Bio-jet fuel challenges and a new technology from non-food resources and residues

CLIB2021 Conference

Düsseldorf, April 17, 2013
Greasoline Company

• Spin-Off of Fraunhofer UMSICHT in Oberhausen (Germany)

• Process for catalytic conversion of bio-based oils and residues into high-quality hydrocarbon biofuels developed over the past 5 years


• Pilot plant built, more than € 4 million invested

• Technical proof of concept demonstrated
Agenda

1. Bio-Jet Fuel Challenges
2. Greasoline Technology from non-food resources and residues
Bio-Jet Fuel Market Drivers

Aviation Industry Growth
• World annual growth of air traffic 4.5% p.a.
• CO₂ emissions +3% p.a.; steady state: emissions triple until 2050

Price Challenge
• Jet fuel main cost driver
• Airline profitability low

Goals for Climate Protection
• EU: By 2020 2 mio tons sustainable kerosene
• Aviation self commitment: CO₂-neutral growth 2020 onwards

Technical Constraints
• Reliant on liquid fuels
• Mere hydrocarbons

Bio-Jet Fuel Market

Source: DG ENER Biofuels Flight Path Technical Paper 2011
With 25% - 40% of operating cost per passenger, jet fuel is main cost driver for airlines
Low profitability of aviation sector doesn’t provide substantial headroom for premium on fossil jet fuel prices.
Technical Constraints

Jet A-1, ASTM D1655 – 12 (extract)

- Distillation diagram: 10 % ≤ 205°C, 100 % ≤ 300 °C
- Aromatics up to 25 vol.-% (ASTM D1319)
- Freezing point max. -47 °C

Compounds

<table>
<thead>
<tr>
<th>Compounds</th>
<th>Serve for</th>
</tr>
</thead>
<tbody>
<tr>
<td>n-Paraffins</td>
<td>high heat to weight ratio, clean burn</td>
</tr>
<tr>
<td>Isoparaffins (+ cycloparaffins)</td>
<td>reduction of the freezing point</td>
</tr>
<tr>
<td>Aromatics</td>
<td>intrinsic lubrication ⇒ mandatory!</td>
</tr>
</tbody>
</table>

Source: ASTM D1655 – 12
L. Rye; C. Wilson / Fuel, 96 (2012), pp. 277-283
State-of-the-art processes for bio-jet fuel

- Summary of state-of-the-art for producing non-fossil-oil based alternative fuels
- Basically two routes are accepted by ASTM:
  1) Fischer-Tropsch processes: Coal-, Gas- and Biomass-to-Liquid
  2) Hydrogenated Vegetable Oils
- Further technologies not yet considered by ASTM but lining up for testing

Source: International Air Transport Association (IATA)
State-of-the-art (1): Fischer-Tropsch

Coal-to-liquid (CTL), Gas-to-liquid (GTL), Biomass-to-Liquid (BTL)

- Gasification of feedstock to syngas (CO/H$_2$) and ash (!)
- FT-synthesis of fuel: mixture of alkanes, naphtha, olefins
- Hydroprocessing of mixture (hydro-treating & -cracking)
- Separation of fuel mixtures by distillation

More than 50% of Fischer Tropsch fuel costs are due to investment
State-of-the-art (2): HVO / HRJ

Hydrogenated Vegetable Oil (HVO) / Hydroprocessed Renewable Jet (HRJ)

- Multistep purification of plant / waste oils
- Synthesis: Hydrotreating, Hydrocracking, Isomerisation, separation of fuel mixtures by distillation
- Major players are Neste Oil and UOP
- Most advanced green technology at the moment

More than 50% of HVO fuel costs are due to raw materials
Agenda

1. Bio-Jet Fuel Challenges
2. Greasoline Technology from non-food resources and residues
Main characteristics of Greasoline process

1. Gaseous phase process with evaporation of raw materials
   - Bio-based raw materials
   - Fatty acids, vegetable oil, algae oil

2. Oxygen-removal via decarboxylation
   - 400 – 500°C

3. Drop-in hydrocarbon products without hydrogen consumption
   - LPG/CO$_x$/CH$_4$

- High-caloric fuel gas
- Fuel components, chemical feedstock
- Fuel gas optionally for reactor heating
- Recycled gas
- Purge
Gaseous phase process with evaporation of raw materials

Europe
- Vegetable oil residues
- Yellow grease

US
- Free Fatty Acids
- Inedible animal fats

Asia
- Waste POME oil
- Camelina oil
- Calophyllum oil
- Jatropha curcas oil

Broad raw material basis: > 7 million mt p.a. in short-term

Residues which cannot be used by competitive technologies

Sources: Jatropha: Marco Schmidt; Camelina: Fornax, Calophyllum: Mauroguanandi; FFA: Magnus Manske; Veg. oil: Greasoline GmbH; Waste POME, Algae oil: Fraunhofer UMSICHT
Drop-In Hydrocarbon products for existing infrastructure

- No blending restrictions: chemically identical with fossil fuel
- High quality: non-oxidation sensitive, non-corrosive, high cetane number
- High value: bio-based jet fuel additives (alkylated benzenes)
- High product fraction in kerosene distillation range even before isomerization
- Sustainable: non-food raw materials, no fossil hydrogen needed for decarboxylation
Product and process fit into existing oil refineries

Existing Oil Refinery

Fossil Raw Oil → Distillation → Greasoline Product Mix

Conversion steps like reforming, hydro-treating, isomerization...

Gas fraction (LPG) → Gasoline/ Naphtha fraction → Jet Fuel fraction

Diesel fraction → Alkylated benzenes fraction for Jet Fuel

Greasoline Feedstock → Greasoline Catalytic Converter

Greasoline Product Mix
Pilot Plant at Oberhausen (GER)

1) Biofuels Synthesis

2) Distillation

3) Catalyst Regeneration
Product Composition for liquid product optimization

Havarie Fat* processing over activated carbon – Energy content yield

**Organic liquid product**

<table>
<thead>
<tr>
<th>Component</th>
<th>Percentage</th>
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<tbody>
<tr>
<td>Alkanes, from C12 on</td>
<td>86</td>
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<tr>
<td>Alkanes, up to C11</td>
<td></td>
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<tr>
<td>Alkylated Benzenes</td>
<td>13</td>
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</table>

**HV-2**

<table>
<thead>
<tr>
<th>Component</th>
<th>Percentage</th>
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<tr>
<td>Organic liquid product (OLP)</td>
<td>79.5</td>
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<tr>
<td>Organic gas product (OGP)</td>
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<tr>
<td>Contaminated pre-processed</td>
<td>14.9</td>
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<tr>
<td>material from plant oil</td>
<td>5.6</td>
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**Organic gaseous product**

<table>
<thead>
<tr>
<th>Component</th>
<th>Percentage</th>
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<tbody>
<tr>
<td>Methane + Ethane</td>
<td>23</td>
</tr>
<tr>
<td>Propane + Butane (LPG)</td>
<td>32</td>
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<tr>
<td>Pentane + Heptane</td>
<td>16</td>
</tr>
<tr>
<td>Ethylene</td>
<td>12</td>
</tr>
<tr>
<td>Propylene</td>
<td>17</td>
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Distillation curves crude Greasoline mixture vs. fossil fuels

~40% Kerosene from waste vegetable oils

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Bio-Jet Fuel Focus – Liquid Product Composition

Oleic Acid, Activated Carbon Catalyst

- Alkanes, from C12 on, 55 wt.-%
- Alkanes, up to C11, 27 wt.-%
- Olefines, 8 wt.-%
- Alkylated Benzenes, 10 wt.-%

Chemical concentrations in g/l:
- Docosane
- Henicosane
- Nonadecane
- Octadecane
- Heptadecane
- Hexadecane
- Pentadecane
- Tridecane
- Tetradecane
- Dodecane
- Undecane
- Decane
- Nonane
- Octane
- Heptane
- Heptadecane
- Undecene
- Methyldecy-Benzen
- Dimethybutyl-Benzene
- Ethyl-Methyl-Benzene
- Dimethyl-Benzene
- Methyl-Benzene
- Other Alkylated Benzenes
## Fuel Market Prices & Greasoline Cost

### €/mt as of December 30, 2011

<table>
<thead>
<tr>
<th></th>
<th>Crude fossil oil</th>
<th>Fossil-based fuels</th>
<th>Greasoline</th>
<th>Other Bio-based fuels incl. Energy-correction</th>
<th>Other Bio-based fuels w/o Energy-correction</th>
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<tbody>
<tr>
<td>Brent Oil</td>
<td>605</td>
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<td>Gasoline</td>
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<tr>
<td>Diesel</td>
<td>740</td>
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<td>Jet Fuel</td>
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<td>Greasoline</td>
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<td>Bioethanol</td>
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<tr>
<td>Biodiesel</td>
<td>1.120</td>
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<tr>
<td>Bio Jet Fuel</td>
<td>&gt; 1.500</td>
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</tbody>
</table>

Greasoline cost: calculation for 200,000 mt/a commercial plant integrated into existing oil refinery.
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