Towards a Biodiesel-based Biorefinery: Chemical and Physical Properties of Reactively Extracted Rapeseed (Canola)

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Overview

Routes to biodiesel production from oils and fats:
- Base-catalyzed transesterification of the oil
- Direct acid-catalyzed transesterification of the oil
- Conversion of the oil to its fatty acids and then to biodiesel
- Enzyme-catalyzed of the oil

Most of the biodiesel produced today use the base-catalyzed reaction for several reasons:
- It is low temperature and pressure
- It yields high conversion (98%) with minimal side reactions
- Lower reaction time
- It is a direct conversion to biodiesel with no intermediate compounds
- No exotic materials of construction are needed
Biodiesel Production: The Transesterification Reaction

Triglyceride (Oil) + 3 CH₃OH → Glycerol (FAME) x 3

Catalyst (usually NaOH, KOH or NaOCH₃)
Transesterification Reaction

Sequence of Reactions

- Triglycerides + CH₃OH ↔ Diglycerides + FAME
- Diglycerides + CH₃OH ↔ Monoglycerides + FAME
- Monoglyceride + CH₃OH ↔ Glycerol + FAME

Typical process parameters (conventional transesterification):

- Molar ratio of TG:MeOH - 6:1
- Catalyst Concentration - 0.5-1 wt% oil
- Atmospheric Pressure
- Low Temperature 25 - 60°C
Biodiesel Production: From Oilseed to Final Product, Conventional Processing

**Crushing:**
- capital and running cost intensive.
- usually performed in very large, centralised plants (to achieve economies of scale)

Whole seeds

- Drying
- Maceration
- CRUSHING
  - Solvent Extraction
  - Refining
  - Transesterification
  - Purification

Hexane

- Meal

Methanol + NaOH

- Glycerol
- Waste water

Biodiesel
Biodiesel Production: Reactive Extraction

Whole seeds

Drying
Maceration
CRUSHING
Solvent Extraction
Refining
Transesterification
Purification

Biodiesel

Hexane

Methanol + NaOH

Waste water

Meal

Glycerol

Purification

Biodiesel

Maceration

Reactive Extraction

Meal

Glycerol

Waste water

Reactive Extraction / In situ transesterification
Biodiesel Production: From Oilseed to Final Product

Reactive Extraction Benefits

- Reduced number of unit operations (⇒ reduced CapEx)
- Eliminate use of hexane
- Reduction in production cost?
- Potential for small-scale and local operation

Whole seeds

Maceration

Reactive Extraction

Meal

Purification

Glycerol

Biodiesel

Waste water

Reactive Extraction / In situ transesterification

Methanol + NaOH
Rape seed

Cotyledon

Carbohydrate (25% )
( Cell wall)
D-glucose, D-fructose, D-galactose, sucrose, raffinose, ...

Protein (20-25% )
Globulin albumin

Lipids (40-45% )
Seed coat
Lignin polyccarides
Antioxidate compounds

Reactive Extraction-based Biodiesel Biorefinery

MeOH/NaOH
↓
Reactive Extraction
↓ 45%?
Seed cake

Glycerol rich phase
Settling
↑ 10%
Protein

Phenolics

Clean BD
45% TG?

Seed cake
Glycerol rich phase
Dirty water

Water
# Effect of by particle size

<table>
<thead>
<tr>
<th>Particle size</th>
<th>Total weight</th>
<th>Time</th>
<th>Mass of ester phase</th>
<th>Yield</th>
</tr>
</thead>
<tbody>
<tr>
<td>300-500 µm</td>
<td>20g</td>
<td>1 hour</td>
<td>9.9g</td>
<td>86.2(±5.3)%</td>
</tr>
<tr>
<td>500-850µm</td>
<td>20g</td>
<td>1 hour</td>
<td>7.5g</td>
<td>65.2(±6.2)%</td>
</tr>
<tr>
<td>1000-1400µm</td>
<td>20g</td>
<td>1 hour</td>
<td>4.9g</td>
<td>43(±7.1)%</td>
</tr>
</tbody>
</table>
Effect of the reactive extraction on carbohydrate and lipid contents:

300-500µm particles size (before and after 1 hour reactive extraction of biodiesel)
SEM (before and after oil extraction 300-500µm)

Cotyledon before

Cotyledon after

Seed coat before

Seed coat after
Microscopy (periodic acid Shiff reaction PAS, before and after oil extraction, 300-500µm)
Microscopy staining with Sudan black B, Before and after oil extraction, 300-500µm
Effect of the reactive extraction on carbohydrate and lipid contents:

1-1.4mm particles (before and after 1 hour reactive extraction)
SEM (before and after reactive extraction, 1-1.4cm)

Cotyledon before

Cotyledon after
Microscopy (staining with periodic acid Shiff regent PAS, before and after extraction, 1-1.4cm)
Microscopy (Staining with Sudan black B, Before and after oil extraction, 1-1.4cm)

Cotyledon before

Cotyledon after
Protein concentration analysis of rapeseed particles before and after biodiesel production

- After oil removal however, almost half of the waste (seedcake/meal) mass ends up with a protein content of about 50%. This is mostly used in animal feed but, researchers say this could be "a source of new food ingredients" with potential functional and health properties.

- Using rapeseed protein as ingredients in experimental sausages boosted taste and aroma of the finished products, as scientists continue the search for novel functional ingredients. (Yumiko Yoshie-Stark from Tokyo University, and Fraunhofer Institute for Process Engineering and Packaging, Freising, Germany)
Rapeseed protein extraction (Sigma, plant total protein extraction kit)

1. Grind 10-250 mg
   -20 °C

2. Methanol removes the phenolics and tannins
   (remove the supernatant)
   -20 °C

3. Acetone removes the lipids
   (remove the supernatant)

4. Plant protein extraction reagent
   25 °C

5. Collect the supernatant as the total protein sample.
Bradford method analyses the total protein concentration (spectrophotometer).

<table>
<thead>
<tr>
<th>Sample</th>
<th>Before</th>
<th>RE</th>
<th>Methanol (only)</th>
<th>Hexane</th>
</tr>
</thead>
<tbody>
<tr>
<td>Protein concentration (mg/ml)</td>
<td>7.59±0.62</td>
<td>6.38±0.86</td>
<td>6.67±0.92</td>
<td>7.26±0.43</td>
</tr>
</tbody>
</table>
Conclusions

- All the lipids were removed from 300-500µm cotyledon particles after 1 hour reactive extraction. However, in particle size range 1-1.4mm, some lipids still remain in the centre of the particles. This result agrees with respectively yields. There is no lipids in the seed coat.

- The carbohydrate is not affected by the reactive extraction (cotyledon and seed coat) at 300-500µm and 1-1.4mm. It is therefore possible to extract this from seed cake.

- Protein contents of seedcake does not have significant affected by reactive extraction as well.

- Generally, antioxidant compounds are found in most seed coats, for example, Almond seed. This research shows that chemical contents in rapeseed’s seed coat are not affected during reactive extraction of biodiesel. Therefore, the antioxidant components can also be extracted from the seed cake.
Acknowledgements

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