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Co-production of bio-oil and propylene through the hydrothermal liquefaction of polyhydroxybutyrate producing cyanobacteria

Jonathan Wagner, a Rachel Bransgrove, b Tracey A. Beacham, b Michael J. Allen, b Katharina Meixner, c Bernhard Drosq, c Valeska P. Ting d and Christopher J. Chuck d*

Supplementary Information

Scheme 1: PHB decomposition pathway to propene and carbon dioxide

1. Yields, ultimate analysis and energy density of oil product phase from HTL of model compounds

<table>
<thead>
<tr>
<th>Compound</th>
<th>300 °C</th>
<th>320 °C</th>
<th>340 °C</th>
<th>360 °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Corn Flour</td>
<td>2.4</td>
<td>3.3</td>
<td>4.0</td>
<td>3.6</td>
</tr>
<tr>
<td>Elemental composition</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C</td>
<td>64.33</td>
<td>67.16</td>
<td>69.41</td>
<td>68.32</td>
</tr>
<tr>
<td>H</td>
<td>4.96</td>
<td>8.54</td>
<td>8.83</td>
<td>7.49</td>
</tr>
<tr>
<td>N</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Energy Density, MJ/kg*</td>
<td>23.34</td>
<td>30.56</td>
<td>32.19</td>
<td>29.47</td>
</tr>
</tbody>
</table>

| Soy Protein       | 16.1   | 24.4   | 21.0   | 28.6   |
| Elemental composition |       |        |        |        |
| C                 | 67.38  | 65.70  | 69.31  | 69.91  |
| H                 | 9.49   | 9.18   | 9.83   | 9.91   |
| N                 | 8.74   | 7.31   | 6.84   | 6.60   |
| Energy Density, MJ/kg* | 33.75  | 32.09  | 35.05  | 35.35  |

| Rapeseed Oil      | 96.3   | 100.1  | 100.6  | 101.3  |
| Elemental composition |       |        |        |        |
| C                 | 75.63  | 74.83  | 74.72  | 69.64  |
| H                 | 12.84  | 13.23  | 11.75  | 12.07  |
| N                 |        |        |        |        |
| Energy Density, MJ/kg* | 36.26  | 37.24  | 35.03  | 36.03  |
2. Product analysis from HTL of PHA-rich cyanobacteria

<table>
<thead>
<tr>
<th></th>
<th>Spirulina</th>
<th>SAn</th>
<th>SAs</th>
<th>SYN</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Solid</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Elemental composition</td>
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<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$C$</td>
<td>5.73</td>
<td>12.34</td>
<td>15.77</td>
<td>38.87</td>
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<tr>
<td>$H$</td>
<td>0.74</td>
<td>2.46</td>
<td>2.85</td>
<td>6.71</td>
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<tr>
<td>$N$</td>
<td>1.05</td>
<td>3.35</td>
<td>4.70</td>
<td>2.97</td>
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<tr>
<td>TGA analysis</td>
<td></td>
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</tr>
<tr>
<td>Ash</td>
<td>nd</td>
<td>61.4</td>
<td>61.2</td>
<td>8.3</td>
</tr>
<tr>
<td>Moisture</td>
<td>nd</td>
<td>3.3</td>
<td>2.8</td>
<td>2.0</td>
</tr>
<tr>
<td>Organic</td>
<td>nd</td>
<td>35.4</td>
<td>35.9</td>
<td>89.7</td>
</tr>
<tr>
<td><strong>Oil</strong></td>
<td>36.9</td>
<td>32.0</td>
<td>31.2</td>
<td>16.6</td>
</tr>
<tr>
<td>Elemental composition</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$C$</td>
<td>71.6</td>
<td>69.8</td>
<td>69.9</td>
<td>70.9</td>
</tr>
<tr>
<td>$H$</td>
<td>9.4</td>
<td>9.5</td>
<td>9.4</td>
<td>8.6</td>
</tr>
<tr>
<td>$N$</td>
<td>7.1</td>
<td>6.1</td>
<td>5.3</td>
<td>4.6</td>
</tr>
<tr>
<td>Energy Density</td>
<td>31.89</td>
<td>34.47</td>
<td>34.22</td>
<td>33.41</td>
</tr>
<tr>
<td><strong>Water Residue</strong></td>
<td>27.3</td>
<td>33.2</td>
<td>23.3</td>
<td>14.8</td>
</tr>
<tr>
<td>Elemental composition</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$C$</td>
<td>40.3</td>
<td>12.4</td>
<td>15.8</td>
<td>68.4</td>
</tr>
<tr>
<td>$H$</td>
<td>6.1</td>
<td>2.5</td>
<td>2.9</td>
<td>5.2</td>
</tr>
<tr>
<td>$N$</td>
<td>8.0</td>
<td>3.4</td>
<td>4.7</td>
<td>5.3</td>
</tr>
<tr>
<td>Ammonia yield</td>
<td>5.7%</td>
<td>2.4%</td>
<td>1.7%</td>
<td>0.6%</td>
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<tr>
<td><strong>Gas</strong></td>
<td>12.6</td>
<td>23.0</td>
<td>17.0</td>
<td>21.2</td>
</tr>
</tbody>
</table>

3. Calculation of theoretical *Spirulina* yields

Theoretical yields from the conversion of *Spirulina* have been calculated based on its biochemical composition, and HTL yields from the conversion of the models representing the three main biochemical compounds found in the algae.

\[
\text{Theoretical Yield (Y}_{T} = A_{CH} x Y_{CH} + A_{P} x Y_{P} + A_{L} x Y_{L}.} \]
Where $Y_T$, denotes the theoretical yield obtained from the conversion of the algae, $A_{CH}$, $A_P$ and $A_L$ stand for the concentration of carbohydrates, protein and lipid in the algae, on a daf basis; and $Y_{CH}$, $Y_P$ and $Y_L$ denote the yields obtained from the HTL of carbohydrates, proteins and lipids (daf basis).

Although the model compounds displayed high purity in their respective biochemical compound fraction, they still included impurities of other biochemical compounds. To correct for this, the yields obtained from the conversion of soy protein, corn flour and rapeseed oil were corrected using a set of three simultaneous equations, as outlined below:

$$Y_{SP} = Y_P \times SP_P + Y_{CH} \times SP_{CH} + Y_L \times SP_L \quad (2)$$

$$Y_{RO} = Y_P \times RO_P + Y_{CH} \times RO_{CH} + Y_L \times RO_L \quad (3)$$

$$Y_{CF} = Y_P \times CF_P + Y_{CH} \times CF_{CH} + Y_L \times CF_L \quad (4)$$

Where $Y_{SP}$, $Y_{RO}$ and $Y_{CF}$ denote the actual yields obtained from the conversion of soy protein, rapeseed oil and corn flour (daf basis), respectively; $SP_P$, $RO_P$ and $CF_P$ stand for the protein concentrations in the three feedstocks (daf basis), and similar denotations were used for the carbohydrate and lipid content.

Rearrange (3):

$$Y_L = \frac{(Y_{RO} - Y_P \times RO_P - Y_{CH} \times RO_{CH})}{RO_L} \quad (5)$$

Insert into (1) and (4):

$$Y_{SP} = Y_P \times SP_P + Y_{CH} \times SP_{CH} + \left((Y_{RO} - Y_P \times RO_P - Y_{CH} \times RO_{CH})/RO_L\right) \times SP_L \quad (6)$$

$$Y_{CF} = Y_P \times CF_P + Y_{CH} \times CF_{CH} + \left((Y_{RO} - Y_P \times RO_P - Y_{CH} \times RO_{CH})/RO_L\right) \times CF_L \quad (7)$$

Rearrange (6) and (7) for $Y_{CH}$:

$$Y_{CH} = (Y_{SP} \times RO_L - Y_P \times SP_P \times RO_L - Y_{RO} \times SP_L + Y_P \times RO_P \times SP_L)/(SP_{CH} \times RO_L - RO_{CH} \times SP_L) \quad (8)$$

$$Y_{CH} = (Y_{CF} \times RO_L - Y_P \times CF_P \times RO_L - Y_{RO} \times CF_L + Y_P \times RO_P \times CF_L)/(CF_{CH} \times RO_L - RO_{CH} \times CF_L) \quad (9)$$

Combine (8) and (9):

$$Y_{CH} = (Y_{CF} \times RO_L - Y_P \times CF_P \times RO_L - Y_{RO} \times CF_L + Y_P \times RO_P \times CF_L)/(CF_{CH} \times RO_L - RO_{CH} \times CF_L) = (Y_{SP} \times RO_L - Y_P \times SP_P \times RO_L - Y_{RO} \times SP_L + Y_P \times RO_P \times SP_L)/(SP_{CH} \times RO_L - RO_{CH} \times SP_L) \quad (10)$$

Rearrange for $Y_P$:

$$Y_P = \frac{(Y_{CF} \times RO_L \times (SP_{CH} \times RO_L - RO_{CH} \times SP_L) + Y_{RO} \times RO_L \times (SP_{L} \times CF_{CH} - CF_L \times SP_{CH}) + Y_{SP} \times RO_L \times (RO_{CH} \times CF_L - CF_{CH} \times RO_L))}{(CF_{P} \times RO_L \times (SP_{CH} \times RO_L - RO_{CH} \times SP_L) + RO_P \times RO_L \times (SP_{L} \times CF_{CH} - CF_L \times SP_{CH}) + SP_{P} \times RO_l \times (RO_{CH} \times CF_L - CF_{CH} \times RO_L))} \quad (11)$$

Now the corrected HTL yields for the protein, carbohydrate and lipid fractions in the algae can be calculated using equations 11, 9 and 5, respectively, and used in equation 1, to determine the theoretical yield for the HTL of the algae.
4. NMR analysis of vegetable oil conversion products