Thermo-chemical conversion of biomass – a route for liquid fuels

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Conceived in 1896 by the inspired vision of the pioneering industrialist Jamsetji Tata

- Established in 1909 as a Trust (Charitable Endowments Act 1890)
- Deemed University from 1957
- Funded by MHRD since 1993
Vision

Founder’s mandate: Institute designed to promote original investigations in all branches of learning and to utilise them for the benefit of India.

21st century: to be among the world’s foremost academic institutions through the pursuit of excellence and the promotion of innovation.
## Composition of biomass

<table>
<thead>
<tr>
<th>Element</th>
<th>Mass fraction (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carbon</td>
<td>52.02</td>
</tr>
<tr>
<td>Nitrogen</td>
<td>0.12</td>
</tr>
<tr>
<td>Sulphur</td>
<td>0.42</td>
</tr>
<tr>
<td>Hydrogen</td>
<td>6.55</td>
</tr>
<tr>
<td>Oxygen</td>
<td>41.43</td>
</tr>
</tbody>
</table>

### Chemical Composition

\[
\text{CH}_{1.4}\text{O}_{0.6}
\]

### Molecular weight

27.89 kg kmol\(^{-1}\)

For liquid fuels – increase the Hydrogen to carbon ratio
Biomass conversion process

Biomass

Bio-chemical conversion platform
Hydrolysis and fermentation

Residues

Combined heat and power

By products

Thermo-chemical conversion platform
Combustion, pyrolysis, gasification

Fuels, Chemicals and other by-products

Sugar, Lignin

CO, H₂, Bio-oil
Biological and Thermo-chemical conversion process

- corn ethanol: 49% as baseline
- cellulosic ethanol: 50%
- butanol: 48%
- ester-diesel: 35%
- sugar: 57%
- methane: 65%
- hydrogen: 60%
- methanol: 54%
- dimethylether: 52%
- FT-diesel: 51%
- FC-power: 45%
- BIGCC-power: 40%
- boiler-power: 32%
Natural available substances with Hydrogen as an element

• Water (H₂O)
  • Electrolysers
    • \(2\text{H}_2\text{O} \rightarrow 2\text{H}_2 + \text{O}_2\)
    • Theoretical H₂ yield is about 100 g/kg of water

• Biomass (C_{1.0} 0.7(H₂O))
  • Bio-chemical and
  • Thermo-chemical
Thermo-chemical conversion - Overall process chemistry for liquid fuels

- $C_{1.0} 0.7(H_2O)$ → C: H 1:1.4
- Air gasification → CO : H$_2$ 1:1
- Oxy-Steam gasification → CO : H$_2$ 1:3
- $CH_3OH$ → C:H 1:4
- $C_2H_5OH$ → C:H 1:3
Possible routes from Biomass to biofuels

• Biological conversion
  • Biogas – biomethane – hydrogen - Methanol

• Thermo-chemical conversion
  • Biomass – Producer gas – Electricity – Electrolyser
  • Biomass – syngas – methanol

• Energy intensive of adding hydrogen

Electrolyser > Biological ~ Thermo-chemical
Thermo-chemical conversion

**Gasification**
- Biomass to mixture of gas and separating hydrogen
- $\text{C}_{1.0} 0.7(\text{H}_2\text{O}) + 0.2 \text{ O}_2 + \text{H}_2\text{O} \rightarrow 1.7\text{H}_2 + \text{CO}_2$
- Theoretical limit $150 \text{ g of } \text{H}_2/\text{kg of biomass}$

**Air gasification**
- $\text{C}_{1.0} 0.7(\text{H}_2\text{O}) + 0.2 + 3.76 \text{ N}_2 \rightarrow 0.2 \text{ H}_2 + 0.2 \text{ CO} + 0.02 \text{ CH}_4 + 0.12\text{CO}_2 + 0.46\text{N}_2$
- Here about $40 – 45 \text{ g of hydrogen per kg of biomass}$

**Oxy-steam**
- $\text{C}_{1.0} 0.7(\text{H}_2\text{O}) + x\text{O}_2 + y\text{H}_2\text{O} \rightarrow 0.25-502 \text{ H}_2 + 0.12 – 0.25 \text{ CO} + 0.04 – 0.05\text{CH}_4 + 0.15 - 0.25\text{CO}_2$
- Up to $100 \text{ g of hydrogen per kg of biomass}$

Challenges - Establishing clean gas and scale-up
Brief history on the gasification technology at IISc

- Gasification research commenced in 1980’s
  - Emphasis was on 5 hp diesel pump sets
- Over 450 Man-Years of R&D effort
- Evolved **State-of-the art** technology
- Undergone critical third party evaluation – by various groups
- Licensed the technology in India and abroad

- **At IISc (Open top down draft technology - distinctly different from other designs)**
  - Multi-fuel capability
  - Power range 5 – 2000 kWe
  - Both power and high quality thermal applications
  - Over **450,000** hours of operational experience
  - Annual operational hours ~ 7000 hours
  - Gas cleaning system for **turbo-charged engines**
  - Developed **indigenous engines for producer gas operation**
Open top Dual air down draft –
The IISc design

- R and D started early 1980’s
- Approx 500 man year’s of effort
- Over 10,000 components

- Features
  - 0.9 – 1.2 kg/kWh
  - 7000 hours of annual operation

- Engine
  - Indigenous engines developed for producer gas 10 kW to 400 kWe

- Technology transfer executed South to North
- Probably the best in the capacity across the globe
- Engine manufacturers provide guarantee and warranty on the product
CHP

Biomass

Power

Activated carbon

Heat (industrial)

Heat (domestic)

Hydrogen

Chemicals

Liquid fuels
Glimpses of the power projects..

Beach Mineral Corporation – Tamil Nadu 1.5 MW

Hindustan pencils – Jammu

A – Plus – Thailand 1.2 MW

Cocodrilo – Cuba

Gomathy mills – 1MW

Wood Power – Switzerland

Ndola, Zambia
R and D at IISc – beyond power from biomass

• Improve H\textsubscript{2} to CO ratio
  ➢ Oxy-steam gasification
    • Hydrogen rich syn-gas
      • Hydrogen
      • Liquid fuels
      • Fuels for Fuel cells
Air gasification – Oxy-steam gasification

Gasification

Single stage process

Air gasification

Yield limited by H₂ content in biomass ~ 60 g/kg of biomass

Low volume fraction (~20% H₂, ~45% N₂) makes it economically non-viable for separation

Oxy-Steam gasification

H₂ yield enhanced by using H₂O as a reactant

Use of O₂ instead of air enhances the H₂ yield to 45-55%
# Oxy-steam gasification results

<table>
<thead>
<tr>
<th>SBR</th>
<th>0.75</th>
<th>1</th>
<th>1.4</th>
<th>1.5</th>
<th>1.8</th>
<th>2.4</th>
<th>2.7</th>
</tr>
</thead>
<tbody>
<tr>
<td>ER</td>
<td>0.21</td>
<td>0.18</td>
<td>0.21</td>
<td>0.23</td>
<td>0.27</td>
<td>0.28</td>
<td>0.3</td>
</tr>
<tr>
<td>H₂ yield (g kg⁻¹ of biomass)</td>
<td>66</td>
<td>68</td>
<td>71</td>
<td>73</td>
<td>94</td>
<td>99</td>
<td>104</td>
</tr>
<tr>
<td>H₂ yield (volume fraction, %) on dry basis</td>
<td>41.8</td>
<td>45.2</td>
<td>43.1</td>
<td>45.2</td>
<td>49.6</td>
<td>51.6</td>
<td>50.5</td>
</tr>
<tr>
<td>CO yield (volume fraction, %) on dry basis</td>
<td>27.6</td>
<td>24.9</td>
<td>26.5</td>
<td>24.9</td>
<td>17</td>
<td>12.4</td>
<td>13</td>
</tr>
<tr>
<td>H₂/CO</td>
<td>1.5</td>
<td>1.8</td>
<td>1.6</td>
<td>1.8</td>
<td>2.9</td>
<td>3.8</td>
<td>3.9</td>
</tr>
<tr>
<td>LHV (MJ Nm⁻³)</td>
<td>8.9</td>
<td>8.6</td>
<td>8.8</td>
<td>8.7</td>
<td>8</td>
<td>7.4</td>
<td>7.4</td>
</tr>
<tr>
<td>Hydrogen efficiency (%)</td>
<td>73.7</td>
<td>63.2</td>
<td>67.2</td>
<td>63.5</td>
<td>70.5</td>
<td>61</td>
<td>63.7</td>
</tr>
<tr>
<td>Gasification efficiency (%)</td>
<td>85.8</td>
<td>76.8</td>
<td>80.8</td>
<td>77</td>
<td>79.5</td>
<td>70.5</td>
<td>71.5</td>
</tr>
</tbody>
</table>
Syngas to fuel cell

Source: Ref. 17, P.L. Spath and D.C. Dayton
Establishing a **National Facility** for Methanol generation by thermo-chemical conversion of biomass – Research and implementation

S Dasappa and team  
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India

**Overall objectives**

- Establishing the pilot scale liquid fuel generation process at the Indian Institute of Science with focused research on adopting oxy-steam gasification system
- Upgrading and adapting the existing facility at BERI for testing and demonstration of multi-fuel gasification coupled to the liquid fuel production plant – **one ton per day**
Syngas from oxy-steam gasification of biomass

99.999% hydrogen

Hydrogen separation

Syn-gas CO and H₂ mixture

Catalytic reactor

Biochemical reactor

Water Gas Shift Reactor

Syngas enrichment

Compression

Conditioned gas

Liquid fuel for separation

• Methanol
• Ethanol
• DME

Syngas from oxy-steam gasification of biomass

Cooling

Particulate and tar removal

Wet scrubbing

Contaminants removal
Importance of syngas chemistry

\[ R = \frac{H_2 - CO_2}{CO + CO_2} \]

- R for methanol synthesis should range from 2 to 2.1 and values are % in volumes.
- There are two routes of adjusting the R ratio:
  - CO$_2$ Separation
    - Water gas shift reaction to convert CO to H$_2$ and CO$_2$, followed by CO$_2$ removal by absorption.
  - Addition of Hydrogen to adjust the stoichiometry.
Challenges and Strategies

• **Gasification Island**
  - Establishing the syngas quality and process conditions for reforming to methanol like temperature, pressure, etc.
  - Fine tuning the gas composition as per the process requirements.
  - Ensuring overall energy balance to ensure minimizing in-house power consumption.

• **Methanol synthesis**
  - Establishing energy efficient small scale systems.
  - Additional expertise on catalysis.
    - Build further on the experience of FT synthesis.
  - Develop reactor configuration.
  - Make available the syngas for various other process developed in the country for evaluation.
Bio-chemical Syn-gas to Methanol Challenges and strategies

- H₂ in syngas is inadequate (limiting) for total conversion of CO₂ + CO → MeOH.
- Gasification to provide higher CO₂ and less of CO for bio-methanol.
- All H₂ available will be primarily reacted with CO₂ to obtain methane (preferred substrate).
- CO kept to acceptable minimum to prevent suppression of CO₂ conversion by methanogens.

### Methanogenesis

- Use solid state biomass support based methanogenic reactor of CO₂+H₂ reaction
- Mesophilic to add diversity /shock resistant
- Mix of medium life and long life biomass support to have 2-3 years of functional life.
- Very low diffusional issues on biomass biofilms
- Use of fortified wastewater as nutrient source

### Bio-methane Oxidation

- Methanotroph consortia at ambient
- Methanotrophs prefers conversion CH₄ to CO₂.
- Growth slows down for MeOH as end product.
- Need to build up biomass for CH₄ → MeOH
- MeOH tolerance low (4-7%, 1-pass ~1%, recycle needed to raise downstream efficiency)
Acknowledgements

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..........Thank you

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