



Thermal decomposition of bio-oil: Focus on the products yields under different pyrolysis conditions

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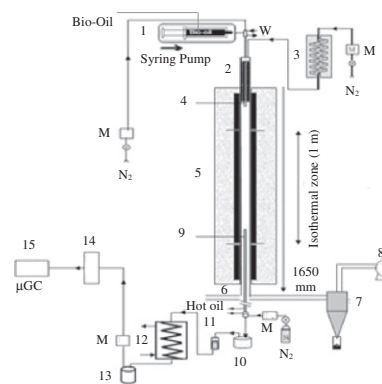
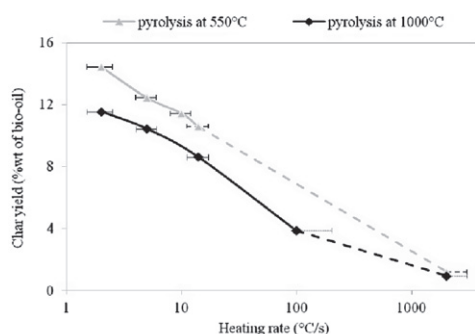
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HIGHLIGHTS

- ▶ Pyrolysis of wood bio-oil in various operating conditions is studied.
- ▶ At very high heating rate, the quantity of formed char is very small.
- ▶ At very high heating rate the char yield depends less on the final temperature.
- ▶ Ash seems to favor repolymerization reactions that lead to an increase in char yield.

GRAPHICAL ABSTRACT



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ABSTRACT

In this study, pyrolysis process of wood bio-oil was studied. The effects of temperature in the range 550–1000 °C, heating rate in the range 2–2000 °C s^{−1} and ash content of the bio-oil on char, tar and gas yields were investigated. The main gas species generated are quantified by Micro-GC: H₂, CO, CO₂, CH₄ and trace amounts of C₂H₄ and C₂H₆.

A temperature increase from 550 to 1000 °C enhanced greatly the gas yield, whilst solid and liquid yields decreased significantly. The heating rate was varied in a range covering rapid pyrolysis using the Horizontal Tubular Reactor (HTR) to flash pyrolysis using an Entrained Flow Reactor (EFR). A decrease of char yield from 11 wt.% down to 4 wt.% was observed when heating rate is changed from 2 to 100 °C s^{−1}. In EFR a flash heating rate of 2000 °C s^{−1} led to a char yield as low as 1 wt.%.

Bio-oil with a natural ash contents of 0.05 wt.% and bio-oil added with 3 wt.% of ash were finally pyrolyzed. Ash seems to favor re-polymerization reactions that lead to an increase in char yield. A decrease in the amount of gas is observed when ash is added while an increase was a priori expected.

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1. Introduction

Among the different thermochemical processes for converting lignocellulosic biomass into energy, fast pyrolysis has gained particular attention for the last years as a process for preconditioning

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of biomass into high yields of bio-oils, as liquid intermediate bio-fuel before its transport to a larger energy production unit. Fast pyrolysis is operated under inert atmosphere, high heating rates, moderate temperature, short vapour residence times and rapid quenching of the pyrolysis vapours. The main advantage of bio-oils is due to their unique and specific properties. Bio-oil has much higher energy volume density than that of solid biomass. This is particularly promising due to the high geographic dispersion of biomass which generally leads to high transportation costs:

bio-oils can easily be stored and transported from scattered gathering stations to a large-scale processing plant. Bio-oil has a wide range of potential industrial uses [1]: combustion for heat and power (boilers, engines or gas turbines), syngas or hydrogen production via gasification/steam reforming process in high-temperature entrained flow reactors, co-refining after upgrading. Moreover, the specific composition of bio-oils (hundreds of organic compounds issued from the depolymerization of cellulose, lignin and hemicelluloses) widens opportunities for the co-production of chemicals (anhydro-sugars like levoglucosan, resins, liquid smoke, wood preservative, etc.).

In the high temperature applications such as gasification, steam reforming or even combustion, the very first step of fuel thermal decomposition is under pyrolysis conditions. It is of particular interest to understand the behaviour of bio-oils in these conditions. However, only few works have been dedicated to this “secondary” pyrolysis process oil conversion under various operating conditions.

The earliest combustion tests of bio-oil droplets were conducted in Sandia National Laboratory [2,3]. In-situ video imaging revealed that biomass oil droplets undergo several distinct stages of combustion. Initially biomass oil droplets burn quiescently in a blue flame, then rapid droplet swelling and distortion, followed by a microexplosion. The same observations were found by Calabria et al. [4].

Thermogravimetric analysis (TGA) is widely used in the literature to characterize the different mechanisms occurring during combustion of bio-oils. Although this methodology is limited to rather low heating rates, these studies concluded that the bio-oil weight loss process in inert atmospheres can be divided into two stages: the evaporation of light volatiles (<150–200 °C) and the subsequent thermal decomposition of unstable heavier components (<350–400 °C). In the presence of air, the weight loss of bio-oils comprises an additional step, corresponding to the combustion of chars formed in the first two stages (>400 °C) [5,6].

Bio-oil evaporation was investigated by Branca et al. [7–9]. They studied separately the devolatilization of several wood bio-oils and the heterogeneous combustion of the resulting secondary char, using an original thermogravimetric system operating. From the weight losses obtained in air with a heating rate of 0.08 °C s^{-1} to final temperature of 600 K, the authors concluded that the bio-oil sample modification and the secondary char formation start at temperatures of about 460–490 K. The yield of secondary char varies from about 25–39% (on a total oil basis). Moreover, a conceptual reaction mechanism, consisting of six main zones was suggested to explain these low-temperature (600 K) devolatilization characteristics [10].

Hallet and Clark [11] established a numerical model for the evaporation and pyrolysis of a single droplet of bio-oil derived

from biomass. The model is compared with the results of suspended droplet experiments, and is shown to give good predictions of the times of the major events in the lifetime of a droplet: initial heating, evaporation of volatile species, and pyrolysis of pyrolytic lignin to char.

van Rossum et al. [12] studied the evaporation of bio-oil and product distribution at varying heating rates ($\sim 1.5\text{--}1.5.104\text{ °C s}^{-1}$) with surrounding temperatures up to 850 °C. A total product distribution (gas, vapor, and char) was measured using two atomizers with different droplet sizes. A big difference is seen in char production, they found that small droplets (undergoing high heating rate) are much quicker evaporated and give much less char compared to larger droplets (undergoing low heating rate).

From this short review, it appears that the decomposition of bio-oil occurring under pyrolysis (inert) conditions is a complex process involving vaporization and thermal cracking reactions with formation of gas, tars and char.

The present work aims to better understand this step, to bridge the lack of knowledge concerning the physicochemical transformation of bio-oil and to investigate the effect of various operating conditions on the pyrolysis products yield. In particular, it will focus on the influence of the heating rate and the final pyrolysis temperature on the product distribution. For this aim, two complementary devices were used to study on the one hand a wide range of heating rates, in the range from 2 to 2000 °C s^{-1} and on the other hand final temperature ranging from 550 to 1000 °C. Finally ash is known for its catalytic effect during thermo-chemical conversion of biomass as approved the works done on solid biomass. In the present work the influence of ash on the bio-oil pyrolysis process has also been evaluated.

2. Materials and methods

2.1. Description of the laboratory device and of the procedure

Two complementary devices, namely: a Horizontal Tubular Reactor (HTR) and a High Temperature – Entrained Flow Reactor (HT-EFR), were used to study a wide range of heating rates, in the range from 2 to 2000 °C s^{-1} and final temperature from 550 to 1000 °C.

2.1.1. Horizontal tubular reactor HTR

The experiments of fast pyrolysis were carried out in a HTR (Fig. 1). This device allowed carrying out experiments in conditions of fast pyrolysis which is not possible in a thermobalance. The reactor consisted of a double-walled quartz pipe. The length and inside diameters were 850 mm and 55 mm respectively for the inner tube, and 1290 mm and 70 mm respectively for the outer tube. The reactor temperature can reach 1100 °C.

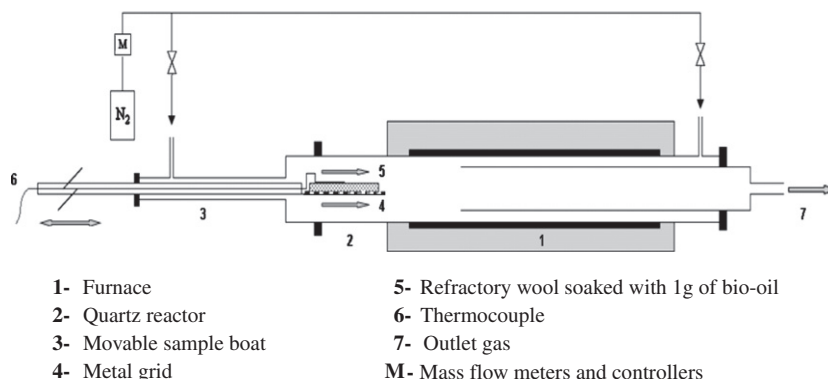


Fig. 1. Horizontal Tubular Reactor (HTR) ready for sample introduction.

The procedure carried out for an experiment was the following. First, the furnace was heated and the gas flowrate (nitrogen) was adjusted using a mass flow meter controller. When the temperature was stabilized, the sample was placed on the metal grid at the unheated section of the reactor. This section was swept by half of the total cold nitrogen flow injected, in order to maintain it cold and under inert atmosphere, and therefore avoid its degradation. Meanwhile the second half of the nitrogen flow was preheated through the double-walled annular section of the reactor as shown in Fig. 1. The sample consisted in 1 g of bio-oil was placed inside a crucible of 25 mm diameter and 40 mm height for studying the effect of temperature and of ash content. In order to achieve higher heating rates, some runs were performed with 1 g of bio-oil previously soaked in a refractory wool sample of 100×20 mm length and width and 3 mm thickness. The choice of this sample holder allowed increasing the exchange surface and subsequently obtaining larger heating rates. We proved that this wool has no catalytic effect on bio-oil pyrolysis. Indeed, previous bio-oil pyrolysis experiments were carried out first with a single crucible, and secondly in the refractory wool deposited in the crucible. The wool didn't induce any change on the products yield.

The reactor outlet was first connected to an O₂ gas analyser to ensure that there is no oxygen in the reactor. Afterwards, a manual insertion enabled to move the sample in the furnace at different velocities, ranging between 0.06 cm s^{-1} and 30 cm s^{-1} . The sample temperature evolution was measured using a thermocouple placed in the middle of the sample in order to determine a heating rate for each experiment. Variation of the heating rate was obtained by varying the sample introduction through the tubular reactor. Four different durations have been used: 16, 8, 4 and finally 0.03 min resulting in four different heating rates. The sample then remained in the middle of the reactor for a definite time and is brought back out of the furnace; the solid residue was weighed after cooling. Even after several experiments, no char deposit was observed inside the reactor. Only tar deposits were observed in the cold outlet of the reactor. The reactor outlet was connected to a sampling bag at $t = 0$ just before sample introduction. The gases formed by pyrolysis were collected in the bag. The duration of all experiments was 10 min with a 2 NL/min N₂ flowrate which enabled to know accurately the volume of N₂ sampled in the bag. In HTR reactor, the volume of formed gas never exceeded 1% of the volume of N₂ sampled in the bag. After the experiment the bag was disconnected from

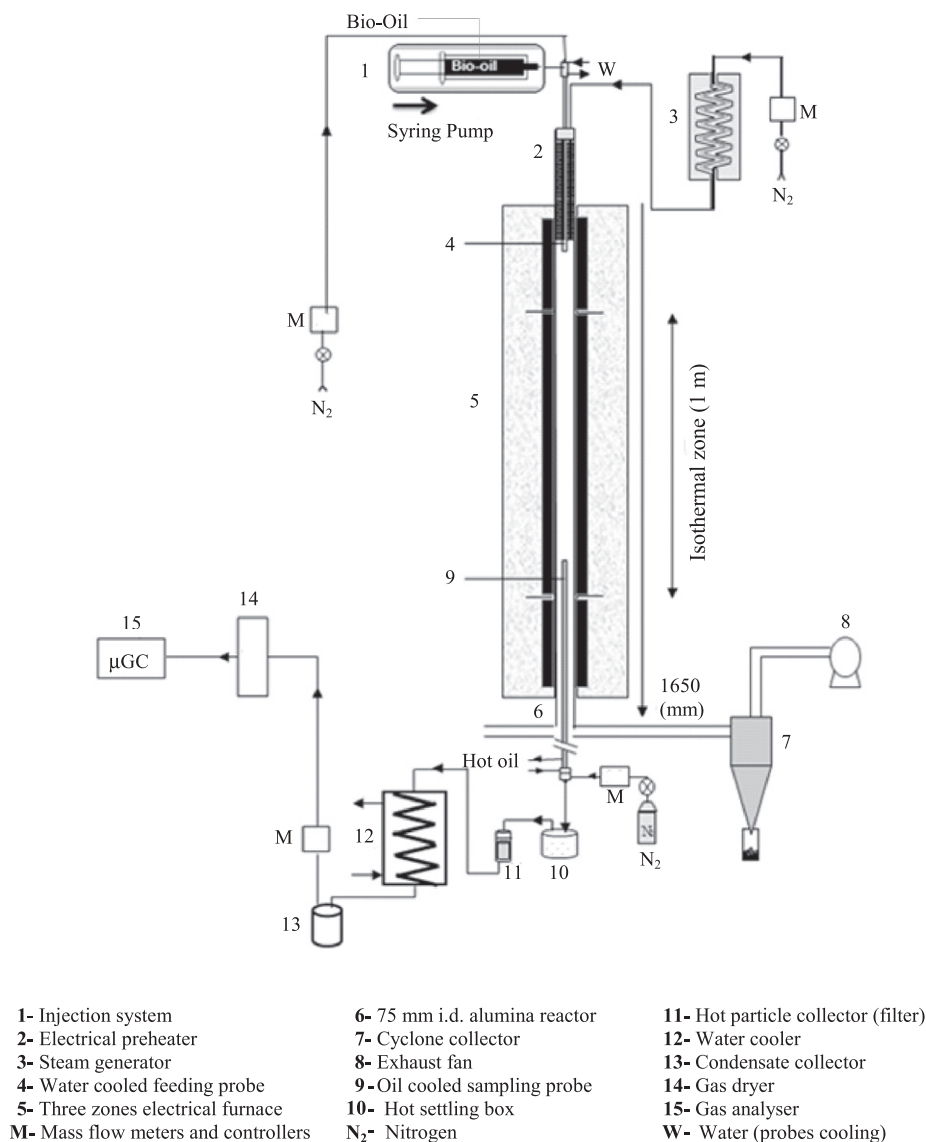


Fig. 2. Entrained Flow Reactor (EFR).

HTR, and connected to the micro-chromatograph analyser (μGC). From the total volume of gas in the bag and measure of the gas concentration, the quantity of each gas formed by 1 g of bio-oil can be precisely calculated.

2.1.2. Entrained flow reactor EFR

To increase heating rate and reach flash pyrolysis conditions, a few additional experiments were carried out in a laboratory scale EFR. It consisted in a vertical tubular reactor electrically heated by a total of 18 kW three-zones electrical furnace, and was able to reach 1600 °C in a 1 m long isothermal reaction zone, as illustrated in Fig. 2. The atmosphere gas was generated by feeding the controlled flows of nitrogen in a 2 kW electrical steam generator. This atmosphere gas was then preheated using a 2.5 kW electrical battery of heating elements before reaching the isothermal reaction zone. EFR was equipped with a specially designed bio-oil spraying feeder, with the aim to obtain a very constant mass flowrate spray [13]. The feeder consisted of a 1 m long and 14 mm o.d. probe cooled with water at 30 °C. At its extremity a stainless steel nozzle was integrated, which allowed uniform distribution with fine atomisation. The microscopic observation of droplets impacted on a surface indicates a size ranging between 20 μm and 400 μm . However, the majority of the droplets were much smaller and not measurable.

The oil was fed with a syringe which is pushed automatically. The expected mass flowrate of 0.3 g min⁻¹ was too low for direct spraying. Therefore, a 3.5 NL min⁻¹ N₂ flowrate was used to entrain oil in the feeding probe and to ensure a thin spray of the oil. The spray of droplets was dispersed on the section of a 75 mm i.d. alumina reactor swept by 15 NL min⁻¹ of N₂ atmosphere. At 1760 mm downstream of the injection point, gases and solid residue were sampled by a hot-oil cooled probe. The sampling flowrate is measured accurately using a mass flow meter. The total gas flowrate at the exit of the reactor is calculated based upon the N₂ flowrate fed to the reactor and upon the produced gas species concentrations that are measured. A mass balance was used to calculate the total flowrate for each gas species. Gas and solid residue were separated using a settling box and a filter, both heated to avoid water condensation. The water and potential remaining tars were first condensed in a heat exchanger, and non-condensable gases were forwarded to a micro-chromatograph analyser (μGC) to quantify H₂, CO, CO₂, CH₄, C₂H₂, C₂H₄, C₂H₆, C₃H₈ and C₆H₆.

2.2. Feedstock

The feedstock used for all experiments was a bio-oil produced by fast pyrolysis of softwood on an industrial-scale fluidized bed unit (Dynamotive, West Lorne, Ontario) and provided by CIRAD, France. Its physico-chemical properties have been measured (see Table 1). The water content of the bio-oil measured by Karl Fischer method (ASTM E203) is around 26 wt.% which is in agreement with the average values reported in the literature. It can be noticed that the solid particles content is rather high (2.3 wt.%) while the ash content remains low (around 0.06 wt.%). This confirms that the solid particles mainly consist of high-carbon content char particles. These particles were entrained during bio-oil production by the gas stream to the bio-oils condensers. Ultimate analysis and LHV of the bio-oil are very similar to those of wood. From the ultimate

analysis, the chemical formula of the bio-oil can be established as CH_{1.18}O_{0.48}0.4 H₂O.

After the production, the bio-oil was stored at 5 °C in a fridge. Before experiments, it was filtered on a 30 μm sieve to eliminate larger solid particles which represented less than 0.01 %wt of the oil.

2.3. Method for char/gas/tar yields measurement and interpretation

The yields of char/gas/tar products are interpreted in the following manner. At first, the water contained by bio-oil vaporizes together with light volatile matters. As the temperature of bio-oil continues to increase, pyrolysis occurs, leading to the release of so-called primary volatile matters and to the formation of char. Primary volatile matters may undergo a complex series of cracking reactions giving rise to non-condensable gases as well as secondary and eventually tertiary volatile matters and re-polymerization inside the sample which leading to formation of solid carbon.

At high furnace temperature (above 1000 °C), the gas species can also undergo reforming reactions, as steam is present in the gas, leading to much more non-condensable gases (including H₂) generated. The progress of the cracking and reforming reactions is influenced by the temperature of the gas phase, and the vapor residence time which was estimated to several seconds both in the HTR and in the EFR as detailed further.

Finally the collected products are:

- the solid residue, or char;
- permanent gases. The major gas species classically identified during pyrolysis are H₂, CO, CO₂, C₂H₂, C₂H₄;
- tars: the condensable volatile organic compounds;
- water which is originating both from the water initially present in bio-oil and from the pyrolysis reaction.

Thereafter the term “condensate” stands for the mix of tars and water. No condensation system is set up. Therefore, the condensate yield is calculated as the complement to 100 wt.% of the yields in gas and solid residue.

3. Results and discussions

3.1. Preliminary runs of bio-oil pyrolysis at two final reactor temperature

Two reactor temperatures were tested in order to evaluate the effect of the final pyrolysis temperature on devolatilization process affecting the yield of gas, condensate and residual solid:

- Moderate temperatures at 550 °C;
- High temperature 1000 °C to approach the severe conditions of gasification.

The yields of final products are listed in Fig. 3. With temperature increasing from 550 to 1000 °C, the total gas yield increased sharply from 12.2 to 43.0 wt.%, while condensate (tar + water) decreased from 73.2 to 47.5 wt.%. Meanwhile, varying temperature shows a great influence on the gas composition. Fig. 4 shows that the main gas products are H₂, CO and CO₂, CH₄ and some C₂ hydro-

Table 1
Ultimate analysis and several characteristics of bio-oil derived from hardwood fast pyrolysis.

Ultimate analysis (wt.%)				H ₂ O	Ash	Solids	LHV	Kinematic viscosity
C	H	O	N	(wt.%)	(wt.%)	(wt.%)	(MJ kg ⁻¹)	at 20 °C (mm ² s ⁻¹)
42.9	7.1	50.58	<0.10	26.0	0.057	2.34	14.5	103

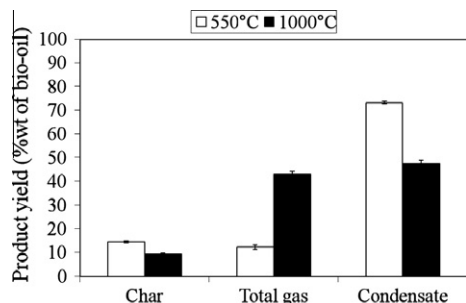


Fig. 3. Product yield of bio-oil pyrolysis in HTR – effect of temperature.

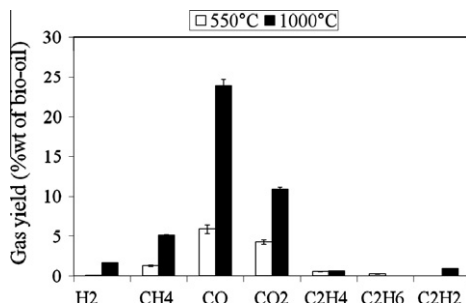


Fig. 4. Gas yield of bio-oil pyrolysis in HTR – effect of temperature.

carbons (C_2H_2 , C_2H_4 and C_2H_6). Among them, the H_2 and CO content increased significantly from 0.056 to 1.65 wt.% and from 5.9 to 23.9 wt.% respectively as temperature increased from 550 to 1000 °C. Yields of CH_4 also increased from 1.2 to 5.0 wt.% whilst that of CO_2 increased from 4.2 to 10.8 wt.%. The yields of C_2H_2 ,

Table 2

Composition of ashes (from combustion of wood) [wt.%, dry ashes].

Ca	K	Mn	Mg	P	Ni	Na	Al
11.67	3.80	1.74	1.54	1.01	0.25	0.24	0.10

C_2H_4 and C_2H_6 are relatively small. The specie C_2H_6 appears only at 550 °C while C_2H_2 appears only at 1000 °C. The thermal cracking of gas-phase hydrocarbons at high temperature might explain the variation of gas product composition observed.

Finally, with increasing temperature from 550 to 1000 °C, the char yield decreased significantly from 14.5 to 9.4 wt.%. However changing the reactor temperature implies a change of both the heat flux density imposed to bio-oil (and hence its heating rate) but also the final temperature reached by the char produced. Therefore the later trend observed might be due to two reasons:

- the char formed at 550 °C contains residual volatile matters which are released when the temperature increases to 1000 °C;
- increasing the heating rate results in the decrease of the char yield. This is actually in good agreement with what is usually observed in the literature from pyrolysis of biomass [14–16].

To check the first assumption, a char first prepared at 550 °C was submitted to a second heating step at 1000 °C. During this second step at 1000 °C, the mass of char did not change, which excluded the first assumption, and highlighted actually the effect of heating rate. In order to confirm this trend, additional experiments were carried out separating the effect of these two parameters. This is studied in details in the following section.

3.2. Effect of heating rate and final temperature on the product yields

The temperature profiles obtained in the HTR are illustrated in Fig. 5. A calculation of the highest heating rate is then made taking into account only the linear part of curves. Details of the calculated heating rates and products yields obtained from experiments are given in Table 3. The temperature profiles curves show that the heating rate ranges from 2 to 14 °C s^{−1} at the final pyrolysis temperature of 550 °C, and from 2 to 100 °C s^{−1} at the final pyrolysis temperature of 1000 °C. The response time of temperature measurement system was characterized by introducing the thermocouple alone and the thermocouple placed in the refractory wool without bio-oil sample introduced together inside the reactor in 0.03 min. The results are also plotted in Fig. 5. At 1000 °C we can notice that the response of the thermocouple and refractory wool does not exceed 100 °C s^{−1}. This means that the actual heating rate for the sample introduced in 0.03 min may be still higher than 100 °C s^{−1}. This is further illustrated on Fig. 6.

In order to highlight the effect of heating rate and final temperature on the yields of char, they were plotted in Fig. 6 with the heating rate as the x scale, using a log scale. The low heating rate experiments, gave higher yields of char. Char yield then decreased significantly: from 14.4 wt.% down to 10.5 wt.% when heating rate increased from 2 to 14 °C s^{−1} at the final temperature of 550 °C, and from 11.5 to 3.8 wt.% when heating rate was increased from 2 to 100 °C s^{−1} at the final temperature of 1000 °C.

In order to increase still the heating rate and reach the flash pyrolysis conditions, we have performed additional experiments in the EFR. This process allows achieving very high heating rate. Indeed it is shown that when a particle or droplet is transported by a cold spraying gas, its heating rate is controlled by mixing of the cold gas with the hot gas in the reactor. CFD modeling was used and derived this order of magnitude. Heating rate estimated at 2000 °C s^{−1} [17]. In these conditions, the char yield measured is

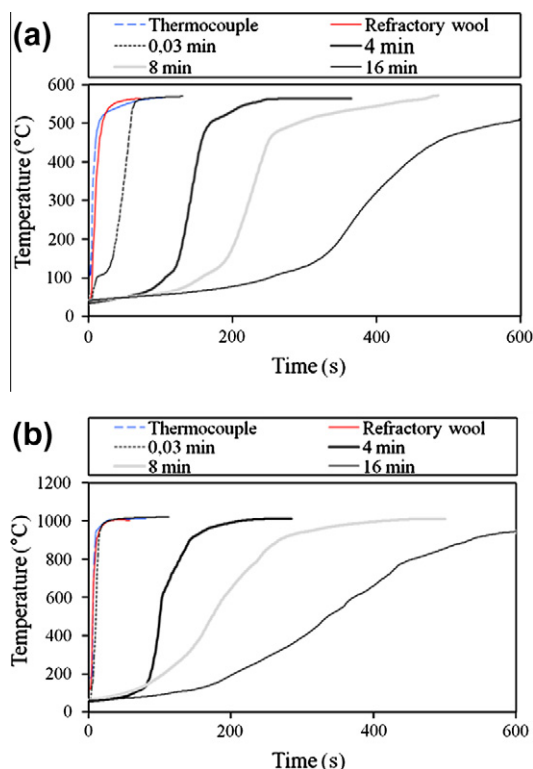
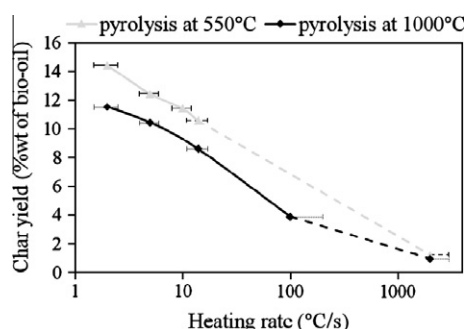
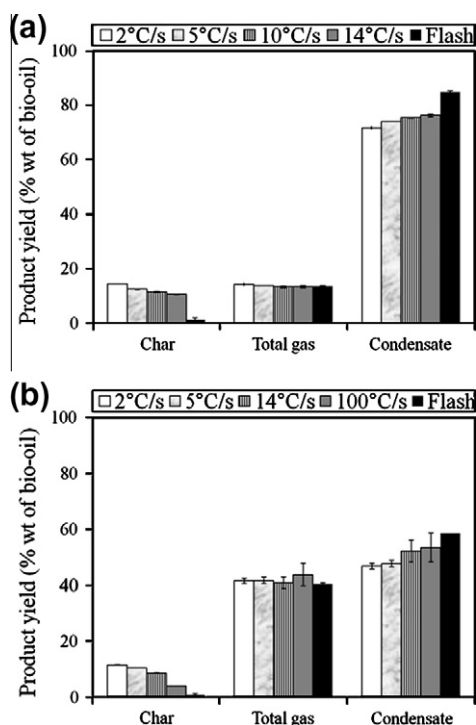


Fig. 5. Temperature evolution of the sample during bio-oil pyrolysis in HTR at different heating rates and two final temperatures. (a) 550 °C, (b) 1000 °C.

Table 3

Product yield of bio-oil pyrolysis at different temperatures and heating rates.

	t (min) ^a	Heating rate (°C s ⁻¹)	Solid (wt.%)	Total gas (wt.%)	Condensate (wt.%)
Pyrolysis at 550 °C	16	2	14.4	14.1	71.4
	8	5	12.4	13.7	73.8
	4	10	11.4	13.3	75.2
	0.03	14	10.5	13.3	76.0
	Flash	>2000	1.2	13.6	85.1
Pyrolysis at 1000 °C	16	2	11.5	41.6	46.8
	8	5	10.4	41.7	47.8
	4	14	8.6	40.9	52.2
	0.03	100	3.8	43.8	53.4
	Flash	>2000	0.9	40.3	58.7

^a Duration of sample introduction in the reactor.**Fig. 6.** Char yield obtained from pyrolysis of bio-oil at two final temperatures: 550 °C and 1000 °C – effect of heating rate.**Fig. 7.** Product yield obtained from bio-oil pyrolysis at two final temperatures. (a) 550 °C, (b) 1000 °C – effect of heating rate.

very low: <1 wt.%. As can be seen in Fig. 6 the char yield obtained with EFR is in rather good agreement with the values obtained in HTR and extrapolated to high heating rates. This result is in agreement with the work carried out by van Rossum et al. [12]. They found that small droplets (undergoing high heating rate) are much

quicker evaporated and give much less char compared to larger droplets (undergoing low heating rate).

Globally from all the data collected, the char yield depends very much on the heating rate, and less on the final temperature, confirming the observation from section 3–1. These results give important information for understanding the pathways occurring during gasification of bio-oil in reactors such as EFR: the amount of char formed by pyrolysis and submitted to subsequent steam-gasification reactions will be very low whereas the main reactions will occur in the gas phase (reforming, partial oxidation, etc.). Considering that solid gasification is rate-limiting, this might be an advantage of using bio-oil instead of biomass as feedstock for EFR gasification.

Fig. 7 shows the effect of heating rate on the product yields at two final pyrolysis temperatures. There is no apparent impact of the heating rate but a drastic influence of the temperature on the total gas yield which remains at about 13–14 wt.% and 40–43 wt.% at 550 °C and 1000 °C, respectively.

On the other hand, we can notice that the total condensate yield increased when the heating rate increased and when the final temperature decreased. A maximum value of 76 wt.% is obtained at 14 °C s⁻¹ and a final temperature of 550 °C, which is about 5 wt.% higher than that obtained at 2 °C s⁻¹. In the same manner, at 1000 °C the total condensate yield increased with the heating rate, up to 53.4 wt.% at 100 °C s⁻¹. This value was about 6 wt.% higher than that of 2 °C s⁻¹.

All these trends can be summarized and explained as follows.

Pyrolysis inside the sample: The volatile matters yield increases with the heating rate of bio-oil, to the detriment of the char yield as reported earlier. The primary volatiles may undergo secondary reactions through two competitive pathways [18,19]:

- re-polymerizing to form char;
- cracking to form lighter volatiles which implies less tar re-polymerization.

The re-polymerization pathway is probably favored by lower heating rates. Indeed, low heating rates lead to longer volatiles residence times inside the sample, and favor secondary reactions of re-polymerization to form solid residue. These conditions are known to favor the formation of secondary char from biomass pyrolysis experiments [18] and apparently, this could be extended to the case of bio-oil pyrolysis.

Gas phase reactions outside the sample: Once the volatiles have escaped from the sample, they can undergo additional secondary gas-phase cracking reactions as previously presented. The conversion rate of this reaction highly increases with the gas temperature, leading to higher gas yields to the detriment of condensates. This result is in agreement with number of pyrolysis works carried out on biomass [19].

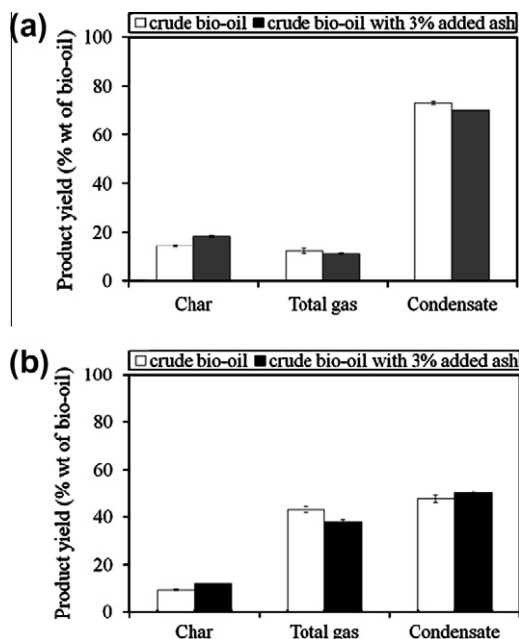


Fig. 8. Product yield of bio-oil pyrolysis at two final temperatures. (a) 550 °C, (b) 1000 °C – effect of ash content.

Let us notice that due to the procedure described, higher heating rate leads to lower residence time of tars in the hot zone because the bio-oil sample is introduced more rapidly to the centre of the heated zone. The estimate of the gas residence time in the HTR was calculated, from their release at the sample position (which varies with time according to the duration of sample introduction) to the exit of the reactor. It varies from 8 to 16 s at 550 °C and from 5 to 10 s at 1000 °C.

3.3. Effect of ash content

Crude bio-oil containing 0.05 wt.% of minerals and crude bio-oil with 3 wt.% of added ash were pyrolysed to highlight effect of minerals on pyrolysis process. The added ash are prepared by burning crushed beech wood (particle size of 300–400 μm) in a furnace equipped with 3 drawers at 600 °C. The choice of this temperature is designed to perform a “mild” heat treatment in order to preserve the properties of minerals present in biomass and keep the same properties as in the case of the production of bio-oil by pyrolysis of wood. The wood is distributed in the drawers on a thin layer of 1.5 cm thickness to ensure good heat transfer and air diffusion. Air was fed to the reactor at low flow rate, 30 NL h^{-1} , to avoid ignition and high temperature rapid combustion of wood. The analysis of the elements most cited in literature was performed on the ashes resulting from this combustion, by ICP-OES (Inductively Coupled Plasma optical emission spectrometry). The results of the main elements are presented in Table 2. Logically for biomass ash Ca, K, Mg and Mn are present in high concentrations. Products yields obtained in experiments are listed in Fig. 8. The results are expressed as a percentage of products on an added ash free basis. At 550 °C, we can notice that when the amount of ash is increased in bio-oil, the char yield increased significantly from 14.5 to 18.5 wt.% and both gas and tar yields reduced. The total gas yield decreased from 12.2 to 11.1 wt.% and tar decreased from 73.3 to 70.4 wt.% as can be seen in Fig. 8a.

Meanwhile, increasing the amount of ash in bio-oil shows a great influence on gas product components as indicated in Fig. 9. Among them, CO_2 content increased from 4.2 to 5.2 wt. while wt.% CO content decreased significantly, from 5.9 to 4.0 wt.%. Also

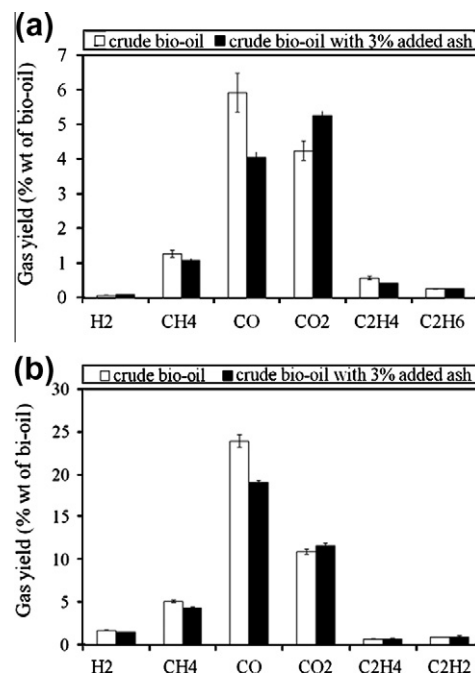


Fig. 9. Gas yield of bio-oil pyrolysis at two final temperatures. (a) 550 °C, (b) 1000 °C – effect of ash content.

a slight decrease of other gases is observed in particular CH₄ and C₂H₄. These phenomena can probably be explained by the catalytic effect of ash, which can favor polymerization reactions. These reactions lead to the formation of larger quantity of solid residue and result in decrease of the amount of gas. The same conclusions are also valid for the case of pyrolysis at 1000 °C (Figs. 8b and 9b).

4. Conclusions

Experiments of pyrolysis have been carried out on bio-oil at different heating rates and different final temperatures. Two different devices have been used in order to cover a wide range of heating rates.

The yields of gas/condensate/char were determined after pyrolysis. They were 12/73/14 wt.% at 550 °C with gas residence time of 8 s, and 43/47/9 wt.% at 1000 °C with gas residence time of 5 s. The composition of the obtained gas was established at the two final temperatures.

The heating rate of bio-oil has little impact on the gas yield, but plays a major role on the char yield. This later decreases from 11 wt.% with a heating rate of 2 °C s^{-1} down to 1 wt.% only for flash heating rate of 2000 °C s^{-1} at final temperature of 1000 °C. At very high heating rate the char yield depends less on the final temperature. These results show that for an EFR type gasification process the quantity of formed char is very small, but will require either complete gasification or removal from the gas produced by the gasifier.

Additional pyrolysis runs performed on wood bio-oil added with 3 wt.% of ash gave some interesting results:

(i) Ash increased the yield of solid products greatly and decreased the yield of gaseous products. Liquid yield undergoes no dramatic change. Ash seems to favor polymerization reactions leading to the formation of char.

(ii) Ash clearly affects the gas composition. When ash is added CH₄ and CO yields decrease, while CO₂ yield increases.

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References

- [1] Goyal HB, Diptendu S, Saxena RC. Bio-fuels from thermochemical conversion of renewable resources: a review. *Renew Sust Energy Rev* 2008;12:504–17.
- [2] Wornat M J, Porter BG, Yang NYC. Single droplet combustion of biomass pyrolysis oils. *Energy Fuel* 1994;8:1131–42.
- [3] Shaddix CR, Huey SP. Combustion characteristics of fast pyrolysis oils derived from hybrid poplar. In: Bridgwater AV, editor. *Developments in thermochemical biomass conversion*. London: Blackie Academic & Professional; 1997. p. 465–80.
- [4] Calabria R, Chiariello F, Massoli P. Combustion fundamentals of pyrolysis oil based fuels. *Exp Therm Fluid Sci* 2007;31:413–20 [ISSN 0894–1777].
- [5] Ba T, Chaala A, Pérez MG, Rodrigue D, Roy C. Colloidal properties of bio-oils obtained by vacuum pyrolysis of softwood bark. Characterization of water soluble and water-insoluble fractions. *Energy Fuel* 2004;18:704–12.
- [6] Ba T, Chaala A, Pérez MG, Roy C. Colloidal properties of bio-oils obtained by vacuum pyrolysis of softwood bark. Storage stability. *Energy Fuel* 2004;18:188–201.
- [7] Branca C, Di Blasi C. Multistep mechanism for the devolatilization of biomass fast pyrolysis oils. *Ind Eng Chem Res* 2006;45:5891–9.
- [8] Branca C, Di Blasi C, Elefante R. Devolatilization of conventional pyrolysis oils generated from biomass and cellulose. *Energy Fuels* 2006;20:2253–61.
- [9] Branca C, Di Blasi C, Russo C. Devolatilization in the temperature range 300–600 K of liquids derived from wood pyrolysis and gasification. *Fuel* 2005;84:37–45.
- [10] Branca C, Di Blasi C, Elefante R. Devolatilization and heterogeneous combustion of wood fast pyrolysis oils. *Ind Eng Chem Res* 2005;44:799–810.
- [11] Hallett WLH, Clark NAA. Model for the evaporation of biomass pyrolysis oil droplets. *Fuel* 2006;85:532–44.
- [12] Van Rossum G, Güell BM, Balegedde Ramachandran RP, Seshan K, Lefferts L, Van Swaaij WPM. Evaporation of pyrolysis oil: Product distribution and residue char analysis. *AIChE Journal* 2010;56:2200–10.
- [13] Chhiti Y, Salvador S, Commandre JM, Broust F, Couhert C. Wood bio-oil non catalytic gasification: influence of temperature, dilution by an alcohol and ash content. *Energy Fuels* 2011;25:345–51.
- [14] Mani T, Murugan P, Abedi J, Mahinpey N. Pyrolysis of wheat straw in a thermogravimetric analyzer: effect of particle size and heating rate on devolatilization and estimation of global kinetics. *Chem Eng Res Des* 2010;88:952–8.
- [15] Ayllón M, Aznar M, Sánchez JL, Gea G, Arauzo J. Influence of temperature and heating rate on the fixed bed pyrolysis of meat and bone meal. *Chem Eng J* 2006;121:85–96.
- [16] Haykiri-Acma H, Yaman S, Kucukbayrak S. Effect of heating rate on the pyrolysis yields of rapeseed. *Renew Energy* 2006;31:803–10.
- [17] Van de Steene L, Salvador S, Charnay G. Controlling powdered fuel combustion at low temperature in a new entrained flow reactor. *Combust Sci Technol* 2000;159:255–79.
- [18] Zaror CA, Hutchings IS, Pyle DL, Stiles HN, Kandiyoti R. Secondary char formation in the catalytic pyrolysis of biomass. *Fuel* 1985;64:990–4.
- [19] Seebauer V, Petek J, Staudinger G. Effects of particle size, heating rate and pressure on measurement of pyrolysis kinetics by thermogravimetric analysis. *Fuel* 1997;76:1277–82.