Catalytic effect of ash on bio-oil thermal conversion

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Abstract
This paper investigated the catalytic effect of inorganic elements in ash on bio-oil thermal conversion process (pyrolysis and gasification). Bio-oil with a natural ash contents of 0.05 wt.% and bio-oil added with 3 wt.% of ash were explored. The influence of ash content of the bio-oil conversion on char, tar and gas yields were investigated over a wide range of temperature from 500°C to 1200°C. A Horizontal Tubular Reactor (HTR) is used for pyrolysis process and an Entrained Flow Reactor (EFR) is used for gasification process. The experimental results showed that ash seems to favor re-polymerization reactions that lead to an increase in char yield and causing a decrease in the yield of gas while an increase was a priori expected.

Key words: ash, catalysis, bio-oil, pyrolysis, gasification

1. Introduction
The energy and the environment are two common preoccupations of modern community. Conventional fuel shortage and severe environmental impacts have attracted a strong focus on the exploitation of clean renewable energies. Biomass appears as a potential attractive feedstock for producing fuel gas as the CO₂ neutral energy supply. The producer gas from biomass can also reduce the emissions of NOₓ and SO₂ outstanding. The biomass share for the production of the worldwide potential energy and heat is about 14% of the total consumption of primary energy [1-5]. Syngas can be produced from biomass mostly via two thermochemical processes, the gasification [6,7] and the fast pyrolysis [8-10] followed by steam reforming of the bio-oil. Fast pyrolysis is a thermal conversion process operated in the absence of air in order to convert solid biomass into liquid products (bio-oil) as the main product together with non-condensable gases and solid carbonaceous residue (char) as by-products. In the few years, fast pyrolysis became one of the promising routes for preconditioning solid biomass into liquid biofuel (bio-oil) as intermediate before its transport to a gasification plant. Indeed, bio-oil have a lot of advantages in comparison to the solid biomass such as: high volume energy density, ease of storage, handling and transport from small decentral production units plan to a large-scale processing plant. During last years, a considerable amount of research
was devoted to fast pyrolysis process [11-13]. The influence of the presence of mineral matter on final products yields from solid biomass pyrolysis has been extensively studied [14-20]. Nik-Azar et al. [15] have studied the effects of cations on the char, tar, and total gas yields from fast pyrolysis of beech wood. Crude wood, washed wood, and impregnated wood with sodium, calcium and potassium cations were pyrolyzed at 1000°C and 1000°C.s⁻¹ heating rate in 1 atm pressure under helium carrier gas. They found that washing wood samples with acid reduces the yields of char and gases. Ming-qiang Chen have investigated catalytic effects of inorganic additives on the pyrolysis of pine wood sawdust by microwave heating at 470°C under nitrogen atmosphere. They found that mineral additives decreased more or less the gas yield and increased significantly the char yield. However, there is no considerable change concerning liquid yield [16]. Skoulou and Masek [17,18] find that the ashes promote catalysis, particularly in tar reforming. Also, during gasification ash lowering the reforming reactions temperature. Silica, is particularly one of the most element which reacts readily with alkali metals to cause fusion and depot problems during the thermal conversion [19]. Calcium is present in significant quantity in wood ashes, while potassium is present in very small quantities and relatively volatile at high temperature. Al, Fe and Ni are present as trace elements, and they are known to participate in several steam reforming reactions [18,20]. As mentioned earlier, there has been much focus in impact of ash on solid biomass gasification but there has been very little assessment on liquid biomass. The objective of this work is to bridge the lack of knowledge concerning this issue.

2. Experimental
2.1. Description of the laboratory device and the procedure
Bio-oil with a natural ash contents of 0.05 wt.% and bio-oil added with 3 wt.% of ash were investigated over a wide range of temperature from 500°C to 1200°C. A Horizontal Tubular Reactor (HTR) is used for pyrolysis process and an Entrained Flow Reactor (EFR) is used for gasification process.

2.1.1. Horizontal Tubular Reactor HTR
The experiments of fast pyrolysis were carried out in a HTR (Figure 1).

![Figure 1. Horizontal Tubular Reactor (HTR) ready for sample introduction](image)

This device allowed carrying out experiments in conditions of fast pyrolysis which is not possible in a thermobalance, and allowed to accurately quantify the solid residue formed (char). 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. 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 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 Figure 1. The sample consisted in 1g of bio-oil was placed inside a crucible of 25 mm diameter and 40 mm height. 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\(^{-1}\) 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
The steam reforming experiments of bio-oils with and without were carried out in a laboratory scale HT-EFR. It consists in a vertical tubular reactor electrically heated by a total 18 kW three-zone electrical furnace, and is able to reach 1600°C in a 1m long isothermal reaction zone, as illustrated in Figure 2. The atmosphere gas is generated by feeding the controlled flows of water and 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, with the aim 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 50°C. At its extremity a stainless steel nozzle is integrated. This allows uniform distribution with fine atomization. Nozzle type (DELAVAL 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 pushed automatically. The expected mass flowrate of 0.3 g/min was too low for direct pulverization. Therefore, a 3.5 NL.min\(^{-1}\) 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 16 NL.min\(^{-1}\) of an atmosphere gas containing 10 vol. % of steam in N\(_2\). The steam to fuel mass ratio (fuel includes inherent water in bio-oil) was S/F=4.5, which equivalent to steam to carbon molar ratio of S/C=8.3. Steam reforming takes place along the reactor during a controlled vapour residence time, which was about 3s. The gas residence time is calculated as ratio of the reaction zone to the average gas velocity in the reactor. At 1760 mm downstream of the injection point, gases and solid residue were sampled by a hot-oil cooled probe. 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.

**Figure 2.** Schematic view of the entrained flow reactor

### 2.2. Feedstock
The feedstock used for all experiments was bio-oil produced by fast pyrolysis of mixture of hardwood (oak, maple, ash) in 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 literature. It can be noticed that the solid particles content is rather high (2.3 wt.%) while the ash content remains very 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-oil 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$_{0.48}$.0.4H$_2$O. 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 largest solid particles which represented less than 0.01 %wt of the oil.

Table 1. Ultimate analysis and physico-chemical properties of bio-oil derived from hardwood fast pyrolysis

<table>
<thead>
<tr>
<th>Ultimate analysis (wt.%)</th>
<th>H$_2$O (wt.%)</th>
<th>Ash (wt.%)</th>
<th>Solids (wt.%)</th>
<th>LHV (MJ/kg)</th>
<th>Kinematic viscosity at 20°C (mm$^2$.s$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C  42.9</td>
<td>H 7.1</td>
<td>O 50.58</td>
<td>N &lt; 0.10</td>
<td>26.0</td>
<td>0.057</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>2.34</td>
<td>14.5</td>
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<td></td>
<td></td>
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<td></td>
<td></td>
<td>103</td>
</tr>
</tbody>
</table>

2.3. Ash preparation
The ash added to bio-oil is prepared by the combustion of the ground beech wood at moderate temperature (600°C) in order to preserve the ash properties. To ensure good air diffusion and heat transfer, the ground wood is spread in several drawers with thin layer about 1.5 cm of thickness. Low air flow rate (30 NL.h$^{-1}$) was injected to the reactor in order to avoid rapid ignition and high temperature and thereafter volatilization of ash. The minerals components were quantified by ICP (Inductively Coupled Plasma Optical Emission Spectrometry), the results are presented in Table 2. It can be noted that Ca, K, Mn, and Mg are present in high concentration. Other minority elements such as Co, Cr, Cu, Fe, Pb, Si, Zn and Cd are present in trace.

Table 2. Composition of ashes (from combustion of wood) [wt%, dry ashes]

<table>
<thead>
<tr>
<th>Ca</th>
<th>K</th>
<th>Mn</th>
<th>Mg</th>
<th>P</th>
<th>Ni</th>
<th>Na</th>
<th>Al</th>
</tr>
</thead>
<tbody>
<tr>
<td>11.67</td>
<td>3.80</td>
<td>1.74</td>
<td>1.54</td>
<td>1.01</td>
<td>0.25</td>
<td>0.24</td>
<td>0.10</td>
</tr>
</tbody>
</table>

3. Results and discussions
3.1. Pyrolysis situation
Figures 3a and 3b show the yield of bio-oil pyrolysis products at 500°C and 1000°C respectively. The pyrolysis products percentages are calculated on an added ash free basis. The results indicate that the addition of ash have increased the yields of char products greatly and decreased yields of gas products more or less as shown in figure 3a. At 550°C we can notice that the yield of char 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.%. At 1000°C both char yield and tar yield increased from 9.5 to 12.0 wt.% and from 47.5 to 50.0 wt.% respectively. However, the yield of tar decrease from 43.0 to 38.0 wt.%. Concerning the composition of gases, ash affects considerably the content of the producer gas; the results are presented in Figure 4. At 550°C (figure 3b), adding the ash involves a significant reduction of CO percentage from 5.9 to 4.0 wt.%. While, the CO$_2$ yield increase from 4.2 wt.% to 5.2 wt.%. Also, other gases undergo a slight decrease as notably CH$_4$ and C$_2$H$_4$. At 1000°C (figure 4b), the same remarks were recorded. CO yield decreased greatly from 23.9 wt.% to 19.0 wt.%. When CO$_2$ yield increase from 10.8 wt.% to 11.5 wt.%. Based on these results, mineral ash acts catalytically on the reactions involved during thermochemical conversion of bio-oil, this promote the formation of same gaseous species and the decline of
others. Also, it promote the reactions of poymérisation which cause an increase in the char yield with a decrease of the total gas yield.

**Figure 3.** Effect of ash content on bio-oil pyrolysis products yields at 550°C and 1000°C

**Figure 4.** Effect of ash content on gas yields of bio-oil pyrolysis at 550°C and 1000°C
3.2. Gasification situation

As indicated above the gasification experiments of bio-oils with and without ash were carried out in a laboratory scale Entrained Flow Reactor at 1200°C. The results are presented in Figure 5, and expressed by g of gas specie per g of bio-oil free ash gasified. For the gasification of bio-oil with added ash, theoretically an increase in the gas yield was expected as in the case of catalytic process, while a significant decrease of all the gas species has been observed.

![Figure 5. Effect of ash content on gas yields of bio-oil gasification at 1200°C with S/F=4.5](image)

Among them, the yield of H\textsubscript{2} decrease from 0.094 to 0.067g/g. CO\textsubscript{2} and CO yields decreased greatly from 0.84 to 0.67g/g and from 0.38 to 0.20 g/g respectively. These results are in harmony with the results of pyrolysis found above and could be attributed to the polymerization reactions catalysed by mineral ash. This leads to the formation of larger amount of char that is not gasified, and consequently causes a decrease of producer gas quantities, especially CO and CO\textsubscript{2} species. The volatilization of alkalis has probably a negative impact on ash catalytic effect at the high temperature. The phenomena of deactivation of minerals at high temperature is explained by the study of Masek et al. [18] who assert that the ash is deactivated at 950°C. In the same direction, Skoulou et al. thought that the high temperature accelerates the iron sintering leading to a loss of Fe dispersion [17].

4. Conclusion

Bio-oil pyrolysis and gasification experiments were carried out in HTR and EFR over a wide temperature range. Emphasis was made on the effect of ash content on gas, char and tar yield. Important findings obtained herein are summarized as follows:

- (i) In pyrolysis situation, ash promote the reactions of poymérisation which cause an increase in the char yield with a decrease of the total gas yield.

Also, ash affects considerably the composition of the producer gas, adding the ash involves a significant reduction of CO yield. Whereas, an increase of CO\textsubscript{2} yield is observed. The other gases undergo a slight decrease as notably CH\textsubscript{4} and C\textsubscript{2}H\textsubscript{4}.

- (ii) In gasification situation, a significant decrease of all the gas species has been observed when ash is added to bio-oil. The volatilization of alkalis has probably a negative impact on ash catalytic effect at the high temperature causing a decrease in the yield of gas.
References