

Preliminary study in using ultrasound as a post-treatment of pyrolytic bio-oils

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Abstract—For many years, studies about producing pyrolysis bio-oils as emerged. Bio-oils can be used as a biofuel or as a source of high value molecules. Therefore, it can be a promising alternative to reduce fossil oil consumption and climate changes. This paper presents the optimization methodology of an ultrasonic post-treatment on pyrolysis bio-oils. Ultrasounds create cavitation bubbles who generate different effects. Their mechanisms have various effects on bio-oils, such as composition modification, calorimetry or water content. To protect the ultrasonic bath and minimize the amount of raw material needed, bio-oils were placed in a sealed plastic bag before the treatment. Different methods were used to characterize the reduction of ultrasonic effects by the plastic bag. In these works, different frequencies (40 and 170 kHz), temperatures (25 and 45 °C), powers (500 and 1000 W) and exposure times (0.5 and 1.5 h) were studied to determine the effect of each parameter on bio-oils, just after post-treatment and after 15 and 30 days. Results have shown that the presence of the plastic bag influences the ultrasound diffusion. Moreover, ultrasonic post-treatment modifies the composition, calorimetry, and time stability of bio-oils.

Keywords—Pyrolytic bio-oils, Ultrasonic post-treatments, Potassium iodide dosimetry, Sonochemistry, Aging

I. INTRODUCTION

Nowadays, the general consumption of fossil energies is growing [1]. This overconsumption causes many troubles, like a reduction of biodiversity and climate changes [2]. Therefore, it is necessary to find new ways to reduce global carbon footprint. The use of biomass to produce biofuels could be a part of the solution for these problems if this resource is intelligently exploited or come from residual biomass. In Canada, a lot of lignocellulosic biomass is available [3]. This high volume of biomass is the result of the decrease of pulp and paper market due to the technological evolution and the competition of emerging countries. Bio-oils can be produced with the pyrolysis process. This transformation consists in heating a lignocellulosic biomass at very high temperature (500 °C) without oxygen. This warm-up breaks molecular bonds of the biomass principal components (cellulose, hemicelluloses and lignin) and creates three products: syngas, biochar and bio-oils [4]. This latter could be considered like biofuels or a compound convertible into high added-value products. However, the bio-oils quality is worse than conventional petroleum. It is less energetic, more viscous,

contained water and is unstable over time. In many studies, different ways were explored to resolve these weak points. Chemical treatment can improve the stability of bio-oils [5, 6], such as catalytic methods or physicochemical treatment directly on bio-oils or upstream of the pyrolysis. Biomass treatments can also modify bio-oils quality or production yield [7]. Ultrasonic treatment could be a method to improve bio-oils. They are often mentioned and effective to catalyze chemical reactions, to help extraction of specific chemical compounds [8]. Moreover, ultrasounds have positive effects on residual oil [9]. This heavy oil formed after fuel production is somewhat similar to pyrolysis bio-oils. Ultrasounds are acoustic waves inaudible to human ears at a frequency between 20 kHz and 1 MHz. They have the capacity to break molecular bonds or to degrade them with the aid of cavitation effects. Indeed, these create super-energetic micro bubbles under vacuum in liquid solution. This cavitation bubbles are growing following the oscillation frequency until their breaking point. During the implosion, large amounts of energy is released and a jet is created toward solid surfaces, which affects the treated sample. The frequency choice influences the type of cavitation bubble to favour mechanical effects or sonochemical effects. Around 20-60 kHz, transient bubbles are created, thus mechanical effects are promoted. Whereas, sonochemical effects are the result of higher frequencies (100-1000 kHz) and induced by more stable bubbles. They lead to the water sonolysis with creation of radicals H[•] and OH[•] [10]. In these study, the objective is to treat the bio-oils with mechanical effects (40 kHz) and sonochemical effects (170 kHz). However, bio-oils could not be inserted directly in an ultrasonic bath due to their corrosiveness. The idea is to insert oil in sealed plastic bag which allows to manage the treated quantity precisely. However, a plastic bag will create a physical border between the ultrasonic transducers and the bio-oils. To determine efficient amount of ultrasounds applied inside the bag, Weissler's method [11] is used to measure the sonochemical effects intensity. For mechanical effects, a simple commercial aluminum foil is irradiated and the mass decreased is measured. These two methods can be used to determine an absorbance coefficient of the plastic bag. Thus, objectives of this work are (1) to find the absorbance coefficient of plastic bags for mechanical and sonochemical effects, (2) to compare bio-oils characteristics before and after ultrasonic post-treatment and (3) to study the aging evolution of treated bio-oils after 15 and 30 days.

II. EXPERIMENTAL SECTION

A. Original bio-oil

The bio-oil used in this work was produced by canmetENERGY (Ottawa, Canada) with a fluidized bed fast pyrolysis process [12]. The feed stock was composed of 60 % softwoods and 40 % hardwoods. The bio-oil produced is a complex mixture formed of around 200 different molecules, which explains the difficulty into analyzing it.

B. Physico-Chemical characterization of the bio-oils

Characterization was done to determine the high heating value (HHV) and the composition of the bio-oils. Oxygen bomb calorimeter (Parr) was used for the first characterization (table I). Approximately 1 gram of bio-oil was collected and burned in the calorific bomb. For the second analysis, to determine bio-oils composition, an Agilent 7890B Gas Chromatograph with flame ionization detectors (GC-FID) was used. Agilent J&W DB-5.625 column was installed with a length of 30 m, an internal diameter of 0.25 mm and a film thickness of 0.25 μm . 1 μL of bio-oils were injected at each analysis with a split ratio of 50:1. The oven heats in steps at different rates of temperature: 3 $^{\circ}\text{C}/\text{min}$ from 40 to 130 $^{\circ}\text{C}$, 1 $^{\circ}\text{C}/\text{min}$ from 130 to 160 $^{\circ}\text{C}$ and 6 $^{\circ}\text{C}/\text{min}$ from 160 to 300 $^{\circ}\text{C}$. At the end of the run, the temperature was maintained at 300 $^{\circ}\text{C}$ during 6 min. A helium flow of 0.6 mL/min browse the column and was carrying the bio-oils components up to the FID detectors. It is difficult to determine the bio-oils composition because of the huge number of different molecules. That is why the classification was done by families and not by single components. Bio-oils composition was therefore classified in 5 families: lights, acids, alcohols, ketones and phenols (table I). To define family limits, the lightest component of each family was injected individually. These retention times was used to determine the separation between two families.

TABLE I: ORIGINAL BIO-OIL CHARACTERIZATION

HHV (kJ.g ⁻¹)	Gas Chromatography (%)				
	Lights	Acids	Alcohols	Ketones	Phenols
23.78	26.79	5.06	1.61	14.14	52.40

C. Ultrasonic bath and experimental conditions

To apply ultrasound to bio-oils, a 34 L ultrasonic bath, model BT90 made in 316L stainless steel (Ultrasonic Power Corporation) was used. Ultrasounds were diffused by 12 transducers installed on the bottom of the bath and generated by commercial frequency generator of 40 and 170 kHz (Ultrasonic Power Corporation). Nominal ultrasonic energy available is between 125 and 1000 W. During post-treatment, the bio-oils were placed in a plastic bag (ULINE, size: 21*30 cm, thickness: 0,09 mm) to protect ultrasonic bath and manage the quantity of bio-oils. The bag was immersed in 3 L of demineralized water and a weighted meshing kept the bag at the bottom of the bath. Water temperature was controlled with a heat exchanger placed in the bath. 100 g of bio-oils were introduced in the plastic bag for each treatment. Finally, the temperature was controlled at 25 or 45 \pm 1 $^{\circ}\text{C}$, for 30 or 90 min with an ultrasonic power of 500 or 1000 W. Ten different

post-treatments were performed on bio-oils (UST-1 to 10), as shown in table II. Characterization was done on each ultrasonic treatment (UST) and a sample without treatment (WT-0) was also characterized as reference.

TABLE II: ULTRASONIC POST-TREATMENT CONDITIONS

Sample	Frequency (kHz)	Time (min)	Temperature ($^{\circ}\text{C}$)	Power (W)
UST-1	40	90	45	1000
UST-2	170	30	25	500
UST-3	170	90	45	1000
UST-4	170	90	45	500
UST-5	170	30	45	1000
UST-6	40	90	25	1000
UST-7	40	30	25	500
UST-8	170	90	25	500
UST-9	40	30	25	1000
UST-10	40	30	45	500

D. Ultrasonic bath mechanical effect characterization with aluminum foil degradation

The presence of the plastic bag between ultrasonic transducers and the bio-oil acted like a border for different ultrasounds effects. Therefore it was necessary to determine an absorbance coefficient of this border for mechanical effects. When ultrasounds are applied to aluminum foil (size 20*29 cm, thickness: 0,01 mm), cavitation bubbles collapse at the foil surface and puncture it. The mass loss is related to the quantity and power of mechanical effects. Two tests were compared. The first without a bag where the aluminum foil was directly placed at the bottom of the bath and submerge with 3 L of demineralized water at 25 \pm 1 $^{\circ}\text{C}$ for different periods of time. The second test with the same conditions as the first, but the foil was placed in a sealed plastic bag filled with 100 mL of demineralized water to help ultrasound diffusion. To measure the bag absorbance coefficient, ratio between the two tests was calculated.

E. Ultrasonic bath sonochemical effect characterization with Weissler's method

To measure the sonochemical effects and their absorbance by plastic bags, Weissler's method was employed. This method consisted in applying ultrasounds on a solution of potassium iodide (KI) at 0.1 M. In presence of ultrasounds, I⁻ ions are oxidized in I₂. The reaction of I⁻ excess and I₂ gives I₃⁻ ions. The concentration of I₃⁻ is directly related to the quantity of sonochemical effect. UV-VIS spectrophotometer (λ = 355 nm, ϵ = 26303 L.mol⁻¹.cm⁻¹, l = 1 cm) is used to measure the solution absorbance. I₃⁻ absorbance and concentration are determined with Beer Lambert relation ($A = \epsilon \cdot l \cdot C$). As for the mechanical effect, two tests were compared, with and without a plastic bag. First, 3 L of KI solution were placed in the ultrasonic bath. The second one, consist in filling a sealed plastic bag with 100 g of KI solution and plunge it in 3 L of demineralized water in the bath. The ratio between the two tests have allowed to obtain sonochemical absorbance coefficients of the plastic bag.

III. RESULTS

A. Ultrasonic effect on aluminum foil

The sealed plastic bag affected the ultrasound diffusion and particularly mechanical effects. As shown on Fig. 1, at low frequencies (40 kHz), the mass loss is more important without a bag. This loss corresponds to an efficiency reduction of 84 %. Thus, mechanical effects are stopped partly by the plastic border. Likewise, for higher frequencies (170 kHz), the presence of the bag reduces, moderately, the post-treatment efficiency is subject to 34 % reduction. In accordance with the literature, as shows in Fig. 1, mechanical effects are more important at low frequencies. That can explain the difference of bags absorption ratios at the two frequencies.

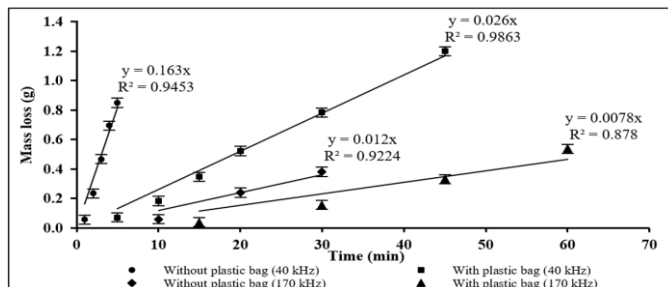


Fig. 1. Mass loss of aluminum foil exposed to ultrasound with and without plastic bags at 40 kHz and 170 kHz

B. Potassium iodide dosimetry

As shows in the previous section, the sealed plastic bag reduces the mechanical effects during the ultrasonic treatment. However, the opposite observation is made for sonochemical effects (Fig. 2). First of all, these effects are lower at 40 kHz than 170 kHz. This can partly explain why the results are in contradiction to common knowledge would suggest. Indeed, sonochemical effects are amplified inside the bag at 40 kHz. Our hypothesis is that additional cavitation bubbles implosions happened at the plastic bag surface.

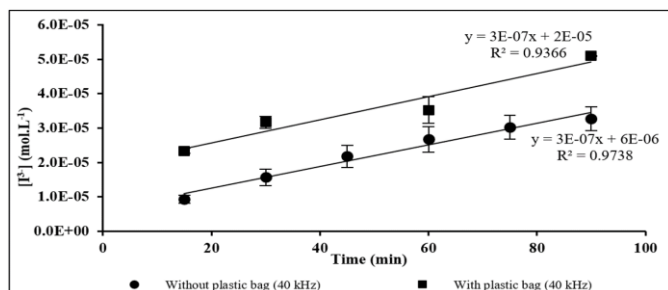


Fig. 2. Evolution of potassium iodide formed during ultrasound exposure, with and without plastic bags at 40 kHz

At 170 kHz, the observation is the same for the first hour of experiments but after that the concentration is higher without plastic bags (Fig. 3). The differences of slopes can be explained by the same hypothesis for 40 kHz. For a short period of time (under 1 h), ultrasonic waves diffusion is lower but more bubble implosions are produced leading to a higher concentration of I_3^- ions in the bag. After 1 h, the additional implosion sites are no longer compensating the diffusion. These results as allowed us to quantify the ultrasound intensity transmitted inside plastic bags. This information is fundamental before the ultrasonic treatment of bio-oils. Finally,

plastic bags significantly affect mechanical effects, especially at low frequency

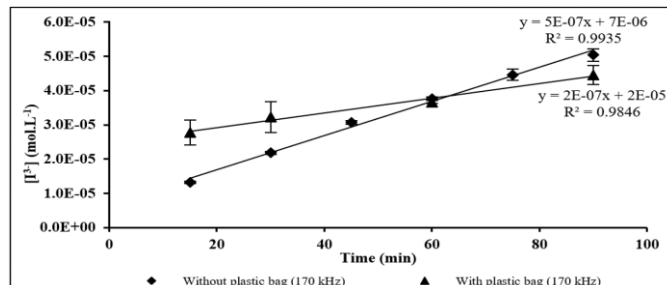


Fig. 3. Evolution of potassium iodide formed during ultrasound exposure, with and without plastic bags at 170 kHz

C. Direct effects of ultrasound on the bio-oil

All results of bio-oil evolutions, just after the ultrasonic treatment, are shown in Table III. To analyze the direct ultrasounds impact, the percentage of change of the High Heat Values (HHV) and the bio-oil composition is calculated between the native bio-oils (Table I) and the treated one.

TABLE III. PERCENTAGE EVOLUTION OF HIGH HEAT VALUE AND FAMILIES

Sample	HHV (%)	Gaz Chromatography (%)				
		Lights	Acids	Alcools	Ketones	Phenols
UST-1	-11.6	-9.8	+56.5	+59.6	+56.2	-19.4
UST-2	-7.5	-21.3	+30.6	+26.7	+17.7	+2.4
UST-3	-6.3	-27.9	+5.5	+8.7	+1.6	+11.1
UST-4	-8.8	-22.4	+29.1	+20.5	+21.9	+2.1
UST-5	-6.7	-10.8	+23.5	+24.8	+32.0	-6.2
UST-6	-7.4	-41.3	+17.8	+4.4	+17.4	+14.5
UST-7	-10.0	-11.1	+39.1	+25.5	+44.7	-11.2
UST-8	-5.1	-30.4	+7.1	+12.4	+10.8	+11.6
UST-9	-8.6	-24.9	+32.2	+26.7	+21.3	+3.0
UST-10	-7.0	-23.3	+27.5	+23.6	17.7	+3.8

Without any treatment (WT-0), the HHV is 23,78 kJ.g⁻¹ but immediately after each ultrasonic treatment this value drop. A decrease from 5 to 11.5 % shows a negative effect of ultrasonic treatment on bio-oils HHV. The ultrasound mechanical effect seems to be the worst. Indeed, an average decrease of 8.9 % was calculated for experiments at 40 kHz while 6.8 % average reduction was observed at 170 kHz. The most energetic molecules forming the bio-oils are degraded. These observations can be related to gas chromatography results. The quantity of lights decreased for each experiment. These lights molecules are needed to maintain the HHV but they are probably fractionated in lighter components, evaporable or reactive with other molecules. For acids, alcohols, and ketones families, an increase is probably found due to the reaction of molecules of treated bio-oils. The phenol part is quite different. Depending on the experiment, phenol amount varied but none of the ultrasonic treatment parameters could be clearly related to this effect. However, the phenol evolution can impact the HHV. Indeed, a significant drop of phenols and HHV have been observed for trials UST-1 and 7. So, there is also a relation between the amount of phenol and the HHV.

D. Chemical evolution of the bio-oils in the time

During aging, the bio-oil composition and HHV evolved. The results are grouped in Fig. 4 and Fig. 5. For each treatment, three different aging times were performed: T1 directly after the ultrasonic treatment, T15 after 15 days and

T30 after 30 days. Bio-oils are stocked in sealed vials placed in a cold room at 4 °C. As shown in Fig. 4, the HHV of bio-oils can change in different ways. First, the biggest drop is observed for the bio-oils without treatment (WT-0). After 30 days the HHV goes from 23,78 kJ.g⁻¹ to 21,68 kJ.g⁻¹, which represents over 8 % decrease. At 40 kHz, all bio-oils HHV declined. So, using ultrasounds at this frequency doesn't completely stabilize the bio-oil but it can strongly limit the HHV drop. At a higher frequency (170 kHz), the observations are different. According to the treatment of conditions, it is possible to observe an increase in the bio-oil HHV with time. Molecules formed during the post-treatment may continue to react to produce higher energetic molecules. These results show the effect of the treatment which stabilizes the bio-oil. However, it was not possible, for now, to correlate the bio-oil stabilization with parameters (time, temperature and power).

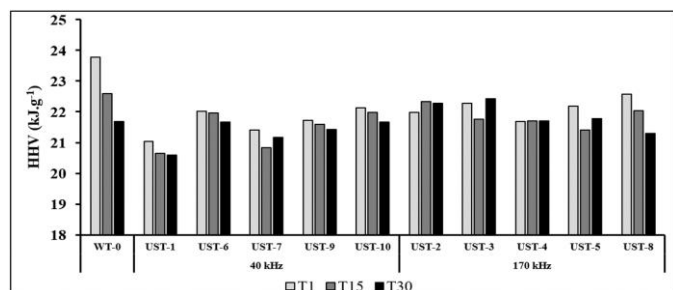


Fig. 4. HHV evolution of bio-oils in the time for all ultrasonic treatments

Ultrasounds changed the bio-oils composition and impact its evolution with time (Fig. 5). To simplify the results, bio-oil composition without treatment (WT-0) is compared to the average of bio-oils treated at 40 kHz and those treated at 170 kHz. Without ultrasonic treatment, the percent of light compounds decrease because of the aging reaction and repolymerization [5, 13, 14]. In the opposite, the amount of light increases in time after ultrasonic treatments. This increase is faster at 40 kHz than 170 kHz. According to the previous results and these observations, we can assume that ultrasonic treatments preserve the stabilized lights in bio-oils. For the acids, alcohols and ketones families the evolution is minimal, but it's slowed by the treatments. Which shows a stabilizing effect of ultrasounds. Finally, the percent of phenols decrease with or without treatment. Ultrasounds has not allowed stabilization of the phenol decomposition. It's difficult to create a correlation between HHV and bio-oil composition due to the complexity of molecules. But lights and phenols are the main families that evolve in time. Therefore, bio-oils HHV modification may be related to these two families.

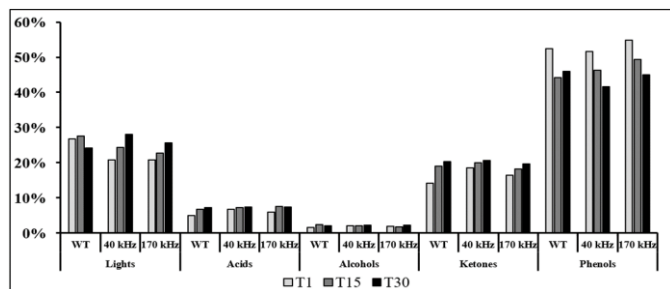


Fig. 5. Untreated bio-oil composition evolution in time compared to the average of bio-oils treated at 40 kHz and at 170 kHz

IV. CONCLUSION

Bio-oils are low-value products due to its very complex mixture, composed of around 200 different molecules, which also make characterization difficult. This paper proposed a new manner to treat the bio-oil with ultrasound. The use of a plastic bag created challenges. The efficiency of mechanical effects are respectively reduced by 84 % and 34 % for treatment at 40 and 170 kHz. The sonochemical effects are amplified inside the bag for the two frequencies due to the increase of implosion sites. The ultrasound modified the bio-oils HHV and composition as well as the aging evolution. Best stabilization is observed with the ultrasound at high frequency.

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