

Biodiesel Processing

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Summary

- Description of a novel simple fractionation process for biodiesel fuels to address product quality issues
- Low energy, environmentally benign, low cost, robust/scalable, compatible with existing/new biodiesel synthesis plants
- Usable with variety of feedstocks (plant, animal, microbial lipids)
- Controllable cold temperature properties suitable for ground, aviation fuels; also potential chemical feedstocks

Overview

- Historical comparison between development of petroleum/biodiesel fuel processing
 - Technologies to create multiple fuel products
- Description of new biodiesel fractionation process
- Opportunities/Applications

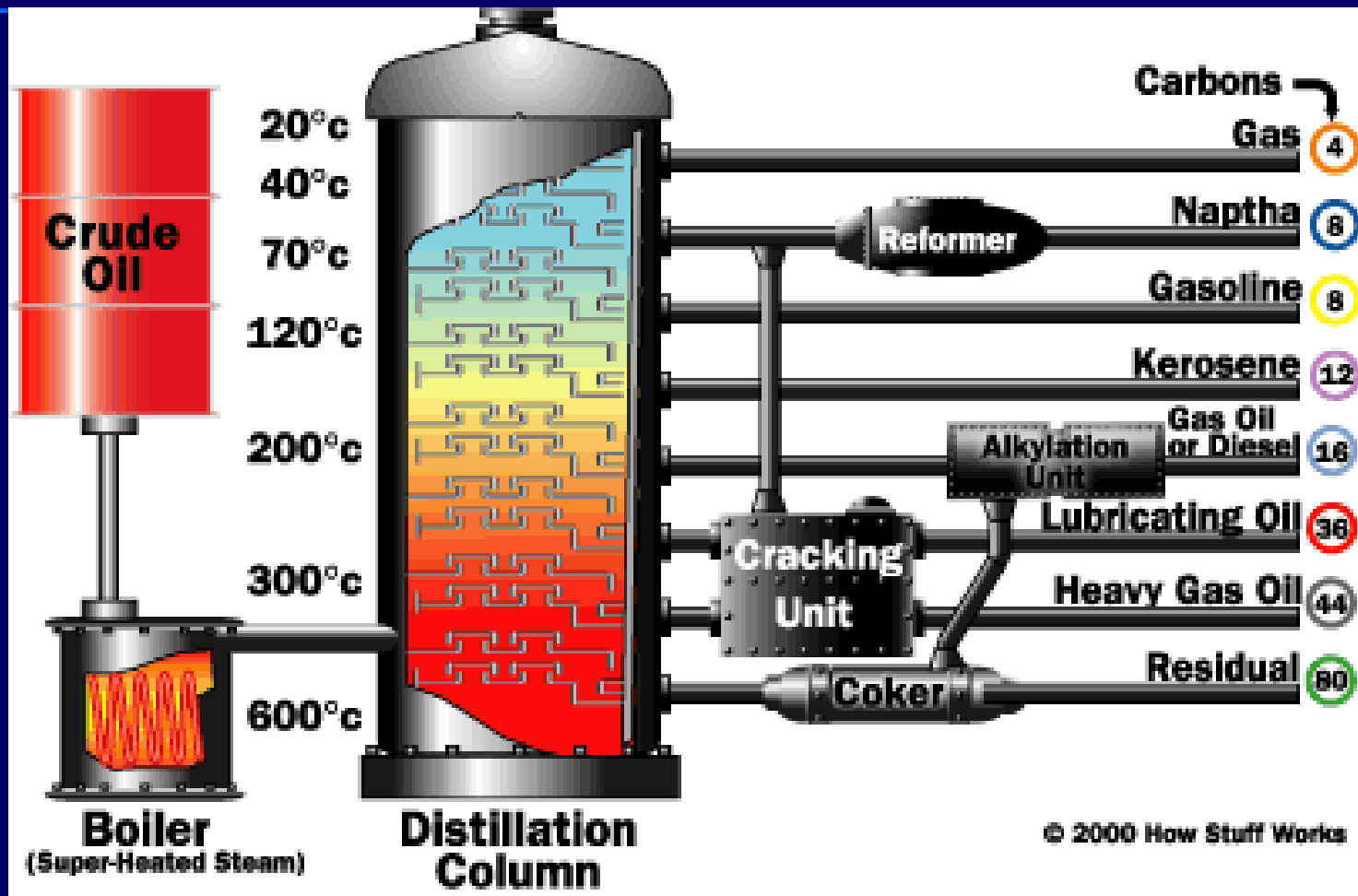
Petroleum Background

- Geologically mined non-renewable resource
- Complex mixture of mainly hydrocarbon structures (alkane/alkene, aromatics, wide range of molecular weights, C₄-C₁₀₀+))
- Multiple sources differing in composition (geographical, contaminants)

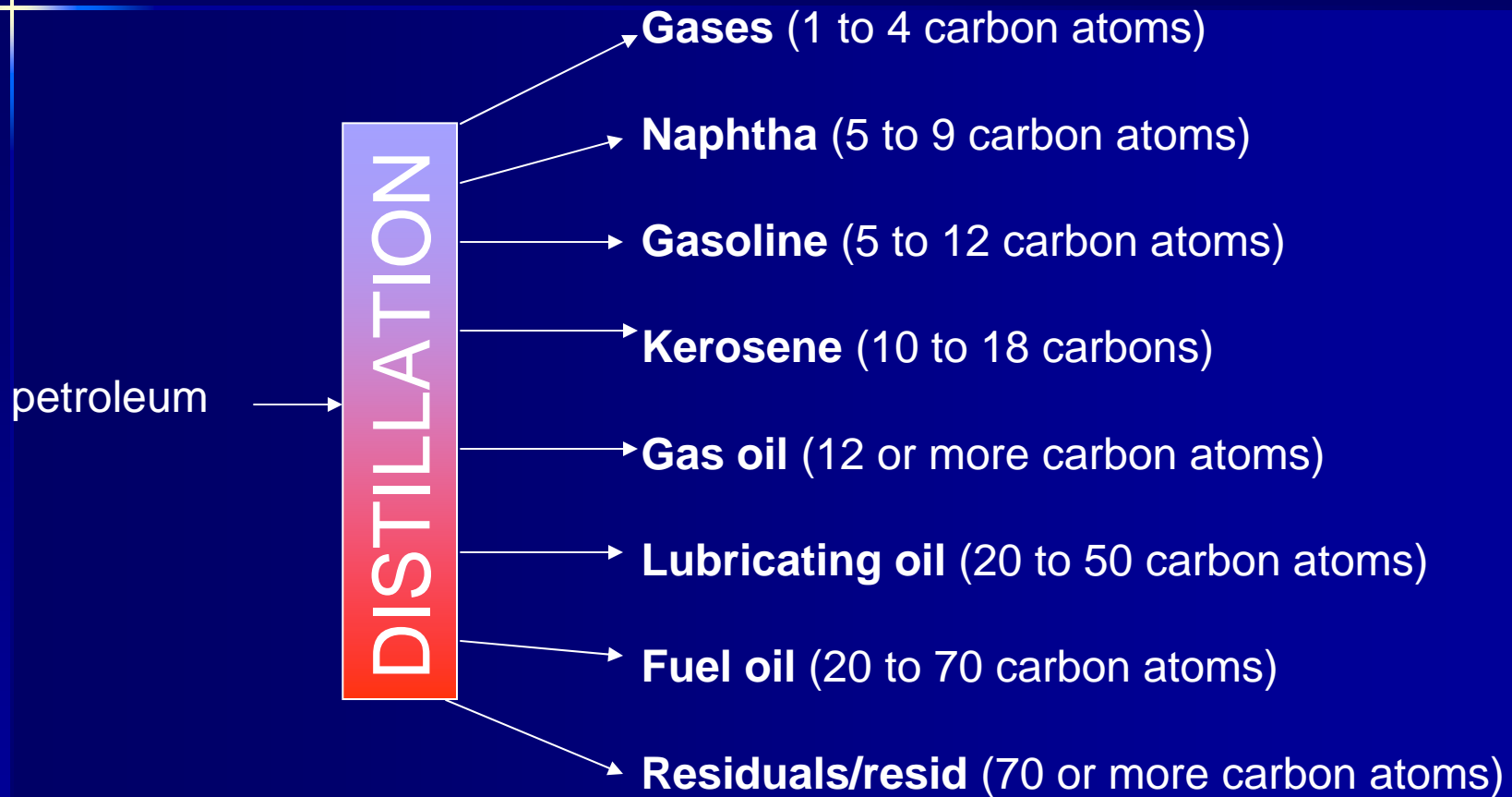
Needs of Petroleum Industry

- Unusable in original state (viscous, black gunk), low cost
- Must be able to handle differing feedstocks and produce consistent products
- Needed processing technology to make useful differentiated products, e.g. gasoline, diesel, kerosene, chemical feedstocks, etc.
- Current issues are economic and political

Schematic of Petroleum Refining



Foundational Technology: Distillation



Scalable/robust, based on volatility, energy intensive (evaporation/condensation)

Biodiesel Background

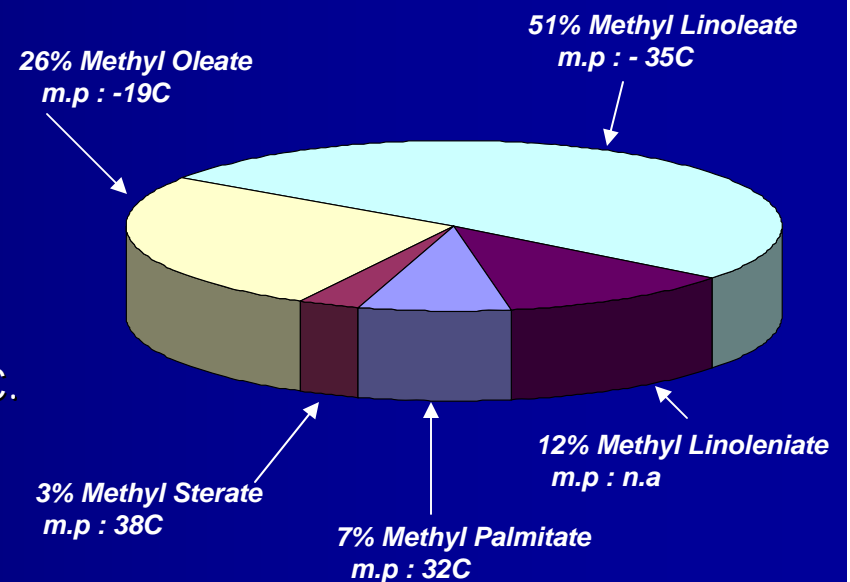
- Biologically produced renewable resource
- Hydrocarbon-like ester structures (mainly alkane/alkene structures, relatively narrow molecular weight distribution (C12-C20))
- Multiple sources differing in composition (plant/animal/microbial, few contaminants)

Needs of Biodiesel Industry

- Useful existing feedstock (oil), high cost
- Quality control; Must be able to handle differing feedstocks and produce consistent products
- Needed processing technology to make differentiated products, e.g. cold flow products
- Major current issue is product performance with respect to cold weather

Cold Flow Properties:

- The formation of crystalline solids in biodiesel fuel is a problem in cold weather situations
- Crystallization is due to alkane/saturate components, which crystallize at higher temperatures
- Soybean B100 crystallizes at approx. 0 C.
- Blending with petrodiesel lower crystallization temperatures slightly (approx. 5 C)
- Removal of the high melting components can result in considerable improvement in freezing behavior



Source: Hawley's 14th Edition.

Biodiesel quality depends on feedstock

source	10:0	12:0	14:0	16:0	18:0	18:1	18:2	18:3	20:n
Coconut	7	48	17	8	3	6	2		
Palm			1	46	5	39	9	1	
Soybean				11	4	22	54	8	
Olive			1	15	3	67	13	1	
Peanut				10	3	52	29		
Canola				3	1	25	17	9	
Beef			3	16	22	42	2	0.2	
Butter	6	6	11	26	10	28	2	1	
fish	6		16		3	15	2	1	14

Source: Bailey's Industrial Oil & Fat Products, 5th ed.

Conventional Biodiesel Fractionation Technologies

1. Thermal fractionation (with or without solvent):
 - Crystallization/filtration process, very low yields, long process time, high losses due to co-crystallization/inclusion
 - Solvent crystallization gives higher yields, but requires significant refrigeration/very low temperatures

2. Adsorption/Chromatographic, Liquid-Liquid extraction techniques
 - Require multiple solvents, expensive processing components, energy intensive
 - High cost, low selectivity, unsuitable for large scale processing

3. Lipase catalysis
 - Relies on the selectivity of certain lipases to hydrolyze only the unsaturates
 - High selectivity but very low yields, process time runs into days
 - Extremely expensive

Urea-biodiesel clathration

- Urea is known to form Channel Type Inclusion complexes with long chain organic compounds.
- Urea forms hexagonal channels into which the organic compounds get included.



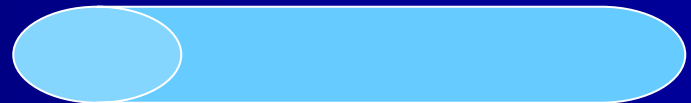
Saturated FAME



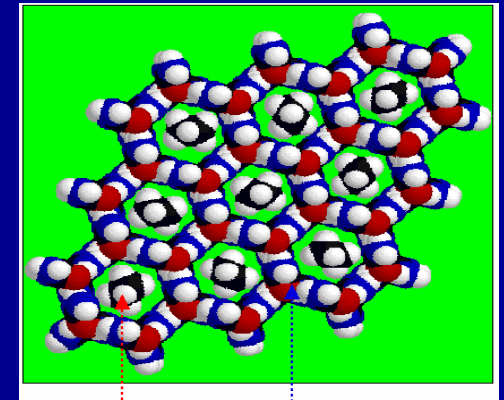
Hexagonal framework Urea Channel



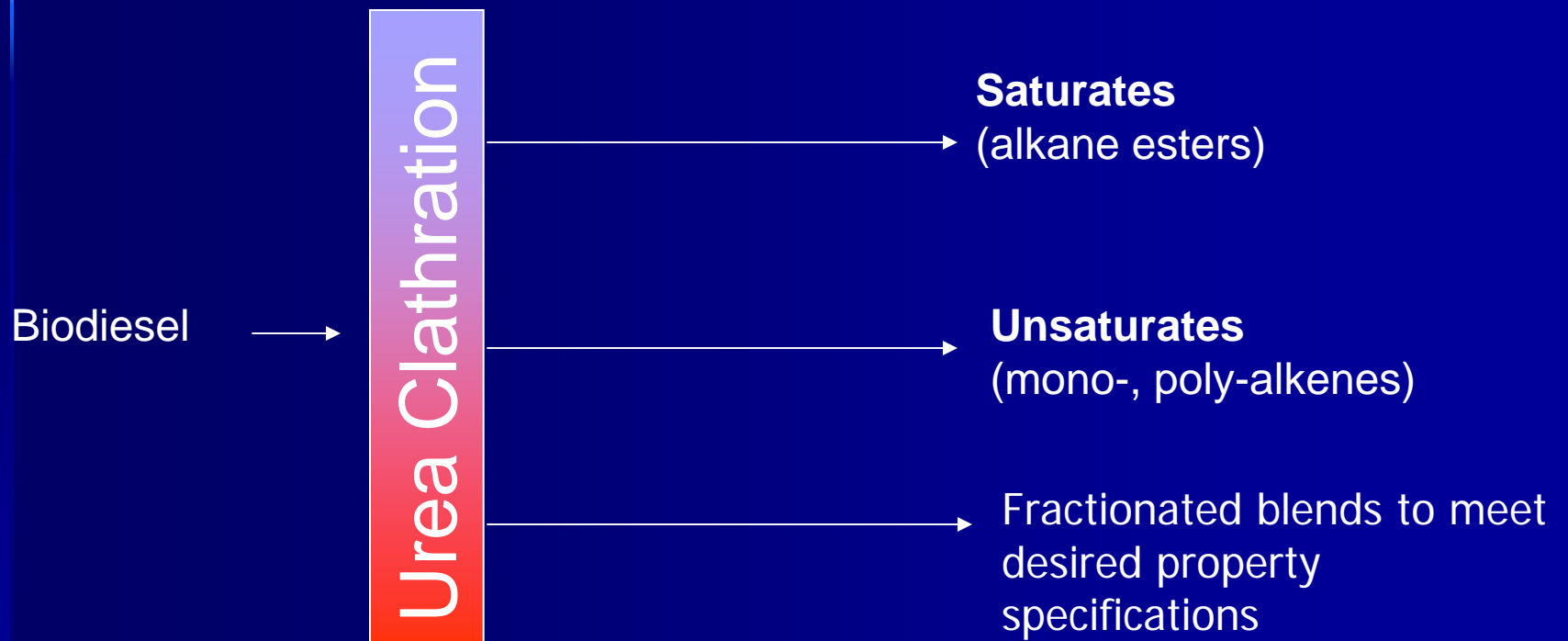
Unsaturated FAME (kink due to cis double bond)



- Separation of saturated and unsaturated methyl esters
- Low cost, very high yields, high selectivity, easily scalable
- All raw materials used are recoverable and reusable

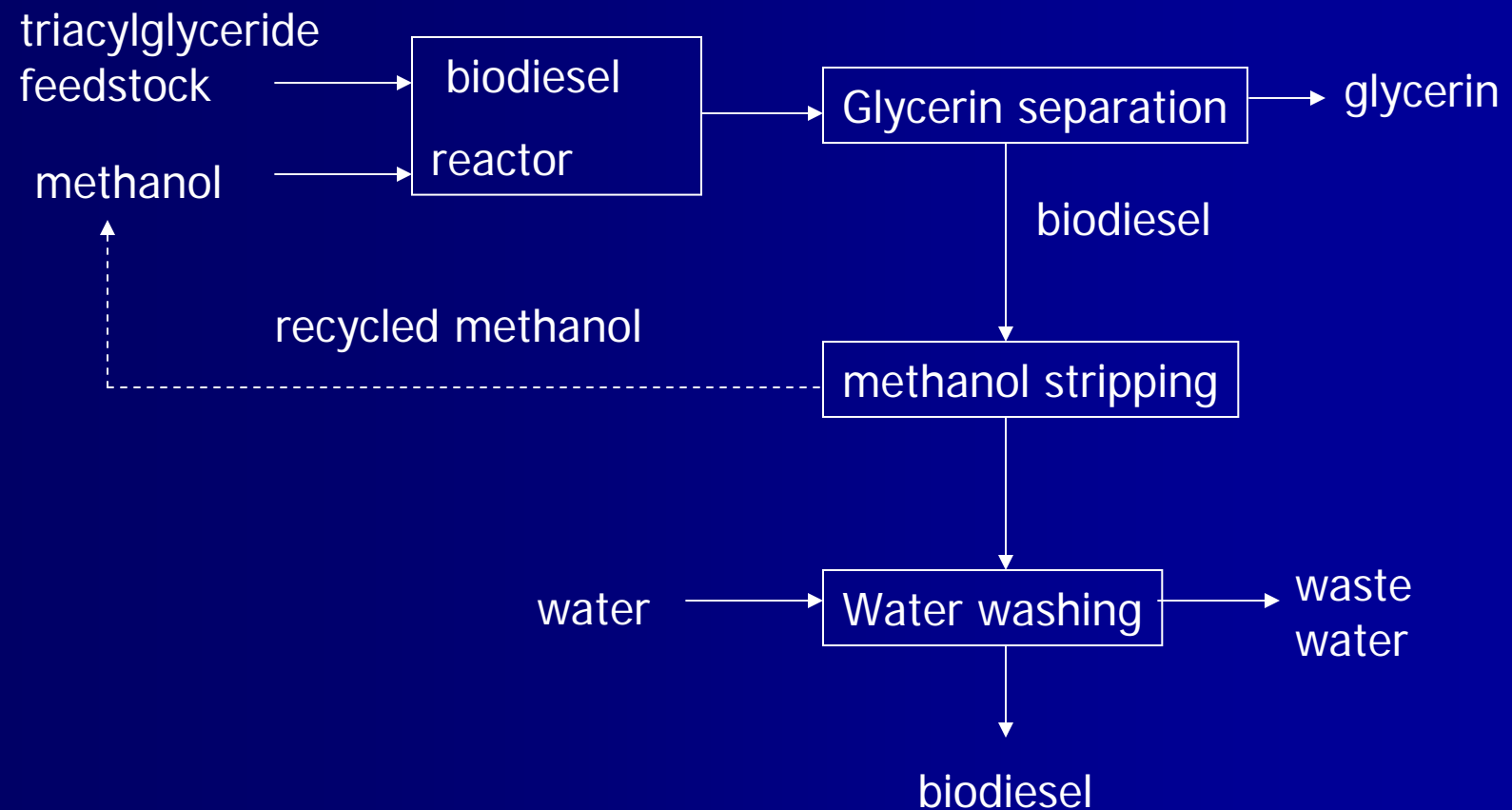


Foundational Technology: Urea Clathration

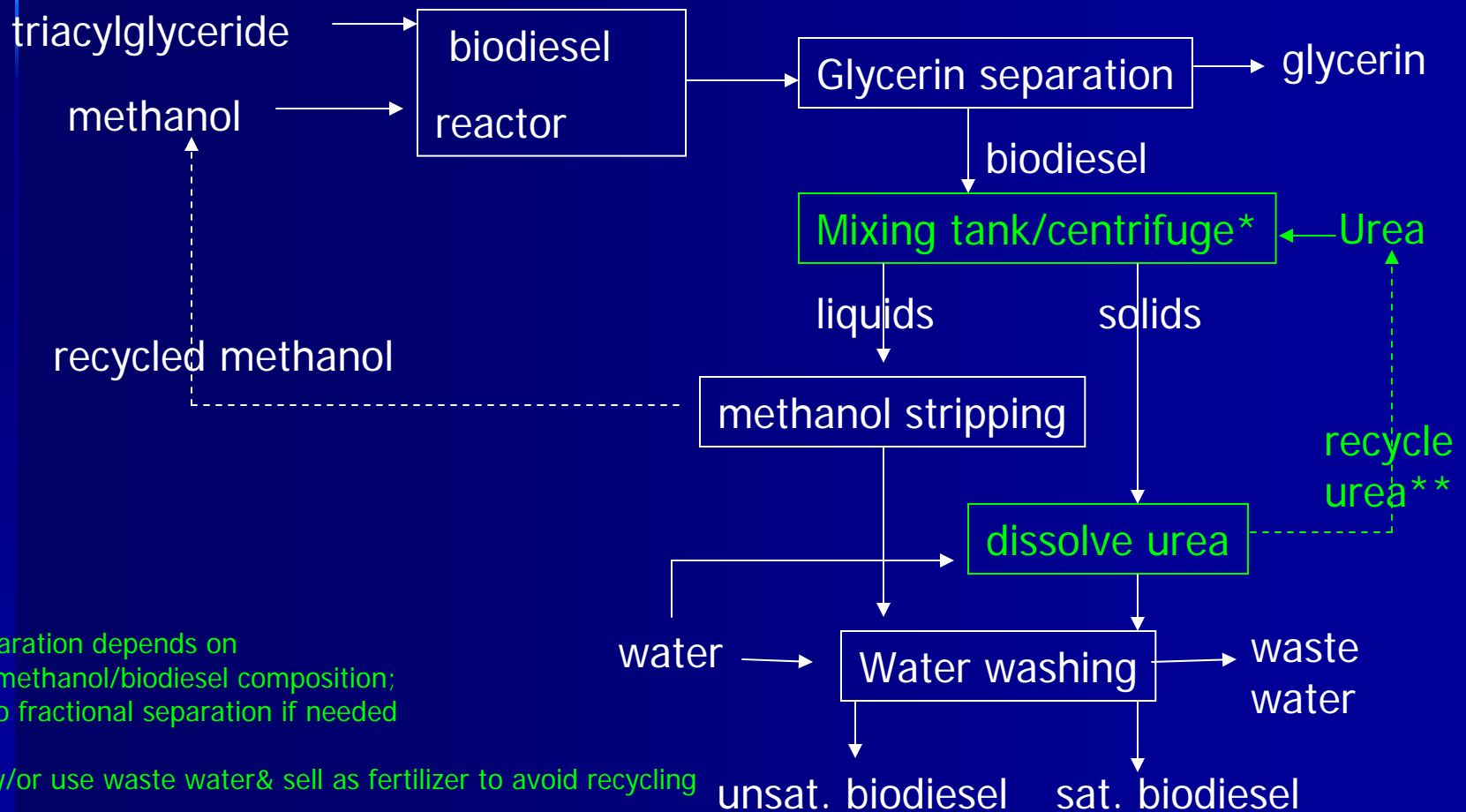


Scalable/robust, based on alkene structure, energy efficient

Biodiesel Standard Process



Biodiesel Fractionation Process



* Separation depends on urea/methanol/biodiesel composition; can do fractional separation if needed

** dry/or use waste water& sell as fertilizer to avoid recycling

Differential Processing

- Urea is only additional component, which is 100% recycled
- Only additional major equipment is mixing tank/centrifuge (some additional tankage)
- Only added energy input is for added methanol evaporation (if any)
- Can be integrated into existing/new biodiesel processing plants
- Scalable, robust, simple process
- Estimated differential costs 5-10 cents/gal

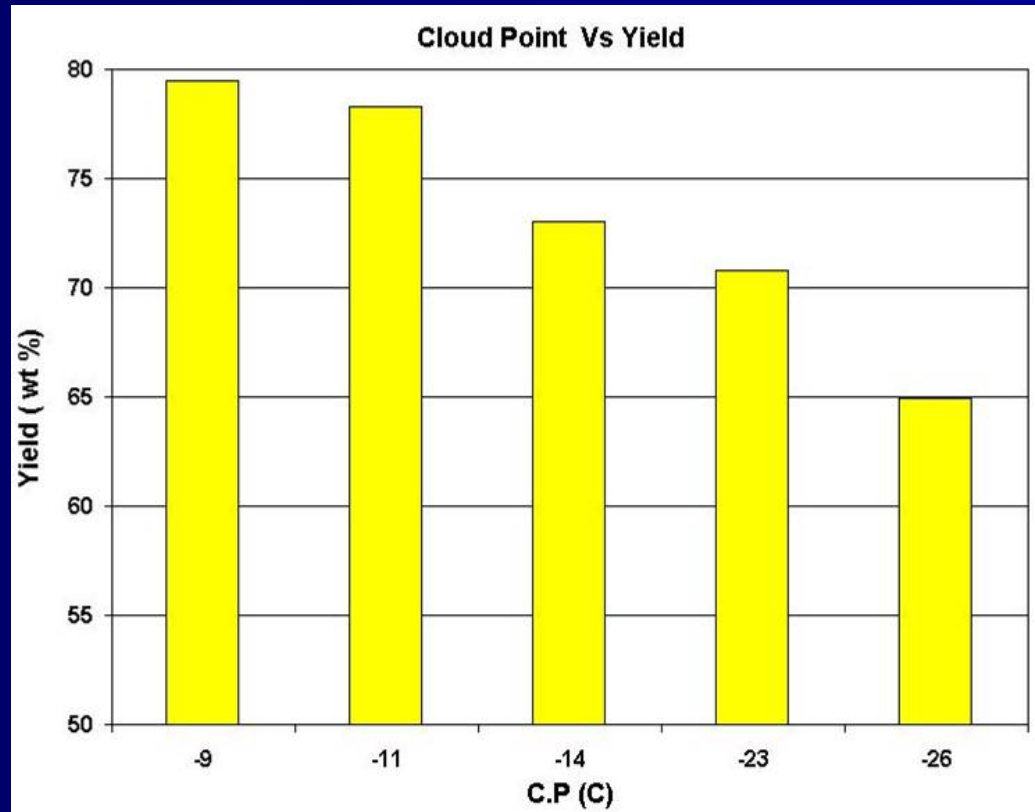
Usable with any biodiesel feedstock or blend, e.g. soybean oil, canola, palm oil, coconut oil, lard, waste restaurant fat, etc.

- Controllable product properties based on alkane/alkene composition, carbon chain length
- Yields will depend on feedstock composition

Serial/staged fractionation is possible to obtain multiple products

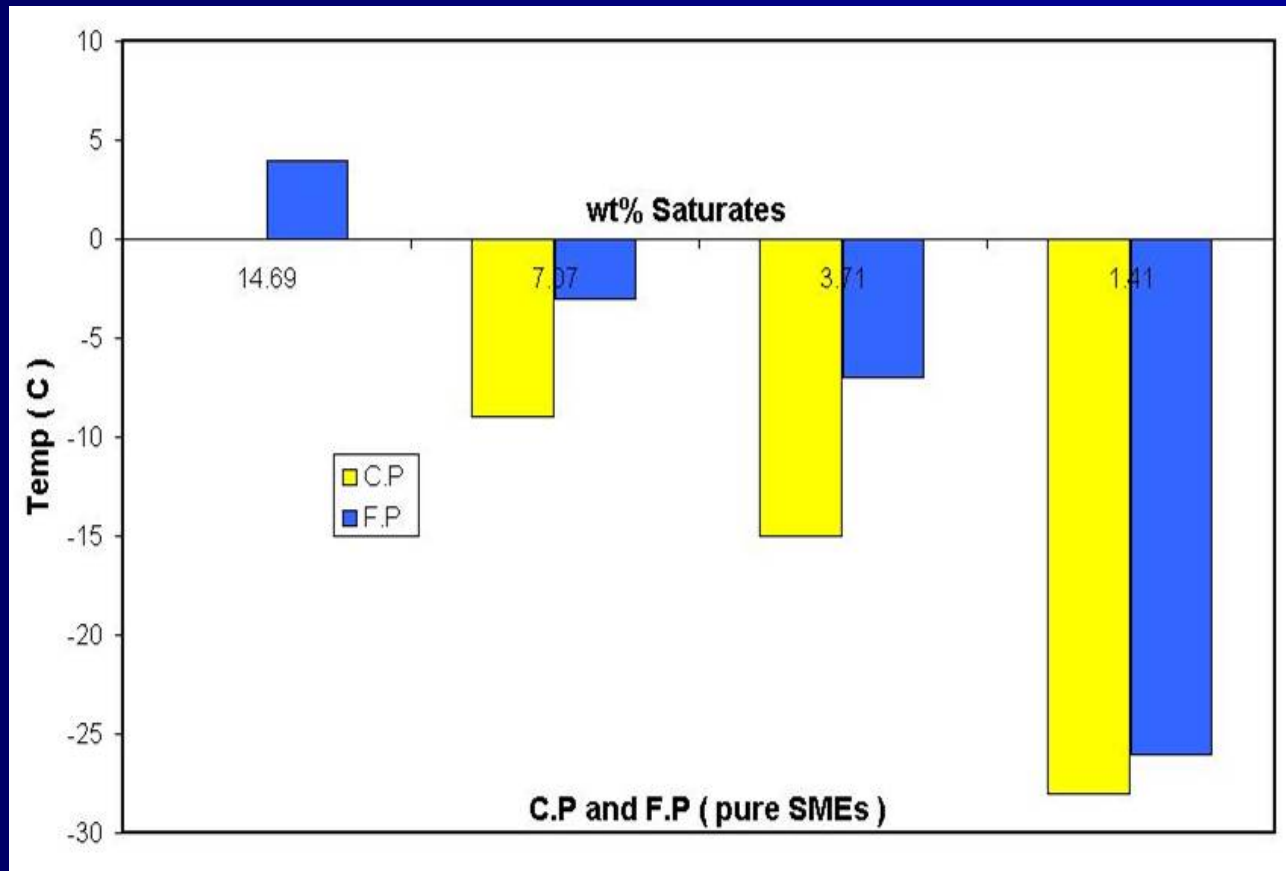
Yield Efficiency (data for soybean oil)

- Cloud Point (C.P.) is defined as the temperature at which crystals appear when cooling
 - C.P of unprocessed SMEs is about 0 C.
 - 9 degree depression in C.P at approx. 80% yield
 - 26 degree depression in C.P at approx. 65% yield
- Note: Max. theoretical yield is approx. 85% (depends on initial composition)



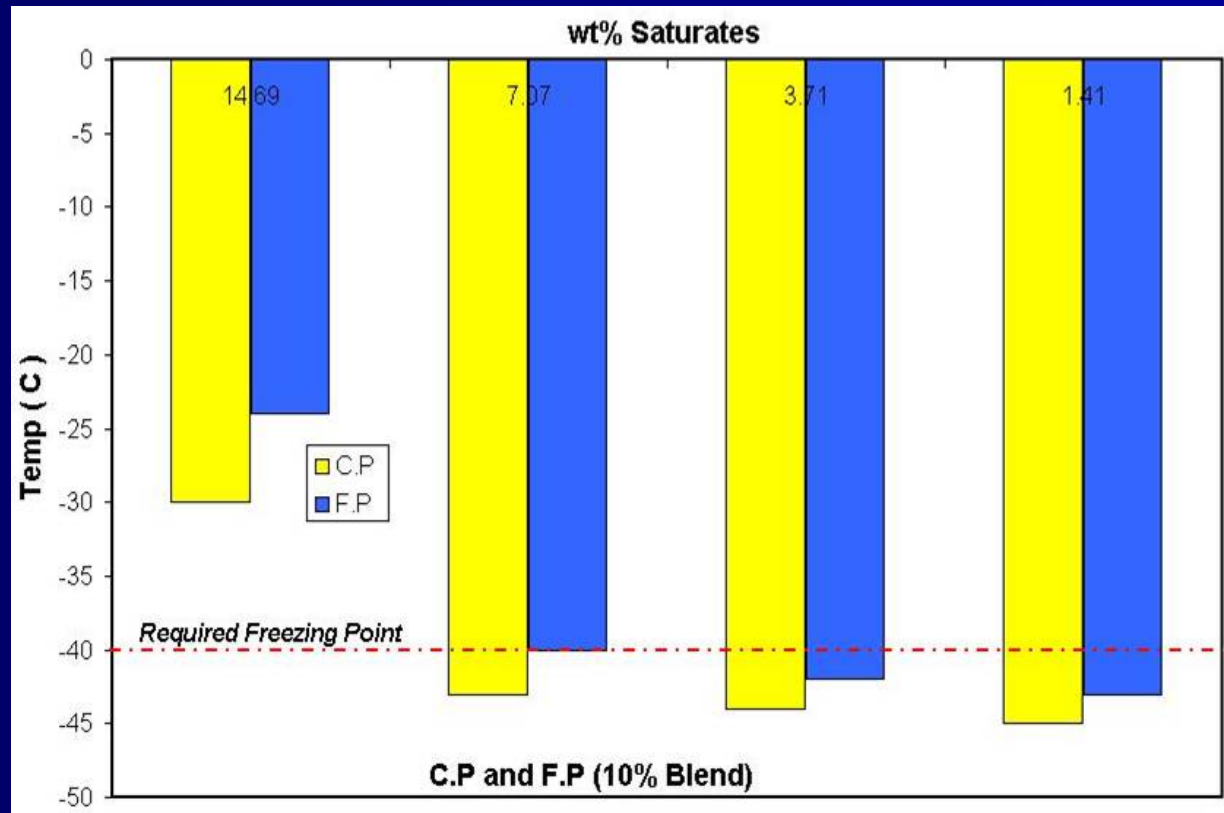
Cloud and Freezing Points vs. composition of B-100 (soybean oil)

- C.P and F.P decrease with decreasing saturated B-100 composition



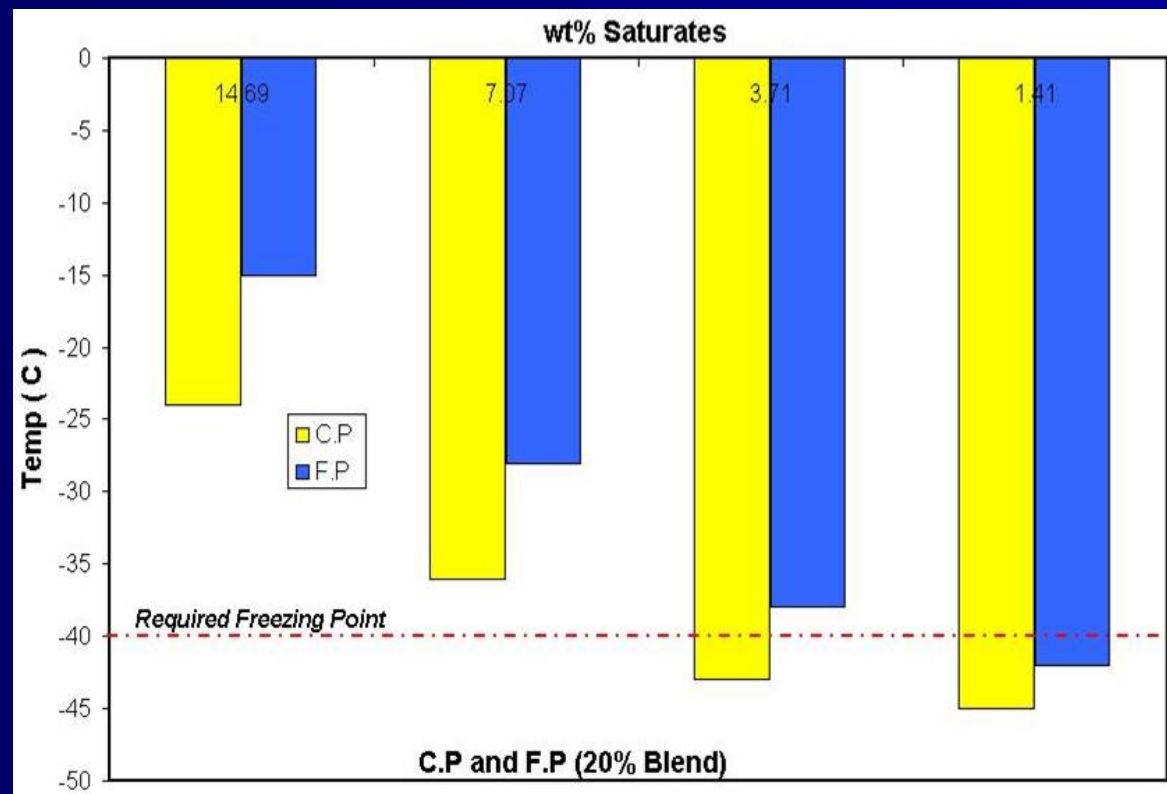
C.P and F.P of 10% vol Aviation Fuel Blends:

- At 10% blend level, all fuels with SMEs containing up to 7.5 wt% saturates are within -40 C freezing specs
- Saturated ester content of less than 2 wt% does not affect on F.P of blends



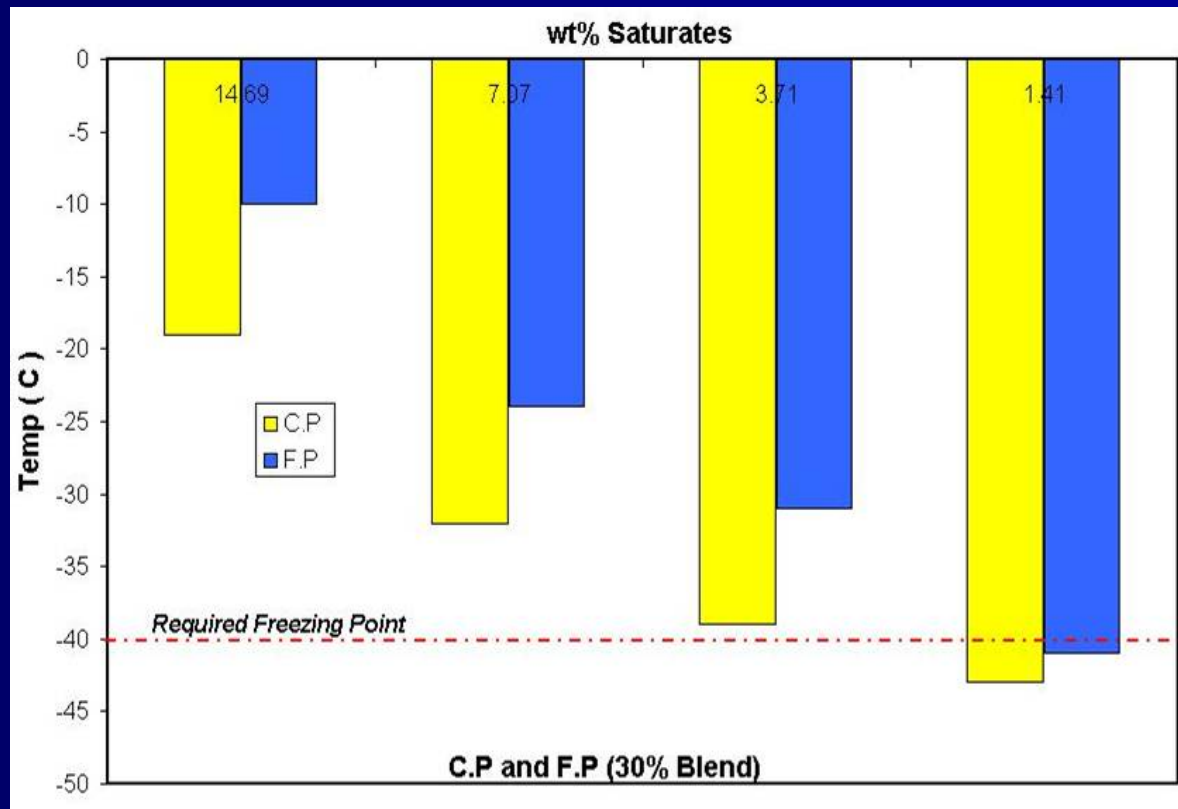
C.P and F.P of 20% vol Aviation Fuel Blends:

- At 20% blend level, fuels with SMEs containing more than 2 wt% saturates are not within the -40C freezing spec
- Thus for blend levels of 20% or higher, SMEs have to be processed to less than 2 wt% saturated esters



C.P and F.P of 30% vol Aviation Fuel Blends:

- At 30% vol blend level, fuel with SMEs containing less than 1.4 wt% saturates is well within -40 C freezing specs.



Applications

Summer/winter diesel fuel blend stocks

Aviation jet fuel

Solvents

Chemical feedstocks (enhanced reactivity)

Future research on catalytic
cracking/reforming/alkylation/cyclization

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Acknowledgements

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