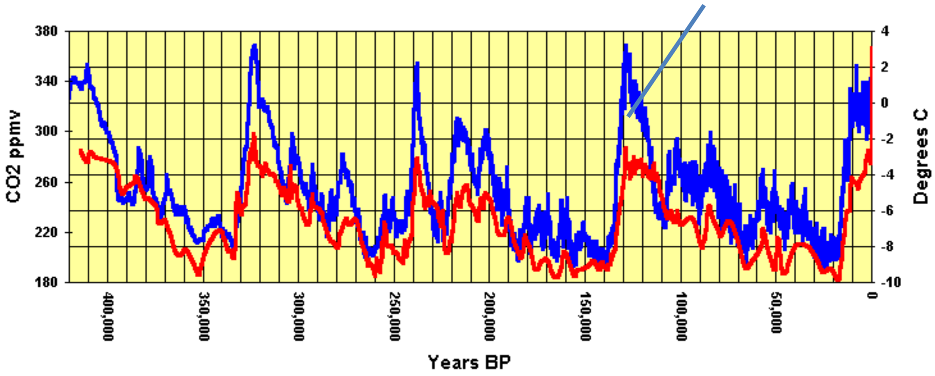
Chapter 12

Carbon Capture and Storage

Temperature Correlation vs. CO_2 concentration


Temperature variation

Source: Petit et. al. , Nature, 2000

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http://www.ipcc.ch/

Global Warming Potentials

GHG Name	Formula	GWP (1995)	GWP (2007)
Carbon dioxide	CO_2	1	1
Methane	CH_4	21	25
Nitrous oxide	N_2O	310	298
Hydrofluorocarbons	HFC	140-11,700	See extended Table 12.1
Perfluorocarbons	PFC	7,400	
Sulfur hexafluoride	SF_6	23,900	

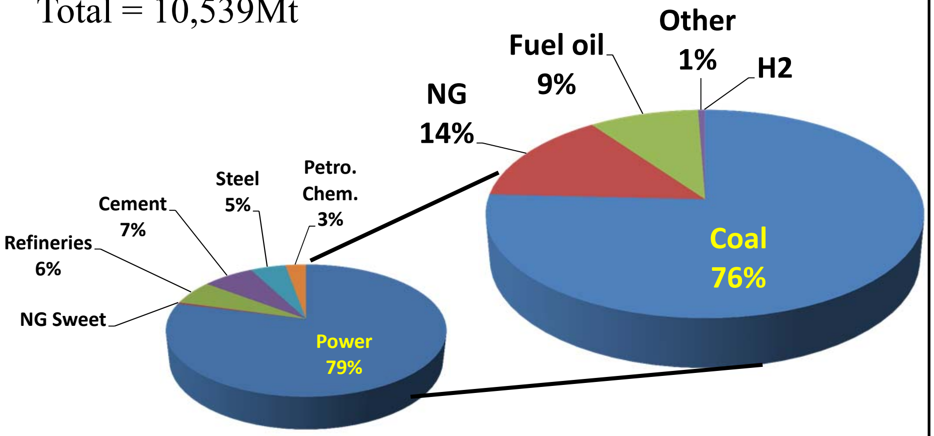
http://www.ghgprotocol.org/files/ghgp/tools/Global-Warming-Potential-Values.pdf

Carbon Dioxide

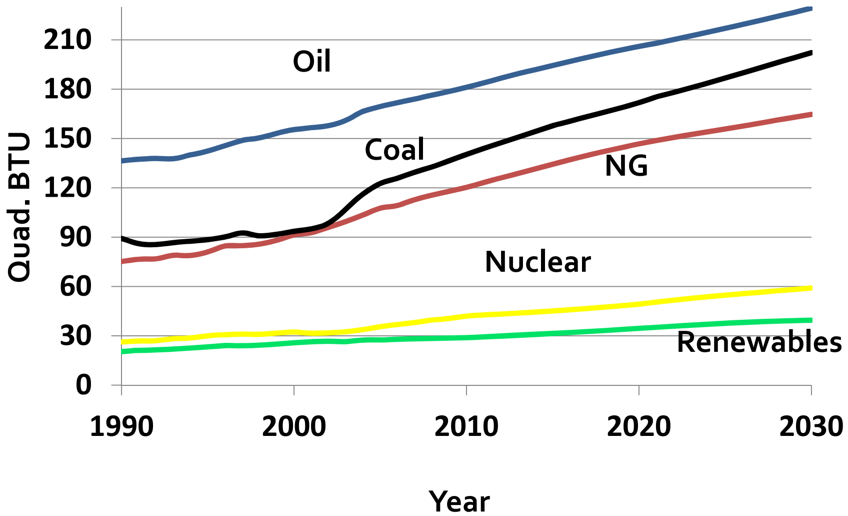
- Levels of GHGs have increased dramatically since industrial revolution. CO_2 concentration is the highest in last 650,000 years
- About 75% human-made carbon dioxide emissions were from burning fossil fuels during the past 20 years.
- About 3.2 billion metric tons is added to the atmosphere annually.
- The U.S. produces about 25% of global CO_2 emissions where 85% of the US energy is produced through fossil fuel combustion (IPCC, 2014).
- Global carbon dioxide emissions continue increasing annually between 2001 and 2025, and the emerging economies (China and India, for example) contribute much of the enhanced GHG effect.
- These developing countries' GHG emissions are expected to grow at 2.7% annually by 2025 (EIA, 2014).

Global Carbon Dioxide Emissions from Electricity in 2007

Total = 10,539Mt



Energy Outlook

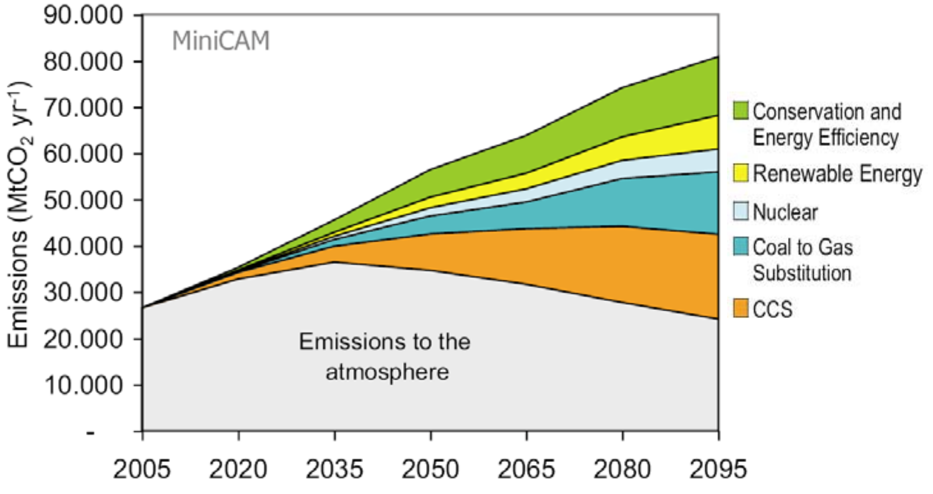


- Source: EIA, International Energy Outlook, 2006

General Approaches to GHG Emission Control

- Enhanced global warming effects can be reduced by reducing the emission of CO_2 and other GHGs.
- Emission reductions of CO_2 can be accomplished by a combination of several of the following approaches:
  - Improved energy conversion efficiency in stationary and mobile combustion processes.
  - Supply and end-use efficiency improvement and conservation
  - Shift to **alternative energy** sources for air pollution control and carbon emission reduction.
  - **Carbon capture and storage (CCS)**

Emissions Mitigation Potential



Source: IPCC Special Report on Carbon Capture and Sequestration

Carbon Capture Options

Technologies Overview

Pre-combustion carbon capture

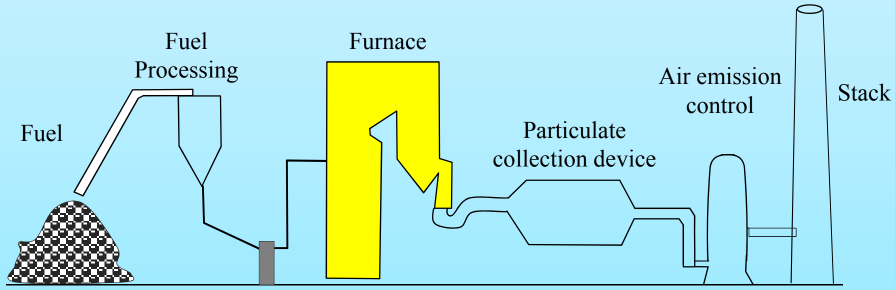
- Gasification and IGCC
- Biofuels fuels

In-combustion carbon capture

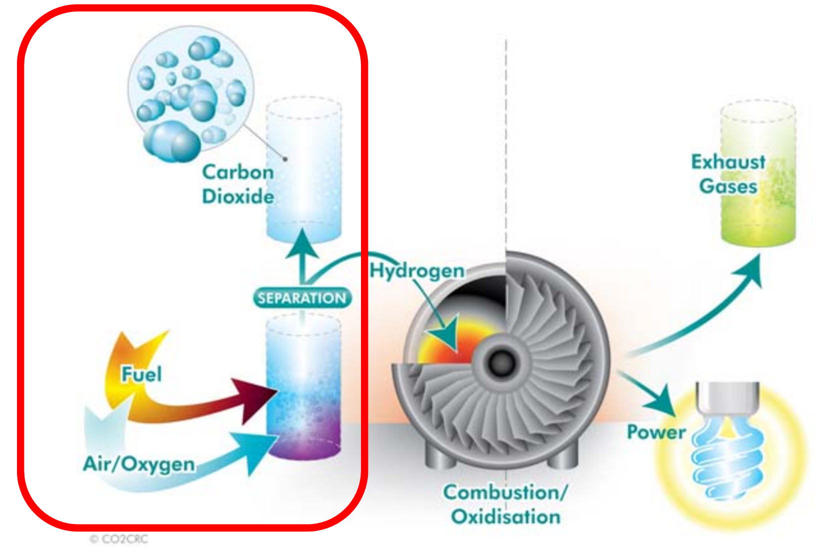
- Oxyfuel combustion
- Chemical-looping combustion

Post-combustion carbon capture

- CO_2 capture from flue gas
- CO_2 capture from atmosphere



Precombustion Carbon Capture



Source: http://www.co2crc.com.au/

Gasification

Synthetic gas (Syn-gas) Production

- *Syngas = CO+H_2*
- $C_\alpha H_\beta + \frac{1}{\phi}\left(\alpha + \frac{\beta}{4}\right) O_2$
  $\rightarrow [xCO_2 + \mathbf{(1-x)CO}] + [yH_2O + \mathbf{(1-y)H_2}]$
- It is a partial oxidation process or say fuel rich combustion

Simplified Reactions

Partial oxidation of carbon

$C(s) + \frac{1}{2}O_2 \rightarrow CO$	Carbon partial oxidation
$C(s) + H_2O \rightarrow CO + H_2$	Carbon-steam reaction
$C(s) + CO_2 \rightarrow 2CO$	Boudouard reaction

Partial oxidation of methane

$CH_4 + \frac{1}{2}O_2 \rightarrow CO + 2H_2$	Methane partial oxidation
$CH_4 + H_2O \rightarrow CO + 3H_2$	Steam-methane reaction (700-950 °C, 1.4-4MPa)

Gasification Chemistry

$\mathrm{C} + \frac{1}{2}\mathrm{O_2} \rightarrow \mathrm{CO}$	(Combustion reaction)	(8-4)
$\mathrm{C} + \mathrm{O_2} \rightarrow \mathrm{CO_2}$	(Combustion reaction)	(8-5)
$\mathrm{C} + \mathrm{CO_2} \leftrightarrow 2\mathrm{CO}$	(Boudouard reaction)	(8-6)
$\mathrm{C} + \mathrm{H_2O} \rightarrow \underbrace{\mathbf{CO + H_2}}$	(Gasification with steam)	(8-7)

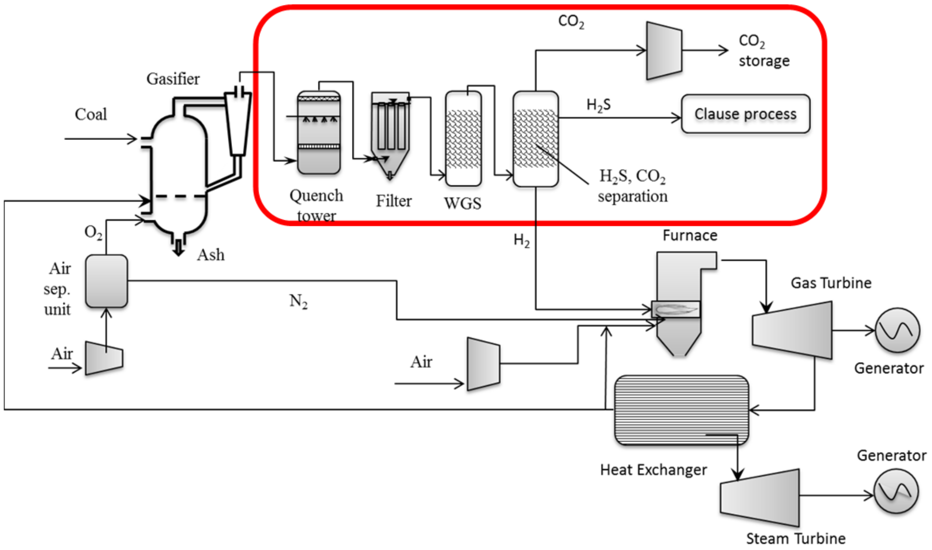
$\mathrm{C} + 2\mathrm{H_2} \rightarrow \mathrm{CH_4}$	(Gasification with $\mathrm{H_2}$)	(8-8)
$\mathrm{CO} + \mathrm{H_2O} \rightarrow \mathrm{H_2} + \mathrm{CO_2}$	(Water gas shift reaction)	(8-9)
$\mathrm{CO} + 3\mathrm{H_2} \rightarrow \mathrm{CH_4} + \mathrm{H_2O}$	(Methanation)	(8-10)
$\mathrm{H_2S} + \mathrm{CO_2} \rightarrow \mathrm{COS} + \mathrm{H_2O}$		**(8-13)**

Water-gas shift reaction for carbon capture purpose

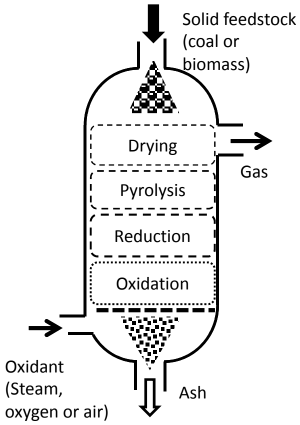
- $CO + H_2O \leftrightarrow CO_2 + H_2$
- Ready for capture

Gases	Mole fraction	
	Pre-combustion syngas after WGS reaction	Postcombustion flue gas
CO_2	37.7%	10-15%
H_2O	0.14%	5-10%
H_2	55.5%	
NOx		< 800 ppm
SOx		< 500 ppm
O_2		3-4%
CO	1.7%	20 ppm
N_2	3.9%	70-75%
H_2S	0.4%	
Temperature	40 °C	40-75 °C
Pressure	30 bar	1 bar

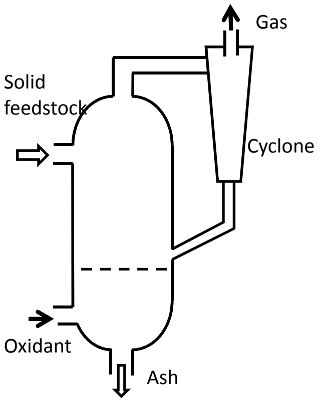
Simplified IGCC with Pre-combustion CO_2 Capture Process



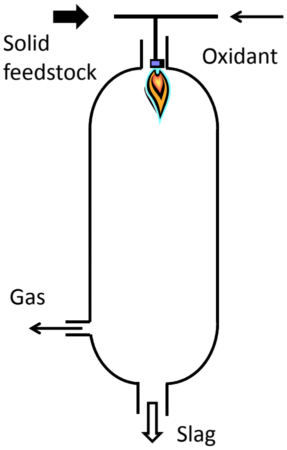
Gasifiers



1. fixed bed gasifier



2. fluidized bed gasifier



3. Entrained flow gasifier

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.

- See Chapter 8 for spray tower wet scrubber design

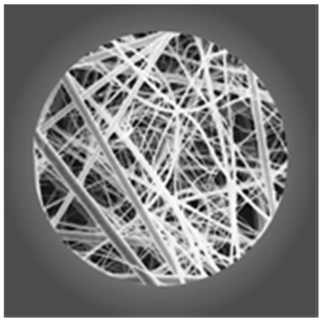
Particulate removal

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.

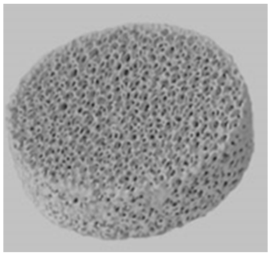
Filter Media

Cotton may be used for the temperatures below 80 ^{o}C



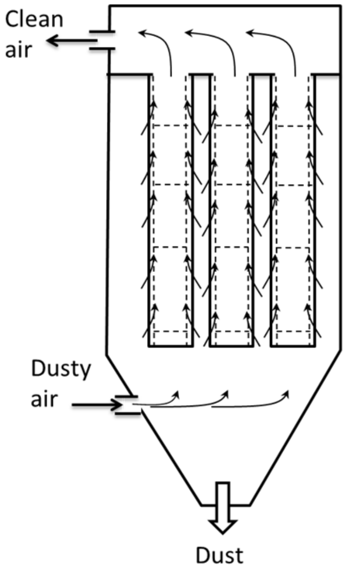
Teflon and **glass** fiber work perfectly up to 260 ^{o}C.

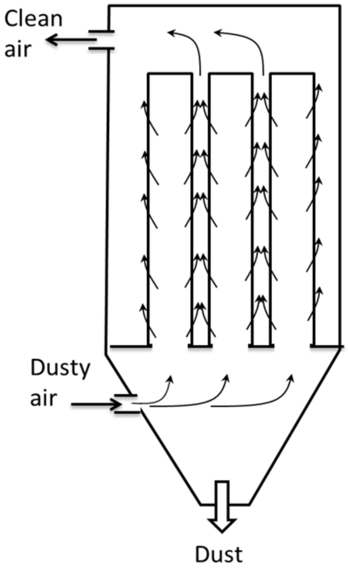
For applications up to 450 ^{o}C **stainless steel** can be used under unfriendly **corrosive** environments.



At higher temperatures, **ceramic** materials are the best choice.

(Gas) Out-In model (Gas) In-Out model



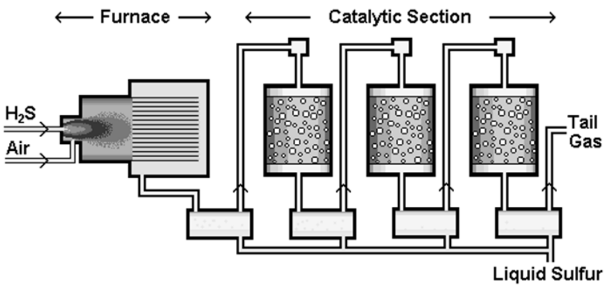


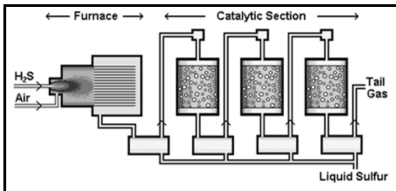
H_2S separation by chemical adsorption

$ZnO + H_2S \rightarrow ZnS + H_2O$ (Adsorption, 315 − 530 °C)	(8-14)
$ZnS + \frac{3}{2}O_2 \rightarrow ZnO + SO_2$ (Regeneration, 590 − 680 °C)	(8-15)

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 °C or higher

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

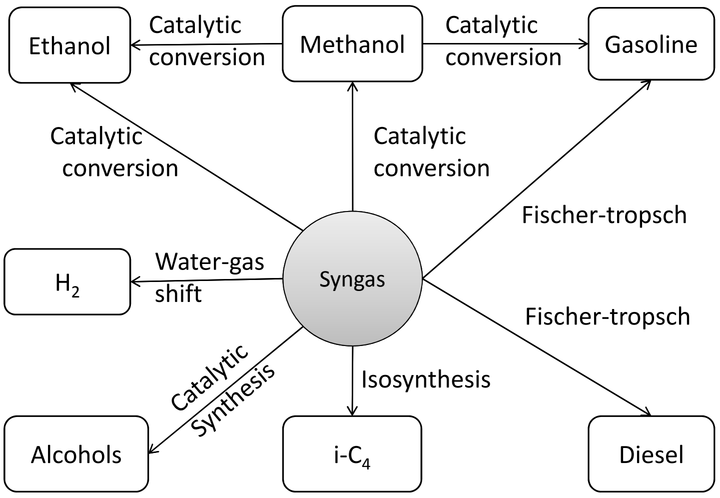
  $2H_2S+SO_2 \rightarrow 3S+2H_2O$
- Overall reaction:

  $10H_2S+5O_2$

  $\rightarrow 2H_2S+SO_2+7/2S_2+8H_2O$
- 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.



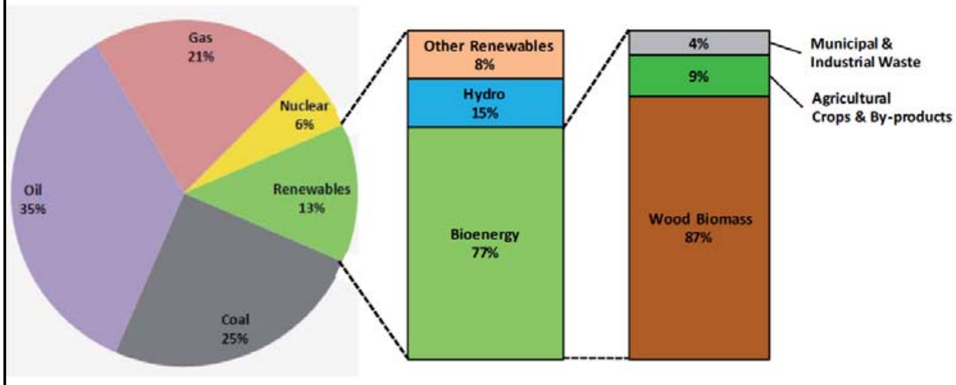
Ethanol
Catalytic conversion
Methanol
Catalytic conversion
Gasoline
Catalytic conversion
Catalytic conversion
Fischer-tropsch
H_2
Water-gas shift
Syngas
Fischer-tropsch
Catalytic Synthesis
Isosynthesis
Alcohols
i-C_4
Diesel

Carbon Capture
(for IGCC before Combustion)

- Adsorption → • Adsorbents
- Absorption → • Absorbents

Bioenergy

Share of bioenergy in the world primary energy mix



Source: based on IEA, 2006; and IPCC, 2007.

- **IEA.** 2006. International Energy Agency, World Energy Outlook 2006. Paris.
- **IPCC.** 2007. Intergovernmental Panel on Climate Change, Mitigation of Climate Change. Working group III, Chapter 4 of the 4th Assessment Report.

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

Solid Biofuels

Wood log

Pulverized wood

Pellets

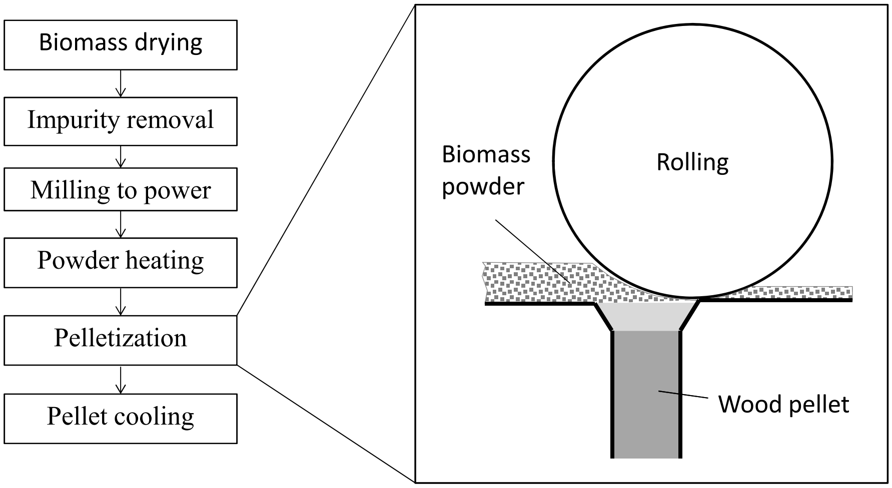
Biomass Pellets

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

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).

Pellet Production Processes



Biomass drying
Impurity removal
Milling to power
Powder heating
Pelletization
Pellet cooling

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 pellitising 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).

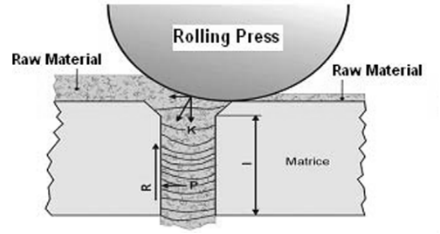
Feedstock Heating

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.



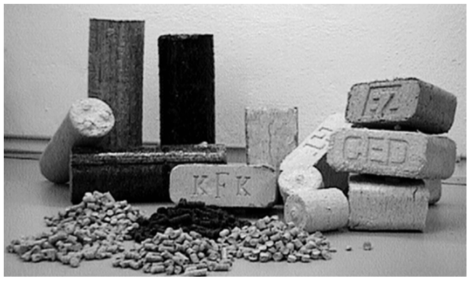
- When the rolling press is once again rolled over the hole, new material is pressed into the hole, thereby compressing the raw material into pellets.

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 another 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

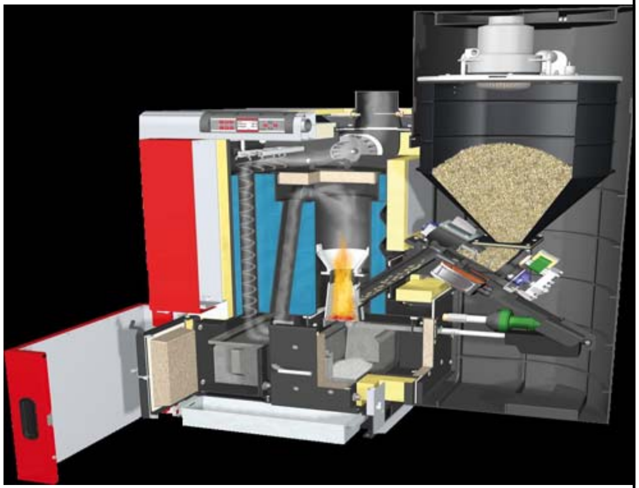
- The quality of fuel pellets may vary considerably depending on raw material, durability and water content.
- The quality of the wood pellets can be difficult to assess and therefore the consumer should make sure that the manufacturer delivers a product that meets a series of minimum standards.
- The 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/

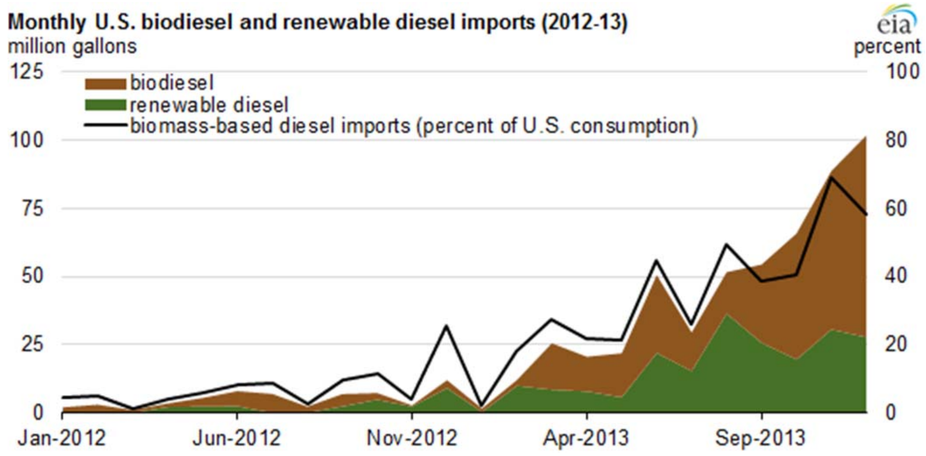
- House pellet heater
- Industrial pellet boilers



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


Monthly U.S. biodiesel and renewable diesel imports (2012-13)

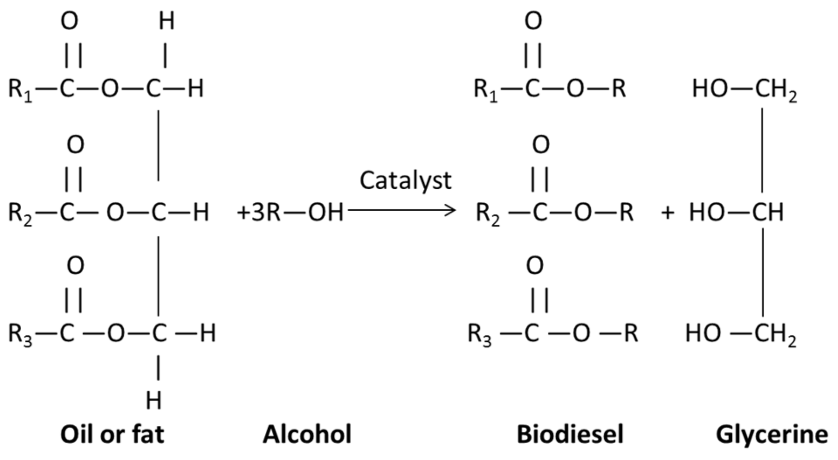
Feedstock for biodiesel (USA)

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

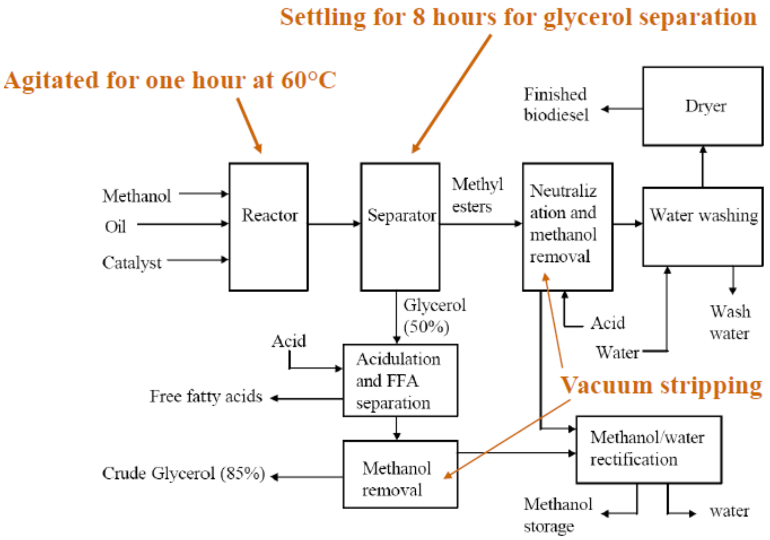
Animal Fats (Billion pounds/yr)	
Edible Tallow	1.625
Inedible tallow	3.859
Lard & Grease	1.306
Yellow Grease	2.633
Poultry Fat	2.215
Total Animal Fat	11.638

[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



Alkali-catalyzed transesterification



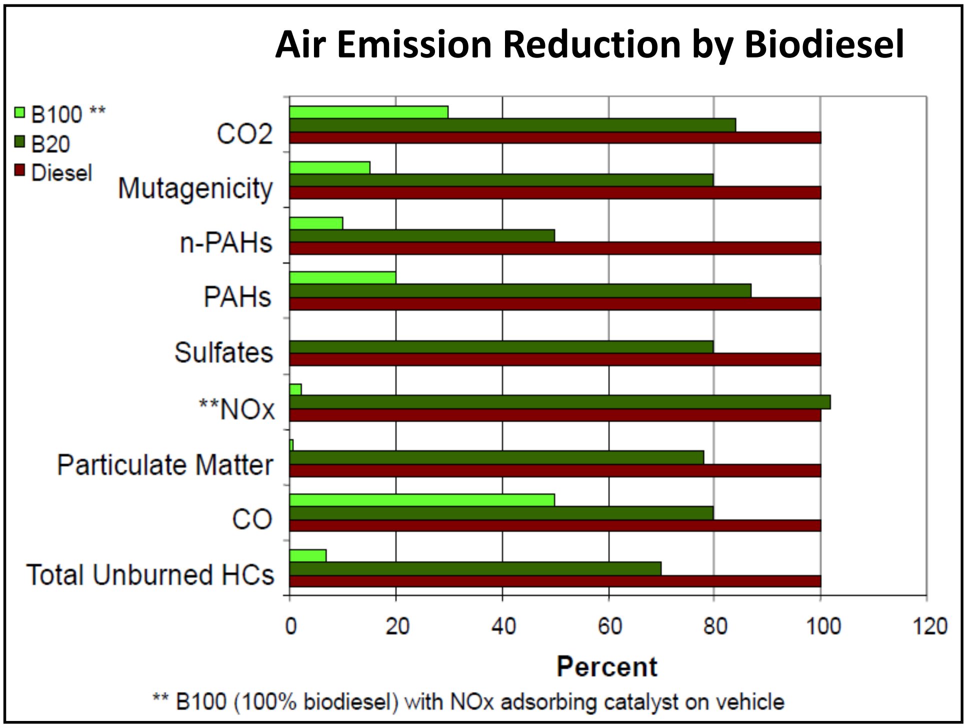
Settling for 8 hours for glycerol separation

Agitated for one hour at 60°C

Vacuum stripping

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



Air Emission Reduction by Biodiesel

** B100 (100% biodiesel) with NOx adsorbing catalyst on vehicle

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 40º F) must be heated to at least 60ºF 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.

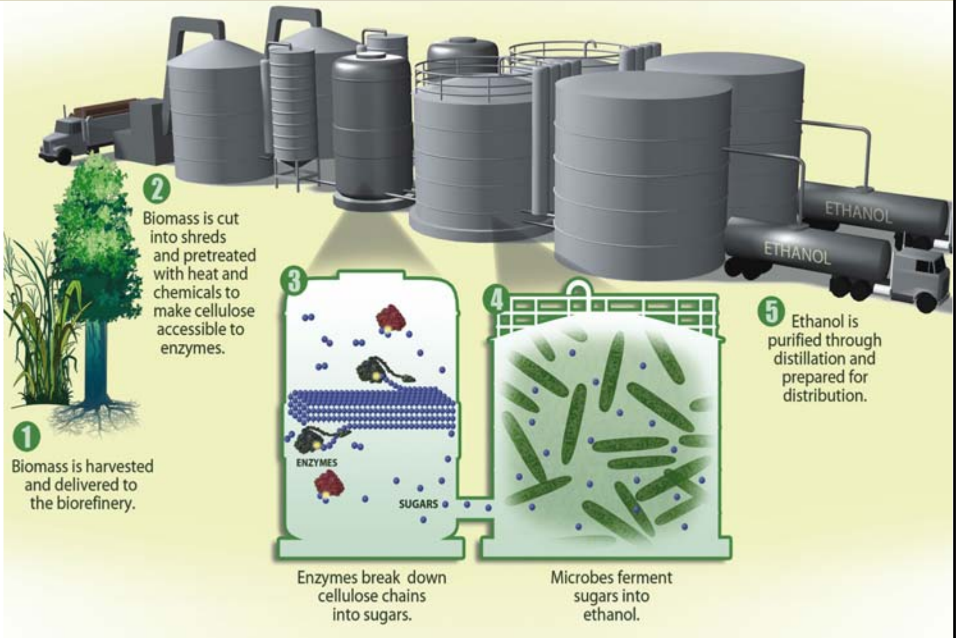
- With any type of blending (splash, in-tank or bottom loading), putting B100 into a cold empty truck can cause the fuel to gel, prohibiting proper mixing.
- Always maintain biodiesel at 10–15º F above its cloud point prior to blending with diesel fuel.

- 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.

Bioethanol



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 ⟶ Glucose

$C_{12}H_{22}O_{11} + H_2O \xrightarrow{\text{Enzyme}} 2C_6H_{12}O_6$	**(8-18)**
$C_6H_{12}O_6 \xrightarrow{\text{Zymase}} 2C_2H_5OH + 2CO_2$	(8-19)

Glucose ⟶ Ethanol

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

Conversion Rate

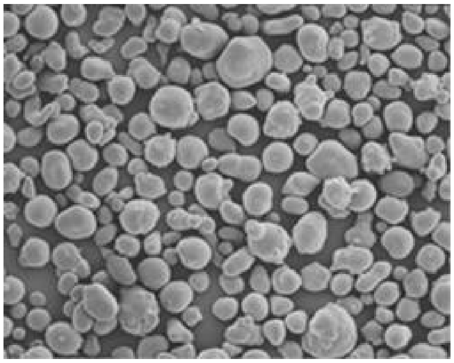
- Maximum theoretical yield of ethanol is 51%
  - Mass ethanol / Mass carbohydrate
  - The rest goes to CO_2
- In reality, no more than 47% of the fermented carbon hydrates is converted into ethanol

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 kids of plant cells where they serve as a storage of carbohydrate

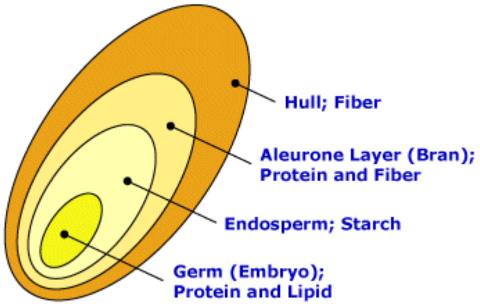


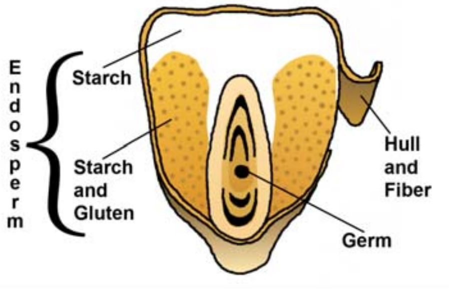
Starch for Fermentation

- Corn
- Wheat
- Barley
- ***They are all cereal grains***
- Grain starch consists of
    - ❑10-20% wt. amylose (<u>soluble</u>)
    - ❑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

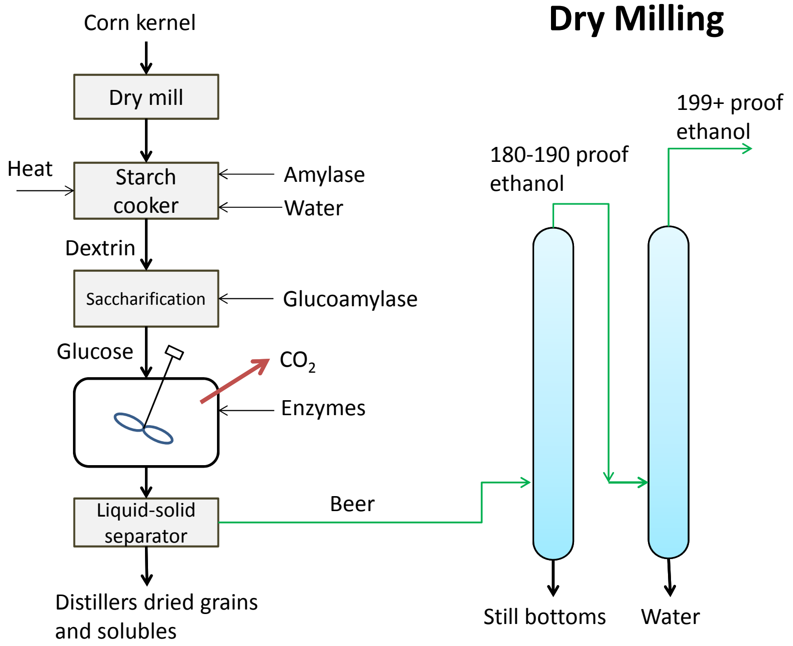




Corn to Ethanol

1. Dry milling process
2. Wet milling process

Production of Fuel-Ethanol by Dry Milling



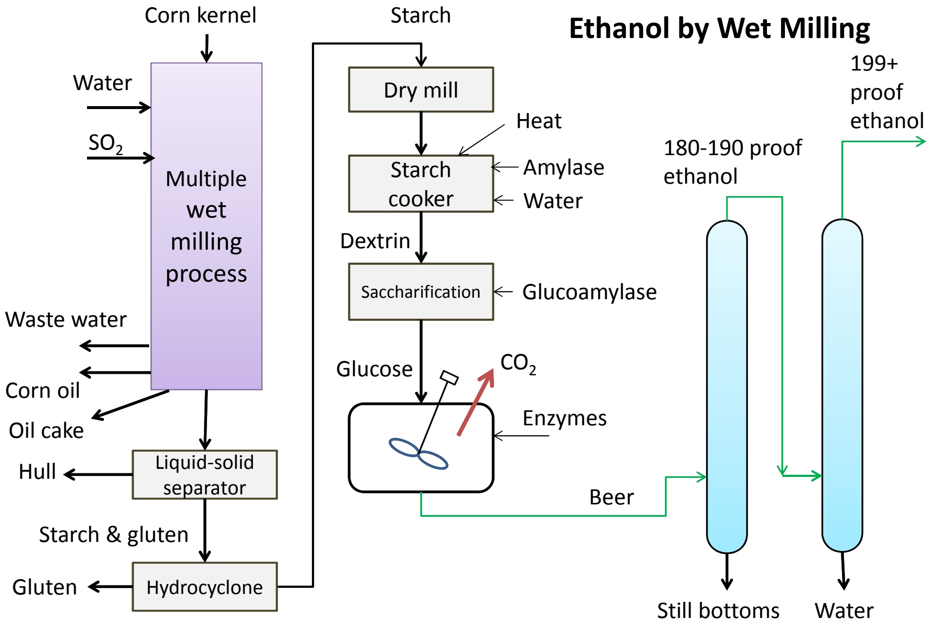
Dry Mill of Corn Steps

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 f ethanol per bushel of corn
  - ❖1 bushel = 35.24 liters
- Co-products:
  - ❖DDG: 7.7-8.2 kg/bushel corn
  - ❖CO_2: 7.3-7.7 kg/bushel corn
    - ❑CO_2 from fermentation
    - ❑CO_2 can be sold to carbonated beverage makers
- <u>Ethanol+DDGS+CO_2</u> about 1/3 for each of the original weight of corn.

Production of Fuel-Ethanol by Wet Milling



Corn kernel

Water

SO_2

Multiple wet milling process

Waste water

Corn oil

Oil cake

Hull

Liquid-solid separator

Starch & gluten

Gluten

Hydrocyclone

Starch

Dry mill

Heat

Starch cooker

Amylase

Water

Dextrin

Saccharification

Glucoamylase

Glucose

CO_2

Enzymes

Beer

180-190 proof ethanol

199+ proof ethanol

Still bottoms

Water

Wet Milling of Corn

Corn $\xrightarrow{\text{Wet milling}}$

- Ethanol
- Starch
- Corn oil
- Gluten (protein-rich materials)
- Fiber (hulls)

Advantage: Higher value by products

Hydrolysis of Starch

- 150-200 ^{o}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 reset 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 CO_2
- Ethanol: Feed: CO_2 = 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

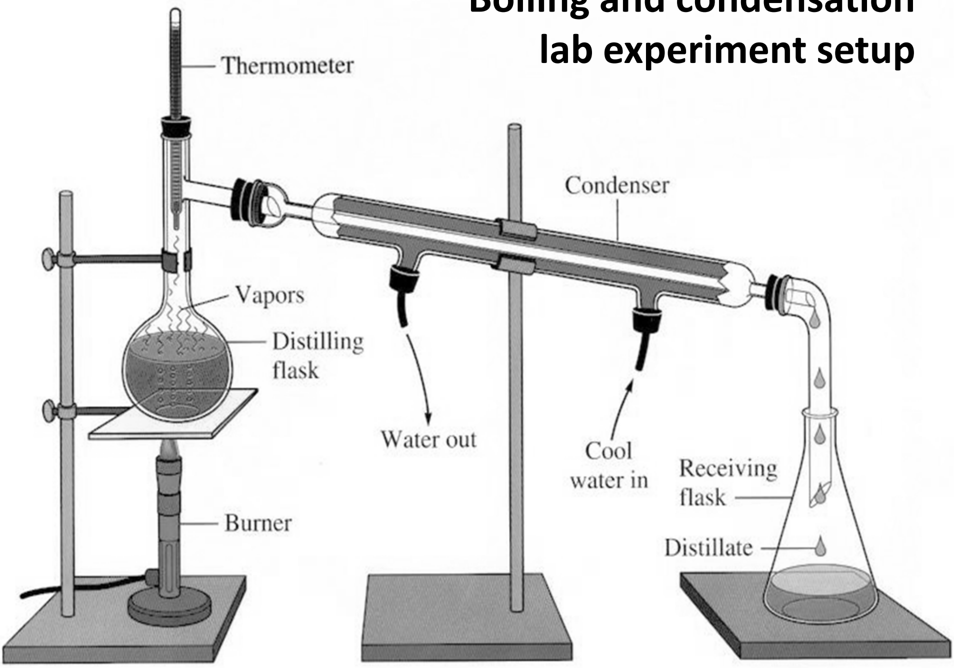
- Low production rate
- Sensitive to both inhibitors and operating conditions, especially temperature and pH
- Recovery of water-soluble products from dilute solutions can be expensive
- Effluent usually contains high biological oxygen demand (BOD) and requires waste-water treatment before discharge

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)

Boiling and condensation lab experiment setup



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:** degress Gay Lussac

  degree GL = % by volume ethanol;
- Degree US proof = 2x% by volume ethanol

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

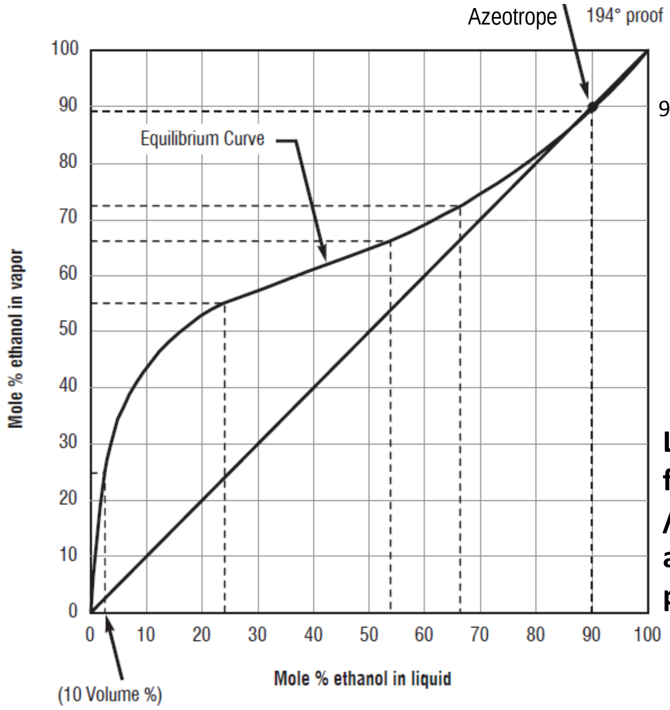
53° GL or 106° US proof

Round 2 (Repeat)

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

---

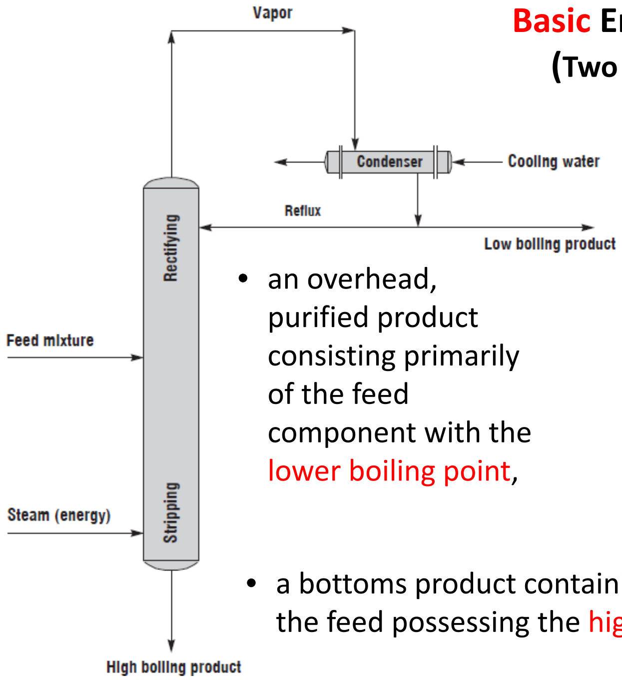
- Repeat the process again and again to a 3rd, 4th, …
- Analysis would reveal that each successive portion of vapor would become richer in ethanol.
- **Infinite times, 100% pure ethanol.**
- Unfortunately, this **oversimplified** process is idealized; and practically speaking, is **impossible**.



97% volume

Liquid equilibrium for the ethanol /water system at atmospheric pressure.

Basic Engineering Practice (Two component system)

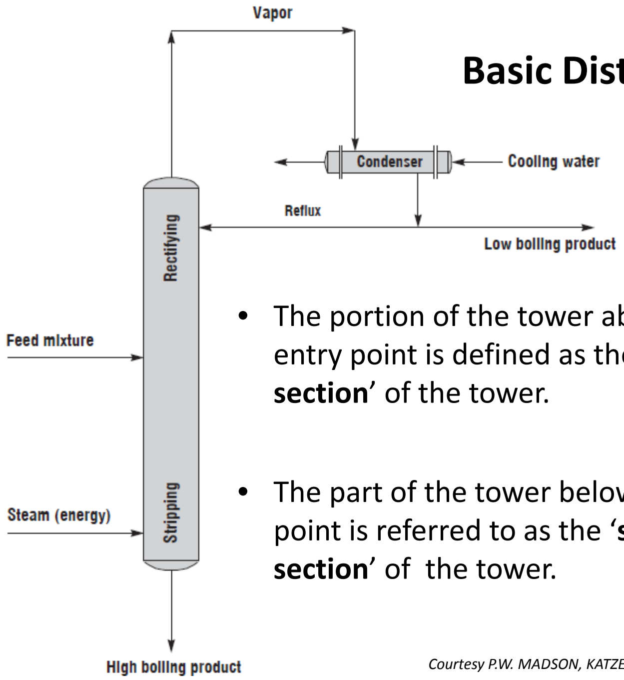


- The overhead vapor, after condensation, is split into two streams.
- One stream is the overhead product
- the other is the **reflux** which is returned to the top of the tower to supply the liquid downflow required in the upper portion of the tower.

- an overhead, purified product consisting primarily of the feed component with the lower boiling point,

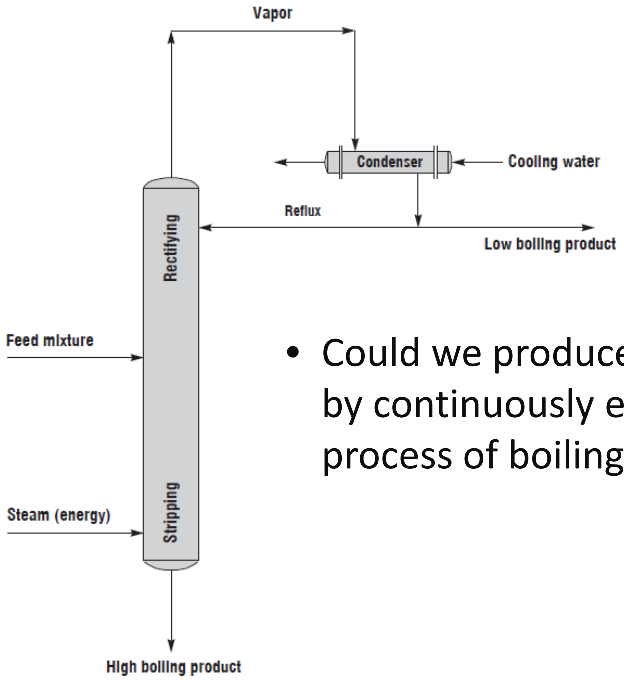
- a bottoms product containing the component of the feed possessing the higher boiling point

Basic Distillation System



- The portion of the tower above the feed entry point is defined as the '**rectifying section**' of the tower.
- The part of the tower below the feed entry point is referred to as the '**stripping section**' of the tower.

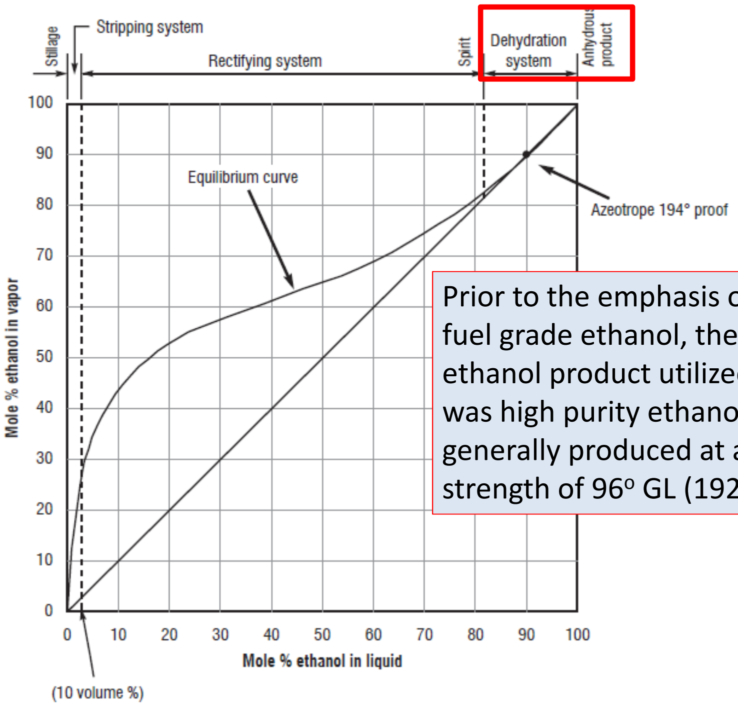
Courtesy P.W. MADSON, KATZEN International, Inc., Cincinnati, Ohio, USA



- Could we produce pure ethanol by continuously extending our process of boiling and reboiling?

Single multistage distillation tower

- **87% volume or 194^o US proof i**s 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.

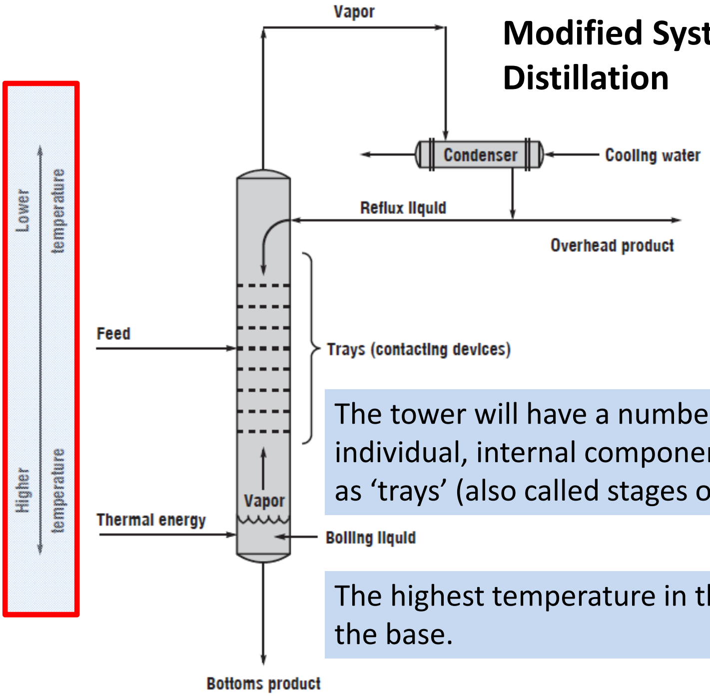


Prior to the emphasis on motor fuel grade ethanol, the major ethanol product utilized worldwide was high purity ethanol, which is generally produced at a strength of 96^o GL (192^o US proof)

Beer from Fermentation

- Is NOT a two component system (Water-ethanol)
  - It is a very complicated system, and many solubiles
- 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.

Modified System for Beer Distillation



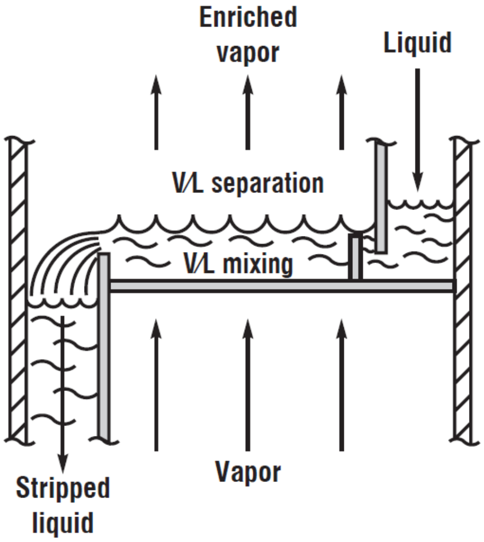
The tower will have a number of similar, individual, internal components referred to as ‘trays’ (also called stages or contactors).

The highest temperature in the tower is at the base.

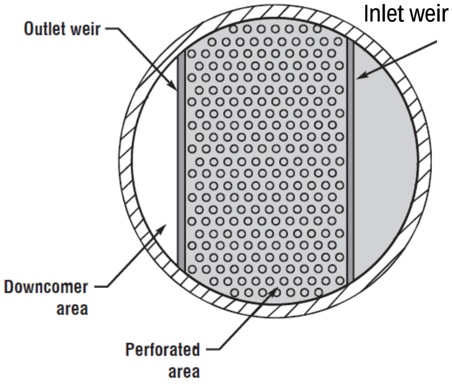
• *Distillation Contactors*

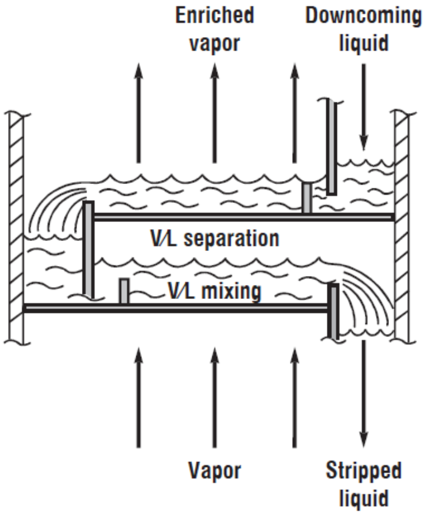
- Trays are the most common contactor in use.
- the primary functions of trays
  - – mixing rising vapor with a falling fluid
  - – allow for separation after mixing
  - – provide path for liquid to proceed down the tower
  - – provide path for vapor to proceed up the tower

Distillation Tray functions

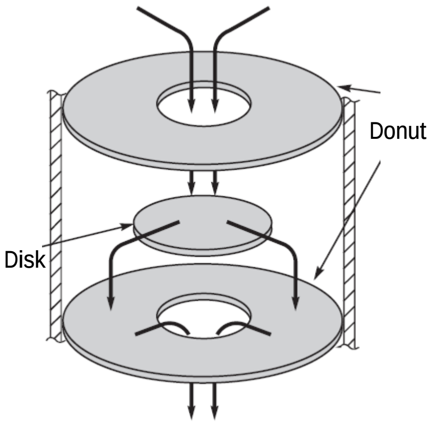


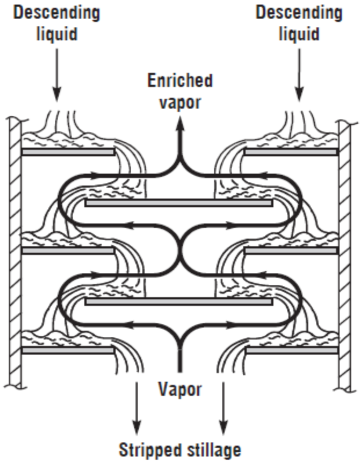
Perforated Trays





Disc-and-donut or baffle tray





This type of contactor make it especially useful for distilling materials such as dry-milled grain beer, which would foul ordinary trays such as perforated, valve, etc.

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

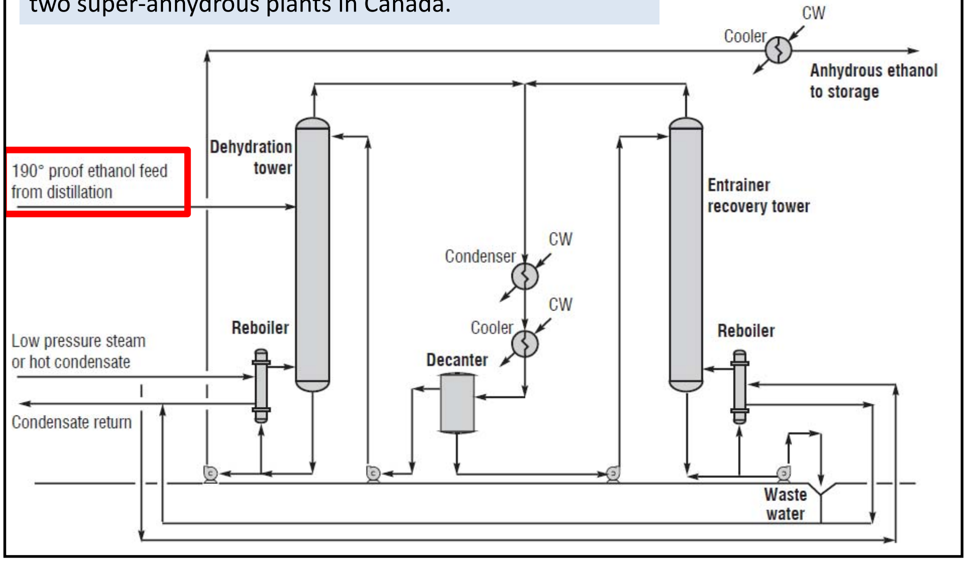
- The operation that has been most subject to critical comment is the distillation process.
- In an early version of this system, installed more than 60 years ago for the production of potable ethanol from grain and from molasses, all towers were operated at atmospheric pressure.
- However, installations 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

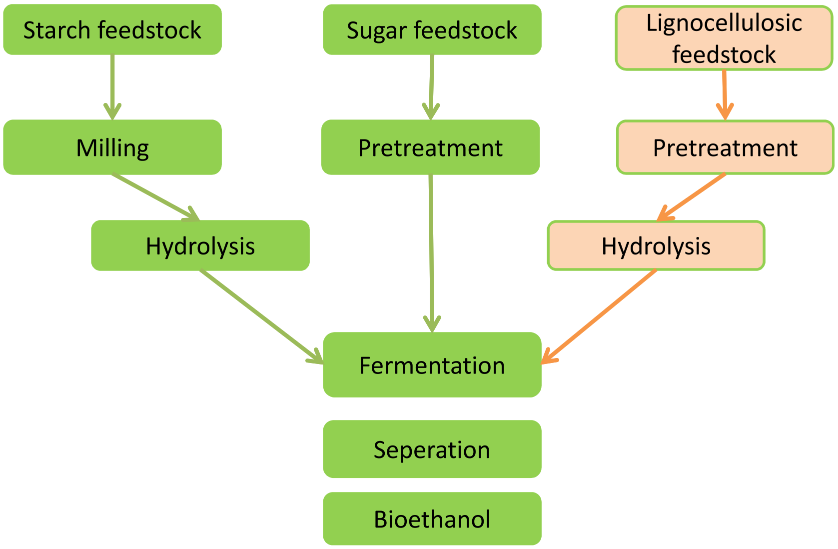
The two tower dehydrating system has been operated in two super-anhydrous plants in Canada.



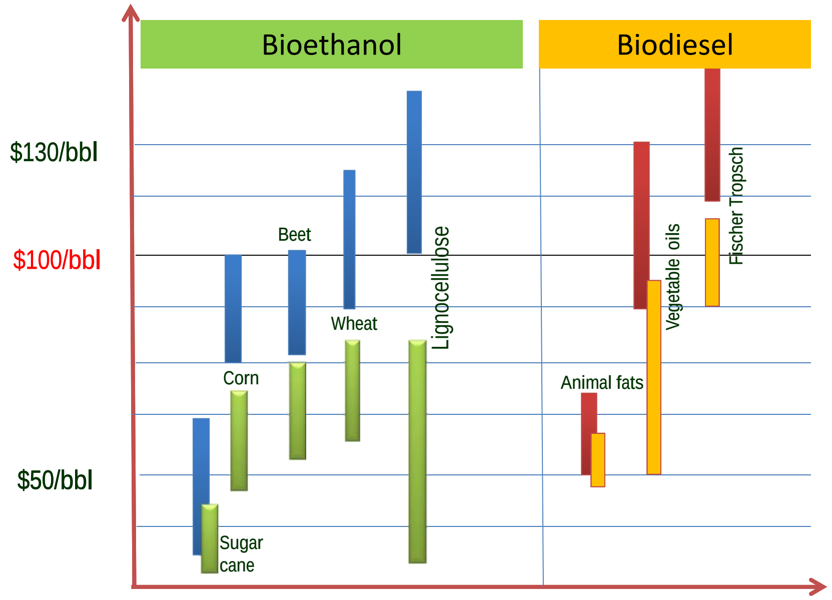
Comments

- 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



Liquid Biofuel Costs (2005~2030)



Alternative Energy Resources

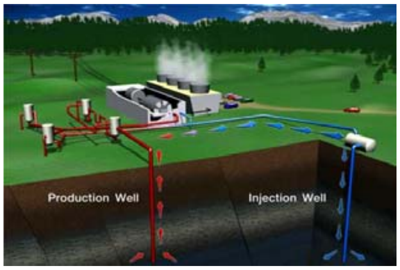

Wind


Solar


Biomass


Fuel Cell

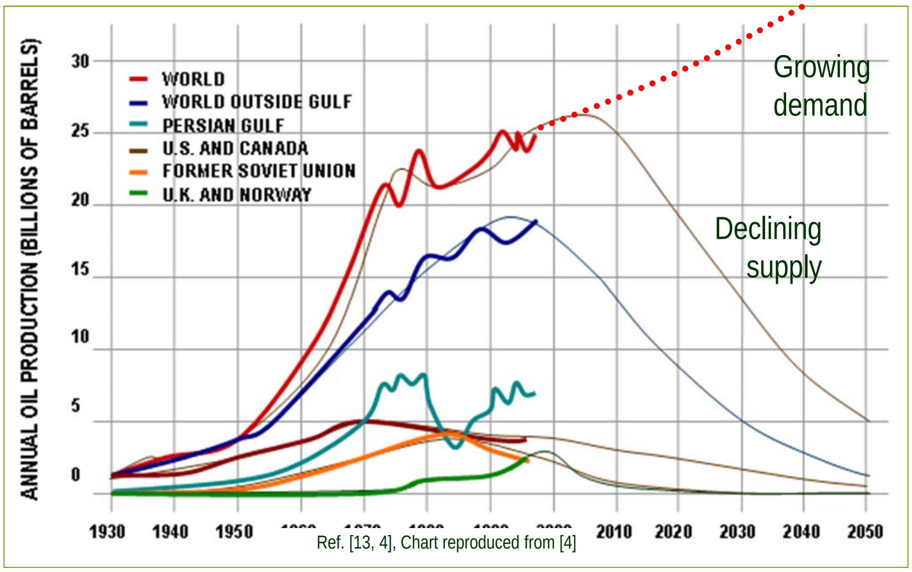

Hydroelectric power



Geothermal


Nuclear energy

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

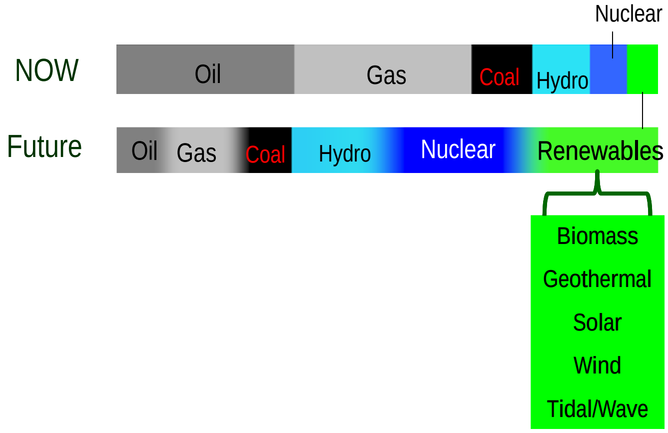


Ref. [13, 4], Chart reproduced from [4]

Table 1 U.S. Energy Consumption by Energy Source, 2005 - 2009 (EIA)

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

In-combustion Approach

- **Oxyfuel combustion**
- **Chemical looping combustion**

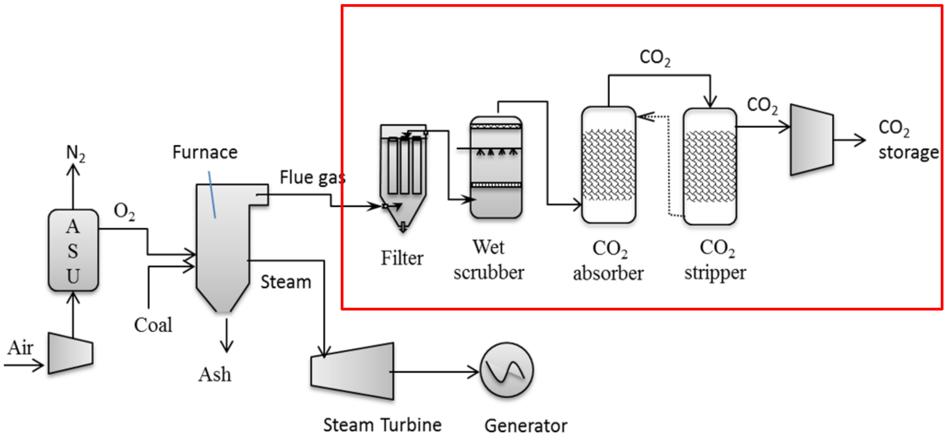
Oxyfuel Combustion

$$C_\alpha H_\beta + \left(\alpha + \frac{\beta}{4}\right) O_2 \rightarrow \alpha CO_2 + \frac{\beta}{2} H_2O$$

- The benefit is a simple process for carbon capture after combustion.
- Without nitrogen and NOx in the flue gas, it contains mainly H_2O and CO_2.
- After removal of soot, and SO_2, if any, CO_2 can be readily separated from water vapor by condensation in the cooler. This highly concentrated CO_2 is ready for transportation and storage.

- Ready for capture

Schematic diagram of the oxyfuel combustion process for CO_2 capture



Technical challenge:
Too High combustion (flame) temperature

$$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O$$

$$\sum_R n_i \left[\left(a_i (T_R - 298K) + \frac{b_i}{2} ({T_R}^2 - (298K)^2 \right) + h^o_{f,i} \right]$$

$$= \sum_P n_i \left[\left(a_i (T_a - 298K) + \frac{b_i}{2} ({T_a}^2 - (298K)^2 \right) + h^o_{f,i} \right]$$

$$h^o_{f,CH_4} + 2h^o_{f,O_2} = \overset{h^o_{f,i}}{\Bigg[} \left(a_{CO_2} (T_a - 298K) + \frac{b_{CO_2}}{2} ({T_a}^2 - (298K)^2 \right) + h^o_{f,CO_2} \Bigg]$$

$$+ 2 \left[\left(a_{H_2O} (T_a - 298K) + \frac{b_{H_2O}}{2} ({T_a}^2 - (298K)^2 \right) + h^o_{f,H_2O} \right]$$

Species	[J/mol]	$C_p(T)$ [J/mol K]	
		a_i	b_i
CO_2	-394,088	44.3191	0.0073
H_2O	-242,174	32.4766	0.00862
O_2	0	30.5041	0.00349
CH_4	-74,980	44.2539	0.02273

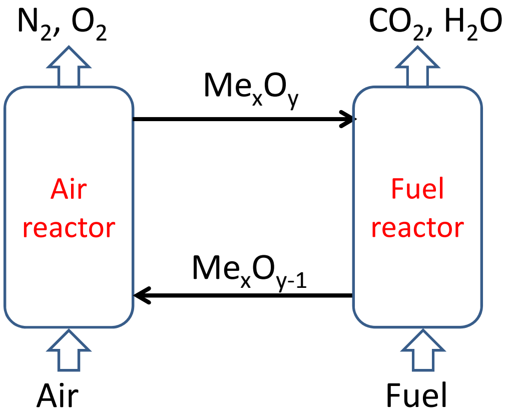
$$0.01227\,T_a^2 + 109.2723\,T_a - 837109 = 0$$

Solving this equation we can get,
$T_a = 4930.8$ K (the value with nitrogen is $T_a = 2341$ K).

Challenges to Oxyfuel Combustion

- As a result, the boiler of the oxyfuel combustion process requires special materials that can survive high temperatures.
- Flue gas circulation can be recirculated to control the combustion temperature.
- Another concern of the oxyfuel combustion process with sulfur containing fuels is the high SOx concentration without the dilution of nitrogen, resulting high corrosion on the ducts.
- Extra costs are associated with concentrated oxygen production by costly air separation.

Chemical looping combustion


N_2, O_2

CO_2, H_2O

Me_xO_y

Air reactor

Fuel reactor

Me_xO_{y-1}

Air

Fuel

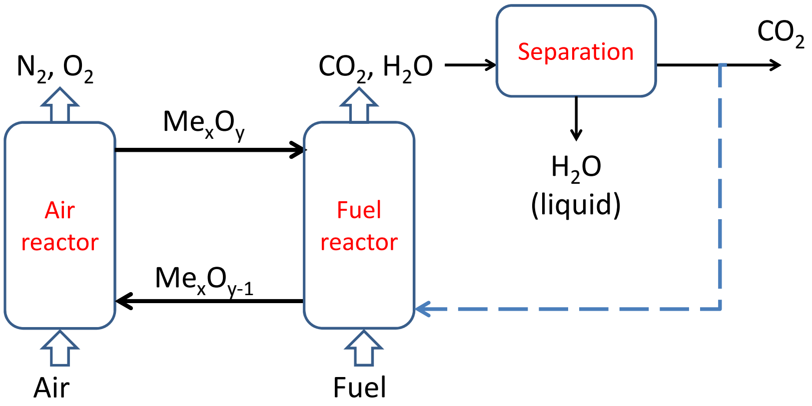
Oxygen carrier materials

$$2Me_xO_y \leftrightarrow 2Me_xO_{y-1} + O_2$$

$$4CuO \leftrightarrow 2Cu_2O + O_2$$

$$6Mn_2O_3 \leftrightarrow 4Mn_3O_4 + O_2$$

$$2Co_3O_4 \leftrightarrow 6CoO + O_2$$


N_2, O_2

CO_2, H_2O

Separation

CO_2

Me_xO_y

H_2O (liquid)

Air reactor

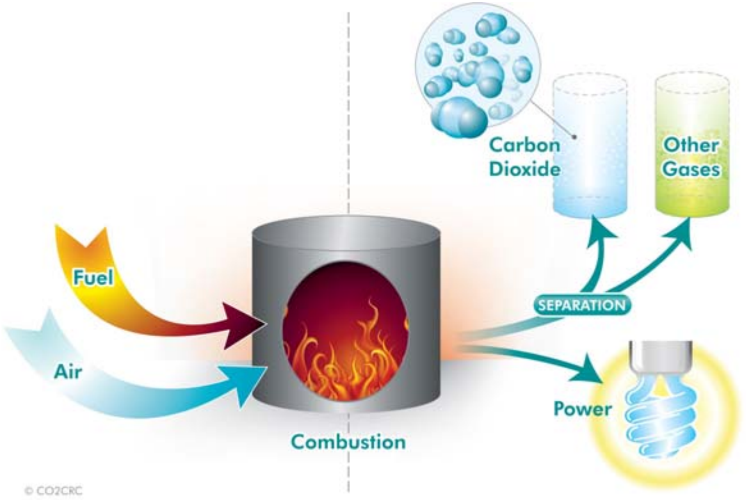
Fuel reactor

Me_xO_{y-1}

Air

Fuel

Post-Combustion
Carbon Capture Options



Source: http://www.co2crc.com.au/

Carbon Separation

- Adsorption – Lime, zeolite, activated carbon
- Absorption– aqueous amines and salts
- See Chapter 5 for Basics of Gas Separation by Ad-/Ab-sorption

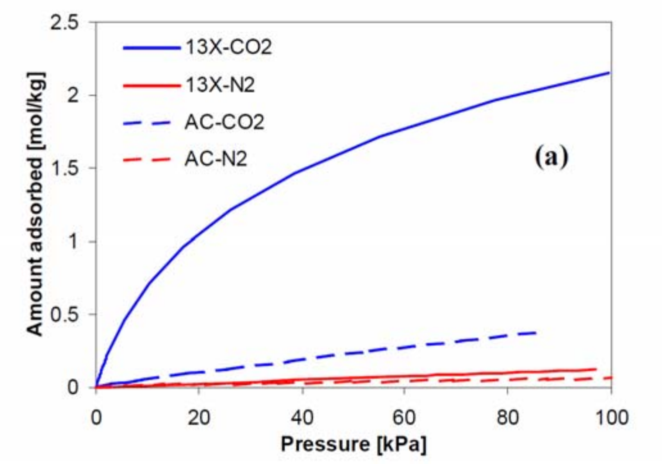
CO_2 Adsorption

- Physical adsorption operates at temperatures that are lower than 100 oC
- Chemical adsorption operates at much high range of 400-600 oC.
- The best adsorbent is expected to be characterized with
  - high CO_2 capacity at low pressure
  - high selectivity for CO_2
  - fast adsorption/desorption kinetics
  - good mechanical properties
  - high hydrothermal and chemical stability
  - low costs of synthesis
- Unfortunately, these criteria are too ideal for any single adsorbent.

Low Temperature Physical Adsorption

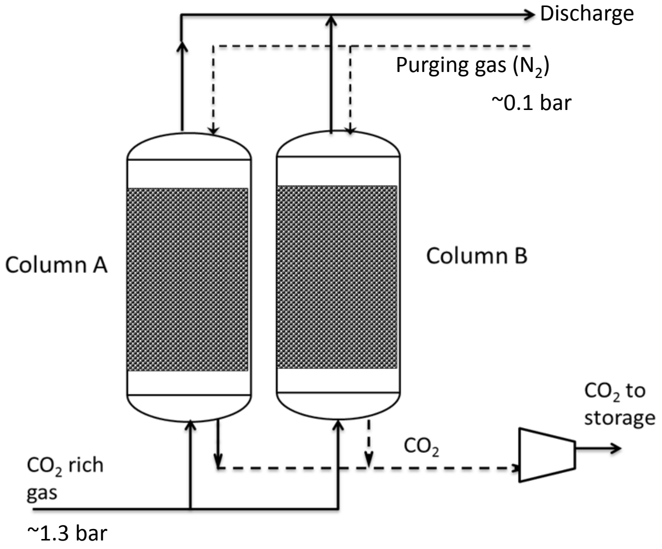
- Zeolites (e.g Zeolite 13 X)
- Activated carbons
- Metal–organic frameworks (MOFs) have recently attracted intense research interest in CO_2 adsorption due to their large porous volume and surface areas

Adsorption equilibrium of carbon dioxide and nitrogen on zeolite 13X (CECA) and Maxorb activated carbon at 373 K.

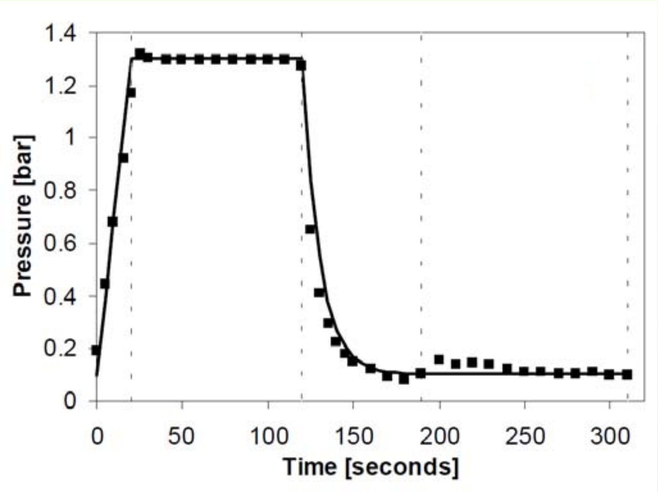


- Carlos A. Grande *, Simone Cavenati, Alírio E. Rodrigues, PRESSURE SWING ADSORPTION FOR CARBON DIOXIDE SEQUESTRATION, **2nd Mercosur Congress on Chemical Engineering**

Schematic Diagram of Pressure Swing Physical Adsorption Process



Pressure vs Time at the Exit of a Column



- Carlos A. Grande *, Simone Cavenati, Alírio E. Rodrigues, PRESSURE SWING ADSORPTION FOR CARBON DIOXIDE SEQUESTRATION, **2nd Mercosur Congress on Chemical Engineering**

Chemical Adsorption

- CaO is one of the oldest sorbent for CO_2 capture by chemical adsorption.
- Calcium oxide reacts with CO_2 at high temperatures to produce carbonates
- A reversible reaction

$$\mathrm{CaCO_{3(s)}} \leftrightarrow \mathrm{CaO_{(s)}} + \mathrm{CO_2}$$

- For this equilibrium reaction at a given temperature, the partial pressure of CO_2 is also the equilibrium constant of CO_2

$$K_P = P_{CO2}$$

$$CaCO_{3(s)} \leftrightarrow CaO_{(s)} + CO_2$$

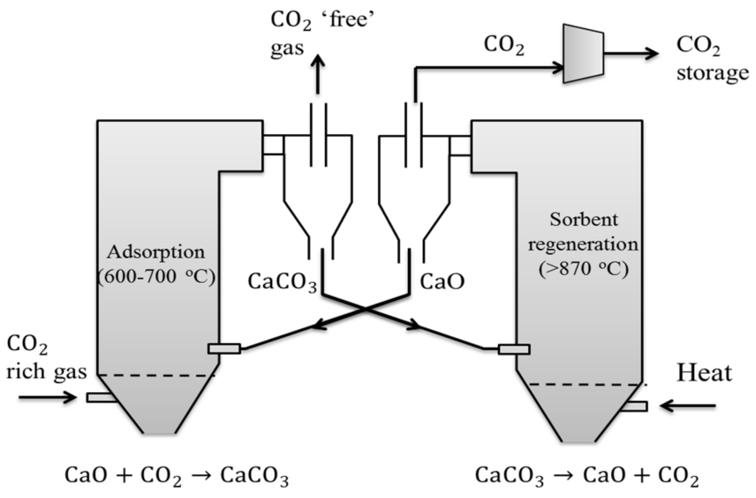
Equilibrium pressure of CO_2 over $CaCO_3$ (P) vs. temperature (T)

P_{CO2} (kPa)	0.055	0.13	0.31	1.80	5.9	9.3	14	24	34	51	72	80	91	101	179
T (°C)	550	587	605	680	727	748	777	800	830	852	871	881	891	898	937

- The reverse reaction is also called thermal decomposition reaction, or calcination
- The reverse reaction is obvious when T> 840 °C
- For the outgassing of CO_2 from calcium carbonate to happen at an economically useful rate, the equilibrium pressure must significantly exceed the ambient pressure of CO_2.
- And for it to happen rapidly, the equilibrium pressure must exceed total atmospheric pressure of 101 kPa, which happens at 898 °C.

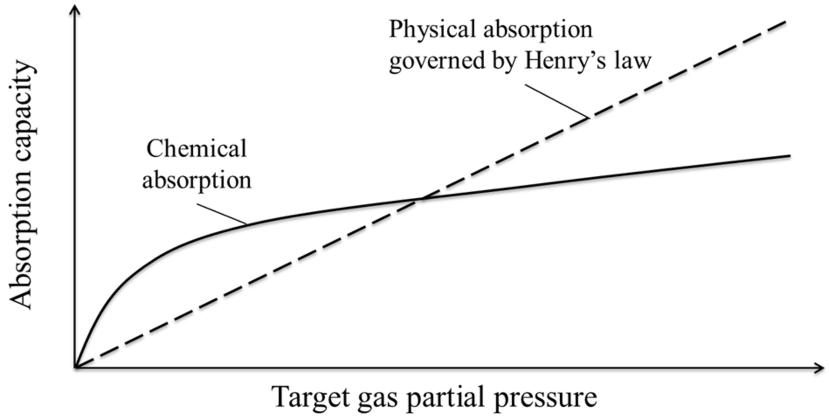
http://www.hbcpnetbase.com/

Temperature Swing Chemical Adsorption Process



Absorption

$$c_{CO_2} = \frac{P_{CO_2}}{H}$$



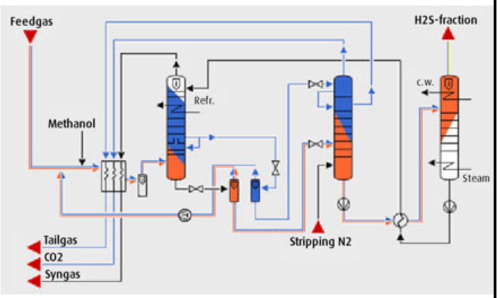
Physical Absorption

$$c_{CO_2} = \frac{P_{CO_2}}{H}$$

- Physical absorption is primarily used for high pressure CO_2 separation to increase the solubility in the solvent.
- Refrigerated methanol (CH_3OH) was considered an effective CO_2 solvent for CO_2 sequestration at low temperature.
- The solubility of CO_2 in methanol at -10 ^oC and P_{CO_2} =1 atm is 10 liters of CO_2 per liter of methanol, which is four times that of water.

RECTISOL®

- Refrigerated methanol has been widely used as a physical solvent for absorption of CO_2 from coal gasification syngas for ammonia and liquid fuel production in Fisher-Tropsch processes.



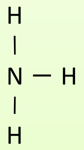
- It is referred to as Rectisol process, which was initially developed in the 1950s by Lurig GmbH and now purifies ¾ of the syngases globally for precombustion carbon capture.
- After the water-gas shift (WGS) reaction, $CO + H_2O \leftrightarrow CO_2 + H_2$, the mixture of H_2 and CO_2 is then delivered to a syngas purification plant.
- The CO_2 is at a partial pressure of 1 MPa and it is removed by contact with refrigerated methanol at -70 to -10 °C. Usually two stages are required to reduce CO_2 from about 33% to a level of 3% or so.

Chemical Absorption

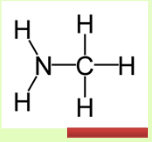
- The sorbents used for chemical absorption include carbonate-based, sodium hydroxide-based, aqueous ammonia-based and amine-based sorbents.
- Amine-based CO_2 absorption is a relatively mature technology used in the ammonia process, steam reforming process, and the natural gas sweetening process.
- Amines are ammonia-derived organic compounds when one or more hydrogen atom(s) of ammonia (NH_3) are replaced with organic substituents.

Amines

- **Amines** are derivatives of ammonia, wherein one or more hydrogen atoms have been replaced by a substituent such as an alkyl or aryl group.
- Amines are organized into four subcategories:
- **Primary amines** - one H atom is replaced by an alkyl or aromatic.
- **Secondary amines** - two H atoms replaced by organic substituents (alkyl, aryl or both).
- **Tertiary amines** - all 3 H atoms are replaced by organic substituents.



Ammonia



Methylamine

Aqueous Amine Solutions are Bases

- The pKa values of typical alkanolamines (Table 12.4)

Amine		pKa
MEA	Monoethanolamine	9.50
DEA	Diethanolamine	8.88
DIPA	Diisopropanolamine	8.80
TEA	Triethanolamine	7.76
MDEA	Methyldiethanolamine	8.57
AMP	2-Amino-2-methyl propanol	9.70
DEMEA	Diethylmonoethanolamine	9.82

Amine Based CO_2 Absorption

- The choice of amine for CO_2 absorption depends on three key factors,
  - Rate of reaction
  - Regeneration energy, and
  - Loading capacity
- The ideal solvent is characterized with
  - a great rate of reaction,
  - low regeneration energy and
  - great loading capacity.
- However, none of them meets all these three requirements.
- Monoethanolamine (MEA) is the most commonly used amine for CO_2 absorption.
  - MEA is a primary amine, and an alcohol too.

MEA

- Among all the amines tested, MEA showed its high reactivity with CO_2, and is predominantly used for CO_2 capture in existing industry.
- Thereby, amines can react with not only CO_2 but also other acidic gases like SO_2, and NO_2 at great rates of reactions.
- Therefore, SO_2 and NO_2 have to be effectively removed first before CO_2 absorption if it is to be used for post-combustion carbon capture.
- It also reduces the contamination to the regenerated solvent and recovered CO_2.

Kinetics of Amine-CO$_2$ Reactions (zwitterion mechanism)

$$CO_2 + AmH \overset{k_{f1}}{\underset{k_{b1}}{\leftrightarrow}} AmH^+COO^- \qquad (R1)$$

zwitterion

$$AmH^+COO^- + Bs \xrightarrow{k_B} AmCOO^- + BsH^+ \qquad (R2)$$

base

carbamate

$H_2O \leftrightarrow H^+ + OH^-$	(12-19)
$CO_2 + OH^- \overset{k_{OH}}{\longleftrightarrow} HCO_3^-$ (R3)	(12-20)
$CO_2 + H_2O \overset{k_{H_2O}}{\longleftrightarrow} HCO_3^- + H^+$ (R4)	(12-21)

Overall Reaction Rate of R1 and R2

$$r_{1,2} = k_{f1}[CO_2][AmH] - k_{b1}[AmH^+COO^-] = k_B[AmH^+COO^-][Bs]$$

$$\Rightarrow \frac{r_{1,2}}{[CO_2][AmH]} = \underbrace{k_{f1} - k_{b1}\frac{[AmH^+COO^-]}{[CO_2][AmH]} = k_B[Bs]\frac{[AmH^+COO^-]}{[CO_2][AmH]}}$$

$$\Longrightarrow k_{f1} = (k_{b1} + k_B[Bs])\frac{[AmH^+COO^-]}{[CO_2][AmH]}$$

$$\Longrightarrow \frac{k_{f1}}{k_{b1} + k_B[Bs]} = \frac{[AmH^+COO^-]}{[CO_2][AmH]}$$

Overall Reaction Rate of R1 and R2 (Cont…)

⇨ $$\frac{\mathrm{r}_{1,2}}{[\mathrm{CO_2}][\mathrm{AmH}]} = \mathrm{k}_{f1} - \mathrm{k}_{b1}\frac{[\mathrm{AmH^+COO^-}]}{[\mathrm{CO_2}][\mathrm{AmH}]} = \mathrm{k}_B[\mathrm{Bs}]\frac{[\mathrm{AmH^+COO^-}]}{[\mathrm{CO_2}][\mathrm{AmH}]}$$

$$\frac{\mathrm{k}_{f1}}{\mathrm{k}_{b1} + \mathrm{k}_B[\mathrm{Bs}]} = \frac{[\mathrm{AmH^+COO^-}]}{[\mathrm{CO_2}][\mathrm{AmH}]}$$

$$\frac{\mathrm{r}_{1,2}}{[\mathrm{CO_2}][\mathrm{AmH}]} = \mathrm{k}_{f1} - \mathrm{k}_{b1}\left(\frac{\mathrm{k}_{f1}}{\mathrm{k}_{b1} + \mathrm{k}_B[\mathrm{Bs}]}\right) = \mathrm{k}_{f1} - \mathrm{k}_{f1}\left(\frac{\mathrm{k}_{b1}}{\mathrm{k}_{b1}+\mathrm{k}_B[\mathrm{Bs}]}\right)$$

$$= \mathrm{k}_{f1}\left(1 - \frac{\mathrm{k}_{b1}}{\mathrm{k}_{b1}+\mathrm{k}_B[\mathrm{Bs}]}\right) = \mathrm{k}_{f1}\left(\frac{\mathrm{k}_B[\mathrm{Bs}]}{\mathrm{k}_{b1}+\mathrm{k}_B[\mathrm{Bs}]}\right) = \left(\frac{\mathrm{k}_{f1}}{\frac{\mathrm{k}_{b1}}{\mathrm{k}_B[\mathrm{Bs}]}+1}\right)$$

$$\frac{r_{1,2}}{[CO_2][AmH]} = \frac{k_{f1}}{1 + k_{b1}/(k_B[Bs])}$$

$$r_{1,2} = \frac{k_{f1}[AmH]}{1 + k_{b1}/(k_B[Bs])}[CO_2]$$

Overall Reaction Rate of R1-4

- Overall reaction rate by considering R1-R4

$$r_{CO_2} = \left\{\frac{k_{f1}[AmH]}{1 + k_{b1}/(k_B[Bs])} + k_{OH}[OH^-] + k_{H_2O}[H_2O]\right\}[CO_2]$$

- A special case

When R_2 is instantaneous

$$\mathrm{k}_{b1} \ll \mathrm{k}_B \xrightarrow{\qquad\qquad} \mathrm{k}_{b1}/(\mathrm{k}_B[\mathrm{Bs}]) \to 0$$

$$\mathrm{r}_{1,2} = \mathrm{k}_{f1}[\mathrm{CO_2}][\mathrm{AmH}]$$

$$r_{CO_2} = \left\{\frac{k_{f1}[AmH]}{1+k_{b1}/(k_B[Bs])} + k_{OH}[OH^-] + k_{H_2O}[H_2O]\right\}[CO_2]$$

$$k_{CO_2} = \frac{k_{f1}[AmH]}{1+k_{b1}/(k_B[Bs])} + k_{OH}[OH^-] + k_{H_2O}[H_2O]$$

↓

Apparent reaction rate constant

$$k_{app} = \frac{k_{f1}[AmH]}{1+k_{b1}/(k_B[Bs])}$$

$$k_{AmH} = \frac{k_{f1}}{1+k_{b1}/(k_B[Bs])}$$

$$\mathrm{k_{CO_2}} = \boldsymbol{k_{AmH}}\mathrm{[AmH] + k_{OH}[OH^-] + k_{H_2O}[H_2O]}$$

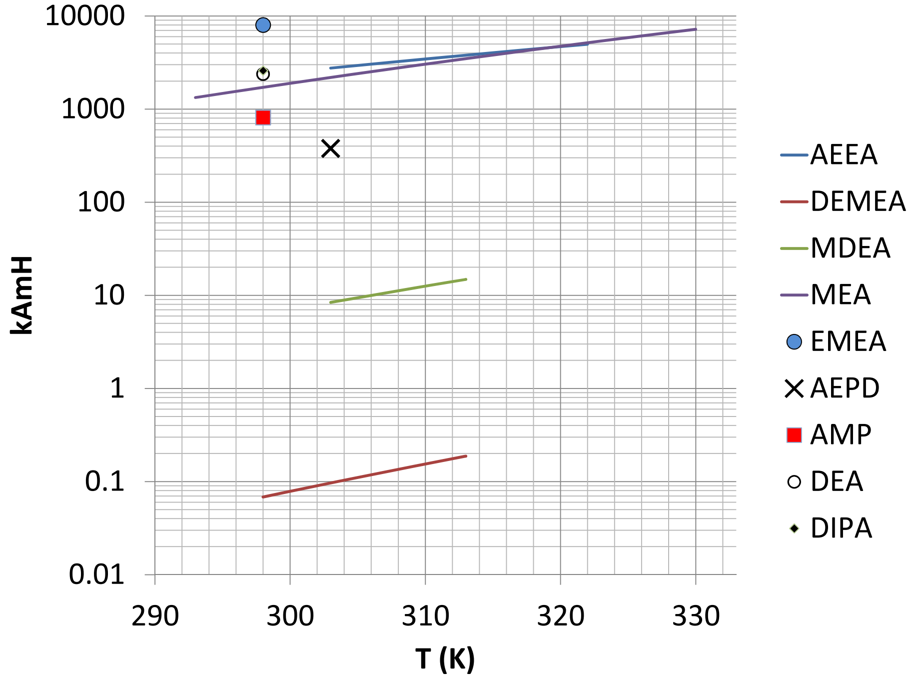
↑

Experimentally determined

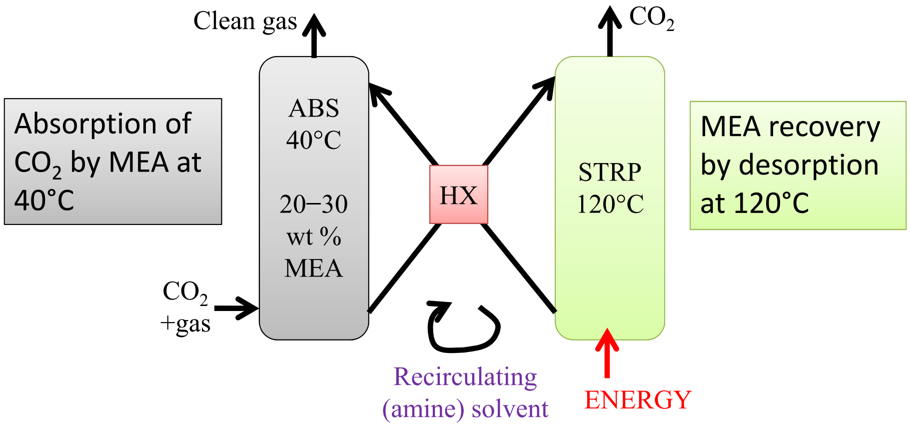
$$\mathrm{r_{CO_2}} = \mathrm{k_{CO_2}[CO_2]}$$

Table 12-5. k_{AmH} for Different Amines

Amine	Reaction rate constant (m³/kmol.s)	T (K)	Conc. (kmole/m³)
AEEA	$k_{AEEA} = 6.07 \times 10^7 exp\left(-\frac{3030}{T}\right)$	305-322	1.19-3.46
DEMEA	$k_{DEMEA} = 9.95 \times 10^7 exp\left(-\frac{6238}{T}\right)$	298-313	
MDEA	$k_{MDEA} = 4.61 \times 10^8 exp\left(-\frac{5400}{T}\right)$	303-313	
MEA	$k_{MEA} = 4.61 \times 10^9 exp\left(-\frac{4412}{T}\right)$	293-333	3–9
EMEA	8000	298	0.028-0.082
AEPD	378	303	5-25 wt %
AMP	810.4	298	0.25-3.5
DEA	2375	298	0.25-3.5
DIPA	2585	298	0.25-3.5



Amine-based Absorption/Stripping Process


Clean gas

CO_2

Absorption of CO_2 by MEA at 40°C

ABS 40°C

20–30 wt % MEA

HX

STRP 120°C

MEA recovery by desorption at 120°C

CO_2 +gas

Recirculating (amine) solvent

ENERGY

- Reboiler provides heat to desorber in the form of steam from the boiler, reducing plant output and efficiency
- Optimize loading, operating temperature, minimize solvent losses

Non-amine-based chemical absorption

- **Sodium hydroxide based chemical absorption**

$CO_2 + H_2O \rightarrow H_2CO_3$	(12-39)
$H_2CO_3 + NaOH \rightarrow NaHCO_3 + H_2O$	(12-40)
$NaHCO_3 + NaOH \rightarrow Na_2CO_3 + H_2O$	(12-41)

- Regeneration of NaOH is usually achieved by adding lime (CaO) into the final product converting Na2CO3 to CaCO3, followed by calcination at 870 ^{o}C or higher to release the pure CO_2 for storage of other applications.
- The corresponding chemical reactions are

$CaO + H_2O \rightarrow Ca(OH)_2$	(12-42)
$Ca(OH)_2 + Na_2CO_3 \rightarrow 2NaOH + CaCO_3$	(12-43)
$CaCO_3 \rightarrow CaO + CO_2$	(12-44)

2. Carbonate-based chemical absorption

Limestone reacts with CO_2 and water as follows.

$CO_2 + H_2O \rightarrow H_2CO_3$	(12-45)
$CaCO_3 + H_2CO_3 \rightarrow Ca(HCO_3)_2$	(12-46)

Potassium carbonate (K_2CO_3) can be used as a regenerable chemical absorbent.

- The corresponding CO_2 absorption reactions are

$K_2CO_3 + H_2O \rightarrow KOH + KHCO_3$	(12-47)
$KOH + CO_2 \rightarrow KHCO_3$	(12-48)

- Since CaO degrades quickly after a few cycles of regeneration, more reliable sorbents have been developed and tested at high temperatures;
- They include
  - Calcium aluminate ($CaAl_2O_4$),
  - Sodium Zirconate (Na_2ZrO_3),
  - Lithium zircanate (Li_2ZrO_3), and
  - Lithium orthosilicate (Li_4SiO_4).

Example

- How much water and $CaCO_3$ is needed to capture 1000 kg of CO_2 from the flue gas? How much calcium biocarbonate ($Ca(HCO_3)_2$) is produced?

Solution

The overall reaction formula is

$$CO_2 + H_2O + CaCO_3 \rightarrow Ca(HCO_3)_2$$

- *It indicates that the mole ratio of the compound in this reaction is 1:1:1:1.*
- *Therefore, in order to capture 1000 kg of CO_2, which is 1000/44 kmole, the same mole amounts of $CaCO_3$ and water are consumed to produced the same mole amount of $Ca(HCO_3)_2$. By considering their molar weight, the corresponding mass can be determined as:*
- *2,300 kg of $CaCO_3$, 400 kg of water and 3,700 kg of $Ca(HCO_3)_2$*

3. Aqueous ammonia-based chemical absorption

- An aqueous ammonia solution reacts with water and CO_2 to form ammonium carbonate and ammonium bicarbonate. The overall reaction can be described as follows.

$$NH_3 + CO_2 + H_2O \rightarrow 2NH_4HCO_3$$

- Ammonia based chemical absorption / scrubbing also can capture SO_2 and NO_2 from a flue gas.
- While it allows multiple air emission control, it is challenging to produce pure acidic gases. The best option is to use the ammonium salts as fertilizer feedstock

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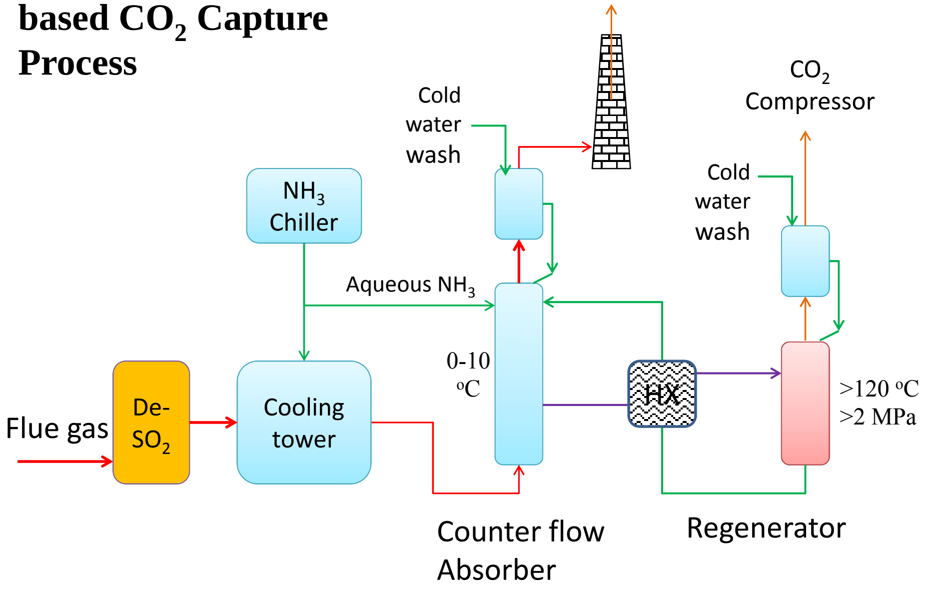
A simplified Ammonia-based CO_2 Capture Process



A Typical Ammonia-based CO_2 Capture Process

- In a counter flow absorption tower flue gas flows upward with aqueous ammonia downward.
- The absorption process operates at near-freezing conditions (0-10 ^oC) with the flue gas cooled by the upstream de-SO_2 process.
- The low temperature allows high absorption capacity and reduces ammonia evaporation, which is also called "*ammonia slip*".
- Downstream the absorption tower, ammonia slip is further reduced by cold-water washing.
- The effluent gas contains mainly nitrogen, oxygen and low-concentration penetrated CO_2.
- The solvent is regenerated at a temperatures of >120 ^oC pressures of >2 MPa.
- Cold-water washing is also employed to reduce ammonia slip in the generation process.

Ionic Liquids as CO_2 Solvents

- Ionic liquids are melting organic slats with unique properties.
- They comprise a large organic cation and a small inorganic anion.
- Ionic liquids have been developed for the physical and chemical absorption of acidic gases including SO_2, NOx, and CO_2.
- The use of ionic liquids (ILs) as CO_2 solvents is believed to have many advantages over conventional amine-based CO_2 separation, such as
  - potentially lower energy consumption for solvent regeneration
  - lower volatility,
  - lower vapor pressure,
  - non-flammability,
  - more thermally stable, and
  - easier recycling.
- All these come with an unusually high cost

- Earlier research on CO_2 capture with ILs focused primarily on physical absorption without chemical reactions.
- In this chapter we concentrate on properties that affect the CO_2 physical absorption including CO_2 solubility and selectivity.
- CO_2 solubility in ionic liquids increases with increasing the increase of the molecular weight, the molar volume, and the free volume of ionic liquids.
- CO_2 solubility in ionic liquids cannot be calculated based on mole fraction (like in Henry's law)
    - Some researchers still use Henry's law though
- It should be determined as a function of molarity

Molarity

- The mole amount of solubility per amount of solvent
    - moles of solute /kg of solvent
    - mole of solute /m^3 of solvent

- What is the molarity of a solution containing 0.30 moles of NaCl in 3 liters of water?

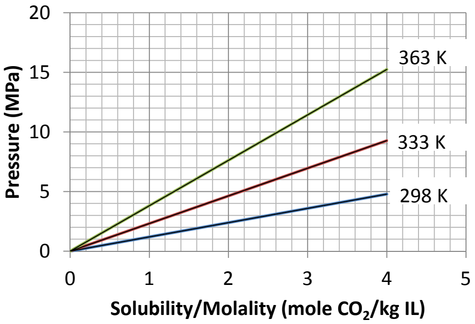
Solution

$$\text{Molarity} = \frac{0.3\ moles\ NaCl}{3\ L\ of\ water} = \frac{0.3\ moles\ NaCl}{3\ kg\ of\ water}$$

$$= 0.1\ (\text{moles NaCl/kg of water})$$

CO_2 Solubility in an IL

$$P = m_i^0 \times exp\left(6.8591 - \frac{2004.3}{T}\right)$$



- P is the pressure in MPa,
- T is temperature in K.
- m_i^0 is the molarity in (mole of CO_2/kg of ionic liquid)
- This equation was obtained using experimental data and it is deemed valid for pressures up to 5 MPa, molarities up to 3 mole/kg, and temperatures ranging from room temperature to 363 K.
- Figure 12.7 shows the calculated solubility *vs.* pressure at three different temperatures. For a fixed temperature, the solubility is in linear relationship with the pressure.

Example 12.4

- *Estimate the amount of CO_2 in kg that can be absorbed into 1000 kg of ionic liquid at 2 MPa and 300 K using the Carvalho and Coutinho (2010) model .*

Solution: *From Equation (12-50) we can get*

$$m_i^0 = \frac{P}{exp\left(6.8591 - \frac{2004.3}{T}\right)} = \frac{2}{exp\left(6.8591 - \frac{2004.3}{300}\right)}$$

$$= 1.6742\ (mole\ CO_2/kg\ IL)$$

The molar weight of CO_2 is 44 g/mole, and that gives the solubility as

$$c_{CO2} = 1.6742 \times 0.044\ (kg\ CO_2/kg\ IL)$$
$$= 0.07357\ (kg\ CO_2/kg\ IL)$$

Gas Selectivity of ILs

Table 12.7. Henry's Law Constants of Different Gases in [hmpy][Tf_2N] Ionic Liquid

Gas	**Temperature**	
	283 K	**298 K**
SO_2		1.54±0.01
CO_2	25.4±0.1	32.8±0.2
CH_4		300±30
O_2	422±220	463±104
N_2		3390±2310

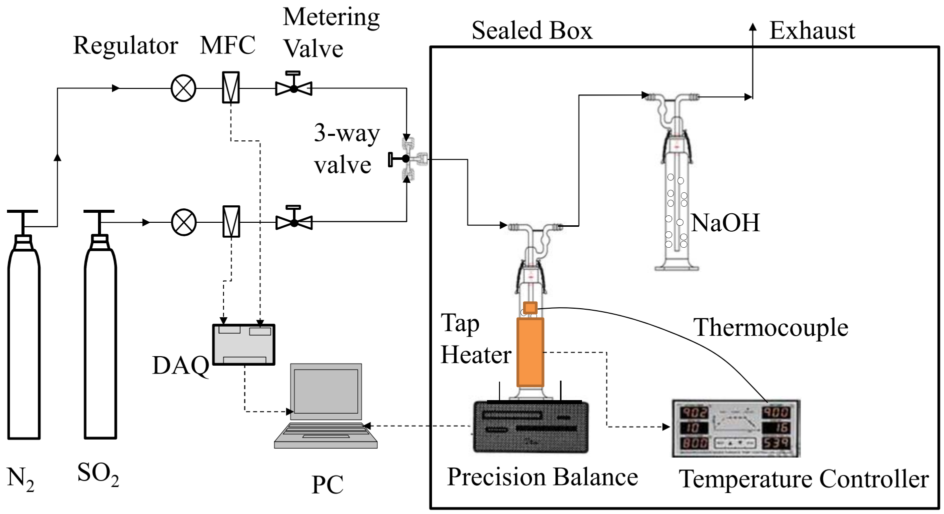
- In general, N_2 and O_2 solubility are much lower compared to CO_2 leading to a high CO_2/N_2 or CO_2/O_2 selectivity.
- On the other hand, SO_2 is very competitive to CO_2 absorption; SO_2 should be removes from stream first before carbon capture.

Our Experimental Test Using SO_2

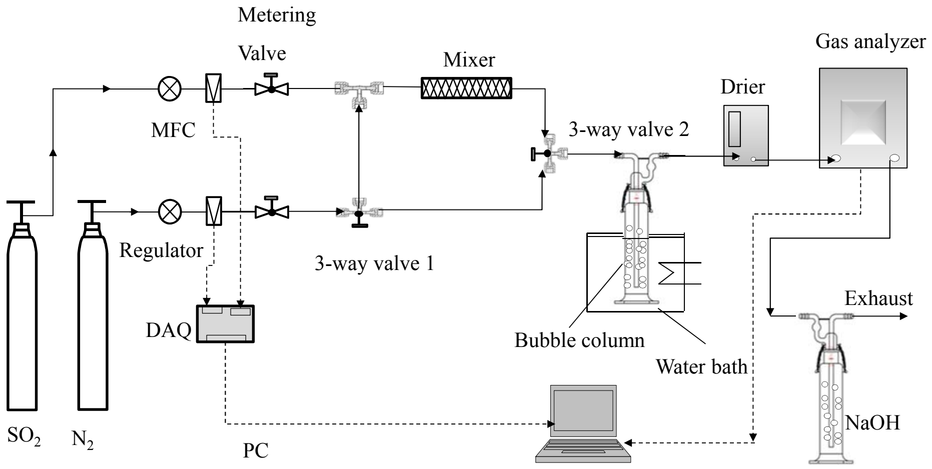
EMIm-MeSO$_4$ Cycling Conditions

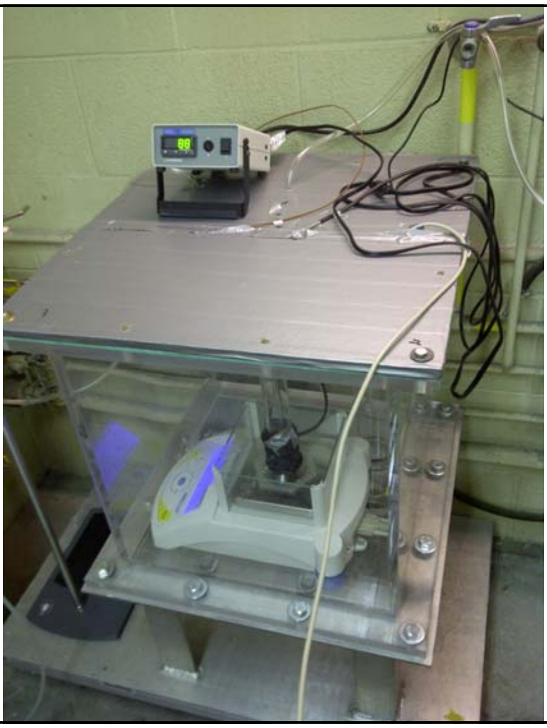
- SO_2 gas concentration: 1% SO_2, balance N_2
- SO_2 gas flow rate: 80 mL/min
- N_2 purge flow rate: 80 mL/min
- Operating temperature:
  Absorption: 23°C
  Desorption: 90°C
- Operating pressure: ambient
- Volume for ionic liquid : 32.81 ml
- Weight measure interval: 5 min

Experimental setup for room temperature tests

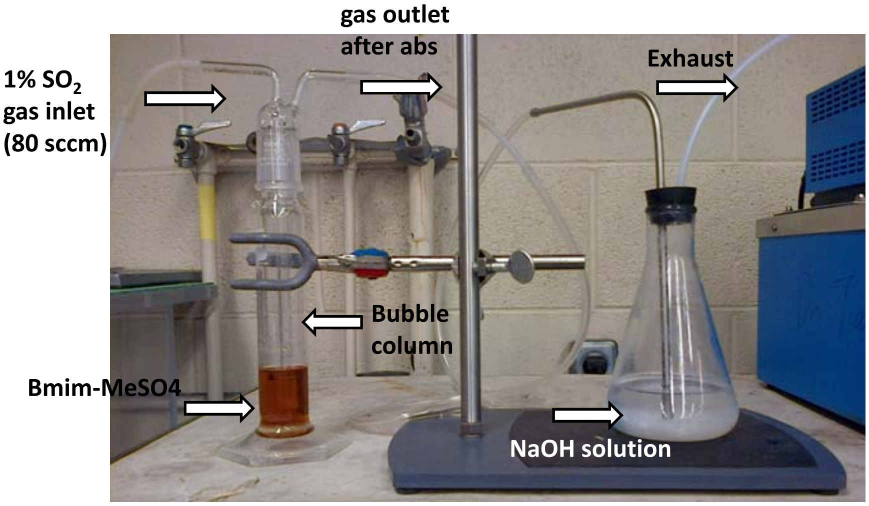


Experimental setup for high temperature test

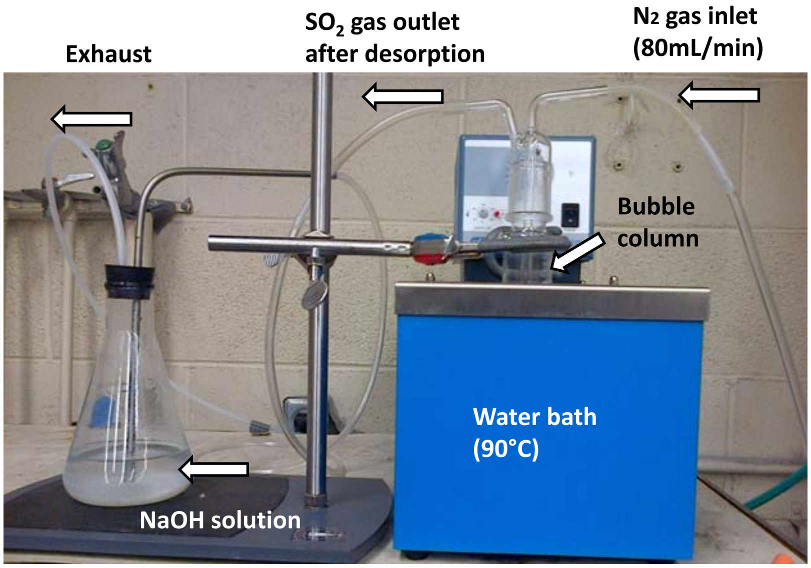




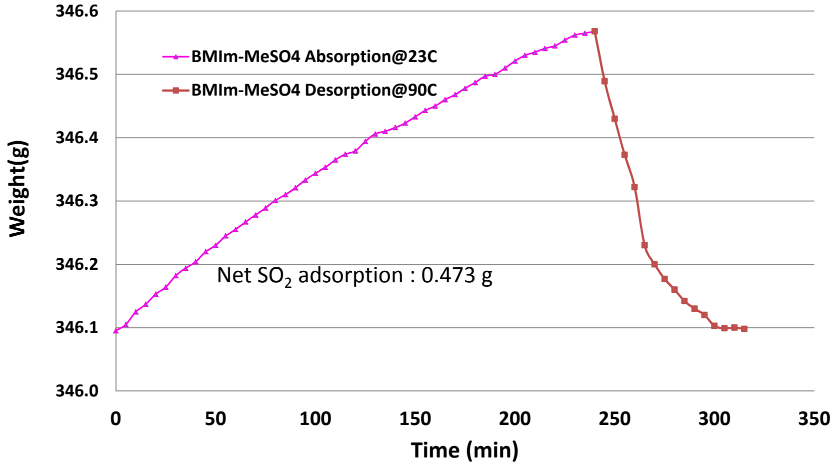
Experiment set-up for SO_2 capture using ionic liquid



Experiment set-up for desorption



Experiment Results for EMIM-MeSO4



Carbon Transport

- Pipeline transportation
- Ship transportation

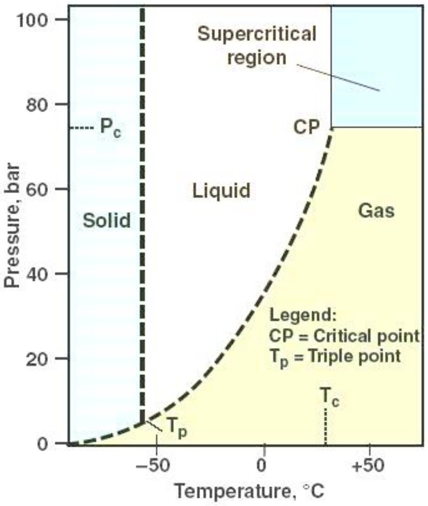
Pipeline Carbon Transport

- 2500 km of pipeline / 50Mtyr^{-1} in western US TODAY
- Use of existing infrastructure – require dry, sweet gas to prevent corrosion
- Challenges are manageable, similar to transport of hydrocarbons

Compressed CO_2

A supercritical fluid is any substance at a temperature and pressure above its critical point, where distinct liquid and gas phases do not exist.

- Prior to transportation via pipeline, CO_2 is compressed to a supercritical fluid or liquid state for efficient pipeline transportation.
- The critical point of CO_2 is 31.1 ^oC and 73 atm.
- However, temperature and pressure drops along the pipeline, therefore, prior to delivery CO_2 is compressed to a pressure that is much more than 73 atm.



The pressure drop per unit length of pipeline

$$\frac{\Delta P}{\Delta L} = f_D\left(\frac{\rho U^2}{2d}\right)$$

- $\frac{\Delta P}{\Delta L}$ is the pressure drop per unit length of pipeline (Pa/m),
- f_D is the dimensionless Darcy friction factor,
- d is the diameter of the pipeline,
- ρ is the density of the fluids, CO_2 in this case,
- U is the average speed of the fluid.

Darcy friction factor

$$f_D^{-1/2} = -2\log_{10}\left(\frac{\varepsilon}{3.7d} + \frac{2.51}{Ref_D^{\frac{1}{2}}}\right)$$

- ε is the pipeline inner surface roughness, which is about 46 μm for typical commercial steel pipes.
- Re is the Reynolds number in pipeline

$$Re = \frac{\rho U d}{\mu} = \frac{4\dot{m}}{\mu \pi d}$$

Example 12.5**:** Pressure drop in a pipeline

- *Consider a pipeline made of commercial steel with an inner diameter of 40 cm for transporting CO$_2$ at a flow rate of 3.5 Mega tons per year. Use CO$_2$ properties under 11 MPa and 25 ^{o}C as follows:* $\rho = 877\ kg/m^3\ and\ \mu = 7.73 \times 10^{-5}\ Pa.s.$ *Estimate the pressure drop over a distance of 100 km.*

Solution

- *Convert the unit of the CO_2 flow rate as*

$$\dot{m} = 3.5\frac{Mt}{yr} = \frac{3.5 \times 10^6 \times 1000\ kg}{365 \times 24 \times 3600\ s} = 111\ kg/s$$

- *The average speed in the pipe can be determined using*

$$U = \frac{4\dot{m}}{\rho \pi d^2} = \frac{4 \times 111}{877 \times \pi \times 0.4^2} = 1.007\quad m/s$$

- *The corresponding Reynolds number is determined using Equation (2-69) above.*

$$Re = \frac{4\dot{m}}{\mu \pi d} = \frac{4 \times 111}{7.73 \times 10^{-5} \times \pi \times 0.4} = 4.57 \times 10^6$$

- *With $\varepsilon = 4.6 \times 10^{-5}$ m, $d = 0.4$ m and $Re = 4.57 \times 10^6$, the Darcy friction factor can be determined using Equation(12-52) as follows.*

$$f_D^{-\frac{1}{2}} = -2\log_{10}\left(\frac{\varepsilon}{3.7d} + \frac{2.51}{Re f_D^{\frac{1}{2}}}\right) = -2\log_{10}\left(\frac{4.6 \times 10^{-5}}{3.7 \times 0.4} + \frac{2.51}{4.57 \times 10^6 f_D^{\frac{1}{2}}}\right)$$

- *By iteration, we can get $f_D = 0.0217$*
- *Then we can calculate the pressure drop over 100 km distance length using Equation (12-51).*

$$\Delta P = f_D\left(\frac{\rho U^2}{2d}\right)\Delta L = 0.0217\left(\frac{877 \times 1.007^2}{2 \times 0.4}\right) \times 100 \times 10^3 = 2.41 \times 10^6\ Pa$$

- *So the pressure drop is about 2.41 MPa over a distance of 100 km. Due to this kind of great resistance, intermediate pumping (or booster) stations are required at certain intervals along the pipeline.*

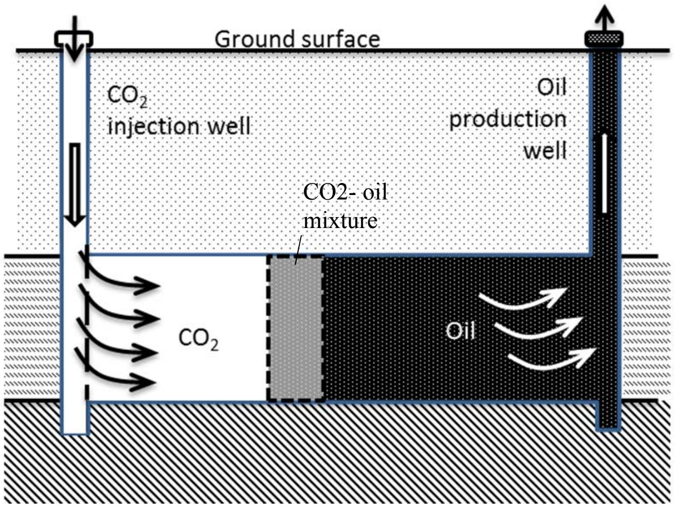
Ship Transportation

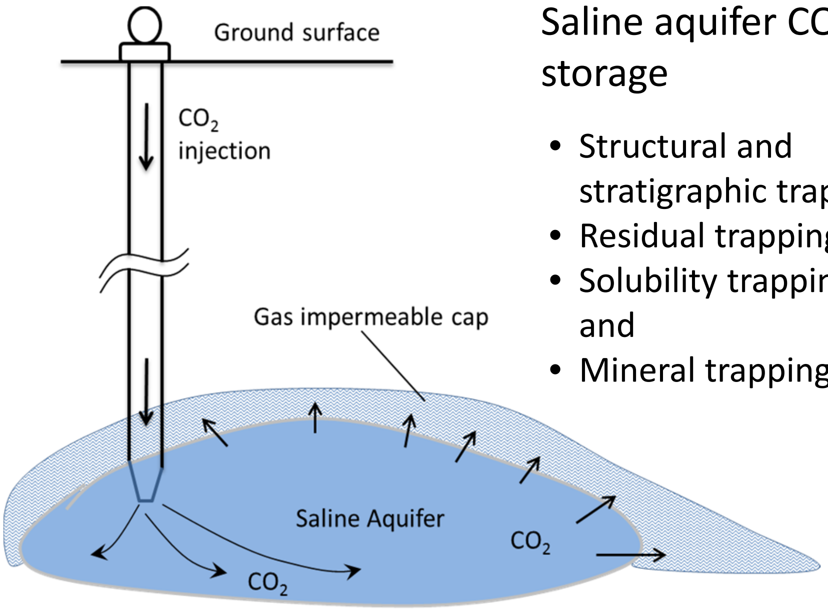
- For CO_2 transport by ship, it is most efficient to transport CO_2 as a cryogenic liquid.
- The best condition for CO2 transport by ship is about 6.4 atm and -51.2 ^oC.
- As it is stored in containers during transportation, there is no pressure drop concern.
- The optimal transport pressure depends on the state of the fluid.
- In short, large-scale transport of CO_2 by ship could be achieved by semi-pressurized vessels of around 20,000 m^3 at pressures of 6.415 atm and -52 ^oC in order to use existing ship and infrastructures.
- This condition also allows low unit cost in transport. The total costs of ship-based transport are estimated to be \$20–30 per ton CO_2.

Carbon Storage

- Geological storage
  1. Enhanced oil recovery (EOR),
  2. Deep saline reservoirs and aquifers.
  3. Unmineable coal beds
- Deep ocean storage
- Ecosystem storage

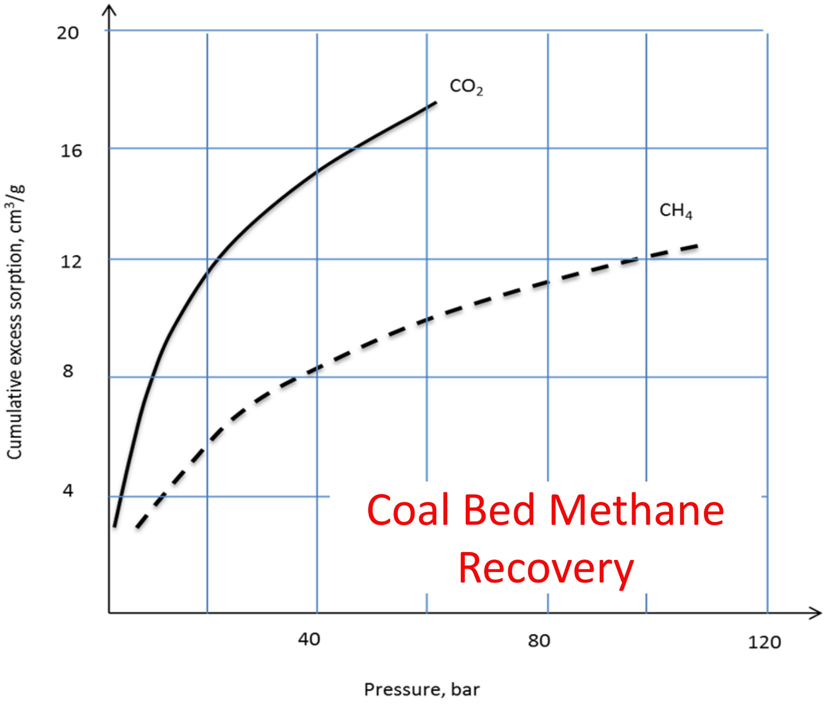
Enhanced Oil Recovery and Enhanced Gas Recovery





Saline aquifer CO_2 storage

- Structural and stratigraphic trapping
- Residual trapping
- Solubility trapping, and
- Mineral trapping



Coal Bed Methane Recovery

Deep Ocean Storage

- The ocean naturally traps over 143,000 Gt of CO_2, which is 50 times more than that in the atmosphere.
- The uptake of CO_2 in ocean has been increasing over the past centuries as a result of the increasing atmospheric CO_2 concentration.
- However, it still can hold much more!
- The solubility of CO_2 in sea water is not constant everywhere; it depends on the pressure, salinity, pH and temperature of the sea water.

Inorganic Carbon in Deep Ocean

- Deeper into the ocean, CO_2 goes through chemical reactions. Several simplified chemical equilibriums define the process as
$$\mathrm{CO_2 + H_2O \leftrightarrow H_2CO_3 \leftrightarrow HCO_3^- + H^+ \leftrightarrow CO_3^{2-} + 2H^+}$$
- All these species are grouped as dissolved inorganic carbon (DIC).
- $\mathrm{H_2CO_3}$ also reacts with dissolved limestone in the ocean, which is a result of weathering the earth surface, and the simplified chemical reaction is
$$\mathrm{CaCO_3 + H_2CO_3 \rightarrow Ca^{2+} + 2HCO_3^-}$$

Biological Conversion of Carbon in Deep Ocean

- Particulate organic carbon (POC)

1. Photosynthesis

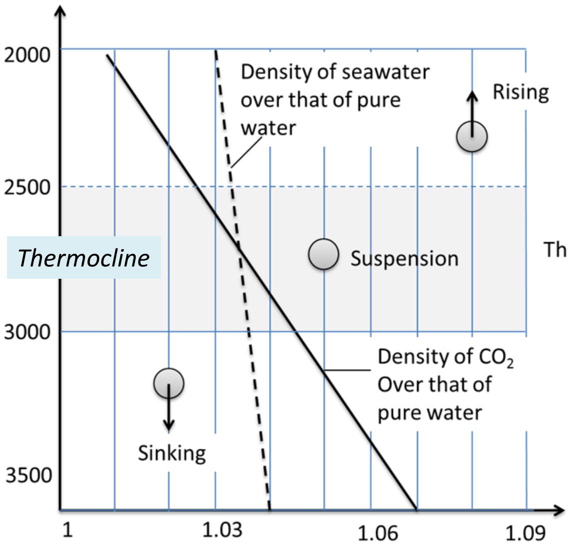
$$6CO_2 + 6H_2O + uv \rightarrow C_6H_{12}O_6 + 6O_2$$

2. Fertilizer

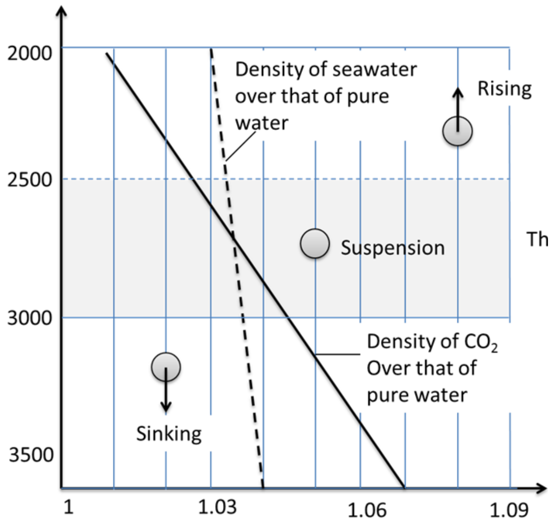
$$106CO_2 + 122H_2O + 16HCO_3^- + H_3PO_4 \\ \rightarrow C_{106}H_{263}O_{110}N_{16}P + 138O_2$$

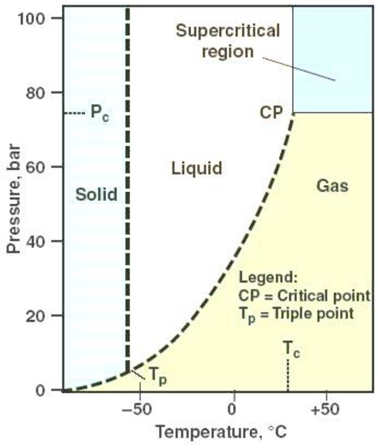
- This process can be expedited by injecting CO_2 into deep ocean. Based on the properties of liquid CO_2 in ocean, engineered deep ocean CO_2 storage can be achieved by
  - ❑direct CO_2 dissolution, and
  - ❑liquid CO_2 isolation

Deep Ocean Storage

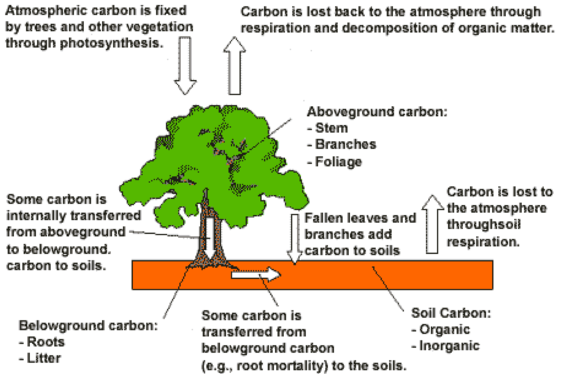


- At a depth of about 500 m CO_2 starts to liquefy and the liquid CO_2 has a density of 860 – 920 kg/m^3.
- liquid CO_2 density is close that of the seawater at the depths of about 2500 – 3000 m.
- Direct CO_2 dissolution below the *__thermocline__* is one option for long term CO_2 storage in the ocean.





Ecosystem Storage

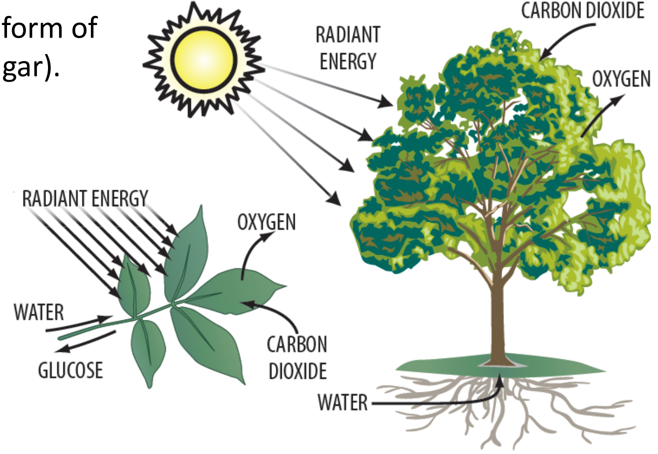


- Agricultural carbon storage
- Change in land use
- **Energy crops production**

Photosynthesis

In the process of photosynthesis, plants convert radiant energy from the sun into chemical energy in the form of glucose (or sugar).

$$6CO_2 + 6H_2O + uv \rightarrow C_6H_{12}O_6 + 6O_2$$



National Energy Education Development Project: http://www.need.org/

Dedicated Energy Crops

- Plants grown specifically for applications other than food or feed
- A dedicated energy crop is planted and harvested periodically
- Examples
  - o Sugar beets, annual
  - o Switch grass, annual
  - o Hybrid polar, 3-10 yrs
  - o Willow, 3-10 yrs

Miscanthus

1 years growth without replanting!

20 tons/acre? (www.bical.net)
10-30 tons/acre (www.aces.uiuc.edu/DSI/MASGC.pdf)

Classifications of Energy Crops

1. Herbaceous energy crops
2. Short-rotation woody crops

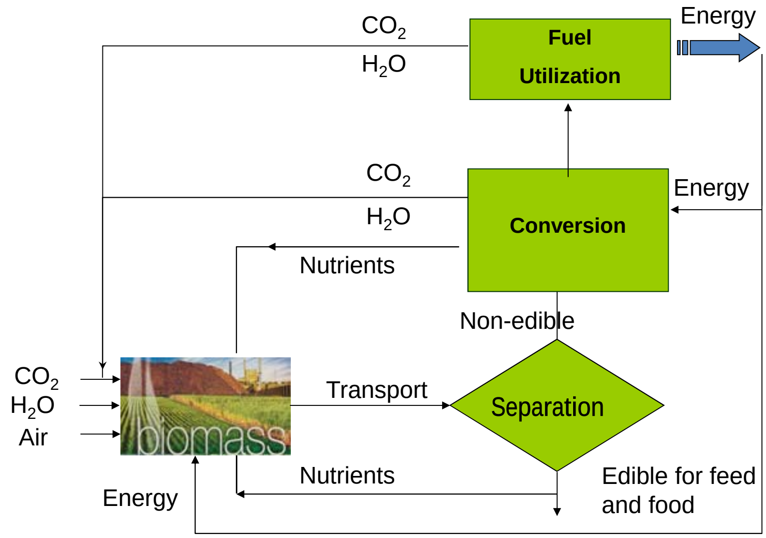
1. Herbaceous energy crops

- Example:
  - Perennials: Sugarcane, Napier grass
  - Annuals: corn, forage sorghum
  - Thin-stemmed, warm season perennial: switch grass
- Characteristics:
  - Low lignin content →Easy to delignify → Improves accessibility to carbohydrate in lignocellulose
  - Relatively high silica content compare to woody crops

2. Woody Energy Crops

- Woody biomass that is fast growing and suitable for use in dedicated supply systems
- Desirable candidates:
  - Rapid juvenile growth
  - Wide site adaptability
  - Pest and disease resistance
- Grown on a sustainable basis, harvested on a rotation of 3-10 yrs
- Examples
  - Hardwood: flowering plants like willow, oak, poplar
  - Softwood: evergreens like pine, spruce, cedar

Sustainable Production of Biofuels: An Integrated Biomass Production System



CO_2

H_2O

Fuel Utilization

Energy

CO_2

H_2O

Conversion

Energy

Nutrients

Non-edible

CO_2

H_2O

Air

biomass

Transport

Separation

Nutrients

Edible for feed and food

Energy

Valuable Components from Energy Crops

- Oils ← soybeans, nuts, grans
- Sugars ← sugar beets
- Starches ←corn, cereal crops
- Lignocellulose (fibre) ←all the residues

Environmental Analysis & Assessment Tools

- Since the 1970s, environmental assessment has been developed as a systematic process to identify, analyze and evaluate the environmental effects of products or activities
  - to ensure that the environmental implications of decisions are taken into account **before** the decisions are made.
- Environmental assessment allows effective integration of environmental considerations and public concerns into decision-making
- For individual projects such as a dam, motorway, factory or a bioenergy plantation or for plans, programs and policies
  - These approaches aim at providing a systematic procedure for identifying potential risks to human health and the environment, and a comparison of the respective risks to alternative options for different environmental compartments (air, soil, water).

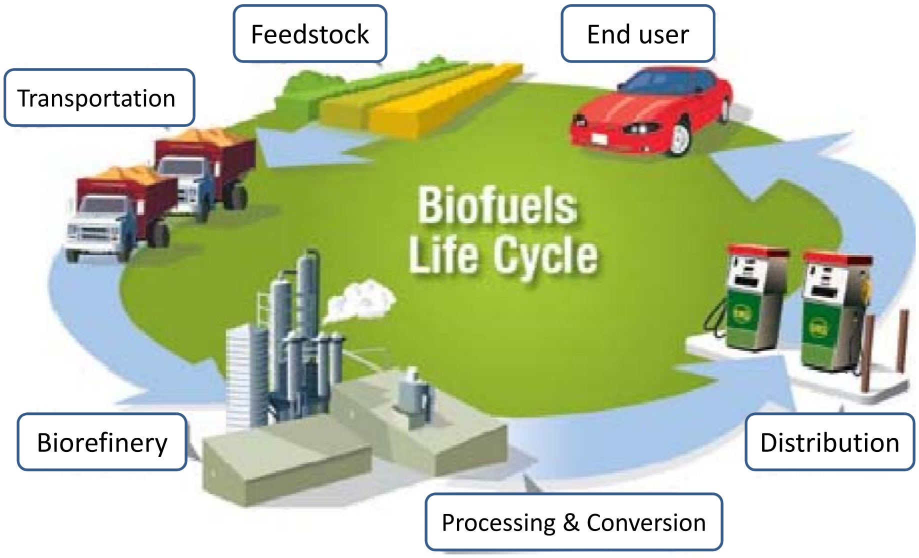
Life Cycle Assessment (Analysis)

- A specific method developed in the 1980s for determining and comparing the potential environmental impacts of product systems or services at all stages in their life cycle
  - from extraction of resources
  - through the production and use of the product
  - to reuse, recycling or final disposal
- It can be applied in strategy formulation, product development, and marketing.
- A number of LCA related standards (ISO 14040-14043) and technical reports have been published within the International Organization for Standardization (ISO) to streamline the methodology.

LCA

- The LCA approach is quite data-intensive to include
  - – direct impacts,
  - – those stemming from “upstream” activities such as mining, processing, and transport, as well as the materials (and energy) needed to manufacture all processes.
- This approach can be applied to **any** system or set of processes, i.e. it is generic.

LCA for Biofuels



Feedstock

End user

Transportation

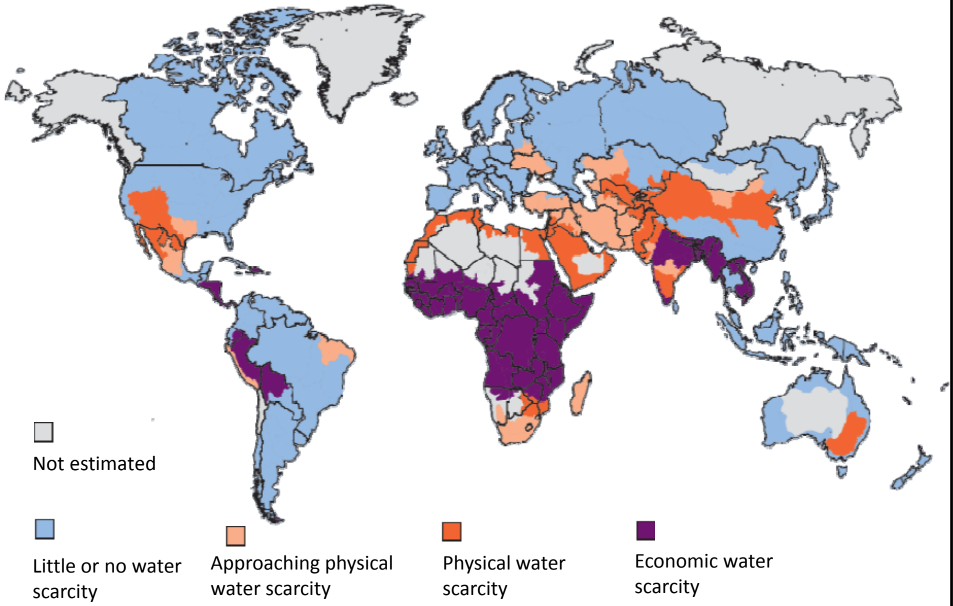
Biorefinery

Distribution

Processing & Conversion

IWMI (2007) based on analysis using the Watersim model

Areas of water Scarcity



Greenhouse Gas Emission Balances

- One of the key reasons for pursuing bioenergy is their potential to reduce GHG emissions when displacing fossil fuels.
- Bioenergy crops could offset their life cycle GHG "burden" in three key ways:
  1. removing CO_2 from the atmosphere and (temporarily) storing it in crop roots and soil as organic carbon;
  2. producing co-products such as protein for animal feed, which could avoid GHG emissions from activities needed to provide feed by other means;
  3. displacing fossil fuels.

On the other hand…

- GHGs are emitted in the production life cycle of bioenergy crops:
  1. in using fertilizers, pesticides, and fuel in farming,
  2. conversion/processing, transport and distribution up to combustion of the bioenergy product
  3. direct and potentially indirect land-use changes.

In determining the potential GHG emissions, it is important to consider all relevant steps in the life cycle.

- **Successful marketing of bioenergy in the EU and the US requires a verifiable GHG balance.**
- GHG balance is the balance between all greenhouse gas emissions from production to use of the equivalent energy amount of the respective fossil fuel.

- *With respect to biofuels, regulations in the EU and currently under consideration in the US require that importers certify the sustainable cultivation of agricultural land, the protection of natural habitats and a minimum level of CO_2 savings for the biofuels, ranging from minimum net savings of 20% (U.S. State of California) to 35% (EU).*
- *With effect from 2017, the EU requires GHG emission saving from the use of biofuels and other bio-liquids of 50%.*

The GHG emissions from fossil reference system used in JRC/EUCAR/Concawe (2007) Model

- **Diesel:** 86.2 kg CO_2-eq. per GJ of diesel
  - crude oil extraction: 3.3;
  - transport 0.8;
  - refinery: 8.6;
  - use: 73.5
- **Gasoline:** 85 kg CO_2-eq. per GJ of gasoline
  - crude oil extraction: 3.3;
  - transport 0.8;
  - refinery: 6.5;
  - use: 74.4

General Consideration

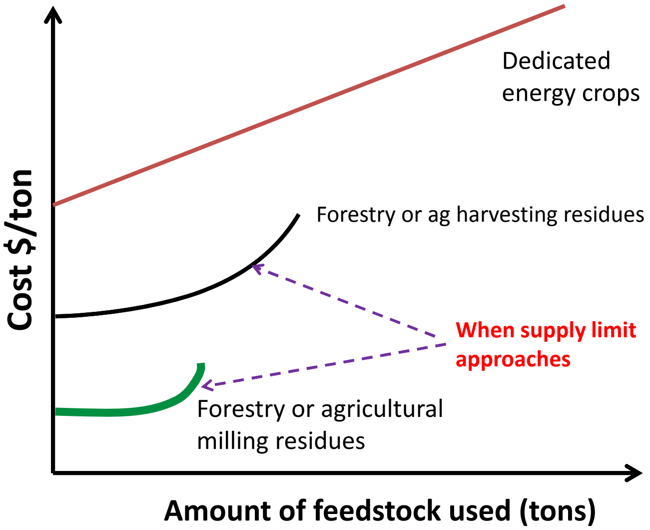
Biofuels Economics Analysis

- Cost estimation only
- Two kinds of costs considered in this content
  1. Cost of feedstock
  2. Unit cost for manufacturing biofuels

Cost estimation for feedstock

- For the purpose of cost estimation, bio-resources are conveniently classified as
  - ☐Processing residues
  - ☐Harvesting residues
  - ☐Dedicated energy crops

Feedstock Costs in General



Actual prices depend on local supply and demand

Unit cost for Production of Annual Crops

Consider

- Harvest machinery
- Labor
- Land
- Transportation
- Harvest machinery
- Land
- Interest on short-term loans
- Labor
- Transportation
- Miscellaneous

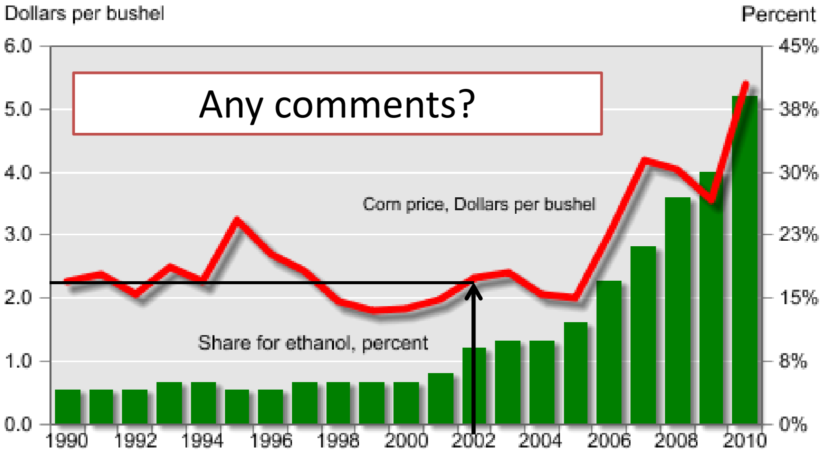
Size of Resource Base

- Canadian biomass potential
- USA biomass crops potentials
- **Highlights**
  1. Now: Biorenewable resources in form of residues and wastes ➔8% USA energy demand
  2. Potential: Energy crops➔35-62% of current USA energy demand.

Comment

"Low" corn price in USA resulted from over production relative to market demand and competition from producers in developing nations who had lower fixed costs (Last century!)

Historical corn price in USA (USDA Data)



Any comments?

1 Bushel of corn = 25.4 kg