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Università degli studi di Napoli “Federico II”



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

Nature Vol. 268 7 July 1977

19

review article

Energy production by microbial photosynthesis

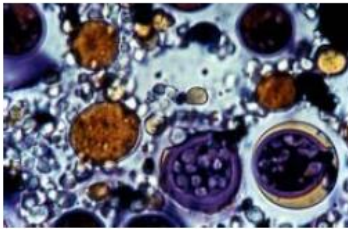
John R. Benemann^a, Joseph C. Weissman, Ben L. Koopman & William J. Oswald

National Renewable Energy Laboratory

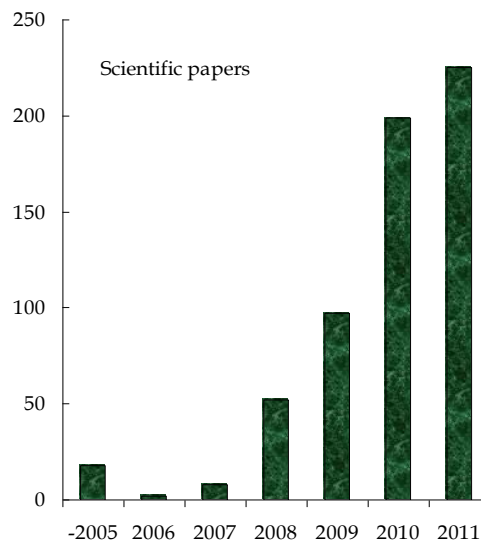


NREL/TP-580-24190

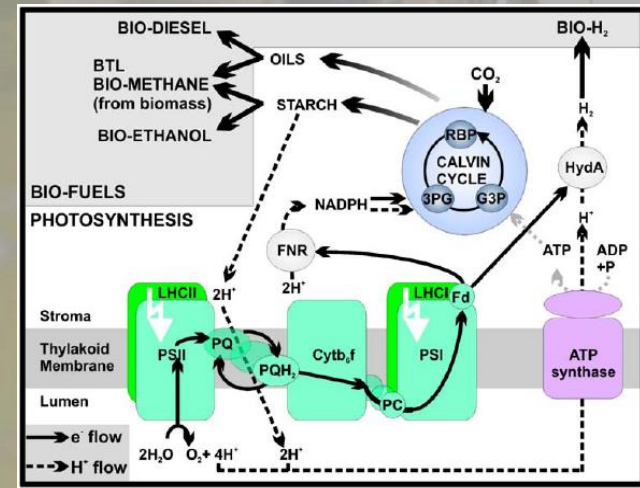
A Look Back at the U.S. Department of Energy's Aquatic Species Program: Biodiesel from Algae



Close-Out Report



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...



Comparison of some sources of biodiesel

Crop	Oil yield (L/ha)	Land area needed (M ha) ^a	Percent of existing US cropping area ^a
Corn	172	1540	846
Soybean	446	594	326
Canola	1190	223	122
Jatropha	1892	140	77
Coconut	2689	99	54
Oil palm	5950	45	24
Microalgae ^b	136,900	2	1.1
Microalgae ^c	58,700	4.5	2.5

^a For meeting 50% of all transport fuel needs of the United States.

^b 70% oil (by wt) in biomass.

^c 30% oil (by wt) in biomass.

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!**

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

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

J. Benemann, MicroBio Engineering, Inc.

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 microalgae 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

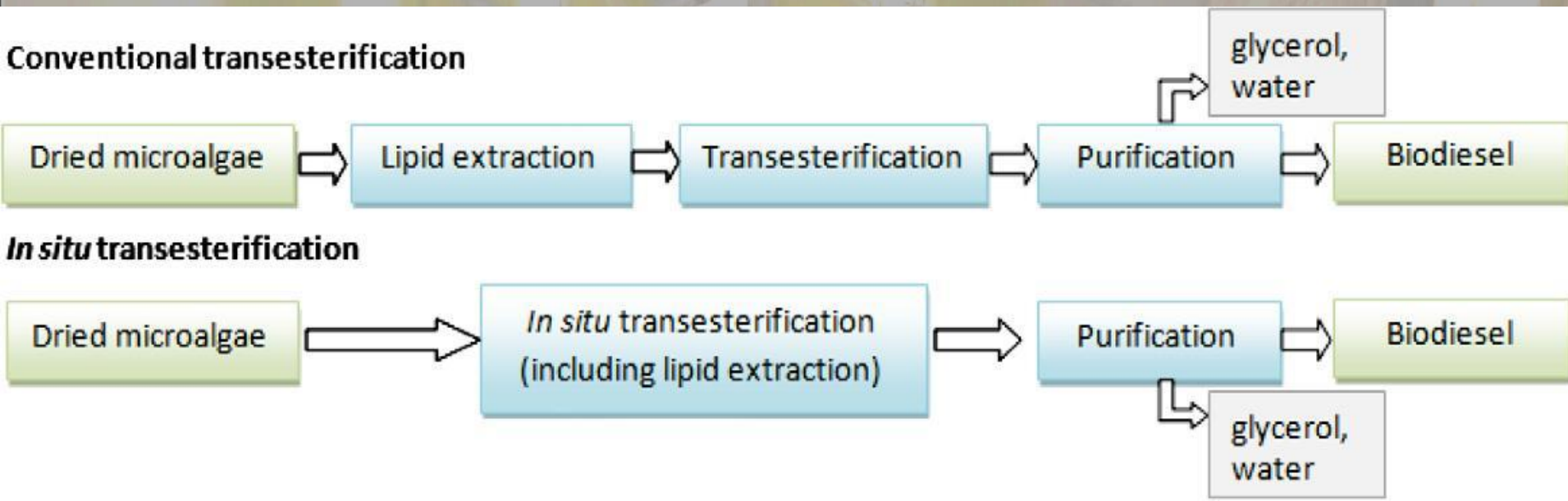
...all appeared in «The fine print of microalgal biofuels», Biotech Bioeng, one week ago....

Conventional transesterification vs in situ transesterification

Biodiesel from microalgae

Conventional protocol:
Soxhlet extraction and
transesterification

New protocol:
In situ transesterification



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.

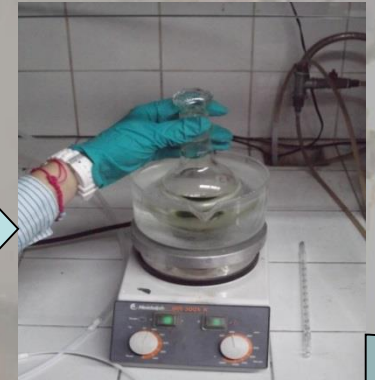
Conventional extraction+transesterification



Biomass growth in photobioreactor



Soxhlet extraction



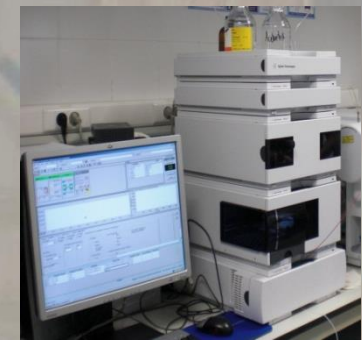
Transesterification



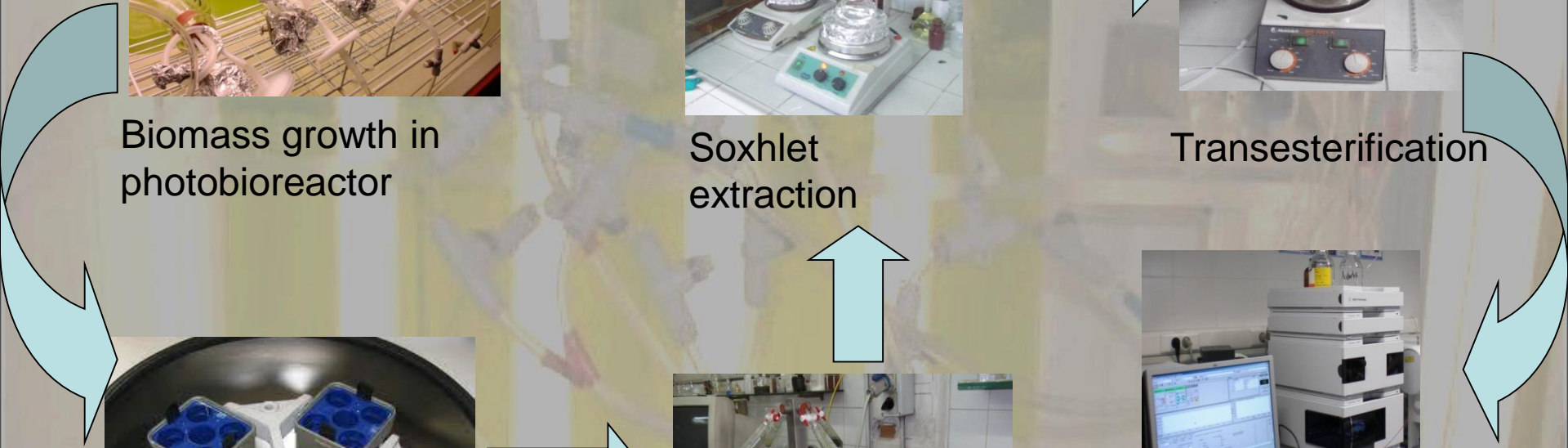
Biomass harvesting



Biomass lyophilization



FAME identification by GC



Direct transesterification



Biomass growth in photobioreactor



Soxhlet extracion



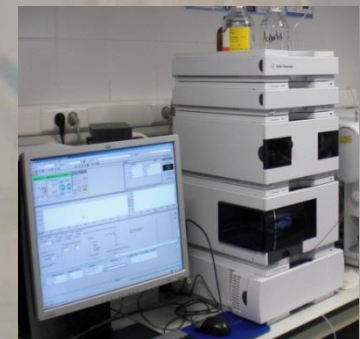
Transesterification



Biomass harvesting



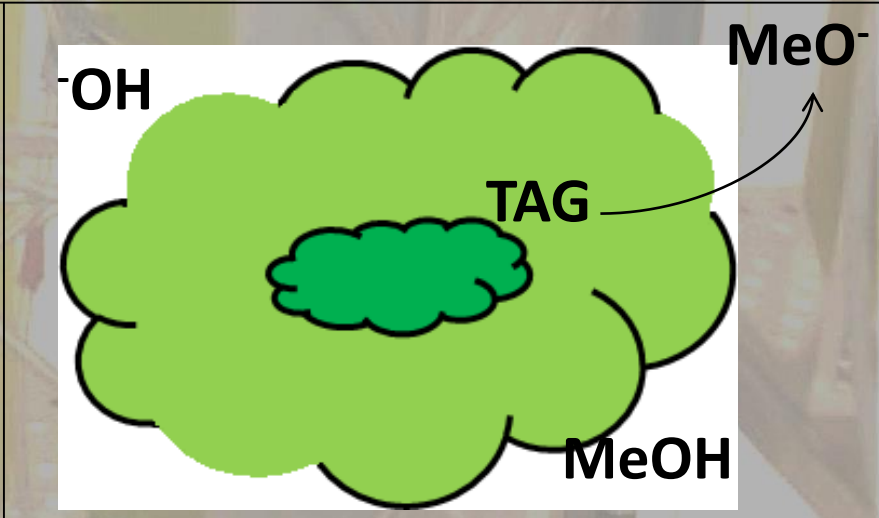
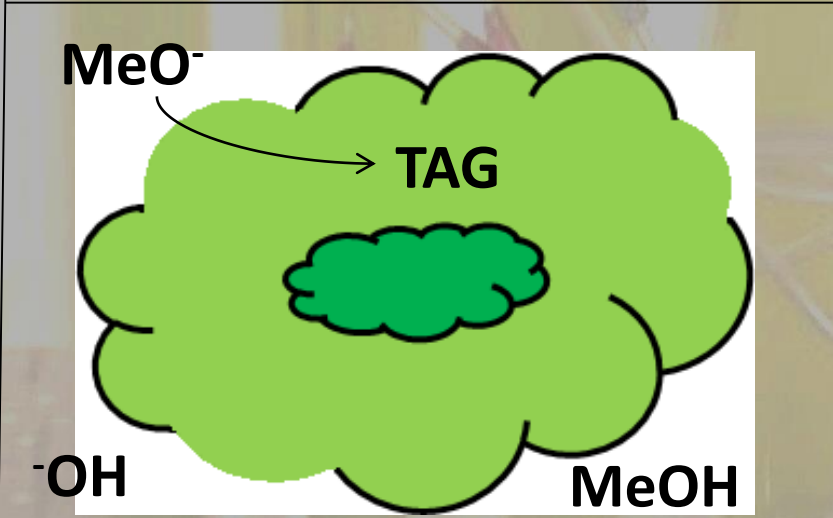
Biomass lyophilization



FAME identification by GC

FAME quantification by HPLC

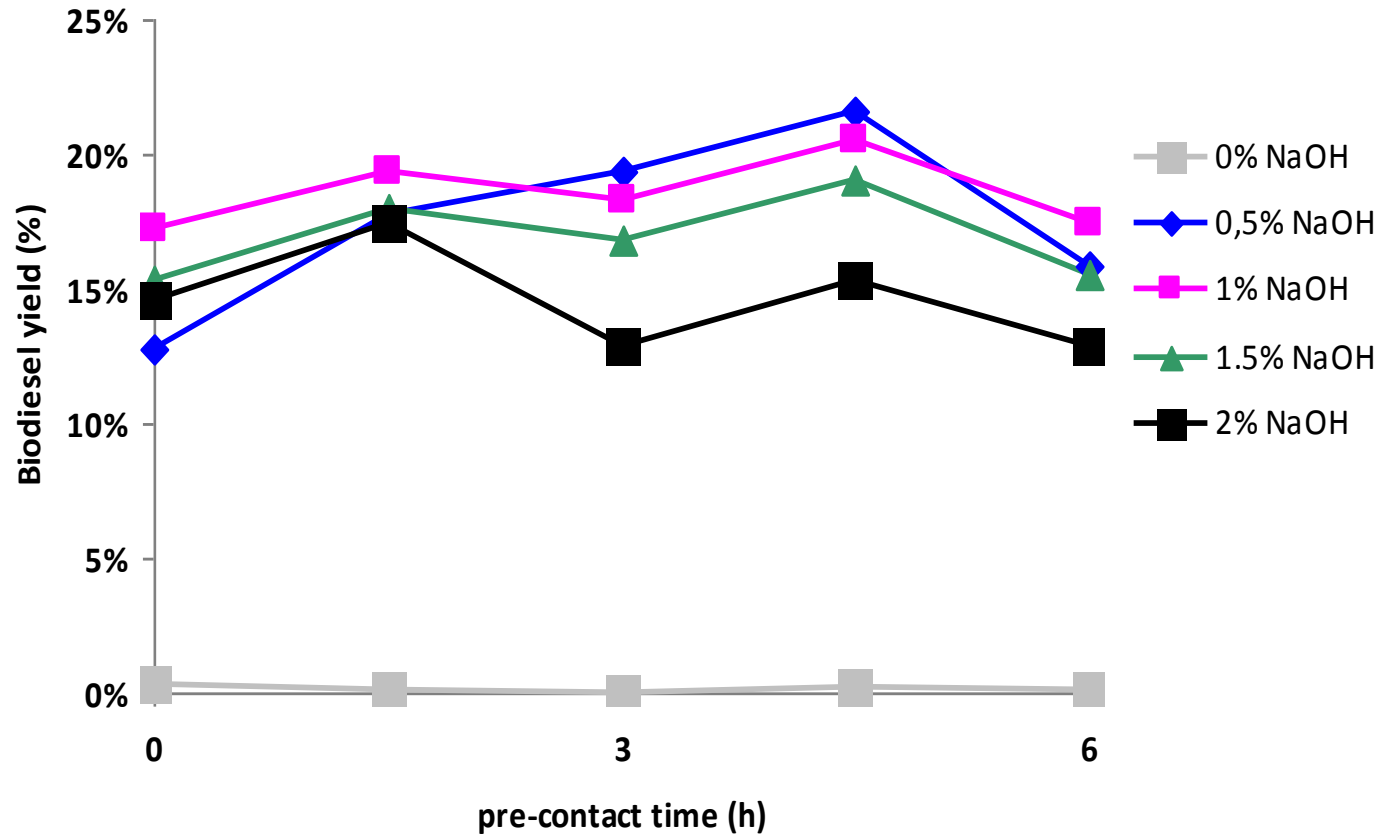
Direct transesterification



Operating conditions

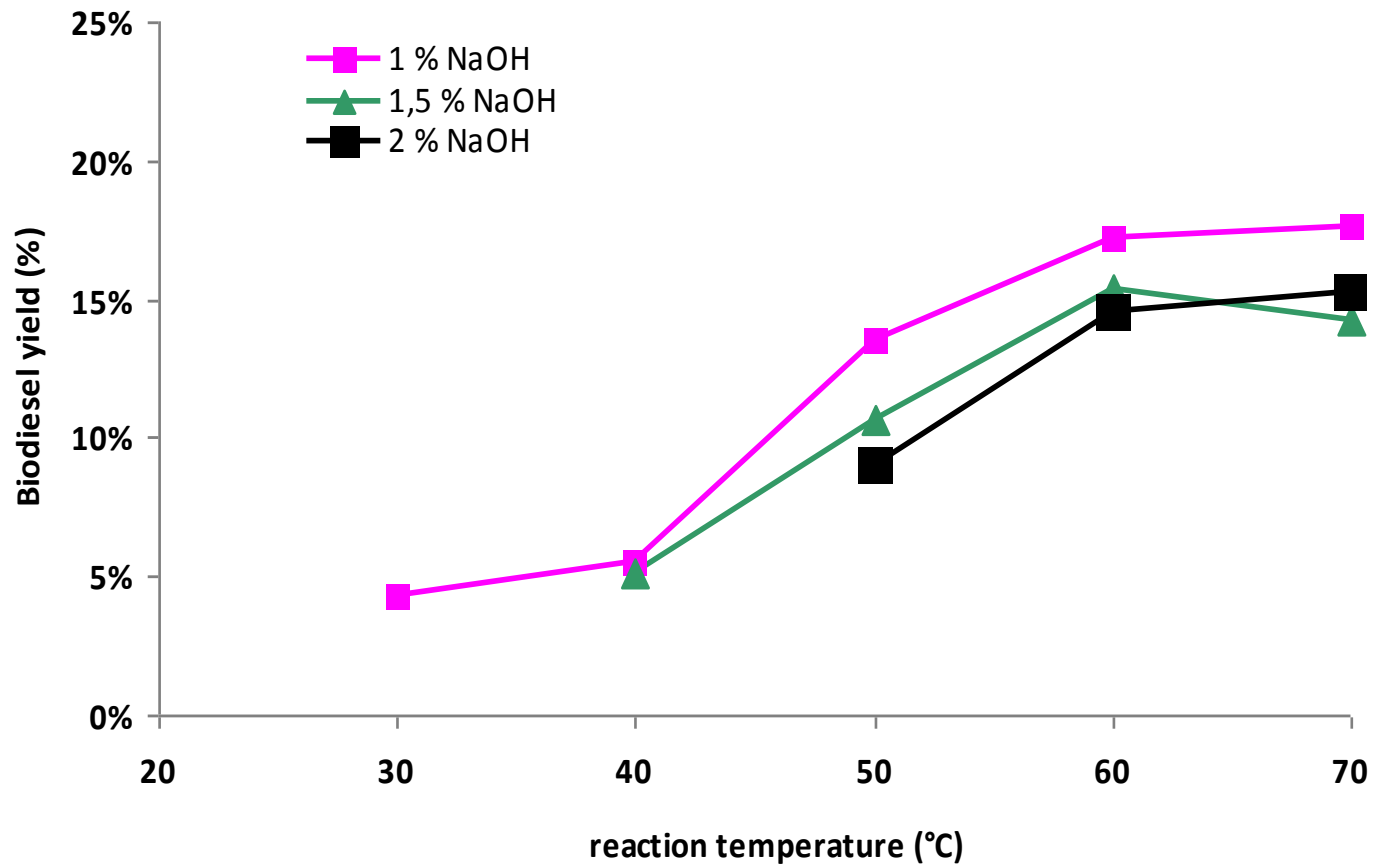
	Velasquez-Orta et al., 2012	This work 2013
Pre-contact time	Not investigated	0-6 h
Reaction time	5-120min	3-12 min
Reaction Temperature	60 °C	30-60 °C
NaOH / MeOH	0.014-0.14 %	0-2 %
MeOH/Biomass	118-316	24-79
Water/Biomass	0%	0-100 %
Strain	<i>Chlorella vulgaris</i>	<i>Stichococcus bacillaris</i>

Effect of pre-contact time



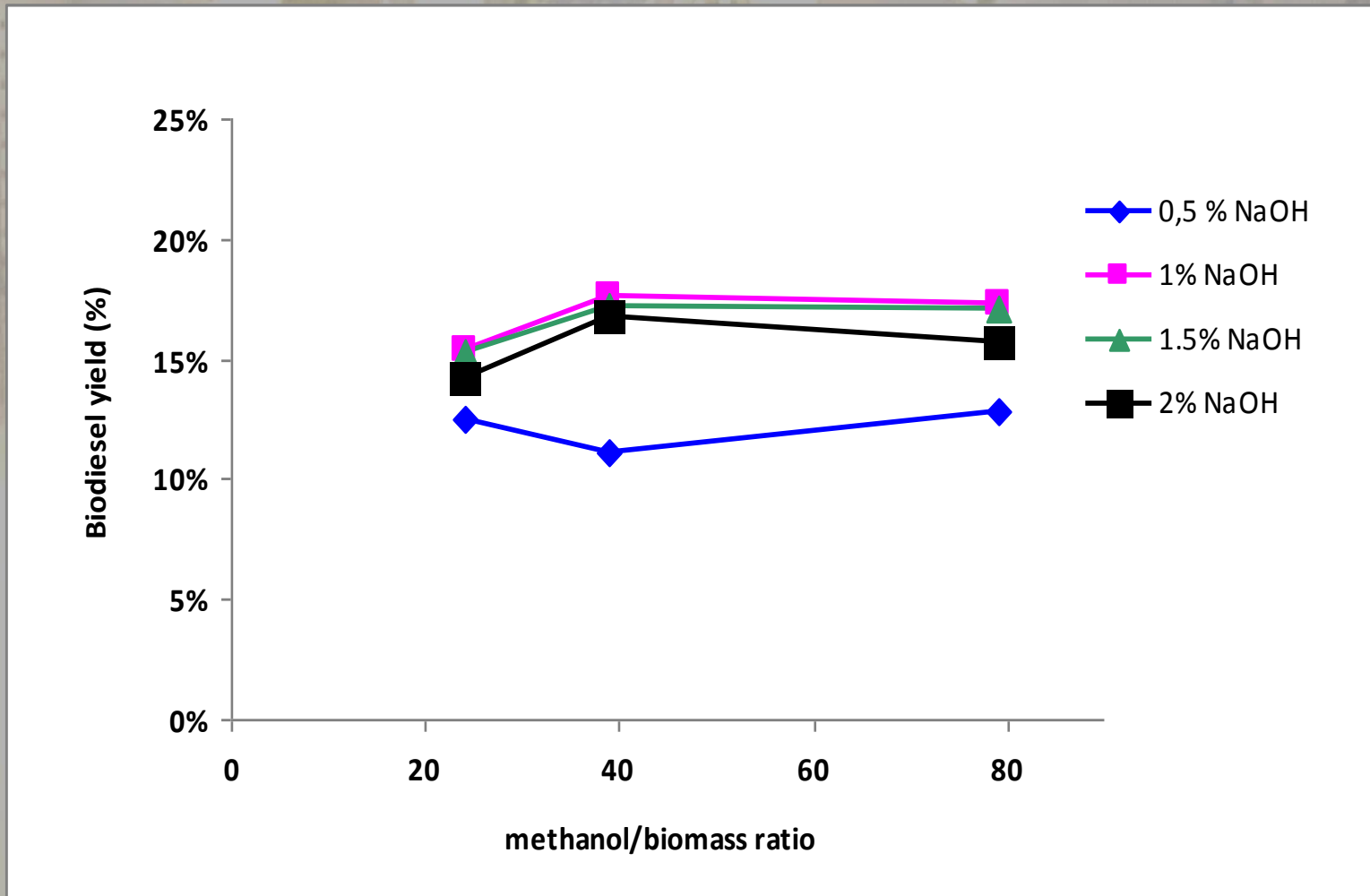
methanol/biomass - 79
reaction Temperature - 60°C
reaction time - 3 min

Effect of reaction temperature



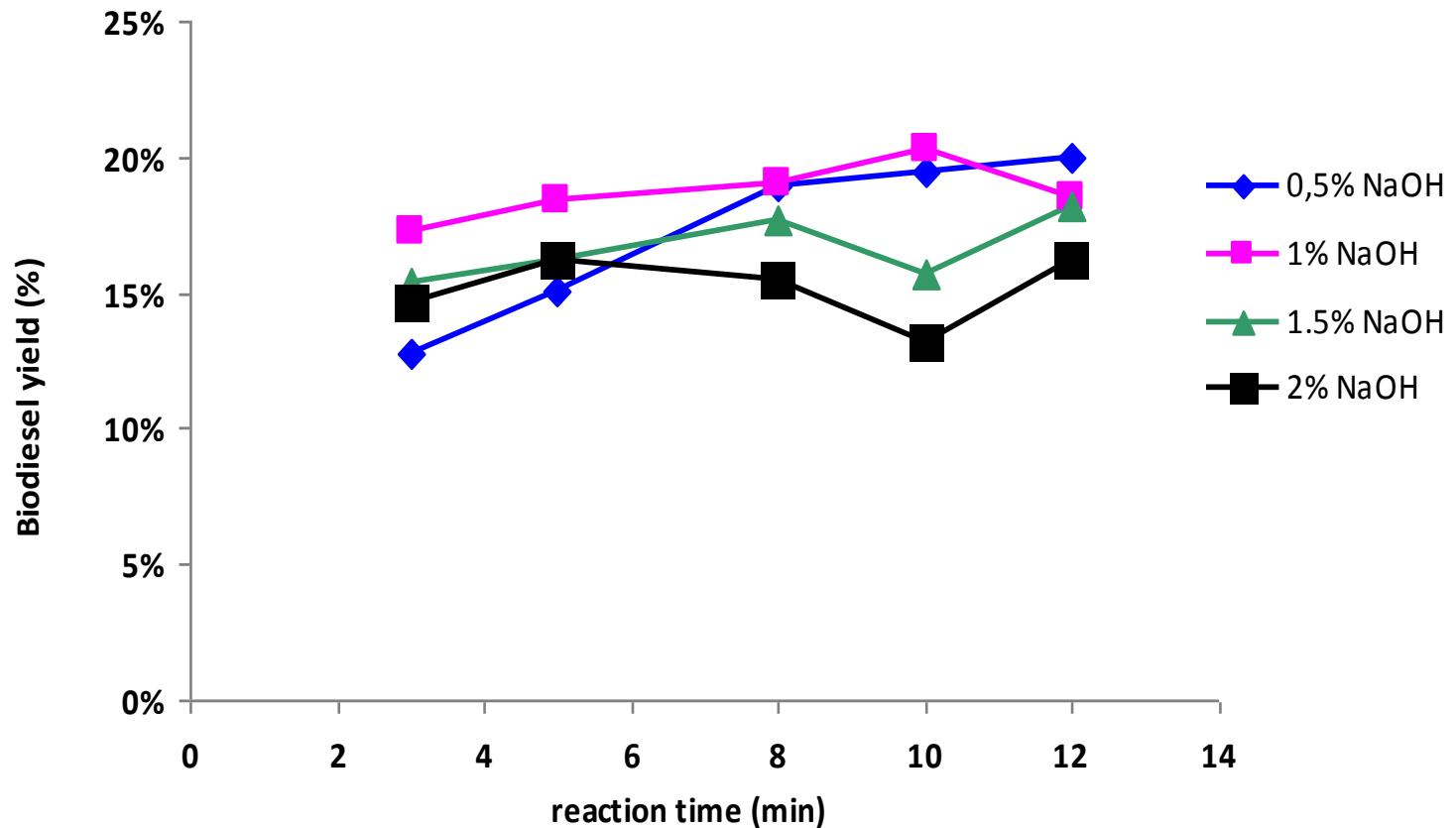
methanol/biomass - 79
pre-contact time - 0 h
reaction time - 3 min

Effect of methanol/biomass



reaction temperature - 60°C
pre-contact time - 0 h
reaction time - 3 min

Effect of reaction time

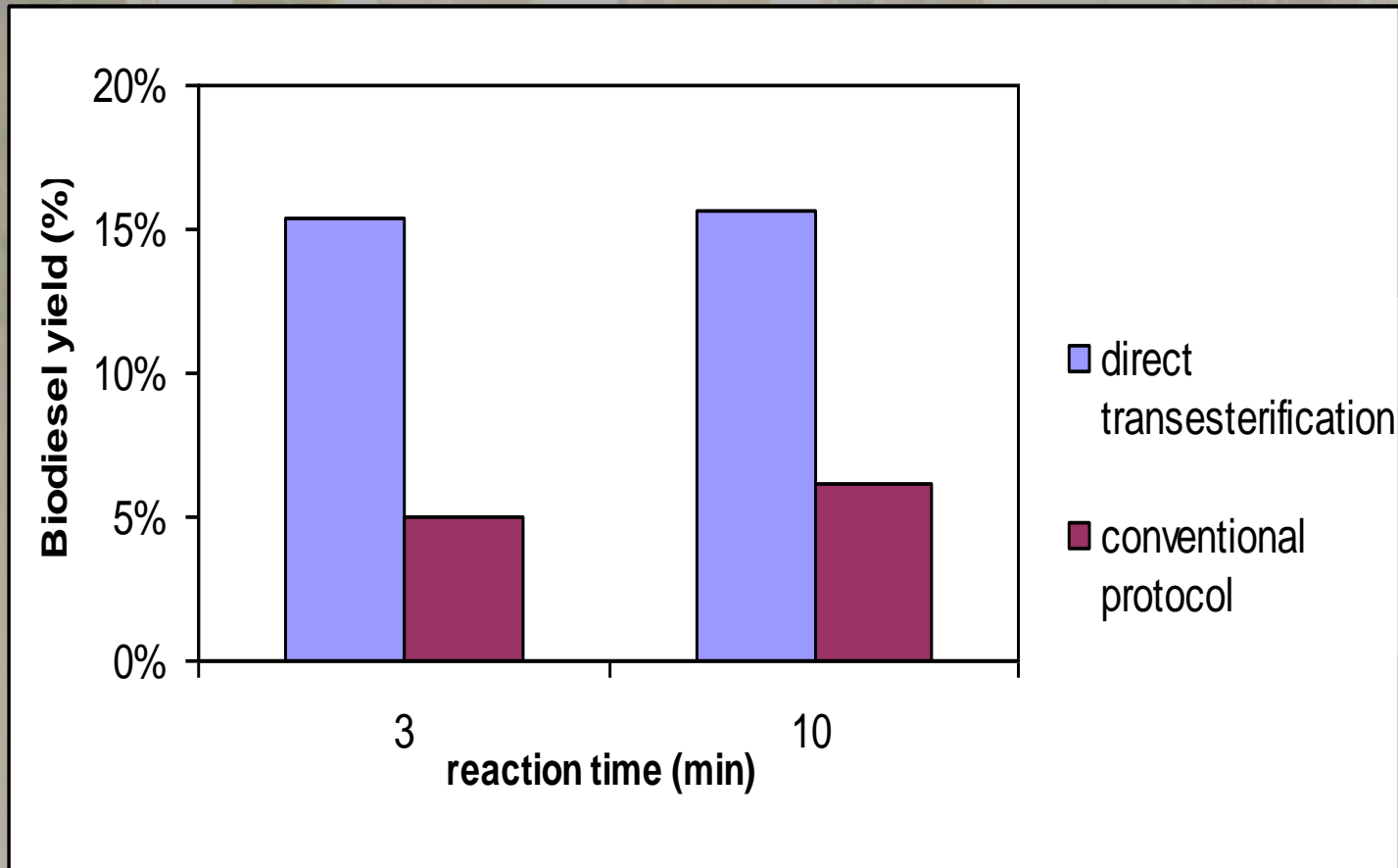


methanol/biomass - 79

pre-contact time - 0 h

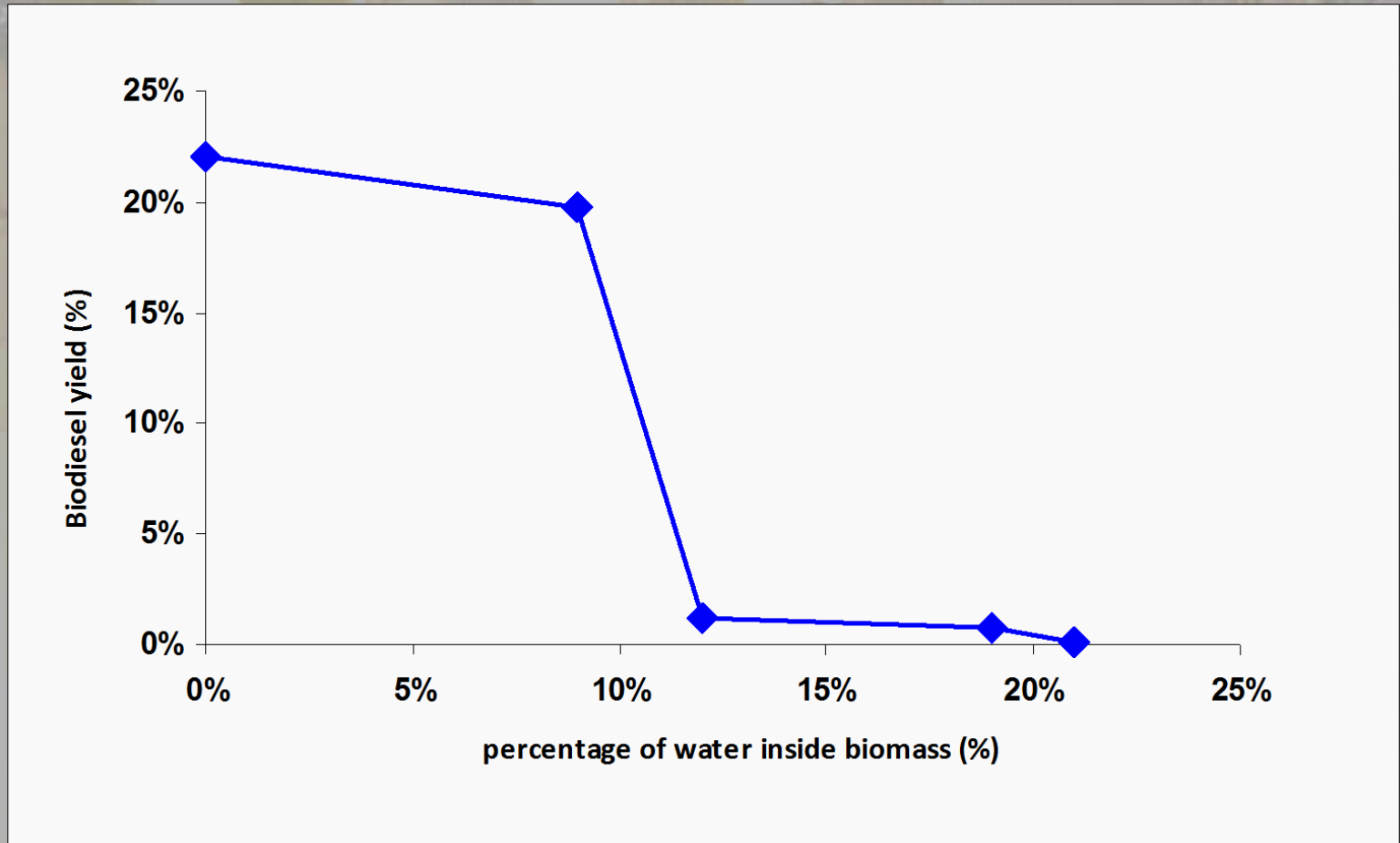
reaction temperature - 60°C

conventional transesterification vs direct transesterification



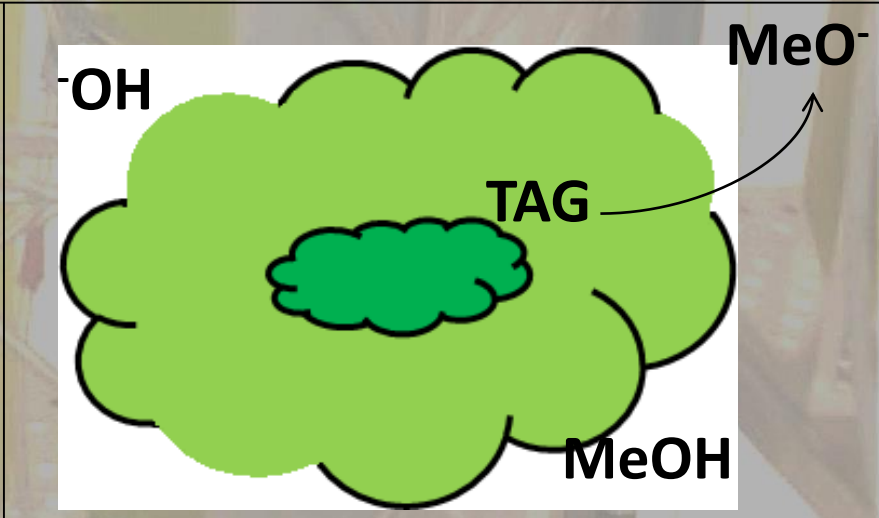
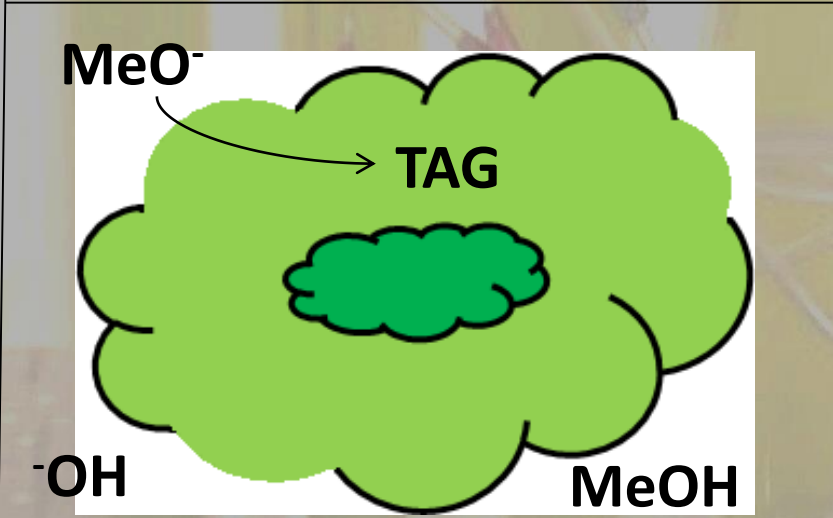
NaOH/methanol - 1.5%
methanol/biomass - 79
reaction temperature - 60°C

Effect of water/biomass



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

Direct transesterification



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