PERFORMANCE OF CARBOXYDOTHERMUS HYDROGENOFORMANS IN A GAS-LIFT REACTOR FOR SYNGAS UPGRADING INTO H₂

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INTRODUCTION: WASTE TODAY

• 2012: 3 billion urbanites ⇔ 1.2 kg MSW / person / day (1.3 billion tonnes per year)

• 2025: 4.3 billion urbanites ⇔ 1.42 kg MSW / person / day (2.2 billion tonnes per year)

• Public Health and environmental concerns

• Actual (downstream) solid waste management:
  • Recycling
  • Anaerobic digestion / Composting
  • Incineration
  • Landfill disposal

An emerging waste to energy technology: Gasification

Inc.: AlterNRG, Dynamis Energy, Enerkem, InEnTec, Plasco Energy Group...

“Conversion at high temperature (800 – 1800°C) at atmospheric or elevated pressures (up to 33 bar) of any carbonaceous fuel to a gaseous product with a useable heating value: syngas (CO, H₂, CO₂)”


http://www.zeep.com/images/gasificationproducts.gif
http://www.syngest.com/images/img_HargestGas.gif
INTRODUCTION: THE WATER-GAS SHIFT REACTION

$$\text{CO} + \text{H}_2\text{O}_{(g)} = \text{H}_2 + \text{CO}_2 \quad \Delta G_0 = -20\text{kJ/mol}$$

Conventional method: catalysts

Two-step process: Nickel ($\approx 350^\circ\text{C}$) and Metal Catalyst ($\approx 200^\circ\text{C}$)
Catalysts need to be regenerated (energy intensive & costly)
High intolerance to sulfur

Innovative approach: a biological catalyst, *Carboxydothermus hydrogenoformans*

Hyperthermophilic (70°C) with High duplication time ($\approx 2$ hours)
CO as sole source of Carbon & Energy
High tolerance to sulfur
High $\text{H}_2$ yield ($\geq 95\%$)

Limitations: low biomass density & low mass transfer of CO at 70°C

Building a continuous system for the biological water-gas shift reaction that:

1. Overrides CO mass transfer limitation
2. Sustains high CO loading (despite the cell low density)
3. Achieves high efficiency conversion of CO into H₂
4. Is reliable (Stable over time, difficult to contaminate)
5. Is economically viable (low OPEX & CAPEX)

?
MATERIAL AND METHODS: SET-UP AND OPERATION

**Set Up**
- 35 L gas-lift reactor, @70°C
- 100% CO & Basal Mineral Medium

**Operation**
- 3 months
- 2 Phases: unsupported vs. supported (1.0 g.L\(^{-1}\) bacto-peptone) growth
- Gradually augmenting CO loading
Schematic representation of the Gas-lift reactor set-up:

1) N2 gas cylinder;
2) CO gas cylinder
3) Gas flow meter
4) Flow controller
5) Gas sampling port
6) Gas Lift Reactor
7) Temperature sensor
8) pH probe
9) Liquid sampling port
10) Electrical heating jacket
11) Temperature controller
12) pH meter and controller
13) Pressure gauge
14) Heat exchanger
15) water bath P
16) Pressure release valve
17) Venting
18) recirculation gas pump
RESULTS: VOLUMETRIC MASS TRANSFER COEFFICIENT

- \( k_L a \) varies linearly with \( Q_{CO} \) regardless of the gas recirculation rate
- Gas recirculation rate had a higher impact than on \( k_L a \) that of \( Q_{CO} \)
- Measured \( k_L a \) (\( \approx 2 \, h^{-1} \)) was lower than values reported in literature (49 – 91 \( h^{-1} \)): probably high \( T^\circ C \)

CONCLUSION

1.5 L.min\(^{-1}\) was used as the standard recirculation rate for the rest of the experiments

Effect of the gas recirculation and CO loading rates on the volumetric mass transfer coefficient (\( k_L a \)) in the abiotic gas-lift reactor

Munasinghe, P. C., & Khanal, S. K. (2010). Syngas fermentation to biofuel: evaluation of carbon monoxide mass transfer coefficient (\( k_L a \)) in different reactor configurations. Biotechnology progress, 26(6), 1616–21
### RESULTS: CO REMOVAL PERFORMANCE

<table>
<thead>
<tr>
<th>Phase</th>
<th>Run</th>
<th>Q&lt;sub&gt;CO&lt;/sub&gt;&lt;sup&gt;a&lt;/sup&gt;</th>
<th>R&lt;sub&gt;CO&lt;/sub&gt;&lt;sup&gt;a&lt;/sup&gt;</th>
<th>E&lt;sub&gt;CO&lt;/sub&gt;&lt;sup&gt;a&lt;/sup&gt;</th>
<th>Y&lt;sub&gt;H2&lt;/sub&gt;&lt;sup&gt;a&lt;/sup&gt;</th>
<th>Q&lt;sub&gt;gas/Q&lt;sub&gt;CO&lt;/sub&gt;&lt;/sup&gt;</th>
<th>d&lt;sub&gt;CO&lt;/sub&gt;&lt;sup&gt;a&lt;/sup&gt;</th>
<th>A&lt;sup&gt;a&lt;/sup&gt;</th>
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<tr>
<td></td>
<td>#</td>
<td>days</td>
<td>mol.L&lt;sub&gt;rxxr&lt;/sub&gt;-1.d&lt;sup&gt;-1&lt;/sup&gt;</td>
<td>mol.L&lt;sub&gt;rxxr&lt;/sub&gt;-1.d&lt;sup&gt;-1&lt;/sup&gt;</td>
<td>%</td>
<td>%</td>
<td>mmol.L&lt;sup&gt;-1&lt;/sup&gt;</td>
<td>mol&lt;sub&gt;CO&lt;/sub&gt;-g&lt;sub&gt;VSS&lt;/sub&gt;-1.d&lt;sup&gt;-1&lt;/sup&gt;</td>
</tr>
<tr>
<td>Unsupported Growth</td>
<td>1</td>
<td>6 – 19</td>
<td>0.08</td>
<td>0.05 ± 0.001</td>
<td>64.0 ± 0.6</td>
<td>74.6 ± 1.8</td>
<td>38</td>
<td>0.11 ± 0.03</td>
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<td>2</td>
<td>22 – 32</td>
<td>0.05</td>
<td>0.04 ± 0.0002</td>
<td>78.9 ± 0.5</td>
<td>83.3 ± 1.6</td>
<td>63</td>
<td>0.08 ± 0.02</td>
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<tr>
<td>Supported Growth</td>
<td>3</td>
<td>33 – 40</td>
<td>0.05</td>
<td>0.05 ± 0.0001</td>
<td>90.4 ± 0.3</td>
<td>96.7 ± 2.2</td>
<td>63</td>
<td>0.05 ± 0.05</td>
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<td>4</td>
<td>40 – 48</td>
<td>0.08</td>
<td>0.07 ± 0.001</td>
<td>82.8 ± 1.2</td>
<td>95.1 ± 0.9</td>
<td>38</td>
<td>0.05 ± 0.04</td>
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<td>5</td>
<td>48 – 55</td>
<td>0.13</td>
<td>0.10 ± 0.0003</td>
<td>76.4 ± 0.2</td>
<td>96.3 ± 0.8</td>
<td>25</td>
<td>0.07 ± 0.01</td>
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<td>6</td>
<td>55 – 61</td>
<td>0.17</td>
<td>0.12 ± 0.001</td>
<td>72.1 ± 0.7</td>
<td>96.6 ± 0.7</td>
<td>19</td>
<td>0.04 ± 0.04</td>
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<td>7</td>
<td>61 – 65</td>
<td>0.23</td>
<td>0.16 ± 0.001</td>
<td>69.2 ± 0.6</td>
<td>94.2 ± 0.9</td>
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<td>0.00 ± 0.00</td>
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<td>8</td>
<td>65 – 68</td>
<td>0.30</td>
<td>0.17 ± 0.003</td>
<td>57.1 ± 0.9</td>
<td>94.7 ± 0.7</td>
<td>11</td>
<td>0.00 ± 0.00</td>
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</table>

**Unsupported Growth**

Y<sub>H2</sub> constant ≈ 80%

E<sub>CO</sub> max (79%) obtained at Q<sub>CO</sub> = 0.05 mol.L<sub>rxxr</sub>-1.d<sup>-1</sup>

Q<sub>CO</sub> max = 0.08 mol.L<sub>rxxr</sub>-1.d<sup>-1</sup>

If Q<sub>CO</sub> = 0.13 mol.L<sub>rxxr</sub>-1.d<sup>-1</sup> → activity drop and reactor failure (biologically limited)

**Supported Growth (peptone)**

Y<sub>H2</sub> constant ≈ 95%

E<sub>CO</sub> max (90%) obtained at Q<sub>CO</sub> = 0.05 mol.L<sub>rxxr</sub>-1.d<sup>-1</sup>

Q<sub>CO</sub> max = 0.30 mol.L<sub>rxxr</sub>-1.d<sup>-1</sup>

If Q<sub>CO</sub> = 0.46 mol.L<sub>rxxr</sub>-1.d<sup>-1</sup> → activity drop and reactor failure (biologically limited)
RESULTS: CO REMOVAL PERFORMANCE

- Logarithmic relationship between $Q_R : Q_{CO}$ and CO Conversion Efficiency and Specific Activity
- mass transfer limited $< Q_R : Q_{CO} = 40 <$ biologically limited

Performance of the gas-lift reactor under supported growth of *C. hydrogenoformans*. 
RESULTS: *C. HYDROGENOFORMANS* GROWTH PROFILE

- Prior peptone addition: plateau $\approx 23$ mg$_{\text{VSS}}$.L$^{-1}$ with growth rate of 0.10 ± 0.01 h$^{-1}$
- After peptone addition, threshold exceeded (4.6x): up to 106 mg$_{\text{VSS}}$.L$^{-1}$ with growth rate of 0.01 ± 0.003 h$^{-1}$
- Final concentration remained low: 0.1 g$_{\text{VSS}}$.L$_{\text{rxr}}^{-1} < <$ previous studies (sessile growth)

*C. hydrogenoformans* concentration (diamonds) in the gas-lift bioreactor as a function of time and CO feeding rate (bold line) modification prior to and after the medium complementation with peptone at 1.0 g·L$^{-1}$ (vertical arrow)

CONCLUSION

• Promising technology: high and stable performances ($Y_{H_2}$, $E_{CO}$, A)

• Importance of 2 parameters: bacto-peptone and $Q_R:Q_{CO}$ ratio

• With biomass concentration of 0.106 g$_{VSS}$.L$_{rxr}^{-1}$ and bioactivity of 2.7 mol$_{CO}$.g$_{VSS}^{-1}$.d$^{-1}$ $\Leftrightarrow$ maximal volumetric CO conversion ca. 0.28 mol$_{CO}$.L$_{rxr}^{-1}$.d$^{-1}$ (8m$^3$.m$_{rxr}^{-3}$.d$^{-1}$)

• Low cell density affected the volumetric activity (18x lower than sessile growth) $\Leftrightarrow$ limitation for higher $Q_{CO}$

• For scale up, gas-lift should be coupled with biofilm based technology (beads) for higher: cell density, biomass retention and volumetric activity
ACKNOWLEDGMENT

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