Fuel & Advanced Combustion

Lecture 1
Fuel

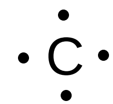
Molecules and Covalent Bonds

Chemical bonds result from a mutual sharing of electrons between atoms, the shared electrons are in the outermost shell, known as valence electrons

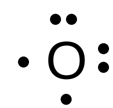
Lewis notation:

Hydrogen Atomic # 1 → 1 valence electron H•

Carbon Atomic # 6 → 4 valence electrons



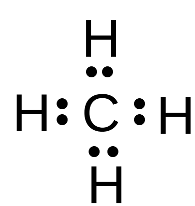
Oxygen Atomic # 8 → 6 valence electrons



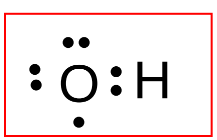
Atoms like to have electron configuration like noble gas, usually eight valence electrons, an octet.

H_2 → H:H

CH_4 →



Atoms and molecules with unpaired valence electrons are called **radicals** e.g. O, H, OH, N, C



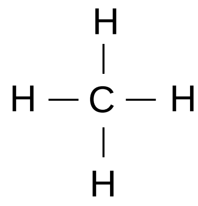
Hydrocarbon Fuels

Common hydrocarbon fuels are grouped as:

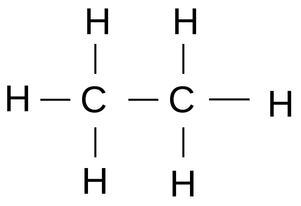
Paraffins:

C_nH_{2n+2}

n= 1 CH_4 methane
n= 2 C_2H_6 ethane
n= 3 C_3H_8 propane
n= 4 C_4H_{10} butane
n= 8 C_8H_{18} octane



methane



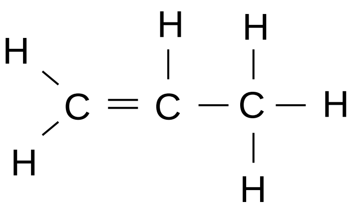
ethane

Olefins:

C_nH_{2n}

n=2 C_2H_4 ethene
n=3 C_3H_6 propene

Note: n=1 yields CH_2 is an unstable molecule

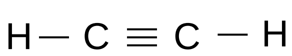


propene

Acetylenes:

C_nH_{2n-2}

n=2 C_2H_2 acetylene
n=3 C_3H_4 propyne



acetylene

Alcohols

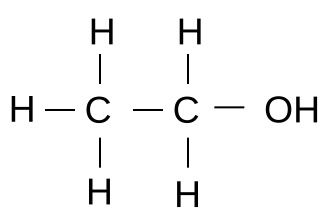
An alcohol molecule is simply a hydrocarbon molecule with one of the hydrogen atoms replaced by a hydroxyl molecule (OH)

The main alcohols used as engine fuels are:

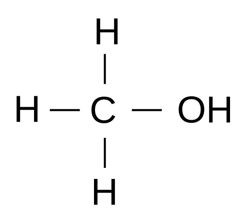
Ethanol – ethyl alcohol (C_2H_5OH) consists of ethane molecule (C_2H_6) with OH substituting one H

Methanol –methyl alcohol (CH_3OH) consists of methane molecule (CH_4) with OH substituting one H

Butanol – (C_4H_9OH) consists of butane molecule (C_4H_{10}) with OH substituting one H



Ethyl alcohol



Methyl alcohol

IC Engine Fuels

Crude oil contains a large number of hydrocarbon compounds (25,000).

The purpose of refining is to separate crude oil into various fractions via a distillation process, and then chemically process the fractions into fuels and other products.

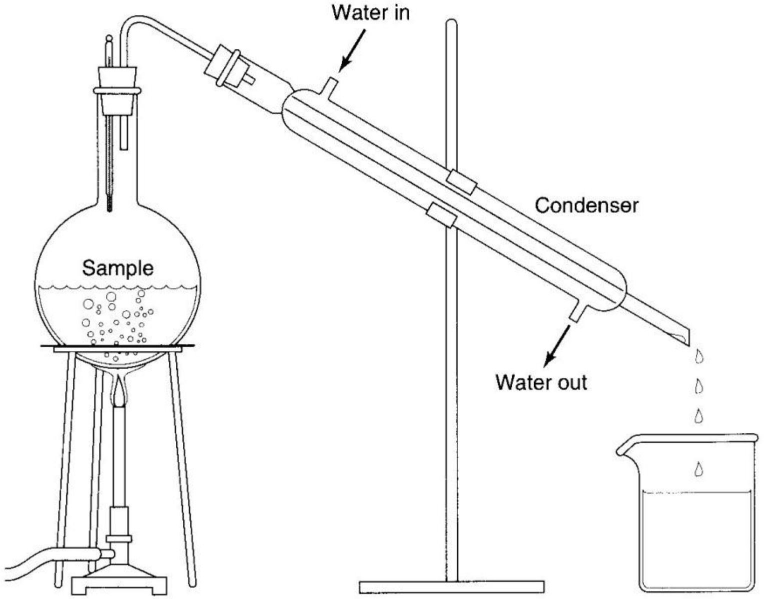
A still is used to heat a sample, preferentially boiling off lighter components which are then condensed and recovered.

The group of compounds that boil off between two temperatures are referred to as fractions.

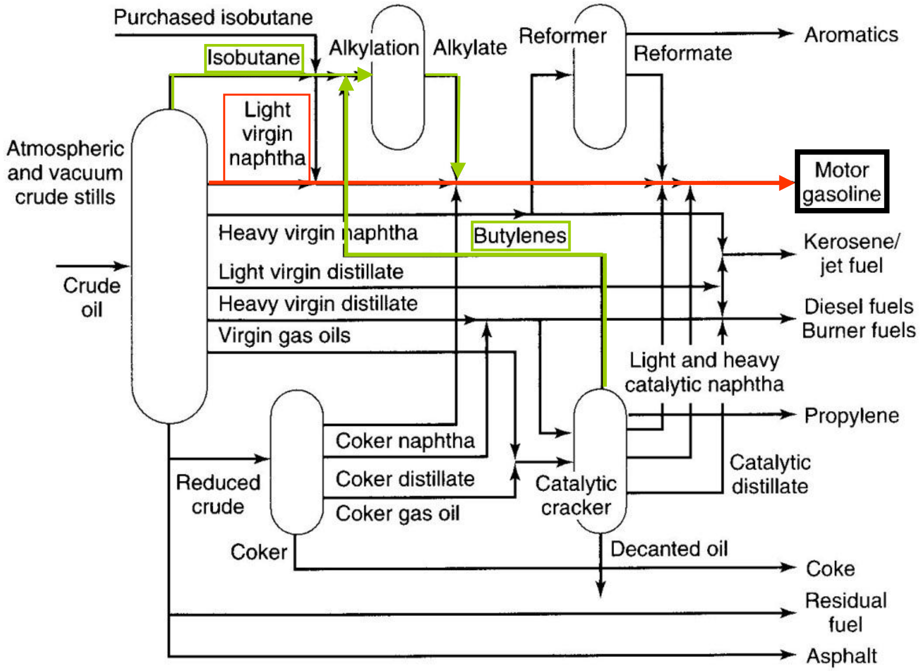
The order of the fractions as they leave the still are *naptha, distillate, gas oil, and residual oil*. These are further subdivided using adjectives *light, middle, and heavy.*

The adjectives *virgin or straight run* are often used to signify that no chemical processing has been performed to a fraction.

Distillation Process



Refining Process



Gasoline

Light virgin (or straight run) naptha can be used as gasoline.

Gasoline fuel is a blend of hydrocarbon distillates with a range of boiling points between 25 and 225^oC (for diesel fuel between 180 and 360^oC)

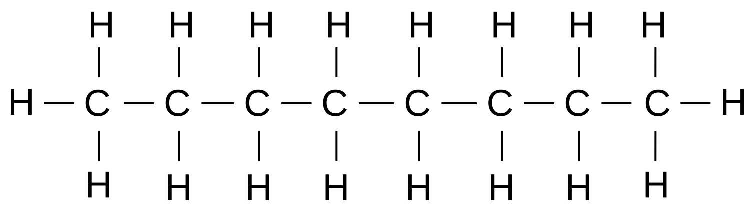
Chemical processing is used to:

- Produce gasoline from a fraction other than light virgin, or

- Upgrade a given fraction (e.g., Alkylation increases the MW and octane number of fuel: produce isooctane by reacting butylenes with isobutane in the presence of an acid catalyst)

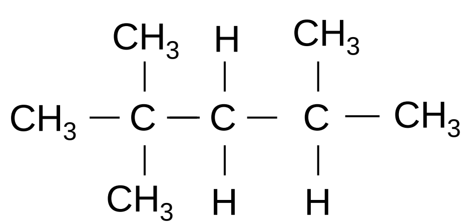
Octane (C_8H_{18})

The octane molecule is often used to simulate the properties of gasoline



n-octane

There are 18 isomers of octane, depending on position of methyl (CH_3) branches which replace hydrogen atoms (eg. a side H is replaced with CH_3)



iso-octane

Reformulated Gasoline (RFG)

In order to reduce emissions such as carbon monoxide (CO) and unburned hydrocarbons (HC) the oxygen content of gasoline is increased to about 3% by weight (U.S. oxygenated fuels program, winter only).

The US Clean Air Act requires certain large US cities to use RFG year-round in order to reduce ozone by requiring a minimum oxygen content of 2% by weight and maximum benzene content of 1%.

The primary oxygenates are MTBE (Methyl tertiary butyl ether) $(CH_3)OC(CH_3)_3$ and ethanol (C_2H_5OH)

As part of the reformulated gasoline program sulfur is restricted to 31 ppm

Renewable Fuels

Currently most automotive IC engines use fossil fuels (gasoline or diesel)

Due to the ever increasing cost of oil, due to diminishing oil reserves and accessibility to the oil reserves, and environmental concerns such as global warming, alternative fuels have become very attractive. The 2007 US Energy Bill set a 36 billion gal target for renewable fuels to be used in autos by 2020

In Canada the Renewable Fuel Mandate that took affect Dec. 2010 requires an average of 5% ethanol content for gasoline and 2% biodiesel

Alcohols such as ethanol, methanol, and butanol are receiving a lot of attention because they can be synthesized biologically, i.e., bioalcohols or biofuels.

Since there is oxygen in the fuel, combustion of alcohols produces no CO but more greenhouse gas carbon dioxide (CO_2) than fossil fuel combustion.

Alcohol Fuels

However, since the fuel is derived from plant matter the CO_2 produced is extracted from the atmosphere during the growth of the plant, i.e.CO_2 neutral

$$\underbrace{6CO_2 + 6H_20 + \text{solar energy}}_{\text{photosynthesis}} \rightarrow \underbrace{C_6H_{12}O_6}_{\text{sugar}} + 6O_2$$

Ethanol used for fuel is obtained by fermentation. Yeast metabolizes sugar ($C_6H_{12}O_6$) in the absence of oxygen to produce ethanol and carbon dioxide

$$C_6H_{12}O_6 \rightarrow 2C_2H_5OH + CO_2$$

In Brazil ethanol is derived from sugar cane whereas in the US and Canada corn is used as the feedstock (sugar cane has 30% more sugar than corn).

Sugars for ethanol fermentation can also be obtained from cellulose $(C_5H_{10}O_5)_n$ that makes up agricultural by products, such as corn cobs, corn stalks, straw, switch grass, and wood, into renewable energy resources

Pros and Cons of Alcohol fuels

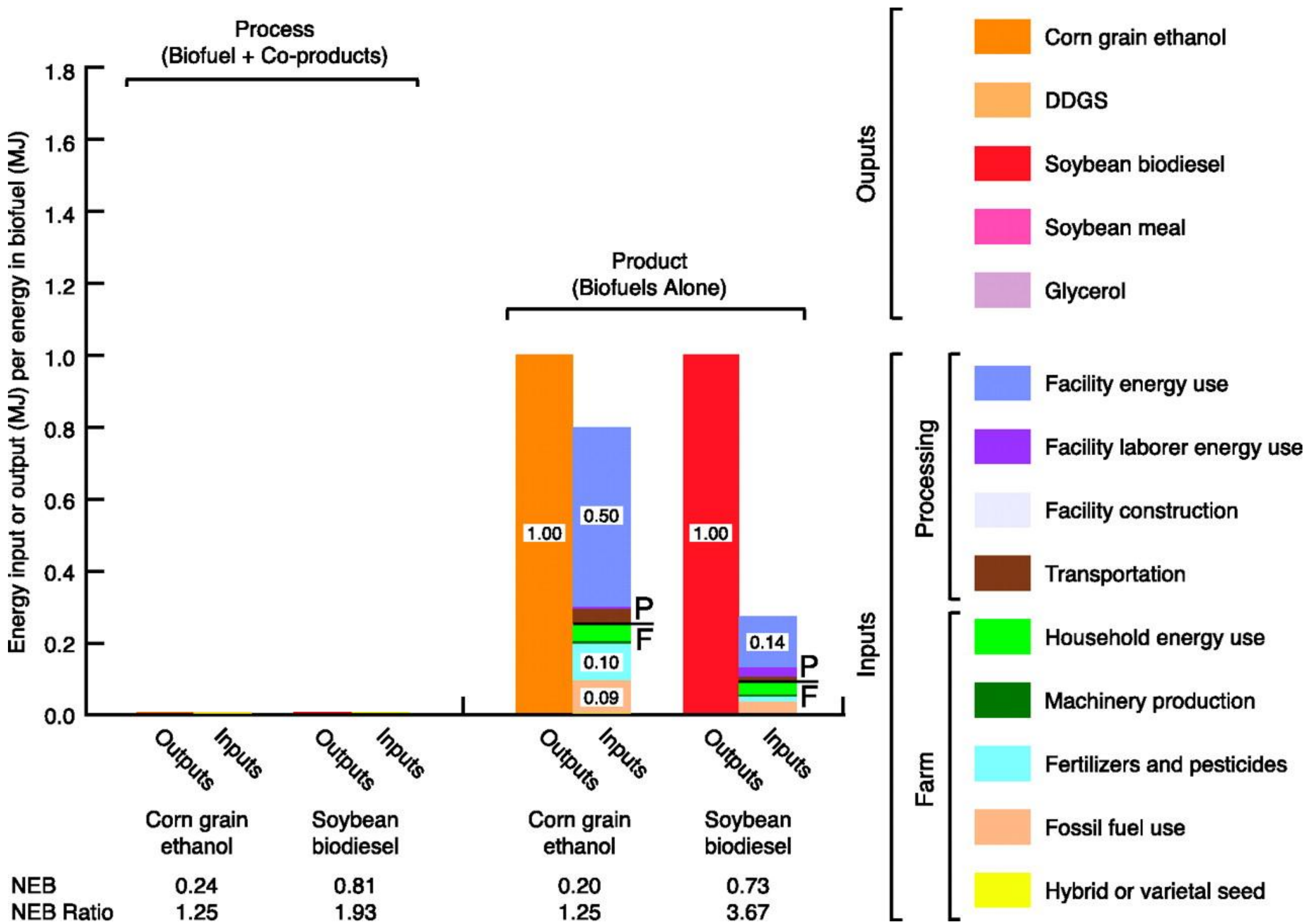
Main advantage of alcohol fuels is they are derived from renewable biomass which is CO_2 neutral when burned

Alcohol fuels have a **higher heat of vaporization** (h_{fg}) than gasoline $\rightarrow$ cools the air during mixing, resulting in **a higher volumetric efficiency**

Alcohol fuels have several drawbacks compared to fossil fuels:

- lower energy density (kJ/m^3) than gasoline (10% less for butanol, 27% less for ethanol, 55% less for methanol),
- corrosive to fuel systems (methanol > ethanol > butanol)
- poor cold temperature start up due to low vapor pressure
- toxicity (methanol)
- use of food crops (i.e., corn, wheat) drives up world prices of food
- production of ethanol is very energy intensive and thus expensive

NEB of corn grain ethanol and soybean biodiesel production



Hill J. et.al. PNAS 2006;103:11206-11210 NEB: net energy balance

PNAS

Ethanol as a Fuel

Ethanol is quickly becoming the alternative fuel of choice for IC engines

An IC engine can run on gasoline with up to 10% ethanol (E10) without any modifications, the use of higher blends requires changing certain components in the fuel system, i.e, use stainless steel fuel lines and tank.

In Brazil half of the cars can run on 100% ethanol including flex-fuel engines that can run on all ethanol, all gasoline, or any combination of the two

Gasoline with up to 85% ethanol (E85) is now starting to enter the US and Canadian markets. Flex-fuel engines in this market can run on E85 or all gasoline, 100% ethanol not yet permitted

Other Alternative Fuels

Biodiesel – made from vegetable oils (soybeans), waste cooking oil, animal fats. It is produced by reacting the oil with an alcohol (usually methanol) and a catalyst (sodium hydroxide). The resulting chemical reaction produces glycerine and alkyl esters (biodiesel). It is a liquid at RTP and has 9% lower energy content than regular diesel, usually mixed with diesel.

Propane has been used for many years as a fuel for IC engines, especially in Europe where the price of gasoline has been historically high. In N.A. mainly used on fork lifts and golf carts. Stored as a liquid in steel tanks $P_v(25^oC)$= 10 bar. Cleaner burning than gasoline.

Dimethyl ether (CH_3OCH_3 same as ethanol) – good diesel fuel because of good autoignition quality. Is a gas at RTP, produced from syngas (biomass) or methanol.

Other Alternative Fuels

The following fuels are in the gaseous state at 25ºC and thus have low energy density and engines using them have low volumetric efficiencies:

Hydrogen (H_2) is the "new" natural gas with similar issues. The main benefit is no CO, CO_2 and HC emissions. Biggest problems with hydrogen is safety, lack of distribution infrastructure, onboard storage, and production energy (hydrogen gas is not found in nature it must be produced). Can be stored as a gas (compressed), a liquid (cryogenic, T_{bpt}=20K), in a metal hydrides

Natural gas (CH_4, C_2H_6,..) Normally stored in tanks at 16-25 MPa. Cleaner burning than gasoline. Limited use in automobiles, mainly used for running pipeline compressors and fixed power generation gas turbines

Producer gas (syngas) engines run on the gaseous products from thermal gasification of biomass such as wood. **The carbon reacts with steam, or a limited amount of air, at high temperature (>700C) to** produce a mixture consisting of roughly 25% CO, 15% H_2, and 5% CO_2 , 50%N_2 …. Drawback is very low energy content, ten times lower than natural gas. Benefit CO_2 neutral. Used to power vehicles during WWII.