Reactive Distillation for Biodiesel Production

M W Tuck

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Background

- Biodiesel is an ester of C\textsubscript{16}-C\textsubscript{20} fatty acids
  - Conventionally methyl ester (FAME), ethyl ester process (FAEE) underdevelopment
- Esterification of Fatty Acids in Resin Catalysed Reactive Distillation Column
- Reaction system developed for BDO and NDA processes
  - Development started in early 1990s.
  - First commercial operation in late 1997
  - About 2.6 million tonnes per year of esters produced in 30 JM Davy licensed reaction columns
- First 2nd generation plant for Endicott Biofuels, start-up Q4 2012
Biodiesel - Market

- Biodiesel consumption is around 2.5% of diesel market (15 million MPTA)
- Installed capacity c. 30 million MPTA – not currently at full load
- Currently market driven by government subsidies and legislation
- European FAME $1200 - $1300 per tonne / European Petrol-diesel $1050 per tonne
- Market has grown at up to 20%/year, mostly virgin oil based – now feedstock limited
### Supply of Virgin Oils

#### Oil Yields per Hectare

<table>
<thead>
<tr>
<th>Crop</th>
<th>Yield (t/ha)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Palm</td>
<td>5</td>
</tr>
<tr>
<td>Peanut</td>
<td>0.9</td>
</tr>
<tr>
<td>Soya</td>
<td>0.4</td>
</tr>
<tr>
<td>Rape (Canola)</td>
<td>0.8</td>
</tr>
</tbody>
</table>
Biodiesel
Key factors for future

- Feedstock is by far the major cash cost
- Finite land area, limits supply of virgin oils.
- Food oil demand is currently c. 110 million tonnes per year
- Population growing at around 1.1% per year

- Vegetable oil production cannot keep up with both demands
- 10,000,000 people generate enough waste oil for 50,000 MTPA of biodiesel
- Need for biodiesel to switch to non food feeds
Biodiesel – New Feeds

Davy process is ideally suited for high acid low cost feeds

✓ High free fatty acid
✓ Fat Splitter removes most impurities

Non-traditional and low value feeds
❖ Non-edible oils (jatropha, algae)
❖ Waste oils (brown/yellow grease)
❖ Rancid oils (spoiled crops and shipments)
❖ Animal waste products
❖ Palm Fatty Acid Distillate (PFAD)
❖ Palm Sludge Oil (PSO)
❖ DDGS (Double distilled grain spirit)
❖ Tallow and other animal fats
❖ Used cooking oil

JM Davy can run other feeds to test suitability
Trans-esterification vs Esterification

Trans-esterification

- Lower CAPEX
- Non-palm virgin oil OPEX lower that Esterification
- Basic catalyst consumed
- Not tolerant of free fatty acids
- Glycerol produced is laden with salt

Fatty Acid Esterification

- Low quality / high free fatty acid feed stocks
- High feedstock efficiency, no losses from soaping
- OPEX benefits With Palm Oil
- Fat splitting route removes many impurities in the hydrolysis step
- Fat splitting by-product glycerol does not contain salts/ash
Esterification Chemistry

\[ \text{R-COOH} + \text{MeOH} \rightleftharpoons \text{R-COO-Me} + \text{H}_2\text{O} \]

\[ \text{Fatty Acid} + \text{Methanol} \rightleftharpoons \text{Methyl Ester} + \text{Water} \]
Increasing concentration of water

Methanol / Preheated Fatty Acid wash

Preheated Fatty Acid

Increasing concentration of ester

Methanol & Water to Methanol Column

Vapour

Methanol

Liquid

Methyl Ester

- Multi-stage countercurrent bubbled slurry reactor

- Methanol provides 3 important functions:

1. It takes part in the reaction
2. It acts as a stripping vapour to remove water from the reaction
3. It provides agitation for the resin catalyst
Column Reaction Profile

- Residual Acid % vs Tray Number
- 3:1 methanol:acid ratio
- 2:1 methanol:acid ratio
Resin Catalyst
Customised for reactive distillation system

- Developed in conjunction with resin manufacturer
  - Activity
  - Selectivity (low ether make)
  - Strength
  - Size distribution
Process Principles

Cross-section of a CCR Tray

- Resin catalyst slurry
- Vapour riser
- Contact slurry with vapour for mass transfer and resin agitation
- Weirs maintain liquid inventory
- Liquid downcomer, screen retains resin on tray
QVF Glass Column

- Ten stage reaction column
- Atmospheric pressure operation
- Used to generate initial operating condition
- 300mls per stage
- Test catalyst life
- Scan parameters
Pilot rig

- Stainless steel pilot column
- Pressure operation
- Simulates commercial column operation
- Demonstrated resin catalyst life
Hydraulic Test Rig

Used to determine:
- Gas / liquid expansion
- Tray height / disengagement space
- Superficial Gas velocity max / min
- Sparger configuration for good mixing and resin suspension
- Sparger holes and tray pressure drop
- Operating stability
- Mass transfer rates by O2 probe
Tray Hydraulics in Operation
Resin Size Distribution

• Resin size distribution varies between resins and method of manufacture

• Resin beads swell to varying extent depending on chemical environment

• Resin size and size distribution is critical in designing screen to avoid blockage and blinding.

• For beads of the wrong size, very small volume is sufficient to block a screen.
Liquid Screen Testing

• Quadrant section of full size stage

• Developed design of liquid take-off screens.

• Design of screen for low Dp, and no resin plugging

• Resin attrition measured over 1000hrs
Commercial Units

Scale-Up

- Initial design, 1m column – same size as hydraulic rig.
- Scaled up to >5m
- Internals modified to ensure resin circulation and gas distribution over whole cross section.
- On-stream resin loading/unloading system developed
Entrainment

- Normal distillation columns will tolerate 1-2% re-entrainment of the liquid
- Different problem for trays with resin. Entrained liquid is returned to tray but not entrained resin.
Tray Hydraulic Study
Commercial Reaction Column
Davy NDA and Biodiesel Plants

Philippines

Indonesia

China
# Fatty Acid Esterification

## Commercial References

<table>
<thead>
<tr>
<th>Client</th>
<th>Location</th>
<th>Annual FAME Capacity (Kilo tonnes/million litres)</th>
<th>Feedstock</th>
<th>Start-Up Date</th>
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</thead>
<tbody>
<tr>
<td>Confidential Client [1]</td>
<td>China</td>
<td>147 / 171</td>
<td>Palm based Fatty Acid</td>
<td>2013</td>
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<tr>
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<td>Asia</td>
<td>80 / 93</td>
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<td>Endicott Biofuels [3]</td>
<td>USA</td>
<td>100 / 116</td>
<td>Tallow &amp; Waste Oil based Fatty Acids</td>
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<td>Ecogreen [1]</td>
<td>Indonesia</td>
<td>78 / 91</td>
<td>Palm based Fatty Acid</td>
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<td>Oxiteno [1]</td>
<td>Brazil</td>
<td>85.5 / 99</td>
<td>Palm based Fatty Acid</td>
<td>2007</td>
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<td>KLK Oleo Mas [1]</td>
<td>Malaysia</td>
<td>111 / 129</td>
<td>Palm based Fatty Acid</td>
<td>2007</td>
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<td>Dahin [1]</td>
<td>Taiwan</td>
<td>55.5 / 65</td>
<td>Palm based Fatty Acid</td>
<td>1999</td>
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<tr>
<td><strong>TOTAL</strong></td>
<td></td>
<td><strong>1,245 / 1,447</strong></td>
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</table>

1. Produces FAME as an intermediate product for conversion to fatty alcohols.
2. Produces FAME suitable for biodiesel and conversion to fatty alcohols.
3. Produces FAME for use as biodiesel.
2nd Generation Biodiesel Plant

- Endicott Biofuels
- JM Davy’s First 2nd Generation Licensee

- 100,000 MTPA per year plant
- Low value waste fat and oil feed
- Commissioned 2012
- High quality G2 Clear™ biodiesel product
2nd Generation Biodiesel

• Process based around fatty acid esterification.

• Feed fatty acid derived from:
  - Virgin oils
  - Waste oils

• Produces fuel in accordance with the American Standard ASTM D-6751 and European Standard EN-14214 for biodiesel.

• Acid resin catalysed reactive distillation - a proven technology.

Oil / Fat → Fat Splitting → Esterification → Biodiesel
The many JM Davy chemists and engineers who have contributed to the development and successful commercialisation of this technology.