From fossil to renewable feedstocks

Kevin M. Van Geem
Outline

• Introduction
• Fast pyrolysis of biomass
• Pyrolysis of renewable fuels: model components
• Biomass to ethylene routes
• Conclusions
Multi-scale Modeling and design of chemical Reactions and Reactors

P6: From fossil to renewable feedstocks
Transition from fossil to renewable resources

- algae
- wood
- sugar cane
- waste
- bagasse
- corn
- short-rotation crops
- wood wastes
- etc.

Biomass
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Lignocellulosic biomass

Composition strongly depends on origin biomass

- **Plant biomass**
  - Macromolecular substances
    - Poly-saccharides
    - Cellulose
    - Hemi-cellulose
  - Low molecular weight substances
    - Lignin
    - Organic molecules
    - Inorganics
    - Extractives
      - Fats, waxes, starches, terpenes etc...
Biomass Biopolymers: Cellulose

Cellulose is an organic compound with the formula $(\text{C}_6\text{H}_{10}\text{O}_5)_n$, a polysaccharide consisting of a linear chain of several hundred to over ten thousand $\beta(1\rightarrow4)$ linked D-glucose units.
A hemicellulose can be any of several heteropolymers (matrix polysaccharides), such as arabinoxylans present in almost all plant cell walls along with cellulose. While cellulose is crystalline, strong, and resistant to hydrolysis, hemicellulose has a random, amorphous structure with little strength. It is easily hydrolyzed by dilute acid or base as well as myriad hemicellulase enzymes.
Genetic engineering allows to modify the lignin structure and fraction of lignin
Biomass: pyrolysis products
Biomass: pyrolysis process

Plant biomass → pyrolysis

- Gas: 15%
  - $\text{CO}_2$, CO, $\text{CH}_4$, $\text{H}_2$, lower amounts of C2’s

- Bio oil: 70%
  - Aldehydes, ketones, phenol ethers, alkyl phenols, polyaromatics etc...

- Char: 15%
  - Active carbon
- Hot sand and biomass mixed by auger
- Suitable for small scale
- Requires hot sand heating and circulation system
Bio oil: main components

Pine wood → Fast Pyrolysis (300 – 600°C, 0.5 – 2s) → Gas & Char → Bio-oil

- Aldehydes, Furans, Ketones & Alcohols
- Carboxylic Acids
- Phenols & Phenols
- Guaicols, Syringols & Catechols
- Anhydrosugars
- Hydroxy Acids
GC×GC set-up

Heated Transfer-line

TOF-MS

GC×GC
Methusalem Advisory Board meeting, Ghent, 17 June 2011

**GC×GC set-up**

- **FID**
  - Quantitative results

- **TOF-MS**
  - Peak identification

**Initial objective**

Maximal agreement between FID and TOF-MS chromatograms

GC×GC: Data Processing

1st dimension separation \rightarrow \text{Modulation} \rightarrow 2nd dimension separation \rightarrow \text{Detection}

- Enhanced Resolution
- Enhanced Signal/Noise Ratio
GC×GC: Data Processing

1. Raw 2D chromatogram (at second column outlet)
2. Transformation
3. Visualization

- 3D plot
- 2D colour plot
- Second-dimension chromatograms stacked side by side
Bio oil: main components

GCxGC-FID & GCxGC-TOF-MS analysis

→ 190 components

Cellulose

- Levoglucosan
- Guaiacol 20%
- Anhydrosugar 13%
- Ketone 8%
- Furan 13%
- Cyclo-ketone 8%
- Aldehyde 9%
- Alcohol 5%
- Phenol 2%
- Syringol 2%
- Catechol 1%

Lignin

- Vanilin
- Guaiacol
- Anhydrosugar 13%
- Ketone 8%
- Furan 13%
- Guaiacol 20%
- Pheno 2%
- Alcohol 5%
- Syringol 2%
- Catechol 1%
- Cyclo-ketone 8%
- Aldehyde 9%
- Carboxylic acid 19%

Methusaleh Advisory Board meeting, Ghent, 17 June 2011
## Bio oil: main components

<table>
<thead>
<tr>
<th>Compound</th>
<th>Relative content (%)</th>
</tr>
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<tbody>
<tr>
<td>Furfural</td>
<td>9.06</td>
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<tr>
<td>Acetoxyacetone, 1-hydroxyl</td>
<td>1.21</td>
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<tr>
<td>Furfural, 5-methyl</td>
<td>1.82</td>
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<tr>
<td>Phenol</td>
<td>2.55</td>
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<tr>
<td>2-Cyclopentane-1-one, 3-methyl</td>
<td>1.58</td>
</tr>
<tr>
<td>Benzaldehyde, 2-hydroxyl</td>
<td>2.70</td>
</tr>
<tr>
<td>Phenol, 2-methyl</td>
<td>5.04</td>
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<tr>
<td>Phenol, 4-methyl</td>
<td>0.51</td>
</tr>
<tr>
<td>Phenol, 2-methoxy</td>
<td>0.27</td>
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<tr>
<td>Phenol, 2,4-dimethyl</td>
<td>9.62</td>
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<tr>
<td>Phenol, 4-ethyl</td>
<td>2.18</td>
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<tr>
<td>Phenol, 2-methoxy-5-methyl</td>
<td>4.15</td>
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<tr>
<td>Phenol, 2-methoxy-4-methyl</td>
<td>0.55</td>
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<tr>
<td>Benzene, 1,2,4-trimethoxy</td>
<td>3.80</td>
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<tr>
<td>Phenol, 2,6-dimethyl-4-(1-propenyl)</td>
<td>4.25</td>
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<tr>
<td>1,2-Benzenedicarboxylic acid, diisooctyl ester</td>
<td>1.80</td>
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<tr>
<td>2-Furanone</td>
<td>5.70</td>
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<tr>
<td>Levoglucosan</td>
<td>6.75</td>
</tr>
<tr>
<td>Phenol, 2,6-dimethoxy-4-propenyl</td>
<td>3.14</td>
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<tr>
<td>Furanone, 5-methyl</td>
<td>0.49</td>
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<tr>
<td>Acetophenone, 1-(4-hydroxy-3-methoxy)</td>
<td>2.94</td>
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<tr>
<td>Vanillin</td>
<td>6.35</td>
</tr>
<tr>
<td>Benzaldehyde, 3,5-dimethyl-4-hydroxyl</td>
<td>4.54</td>
</tr>
<tr>
<td>Cinnamic aldehyde, 3,5-dimethoxy-4-hydroxyl</td>
<td>2.19</td>
</tr>
</tbody>
</table>
Bio oil: untreated
Bio oil: hydrotreated
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Validation: pyrolysis in laminar flow reactor

GCxGC Tof-MS methyldecanoate

Pyl et al., 2011
Influence COT MD pyrolysis

- C3:1
- C4:1
- C5:1
- C6:1
- C7:1
- C8:1
- C9:1
- MD

- Aromatics
- Esters
- 1-Olefins
- 1-Octene
- 1-Nonene
- 1-Heptene
- 1-Hexene

Pyrolysis at 620 °C
Influence COT MD pyrolysis
Influence COT: MD pyrolysis
Influence dilution: MD pyrolysis

![Graph showing the influence of dilution on conversion in MD pyrolysis. The graph compares low dilution (blue diamonds) and high dilution (red squares) with temperature (in °C) on the x-axis and conversion (in wt%) on the y-axis. The low dilution curve is consistently above the high dilution curve, indicating a greater conversion at the same temperature.]
Mechanism validation

![Graph showing conversion vs. temperature for different models: Zhaoyu Luo et al., Herbinet et al. (Red), Herbinet et al. (Full), and Experimental. The graph plots conversion in wt% against temperature in °C.]
Mechanism validation
Reaction path analysis

C3:1-2 Yield [wt%]

Conv. [wt%]

Zhaoyu Luo et al.
Herbinet et al. (Red.)
Herbinet et al. (Full)
Experimental

m02j

m0d

m817-1

m2ej

m3j

m2o

h0c

ch3co

co

nc3h7

c5h11-1

c7h15-1

C3h6

c2h4

Experimental

(9.7%)

(41.5%)

(24.4%)

(34.4%)

(45.4%)

(49.9%)

(50.0%)

(50.0%)

(5.8%)

(17.0%)

(6.4%)

(39.7%)

(39.7%)

(43.7%)

Zhaoyu Luo et al.
Butanol work

✔ Oxygenated fuels
  ▪ Improve octane rating
  ▪ Impede sooting and particulate formation
  ▪ Promote formation of toxic byproducts

✔ Examples of oxygenated fuel additives
  ▪ 1979 (US): MTBE ($H_2O$ decontamination)
  ▪ Late 70’s (US): Ethanol (21.2 MJ/L)
  ▪ 2000’s (Dupont/BP): 1-Butanol (29.2 MJ/L)
  ▪ 2015: 2-methyl-1-propanol or 2-butanol?

Van Geem et al., 2010; Harper et al. 2011
Acetone/butanol/ethanol pyrolysis/combustion
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Biomass to hydrocarbon routes

• Biomass to hydrocarbons
  – Gasification and enzyme routes not commercial
  – Hydrotreated Vegetable Oil (e.g. Bio-Synfining™) commercialized

• Economics based on diesel and jet fuel

• Naphtha co-product tested as feedstock for conventional steam crackers
Feedstock

- Algal oils
- Tall oil fatty acid
- Seaweed oils
- Seed oils
- Yellow grease
- Brown grease
- Waste animal fats

U.S. sources ~ 360,000 BPD (16 million tonne/y) hydrocarbon equivalent ...and increasing
Simple, low capital cost process
Paraffinic hydrocarbons from bio oils via hydrodeoxygenation (Eqs 1a-b) and hydrocracking (Eq 2)
Renewable kerosene vs Petroleum kerosene

**Paraffinic Kerosene**

- n-paraffins: 12%
- iso-paraffins: 86%
- naphthenes: 2%
- aromatics: 17%

- C10 – C18
- Aromatics free

**Petrochemical Kerosene**

- n-paraffins: 12%
- iso-paraffins: 86%
- naphthenes: 2%
- aromatics: 17%

- Paraffinic kerosene
- Aromatics free

**GC × GC - FID analysis**
GC-GC analysis of renewable naphtha

Hydrodeoxyxygenation → Naphtha → Hydrocracking → Kerosene

- Benzene
- Toluene
- Ethyl-benzene
- Propyl-benzene
- Butyl-benzene
- n-Paraffins (32.4%)
- iso-Paraffins (59.9%)
- Olefins (0.4%)
- Naphthenes (6.5%)
- Aromatics (0.8%)

Pyl et al., accepted
Follow up story

- Hydrodeoxygenation
- Hydrocracking

Paraffinic Kerosene

→ C10 – C18
→ Aromatics free
## Simulation results

<table>
<thead>
<tr>
<th>Product Yield (wt%)</th>
<th>COT = 820°C</th>
<th>COT = 850°C</th>
<th>COT = 880°C</th>
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</thead>
<tbody>
<tr>
<td>hydrogen</td>
<td>0.9</td>
<td>1.0</td>
<td>1.1</td>
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<tr>
<td>methane</td>
<td>8.2</td>
<td>9.7</td>
<td>10.9</td>
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<tr>
<td><strong>ethylene</strong></td>
<td><strong>37.3</strong></td>
<td><strong>39.9</strong></td>
<td><strong>40.4</strong></td>
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<tr>
<td>ethane</td>
<td>3.0</td>
<td>2.9</td>
<td>2.8</td>
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<tr>
<td><strong>propylene</strong></td>
<td><strong>14.6</strong></td>
<td><strong>14.0</strong></td>
<td><strong>12.4</strong></td>
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<tr>
<td>propane</td>
<td>0.3</td>
<td>0.3</td>
<td>0.3</td>
</tr>
<tr>
<td>isobutene</td>
<td>0.2</td>
<td>0.3</td>
<td>0.3</td>
</tr>
<tr>
<td>2-butene</td>
<td>0.7</td>
<td>0.7</td>
<td>0.6</td>
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<tr>
<td>1-butene</td>
<td>3.9</td>
<td>1.9</td>
<td>0.7</td>
</tr>
<tr>
<td>1,3-butadiene</td>
<td>7.3</td>
<td>6.6</td>
<td>5.6</td>
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<tr>
<td>n-butane</td>
<td>0.1</td>
<td>0.1</td>
<td>0.1</td>
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<tr>
<td><strong>benzene</strong></td>
<td><strong>6.7</strong></td>
<td><strong>8.6</strong></td>
<td><strong>9.5</strong></td>
</tr>
<tr>
<td>toluene</td>
<td>2.5</td>
<td>3.3</td>
<td>3.8</td>
</tr>
<tr>
<td>Et-benzene</td>
<td>0.2</td>
<td>0.4</td>
<td>0.7</td>
</tr>
<tr>
<td>xylene</td>
<td>0.1</td>
<td>0.1</td>
<td>0.1</td>
</tr>
<tr>
<td>styrene</td>
<td>0.4</td>
<td>1.0</td>
<td>1.9</td>
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<tr>
<td>indene+ vinyl toluene</td>
<td>0.3</td>
<td>0.5</td>
<td>0.7</td>
</tr>
<tr>
<td>naphthalene</td>
<td>0.1</td>
<td>0.4</td>
<td>1.2</td>
</tr>
</tbody>
</table>
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Talloil: byproduct of Kraft process

<table>
<thead>
<tr>
<th>Compounds</th>
<th>Pine</th>
<th>Spruce</th>
<th>Birch</th>
</tr>
</thead>
<tbody>
<tr>
<td>Esters, %</td>
<td>40</td>
<td>43</td>
<td>58</td>
</tr>
<tr>
<td>Free fatty acids, %</td>
<td>18</td>
<td>10</td>
<td>6</td>
</tr>
<tr>
<td>Free rosin acids, %</td>
<td>34</td>
<td>25</td>
<td>0</td>
</tr>
<tr>
<td>Total, %</td>
<td>92</td>
<td>78</td>
<td>64</td>
</tr>
</tbody>
</table>
Pilot plant set-up

- **FEED**
  - \( \text{H}_2\text{O} \)
  - hydrocarbons

- **FURNACE & REACTOR**
  - cell 1
  - cell 2
  - cell 3
  - cell 4
  - cell 5
  - cell 6
  - cell 7
  - preheating & mixing
  - reactor zone

- **TLE**

- **ANALYSIS**
  - oven
  - GC×GC
  - DHA
  - condensate
  - IR-GA
  - water
  - PGA
  - RGA
Nitrogen is used as internal standard

RGA (TCD)  |  H₂  CO₂  C₂H₄  C₂H₆  C₂H₂  N₂  CH₄  CO
RGA (FID)  |  CH₄  C₂  C₃  C₄
PGA (TCD)  |  CO₂  C₂H₄  C₂H₆  C₂H₂  N₂  CO  CH₄
DHA (FID)  |  CH₄  C₂  C₃  C₄  C₅  C₆  ...  C₁₆
GC×GC (FID)  |  CH₄  ...  C₂₅

Methane functions as a second internal standard
TOFA GC

1st dimension retention time (min)

0 25

2nd dimension retention time (s)

0

5 phenanthrene C1-triaro

50 75 100

nC16

nC18

nC20

Norabitane

C12H14O

Norabitane-aro

iC8

nC8

nC10

nC12

nC14

nC16

nC18

nC20

nC22

nC24

nC26

C18:1

C16:1
DTO feedstock analysis

- 1st dimension retention time (min)
  - 0
  - 25
- 2nd dimension retention time (s)
  - 0
  - 5

- Phenanthrene C1-triaro
- Norabitane C12H14O

![Chemical structures](image-url)
Naphtha/DTO

2nd dimension retention time (s)

1st dimension retention time (min)

C2 arom

benzene
toluene

Norabitane-aromatic

Norabitane

naphthenes

nC10

nC16

nC18

nC20

nC4

nC12H14O

xylenes
## TOFA/DTO feedstock analysis

<table>
<thead>
<tr>
<th>Component</th>
<th>TOFA Wt%</th>
<th>DTO Wt%</th>
</tr>
</thead>
<tbody>
<tr>
<td>C12H14O</td>
<td>0.053</td>
<td>0.802</td>
</tr>
<tr>
<td>C16:0 FAME</td>
<td>0.713</td>
<td>0.371</td>
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<tr>
<td>C18:1 FAME</td>
<td>2.280</td>
<td>0.243</td>
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<tr>
<td>C18:2 FAME</td>
<td>0.591</td>
<td>0.626</td>
</tr>
<tr>
<td>cyclo C18</td>
<td>0.912</td>
<td>0.117</td>
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<tr>
<td>decane</td>
<td>0.137</td>
<td>0.218</td>
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<tr>
<td>dodecane</td>
<td>0.084</td>
<td>0.150</td>
</tr>
<tr>
<td>eicosane</td>
<td>3.148</td>
<td>6.194</td>
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<tr>
<td>heneicosane</td>
<td>0.604</td>
<td>0.575</td>
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<tr>
<td>heptadecane</td>
<td>13.235</td>
<td>8.844</td>
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<tr>
<td>heptane</td>
<td>0.279</td>
<td>0.392</td>
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<tr>
<td>hexadecane</td>
<td>0.424</td>
<td>0.412</td>
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<tr>
<td>hexane</td>
<td>0.790</td>
<td>15.657</td>
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<tr>
<td>isoparaffin C16</td>
<td>0.062</td>
<td>0.046</td>
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<tr>
<td>isoparaffin C17</td>
<td>0.780</td>
<td>0.282</td>
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<tr>
<td>isoparaffin C18</td>
<td>1.594</td>
<td>1.062</td>
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<tr>
<td>isoparaffin C19</td>
<td>0.717</td>
<td>0.867</td>
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<tr>
<td>isoparaffin C20</td>
<td>0.151</td>
<td>0.194</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Component</th>
<th>TOFA Wt%</th>
<th>DTO Wt%</th>
</tr>
</thead>
<tbody>
<tr>
<td>nonadecane</td>
<td>1.164</td>
<td>1.829</td>
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<tr>
<td>nonane</td>
<td>0.113</td>
<td>0.145</td>
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<tr>
<td>norabietane</td>
<td>6.128</td>
<td>9.984</td>
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<td>norabietane-1aro</td>
<td>1.592</td>
<td>3.521</td>
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<tr>
<td>octadecane</td>
<td>59.520</td>
<td>42.797</td>
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<tr>
<td>octane</td>
<td>0.136</td>
<td>0.180</td>
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<tr>
<td>olefin C18</td>
<td>2.247</td>
<td>2.016</td>
</tr>
<tr>
<td>olefin C20</td>
<td>0.781</td>
<td>0.644</td>
</tr>
<tr>
<td>paraffin C22</td>
<td>0.292</td>
<td>0.518</td>
</tr>
<tr>
<td>paraffin C23</td>
<td>0.250</td>
<td>0.235</td>
</tr>
<tr>
<td>paraffin C24</td>
<td>0.359</td>
<td>0.158</td>
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<tr>
<td>paraffin C25</td>
<td>0.282</td>
<td>0.122</td>
</tr>
<tr>
<td>paraffin C26</td>
<td>0.195</td>
<td>0.207</td>
</tr>
<tr>
<td>paraffin C27</td>
<td>0.108</td>
<td>0.138</td>
</tr>
<tr>
<td>tetradecane</td>
<td>0.051</td>
<td>0.077</td>
</tr>
<tr>
<td>tridecane</td>
<td>0.075</td>
<td>0.156</td>
</tr>
<tr>
<td>undecane</td>
<td>0.152</td>
<td>0.220</td>
</tr>
</tbody>
</table>
DTO/naphtha feedstock analysis

Weight fraction %

Carbon number

0 5 10 15 20 25 30 35 40 45 50

3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 23 24 25 26 27 28 29
GC×GC FID chromatogram TOFA

- Benzene
- Ethyl-benzene
- Toluene
- Styrene
- Naphthalene
- Acenaphthylene
- Methyl-naphthalenes
- Phenanthrene
- Cyclopentadiene
- Indene
- Mono-aromatics
- Di-aromatics
- Unconverted TOFA
- C_{18}:1 ester
- nC_{16}
- nC_{18}
Detailed effluent with GC×GC FID

Over 100 components are identified and quantified each run

<table>
<thead>
<tr>
<th>Feed</th>
<th>Naphtha (N)</th>
<th>N+DTO</th>
<th>TOFA</th>
<th>N+TOFA</th>
<th>N+TOFA</th>
<th>N+TOFA</th>
<th>N+TOFA</th>
<th>N+TOFA</th>
</tr>
</thead>
<tbody>
<tr>
<td>HC-flow (g/hr)</td>
<td>3999</td>
<td>3987</td>
<td>4039</td>
<td>3987</td>
<td>3995</td>
<td>4011</td>
<td>3006</td>
<td></td>
</tr>
<tr>
<td>H₂O-flow (g/hr)</td>
<td>1809</td>
<td>1797</td>
<td>1815</td>
<td>1797</td>
<td>1797</td>
<td>1804</td>
<td>2124</td>
<td></td>
</tr>
<tr>
<td>Dilution (kg/kg)</td>
<td>0.45</td>
<td>0.45</td>
<td>0.45</td>
<td>0.45</td>
<td>0.45</td>
<td>0.45</td>
<td>0.71</td>
<td></td>
</tr>
<tr>
<td>COT (°C)</td>
<td>851</td>
<td>850</td>
<td>850</td>
<td>850</td>
<td>822</td>
<td>880</td>
<td>852</td>
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</tr>
<tr>
<td>COP (Bar abs)</td>
<td>1.69</td>
<td>1.67</td>
<td>1.69</td>
<td>1.67</td>
<td>1.68</td>
<td>1.71</td>
<td>1.67</td>
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</tr>
</tbody>
</table>

Yields (wt%)

<table>
<thead>
<tr>
<th>Component</th>
<th>Base case</th>
<th>Influence feed</th>
<th>Influence COT</th>
<th>Influence dilution</th>
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<tbody>
<tr>
<td>ΣC₄⁺</td>
<td>79.71</td>
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<tr>
<td>[C₅⁺,C₆H₆]</td>
<td>7.42</td>
<td></td>
<td></td>
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</tr>
<tr>
<td>[C₆H₆, Naphthalene]</td>
<td>11.92</td>
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<tr>
<td>[Naphthalene, ...]</td>
<td>1.13</td>
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</tr>
<tr>
<td>P/E</td>
<td>0.55</td>
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</tr>
<tr>
<td>CO</td>
<td>0.03</td>
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</tr>
<tr>
<td>methane</td>
<td>15.62</td>
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<tr>
<td>ethylene</td>
<td>29.97</td>
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<tr>
<td>propylene</td>
<td>16.51</td>
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<tr>
<td>1,3-butadiene</td>
<td>1.44</td>
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<tr>
<td>1-butene</td>
<td>2.75</td>
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<td>isobutene</td>
<td>5.32</td>
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<td>1,3-cyclopentadiene</td>
<td>1.84</td>
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<td>benzene</td>
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<td>toluene</td>
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<td>naphthalene</td>
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<tr>
<td>norabietane</td>
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</table>
Conclusions

- GC×GC analysis of bio-oils produced by fast pyrolysis of biomass allows to quantify more than 50 components qualitatively.

- Pyrolysis of model components for renewable fuels provides valuable information to validate the combustion chemistry.

- Hydrodeoxygenation of waste fats and greases gives a highly paraffinic renewable feedstock.
  - Excellent feedstock for conventional steam crackers
    - High Ethylene and Propylene yields
    - Low Coking tendency = long run lengths

- Opportunity for petrochemical producers to transition to biorenewable feeds without modifying process.

- Hydrodeoxygenated tall oil is also a valuable feed for producing light olefins, but smaller ethylene and propylene yields are obtained compared to the DHO product of waste fats.
**Glossary**

*Lignin*: a polyaromatic structure, part of cell walls of plants and algae

*Cellulose*: a polysaccharide consisting of a linear chain of several hundred to over ten thousand $\beta(1\rightarrow4)$ linked D-glucose units

*Hemicellulose*: a polysaccharide consisting of include xylose, mannose, galactose, rhamnose, and arabinose monomers

*Bio-oil*: oil produced from lignocellulosic biomass via pyrolysis

*Tall oil*: by-product of the Kraft process of wood pulp manufacture