Microwave assisted pyrolysis of kraft lignin at reduce pressure in a multimode oven

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MICROWAVE ASSISTED PYROLYSIS OF KRAFT LIGNIN AT REDUCE PRESSURE IN A MULTIMODE BATCH OVEN

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Mont Tremblant 19-24 June 2016
LIGNIN AND KRAFT LIGNIN

- Lignin is the second most abundant natural polymer (up to 30%).
- It is the only aromatic natural polymer.
- It is raised in economical relevance year by year.
- Kraft lignin gained neglectable global market.
- It is used like energy solid fuels, dispersant in high performance conglomerate, for water treatment and for chemicals productions.

RESEARCH AIMS

- Use of Microwave based approach to process Kraft lignin at reduce pressure.
- Improve the recovery of aromatics from lignin.
The heating occurs when dipolar molecules exposed to an electromagnetic field try to rotate in phase with the alternating electric current. Resistance to this rotation on molecular level results in friction between molecules and heat is generated.

Three interaction mechanisms:

1. Dipole reorientation
2. Interfacial or Maxwell-Wagner polarization (multicomponent systems)
3. Conduction (metals and conducting materials)
The energy absorbed is function of the intensity of electromagnetic field and the loss-factor.

In dielectric multi materials MW absorption is different point by point, depending on their characteristics as MW absorber.

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MICROWAVE OVEN PLANT: SET UP B

## EXPERIMENTAL CONDITIONS

<table>
<thead>
<tr>
<th></th>
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<td>58.4</td>
<td>27.1</td>
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PRELIMINARY CHARACTERIZATIONS: $^1$H-NMR

$^1$H-NMR OF ID 5 WITHOUT WATER SIGNAL

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$^{1}$H-NMR ANALYSIS: ALTERNATIVE WAY TO WATER WATER ESTIMATION

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PRELIMINARY CHARACTERIZATIONS: FT-IR ATR

- $\nu_{O-H}$ due to water and carboxylic acid (mainly acetic acid)
- $\nu_{C-H}$ due to the presence of alkyl groups ($\text{CH}_3$, $\text{R-CH}_2$-$\text{Ar}$, ecc.)
- $\nu_{C=O}$ due to the presence of carbonyl and carboxylic compounds
- $\nu_{C=C}$ due to the presence of aromatic ring (ring breathing)

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BIO-OILS CHALLENGE: THE COMPOSITION

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Bio-oils contains up to several hundreds of compounds.

Difficult evaluation of concentrations of different bio-oils components.

A theoretical method to calculate relative response factors (RRF) and concentrations of compounds inside the bio-oils was developed and improved for GC-MS and GC-MS/FID.

Concentration was calculated using the RRF referred to DIPHENYLE as standard:

$$RRF_i = \frac{MW_i \cdot A_i \cdot C_S}{MW_S \cdot A_S \cdot C_i}$$

where $i$ is referred to compound and $s$ to internal standard.

When RRF were not available they were predicted using the contribution factors following the equation:

$$RRF_{calc} i = \frac{rt_S \cdot MW_i \cdot \sum_k (P_k \cdot n_{kS}^Z + Q)}{rt_i \cdot MW_S \cdot \sum_k (P_k \cdot n_{ki}^Z + Q)}$$

$rt$, retention time; $MW$, molecular weight; $P$ and $Z$, parameters to be refined for each group; $n$ number of atoms of carbon, hydrogen, oxygen, aromatic rings, double bonds, ketone groups, carboxylic groups (in acids, esters, anhydride), alcoholic groups, aldehydic groups, and ether groups, $Q$ a constant.

CHARACTERIZATION OF BIO-OILS: QUANTITATIVE GC-MS METHOD

Sample preparation:
- 100 mg of bio-oil or 1 mg of standard compound in 1 mL of acetonitrile
- 1 mg of diphenyle
- Mix with ultrasound bath for 5 min
- filtered onto PTFE filter (0.4 mm)

GC-MS set-up:
- capillary column Petrocol™ DH 24160-U, (100 m length, 0.25 mm diameter, 0.5 µm stationary phase)
- detector quadrupole (EI 70 eV)
- split ratio 1:30
- 298 K for 15 min then heated at 2.5 K/min up to 523 K and kept at this temperature for 15 min


<table>
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<tr>
<th>Standard compounds</th>
<th>RRF found</th>
<th>RRF calc</th>
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<tbody>
<tr>
<td>1 3-Penten-2-one</td>
<td>0.11</td>
<td>0.18</td>
</tr>
<tr>
<td>2  Furural</td>
<td>0.13</td>
<td>0.16</td>
</tr>
<tr>
<td>3  Pyridine</td>
<td>0.16</td>
<td>0.14</td>
</tr>
<tr>
<td>4  Toluene</td>
<td>0.16</td>
<td>0.25</td>
</tr>
<tr>
<td>5  3-Methyl-2-butanone</td>
<td>0.17</td>
<td>0.16</td>
</tr>
<tr>
<td>6  Acetic acid</td>
<td>0.18</td>
<td>0.07</td>
</tr>
<tr>
<td>7  2,4-Pentandiol</td>
<td>0.18</td>
<td>0.26</td>
</tr>
<tr>
<td>8  3,3-Dimethyl-2-butanol</td>
<td>0.19</td>
<td>0.26</td>
</tr>
<tr>
<td>9  Butyraldehyde</td>
<td>0.20</td>
<td>0.10</td>
</tr>
<tr>
<td>10 Valerolactone</td>
<td>0.21</td>
<td>0.29</td>
</tr>
<tr>
<td>11 2-Pentanone</td>
<td>0.21</td>
<td>0.17</td>
</tr>
<tr>
<td>12 Anilin</td>
<td>0.21</td>
<td>0.28</td>
</tr>
<tr>
<td>13 p-Benzoquinon</td>
<td>0.22</td>
<td>0.22</td>
</tr>
<tr>
<td>14 Cyclopentanol</td>
<td>0.25</td>
<td>0.23</td>
</tr>
<tr>
<td>15 Salicylaldehyde</td>
<td>0.31</td>
<td>0.30</td>
</tr>
<tr>
<td>16 Cyclohexanone</td>
<td>0.31</td>
<td>0.31</td>
</tr>
<tr>
<td>17 1-Hydroxy-1-methyclohexane</td>
<td>0.33</td>
<td>0.43</td>
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<tr>
<td>18 Vanilin</td>
<td>0.33</td>
<td>0.41</td>
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<tr>
<td>19 Phenol</td>
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<td>0.29</td>
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<tr>
<td>20 Sesamol</td>
<td>0.38</td>
<td>0.43</td>
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<tr>
<td>21 Guaiacol</td>
<td>0.43</td>
<td>0.34</td>
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<tr>
<td>22 Acetophenone</td>
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<td>0.43</td>
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<tr>
<td>23 p-Xylene</td>
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<td>0.39</td>
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<tr>
<td>24 Cinnamaldehyde</td>
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<td>0.55</td>
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<tr>
<td>25 1,3,5-Trimethylbenzene</td>
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<tr>
<td>26 7-Methylcyclohexadiene</td>
<td>0.55</td>
<td>0.49</td>
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<tr>
<td>27  (+) Carveol</td>
<td>0.66</td>
<td>0.69</td>
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<tr>
<td>28 Benzilidenacetone</td>
<td>0.66</td>
<td>0.68</td>
</tr>
<tr>
<td>29 4-Phenyl-2-butanone</td>
<td>0.67</td>
<td>0.65</td>
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<tr>
<td>30 4-Phenyl-2-butanol</td>
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<tr>
<td>31 Menthol</td>
<td>0.79</td>
<td>0.77</td>
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<tr>
<td>32 Endo (+) borneol</td>
<td>0.85</td>
<td>0.79</td>
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<tr>
<td>33 2,6-Diterbutyl-4-methylphenol</td>
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</tr>
<tr>
<td>34 Phenantrene</td>
<td>1.82</td>
<td>1.85</td>
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</table>

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BIO-OILS CHALLENGE: THE COMPOSITION

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BIO-OILS FROM LIGNIN: RESIDENCE TIME EFFECT

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CONCLUSIONS

- Bio-oils obtained were dark brown liquids and showed a low viscosity and density (close to 1cP and 1 g/mL respectively).
- MAP was carried out in 9 min.
- Maximum yield (37%) was obtained at residual pressure of 0.013 kPa with set-up A.
- and at the same pressure with fractionating when process was carried out in 9 min. Analysis showed the presence multisubstituited aromatic ring and few light hydrocarbons/organic acids from advanced thermal degradation of lignin structure. A degradation mechanism was proposed to explain the result observed.
University of Florence

- Dr. Marco Frediani
- Dr. Luca Rosi
- Prof. Piero Frediani

And a special thank to Alfredo Maione
Thanks for your kind attention!

...ANY QUESTIONS?