Biomass to Olefins:
Steam Cracking of Renewable Feedstocks

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# Outline

## Introduction: Green Olefins

## Pilot Plant Steam Cracking of Hydrodeoxygenated Biomass
- Feedstock analyses
- Effect of feedstock on product yields
- Effect of feedstock on run-length

## Reactor and Kinetic modeling
- Effect of Coil Outlet Temperature on product yields

## Conclusions
Poultry Fat to Olefins

Poultry Fat & Yellow Grease → Hydro-deoxygenation → CO, CO₂, H₂O

→ HDO – FAT (C₁₄-C₂₆ n-Paraffins) → Hydrocracking + Fractionation

→ LPG (C₃-C₄) Jet Fuel (C₁₀-C₁₅) → Renewable Naphtha (C₄-C₁₀)

Steam Cracking → GREEN OLEFINS
Crude Tall Oil Refining

Pine Wood → Kraft Pulping Process → Crude Tall Oil → Fractionation

Fractionation:
- Heads
- TOFA
- DTO
- Pitch

TOFA → Hydro-deoxygenation → HDO – TOFA (C_{14}-C_{26} n-Paraffins) → Steam Cracking → GREEN OLEFINS
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Detailed Feedstock Analyses

→ Hydrodeoxygenated Tall Oil Fatty Acids (TOFA)

→ Using comprehensive 2D gas chromatography
Fossil vs. Renewable Feedstocks

**Renewable Naphtha**
- n-paraffins: 33%
- naphthenes: 7%
- iso-paraffins: 60%
- aromatics: 0.8%

**HDO-FAT**
- n-paraffins: 96%
- naphthenes: 1%
- iso-paraffins: 3%
- aromatics: 0.8%

**HDO-TOFA**
- n-paraffins: 91%
- naphthenes: 6%
- iso-paraffins: 3%
- aromatics: 0.1%
- FAME: 0.2%

**Naphtha**
- n-paraffins: 35%
- naphthenes: 16%
- iso-paraffins: 46%
- aromatics: 3%

**Gas Oil**
- n-paraffins: 24%
- aromatics: 29%
- iso-paraffins: 33%
- thiophenes: 1%

**Natural Gas Condensate**
- n-paraffins: 18%
- naphthenes: 35%
- iso-paraffins: 32%
- aromatics: 14%
Steam Cracking Pilot Plant

High temperature sampling system

Online Analysis Section

$CH_4 \rightarrow PAHs$

Gas-Fired Furnace + Reactor

Control Room

$H_2O$

HC Feed
## Effect of feedstock on product yields

### P/E = 0.50

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<th>Reference Feedstock</th>
<th>Renewable Feedstocks</th>
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<tr>
<td></td>
<td>Full-range Naphtha</td>
<td>Renewable Naphtha</td>
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<tr>
<td></td>
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<td>HDO-FAT</td>
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<tr>
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<td>HDO-TOFA</td>
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<tr>
<td>Methane</td>
<td>16.9</td>
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<td>COT</td>
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<td></td>
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<td>835°C</td>
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<tr>
<td></td>
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<td>820°C</td>
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**Yields [wt%]**

\[ \delta = 0.45\text{kg/kg} \]

**COT**

- Methusalem Advisory Board Meeting, June 19, 2012
COT = 850°C

Effect of feedstock on run-length

Pilot plant cokes test → Cokes formation during 6-h steady state operation

Renewable Naphtha: 3.5 g cokes / 6 h
HDO-FAT: 5.55 g cokes / 6 h
HDO-TOFA: 5.8 g cokes / 6 h
Ethane: 2.5 g cokes / 6 h
Petroleum Naphtha: 4.4 g cokes / 6 h
Natural Gas Condensate: 5.8 g cokes / 6 h

Renewable Feedstocks
Reference Feedstocks

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Reactor and Kinetic Modeling

Microkinetic Model

- $R_1 - R_2 \leftrightarrow R_1^* + R_2^*$
- $R_1 - H + R_2^* \leftrightarrow R_1^* + R_2 - H$
- $R_1 = R_2 + R_3^* \leftrightarrow R_1^* - R_2 - R_3$

Free Radical Mechanism

System of Differential Equations

- $\frac{dF}{dz} = \left( \sum_{k=1}^{n} \nu_k r_k \right) \Omega$
- $\sum_j F_j c_{pj} \frac{dT}{dz} = \omega q + \Omega \sum_k r_{v,k} (-\Delta H_k)$
- $-\frac{dp_i}{dz} = \alpha \left( \frac{2f}{d_i} + \frac{\zeta}{\pi r_b} \right) \rho_g u^2 + \alpha \rho_g u \frac{\partial u}{\partial z}$

numerical integration

Plug flow

Reactor Model

Concentration Profiles & Product Yields
Temperature and Pressure Profile
Single-event Microkinetic Model

1. Automatic reaction network generation
2. Group-additive calculation of rate coefficients
3. Quasi steady state approximation for $\mu$ radicals
4. In situ lumping of primary products
5. A posteriori lumping of feed molecules

Microkinetic Model

- 51 paraffins: $C_0 - C_{26}$
- 168 olefins: $C_2 - C_{26}$
- 14 aromatics: $C_6 - C_{14}$
- 43 radicals: $C_0 - C_7$

276 species: $C_0 - C_{26}$
HDO-FAT Steam Cracking

simulated yields (lines) vs. pilot plant yields (symbols)

\[ \delta = 0.45 \text{ kg/kg} \]

Coil Outlet Temperature (COT)
755°C → 865°C
Renewable Naphtha Steam Cracking

Simulated yields (lines) vs. pilot plant yields (symbols)

\[ \delta = 0.45 \text{ kg/kg} \]

Coil Outlet Temperature (COT)

820°C → 860°C
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## Conclusions
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• Biowaste is a promising starting material for the production of *green olefins*

• Hydrodeoxygenation of waste fats as well as tall oils produces highly paraffinic liquids

• Steam cracking of these liquids results in high light olefin yields

• Microkinetic modeling provides a rigorous fundamental basis for industrial reactor models
Thank you for your attention!
<table>
<thead>
<tr>
<th>Term</th>
<th>Definition</th>
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<tr>
<td>Biowaste</td>
<td>A variety of renewable animal and vegetal waste streams arising from households, commerce and the food manufacturing industry.</td>
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<tr>
<td>Comprehensive two-dimensional gas chromatography</td>
<td>Advanced analytical technique that provides two-dimensional separation by combining two different analytical columns connected with an interface, called the modulator, that ensures that the entire sample is comprehensively subjected to both separations.</td>
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<tr>
<td>Group additive framework</td>
<td>Framework that enables automated calculation of thermodynamic or kinetic data from the structure of the molecule or transition state respectively by summation of group-additive values.</td>
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<td>Hydrodeoxygenation</td>
<td>A catalytic process which, in the presence of hydrogen, removes oxygen from organic components in the form of water. Common side-reactions are decarboxylation and decarbonylation producing carbon dioxide and carbon monoxide respectively.</td>
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<tr>
<td>Tall oil</td>
<td>A viscous yellow-black odorous liquid obtained as a by-product of the Kraft process of wood pulp manufacture when pulping mainly coniferous trees. The name originated as an Anglicization of the Swedish &quot;tallolja&quot; (&quot;pine oil&quot;). Crude tall oil can be fractionated into several fractions, including so-called tall oil fatty acids (TOFA) and distilled tall oil (DTO).</td>
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