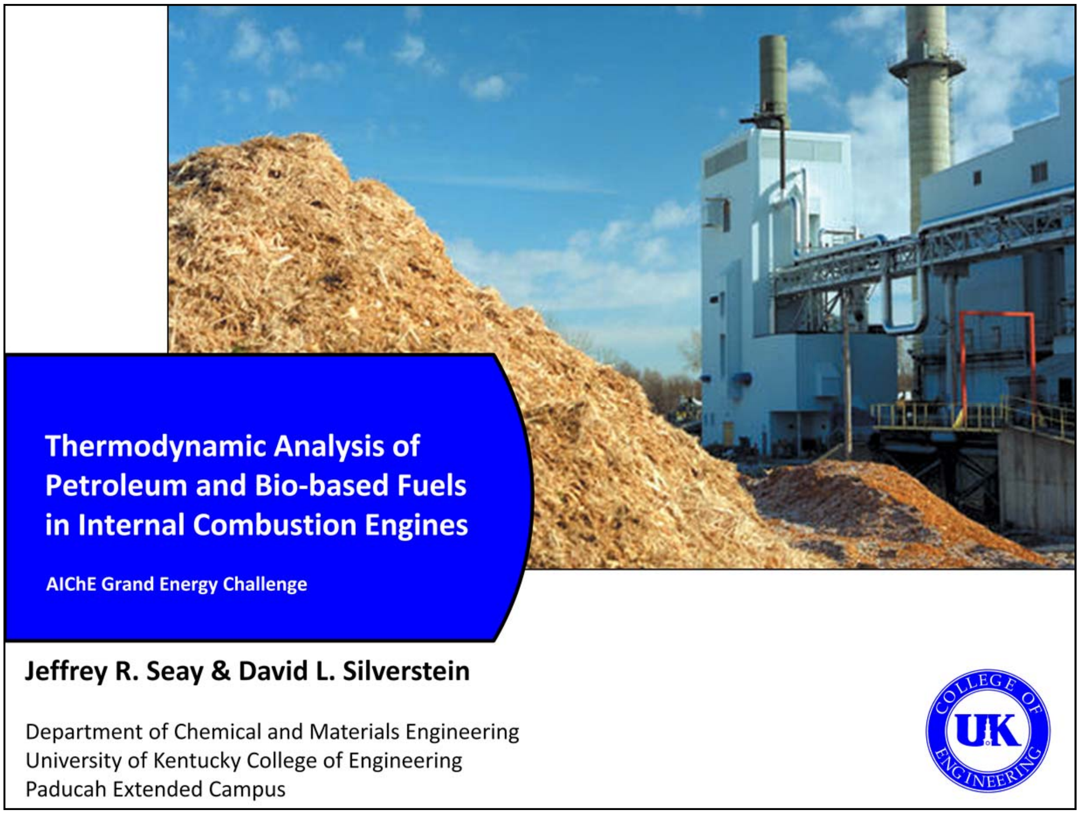

This module is designed to introduce undergraduate Chemical Engineering students to the topic of liquid transportation fuels generated from renewable and petroleum based resources from a thermodynamics prospective.

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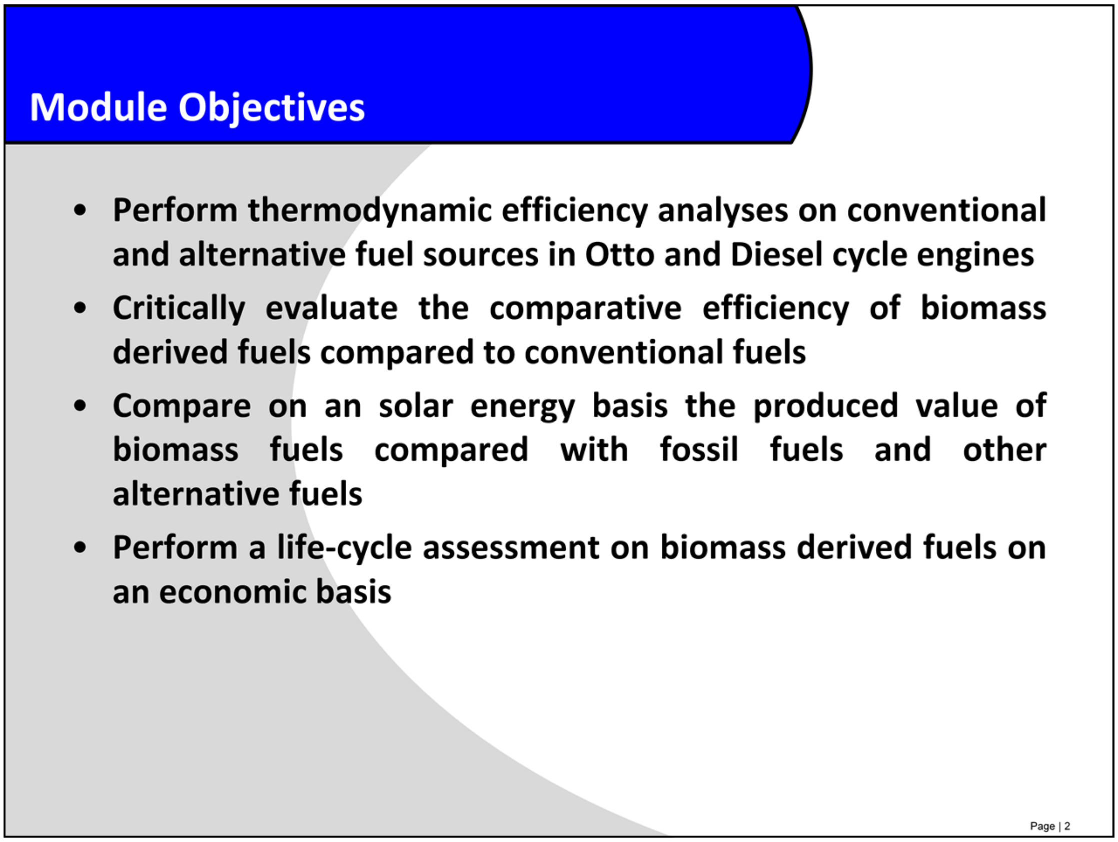
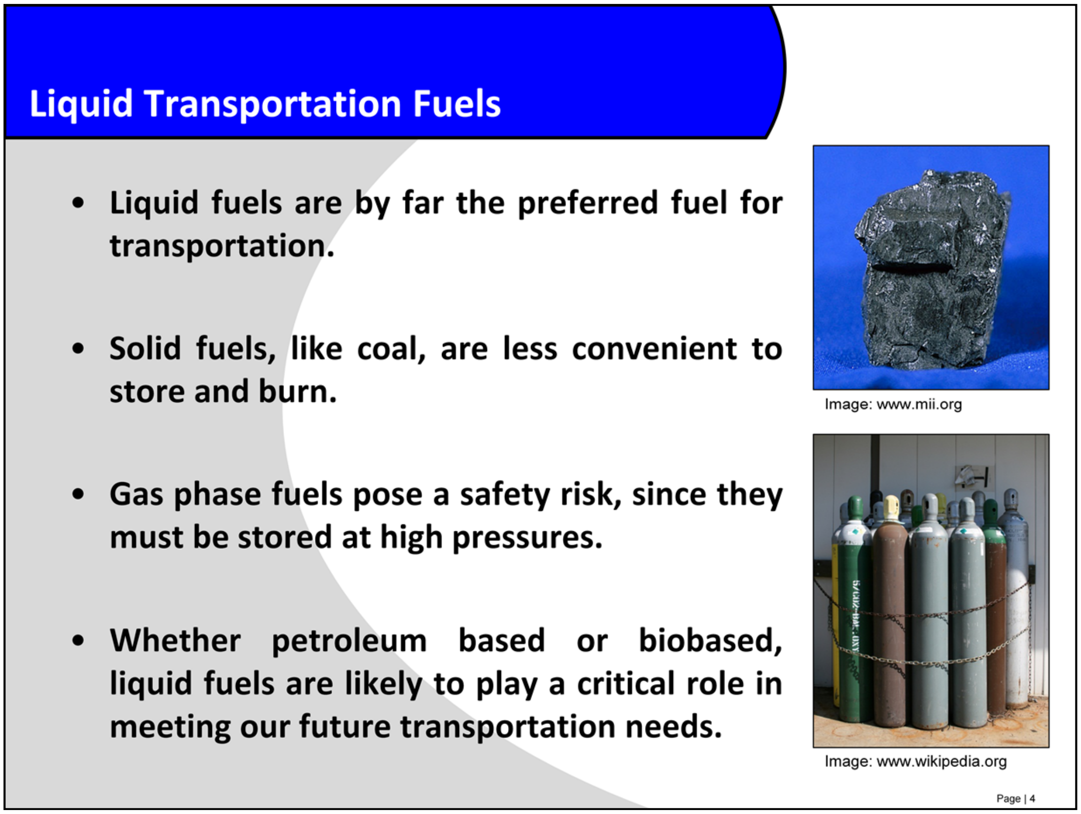
Image reference: www.ctcleanenergy.com



This module will introduce students to the principle types of internal combustion engines and the thermodynamic principles behind them, provide an overview of the most common petroleum and bio-based liquid transportation fuels and introduce the concept of life cycle assessment, as it applies to liquid transportation fuels.

Liquid fuel are the current preferred means of powering engines used for transportation. The objectives of this section are:

- To provide an overview of the advantages of liquid fuels over solid and gas phase fuels for transportation
- Introduce the concept of Heating Value as a measure of the energy density in a fuel
- Describe two methods of estimating Heating Value using empirical formulae
- Describe the importance of experimentation when more accurate measures of heating value is required.



Although less energy dense, liquid fuels are cleaner and more convenient than solid fuels, like coal. Coal was the primary transportation fuel in the 19th century, powering locomotives and steam ships.

Liquids are safer than gas phase fuels since they can be stored and transported at ambient pressures. Hydrogen fuel cells represent a potential technology for utilizing gas phase fuels, however, problems of on-board storage and filling still present challenges for engineers and designers.

Our current transportation infrastructure, whether by road, air, sea or rail, is linked to liquid fuels and will be for the foreseeable future.

Higher and Lower Heating Values of Liquid Fuels

- **The amount of energy potentially liberated from a fuel by combustion is the *heating value***
  - The *Higher Heating Value* (HHV) is where the useful energy of the process is maximized by not vaporizing the water product
  - The *Lower Hearing Value* (LHV) assumes water vapor as the phase of that combustion product
- **Heating values are calculated from heats of combustion at standard conditions**
- **HHV and LHV are related by the heat of vaporization of water**
  - $HHV = LHV + n\Delta\hat{H}_v(H_2O, 25°C)$, where *n* is the moles water produced per mole fuel combusted
- **For mixtures, the HV is a weighted average**
  - $HV = \sum x_i (HV)_i$

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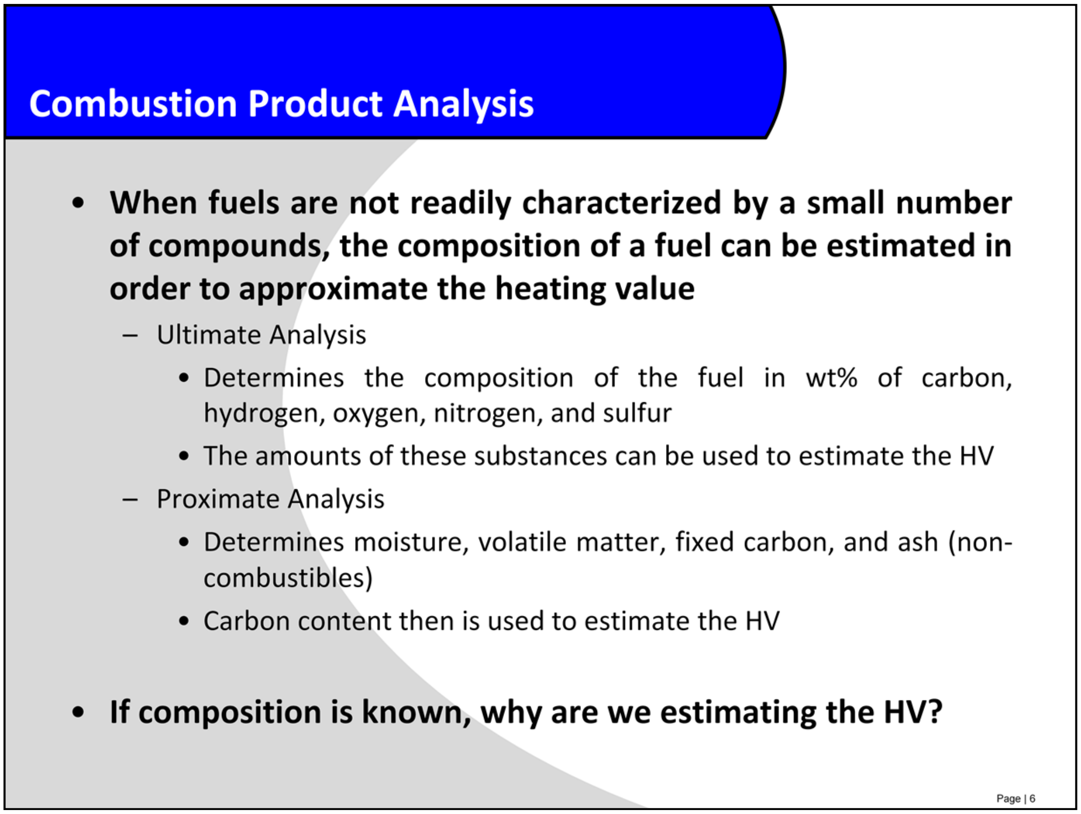
The *Heating Value* of a material is an important component in determining its usefulness as a fuel. The heating value is a measure of the energy density of a fuel. Fuels with a high energy density are desirable because this minimizes the volume of fuel that must be stored on-board in order to achieve an acceptable vehicle range.

As we will see, many fuels are not pure components, and therefore estimating the heating value is not necessarily straightforward. As a result we must utilize empirical methods or direct experimentation to determine the heating value of some fuels.



Many fuels, especially biomass based fuels, are mixtures of large numbers of components. Therefore, estimating the combustion properties from the molecular composition is difficult and impractical. It is common practice to use an elemental analysis to estimate the combustion properties of a fuel.

Two common analytical techniques are Ultimate Analysis and Proximate Analysis.

Answer to question: The elemental composition does not reveal the bond structure in the fuel, and energy is being released when the net energy cost of breaking bonds is less than that of forming bonds in combustion products.

Estimating Heating Values from Compositions

- **Dulong equation (McGowen, 2009)**
  - $HHV\left(\frac{kJ}{kg}\right) = 33{,}801(C) + 144{,}158[(H) - 0.125(O)] + 9413(S)$
    - Here C,H, O, and S are mass fractions of the corresponding elements
- **Equation from Dimirbas (1997)**

$$HHV\left(\frac{MJ}{kg}\right) = [33.5(C) + 142.3(H) - 15.4(O) - 14.5(N)]x10^{-2}$$

- **Using a calorimeter is preferred!**

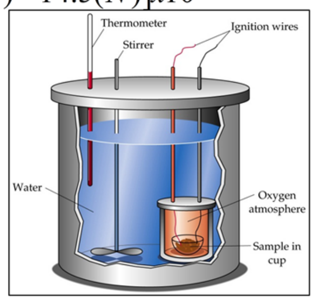


Image: www.itl.chem.ufl.edu

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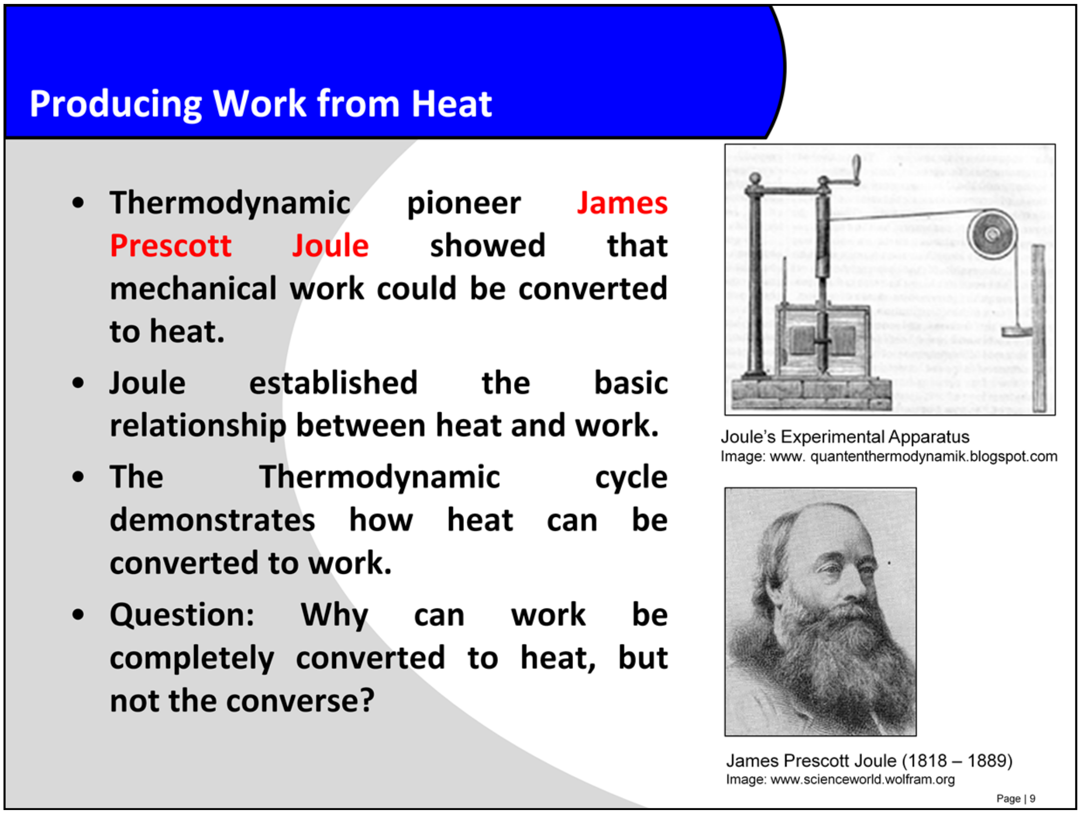
Estimating heating values can be done using empirical formulas. Numerous formulae are available in literature, two of which are presented here. References are included for both equations.

A calorimeter is an experimental device for determining (among other things) the combustion properties of a material. If knowing the precise heating value of a given fuel is required, a calorimeter is the preferred device to measure it. One should always take care when using empirical methods for estimating any physical property!

Thermodynamic cycles are an important concept for describing the conversion of heat to work.

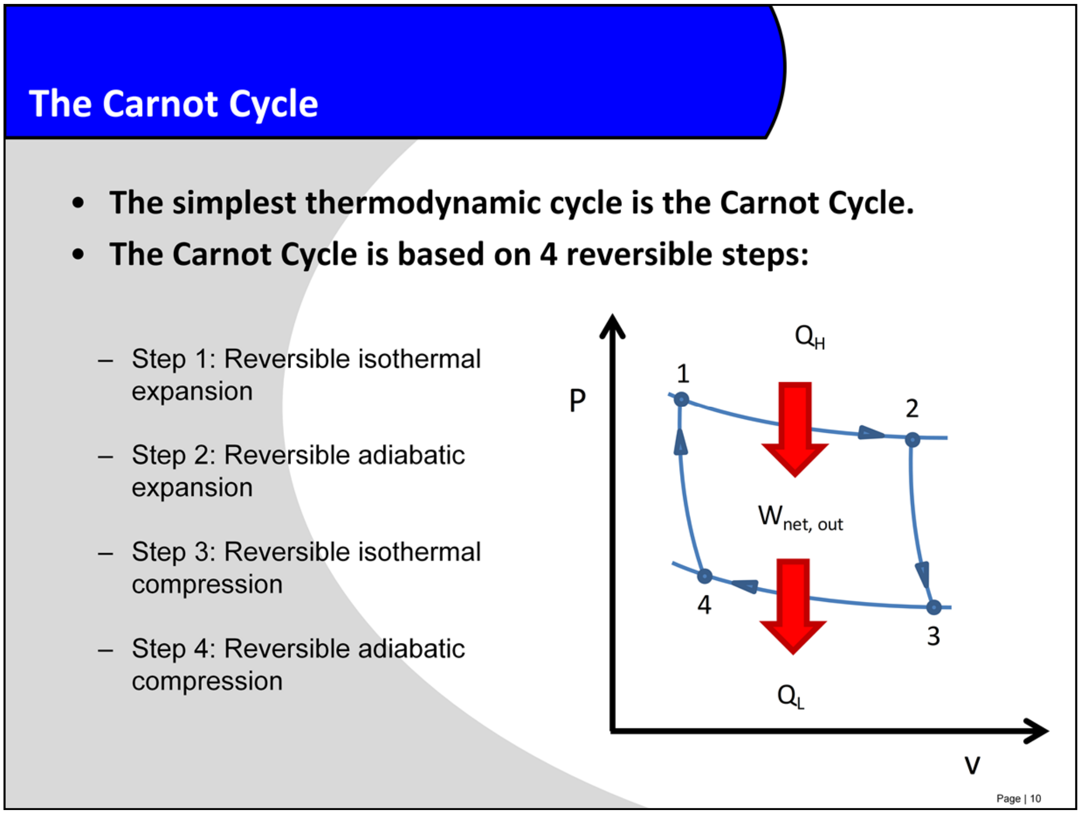
The objectives of this section are:

- Introduce the concept of thermodynamic cycles.
- Describe the step of the ideal Carnot cycle.



Heat released from combustion reactions, such as burning a fuel, is converted to work, which is used to power the engines that move our automobiles. This conversion of chemical energy to heat to work is carried out in a series of steps called a cycle. Therefore, a thermodynamic cycle is a series of individual thermodynamic processes carried out at differing temperatures, pressures, or other state variables. The system eventually returns to its starting state, thus completing the cycle. By completing the cycle, the system produces work on its surroundings – in this way heat is converted to work.

Discussion question: Heat can not be completely converted to work due to irreversibilites in the process, such as frictional losses.



In this P-v diagram, the area under the curve 1-2-3 is the work done by the gas in the expansion part of the cycle.

The area under the curve 3-4-1 is the work done by the gas during the compression part of the cycle.

The area enclosed by the path is the net work done during the cycle.

Since it is reversible, the Carnot Cycle is the most efficient cycle operating between two specified temperature limits.

The cycles that describe the operation of internal combustion are variations of this cycle, including irreversibilities. The Carnot efficiency is the maximum theoretical efficiency of any engine operating between two temperatures.

Overview of Internal Combustion Engines

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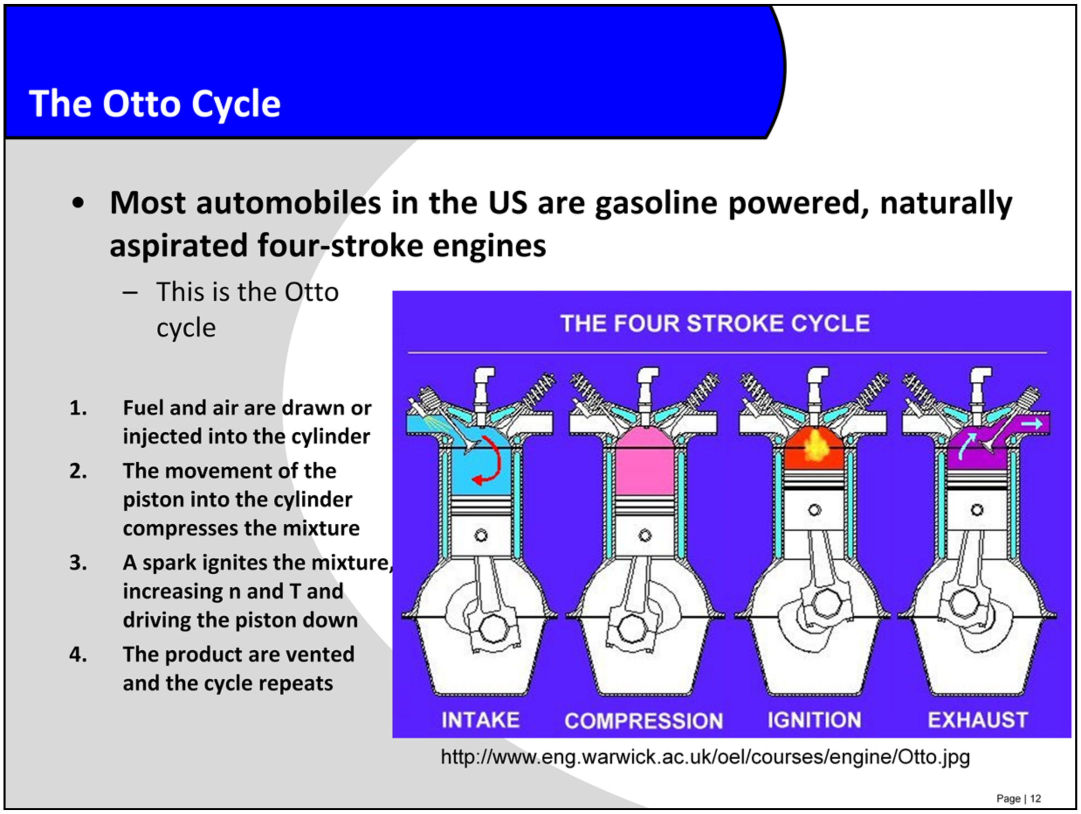
Internal combustion engines are the focus of this module. In this section, the main types of internal combustion engines will be described.

The objectives of this section are:

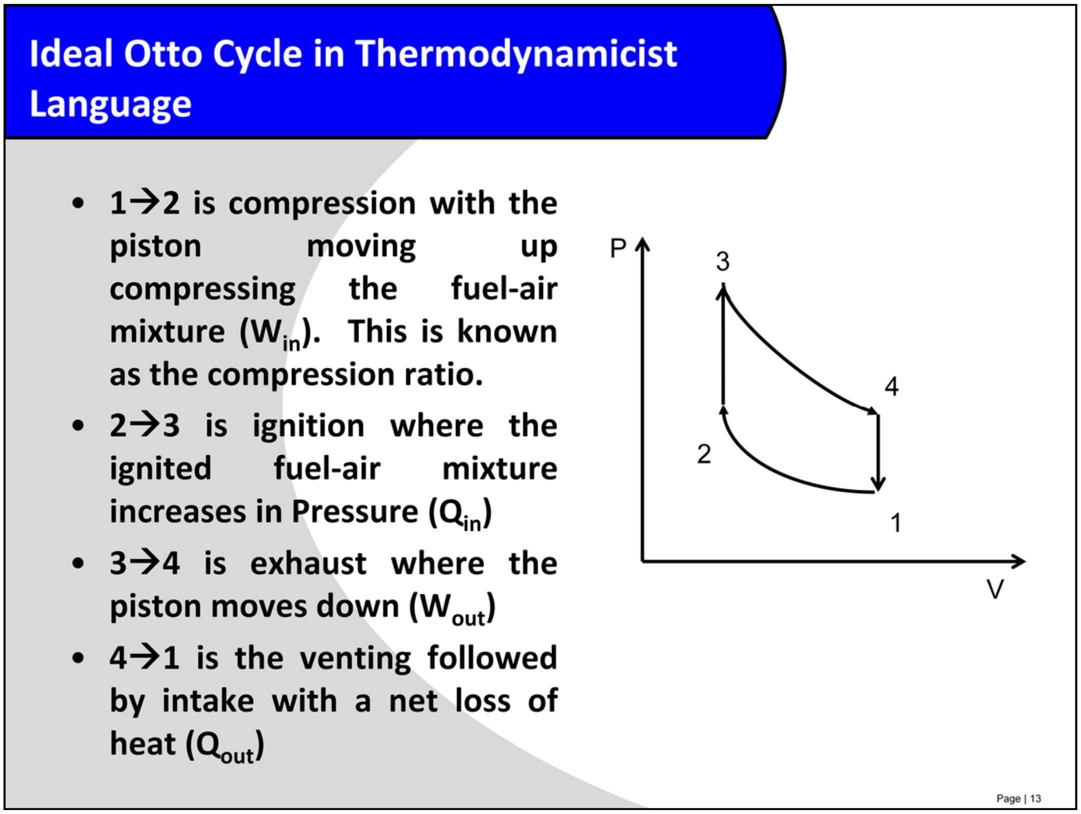
- Describe the Otto cycle as the basis for modern gasoline engines.
- Describe the Diesel Cycle as the basis for modern compression ignition engines.
- Describe the concept to turbo charging and how it applies to internal combustion engines.
- Provide some background data on fuel economies of various vehicles powered by gasoline and diesel engines.



The Otto Engine was developed by German **Nikolaus August Otto** in the 19th century. The Otto Engine is an internal combustion engine, and the basis for the gasoline engines used in automobiles today.

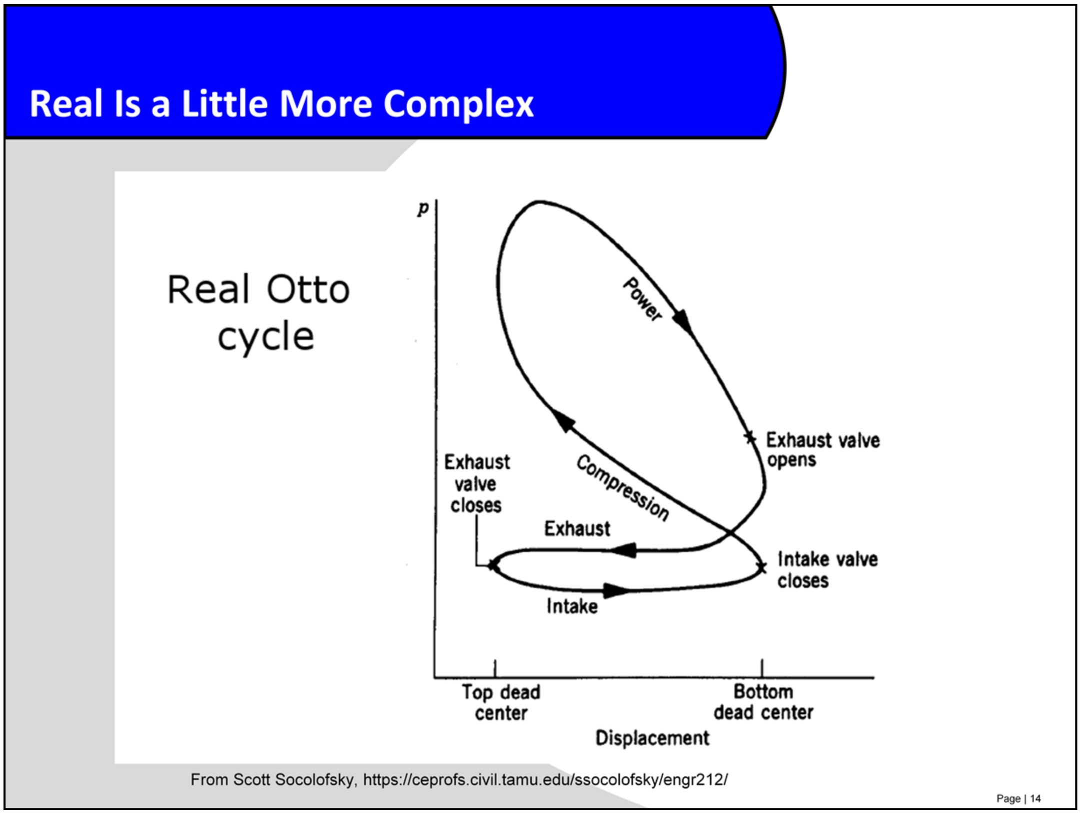
Question for class discussion: What are some recent innovations applied in engines to increase efficiency?

Possible Answers: Variable valve timing, cylinder shutdown, fuel injection, turbocharging

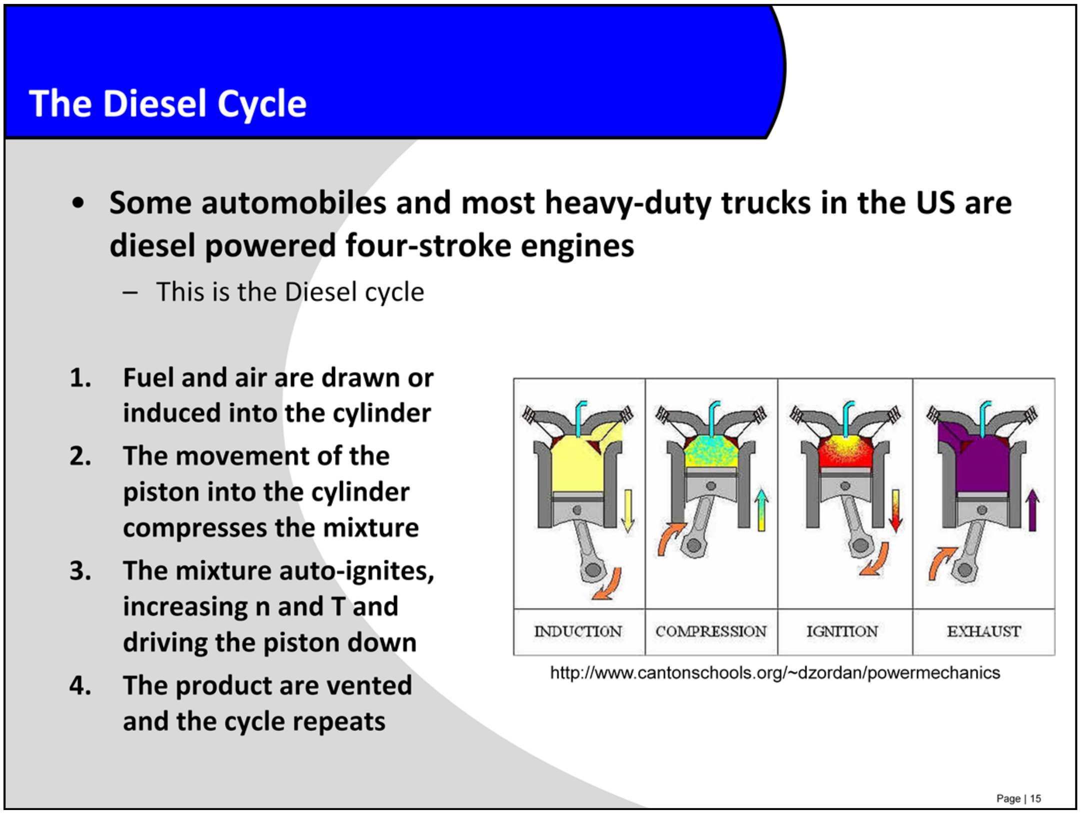


Each step in the 4-cycle spark ignition engine is a separate thermodynamic process. These processes, working together, convert the chemical energy of the liquid fuel to the work needed to move the vehicle it is powering.

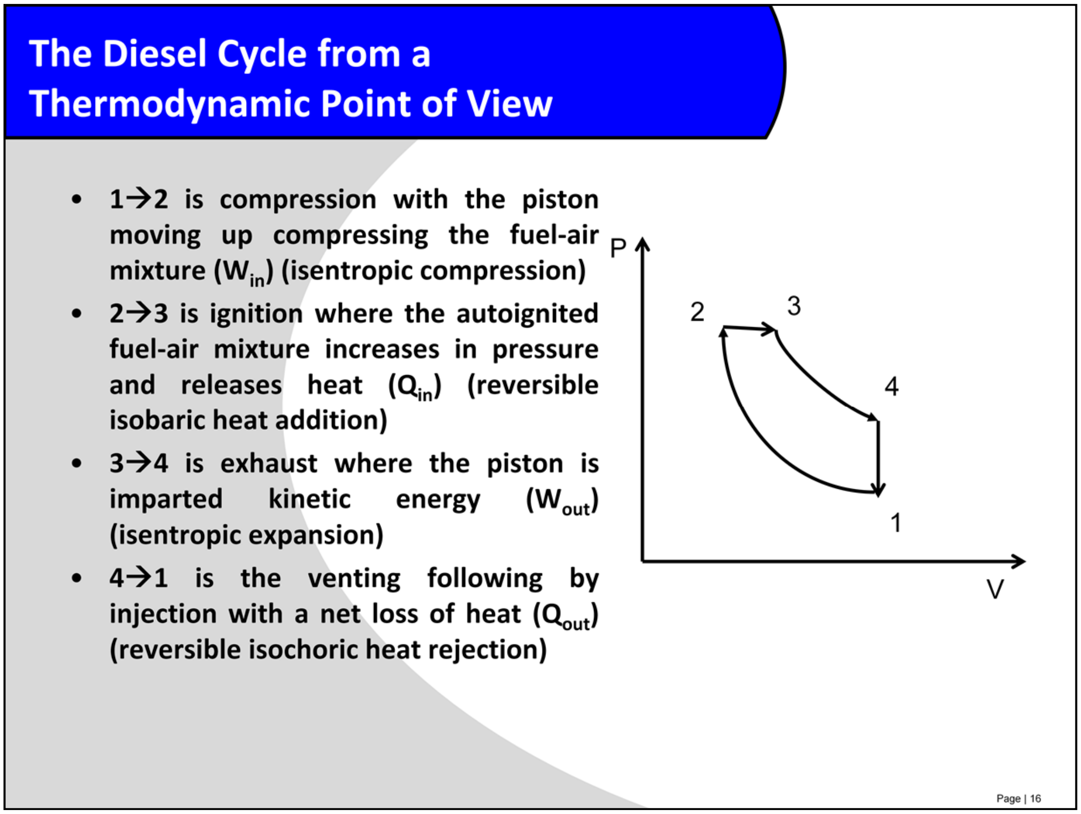
The degree to which the piston volume is compressed from step 1 → 2 in the thermodynamic cycle is known as the compression ratio. As we will see later, compression is an important variable in determining the power and efficiency on an internal combustion engine.



Because the steps in a real engine are not truly adiabatic, and irreversibilities like friction rob efficiency, the real Otto cycle looks quite different from the ideal cycle shown on the previous slide.



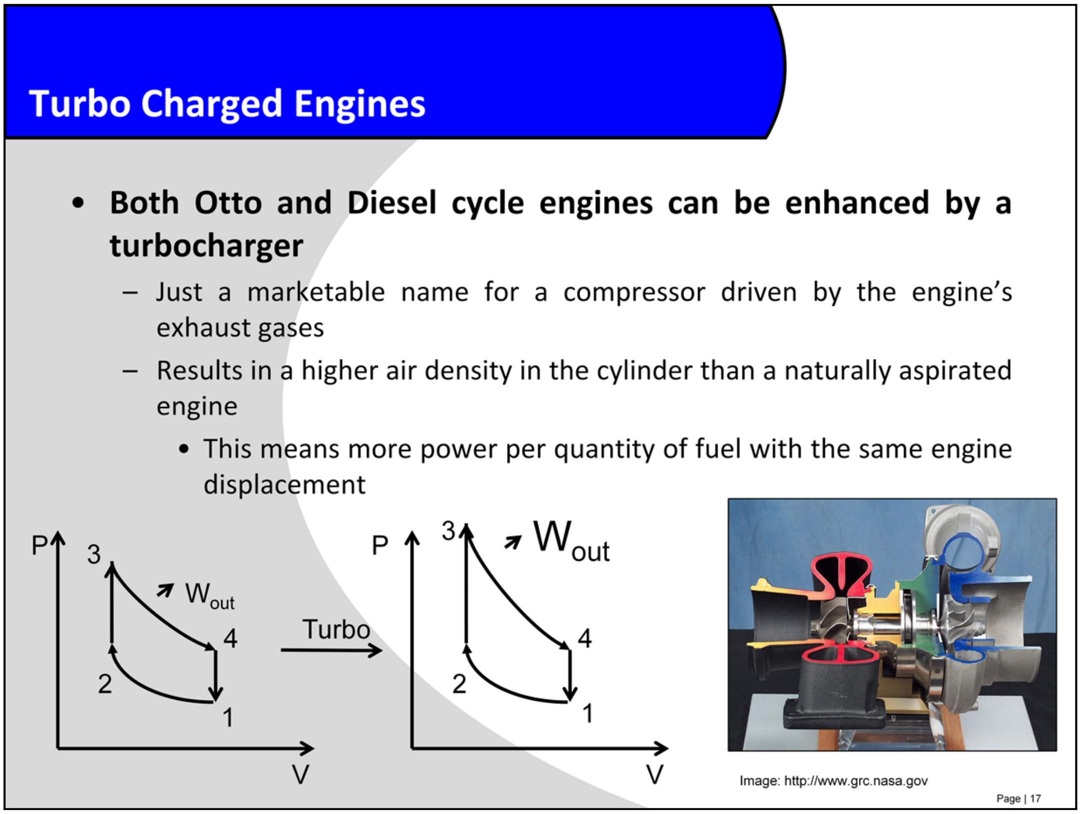
The Diesel Cycle is the thermodynamic basis for the Diesel Engine, developed by German engineer and inventor **Rudolf Diesel**. The chemical energy that is released to drive the engine come from the compression step of the cycle. Therefore, an engine based on the Diesel Cycle is a compression ignition engine (as opposed to the spark ignition of the Otto cycle)



Like the spark ignition Otto engine, each step in the 4-cycle compression ignition engine is also a separate thermodynamic process. These processes, working together, convert the chemical energy of the liquid fuel to the work needed to move the vehicle it is powering.

As with the Otto cycle, the compression ratio is the ratio of the change in the volume of the cylinder from point 1 → 2. As we will see later, Diesel cycle engines operate at higher compression ratios than Otto cycle engines, which has an influence on engine efficiency.

Note the differences between the ideal Otto and ideal Diesel cycles. As with the Otto cycle, irreversibilities and non-adiabatic operation will cause the real Diesel cycle to look quite different from the ideal version shown here.



Turbocharging got its start with aircraft engines to overcome the loss of engine efficiency due to falling atmospheric pressure as the aircraft climbs in altitude. Although this drop in atmospheric pressure is not typically a problem for automobiles, turbochargers can be used to increase engine efficiency or (more commonly) to boost power output without increasing the available combustion volume of the engine.

Disadvantages to turbo charging include "turbo lag", which occurs when the engine rpms increase, but the turbocharger lags behind, and additional wear and tear on the drive train.

Fuel Economy Data for 2011 Model Year Vehicles

2011 Most Fuel Efficient Cars by EPA Size Class* (excluding Electric Drive Vehicles)

EPA Class	Automatic Transmission	Fuel Economy City	Fuel Economy Hwy	Manual Transmission	Fuel Economy City	Fuel Economy Hwy
Two-Seaters	Honda CR-Z 4 cyl, 1.5 L, Auto (AV-S7), Regular Gasoline	35	39	Honda CR-Z 4 cyl, 1.5 L, Manual (M6), Regular Gasoline	31	37
Minicompacts	MINI Cooper 4 cyl, 1.6 L, Auto (S6), Premium Gasoline	28	36	MINI Cooper 4 cyl, 1.6 L, Manual (6), Premium Gasoline	29	37
Subcompacts	Ford Fiesta SFE FWD 4 cyl, 1.6 L, Auto (AM6), Regular Gasoline	29	40	Toyota Yaris 4 cyl, 1.5 L, Manual (5), Regular Gasoline	29	36
Compacts	Lexus CT 200h 4 cyl, 1.8 L, Automatic (CVT), HEV, Regular	43	40	Volkswagen Golf 4 cyl, 2.0 L, Manual (6), Diesel	30	42
				Volkswagen Jetta 4 cyl, 2.0 L, Manual (6), Diesel	30	42
Midsize	Toyota Prius Hybrid 4 cyl, 1.8 L, Auto (CVT), HEV, Regular Gasoline	51	48	Hyundai Elantra 4 cyl, 1.8 L, Manual (6), Regular	29	40
Large	Honda Accord 4 cyl, 2.4 L, Auto (5), Regular Gasoline	23	34	Hyundai Sonata 4 cyl, 2.4 L, Manual (6), Regular Gasoline	24	35
Small Station Wagons	Audi A3 4 cyl, 2.0 L, Auto (S6), Diesel	30	42	Volkswagen Jetta SportWagen 4 cyl, 2.0 L, Manual (6), Diesel	30	42
Midsize Station Wagons	Kia Rondo 4 cyl, 2.4 L, Auto (4), Regular Gasoline	20	27			

Source: www.fueleconomy.gov

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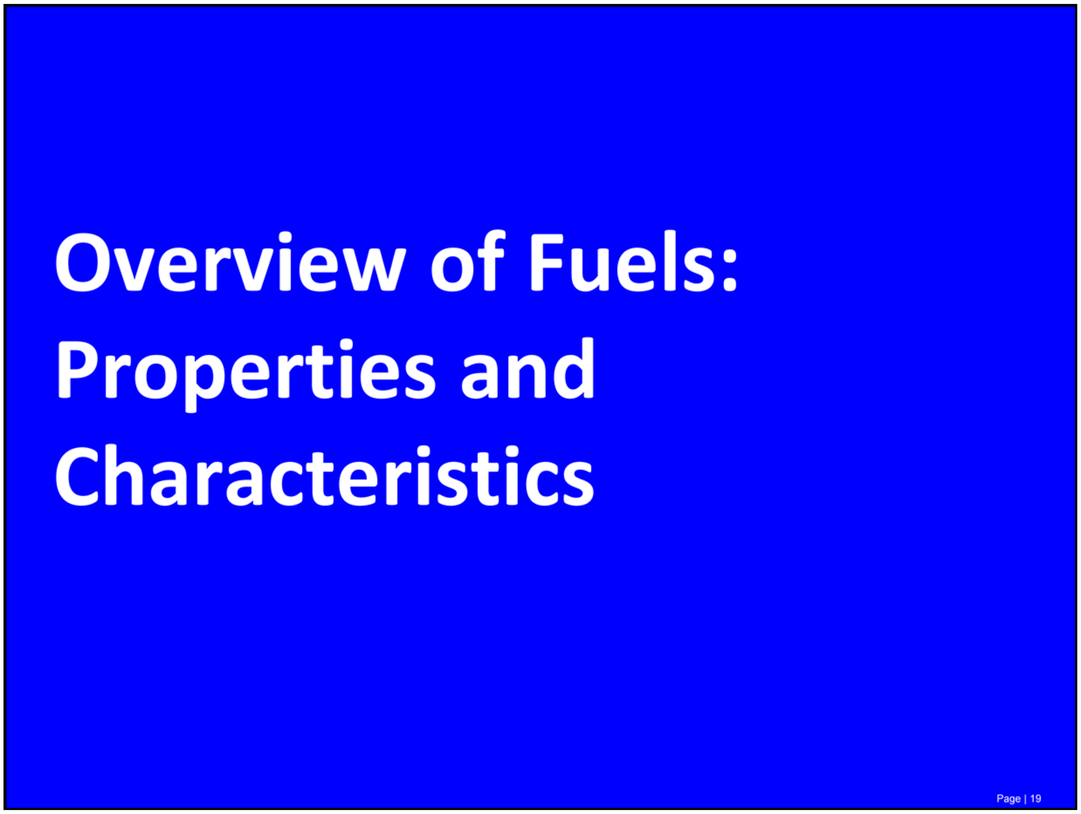
For comparison, note that the Hybrid Toyota Prius gets an EPA rated 48 MPG HWY and 51 MPG City.

Generally speaking, diesel engines get better fuel economy that gasoline engines. This is attributed to both the greater energy density of the fuel and the higher compression ratios achieved by the diesel cycle.

Point for class discussion: Why aren't all engines diesel, since they get better fuel economy?

- Discussion points may include the following:
- Because of the higher compression ratio, diesel engines tend to be high torque, rather than high RPM. This means that they can seem sluggish when compared with gasoline engines. Note that trucks designed to haul heavy loads are overwhelmingly powered by diesel engines.
- Due to the compression ignition, diesel engines tend to vibrate, leading to a less comfortable ride than gasoline engines.
- Historically, diesel engines have been heavier, and thus more expensive than their gasoline powered counterparts.
- Until recently, diesel fuel standards allowed a higher sulfur content, leading diesel powered vehicles to have an unpleasant, "rotten egg" smell.
- Diesel engines can be difficult to start in cold weather.

Many of these issues have been addressed in modern diesel engines, however, the public is often slow to let go of old stereotypes, so diesel engines have been slow to gain market share outside of the trucking industry, where the need for higher torque outweighs any other drawbacks of using diesel fuel.



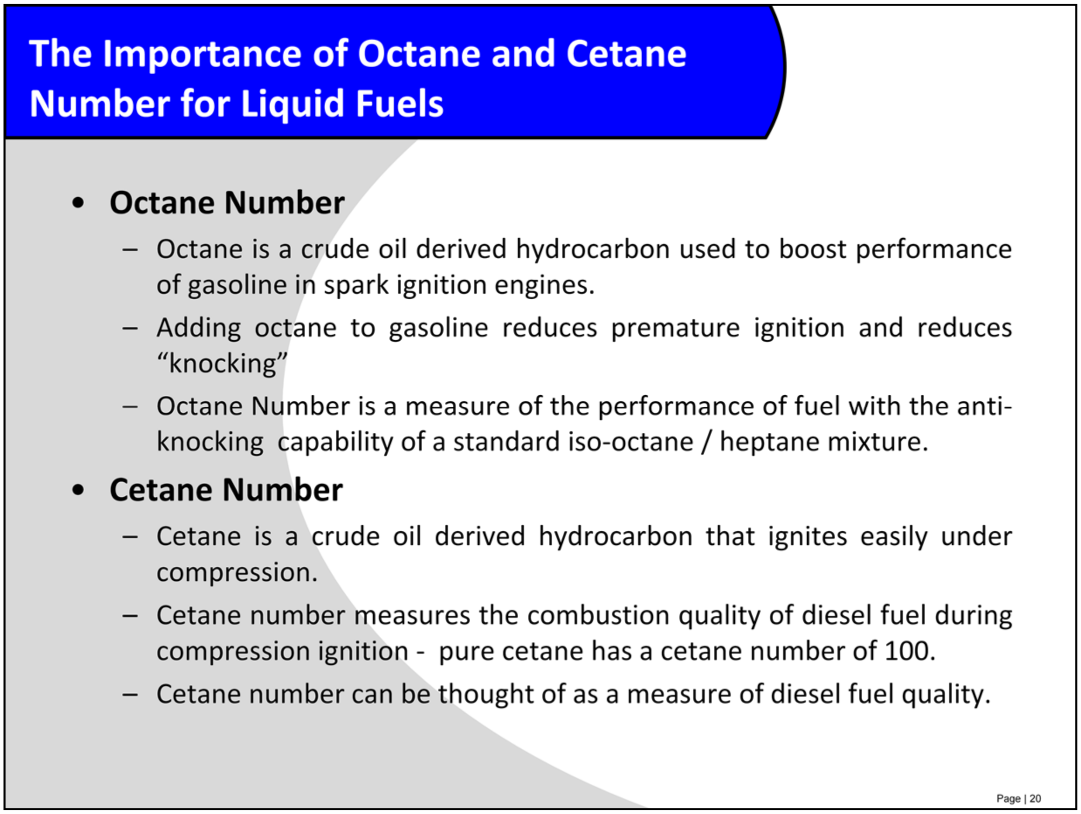
There are numerous choices available for liquid fuels, including those derived from petroleum and those derived from biomass.

The physical properties of these fuels vary greatly and each has its own advantages and disadvantages for use as a transportation fuel. This section will provide an overview of the most common transportation fuels.

The objectives of this section are:

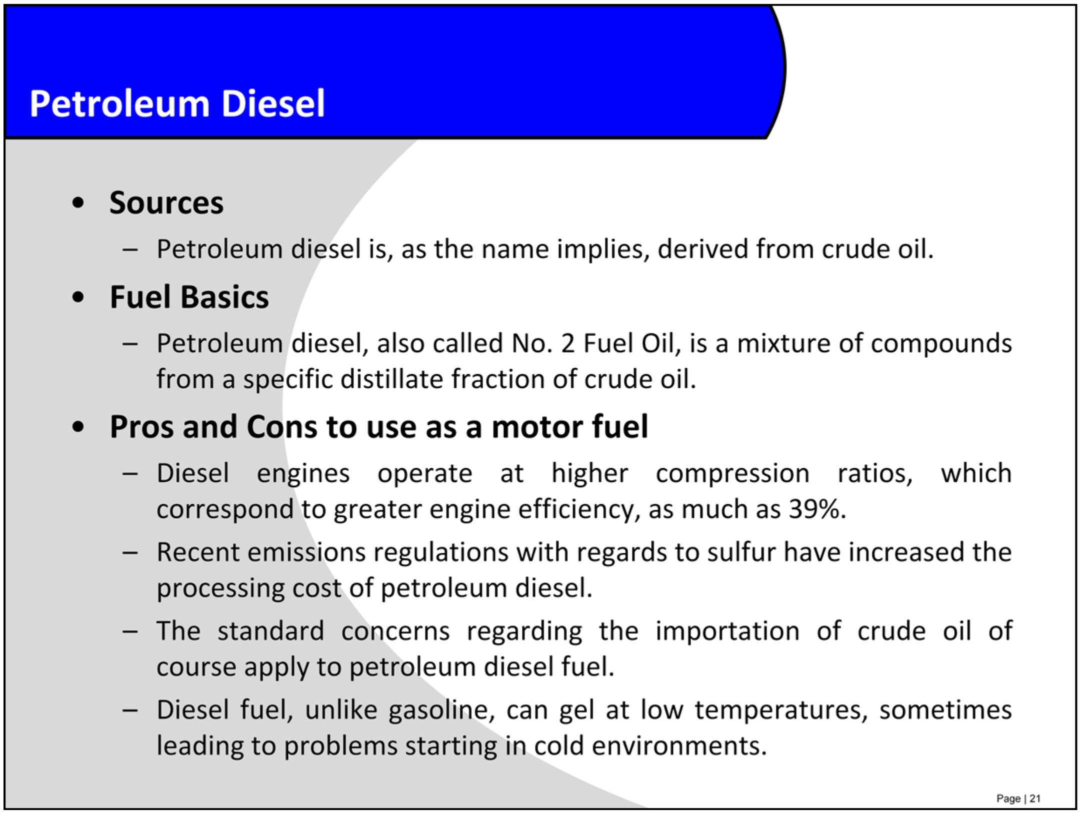
- Provide an overview of commonly used terms to describe liquid fuels like Octane Number and Cetane Number

- Provide an overview of commonly used petroleum based and biobased liquid fuels



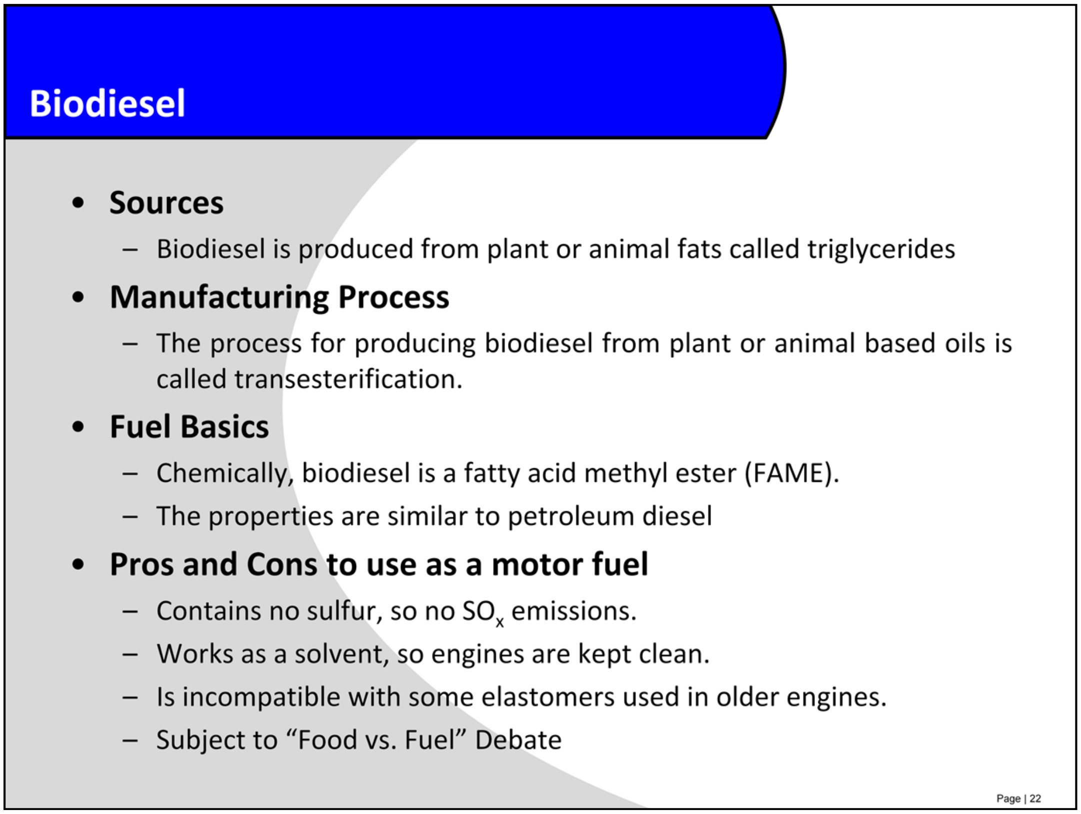
Although octane does not increase the heating value of a fuel, it improves the ability of the fuel to burn in a controlled way, instead of exploding. This exploding in the engine cylinder is called "knocking." Octane number for gasoline refers to the anti-knocking capacity of the fuel in comparison with a mixture of iso-octane and heptane. "Regular Gasoline" sold at most gas stations has an octane number of 87. This means that the anti-knocking capacity of that fuel is equivalent to a mixture of 87% iso-octane / 13% heptane. In years past, tetra-ethyl lead was used as an anti-knocking agent (hence the term "leaded gasoline"), however, this has been phased out due to environmental and public health concerns. Some fuel blends have an anti-knocking capacity greater that 100% iso-octane, leading to octane number greater than 100%. Other additives, like MTBE, toluene and ethanol can also reduce knocking.

Cetane number is a measure of the ignition delay of a fuel in a compression ignition engine. Much like octane number in gasoline, the cetane number of a diesel fuel is a measure of the ignition delay properties of a diesel fuel relative to a standard mixture of cetane and isocetane. Diesel engines typically require a cetane number between 40 and 55. Since Diesel fuel is a mixture of hundreds of molecules, the cetane number, which is determined experimentally, is an average of the cetane number of all the species in a fuel sample.



Petroleum diesel (No. 2 fuel oil) is the most commonly used fuel for trucking and heavy equipment in the United States. Its high energy density makes it an ideal fuel for Diesel engines. The principle drawbacks include:

- The current volatility of the crude oil market.
- The fact that most crude oil used in the United States is imported.
- Potential future supply shortages (although there is little debate on this point, the time horizon for this occurrence is highly speculative and open to robust debate).
- Concerns over carbon dioxide emissions as well as other combustion products like NOx and SOx.



Biodiesel is a biobased fuel made from oils or fats. It can be burned in a standard Diesel engine, provided no natural rubber products are used. Biodiesel is an excellent solvent and will dissolve natural rubber, however all US Diesel engines currently produced are biodiesel compatible. The feedstock can come from used cooking oil or dedicated crops, such and soybeans or canola (rapeseed). In fact, the Diesel Engine was originally envisioned to burn vegetable oil based fuel, giving farmers the means to "grow" their own fuel. Data from the US Department of Agriculture show that by dedicating as little as 6% of crop land to oil seeds, a farmer can produce enough fuel to power farming equipment for an entire growing season. Additionally, use of biodiesel, as opposed to petroleum diesel, keeps engines cleaner and eliminates SOx emissions.

However, in addition to oil, methanol and a catalyst (usually sodium hydroxide) are also required. Finally, in addition to biodiesel, the transesterification reaction also produces glycerol as a side product. Unless there is a nearby use for this glycerol, it becomes a waste product, reducing the overall efficiency of the process. At current market conditions, biodiesel is not cost competitive with petroleum diesel without additional tax incentives. However, rising crude oil prices and ongoing research into processes to utilize crude glycerol could result in making biodiesel competitive with petroleum diesel.

The most pressing point of debate regarding the use of biodiesel is the so called "food vs. fuel" debate. This debate involves the long term sustainability of producing transportation fuel from a food product. Although production of biodiesel only utilizes the oil and leaves the protein behind for food usage, some food yield is lost through biodiesel production. The food vs. fuel debate is certainly one that must be addressed, however, it is likely that biodiesel will remain part of the renewable energy picture moving forward.

Fischer-Tropsch Liquid Fuels

- **Sources**
  - Can be derived from any hydrocarbon source, such as coal or biomass.
- **Manufacturing Process**
  - Hydrocarbons are converted to a mixture of CO and H_2 called synthesis gas (syngas) by reaction with steam in the absence of O_2.
  - Syngas is then converted using a catalyst to long chain alkanes.
- **Fuel Basics**
  - Fischer-Tropsch fuels are long chain alkanes that can be used to fuel diesel engines.
- **Pros and Cons to use as a motor fuel**
  - Can be used to displace crude oil derived fuels.
  - Can convert waste biomass such as crop residues into useful fuels.
  - Currently not economically competitive with fossil fuels at current oil prices.

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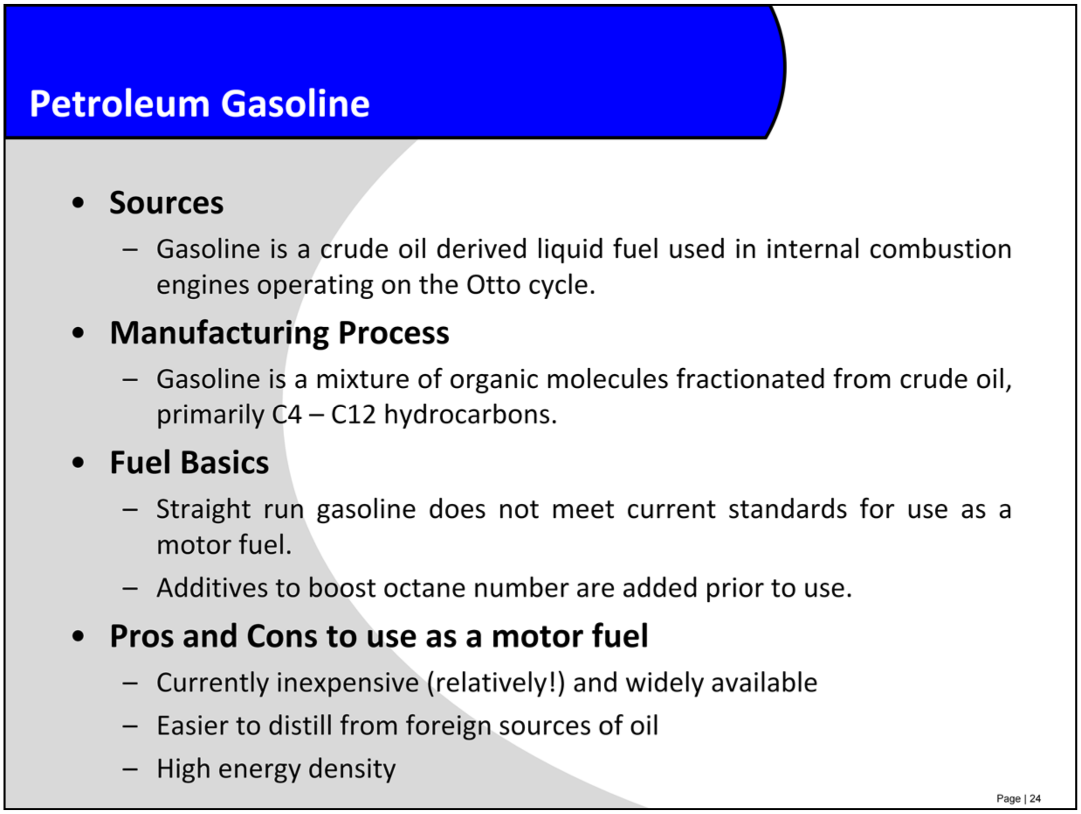
The process for converting coal into syngas has been around since the 19th century. Before reliable supplies of natural gas were discovered, gasified coal, called “towngas” was used for streetlights in many cities.

The Fischer-Tropsch process for converting syngas to liquid fuels using a catalyst was developed in Germany during World War II. As the German army lost access to petroleum supplies, they developed the technology to convert coal, which was abundantly available in Germany, to a diesel equivalent to fuel their military operations.

After the war, this process fell out of favor since converting petroleum was far easier and cheaper. Recently, however, Fischer-Tropsch synthesis has gained new life as a process for converting biomass into liquid transportation fuel.



Petroleum gasoline is the most commonly used fuel for passenger cars in the United States. Its high energy density and performance in cold weather make it an ideal liquid transportation fuel for passenger road travel. The principle drawbacks are similar to the drawbacks of petroleum diesel and include:

- The current volatility of the crude oil market.
- The fact that most crude oil used in the United States is imported. Foreign oil tends to be "light, sweet" crude which is more readily distilled to gasoline.
- Potential future supply shortages (although there is little debate on this point, the time horizon for this occurrence is highly speculative and open to robust debate).
- Concerns over carbon dioxide emissions as well as other combustion products like NOx and SOx.

Ethanol and Ethanol / Gasoline Blends

- **Sources**
  - Ethanol is typically produced from agricultural sources such as corn or sugarcane.
- **Manufacturing Process**
  - Ethanol is produced in a biological process called fermentation.
- **Fuel Basics**
  - Ethanol is an alcohol and has a high octane rating when used in internal combustion engines operating on the Otto cycle.
- **Pros and Cons to use as a motor fuel**
  - Higher octane level of ethanol can boost engine horsepower and allow operation at higher compressions ratios, improving engine efficiency.
  - Loss of MPG rating in flex fuel vehicles using E85 blend.
  - Standard "food vs. fuel" debates apply unless ethanol is produced from waste cellulose

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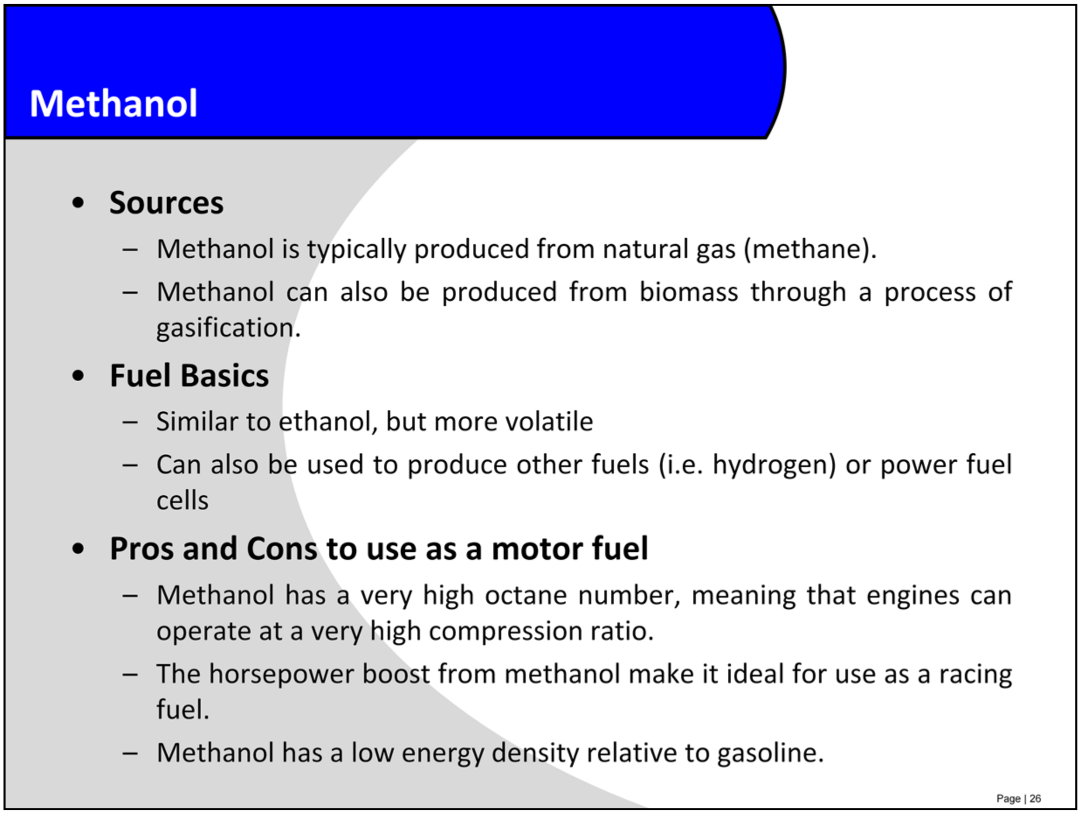
Ethanol has been used for years as an additive to boost the octane number of petroleum gasoline. Ethanol is a less toxic alternative to a compound called MTBE which is the primary octane boosting additive to petroleum gasoline. Unmodified gasoline engines can run on mixtures of up to 10% ethanol, added as an octane booster. However, many gasoline engines have been modified to run on a blend of up to 85% ethanol, called E85. The principle drawback to the use of E85 is a loss in fuel economy due to the low heating value of ethanol as compared to gasoline. However, many people tout the environmental benefits of ethanol, particularly with regard to reduction of carbon dioxide emissions.

The viability of ethanol as a liquid transportation fuel depends in large part on the feed stock used. Using a starch, like corn, requires a two step process – first converting the starch to sugar, then converting the sugar to alcohol. This greatly reduces the efficiency of the process and increases the production cost. If ethanol is produced from sugarcane or sugar beets, the efficiency is much improved. In addition to the simpler production process, sugar cane and sugar beets contain much more sugar per plant volume than corn, improving the yield per acre.

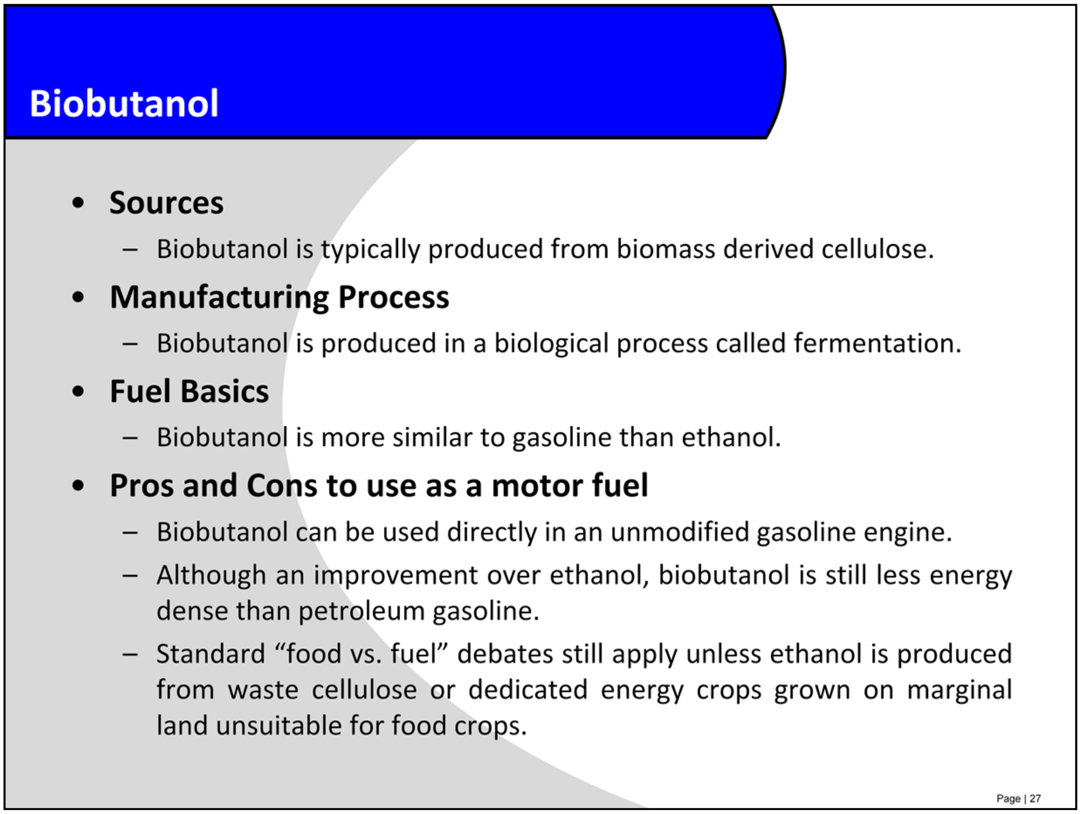
As with biodiesel, a major point of debate regarding the use of ethanol as a fuel involves the production of fuel from a food item – the so called "food vs. fuel" debate. Although the ethanol production process still leaves much of the corn behind as "distillers mash", which is used as an animal feed, some of this food crop is converted to fuel. This problem can be solved using a process called cellulosic ethanol. In this process, the non-food part of the plant, the stalk and the cobs are converted to ethanol through an enzymatic process.

Unfortunately, this process is not yet economically viable at current market conditions, although ongoing research aims to improve the economics of this process.



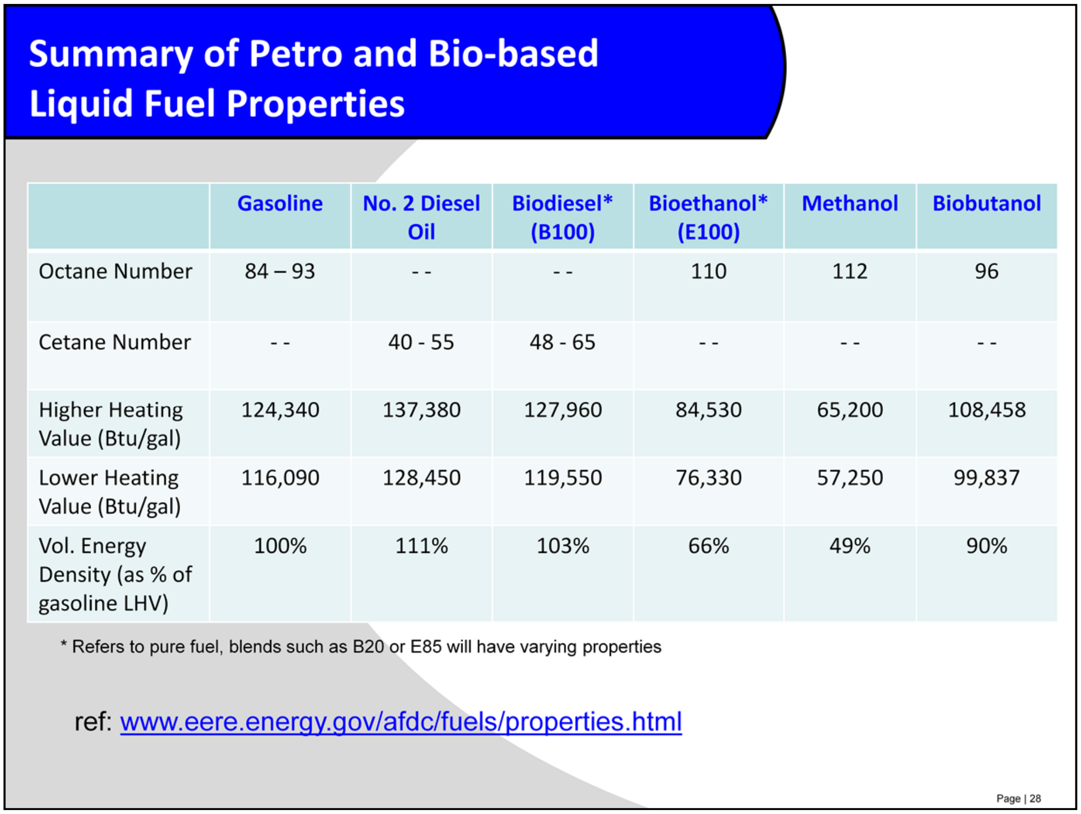
Methanol has not found widespread use as a road transportation fuel. Its low energy density makes it impractical for long distance travel, and it is significantly more expensive than gasoline. It is, however often used to fuel racecars, due to its high octane number. Additionally, methanol is less explosive than gasoline, leading to improved driver safety in the event of a crash.

Although methanol can be produced from biomass (via a process called destructive distillation of wood), most commercially produced methanol uses natural gas (methane) as a raw material.



Biobutanol shows a lot of promise as a liquid transportation fuel. Unlike ethanol or methanol, it can be burned directly in an unmodified gasoline engine. Although still less energy dense than gasoline, biobutanol, due to its additional C-C bonds is much more energy dense than ethanol.

Currently, biobutanol is not cost competitive with petroleum gasoline at current prices, however, ongoing research aims to close this gap.



Summary of Petro and Bio-based Liquid Fuel Properties

	Gasoline	No. 2 Diesel Oil	Biodiesel* (B100)	Bioethanol* (E100)	Methanol	Biobutanol
Octane Number	84 – 93	- -	- -	110	112	96
Cetane Number	- -	40 - 55	48 - 65	- -	- -	- -
Higher Heating Value (Btu/gal)	124,340	137,380	127,960	84,530	65,200	108,458
Lower Heating Value (Btu/gal)	116,090	128,450	119,550	76,330	57,250	99,837
Vol. Energy Density (as % of gasoline LHV)	100%	111%	103%	66%	49%	90%

* Refers to pure fuel, blends such as B20 or E85 will have varying properties

ref: www.eere.energy.gov/afdc/fuels/properties.html

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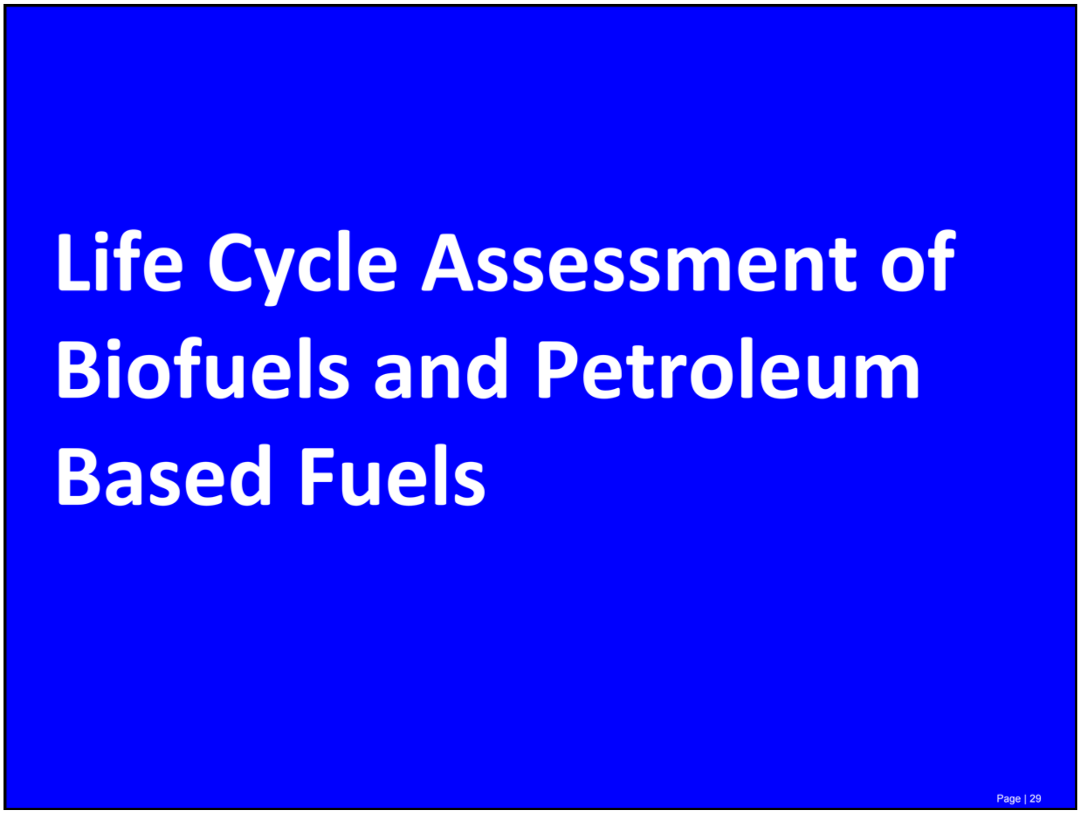
This table summarizes some of the key physical property differences between some of the most common petroleum and bio-based liquid transportation fuels. From an energy content perspective only, the advantages of petroleum derived fuels are clear. However, when considering societal and environmental factors, along with future supply concerns, renewable fuels become more attractive.

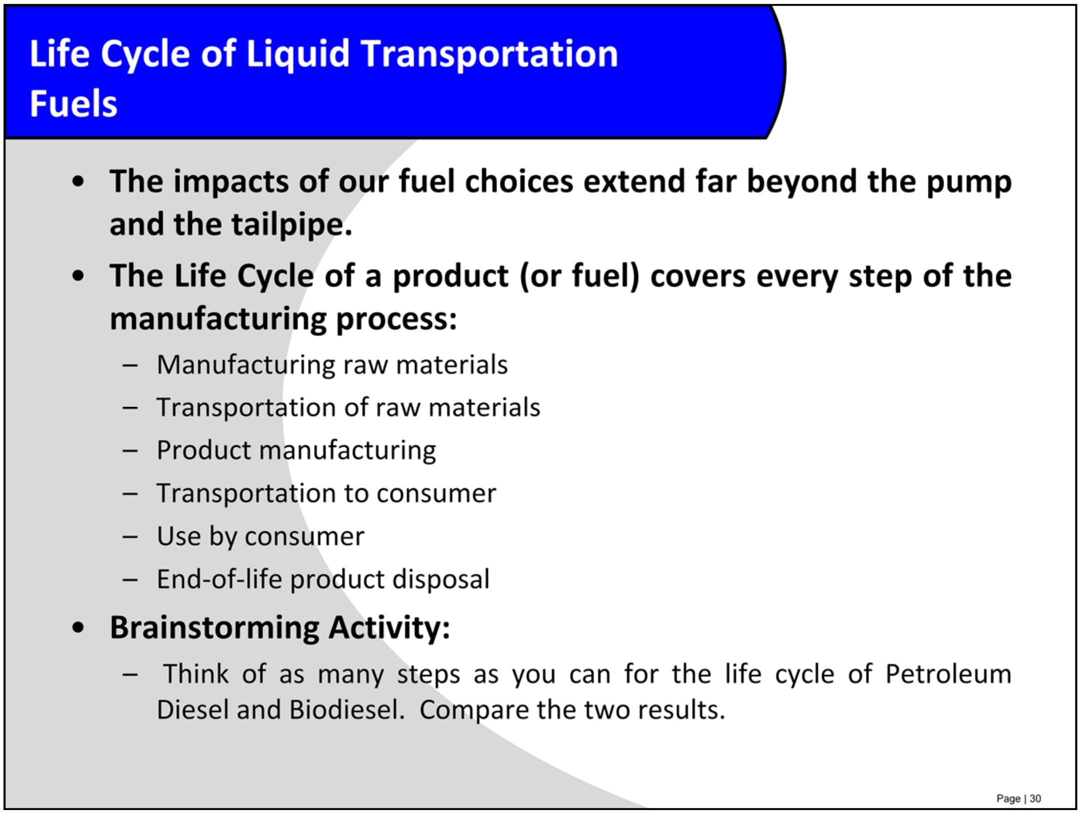


Any assessment of the social, economic and environmental impacts of a product, including fuels, must include the entire lifecycle in order to be accurate.

The objectives of this section are:

- Illustrate the importance of considering the entire product lifecycle in assessment of fuels.

- Provide an overview of the petroleum based and biobased fuel lifecycle.



Life cycle analysis is technique to determine the costs (environmental, economic and social) for every step in the life of a product – from acquiring and processing raw materials to the disposal of the final product after use.

Life cycle analysis is often thought of as a "cradle to grave" accounting of a product, or in this case a fuel.

Life cycle analysis is complex, because so many steps are involved in the manufacture of a product. However, the true cost (again, environmental, economic and societal) can not be accurately evaluated until a life cycle analysis is complete.

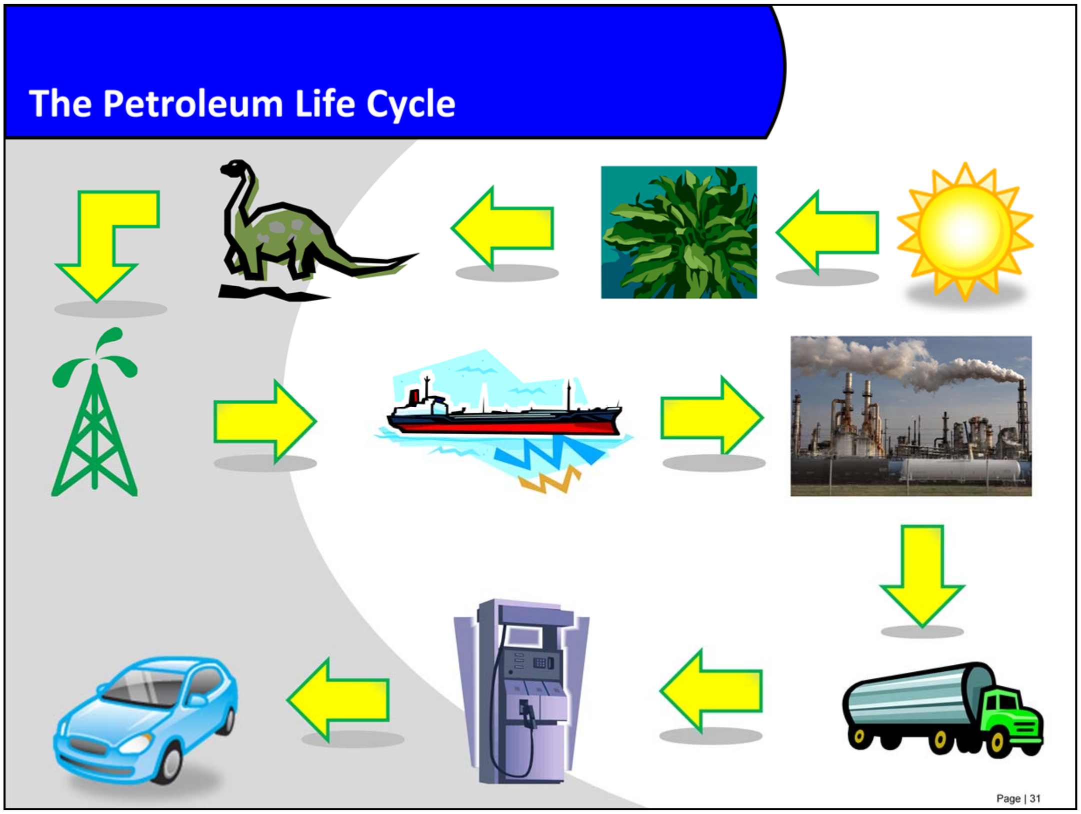
Possible results for Brainstorming Activity (results illustrated on the next two slides):

Petroleum Diesel

Oil Wells
Transportation (often over long distances)
Refining
Distribution
Combustion in your engine

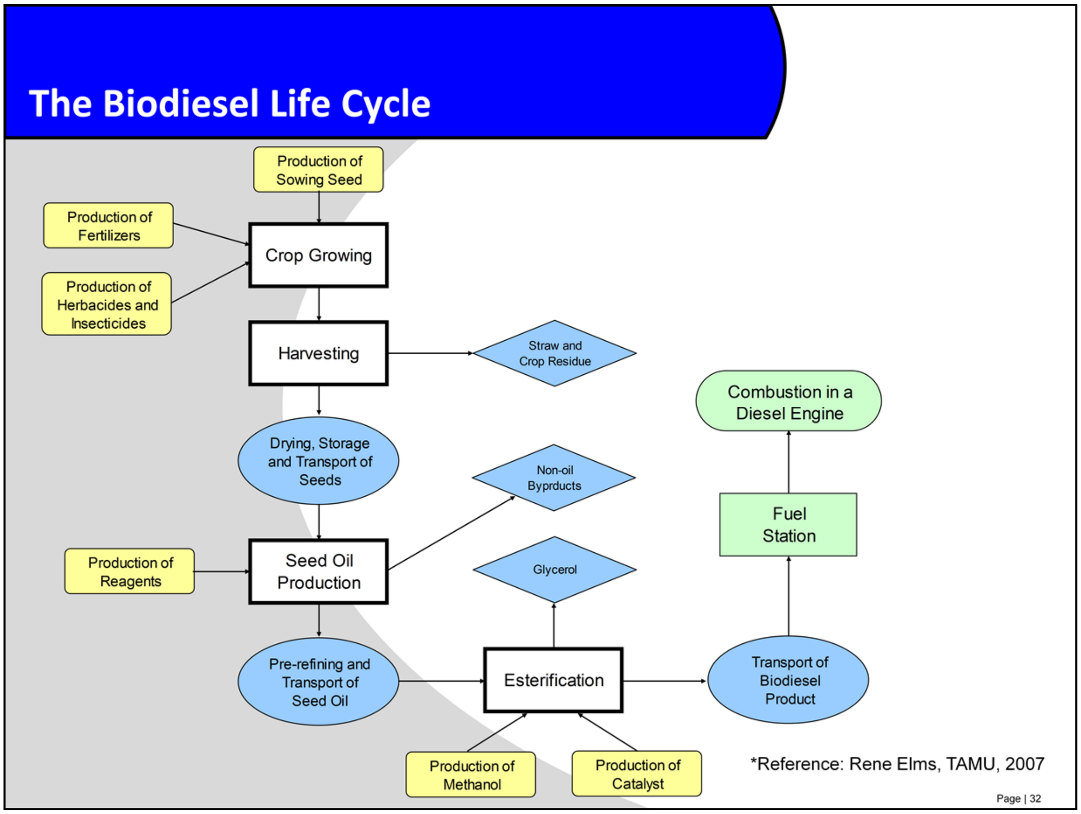
Biodiesel

Crop Production (planting, fertilizing, insect and weed control)
Transportation (usually short distances)
Chemical conversion or fermentation
Distribution
Combustion in your engine



Petroleum can really be thought of as "vintage biomass". Plants convert carbon dioxide from the atmosphere into biomass as they grow using energy from the sun. As the plants die, or are consumed by animals who later die, they are converted over time (under the right conditions) into crude oil.

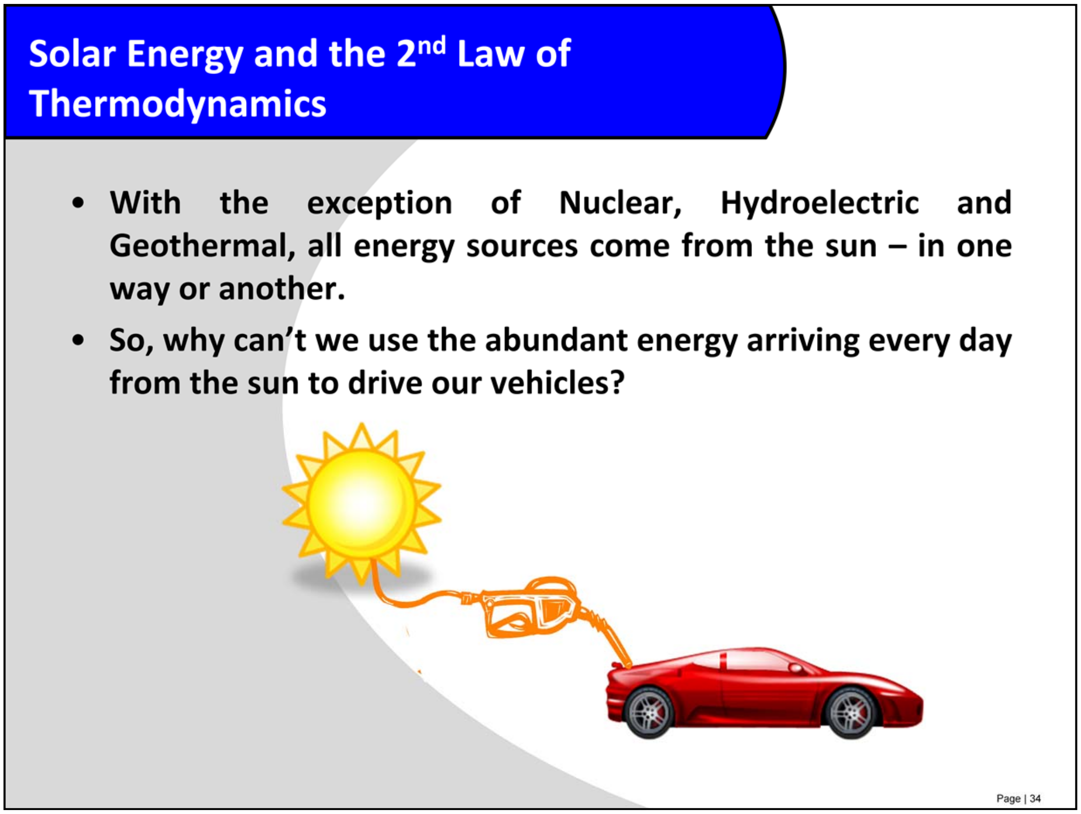
This crude oil must be extracted from underground, shipped (often over long distances) to a refinery where it is processed into fuels and other products. Finally, this fuel is transported to a distributor where it is sold and burned in an internal combustion engine. This combustion process releases the carbon dioxide that was originally stored in the biomass back into the atmosphere



The biodiesel lifecycle goes much further than simply converting vegetable oils and/or animal fats via the transesterification reaction. Biodiesel is often considered to be "carbon neutral" since the carbon dioxide released by combustion is offset by the growth of the plants needed to produce the vegetable oils. However, this assessment is overly simplistic. A true evaluation of the environmental impacts of biodiesel must also include the production of the alcohol (usually methanol) and catalyst (usually sodium hydroxide) used to product the fuel.

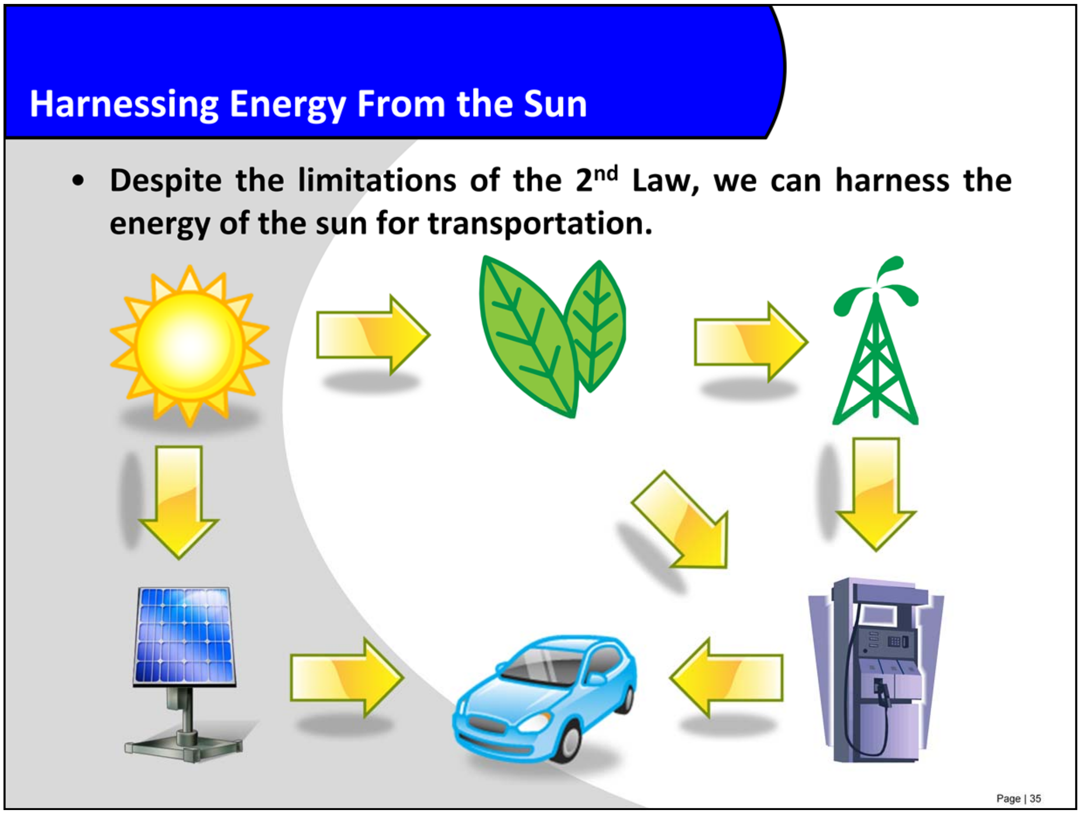
Additionally, the production of insecticides, herbicides and fertilizers must be considered, along with the fuel needed to plant and harvest the oil seeds. This is not to say that biodiesel is not environmentally friendly, but to point out that determining its impacts is not an easy process!

All energy derived from crude oil or biomass sources originally came from the sun. This section will provide an overview of the solar basis for the energy found in liquid fuels.



Since we now understand that heat can be converted to work, it stands to reason that a heat engine driven by heat reaching the earth's surface from the sun could provide all our energy needs. The 1st Law would seem to be in agreement with this assumption. However, even though the sun does provide a tremendous amount of energy, the 2nd Law tells us that this heat cannot provide a useful quantity of work for transportation due to the temperatures at which ambient solar heat is collected and rejected. (Refer to Heat Engine Example Problem).

Estimates of the amount of solar energy that reach the ground on earth are in the range of 0 W/m^2 at night to 1,050 W/m^2 under sunny summertime conditions (Testor, *et al*., 2005), however, despite this large amount, the solar energy reaching the ground has a low energy density. Therefore, in order to be useful as a transportation fuel, solar energy must be concentrated, such as by charging batteries using a photovoltaic collector. However, nature already provides a means of collecting and concentrating solar power – through the growth of plants. As we know, biomass can be either converted directly to liquid fuel, or converted to crude oil through geologic processes.

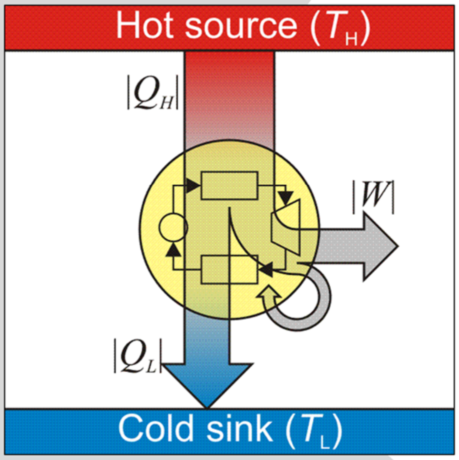


Solar energy can be directly converted to electricity to operate an electric vehicle or to biomass which can be converted to crude oil in geologic processes or directly to liquid fuels in a biorefinery.

As previously illustrated, petroleum is really just vintage biomass – solar energy that has been converted to biomass by plants and into crude oil by heat, pressure and time.

These in-class example problems are provided in addition to the homework problems included with this module.

Solar Heat Engine Example Problem



- Consider a vehicle powered by passive solar energy alone.
- This vehicle consists of a high temperature reservoir heated to 175°F by the sun.
- The heat engine powering the vehicle rejects heat to the atmosphere which we will assume to be 95°F.
- If the maximum heat input from the sun, Q_H, is 1.05 kW, what is the power available to drive the vehicle?
- Is this reasonable?

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Note the QH value assumes a 1 m^2 solar collector at peak capacity.

Solar Heat Engine Solution

- **First, we calculate the maximum theoretical efficiency of the heat engine operating between the two reservoirs:**

$$\eta = 1 - \frac{T_C}{T_H} = 1 - \frac{555°R}{635°R} = 0.127$$

- **Next, we calculate the available work, and convert to horsepower.**

$$|Work| = \eta \cdot Q_H = 0.127 \cdot 1.05kW = 0.133kW = 0.178hP$$

- **Considering that a small passenger sedan typically comes equipped with an engine in the range of 100 hP, a solar powered heat engine would not be practical.**

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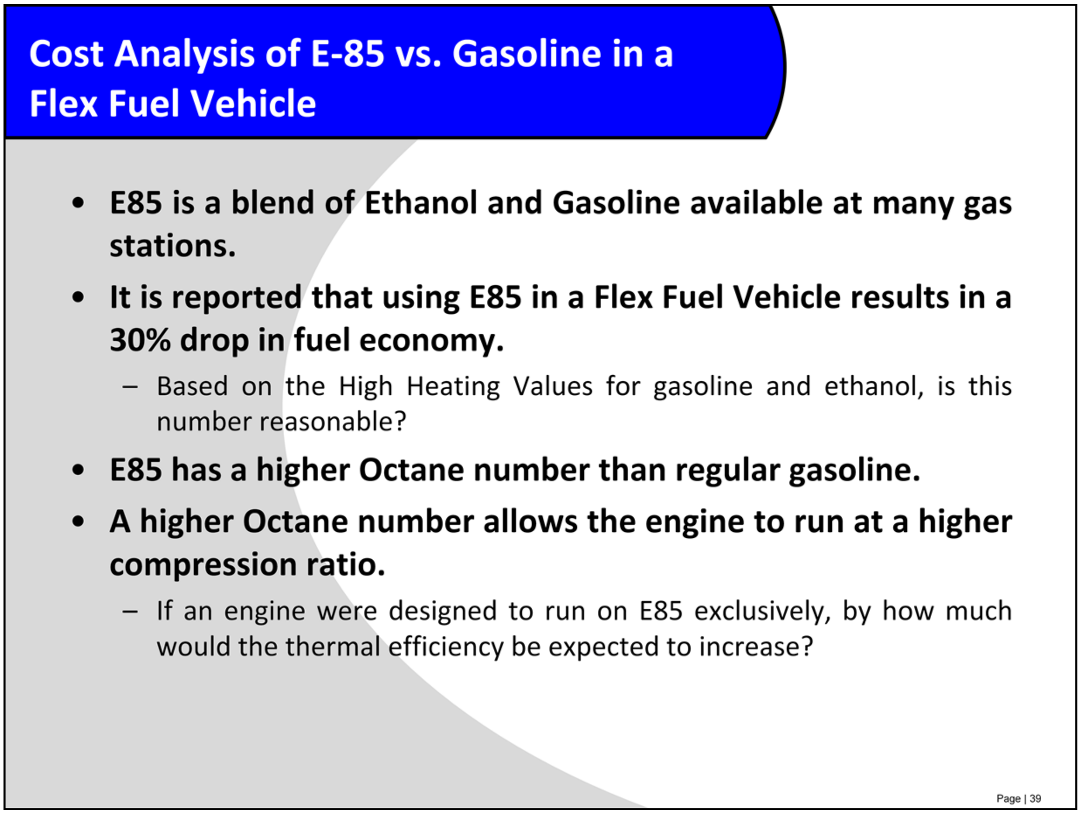
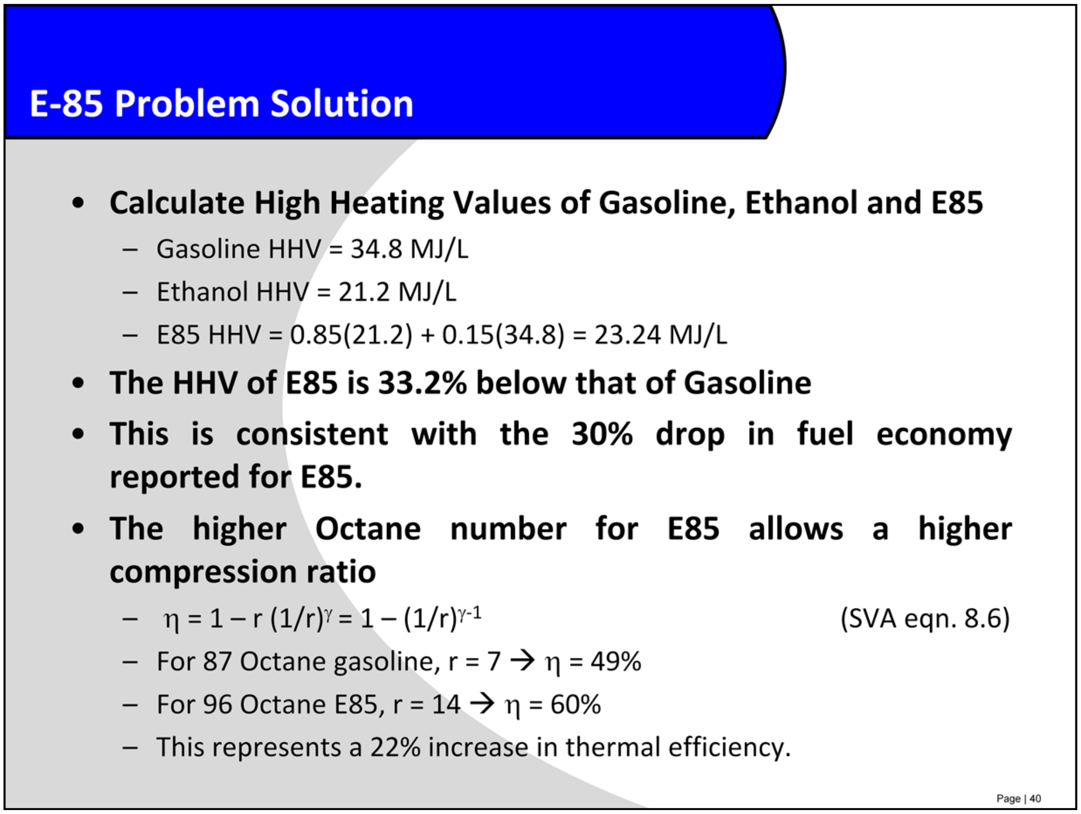
From this example we see the problems imposed by the 2^{nd} Law. Even in this idealized case with no irreversibilities we see that, although solar energy is abundant, the energy density is simply too low be useful without concentrating it.

To power a small sedan, we would need 562 m^2 of solar collectors always trained on the sun under cloudless conditions.



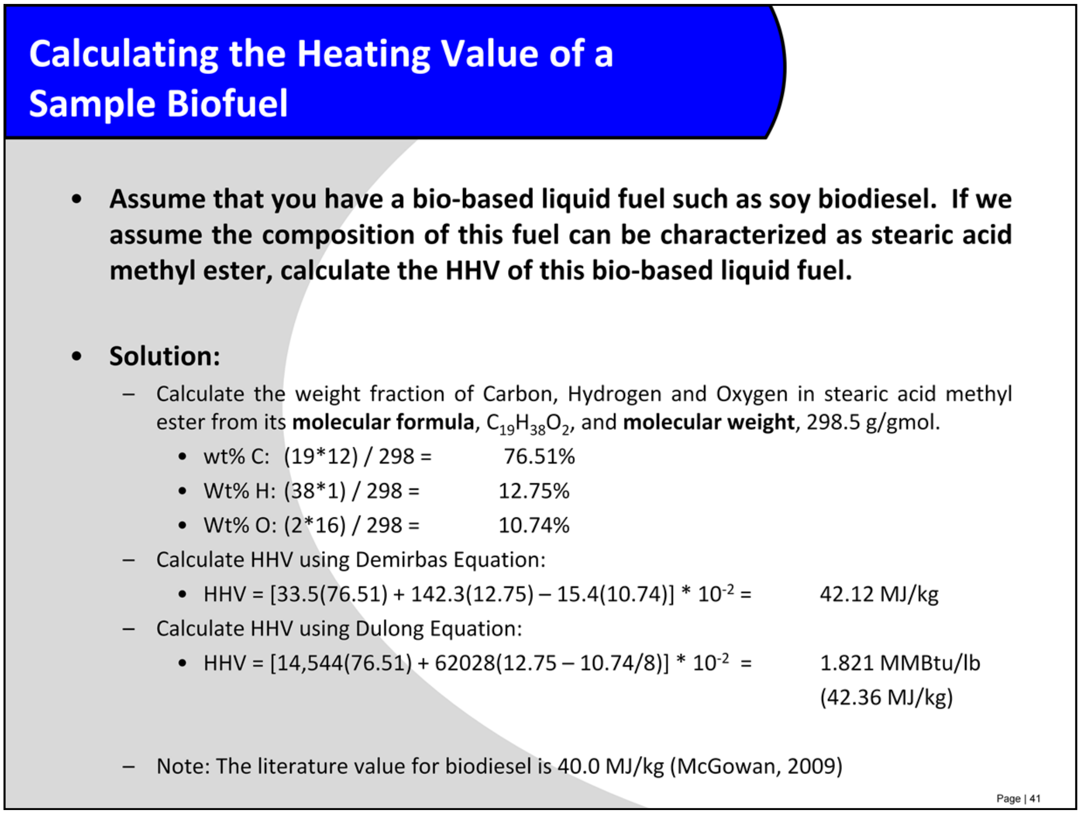
It is widely reported that the use of E85 fuel in a flex fuel vehicle results in a drop in fuel economy. This problem illustrates the reasons for this loss of efficiency, and how some efficiency can be regained by operating at a higher compressions ratio.



In this example we see the effects of both energy density and compression ratio on engine efficiency.

Note: Calculated values assume a value of 1.35 for the heat capacity ratio.

SVA refers to Smith/VanNess/Abbot



Biofuels are typically composed by hundreds of different molecular compounds, however, it is often possible to estimate the higher heating value by only considering a handful of the most prevalent components. This example illustrates how the HHV of a compound can be estimated through the use of empirical relationships.

Example Internal Combustion Engine Problem

- **Plot the thermal efficiency of two internal combustion engines operating on the Otto cycle and the Diesel cycle as a function of compression ratio.**
  - For the Otto Engine, assume the heat capacity ratio, γ, is 1.35, and the compression ratio varies between 4 : 1 and 8 : 1.
  - For the Diesel Engine, again assume the heat capacity ratio , γ, is 1.35, but the compression ratio varies between 14 : 1 and 25 : 1 and the expansion ratio is 10.
- **Solution**
  - Otto cycle: $$\eta = 1 - \left(\frac{1}{r}\right)^{\gamma - 1}$$ (SVA Eqn. 8.6)
  - Diesel cycle: $$\eta = 1 - \frac{1}{\gamma} \cdot \left[\frac{(1/r_e)^{\gamma} - (1/r)^{\gamma}}{(1/r_e) - (1/r)}\right]$$ (SVA Eqn. 8.7)

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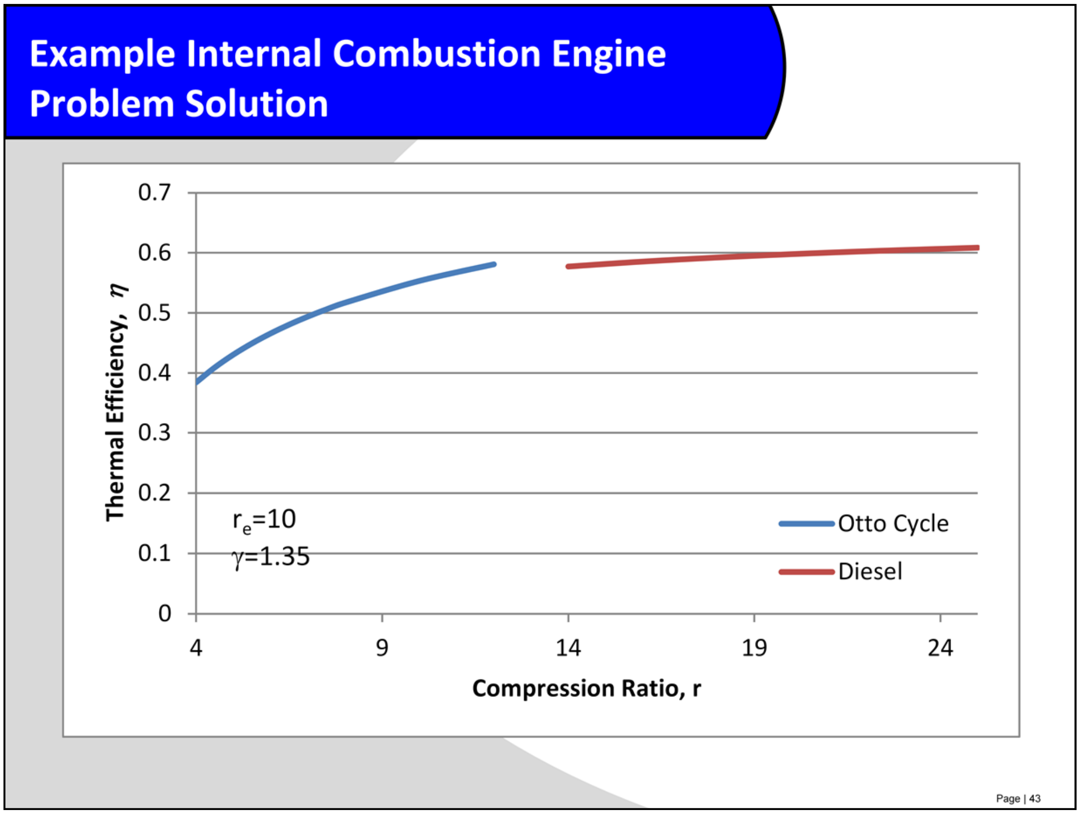
This problem illustrates the effect of compression ratio on engine efficiency.

Note: The efficiency equations used are from the Smith, Van Ness and Abbott text. Two forms of this equation are available, however both give the same result.



From these results, it is clear that increasing the compression improves the engine efficiency. Because of the higher compression ratio, the diesel engine does exhibit higher efficiency, but this is only part of the story. The higher energy density of diesel fuel oil generates more power per stroke versus a gasoline engine with the same cylinder volume.

In addition, higher compression gasoline engines require higher octane fuel to prevent “knocking”, or premature fuel ignition.

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