Direct Conversion of Algal Biomass Under Supercritical Methanol and Microwave Irradiation Conditions

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Outline

• Project Background
• Supercritical Conversion Process for Wet Algae
• Microwave-assisted Transesterification of Dry Algae (Nannochloropsis sp.) to Biodiesel
• Experimental Design & Process Optimization
• Analysis of Algae and Algal Biodiesel
Feed Stocks for Biodiesel

- Rapeseed oil (Europe)
- Sunflower oil (Italy and France)
- Soybean oil (USA & Brazil)
- Palm oil (Malaysia)
- Cottonseed oil (Greece)
- Jatropha (India & Nicaragua)

<table>
<thead>
<tr>
<th>Crop</th>
<th>Oil yield (L/ha)</th>
<th>Land Area* (M ha)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Corn</td>
<td>172</td>
<td>1,540</td>
</tr>
<tr>
<td>Soybean</td>
<td>446</td>
<td>594</td>
</tr>
<tr>
<td>Canola</td>
<td>1,190</td>
<td>223</td>
</tr>
<tr>
<td>Jatropha</td>
<td>1,892</td>
<td>140</td>
</tr>
<tr>
<td>Coconut</td>
<td>2,689</td>
<td>99</td>
</tr>
<tr>
<td>Oil palm</td>
<td>5,950</td>
<td>45</td>
</tr>
<tr>
<td><strong>Microalgae</strong></td>
<td><strong>136,900</strong></td>
<td><strong>2</strong></td>
</tr>
</tbody>
</table>

* 50% of USA transportation fuel needs

What is Microalgae?

- Sunlight-driven cell factories
- They contain lipids and fatty acids as Storage
- They contain up to 40-60% of lipids/oils
- They need light, nutrients and warmth to grow
- Complete set of photosynthetic machinery

Algal Biomass-Based Biorefinery

1. Water + Nutrients
2. Algal Biomass Production
3. Power Generation
4. Power to Grid
5. Biomass Recovery
6. Biogas
7. Anaerobic Digestion
8. Effluent:
   - Fertilizer
   - Irrigation
9. Algal Oil
10. Biodiesel
11. Gasoline
12. Other Products
13. Biomass Extraction
14. Alternatives
15. Pyrolysis
16. Solid → Gas
17. Liquid into Fuel
18. Animal Feed
19. Other Products

H₂O/Nutrients
Light
CO₂

NM STATE UNIVERSITY
Main Challenges in Algal Biofuels

- Algal biology and cultivation
- Harvesting and dewatering
- Extraction and conversion
- Development of co-products
Transesterification Mechanism in SCM

One-Step Conversion Process (Supercritical Methanol) for Wet Algae (Nannochloropsis sp.)

\[
\begin{align*}
\text{CH}_2\text{OOOCR}_1 & \quad \text{CHOOOCR}_2 & \quad \text{CH}_2\text{OOOCR}_3 \\
\text{CHOOCR}_2 \quad \text{Methanol} & \quad \text{High Temp} & \quad \text{High Pressure} \\
\text{CH}_2\text{OOOCR}_3 \quad \text{(SCM)} & \quad \text{R}_1\text{COOCH}_3 & \quad \text{R}_2\text{COOCH}_3 & \quad \text{R}_3\text{COOCH}_3 & \quad \text{CH}_2\text{OH} & \quad \text{CHOH} & \quad \text{CH}_2\text{OH} & \quad \text{Glycerol} \\
\text{Triglyceride} & \quad \text{3 CH}_3\text{OH} & \quad \text{Methyl Ester} & \quad \text{R}_1, \text{R}_2 \text{ and } \text{R}_3 = \text{Long Chain Hydrocarbons, may be same or different} \\
\text{ROOCR}_1 & \quad \delta^- & \quad \delta^- & \quad \delta^+ & \quad \delta^- & \quad \delta^- & \quad \delta^+ & \quad \delta^- & \quad \delta^- & \quad \delta^+ & \quad \delta^- & \quad \delta^- & \quad \delta^+ & \quad \delta^- & \quad \delta^- & \quad \delta^+ & \quad \delta^- & \quad \delta^- & \quad \delta^+ \\
\text{ROOCR}_1 & \quad \text{ROOCR}_1 & \quad \text{HOR} & \quad \text{ROH: Diglyceride, } \\
\text{R'}: \text{Alkyl Group} & \quad \text{R}_1: \text{Long Chain Hydrocarbon} & \\
\end{align*}
\]
One-Step Conversion of Wet Algae

Why Wet Algae?

• Residual water in Wet Algae becomes an excellent organic solvent at near-critical conditions and is non-toxic.

• Conversely, removing residual water from algal biomass is expensive and energy demanding.

Why Supercritical Methanol?

• Single-Step Conversion Process

  Simultaneous Extraction and Transesterification!!

• Non-catalytic-Simpler purification of products

• Lower reaction time and More environmental friendly
# Analysis of Energy for Algae Drying

Basis: 1 kg of algal biodiesel production

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Algae culture and harvesting</td>
<td>7.5</td>
<td>10.6</td>
<td>90%</td>
<td>113%</td>
</tr>
<tr>
<td>Drying</td>
<td>90.3</td>
<td>0</td>
<td>80%</td>
<td>50%</td>
</tr>
<tr>
<td>Extraction</td>
<td>8.6</td>
<td>30.8</td>
<td>70%</td>
<td>29%</td>
</tr>
<tr>
<td>Oil transesterification</td>
<td>0.9</td>
<td>0.9</td>
<td>60%</td>
<td>19%</td>
</tr>
<tr>
<td>Total</td>
<td>107.3</td>
<td>42.3</td>
<td>50%</td>
<td>13%</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>40%</td>
<td>8%</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>30%</td>
<td>5%</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>20%</td>
<td>3%</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>10%</td>
<td>1%</td>
</tr>
</tbody>
</table>

# Lipid Extraction Report

**Nannochloropsis CCMP 1776 sp.**

<table>
<thead>
<tr>
<th>Sample Label</th>
<th>CCMP 1776</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ash Free Dry Weight</td>
<td>68.64%</td>
</tr>
<tr>
<td>(dry/wet *%)</td>
<td></td>
</tr>
<tr>
<td>Lipid Yield (wt% Dry Mass)</td>
<td>50%</td>
</tr>
<tr>
<td><strong>Lipid composition</strong></td>
<td></td>
</tr>
<tr>
<td>Triglycerides (%)</td>
<td>37.74 %</td>
</tr>
<tr>
<td>Other Non-polars (%)</td>
<td>8.72%</td>
</tr>
<tr>
<td>Polars-Glyco &amp; Phospholipids</td>
<td>3.54 %</td>
</tr>
</tbody>
</table>

A gross estimation of non-polar lipids and triglycerides is done using Thin Layer Chromatography (TLC) and densitometry.
FTIR Transmission Spectrum of Nannochloropsis Algal sp.

- Aliphatic character: 650-720 cm\(^{-1}\)
- Phenols and Alcoholic group: 1300-1400 cm\(^{-1}\)
- Carboxyl group: 1600-1700 cm\(^{-1}\)
- Hydroxyl group: 3200-3300 cm\(^{-1}\)
# Elemental and Fatty Acid Composition of Nannochloropsis Algae

## Elemental Composition

<table>
<thead>
<tr>
<th>Elements</th>
<th>Weight (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carbon (C)</td>
<td>72</td>
</tr>
<tr>
<td>Oxygen (O)</td>
<td>21</td>
</tr>
<tr>
<td>Sodium (Na)</td>
<td>1.5</td>
</tr>
<tr>
<td>Magnesium (Mg)</td>
<td>0.41</td>
</tr>
<tr>
<td>Silicon (Si)</td>
<td>0.93</td>
</tr>
<tr>
<td>Phosphorous (P)</td>
<td>0.47</td>
</tr>
<tr>
<td>Chlorine (Cl)</td>
<td>1.52</td>
</tr>
<tr>
<td>Potassium (K)</td>
<td>0.96</td>
</tr>
</tbody>
</table>

## Fatty Acid Composition

<table>
<thead>
<tr>
<th>Fatty acids</th>
<th>Area (% total)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Myristic acid, C14:0</td>
<td>0.3</td>
</tr>
<tr>
<td>Palmitic acid, C16:0</td>
<td>10.4</td>
</tr>
<tr>
<td>Palmitoleic acid, C16:1 n7</td>
<td>35.7</td>
</tr>
<tr>
<td>Oleic acid, C18:1 n9</td>
<td>30.7</td>
</tr>
<tr>
<td>Linoleic acid, C18:2 n6</td>
<td>5.6</td>
</tr>
<tr>
<td>gamma-Linolenic acid, C18:3 n6</td>
<td>0.7</td>
</tr>
<tr>
<td>Arachidic acid, C20:0</td>
<td>0.5</td>
</tr>
<tr>
<td>Arachidonic acid, C20:4 n6</td>
<td>1.2</td>
</tr>
<tr>
<td>EPA, C20:5 n3</td>
<td>6.2</td>
</tr>
<tr>
<td>Lignoceric acid, C24:0</td>
<td>0.3</td>
</tr>
<tr>
<td>Nervonic acid, C24:1 n-9</td>
<td>0.2</td>
</tr>
</tbody>
</table>
One-Step SCM Algal Biodiesel Process

Wet Algae + Methanol → Supercritical methanol reactor → Crude Biodiesel

4 g of wet algae (80% water) = 0.8 g solid,
Lipid yield (% dry mass) = 50% = 0.4 g Lipids,
Triglyceride (%) = 37.74% of Lipid = 0.1509 g,
FAME Yield (%) ≈ 70% = 0.1056 g Biodiesel

FAME: Fatty Acid Methyl Esters
Supercritical Methanol Reactor

(PARR-4593 with 4843 Controller)

- Non-catalytic process
- Simple process and high yield
- Easy separation
- Shorter reaction time

Operating range:
- 0-140 bar
- 273-623 K
Statistical Analysis of Experimental Design

General Linear Model:

\[ \mu = \beta_0 + \sum_{i=1}^{3} \beta_i x_i + \sum_{i=1}^{3} \beta_{ii} x_i^2 + \sum_{i=1}^{2} \sum_{j=i+1}^{3} \beta_{ij} x_i x_j \]

ANOVA for Response Surface Quadratic model:

<table>
<thead>
<tr>
<th>Source</th>
<th>DF</th>
<th>Seq SS</th>
<th>Adj SS</th>
<th>Adj MS</th>
<th>F</th>
<th>Prob &gt; F</th>
<th>Significance at 95%</th>
</tr>
</thead>
<tbody>
<tr>
<td>Model</td>
<td>9</td>
<td>9870.7</td>
<td>9870.7</td>
<td>1096.7</td>
<td>34.1</td>
<td>0</td>
<td>Yes</td>
</tr>
<tr>
<td>Temp, Meth, Time</td>
<td>3</td>
<td>5280.7</td>
<td>5280.7</td>
<td>1760.2</td>
<td>54.7</td>
<td>0</td>
<td>Yes</td>
</tr>
<tr>
<td>Temp^2, Meth^2</td>
<td>3</td>
<td>3656.5</td>
<td>3656.5</td>
<td>1218.8</td>
<td>37.9</td>
<td>0</td>
<td>Yes</td>
</tr>
<tr>
<td>Temp<em>Meth, Temp</em>Time</td>
<td>3</td>
<td>933.5</td>
<td>933.5</td>
<td>311.17</td>
<td>9.67</td>
<td>0.001</td>
<td>Yes</td>
</tr>
<tr>
<td>Residual Error</td>
<td>18</td>
<td>578.9</td>
<td>578.9</td>
<td>32.16</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Lack-of-Fit of model</td>
<td>5</td>
<td>257.6</td>
<td>257.6</td>
<td>51.51</td>
<td>2.08</td>
<td>0.133</td>
<td>No</td>
</tr>
<tr>
<td>Pure Error</td>
<td>13</td>
<td>321.4</td>
<td>321.4</td>
<td>24.72</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Total</td>
<td>27</td>
<td>10450</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

\[ R^2 = 94.46 \%, \ R\text{-S}q \ (\text{pred}) = 84.35 \%, \ R\text{-S}q \ (\text{adj}) = 91.69 \% \]
RSM Design for SCM Algal Biodiesel Process

Effect of Time

Optimal Conditions: 1:9 (wt/vol) MeOH Ratio, around 255 °C & 25 min, Pressure-1200 psi (fixed)

FT-IR Analysis On The Product Sample At Reaction Temperature (a) 250 °C, (b) 270 °C
The intense C=O stretching band of methyl ester appears at 1743 cm\(^{-1}\) for algal and camelina biodiesel which is absent in petro-diesel spectra.

Algal biodiesel contains a major proportion of mono and poly-unsaturated fatty acid methyl esters.

One-Step Conversion of Dry Algae

Why Microwave Heating?

• Easy, Fast and requires shorter Reaction Time
• Single-Step Conversion Process

Simultaneous Extraction and Transesterification!!

• Efficient Extraction of Algal Oils and FAME recovery from reaction mixture is quicker
• Lower Energy Consumption (for Extraction-transesterification) compared to Conventional Heating for biodiesel production
Microwave Heating Basics

Conventional and microwave heating methods

Ionic conduction, dipolar polarization dielectric heating

Dariusz Bogdal, Microwave-assisted organic synthesis, 2005 Elsevier Ltd.
Microwave Transesterification Process for Dry Algal Biodiesel

FAME: Fatty acid methyl ester; SPE: Solid phase extraction

RSM Design for Microwave Algal Biodiesel Process

Optimal Conditions: 1:12 (wt/vol) MeOH Ratio, Catalyst Conc.- 2 wt%, 4-5 mins, 60-64 °C

TEM Analysis of Raw and Residual Algal Biomass

Supercritical Methanol

Fresh (Raw)

Residue

Microwave
TLC Chromatograms of Algal Biodiesel

- TLC plates for experiments 8 & 9 indicating 50 to 60% of FAME yield.
- Retention factor ($R_f$) value for methyl ester and Triglyceride is calculated as 0.645 and 0.564, resp.

(A)- Initial Development of TLC Plate
(B)- Fully Developed FAME TLC plate
(A) Eicosapentaenoic acid methyl ester (EPA, C20:5)
(B) Docosahexanoic acid methyl ester (DHA, C20:6)
(C) Arachidonic acid methyl ester (C20:4).
## High Value Bioproducts Extracted from *Nannochloropsis* sp.

<table>
<thead>
<tr>
<th>Product group</th>
<th>Applications</th>
<th>Bioproducts</th>
</tr>
</thead>
<tbody>
<tr>
<td>Phycobiliproteins carotenoids</td>
<td>Cosmetics, pigments, surfactants, plasticizer</td>
<td>Indole, oxalic acid, diethyl phthalate, naphthalene</td>
</tr>
<tr>
<td>Polyunsaturated fatty acids (PUFAs)</td>
<td>Food additive, nutraceuticals</td>
<td>Eicosapentaenoic acid (EPA), arachidonic acid, docosahexanoic acid (DHA)</td>
</tr>
<tr>
<td>Vitamins</td>
<td>Nutrients, precursors</td>
<td>Ascorbic acid, phytols</td>
</tr>
</tbody>
</table>
# Comparison Between MW and SCM Extraction- Transesterification

## Energy Consumption

<table>
<thead>
<tr>
<th>Species</th>
<th>Feed type</th>
<th>Process</th>
<th>Optimum parameter</th>
<th>FAME (%)</th>
<th>Feed amt</th>
<th>MeOH amt</th>
<th>Energy Consumption (kJ/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td><em>Nannochloropsis</em> (CCMP 1776)</td>
<td>Dry</td>
<td>MW</td>
<td>Cat. 2 wt% 9 (wt/vol) 6 min</td>
<td>80.13</td>
<td>2g</td>
<td>18 mL</td>
<td>Thermal 476.6, Mechanical 47.6, Total 524.2</td>
</tr>
<tr>
<td></td>
<td>Wet</td>
<td>SCM</td>
<td>250 C, 8 (wt/vo) 25 min</td>
<td>84.15</td>
<td>4g</td>
<td>32 mL</td>
<td>Thermal 4966.5, Mechanical 709.5, Total 5676</td>
</tr>
</tbody>
</table>

- MW-524.2 kJ/g ; SCM- 5676 kJ/g (For Extraction-transesterification process only). The energy calculated is based on the 1 g of final product.
Microwave Synthos 3000

Major Benefits:
- Rate Enhancement
- Increased Yield
- Improved Purity

Rotor 8SXQ80

Operating range:
- Microwave Power: 0-1400 W
- Operating Pressure: 0-80 bar
- Maximum Temperature: 300 ºC
- Operating Volume: 12-60 mL
Concluding Remarks

• Algae is an important feedstock for biodiesel production in both economical and environmental-friendly manner.
• Supercritical methanol (one-step) process—simultaneous extraction and transesterification, is a promising method.
• Microwave heating (one-step) process—simultaneous extraction and transesterification, is a promising method as it is Fast, Easy and energy efficient method.
• Considering availability of dry algal biomass, microwave-assisted extraction and transesterification of algal biomass seems to be an attractive solution.
Acknowledgements

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Instruments

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