We are IntechOpen, the world's leading publisher of Open Access books Built by scientists, for scientists

6,900
Open access books available

185,000
International authors and editors

200M
Downloads

Our authors are among the

154
Countries delivered to

TOP 1%
most cited scientists

12.2%
Contributors from top 500 universities



WEB OF SCIENCE™

Selection of our books indexed in the Book Citation Index in Web of Science™ Core Collection (BKCI)

Interested in publishing with us?
Contact book.department@intechopen.com

Numbers displayed above are based on latest data collected.
For more information visit www.intechopen.com



Chapter 4

Gasification of Wood Bio-Oil

Younes Chhiti and Sylvain Salvador

Additional information is available at the end of the chapter

http://dx.doi.org/10.5772/48553

1. Introduction

Energy and environmental issues are two common concerns of modern society. Energy is a central part of every human being's daily life. In all its forms, such as chemical energy (food), thermal energy (heat), or electricity, energy has the ability to transform the daily lives of humans across the world by easing workloads, boosting economies and generally increasing the comfort of our lives. Worldwide energy consumption has been increasing rapidly. This has been accelerated by the improvement of the quality of life that almost directly relates to the amount of energy consumed. At present, fossil fuels based energy resources, such as coal, gas, and oil supply the majority of the total world energy requirement.

The global warming owing to the emissions of greenhouse gas is the most drastic consequence of the use of fossil fuels. According to experts in the field, global warming can disturb the natural equilibrium of the Earth's ecosystem. If CO_2 emissions are not regulated, global warming can have severe consequences for environment. These consequences, although some of them are not fully corroborated, are increasing sea and ocean levels, ocean acidification, change in rainfall patterns, hurricanes, volcanic eruptions, earthquakes and plant or animal extinctions, among others.

The development of non-conventional sources like wind, sunlight, water, biomass, etc., is inevitable. Among the renewable sources of energy, substantial focus of research is currently on the use of biomass. Besides being a renewable source of energy, there are many other advantages associated to the use of biomass. It is available abundantly in the world. Its use does not increase the net amount of CO_2 in the atmosphere and can reduce the emissions of SO_2 and NO_x remarkably.

Biomass gasification is a promising technology, which can contribute to develop future energy systems which are efficient and environmentally friendly in order to increase the share of renewable energy for heating, electricity, transport fuels and higher applications.

INTECH
open science | open minds

© 2012 Chhiti and Salvador, licensee InTech. This is an open access chapter distributed under the terms of the Creative Commons Attribution License (http://creativecommons.org/licenses/by/3.0), which permits unrestricted use, distribution, and reproduction in any medium, provided the original work is properly cited.

The gasification of carbon-containing materials to produce combustible gas is an established technology. Biomass gasification is a thermochemical process that produces relatively clean and combustible gas through pyrolytic and reforming reactions. The syngas generated can be an important resource suitable for direct combustion, application in prime movers such as engines and turbines, or for the production of synthetic natural gas (SNG) and transportation fuels e.g. Fischer-Tropsch diesel.

For energy production, the major concerns about syngas are its heating value, composition, and possible contamination. The proportion of the combustible gas hydrogen (H_2), methane (CH_4), carbon monoxide (CO), and moisture determines the heating value of the gas. The composition of syngas depends on the biomass properties and gasifier operating conditions. For a specific gasification system, operating conditions play a vital role in all aspects of biomass gasification. These include carbon conversion, syngas composition, tars and soot formation and oxidation (Devi et al., 2003).

The main hurdles for large-scale implementation of energy production from solid biomass are the nature of biomass - non uniform, low-energy density, sometimes large ash content - together with the usual inconsistency between the local availability of biomass and the demand for biomass related products: heat, electricity, fuels and chemicals. Usually, import/transport of fossil fuels is cheaper. Pyrolysis may be a process to overcome these hurdles: biomass is transformed into a versatile liquid called bio-oil, easy to handle and to transport. This bio-oil would then be transported to centralized air/steam gasification units. Bio-oil is an intermediate product which is produced from relatively dry biomass via fast pyrolysis process. It is a liquid with similar elemental composition to its original feedstock and with high bulk and energy density. The high bulk and energy density of bio-oil can reduce transportation costs to large scale centralized gasification plants; these costs have been a detrimental factor in large scale use of solid biomass resource. Bio-oil can be produced where the biomass is available and then be transported over long distances to central processing units of similar scales as the current petrochemical industry. Besides technical and logistic advantages, this conversion chain may also give incentives for economic development and job creation especially in rural areas.

The essential features to obtain high yields of bio-oil (up to 75 wt% on dry basis) are a moderate pyrolysis temperature (500°C), high heating rates (10^3-10^5°C/s), short vapour residence times (<2 s) and rapid quenching of the pyrolysis vapours.

The combination of fast pyrolysis of biomass followed by transportation in large units for steam reforming has attracted considerable attention of the research community, as one of the most promising viable methods for hydrogen production. For the high temperature applications such as gasification, steam reforming or even combustion, it is of particular interest to understand the behavior of bio-oils during the very first step of its decomposition under pyrolysis conditions. However, only few works can be found on the understanding of processes occurring during thermal conversion of bio-oils.

The earliest combustion tests of bio-oil droplets were conducted in Sandia National Laboratory (Wornat et al., 1994). Streams of monodispersed droplets were injected into a

laminar flow reactor. The experimental conditions were as follows: droplet diameter of about 300 μm, reactor temperature of 1600 K and O_2 concentrations of 14–33%. In-situ video imaging of burning droplets reveals that biomass oil droplets undergo several distinct stages of combustion. Initially biomass oil droplets burn quiescently in a blue flame. The broad range of component volatilities and inefficient mass transfer within the viscous biomass oils bring about an abrupt termination of the quiescent stage, however, causing rapid droplet swelling and distortion, followed by a microexplosion.

Thermogravimetric analysis (TGA) is widely used to characterize the evaporation, thermal decomposition and combustion properties of bio-oils. The weight loss process of bio-oils 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 case of TGA tests performed in the presence of air, the weight loss of bio-oils can be divided into three stages. The first two stages are similar to those in inert atmospheres and the third stage is the combustion of chars formed in the first two stages (>400°C) (Ba et al., 2004a, 2004b).

Branca et al. (Branca, 2005a) studied the devolatilization and heterogeneous combustion of wood fast bio-oil. Weight loss curves of wood fast bio-oil in air have been measured, under controlled thermal conditions, carrying out two separate sets of experiments. The first, which has a final temperature of 600 K, concerns evaporation/cracking of the oil and secondary char formation. A heating rate of 0.08 °C/s was applied. The yield of secondary char varies from about 25% to 39% (on a total oil basis). After collection and milling, in the second set of experiments, heterogeneous combustion of the secondary char is carried out to temperatures of 873 K. In another study, Branca et al. (Branca et al., 2005b) found that thermogravimetric curves of bio-oil in air show two main reaction stages. The first (temperatures ≤ 600 K) concerns evaporation, formation and release of gases and formation of secondary char (coke). Then, at higher temperatures, heterogeneous combustion of secondary char takes place. They found that the pyrolysis temperature does not affect significantly weight loss dynamics and amount of secondary char (approximately equal to 20% of the liquid on a dry basis).

Hallet et al. (Hallett et al., 2006) 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.

Guus van Rossum et al. (Van Rossum et al., 2010) studied the evaporation of bio-oil and product distribution at varying heating rates (~1.5×10^{-2}–1.5×10^{4}°C/s) 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 between the two atomizers where the ultrasonic atomizer gives much less char compared to the needle atomizer, ~8 and 22% (on carbon basis), respectively. Small droplets (88-117μm generated by ultrasonic atomizer, undergoing high heating rate) are much quicker

evaporated than larger droplets (~ 1.9 mm, generated by needle atomizer, undergoing low heating rate).

Calabria et al. carried out lots of studies on the combustion behaviors of fibre-suspended single bio-oil droplets. The droplet size varied between 300 and 1100 μm and the furnace temperature changed in the range of 400–1200°C. The droplets were observed to undergo initial heating, swelling and microexplosion before ignition. During this stage, the temperature–time curves showed two zones with constant temperatures (100 and 450°C), which corresponded to the evaporation of light volatiles and the thermal cracking of unstable components, respectively. The droplets were ignited at around 600°C. The combustion of the droplets started with an enveloping blue flame. Then, the flame developed a yellow tail with its size increasing, which indicated the formation of soot. After that, the flame shrank and extinguished, and the remaining solid carbonaceous residues burned leading to the formation of ash (Calabria et al., 2007).

In air/steam gasification process the essential steps are pyrolysis, partial oxidation, cracking of tar, solid carbon residue gasification, reforming (steam and/or dry), and water gas shift to yield syngas, water, carbon dioxide, and unwanted products like tars, methane and carbon (Levenspiel et al., 2005). As a summary, a schematic representation of air/steam gasification of single droplet of bio-oil is proposed in Figure 1.

The steam reforming of the bio-oil can be simplified as the steam reforming of an oxygenated organic compound ($C_nH_mO_k$) following:

$$C_nH_mO_k + (n - k)H_2O \leftrightarrow nCO + (n + m/2 - k)H_2 \quad (1)$$

During the last decade, catalytic steam reforming of bio-oil components has been widely studied, focusing on acetic acid as one of the most representative compounds.

Production of hydrogen from catalytic steam reforming of bio-oil was extensively investigated by NREL (Wang et al., 1997, 1998). Czernik et al. obtained hydrogen in a fluidized bed reactor from the carbohydrate derived fraction of wood bio-oil with a yield of about 80% of theoretical maximum (Czernik et al., 2002). The catalytic steam reforming of the bio-oil or the model oxygenates (e.g., ethanol, acetic acid) has been widely explored via various catalysts, e.g., Ni-based catalysts (Sakaguchi et al., 2010), Mg-doped catalysts (Garcia et al., 2000) and noble metal-loaded catalysts (Goula et al., 2004; Rioche et al., 2005; Trimm et al., 1997). Noble metals (Pt, Ru, Rh) are more effective than the Ni-based catalysts and less carbon depositing. Such catalysts are not common in real applications because of their high cost. Catalytic steam reforming of bio-oil is a costly process and presents several disadvantages such as carbon deposit and the deactivation of catalysts due to coke or oligomer deposition even in the presence of an excess of steam (S/C > 5) (Trimm et al., 1997; Rostrup-Nielsen et al., 1997). For these reasons, there is an interest in developing non catalytic gasification of bio-oil.

Only very few works can be found on the non catalytic reforming of whole bio-oil. Bimbela et al. studied catalytic and non catalytic steam reforming of acetol (bio-oil model compound)

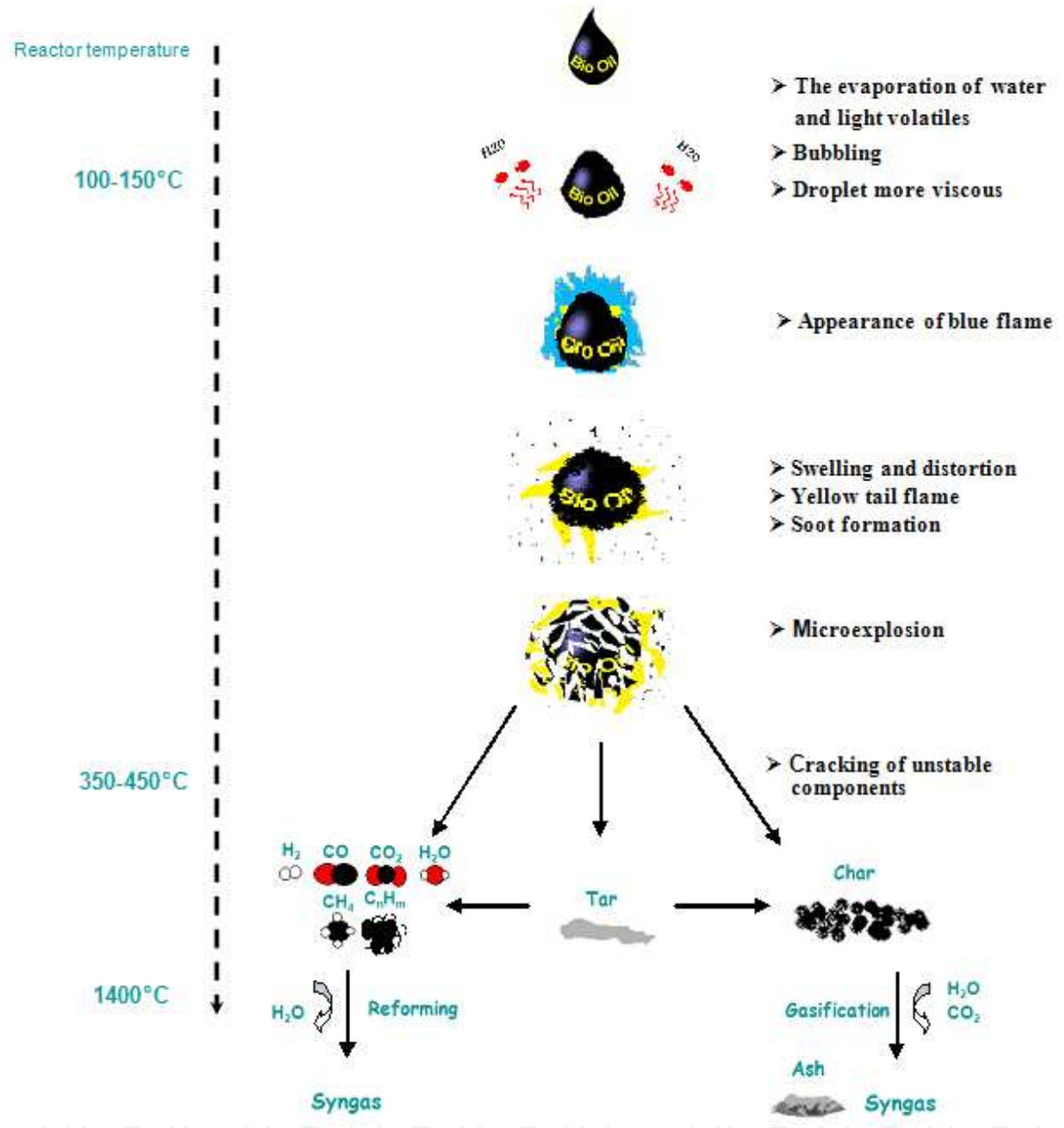


Figure 1. Schematic representation of air steam gasification of bio-oil droplet

in fixed bed at low temperature (550-750°C) in order to highlight the specific role of the catalyst in this process (Bimbela et al., 2009). The same study is carried out by Guus van Rossum et al. concerning catalytic and non catalytic gasification of bio-oil in a fluidized bed over a wide temperature range (523-914°C) (van Rossum et al., 2007). Marda et al. has developed a system for the volatilization and conversion of a bio-oil mixed with methanol to syngas via non-catalytic partial oxidation (NPOX) using an ultrasonic nozzle to feed the mixture. The effects of both temperature (from 625 to 850°C) and added oxygen (effective O/C ratio from 0.7 to 1.6) on the yields of CO and H_2 have been explored. They obtained hydrogen yield of about 75% of theoretical maximum (Marda et al., 2009). Panigrahi et al. gasified biomass-derived oil (BDO) to syngas and gaseous fuels at 800°C. They obtained syngas (H_2 + CO) yield ranging from 75 to 80

mol % (Panigrahi et al., 2003). Henrich et al. gasified lignocellulosic biomass. The first process step is a fast pyrolysis at atmospheric pressure, which produces large condensate that was mixed to slurries. The slurries are pumped into a slagging entrained flow gasifier and are atomized and converted to syngas at high operating temperatures and pressures (Henrich et al., 2004).

The objective of this work is to bridge the lack of knowledge concerning the physicochemical transformation of bio-oil into syngas using non catalytic steam gasification in entrained flow reactors. This complex process involves vaporization, thermal cracking reactions with formation of gas, tars and char that considered as undesirable product. This is followed by steam reforming of gas and tars, together with char conversion. To better understand the process, the first step of gasification (pyrolysis) and thereafter the whole process (pyrolysis + gasification) were studied. The pyrolysis study focused on the influence of the heating rate and the final pyrolysis temperature, for this aim, two complementary devices namely: a Horizontal Tubular Reactor (HTR) and a High Temperature - Entrained Flow Reactor (HT-EFR) were used to study on the one hand a wide range of heating rates, in the range from 2 to 2000°C/s and on the other hand final temperature ranging from 550 to 1000°C. Concerning gasification, the effect of temperature on syngas yield and composition was studied over a wide range from 1000°C to 1400°C, for this aim HT-EFR was used.

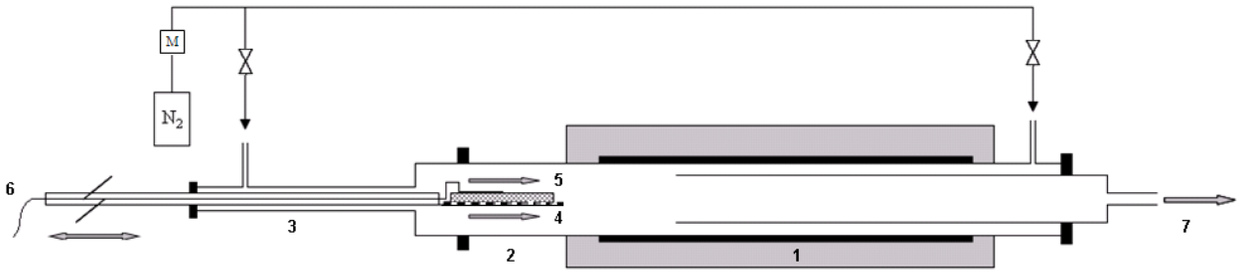
2. Materials and methods

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 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. 2). 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.



1- Furnace; **2-** Quartz reactor; **3-** Movable sample boat; **4-** Metal grid; **5-** Refractory ceramic wool soaked with 1g of bio-oil; **6-**Thermocouple; **7-** Gas outlet; **M**- Mass flow meters and controllers

Figure 2. 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 1g 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 1g of bio-oil previously soaked in a refractory ceramic wool sample of 100x20 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 ceramic wool deposited in the crucible. The wool didn't induce any change on the products yield.

The reactor outlet was first connected to an O_2 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 and 30 cm/s. 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 N_2 flowrate which enabled to know accurately the volume of N_2 sampled in the bag. In HTR reactor, the volume of formed gas never exceeded 1% of the volume of N_2 sampled in the bag. After the experiment the bag was disconnected from 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 1g of bio-oil can be precisely calculated.

2.1.2. Entrained Flow Reactor EFR

A laboratory scale high temperature entrained flow reactor HT-EFR was used in this work. 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 1m long isothermal reaction zone, as illustrated in Fig. 3.

The atmosphere gas is generated by feeding the controlled flow of nitrogen in a 2 kW electrical steam generator. This atmosphere gas is then preheated to 900°C using a 2.5 kW

electrical battery of heating elements before reaching the isothermal reaction zone. The HT-EFR was initially set up to achieve high heating-rate gasification of solid biomass, and was equipped for the present work with a specially designed bio-oil pulverization feeder, in order to obtain a very constant mass flowrate spray.

The feeder consists of a 1 m long and 14 mm o.d. probe cooled with water at 30°C. At its end a commercial stainless steel nozzle is integrated. This allows uniform distribution with fine atomization. Nozzle type (DELAVAN WDB) is a solid cone, with orifice diameter of 0.46mm and a spray angle of 60°.

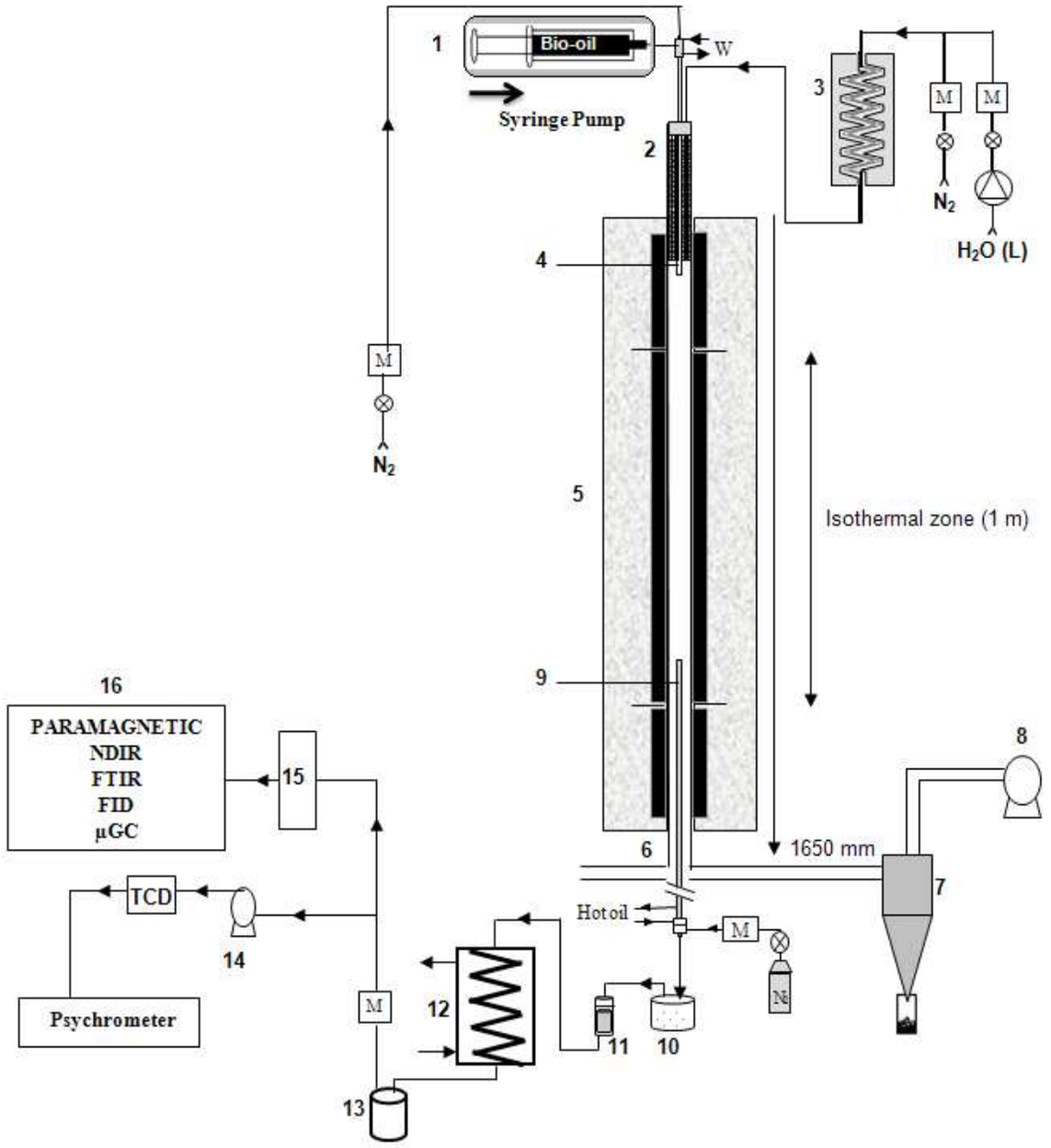
The oil is fed with a syringe which is automatically pushed. The expected mass flowrate of 0.3 g/min was too low for direct pulverization. Therefore, a 3.5 NL/min N_2 flowrate was used to entrain oil in the feeding probe and to ensure a thin spray of the oil. The spray of droplets is dispersed on the section of a 75 mm i.d. alumina reactor swept by 15 $NL.min^{-1}$ of atmosphere gas. The steam gasification experiments were carried out in HT-EFR with steam to fuel mass ratio (fuel includes inherent water in bio-oil) of S/F=4.5.

Reactions take place along the reactor during a controlled gas residence time, which was of about 3-4s. The residence time of droplets or solid residue after reaction is assumed to be similar to that of the gas because of the very small particle size. The gas residence time was calculated as the ratio of the reaction zone length to the average gas velocity in the reactor. At 1650 mm downstream of the injection point, gases and solid residue were sampled by a hot-oil cooled probe at 150°C. 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 H_2, CO, CO_2, CH_4, C_2H_2, C_2H_4, C_2H_6, C_3H_8 and C_6H_6. The μGC offers excellent resolutions of all analyze species at higher concentrations with repeatability of ± 2 percent relative standard deviation, the system offers also a minimum detectable quantity of about 10 ppm for most gases species.

Gases were also analyzed by other analyzers that allowed checking the absence of O_2, to confirm the analysis and to control continuously gas production: a Fourier Transform InfraRed (FTIR) analyser, a Non-Dispersive InfraRed (NDIR) analyser coupled with a paramagnetic analyser for O_2 and a Thermal Conductivity Detector (TCD) to quantify H_2.

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



1- Injection system; **2-** Electrical preheater; **3-** Steam generator; **4-** Water cooled feeding probe; **5-** Three zones electrical furnace; **6-** 75 mm i.d. alumina reactor; **7-** Cyclone collector; **8-** Exhaust fan; **9-** Oil cooled sampling probe; **10-** Hot settling box; **11-** Hot particle collector (filter); **12-** Water cooler; **13-** Condensate collector; **14-** Sampling pump; **15-** Gas dryer; **16-** Gas analyser; **M-** Mass flow meters and controllers; **N_2-** Nitrogen; **W**- Water (probes cooling)

Figure 3. Entrained flow reactor

similar to those of wood. From the ultimate analysis, the chemical formula of the bio-oil can be established as $CH_{1.18}O_{0.48}.0.4H_2O$.

Ultimate analysis (wt.%)					H_2O	Ash	Solids	LHV	Kinematic viscosity
C	H	O	S	N	(wt.%)	(wt.%)	(wt.%)	($MJ.kg^{-1}$)	at 20 °C ($mm^2.s^{-1}$)
42.9	7.1	50.58	< 0.10	< 0.10	26.0	0.057	2.34	14.5	103

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

3. Results and discussions

3.1. Thermal decomposition of bio-oil: focus on the products yields under different pyrolysis conditions

3.1.1. Preliminary runs of bio-oil pyrolysis at two final reactor temperatures (The experiments were carried out in a HTR)

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 Figure 4. With temperature increasing from 550 to 1000°C, the total gas yield sharply increases from 12.2 to 43.0 wt.%, while condensate (tar + water) decreases from 73.2 to 47.5 wt.%. Varying temperature shows a great influence on the gas composition as well.

Figure 5 shows that the main gas products are H_2, CO, CO_2, CH_4 and some C_2 hydrocarbons (C_2H_2, C_2H_4 and C_2H_6). Among them, the H_2 and CO content increased significantly from 0.056 wt.% 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, C_2H_4 and C_2H_6 are relatively small. The specie C_2H_6 only appears at 550°C while C_2H_2 only appears 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°C 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 emperature 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 (Ayllón et al., 2006; Haykiri-Acma et al., 2006; Mani et al.,2010).

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, 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 to separate the effect of these two parameters. This is studied in details in the following section.

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

The temperature profiles obtained in the HTR are illustrated in Figure 6. 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 2.

The temperature profiles curves show that the heating rate ranges from 2 to 14°C/s at the final pyrolysis temperature of 550°C, and from 2 to 100°C/s at the final pyrolysis temperature of 1000°C. The response time of temperature measurement system was characterized by placing the thermocouple alone and the thermocouple placed in the refractory ceramic wool without bio-oil sample together inside the reactor in 0.03 min. The results are also plotted in Figure 6. At 1000°C we can notice that the response of the thermocouple and refractory ceramic wool does not exceed 100°C/s. But, it appears that the actual heating rate for the sample introduced in 0.03min may be still higher than 100°C/s. This is further illustrated on Figure 6.

	t (min)[a]	Heating rate °C/s	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

Table 2. Product yield of bio-oil pyrolysis at different temperatures and heating rates

In order to highlight the effect of heating rate and final temperature on the yields of char, they were plotted in figure 7, 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 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 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 HT-EFR. This process allows achieving very high heating rate.

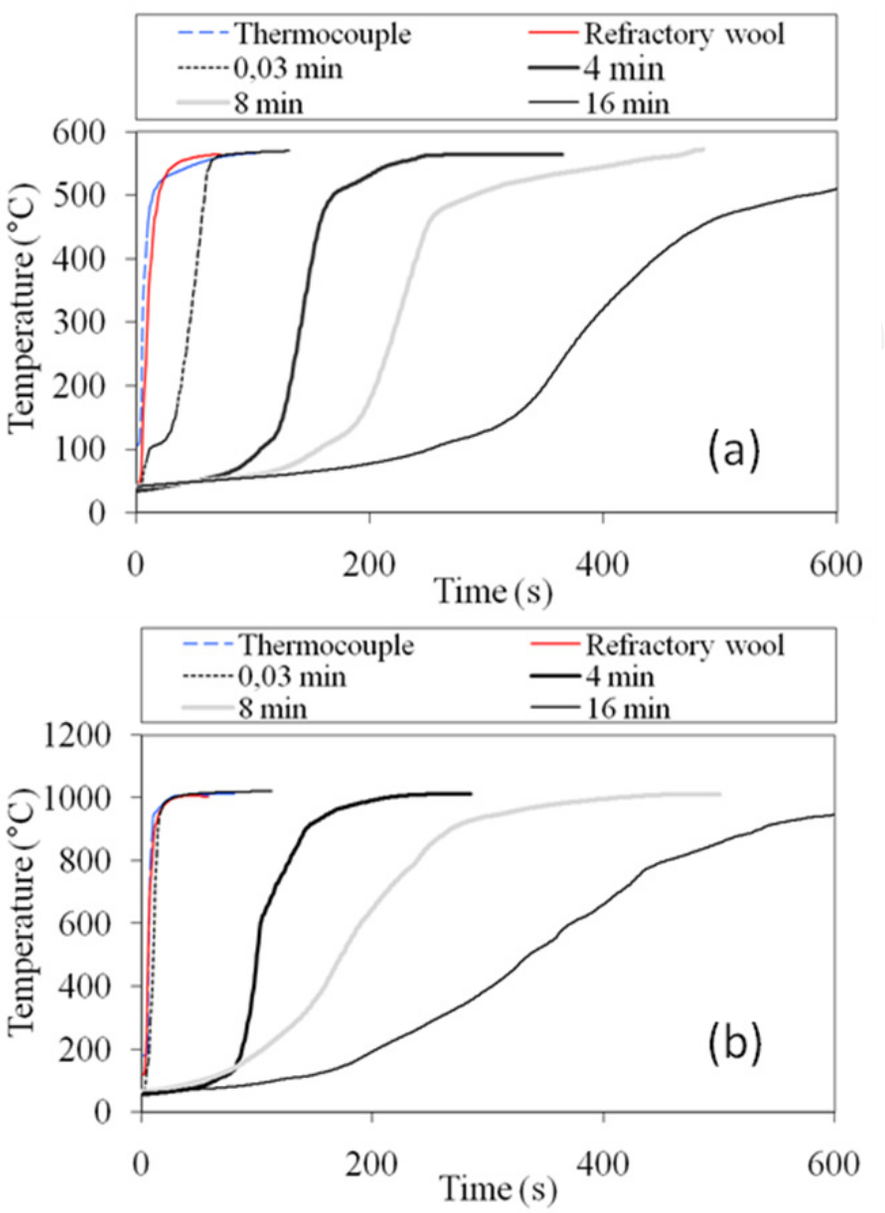


Figure 4. Temperature evolution of the sample during bio-oil pyrolysis in HTR at different heating rates and two final temperatures. **a:** 550°C, **b:** 1000°C

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 was estimated at 2000°C/s (Van de Steene et al., 2000). Under these conditions, the char yield measured is very low: < 1 wt.%. As can be seen in Figure 7, the char yield obtained with HT-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 Guus van Rossum et al. (Van Rossum et al., 2010). They found that small droplets (undergoing high heating rate) are much quicker evaporated and give fewer char compared to larger droplets (undergoing low heating rate pyrolysis).

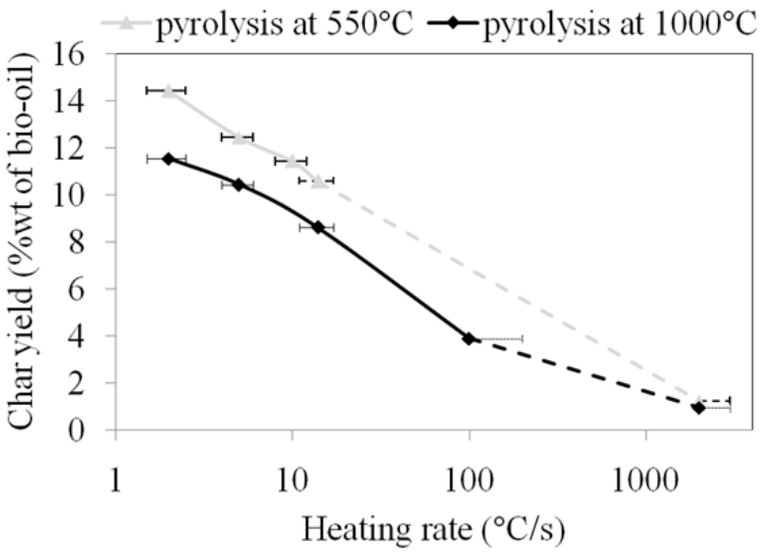


Figure 5. Char yield obtained from pyrolysis of bio-oil at two final temperatures: 550°C and 1000°C - effect of heating rate

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…). Considering that solid gasification is rate-limiting, this might be an advantage of using bio-oil instead of biomass as feedstock for EFR gasification.

Figure 8 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 of 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 value of 76 wt.% is obtained at 14°C/s and a final temperature of 550°C, which is about 5 wt.% higher than that obtained at 2°C/s. 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. This value was about 6 wt.% higher than that of 2°C/s.

All these trends can be summarized and explained as follows.

i. 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 (Zaror et al., 1985; Seebauer et al., 1997):

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

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 (Zaror et al., 1985) and apparently, this could be extended to the case of bio-oil pyrolysis.

ii. 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 (Seebauer et al., 1997).

Let's 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 16s at 550°C and from 5 to 10s at 1000°C.

3.2. Gasification of wood bio-oil (The experiments were carried out in a HT-EFR)

3.2.1. Effect of temperature

The first objective was to study the influence of temperature - over a wide range - on the syngas yield and composition.

Generally the gas mixture formed from catalytic reforming of bio-oil is composed of hydrogen, carbon monoxide and dioxide, methane, acetylene, unconverted steam, coke (carbon) and soot. Figure 9, presents the mole fraction of the gaseous products from this work (in dry basis and without N_2) as a function of temperature in the range 1000 to 1400°C. Error bars were established by repeating each test 2 or 3 times. The species C_2H_4, C_2H_6, C_3H_8 and C_6H_6 are not detected by chromatography. Whatever the operating temperature between 1000°C and 1300°C, bio-oil is mainly decomposed to H_2, CO, CO_2, CH_4 and C_2H_2. Above 1300°C C_2H_2 disappears, while CH_4 disappears above 1400°C. As the temperature rises, the fraction of H_2 increases monotonically at the expense of carbon monoxide, methane and acetylene. Above 1300°C the hydrogen content remains almost stable. At 1400°C hydrogen mole fraction reaches the maximum value of 64 mol% of the syngas.

The reactions that may explain the increase of hydrogen with temperature are:

The steam reforming of CH_4 and C_2H_2 into H_2 and CO (2)

The water gas shift reaction $CO + H_2O \leftrightarrow CO_2 + H_2$ (3)

The water gas shift reaction can also explain the increase of carbon dioxide and the decrease of carbon monoxide between 1000 and 1200°C. Above 1200°C, carbon monoxide slightly

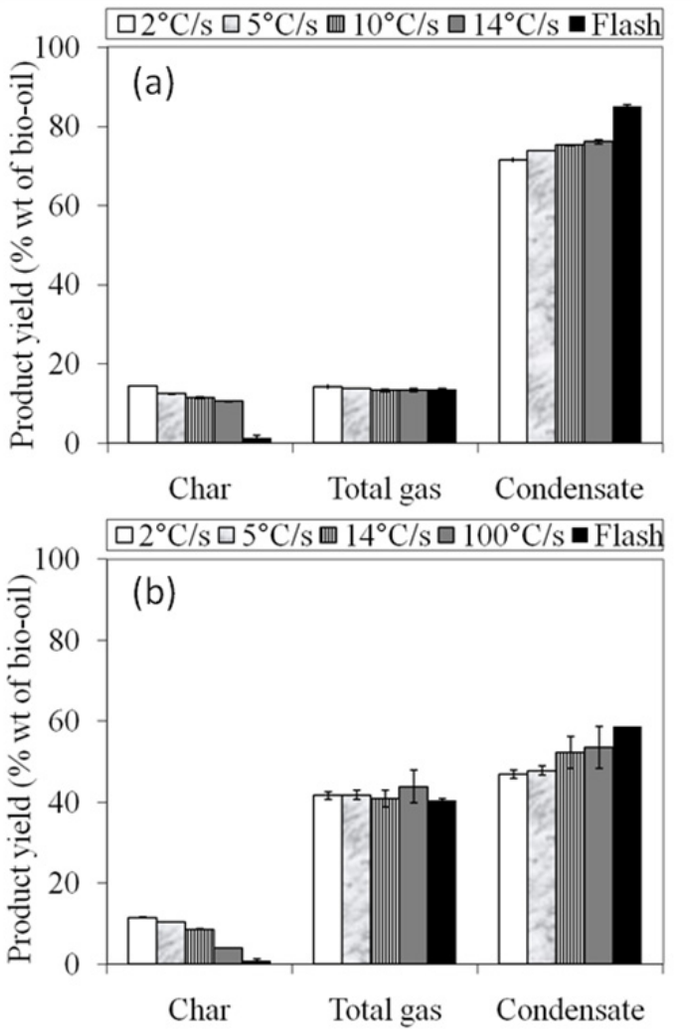


Figure 6. Product yield obtained from bio-oil pyrolysis at two final temperatures. **a:** 550°C, **b:** 1000°C- effect of heating rate

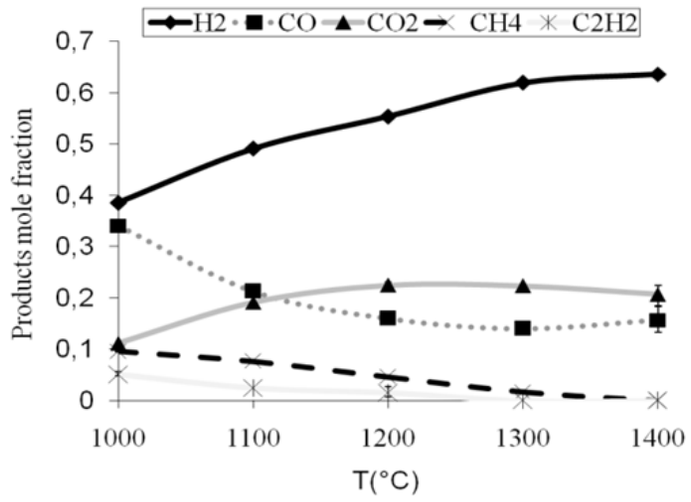


Figure 7. Composition of the produced syngas (dry basis and without N_2) - effect of temperature, at S/F=4.5

increases. This may be explained by steam gasification of the solid carbon residue (char and soot) resulting from the pyrolysis of oil droplets to yield carbon monoxide and hydrogen following the reaction:

$$C + H_2O \leftrightarrow CO + H_2 \quad (4)$$

and potentially following the Boudouard reaction which would explain the slight decrease of CO_2:

$$C + CO_2 \rightarrow 2CO \quad (5)$$

It was observed that as the temperature increases the amount of collected solid decreases significantly above 1000°C. The process allows achieving very high heating rate estimated at 2000°C/s (Van de Steene et al., 2000). Under these conditions, the char yield measured is very low: < 1 wt.%. At 1400°C more than the 99.9% the bio-oil is converted to gas.

3.2.2. Equilibrium calculation

The thermodynamic equilibrium calculation is independent of reactor and predicts the yield of final products, based on the minimization of the Gibbs free energy of the system. It was conducted here using FactSage software 5.4 to establish whether the syngas was close or not to equilibrium at the different temperatures. Operating temperature varied from 1000°C to 1400°C; pressure was fixed at 1 atm. The software is not presented in detail in this paper; details of the thermodynamic calculation could be found on FactSage web site.

The results of prediction are presented in Figure 10, expressed in g of gas produced per g of crude bio-oil injected. As the temperature increases from 1000 to 1400°C the calculated equilibrium yield of H_2 remains approximately constant at 0,11g/g, while the yield of CO increases from 0.3 at 1000°C to 0.45g/g at 1400°C. The CO_2 yield decrease from 1.1 g/g at 1000°C down to 0.9 at 1400°C.

At 1000°C the calculation yields are far away from the experimental results. The deviation from equilibrium at lower temperatures is also reported by Sakaguchi et al (Sakaguchi et al., 2010). At 1200°C the thermodynamic equilibrium begins to establish. The calculation nevertheless does not retrieve the presence of CH_4 and C_2H_2. At 1400°C the experimental yields are very close to the equilibrium calculation yields: 0.11 and 0.12 respectively for H_2, 0.45 and 0.45 respectively for CO, and 0.86 and 0.88 respectively for CO_2. It can be concluded that at this temperature the equilibrium is reached.

It is also interesting to compare the obtained experimental yields at 1400°C to the theoretical yields corresponding with complete gasification of oil that would follow:

$$CH_{1.18}O_{0.48}.0.4H_2O + 1.12\ H_2O \rightarrow CO_2 + 2.11\ H_2 \quad (6)$$

The maximum stoichiometric H_2 yield for this oil would be 0.150g per 1g crude bio-oil while a value of 0.126 g was obtained experimentally. This shows that under our experimental

conditions and at 1400°C steam reforming of bio-oil lead to a production of H_2 with a yield of about 84% of theoretical yields corresponding with complete gasification of oil (reaction 6).

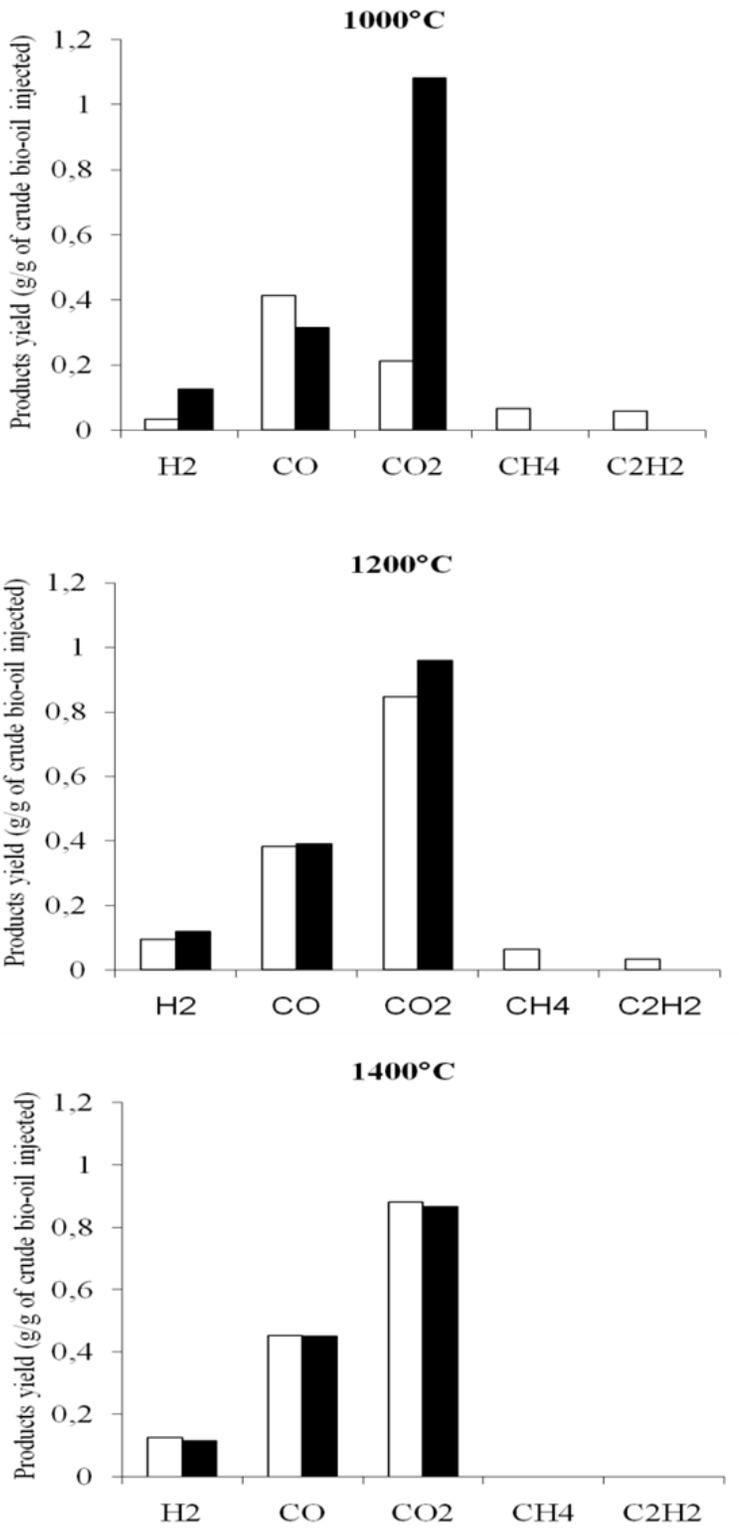


Figure 8. Gas yield from bio-oil reforming at 1000, 1200 and 1400°C, S/F=4.5. □ Experiments; ■ Equilibrium calculation

4. Conclusion

Gasification of biomass is one of the leading near-term options for renewable energy production. When large scale units are considered, bio-oil shows lots of advantages compared to solid biomass. The combination of decentralized fast pyrolysis of biomass followed by transportation and gasification of bio-oil in bio-refinery has attracted great attention.

The overall purpose of this research was to investigate the feasibility of a whole bio-oil non catalytic steam gasification process for the production of high quality syngas in entrained flow reactor.

From a chemical point of view, bio-oil gasification process is quite complex and consists of the following main stages: vaporization, thermal cracking reactions with formation of gas, tars and char that considered as undesirable products. This is followed by steam reforming of gas and tars, together with char oxidation. To better understand the process, the first step of gasification (pyrolysis) and thereafter, the whole process (pyrolysis+gasification) were separately studied.

In the pyrolysis step, a temperature increase from 550°C to 1000°C greatly enhanced the gas yield, whilst solid and liquid yields decreased significantly in agreement with the literature. The heating rate of bio-oil has little impact on the gas yield, but plays a major role on the char yield. Hence the char yield decreases from 11 wt.% with a heating rate of 2°C/s down to 1 wt.% for flash heating rate of 2000°C/s at a final temperature of 1000°C. At very high heating rate, the final temperature has little influence on the char yield. These results show that for gasification under industrial EFR conditions, the quantity of char is very small. Thus the gasification process mainly consists in gas/tar reforming. Nevertheless, the production of clean syngas will require either complete gasification of char or its removal from the gas produced by the gasifier.

In steam gasification process, whole bio-oil was successfully steam gasified in HT-EFR. An increase in the reaction temperature over a wide range from 1000°C to 1400°C implies higher hydrogen yield and higher solid carbon conversion. A thermodynamic equilibrium calculation showed that equilibrium was reached at 1400°C. At this temperature steam reforming of bio-oil leads to yield of equal 84% of theoretical yields corresponding with complete gasification of oil.

Author details

Younes Chhiti
Université de Pau/LaTEP-ENSGTI

Sylvain Salvador
Ecole des Mines d'Albi – Carmaux/RAPSODEE

Acknowledgement

The authors gratefully acknowledge the financial support from EnerBio Program of Fondation Tuck France, and express their gratitude to Mr. Bernard AUDUC technician in

Ecole des Mines d'Albi-Carmaux for his assistance and contribution to experimental device design and operation.

5. References

Ayllón, M.; Aznar, M.; Sånchez, JL.; Gea, G. & Arauzo, J. (2006). Influence of temperature and heating rate on the fixed bed pyrolysis of meat and bone meal. *Chemical Engineering Journal,* Vol.121, No.2-3, (June 2006), pp. 85–96, ISSN 13858947

Ba, T.; Chaala, A.; Pérez, MG.; Rodrigue, D. & Roy, C. (2004a).Colloidal properties of bio-oils obtained by vacuum pyrolysis of softwood bark. Characterization of water soluble and water-insoluble fractions. *Energy Fuel*, Vol.18, No.5, (August 2004), pp. 704–12, ISSN 0887-0624

Ba, T.; Chaala, A.; Pérez, MG. & Roy, C. (2004b). Colloidal properties of bio-oils obtained by vacuum pyrolysis of softwood bark. Storage stability. *Energy Fuel,* Vol.18, No.1, (December 2003), pp. 188–201, ISSN 08870624

Branca C.; Di Blasi C. & Elefante R. (2005a). Devolatilization and Heterogeneous Combustion of Wood Fast Pyrolysis Oils. *Ind. Eng. Chem. Res* Vol. 44, No.4, (January 2005), pp. 799-810, ISSN 08885885

Branca C.; Di Blasi C. & Russo C. (2005b). Devolatilization in the temperature range 300–600 K of liquids derived from wood pyrolysis and gasification. *Fuel,* Vol.84, No.1, (August 2004), pp. 37–45, ISSN 0016-2361

Bimbela, F.; Oliva M.; Ruiz J.; Garcia L. & Arauzo, J. (2009). Catalytic steam reforming of model compounds of biomass pyrolysis liquids in fixed bed: Acetol and n-butanol. *J. Anal. Appl. Pyrolysis,* Vol.85, No.1-2, (December 2008), pp. 204-213, ISSN 01652370

Calabria, R.; Chiariello, F. & Massoli, P. (2007). Combustion fundamentals of pyrolysis oil based fuels. *Exp Therm Fluid Sci,* Vol.31, No.5, (July 2006), pp. 413–20, ISSN 0894-1777

Czernik, S.; French, R. & Feik, C. (2002). Hydrogen by catalytic steam reforming of liquid byproducts from biomass thermoconversion processes. *Ind Eng Chem Res*, Vol.41, No.17, (July 2002), pp. 4209–15, ISSN 0888-5885

Garcia, L.; French, R.; Czernik, S. & Chornet, E. (2000). Catalytic steam reforming of bio-oils for the production of hydrogen: effects of catalyst composition. *Appl. Catal.,* Vol.201, No.2, (January 2000), pp. 225–239, ISSN 0926860X

Devi, L.; Ptasinski, KJ. & Janssen, FJ.JG. (2003). A Review of the Primary Measures for Tar Elimination in Biomass Gasification Processes. *Biomass and Bioenergy,* Vol.24, No.2, (September 2002), pp. 125-140, ISSN 09619534

Goula, MA.; Kontou, SK. & Tsiakaras PE. (2004). Hydrogen production by ethanol steam reforming over a commercial Pd/γ-Al2O3 catalyst. *Appl. Catal.,* Vol.49, No.2, (February 2004), pp. 135–144, ISSN 09263373

Hallett, WLH & Clark, NAA. (2006). Model for the evaporation of biomass pyrolysis oil droplets. *Fuel,* Vol.85, No.4, (September 2005), pp. 532–544, ISSN 0016-2361

Haykiri-Acma, H.; Yaman, S & Kucukbayrak, S. (2006). Effect of heating rate on the pyrolysis yields of rapeseed. *Renewable Energy,* Vol.31, No.6, (May 2005), pp. 803–810, ISSN 0960-1481

Henrich, E. & Weirich, F. (2004). Pressurized Entrained Flow Gasifiers for Biomass. *Environmental Engineering Science,* Vol.21, No.1, (July 2004), pp. 53-64, ISSN 1092-8758

Levenspiel, O. (2005). What will come after petroleum. *Ind. Eng. Chem. Res.,* Vol.44, No.14, (February 2005), pp. 5073-5073, ISSN 0888-5885

Mani, T.; Murugan, P.; Abedi, J & Mahinpey, N. (2010). Pyrolysis of wheat straw in a thermogravimetric analyzer: Effect of particle size and heating rate on devolatilization and estimation of global kinetics. *Chemical Engineering Research and Design,* Vol.88, No.8, (August 2010), pp. 952-958, ISSN 0263-8762

Marda, JR.; DiBenedetto, J.; McKibben, S.; Evans, RJ.; Czernik, S.; French, RJ. & Dean, AM. (2009). Non-catalytic partial oxidation of bio-oil to synthesis gas for distributed hydrogen production. *International journal o f hydrogen energy,* Vol.34, No.20, (October 2009), pp. 8519–8534, ISSN 0360-3199

Panigrahi, S.; Dalai, AK.; Chaudhari, ST. & Bakhshi, NN. (2003). Synthesis Gas Production from Steam Gasification of Biomass-Derived Oil. *Energy Fuels,* Vol.17, No.3, (April 26, 2003), pp. 637–642, ISSN 0887-0624

Rioche, C.; Kulkarni, S.; Meunier, FC.; Breen, JP. & Burch, R. (2005). Steam reforming of model compounds and fast pyrolysis bio-oil on supported noble metal catalysts. *Appl. Catal.,* Vol. 61, No.1-2, (October 2009), pp. 130–139, ISSN 09263373

Rostrup-Nielsen, JR. Industrial relevance of coking. (1997). *Catal. Today,* Vol.37, No.3, (August 1997), pp. 225–23, ISSN 0920-5861

Sakaguchi, M.; Paul Watkinson, A. & Naoko, E. (2010). Steam Gasification of Bio-Oil and Bio-Oil/Char Slurry in a Fluidized Bed Reactor. *Energy Fuels,* Vol.24, No.9, (August 2010), pp. 5181–5189, ISSN 0887-0624

Seebauer, V.; Petek, J & Staudinger, G. (1997). Effects of particle size, heating rate and pressure on measurement of pyrolysis kinetics by thermogravimetric analysis. *Fuel,* Vol.76, No.13, (October 1997), pp. 1277-1282, ISSN 0016-2361

Trimm, DL. (1997). Coke formation and minimization during steam reforming reactions. *Catal. Today,* Vol.37, No.3, (August 1997), pp. 233–238, ISSN 09205861

Van de Steene, L.; Salvador, S & Charnay, G. (2000). Controlling powdered fuel combustion at low temperature in a new entrained flow reactor. *Combustion Science and Technology,* Vol.159, No.1, (January 2000), pp. 255-279, ISSN 0010-2202

Van Rossum, G.; Kersten, SRA. & van Swaaij, WPM. (2007). Catalytic and Noncatalytic Gasification of Pyrolysis Oil. *Ind. Eng. Chem. Res.,* Vol.46, No.12, (March 2007), pp. 3959-3967, ISSN 0888-5885

Van Rossum, G.; Güell, BM.; Balegedde Ramachandran, RP.; Seshan, K.; Lefferts, L.; Van Swaaij, WPM & Kersten, SRA. (2010). Evaporation of pyrolysis oil: Product distribution and residue char analysis. *AIChE Journal,* Vol.56, No.8, (August 2010), pp. 2200–2210, ISSN 0001-1541

Wang, D.; Czernik, S. & Montane, D. (1997). Biomass to hydrogen via pyrolysis and catalytic steam reforming of the pyrolysis oil and its fractions. *Ind Eng Chem Res,* Vol.36, No.5, (May 1997), pp. 1507–18, ISSN 0888-5885

Wang, D.; Czermik, S. & Chornet, E. (1998). Production of hydrogen from biomass by catalytic steam reforming of fast pyrolytic oils. *Energy Fuels,* Vol.12, No.1, (January 1998), pp. 19–24, ISSN 08870624

Wornat, MJ.; Porter, BG & Yang, NYC. (1994). Single droplet combustion of biomass pyrolysis oils. *Energy Fuel,* Vol.8, No.5, (September 1994), pp. 1131–1142, ISSN 1520-5029

Zaror, CA.; Hutchings, IS.; Pyle, DL.; Stiles, HN & Kandiyoti, R. (1985). Secondary char formation in the catalytic pyrolysis of biomass. *Fuel,* Vol.64, No.7, (july 1985), pp. 990–994, ISSN 0016-2361