SUSTAINABLE HEFAS FOR AVIATION

Dr. Stella Bezergianni,
Dr. Loukia P. Chrysikou
Biomass Conversion to Biofuels

- Renewable
- Low H/C ratio
- Contains water
  - Corrosion problems
- High oxygen content (aldehydes, acids, ketones)
  - Reduced heating value
  - Reduced oxidation stability
  - Increased acidity

Biomass requires H/C increase, oxygen and H₂O removal
Biofuels are the only way to meet the 2050 CO₂ emission targets.
Which Biofuels Technology?

Presentation of Lucy Nattrass in Flightpath 2020 Workshop, Brussels, February 12, 2015

Sustainable Aviation Sustainable Fuels

UK Road-Map, 2014

S. Bezergianni and L. Chrysikou, Sustainable HEFAs for Aviation
Limit aviation GHG emissions’ impact on global climate
  — Target: 60% GHG emissions reduction over fossil fuels

Limit aviation emissions’ impact on local air quality

Meet stringent sustainability standards with respect to land, water and energy use
  — Avoid direct and indirect land use change impacts
  — Not displace or compete with food/feed crops

Provide a positive socio-economic impact

Exhibit minimal impact on biodiversity

Reduce the number of people affected by significant aircraft noise

Enable harmonisation of sustainability standards in all countries
Bio kerosene specifications relevant for Europe

- ASTM D1655 and D7566 (US specifications)
  - ASTM D1655: Standard specification for Jet A-1 kerosene for civil aviation use
  - ASTM D7566: Specification for Synthetic kerosene & blends of synthetic (max 50%) and conventional kerosene (Blends meeting ASTM D7566 are by definition ASTM D1655 kerosene and can be used like conventional kerosene)
- DefStan 91-91 (European specification)
## Aviation Biofuels’ Quality Challenge

<table>
<thead>
<tr>
<th>Property</th>
<th>ASTM D1655</th>
<th>ASTM D7566</th>
<th>Reason of expanded quality requirements of aviation biofuels</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aromatics (% v)</td>
<td>25 (max)</td>
<td>8-25</td>
<td>Minimum enforced to maintain engine components (e.g., seals), as some biofuels do not have aromatics</td>
</tr>
<tr>
<td>Distillation T50-T10 (°C)</td>
<td>NA</td>
<td>15 (min)</td>
<td>Ensure proper and smooth range distribution</td>
</tr>
<tr>
<td>Distillation T90-T10 (°C)</td>
<td>NA</td>
<td>40 (min)</td>
<td>Ensure proper and smooth range distribution</td>
</tr>
<tr>
<td>Lubricity (mm)</td>
<td>NA</td>
<td>0.85</td>
<td>Specified to ensure smooth operation of moving engine parts, as biofuels are pure HC w/o polar acids</td>
</tr>
</tbody>
</table>

All other quality specs are identical (acidity, sulfur, mercaptans, density, flash point, viscosity, energy density, smoke point, distillation residue, corrosion, thermal stability, electrical conductivity, contaminants)
### Aviation Biofuels Types

<table>
<thead>
<tr>
<th>Pros</th>
<th>Cons</th>
<th>Applications</th>
</tr>
</thead>
</table>
| **FTs** | • Lignocellulosic feedstock (agro/forest residues)  
• High sustainability | • High capital costs  
• Questionable economics  
• Low aromatics | • No commercial production  
• BioTfuel project pilot (2016 ?) |
| **HEFAs** | • Technology available | • High production costs (1700-2400$/t)  
• Low aromatics | • Plants in operation  
• Fuel tested in flights |
| **ATJs** | • Under development | • Low aromatics (need additives) | • Demo plant in operation  
• Fuel tested in flights |
| **CH** | • High aromatics | • Low aromatics | • Demo plant in operation |
Which Biofuels Technology?

Sustainable Aviation Sustainable Fuels
UK Road-Map, 2014

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S. Bezergianni and L. Chrysikou, Sustainable HEFAs for Aviation
HEFAs Production Technology

- Flexibility of feedstock types
- High selectivity on biojet fuel
- Well established technology used in refining industry

- In-line separation of water and acid gases
- Relatively high production cost
  - Mostly attributed to \( H_2 \) consumption

Deoxygenation

- Vegetable oils
- Animal fats
- Greases
- Microalgal oil

Isomerization/ Hydrocracking

Fresh \( H_2 \) (make up)

Product separation

- Light fuels
- Jet
- Diesel

\( H_2 S, CO, CO_2 \)

Water

S. Bezergianni and L. Chrysikou, Sustainable HEFAs for Aviation
Hydrotreating Reactions (1/2)

- ρ reduction
- Diesel yield increase
- H/C increase
- Br# decrease
- TAN decrease
- Induction time increase

\[
\begin{align*}
\text{O} & \quad \text{H}_2\text{C}-\text{O}-\text{C}-\text{R} \\
\text{O} & \quad \text{HC}-\text{O}-\text{C}-\text{R} \\
\text{O} & \quad \text{H}_2\text{C}-\text{O}-\text{C}-\text{R} \\
\end{align*}
\]

$\text{H}_2\text{R} + \text{CO}_2$ Decarboxylation
$\text{H}_2\text{R} + \text{CO} + \text{H}_2\text{O}$ Decarbonylation
$\text{H}_3\text{C} - \text{R} + 2\text{H}_2\text{O}$ Deoxygenation

$\tilde{\text{R}}$: unsaturated aliphatic chain
$\text{R}$: saturated aliphatic chain

\[ \text{O} \quad \text{H}_2\text{C}-\text{O}-\text{C}-\text{R} \quad +\text{H}_2 \quad \text{H}_2\text{C}-\text{O}-\text{C}-\text{R} \quad +\text{H}_2 \quad \text{H}_2\text{C}-\text{O}-\text{C}-\text{R} \quad +\text{H}_2 \]
Hydrotreating Reactions (2/2)

- Cold flow properties improvement
- Tailoring jet fuel molecules

\[ R_1-\text{CH}_2-\text{CH}_2-\text{CH}_3 + \text{H}_2 \rightarrow R_1-\text{CH}-\text{CH}_3 \]

\[ \text{R}_1 = \text{R}_2 + \text{R}_3 \]
Reactions associated with HEFA production based on a range of large and unsaturated fatty acids content of lipid feedstocks

<table>
<thead>
<tr>
<th>Reaction type</th>
<th>Reaction</th>
<th>H₂/oil (mol/100mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 Triglyceride hydrogenolysis*</td>
<td>![Triglyceride hydrogenolysis reaction]</td>
<td>2×100</td>
</tr>
<tr>
<td>2 Saturation</td>
<td>R-(CH=CH)_n·CH₃ + n H₂ → R-CH₂CH₂CH₃</td>
<td>3×n·(50-225)***</td>
</tr>
<tr>
<td>3 Deoxygenation**</td>
<td>![Deoxygenation reactions]</td>
<td>3×100·(1-3)</td>
</tr>
<tr>
<td>4 Isomerization</td>
<td>R-CH₂CH₂CH₃ → R-CH·CH₃</td>
<td>0</td>
</tr>
<tr>
<td>5 Hydrocracking</td>
<td>R-CH₂CH₂CH₃ + H₂ → R-H + CH₃-CH₂CH₃</td>
<td>3×(78-95)***</td>
</tr>
</tbody>
</table>
Lipid Sources

- **Plant oils**
  - Triglycerides
  - Coconut oil renders 85% jet range (C10-C14) molecules

- **Microalgaee oils**
  - Mostly FFAs
  - *Trichodesmium erythraeum* renders 55% of jet molecules

![Fatty acids composition graphs](image)
## Lipid Source Type vs. $H_2$ Consumption

<table>
<thead>
<tr>
<th>Reaction type</th>
<th>Plant oils</th>
<th>Microalgae oils</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Sunflower</td>
<td>Rape</td>
<td>Palm</td>
</tr>
<tr>
<td>1. Hydrogenolysis</td>
<td>2.0</td>
<td>2.0</td>
<td>2.0</td>
</tr>
<tr>
<td>2. Saturation</td>
<td>6.3</td>
<td>1.4</td>
<td>0.6</td>
</tr>
<tr>
<td>3. Deoxygenation</td>
<td>6.0</td>
<td>6.0</td>
<td>6.0</td>
</tr>
<tr>
<td>4. Isomerization</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
</tr>
<tr>
<td>5. Hydrocracking</td>
<td>2.6</td>
<td>2.6</td>
<td>2.5</td>
</tr>
</tbody>
</table>

Total (mol $H_2$/mol oil) | 16.9 | 12.0 | 11.1 | 8.5 | 2.9 | 2.8 | 2.7 | 2.4 |

Total (mol $H_2$/mol jet) | 5.6 | 4.0 | 3.7 | 2.8 | 2.9 | 2.8 | 2.7 | 2.4 |

- No $H_2$ consumption during hydrogenolysis of microalgal lipids
- Significant $H_2$ consumption during this step
- Need for saturated lipids feedstocks (some plant oils)
- Can be improved for microalgae-based species by improving cultivation strategy & genetic modification of algae strain
- Highest $H_2$ consumption
- Can be improved by catalyst design optimization
- Comparable consumption (negligible)
- Comparable $H_2$ consumption for all species
- Can be improved for microalgae-based species only by improving cultivation strategy & genetic modification of algae strain
Microalgae Oil Experimental Tests

- Evaluate different microalgae species
  - *Stichococcus* sp., *Nannochloropsis* sp., *Botryococcus braunii*
- Develop technology for microalgal oil extraction and conversion to 3G-biofuels

A. Karapatsia, et.al., 10th European Symposium on Biochemical Engineering Sciences and 6th International Forum on Industrial Bioprocesses, September 7-10, 2014, Lille, France
Overall HEFAs Production Carbon Footprint

<table>
<thead>
<tr>
<th>Plant oils</th>
<th>Microalgae oils</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sunflower</td>
<td>Dunaliella sp.</td>
</tr>
<tr>
<td>Rape</td>
<td>Chlorella sp.</td>
</tr>
<tr>
<td>Palm</td>
<td>Nannochloropsis Oceanica</td>
</tr>
<tr>
<td>Coconut</td>
<td>Trichodesmium erythraeum sp.</td>
</tr>
</tbody>
</table>

A. Cultivation & lipid production

<table>
<thead>
<tr>
<th></th>
<th>Sunflower</th>
<th>Rape</th>
<th>Palm</th>
<th>Coconut</th>
</tr>
</thead>
<tbody>
<tr>
<td>5.288</td>
<td>8.609</td>
<td>6.489</td>
<td>5.835</td>
<td></td>
</tr>
</tbody>
</table>

B. Hydrogenation

<table>
<thead>
<tr>
<th></th>
<th>Dunaliella sp.</th>
<th>Chlorella sp.</th>
<th>Nannochloropsis Oceanica</th>
<th>Trichodesmium erythraeum sp.</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.410</td>
<td>3.160</td>
<td>3.676</td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.171</td>
<td>0.122</td>
<td>0.113</td>
<td>0.085</td>
<td></td>
</tr>
<tr>
<td>0.089</td>
<td>0.085</td>
<td>0.082</td>
<td>0.073</td>
<td></td>
</tr>
<tr>
<td>0.085</td>
<td>0.082</td>
<td>0.073</td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.073</td>
<td>0.073</td>
<td>0.073</td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.073</td>
<td>0.073</td>
<td>0.073</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Total (g CO₂-eq/MJ jet)

<table>
<thead>
<tr>
<th></th>
<th>Sunflower</th>
<th>Rape</th>
<th>Palm</th>
<th>Coconut</th>
</tr>
</thead>
<tbody>
<tr>
<td>5.459</td>
<td>8.731</td>
<td>6.602</td>
<td>5.920</td>
<td></td>
</tr>
</tbody>
</table>

Sources:
Limits & Opportunities of HEFAs

- High production costs
  - Mostly related with lipid cultivation/extraction
- Current low crude oil prices
- Low aromatics

- Favorable carbon footprint
  - For some (not all) lipid sources
- Potential lipid integration in underlying refineries
  - Hybrid jet
Horizon 20-20 project: Reliable Bio-based Refinery Intermediates - BIOMATES
Thank you for your attention.

For more information:

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● Common refining conversion technology
  — H/C ratio increase
  — Heteroatom (S, N, O) and metals removal
  — High conversion
  — Feedstock variability
  — No by-products

● Most effective technology for biomass upgrading
Waste Lipids Upgrading ...

- Better combustion (increased cetane)
- More economic (high HHV)
- More stable (no TAN, high IP)
- Sustainable

Potential to cover 9.5% of Greek diesel demand

Potential to cover 9,5% of Greek diesel demand

- Bezergianni, S. et al. (2014) Fuel 118:300
- Bezergianni, S., et al. (2012), Fuel, 93:638

Large-scale units require large investments
Is it possible to integrate biomass in refineries?
A. Technical feasibility
- Utilize existing infrastructure
- Maintain similar operation
- Maintain same product quality

B. Environmental performance
- Mitigate energy consumption
- Reduction of emissions (WTT)

www.sustaindiesel.gr
Technical Feasibility Assessment

1. Evaluation of hydrotreating catalyst
2. Determine optimal operating conditions
   - T, P, H₂/oil, LHSV
3. Determine max WCO mixing ratio
4. Evaluate hybrid diesel
   - GHG emissions
   - engine performance
- NiMo catalyst showed a performance increase for the feedstock with the largest WCO content.
- NiMo catalyst exhibited increased HDN performance with increasing WCO content.

WCO addition does not decrease product quality when NiMo catalyst is used.
Catalyst deactivation rate is extremely important for catalyst selection.

- Deactivation rate determined based on desulfurization efficiency at different DOS.
- WCO by-product CO₂ has a suspending role in HDS/HDN.

NiMo deactivation rate is 3 times smaller than CoMo.


S. Bezergianni and L. Chrysikou, Sustainable HEFAs for Aviation
Effect of Biomass Content
Heteroatom Removal & Diesel Yields

- Diesel yield favored with increasing WCO
  - WCO contained triglycerides can be more easily converted into diesel range hydrocarbons
- Desulfurization is not limited by WCO

Biomass integration favors diesel yields and renders low S diesel

Hydrogen consumption affects process economics.

Hydrogen consumption increases due to underlying HDO kinetics.

Smaller WCO rates (<90%) are preferred for economic feasibility of WCO integration.

- 5-10% WCO $\rightarrow$ 7.5-8.5% increase in H$_2$ consumption.

No more than 10% H$_2$ consumption increase for less than 10% WCO.
## Quality Assessment
### Hybrid vs. Market Diesel

<table>
<thead>
<tr>
<th>Properties</th>
<th>Units</th>
<th>Hybrid diesel</th>
<th>Market diesel</th>
</tr>
</thead>
<tbody>
<tr>
<td>Density</td>
<td>kg/m³</td>
<td>825,8</td>
<td>829,2</td>
</tr>
<tr>
<td>Flash point</td>
<td>°C</td>
<td>61</td>
<td>67</td>
</tr>
<tr>
<td>Sulfur</td>
<td>wppm</td>
<td>8,2</td>
<td>5,8</td>
</tr>
<tr>
<td>Viscosity (40°C)</td>
<td>cSt</td>
<td>2,996</td>
<td>3,066</td>
</tr>
<tr>
<td>Cetane index</td>
<td></td>
<td>59,1</td>
<td>58,3</td>
</tr>
<tr>
<td>Cetane number</td>
<td></td>
<td>56,7</td>
<td>55,7</td>
</tr>
<tr>
<td>Water</td>
<td>wppm</td>
<td>100</td>
<td>60</td>
</tr>
<tr>
<td>CFPP</td>
<td>°C</td>
<td>-2</td>
<td>0</td>
</tr>
<tr>
<td>Polyaromatics</td>
<td>%w/w</td>
<td>1,1</td>
<td>1,4</td>
</tr>
<tr>
<td>Lubricity</td>
<td>μm</td>
<td>181</td>
<td>174</td>
</tr>
<tr>
<td>Recovery 95% v/v</td>
<td>°C</td>
<td>353</td>
<td>353,2</td>
</tr>
<tr>
<td>Recovery at 250°C</td>
<td>%v/v</td>
<td>26,8</td>
<td>25,8</td>
</tr>
</tbody>
</table>
### Environmental Performance Assessment

<table>
<thead>
<tr>
<th>Fuel* type</th>
<th>gCO₂ eq/MJ</th>
</tr>
</thead>
<tbody>
<tr>
<td>Market diesel</td>
<td>16.97</td>
</tr>
<tr>
<td>Hybrid diesel (WCO co-processing)</td>
<td>9.32</td>
</tr>
<tr>
<td>Diesel with WCO-based HVO</td>
<td>14.15</td>
</tr>
</tbody>
</table>

*All fuels have a total 7% v/v bio-content

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Expected reduction of GHG emissions by 45%

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Co-processing of biomass in refinery is environmentally and economically more sustainable allowing extended integration of biomass in transportation sector.

---

### Stand-alone Biomass Upgrading vs. Biomass Co-processing

<table>
<thead>
<tr>
<th>Stand-alone biomass upgrading</th>
<th>Biomass co-processing</th>
</tr>
</thead>
<tbody>
<tr>
<td>Produces drop-in biofuels (FAME, ethanol, HVOs, etc)</td>
<td>Renders hybrid fuels (decarb gasoline, jet, diesel)</td>
</tr>
<tr>
<td>– Technical limitations may be associated with end-use</td>
<td>– Fully compatible with fossil counterparts</td>
</tr>
<tr>
<td>Requires infrastructure ➔ large CAPEX</td>
<td>Utilizes existing infrastructure ➔ low CAPEX</td>
</tr>
<tr>
<td>Utility intensive processes (fuel, NG, H₂ etc)</td>
<td>Employs underlying utilities of refineries</td>
</tr>
<tr>
<td>Ambiguous environmental benefits</td>
<td>Clear reduction of CO₂ emissions during production</td>
</tr>
</tbody>
</table>

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*S. Bezergianni and L. Chrysikou, Sustainable HEFAs for Aviation*
Conclusions

- Catalytic hydrotreatment is a key technology for biomass upgrading
  - Bio-based intermediates & lipids upgrading
  - Compatibility with fossil fuels, attractive properties
- Co-hydroprocessing can allow immediate and sustainable biomass integration with energy markets
  - No requirement of investments on new infrastructure
  - No significant technology limitations
  - Improvement of fuel sustainability (lower carbon foot-print)
  - Optimal way of integrating biomass in transportation sector from an environmental and economic point of view
Biomass & Biofuels

**Biomass**

- **Energy crops**
  - Sunflower, rapeseed, cotton, corn, barley, soy, sweet- sorghum, sugar-beet etc
- **Lignocellulosic material**
  - Wood, paper industry waste, forestry waste etc
- **Animal fats**
- **Agricultural and municipal waste**
- **Waste cooking oil/fats**
- **Algae**
- **...**

**Biofuels**

Fuels produced from biomass
FAME Biodiesel
Most Common Biofuel in EU

- Fatty Acid Methyl Esters, FAME
  - Produced via transesterification of fatty acids
- Lipid feedstocks / Triglycerides
  - Rape-seed oil, sunflower oil, cotton oil, tallow, waste cooking oil etc
  - Require dedicated cultivated areas ➔ Food vs. Fuel
- Properties
  + Environmentally friendly (reduced SO$_x$, CO, aromatics)
  + Higher cetane number and lubricity
  - Reduced cold flow properties
  - Low oxidation stability
  - Tend to decompose ➔ hydroperoxides, acids, cetones
- Utilized as mixture with conventional diesel
  - B5 to B20 (higher FAME content renders problems in warmer countries)
  - No major engine modifications required
Bioethanol

Most Popular Biofuel Worldwide

- Sugar and starch feedstocks
  - Sugar-cane, sugarbeet, sweet-sorghum, corn, potato, etc
  - Require dedicated cultivated areas
    Food vs. Fuel

- Properties
  - Similar combustion with gasoline
  - Reduction of emissions
  - Higher octane number
    » Employed as octane booster
  - Increase engine performance
  - Requires high purity ethanol in gasoline mixtures (99.5-99.9%)

- Utilized in mixtures with gasoline
  - Most common E10, ideal E85 (FFVs)