National Renewable Energy Laboratory

Biodiesel Technology and Feedstocks

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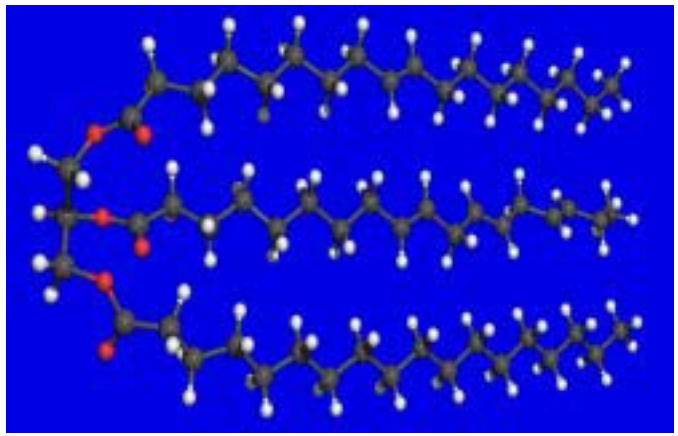
Selecting a Feedstock/Technology

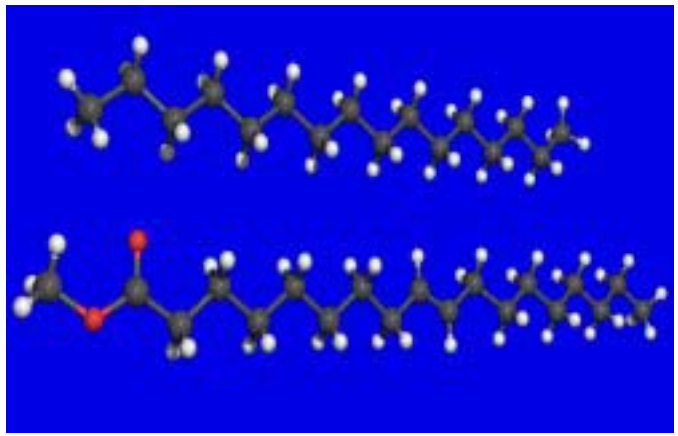
- Feedstock cost
- Feedstock quality
  - Free Fatty Acid (FFA)
  - Moisture, impurities, unsaponifiable matter
  - Color and odor
- Technology
- Capital and production costs
- Glycerin quality
- Agricultural and recycling incentives
- Coproduct and revenue targets
- Expertise of staff
- Risk management

Biodiesel Feedstocks

Fat molecule (triglyceride)



A “free fatty acid” (FFA) chain that has broken off the “fat” molecule



One FFA + One methanol = One biodiesel

FFA break off through hydrolysis

- steam from cooking foods, salts, chemicals, heat, etc., work together to break chains off triglycerides

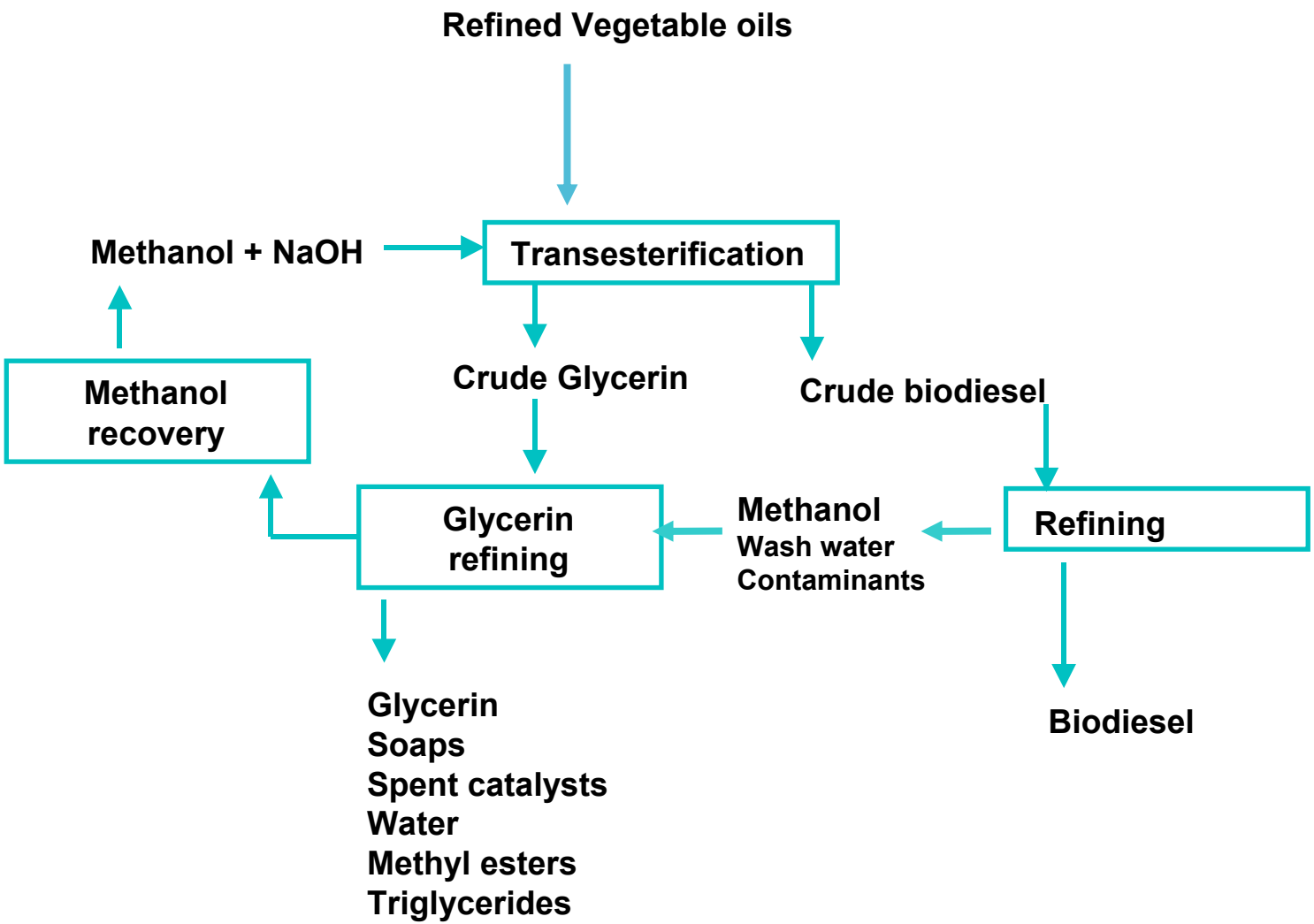
Transesterification

- Transesterification converts Triglycerides to biodiesel

• Triglycerides + methanol + NaOH (base) +FFA (if any)	➲	fatty acid methyl esters + glycerin + NaOH + soaps (if any)

- Temperatures of 60-70^{o}C, at atmospheric pressure
- Crude glycerin and crude biodiesel are separated
- Crude biodiesel is washed with mildly acidic water to remove:
  - Neutralized catalysts
  - Water soluble glycerin
  - Soaps
  - Methanol
- Crude Glycerin can be refined to various grades

Transesterification



Selected Feedstocks

Feedstock	Cost $/lb	FFA %	MIU %	Glycerin Quality
Crude Soy Oil	0.14-.25	<1.0	<1.0	Good
Refined Soy Oil	0.16-.28	0.1	0.5	Good
Yellow Grease	0.06-.16	1-15	<2	Depends
Edible Tallow	0.12-.20	<1	<.25	Good
Inedible Tallow	0.08-.16	2-35	1-2	Depends
Raw Trap Grease	-1 to -5	50-100	1-20	Little Poor

Feedstock Pretreatment

- Most (but not all) feedstocks pretreated
  - Vegetable oils - refined and degummed
  - Yellow grease - filtered, dewatered
  - Tallow and fat - various preparations and grades
  - Trap grease - filtered, dewatered, but still contans fines and other contaminates
- Technologies can be adapted to crude feedstocks
  - Lower feedstock cost
  - Higher production and capital cost
  - Lower yields

Pretreatment Technologies

- Depends on
  - FFA content
  - MIU
  - Esterification technology
- Types of pretreatment include:
  - Degumming
  - Deodorization
  - FFA reduction: Steam stripping, caustic stripping, solvent extraction, glycerolysis, acid esterification
  - Hydrolysis
  - Bleaching
- Some pretreatment steps can occur after biodiesel is made

Degumming

- Necessary if large amounts of phosphatides are present in feedstock
- Phosphoric acid and steam swells the gums for removal
- Common process for crude vegetable oils, fats
- Could be used more with recycled greases if warranted

Bleaching

a) Adsorb trace metals, moisture, insolubles, pigments
b) Reduce oxidation products (peroxides etc)
c) Absorb any phospholipids precipitated during degumming
d) Removes phosphoric acid left from degumming

Deodorization

- Used with feedstocks up to 30% FFA
- Basically a vacuum distillation
  - 240 to 270°C
  - 2-5 mmHg (.3 - .8 kPa)
- Energy intensive
- Small plants add about 4 cents/lb to feedstock costs
- Large plants add about 1.5 to 2 cents/lb to feedstock costs

It May be Worthwhile to Deodorize

- Possible contaminants in feedstocks
  - Remove aldehydes, ketones, and smelly products
  - Lighten up the product by destroying caroteinoids
  - Pesticides, fungicides, herbicides
  - Polycyclic hydrocarbons
  - Polychlorinated cyclic hydrocarbons
  - Trace metals
  - Aflatoxins (from molds)
  - Perchloroethylene (PCE from dry cleaning operations)
  - PCB
  - Detergents and cleansers
- Oil refining has demonstrated reduction in these contaminates of 50% or more when present

Caustic Stripping

- Reduces FFA content of feedstocks
- FFA reacts with base catalyst (NaOH, KOH) to form soaps
- Soaps can be removed prior to other treatments
  - e.g., deacidification of crude soybean oil
  - pretreatment of low FFA (<4%) yellow grease
- Often combined with biodiesel technology using feedstocks < 4% FFA

Solvent Extraction

- Ethanol can reduce FFA in olive oil from 20%+ to less than 3%
- Furfurol extracts FFA
  - Also phase separates saturates and unsaturated glycerides
  - Might be an interesting benefit to control cold flow
- Neither alcohol currently used to manage FFA in biodiesel production
- Liquid propane (Solexol process) removes triglycerides and leaves everything else
  - Very good at reducing color

Hydrolysis

- Hydrolysis converts Triglycerides to FFA

Triglycerides	➲	free fatty acids
+ steam		+ water

- Can be batch or continuous
- Acid resistance steel required
- Yields approached 99% in counter current systems

Glycerolysis

- Glycerolysis converts FFA into monoglycerides

  Glycerol + FFA ➲ Fat + water

- Temperatures of 250-260^{o}c
  - If using a catalyst like zinc power or zinc chloride, reduce temperatures to 220^{o}C
- Reduced pressures: 5-6 hPa
- Commercialized to produce various monoglyceride products

Acid Esterification Technology

- Acid esterification converts FFA to biodiesel

FFA + methanol + sulfuric acid + triglycerides (if any)	➲	fatty acid methyl esters (aka biodiesel) + water + sulfuric acid + triglycerides (if any)

- Can be batch or continuous
- 200-250^{o}C and pressures up to 1000 kPa
- Need continuous water removal (water shuts off catalyst)
- Acid resistance steel required
- Yields approached 99% in counter current systems
- Unreacted FFA can be removed with caustic stripping

Commercial Technology: 1

- Buy refined, degummed feedstock
  - mostly soy oil
  - Could request yellow grease be pretreated, but it isn't commonly done yet, and would add to feedstock price
- Transesterify
- Recycle any soaps
  - Convert to FFA with acid treatment
  - Sell separately as coproducts
  - Or save up and convert to methyl esters in small batches
- Sell crude glycerin or upgrade or convert into coproducts

Commercial Technology: 2

- FFA < 4%
- Caustic strip and remove soaps and water before transesterification
- Process triglycerides with transesterification
  - few problems
- Recover soaps and react with acids to recover FFA
- Convert FFA to methyl esters with acid esterification
  - Small batch process
  - Neutralize remaining FFA in biodiesel output and recycle
- Glycerin is slightly better quality
  - no soaps

Commercial Technology: 3

- FFA < 4%
- Caustic strip during transesterification
- Process triglycerides with transesterification
  - High soap levels can cause foaming, emulsifications that reduce yields, create problems
- Soaps come out in glycerin
- Recover soaps and convert FFA to biodiesel as in #2

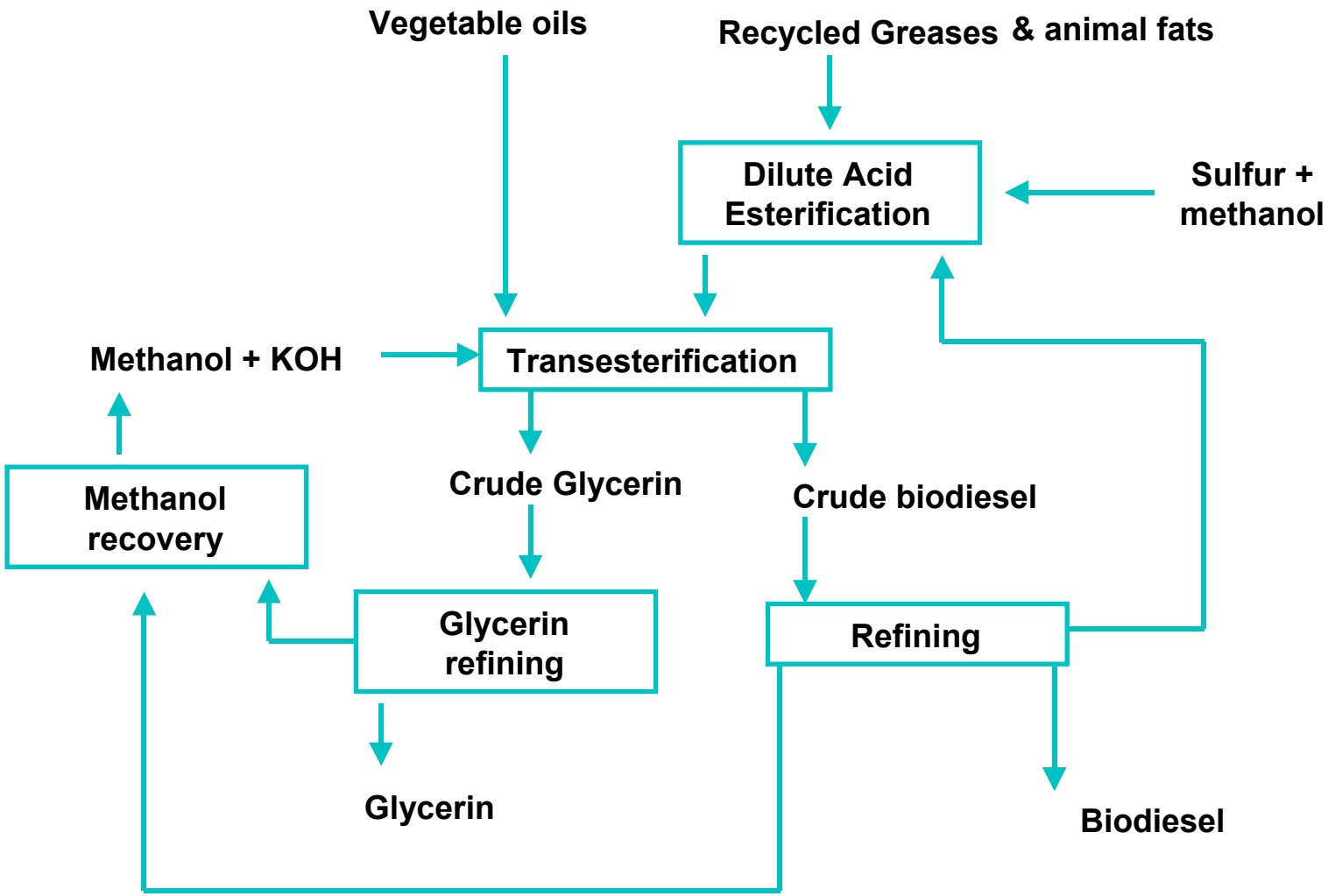
Commercial Technology: 4

- FFA < 20%
- React entire feedstock in acid esterification
  - converts FFA to biodiesel
  - Remove water of reaction
  - Remove excess methanol and acids
- React entire feedstock in transesterification
  - use extra catalyst to neutralize acids, remaining FFA
- Recycle remaining soaps, FFA and reintroduce into raw feedstock

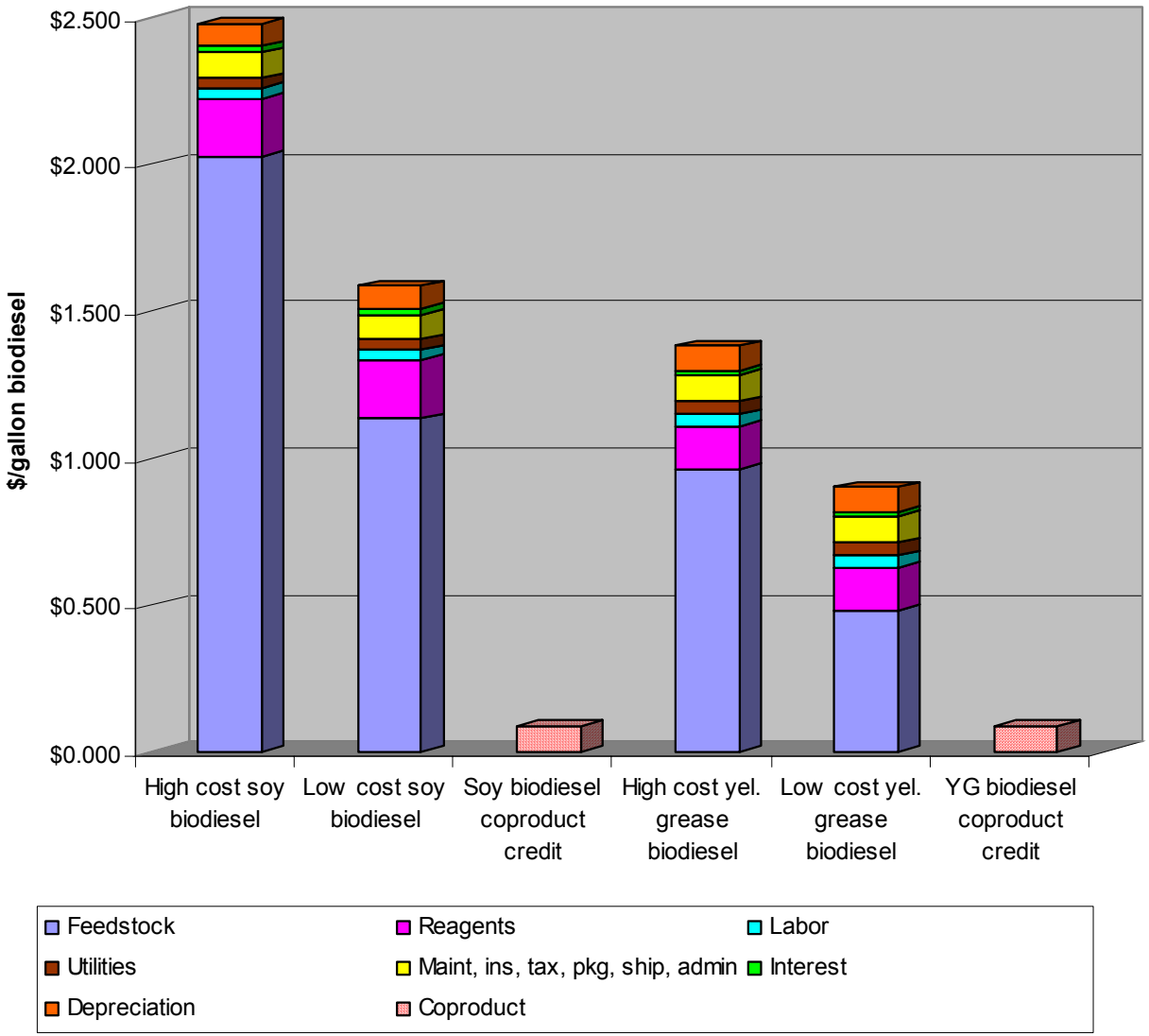
Other Commercial Technologies Used for Biodiesel

- FFA 4-20%
- Blend feedstocks to achieve desired FFA level, other objectives
- Use commercial technology 2-4
- Also, some batch conversions of up to 50% FFA have been achieved with multiple steps
  - 2 sequential acid esterifications with water separation in between followed by a transesterification
  - Multiple caustic stripping steps with water removal

Acid-Base Esterification Technology



Production Costs



Low Cost Feedstock Issues

- Color
  - Not an indication of technical quality
    - ASTM quality biodiesel can range from clear to black
  - Is a consumer issue, raises uncertainties
    - may need bleaching, carbon filtration
    - bleaching will remove other impurities
- Odor
  - Not an indication of technical quality
    - ASTM quality biodiesel can range from clear to black
  - Is a consumer issue, raises uncertainties
    - may need deodorization
    - deodorization will remove other impurities

Low Cost Feedstock Issues

- Glycerin quantity
  - high FFA feedstocks contain less glycerin
    - smaller coproduct revenue per gallon biodiesel
  - Impurities tend to be concentrated in the glycerin
    - reduces value of glycerin because upgrading becomes more expensive
    - not many buyers for the glycerin, could get stuck with it
- Glycerin quality
  - color and odor bodies reduce glycerin value drastically
  - salt, methanol, methyl esters, triglycerides, cosolvents reduce glycerin value
  - upgrading may be expensive

Trap Grease Issues

- FFA content varies from 50-100% of raw material
  - Based on 50 U.S. samples
- Composition of fatty acids similar to yellow grease
- Creates unique processing issues for biodiesel
  - water, fine grit, emulsifications, odor issues, water disposal
  - No technology commercial for 50%+ FFA feedstocks
    - will need to use some of the technologies discussed today in a variety of configurations
    - Could blend trap grease into other feedstocks up to 20% FFA
- May reduce quality of glycerin if trap grease is blended into other feedstocks
- Need to determine any contamination issues in the biodiesel product for amounts of trap grease used in feedstock blends

Other Energy Uses of Trap Grease

- Hydrogen production via steam reforming in commercial fixed bed reactor systems
  - May need sulfur removal
  - Could be cost-competitive with natural gas
  - Need a commercial demonstration
- Combustion (as No. 6 or No. 4 Fuel Oil replacement)
  - No. 4 & 6 systems already have fuel heating capability
  - Industrial fuel use in many sewage systems
- Use in turbines designed for heavy fuel oils, pyrolysis oils, or crude oil

Emerging Technologies

- Cosolvent Processes
  - Bioxx, Resoydyn
- Enzymatic conversion of triglycerides
  - slow, low yields (high triglyceride content of biodiesel)
  - enzyme cost issues
- Enzymatic conversion of FFA
  - need more data
  - enzyme cost issues
- In situ conversion of oil in seeds
  - no glycerine coproduct
  - Need further data

Cosolvent Technologies

- FFA < 20%
  - Claims that even higher (up to 50% FFA) feedstocks can be treated, but commercial demonstrations needed
- Simultaneous conversion of FFA and triglycerides
- Using hexane, MTBE, THF, other solvents
  - makes methanol, FFA, and triglycerides misible
  - speeds up reaction
- React entire feedstock mixed with cosolvent with methanol and a catalyst
- Separate biodiesel, glycerin, cosolvent, methanol using existing technology
- Address unintended coproducts: peroxides, etc.

Possible Technologies

- Glycerolysis to treat FFA
  - commercial, not currently used in biodiesel
  - convert FFA to monoglycerides, then transesterify feedstock
- Hydrolyze high FFA feedstocks followed by acid esterification
  - commercial, not currently used in biodiesel, energy intensive
  - turn feedstock in FFA, convert to methyl esters with acid esterification
  - Existing commercial processes 99% yields, caustic stripping of remaining FFA would be sufficient
- Solvent Extraction technologies
  - remove FFA or triglycerides and treat separately with acid or base esterification

Emerging Coproduct Technologies

- Make more coproducts from fatty acids
- Make more coproducts from glycerin
- Extract more trace compounds
- Risk
  - Competing with P&G, Cargill-Dow, Uniqema, Stepan Chemicals, Cognis, etc.
- Benefits
  - Existing technology and markets
  - increase revenue steam
  - increase financial stability

Future Technologies

- Better separation technologies
  - oxidize saturates
  - fragment polyunsaturates into high value small chain esters
  - process specific FA into existing or new products
  - separate out high value coproducts
    - omega acids, other rare acids, sterols, pigments, etc.
- Ferment crude glycerin into high value coproducts
- Enzymatic transformation of crude glycerin in high value coproducts

Future Technologies

- Super critical processes
  - methanol
  - Propane
  - CO2

Contact Information

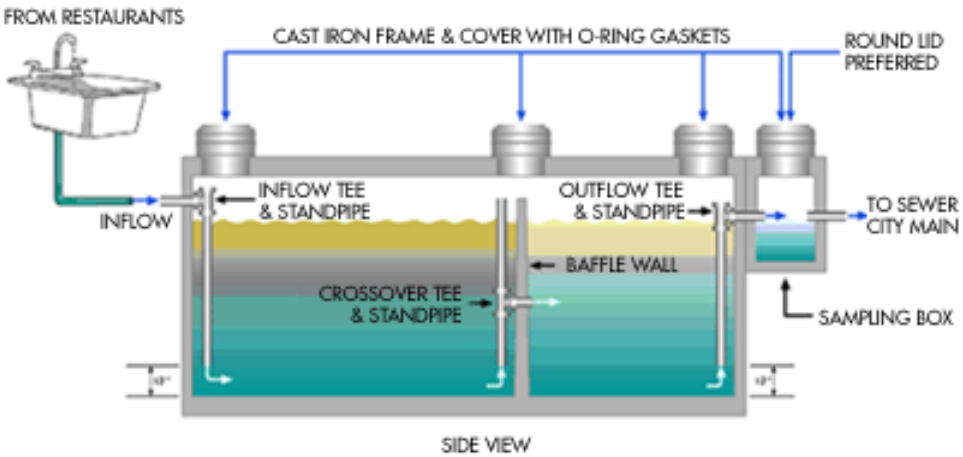
- National Renewable Energy Laboratory
  - www.nrel.gov
- National Biodiesel Board
  - www.biodiesel.org

Feedstock Composition

Fatty Acids: C# carbons: # C=C bonds

	≤C12	C14:0	C16:0	C16:1	C18:0	C18:1	C18:2	C18:3	≥C20
Soy	0	0	12	0	4	23	55	7	1
Corn	0	1	9	1	3	40	45	0	1
Yel Grease	0	1	23	1	10	50	15	0	0
Rape	0	0	4	0	1	10	15	10	60
Mustard	0	0	3	0	2	39	15	9	30
Sunflower	0	0	6	0	4	19	69	0	2
Lard	0	1	25	2	14	46	10	0	3
Tallow	0	2	27	2	25	40	2	0	2

Grease Traps



Grease Trap

- A grease trap works by slowing down the flow of warm/hot greasy water and allowing it to cool. As the water cools, the grease and oil separate and float to the top of the grease trap. The cooler water (less grease) continues to flow down the pipe to the sewer. The grease is actually trapped by baffles, which cover the inlet and outlet of the tank, preventing grease from flowing out of the trap.