



“Drop-in” Jet and Diesel Fuels from Renewable Oils

11 May 2011

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ReDiJet™
ReDiDiesel™

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Report Documentation Page

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Overview

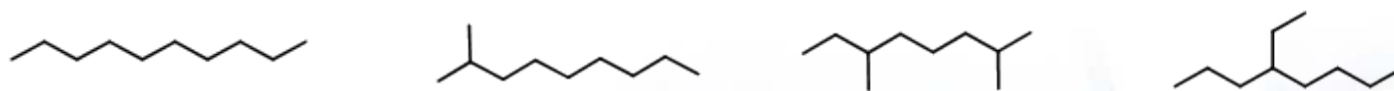
- **ARA Introduction**
- **Catalytic Hydrothermolysis (CH) Process**
- **CH Product Chemistry**
- **Naphtha Data**
- **Recent Algal Oil Tests**
- **Byproduct Potential**
- **Pilot System**
- **Engineering Challenges**
- **Feed Stock Availability**
- **Commercialization Approach**

Current Alternate Fuel Technologies

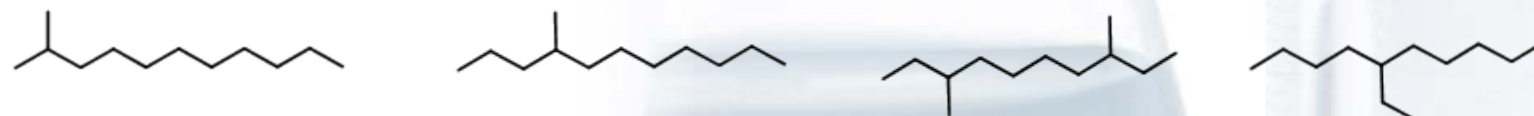
- **Fischer-Tropsch (FT) and Syngas Fuels**
 - First used in WWII Germany
 - Gasify coal or other biomass to CO and H₂
 - Catalytically convert syngas to hydrocarbons
 - Paraffins and isoparaffins
- **Hydrotreated Renewable Jet (HRJ)**
 - Converts renewable plant oils or fats
 - Conventional catalytic petroleum refining processes
 - Hydrotreating, hydrocracking, hydroisomerization
 - Produces paraffins and iso paraffins
- **Jet Fuel from Current Technologies Require Blending**
 - Up to 50:50 with petroleum-derived jet fuel
 - Alternate fuels exhibit low density – below specification requirement
 - Alternate fuels contain no aromatic compounds
 - Necessary for O-ring swelling

Current Alternate Fuel Technologies

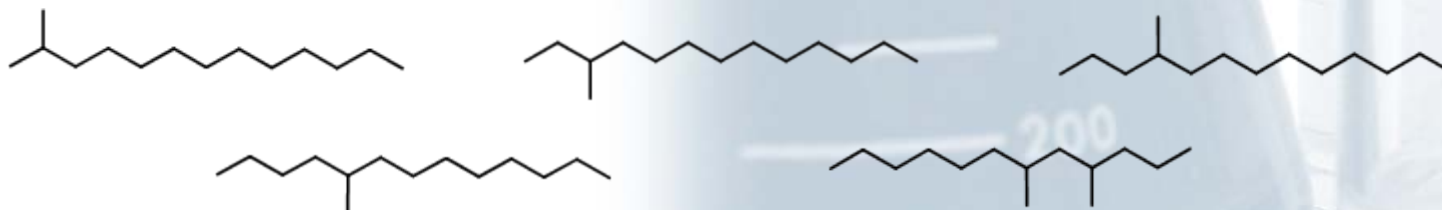
- **Typical jet fuel hydrocarbons from HRJ and FT**
 - 8 to 14 carbon paraffins are typical for the jet fuel fraction
 - C10 examples



- **C12 examples**



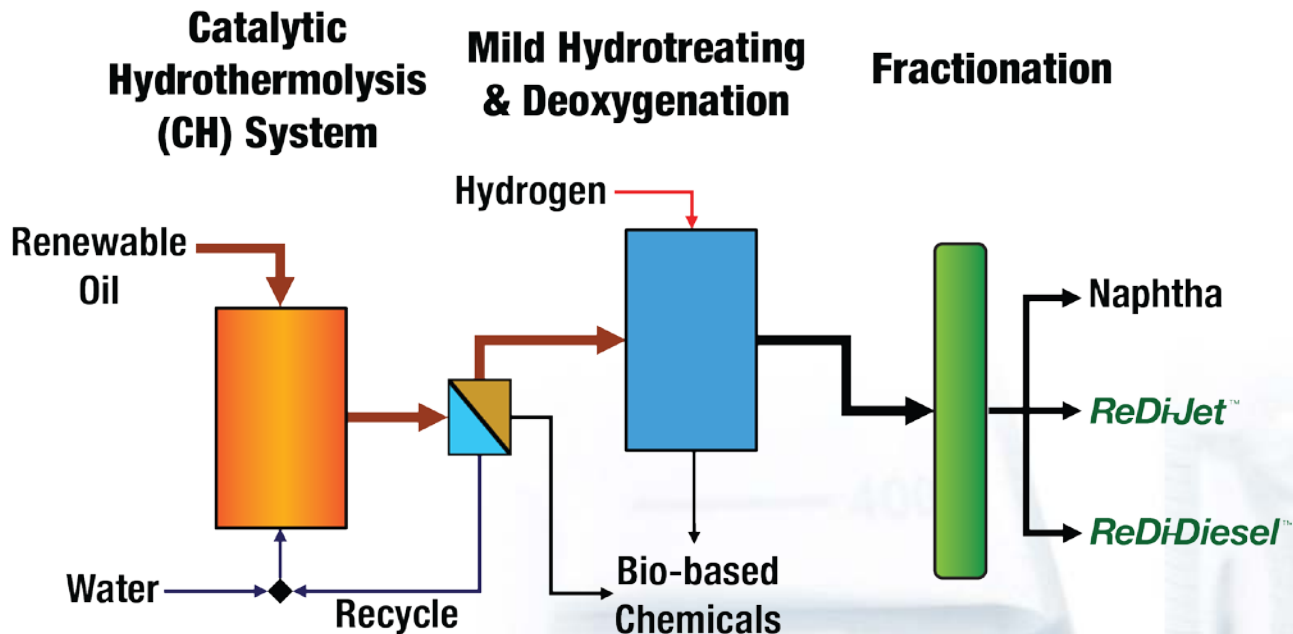
- **C14 examples**



CH Process Background

- ARA developed “Catalytic Hydrothermolysis “ (CH) in 2006
 - A hydrothermal process where water mediates the CH reactions
 - Dr Lixiong Li, inventor, expert in hydrothermal technology
 - U.S. patent 7,691,159 was awarded April 6, 2010
- Goals of the CH process:
 - Produce Renewable Drop-in Jet fuel – **ReDi** Jet™ and
 - Renewable Drop-in diesel fuel – **ReDi** Diesel™
 - Avoid blending and equipment or infrastructure modifications
- A commercially viable process without subsidies
 - Reduce hydrogen consumption and carbon footprint
 - Eliminate hydrocracking, hydroisomerization and catalysts consumption
 - Produce valuable chemical byproducts
- Improve energy security

ARA Hydrothermal Process (patented)



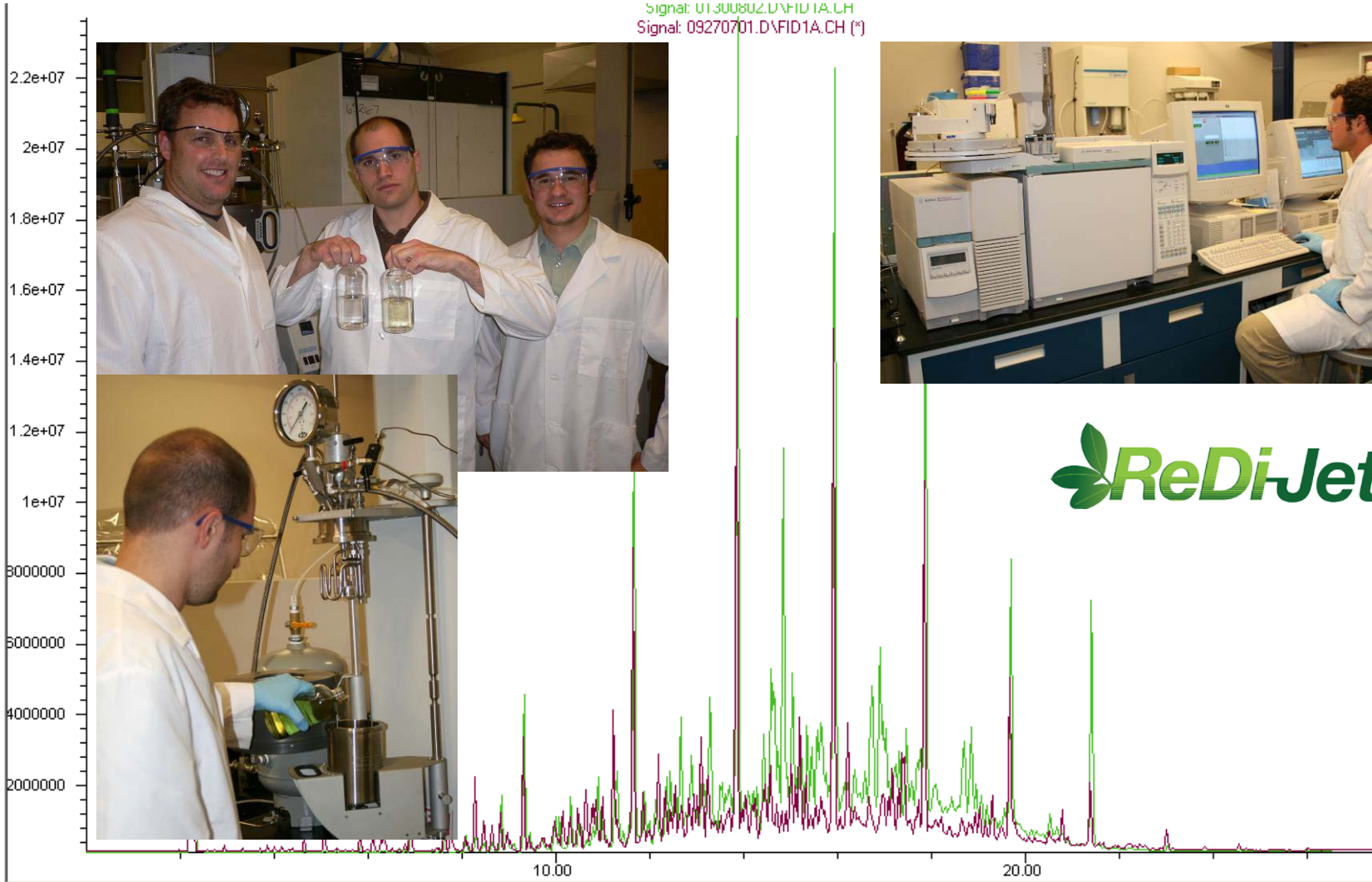
- Hydrolysis and cyclization reactions reduce hydrogen requirements compared to conventional hydrocracking and hydroisomerization
 - Reduces hydrogen consumption up to 74%
 - Reduces CO₂ generation up to 65%
- High-density cycloparaffins and aromatics are produced
- Valuable bio-based chemicals are produced

Catalytic Hydrothermolysis Reactions

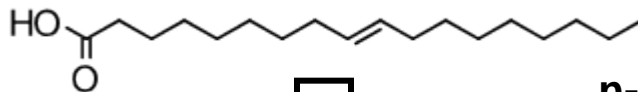
- **Hydrolysis**
- **Isomerization of the double bonds in unsaturated fatty acids**
- **Decarboxylation of fatty acids to the corresponding paraffin**
- **Cyclization of unsaturated fatty acids into alkyl cycloparaffins and aromatics**
- **Cyclization of polyunsaturated fatty acids into alkyl aromatics**
- **Cracking of fatty acids into linear carboxylic acids and corresponding cycloparaffin**
- **Cracking of fatty acids into linear carboxylic acids and corresponding aromatics**
- **Formation of dicarboxylic acids**
- **Skeletal isomerization of intermediate and product compounds**

GC of ReDi Jet from CH and Petroleum JP-8

Signal: 01300802.D\FID1A.CH
Signal: 09270701.D\FID1A.CH (*)



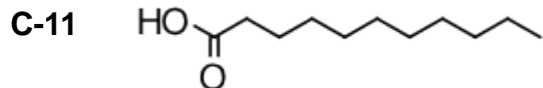
Oleic Acid – Hydrothermolysis Products



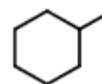
Carboxylic Acids



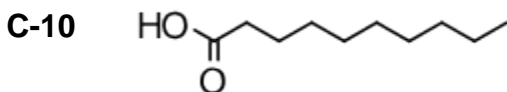
n-Alkylcyclohexanes



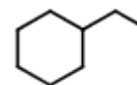
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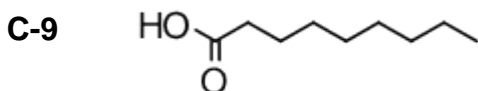
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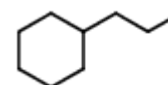
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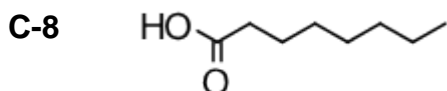
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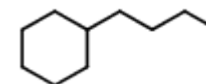
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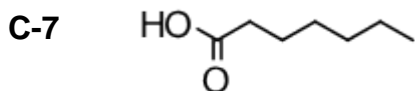
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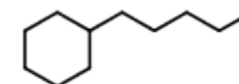
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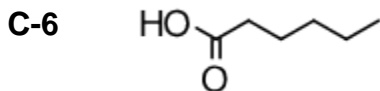
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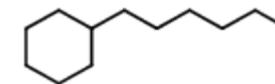
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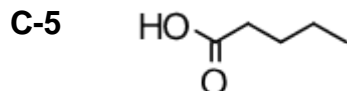
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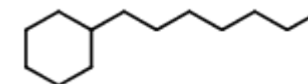
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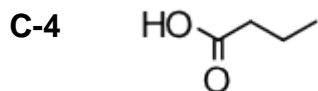
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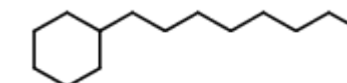
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C-13

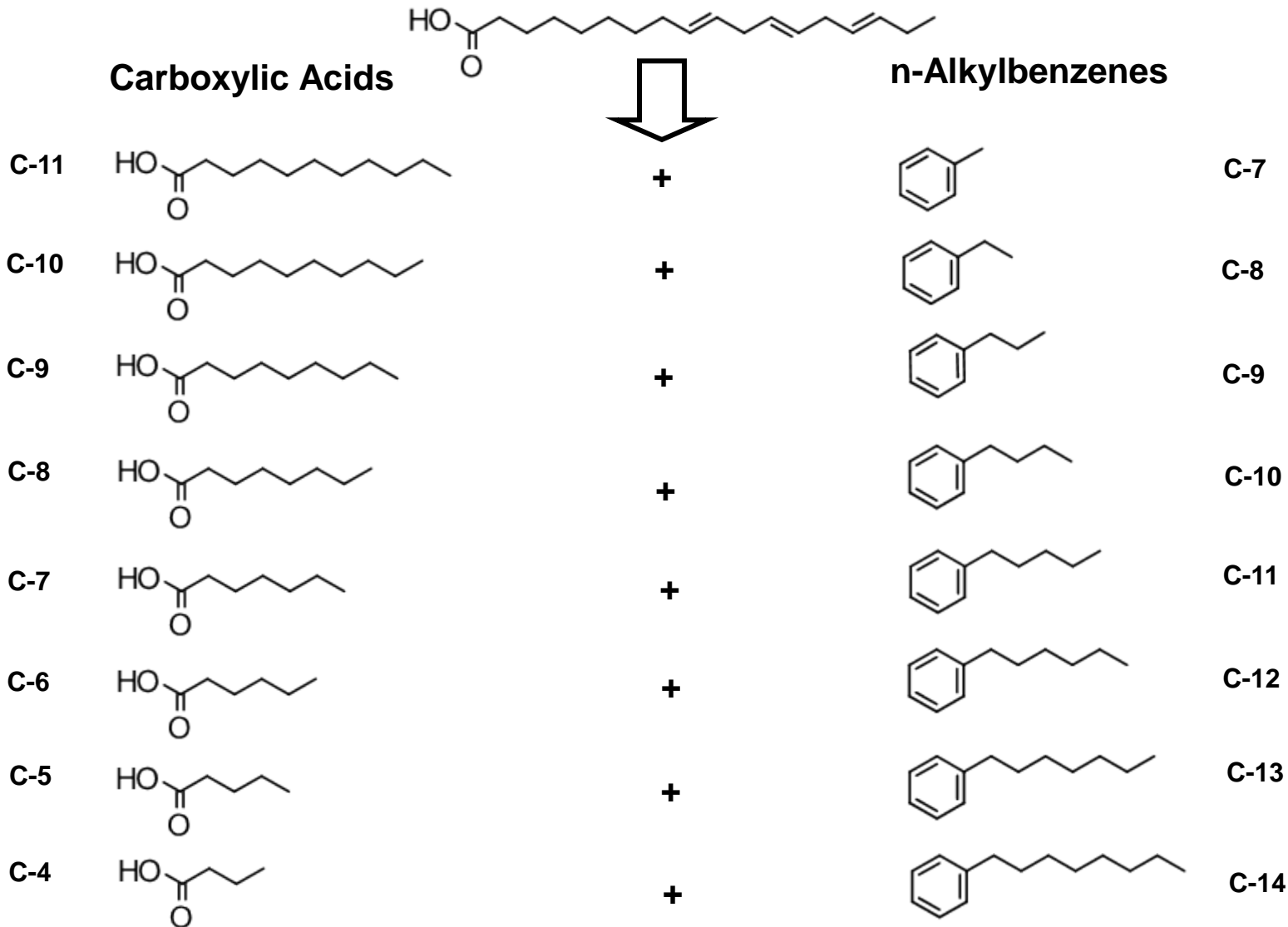


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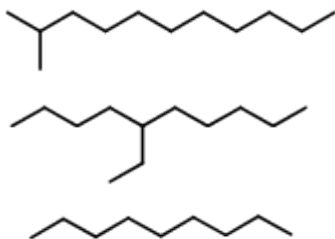
C-14

Linolenic Acid – Hydrothermolysis Products

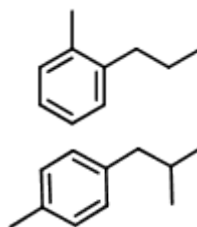


Other Products of Hydrothermolysis

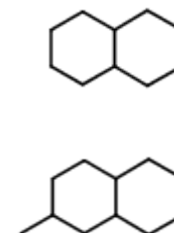
Isoparaffins



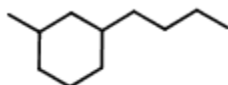
Alkylbenzenes



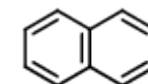
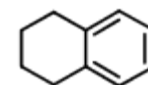
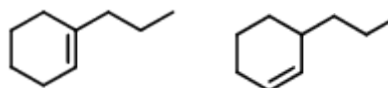
Polycyclics



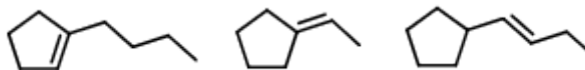
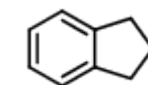
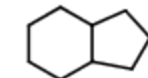
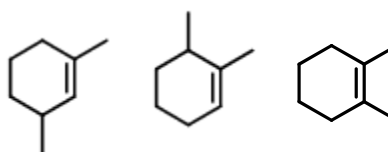
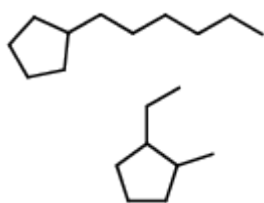
Cyclohexanes



Olefins



Cyclopentanes

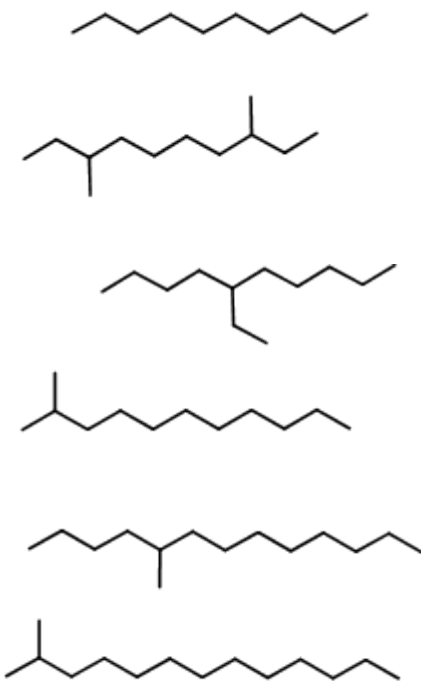


Typical Alternate Fuel Hydrocarbons

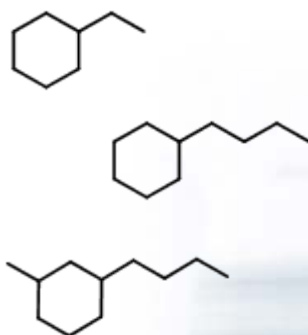
FT & HRJ

Catalytic Hydrothermolysis (CH)

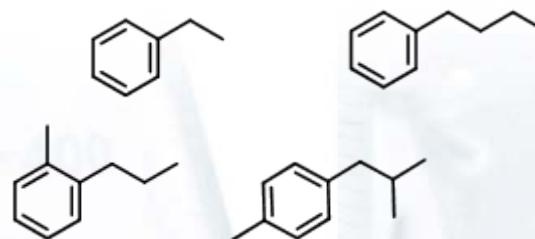
Paraffins



+ Cyclohexanes

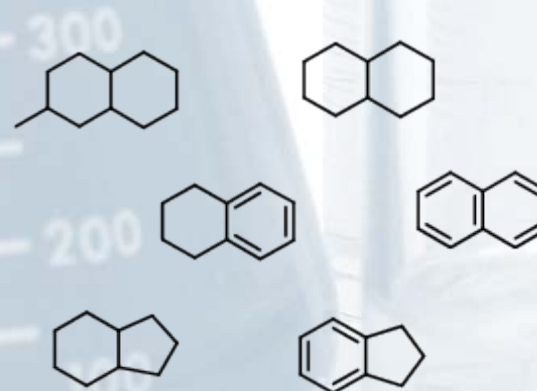
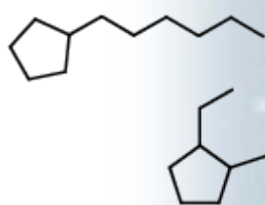


+ Alkylbenzenes

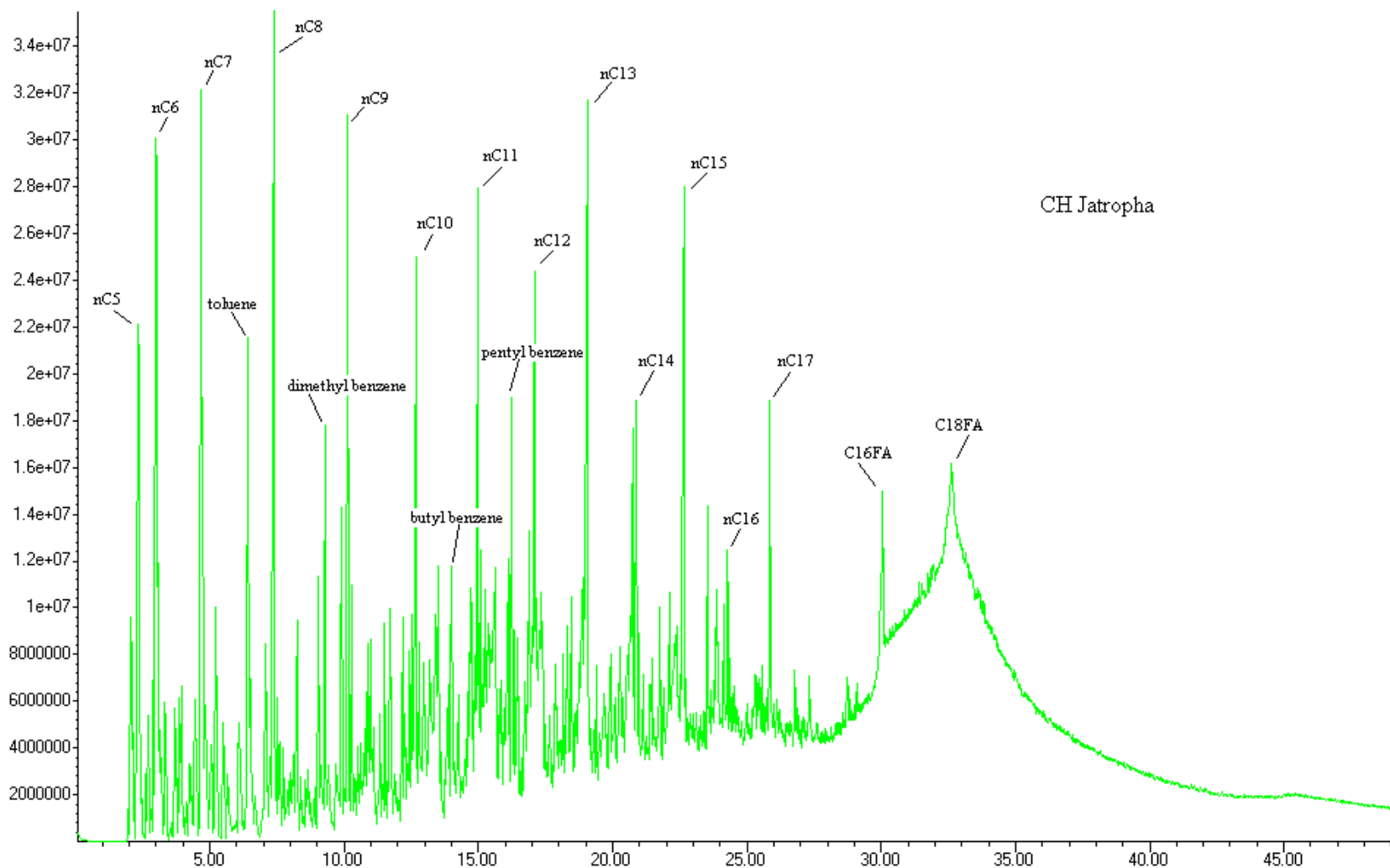


+ Polycyclics

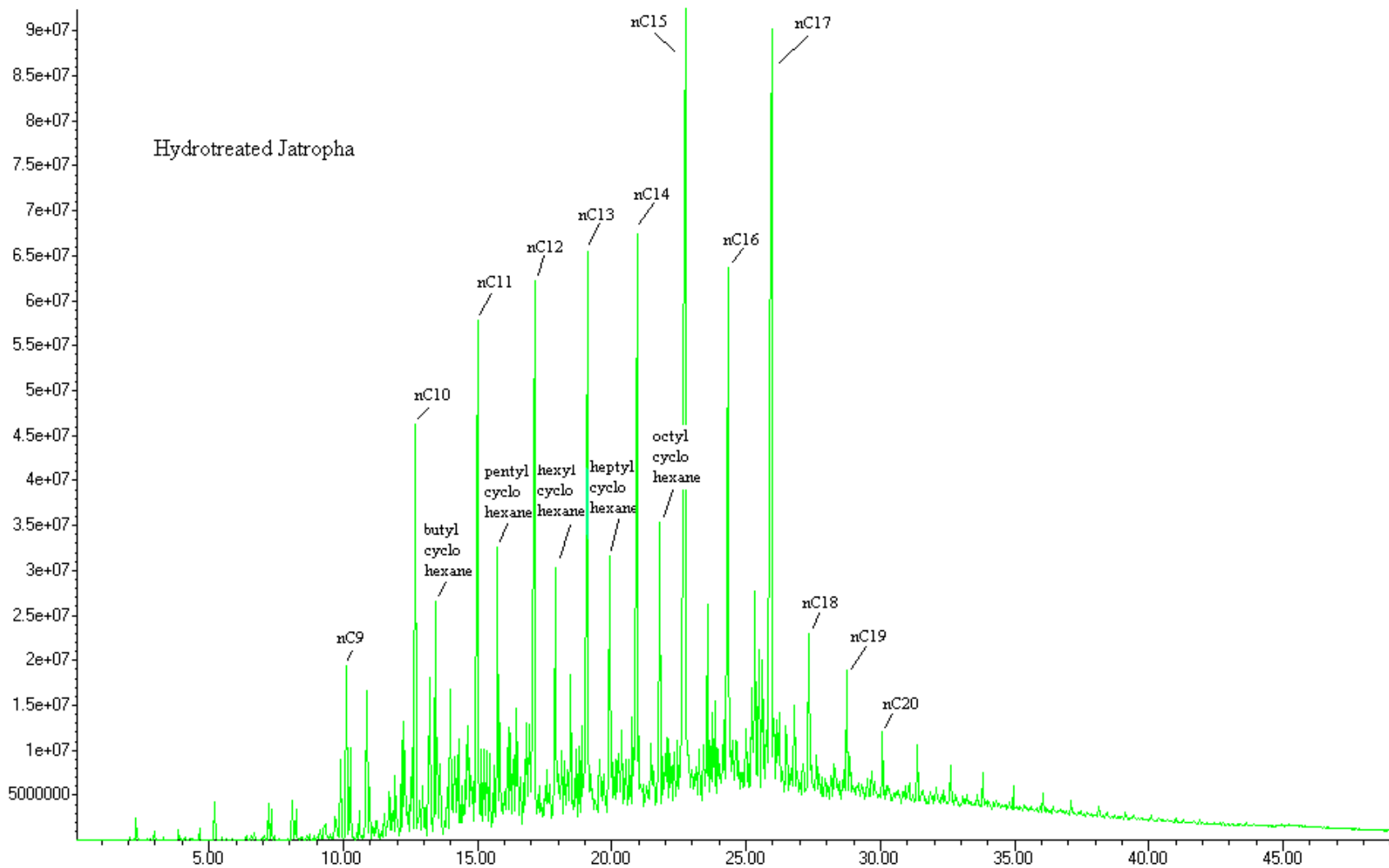
+ Cyclopentanes



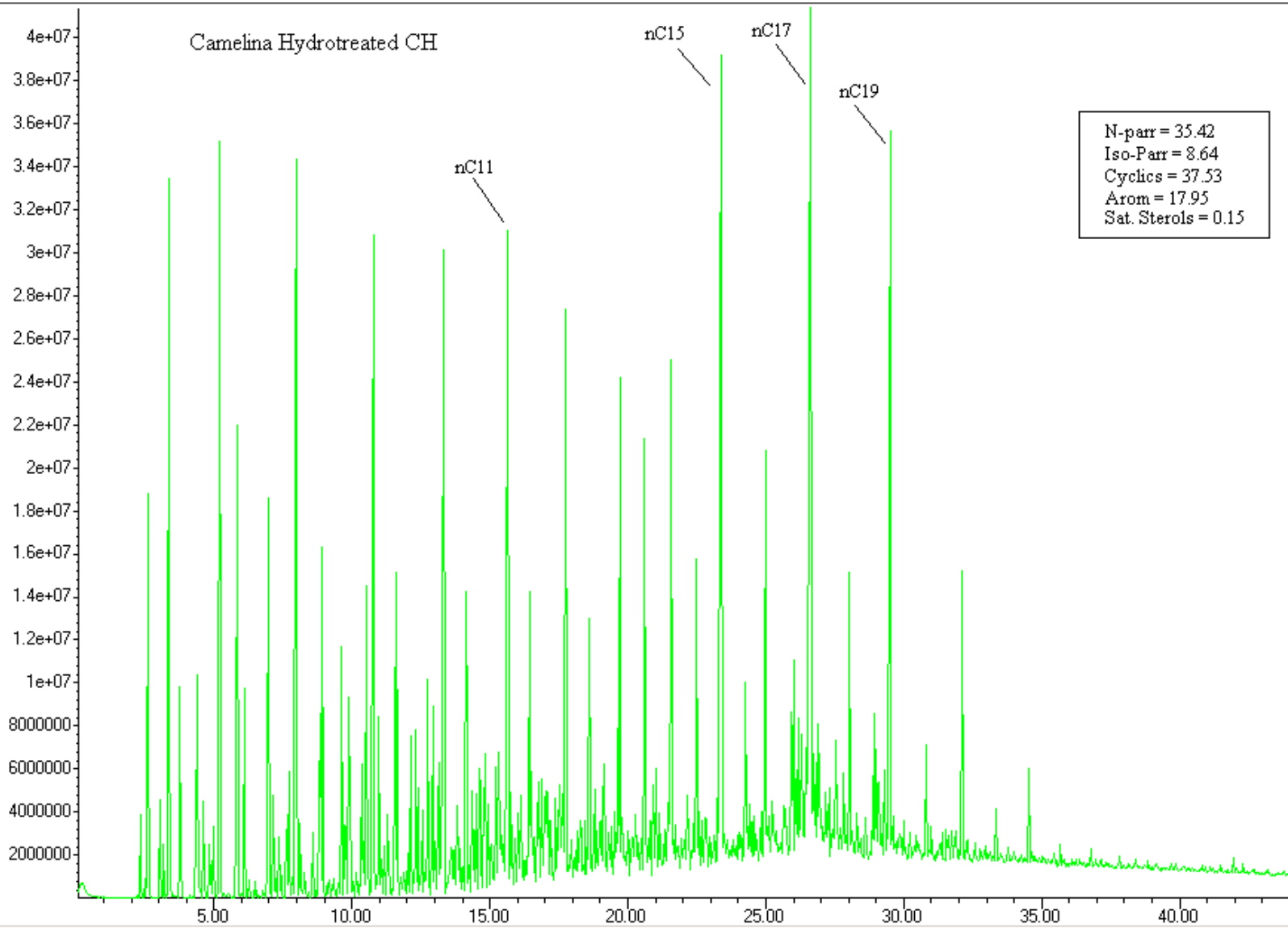
GC of CH Crude from Jatropha Oil



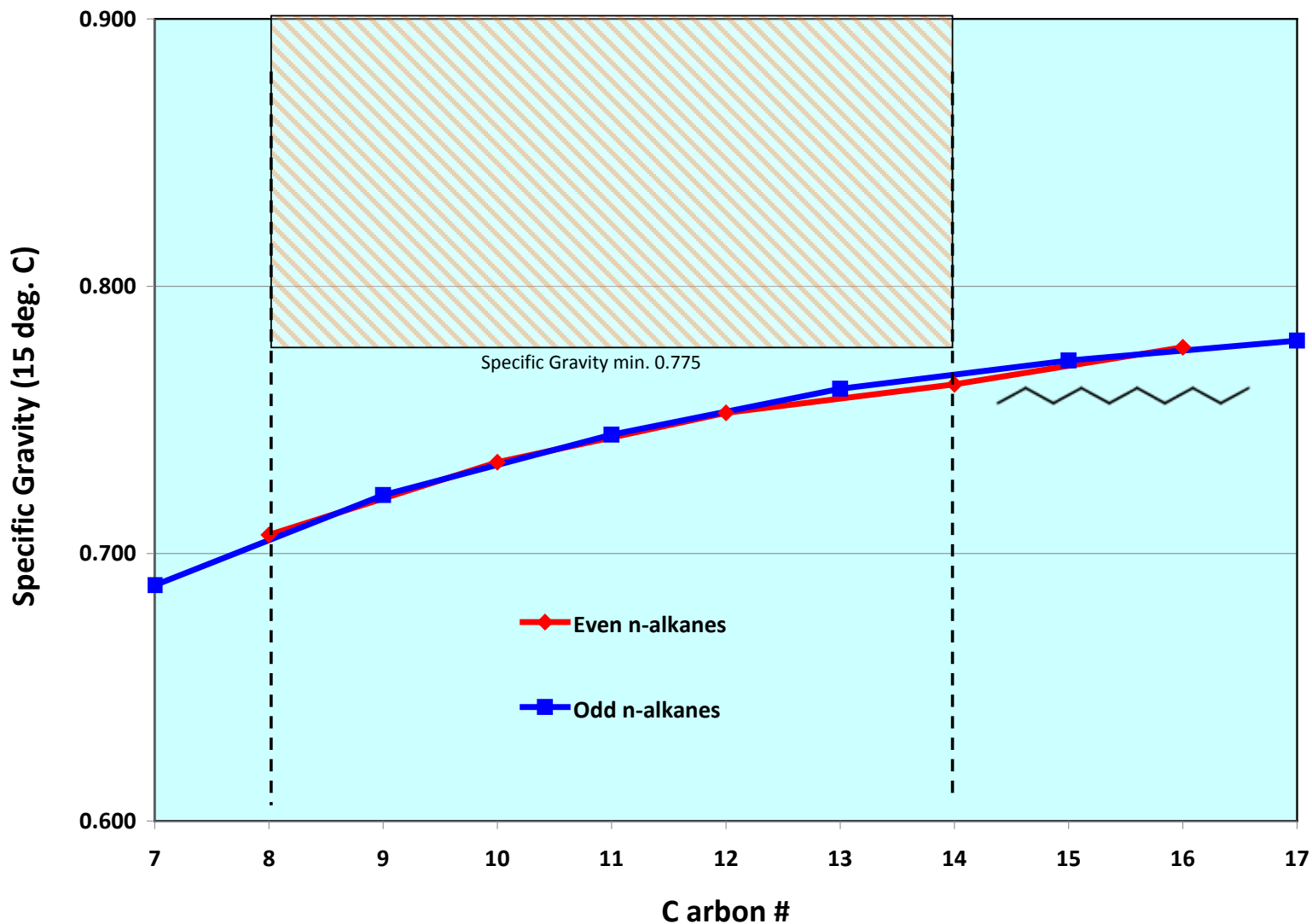
GC of Hydrotreated CH Crude Jatropa Oil



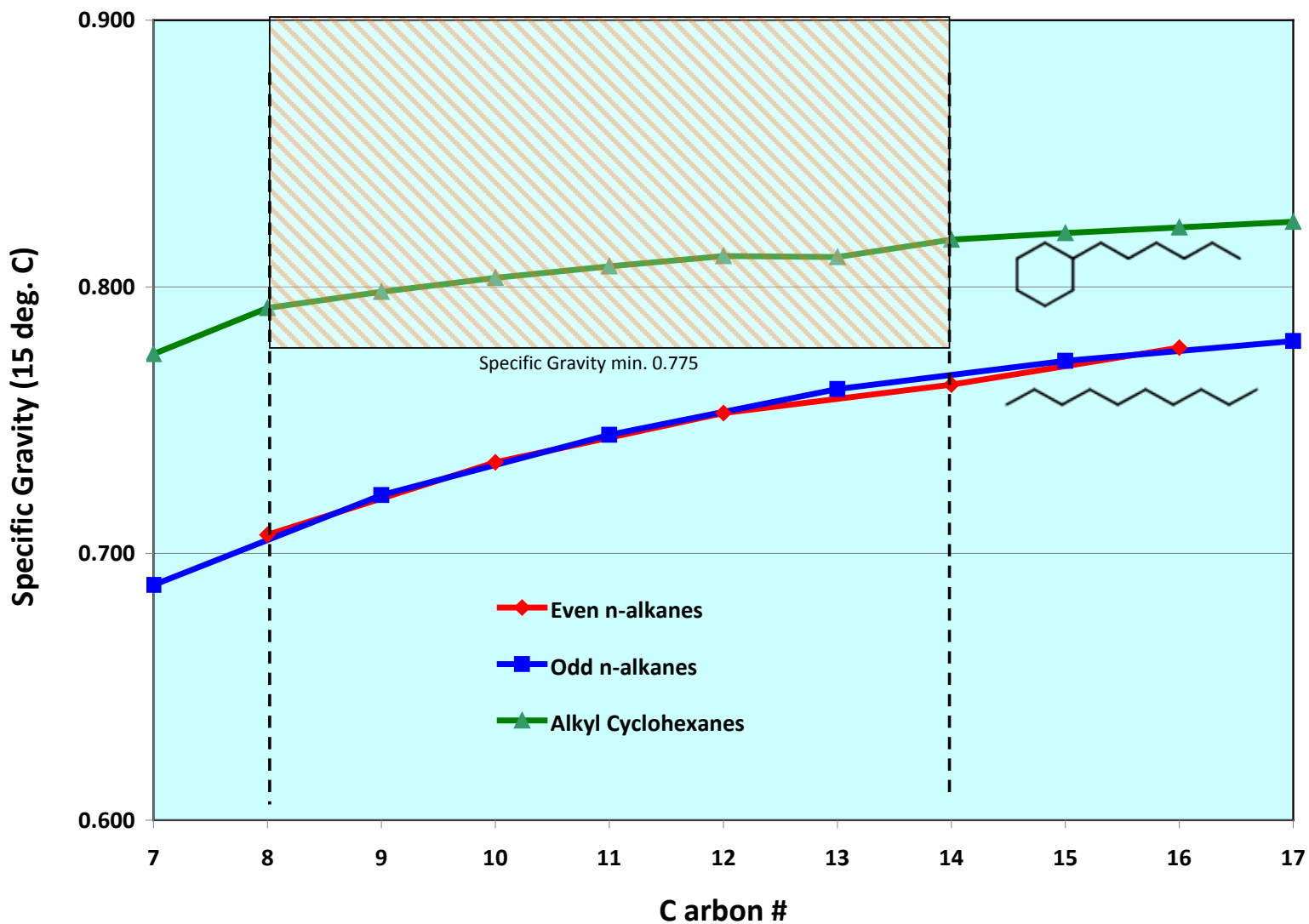
GC of Hydrotreated CH Crude Camelina Oil



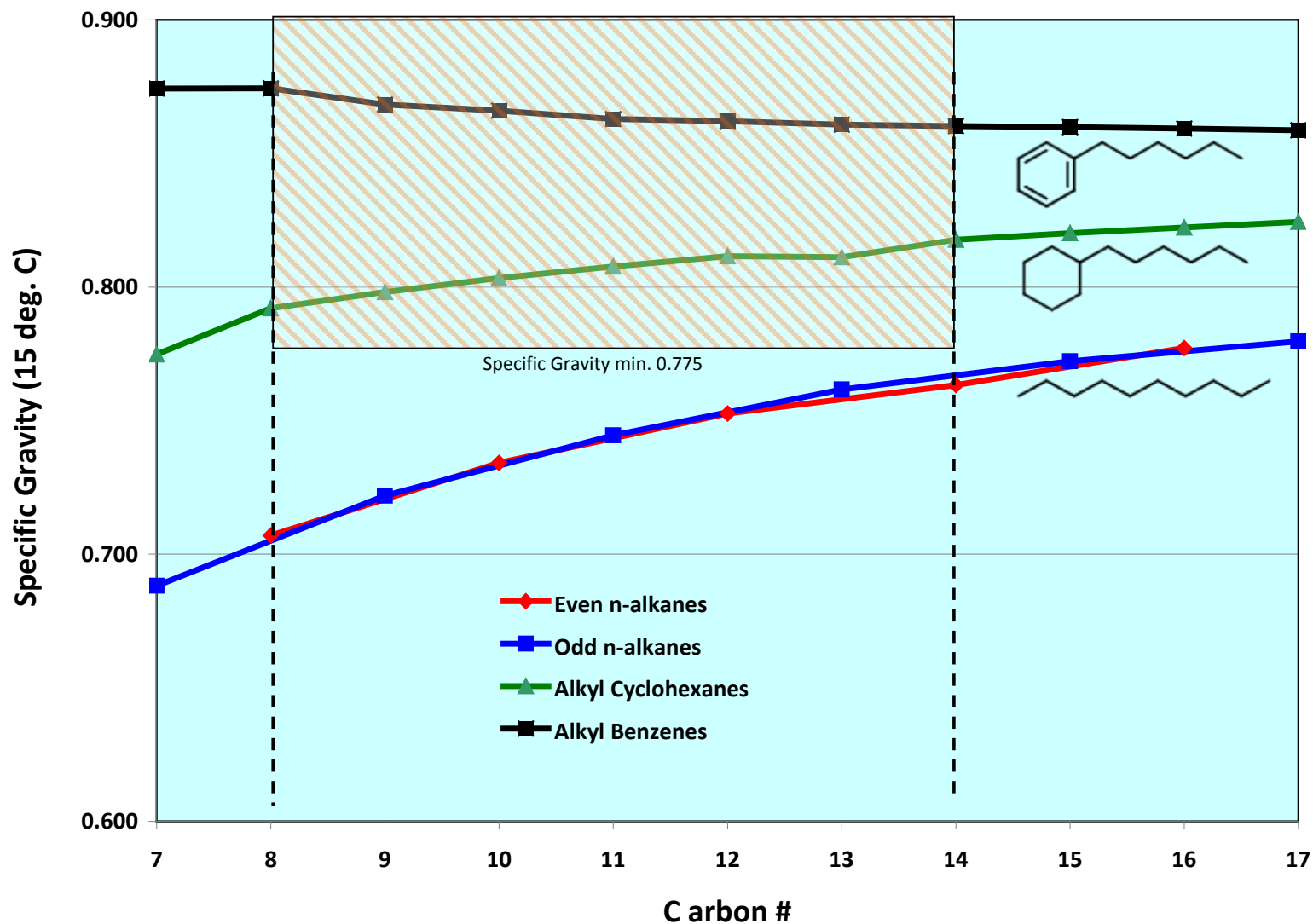
Hydrocarbon Type – Specific Gravity Effect



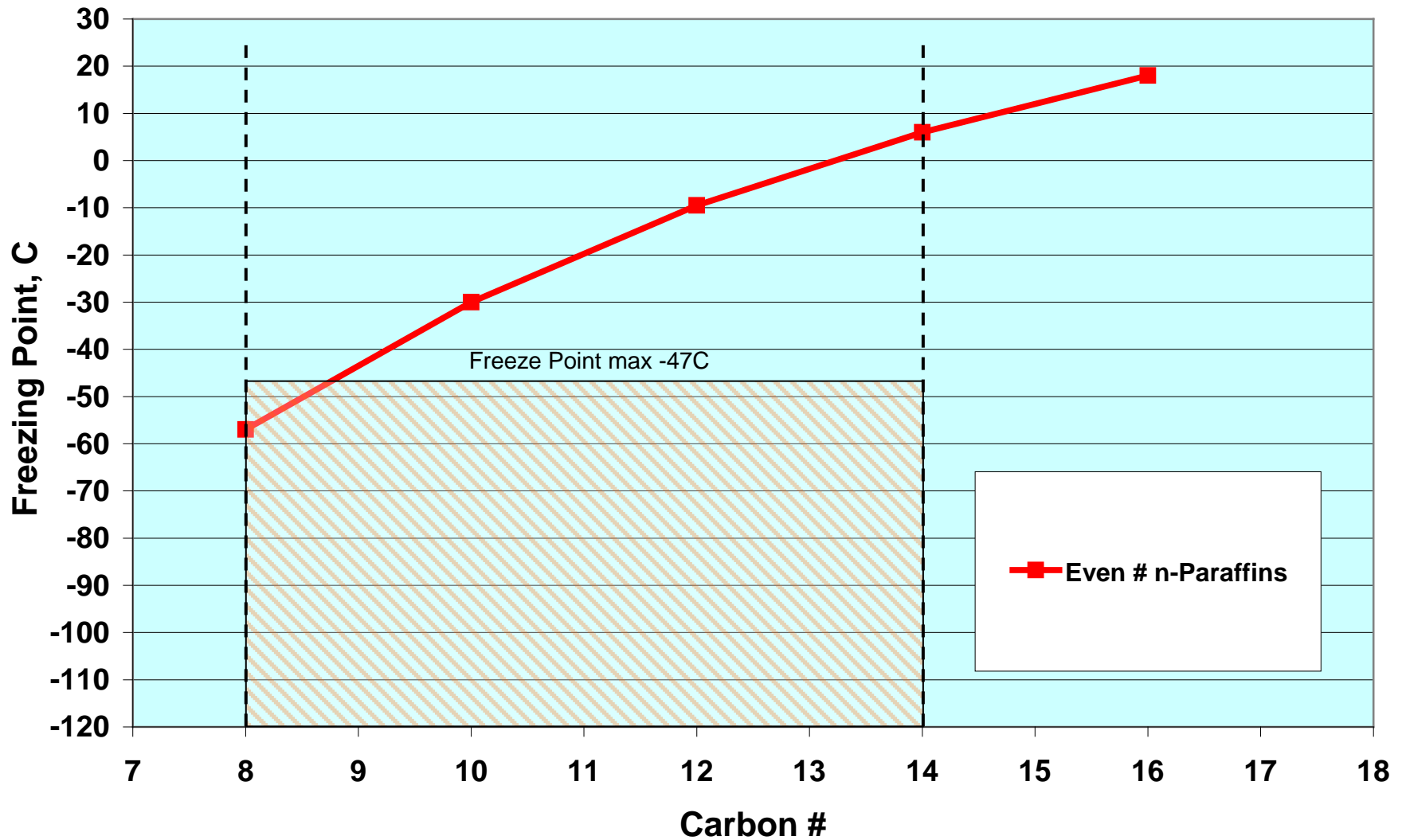
Hydrocarbon Type – Specific Gravity Effect



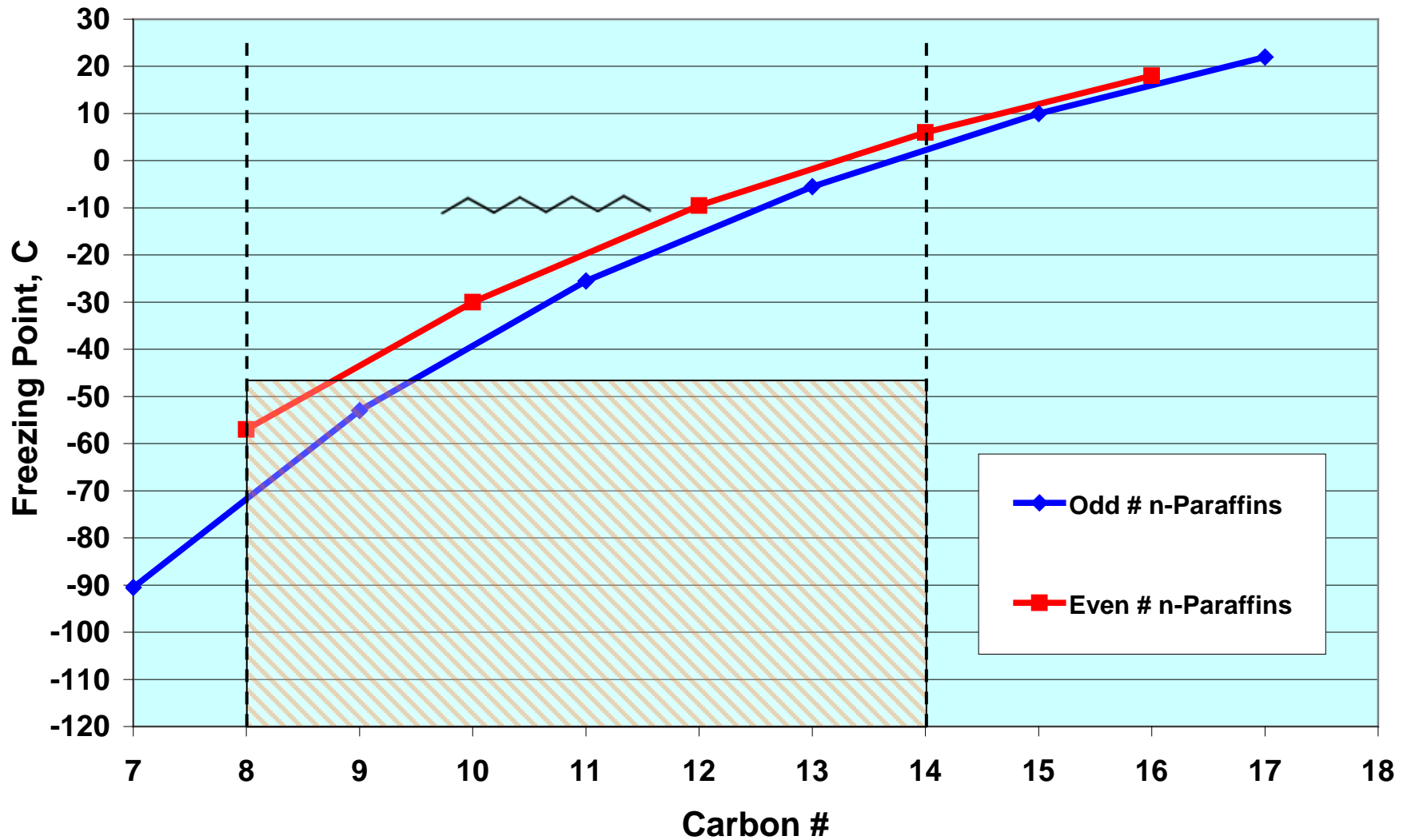
Hydrocarbon Type – Specific Gravity Effect



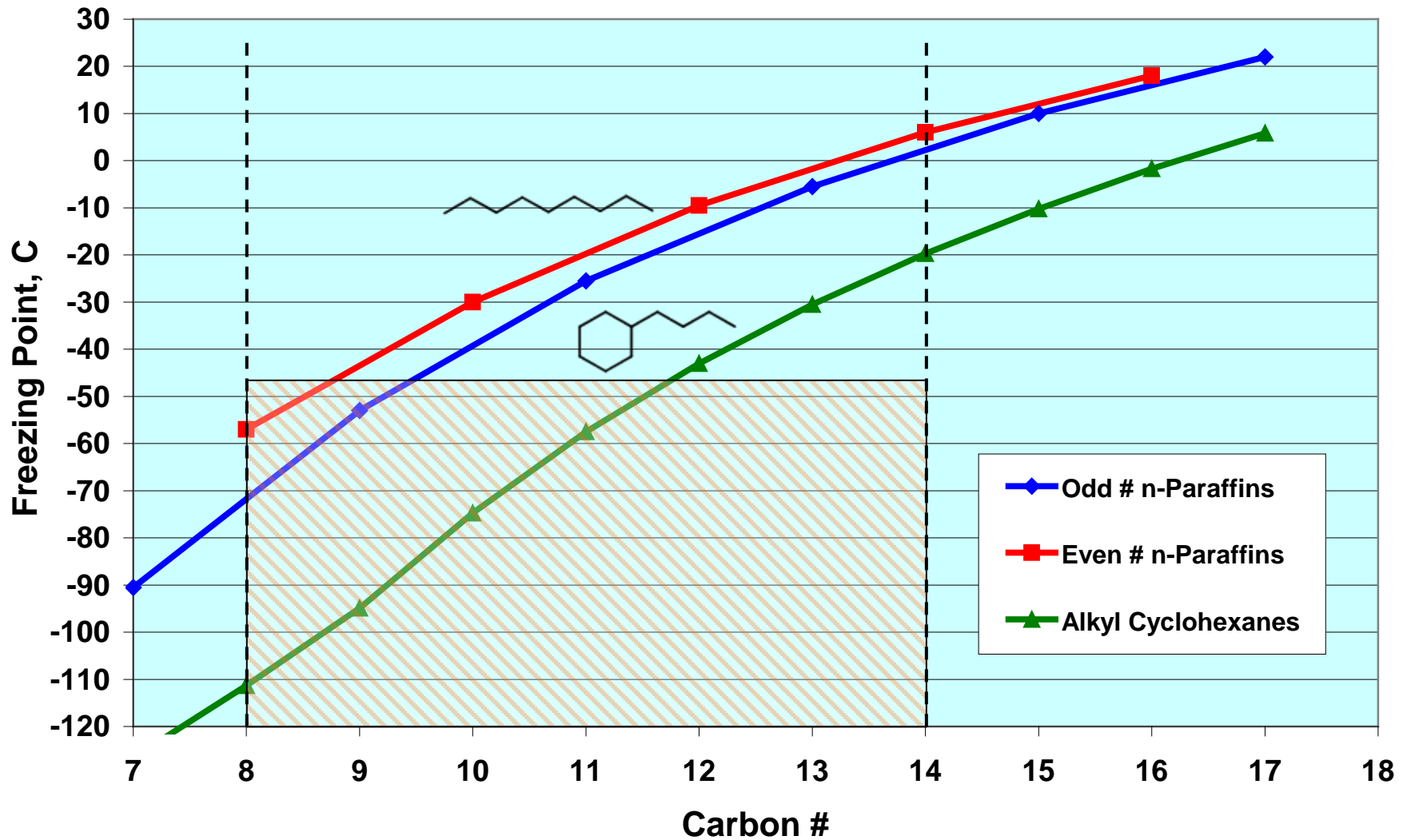
Hydrocarbon Type – Freezing Point Effect



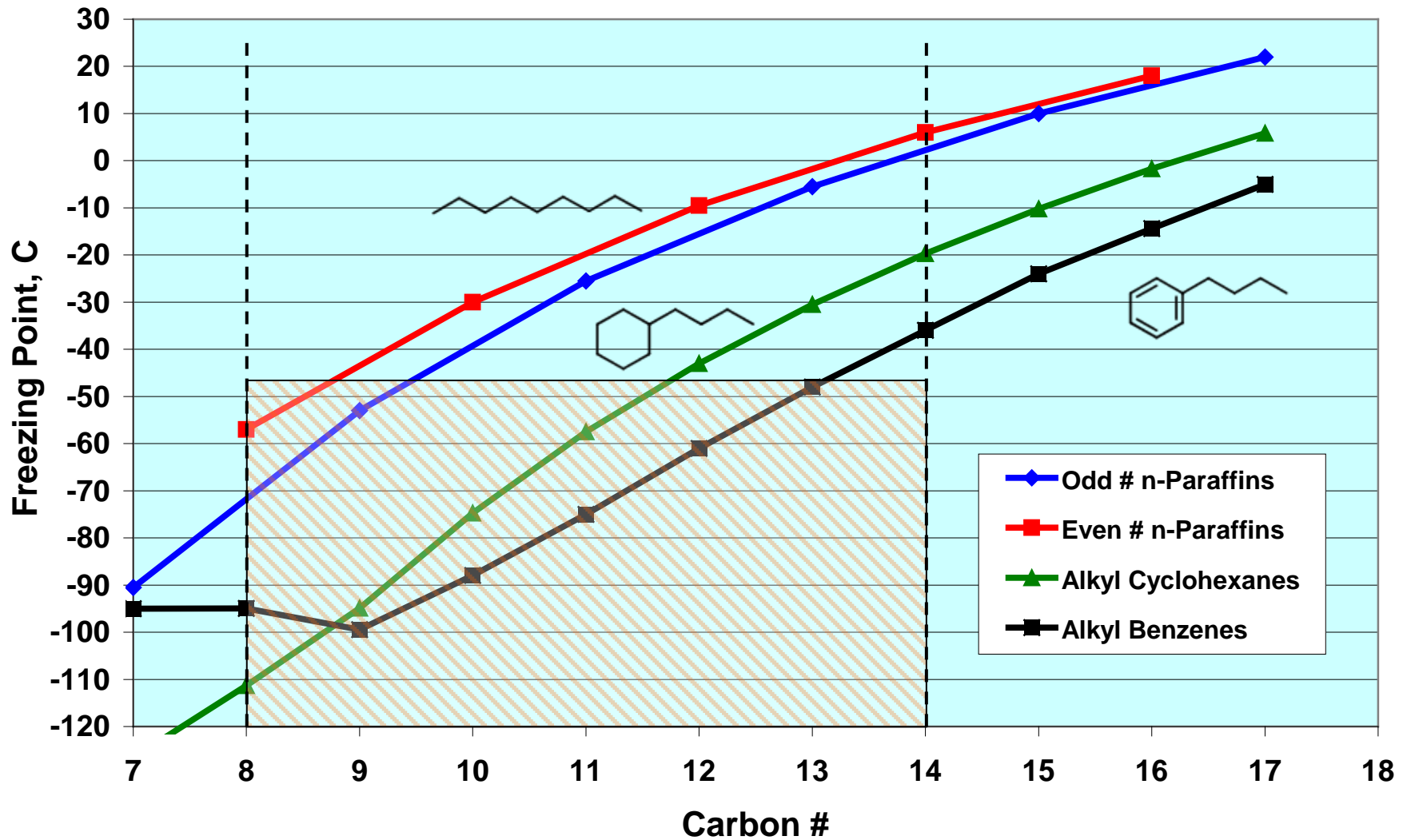
Hydrocarbon Type – Freezing Point Effect





Hydrocarbon Type – Freezing Point Effect



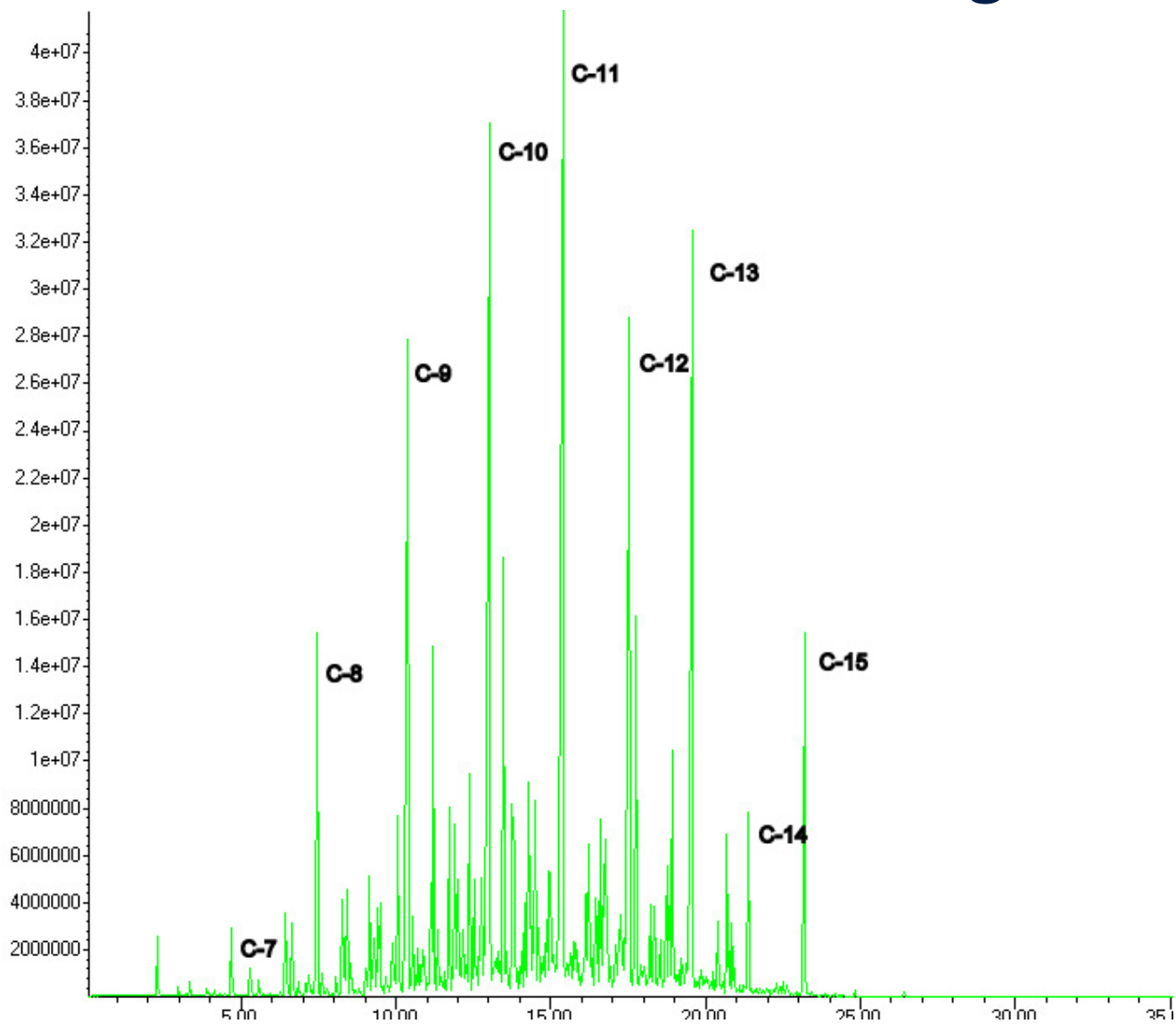
Hydrocarbon Type – Freezing Point Effect



Properties of ReDi Jet™ and ReDi Diesel™ Fuel Produced by CH

	 ReDiJet™	JP - 8 Spec	 ReDiDiesel™	F -76** Spec
Aromatics, wt%	11	25 max	14.5	-
Cycloparaffins, vol%	39	-	-	-
Heat of combustion, MJ/kg	43.4	42.8 min	43.6	-
Smoke point, mm	28	25 min	-	-
Freeze point, °C	<-47	-47 max	-	-
Flash point, °C	45	38 min	78	60 min
Density, kg/L	0.804	0.775 min	0.826	-
Acid #, mg KOH/g	<0.01	0.015 max	0.004	0.30 max
Hydrogen, wt%	14.0	13.4 min	14.1	12.5 min
Cloud point, °C	-	-	-8	-1 max
Pour point, °C	-	-	-9	-6 max
Viscosity @40 °C, cSt	-	-	3.45	1.7-4.3
Demulsification, min	-	-	1	<10
Cetane Index	44	Report	62	>43

GC of Jet Fuel Fraction from Algal Oil

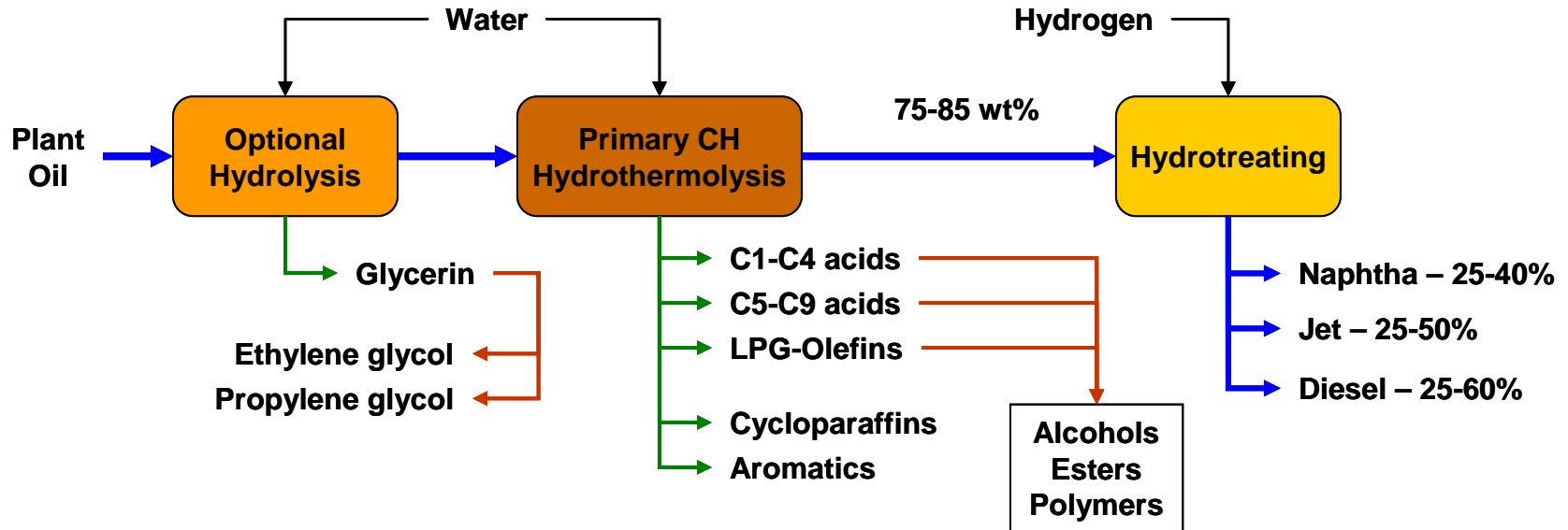


JP-8 from Algal Oil

- Refined algal oil from an AFRL contractor
- Processed in bench-scale CH unit
- Properties are very similar to petroleum reference fuel
- Results indicate insufficient hydrotreating for this sample

Specification Test	MIL-DTL-83133G	Algal Jet 7451	Petroleum JP-8 4751
Aromatics, vol%	< 25	18.8	18.8
Olefins, vol%		1.8	0.8
Heat of Combustion, MJ/Kg	>42.8	42.7	43.3
Flash Point, °C	>38	40	51
Freeze Point, °C	<-47	-49	-50
Density @15°C, Kg/L	0.775-0.840	0.792	0.804
Other Tests			
Paraffins (normal + iso), wt%		55	49
Cycloparaffins, wt%		27	30
Alkylbenzenes, wt%		13	13
Indans and Tetralins, wt%		4.9	5.8
Phenolic Polars by HPLC, mg/L		5000	160

Product and Byproduct Potential



- **Optional two-step CH process for clean glycerin recovery**
- **Primary and secondary byproducts of higher value**
- **Less than 5% water consumption**
- **Up to 100% process water recycle**

Pilot Testing – Panama City, FL

- **CH Crude oil production**
 - > 24-hour continuous operation
 - Steady-state performance
 - 90-93% FA conversion
 - 5+ gal/hr
- **Camelina oil feed**
 - Crude and degummed
- **CH crude product**
 - Water wash
 - Acid no. ~150



Air Force Research Lab (AFRL)

- **Awarded 2nd contract effective 1 Dec 2010**
- **Primary tasks**
 - **Optimize 100 gpd pilot system**
 - Increase capacity – decrease residence time
 - Conceptual engineering for commercial module
 - **Optimize byproduct recovery/value**
 - **Demonstrate water management**
 - **Optimization hydrotreating**
 - **Evaluate additional feed stocks**
 - Algal oil, Camelina oil, other plant oils
 - **Deliver 150 gallons of CH crude**
 - **Deliver 100-gal samples of JP-8**
 - Different aromatic concentrations
 - Different cycloparaffin concentrations



Engineering Challenges for Scale up

- **CH process**
 - Heat transfer - heat recovery
 - Reactor design
 - 3000 psig operating pressure
 - Up to 500°C operating temp
 - Materials of construction
 - Exothermic reaction
 - Turbulent flow
 - Short residence time < 1 min
 - Byproduct optimization
 - Water management
- **Hydrotreating**
 - Optimize decarboxylation
 - Acid tolerant catalysts
 - Address deactivation
 - Preserve aromatics and cycloparaffins



Benefits of Catalytic Hydrothermolysis

- Produces high yields of pure hydrocarbon fuels
- Produces cycloparaffin and aromatic compounds
 - Ideal composition for *ReDi* Jet and *ReDi* Diesel fuels
- Produces valuable bio-based chemicals
- Effective for any renewable feed stock
- Reduces hydrogen consumption vs FT & HRJ
- Reduces CO₂ emissions vs FT & HRJ
- Minimizes water, chemical, catalyst and energy consumption



Acknowledgements

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- **Robert Allen, Air Force Research Laboratory**
- **Don Minus, Air Force Research Laboratory**
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- **Richard Kamin, NAVAIR**
- **Bill Varden, USCJO, FFGA**