

Chapter 8

Pre-combustion Air Emission Control

Introduction

- Air pollution control costs – it is a luxury.
- A logical goal is to have an appropriately clean environment, obtained at an appropriate cost, with this cost appropriately distributed among industry, car owners, homeowners, and other sources of pollutants.
- The detailed regulations can be set in a strict way or a lax way.
- An ideal approach to air pollution control and its implementing regulation are cost-effective, simple, enforceable, flexible, and evolutionary.

Pre-combustion Approaches

- The most cost effective approach is to control emissions before combustion, which reduces the load of the downstream unit.
- Include
 - Fuel cleaning,
 - Fuel substitute,
 - Alternative fuels, and
 - Alternative energy resources.

Fuel Cleaning Examples

- Coal preparation, coal washing
 - In the United States, about 50% of all coals supplied to power plants are washed before delivery.
 - In Germany, almost all coals are washed before firing.
- Oil and gas refinery
 - Crude oils and sour gases are refined globally following specific government regulations.

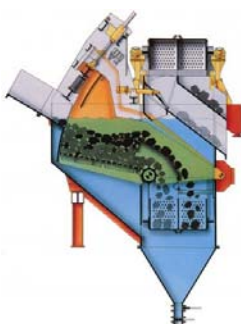
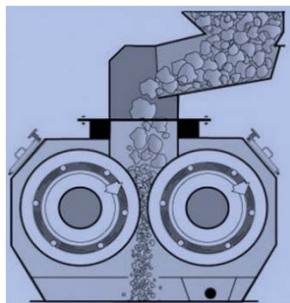


Coal cleaning

- Coal cleaning is a process by which impurities such as sulfur, ash, and rock are removed from coal to upgrade its value.
- Coal cleaning processes are categorized as
 - physical cleaning
 - chemical cleaning.
- Physical coal cleaning processes
 - the mechanical separation of coal from its contaminants using differences in density, are by far the major processes in use today.
- Chemical coal cleaning processes
 - are currently being developed, but their performance and cost are undetermined at this time.
 - Therefore, chemical processes are not included in this discussion.

Conventional coal cleaning steps

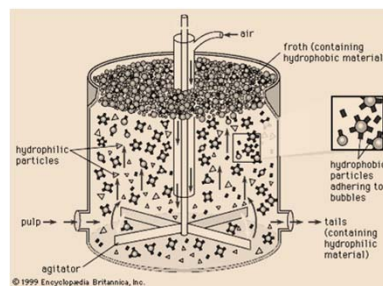
- **Crushing of the coal:** Grinding into smaller particles with diameters less than 50-mm results in higher separation. It also liberates ash-forming minerals and inorganically bound sulfur.
- **Particle screening:** The crushed coal particles are screened into three modes; coarse, intermediate, and fine.



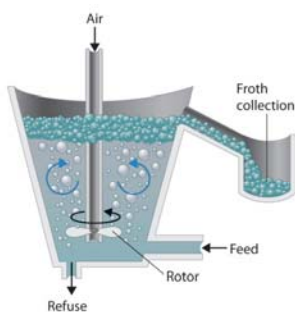
http://dsmac.com.ng/news/2PG_roller_crusher_for_high_moisture_coal_in_Nigeria_139.htm

Flotation

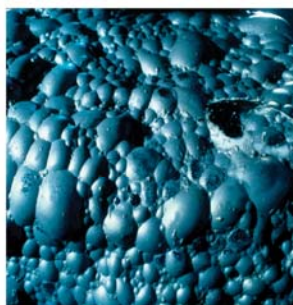
- It involves separation of ash and sulfur compounds from the coal before it is pulverized and introduced into combustion. The lighter coal particles float on top while the heavier minerals sink to the bottom in a stream of water.



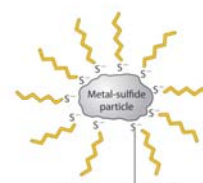
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(a) Froth flotation



(b) Precious-metal-sulfide froth

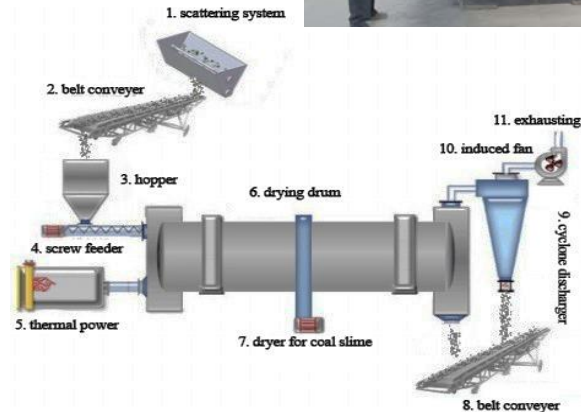


(c) Anionic organic sulfur ligands bound to metal-sulfide particle

<http://2012books.lardbucket.org/books/principles-of-general-chemistry-v1.0m/s27-the-d-block-elements.html>

Drying

- In this step wet coal particles are dried using a dewatering device, generally a vacuum filter, centrifuge, or a cyclone, to separate water from the solid, followed by further drying in hot air.



Effectiveness of coal cleaning

- Coal washing can remove about 60% of ash-forming materials.
- A significant amount of Pyrite (FeS_x), As, Se and Hg can be removed by coal pre-cleaning.
 - Coal washing alone can remove up 10-25 % removal of the total sulfur content of the coal.
 - Ninety percent of the inorganic fuel sulphur, especially pyritic sulphur, FeS_2 , can be easily removed by coal washing.
- The organically bound sulphur cannot be removed by physical cleaning methods;

<ul style="list-style-type: none"> • Reduced SO₂ formation in the flue gas: The reduction could be 10 to 40% lower than burning coals without pre-cleaning. • Decrease of ash content: This allows the cleaned coal to be used for many higher pulverizer and boiler. It also reduces the loading of downstream particle separators such as ESPs and bag houses. • Lower maintenance costs for boilers: The reduction of ash content leads to less wear and tear on coal preparation before combustion and on boiler during combustion. • Smooth operation: Less operational problems such as boiler slagging and fouling. 	<ul style="list-style-type: none"> • Extra intensive energy required for coal grinding and drying. • Moisture added to the coal may reduce the efficiency of the boiler and the entire plant. There may be 2-15% of energy loss to preheating of coal. • Waste liquid stream from coal cleaning may contain acidic toxic metals, which poses an extra challenge and cost in waste treatment or disposal. • Strict regulations have been introduced in the United States and elsewhere to prevent dumping of these toxic acidic streams into the environment without prior treatment.
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Secondary air Emissions from Coal Washing

- The major emission source in the fine or coarse coal processing phases is the air exhaust from the air separation processes.
- For the dry cleaning process, these emissions are generated when the coal is stratified by pulses of air.
- Particulate matter emissions from this source are normally controlled with cyclones followed by fabric filters.
- Potential air emissions from wet cleaning processes are very low.
 - Pollution goes to liquid
- The major source of emissions from the final preparation phase is the **thermal dryer exhaust**.
- This emission stream contains coal particles entrained in the drying gases and volatile organic compounds (VOC) released from the coal, in addition to the standard products of coal combustion resulting from burning coal to generate the hot gases
- The most common technology used to control dryer emissions is venturi scrubbers and mist eliminators downstream from the product recovery cyclones.

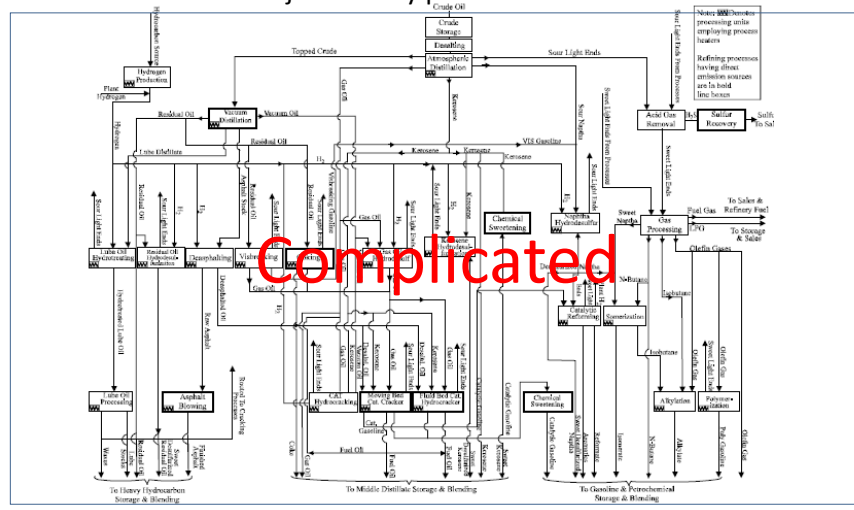
Petroleum Refinery



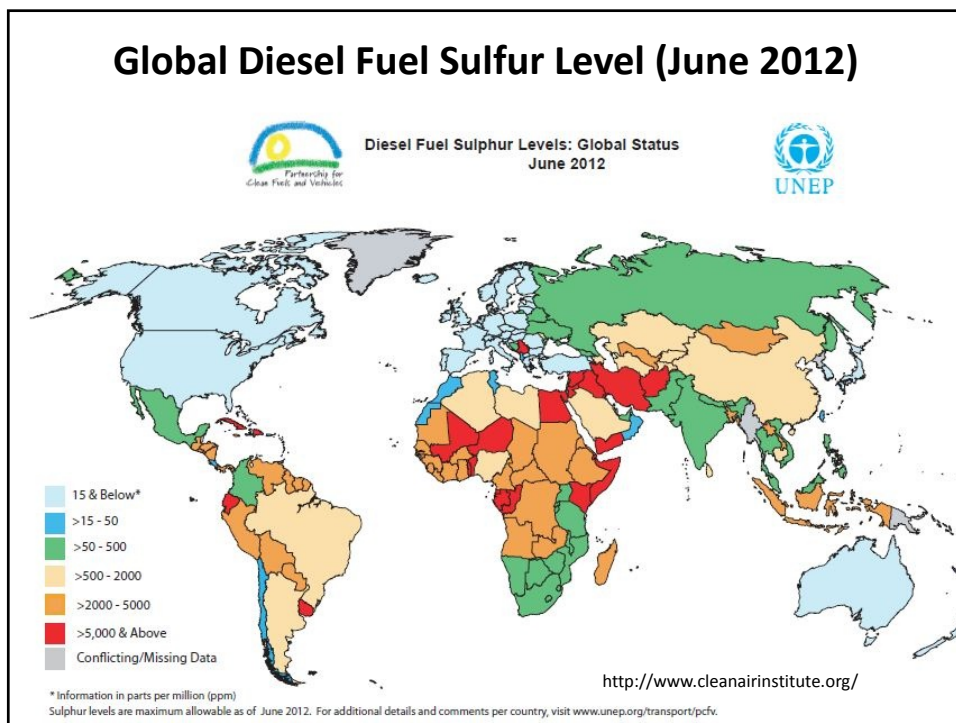
- The petroleum refining industry converts crude oil into more than 2500 refined products,
- These products include
 - liquefied petroleum gas (LPG)
 - Gasoline
 - Kerosene
 - aviation fuel
 - diesel fuel
 - fuel oils
 - lubricating oils, and
 - feedstocks for the petrochemical industry.

Petroleum Refining Processes

- A refinery's processing flow scheme is largely determined by composition of the crude oil feedstock and the chosen slate of petroleum products.
- This figure shows the general processing arrangement used by refineries in the United States for major refinery processes.

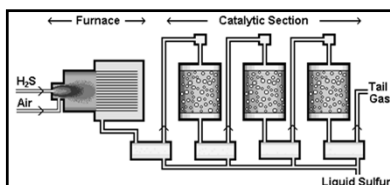
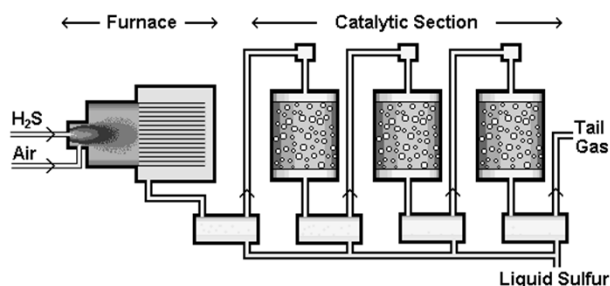


- Crude oil contains up to 25,000 hydrocarbon compounds.
- At refinery, crude oil is decomposed into various fractions and transformed into fuels including oil, gas, and other products.
- The oil after the refinery process contains a specified amount of sulfur, nitrogen, and ash contents.
 - For example, the average sulphur content in Canadian diesel was 350 ppm in 2000, and
 - ultra-low sulphur diesel with 15 ppm sulphur became mandatory in North America for highway vehicles in 2006.
 - In 2009, all EU vehicles will run on 10 ppm sulphur diesel including off-roads.



Claus Process for desulfurization

- The **Claus process** is the most significant gas desulfurizing process
- A catalytic reduction-oxidation process first reduces sulfur compounds in the oil to H_2S .
- Then H_2S is oxidized to SO_2 by oxygen in the air, and simultaneously, SO_2 reacts with H_2S in the presence of a catalyst to form elemental sulfur.



Step 1. Thermal step

- A sub-stoichiometric combustion at temperatures $850\text{ }^\circ\text{C}$ or higher

$$2H_2S + 3O_2 \rightarrow 2SO_2 + 2H_2O$$

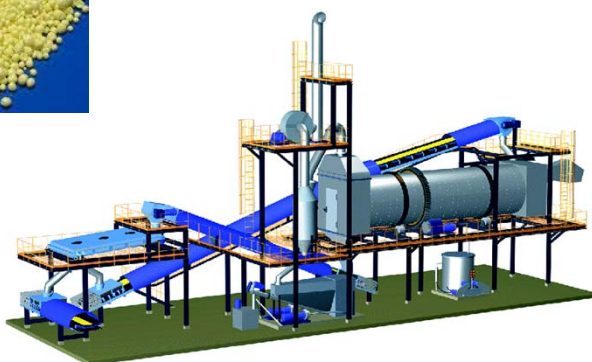
$$2H_2S + SO_2 \rightarrow 3S + 2H_2O$$
- Overall reaction:

$$10H_2S + 5O_2 \rightarrow 2H_2S + SO_2 + 7/2S_2 + 8H_2O$$
- Elemental sulfur precipitates in the downstream process gas cooler
- Usually, 60 to 70% of the total amount of elemental sulfur produced in the process are obtained in the thermal process step.

Step 2 Catalytic Step

- $2H_2S + SO_2 \rightarrow 3S + 2H_2O$
- This sulfur can be S_6 , S_7 , S_8 or S_9 .
- Typical catalysts for Claus processes are activated alumina, activated bauxite, or cobalt molybdenum hydrogenation catalyst.
- By 2- or 3-stage processes, the H_2S conversion efficiencies could be about 95% or 97%, respectively.
- Alternatively, with the super-Claus process special catalysts, efficiencies $> 99\%$ can be obtained.
- A separate hydrogenation reactor has to be employed between the 2nd and 3rd stages.
- Oxygen enrichment of the air to the burner in the final Claus stage also reduces soot formation and poisoning of the catalysts.

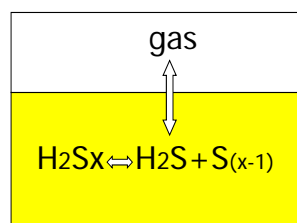
- Due to stringent regulation on sulfur content in fuels, a significant amount of sulfur compound is produced as byproduct of oil refinery.
- The elemental sulfur is often an important byproduct of oil refining and it is also a major raw material for the productions of fertilizer and sulfuric acid.



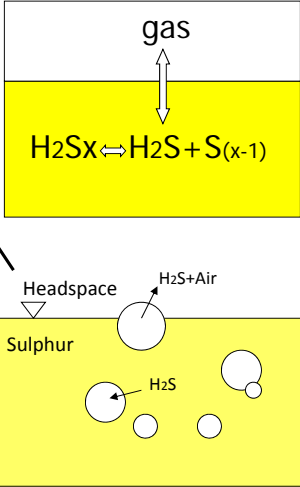
Enersul.com

H₂S in Sulphur

- The liquid sulphur produced from Claus process usually contains 150~350 ppm H₂S and H₂S_x.
- H₂S can be released from liquid sulphur to gas phase during shipping and handling – safety problem
- H₂S is very toxic and easy to explode.
- It needs to be degassed to a level of 10 ppm or lower for safe shipping and handling

H₂S

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The diagram illustrates the degassing process in three stages. The top part shows a yellow liquid phase with the chemical equilibrium $H_2S_x \leftrightarrow H_2S + S_{(x-1)}$ and a double-headed arrow pointing to a 'gas' phase above. The middle part shows a cross-section of a liquid containing 'Sulphur' and 'H₂S' bubbles, with an arrow pointing to a 'Headspace' containing 'H₂S+Air'. The bottom part shows a 'Final step' where gas is swept away from the headspace.

Basic degassing principles

First step: Depolymerization in liquid

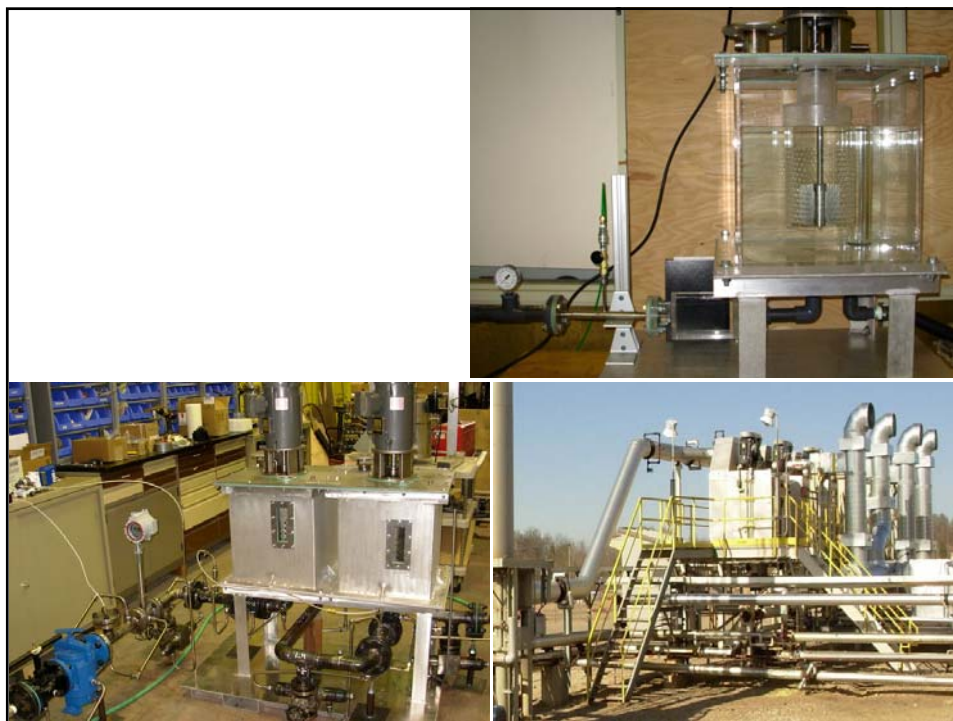
$$H_2S_x \xrightleftharpoons{\text{Catalyst}} H_2S + S_x$$

Second step:
Release from liquid to gas (head space)
Henry's law governed mass transfer (degassing)

Final step: Sweeping from head space

Degassing efficiency can be increased by increasing

- Concentration difference
- (Interfacial) Contact area
- (Residence) Time



Reformulated Gasoline (RFG)

- Reformulated gasoline (RFG) is gasoline blended to burn more cleanly than conventional gasoline and to reduce smog-forming and toxic pollutants in the air we breathe.
- The RFG program was mandated by Congress in the 1990 Clean Air Act amendments. The first phase of the RFG program began in 1995 and the second (current) phase began in 2000.
- RFG reduces smog levels in cities.
- About 30 percent of gasoline sold in the U.S. is reformulated.
 - The air quality benefits RFG has achieved represent a significant part of the country's smog reduction strategy. The RFG program, combined with other industrial and transportation controls aimed at smog reduction, is contributing to the long-term downward trend in U.S. smog levels.

• <http://www.epa.gov/otaq/fuels/gasolinefuels/rfg/index.htm>

Reformulated Gasoline (RFG)

- 15% reduction of emissions of ozone-forming volatile (VOCs)
- A 15% reduction in air toxics such as benzene.
- Adding oxygenates to gasoline is another way to decrease CO and VOC emissions.
 1. Methyl tertiary butyl ether (MTBE): derived from methanol
 2. Ethyl tertiary butyl ether (ETBE) : derived from ethanol
- They are less volatile than their parent alcohols and therefore better satisfy the 1990 Clean Air Act Amendments

Comments:

- MTBE derived from natural gas and coal and supported by petroleum industry
- ETBE derived from ethanol and supported by agricultural industry

Source: Heinsohn and Kabel, Source and Control of Air Pollution, pg316-7

Fuel Substitute

- Air emissions depend on the fuel types.
- It is technically feasible to use fuel substitutions such as co-combustion of oil and coal, in order to reduce some air emissions
- In reality, other factors, likely economical considerations also contribute to the final decision of which fuel is used for certain processes.
- Coal is still the cheapest and also most polluted fuel in the environment.
- Although oil is more expensive to recover than coal, it can be easily transported by pipelines.
- Like oil, natural gas is more expensive to recover from wells, but contrary to oil it cannot be easily stored or shipped.
- Nonetheless, natural gas is widely used because of its availability, efficiency, and cleanliness of combustion.

Air Emission Reduction by Fuel Substitute

1. SO_x and particulate matter (PM)

- Replacing a high-sulphur fuel with a low-sulphur fuel will reduce the amount of SO_x in the flue gas.
- Replacing solid fuel with oil or gas can also reduce the ash (PM) formation.
- In some countries, local authorities may enforce fuel substitutions to improve the local air quality.
 - For example in Beijing, China, a low sulfur coal must be burned in the plants within this capital city.
 - It is found that fuels with different sulfur contents may have different effects on the performances of an ESP in terms of particulate emission control.
- In addition, the success of fuel substitution depends on the fuel-flexibility of the burner and the economics of operation with another fuel.

2. Control of Volatile Organic Compounds (VOCs)

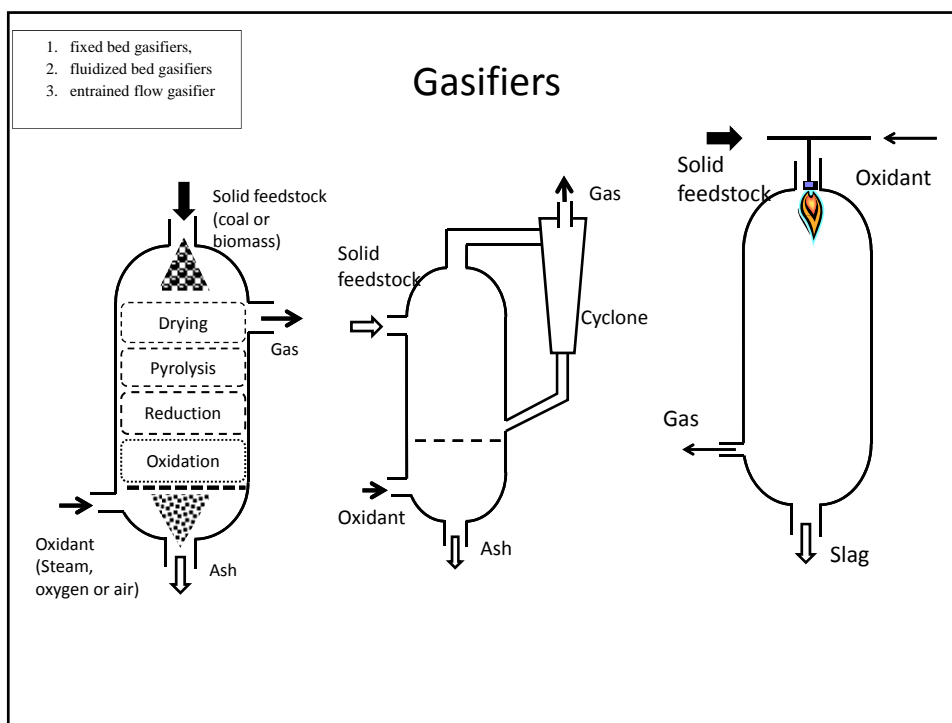
- Replacing gasoline with natural gas or propane can reduce the emissions of VOCs.
- This replacement is not limited to stationary combustion sources, but also to engines when the natural gas or propane is compressed.
- Extensive R&D is being conducted in the petroleum industry to improve the combustion properties, handling, and use of natural gas as a substitute of gasoline to dominate the auto fuel market, although it is still not yet the case.



A video: <http://ventrac.com/advantages/green/propane?gclid=CNaznpfUy7oCFSgSMwoda3cAJQ>

Thermochemical Conversion of Fuels

- Pyrolysis
 - Pyrolysis is a process where organic matter is degraded by thermal reactions in the absence of added oxidizing agents.
- Gasification,
 - Solid to gaseous fuels
- Liquefaction
 - Solid to liquid fuels



Gasification Chemistry

$C + \frac{1}{2}O_2 \rightarrow CO$	(Combustion reaction)	(8-4)
$C + O_2 \rightarrow CO_2$	(Combustion reaction)	(8-5)
$C + CO_2 \leftrightarrow 2CO$	(Boudouard reaction)	(8-6)
$C + H_2O \rightarrow \mathbf{CO + H_2}$	(Gasification with steam)	(8-7)
$C + 2H_2 \rightarrow CH_4$	(Gasification with H_2)	(8-8)
$CO + H_2O \rightarrow H_2 + CO_2$	(Water gas shift reaction)	(8-9)
$CO + 3H_2 \rightarrow CH_4 + H_2O$	(Methanation)	(8-10)
$H_2S + CO_2 \rightarrow COS + H_2O$		(8-13)

Table 8-2. Pre-combustion Syngas after Water Gas Shift Reaction

Gas	Mole fraction
H ₂	55.5%
CO ₂	37.7%
N ₂	3.9%
CO	1.7%
H ₂ O	0.14%
H ₂ S	0.4%
Others	0.66%

Syngas cleaning and separation

- Particulate removal
- Acidic gas removal
- Carbon capture
- Carbon separation
- Carbon storage

Particulate removal

- Particulate cleaning of the hot syngas is necessary not only to reduce air emissions, but also to prevent corrosion and erosion of downstream gas separation components.

Water spray

- Ash and char materials can be removed by water spray (quenching)
- Around 95% of the char carbon can be removed by direct water spray.
- The residual carbon is handled in the following wet scrubbers.
- Because of the cooling of the syngas, the thermal efficiency is greatly reduced in the entire process if the syngas will be used immediately, like in an IGCC process.

Hot gas filtration

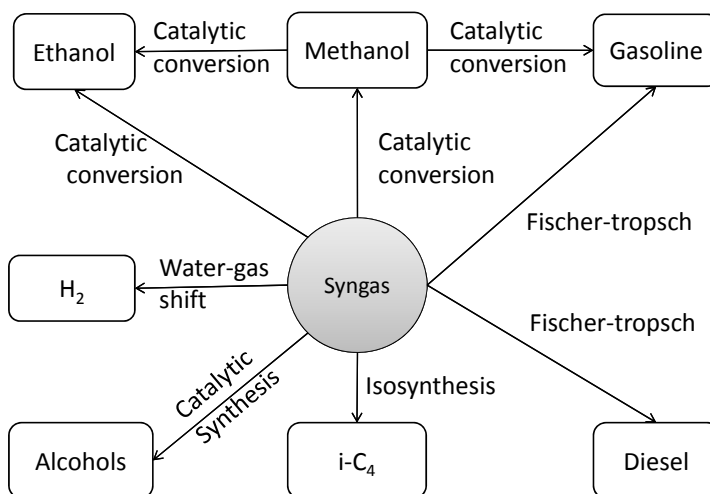
- Temperatures above 260 °C; sometimes it can reach 900 °C.
- Special filtration materials that can endure the high temperature as well as the acidic gases in the raw syngas.
- Common materials are ceramic and metallic.
- The filters can be shaped like candles, as long as a few meters, or honeycomb structure.
- High costs and system failure due to filter clogging are the main challenges to hot gas filtration.

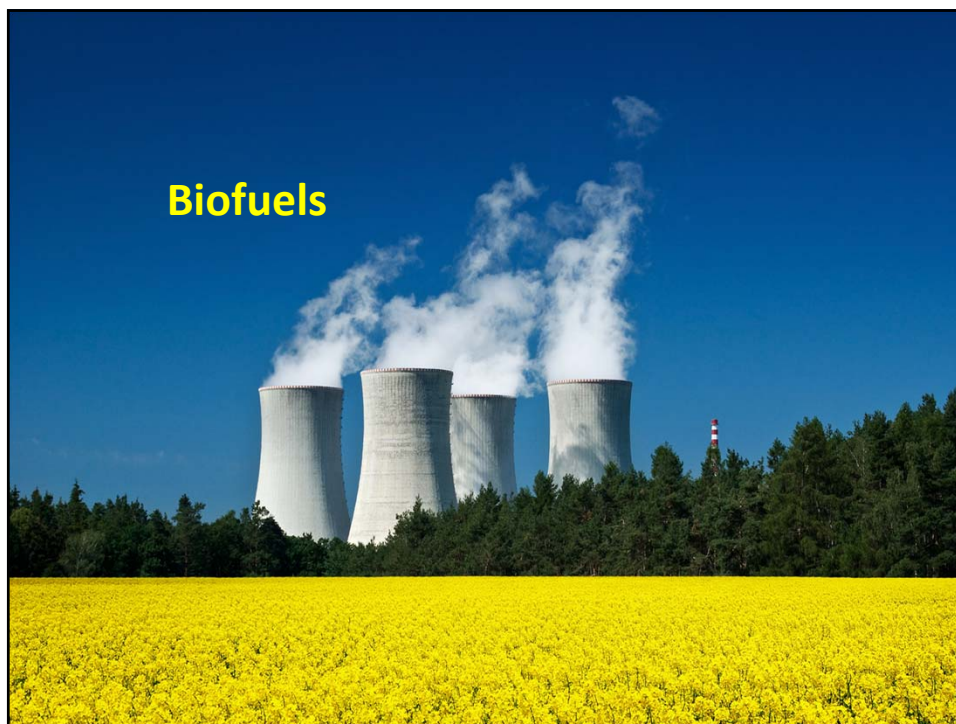
H₂S separation

$\text{ZnO} + \text{H}_2\text{S} \rightarrow \text{ZnS} + \text{H}_2\text{O}$ (Adsorption, 315 – 530 °C)	(8-14)
$\text{ZnS} + \frac{3}{2}\text{O}_2 \rightarrow \text{ZnO} + \text{SO}_2$ (Regeneration, 590 – 680 °C)	(8-15)

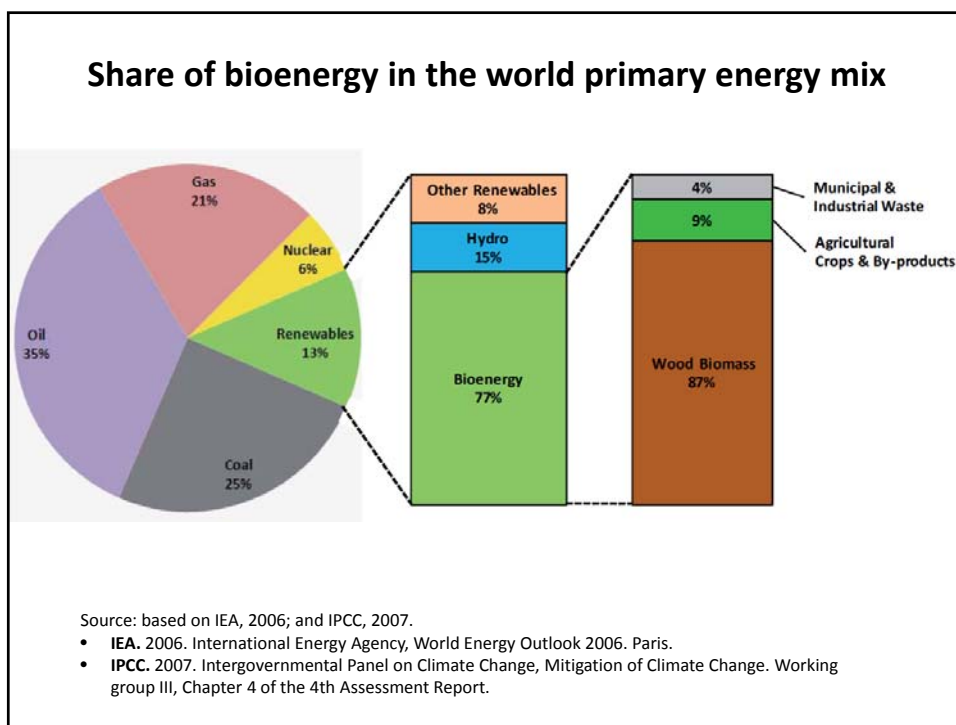
Carbon capture

- See Chapter 12

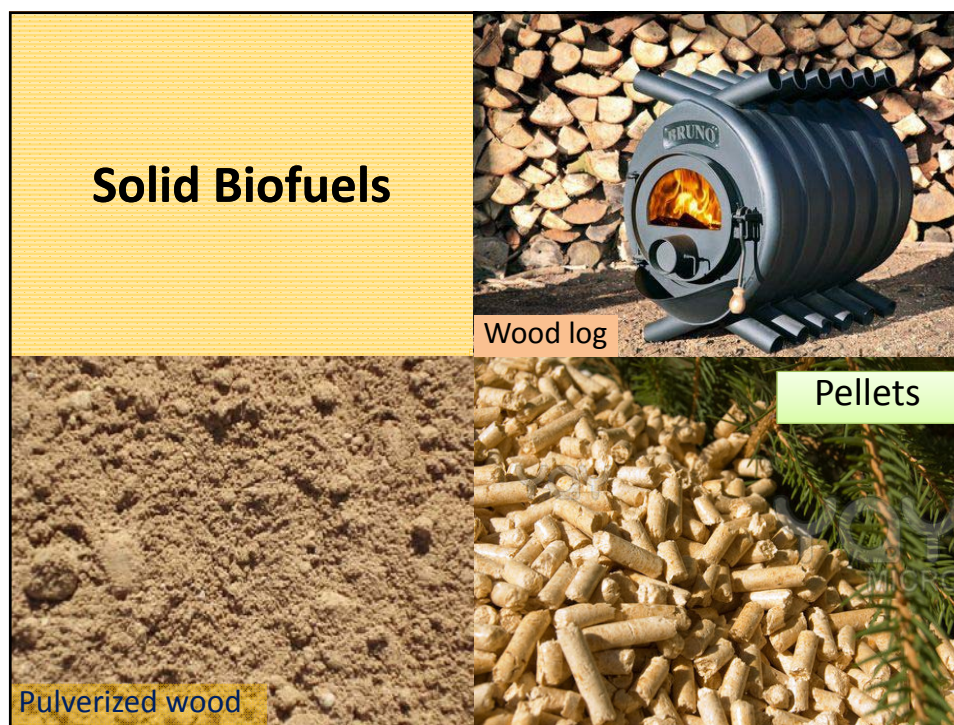




Biofuels



Biomass		Biofuel production			
Type	Examples	Technology	Immediate products	Post processing	Final Biofuel products
Lignocellulosic biomass	Wood, grass	Pulverization	Powder		Co-firing
		Pelletization			Pellets
		Anaerobic digestion	Biogas	Gas separation	H ₂ , CH ₄ , CO
		Gasification	Syngas	Fischer-Tropsch Fermentation	FT-diesel, jet fuel, ethanol
		Pyrolysis	Biooil	Refining	Bioler oil, diesel
		Liquefaction	Biooil	Refining	Bioler oil, diesel
Starch-based plants	Corn, sugarcane	Hydrolysis	Sugar	Fermentation	Bioethanol, biobutanol
Triglyceride-producing plants	Canola, soybean	Extraction	Edible oil	Transesterfication	Biodiesel
	Cooking oil	Purification		Transesterfication	Biodiesel



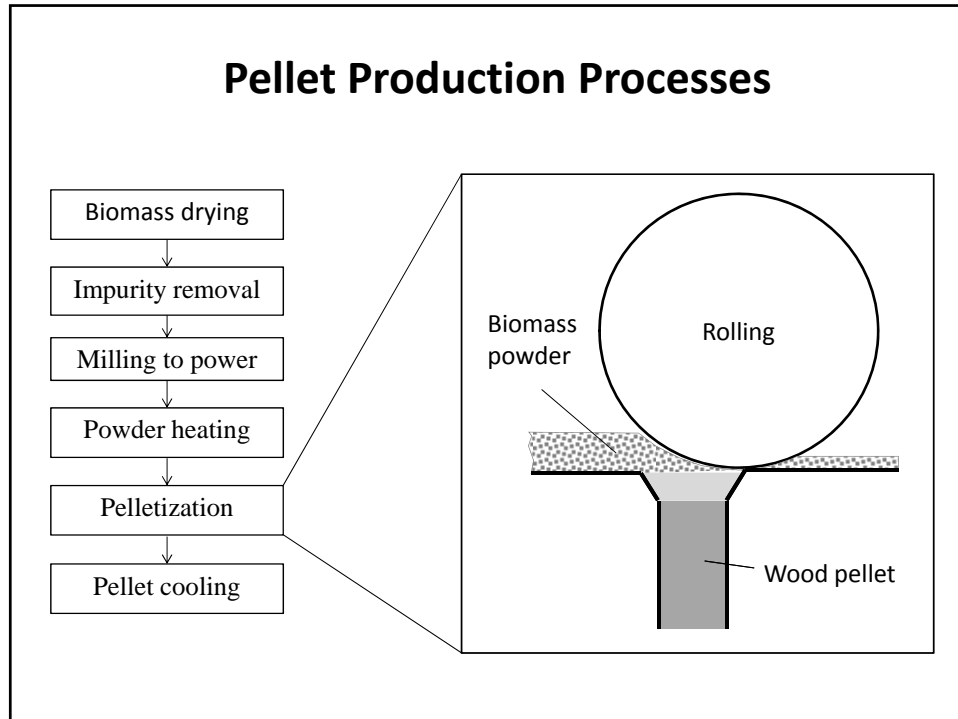
Biomass Pellets

- Pellets = Densified biomass
- Mainly produced by wood residues; should also be produced by mixed other biomass residues through a quite simple process of milling, drying and compacting.



Biomass Pellets

- European technology is leading this sector.
- The cheap process technologies already exist and are highly competitive in comparison with the fossil fuels.
- Actually, around 1.4 tons oil equivalent per dwelling is used in Europe for households (EEA, 2008).



Drying

- The content of water in the raw material must be about 10 % before the pelletising process begins.
- If the content of water in the raw material is too high, it has to be dried.
- The drying is of high importance for the final product, since raw material with a water content higher than 15 % is difficult to pelletise.
- The extent to which a material needs to be dried before pelletising makes a big difference to the energy required in the manufacture of wood pellets.

Cleansing

- On delivery of the raw material to the pelletising factory unwanted material, for example metal, is removed with the help of magnets and a screen.
- This is particularly important when using recycled biomass.

Grinding

- After cleansing, the raw material is ground in a hammer mill
- The resulting wood flour is then separated in a cyclone, alternatively in a filter. The grinding is necessary because the raw material, at delivery can be very heterogeneous in size (although it will typically be below 5 mm in diameter).

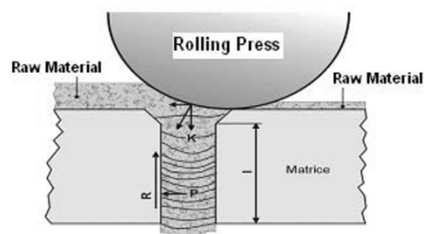
Feedstock Heating

Heating the feedstock to 70 °C to soften lignin

- The heating ensures that the content of lignin in the wood is released and this contributes to the increased binding of the particles together in the final product.

Pellet Processing

- The raw material lies in a layer in front of a rolling press, which presses the material down into the die block.
- When the rolling press is once again rolled over the hole, new material is pressed into the hole, thereby compressing the raw material into pellets.

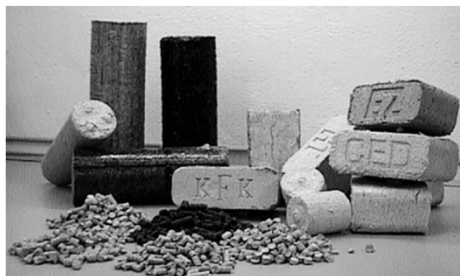


Pellet Cooling

- The still warm and elastic pellets are transported to a **cooling device** to be cooled to just above room temperature.
- The cooling increases the **durability** of the pellets, and this decreases the formation of dust during the following transportation and handling.
- During counter-current cooling pellets and cooling air are moved towards each other so that warm air is used to cool the warmest pellets and vice versa.
- The counter-current cooling gives a gradual cooling of the pellets, which reduces the amount of heat stress that the pellets are exposed to (which may decrease the quality of the product).

Dimension

- The dimensions of fuel pellets vary between 3 and 25 mm in diameter depending on the die block that is used in production.
- The length generally varies between 5 and 40 mm.
- If the product exceeds 25 mm in diameter it is called a briquette.



Dust removal and packing

- After cooling the pellets are screened in order to remove dust and fine particles formed during the production process.
- The pellets are then stored loose or packed in bags and the residue is recycled back into the production process.



Pellet Quality

- The quality of fuel pellets may vary considerably depending on raw material, durability and water content.
- The quality of the wood pellets can be difficult to assess and therefore the consumer should make sure that the manufacturer delivers a product that meets a series of minimum standards.
- The varying quality of wood pellets has created problems for users with smaller boiler systems. Several have complained about combustion problems in systems which up till then had worked fine.

*Wood Pellet in Canada

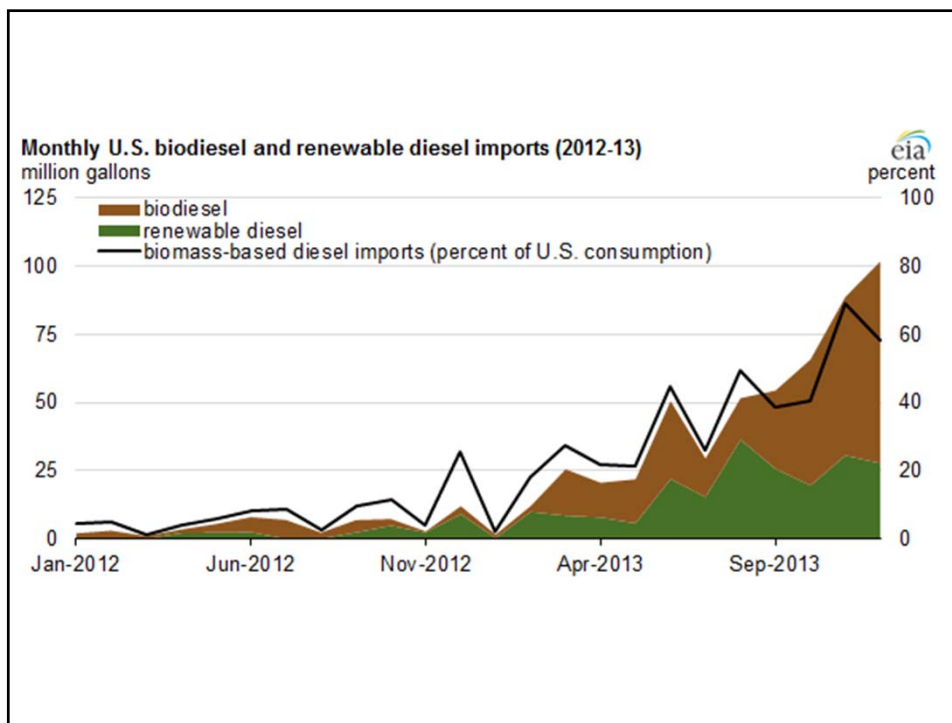
Refer to:

- Wood Pellet Association Canada:
<http://www.pellet.org/>



Biodiesel

- A substitute of (petroleum) diesel
- **Biodiesel** is a generic name given to modified vegetable oils and animal fats that yield diesel-engine fuels
- **Process:**
Triglycerides → Methyl or ethyl esters
- **Feedstock**
 - Soybeans, sunflowers, cotton seeds, corn, peanuts, safflower seeds rapeseeds waste cooking oils and animal fats



Feedstock for biodiesel (USA)

Vegetable Oil Production (Billion pounds/yr)	
Soybean	18.34
Peanuts	0.22
Sunflower	1
Cottonseed	1.01
Corn	2.42
Others	0.669
Total Veg. Oil	23.659

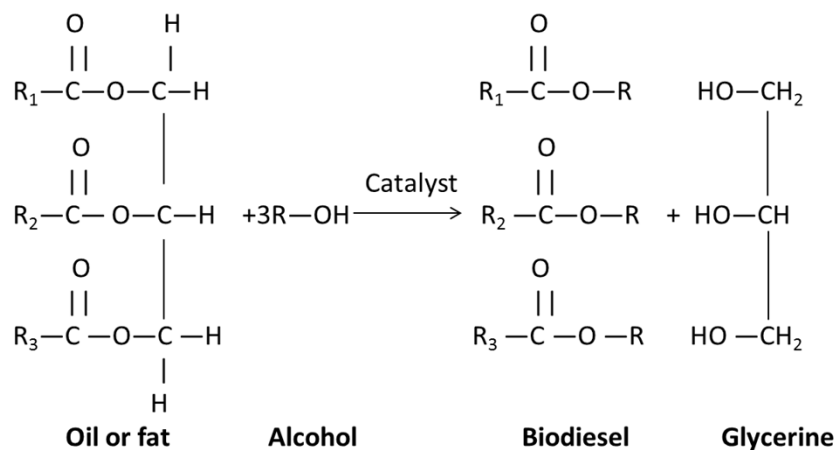
Animal Fats (Billion pounds/yr)	
Edible Tallow	1.625
Inedible tallow	3.859
Lard & Grease	1.306
Yellow Grease	2.633
Poultry Fat	2.215
Total Animal Fat	11.638

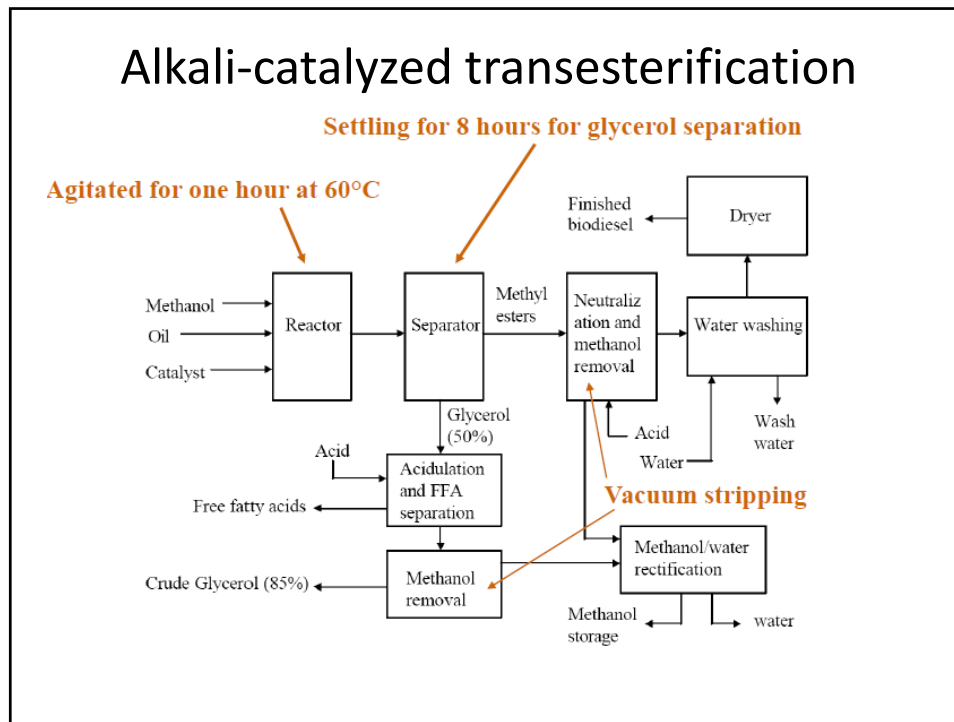
[from Pearl, G.G., "Animal Fat Potential for Bioenergy Use" Bioenergy 2002]

✦ Total oils available:
35.3 billion pounds

✦ Equals to about
4.64 billion gallon
biodiesel (7.6
lbs/gallon)

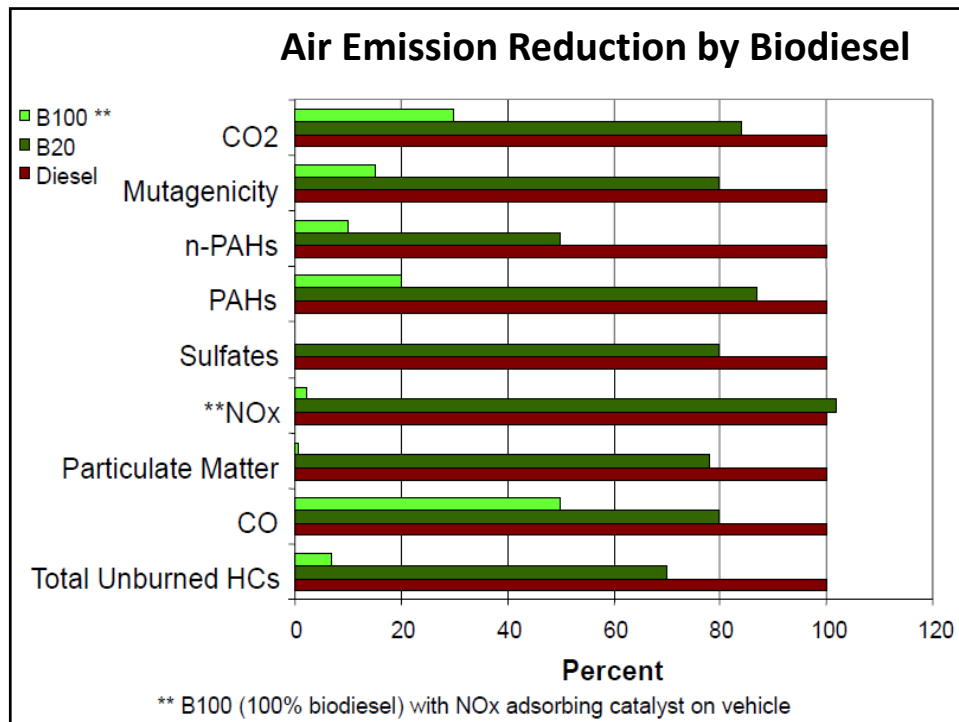
✦ U.S. diesel
consumption: 60
billion gal./year





Biodiesel B-factor, Bx

- Bx: x volume % of biodiesel mixed with petroleum diesel
- B20: 20 vol % biodiesel in the mixture
- Lower than 20% does not require major modifications to existing engines



Biodiesel has less energy content

- 8% less energy per gallon
- 12.5% less energy per pound
- 8% less in power and torque
- 8% more fuel consumption or less MPG
- B20 resulted in 1% to 2% reduction in power
- For B5 or lower, no noticeable differences
- **Adjust engine fuel injection system**

Biodiesel stability issue

- Long term storage or aging
- Stability at elevated temperature and/or pressures as the fuel is recirculated through an engine's fuel system
- The higher the level of unsaturation, the worse stability is
- Heat and sunlight will accelerate oxidation
- Certain metals such as copper, brass, bronze, lead, tin and zinc will accelerate the degradation process
- Keeping oxygen from the fuel reduces or eliminates fuel oxidation
- Antioxidants, whether natural or incorporated as an additive, can increase storage life or stability
- Fuel turn over between 2 and 4 months has no problem
- NBB recommends 6 month storage life for B100

Don't leave biodiesel in vehicle for too long

Biodiesel Blending and Cold Weather Operability

- Generally, the better the cold flow characteristics of the base diesel fuel, the greater the effect of blending biodiesel on its cold flow properties.
- Blending biodiesel with #1-D and premium diesel fuels tends to affect cold flow properties more than blending biodiesel with #2-D.

B100 Cold Weather Storage and Delivery Precautions

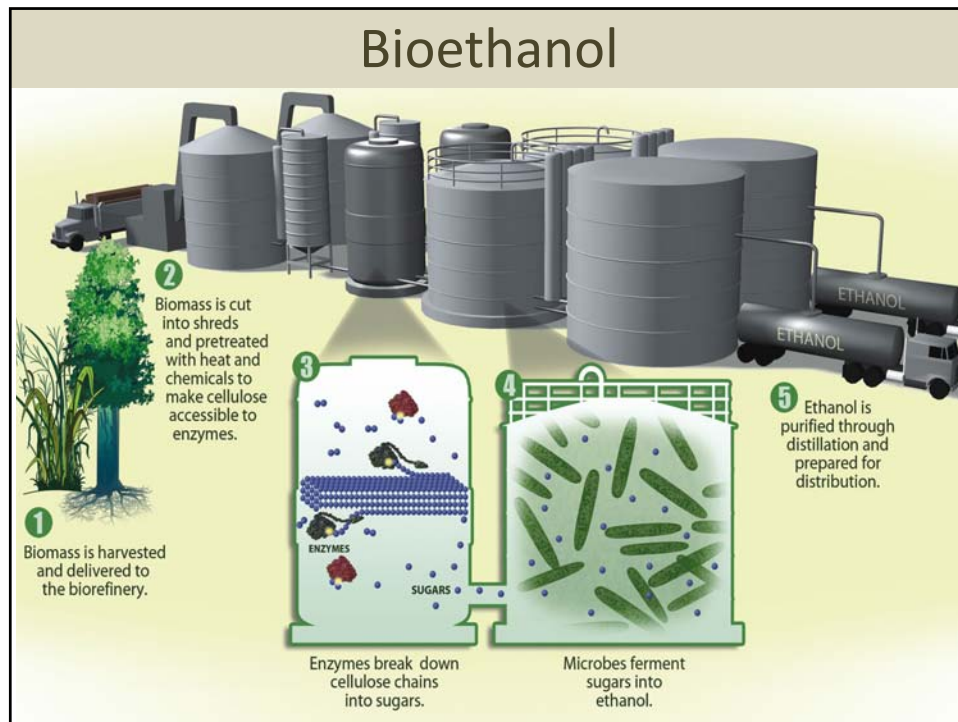
- B100 stored in cold temperatures (less than 40° F) must be heated to at least 60°F prior to distribution or blending into middle distillates of any grade.
- If pumping biodiesel in cold weather through a conventional fuel pump, keep the hose and supply line to the pump equally protected with heat.
- An option to heating the systems is to blend B100 with 50% kerosene to dilute the cold weather properties of the biodiesel.

- With any type of blending (splash, in-tank or bottom loading), putting B100 into a cold empty truck can cause the fuel to gel, prohibiting proper mixing.
- Always maintain biodiesel at 10–15° F above its cloud point prior to blending with diesel fuel.

- Blends of 2% and 5% biodiesel with diesel fuel have little impact on cold flow properties.
- Only small increases in cloud and pour point were observed.
- As long as the B2 or B5 blend is made using an appropriate “winter grade” diesel fuel, no special provisions are required for storing, transferring or using the fuel.

Biodiesel and Cold Flow Additives

- Cold flow additives essentially work only on the diesel portion of the biodiesel blend as U.S. oils and fats contain too high a level of saturated compounds for most additives to be effective.
- The cold flow additive effectiveness can also change dramatically depending on the exact type of biodiesel and the processing it has undergone; much like the situation found with diesel fuel.



Depending on the biomass feedstock, there are several major steps that may apply to bioethanol production (Humbird et al. 2011).

- Feedstock pre-treatment
- Hydrolysis
- Fermentation
- Separation
- Storage

BRAZIL Example

- World leader in production and export of ethanol from sugarcane.
- Ethanol produced per day equivalent to 200,000 barrels of gasoline.



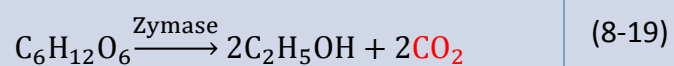
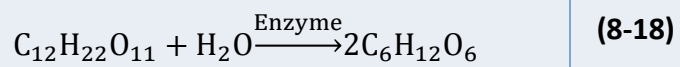
Fermentation

- From sugars and starches
- A biological process
 - Enzymes catalyze energy-releasing reactions that breakdown complex organic substrates
- Products:
 - Mostly: organic acids and alcohol
 - Some: many other chemicals



Simplified Chemical Reactions

Sucrose \longrightarrow Glucose



Glucose \longrightarrow Ethanol

- What is the stoichiometric mass ratio of conversion by fermentation?

Conversion Rate

- Maximum theoretical yield of ethanol is 51%
 - Mass ethanol / Mass carbohydrate
 - The rest goes to CO₂
- In reality, no more than 47% of the fermented carbon hydrates is converted into ethanol

Feedstocks

- Traditional sugar crops:
 - Apples, grapes other fruits
 - Sugar canes, sugar beets, sweet sorghum
- Waste surgars
 - Pulp and paper mill sludges
 - <40-50% wt. cellulose
 - Fermentation → glucose, mannose, fructose, and galactose

Starch Crops

- Starch = a polymer that accumulates as granules in many kinds of plant cells where they serve as a storage of carbohydrate



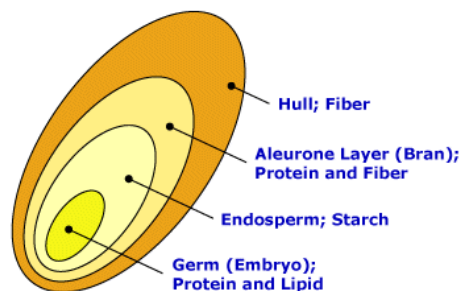
Starch for Fermentation

- Corn
- Wheat
- Barley
- ***They are all cereal grains***
- Grain starch consists of
 - 10-20% wt. amylose (soluble)
 - 80-90% wt. amylopectin (insoluble)



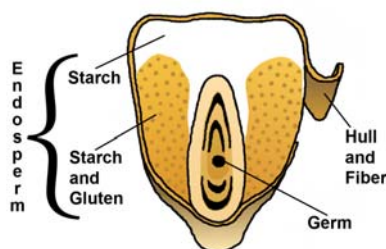
Grain Structure

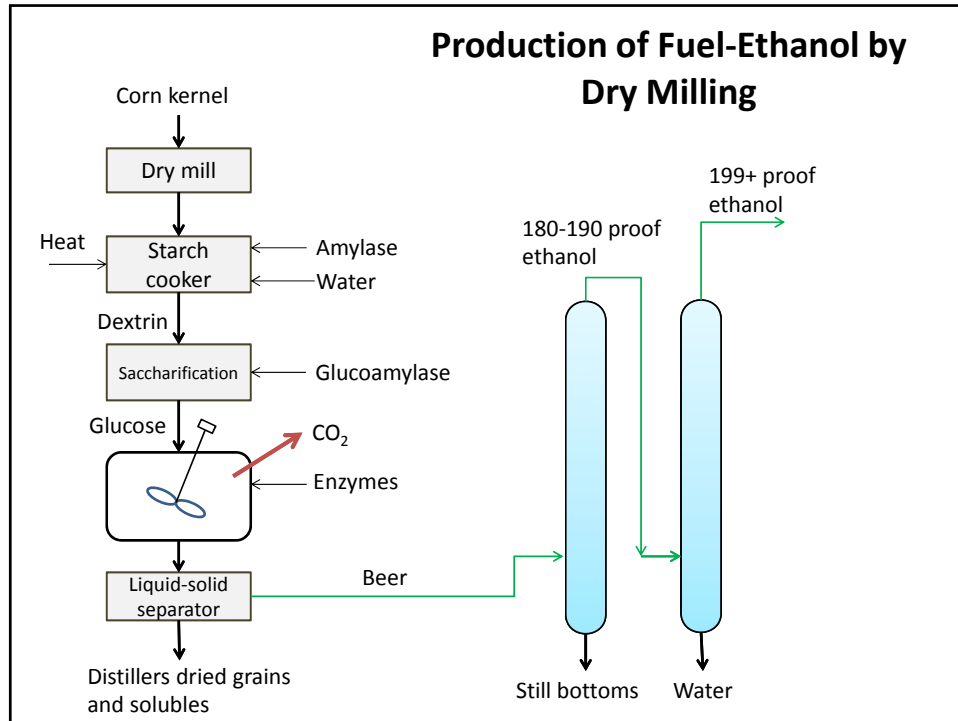
- Cereal grains also contains
 - Protein
 - Oil
 - Fibre
- Cell walls of grains must be disrupted to expose starch polymers before they can be hydrolyzed to fermentable sugars



Corn to Ethanol

1. Dry milling process
2. Wet milling process



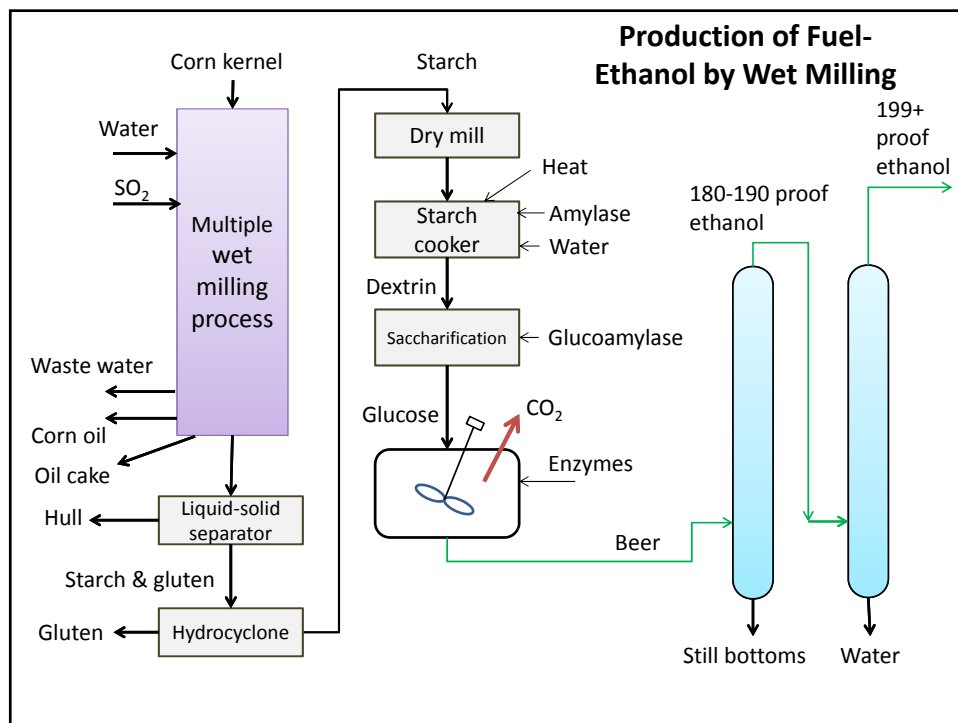


Dry Mill of Corn Steps

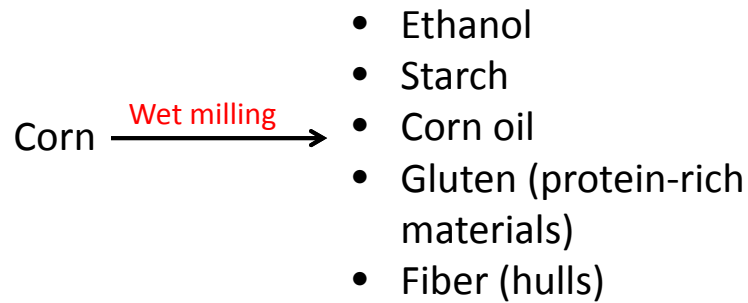
1. Dry and condition Corn for 24 hours → 15-20% wt of moisture
2. Roller mill or crusher → separate the kernel into germ, endosperm and fibrous hull by gravity → germ containing 18-25% wt oil, can be solvent-extracted
3. The starchy particles of the endosperm can be further grained and sieved to flour, corn meal, and grits:
 - Typically 75% wt of kernel becomes flour, corn meal, grits
 - 5% recovered as oil
 - 11% as fibrous feed

Dry Milling Process Yield

- A typical dry-milling plant will produce about 9.5-9.8 liters of ethanol per bushel of corn
 - ❖ 1 bushel = 35.24 liters
- Co-products:
 - ❖ DDG: 7.7-8.2 kg/bushel corn
 - ❖ CO₂: 7.3-7.7 kg/bushel corn
 - ☐ CO₂ from fermentation
 - ☐ CO₂ can be sold to carbonated beverage makers
- Ethanol+DDGS+CO₂ about 1/3 for each of the original weight of corn.



Wet Milling of Corn



Advantage: Higher value by products

Hydrolysis of Starch

- 150-200 °C
- Acid catalytic hydrolysis
- Enzymatic hydrolysis
- Acid/enzymes: starch = 1:100 by weight
 - ➔ Low cost of hydrolysis

Wet milling By products

- **Gluten** is a protein composite from grain processing, Contains 60% of protein, Used primarily as poultry feed
- **Oil cake:** dairy cattle feed



Wet Milling Steps

1. **Soaking:** Soak corn using a dilute solution of SO_2 for 24-36 hours
2. **Separate** “corn-steep liquor” from the corn
3. Coarsely **grind** the wet kernels to release the hull and germ from the endosperm
4. Separate the **germ** from the rest of the components using hydro-cyclone or mesh
5. **Drying**
6. **Extract oil** from the germ by either solvents or a screw press → residue oil cake
7. **Milling:** Mill the hull and endosperm using rotating disk mills → starch, gluten, and coarse fiber
8. **Separation:** using centrifugal separation for final products, screen for coarse ones

Wet Milling Process Production Rate

- Ethanol:
 - Same as dry milling process
- Co-products:
 - 0.7 kg of corn oil
 - 1.4 kg of corn gluten meal (60% of protein)
 - 5.9 kg of corn gluten feed (21% of protein)
 - 7.7 kg of CO₂
- Ethanol: Feed: CO₂ = 1:1:1

Separation of Fermentation Products

- A mixture of solids, liquids and dissolved gases
- It is relatively easy to separate gaseous and precipitated products from spent fermentation broth
 - Liquid-solids separation by gravity settling, centrifugal separation and filtration
 - Dissolved gas is a NOT big concern



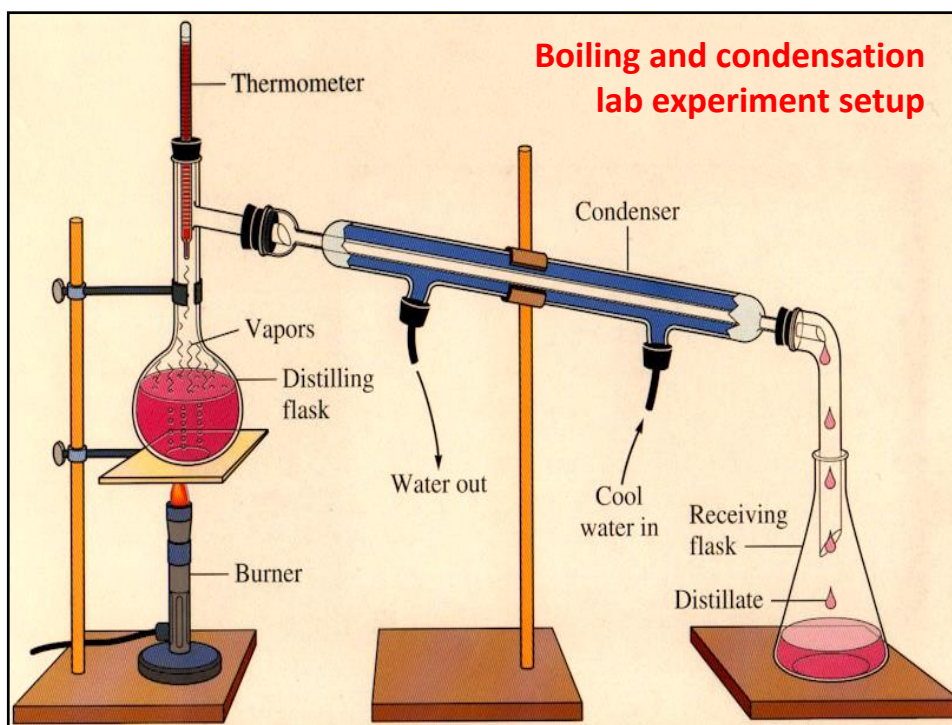
Fermentation Challenges

- Low production rate
- Sensitive to both inhibitors and operating conditions, especially temperature and pH
- Recovery of water-soluble products from dilute solutions can be expensive
- Effluent usually contains high biological oxygen demand (BOD) and requires wastewater treatment before discharge

Introduction to Ethanol Distillation*

Distillation

- To separate a mixture of liquids, the liquid can be heated to force components, which have different **boiling points**, into vapor. The vapor is then **condensed** back into liquid form and collected.
- Repeating the process on the collected liquid to improve the purity of the product is called double distillation.
- **Distillation is used for many commercial processes, such as production of gasoline, distilled water, xylene, alcohol, paraffin, kerosene, and many other liquids.**
- **Distillation** is an energy intensive process to recover **water-soluble** products (of fermentation)



Experiments

Round 1

- Consider the flask filled with a mixture of ethanol in water (a beer) containing 10% by volume ethanol (3.3 mole %).
- Heating would add thermal energy to the system.
- Shortly, boiling takes place and vapor generated.
- Gather a small portion of the vapor for analysis
 - ❖ 24 mole % ethanol (53 volume %).
- ❖ Now we condense this vapor

Ethanol Grade

- **Degree GL:** degrees Gay Lussac
degree GL = % by volume ethanol;
- **Degree US proof** = 2x% by volume ethanol

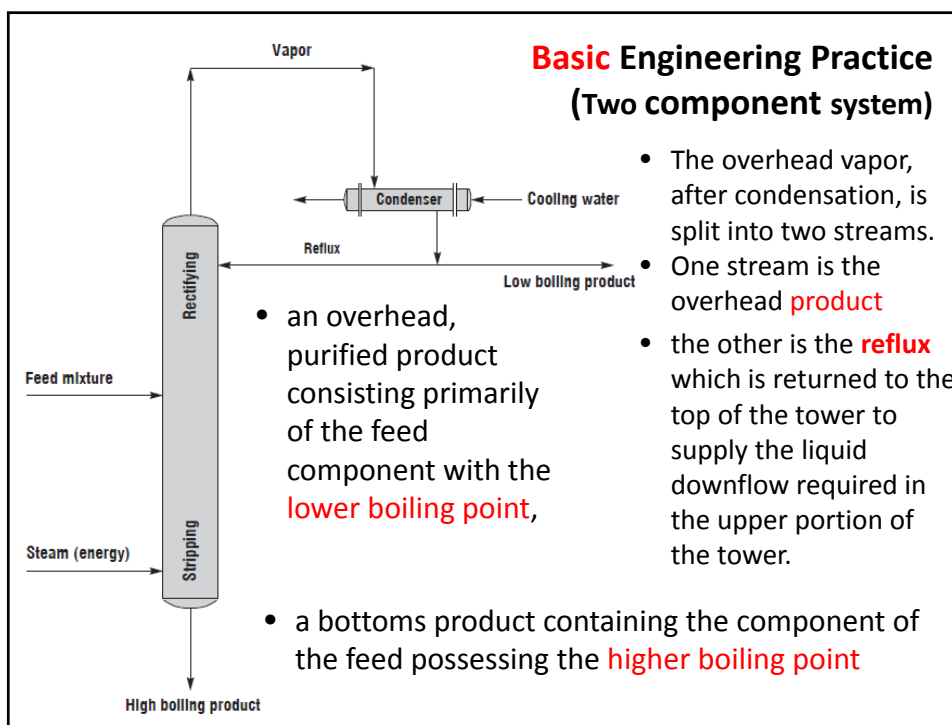
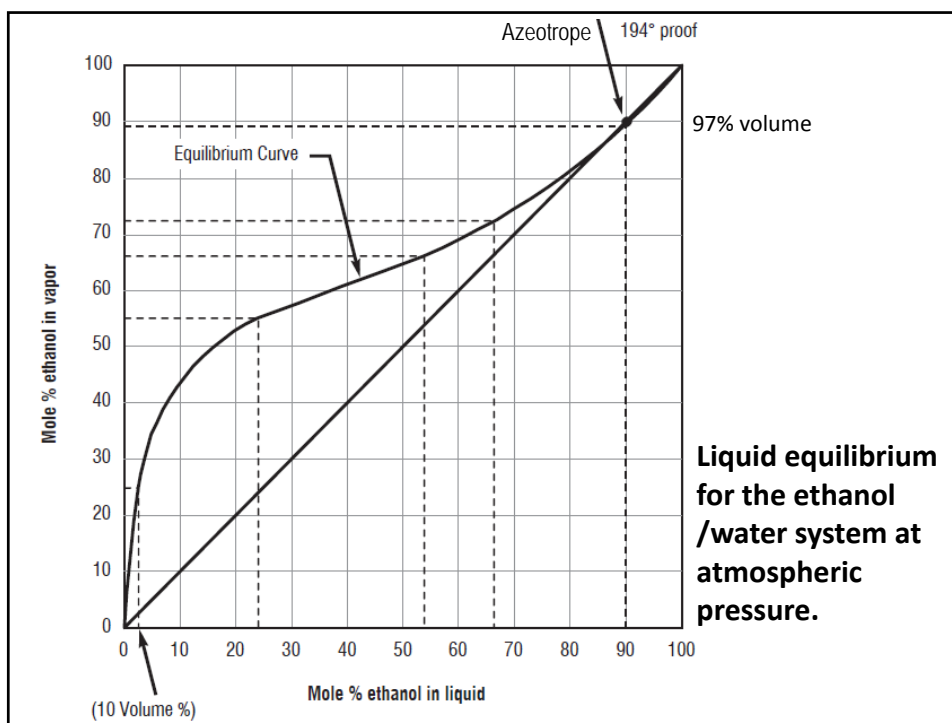
Example: Last slide, 24 mole % ethanol (53 volume %). it is graded as

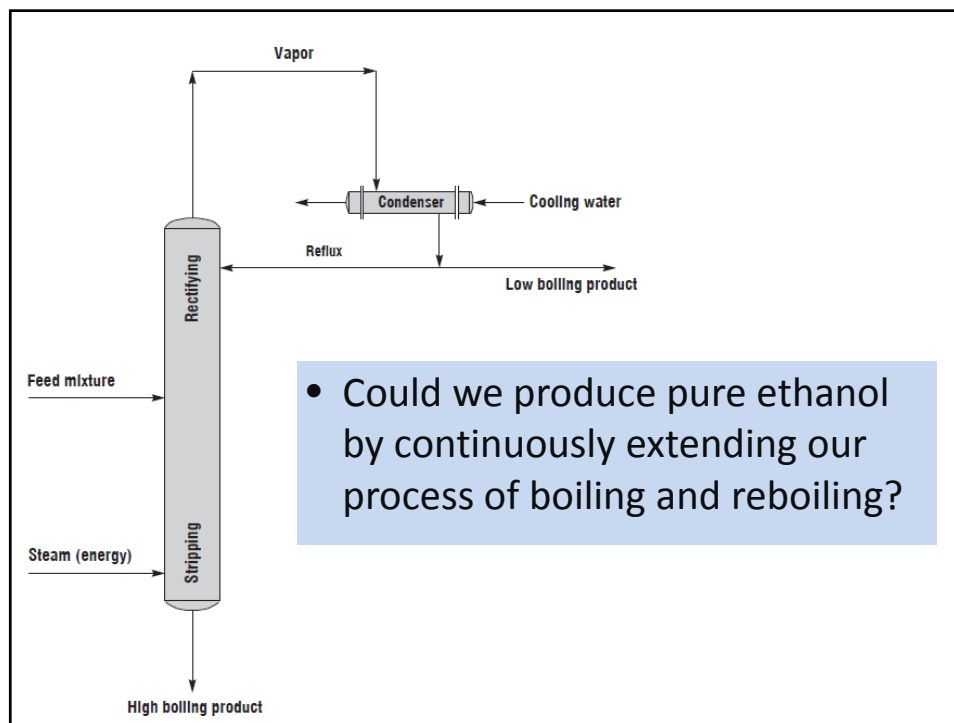
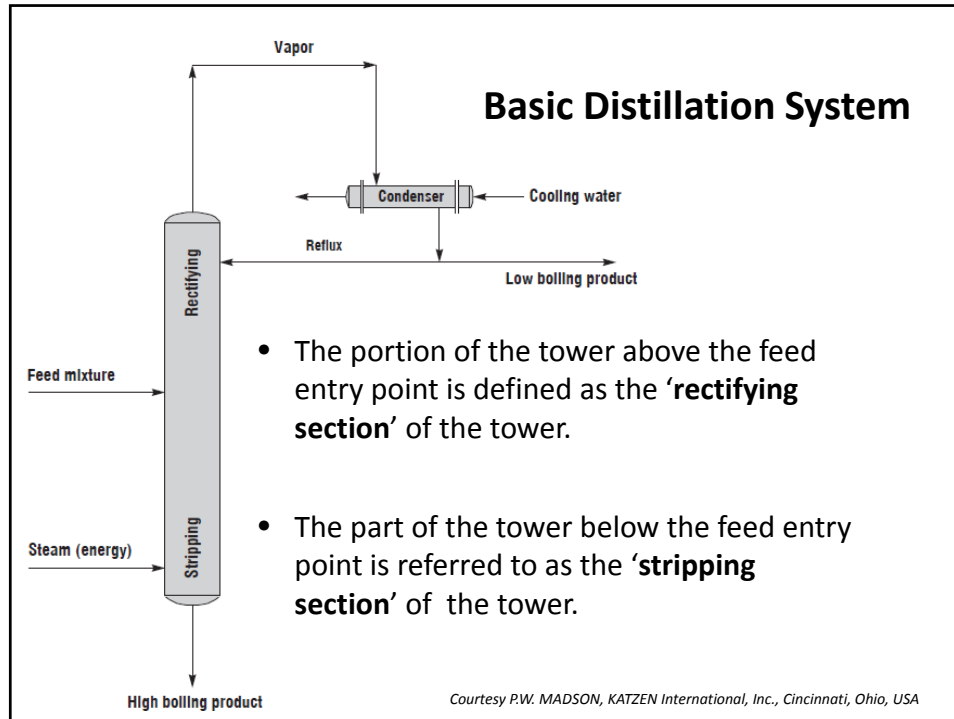
53° GL or 106° US proof

Round 2 (Repeat)

- *Boil the condensate obtained in Round 1* boil it in a second flask
- Collect a small amount of the initial vapor generated for analysis
 - ❖ this second vapor would contain about 55 mole % (83 volume %) of ethanol

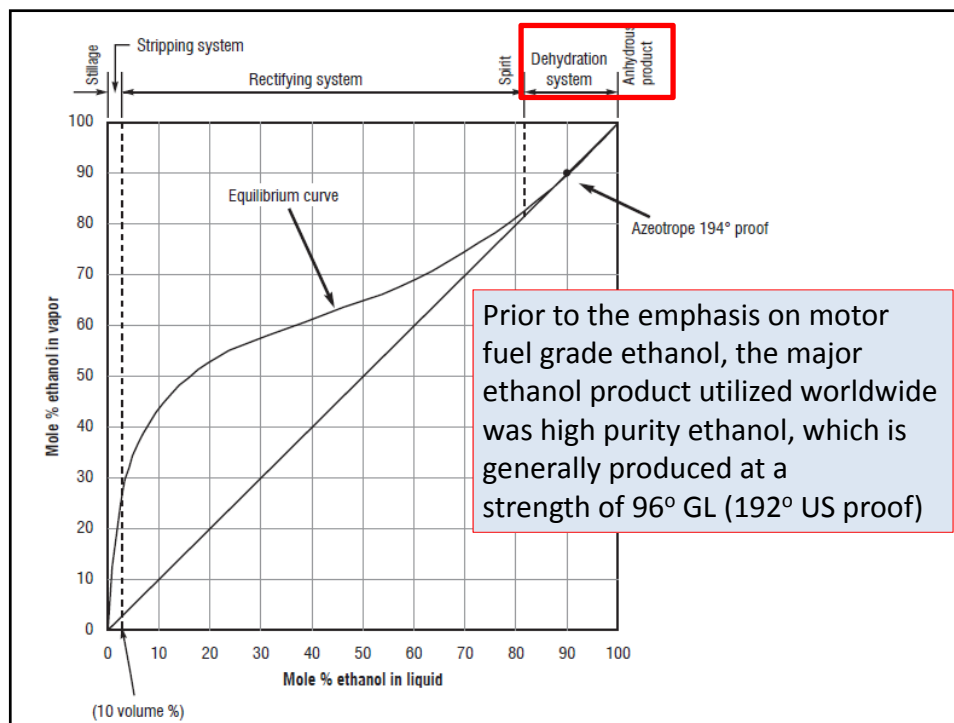
- Repeat the process again and again to a 3rd, 4th, ...
- Analysis would reveal that each successive portion of vapor would become richer in ethanol.
- **Infinite times, 100% pure ethanol.**
- Unfortunately, this **oversimplified** process is idealized; and practically speaking, is **impossible**.





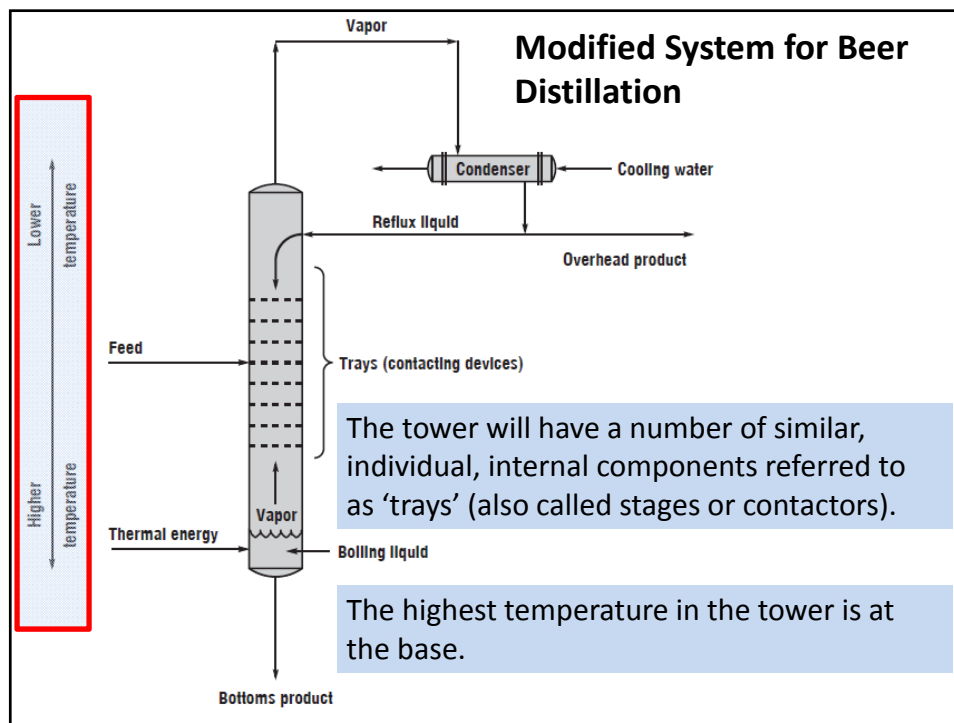
Single multistage distillation tower

- **87% volume or 194° US proof** is the limit in ethanol/water purification in any to the production of azeotropic ethanol-water mixtures.
- These azeotropic solutions of ethanol and water are also known as constant boiling mixtures (CBM) since the azeotropic liquid will have the same temperature as the azeotropic equilibrium vapor being boiled from itself.



Beer from Fermentation

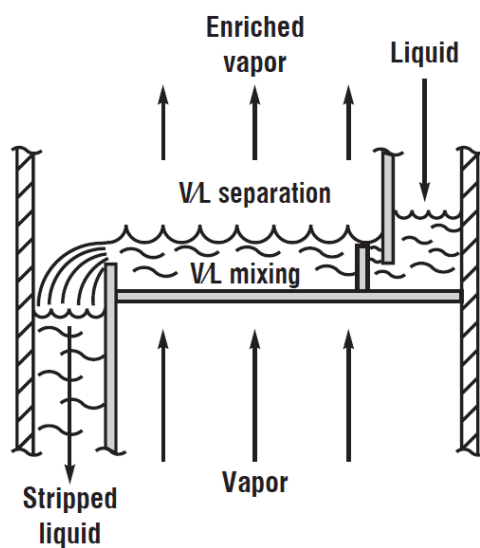
- Is NOT a two component system (Water-ethanol)
 - It is a very complicated system, and many solubles
- modifications required based on the simple distillation system in order to make it effective for the separation of a very pure ethanol product, essentially free of its water content.



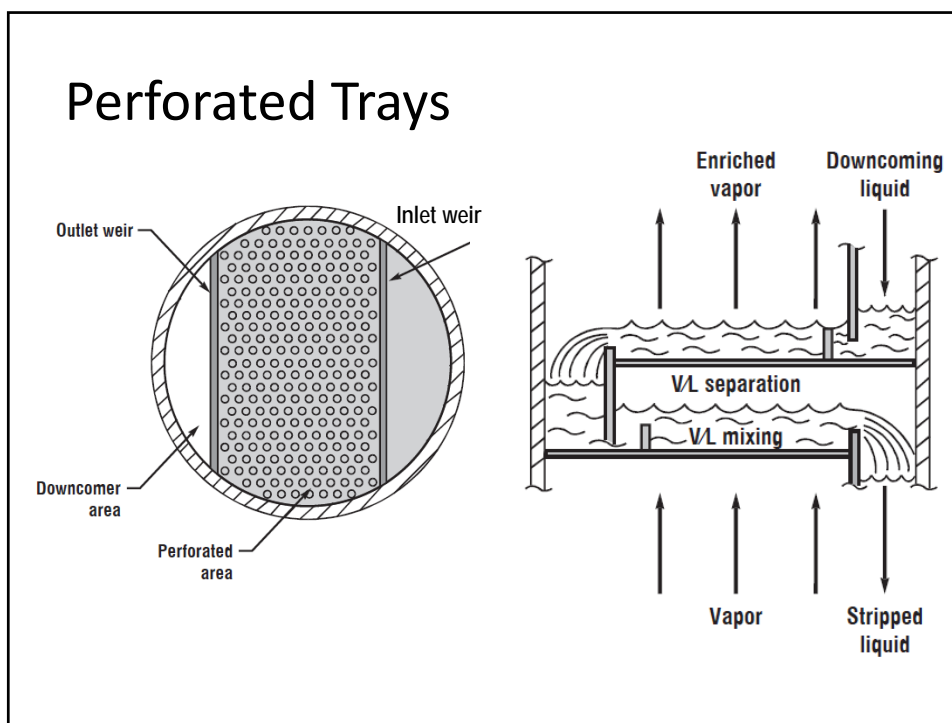
- *Distillation Contactors*

- Trays are the most common contactor in use.
- the primary functions of trays
 - mixing rising vapor with a falling fluid
 - allow for separation after mixing
 - provide path for liquid to proceed down the tower
 - provide path for vapor to proceed up the tower

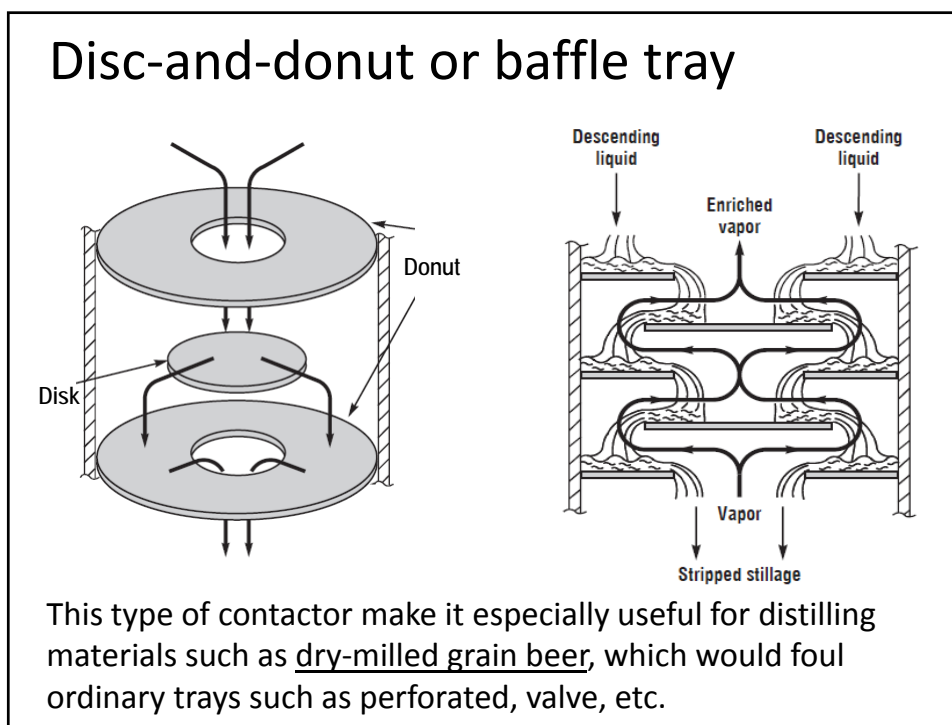
Distillation Tray functions



Perforated Trays



Disc-and-donut or baffle tray



Modern distillation systems

- multi-stage,
- continuous,
- countercurrent,
- vapor-liquid contacting systems

different materials boil at different temperatures

With outdoor installations, literally the 'sky is the limit', and refinery and petrochemical towers of 200 feet in height are not uncommon.



www.odfjell.com

- In the case of synthetic ethanol, the beer stripping tower is not required and the refining system is a simple three tower unit, which achieves 98% recovery of the ethanol in the crude feed as a first grade product.
- The final product may contain less than 5 ppm total impurities

Advances in R&D have reduced energy consumptions

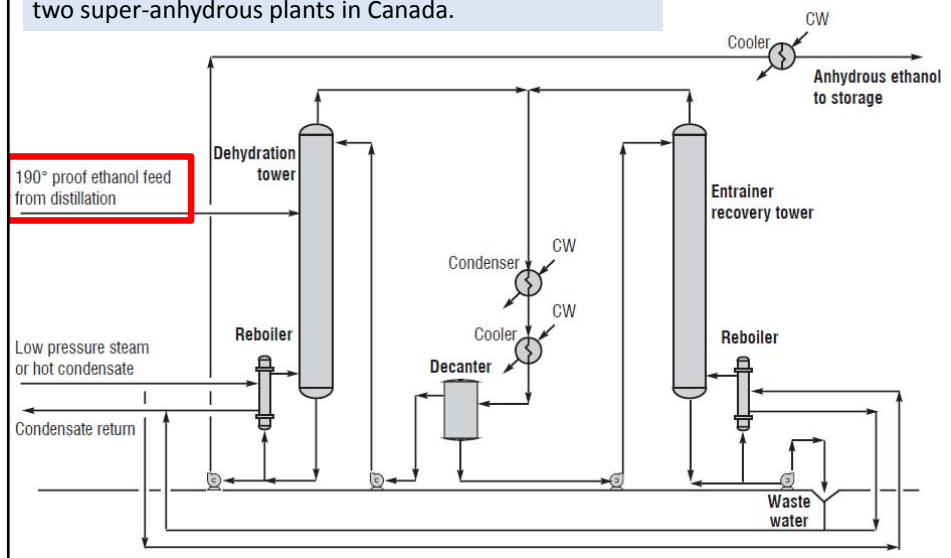
- The operation that has been most subject to critical comment is the distillation process.
- In an early version of this system, installed more than 60 years ago for the production of potable ethanol from grain and from molasses, all towers were operated at atmospheric pressure.
- However, installations made within the past 40 years utilize the multistage pressure system to reduce energy consumption to a level of about 50% of the all-atmospheric system.

Anhydrous ethanol

- Systems have been designed and installed for production of extremely dry and very pure – anhydrous ethanol for food and pharmaceutical use, primarily in aerosol preparations.
- These systems, as shown in next slide, yield ethanol containing less than 200 ppm water (99.98° GL).

High grade anhydrous ethanol system

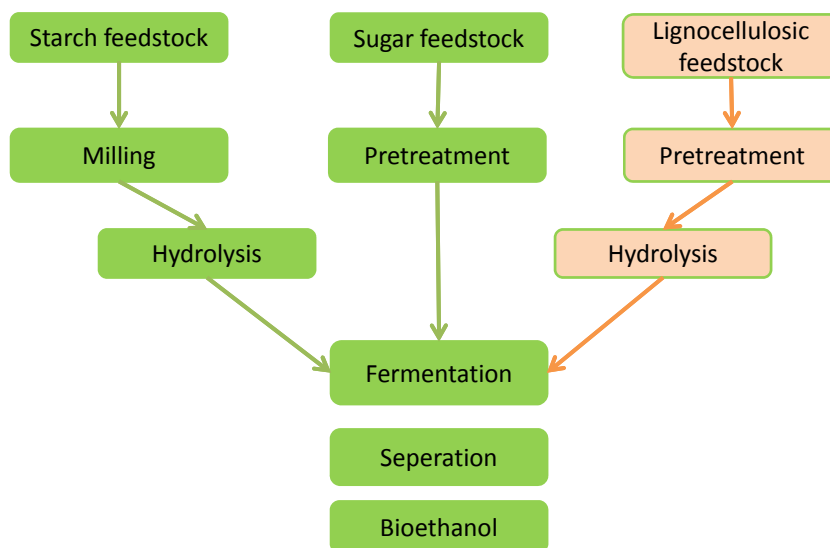
The two tower dehydrating system has been operated in two super-anhydrous plants in Canada.

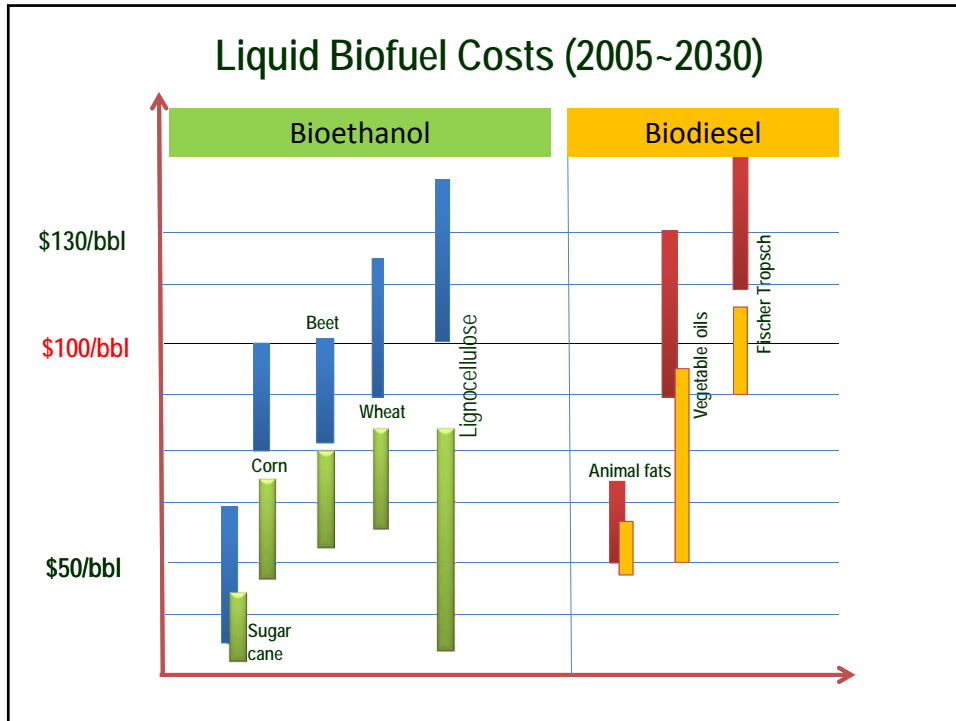


Comments


- Ethanol production by fermentation and distillation has been criticized for Consuming more energy than it produces because of
 - Distillation
 - Sometimes pretreatment

Lignocellulosic Feedstock to Sugar for Fermentation







Alternative Energy




Wind




Solar



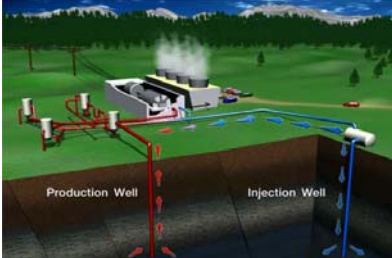
Biomass




Fuel Cell



Hydroelectric power

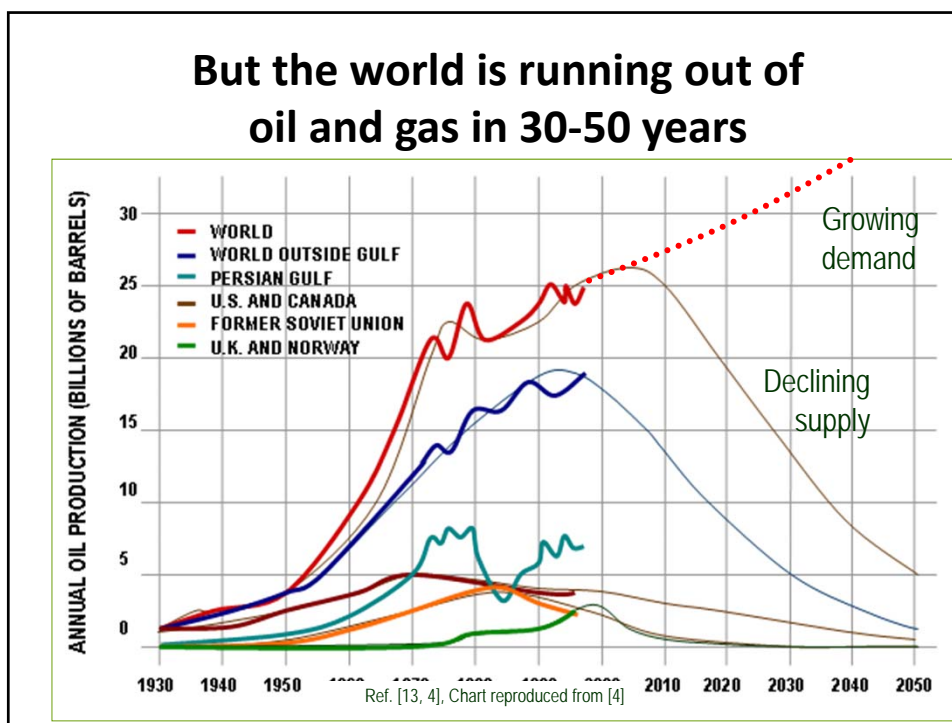


Geothermal



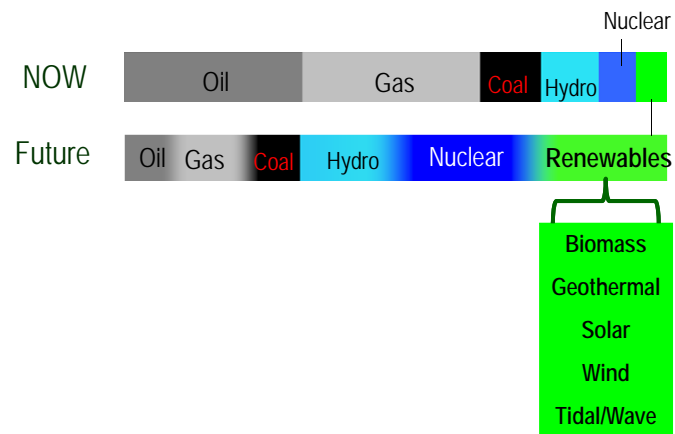
Nuclear energy

But the world is running out of oil and gas in 30-50 years



Energy Source ¹	2005	2006	2007	2008	2009
Total	100.47	99.79	101.5	99.44	94.82
Fossil Fuels	85.815	84.69	86.223	83.53	78.63
Coal	22.797	22.45	22.749	22.4	20
Coal Coke Net Imports	0.045	0.061	0.025	0.04	-0.023
Natural Gas ²	22.583	22.22	23.679	23.81	23.42
Petroleum ³	40.391	39.96	39.769	37.28	35.24
Electricity Net Imports	0.084	0.063	0.106	0.113	0.116
Nuclear Electric Power	8.161	8.215	8.455	8.427	8.328
Renewable Energy	6.407	6.825	6.719	7.367	7.745
Biomass ⁴	3.117	3.277	3.503	3.852	3.884
Biofuels	0.577	0.771	0.991	1.372	1.546
Waste	0.403	0.397	0.413	0.436	0.447
Wood and Derived Fuels	2.136	2.109	2.098	2.044	1.891
Geothermal Energy	0.343	0.343	0.349	0.36	0.373
Hydroelectric Conventional	2.703	2.869	2.446	2.512	2.682
Solar Thermal/PV Energy	0.066	0.072	0.081	0.097	0.109
Wind Energy	0.178	0.264	0.341	0.546	0.697

The Coming Decades Will See Growing Shares of Renewables



- ME 459, Energy Conversion