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

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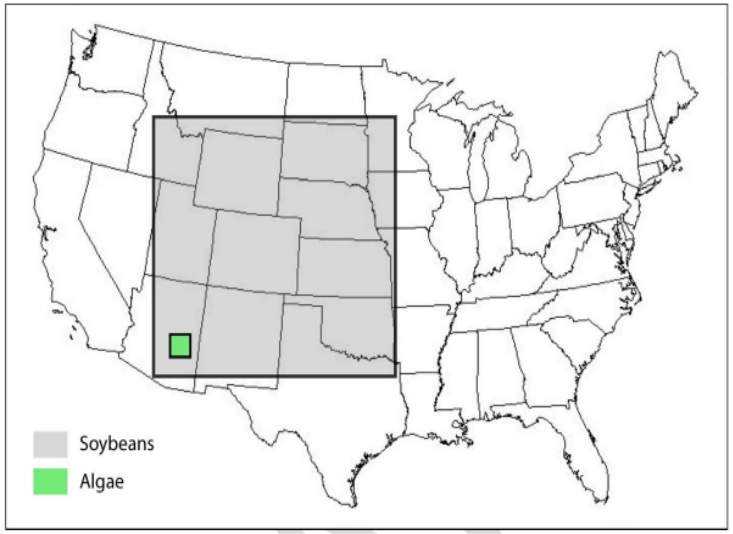
Feed Stocks for Biodiesel

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



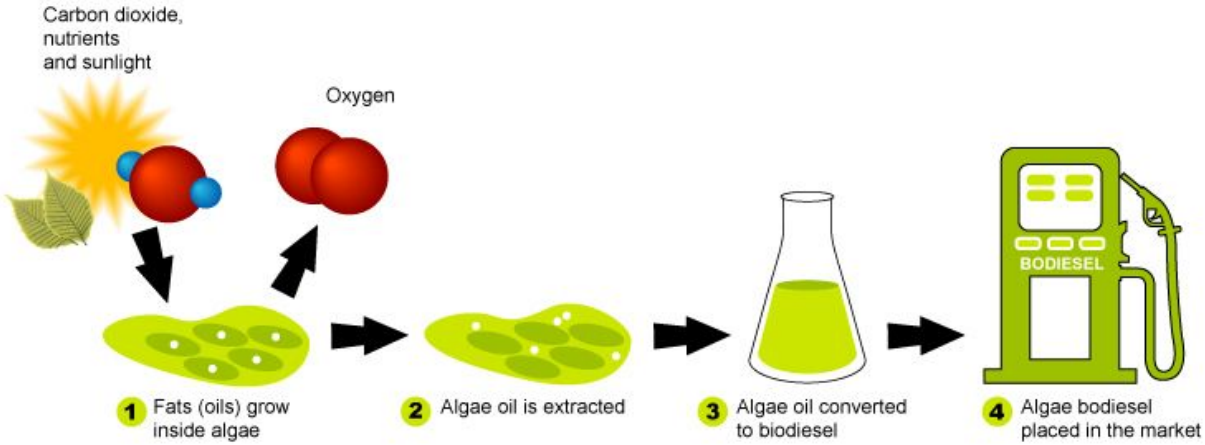
Crop	Oil yield (L/ha)	Land Area* (M ha)
Corn	172	1,540
Soybean	446	594
Canola	1,190	223
Jatropha	1,892	140
Coconut	2,689	99
Oil palm	5,950	45
Microalgae	**136,900**	**2**

* 50% of USA transportation fuel needs

Chisti, Y. Biodiesel from microalgae. *Biotechnology Advances* 2007, 25, 294-306.

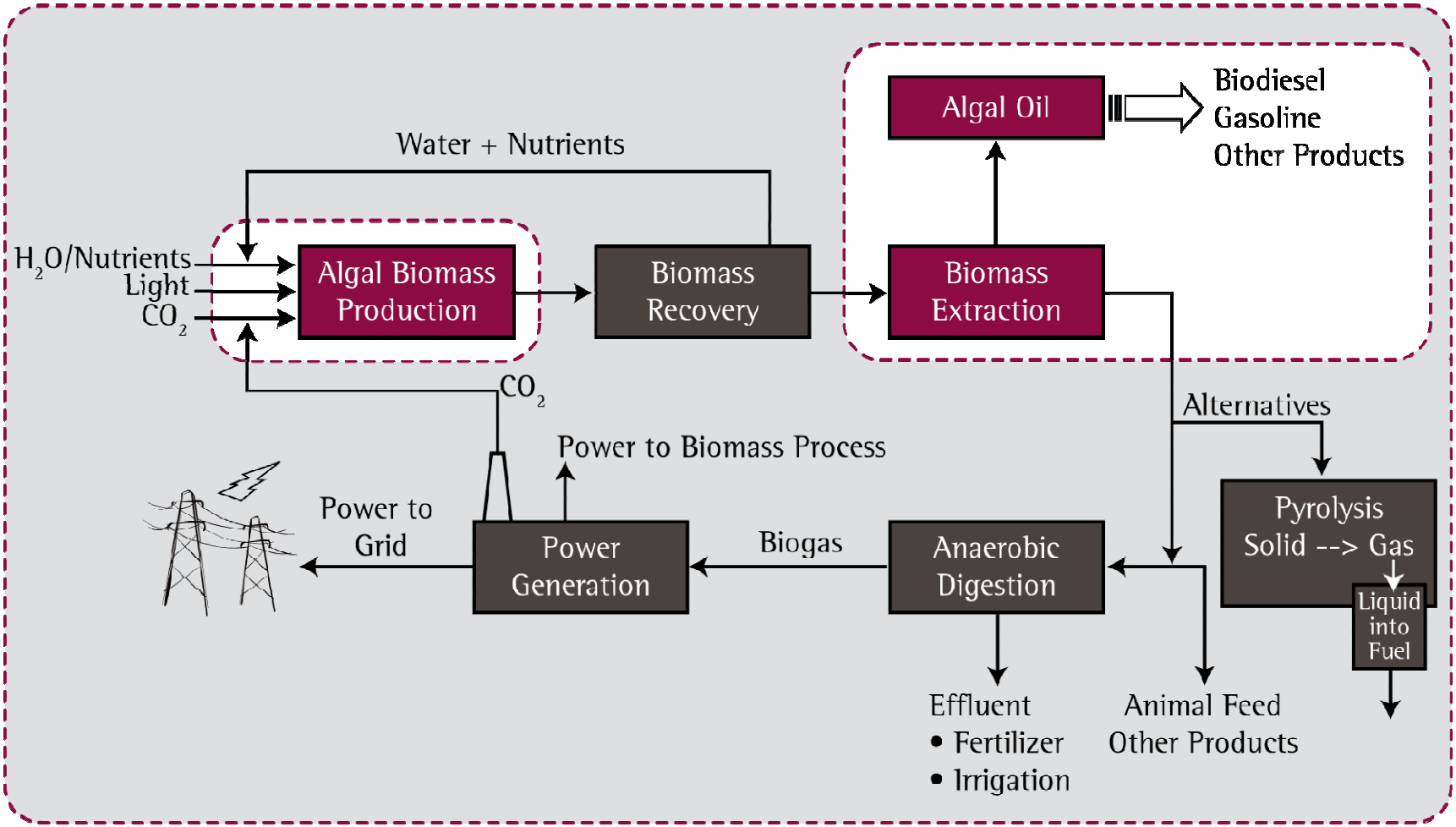
What is Microalgae ?

- 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



Metting, B., Pyne, J.Biologically active compounds from microalgae. *Enzyme Microb Technol* 1986; 8: 386-94.

Algal Biomass-Based Biorefinery



Main Challenges in Algal Biofuels

- Algal biology and cultivation
- Harvesting and dewatering
- Extraction and conversion
- Development of co-products

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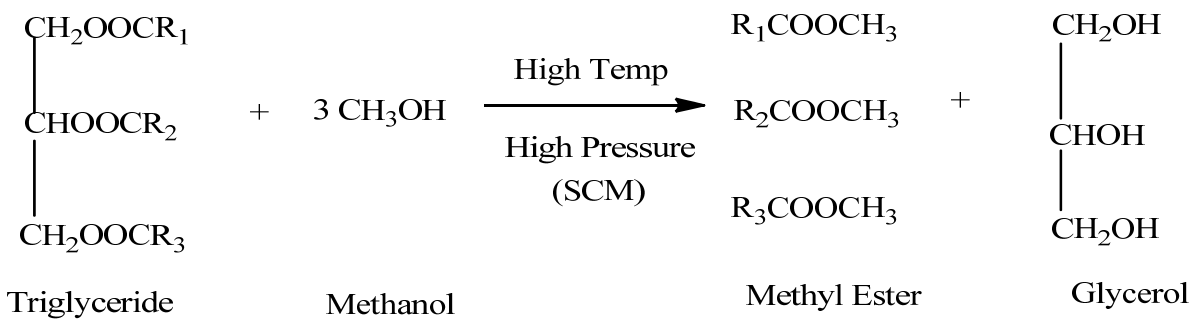
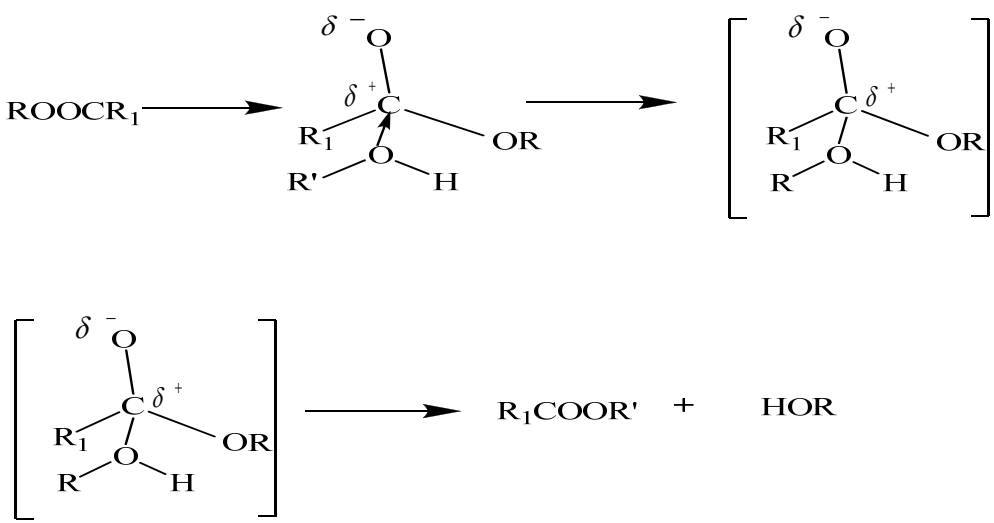
Transesterification Mechanism in SCM

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



R_1, R_2 and R_3 = Long Chain Hydrocarbons, may be same or different



ROH: Diglyceride,

R': Alkyl Group

R_1 : Long Chain Hydrocarbon

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

Biodiesel production step	Dry algal biomass [MJ/kg]	Wet algal biomass [MJ/kg]
Algae culture and harvesting	7.5	10.6
Drying	90.3	0
Extraction	8.6	30.8
Oil trans-esterification	0.9	0.9
Total	107.3	42.3

Water Content in Wet Algae	Percentage of Energy Spent on Algae Drying
90%	113%
80%	50%
70%	29%
60%	19%
50%	13%
40%	8%
30%	5%
20%	3%
10%	1%

Dept of Biomass Program- National Algal Biofuel Technology Roadmap 2010 ; Lardon et al. Environmental science and technology 2009, 43, 6475-81.

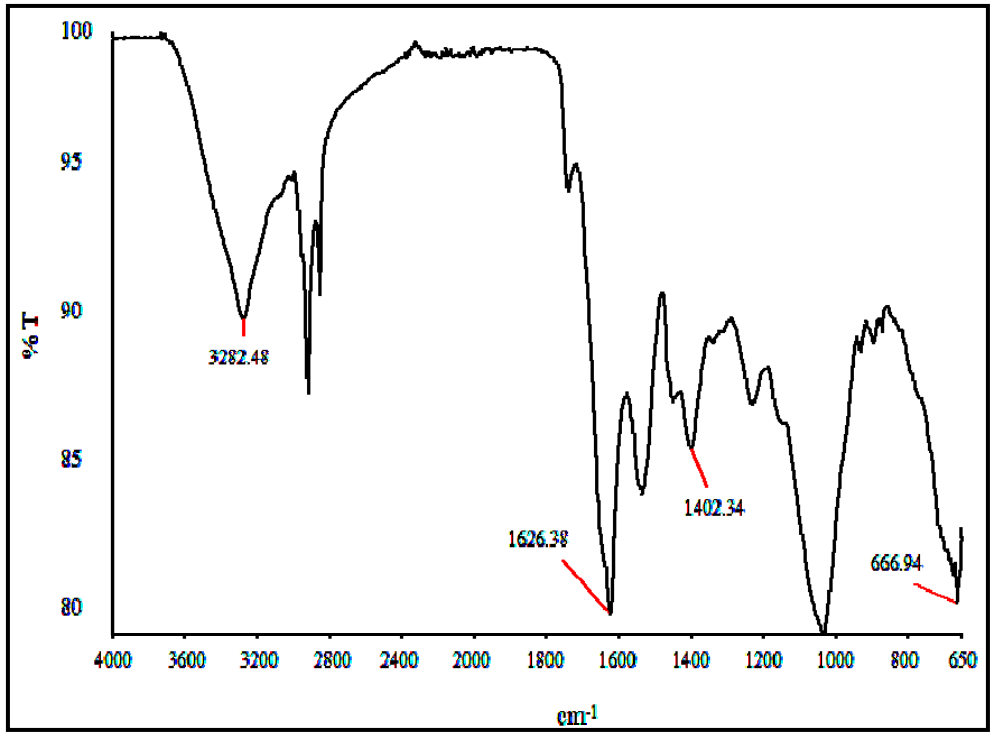
Lipid Extraction Report

Nannochloropsis CCMP 1776 sp.

Sample Label	**CCMP 1776**
Ash Free Dry Weight (dry/wet *%)	68.64%
Lipid Yield (wt% Dry Mass)	50%
Lipid composition	
Triglycerides (%)	37.74 %
Other Non-polars (%)	8.72%
Polars-Glyco & Phospolipids	3.54 %

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.*



FTIR Spectrum

- ✓ 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

Elements	Weight (%)
Carbon (C)	72
Oxygen (O)	21
Sodium (Na)	1.5
Magnesium (Mg)	0.41
Silicon (Si)	0.93
Phosphorous (P)	0.47
Chlorine (Cl)	1.52
Potassium (K)	0.96

Fatty acid Composition

Fatty acids	Area (% total)
Myristic acid, C14:0	0.3
Palmitic acid, C16:0	10.4
Palmitoleic acid,C16:1 n7	35.7
Oleic acid ,C18:1 n9	30.7
Linoleic acid, C18:2 n6	5.6
gamma-Linolenic acid, C18:3 n6	0.7
Arachidic acid, C20:0	0.5
Arachidonic acid, C20:4 n6	1.2
EPA, C20:5 n3	6.2
Lignoceric acid, C24:0	0.3
Nervonic acid, C24:1 n-9	0.2

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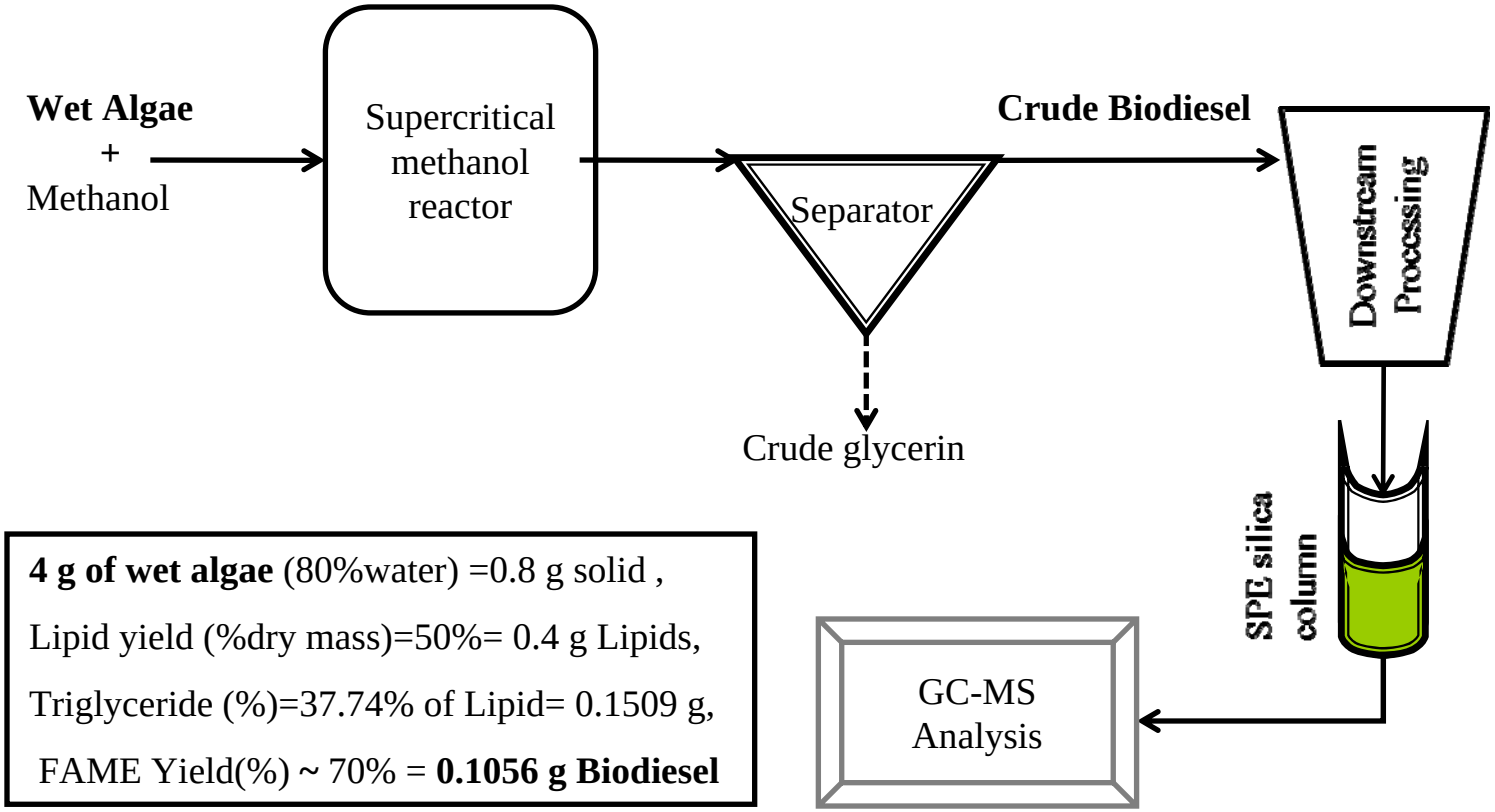
One-Step SCM Algal Biodiesel Process



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

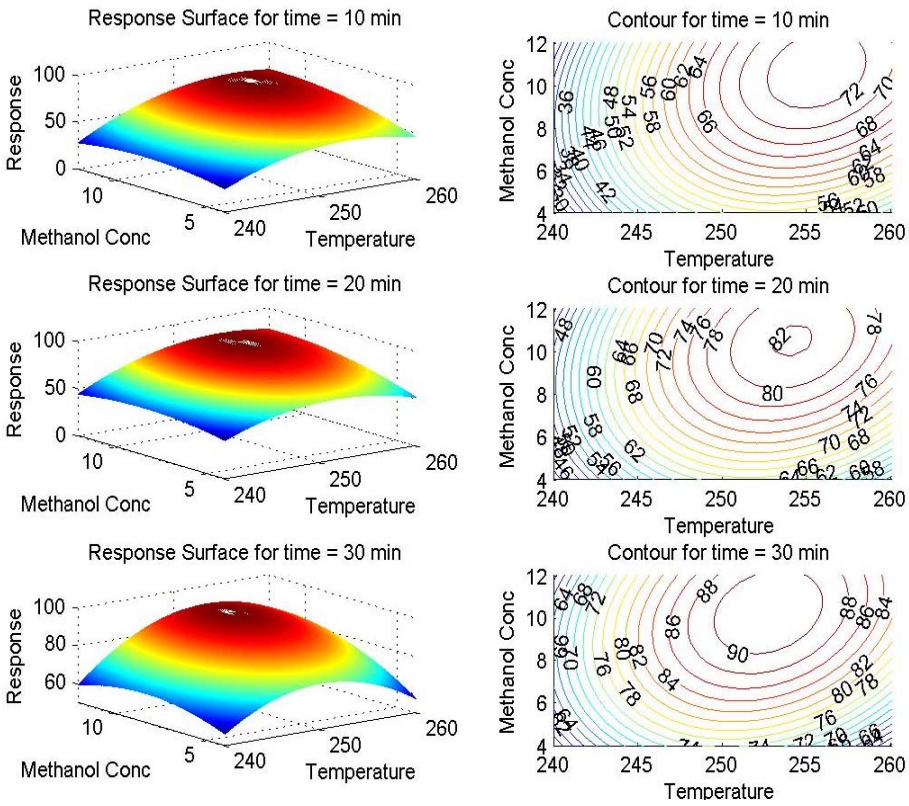
ANOVA for Response Surface Quadratic model :

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

R^2 = 94.46 %, R-Sq (pred) =84.35 %, R-Sq (adj) =91.69 %

RSM Design for SCM Algal Biodiesel Process

Effect of Time

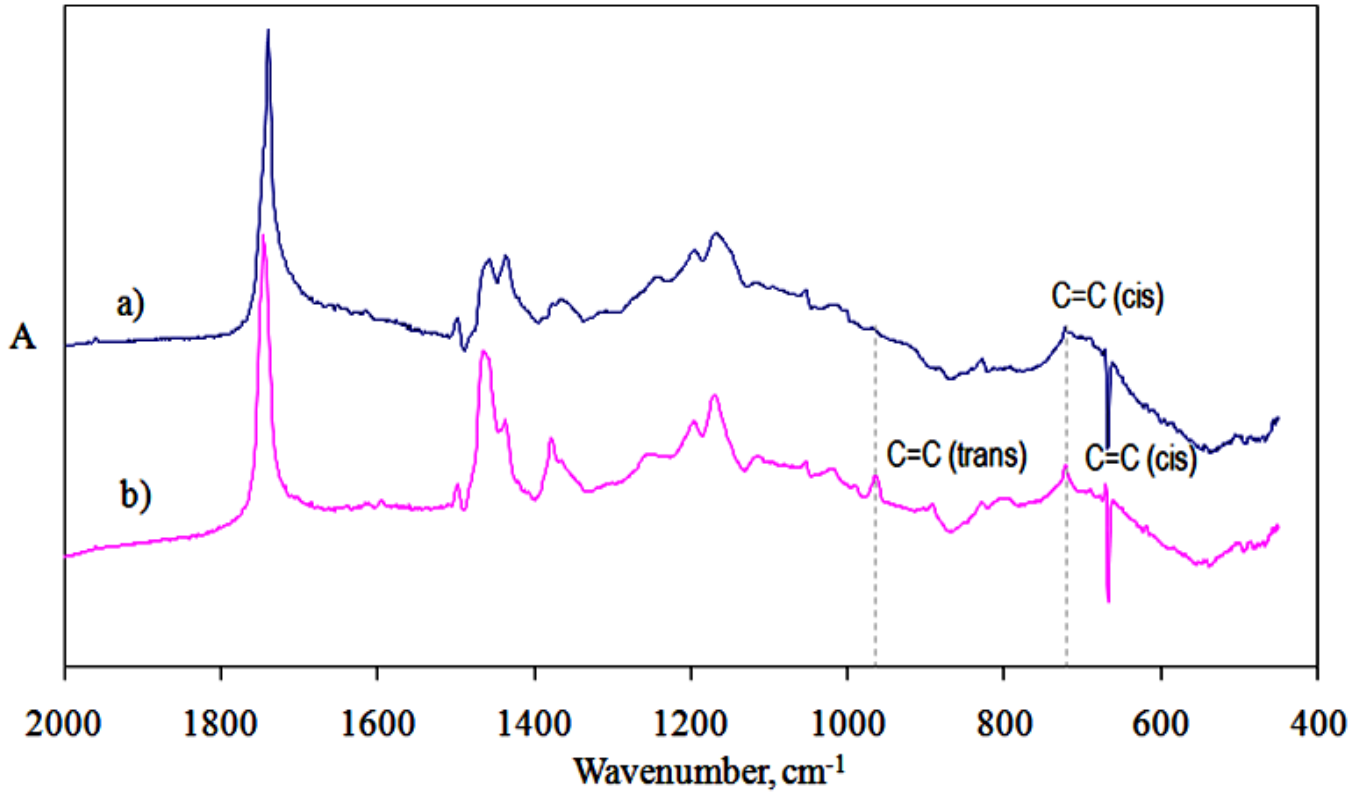


Run Order	Std Order	Temperature (°C)	Methanol (wt/vol)	Reaction Time (min)	Observed FAME %	Predicted FAME %
1	1	240	4	10	25.12	24.38
5	2				20.15	
6	3	240	4	30	68.13	56.02
26	4				53.15	
11	5	240	8	20	38.35	49.32
20	6	240	12	10	32.05	27.37
25	7				28.15	
24	8	240	12	30	55.15	59.01
13	9				62.62	
16	10	250	4	20	55.56	63.03
3	11	250	8	10	76.05	66.70
12	12	250	8	20	82.15	77.79
22	13				77.20	
19	14				83.25	
7	15				79.15	
14	16				78.15	
9	17				76.07	
15	18	250	8	30	84.15	88.88
17	19	250	12	20	70.91	77.30
27	20	260	4	10	45.07	44.43
8	21				39.31	
18	22	260	4	30	66.37	57.15
21	23				54.12	
4	24	260	8	20	68.30	71.19
23	25	260	12	10	70.00	69.97
10	26				72.35	
2	27	260	12	30	78.40	82.69
28	28				85.75	

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

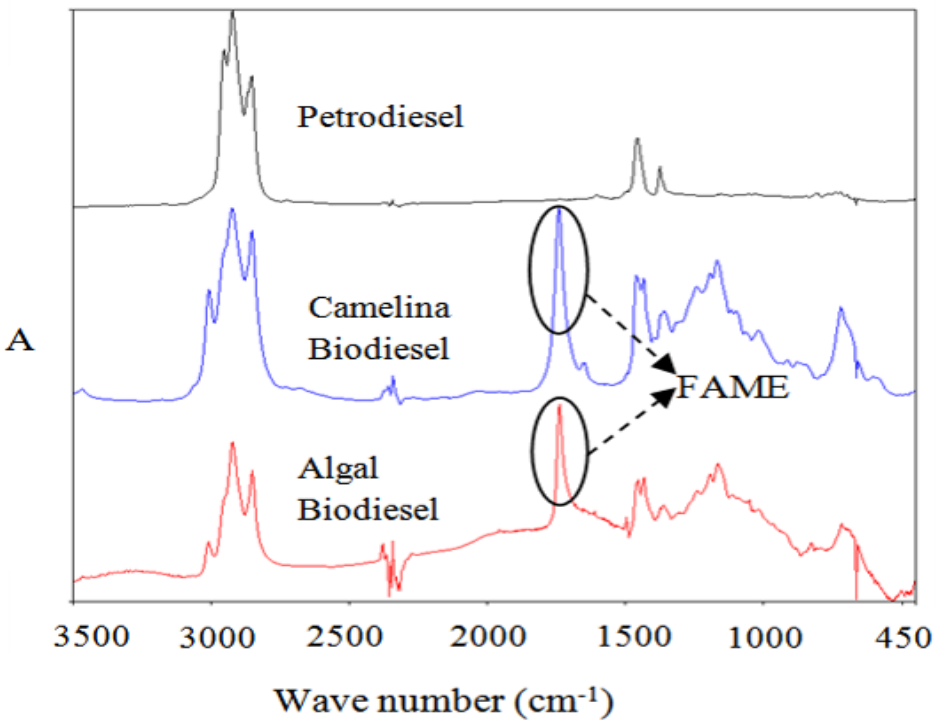
Patil, P.D., et al. Bioresour. Technol. (2011),102(1),118-122

FT-IR Analysis On The Product Sample At Reaction Temperature (a) 250 ºC, (b) 270 ºC



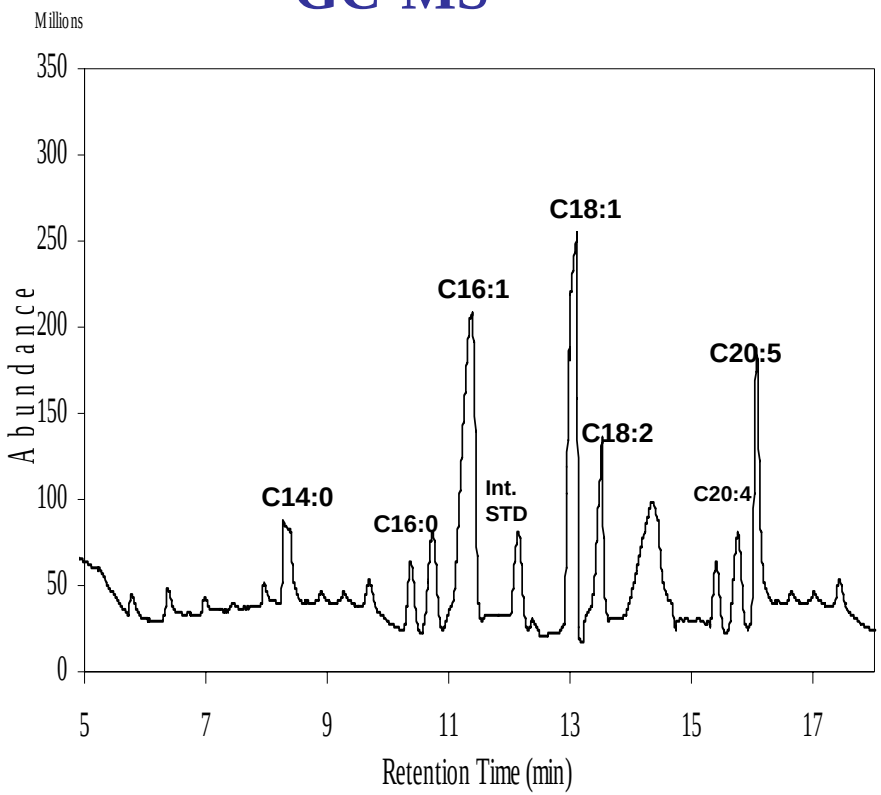
Analysis of Biodiesel from Algae

ATR-FTIR



✓ 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.

GC-MS



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

Patil, P.D., et al. Bioresour. Technol. (2011),102(1),118-122

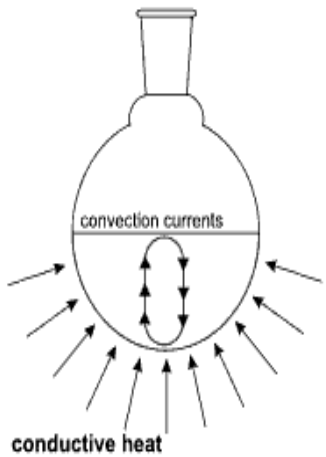
One-Step Conversion of Dry Algae

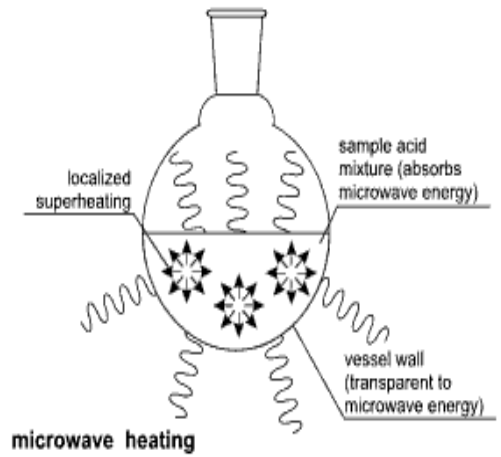
Why Microwave Heating ?

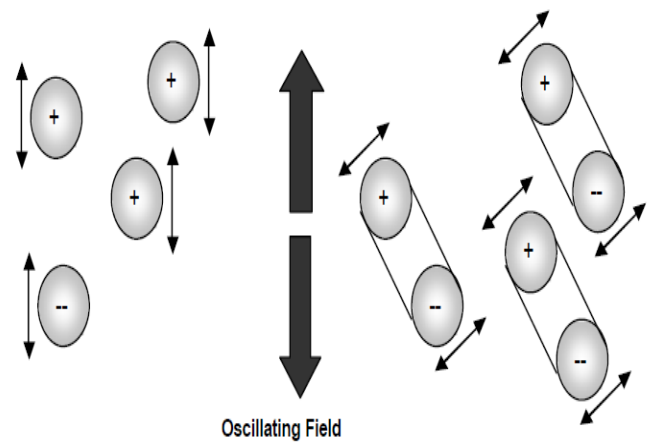
- Easy, Fast and requires shorter Reaction Time
- Single-Step Conversion Process

  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







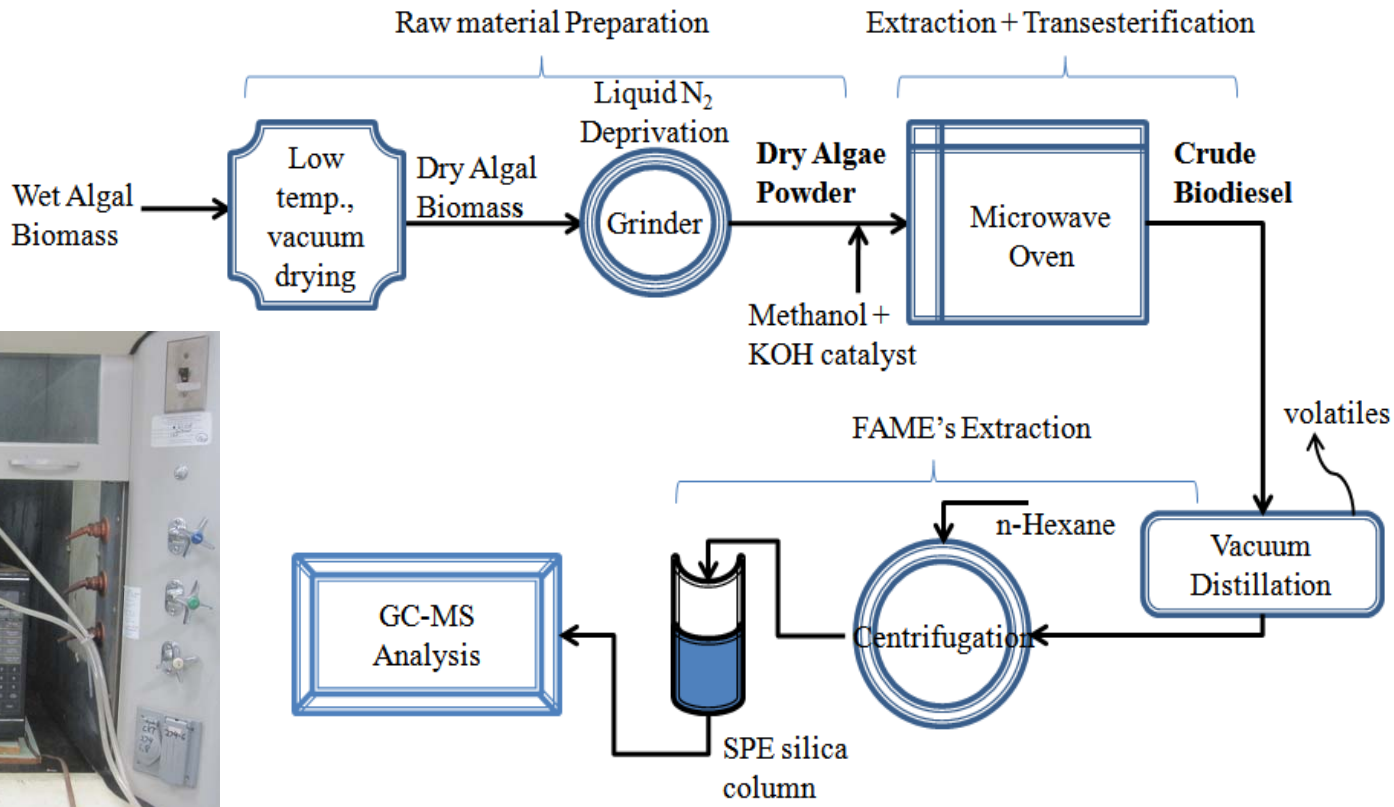
Conventional and microwave heating methods

Ionic conduction, dipolar polarization dielectric heating

Y. Groisman and A. Gedanken, *J. Phys. Chem. C* 2008, *112,* 8802–8808;

Dariusz Bogdal, Microwave-assisted organic synthesis, 2005 Elsevier Ltd.

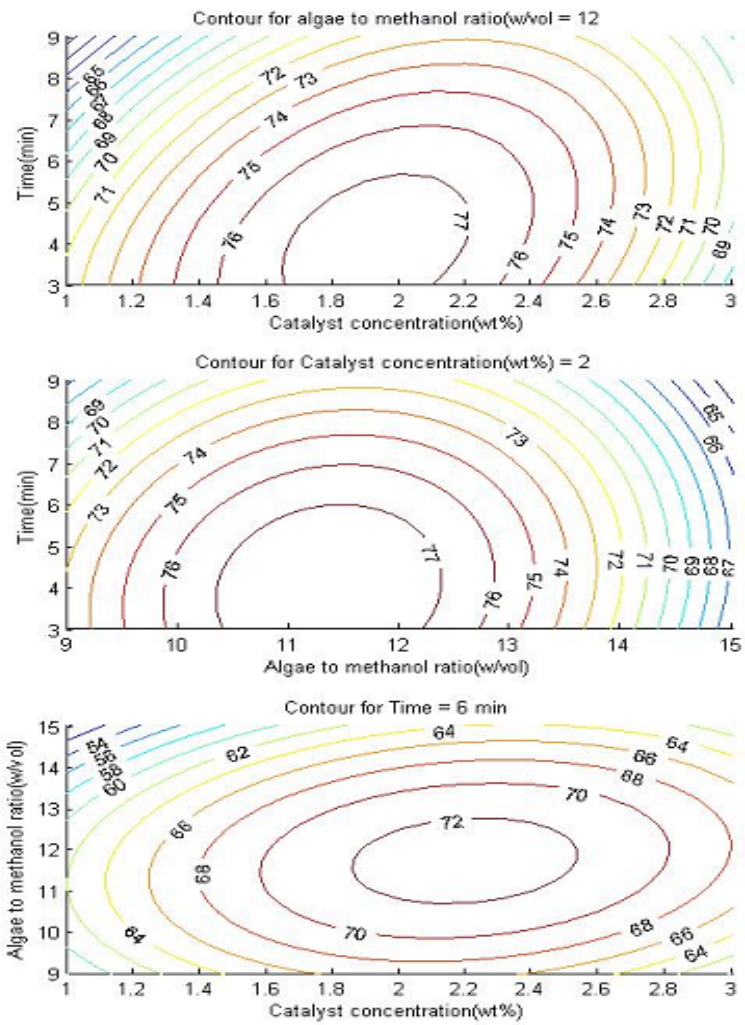
Microwave Transesterification Process for Dry Algal Biodiesel

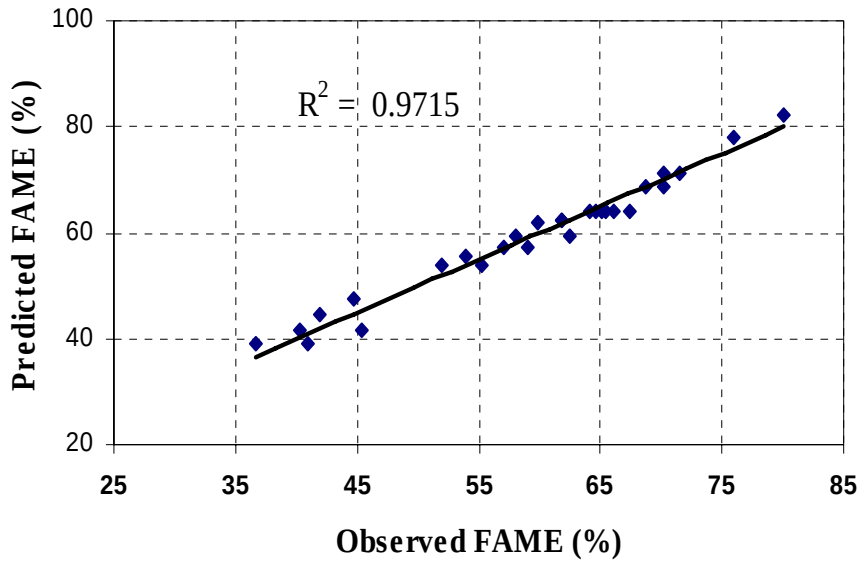


FAME: Fatty acid methyl ester; SPE: Solid phase extraction

Patil, P.D., et al. Optimization of microwave transesterification of dry algal biomass using RSM. Bioresource Technology 102 (2011) 1399–1405

RSM Design for Microwave Algal Biodiesel Process





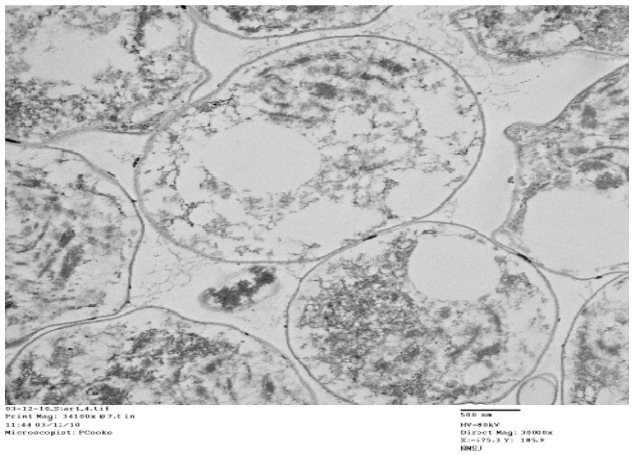
Optimal Conditions: 1:12 (wt/vol) MeOH Ratio, Catalyst Conc.- 2 wt%, 4-5 mins, 60-64 °C

Patil, P.D., et al. Optimization of microwave transesterification of dry algal biomass using RSM. Bioresource Technology 102 (2011) 1399–1405

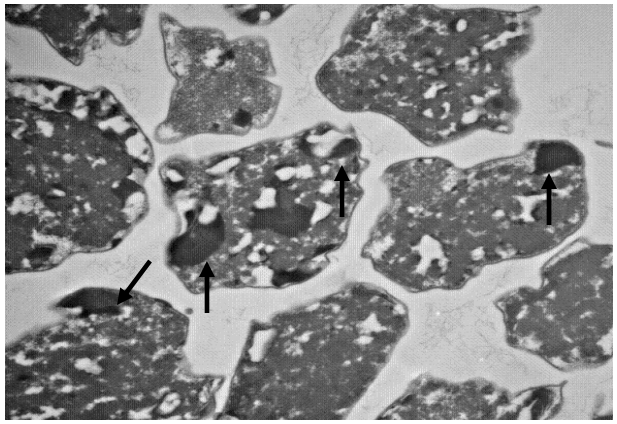
TEM Analysis of Raw and Residual Algal Biomass

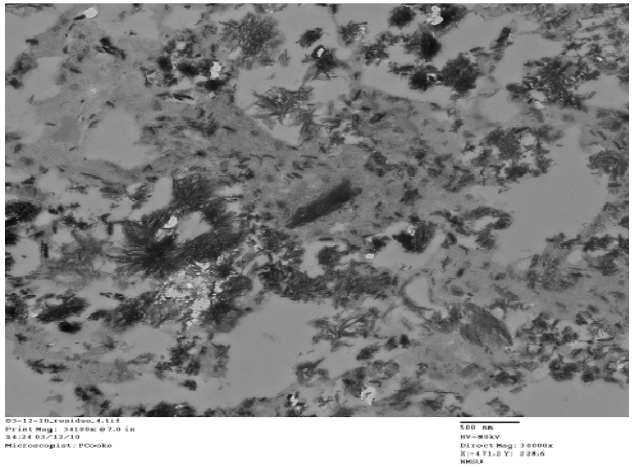
Supercritical Methanol

Microwave

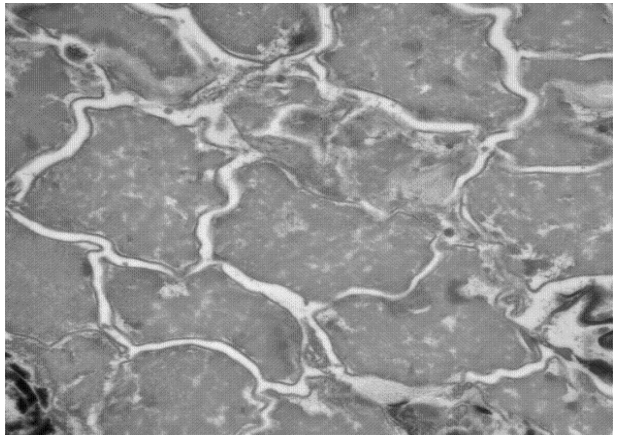


Fresh (Raw)

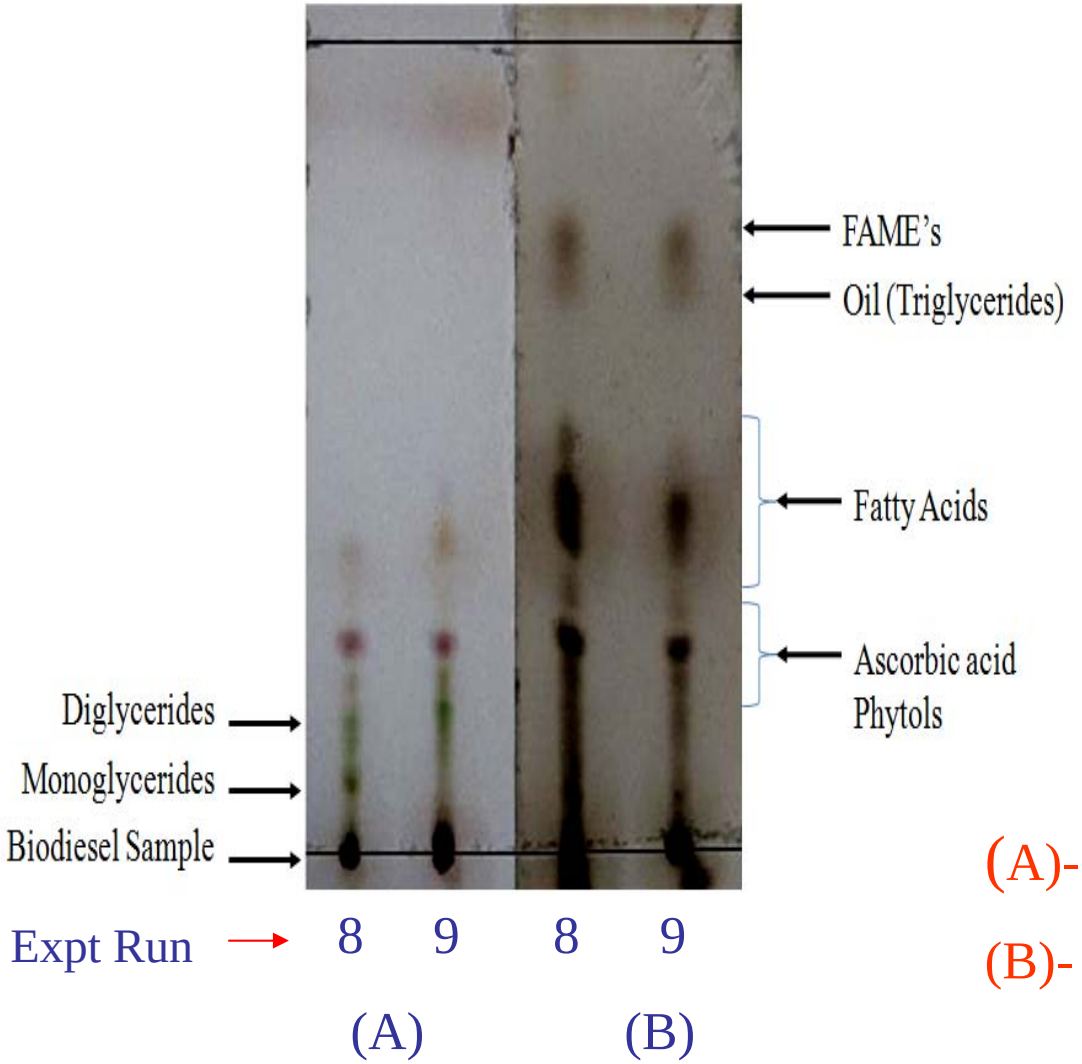




Residue



TLC Chromatograms of Algal Biodiesel

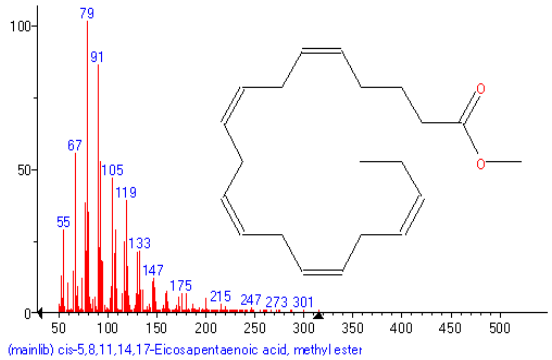


- ✓ TLC plates for experiments 8 & 9 indicating 50 to 60 % of FAME yield.
- ✓ Retention factor (R_f) value for methyl ester and Triglyceride is calculated as 0.645 and 0.564, resp.

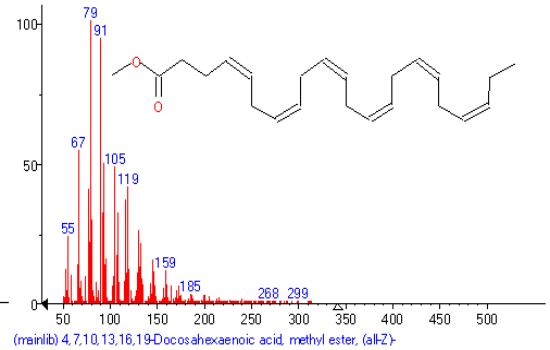
(A)- Initial Development of TLC Plate

(B)- Fully Developed FAME TLC plate

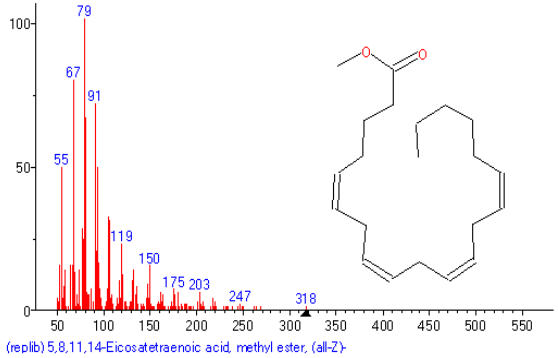
Mass Spectra of PUFA Methyl Esters Found in *Nannochloropsis* Microalgae



(A)



(B)



(C)

(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.

Product group	Applications	Bioproducts
Phycobiliproteins carotenoids	Cosmetics, pigments, surfactants ,plasticizer	Indole, oxalic acid, diethyl phthalate, naphthalene
Polyunsaturated fatty acids (PUFAs)	Food additive, nutraceutics	Eicosapentaenoic acid (EPA), arachidonic acid, docosahexanoic acid (DHA)
Vitamins	Nutrients, precursors	Ascorbic acid, phytols

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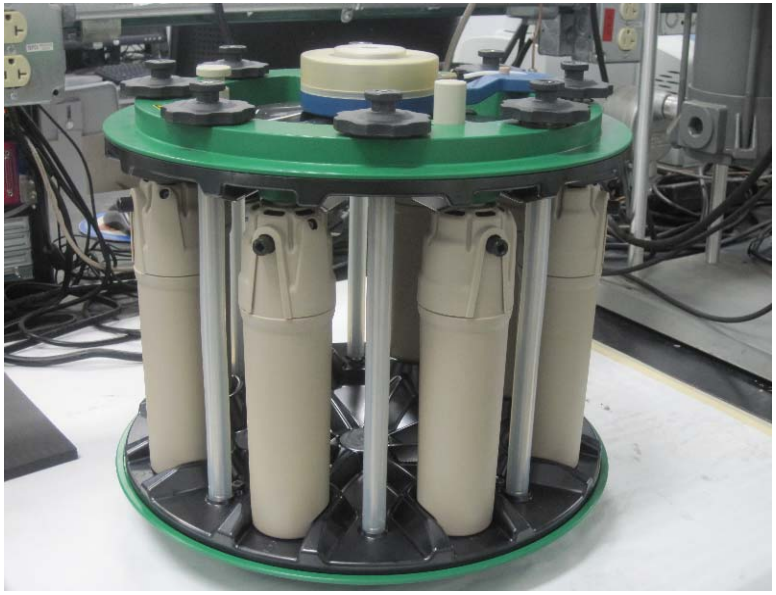
Comparison Between MW and SCM Extraction- Transesterification

Energy Consumption

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

- ✓ 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



Rotor 8SXQ80

Major Benefits:

- ✓ Rate Enhancement
- ✓ Increased Yield
- ✓ Improved Purity

Operating range:

- ✓ Microwave Power : **0-1400 W**
- ✓ Operating Pressure : **0-80 bar**
- ✓ Maximum Temperature : **300 °C**
- ✓ Operating Volume : **12-60 mL**

Concluding Remarks

- Algae is a important feed stock 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.

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Instruments

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