Making Your Own Biodiesel
David Thornton
What is Biodiesel?

- Clean Burning, Renewable, Domestically produced fuel
- Drop-in diesel replacement fuel
- Less toxic than table salt, more biodegradable than sugar
- Carbon neutral
- Made from plant oils, animal fats and other lipids
- Long Chain Fatty Acid Methyl Ester
Rudolf Diesel

- patented diesel engine in 1892 (Berlin, Germany) with Linde Enterprises
- demonstrated production scale system in 1894 (3 m height)
- demonstrated working system at World’s Fair in Paris (running on peanut oil)
- stated “the use of vegetable oils as engine fuels may seem insignificant today by such oils may become, in the course of time, as important as petroleum and coal tar products of present time.”
- Died 1913 mysteriously falling off passenger ship.
Fractional Distillation of Petroleum

- Gas: 30°C–180°C
- Naphtha: 110°C–195°C
- Kerosene: 170°C–290°C
- Heating oil: 260°C–350°C
- Lubricating oil: 300°C–370°C
- Residue

Heated crude oil at 370°C
## Major Fractions of Petroleum

<table>
<thead>
<tr>
<th>Fraction</th>
<th>Carbon Atoms*</th>
<th>Boiling Point Range (°C)</th>
<th>Uses</th>
</tr>
</thead>
<tbody>
<tr>
<td>Natural gas</td>
<td>$C_1$–$C_4$</td>
<td>−161 to 20</td>
<td>Fuel and cooking gas</td>
</tr>
<tr>
<td>Petroleum ether</td>
<td>$C_5$–$C_6$</td>
<td>30–60</td>
<td>Solvent for organic compounds</td>
</tr>
<tr>
<td>Ligroin</td>
<td>$C_7$</td>
<td>20–135</td>
<td>Solvent for organic compounds</td>
</tr>
<tr>
<td>Gasoline</td>
<td>$C_6$–$C_{12}$</td>
<td>30–180</td>
<td>Automobile fuels</td>
</tr>
<tr>
<td>Kerosene</td>
<td>$C_{11}$–$C_{16}$</td>
<td>170–290</td>
<td>Rocket and jet engine fuels, domestic heating</td>
</tr>
<tr>
<td>Heating fuel oil</td>
<td>$C_{14}$–$C_{18}$</td>
<td>260–350</td>
<td>Domestic heating and fuel for electricity production</td>
</tr>
<tr>
<td>Lubricating oil</td>
<td>$C_{15}$–$C_{24}$</td>
<td>300–370</td>
<td>Lubricants for automobiles and machines</td>
</tr>
</tbody>
</table>

* The entries in this column indicate the numbers of carbon atoms in the compounds involved. For example, $C_1$–$C_4$ tells us that in natural gas the compounds contain 1 to 4 carbon atoms, and so on.
# ASTM and EN standards

**ASTM D 6751-08**

<table>
<thead>
<tr>
<th>Property</th>
<th>Test Method</th>
<th>Specification Limits</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acid Number</td>
<td>ASTM D 664</td>
<td>0.50 maximum mgKOH/g</td>
</tr>
<tr>
<td>Calcium and Magnesium</td>
<td>EN 14538</td>
<td>5 ppm maximum</td>
</tr>
<tr>
<td>Carbon Residue</td>
<td>ASTM D 4530</td>
<td>0.050 maximum Wt %</td>
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<tr>
<td>Cetane Number</td>
<td>ASTM D 613</td>
<td>47 min</td>
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<tr>
<td>Cloud Point</td>
<td>ASTM D 2500</td>
<td>Report in °C</td>
</tr>
<tr>
<td>Cold Soak Filterability</td>
<td>ASTM Annex A1</td>
<td>360 max F Seconds</td>
</tr>
<tr>
<td>Copper Strip Corrosion</td>
<td>ASTM D 130</td>
<td>No. 3 maximum</td>
</tr>
<tr>
<td>Distillation-Atmospheric</td>
<td>ASTM D 1160</td>
<td>360 maximum °C</td>
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<tr>
<td>Equivalent Temperature 90%</td>
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<tr>
<td>Flash Point</td>
<td>ASTM D 93</td>
<td>130 minimum °C</td>
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<tr>
<td>Glycerin – Free</td>
<td>ASTM D 6584</td>
<td>0.020 maximum Wt %</td>
</tr>
<tr>
<td>Glycerin – Total</td>
<td>ASTM D 6584</td>
<td>0.240 maximum Wt %</td>
</tr>
<tr>
<td>Kinematic Viscosity - 40°C</td>
<td>ASTM D 445</td>
<td>1.9 – 6.0 mm²</td>
</tr>
<tr>
<td>Methanol Content</td>
<td>EN 14110</td>
<td>0.20 maximum Wt %</td>
</tr>
<tr>
<td>Oxidation Stability</td>
<td>EN 14112</td>
<td>3 hours minimum</td>
</tr>
<tr>
<td>Phosphorus Content</td>
<td>ASTM D 4951</td>
<td>0.001 Wt % or 10 ppm</td>
</tr>
<tr>
<td>Sodium and Potassium</td>
<td>EN 14538</td>
<td>5.00 ppm maximum</td>
</tr>
<tr>
<td>Sulfate Ash</td>
<td>ASTM D 874</td>
<td>0.020 maximum Wt %</td>
</tr>
<tr>
<td>Sulfur (S15)</td>
<td>ASTM D 5453</td>
<td>15.0 ppm maximum</td>
</tr>
<tr>
<td>Sulfur (S500)</td>
<td>ASTM D 5453</td>
<td>500 ppm maximum</td>
</tr>
<tr>
<td>Water and Sediment</td>
<td>ASTM D 2709</td>
<td>0.050 maximum Vol. %</td>
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</tbody>
</table>

**EN 14214 – 03**

<table>
<thead>
<tr>
<th>Property</th>
<th>Test Method</th>
<th>Specification Limits</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acid Number</td>
<td>EN 14104</td>
<td>0.50 mgKOH/g maximum</td>
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<tr>
<td>Carbon residue (10% Etchons)</td>
<td>EN ISO 10370</td>
<td>0.30 % (m/m) maximum</td>
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<tr>
<td>Cetane Number</td>
<td>EN ISO 5165</td>
<td>51.0 minimum</td>
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<tr>
<td>Copper Strip Corrosion 1hr @ 50°C</td>
<td>EN ISO 2160</td>
<td>Class 1 rating</td>
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<tr>
<td>Density @ 15°C</td>
<td>EN ISO 3675, EN</td>
<td>860.900 Kg/m²</td>
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<tr>
<td>Ester Content</td>
<td>EN 14103</td>
<td>96.5 % (m/m) minimum</td>
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<tr>
<td>Flash Point</td>
<td>ISO/CD 3679</td>
<td>Above 101°C minimum</td>
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<tr>
<td>Glycerol – Free</td>
<td>EN 14105, EN 14106</td>
<td>0.02 % (m/m) maximum</td>
</tr>
<tr>
<td>Glycerol – Total</td>
<td>EN 14109</td>
<td>0.25 % (m/m) maximum</td>
</tr>
<tr>
<td>Monoglyceride Content</td>
<td>EN 14105</td>
<td>0.80 % (m/m) maximum</td>
</tr>
<tr>
<td>Diglyceride Content</td>
<td>EN 14108</td>
<td>0.20 % (m/m) maximum</td>
</tr>
<tr>
<td>Triglyceride Content</td>
<td>EN 14105</td>
<td>0.20 % (m/m) maximum</td>
</tr>
<tr>
<td>Iodine Value</td>
<td>EN 14111</td>
<td>120 maximum</td>
</tr>
<tr>
<td>Linoleic acid methyl ester</td>
<td>EN 14103</td>
<td>12 % (m/m) maximum</td>
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<tr>
<td>Methanol Content</td>
<td>EN 14110</td>
<td>0.20 % (m/m) maximum</td>
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<tr>
<td>Oxidation Stability @ 110°C</td>
<td>EN 14112</td>
<td>6 hours minimum</td>
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<tr>
<td>Phosphorus Content</td>
<td>EN 14107</td>
<td>10.0 mg/Kg maximum</td>
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<tr>
<td>Polysaturated (4-4 double bonds) methyl esters</td>
<td></td>
<td>1.00 % (m/m) maximum</td>
</tr>
<tr>
<td>Sodium and Potassium</td>
<td>EN 14108, EN 14109</td>
<td>5.00 mg/Kg maximum</td>
</tr>
<tr>
<td>Sulfate Ash Content</td>
<td>ISO 3987</td>
<td>0.02 % (m/m) maximum</td>
</tr>
<tr>
<td>Sulfur</td>
<td>ASTM D 5453 or other total sulfur method</td>
<td>10 mg/Kg maximum</td>
</tr>
<tr>
<td>Total Contamination</td>
<td>EN 12662 (ASTM D 5452)</td>
<td>24.0 mg/Kg maximum</td>
</tr>
<tr>
<td>Viscosity @ 40°C</td>
<td>EN ISO 310</td>
<td>3.50 – 5.00 mm²</td>
</tr>
<tr>
<td>Water Content</td>
<td>EN ISO 12937</td>
<td>500 mg/Kg maximum</td>
</tr>
</tbody>
</table>
Energy Balance

Biodiesel versus Petroleum Diesel Fuel
• Diesel 0.843 (15.7 percent loss)
• Biodiesel (soy) 5.50 (450 percent gain)

Gasoline versus Ethanol
• Gasoline 0.805 (19.5 percent loss)
• Ethanol (corn) 1.34 (34 percent gain)
NOT SUSTAINABLE
List of Raw Materials

- **Oil or Fat**
  - Soy
  - Canola
  - Cottonseed
  - Poultry Fat
  - Beef Tallow
  - Pork Lard
  - Restaurant Grease

- **Alcohol**
  - Methanol
  - Ethanol
  - Isopropanol
  - Butanol

- **Catalyst**
  - Sodium Hydroxide
  - Potassium Hydroxide
  - Enzymes
Transesterification

• **Ester** – an alcohol reacted with an acid

• **Transesterification** – swapping the alcohol that is bonded to the fatty acid

• When making biodiesel, we are typically replacing the glycerol with methanol in a **transesterification** reaction
Transesterification

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

Vegetable oil molecule (Triglyceride)

FFA combines with alcohol molecule to make an alkyl ester (Biodiesel)

Steam from cooking foods, salts, chemicals, and heat break chains off triglycerides to produce FFAs
Transesterification

One triglyceride molecule is converted into three mono-alkyl-ester (biodiesel) molecules.
Step 1: Catalyst generates active species

\[
\text{CH}_3\text{OH} + \text{KOH} \rightarrow \text{CH}_3\text{OK}^+ + \text{H}_2\text{O}
\]

Potassium methoxide salt

Step 2: Active species reacts with triglyceride

\[
\text{triglyceride} + \text{CH}_3\text{OK} \rightleftharpoons \text{diglyceride salt} + \text{fatty acid methyl ester}
\]

Step 3: Active species regenerated

\[
\text{diglyceride salt} + \text{CH}_3\text{OH} \rightleftharpoons \text{diglyceride} + \text{potassium methoxide}
\]
Steps 2-3 repeat for remaining glycerides

\[
\text{diglyceride} + \text{CH}_3\text{OK} \rightleftharpoons \text{monoglyceride} + \text{fatty acid methyl ester}
\]

\[
\text{monoglyceride} + \text{CH}_3\text{OK} \rightleftharpoons \text{glycerol} + \text{fatty acid methyl ester}
\]
Hydrolysis is a chemical reaction during which one or more water molecules are split into hydrogen and hydroxide ions which may go on to participate in further reactions

\[ R\text{-COOCH}_3 + H_2O \rightarrow R\text{-COOH} + CH_3OH \quad (R = \text{alkyl}) \]

methyl ester + water → fatty acid + methanol

Excess water in a biodiesel reaction greatly reduces potential yield as well as conversion quality. Feedstocks should have under 1% water in them prior to transesterification.
Saponification

• **Saponification** is the hydrolysis of an ester under basic conditions to form an alcohol and the salt of a carboxylic acid. Saponification is commonly used to refer to the reaction of a metallic alkali (base) with a fat or oil to form soap. Saponifiable substances are those that can be converted into soap.

\[
\begin{align*}
\text{R-COOH} & \quad + \quad \text{KOH} \quad \rightarrow \quad \text{R-COOK} \quad + \quad \text{H}_2\text{O} \\
\text{Fatty acid} & \quad \text{Potassium hydroxide} \quad \text{Potassium soap} \quad \text{Water}
\end{align*}
\]

• Soap is created when free fatty acids in the oil combine with the caustic. Water is created as a by-product of this reaction which can then hydrolyze more oil creating more free fatty acids.

• Soap is an emulsifier – it is hydrophobic on one end and hydrophilic on the other.

• Excess soap can prevent the separation of glycerol from the oil.
Esterification

- **Esterification** is the general name for a chemical reaction in which two reactants (typically an alcohol and an acid) form an ester as the reaction product.

\[ \text{Fatty acid} + \text{CH}_3\text{OH} \rightarrow \text{R-COOC_2H}_3 + \text{H}_2\text{O} \]

- Esterification (aka acid pretreatment) can be used to treat high FFA oils. The FFA’s are converted to methyl esters (biodiesel) and then the remaining oil is transesterified. This process results in greatly increased yields, although it increases the complexity of the process.
Lipids – Fats & Oils

- **Lipids** are broadly defined as any fat-soluble (lipophilic), naturally-occurring molecule, such as fats, oils, waxes, cholesterol, sterols, fat-soluble vitamins (such as vitamins A, D, E and K), monoglycerides, diglycerides, phospholipids, and others.

  - Sources of lipids include:
    - Vegetable oils such as canola, soybean, and palm.
    - Rendered animal products - beef, chicken, and pig fat.
    - Used cooking oils – yellow and brown grease.

- “Fats” generally means solid at room temperature
- “Oils” generally means liquid at room temperature
Oil Processing

• Vegetable oils are obtained by the extraction or the expression of the oil from the oilseed source.
  – Historically, cold or hot expression methods were used. These methods have largely been replaced with solvent extraction which gives a better oil yield.
  – <100,000kg/day = mechanical extraction
  – >300,000kg/day = solvent extraction

  – Oil is extracted from the oilseed by hexane (a light petroleum fraction) and the hexane is then separated from the oil, recovered, and reused. Because of its high volatility, hexane does not remain in the finished oil after processing.

• The fats and oils obtained directly from rendering or from the extraction of the oilseeds are termed “crude” fats and oils.

https://www.youtube.com/watch?v=iCXvwElG9iY
Oil Processing

- **Crushing** - breaks cell membranes retaining the oil
- **Expelling** - extraction of the oil from the meal (mechanical or solvent)
- **Degumming**
  - treating the crude oil with a limited amount of water to hydrate the phosphatides and make them separable by centrifuge. Soybean oil is the most common oil to be degummed
- **Refining**
  - treating of the fat or oil with an alkali/water solution. This results in a large reduction of free fatty acids through their conversion into soaps
- **Bleaching**
  - adsorption of the color producing substances on an adsorbent material. Acid-activated bleaching earth or clay, sometimes called bentonite, is the adsorbent material that has been used most extensively for removal of soaps, metals, phosphatides and sulfur compounds
- **Deodorization** - a vacuum steam distillation process for the purpose of removing trace constituents that give rise to undesirable flavors, colors and odors in fats and oils.
Oil Processing

• Before oil can be extracted:
• Stems and seeds are removed by sifting/cleaning
• Metals are removed by magnets
• Extruder compresses seeds to produce heat to denature unwanted enzymes
• Moisture is reduced to < 10% for good extraction (too high = high solids content, too low burns the meal)
Overview of Oil Crops for the South East

1st Place = Sunflower and Canola

2nd Place = Soy .... ¿ Soy Biodiesel? 
...(I am biodiesel?)

3rd = Oilseed radish and high glucosinolate brassicas for the future!!!

....Niche markets? Grapeseed, Chinese Tallow Seed, Pumpkins, Watermelon? ...insects, fungi, algae?
Clemson Organic Testplot

In this study Mid Oleic NuSun sunflower seed was used to test low nutrient input production of potentially organic sunflower. The test plot consisted of (3) 210 ft rows spaced 12 inches apart with seed spacing (4) inches apart and planted 1.5 inches deep using an Earthway walk behind seeder with sweet corn seeding implement. The minimum 70 units of nitrogen equivalent per acre was achieved using a cover crop of red clover prior to planting. No herbicide, pesticide, fungicide or additional fertilizer was used and the plot was not irrigated. The plot yielded 52 lbs of cleaned seed, with 10.9 lbs of refined sunflower oil and 38 lbs of pelletized meal utilizing a quarter ton Swedish Tabby Press. On a per acre equivalent this yield equals 99.3 gallons of refined oil (washed with warm water to remove hydratable gums and sediment, dried, and filtered to .5 micron) and 1.3 tons of meal (hull in).
Drying, Threshing, Cleaning
Drawbacks of Sunflower?

- Shares Many Pests with Soy
- Recommended 2-3 years between planting again
- ...will we saturate the market? How much sunflower can we possibly consume in the Carolinas?
- Ever tried some?
- Where will we crush it?
Canola? Is that Rapeseed?

- NO!!!!!!!!!! It’s better!
- Thank you Canada
- We can eat the meal?
- How do I harvest?
Table 3. Canola Processing Costs of 20 acre scale Capital Costs

- Seed storage (super sacks) $300
- Oil press $18,000
- Frame, hopper $200
- 4-110 gallon cone bottom tanks $800
- Fittings, valves, pumps, and filters $550
- Meal storage (covered concrete pad) $150
- Total Capital Cost $20,000
- Annualized Capital Cost $2,981

Operating Costs
- Cost of feedstock $4,600
- Labor $2385
- Electricity $288
- Annual maintenance $500
- Overhead $317
- Total Operating Cost $7,773
- Total Processing Cost $10,754
- Annual (Operating) Cost / Gallon of Crude Oil $7.31

Returns
- Canola meal $2,880
- Net Processing Cost $6,624
- Annual Net (Operating) Cost / Gallon of Crude Oil $5.34
Seed storage (5,550-bu. corrugated metal bin w/ ladders, roof, 3-HP fan, concrete pad, floor sweep) $27,415
Oil press $18,000
Frame, hopper $1,100
Filter press $16,500
Unfiltered oil storage (1,000-gallon cone-bottomed tank) $1,700
Filtered oil storage (10 250-gallon storage cubes) $5,400
Meal storage: concrete pad $1,100
Meal storage: tarps $650
Automation system: 100-amp service, wiring, controls $7,500
Grain auger $850
Meal conveyor $1,250
Fittings, valves, pumps, filters $2,200
Total Capital Cost $83,665
Annualized Capital Cost $12,469

Operating Costs
Cost of feedstock $28,980
Labor $3,150
Electricity $2,268
Annual maintenance $2,092
Overhead $750
Total Operating Cost $37,240
Total Processing Cost $49,709
Annual (Operating) Cost / Gallon of Crude Oil $5.35

Returns
Canola meal $18,144
Net Processing Cost $31,565
Annual Net (Operating) Cost / Gallon of Crude Oil $3.40
What do we need to try?

Camelina

Oilseed radish
More on Mustard:


http://www.farmfuelinc.com/

http://www.oilpress.com/
Black Soldier Fly Production from Cafeteria Food Waste

• This project began April 2012 as a collaboration between Student Organic Farm Manager Shawn Jadrnicek and BE Research Associate David Thornton Via a creative inquiry section on Creating Value Added Co-products from Waste
This group has constructed a biodigester utilizing BSF larvae to process 500 lbs of food waste per week.
Why BSF?

- *Hermetia illuscens*, ubiquitous throughout North America, are voracious consumers of nitrogen-dominant decaying materials, such as kitchen food scraps or manures.
- Dried pre-pupae contain 42% protein and 35% fat, and as a component of a complete diet they can provide an excellent feed for chicks, swine, rainbow trout and catfish.
- BSF have been demonstrated to digest over 15 kilograms per day of waste per square meter of feeding surface area per day.
Integrated BSF Process

Brewery and food waste is loaded into the digester

Mature larvae are harvested

Compost harvested from the digester is used
To plant energy crops and beer crops

An expeller is used to separate oils for biodiesel, and meal pellets as livestock feed
# Analysis of BSF Meal Pellets

*VALUES CALCULATED FROM CURRENT RESEARCH FORMULAS*

**MINERAL ANALYSIS**

<table>
<thead>
<tr>
<th></th>
<th>CALCULATED AS-SAMPLED</th>
<th>100PERCENT DRY-MATTER</th>
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</thead>
<tbody>
<tr>
<td>P</td>
<td>0.58 %</td>
<td>0.59 %</td>
</tr>
<tr>
<td>K</td>
<td>0.91 %</td>
<td>0.93 %</td>
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<tr>
<td>Ca</td>
<td>5.53 %</td>
<td>5.66 %</td>
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<tr>
<td>Mg</td>
<td>0.36 %</td>
<td>0.36 %</td>
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<tr>
<td>S</td>
<td>0.34 %</td>
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<td>Zn</td>
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<td>Cu</td>
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<td>Mn</td>
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<td>Fe</td>
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<td>Na</td>
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<td>Ca/P</td>
<td>9.53</td>
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**OTHER ANALYSES**

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<th>CALCULATED AS-SAMPLED</th>
<th>100PERCENT DRY-MATTER</th>
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<td>FAT</td>
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<td>NO3-N</td>
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<td>ppm</td>
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<td>ASH</td>
<td>%</td>
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<tr>
<td>Chloride</td>
<td>%</td>
<td>%</td>
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<tr>
<td>Selenium</td>
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<td>pH(SILAGE)</td>
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<tr>
<td>MOISTURE</td>
<td>2.2 %</td>
<td>97.8 %</td>
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<td>DRY MATTER</td>
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**CRUDE PROTEIN**

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<th>CALCULATED AS-SAMPLED</th>
<th>100PERCENT DRY-MATTER</th>
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<tbody>
<tr>
<td></td>
<td>41.1 %</td>
<td>42.1 %</td>
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## COMPOST ANALYSIS

<table>
<thead>
<tr>
<th></th>
<th>Wet Basis</th>
<th>Dry Basis</th>
<th>lbs/ton Wet Basis</th>
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<tbody>
<tr>
<td>Ammonium Nitrogen</td>
<td>0.04 %</td>
<td>0.18 %</td>
<td>0.80</td>
</tr>
<tr>
<td>Total Nitrogen</td>
<td>0.84 %</td>
<td>3.79 %</td>
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<tr>
<td>Carbon</td>
<td>9.41 %</td>
<td>42.64 %</td>
<td>188.25</td>
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<tr>
<td>Carbon:Nitrogen (C:N) Ratio</td>
<td>11.25</td>
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<tr>
<td>Phosphorus as P2O5</td>
<td>0.50 %</td>
<td>2.25 %</td>
<td>9.95</td>
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<tr>
<td>Potassium as K2O</td>
<td>0.67 %</td>
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<tr>
<td>Calcium</td>
<td>1.30 %</td>
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<tr>
<td>Magnesium</td>
<td>0.08 %</td>
<td>0.38 %</td>
<td>1.66</td>
</tr>
<tr>
<td>Sulfur</td>
<td>0.14 %</td>
<td>0.65 %</td>
<td>2.87</td>
</tr>
<tr>
<td>Zinc</td>
<td>31 ppm</td>
<td>141 ppm</td>
<td>0.06</td>
</tr>
<tr>
<td>Copper</td>
<td>8 ppm</td>
<td>36 ppm</td>
<td>0.02</td>
</tr>
<tr>
<td>Manganese</td>
<td>30 ppm</td>
<td>134 ppm</td>
<td>0.06</td>
</tr>
<tr>
<td>Iron</td>
<td>808 ppm</td>
<td>3662 ppm</td>
<td>1.62</td>
</tr>
<tr>
<td>Sodium</td>
<td>991 ppm</td>
<td>4491 ppm</td>
<td>1.98</td>
</tr>
<tr>
<td>Aluminum</td>
<td>1176 ppm</td>
<td>5327 ppm</td>
<td>2.35</td>
</tr>
<tr>
<td>Organic Matter (LOI)</td>
<td>15.65 %</td>
<td>70.90 %</td>
<td>312.99</td>
</tr>
</tbody>
</table>

| EC (Soluble Salts)        | 12.48 mmhos/cm |
| pH                        | 6.9           |
Reactions of Fats & Oils

• **Hydrolysis**
  – Glycerides can be hydrolyzed readily, breaking down the triglycerides
  – With water and an acid catalyst, the mono-, di-, and triglycerides will hydrolyze to yield glycerol and free fatty acids
  – With water and a base (like sodium hydroxide), glycerol and soaps are made

• **Oxidation**
  – Autoxidation occurs at room temperature over time and causes rancidity
  – Oxidation occurs faster at higher temperatures
  – Occurs more rapidly with unsaturated oils due to the breaking of a double bond and the addition of oxygen

• **Polymerization**
  – Fats and oils (particularly those high in polyunsaturated fatty acids) tend to form larger molecules (known broadly as polymers) when heated under extreme conditions of temperature and time.
  – Under normal processing and cooking conditions, polymers are formed in insignificant quantities.
  – When an appreciable amount of polymer is present, there is a marked increase in viscosity.
Vegetable Oils

- **Palm**: currently most abundant.
  - Palm kernel oil extracted from the seed kernel
  - Palm Oil is extracted from the seed pulp
  - Semi-solid at room temp
- **Soy**: co-product of soy meal production
  - Most common in the U.S.
  - Extracted and Expeller pressed
  - Excellent cold flow characteristics
- **Rapeseed**: primary feedstock in Europe
  - High in inedible erucic acid
  - Used in high performance lubricants, corrosion inhibitors, biodiesel
  - Canola oil is a low erucic acid oil derived from the rape family.
- **Corn Oil**: co-product of corn wet milling.
  - Similar properties to soy bean oil
  - More expensive than soy bean oil
  - In SC, cottonseed, sunflower, and peanut may also be good feedstock
Fatty Acid Profile

Physical performance of the oil

- Cold flow, Viscosity, Ox stability, Cetane

- **Free Fatty Acid Content** -
  - Key factor in determining the degree of processing required.

- **Acid Number** - The number of miligrams of KOH required to saponify the FFA’s in 1g of oil or fat.
  
  1 unit of acid number = 0.503 %FFA (assuming oleic)
Major Component - Triglycerides

- One unit of glycerol and three units of fatty acids
- Insoluble in water, but soluble in most organic solvents
- Lower density than water – typically 7.6 lbs/gal vs 8.3 lbs/gal for water
- Triglycerides are an ester – i.e. the condensation product of an alcohol and an acid
Fatty Acids

- Lipids are mostly made of fatty acids ~95% by weight
- Both the physical and chemical properties of the fat or oil are greatly influenced by the kinds and proportions of fatty acids present
- **Saturated Fatty Acids** are those containing only single carbon-to-carbon bonds
- **Unsaturated Fatty Acids** are those containing one (or more) double carbon-to-carbon bonds
Saturated, Unsaturated, & Polyunsaturated Fatty Acids

- arachidic
- stearic
- palmitic
- erucic
- oleic
- arachidonic
- linoleic
- linolenic
# Saturated Fatty Acids

## TABLE II

<table>
<thead>
<tr>
<th>Systematic Name</th>
<th>Common Name</th>
<th>No. of Carbon Atoms*</th>
<th>Melting Point °C</th>
<th>Typical Fat Source</th>
</tr>
</thead>
<tbody>
<tr>
<td>Butanoic</td>
<td>Butyric</td>
<td>4</td>
<td>-7.9</td>
<td>Butterfat</td>
</tr>
<tr>
<td>Hexanoic</td>
<td>Caproic</td>
<td>6</td>
<td>-3.4</td>
<td>Butterfat</td>
</tr>
<tr>
<td>Octanoic</td>
<td>Caprylic</td>
<td>8</td>
<td>16.7</td>
<td>Coconut oil</td>
</tr>
<tr>
<td>Decanoic</td>
<td>Capric</td>
<td>10</td>
<td>31.6</td>
<td>Coconut oil</td>
</tr>
<tr>
<td>Dodecanoic</td>
<td>Lauric</td>
<td>12</td>
<td>44.2</td>
<td>Coconut oil</td>
</tr>
<tr>
<td>Tetradecanoic</td>
<td>Myristic</td>
<td>14</td>
<td>54.4</td>
<td>Butterfat, coconut oil</td>
</tr>
<tr>
<td>Hexadecanoic</td>
<td>Palmitic</td>
<td>16</td>
<td>62.9</td>
<td>Most fats and oils</td>
</tr>
<tr>
<td>Heptadecanoic</td>
<td>Margaric</td>
<td>17</td>
<td>60.0</td>
<td>Animal fats</td>
</tr>
<tr>
<td>Octadecanoic</td>
<td>Stearic</td>
<td>18</td>
<td>69.6</td>
<td>Most fats and oils</td>
</tr>
<tr>
<td>Eicosanoic</td>
<td>Arachidic</td>
<td>20</td>
<td>75.4</td>
<td>Peanut oil</td>
</tr>
<tr>
<td>Docosanoic</td>
<td>Behenic</td>
<td>22</td>
<td>80.0</td>
<td>Peanut oil</td>
</tr>
</tbody>
</table>

*A number of saturated odd and even chain acids are present in trace quantities in many fats and oils.
### TABLE III

**SOME UNSATURATED FATTY ACIDS IN FOOD FATS AND OILS**

<table>
<thead>
<tr>
<th>Systematic Name</th>
<th>Common Name</th>
<th>No. of Double Bonds</th>
<th>No. of Carbon Atoms</th>
<th>Melting Point °C</th>
<th>Typical Fat Source</th>
</tr>
</thead>
<tbody>
<tr>
<td>9-Decenoic</td>
<td>Caproleic</td>
<td>1</td>
<td>10</td>
<td>-</td>
<td>Butterfat</td>
</tr>
<tr>
<td>9-Dodecanoic</td>
<td>Lauroleic</td>
<td>1</td>
<td>12</td>
<td>-</td>
<td>Butterfat</td>
</tr>
<tr>
<td>9-Tetradecenoic</td>
<td>Myristoleic</td>
<td>1</td>
<td>14</td>
<td>-4.5</td>
<td>Butterfat</td>
</tr>
<tr>
<td>9-Hexadecenoic</td>
<td>Palmitoleic</td>
<td>1</td>
<td>16</td>
<td>-</td>
<td>Some fish oils, beef fat</td>
</tr>
<tr>
<td>9-Octadecenoic</td>
<td>Oleic</td>
<td>1</td>
<td>18</td>
<td>16.3</td>
<td>Most fats and oils</td>
</tr>
<tr>
<td>9-Octadecenoic*</td>
<td>Elaidic</td>
<td>1</td>
<td>18</td>
<td>43.7</td>
<td>Partially hydrogenated oils</td>
</tr>
<tr>
<td>11-Octadecenoic*</td>
<td>Vaccenic</td>
<td>1</td>
<td>18</td>
<td>44</td>
<td>Butterfat</td>
</tr>
<tr>
<td>9,12-Octadecadienoic</td>
<td>Linoleic</td>
<td>2</td>
<td>18</td>
<td>-6.5</td>
<td>Most vegetable oils</td>
</tr>
<tr>
<td>9,12,15-Octadecatrienoic</td>
<td>Linolenic</td>
<td>3</td>
<td>18</td>
<td>-12.8</td>
<td>Soybean oil, canola oil</td>
</tr>
<tr>
<td>9-Eicosenoic</td>
<td>Gadoleic</td>
<td>1</td>
<td>20</td>
<td>-12.8</td>
<td>Some fish oils</td>
</tr>
<tr>
<td>5,8,11,14-Eicosatetraenoic</td>
<td>Arachidonic</td>
<td>4</td>
<td>20</td>
<td>-49.5</td>
<td>Lard</td>
</tr>
<tr>
<td>5,8,11,14,17-Eicosapentaenoic</td>
<td>Erucic</td>
<td>5</td>
<td>20</td>
<td>-53.5</td>
<td>Some fish oils</td>
</tr>
<tr>
<td>13-Docosenoic</td>
<td>Erucic</td>
<td>1</td>
<td>22</td>
<td>33.4</td>
<td>Rapeseed oil</td>
</tr>
<tr>
<td>4,7,10,13,16,19-Docosahexaenoic</td>
<td>-</td>
<td>6</td>
<td>22</td>
<td>-</td>
<td>Some fish oils</td>
</tr>
</tbody>
</table>

*All double bonds are in the *cis* configuration except for elaidic acid and vaccenic acid which are *trans*.

---

![Fatty Acid Structures](image-url)

- **oleic (18:1)**
- **linoleic (18:2)**
- **linolenic (18:3)**
- **arachidonic (20:4)**
- **erucic (22:1)**
Appleseed Biodiesel Reactor
Utahbiodieselsupply.com
Transesterification

Heat

Time \quad Agitation
Biodiesel Process Design

Settling Tanks

Ion-exchange columns

Reactor

Finished Biodiesel

Methanol Mix Tank

Glycerin Recovery Tank

Gravy

Filter

Flow control pump

Flow meter

Biofuel, methanol, KOH added
- Insulated and heated
- Mixed through cavitation
- Reacted for 1-2 hours

MeOHCH3OH + KOH
- 50 gal

Glycerin processing
- 50 gal

FINISHED BIODIESEL

ION-EXCHANGE COLUMNS

FILTER

Biodiesel
Process Review

• Feedstock Treatment
• Transesterification
• Washing
  - Wet
  - Dry
• Drying
• Methanol Recovery

• Quality Control Testing
• Acid Esterification
• Caustic Stripping
• Safety Concerns – Lab, Equipment, Chemicals (15 min)
Home Quality Testing

• Feedstock
  – Less than 7% FFA (using acid value titration)
  – less than 5000 ppm moisture (using Sandy Brae)

Finished Fuel
- Passes 27/3 (27mL methanol, 3mL biodiesel)
- moisture test (Sandy Brae)
- Water Test (50/50 mix water in biodiesel)
- soap test (Soap Titration)
Additional Resources

- Utahbiodieselsupply.com
- https://www.youtube.com/user/clemsonbiofuels