Upgrading of Algae Oil to Hydrocarbon Fuels

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Overview

- Introduction
- Algae oil extraction
- Algae oil upgrading
- Conclusions

Introduction

Conversion of Natural Oils to Hydrocarbon Fuels:

- **Hydrotreating**
  - Used commercially, e.g., Neste Oil NExBTL process
  - Either singular processing of fats and oils or co-processing with heavy petroleum feedstock
- **Thermal cracking (pyrolysis)**
  - Used during WWI and II to produce hydrocarbon fuels
  - High temperatures required (>600 °C), unselective

Hydrotreating

- Current technology for production of “Green Diesel” from vegetable oils and animal fats (triglycerides):

  - Conventional hydrotreating catalysts and conditions: e.g., 350-450 ^{o}C, H_2 pressure = 50-100 bar, catalyst = sulfided $Ni/Mo/Al_2O_3$, $Co/Mo/Al_2O_3$, etc.

  - Results in hydrogenation, hydrodeoxygenation, decarboxylation and decarbonylation

  - Product closely resembles current petroleum diesel

  - Suitable for refineries but not for distributed processing of triglycerides

Alternatives to Hydrotreating for Production of Hydrocarbon Fuels

- Acid cracking (e.g., over zeolites):
  - No H_2 required
  - Oxygen mainly removed as CO_2 (decarboxylation) and H_2O (dehydration)
  - Catalyst deactivates rapidly due to coking ($\Rightarrow$ continuous regeneration)
  - Unselective: C and light HCs formed, as well as liquid products

- Decarboxylation/decarbonylation over metal catalysts:
  - No H_2 required
  - Pd/C shown to be active for deoxygenation of fatty acids and methyl esters (Murzin and co-workers)
  - Effective for triglycerides??

Extraction of Algae Oil

- Solvent extraction (hexane; chloroform/iso-propanol)
- Expression via expeller press
- Supercritical fluid extraction (e.g., CO_2)
- Ultrasound-assisted extraction
- Osmotic shock

Algae Oil Extraction: Results

Solvent extraction

Algae form	Reagents	Conditions	Oil yield
Dried	Hexane	Soxhlet extraction, 16 h	17.7 wt%
Wet	1:1 hexane:methanol	Soxhlet extraction, 16 h	4.9 wt%
Wet	40:1 hexane:methanol	Soxhlet extraction, 16 h	7.2 wt%
Wet	10:1 hexane:methanol	Reflux, 16 h	16.0 wt%

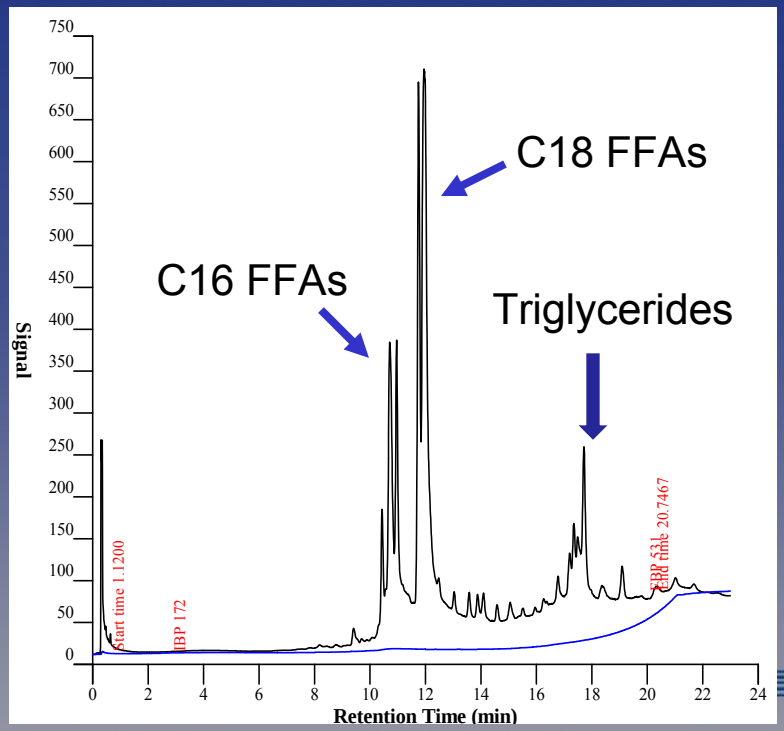
"Dry" algae: 8 wt% water. "Wet" algae: ca. 90 wt% water.

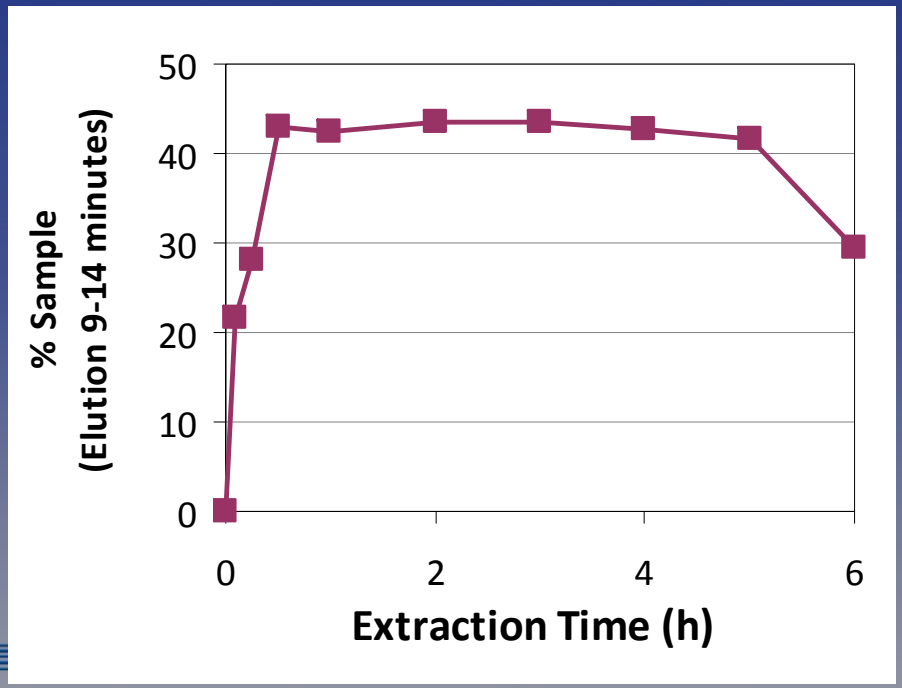
Algae provided by APS.

→ ~80% recovery of lipids is possible using "wet" algae (algae paste)

Algae Oil Extraction: Results

- Extraction of wet algae using 1:1 hexane/methanol under reflux
- GC indicates:
  - maximum lipids removal achieved after 30 min
  - high FFA content of extracted lipids



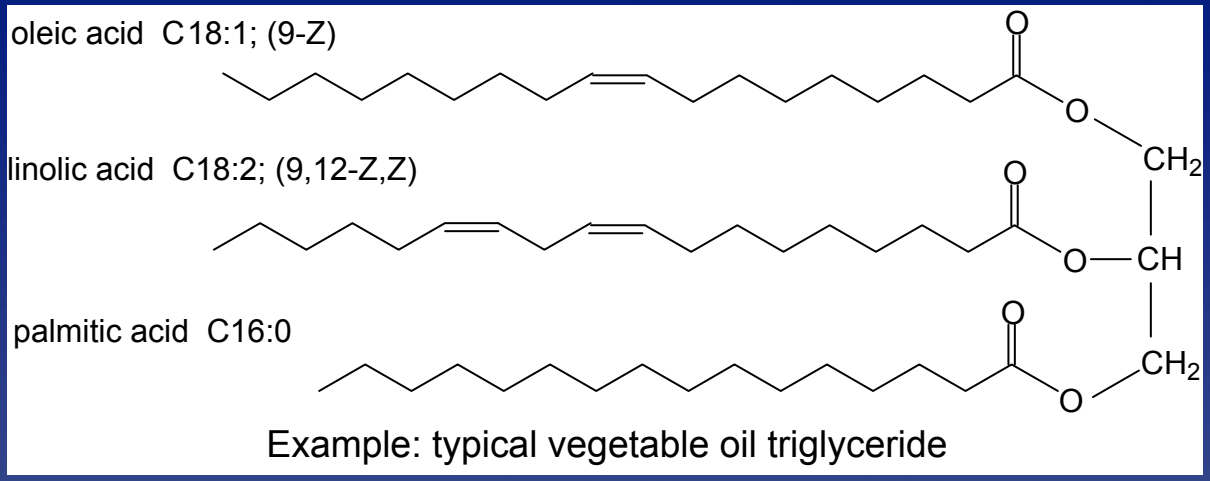


Algae Oil Upgrading: Objective

- Develop a catalyst for the direct conversion ("upgrading") of triglycerides to diesel fuel/jet fuel:
  - diesel fuel: mainly linear paraffins, C_{10}-C_{15}
  - jet fuel: mainly linear paraffins, C_8-C_{16}

- Catalyst requirements:
  - high selectivity to hydrocarbons boiling in the C_8-C_{16} range, hence mild activity for C-C cracking required
  - high activity for triglyceride deoxygenation, i.e., C-O scission
  - inexpensive

Algae Oil Upgrading: Objective



Example: typical vegetable oil triglyceride

↓ Catalyst

C_8-C_{16} hydrocarbons + CO_2 (+ CO + O_2 + light HCs + …)

Hydrocarbon Fuels

- Gasoline:
  - $C_5 – C_{12}$
  - b.p. range: 80-400 °F (27-204 °C)
- Diesel:
  - $C_{10} – C_{15}$ (C_{12} as average)
  - ~75% saturated paraffins, ~25% aromatics
  - b.p. range (# 2 diesel): 350-650 °F (177-343 °C)
- Jet Fuel (JP8):
  - $C_8 – C_{16}$
  - b.p. range: 302-554 °F (150-290 °C)

Approach

- Screen Pt and Pd catalysts:
  - known catalysts for deoxygenation of fatty acids and fatty acid methyl esters
  - triglycerides also mentioned in some publications, but no data given

- Examine lower cost alternatives, i.e., Ni catalysts:
  - Ni is known to have high activity for C-C and C-O bond breaking ("cracking")
  - risk is that high C-C cracking activity may give rise to mainly light hydrocarbons (i.e, $< C_8$)

Experimental Details

- Mechanically stirred 300 ml autoclave, flushed with N_2 and pressurized to 100 psi
- Tristearin and algae oil experiments:
  0.25 g catalyst, 30 g feed
- Reaction temp. = 350 °C (4 h)
- Product analysis:
  GC (gases), simulated distillation GC ("SIMDIST"), elemental analysis (C & H, O by difference), ^{13}C NMR

Catalysts

- 5 wt% Pd/C: Aldrich
- 1 wt% Pt/Al_2O_3: prepared in house
- 1 wt% Pt/C: prepared in house
- Various Ni catalysts prepared in house

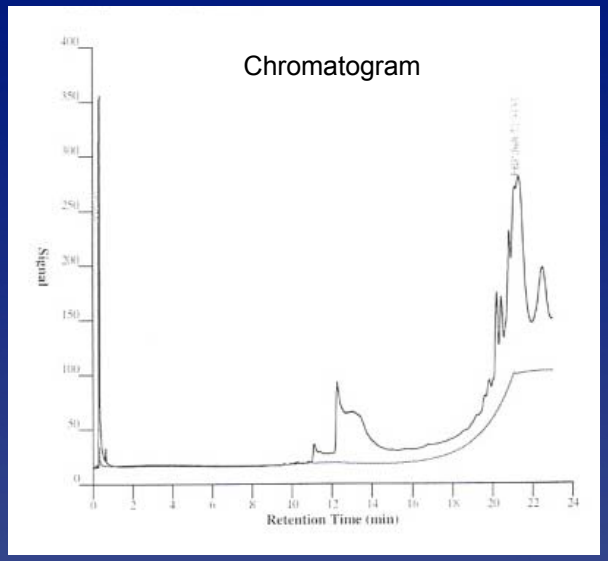
Oil Upgrading Experiments

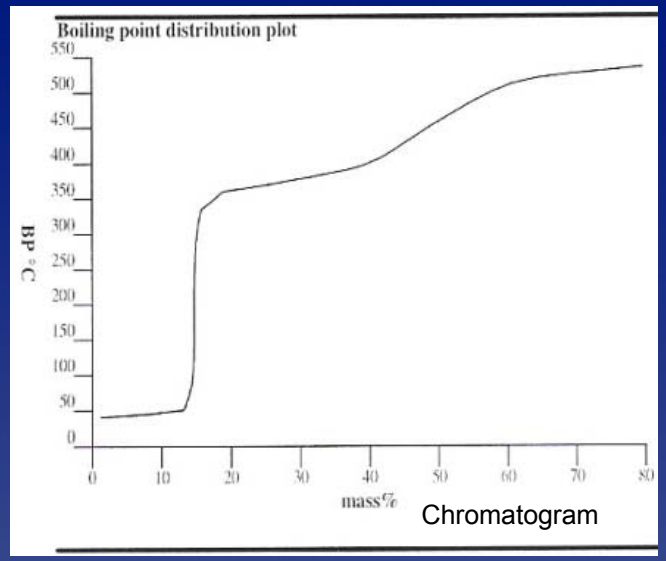
- Algae oil:
  - Provided by APS
  - Acid number (AN) = 1.47 mg KOH/g
- Salad Oil:
  - Refined soybean oil
  - AN = 0.07 mg KOH/g

<u>Tristearin</u>:

- Triglyceride with saturated C_{18} chains
- AN = 3.12 mg KOH/g

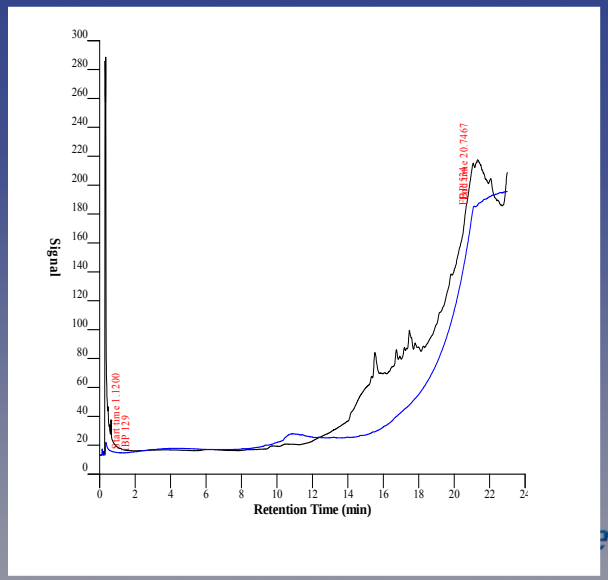
SIMDIST Analysis of Tristearin and Algae Oil Feed

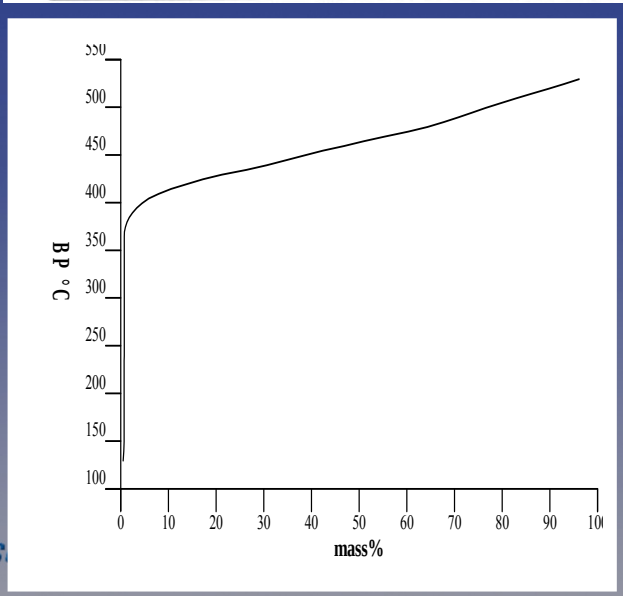




Analysis according to ASTM D2887

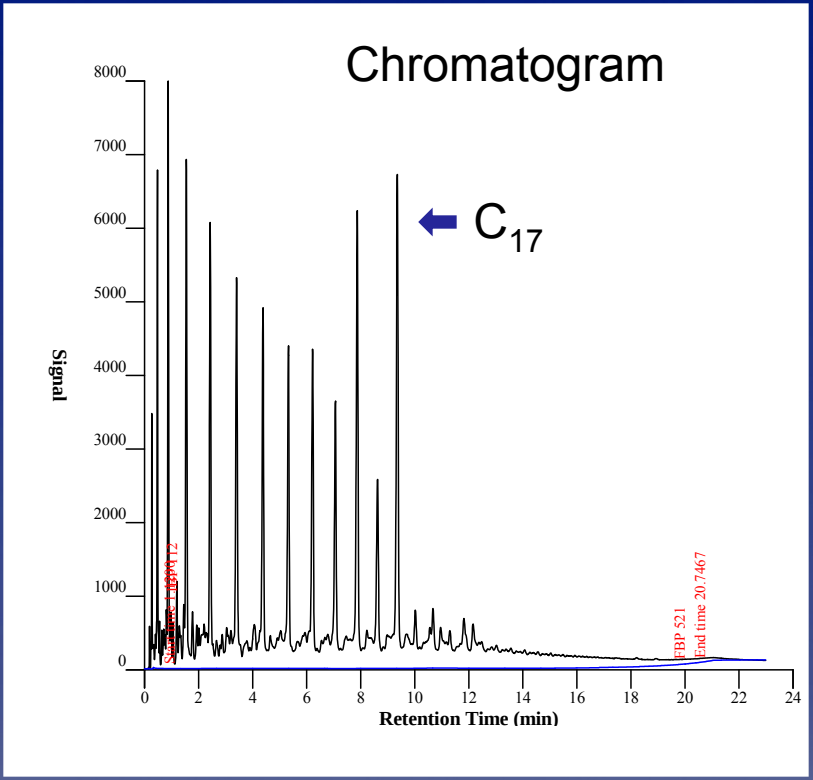
Tristearin: 50% mass recovered at 458 °C

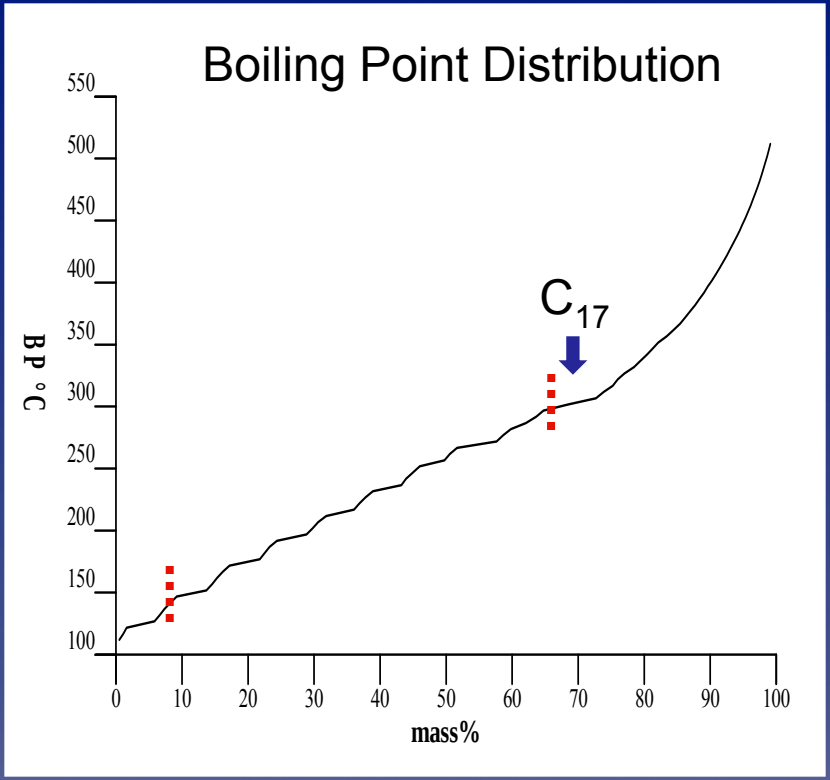




Algae oil: 50% recovered at 464 °C

Tristearin Upgrading Using 5% Pd/C





$\leq C_{17}$ = 75.3 wt% of liquid

Yield of C_8-C_{17} = 61.7%

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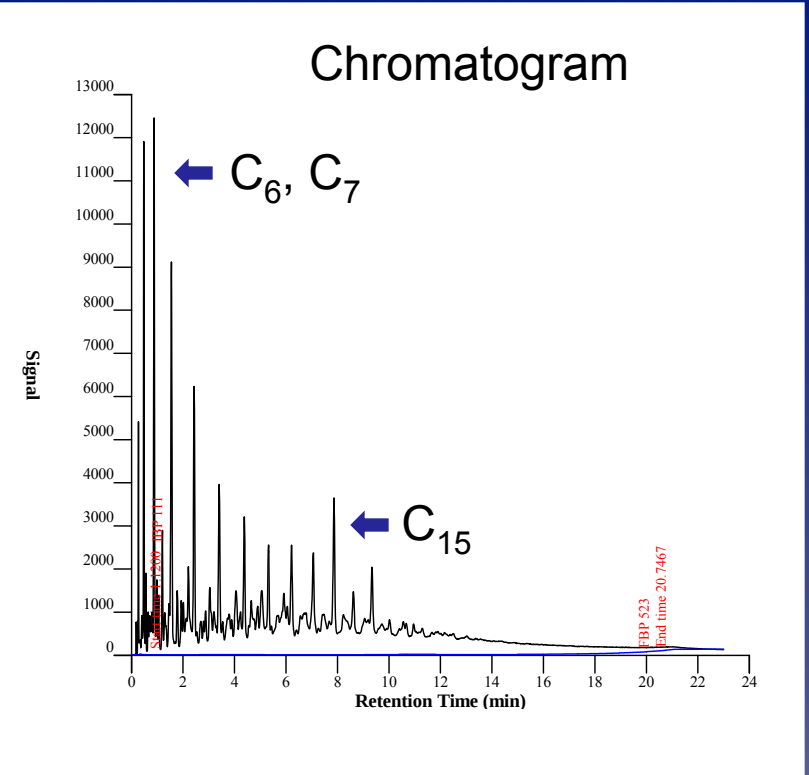
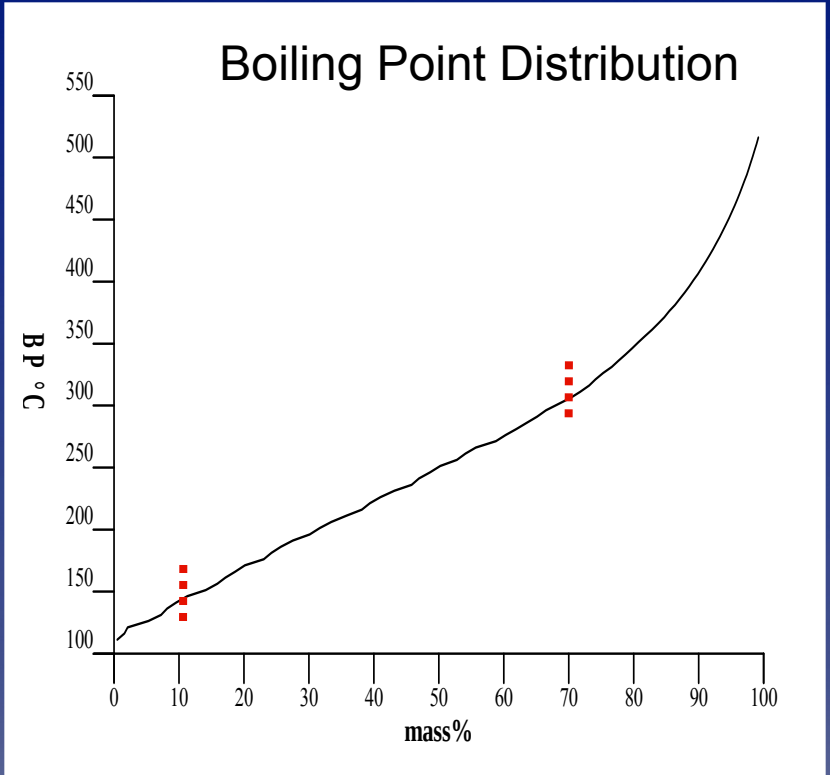
Salad Oil Upgrading Using 5% Pd/C





$\leq C_{17}$ = 70.0 wt% of liquid

Yield of C_8-C_{17} = 51.2%

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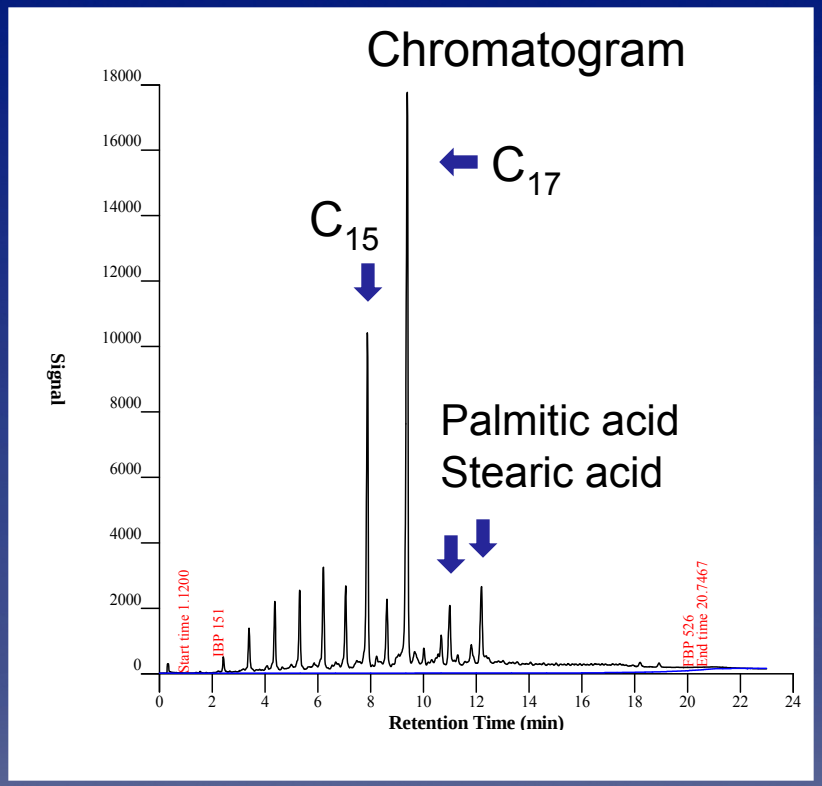
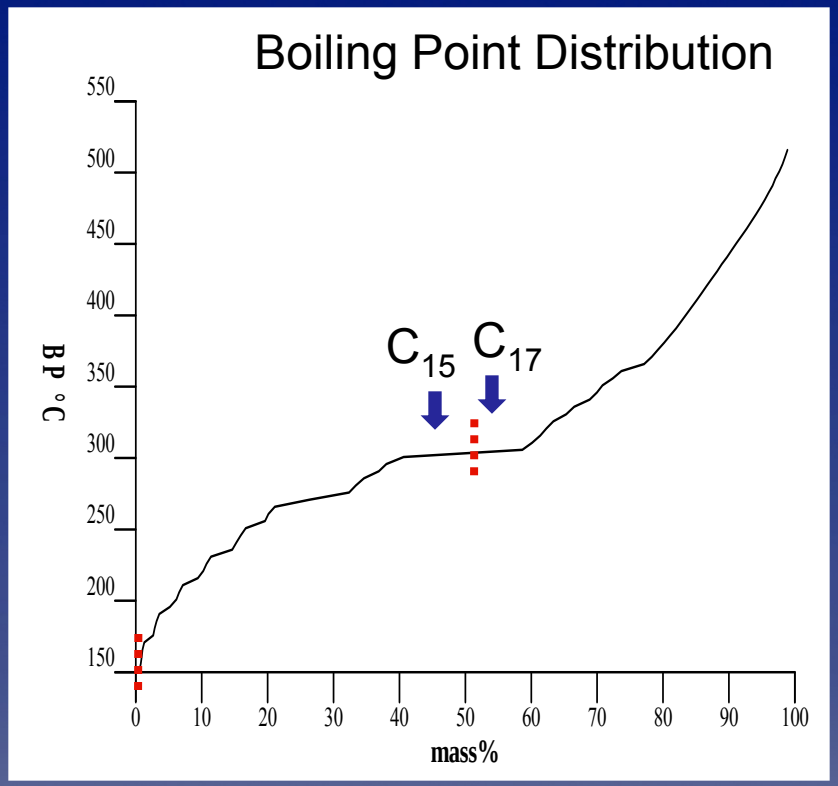
Tristearin Upgrading Using Ni-1





$\leq C_{17}$ = 58.5 wt% of liquid

Yield of C_8-C_{17} = 47.3%

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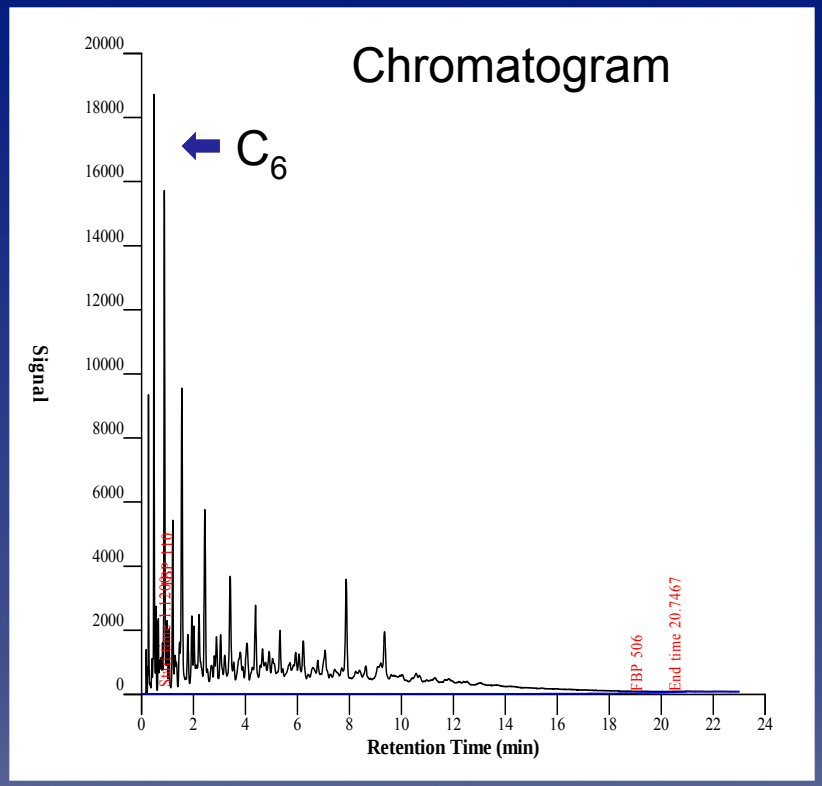
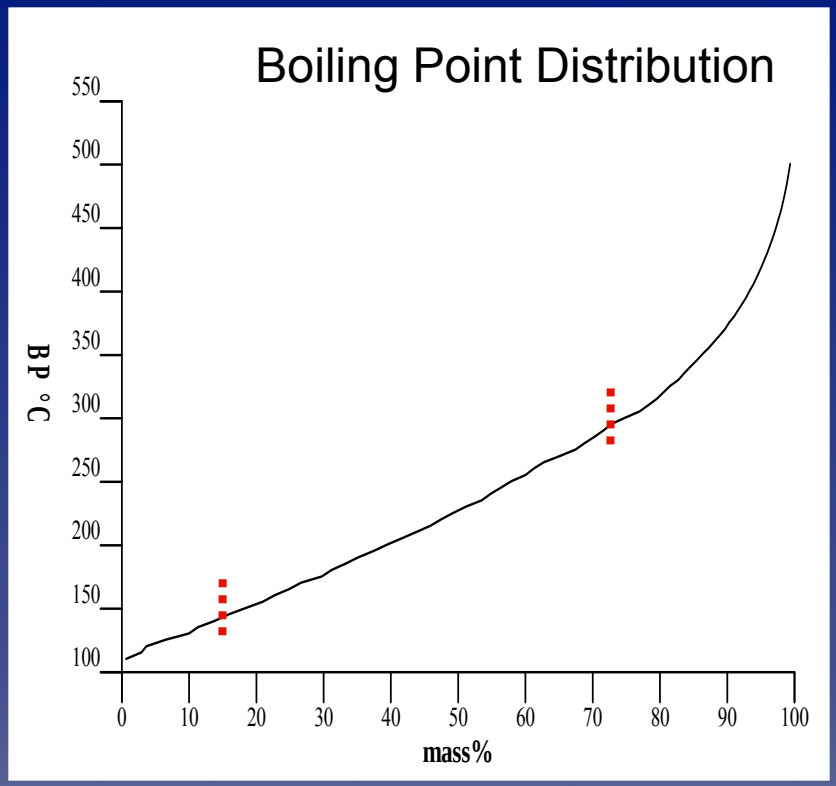
Salad Oil Upgrading Using Ni-1





$\leq C_{17}$ = 76.8 wt% of liquid

Yield of C_8-C_{17} = 63.2%

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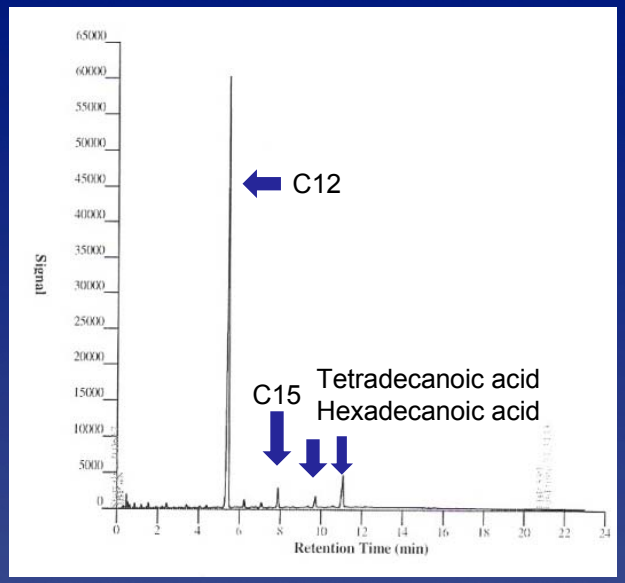
Oxygen Content of Heavy Ends
(Tristearin Upgrading)

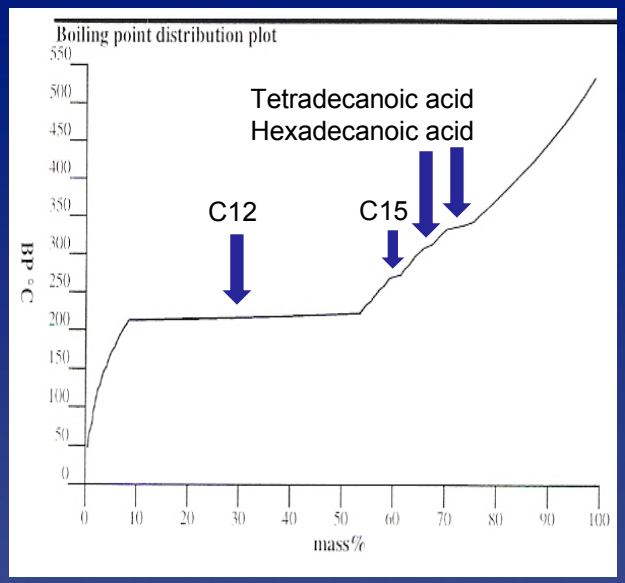
- Discrepancies between CO_x yield and SIMDIST results: in general, conversion based on CO_x yield > conversion based on SIMDIST $\Rightarrow$ heavy HCs being formed
- Elemental analysis of oil indeed suggests that "unconverted oil" may contain significant fraction of O-deficient heavy ends:

Catalyst	% conversion to $\leq C_{17}$	Wt% O (found)	Wt% O (theory)*
Ni-1	76	0.83	2.2
Ni-2	52	0.91	4.08

* Theoretical wt% O based on SIMDIST data (conversion by mass)

Comparison of Algae Oil Upgrading over 1 wt% Pt/C and 5 wt% Pd/C

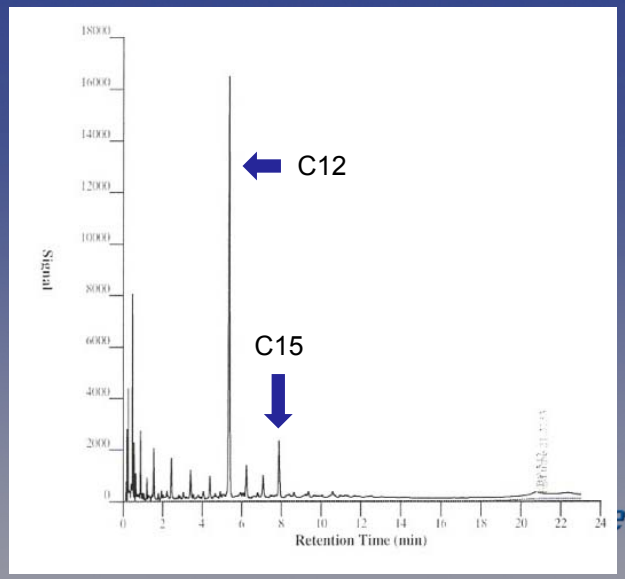


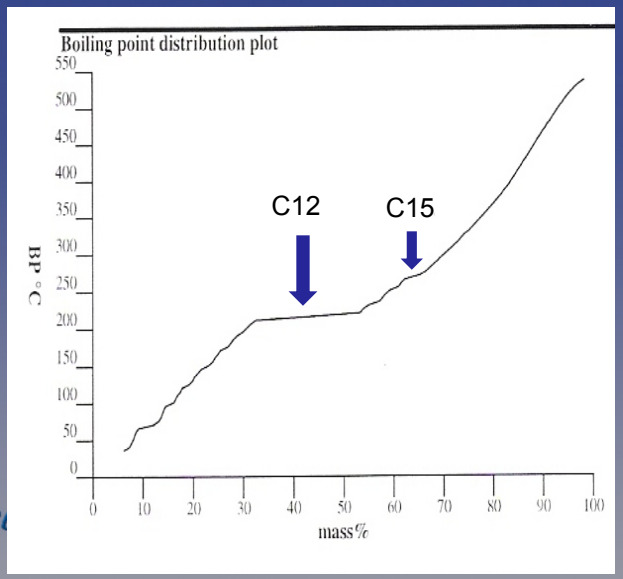


Dodecane as solvent

1 wt% Pt/C:

$\leq C_{17}$ = 40.9 wt%





5 wt% Pd/C:

$\leq C_{17}$ = 64.0 wt%

Summary of Algae Oil Upgrading Experiments

Catalyst	Product			Selectivity to liquid products			**Yield C8-C17 (%)**
	Solid (%)	Gas (%)	Liquid (%)	≤C7 (%)	C8-C17 (%)	≥C18 (%)	
1% Pt/C	3.0	6.7	90.3	3.8	37.1	59.1	33.5
5% Pd/C	12.0	12.2	75.8	22.6	41.4	36.0	31.4

Yield C_8-C_{17} = liquid yield (%) x selectivity to C_8-C_{17} (%)

- Fairly high yield of liquid products although some coke formed
- Selectivity to C_8-C_{17} HCs is only moderate; high degree of oil unsaturation may be responsible for excess cracking / heavy ends formation
- ^{13}C NMR spectroscopy indicates that product HCs are saturated

Summary: Pt and Pd catalysts

- Preliminary experiments indicate that triglycerides can be converted to hydrocarbons over Pt/C and Pd/C catalysts (as can fatty acids and fatty acid methyl esters)
- In triglyceride conversion, 1 wt% Pt/C and 5 wt% Pd/C show similar activity and product distributions
- The main products are C_5-C_{15} hydrocarbons
- ^{13}C NMR data indicate that the hydrocarbons are saturated
- Compared to tristearin and salad oil, the algae oil tested to date affords fairly similar product distributions

Summary: Ni catalysts

- Ni catalysts also show promise for triglyceride deoxygenation:
  - activity similar Pd and Pt catalysts
  - in general, Ni catalysts show slightly higher cracking activity than Pd and Pt catalysts
  - for best Ni catalysts, selectivity to C_8-C_{17} HCs is similar to Pd and Pt catalysts
- For all catalysts, the degree of C-C cracking is heavily influenced by the degree of unsaturation of the fatty acid chains
- In some runs catalyst coking is observed
- P and S content of algae oil could be a concern w.r.t. catalyst deactivation