Preliminary assessments of microalgae direct transesterification for biodiesel production

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Preliminary assessments of microalgae direct transesterification for biodiesel production

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Bio-fuel and microalgae: it’s a long story…

“...the use of vegetable oils as engine fuels may seem insignificant today but such oils may become, in the course of time, as important as petroleum and the coal tar products of the present time…”

Rudolph Diesel, 1913

A Look Back at the U.S. Department of Energy’s Aquatic Species Program: Biodiesel from Algae

Benneman 1977, Nature
Sheenan 1998, NREL
Williams 2007, Nature
Chisti 2007, Biotechnol Adv
Schenk 2008, Bioenerg Res
Waltz 2009, Nature
Wijffels 2010, Science
Stephens 2010, Nature
Christenson 2011, Biotechnol Adv....
### Bio-fuel and microalgae: it’s a long story...

| microalgae could make a significant contribution to renewable biofuels, feeds and GHG reduction |
| J. Benemann, MicroBio Engineering, Inc. |

...genetic and genomic methods are already being applied to improve production and recovery of algal fuels ...

...production of algal oil for 5% of US consumption is feasible if the inorganic nutrients are recycled, energy is recovered from the spent biomass, the CO₂ supply bottleneck is overcome, and the cost ...is reduced to about $0.25/kg ... all with sustained R&D....

Y. Chisti, Massey University

| Microalgae are photosynthetically more efficient compared with land plants ...but unsustainable on freshwater, nitrogen, phosphorous and on low-cost concentrated CO₂ demands ...
| Y. Chisti, Massey University |

The challenge for microalgal biofuel production is ...securing sustainable supplies of N, P and C

D.Lewis, University of Adelaide

| President Obama (2012) projected that algae oil might replace 17% of imported transportation fuels. ...ignoring CO₂ and freshwater availability!
| J. Benemann, MicroBio Engineering, Inc. |

...projections for major reductions in CO₂ emissions ...are not credible.

...the algal biorefineries ...is also not plausible, due to large disparities in market sizes...

D. Lewis, University of Adelaide

LCA studies suggest that ...commercial reality in a niche fuel market is inevitable

D. Lewis, University of Adelaide
...there are methodical and comprehensive analyses based on the same premises, the results of which are often used to tout the promise of microalgal biofuels (Wiffels and Barbosa, 2010, Science, ....)

D. Klein-Marcuschamer, Lawrence Berkeley National Laboratory

...currently produced microalgal biomass is several orders of magnitude smaller in production scale and higher in costs than required for the production of biofuels or commodity feeds, the aim of most of the hundreds of start-up companies, research consortia and university projects, ten thousand researchers and engineers, hundreds of patents and publications

J. Benemann, MicroBio Engineering, Inc.

...There are places in the world with sufficient year-round levels of sunlight, close to plenty of water, to carbon intensive industries that can supply inexpensive CO₂, and with developed road and rail networks..... But by no stretch of the imagination are these locations commonplace.

D. Klein-Marcuschamer, Lawrence Berkeley National Laboratory

...closed photobioreactors are superior to open ponds (Chisti, 2007), .... researchers favor PBRs vs open ponds (Wijffels and Barbosa, 2010) ...but about a dozen commercial PBR systems have been built, 100-times higher cost than open ponds, all failed!!!

J. Benemann, MicroBio Engineering, Inc.

...the tendency to bundle all species and all strains of microalgae into a single entity of interest to biotechnology......microalgae, again as a group, will solve the world’s energy problems is at odds with the principles of process engineering and design...

D. Klein-Marcuschamer, Lawrence Berkeley National Laboratory

...all appeared in «The fine print of microalgal biofuels», Biotech Bioeng, one week ago....
Conventional transesterification vs in situ transesterification

Biodiesel from microalgae

Conventional protocol:
Soxhlet extraction and transesterification

New protocol:
In situ transesterification

**Conventional transesterification**

Dried microalgae → Lipid extraction → Transesterification → Purification → Biodiesel

**In situ transesterification**

Dried microalgae → In situ transesterification (including lipid extraction) → Purification → Biodiesel

Glycerol, water
Aim of the work

Characterization of direct alkaline transesterification process of *Stichococcus bacillaris*.

Optimisation of methyl ester yield:

- pre-contact time
- catalyst concentration
- methanol/biomass
- reaction temperature
- reaction time
- water/biomass.
Conventional extraction + transesterification

- Biomass growth in photobioreactor
- Soxhlet extraction
- Transesterification
- FAME identification by GC
- Biomass harvesting
- Biomass lyophilization
Direct transesterification

Biomass growth in photobioreactor

Biomass harvesting

Soxhlet extraction

FAME identification by GC

Biomass lyophilization

FAME quantification by HPLC

Transesterification
Direct transesterification

MeO\(^{-}\) - MeOH - OH

MeOH

MeO\(^{-}\)
## Operating conditions

<table>
<thead>
<tr>
<th></th>
<th>Velasquez-Orta et al., 2012</th>
<th>This work 2013</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Pre-contact time</strong></td>
<td>Not investigated</td>
<td>0-6 h</td>
</tr>
<tr>
<td><strong>Reaction time</strong></td>
<td>5-120 min</td>
<td>3-12 min</td>
</tr>
<tr>
<td><strong>Reaction Temperature</strong></td>
<td>60 °C</td>
<td>30-60 °C</td>
</tr>
<tr>
<td><strong>NaOH / MeOH</strong></td>
<td>0.014-0.14 %</td>
<td>0-2 %</td>
</tr>
<tr>
<td><strong>MeOH/Biomass</strong></td>
<td>118-316</td>
<td>24-79</td>
</tr>
<tr>
<td><strong>Water/Biomass</strong></td>
<td>0%</td>
<td>0-100 %</td>
</tr>
<tr>
<td><strong>Strain</strong></td>
<td><em>Chlorella vulgaris</em></td>
<td><em>Stichococcus bacillaris</em></td>
</tr>
</tbody>
</table>
Effect of pre-contact time

- Methanol/biomass: 79
- Reaction Temperature: 60°C
- Reaction time: 3 min

Biodiesel yield (%) vs. pre-contact time (h)
- 0% NaOH
- 0.5% NaOH
- 1% NaOH
- 1.5% NaOH
- 2% NaOH
Effect of reaction temperature

- Methanol/biomass: 79
- Pre-contact time: 0 h
- Reaction time: 3 min
Effect of methanol/biomass ratio on biodiesel yield over different concentrations of NaOH. The reaction temperature was set at 60°C, pre-contact time was 0 h, and reaction time was 3 min.
Effect of reaction time

methanol/biomass - 79
pre-contact time - 0 h
reaction temperature - 60°C
conventional transesterification vs direct transesterification

NaOH/methanol - 1.5%
methanol/biomass – 79%
reaction temperature - 60°C
Effect of water/biomass

NaOH/methanol - 1.5%
methanol/biomass – 79
reaction temperature - 60°C
reaction time – 3 min
Direct transesterification

MeO⁻ - MeOH - OH

MeO⁻ - TAG - TAG

MeOH - OH

MeO⁻ - TAG

MeOH
Final remarks

• The yield of direct transesterification is larger than that by conventional protocol.
• Biodiesel yield decreases with biomass water content higher than 10%.
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Thanks for your attention