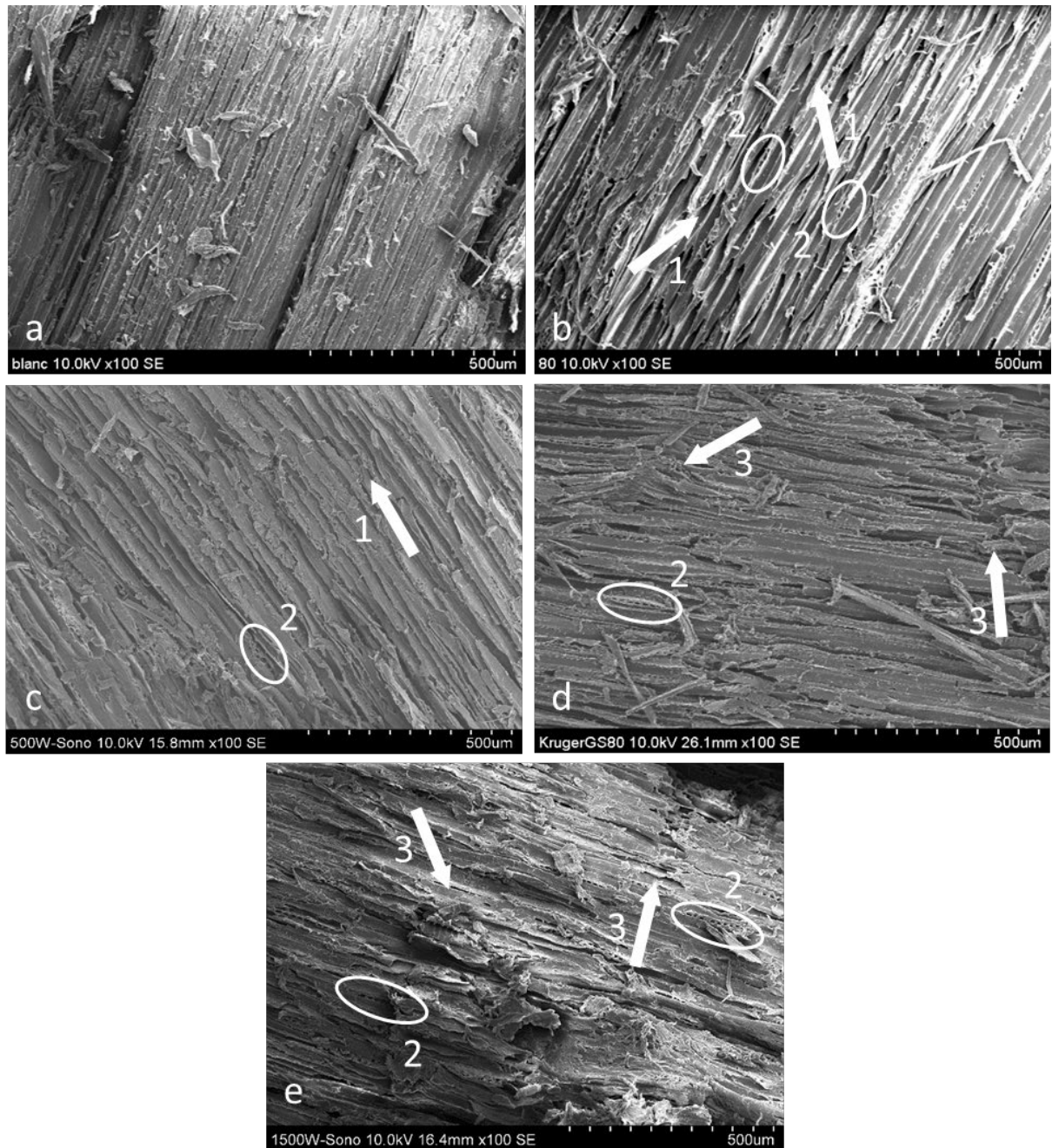


Figure 10: MEB images of untreated wood (a), wood treated in the bath (b) and wood treated in the pilot scale unit at 500 W(c), at 1000 W (d) and at 1500 W (e)

MEB images from PSU at 500 W, 1000 W and 1500 W in Figure 10.c, d and e, respectively, show that the surface morphology from wood chips has also been modified compared to that of the untreated wood. However, the modifications are different from those occurring in the bath-treated wood (Figure 10.b). Indeed, in the case of the PSU, for the three power settings, microfibrils on wood chips surface have not been entirely removed by ultrasonic treatment, although “pits” are visible (2). There is no cleaning of the wood surface as

observed in the bath, thus the structure is less open, explaining the lower bio-oil yield. Although microfibers have not been removed from the wood chip, it appears that the force from the shockwave moved the wood fibers from their original position on the wood chips. Indeed, this phenomenon, observable in Figure 10.c, d and e, resulted in the formation of breaches and mountain-like shapes (3). This phenomenon is more observable with the increase in power. The oddness of this modification can be explained by Bussemaker et al. [23], who explained that the depolymerization that occurs when lignocellulosic biomass is exposed to ultrasounds (in conditions different than ours) takes place in two steps: “the initial scission in the midsection of large polymer chains is followed by depolymerization of smaller molecular structures.” The surface morphology of the PSU 500 W sample seems to be the most similar to that of the bath-treated wood, even if substantial differences still remain, which is a result that concurs with that of the bio-oil yields (Figure 6) showing that this treatment allows a larger yield than the two other PSU treatments. These observations confirm that too much power, in this particular case, will have a detrimental effect, because a greater power input will cause the surface morphology to be different from what appears to be the result of an efficient ultrasonic treatment prior to pyrolysis (Figure 10.b).

4. CONCLUSIONS

This work has demonstrated that laboratory-scale ultrasonic wood pretreatment prior to pyrolysis cannot be scaled up to the pilot scale in the conditions given by a previous work from our laboratory. Preliminary results show that time exposure and power input are the main limiting factors. Indeed, the powerfulness of the PSU, especially at high frequencies, seemed too strong for our goal of increasing pyrolytic bio-oil yield.

Therefore, some processing parameters must be modified to make them more suitable for the new scale. Further studies will need to be carried out in order to find new optimum conditions for the pretreatment of biomass at the pilot scale. It will be necessary to conduct more work on the time exposure, likely in an effort to decrease it, but with the initial use of the same chemical effect and mechanical effect ratio (1:3), as it has shown the best results. However, considering the great sonochemical power of the PSU, lower frequency exposure could benefit our treatment for the present purpose. To the best of our knowledge, this preliminary study of wood pretreatment scale-up from laboratory to pilot units is among the first on the subject. We have reported some of the limitations and possibilities that need to be further explored before assessing the full potential of this technology.

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