Brown Grease to Biodiesel

Presentation to Nu-Energie

May 1, 2008

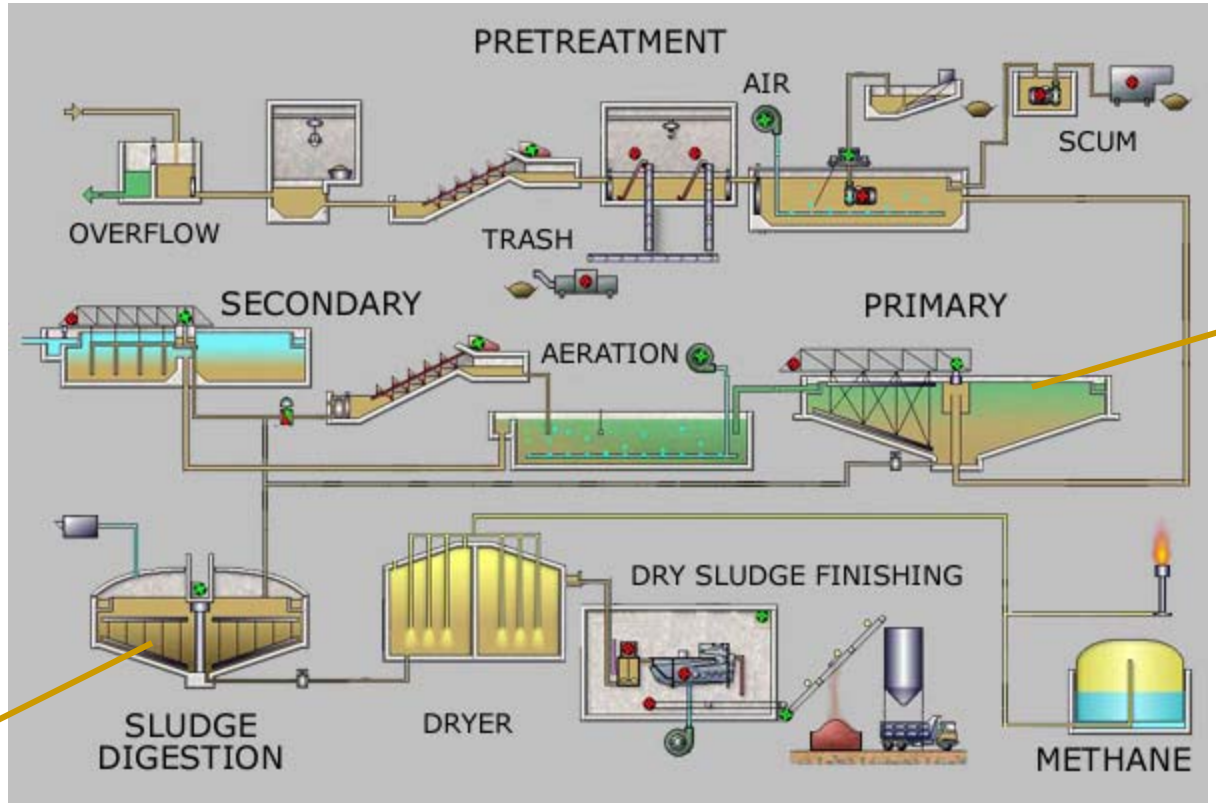
There is broad interest in biofuels from waste materials

- Web of Science search
  - 193 “hits” on (biodiesel) AND (waste)
  - ½ in the last year
  - World-wide interest
- Wastes:
  - Fish processing waste
  - Frying fats
  - Microbes, algae, waste lipids
  - Leather industry (animal fats)
  - Fire debris
  - Agricultural waste

Small and mid-sized companies are investing in recycling waste materials

- Example: Rendering companies
  - http://www.valleyproteins.com/index.asp
  - Valley Proteins, one of the largest rendering companies in the United States, is now offering BioFuel, an alternative source of reliable energy made from rendered animal fat.
- www.rendermagazine.com: **"Turning Trap Grease into Fuel" (Dec. 2006)**
  - "Mike Haas, a chemist at the Agriculture Research Service (ARS) Eastern Regional Research Center in Wyndmoor, PA, is working with Philadelphia Fry-o-Diesel to demonstrate that trap grease can be converted into biodiesel.…Trap grease, the grease that restaurants and food companies collect from their drains, currently has a limited market. According to Philadelphia Fry-o-Diesel, restaurants in southeastern Pennsylvania and New Jersey collect more than **two million gallons of trap grease every month** that must be removed at a cost of about five cents per gallon. Illegal disposal and sloppy collection often lead to clogged sewers and polluted water. "

Municipal waste provides different options for biodiesel feedstocks



Grease

Bio-solids

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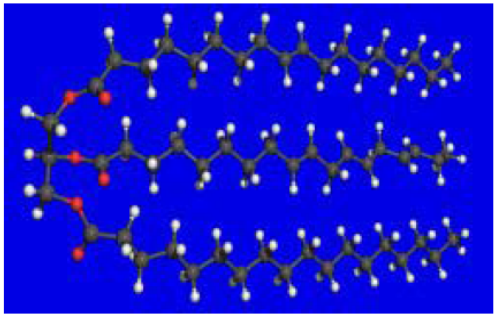
Brown Grease is removed during primary treatment

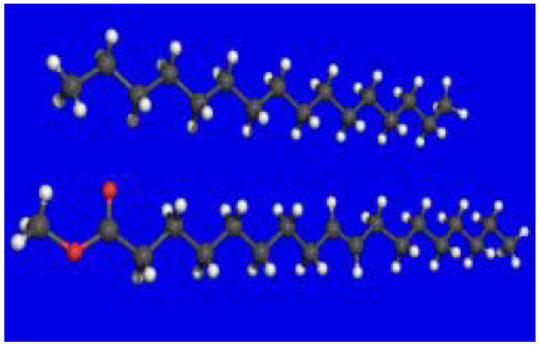
- FOG – Fat Oil Grease (http://www.nrbp.org/pdfs/pub32.pdf)
  - Floating material from primary treatment
  - Semi-solid, gelatinous
  - Mixture of triglycerides and free fatty acids
  - Free fatty acid content >20%, so not fit for animal feed

Fat molecule
(triglyceride)



"oil"

Free Fatty acids



Source of pictures:
K. Shane Tyson
NREL
June 19, 2002

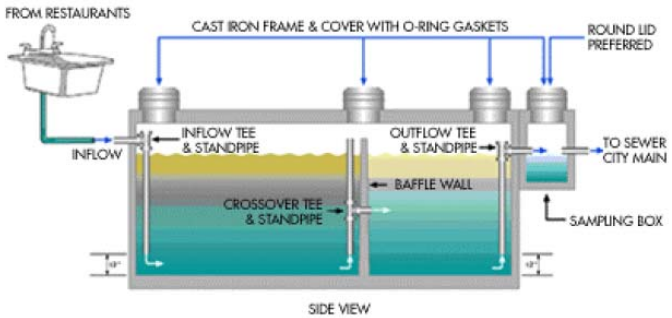
Pretreatment is less involved for brown grease than sewage sludge

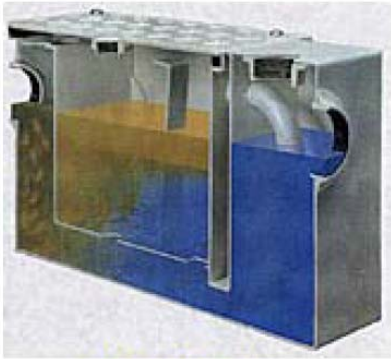
- Sewage sludge – biosolids
  - Municipal treatment facilities
  - Contains grease and waste lipids, plant micro-organisms, other organics
  - USA produces 6900 million tons dry solids/year
  - 41% spread on crop land, 17% goes to landfill, 22% incinerated (EPA 1999)
  - Heavy metals of concern: Cd, Zn, Cu, Cr, Ni, Hg
  - http://cwmi.css.cornell.edu/sewagesludge.htm

- Pretreatment requirements for sludge pretreatment are much greater than for waste oil and grease
  - Biological materials in sludge need to be broken down into fatty acids before transesterification reaction. (Peregrina et al. *J. Environmental Management* 86, 246, 2008).

NREL assessed grease sources

Grease Traps





Grease Trap

- Traps are pumped at intervals to collect grease
- Waste taken to water treatment plant or landfill (dumping fee)
- Currently, grease is burned, digested anaerobically, or composted

Environmental regulations apply to disposal of oil and grease down drains (http://www.kentcountydpw.com/oil_and_grease_interceptor_and_t.htm)

NREL assessment:

- 8.9 lbs used oil/person/year
- 13.4 lbs trap grease/person/year,
- 3.8×10^9 lbs in US/year, **equivalent to 495 million gallons biodiesel**

Source of Figure: K. Shane Tyson, NREL 2002

Composition of trap grease is different from seed oils

FFA in brown grease 50-100%
FFA in yellow grease 4-15%
FFA in seed oil 1-4%

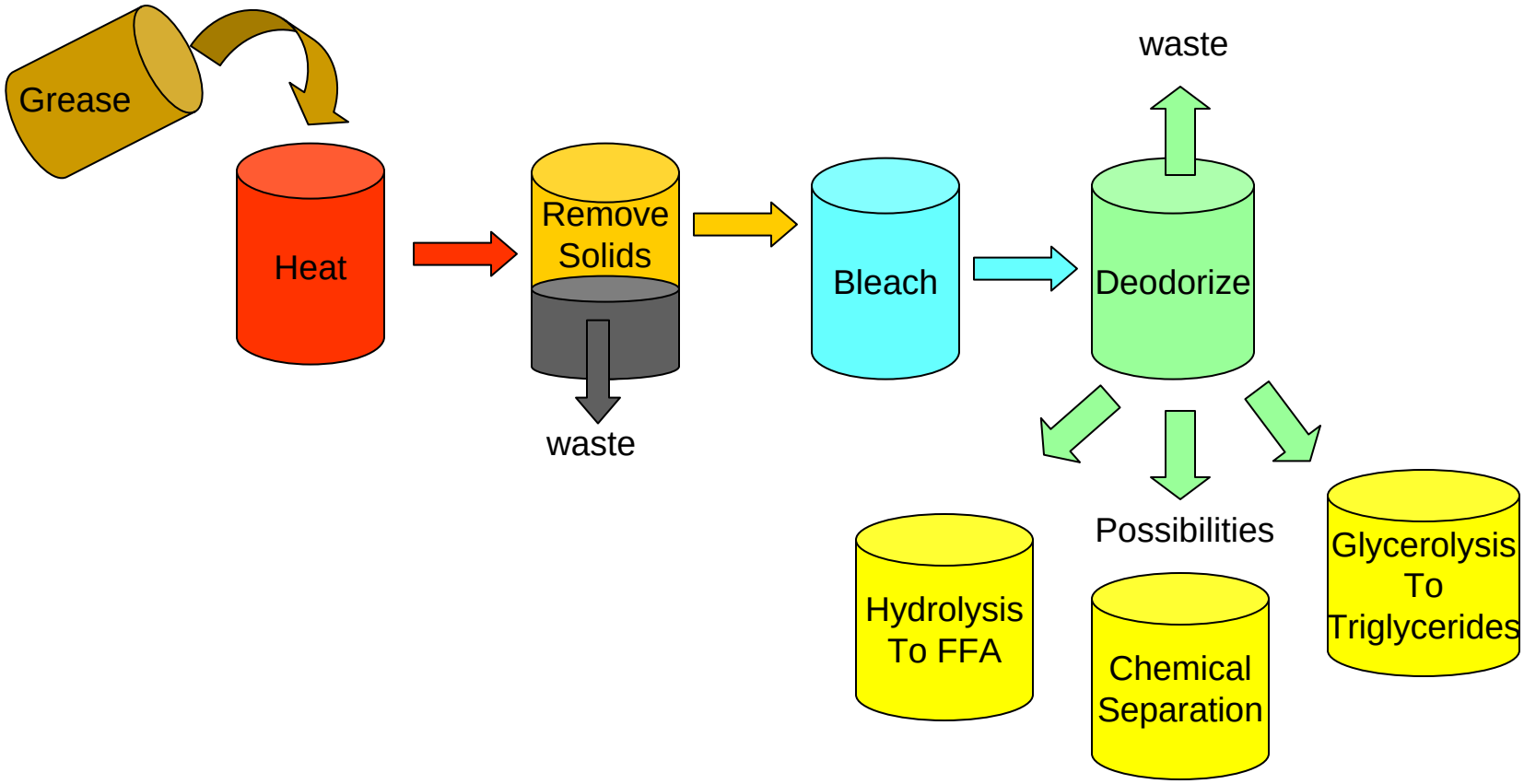
Possible contaminants
Aflatoxins, trace metals, pesticides
PAH, chlorinated compounds

	≤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

Source of Table: Tyson, NREL 2002.

Need to develop pretreatment for brown grease

- Multi-step - Will depend on source and analysis
- Can use commercial processes and devices where possible

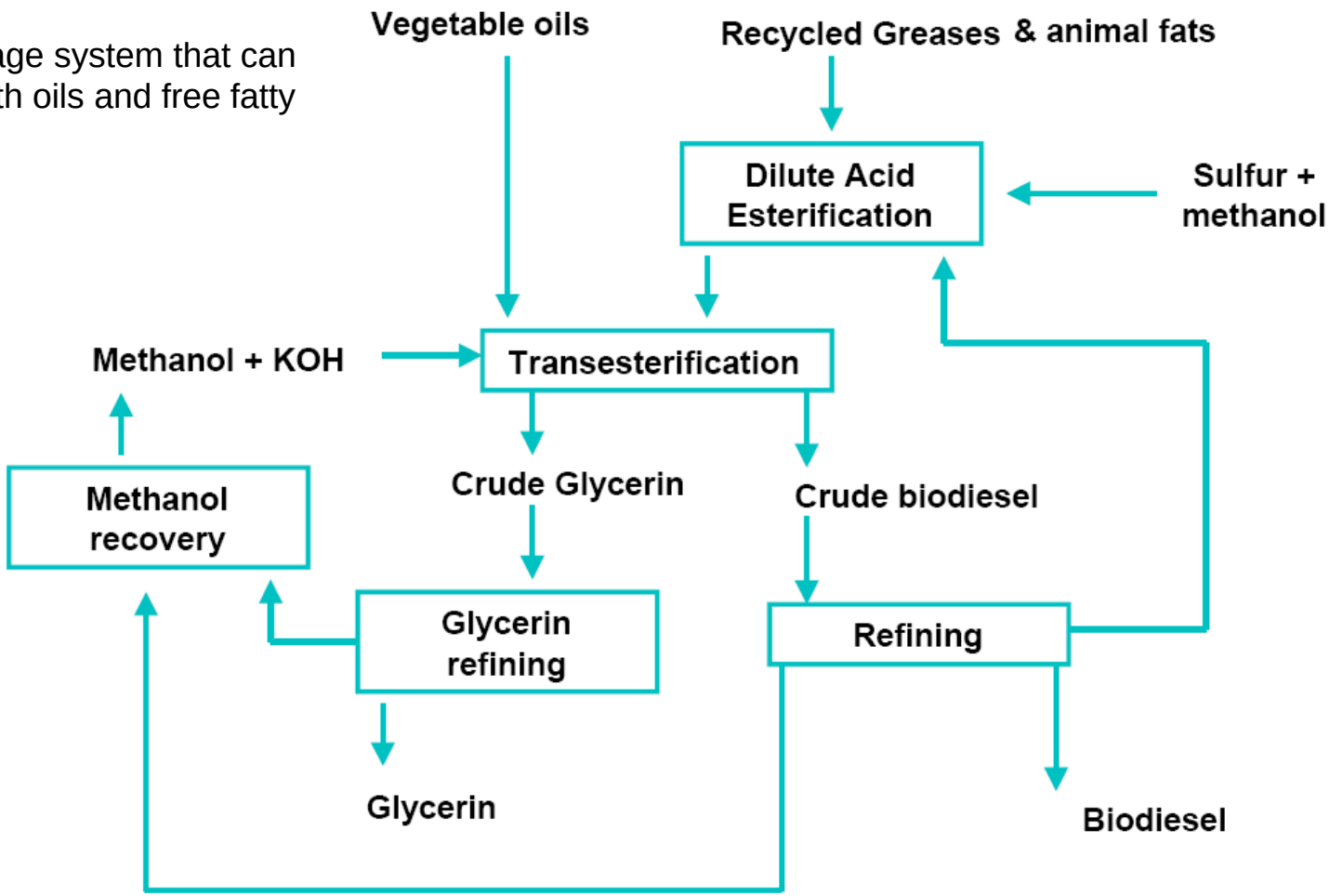


Chemical processing needed for feedstock

- Without pretreatment, free fatty acids (>4%) cause standard base-catalyzed esterification to generate too much soap from waste materials
- There is no proven technology for 50-100% FFA content
  - have to separate or convert FFA and oils
- Acid esterification process needed for FFA
  - Hot - 200-250˚C
  - High pressure - 1000kPa
  - Need acid-resistant steel vessels
  - High yields possible (99%)
  - Remove water continuously to prevent emulsions
  - pH control: Need extra base to neutralize sulfuric acid and residual FFA

Acid-Base Esterification Technology

A multi-stage system that can handle both oils and free fatty acids.



Source of Figure: K. Shane Tyson, NREL 2002

Work scope estimate to introduce brown grease feedstock into continuous-mode biodiesel production

- Characterization and analysis of feedstocks ($50k)
  - Required to develop pretreatment options
- Pretreatment: Investigation and optimization of fatty acid and triglyceride separation ($125k)
  - Minimize loss of oil, FFA into soaps, solvents and other treatment chemicals
  - Up to 10% FFA standard, but beyond that technology not optimized
- Esterification by acid catalysis and product recovery in continuous process ($75k)

Background material

Involves physical and chemical processing…

- Heat feedstock to permit flow – microwave or thermal treatment
- Solid removal
  - Counter flow filter
  - Degum with phosphoric acid and steam (to remove phosphatides)
- Bleach
  - Remove contaminants (metals, pigments), water
  - Reduce oxidation products such as peroxides
  - Absorb phospholipids
  - Remove phosphoric acid from degumming
- Deodorize by removing ketones, aldehydes, etc.
  - Current technology is vacuum distillation (240-270 deg.C, 0.3-0.8 atm)

And separation of FFA from triglycerides…

Challenge

- Solvent extraction
  - Ethanol reduces FFA in olive oil from 20% to less than 3%
  - Furfural removes FFA, also separates sat'd and unsat'd triglycerides
  - Isopropanol
  - Liquid propane extracts triglycerides (Solexol)
- Physical methods
  - steam stripping,
  - caustic refining (centrifuge separation of resulting soaps),
  - adsorption

Acid catalysis method needs to be developed for continuous production

- Without pretreatment, free fatty acids (>4%) cause standard base catalyzed esterification to generate too much soap from waste materials
- No proven technology for 50-100% FFA
- Options include
  - No separation: Multiple stages (acid and alkali catalysis)
    - Standard homogeneous catalysis for FFA to give methyl esters, and transesterify the triglyceride
  - Pretreat feedstock to hydrolyze to 100% FFA and then esterify by acid catalysis
  - Convert FFA to glycerides by glycerolysis (250-260 deg.C, 5-6 kPa, Zn catalyst)
  - Heterogeneous technologies
    - Sulfonic exchange acid resin
    - Zeolite “Y”