Syngas from renewables

Production of green methanol

Jim Abbott, JMPT

2015 European Methanol Policy Forum

Brussels, 14 Oct 2015
Renewable energy usage

1.1 Renewable power generation by technology

- **2000**: 2,700 TWh
  - Bioenergy: 220 TWh
  - Geothermal: 360 TWh
  - Wind: 723 TWh
  - Ocean: 1,566 TWh
  - Solar: 3,516 TWh
  - Hydropower: 4,102 TWh

- **2015 projection**: 4,571 TWh
  - Bioenergy: 2,864 TWh
  - Geothermal: 1,566 TWh
  - Wind: 723 TWh
  - Ocean: 1,566 TWh
  - Solar: 3,516 TWh
  - Hydropower: 4,102 TWh

Progress of renewable power use towards 2020 2°C target
[reproduced from Tracking Clean Energy Progress 2013, IEA]

- **14%** Annual growth of renewables 2000 - 2015
- **13%** Required annual growth of renewables to 2020

Legislated targets for ‘green’ fuels
Market for ‘green’ chemicals
Methanol in a carbon neutral cycle

1. Green methanol from biomass gasification

2. Green methanol from renewable electricity

Beyond Oil and Gas: The Methanol Economy [Olah et al., Wiley, 2011]
Syngas from biomass gasification

- High yield – uses ‘not for food’ biomass/waste resources
  - Efficient power production
  - Building block for chemicals, fuels – e.g. methanol

Syngas from biomass gasification:

- Biomass
  - Fluidizing oxidant
  - Fluidized bed
  - Freeboard
  - Orifice plate
  - Windbox
  - Raw syngas
Gasification is a flexible process to convert a wide range of biomasses to syngas from which useful chemicals can be efficiently produced.
Bio-syngas from gasification

**Review of technology for the gasification of biomass and wastes, E4Tech, June 2009**

**Low temperature gasifiers**
- Low pressure, inexpensive
- Particulate feed

**High temperature gasifiers**
- High pressure, expensive
- Powder feed – difficult for biomass

Gasifier capacity (odt/day biomass input):
- 10tpd
- 100tpd
- 1000tpd
- 10000tpd
- Methanol

Entrained flow
- High temp, no tar

Pressurized BFB, CFB & dual
- Low temp, with tar

Atmospheric CFB & dual
- High temp, no tar

Plasma
- High temp, no tar

Atmospheric BFB
- Low temp, with tar

Updraft fixed bed
- Low temp, with tar

Down draft fixed bed
- Low temp, With tar
## Syngas from low temperature gasifiers

### Tars & aromatics
- Downstream fouling and poisoning
  - Equipment & catalysts
  - Downstream effluents
  - Represent loss of product

### Methane and light hydrocarbons
- Represent loss of product
- Represent inerts in downstream syngas conversion processes

### Critical to convert (or remove) tars

On ‘dry’ and ‘N₂’ free basis

* + other contaminants
halides, alkali metals, HCN

### Methane and light hydrocarbons

<table>
<thead>
<tr>
<th>Component</th>
<th>Unit</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH₄, C₂⁺</td>
<td>%</td>
<td>2-15</td>
</tr>
<tr>
<td>CO</td>
<td>%</td>
<td>10-45</td>
</tr>
<tr>
<td>CO₂</td>
<td>%</td>
<td>10-30</td>
</tr>
<tr>
<td>H₂</td>
<td>%</td>
<td>6-40</td>
</tr>
<tr>
<td>NH₃</td>
<td>%</td>
<td>0.2</td>
</tr>
<tr>
<td>C₆H₆/tars</td>
<td>g/Nm³ (oz/scf)</td>
<td>1-40 (0.009-0.37)</td>
</tr>
<tr>
<td>H₂S*</td>
<td>ppmv</td>
<td>20-200</td>
</tr>
<tr>
<td>Dust</td>
<td>g/Nm³ (oz/scf)</td>
<td>0-10 (0-0.93)</td>
</tr>
<tr>
<td>Temperature</td>
<td>°C (°F)</td>
<td>550-900 (1022-1652)</td>
</tr>
<tr>
<td>Pressure</td>
<td>Bara (psia)</td>
<td>1-5 (14.5-72.5)</td>
</tr>
</tbody>
</table>

Highly desirable to steam reform

Methane and light hydrocarbons
For downstream conversion processes
The amazing tar reformer

Syngas (with tars, aromatics, S, NH3, contaminants)

- Coated, Shaped catalyst
  - High GSA, Low PD

- Coated monolith catalyst
  - High GSA, Low PD
  - For dusty gas

\[
\text{Anthracene} + 15\text{H}_2\text{O} \rightarrow 9\text{CO} + 3\text{CO}_2 + 16\text{H}_2 + 2\text{CH}_4
\]

650-850°C

Oxygen

- Oxygen burner
  - Good mixing

\[
\text{CH}_4 + \text{H}_2\text{O} \rightarrow \text{CO} + 3\text{H}_2
\]

\[
\text{CO} + \text{H}_2\text{O} \rightarrow \text{CO}_2 + \text{H}_2
\]

800 - 1000°C

Tar reformer

Tar free syngas
Tar reforming catalyst

Advantages of PGM

- Faster inherent kinetics
- Slower sintering of metal crystallites
- Much superior resistance to sulphur
- Precision coating
  - Applies metal only where effective
- Recovery and recycle of PGM
- Regenerable

Catalysis Today 214 (2013) 74-81,
[Steele, Poulston, Magrini-Blair, Jablonski]
Methane conversion – oak derived syngas

(1) Ni catalyst (~20% CH₄ convn.)
(2) PGM catalyst (80-85% CH₄ convn.)
T = 850-900°C
H₂S = 10-15 ppmv

PGM catalyst has stable Long-term performance


Raw gas → Ni → PGM → Reformed gas
Industrial application of tar reforming

- Tar reforming in CHP
  - Market developing now
  - Typically smaller scale
  - 0.5 – 20 MW\textsubscript{el}

JM tar reforming catalyst installed in Ecorel 1MW\textsubscript{el} biomass CHP plant
Methanol from bio-syngas
Methanol from bio-syngas

Import of hydrogen improves carbon efficiency
Methanol case study

- Basis - 4300 odtd wood feed & low temperature gasification
- Flowsheet
  - Tar scrubbing comparison vs tar & methane reforming with Ni or pgm catalyst
  - Water gas shift and carbon dioxide removal

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Tar removal process</th>
<th>Temperature °C</th>
<th>Oxygen MTPD</th>
<th>Methanol MTPD</th>
</tr>
</thead>
<tbody>
<tr>
<td>None</td>
<td>Solvent washing</td>
<td>n/a</td>
<td>0</td>
<td>1334</td>
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<tr>
<td>Nickel</td>
<td>Tar &amp; CH₄ reforming</td>
<td>950</td>
<td>496</td>
<td>1760</td>
</tr>
<tr>
<td>PGM</td>
<td>Tar &amp; CH₄ reforming</td>
<td>775</td>
<td>286</td>
<td>1877</td>
</tr>
</tbody>
</table>

Catalysis Today 214 (2013) 74-81, [Steele, Poulston, Magrini-Blair, Jablonski]

- Tar and methane reforming delivers 30-40% more methanol
  80% methane conversion
- PGM vs nickel catalyst
  45% less oxygen
  5-10% more methanol
The growth of power from wind and solar

Share of renewables in German electricity consumption

German power generation mix 2013

The German Energiewende and its climate paradox – causes and challenges
[Agora Energiewende, Graichen, Berlin]
Power balancing: the supply side

Recreated from Rapid Response Electrolysis [ITM Power, 2013, Hannover]

- Grid balancing and stability problems occur typically when share of renewables is >20%
- This leads to curtailment of power
Electricity storage technologies

- Power to chemicals/fuels (gas, liquids) is an efficient, bulk energy storage process

Recreated from Power to gas webinar [ITM Power, 2014]
Electrolysis features (PEM*)

- Dynamically responsive (seconds)
- Can be operated to provide $\text{H}_2$ at high pressure
- High efficiency, low temperature process
  - 75-80% of electrical energy used to split water
- Now scaled up to 1-2MW modules
- Projected costs (p/kWhr consumed) falling
  - Larger scale equipment
  - Increasing manufacturing capacity

* Proton exchange/ polymer electrolyte membrane
H₂ from green power by electrolysis

- Methanol synthesis from H₂ and CO₂
  - JM industrial experience
- Purification of CO₂ required

Renewable or Fossil CO₂ → Methanol synthesis

Wind → Solar → PEM electrolysis

\[
\begin{align*}
\text{H}_2\text{O} & \rightarrow 2\text{H}^+ + \frac{1}{2}\text{O}_2 + 2\text{e}^- \quad \text{(Anode)} \\
2\text{H}^+ + 2\text{e}^- & \rightarrow \text{H}_2 \quad \text{(Cathode)} \\
\text{H}_2\text{O} & \rightarrow \text{H}_2 + \frac{1}{2}\text{O}_2 \quad \text{(Total Reaction)}
\end{align*}
\]
Methanol from renewable H₂ and CO₂

- Technology requirements
  - Optimized designs and catalysts
    - Methanol from CO₂/H₂ only
  - Flexibility/agility
    - For fast load change
    - High conversion over wide operating range

- Reduced CAPEX for small scale
  - 10 – 100 MTPD methanol
  - Skid mounting & miniaturization

[www.carbonrecycling.is]
Summary

• Low carbon energy and fuels continue to be a key requirement for 2020 sustainability targets and beyond.
• Technologies to produce green power, fuels and chemicals are developing
  • From renewable power via electrolysis and carbon dioxide recovery
  • From biomass-derived syngas.
• Johnson Matthey is developing catalysis & technology
  • In bio-syngas purification and conditioning
  • For methanol production from renewable power