Supercritical Water
Biomass Gasification:
Fuel Gas from Waste

Dr. Paul Hamley
Clean Technology Group
School of Chemistry   University of Nottingham
www.nottingham.ac.uk/supercritical
Menu

• Waste Sources
• Gasification Technologies
• Properties of Supercritical Water (SCW)
• SCW Gasification – Process and Potential
Waste Sources

- Animal waste
- Animal carcasses
- Domestic / Municipal
- Forestry
- Packaged food
- Vegetable
Gasification Technologies

<table>
<thead>
<tr>
<th>Temperature</th>
<th>Pressure</th>
</tr>
</thead>
<tbody>
<tr>
<td>1200°C</td>
<td>220 Atm</td>
</tr>
<tr>
<td>1000°C</td>
<td>220 Atm</td>
</tr>
<tr>
<td>800°C</td>
<td>220 Atm</td>
</tr>
<tr>
<td>600°C</td>
<td>220 Atm</td>
</tr>
<tr>
<td>400°C</td>
<td>220 Atm</td>
</tr>
<tr>
<td>200°C</td>
<td>220 Atm</td>
</tr>
</tbody>
</table>

- Conventional
- Pyrolysis
- Low temperature
- Pyrolysis (charcoal)
- Supercritical water
- Supercritical water + catalyst
Pyrolysis

• 400-550°C, 1-5 bar

• Anaerobic

• Slow – charcoal

• Fast – dark brown mobile liquid
Conventional Gasification

- 700 – 1200°C
- Need to drive off water before gasification
- Water content can be ca. 90% by mass
- Inefficient for high water content materials
- Suited to dry materials (e.g. sawdust)
- Problems:
  - Char (always at 1 bar), tar
## Tar Avoidance Options

- >1000°C
- Dolomite
- Alkali metal oxides
- Catalyst
- Secondary air injection
Char

- Result of polymerisation of fragments broken down by hydrolysis
- Builds up at low temperatures
- Can be burnt off at high T

Avoidance strategies
- Rapid heating zone
- Catalyst
- SCW
Properties of Water

- Covalent molecule
- Extensive hydrogen bonding
- Dissociation: Acid/Base
- Dielectric constant
- Unusual properties of ice
A significant change of the dielectric constant can be obtained by changing P and T. 

Change of $\varepsilon$ with P and T increase the dissolving power. At 300°C, the $H_2O$ is similar to acetone: dissolving organic compounds and precipitating inorganic salts.
Supercritical Water

- $T_c$ 374 °C; $p_c$ 218 atm.
- $\text{H}_2\text{O}$, 374°C
- Hexane
  - $\varepsilon$ 6
  - 1.8
- $\rho$ 0.3
- 0.8

- Organics dissolve; salts precipitate
- $O_2$ is miscible with $H_2O$ above $T_c$
The ionic product ($K_w$)

$K_w$ depends significantly on the temperature and/or pressures.

$$KW = [H^+] [OH^-]$$

As the dissociation proceeds, the nature of the water itself changes. Water becomes an **acidic** or **alkaline catalyst**.

$-\log K_w = 11$

$-\log K_w = 14$

Optimisation of acid/based-catalysed reaction by $P$ and $T$

$K_w$ depends significantly on the temperature and/or pressures.
SCW Gasification

- SC Water miscible with nonpolar organic compounds
- Self dissociation – high OH⁻
- Hydrolysis

- 600-800°C (no catalyst)
- 500-650°C (with metal catalyst)
- 220-250 bar – gases produced at pressure
SCW Gasification

- No need to drive off water
- Suitable for high moisture content materials
- Optimum 700°C, 3% aqueous feedstock
  100% gasification achievable
- Need energy source for preheating incoming feedstock slurry to ca. 400°C
sc Water conditions are routinely in use

- Ratcliffe-on-Soar Power Station
  - 4x 500MW Steam Turbines
    - 165 bar
    - 568°C
Heating Energy

• Externally
  Burn portion of biomass to heat incoming slurry

• Internally
  Inject $O_2$ in first stage, combust part of feed in SCW
Supercritical Water Gasification Process

- Feed Solution
  - 400-500°C
- Air
  - 600-700°C
- Gas Saturated water 250 bar
- Gas 250 bar
- Power generation
- Gas 1 bar
  - water
Supercritical Water Reactor
Feedstocks

- Dry waste – thermal gasification optimum
- Wet waste – supercritical water optimum


Bulbs
Cabbage
Cereal residue
Distillers dried grain
Ethanol fermentation residue
Food waste, potato waste
Food packaging
Manure
Sawdust, wood
Straw
Sugarcane bagasse
Chemical Composition

- Cellulose
- Hemicellulose
- Proteins
- Lignin
  - waste product of paper pulping
  - difficult to process
  - reduces $H_2$ yield
## Feedstocks

<table>
<thead>
<tr>
<th></th>
<th>Glucose</th>
<th>Trester</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(Sparqle, NL)</td>
<td>(Winegas project)</td>
</tr>
<tr>
<td></td>
<td>Mol%</td>
<td>Vol%</td>
</tr>
<tr>
<td>H₂</td>
<td>54</td>
<td>H₂</td>
</tr>
<tr>
<td>CH₄</td>
<td>3</td>
<td>CH₄</td>
</tr>
<tr>
<td>CO₂</td>
<td>34</td>
<td>CO₂</td>
</tr>
<tr>
<td>CO</td>
<td>3</td>
<td>CO</td>
</tr>
<tr>
<td>Cₓ</td>
<td>0</td>
<td>Cₓ</td>
</tr>
</tbody>
</table>

Penninger JML et al  
EU Project CRAF-1999-70995
Gas Optimisation

- Hydrogen
  Favoured at higher temperature
  Water – gas shift

- Methane
  Lower temperature
  Ni Catalyst (Kruse, FZK)
Gas Use

• Gases are pre scrubbed by water

• No SOx, NOx in SCWO; (converted to corresponding acids)

• Claimed gases are “turbine suitable”

• At 250 bar, CO$_2$ sequestration easy
CHOREN Industries
Carbo-V Process

Biomass $\rightarrow$ gas + tar + char

1. gas
2. pulverisation
3. syngas
4. compression
5. F-T synthesis

Synthetic diesel fuel

www.choren.com
Routes to Syngas

• Steam Reforming: $\text{CH}_4 + \text{H}_2\text{O} \rightarrow \text{CO} + 3\text{H}_2$

• Partial Oxidation: $\text{CH}_4 + 3/2\text{O}_2 \rightarrow \text{CO} + 2\text{H}_2\text{O}$

• Water Gas Shift: $\text{CO} + \text{H}_2\text{O} \rightarrow \text{CO}_2 + \text{H}_2$
Fischer-Tropsch

• Step 1
  Production of syngas  [CO + H2]

• Step 2
  Syngas to a broad range hydrocarbon stream
  \[ CO + 2H_2 \rightarrow [-CH_2-] + H_2O \]
150,000 barrels/day

SASOL II and III
Who & Where?

SCW expertise:
- China, Japan
- US – PNW Labs / Hawaii
- EU – Austria, Germany, Holland
- Vienna Institute of Technology
- CHOREN industries
- Sparql
- Univ Twente
- UK
- SC Water at Nottingham, Birmingham
  [Hamley, Poliakoff] [Al-Duri]
- Pyrolysis expertise at Aston
  [Tony Bridgwater]  www.aston-berg.com
Acknowledgements

• Professor Martyn Poliakoff, F.R.S.
• Dr. Eduardo Verdugo
• Dr. Thomas Ilkenhans

• Invista Performance Technologies
• National Non Food Crops Centre
• Beacon Energy
• Chematur A.G.