Bio-Oil Treatment by Non Thermal Plasma

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1. Introduction
Evolution of the fossil energy resources reveals a great interest for prospecting new energy vectors. Molecular hydrogen (H$_2$) is supposed to have an important role in future worldwide energy vector supply and environmental safe technologies. Traditionally, direct conversion of methane (natural gas) into valuable products such as higher hydrocarbons, liquid hydrocarbons, oxygen-contained compounds and synthesis gas (syngas) received increasing attention. This was motivated in part by the need to utilize natural gas from remote sources and also by novel fuel cell applications.

In contrast to fossil fuels, the use of renewable biomass for energy provides significant environmental advantages such as greenhouse effect reduction and could be a logical choice to replace oil [1]. Biomass conversion is achieved by thermo-chemical processes such as pyrolysis, gasification, and combustion. Pyrolysis which is the thermal decomposition in the absence of oxygen is currently one of the most used techniques for recovering energy from biomass [2-4]. Main products from biomass pyrolysis could be liquid, solid charcoal and gases in different proportion depending on the operation conditions. In general, the process is usually optimized for bio-oil production in well defined conditions for a great number of applications [2]: heat and electricity productions, preparation of chemicals and H$_2$, fuel for transport, etc.

Recently, research interest focuses on the Non Thermal Plasma (NTP) treatment of hydrocarbons and alcohol aimed to improve the yield of hydrogen production [5-15]. NTP, where the electron temperature exceeds the heavy species temperature, could replace catalysts and accelerate chemical reactions due to both temperature and active species effects. NTP reactors present some advantages over the conventional technologies such as their simplicity, compactness, and low energetic cost of the treatment.

In the present paper, we have investigated stationary discharge under non equilibrium conditions as a method for bio-oil conversion. Conversion experiments were conducted with pure and diluted (in water) bio-oils at different flow rates. Preliminary results concerning the gas phase of bio-oils conversion are reported and show that NTP bio-oil treatment was effective in the selective formation of H$_2$, CO, CO$_2$, and CH$_4$. When bio-oil diluted in water was fed in the plasma reactor, H$_2$ mole fraction up to 70% was obtained under conditions of ambient temperature and atmospheric pressure without any catalyst. In addition, high H$_2$ to CO ratios could be obtained and significant modification of physico-chemical properties of the condensable products achieved.

2. Experimental
The bio-oils used in these experiments were resulting of fast wood biomass pyrolysis. The wood biomass was a commercial wood pellets made of mixture of pressed oak and beech sawdust [4]. The viscosity of these bio-oils varied between 0.15 and 0.05 Pa.s depending of the temperature (20 - 40°C). Two samples of bio-oils are treated in these experiments: light and heavy bio-oils (L-oil and H-oil) which are characterized by low and high viscosity, respectively.
The experimental arrangement consists of 4 parts: plasma reactor, high voltage power supply, gas and oil handling system, and analysis system. Figure 1 shows the plasma reactor together with a photography of the plasma created. The Bio-oils used pure or diluted in water, as a source, were introduced using a dosing pump into a cylindrical reactor under atmospheric pressure and room temperature. Experiments were conducted at two bio-oil flow rates: 1.6 and 4 mL h⁻¹.

Fig. 1 Plasma reactor and plasma column photography (2 mm diameter - 10 mm length).

The plasma reactor was powered by a 50 Hz high voltage (15 kV) step-up transformer with leakage flux allowing sinusoidal current waveform with a constant RMS (root mean square) value of 155 mA. In operation, the plasma reactor temperature can reach up to 200°C and the system can handle a maximum operating temperature of 400°C. To ensure uniform gas temperature throughout the setup, sufficient time (30 min) is devoted to attain a steady state. Dry outlet gases were analysed online and H₂, CO, CO₂, CH₄, C₂H₂, C₂H₄, C₂H₆ species were quantified using gas phase chromatography analyzer (GC Varian CP2008). The GC was equipped with Molsieve 5Å and Hayesep A columns and the detection was assured by thermal conductivity (TCD) and flame ionisation (FID) detectors.

The electrical diagnostics were performed using Tektronix current and voltage probes (TCP202 and P5205, respectively). Signals from the probes were recorded on a transient digitizer (Tektronix TDS3034B) and processed on a PC. Typical voltage and current waveforms (u(t) and i(t), respectively) are shown in the figure 2. The mean electrical discharge power P_m is determined from the equation (1) by averaging results over a large number of discharges. In all the cases studied, the mean power is lower than 200 W.

\[ P_m = \frac{1}{T} \int u(t) i(t) \, dt \] (1)
3. Results

Gas analysis results obtained after plasma treatment of samples of light and heavy bio-oils used pure or diluted in water are shown in Table 1. Equilibrium concentrations of reaction products show that bio-oils mainly decomposed into hydrogen (from 55 to 69%), carbon monoxide (from 5 to 33%) and carbon dioxide (from 11 to 25%). The maximum of hydrogen concentration was obtained when bio-oils are diluted in water. On the other hand, in all cases studied, approximately less than 1% of methane and 0.3% of C₂-hydrocarbon species were produced.

<table>
<thead>
<tr>
<th></th>
<th>Light Bio-oil</th>
<th>Heavy Bio-oil</th>
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<tbody>
<tr>
<td></td>
<td>Pure + H₂O</td>
<td>Pure + H₂O</td>
</tr>
<tr>
<td>H₂ (%)</td>
<td>63.53</td>
<td>68.54</td>
</tr>
<tr>
<td>CO (%)</td>
<td>14.50</td>
<td>5.39</td>
</tr>
<tr>
<td>CO₂ (%)</td>
<td>21.53</td>
<td>25.39</td>
</tr>
<tr>
<td>CH₄ (%)</td>
<td>0.38</td>
<td>0.47</td>
</tr>
<tr>
<td>C₂H₂ (%)</td>
<td>0.03</td>
<td>0.08</td>
</tr>
<tr>
<td>C₂H₄ (%)</td>
<td>0.03</td>
<td>0.10</td>
</tr>
<tr>
<td>C₂H₆ (%)</td>
<td>0.00</td>
<td>0.03</td>
</tr>
<tr>
<td>H₂/CO</td>
<td>4.38</td>
<td>12.72</td>
</tr>
</tbody>
</table>

Table 1 Composition of gases at the output of the plasma reactor

One can note that NTP treatment of pure light bio-oils produced higher H₂ and CO₂ concentrations and lower CO, CH₄ and C₂-species concentrations compared to those of pure heavy bio-oils in the same experimental conditions.

When water is added into the plasma, H₂ to CO ratio can be improved by a factor of 3. In that case, O and OH radicals created by the plasma could be effective to oxidize CO into CO₂. Moreover, L-oils or H-oils conversion into CH₄ and C₂-species can be observed by the concentration increasing of these species and could be done by partial oxidation or steam reforming reactions.

In further experiments, we will focused our attention on the kinetics of such a complex media together with the optimization of the H₂ production and energy efficiency.
4. Conclusion

This preliminary study successfully demonstrated that bio-oils were easily decomposed in a stationary discharge under non equilibrium conditions. It was assumed that this was due to the high-energy electrons creating reactive species/radicals by way of collision. Synthesis gas with high content of hydrogen and high H$_2$ to CO ratio was produced. The concentration of hydrogen is higher than the maximum values reported for classical treatment of bio-oils. The content of other gases (especially C$_2$-hydrocarbons) is very low. Further investigations are in progress in order to understand the kinetics of such a complex systems and to improve hydrogen concentration as well as energy efficiency of the process.

5. Acknowledgment

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6. References