Ultrasonic pretreatment effects on the bio-oil yield of a laboratory-scale slow wood pyrolysis

Lucie CHERPOZAT[1], Eric LORANGER[1,*], Claude DANEAULT[1]

1   Lignocellulosic Materials Research Centre, Université du Québec à Trois-Rivières, 3351 boul. des Forges, C.P. 500, Trois-Rivières, QC, Canada G9A 5H7

*   Corresponding author: eric.loranger1@uqtr.ca

lucie.cherpozat@uqtr.ca

eric.loranger1@uqtr.ca

claude.daneault@uqtr.ca

ABSTRACT

Research on biomass conversion into energy through pyrolysis has emerged in the past several years. Pyrolysis is believed to have a real future for green-fuel production and as the means of the revitalization of the Canadian pulp and paper industry. As pyrolysis has recently been successfully optimized through the use of heterogeneous catalysts, attention has been drawn to ultrasound for its ability to cleave lignocellulosic bonds. In this study, we investigated the use of ultrasound techniques as a pretreatment for biomass before wood pyrolysis with respect to bio-oil yields. Different conditions in terms of frequency (40, 68 and 170 kHz), time (0.5, 1 and 1.5 h) and power (125, 250, 500 and 1000 W) were explored to include the primary action mechanisms of ultrasound: mechanical and sonochemical effects. The combination of using 40 kHz and 170 kHz frequencies in a sequence of 0.5 h at 170 kHz and 1.5 h at 40 kHz and a power of 1000 W has been demonstrated to be the best, achieving a 12% increase in bio-oil yield compared to untreated wood. However, contrary to what was thought at first, the best energy efficiency was obtained at low power (125 W) with a Watt per percentage of extra oil produced ratio of 47. Therefore, depending on the final production goal, the ultrasonic conditions could be adjusted accordingly. Finally, the chemical analysis of the oils by GC indicated no influence of the pretreatment on the final composition of the recovered oils.

Keywords: wood; ultrasonic pretreatment; slow pyrolysis; bio-oil yield; sonochemistry

1.   INTRODUCTION

For several years, the pulp and paper industry has sought to renew itself in the face of constant decreases in the traditional pulp and paper market, partly due to the rise of electronic media, as well as the emergence of the paper industry in China, which has led to a more competitive market [1]. To revive this industry, research has focused on new utilizations of raw wood that move away from conventional uses, especially the thermochemical conversion of forest biomass. Many technologies are already available, such as gasification, carbonization, and liquefaction. Among all of these technology, pyrolysis has attracted the most interest [2,3]. Since one of the products of pyrolysis are bio-oils, which are a great carbon source, pyrolysis represents a potential source of energy. Beyond economic reasons, there is also an environmental aspect that has motivated this work. The human dependence on fossil fuels is a problem, especially because these energies cause considerable pollution and are not renewable, making their replacement a priority that we must address now in order to reduce their negative impact on the environment in the future [4].

The pyrolysis of wood biomass for the production of bio-oils has been found to be both a solution and a problem. Indeed, it is a simple process that is well-understood. This thermochemical conversion typically occurs at temperatures between 500°C and 800°C under an inert atmosphere and uses biomass with minimal water content (under 10 wt%) [5]. The process itself currently

45 possesses good efficiency. For example, flash pyrolysis can achieve bio-oil yields ranging from
46 75 to 80 wt%. However, for the sake of the cost of production, we are seeking to optimize this
47 process in order to have it work at lower temperatures and with fewer chemicals involved, thus
48 emitting a minimal amount of pollutants into the atmosphere. We are also especially seeking to
49 obtain the purest products possible in greater amounts.

50 To realize such ambitious objectives, studies of pyrolysis were undertaken. From the many
51 possibilities, it was shown that fluidized bed reactors have given the best results in term of oil
52 production [6]. The choice of cooling system was also shown to be of importance because its
53 effectiveness determines the capability to recover the pyrolytic vapours. As systems
54 configurations are reaching their limits, the use of homogeneous or heterogeneous catalysts (e.g.,
55 metal salts and ultrasound) are now explored. [7, 8]

56 By definition, ultrasound is acoustic energy at a frequency higher than the upper normal human
57 hearing limit (20 kHz) and is normally limited up to 1 MHz. However, the efficiency range of
58 power ultrasounds are more limited. In fact, from [9], the sonochemistry efficiency is at a
59 maximum in the range of 200 kHz while the maximum mechanical effect is found at 20 kHz. The
60 use of ultrasound as a technique for process optimization is of great interest as a result of its
61 ability to promote chemical and thermal decomposition reactions [10]. In addition, studies have
62 clearly shown that, thanks to the cavitation effect, the use of ultrasound can reduce the time of a
63 biomass hydrolysis reaction up to 80% [11], which is useful while producing biofuels. Even more
64 interesting, ultrasound has considerable potential to cleave the chemical bonds of the biomass
65 components and thus could facilitate the extraction of compounds of interest, such as cellulose,
66 hemicellulose or lignin [12]. With the partial destruction of lignocellulosic molecules, the energy
67 needed for the complete thermal decomposition of biomass should not be as high [13], thus
68 making the process easier through the use of ultrasound. Ultrasound can exhibit mechanical
69 effects, mainly at low frequencies (20 - 60 kHz), and sonochemical effects, mainly at high
70 frequencies (100-1000 kHz), that need to be explored [14, 15]. The acoustic energy resulting
71 from ultrasound allows the formation of stable cavitation bubbles (at high frequencies) or
72 transient bubbles (at low frequency). Transient bubbles quickly grow to their breaking point,
73 while stable cavitation bubbles oscillate in diameter over several acoustic cycles before also
74 breaking [10]. When the bubbles implode, they create a violent jet of matter and energy. Surface
75 tension variation in the fluid always guides the jet in the direction of a solid surface, resulting in
76 an intense mechanical shock of up to 10^3 MPa. This violent fluid movement promotes
77 microconvections, increasing the transport of fluids and solid particles [16]. At this stage,
78 temperatures near 5000°C and pressures of approximately 500 atmospheres in the vacuum
79 cavitation bubble lead to water sonolysis and promote the formation of short-lived radicals,
80 principally H˙ and OH˙, [17] thus giving rise to sonochemical effects, especially when a high
81 frequency is used (≈100 - 1000 kHz).
82 Unfortunately, the introduction of transducers directly into a pyrolysis reactor is not possible due
83 to high temperature maintained inside, which would permanently damage them. Modern
84 piezoelectric transducers cannot be used at such a high temperature (500°C) because of the Curie
85 point of the material they are composed of, thus limiting their use as well. To solve this limitation
86 and still use ultrasound in a pyrolysis process, it is possible to incorporate ultrasound prior to the
87 use of the pyrolysis reactor. The second possibility is to use ultrasound directly on the pyrolysis
88 end products, which in our case are pyrolytic oils. This work was focused on the first of these
89 solution: an ultrasonic pretreatment of wood chips at 40, 68 and 170 kHz, thereby enabling an
90 investigation of both ultrasound effects at different exposure times (0.5, 1, and 2 h), as well as
91 different combinations of these two parameters.

92 **2.   EXPERIMENTAL**

2.1. Wood Chips

The wood chips were provided by an eastern Canadian pulp and paper mill, which is mainly fed by softwood (spruce, fir, pine, and larch). Before being used, the chips were washed in water to remove impurities such as sand or plastic, dried in ambient air, and then ground down to 5 mm by 5 mm needles before being pretreated with the ultrasound if needed. The wood chips were dried at 105°C for at least 24 h before being used in the pyrolysis reactor.

2.2. Ultrasonic Bath

Ultrasonic treatments were performed in a 34 l ultrasonic bath, model BT90 from Ultrasonic Power Corporation (USA), made of 316 L stainless steel, as previously used by Loranger et al. [18]. It was equipped with 12 transducers, all of which were located below the bottom plate of the bath. Commercial frequency generators of 40, 68 and 170 kHz were used to produce between 125 and 1000 W of nominal ultrasonic energy. The exposure time at a given frequency or frequency combination was varied from 30 min to 2 h. For each treatment, the wood chips (200 g) were dipped into 4 l of deionized water ($\Omega < 0.8$ µS). The wood chips were kept on the bottom of the bath with a weighted meshing, which allowed the wood chips to remain fully submerged and ensured that all introduced biomass was being treated by ultrasound. During the experiments, the temperature over time was recorded. The system was calibrated as described by M. Paquin et al. [19] for various ultrasonic frequencies and for the corresponding mechanism (sonochemical or mechanical effects).

2.3. Ultrasonic Treatments

In order to assess the ultrasound effects mechanisms in our system configuration, i.e., sonochemical or mechanical, we have tried three frequencies, 40 kHz, 170 kHz and 68 kHz, to study respectively mechanical effect, sonochemical effect, and an intermediate. According to Paquin et al. [19] and Loranger et al. [20,21], who measured the effect on those ultrasonic apparatus thanks to power calibration (temperature increase) and iodide dosimetry as reported in Koda et al. [22], both effects are more or less observable depending on the range of frequencies used for the experiment. Thus, for each frequency, a ratio of observable mechanical effect/sonochemical effect could be estimated for the system. At 40 kHz, the ratio was close to 80/20, while at 170 kHz, the ratio was closer to 20/80. 68 kHz was found to have a value in the middle of the range as the ratio was about 50/50. Once an optimal condition was found, we then focused our attention on the best exposition time combinations for the bio-oil production. Each experiment was conducted at least three times, and the mean was reported as a single result. All ultrasonic treatments are shown in Table 1.

Table 1: Ultrasonic treatment conditions (power, frequency, time of exposure)

Ultrasonic conditions.					
		Step #1		Step #2	
Experiments	Power (W)	Frequency (kHz)	Time (h)	Frequency (kHz)	Time (h)
A					
B		40	1		
C	1000	68	1		
D		170	1		

E		Soaking only	1	40	1
F		Soaking only	1	170	1
G		40	1	170	1
H		170	1	40	1
I*		170	0.5	40	0.5
J		170	0.5	40	1.5
K		170	1.5	40	0.5
L	500	170	1	40	1
M		170 kHz and 40 kHz, simultaneously for 2 h			
N	250	170	1	40	1
O	125	170	1	40	1
*: Repeated to achieve a total of 2 h of treatment (sequence Step 1/Step 2/Step 1/Step 2)					

127 Once the treatment was over, the totality of the exposed wood was recovered and dried in an oven
128 (105°C). After the ultrasound treatments, a slight water coloration was observed. Thus, the water
129 from the bath was also recovered and analysed by GC-FID according to the method presented in
130 section 2.6. From these results (data not shown) no significant amount of organic compounds was
131 found in the remaining water. To further confirm, weight measurement before and after the
132 treatment J were also performed. Being the most conclusive condition, any change, if any, should
133 be more evident. Weight measurement (data not shown) did not present any significant weight
134 change of our sample, especially considering the potential errors coming from wood manipulation
135 and recovery as well as the humidity content of wood chips, which can also be of influence.

2.4. Thermal Treatment

137 As ultrasound is applied to a closed system, the energy is trapped in the medium, resulting in an
138 increase in temperature. In pulp and paper applications, it is well-known that hot water alone
139 could be used as an extraction medium [23]. Thus, the exact effect of an increased water
140 temperature was determined in preliminary testing, and disregarding the heating rate of each
141 experiments which could be slightly different, a maximum temperature of about 80°C was
142 achieved under ultrasounds. Thus, it has been chosen as a setpoint for thermal treatments. Exactly
143 200 g of wood chips was placed in a 2 l crystallizer filled with tap water and preheated to 80°C
144 for a period of 1 to 2 h. The water temperature was controlled by a hotplate, and the wood chips
145 were stirred to ensure homogeneity. Afterwards, they were dried at 105°C for 48 hours before
146 going through the pyrolysis process.

2.5. Lab-Scale Pyrolyser

148 To produce bio-oil, a stainless steel lab scale pyrolyser was built as described by Loranger et al.
149 [18]. Wood chips (140 g) were added into the cylindrical reactor (36 cm long with an 8 cm inner
150 diameter) that was sealed using a bolted flange. Heating was accomplished at a rate of
151 approximately 16°C/min by two natural gas burners. However, as the necessary time for complete
152 pyrolysis is between 1 and 1.5 h, depending on the treatment, our pyrolysis system belonged to
153 the slow pyrolysis category. The reactor was connected to a thermocouple that indicated the
154 temperature in the reactor. The produced vapours were recovered with a multiple stage
155 condensing system made of three baths. The first flask was cooled with tap water (15°C), the
156 second with an ice-water mix (0°C) and, finally, the third flask was placed into brine (-15°C).

157   This system permitted a better separation of the different components according to their volatility
158   and thus to their molecular weight. In our experiments, flask 1 mainly contained water and a
159   small fraction of oils, flask 2 mainly contained oils, although a small quantity of water was still
160   recovered, and flask 3 only contained a very small amount of oil. To ensure an inert atmosphere,
161   a flow of nitrogen (10 mL/min) travelled in the entire system throughout the experiment. As the
162   gas outlet was composed of various non-condensable chemicals, a flame was ignited at the outlet
163   to prevent any accumulation.

164
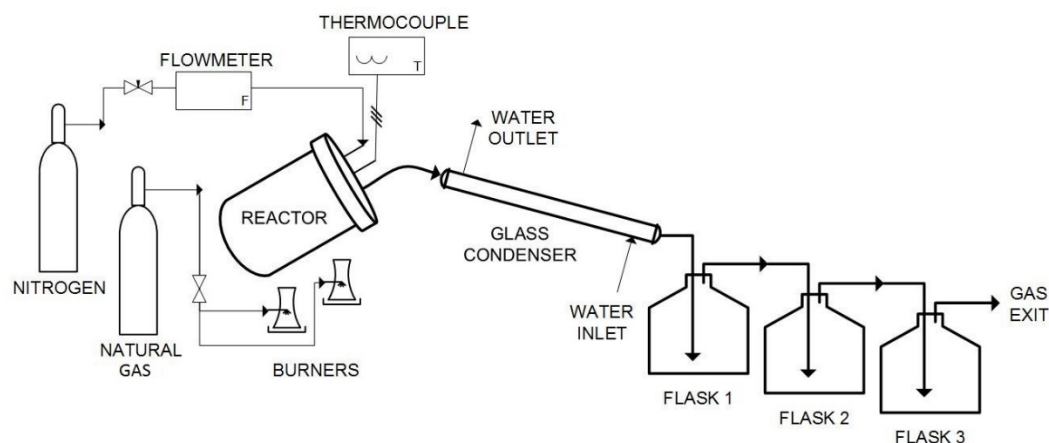
165

166   *Figure 1: Schematic diagram of the laboratory-scale pyrolyser [18].*

167   2.6   GC Analysis

168   The bio-oil composition was established using an Agilent 7890B Gas Chromatograph equipped
169   with a flame ionization detector (FID) and a J&W Scientific DB-5.625 column (length: 30 m,
170   internal diameter: 0.25 mm, film thickness: 0.25 µm). The 1 µL injection sample underwent two
171   temperature ramps at 3°C/min from 40 to 200°C and at 6°C/minutes from 200 to 300°C. The
172   sample was injected in split mode (50:1 ratio) before being carried through the column by a 0.6
173   mL/min helium gas flow to the FID detector. Considering the high chemical complexity of bio-
174   oils, exact quantification was not carried out. Instead, the components were classified into five
175   categories: lights, acids, alcohols, ketones and phenols. To obtain the retention time of these
176   categories, a 44 component standard with various representatives of each chemical family was
177   injected, measured and classified. The oils from flask 1 and flask 2 were analysed separately, then
178   the total composition of oil was calculated from these results.

179   2.7   Experimental Process Diagram

180   For an easier understanding our entire experimental process, Figure 2 presents the process
181   diagram.
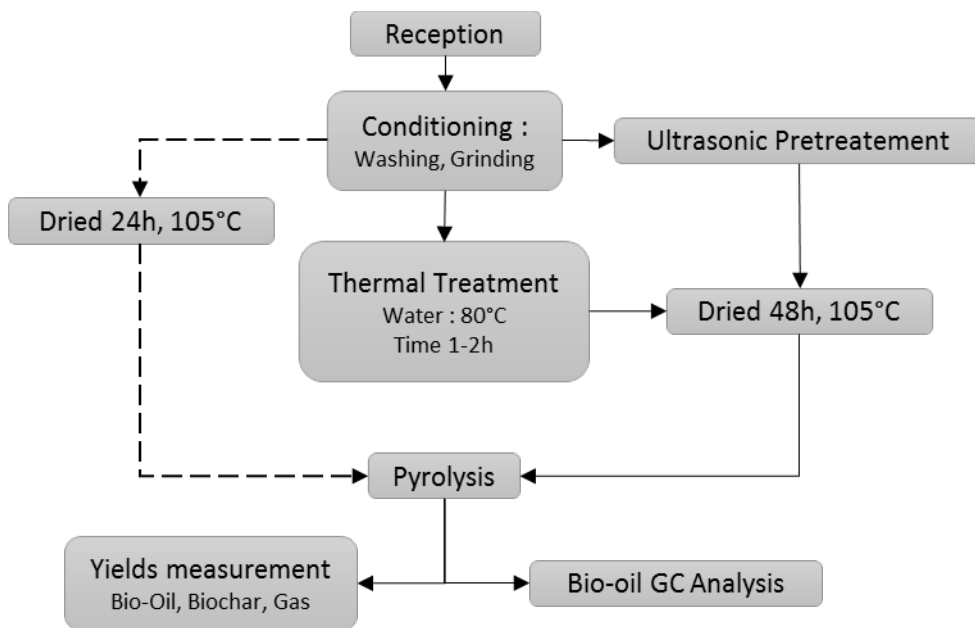
182

183 *Figure 2: Experimental process diagram.*

3. RESULTS AND DISCUSSION

184

185 As a result of the number of experiments completed in this work to cover the principal parameters
186 and find the optimum combinations between frequencies and times, the results have been
187 separated into the different stages of research. As a first step, we determined which frequency was
188 the most advantageous in terms of bio-oil yields. In all the mass yield graphics in this section, the
189 liquid fraction represents the sum of the oil phase and aqueous phase, the latter being mainly
190 composed of water and low weight organic parties. The residues corresponded to the fraction
191 remaining in the reactor that was not recovered with the biochar (mainly tars and wax). Starting
192 with section 3.2, the green dashed line represents the untreated wood values, considered here as
193 the control.

194 Considering the novelty of this work, there was no literature to compare to our results. Indeed,
195 research on the improvements of pyrolysis through physical techniques has largely been focused
196 on microwaves [24,25] instead of ultrasound. The closest work that we found is from Z. Wang et
197 al. [26] and Loranger et al. [27]. However, these reports did not investigate exactly the same
198 subject as the current study.

3.1. Ultrasound Frequency Effects on the Bio-Oil Yield

199

200 This first stage in our work was aimed at identifying the frequency to use in the subsequent
201 stages. However, as shown in Figure 3, no significant effect was observed at 1000 W. With
202 respect to the standard deviation of the measurement, we could only observe trends. Gas, for
203 example, tended to increase when the frequency increased. On the other hand, biochar was found
204 to undergo the opposite effect. With respect to the bio-oil yield, the only significant conclusion
205 was that the utilization of the 68 kHz frequency was detrimental to achieve our initial goal, which
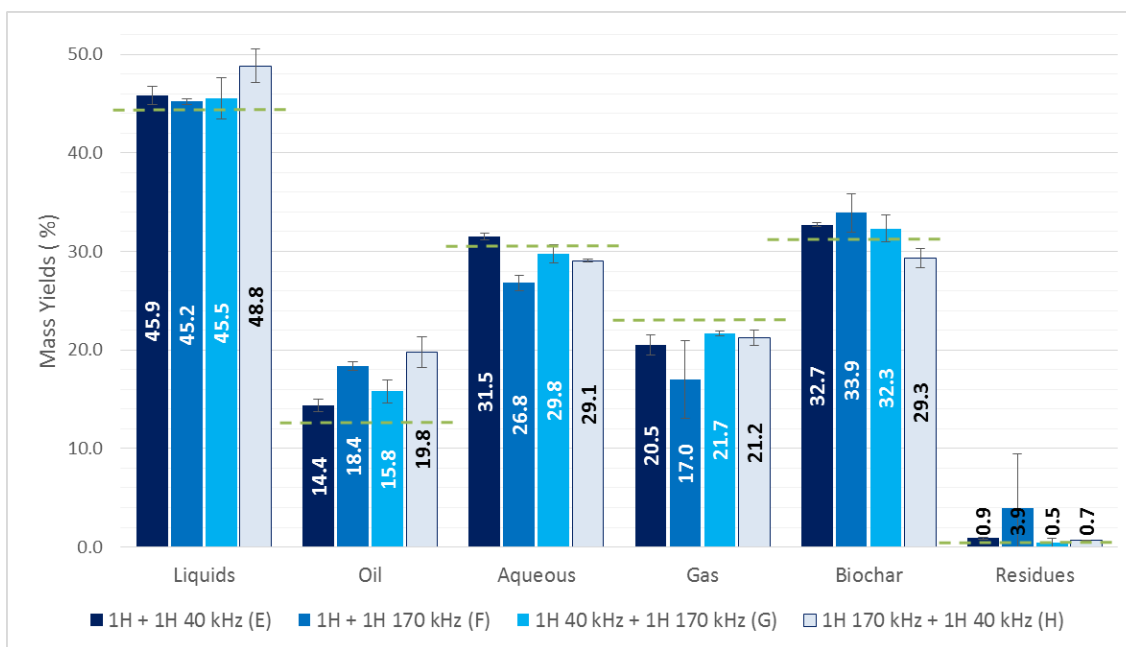206 was to increase the bio-oil yield.
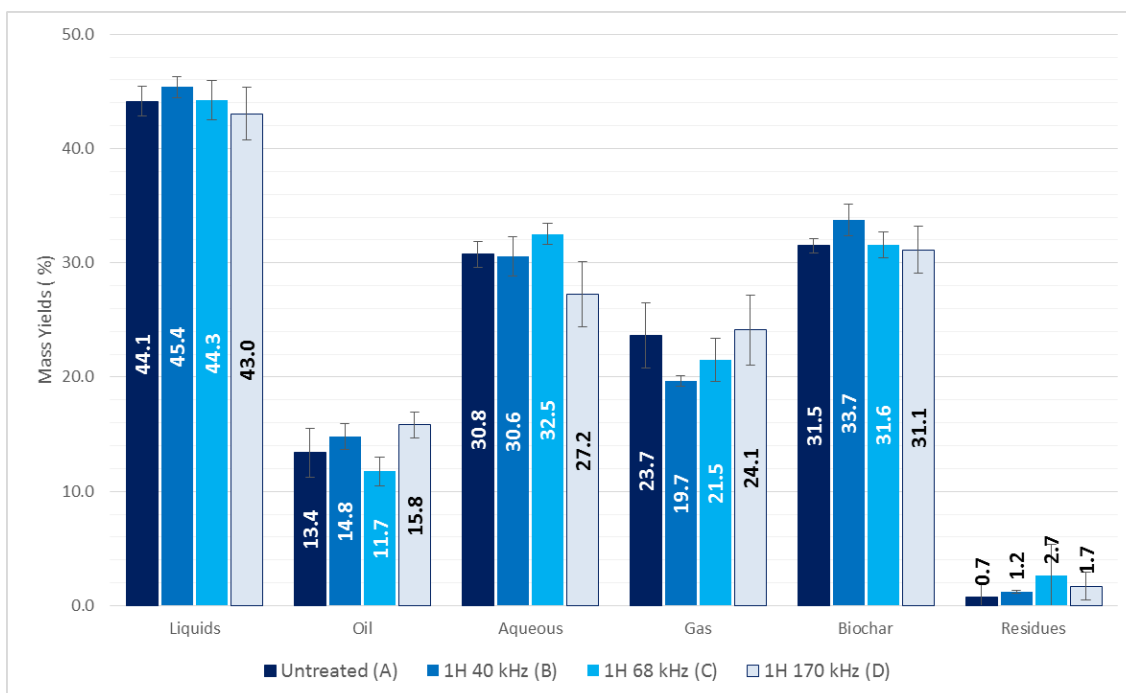
Figure 3: Effects of 40, 68 and 170 kHz ultrasound frequencies on bio-oil yield compared to untreated wood.

This lack of effect despite the high ultrasonic power used (1000 W) led to the development of four hypotheses: (i) the exposure time is too short, meaning that ultrasound did not have sufficient time to act properly; (ii) only the wood surface was attacked by ultrasound, thus leaving a significant amount of its internal matrix untouched; (iii) the ultrasonic bath was ineffective and needed to be replaced by a more efficient delivery system (an ultrasonic tube reactor[20], for example); or (iv) 1000 W is not enough power to deliver the required energy to obtain a noticeable effect. Hypotheses (iii) and (iv) are related to physical limitations of our experimental apparatus; thus, further experiments with another system would have to be done. Complementary experiments have been done for an increased exposure time (2 h) but the results were similar to Figure 3 and therefore are not shown. Moreover, Loranger *et al.*. [27], have found similar behaviour even after 8 hours of treatment. By deduction, hypothesis (ii) was further investigated in this study.

In the following studies, the 68 kHz frequency was been abandoned because it gives minimal results and even potential detrimental effects. Furthermore, because 68 kHz represents the combination of 50% mechanical and 50% sonochemical effects, it was difficult to draw any conclusions. Hence, the mechanical effects were explored at 40 kHz and the sonochemical effects at 170 kHz.

3.2. Soaking Treatment and Frequency Combination Effects on the Bio-Oil Yield

The propagation of ultrasound occurs through water. Therefore, if there is no water inside the matrix of wood, ultrasound cannot have its complete effect on the wood components. The purpose of the soaking treatment was to determine if the wood only needed time to absorb water to allow cavitation to occur inside the wood particles and if the addition of ultrasonication at 40 kHz or 170 kHz could help to achieve that effect as well. Soaking was done at room temperature for experiments E and F, and the results are presented in Figure 4.

Figure 4: Effect of soaking treatment and 40 and 170 ultrasound frequencies on the bio-oil yield.

This pretreatment stage allowed us to observe significant effects, with the best result being obtained with treatment H. This result was significantly different from what was expected. Our first thought was that the use of 40 kHz frequency would be more efficient because the mechanical effect would "smash" the surface particles [28]. Its action would then resume on the newly exposed surface, which was inaccessible at first. At 170 kHz, ultrasound has a sonochemical effect, namely, the production of radical inside the propagation medium. Using water as the fluid of propagation, H˙ and OH˙ radicals are created [19]. At 40 kHz, the mechanical effect is observable [9,14,15,21], which should pulverize the wood into smaller particles that were recovered at the end of the treatment. This combination of both effects allowed us to devise an explanation: during the first hour, generated radicals attack the biomass linkages and weaken them, making it easier for the mechanical effect to reduce wood particle size and exposing the matrix, which facilitates thermal degradation. The use of the 170 kHz frequency was necessary to improve bio-oil yield, as shown by treatment (F). When comparing treatments E and F with treatments B and D from Figure 3, it was possible to see that the 40 kHz frequency alone (B) or the 40 kHz frequency preceded by soaking (E) gave almost the same bio-oil yields. Therefore, we could state that soaking did not improve the mechanical effect. Furthermore, one hour treatment at 170 kHz (D) gave the same results as (E), which confirmed the ineffectiveness of soaking when using only the 40 kHz frequency. In contrast, soaking did enable improvement when using the 170 kHz frequency, as shown by the increase of 2.6% yield between treatments (D) and (F). This treatment showed better results than the combination tested in treatments E and G. These observations allowed us to state that the sonochemical effect obtained at 170 kHz was more crucial than any other treatment, as shown by the yield of trial (H).

3.3. Bio-Oil Composition

As the ultrasound treatment had an effect on the pyrolysis yield of the biomass, it could also have an effect on the oil composition. For comparison, the composition analysis of untreated wood (A), 1 h 170 kHz (D) and 1 h 170 kHz + 1 h 40 kHz (H) has been gathered in Figure 5.
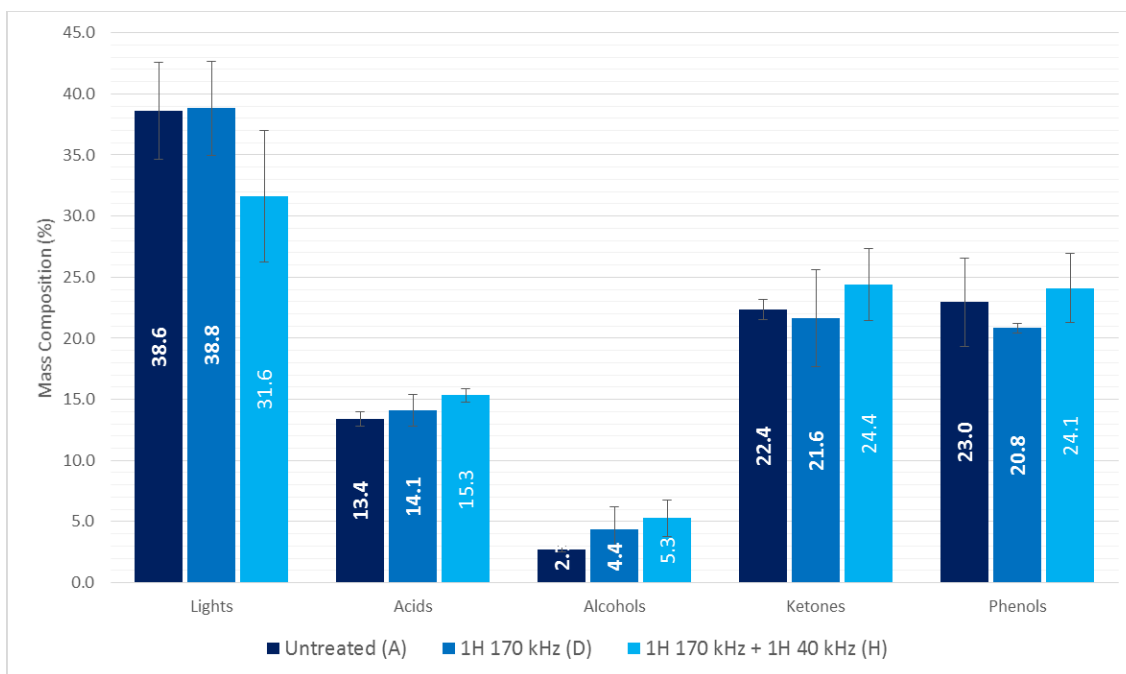
Figure 5: Bio-oil compositions for a few ultrasonic treatments.

Although the yields were considerably different (Figure 4), the composition of the oil did not seem to be significantly affected by the ultrasound treatments, which was also shown by García et al. [13] and Loranger *et al*. [27]. Because of the large standard deviations, no remarkable changes are evident; thus, the effect of ultrasound seems to be limited to an increased yield. All the compositions were measured (data not shown) but they were similar to Figure 5. At first, results seem to be in contradiction with some of the works of others [26, 29] who have found modifications in the biomass after an ultrasound's treatment. However, conclusions were made on very subtle changes (e.i. carbon content decrease from 49.86% to 49.39% in [26]) which is difficult to consider as significant results. Moreover, both references [26, 29] used more aggressive media (acetic acid, benzene-alcohol solvent, soda, etc.) on an easier biomass to process as it is in powder. Finally, unlike their research who uses only low frequencies (28 and 40 kHz), we use a combination of low and high frequencies (40 and 170 kHz) which effects have not been studied yet. Therefore, it proves that ultrasounds effect on lignocellulosic biomass is unclear and depending on all possible conditions such as biomass, particles size, reaction medium, frequency, etc. If any chemical modifications had occurred on wood, like extraction of some sort, it should appear on the composition chart, which from our results has not. The unchanged composition in our case was considered to be a positive aspect of the present research because it means that ultrasound treatment could be appropriate for incorporation into an already established process of wood conversion without interfering with the final quality of the product.
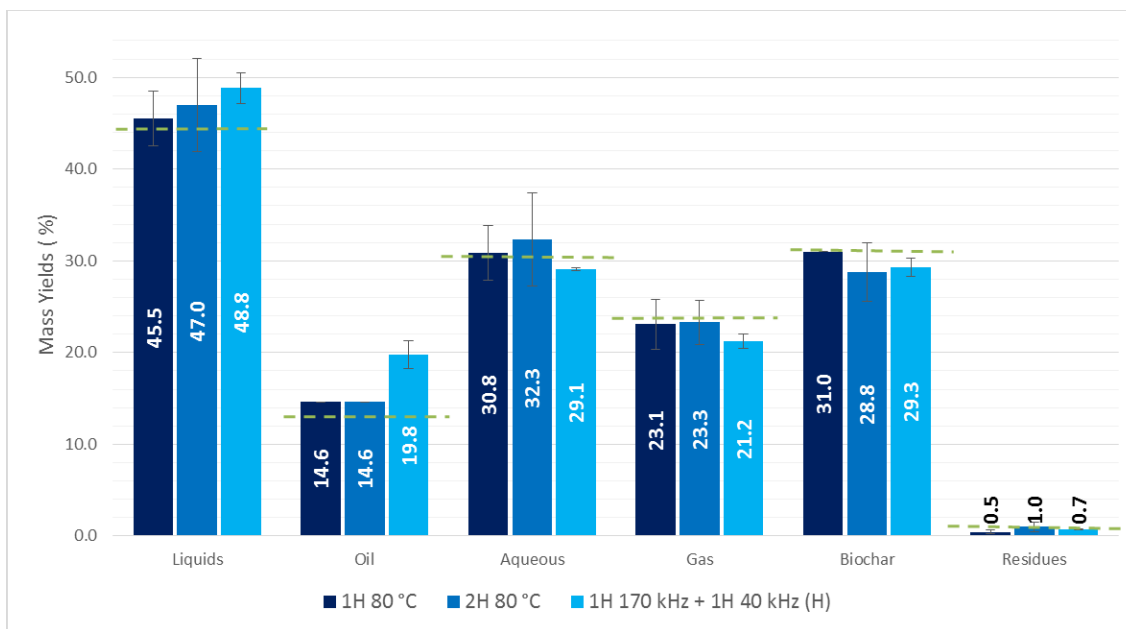
3.4. Water Temperature Effects on the Bio-Oil Yield

During our experiments, it was noticed that the water temperature rose to 76 °C. This situation resulted from the bubble implosions that occurred during ultrasound treatment and from the irreversible losses caused by the conversion of electrical energy to vibrational energy. Consequently, the effect of hot water must be accounted for to certify that the results presented in previous study (Figure 4) were due to ultrasound and not to the increase in temperature during the

treatment. As shown in Figure 6, temperature had a positive effect. Temperature increased the bio-oil yield to 14.6 % from 13.4 % for untreated wood (Figure 3), a small increase of 1.2 %. However, the time of exposure to hot water did not seem to be relevant because the bio-oil yields after 1 h and 2 h were exactly the same.


Figure 6: Ultrasonic bath temperature effect on bio-oil yield.

In conclusion, a simple hot water extraction did occur during the ultrasound treatment but was responsible for 1.2 % of the total increase of 5.2 % with the optimized ultrasound treatment. Therefore, close to 80 % of the increase was attributable only to ultrasound. Nevertheless, we consider temperature to be a small help for further wood decomposition.

3.5. Treatment Time Combination Optimization

As the given frequency and sequence seemed to be optimal at 1 h 170 kHz + 1 h 40 kHz (H), we tried to change the exposure time to assess whether it was also optimized. From Figure 7, we can clearly see a pattern emerging concerning the bio-oils yield, which also affected the other products of pyrolysis. We noted that a reduction in the exposure time to the 170 kHz frequency and an increase in exposure time to the 40 kHz frequency were beneficial because bio-oil yields reached 22.0 % and 25.4 % with treatments I and J, respectively, for a total increase of 12 % compared to untreated wood. Another advantage was that the bio-oil yield increase was due to a decrease in the aqueous phase and not to an overall increase in the amount of recovered liquids. As the water content is a common problem in pyrolysis oil production, this effect should not be ignored. In addition, gas production decreased by 3 % compared to untreated wood, which was beneficial for slow pyrolysis because the gases are burned most of the time for security reasons.
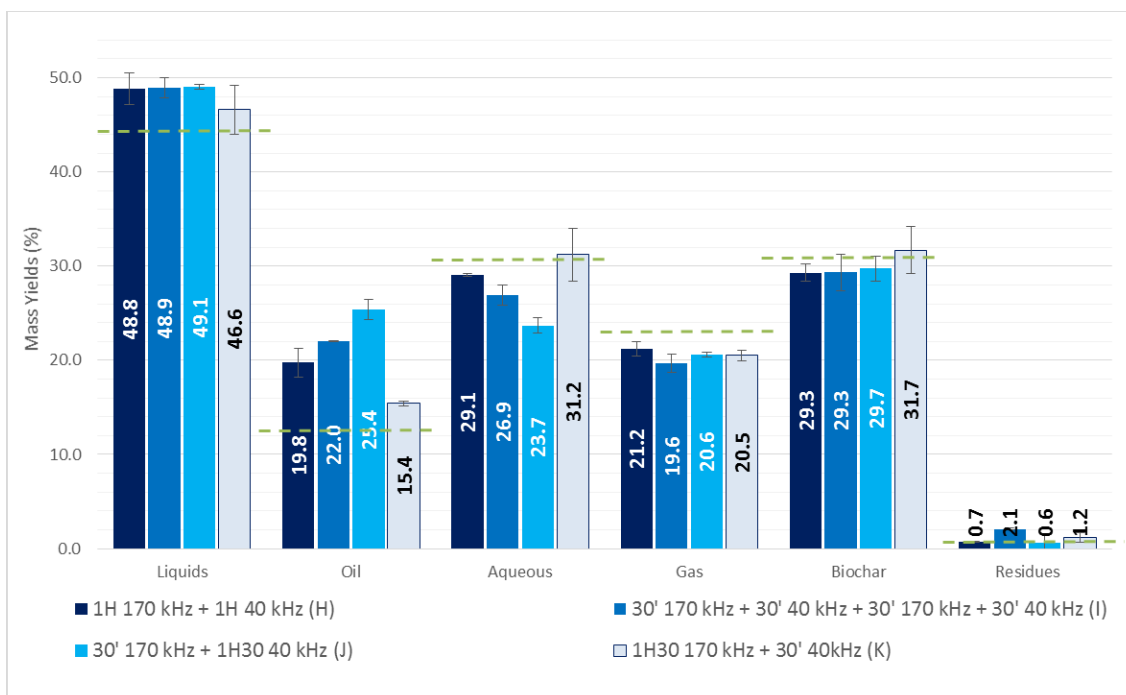
Figure 7: Effect of different time combinations on the bio-oil yields

Finally, treatment K showed significant differences in its bio-oil and aqueous phase yields. Unlike the two previous treatments, the bio-oil yield was lower than that obtained with treatments H and even D, which in turn benefited the aqueous phase. To explain this phenomenon, we assumed, according to all the observations made above, that the radicals formed during the phase at 170 kHz attacked the surface of the wood particles and weakened or even destroyed easily accessible or weaker bonds. An increased exposure rate could readily promote this type of catalytic degradation reaction, as shown in [13]. Then, in the subsequent phase at 40 kHz, the mechanical effect and the high energy involved finished breaking the bonds already weakened by the radicals, all of which has acted to break up the surface of the wood particles and thus expose a portion that lies deeper in matrix [29]. This newly released and revealed surface is therefore available to be attacked by radicals again. However, the mechanical attack would only result in weakening the newly accessible links. Therefore, you could end up with macroscopic particles (visible to the naked eye at the bottom of the ultrasonic bath), which could eventually decompose during pyrolysis be part of the bio-oil fraction.

This reasoning explained that prolonged exposure to the chemical effect was not recommended because if the radicals were formed in excessively large quantities, once the weakest links were destroyed, then the radicals would attack the bonds of larger molecules (the aromatic rings of the lignin, for example). Next, these large molecules, already weakened by the chemical effect, would be broken due to the mechanical effect. Therefore, a larger amount of small molecular weight molecules that were more soluble in the water phase was created, thus preventing them from being found in the bio-oil. Additionally, it was possible to lose a certain amount of particles in the bath water, which were always discarded and not involved in the pyrolysis process.

3.6. Ultrasound Power Effects on the Bio-Oil Yield

All previous experiments were conducted at 1000 W to ensure that any effects of ultrasound would be observable. However, a lower power could lead to the same results and be economically more advantageous. Thus, we have studied in this work the impact of power on the bio-oil yield, using the optimal treatment of 1 h 170 kHz + 1 h 40 kHz (H). The product yields from this experiment are shown in Figure 8.
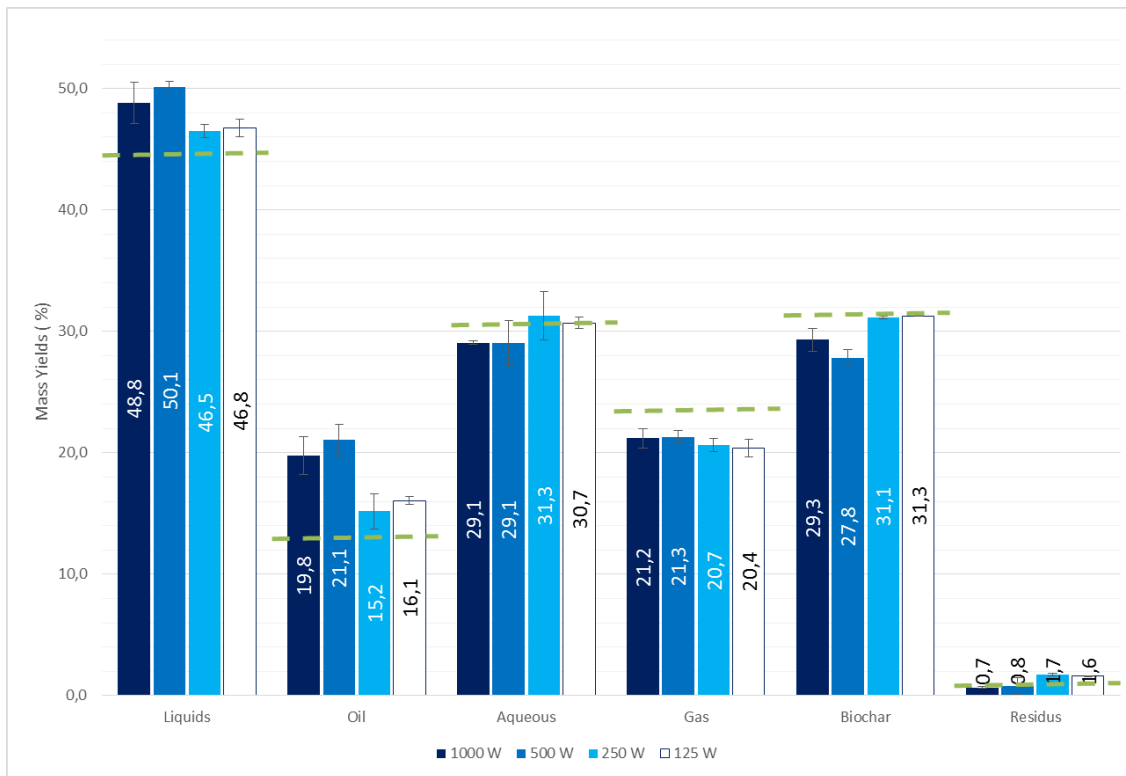

Figure 8: Ultrasound power effects on bio-oil yield.

In Figure 8, two plateaus are observable, the first at 125 W and the second at 500 W, which shows that the use of too much power (i.e., 1000 W) was unnecessary. At 125 W and 500 W, the system seemed to reach an operating equilibrium beyond which additional energy is dissipated without significant effects on the medium. This theory was confirmed by the differences in the temperatures of the ultrasonic bath water between treatments at different levels, along with the calculation of the power per the percentage of additional oil ratio (W/% $_{\text{Oil Yield Gain}}$). Indeed, values of 46.64, 138.122, 65.18 and 156.49 for 125, 250, 500 and 1000 W, respectively, were calculated. In other words, an increase of the power allocated per percentage of extra oil was 2.96 for the first level and 2.40 for the second level to achieve similar bio-oil yields. According to this data, at 500 W was the level at which the largest increase is obtained (7.67 %) compared to untreated wood (green dashed lines). However, from an energy efficiency point of view, a power of 125 W could also be used. This condition was especially favourable for biochar production as the lowest power tended to lead to higher yields. To confirm this observation, however, further work is needed.

3.7. Ultrasound Application Mode Effects on the Bio-Oil Yield

As the best yield was obtained by sequencing two frequencies, it was of interest to couple them differently. Although they were only used sequentially at first, the use of these two frequencies

359 simultaneously could be of interest, especially in industrial applications. To answer this question,
360 treatments L and M, again at the same frequencies that had been identified as optimal, were
361 completed at 500 W. The results are presented in Figure 9. As half of the transducer bank were at
362 40 kHz and the other half at 170 kHz, the ultrasonic bath wiring configuration gave a combined
363 power of 500 W.
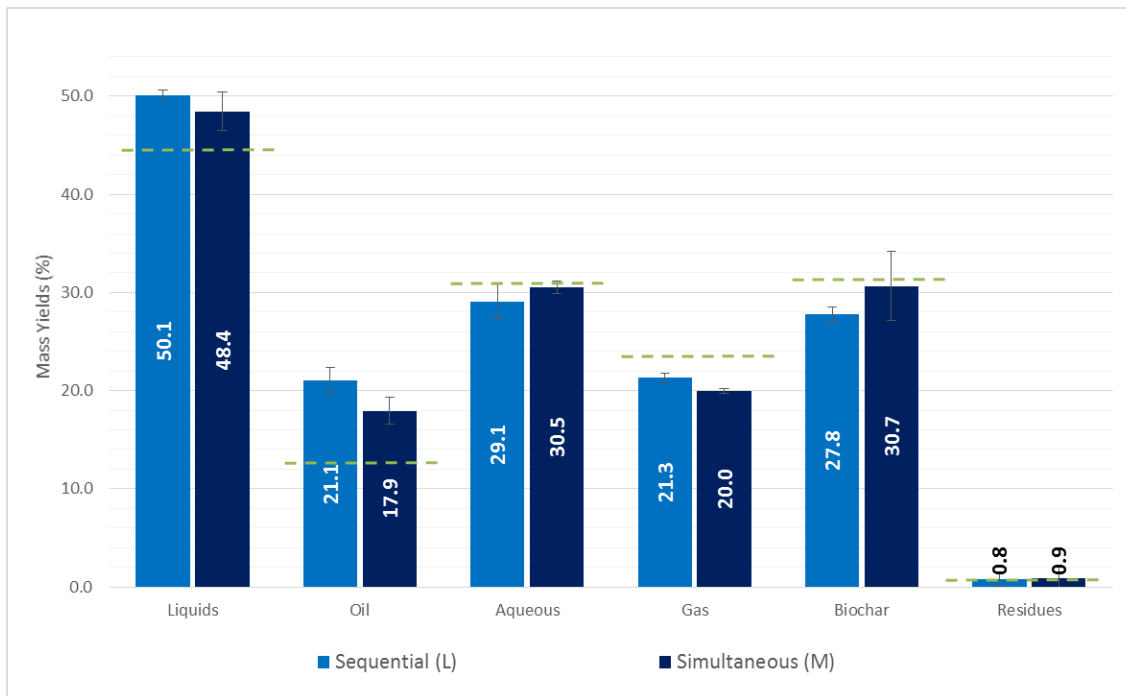
364

365 *Figure 9: Ultrasound application mode effect on the bio-oil yield*

366 The results shown in Figure 9 revealed a negative effect of the simultaneous use of the
367 frequencies. An increase the aqueous phase and a decrease the oil phase compared to the
368 sequential treatment was found. Thus, the simultaneous use of frequencies was not as efficient as
369 in sequence but is nevertheless still better than pyrolysis without any ultrasound applied (green
370 dash line).

371 **4. CONCLUSIONS**

372 In the field of energy production from renewable sources, product yields are important because it
373 will often determine the viability of a project. This work has demonstrated the added value of
374 ultrasound techniques used as a pretreatment for wood pyrolysis for the production of bio-oil. For
375 this purpose, the combination of two frequencies, 40 and 170 kHz, and thus two notably different
376 action mechanism was required to take advantage of their synergistic effects. In this sense, the
377 combination of 0.5 h at 170 kHz and 1.5 h at 40 kHz (J) was proved to be the most effective,
378 enabling an increase of almost 12% of bio-oil yield compared to untreated wood.

379 Although excessive chemical effect was shown to be detrimental to bio-oil production, its
380 presence was still necessary in STEP 1 to optimize the mechanical effect in STEP 2, although the
381 reverse is not true. In contrast, the simultaneous use of both ultrasonic effects did not appear to be
382 sufficiently significant, as shown by treatments C and M. Although water bath temperature
383 increased during processing, thus subjecting the wood to a hot water extraction of certain
384 compounds, especially at higher power, ultrasound was shown to have an additional beneficial

385 effect. The temperature increase was responsible for only 2% of the total increase of 12% in
386 comparison to the untreated wood.

387 Finally, contrary to what seems logical at first, increasing the power allocated to the treatment did
388 not lead to a proportional increase in oil yield. Indeed, we have seen two levels of efficiency: a
389 first at 125 W and a second at 500 W. Even though the optimal bio-oil yield was found for a
390 power of 500 W, the best energy efficiency was found at 125 W, with approximately 47 W per
391 percentage of extra oil against 138, 65 and 156 W/% for 250, 500 and 1000 W, respectively. All
392 obtained results obeyed the overall mass balance, thus remaining plausible and reasonable each
393 time.

394 This work has demonstrated great progress for ultrasound-enhanced lab-scale pyrolysis bio-oil
395 production. However, further studies are still necessary to explore all possibilities that arise from
396 this new technology and to fully access its potential.

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