BIODIESEL LAB EXERCISE WITH HYDROGEN ENRICHMENT

Developed for the 2012 SEET Workshop

ATEEC

COLORADO SCHOOL OF MINES
EARTH • ENERGY • ENVIRONMENT

NSF

THE CREW

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THE CREW
HARLEY-DAVIDSON
Hard Rock

A BRIEF HISTORY

- 1853: First transesterification of a vegetable oil
  - Conversion of fat into diesel
  - Use of an alcohol (such as ethanol or methanol) in the presence of a catalyst (like sodium hydroxide or potassium hydroxide) to chemically break the molecule of the raw renewable oil into methyl or ethyl esters
  - Creates glycerol by-product
- 1893: First biodiesel-powered vehicle—Rudolf Diesel, Augsburg, Germany
  - Prime model: a single 10-ft iron cylinder with a flywheel at base
  - 1900: Received Grand Prix award in Paris for engine powered by peanut oil
  - 1912: Believed that the utilization of a biomass fuel was the future of his engine—“The use of vegetable oils for engine fuels may seem insignificant today, but such oils may become, in the course of time, as important as petroleum and the coal-tar products of the present time."

BIODIESEL BASICS

NOTE: This presentation will begin with biodiesel basics, and will conclude with two excellent videos of actual engine performance testing using various blends of fuel, and with hydrogen enrichment. Procedures and videos for making biodiesel and titration are included in supplementary materials that will be available as pdfs on the ATEEC Web site (http//ateec.org/ateec-downloads) in Oct.

- Biodiesel can be manufactured from several base stocks, including:
  - Waste vegetable oil (WVO)
  - Virgin oils—peanut, canola, soybean, etc.
  - Waste organic products, switchgrass, wood chips
  - Algae

- For this project, we focus on WVO:
  - Easily obtained from your school cafeteria
  - Prevents oil from entering waste stream
  - Converts waste oil into a useful product.

SOURCE OF FEEDSTOCK

- Yellow grease (recycled)
  - 2.75 billion pounds
- Soy bean oil
  - 11 billion pounds
- Animal fats (Byproduct)
  - 17 billion pounds

SOURCE OF FEEDSTOCK (cont.)

- Yellow grease (recycled)
  - Advantages
    - Cheaper than soybean oil
    - Waste oil source
  - Disadvantages
    - Limited quantities (100 million gallons of biodiesel)
    - U.S. diesel consumption 37 billion gallons

SOURCE OF FEEDSTOCK (cont.)

- Animal fats
  - Advantages
    - Animal processing waste product
  - Disadvantages
    - Solidification at low temperatures
    - Fuel contaminations

SOURCE OF FEEDSTOCK (cont.)

- Soy bean oil (Primary U.S. feedstock)
  - Advantages
    - Large supply
    - Local economy and jobs

  - Disadvantages
    - Uses food production resources
    - Food demand is expected to increase
    - Agricultural environmental damage

AGRICULTURAL ENVIRONMENTAL DAMAGE

- Climate Change
- Deforestation
- Ground Erosion
- Chemical use
  - Fertilizer – limited supply
  - Petroleum products – limited supply
  - Pesticides
  - Insecticide
- Aquifers – limited supply

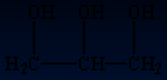
ENVIRONMENTAL IMPACT

- Fertilizer requirements
  - Limited resources
- Land requirements
  - 325 million acres and declining
- Food resource

Recycled waste has lowest environmental impact, therefore, recycled cooking oil will be used as feedstock for this project.

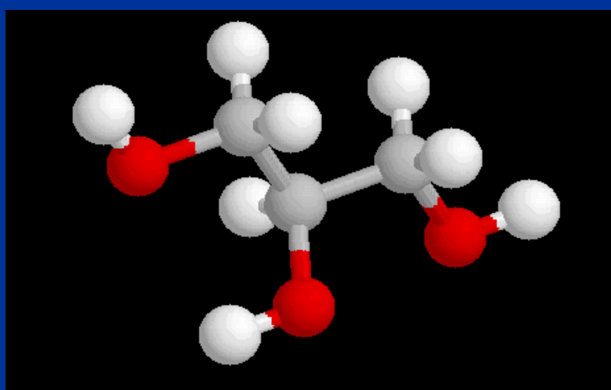
THE PROCESS

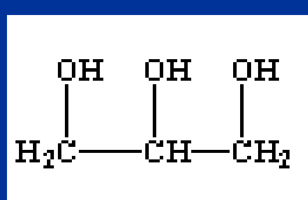
- TRANSESTERIFICATION
  - Conversion of vegetable oil to biodiesel
  - Replaces one type of alcohol (glycerol) with another (in biodiesel ethanol or methanol is used)
  - Vegetable oil combined with ethanol or methanol in the presence of a catalyst (sodium/potassium hydroxide)
  - In resulting transesterification reaction, the triglyceride structure is "broken" and three ethanol/methanol molecules replace the glycerol molecule.
  - Result is three separate fatty acid chains and a waste byproduct of glycerin, from the glycerol molecule
  - A specific example of a fatty acid found in biodiesel is linoleic acid which has 18 carbon atoms, two of which have double bonds.

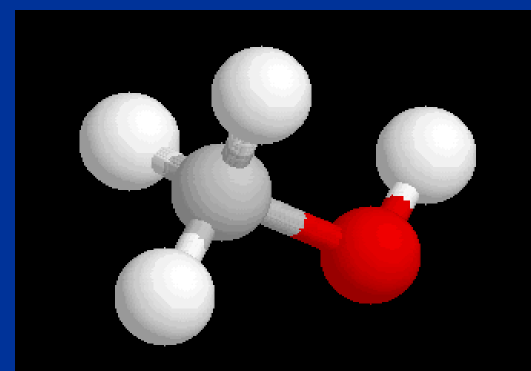


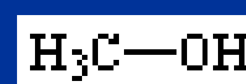
THE PROCESS

- Glycerol and methanol, both alcohol molecules



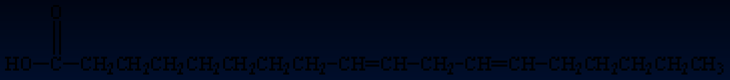






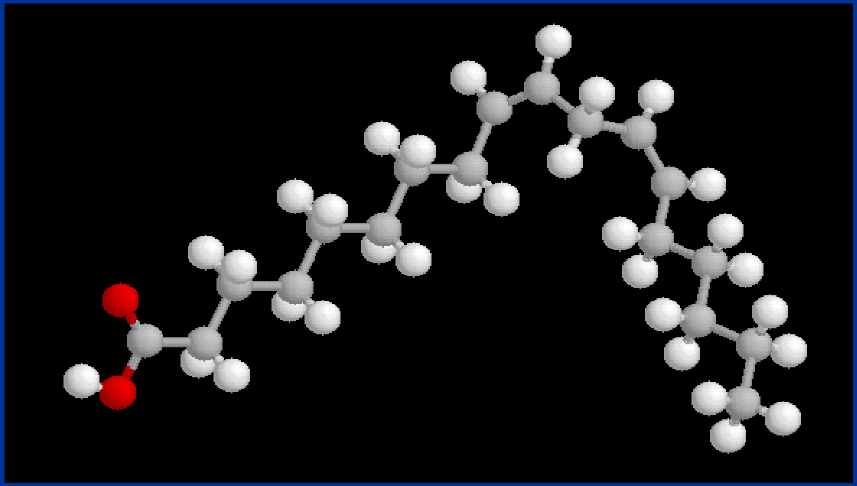
THE PROCESS

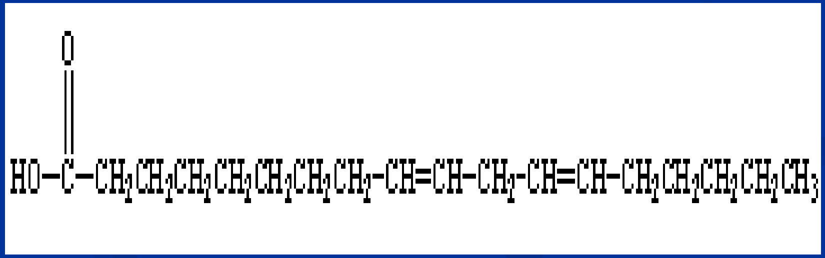
- Fatty acids that have no double bonds are termed "saturated." These chains contain the maximum number possible of hydrogen atoms per carbon atom. Stearic acid is a saturated fatty acid.
- Fatty acids that have double bonds are "unsaturated." These chains do not contain the maximum number of hydrogen atoms possible due to the double bond(s) present on some carbon atoms. Linoleic acid is an unsaturated fatty acid.
- Acids with one double bond are termed "mono-unsaturated” while more than one double bond are termed “poly-unsaturated.”



THE PROCESS

- Linoleic acid, a common component of soy biodiesel





THE PROCESS

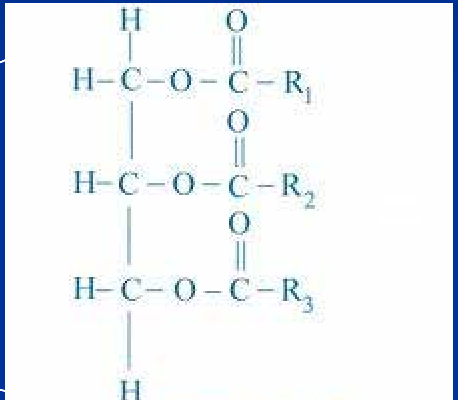
- An examination of soybean oil, and biodiesel made from soybean oil through transesterification, reveals 5 variations of fatty acid chains, in approximately this mix:
  - Composition of soy oil 8% with 16 carbon atoms (palmitic acid)
  - Composition of soy oil 3% with 18 carbon atoms (stearic acid)
  - Composition of soy oil 25% with 18 carbon atoms and 1 double bond (oleic acid)
  - Composition of soy oil 55% with 18 carbon atoms and 2 double bonds (linoleic acid)
  - Composition of soy oil 8% with 18 carbon atoms and 3 double bonds (linolenic acid)

- Linoleic acid is a common component of soy biodiesel.

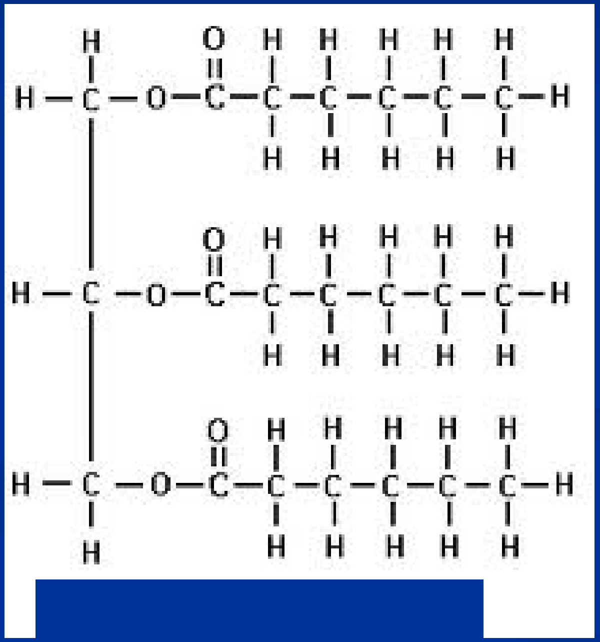
THE PROCESS

- Biodiesel produced from different source oils (feedstocks) will contain different proportions and types of fatty acid chains.
- This is why Soy Methyl Ester (SME)—biodiesel produced from soybean oil using methanol during transesterification—does not have the identical chemical properties of Rapeseed Methyl Ester (RME)—biodiesel produced from rapeseed oil.

What do all these symbols mean?



Triglyceride



See Supplementary Materials for more chemistry details.

REQUIRED EQUIPMENT








See Supplementary Materials for details and videos on making biodiesel & titration procedure.

ENGINE MANUFACTURER'S CONCERNS (Cummins)

Voice of the Customer

- B2, B5
  - Available in many states, supported by farmers, sold as premium fuel due to the lubricity benefits of biodiesel
- B20
  - School buses (becoming de facto fuel, PM and odor reduction), Transit fleets
  - Military ground support (mandatory and strategic)
  - Municipal, State and Federal fleets (mandatory alternative fuel use)

EVERY TIME.

VOICE OF THE CUSTOMER (cont.)

- B100
  - Marine (biodegradable in case of spills)
  - Parks (same as above, renewable)
  - Power generation (green power, renewable)
  - Passenger vehicles (especially California)

VOICE OF THE TECHNOLOGY

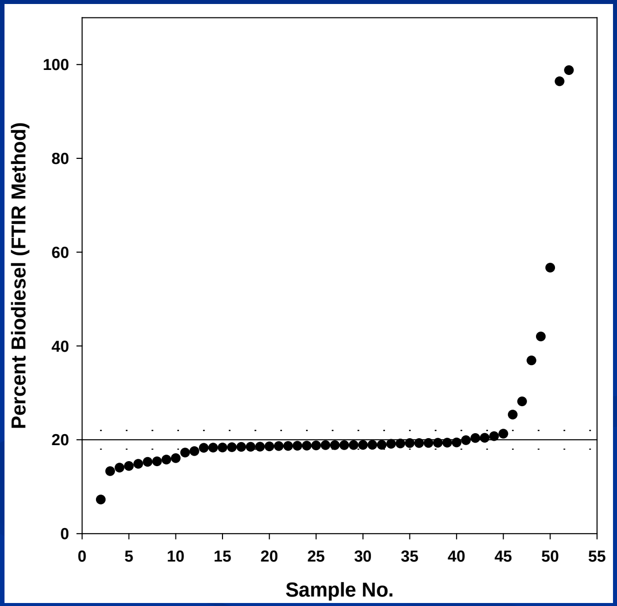
- Cummins today allows only B5 blends. (Biodiesel used to make the blend must meet ASTM D6751 or European EN14214.)
- Key challenges for higher blends
  - Cost
  - Fuel quality
  - Fuel oxidation stability
  - Contamination, microbe growth
  - High cloud point
  - Cleansing effect on fuel systems upon initial use

VOICE OF THE TECHNOLOGY (cont.)

- Key challenges for higher blends (cont.)
  - Materials interaction
  - NOx increase
  - Power loss vs. #2 diesel
  - Higher fuel consumption
  - Fuel filter water separation efficiency
  - Potential increased fuel dilution of engine oil due to higher viscosity
  - Joint Fuel Injection Equipment statement, limiting use to B5 blends only

VOICE OF THE TECHNOLOGY (cont.)

- Fuel quality
  - Recent study by U.S. Department of Energy on B20 biodiesel blend suppliers determined that 36% of the samples didn't meet the 18-22% blend ratio.



VOICE OF THE TECHNOLOGY (cont.)

- Materials impact
  - Degradation/swelling of elastomers (natural and nitrile rubber), nylon 66
  - Attacks brass, bronze, copper, lead, tin, and zinc
  - Bosch pump overpressure valve, removal of zinc coating after 1-year stand-by genset operation with B20 (300 hours):

#2 diesel

Zinc coating removed by the fuel

TESTING

- We are going to demonstrate the output of the newly-made fuel, using a Cummins N-14 microprocessor-controlled diesel engine, mounted on a Taylor 1000-HP engine dynamometer.

TESTING

- The engine will be set at 2250 RPMs and the dyno load adjusted to 200 HP with the engine running on No 2 Diesel Fuel and the engine fuel rate will be recorded from the engine microprocessor control module (ECM). This will be considered our test state.
- The engine will be shut down, and the fuel will be changed to a B5 mixture and the engine will be returned to the test state. The fuel rate will be recorded from the engine ECM.

TESTING

- The engine will be shut down, the fuel will be changed to a B10 and then a B20 mixture, and the engine will be returned to the test state. The fuel rate will be recorded from the engine ECM.
- The engine will be shut down, the fuel will be changed to a B100 fuel mixture and the engine will be returned to the test state. The fuel rate will be recorded from the engine ECM.

TESTING

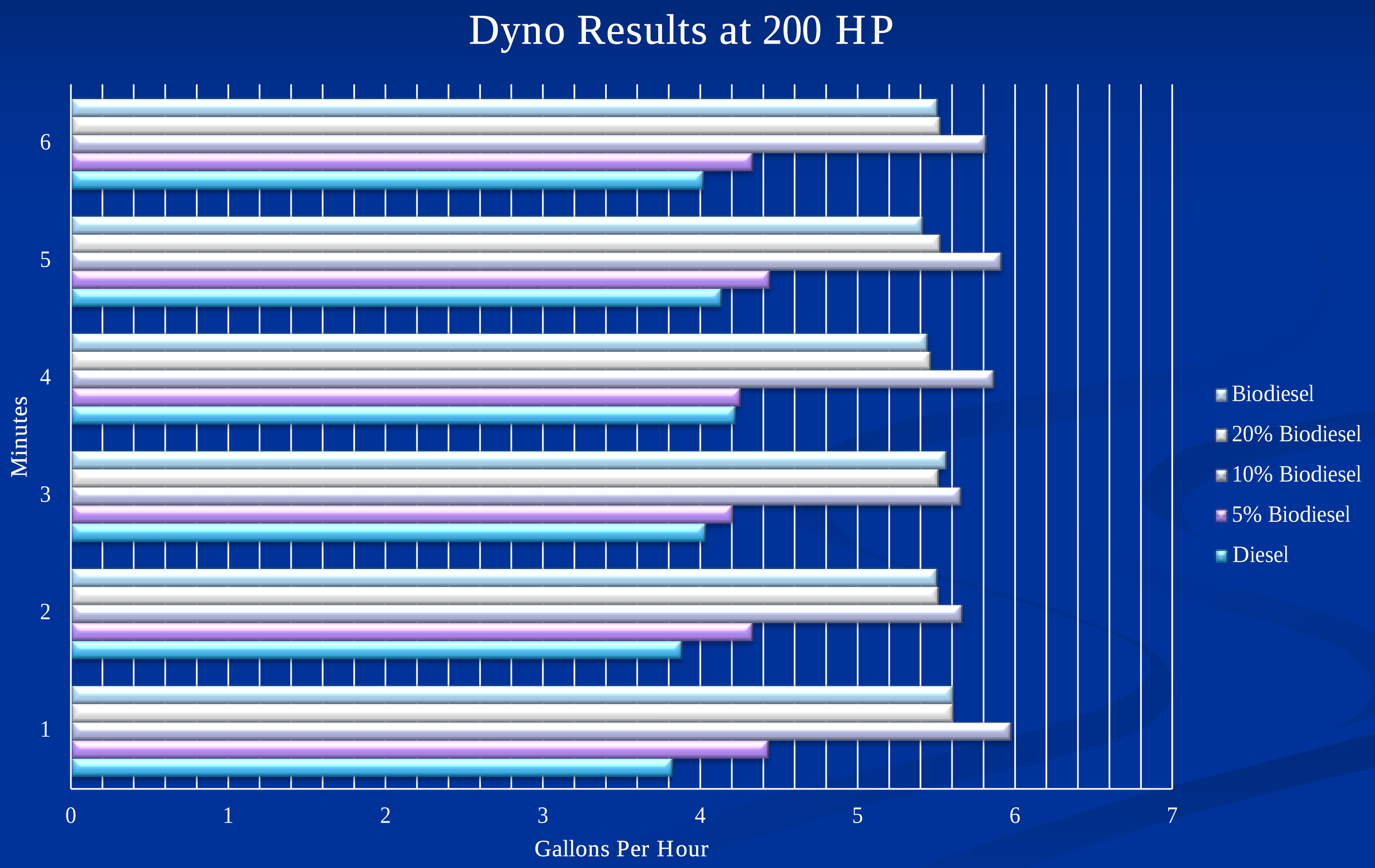
- The engine will be shut down, the fuel will be changed to a #2 diesel mixture, and the engine will be run at 800 RPM with a 40-HP load.
  - A hydrogen generator will be added to the turbocharger intake and the fuel rate will be recorded from the engine ECM.
  - A lower load and speed was selected because of the small size of the HHO generator relative to the displacement of the engine.

TESTING

Testing Engine Performance Using Various Fuels

http://youtu.be/6DdmtpIP-74

TEST RESULTS

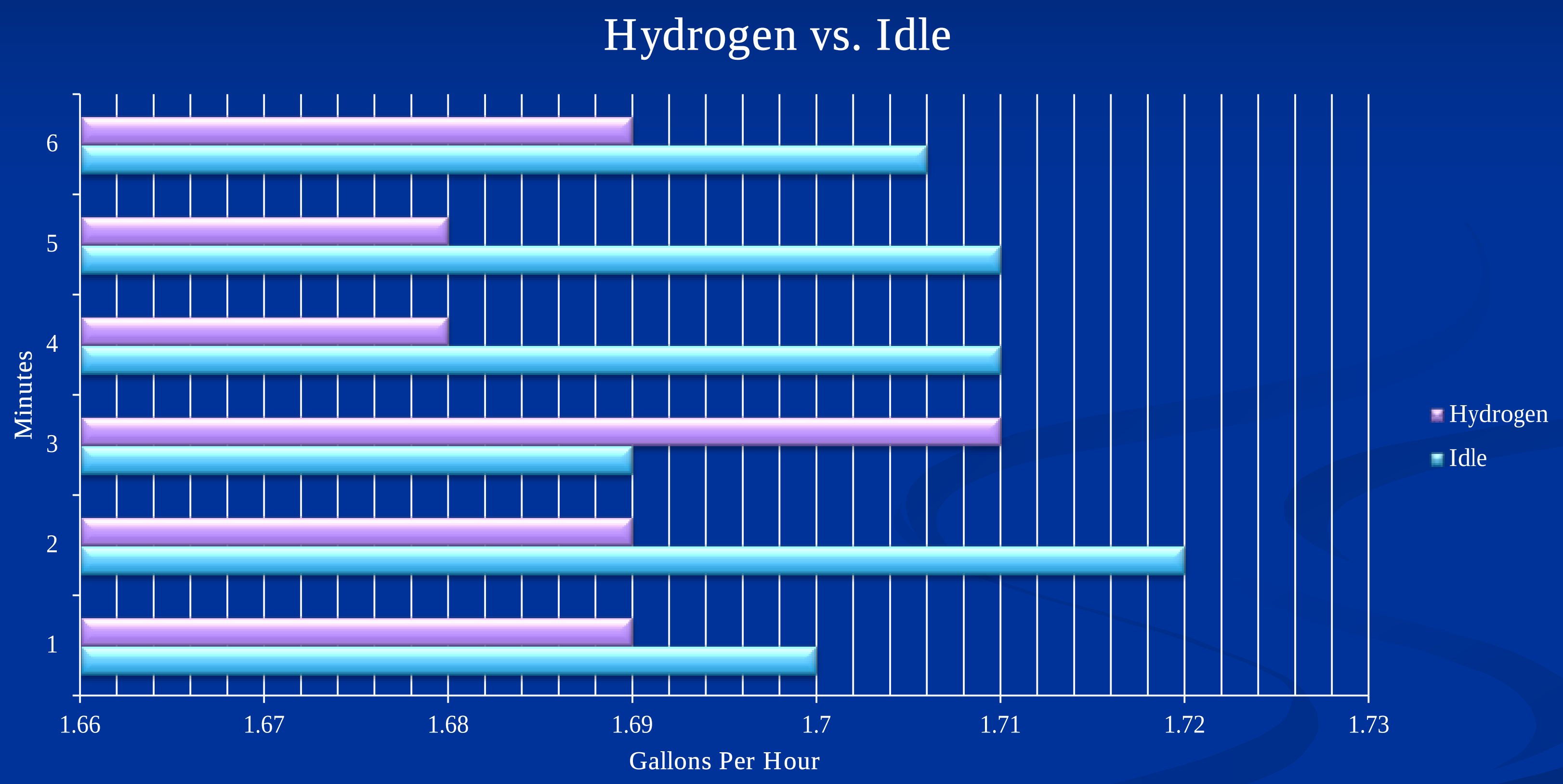


TESTING

Testing Engine Performance Using Hydrogen Enrichment

http://youtu.be/QKwznITT3vc

TEST RESULTS



For more information on the SEET Energy Webinar Series, please contact Melonee at ATEEC mdocherty@eicc.edu.

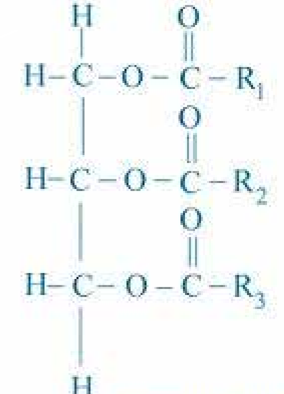
This webinar will be available for viewing at: http://ateec.org.

For a free, downloadable pdf version of this presentation: http://ateec.org/energy.

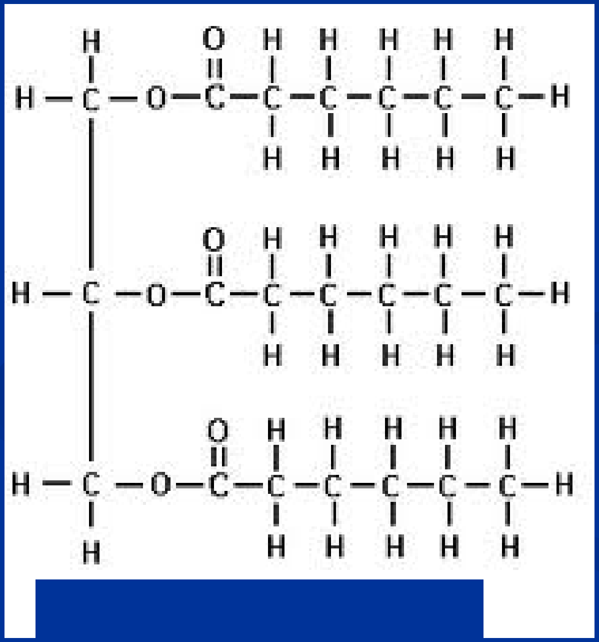
SUPPLEMENTARY MATERIALS

The CHEMISTRY of making biodiesel

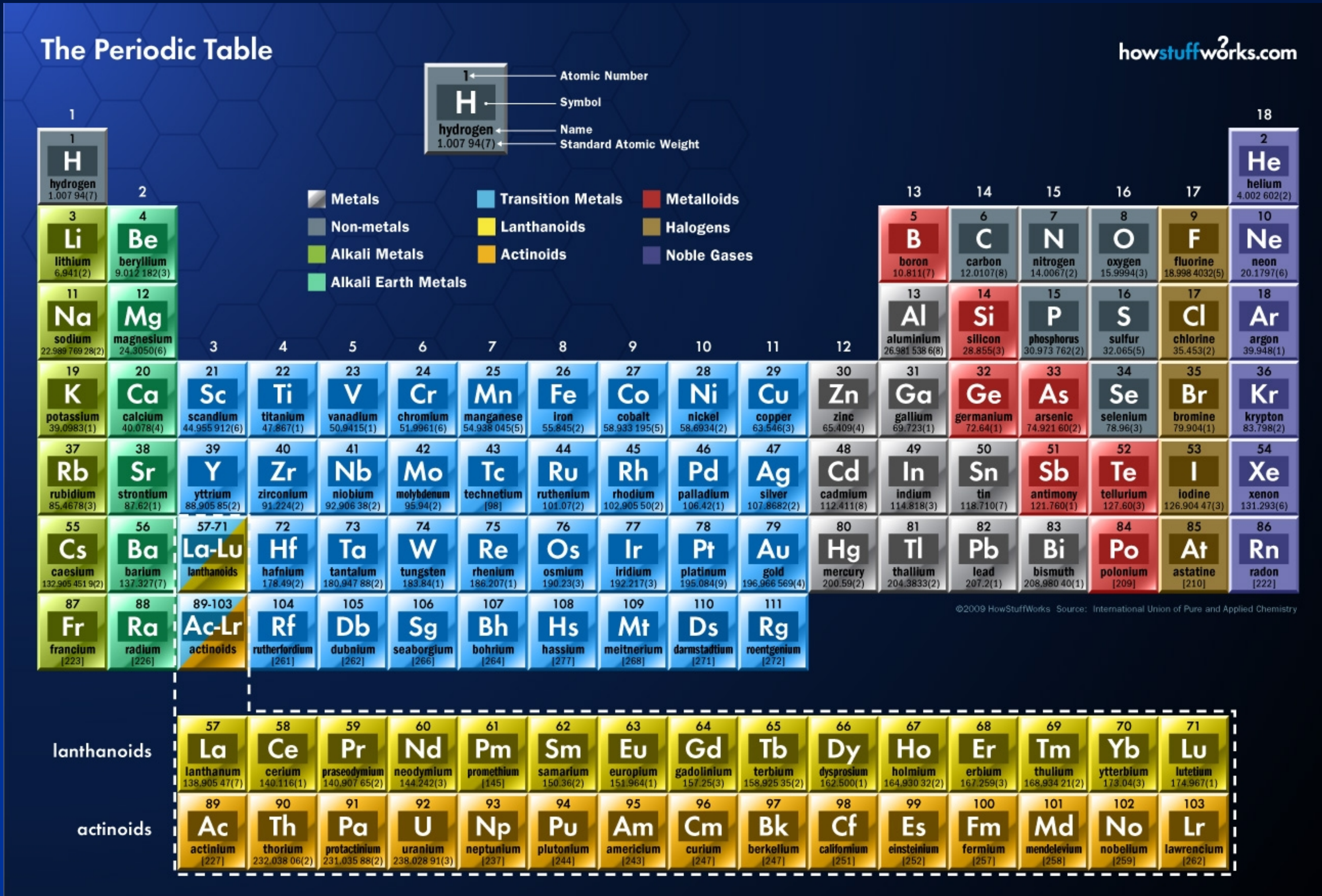
What do all these symbols mean?



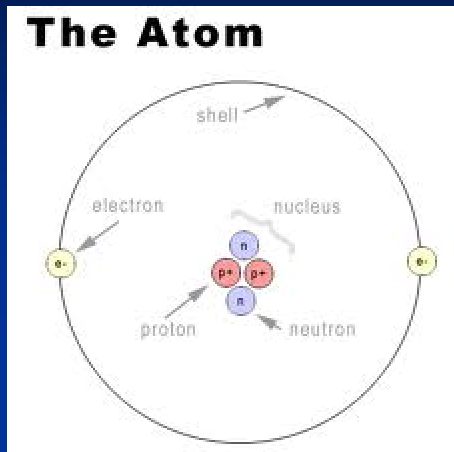
Triglyceride

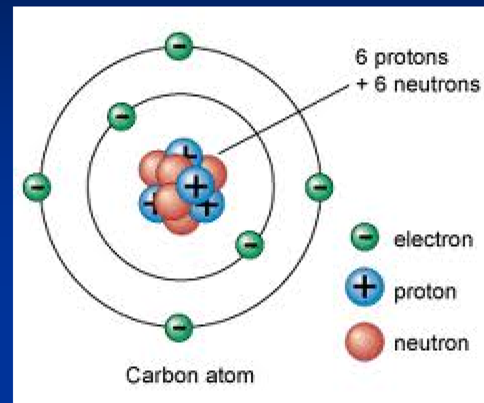


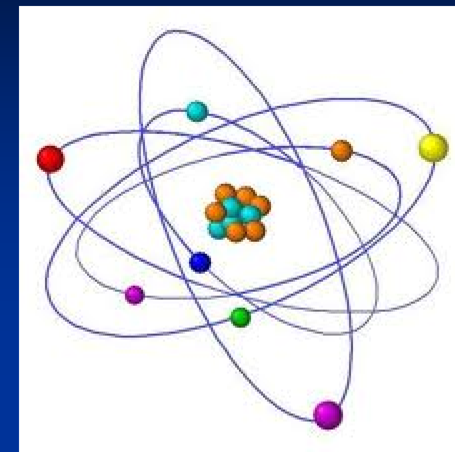
Periodic Table

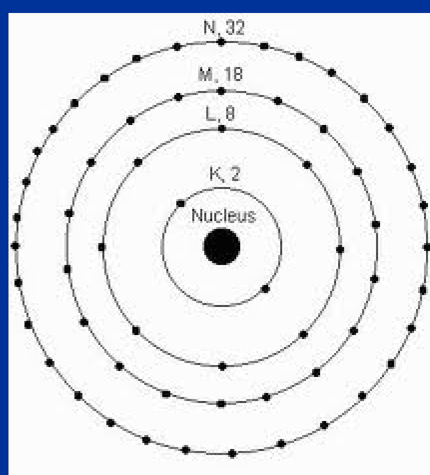


Atoms and Shells



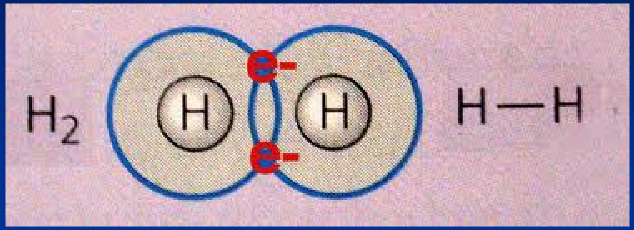




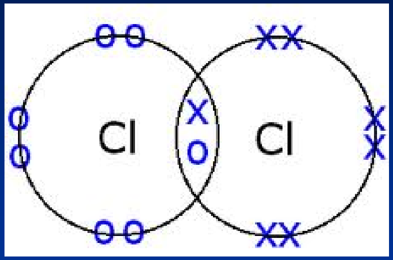


Energy Level (Principal Quantum Number)	Shell Letter	Electron Capacity
1	K	2
2	L	8
3	M	18
4	N	32
5	O	50
6	P	72

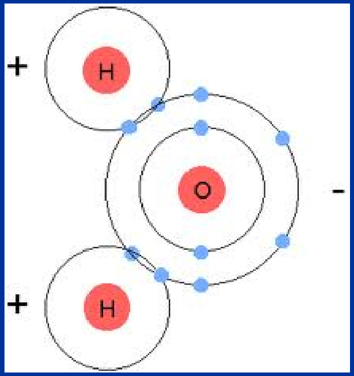
Sharing of electrons between various atoms to form single bond.



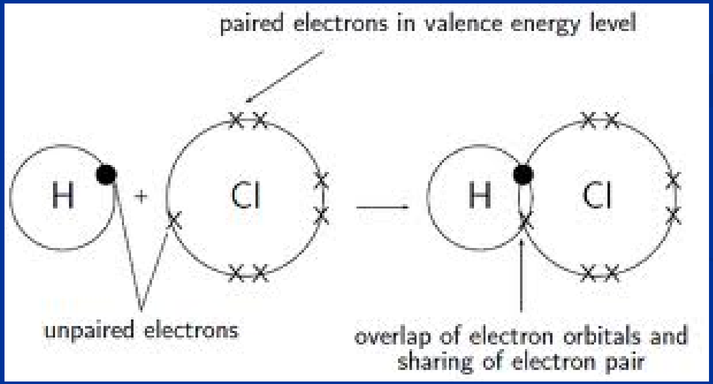
H_2 – hydrogen gas



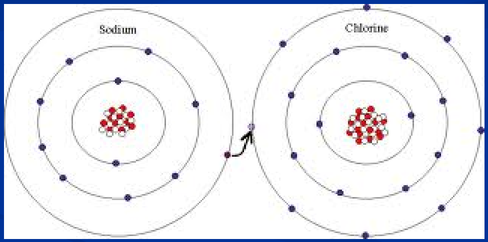
Cl_2 – chlorine gas



H_2O – water



HCL – hydrochloric acid

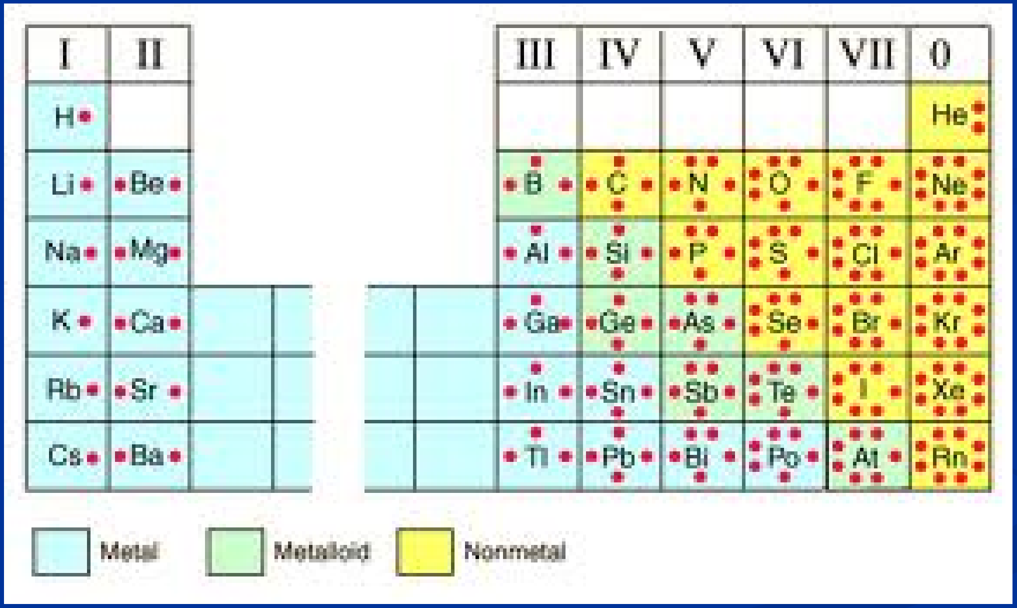


NaCl – sodium chloride (salt)

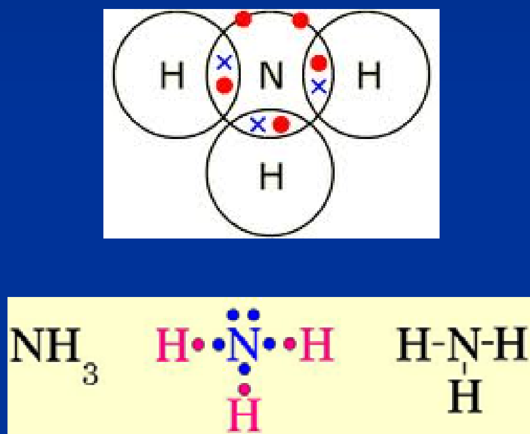
Valence Electrons

valence electrons – electrons at its outermost shell

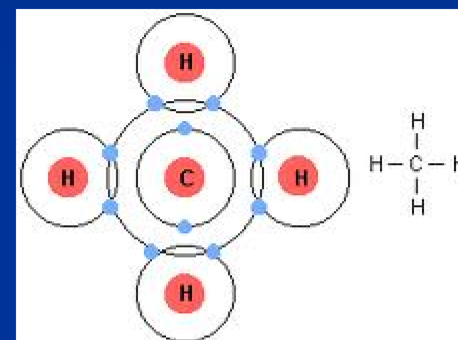
Periodic Table of Valence Electrons of Atoms:



Sharing of electrons between various atoms to form single bond.

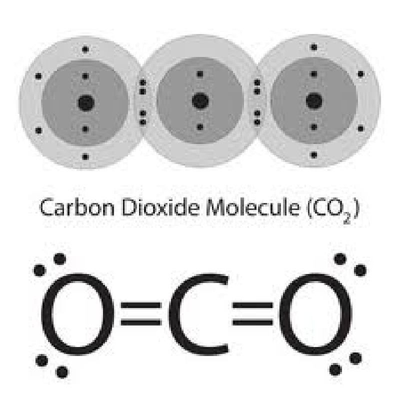


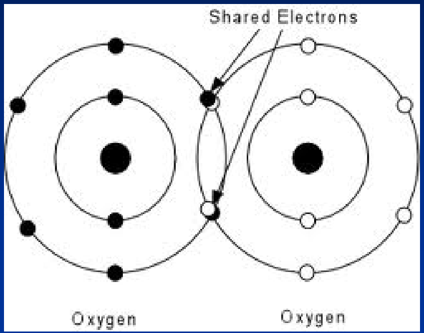
ammonia



methane

Sharing of electrons between various atoms to form double bond.

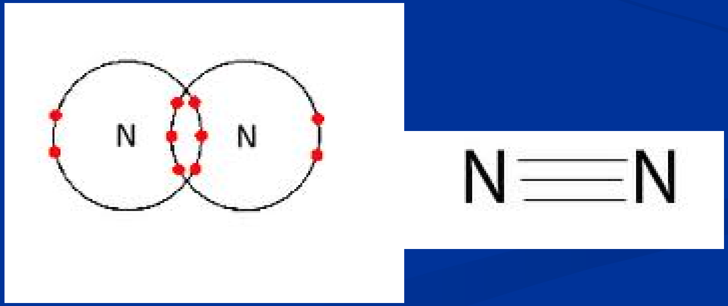




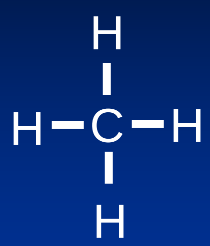
O = O

O_2 – oxygen gas

Sharing of electrons between various atoms to form triple bond.

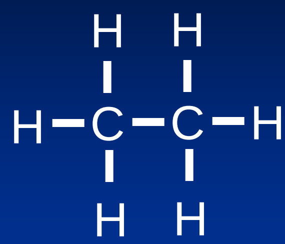


N_2 – nitrogen gas



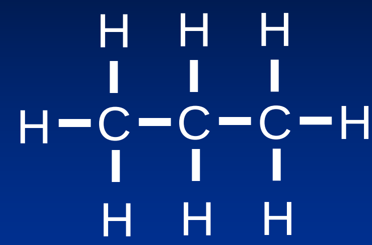
CH_4

methane



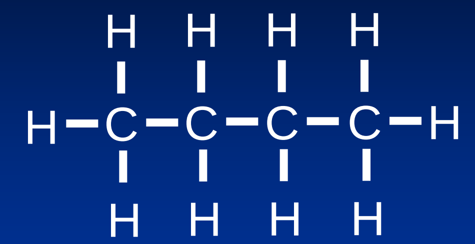
C_2H_6

ethane



C_3H_8

propane



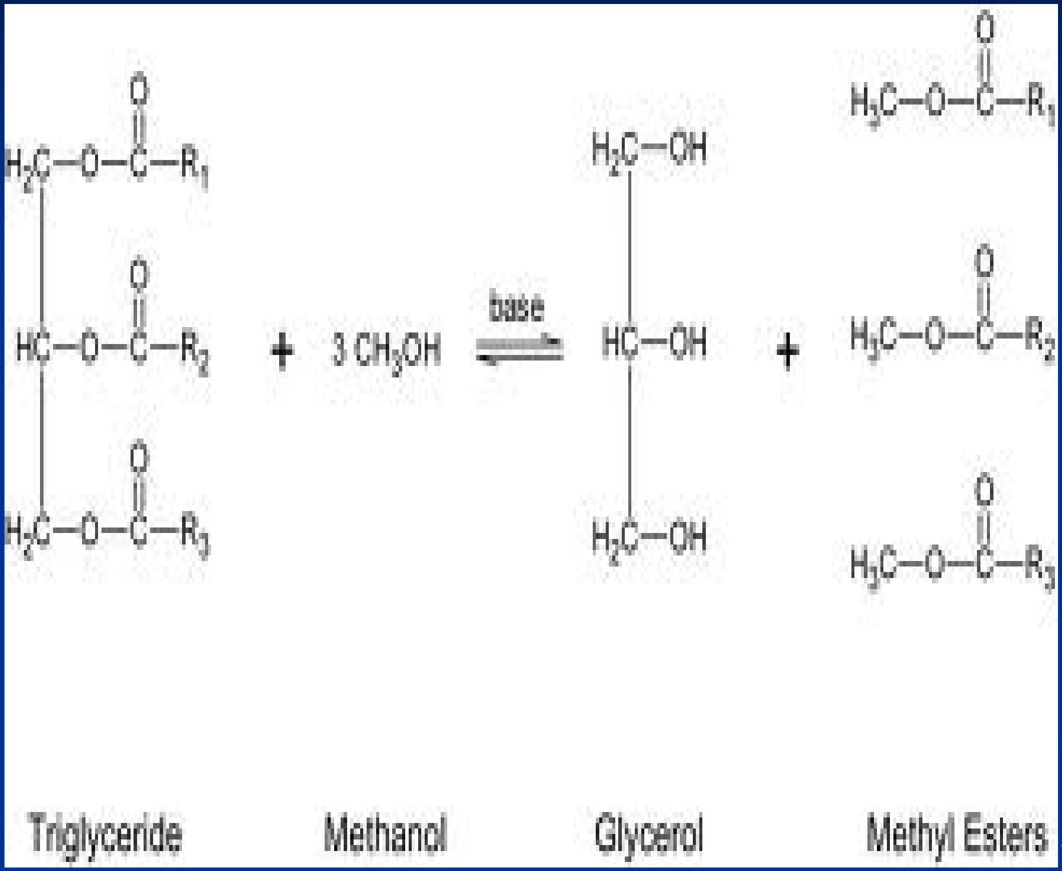
C_4H_{10}

butane

C_5H_{12} C_6H_{14} C_7H_{16} C_8H_{18} C_9H_{20} $C_{10}H_{22}$ $C_{11}H_{24}$ $C_{12}H_{26}$ $C_{13}H_{28}$ $C_{14}H_{30}$

$C_7H_{16} \longrightarrow C_{11}H_{24}$ gasoline

$C_{12}H_{26} \longrightarrow C_{15}H_{32}$ kerosene



base
3 CH3OH
Triglyceride
Methanol
Glycerol
Methyl Esters

biodiesel

STABILITY MEASUREMENT IODINE VALUE "IV"

- To compare the chemical stability properties of different biodiesel fuels, it is desirable to have a measurement for the stability of the fuel against oxidation. Currently the most common method for doing this, and the one specified in many of the biodiesel fuel specifications is called the Iodine Number or Iodine Value. The Iodine Value is not determined by measuring the stability of the fuel, rather it is determined by measuring the number of double bonds in the mixture of fatty acid chains in the fuel by introducing iodine into 100 grams of the sample under test and measuring how many grams of that iodine are absorbed. Iodine absorption occurs at double bond positions - thus a higher IV number indicates a higher quantity of double bonds in the sample. Numbers range from 10 for Coconut oil, 94-120 for Rapeseed oil, 117-143 for Soybean oil, up to 185 for Sardine oil. Biodiesel from these oils have Iodine values something like 97 for Rapeseed Methyl Ester, 100 for Rapeseed Ethyl Ester, 123 for Soy Ethyl Ester and 133 for Soy Methyl Ester.

STABILITY MEASUREMENT IODINE VALUE “IV”

- The Iodine Value can be important because many Biodiesel fuel standards specify an upper limit for fuel that meets the specification. For example, Europe’s EN14214 specification allows a maximum of 120 for the Iodine number, Germany's DIN 51606, tops out at 115. The USA ASTM D6751 does not specify an Iodine value. Since Soy has a value of 133 utilizing these two standards, it is not allowed for biodiesel production in Europe. The Iodine value (IV) does not necessarily make the best measurement for stability as it does not take into account the positions of the double bonds available for oxidation. In some cases this can lead to IV values that are misleading.

STABILITY MEASUREMENT

- After oxidation, hydro peroxides (one hydrogen atom and 2 oxygen atoms) are attached to the fatty acid chain. In a food oil this leads to rancidity. In biodiesel these degraded chains can polymerize, hooking together into various substances including insoluble gums that clog up injectors, metering drillings in distributor pumps and delivery valves in inline injector pumps.

STABILITY MEASUREMENT

- Other measurements of stability are available which *do take into account double bond position*. One is termed "Oil Stability Index" or OSI and is measured in hours by looking at the conductivity in water of the degraded fatty acids at a specific temperature. Another stability specification is known as "APE" and "BAPE" for "allylic position equivalents" and "bis-allylic position equivalents" which takes into account both the number and position of double bonds in the fatty acid chains.

LAB—REQUIRED EQUIPMENT

- Rubber gloves
- Safety glasses
- Hydrogen generator
- Diesel engine
- Sodium hydroxide or potassium hydroxide
- WVO
- Methanol
- Phenolphthalein solution

REQUIRED EQUIPMENT (cont.)

- Precision scale
- Graduated cylinder
- Thermometer 200 ° F
- Heat plate
- Mixing apparatus
- Spray bottle
- Blender

OPTIONAL EQUIPMENT

- Microprocessor-controlled diesel engine
- Engine dynamometer
- Computer and software to communicate with engine ECM
- Hydrogen generator

REQUIRED EQUIPMENT








TITRATION

- Dissolve 1 gm of lye (KOH or NaOH) in 1 liter of distilled water to make 0.1% w/v lye solution (weight-to-volume).

  In a smaller beaker, dissolve 1 ml of the oil to be tested in 10 ml of pure isopropyl alcohol (isopropanol).

  Warm the beaker gently by standing it in some hot water, stir until all the oil dissolves in the alcohol and turns clear. (Wooden chopsticks make good stirrers for titration.)

  Add 2 drops of phenolphthalein solution.

  Using a graduated syringe or a pipette, add 0.1% lye solution drop by drop to the oil-alcohol-phenolphthalein mixture, stirring all the time. It might turn a bit cloudy, keep stirring. Keep on carefully adding the lye solution until the mixture just starts to turn pink (magenta) and stays that way for 15 seconds.

TITRATION

- Take the number of milliliters of 0.1% lye solution you used and add the basic amount of lye needed to process fresh oil -- 3.5 grams for NaOH or 4.9 grams for (pure) KOH. This is the number of grams of lye you'll need per liter of the oil you titrated. (Don't worry that you seem to be adding milliliters to grams, that's the way it works.)

TITRATION

http://youtu.be/--7zu-DB_mM

THE PROCESS

- After titration of the feed stock we will add the calculated amount of sodium hydroxide to 1 liter of methanol and then mix thoroughly in the blender. After mixing is completed, we will add the meth-hydroxide solution to 10 liters of WVO and heat to 130 degrees f while stirring constantly for 45 minutes. It is important to keep the temperature below 130 degrees to prevent the methanol from evaporating.

THE PROCESS

- After mixing for 45 minutes, remove the heat source and let the mixture sit foe 24 hours.
- After 24 hours the glycerin will have settled to the bottom and depending on how much other fats were in the WVO there could be a viscous layer mixed in with the glycerin.
- The Bio-fuel can now be drained off the top of this layer and is ready for washing to remove the soap formed by the lye.

THE PROCESS

- Washing the fuel is easily accomplished by spraying finely misted water out of a spray bottle over the top of the fuel.
- As the water migrates through the fuel it will pick up the soap and will become cloudy.
- Repeat this process until the water precipitates through the fuel without becoming cloudy

THE PROCESS

- Filter the fuel through a fuel filter/water separator assembly and the fuel is ready to use.
- The glycerin can be further refined into soap or can be used as an oil candle, further limiting the waste trail of the WVO.

TRANSESTERIFICATION

Making the Biodiesel

http://youtu.be/Y8_qAgS2_dA