CATALYTIC PROCESSING OF TRIGLYRICERIDES INTO BIOJET FUEL

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1st FERIA Conference
The European Conference on Fuel and Energy Research and its Applications
September 6 – 8, 2021, Nottingham, United Kingdom
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Introduction

• About 10% of global crude oil production goes into jet fuel

• Graph shows a steady increase since 2009.
  • In 2019, 432 billion litres of oil consumed
  • Dropped to about 236 billion litres in 2020 due to COVID\(^1\)

• Sustainable development goals and Net Zero agenda require replacement with environmentally-friendly alternatives
  • Renewable hydrocarbon fuels from biomass (BioJet)
  • Electrification

\[1\) https://www.statista.com/statistics/655057/fuel-consumption-of-airlines-worldwide/
Drivers for BioJet Fuel Production and Utilisation

- The aviation sector accounts for about 3% of the global CO\textsubscript{2} emissions (36 billion tonnes in 2019)\textsuperscript{2} but air travel is forecasted to increase.

- The International Air Transport Agency (IATA) the aviation industry is to meet a target set at 50% or less than the 11.4 Gtoe consumed in 2005 and net zero by 2060\textsuperscript{3}.

- The International Civil Aviation Organization (ICAO) has put in place policies to improve aircraft efficiency and limit the growth in CO\textsubscript{2} emissions of international flights\textsuperscript{4}.

- The electric plane is a possible prospect but there is need to fill the gap until this is established.

- About 10% bioenergy (biojet fuel) contribution currently.

- Production of biojet fuel can be beneficial for the socio-economics of poorer communities and developing countries.

\textsuperscript{[2]} https://ourworldindata.org/co2-emissions
\textsuperscript{[3]} https://inis.iaea.org/collection/NCLCollectionStore/_Public/48/026/48026313.pdf?r=1&r=1
\textsuperscript{[4]} https://www.frontiersin.org/articles/10.3389/fenrg.2020.00110/full
(Potential) Commercial Routes for BioJet Fuel Production

- ASTM D7566 approved

**OIL TO BIOJET**

- Vegetable oil/Tallow/Fats → HYDRODEOXYGENATION → Long chain hydrocarbons → HYDROCRACKING → Fuel-range hydrocarbons → FRACTIONATION → BIOJET FUEL

**GAS TO BIOJET**

- Biomass → GASIFICATION → Syngas → FISCHER-TROPSCH SYNTHESIS (FT) → Fuel-range hydrocarbons → FRACTIONATION → BIOJET FUEL

**ALCOHOL TO BIOJET**

- Biomass → HYDROLYSIS → Sugars → FERMENTATION → Alcohols → DEHYDRATION → HYDROGENATION → Fuel-range hydrocarbons → FRACTIONATION → BIOJET FUEL

- *2 different process routes possible

**SUGAR TO BIOJET**

- Biomass → HYDROLYSIS → Sugars → FERMENTATION → Farnesene → HYDROGENATION → Fuel range hydrocarbons → FRACTIONATION → BIOJET FUEL

- *2 different process routes possible
Challenges of Existing BioJet Routes

- Apart from FT, existing routes require large external hydrogen input, with high environmental and economic implications.
- Successful oil-to-jet tests require hydrogen/oil molar ratio of around 1000; 40 – 50 kt/y plants
- About 50% of hydrogen is produced via steam methane reforming (SMR), giving the cheapest hydrogen selling price ($1.5/kg) but has high carbon footprint, even with carbon capture and storage (CCS).
- Green hydrogen from electrolysis of water is still costly; at about $12/kg.
- Case study: Vegetable oil to Aviation Fuel via HRJ
  - 50,000 tonnes of vegetable oil per year
  - 17,500 tonnes of hydrogen per year
  - Average biojet yield is 45 wt%
  - ≈ Hydrogen cost of £9333 per tonne of biojet fuel (if using hydrogen from electrolysis)
  - ≈ Hydrogen cost of £1160 per tonne of biojet fuel (if using hydrogen from SMR)
  - In comparison, fossil jet fuel sells for about £780 per tonne!

Research Aim

- To investigate a **hydrogen-free** multi-step catalytic process route which converts fats and oils (triglycerides) into high yields of biojet fuel.
- To determine optimum conditions for each reaction step in the multi-step process for biojet fuel production.
Experimental Methodology

Batch Reactors
- Temperature
- Feed ratio
- Reaction time

- 450 ml 4575A Stainless Steel batch reactor
  - Max. temp. 350 °C
  - Max. press. 345 bar

- 75 ml Parr Instruments Co. Hastelloy-C batch reactor
  - Max. temp. 600 °C
  - Max. press. 450 bar

- FEEDSTOCK
- Catalyst & solid residue
- Gas
- Aqueous phase
- Organic phase

(Catalytic) Thermal Processing
- Hydrolysis (non-catalytic)
- Deoxygenation (catalytic)
- Cracking (catalytic)

Products Separation & Analysis
Feedstock and Materials

- Rapeseed oil
- Deionised water
- Pt/C catalysts (Sigma-Aldrich), powder, used as received
- ZSM-5 (Alfa Aesar); Si/Al ratio, 360:1, surface area 620 m²/g

Fatty acid compositions of rapeseed oil

<table>
<thead>
<tr>
<th>Common Name</th>
<th>Scientific Name</th>
<th>Lipid Number</th>
<th>% Composition ( Typical )</th>
<th>% Composition *(UK Basis)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Palmitic acid</td>
<td>Hexadecanoic acid</td>
<td>C16:0</td>
<td>1.5 - 4</td>
<td>3-6</td>
</tr>
<tr>
<td>Stearic acid</td>
<td>Octadecanoic acid</td>
<td>C18:0</td>
<td>0.4 - 3</td>
<td>0-3</td>
</tr>
<tr>
<td>Oleic acid</td>
<td>9-Octadecenoic acid</td>
<td>C18:1</td>
<td>22 - 60</td>
<td>61-66</td>
</tr>
<tr>
<td>Linoleic acid</td>
<td>9,12-Octadecadienoic acid</td>
<td>C18:2</td>
<td>12 - 14</td>
<td>21-27</td>
</tr>
<tr>
<td>Alpha-Linolenic acid</td>
<td>9,12,15-octadecatrienoic acid</td>
<td>C18:3</td>
<td>5 - 7</td>
<td>9.6</td>
</tr>
<tr>
<td>Arachidic acid</td>
<td>Eicosanoic acid</td>
<td>C20:0</td>
<td>3 - 5</td>
<td>1-2</td>
</tr>
<tr>
<td>Gondoic acid</td>
<td>11-Eicosenoic acid</td>
<td>C20:1</td>
<td>0 - 1</td>
<td>0-1</td>
</tr>
<tr>
<td>Behenic acid</td>
<td>Docosanoic acid</td>
<td>C22:0</td>
<td>0 - 3</td>
<td>0-1</td>
</tr>
<tr>
<td>Gondoic acid</td>
<td>13-Docosenoic acid</td>
<td>C22:1</td>
<td>0 - 5</td>
<td>0-1</td>
</tr>
<tr>
<td>Lignoceric acid</td>
<td>Tetracosanoic acid</td>
<td>C24:0</td>
<td>0 - 3</td>
<td>0-1</td>
</tr>
</tbody>
</table>

*https://www.cambridge.org/core/journals/british-journal-of-nutrition/article/can-rapeseed-oil-replace-olive-oil-as-part-of-a-mediterraneanstyle-diet/09863075B1598A2CDBA1A056E4FA1268#
Stage 1: Hydrolysis

- Use of subcritical water (with no added catalysts)

**Parameters**
- Temperature: 300 °C
- Oil/water mass ratio: 1:1, 1:2, 1:3, 1:4
- Time: 1 hr, 2 hrs, and 3 hrs
- Reaction environment: Nitrogen

**PRODUCT ANALYSIS**

- Organic phase (liquid)
  - Titration
  - GC-FID
  - CHNS

- Aqueous phase
  (For future analysis)
### RESULTS FROM HYDROLYSIS OF VEGETABLE OIL

**Example of mass balances from hydrolysis tests (oil/water mass ratio= 1:2) at 300 °C for 1 hr under 5 bar Nitrogen gas**

<table>
<thead>
<tr>
<th>VEGETABLE OIL (g)</th>
<th>WATER FEED (g)</th>
<th>SOLID (g)</th>
<th>SEMI-SOLID PRODUCT (g)</th>
<th>AQUEOUS PHASE (g)</th>
<th>GASES (g)</th>
<th>% BALANCE</th>
</tr>
</thead>
<tbody>
<tr>
<td>20.00</td>
<td>40.00</td>
<td>-</td>
<td>17.68</td>
<td>41.84</td>
<td>-</td>
<td>99.20</td>
</tr>
<tr>
<td>20.00</td>
<td>40.05</td>
<td>-</td>
<td>17.83</td>
<td>41.74</td>
<td>-</td>
<td>99.20</td>
</tr>
<tr>
<td>19.99</td>
<td>40.00</td>
<td>-</td>
<td>17.51</td>
<td>40.39</td>
<td>-</td>
<td>96.52</td>
</tr>
<tr>
<td>20.00</td>
<td>40.02</td>
<td>-</td>
<td>17.57</td>
<td>42.10</td>
<td>-</td>
<td>99.43</td>
</tr>
</tbody>
</table>

- Organic phase (long chain carboxylic acids)
- Semi-solid due to loss of glycerol
- Formation of intermolecular bonds between the long carbon chains
RESULTS FROM HYDROLYSIS: FATTY ACIDS YIELDS FROM TITRATION

Back titration method
- Hydrolysis product dissolved in DCM
- 2 ml of solution taken for titration analysis
- 25 ml of 0.1 M NaOH (ethanolic)
- Mixed thoroughly and titrated with 0.1 M HCl

Yield of fatty acid:

\[
\text{Yield} = \frac{(B-S) \times M \times V \times MR}{10000}
\]

S = volume of 0.1 M HCl used in titration (mL)
B = volume of 0.1 M HCl used in blank titration (mL)
M = concentration of HCl (mol/L)
V = volume of aqueous phase collected (mL)
MR = molecular mass of main fatty acid (g/mol)

Optimum condition: 1:2 oil/water ratio, 300 °C, 1 hr
Results from Hydrolysis of Rapeseed oil

Elemental Compositions of Fresh Vegetable Oil and Hydrolysed Vegetable oil

<table>
<thead>
<tr>
<th>SAMPLE</th>
<th>NITROGEN</th>
<th>CARBON</th>
<th>HYDROGEN</th>
<th>SULPHUR</th>
<th>OXYGEN</th>
<th>HHV (MJ/kg)*</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rapeseed oil</td>
<td>0.125</td>
<td>77.00</td>
<td>12.01</td>
<td>0</td>
<td>10.87</td>
<td>41.4</td>
</tr>
<tr>
<td>Hydrolysed oil (Fatty acids)</td>
<td>0.157</td>
<td>73.14</td>
<td>11.92</td>
<td>0</td>
<td>14.78</td>
<td>39.3</td>
</tr>
</tbody>
</table>

* Dulong’s formula: \( HHV = 0.3383C + 1.443(H – (O/8) + 0.0942S \)

64% oleic acid yield obtained from GC analysis, which correlates with the values from literature
Stage 2: Deoxygenation

There are three main deoxygenation routes for carboxylic acids. These are:
- Decarbonylation
- Decarboxylation
- Hydrodeoxygenation

Both decarbonylation and decarboxylation will produce a hydrocarbon with one less carbon than the original carboxylic acid.

Among these three, only decarboxylation does not require hydrogen input and will be targeted in this project.

Decarboxylation Tests

Main reaction (using oleic acid)

\[ \text{C}_{17}\text{H}_{33}\text{COOH} + \text{H}_2 \rightarrow \text{C}_{17}\text{H}_{36} + \text{CO}_2 \]

**Parameters**
- Temperature: 400 °C
- Catalyst: 1 g Pt/C
- Time: 1 hr
- Pressurised with 5 bar N₂

At the end of reaction
- Gas sampled for GC-FID/TCD analysis
  - GC-FID for hydrocarbon gases
  - GC-TCD for permanent gases
- No aqueous phase
- Oil separated from solid residue by filtration
  - Oil analysed by GC-FID and GC-MS
  - Solid residue dried, weighed, and stored for future analysis

**PRODUCT ANALYSIS**

- **Liquid organic product**
  - GC-MS
  - GC-FID
  - CHNS

- **Gas product**
  - GC-FID
  - GC-TCD

In-situ hydrogenation without external hydrogen supply
Results from Decarboxylation of Hydrolysis Products and Model Fatty Acid

Mass balances from decarboxylation tests

<table>
<thead>
<tr>
<th>SAMPLE NAME</th>
<th>FEED (g)</th>
<th>SOLID (g)</th>
<th>ORGANIC PRODUCT (g)</th>
<th>AQUEOUS PHASE (g)</th>
<th>GAS PHASE (g)</th>
<th>% BALANCE</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hydrolysed Oil 1</td>
<td>18.63</td>
<td>0.22</td>
<td>14.64</td>
<td>-</td>
<td>3.28</td>
<td>97.37</td>
</tr>
<tr>
<td>Hydrolysed oil 2</td>
<td>19.15</td>
<td>0.66</td>
<td>16.21</td>
<td>-</td>
<td>1.94</td>
<td>98.22</td>
</tr>
<tr>
<td>Palmitic acid</td>
<td>20.00</td>
<td>0.28</td>
<td>16.07</td>
<td>-</td>
<td>2.76</td>
<td>95.55</td>
</tr>
</tbody>
</table>

From Rapeseed oil

Elemental Composition of decarboxylated oils

<table>
<thead>
<tr>
<th>SAMPLE</th>
<th>NITROGEN %</th>
<th>CARBON %</th>
<th>HYDROGEN %</th>
<th>SULPHUR %</th>
<th>OXYGEN %</th>
<th>HHV (MJ/kg)*</th>
</tr>
</thead>
<tbody>
<tr>
<td>Decarboxylated Oil 1</td>
<td>0.190</td>
<td>85.56</td>
<td>14.25</td>
<td>0</td>
<td>0</td>
<td>49.5</td>
</tr>
<tr>
<td>Decarboxylated Oil 2</td>
<td>0.222</td>
<td>86.24</td>
<td>13.54</td>
<td>0</td>
<td>0</td>
<td>48.7</td>
</tr>
<tr>
<td>Decarboxylated Palmitic acid</td>
<td>0.171</td>
<td>84.85</td>
<td>14.97</td>
<td>0</td>
<td>0</td>
<td>50.3</td>
</tr>
</tbody>
</table>

* Dulong’s formula
Comparison with Model Fatty acid (Palmitic acid)

- Oleic acid, a C18 carboxylic acid is the main component (about 60%) in Rapeseed oil.
  - Its decarboxylation would yield heptadecane, which can be seen in chromatogram A (largest peak)
- Palmitic acid is a C16 carboxylic acid.
  - Its decarboxylation yielded pentadecane as shown in the chromatogram B (largest peak)
- The differences in the physical states could be due to the presence of higher concentrations of lower molecular weight hydrocarbons in the liquid oil compared to the palmitic acid
Stage 3: Cracking

Example: $\text{C}_{15}\text{H}_{32} \rightarrow \text{C}_{10}\text{H}_{22} + \text{C}_{5}\text{H}_{10}$

Parameters
- Temperature: 400 °C
- Catalyst: 1 g ZSM-5 (Alfa Aesar); Si/Al ratio, 360:1, surface area 620 m$^2$/g
- Time: 1 hr
- Pressurised with 5 bar N$_2$

At the end of reaction
- Gas sampled for GC-FID/TCD analysis
  - GC-FID for hydrocarbon gases
  - GC-TCD for permanent gases
- No aqueous phase
- Oil separated from solid residue by filtration
  - Oil analysed by GC-FID and GC-MS
  - Solid residue dried, weighed, and stored for future analysis
## Results from Cracking Stage

### Mass Balances from the Cracking Stage

<table>
<thead>
<tr>
<th>SAMPLE NAME</th>
<th>FEED (g)</th>
<th>SOLID (g)</th>
<th>ORGANIC PRODUCT (g)</th>
<th>AQUEOUS PHASE (g)</th>
<th>GAS PHASE (g)</th>
<th>% BALANCE</th>
</tr>
</thead>
<tbody>
<tr>
<td>Decarboxylated oil 1</td>
<td>13.64</td>
<td>0.34</td>
<td>9.94</td>
<td>-</td>
<td>1.33</td>
<td>85.09</td>
</tr>
<tr>
<td>Decarboxylated oil 2</td>
<td>10.49</td>
<td>0.55</td>
<td>7.28</td>
<td>-</td>
<td>1.48</td>
<td>88.76</td>
</tr>
<tr>
<td>Decarboxylated Palmitic acid</td>
<td>8.76</td>
<td>0.49</td>
<td>6.34</td>
<td>-</td>
<td>0.84</td>
<td>87.58</td>
</tr>
</tbody>
</table>

### Elemental compositions of oils from the Cracking Stage

<table>
<thead>
<tr>
<th>SAMPLE</th>
<th>NITROGEN</th>
<th>CARBON</th>
<th>HYDROGEN</th>
<th>SULPHUR</th>
<th>OXYGEN</th>
<th>HHV (MJ/kg)*</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cracked Oil 1 from Stage 2</td>
<td>0.244</td>
<td>87.63</td>
<td>12.12</td>
<td>0</td>
<td>0</td>
<td>47.2</td>
</tr>
<tr>
<td>Cracked oil 2 from Stage 2</td>
<td>0.269</td>
<td>88.55</td>
<td>11.18</td>
<td>0</td>
<td>0</td>
<td>46.1</td>
</tr>
<tr>
<td>Cracked oil from Palmitic acid</td>
<td>0.191</td>
<td>85.68</td>
<td>14.13</td>
<td>0</td>
<td>0</td>
<td>49.4</td>
</tr>
</tbody>
</table>

* Dulong’s formula
Comparison of Chromatograms from GC Analysis Before and After Cracking

• The GC-MS was used to identify the compounds in the oil
• GC-FID used to quantify the compounds in the oil
  • About 72% of compounds quantified
• Diphenyl ether used as internal standard for the GC-FID quantification
Effect of Cracking Stage on Oil Compositions

Weight % composition of oil products

Decarboxylated oil
Cracked oil
Cracking: Comparison with Model Product

- Kerosene standard has mainly $C_{10} - C_{15}$ hydrocarbons
- About 45% selectivity to kerosene already achieved
- Further optimization required to get cracked oil to jet fuel range
Overall Yields

**VEGETABLE OIL**

**HYDROLYSIS:**
average yield = 88.22%

**DECARBOXYLATION:**
average yield = 81.61%

**CRACKING:**
average yield = 71.14%

**Overall yield = 51.22%**

**PALMITIC ACID**

**DECARBOXYLATION:**
average yield = 80.35%

**CRACKING:**
average yield = 72.37%

**Overall yield = 58.15%**
Conclusions

• Research focus on conversion of vegetable oil to bio-derived aviation fuel (BioJET) via thermo-catalytic processing
• Hydrothermal hydrolysis (first) stage optimised
• Preliminary experimental work carried out on decarboxylation and cracking stage
• Fuel range hydrocarbons (alkanes and aromatics) obtained but further work needed to improve proportion of jet fuel
• Higher heating values of hydrocarbon products ranged from 46.1 – 50.3 MJ/kg (fossil kerosene = 46.2 MJ/kg; rapeseed oil (feedstock)= 41.4 MJ/kg)
• Starting from rapeseed oil, over 80% of liquid hydrocarbon product obtained after decarboxylation (theoretical yield = 81.5%)\(^7\)
• Cracking stage led to reduction to about 71% of fuel range hydrocarbons!

Future work

• Optimisation of decarboxylation and cracking stage/stages
  • Effect of temperature
  • Effect of reaction time
  • Effect of catalyst types and loading
  • Effect of feedstock loading

• Process synthesis and process modelling

• Economic evaluation
Acknowledgements

Thank you for your attention!!!

Research team (current)
Dr Iram Razaq (PDRA)
Dr Cristiane Scaldaferrri (PDRA)
Morenike Peters (PhD student)
Danielle Nouwe Edou (RA)
Qasim Hussain (RA)