National Renewable Energy Laboratory

Brown Grease Feedstocks for Biodiesel

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Overview

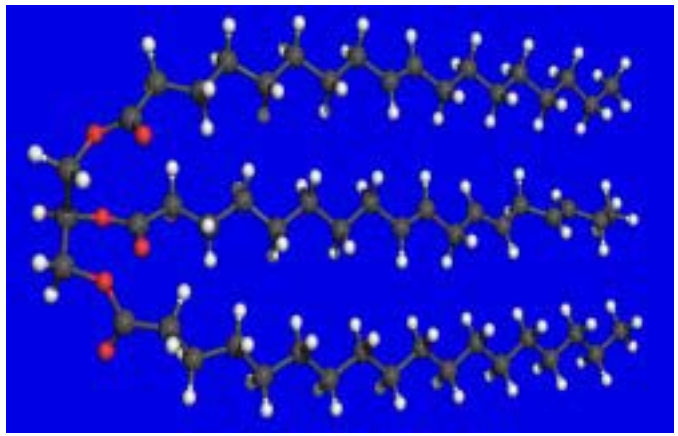
- Definitions
- Composition
- Supply
- Infrastructure needs
- Cost
- Conversion
- Benefits
- Policies

What is Brown Grease?

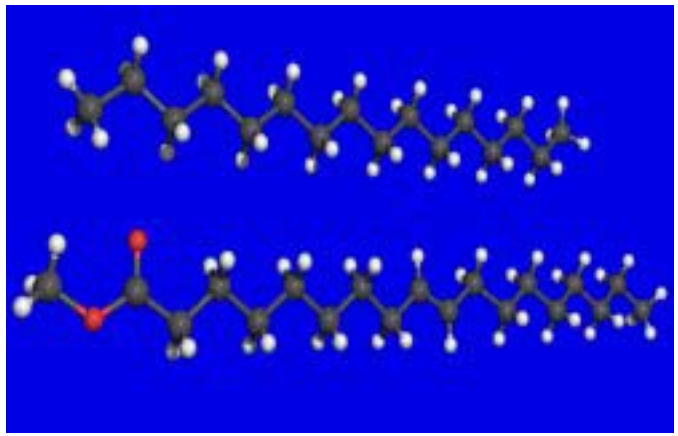
- Generic Term
  - Also includes trap grease, sewage grease, black grease
- Greases from traps and sewage plants cannot be used for animal feed
- Greases from other sources whose free fatty acid (FFA) content exceeds limits for animal feed
  - e.g., FFA >20%
- Gelatinous at ambient temperatures
- VERY Smelly

What is a Free Fatty Acid?

Fat molecule (triglyceride)



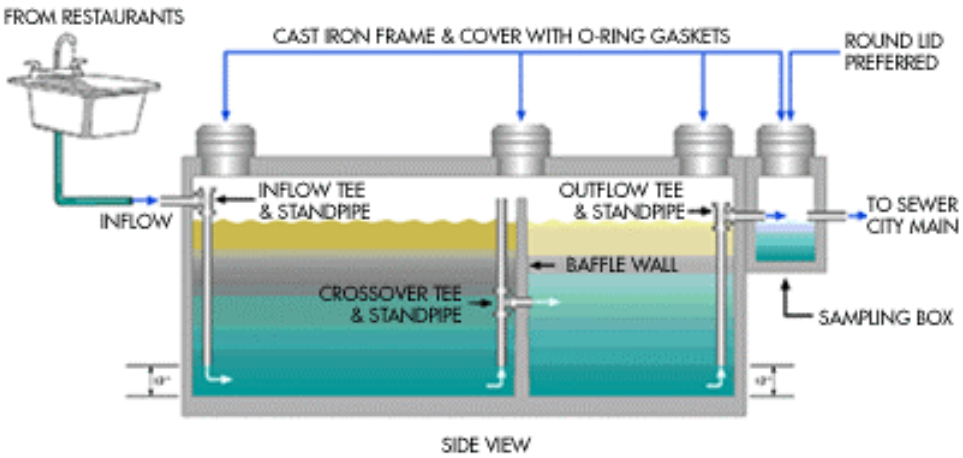
- A "free fatty acid" (FFA) chain that has broken off the "fat" molecule



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

- One FFA + One methanol = One biodiesel
- Need acidic catalyst

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.

Traps Maintenance

- Traps are required to be pumped at specific intervals by law
  - Mostly ignored
  - Traps pumped when they start to smell or back up
- Commercial firms provide the service
  - Septic firms
  - Grease collectors
  - Other
- Poorly maintained traps cause sewage backups
  - WTP have to clear sewer lines
  - Back ups damage private property
  - Create occasional rat population booms

Waste Water Treatment Plants

- The pumped trap waste can be disposed at a WTP or a landfill
  - Typically a tipping fee is paid for disposal
  - Disposal at the WTP “gums up the works”
  - Previous practice of dumping trap waste down sewer mains is being discouraged and banned
- WTP must collect, treat and dispose of greases
- Typical disposal methods
  - Landfills (mixes with lime, dumping fees)
  - Burns greases
  - Composts greases
  - Anaerobic digestion

Resource Assessment

- Urban Waste Grease Resource Assessment
  - 8.87 lbs/person/year Yellow grease (recycled cooking oil)
  - 13.37 lbs/person/year Trap grease
    - Probably a little high
    - George tried to adjust for water
    - But estimate may include some water
  - Documented tipping fees of up to 11 cents/gal
  - 3,800 million lbs produced annually in US
  - Equivalent to 495 million gallons of biodiesel with good yields

Biodiesel Model

- Collect trap grease at specialized collection facilities
  - Separate out greases, water, solids
    - Water to sewer
    - Solids to compost, combustion, or landfill
  - Take grease to biodiesel plant
- Saves the sewage plant the cost of:
  - Collecting
  - Neutralizing
  - Disposal
- Also saves on preventative maintenance
  - Reducing plugged sewage lines
  - Reducing private property damage
- Increase enforcement of trap pumping to increase availability of trap grease

Trap Grease Composition

- FFA content varies from 50-100% of raw material
  - Based on 50 U.S. samples
  - Creates unique processing issues for biodiesel
  - FFA in yellow grease (recycled cooking oil) ranges from 4% to 15% typically
  - FAA in crude vegetable oils range from 1-4% (olive oil up to 20%)
- Composition of fatty acids similar to yellow grease
  - Biodiesel characteristics in the known range for cold weather performance, and other fuel properties
  - Need to analyze the FINAL BIODIESEL PRODUCT for
    - Aflatoxins (products of mold)
    - Trace metals and pesticides
    - Polycyclic aromatic hydrocarbons
    - Chlorinated polycyclic hydrocarbons

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

Other Energy Uses of Trap Grease

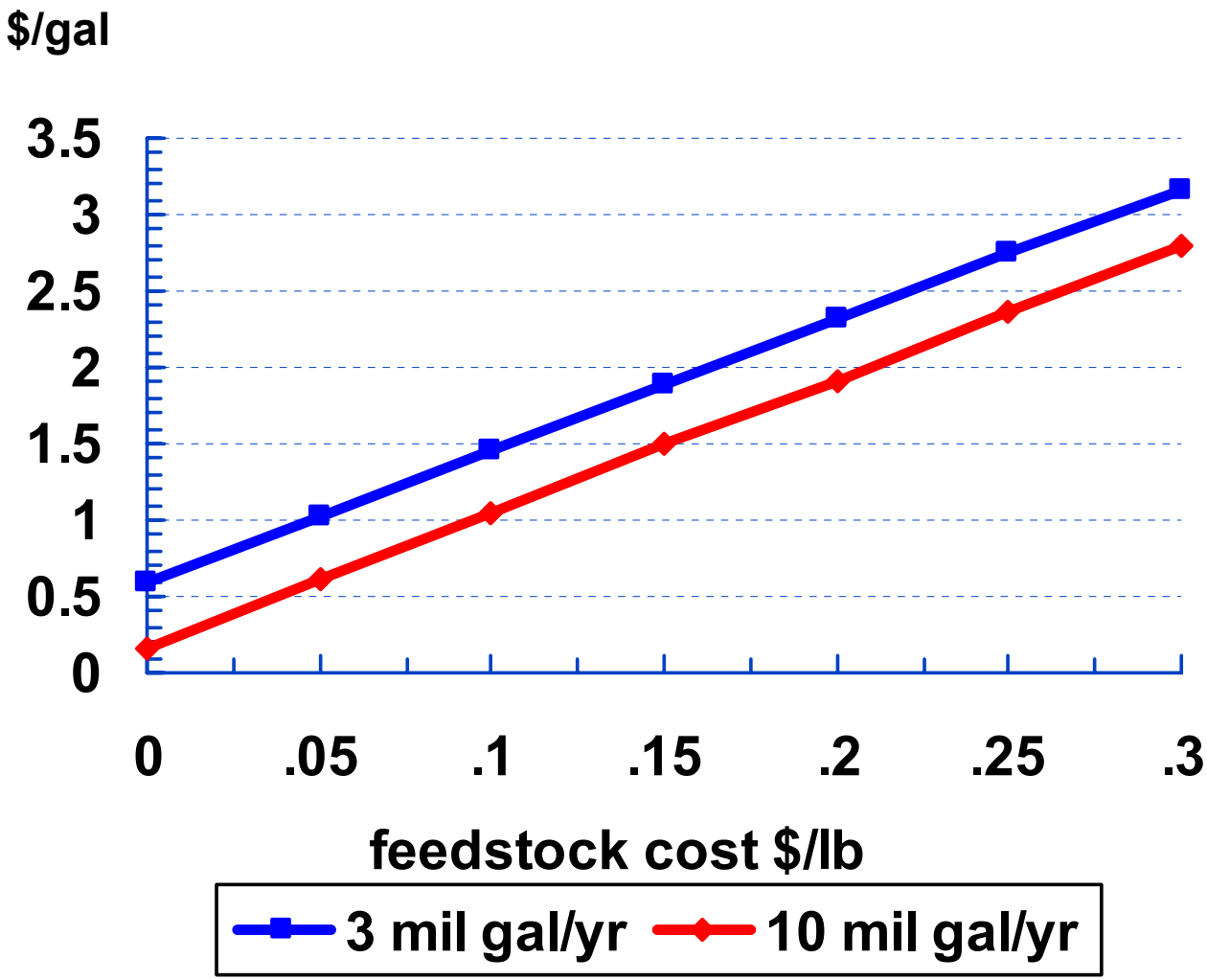
- Hydrogen production via steam reforming in commercial fixed bed reactor systems
  - Need sulfur removal
  - Could be cost-competitive with natural gas
  - Need a commercial demonstration
- Combustion (as No. 6 or No. 4 Fuel Oil replacement)
  - No. 4 & 6 systems already have fuel heating capability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

Why Biodiesel?

- With a dumping fee, collectors can acquire trap grease for <5 cent per pound revenue
  - Cost of clean up mostly in capital
  - Tipping fee to cover operating costs, waste disposal
- Conversion costs can be similar to other biodiesel unless extensive processing is needed
  - May cost a little more to convert, don't know this yet
- It's a value-added product compared to combustion
- Creates local biodiesel supply
  - Fuel security
  - Increases liquid fuel diversity
  - Dampens petroleum price spikes
  - Creates local jobs

Theoretical Production Cost

per Gallon Biodiesel



Prices:	August 9, 2001
Sunflower:	20 ¢/lb
Corn:	19 ¢/lb
Soy:	18 ¢/lb
Inedible Tallow:	14 ¢/lb
Yellow Grease:	9 ¢/lb
Brown Grease:	-5 to 5 ¢/lb
Mustard target	10 ¢/lb

Biodiesel Technology Issues

- Transesterification handles <4% FFA
  - FFA typically removed with caustic
  - Caustic stripping typically done for 1% FFA or less during crude oil refining
- 4% - 20% FFA uses two esterification technologies
  - Acid esterification and base transesterification
- 100% FFA can be converted to biodiesel using 50+ year old acid esterification technology
- FFA are difficult to separate from triglycerides
- No proven technology for 50+% FFA mixes

Vegetable Oil Pretreatment

- Raw vegetable oils typically are refined prior to transesterification
  - removes 1-2% FFA, gums, proteins, minor contaminants
  - Phosphoric acid and steam swells the gums for removal
  - Caustic soda (NaOH) bonds to the FFA to produce soaps
  - Soap, gums and water are removed
  - The refined soybean oils are then transesterified
- Same process can be used for yellow grease with <4% FFA before transesterification
- According to Cargill, refining adds 1.5-2 cents per pound to feedstock costs

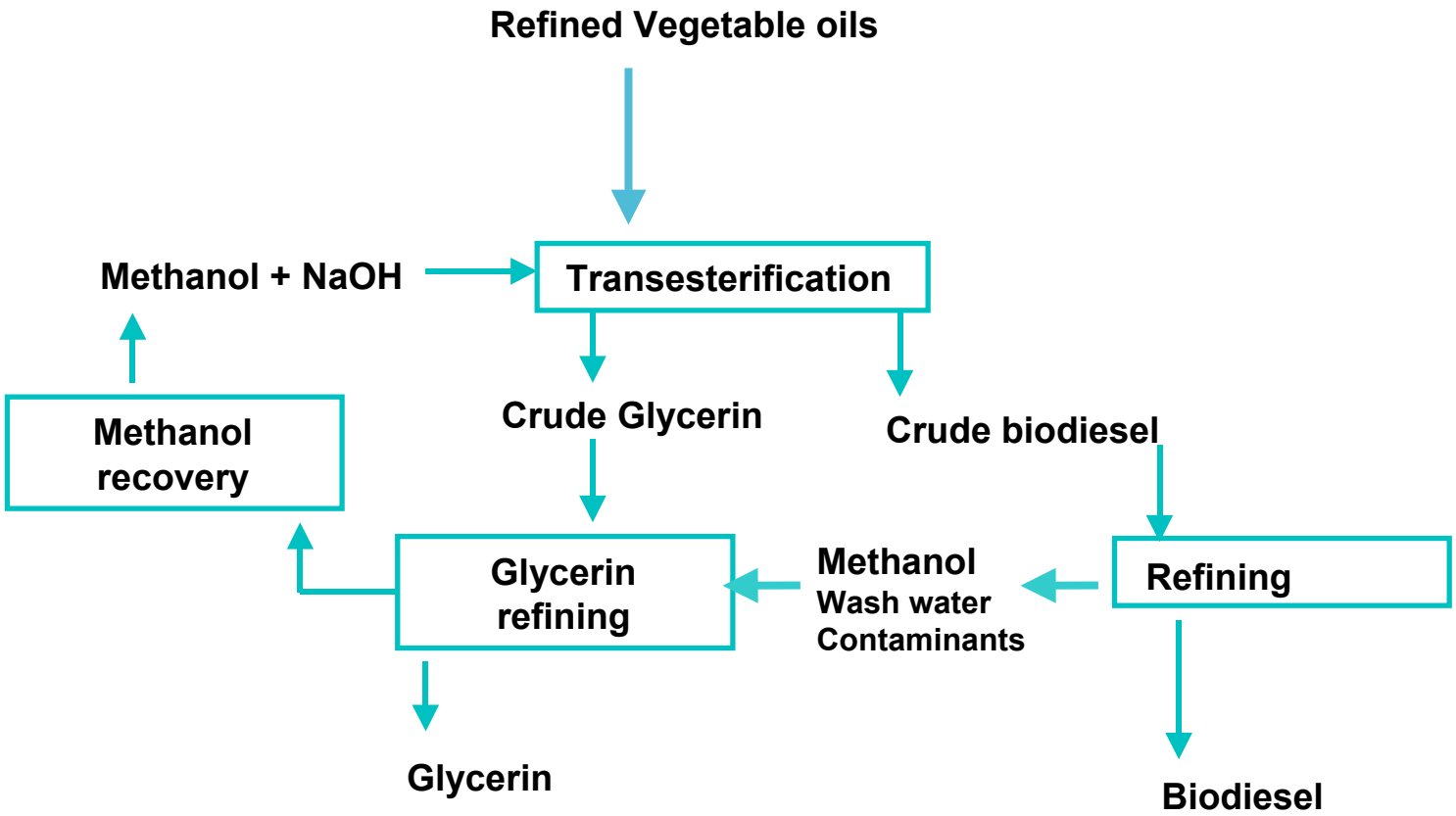
Transesterification

- 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

Transesterification



Technical Options When FFA Equals or Exceeds 4%

- A number of technical approaches exist
  1. Remove FFA with NaOH and centrifuge (caustic stripping)
  2. Convert FFA into methyl esters with acid esterification then proceed with transesterification
  3. Convert feedstock into 100% FFA and convert via acid esterification
  4. Convert the FFA into monoglycerides then proceed with transesterification
  5. Separate the FFA and triglycerides and treat separately
- Combined processes for ASTM quality biodiesel not well developed
  - Technical and economic questions exist

Pros and Cons of Caustic Stripping

- Biodiesel companies are doing it up to 10% FFA
- Expensive in terms of chemical usage
- Yield losses can mount quickly
  - You loose 1-2% clean oil with each 1% FFA converted into soaps up to about 4% FFA
  - Beyond 4% FFA you loose more clean oil with each 1% FFA converted into soaps
  - For example, 10% FFA can result in a 30%+ yield loss
- FFA can be packaged as consumer products by themselves without converting to biodiesel
  - Limited market potential beyond some point as industry grows
- Oleochemists recommend physical refining for FFA >1%

Acid Esterification

- Typically used on 100% FFA feeds
- Since trap grease >50% FFA, it may be cost effective to hydrolyze grease into 100% FFA
  - Then proceed with acid esterification on a commercial scale
- Acid esterification has been used to treat small FFA levels in batch plants in a two step acid-base esterification

Acid Esterification Technology

- Acid esterification converts FFA to biodiesel

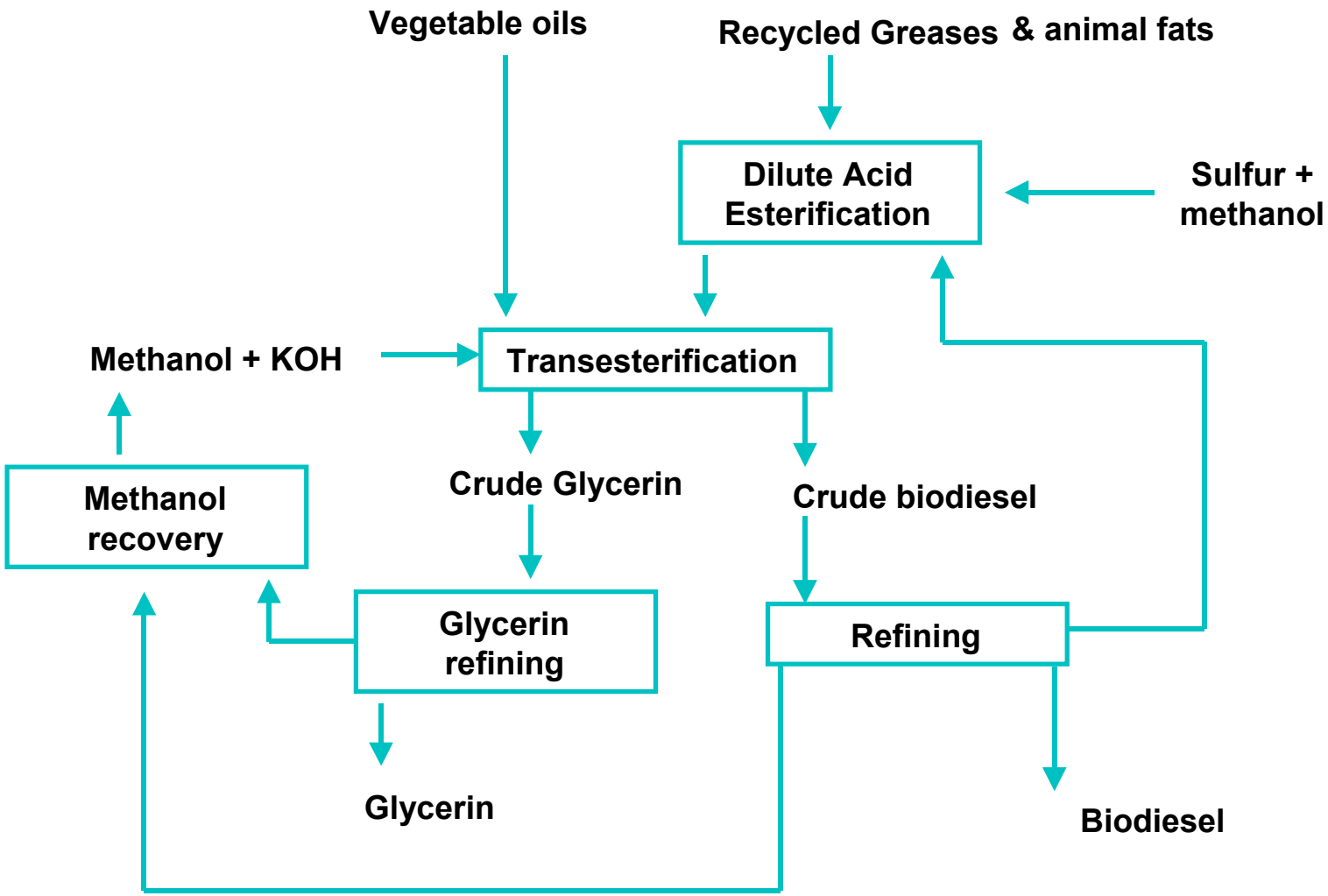
FFA + methanol + sulfuric acid + triglycerides (if any)	➲	fatty acid methyl esters (aka biodiesel) + water + sulfuric acid + triglycerides (if any)

- 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

Combined Acid-Base Systems

- Feedstock up to 20% FFA goes into acid esterification
  - A hypothetical 80% conversion yield results in an output consisting of 4% FFA, 16% methyl esters, 80% triglycerides, H20, methanol, and sulfur catalyst
- Must remove water continuously for high yields
- Could remove soaps with centrifuge prior to next step
- Output from acid stage goes to transesterification
  - Extra base will be required to neutralize sulfuric acid plus extra base to neutralize any remaining FFA

Acid-Base Esterification Technology



Pros and Cons of Acid-Base Esterification

- You need to treat the entire feedstock in the acid step just to react the small fraction of FFA present
- By-product water from acid step can:
  - Reduce yields in acid step
  - Reduce yields in base step
  - Generate emulsifications
  - Reduce biodiesel quality
- Low acid esterification yields will increase FFA soap production
  - Soaps cause emulsifications unless reaction time increases and mixing speeds reduced
- Chemical cost increases
- Acid resistant tanks for acid step increases capital

Glycerolysis

- Turn FFA back into glycerides, then transesterify
- Glycerolysis converts FFA to triglycerides

  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
- Same problems as Acid-Base systems before

Separating FFA and Oil before reactions

- Caustic refining
  - Already discussed in slide 15 and 19
- Physical refining
  - Also known as steam stripping
- Solvent extraction
- Adsorption

Physical Refining for Trap Grease

- **Could have as many as 5 basic steps**

1. Degumming
   a) Necessary if large amounts of phosphatides are present in feedstock
2. 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

Physical Refining for Trap Grease

3. Deodorizing and Deacidification
   a) Remove aldehydes, ketones, and smelly products
   b) Lighten up the product by destroying caroteinoids
   c) Remove 92-95% FFA
4. FFA go to esterification after light thermal quenching
   a) Hot oil is used to heat incoming oil for thermal efficiency
5. Triglycerides go to transesterification

Deoderization

- Up to 30% FFA feedstocks commercial
- Basically a vacuum distillation
  - 240 to 270^{o}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 trap grease
  - 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

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
- Isopropanol
- Liquid propane (Solexol process) removes triglycerides and leaves everything else
  - Very good at reducing color

Attractive Approaches for Feedstocks >50% FFA

- Evaluate limits to acid-base combined approaches based on current practices
  - Then blend trap grease into feedstocks up to technical limits
- Evaluate hydrolysis to FFA followed by acid esterification
- Evaluate physical refining with both acid and base esterification conducted separately
- Evaluate final biodiesel products from various processes for contaminants

What we are currently doing

- Ocean Air Environmental
  - selected as NREL's demonstration partner
  - Had converted feedstocks up to 50% FFA
  - Has an idea about how to convert trap grease cost effectively
  - Will document benefits to WTA
  - Will document technology issues: mass-energy
  - Will document costs
  - Will demonstrate a commercial approach
- Other R&D
  - Will depend on OAE's progress