GREEN DIESEL FROM BIOMASS BY FISCHER-TROPSCH SYNTHESIS: NEW INSIGHTS IN GAS CLEANING AND PROCESS DESIGN

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<table>
<thead>
<tr>
<th>Revisions</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
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<tr>
<td>B</td>
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</tbody>
</table>

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Checked by: R. van Ree
Purpose: first-order and qualitative discussion to obtain new insights

- Renewable transportation fuels
- Biomass gasification & Fischer-Tropsch synthesis
- Evaluated system & Design approaches
- Experimental demonstration
- Conclusions
Renewable fuels

motivation for BG-FT

• Biomass-based fuels
  - reduction of CO₂ emissions (objectives Kyoto protocol)
  - important renewable energy source

• Directives from European Commission
  - 2% share in 2005 (for bio-fuels) to 6% in 2010

• Biomass gasification & Fischer-Tropsch synthesis
  = one of most promising routes *(GAVE study)*

Definitions

for renewable fuels

**Bio-diesel**
liquid product from esterification of vegetable oils (*e.g.* rapeseed oil = RME)

**Green diesel**
high-quality ultra-clean diesel-like product from Fischer-Tropsch synthesis

**Biosyngas**
gas rich in H₂ and CO obtained by gasification of biomass

**Syngas**
comparable to biosyngas, but from fossil origin

**Bio-gas**
from digestion of organic matter, consisting mainly of CH₄ and CO₂
Fischer-Tropsch Synthesis

chemistry

• Synthesis of long-chain hydrocarbons from CO en H₂

• Catalytic reaction: CO + 2 H₂ \rightarrow -\text{CH}_2 - + \text{H}_2\text{O}

• Cobalt (Co) catalyst: superior activity and selectivity

• Exothermic reaction: 20% of energy released as heat

• Ratio H₂/CO adjustment by water-gas-shift:
  \[ \text{CO} + \text{H}_2\text{O} \leftrightarrow \text{CO}_2 + \text{H}_2 \]

Products from FT Synthesis

Anderson-Schulz-Flory (ASF) relation

Diagram showing the Anderson-Schulz-Flory distribution of different hydrocarbons with weight fractions of methane, ethane, LPG, naphtha, diesel, light wax, and heavy wax. The diagram illustrates the maximum naphtha yield and the high C₅+ yield.
Diesel with Fischer-Tropsch
from feed to diesel

Partial Oxidation → Gas Cleaning → Product Upgrade

- natural gas (Shell)
- coal (SASOL)
- biomass

- Water-Gas Shift
- CO₂ removal
- recycle
- reforming

Gas cleaning is most critical and uncertain step

Biomass Gasification & FT
integrated system

Biomass → Gasification → Gas Cleaning → Fischer-Tropsch Synthesis → Product

- Electricity & Heat ("trigeneration")
- 'Green' Diesel
**Evaluated System**

assumptions and choices

- Integrated BG-FT system, focus on gas cleaning
- Circulating Fluidised Bed (CFB) gasifier
  - robust, scaleable, fuel-flexible, widely used
  - state-of-the-art = air-blown, atmospheric CFB
- FT synthesis treated as black-box
  - no optimisation and no product upgrading
- Goal is to maximise production of FT liquids
- Technical assessment !!!

<table>
<thead>
<tr>
<th>Impurity</th>
<th>Removal level</th>
</tr>
</thead>
<tbody>
<tr>
<td>H$_2$S + COS + CS$_2$</td>
<td>&lt; 1 ppmV</td>
</tr>
<tr>
<td>NH$_3$ + HCN</td>
<td>&lt; 1 ppmV</td>
</tr>
<tr>
<td>HCl + HBr + HF</td>
<td>&lt; 10 ppbV</td>
</tr>
<tr>
<td>alkaline metals</td>
<td>&lt; 10 ppbV</td>
</tr>
<tr>
<td>solids (soot, dust, ash)</td>
<td>essentially completely</td>
</tr>
<tr>
<td>organic compounds (tars)</td>
<td>below dew point</td>
</tr>
<tr>
<td>- class 2 (hetero atoms)</td>
<td>&lt; 1 ppmV</td>
</tr>
</tbody>
</table>

- class 2 tars: phenol, pyridine, thiophene
- organic compounds also include BTX
Biomass Gasification

raw CFB biosyngas

<table>
<thead>
<tr>
<th>Main Constituents</th>
<th>[vol%, dry]</th>
<th>[LHV%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO</td>
<td>18</td>
<td>27.8</td>
</tr>
<tr>
<td>H₂</td>
<td>16</td>
<td>21.1</td>
</tr>
<tr>
<td>CO₂</td>
<td>16</td>
<td>-</td>
</tr>
<tr>
<td>N₂</td>
<td>42</td>
<td>-</td>
</tr>
<tr>
<td>CH₄</td>
<td>5.5</td>
<td>24.1</td>
</tr>
<tr>
<td>C₂H₆ (ethene)</td>
<td>1.7</td>
<td>12.4</td>
</tr>
<tr>
<td>C₂H₄ (ethane)</td>
<td>0.1</td>
<td>0.8</td>
</tr>
<tr>
<td>BTX</td>
<td>0.53</td>
<td>10.5</td>
</tr>
<tr>
<td>sum of tars</td>
<td>0.12</td>
<td>2.8</td>
</tr>
<tr>
<td>TOTAL</td>
<td>100</td>
<td>100</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Impurities</th>
<th>[mg/m³]</th>
</tr>
</thead>
<tbody>
<tr>
<td>NH₃</td>
<td>2200</td>
</tr>
<tr>
<td>HCl</td>
<td>130</td>
</tr>
<tr>
<td>H₂S</td>
<td>150</td>
</tr>
<tr>
<td>all COS, CS₂, HCN, HBr</td>
<td>&lt; 25</td>
</tr>
<tr>
<td>dust, soot, ash</td>
<td>2000</td>
</tr>
</tbody>
</table>

CFB gasifier, 850°C, air-blown, atmospheric wood; 15 wt% moisture

dilution
energy loss for FT

catalyst poison

Front-end Approach

economic considerations

- scale: available gasifiers; 10-100 MWₜʰ
- air-blown gasifier *(air separation is expensive)*
- no recycle *(due to N₂ in gas)*
- no CO₂ removal *(expensive)*
- no adjustment of H₂/CO ratio *(simplicity)*

Thus, operated in once-through mode: *tri-generation*
**Base-case**

production of liquids, electricity, and heat

- **H₂ is limiting compound**

\[ \text{Yield FT products} = 100 \times 33.5\% \times 90\% \times 80\% \times 90\% \]

- \( \text{H₂/CO ratio} = 0.89 \) (containing 49% of the chemical energy)

- energy content of product gas used for FT synthesis: 33.5%
- FT conversion, once-through: 90% (of limiting compound)
- heat generated: 20% of converted energy
- FT selectivity to C₅⁺ products (wax and liquids): 90%
- electrical efficiency CC: 50%
- assume clean gas and tars as inert

**Importance of H₂/CO ratio**

maximising conversion

- **shift to H₂/CO = 2**

\[ \text{Yield FT products} = (100-1.5) \times 48.2\% \times 90\% \times 80\% \times 90\% \]

- energy content of product gas used for FT synthesis: 48.2%
- FT conversion, once-through: 90% (of syngas)
- heat generated: 20% of converted energy
- FT selectivity to C₅⁺ products (wax and liquids): 90%
- electrical efficiency CC: 50%
**Gas Cleaning**

general remarks

- state-of-the-art gas cleaning = for gas engine
  - 2 g/m³ tars, tar dewpoint ~40°C

  required: removal of organic compounds below dew-point
  - 2 ppmV naphthalene, 2500 ppmV BTX (@40 bar)

- conventional wet gas cleaning is sufficient for NH₃, H₂S, etc.
  - wet scrubbers & active carbon and ZnO guard beds

  active carbon also captures BTX - not preferred!

**Design of Gas Cleaning (1)**

are tars the issue?

- removal of BTX is strongly preferred
- tars are readily removed under BTX removal conditions

Thus, the removal of BTX is the issue in gas cleaning

Process line-up:

![Process diagram]

Details on the novel and powerful OLGA technology for complete tar removal are presented in the poster session.
**Back-end Approach**

maximised production FT liquids

- scale: economically desired for FT unit; \(\sim 1000 \text{ MW}_{\text{th}}\)
- electricity is by-product
- FT off-gas recycled (oxygen-blown gasifier required)
- \(\text{CO}_2\) removal required
- adjustment of ratio \(\text{H}_2/\text{CO} = 2\)
- high \(\text{H}_2+\text{CO}\) yield (*tar cracker*)

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**Importance of \(\text{H}_2+\text{CO}\) yield**

maximising FT production

- energy content of product gas used for FT synthesis: 100%
- FT(*) conversion, including recycle: 95% (of syngas)
- \(\text{CO}_2\) removal
- and shift to \(\text{H}_2/\text{CO} = 2\)
- oxygen-blown gasification

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Yield FT products = \(100-15\) × 100% × 95% × 80% × 90%

- all \(\text{CH}_4\) (24%), \(\text{C}_x\text{H}_y\) (12%), and BTX (11%) converted, and all tar cracked

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Design of Gas Cleaning (2)
maximised H₂+CO yield

- high-temperature step, i.e. tar cracker
- all BTX and tars are also removed/destructed

Thus, conversion of all chemical energy into H₂+CO

Process line-up:

1. Gasifier
2. Tar Cracker
3. Wet Cleaning
4. Active carbon & ZnO filters
5. Clean biosyngas

Integrated Test
process line-up

1. Tar cracker
2. Aqueous scrubber
3. Compressor
4. Fischer-Tropsch micro flow unit
5. Bottles

--- Biosyngas production ---
--- Gas cleaning ---
--- FT synthesis ---
**Demonstration**

gas cleaning for large-scale systems

<table>
<thead>
<tr>
<th>Gas</th>
<th>Raw biosyngas</th>
<th>Cracked biosyngas</th>
<th>FT feed gas</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH₄</td>
<td>6.42</td>
<td>0.01</td>
<td>0.01</td>
</tr>
<tr>
<td>C₂H₄</td>
<td>5936</td>
<td>&lt; 5</td>
<td>&lt; 5</td>
</tr>
<tr>
<td>C₂H₆</td>
<td>7359</td>
<td>&lt; 5</td>
<td>&lt; 5</td>
</tr>
<tr>
<td>BTX</td>
<td>1266</td>
<td>&lt; 5</td>
<td>&lt; 5</td>
</tr>
<tr>
<td>Tars</td>
<td>+/- 50%</td>
<td>&lt; 10</td>
<td>&lt; 10</td>
</tr>
<tr>
<td>NH₃</td>
<td>~</td>
<td>516</td>
<td>0.02</td>
</tr>
<tr>
<td>H₂S</td>
<td>~</td>
<td>23789</td>
<td>&lt; 10</td>
</tr>
<tr>
<td>COS</td>
<td>~</td>
<td>47578</td>
<td>278</td>
</tr>
<tr>
<td>CS₂</td>
<td>~</td>
<td>207</td>
<td>&lt; 10</td>
</tr>
<tr>
<td>TOTAL</td>
<td>[vol%]</td>
<td>100.0</td>
<td>100.0</td>
</tr>
</tbody>
</table>

(Experimental data)

1. high-temperature tar cracker
2. wet scrubbers
3. active carbon en ZnO guard beds

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**Technical Feasibility**

demonstration of integrated system

Two tests for 150 h and 500 h:

1. gasification of willow
2. cleaning of biosyngas to FT specifications
3. operating a micro-flow FT unit on the cleaned gas

**Successful:**

- No loss of catalyst activity
- Constant gas consumption and off-gas composition
- FT products similar to fossil equivalents
“Product in Bottle”

Conclusions

insights on gas cleaning and process design

• BTX are the design guideline for gas cleaning (not tars)
• H₂/CO ratio in raw biosyngas is irrelevant
• Tar cracker is required for high FT yields (high H₂+CO yield)
• Oxygen-blown gasification is required (with a CFB) for high syngas conversions (to allow a recycle)
• Scale of the plant determines line-up of gas cleaning
• Technical feasibility of gas cleaning for BG-FT is successfully demonstrated
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