Distillation and Ethanol Recovery

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Topics of Discussion

- Distillation Principles
- Ethanol Distillation
- Ethanol Dehydration
- Coproduct Recovery

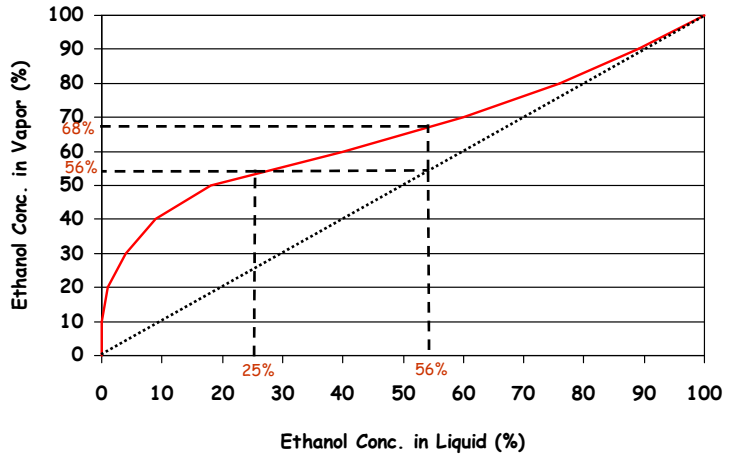
What is Distillation?

- Separation Process
- Purification Process
  - Distilled water
- Individual components in a mixture will boil off differently
  - Volatility of components

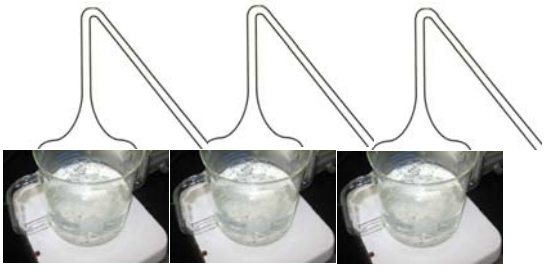
Equilibrium Curve

- Vapor pressure of each component varies with liquid concentration
  - Concentration in vapor mixture varies with the liquid concentration
- Equilibrium curve is vapor concentration as a function of liquid concentration

Equilibrium Curve for Water Ethanol Mixture

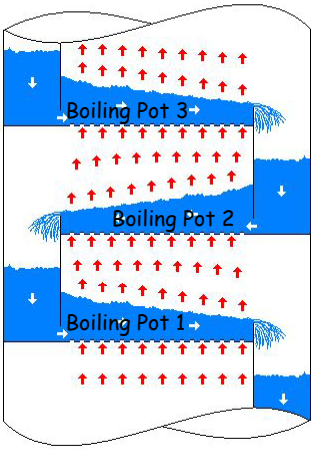


Distillation Basics



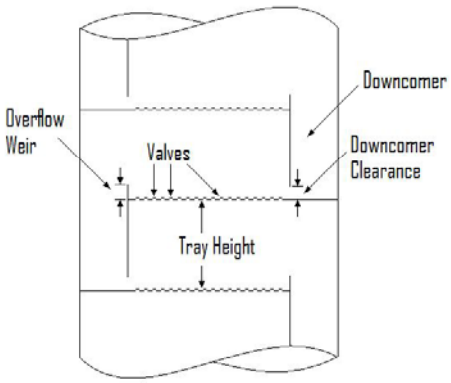
Boiling Pot 1 Boiling Pot 2 Boiling Pot 3

The whole distillation column functions as if it were composed of lots of individual "boiling pots" stacked on top of each other.



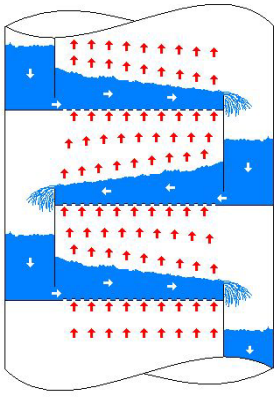
Distillation Basics

Distillation columns consist of many trays that are designed to maximize mass transfer area between the liquid and vapor.



Distillation Basics

- The liquid flows across each tray while the vapor flows up through the tray and mixes with the liquid.
- The velocity of the vapor going through the valves keeps the liquid on the top of the tray and prevents it from leaking through the tray (known as weeping).
- Most distillation columns use fixed orifice valves that are stamped from a single metal plate.



Distillation Basics Cont.

Each tray acts as a boiling pot!

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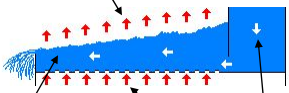


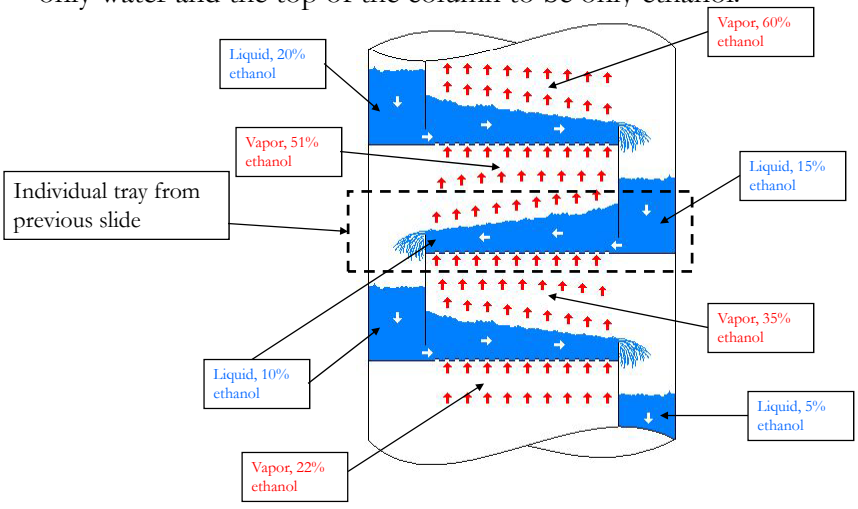
Vapor at 51% ethanol

Liquid and Vapor going into the tray to make up for what is leaving. Liquid is 15% ethanol, vapor is 35% ethanol.

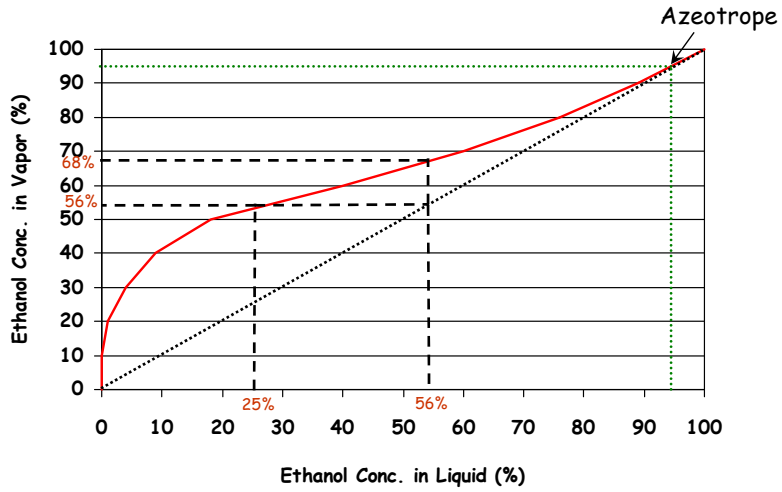
Liquid leaving at 10% ethanol

Distillation Basics Cont.

The overall function of the distillation column is to separate the ethanol from the water. We want the bottom of the column to be only water and the top of the column to be only ethanol.

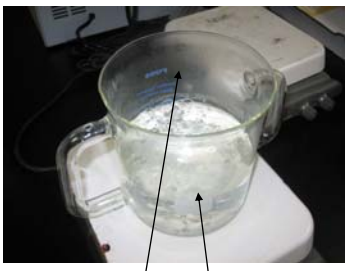


Equilibrium Curve for Water Ethanol Mixture

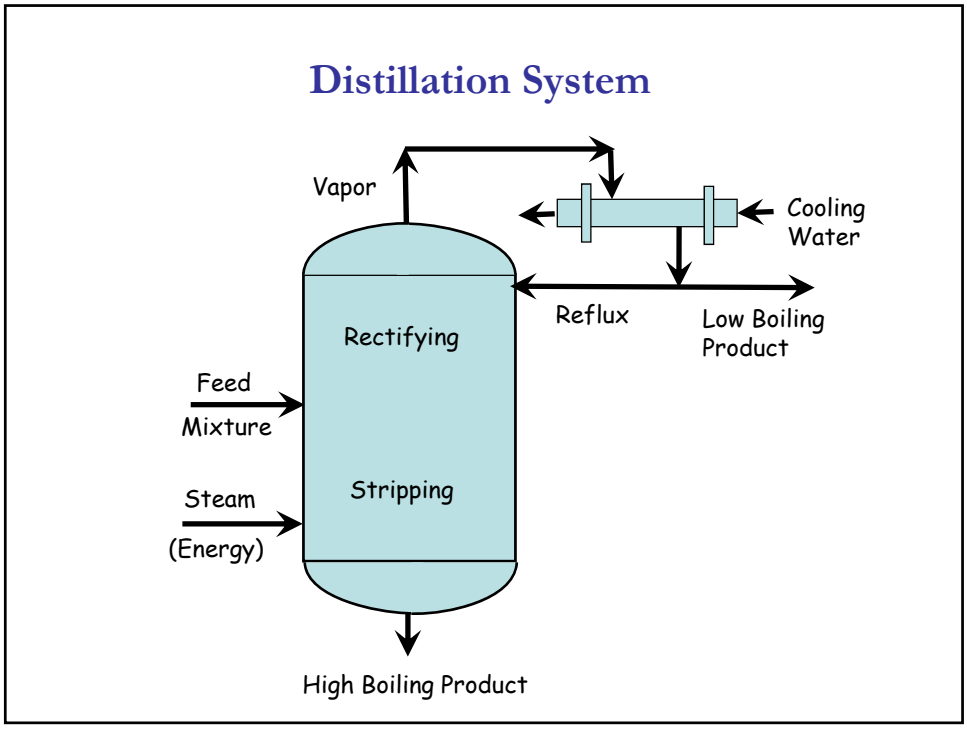


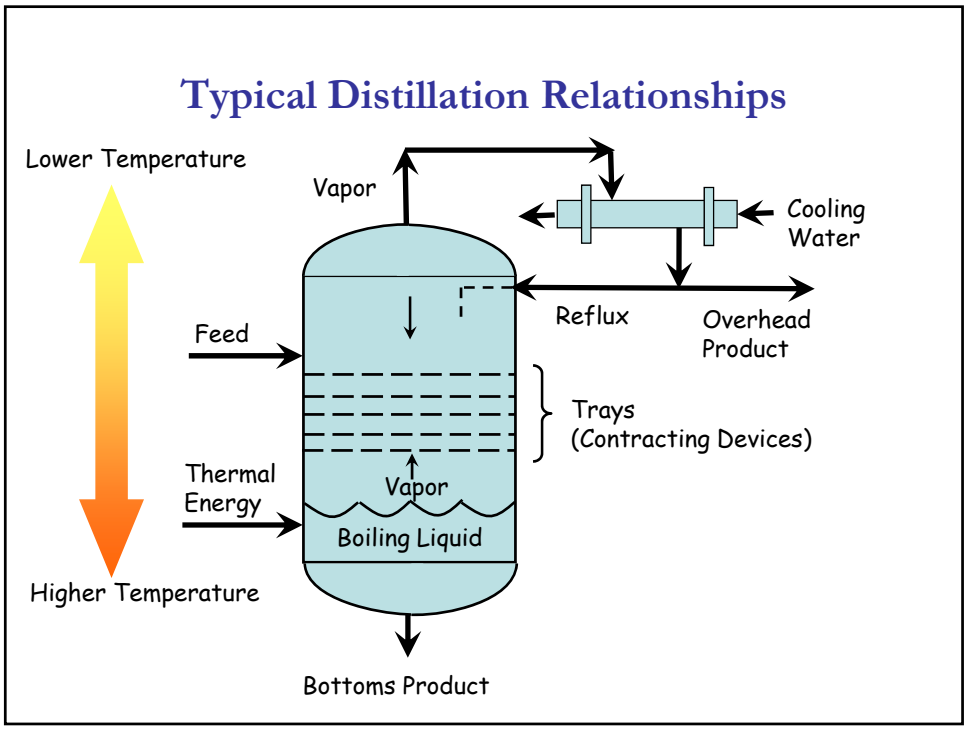
Azeotrope

- We cannot use distillation to get 100% ethanol because of the azeotrope
- Composition of vapor mixture is the same as the liquid mixture
  - Separation by distillation is impossible
  - Equilibrium curve intersects 45° line
- Azeotrope of ethanol water mixture is at 194° Proof
- Typically distill to 190 proof and use molecular sieves to remove the rest of the water



At the azeotrope both the liquid in the pot and the vapor boiling off are at 194 proof.

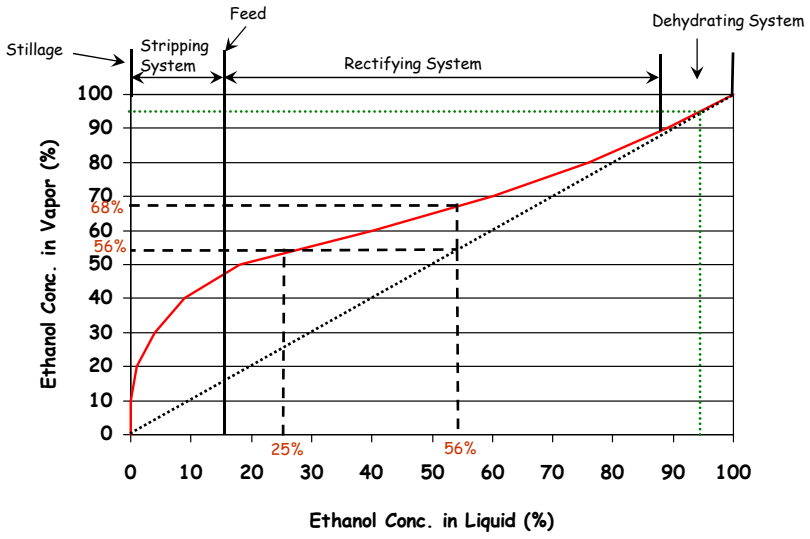

Distillation System
Vapor
Cooling Water
Reflux
Low Boiling Product
Rectifying
Feed Mixture
Stripping
Steam (Energy)
High Boiling Product


Typical Distillation Relationships
Lower Temperature
Vapor
Cooling Water
Reflux
Overhead Product
Feed
Trays (Contracting Devices)
Thermal Energy
Vapor
Boiling Liquid
Higher Temperature
Bottoms Product

Distillation Design

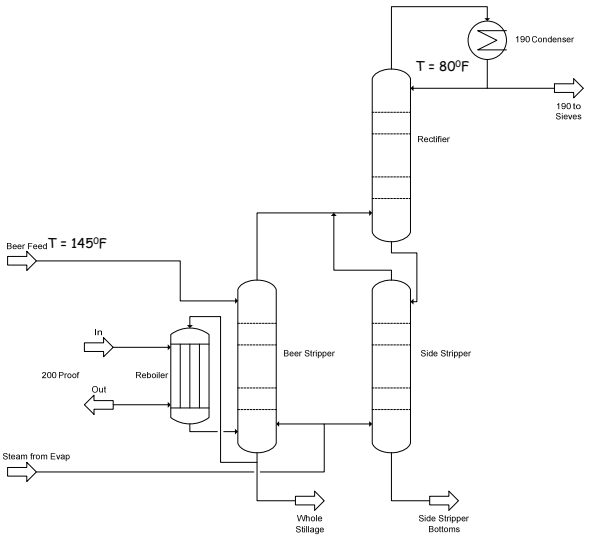
- What sort of contacting devices should be used?
- How much vapor is needed?
- How much liquid reflux is required?
- How much steam (energy) will be required?
- What are the general dimensions of the distillation tower?

Distillation Systems



Distillation System

- Typical design uses three separate distillation columns: beer stripper, rectifier, and side stripper.
- Bottom temperature of both stripper columns are controlled by steam flow to prevent ethanol from leaving in either whole stillage or side stripper bottoms
- Top temperature of the rectifier is controlled by reflux rate to achieve desired concentration of 190 proof.
- Controlled temperature points are typically 5 trays up from the bottom or down from the top.



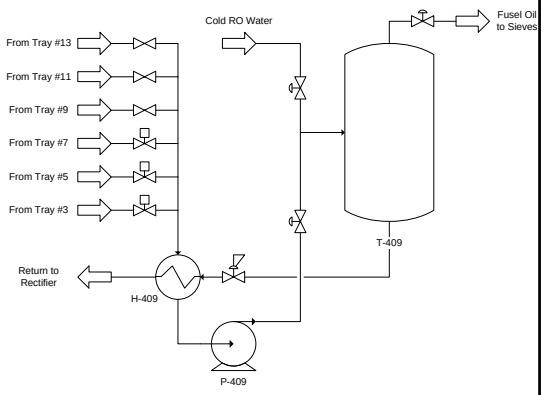
Fusel Oil System

Fusel oils are made up of longer chain alcohols.

Water : $H-O-H$

Ethanol : $H-C(H)(H)-C(H)(H)-O-H$

Fusel Oil : $H-C(H)(H)-C(H)(H)-C(H)(H)-C(H)(H)-O-H$

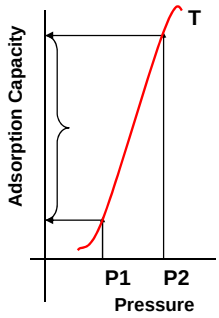


The fusel oils separate and form an oil layer on top when mixed with cold water. The fusels are then taken directly to the sieves.

Distillation

Technologies for Ethanol Dehydration

- Molecular Sieve Dehydration
  - Pressure Swing Adsorption
  - Selective adsorption of water using special adsorbents
  - Adsorption Isotherm



Dehydration History

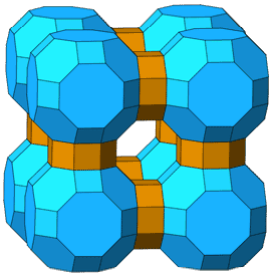
- Synthetic Zeolyte First used in 1957 to dry Air
- Synthetic Zeolyte were then called as Molecular Sieves due to very precise pore size that enabled them to select and remove one molecule from other based on their sizes
- First application to Ethanol drying in early 80's

Molecular Sieves

- Type 3Å
  - Chemical Formula: $(K_2O.Na_2O).Al_2O_3.2SiO_2.xH_2O$
- Strongest Known Adsorbent
- Normally referred as Zeolite
- Crystalline, hydrated Metal Alumino Silicates (normally Sodium)

Mol Sieve Structure

Zeolite X
3^0A
Na Metal



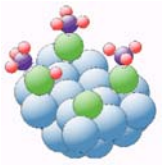
Zeolite A
4^0A
K Metal

Properties of Molecular Sieve

- Crystalline Structure
- Affinity to adsorb Polar compounds
- Form very uniform three dimensional array
- Permit very selective adsorption because of uniform pore size distribution

Adsorption

- Molecules diffuse from the bulk of the fluid to the surface of the solid adsorbent forming a distinct adsorbed phase
- These adsorbed molecules adhere to the surface of adsorbents by weak cohesive forces called as Vander wall's forces
- Separation depends on relative degree of adsorption of one component over other. For e.g. In ethanol water mixture, Water is more readily adsorbed on Zeolite than Ethanol
- Exothermic Process: Heat of adsorption



Regeneration

- When Adsorbent surface gets saturated by the adsorbed component it becomes essential to desorb the adsorbate from adsorbent. This process is known as Regeneration
- In Regeneration, adsorbate is removed from the adsorbent by raising it's Temperature or decreasing it's Pressure

Mechanism of Adsorption

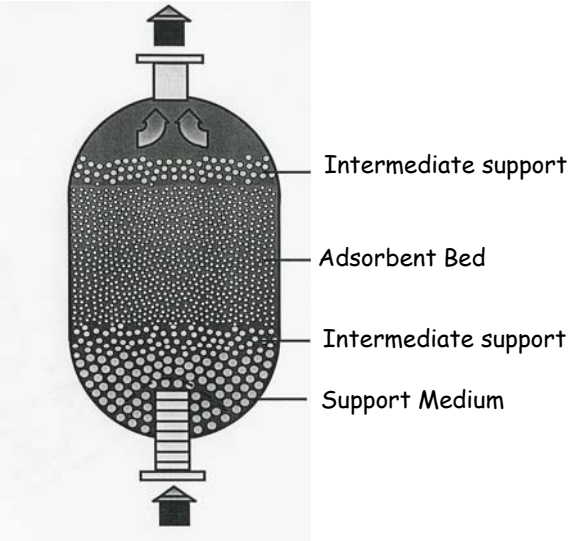
Adsorption bed is divided into Three Zones

- Active Zone
- Mass Transfer Zone
- Equilibrium Zone

Mechanism of Adsorption

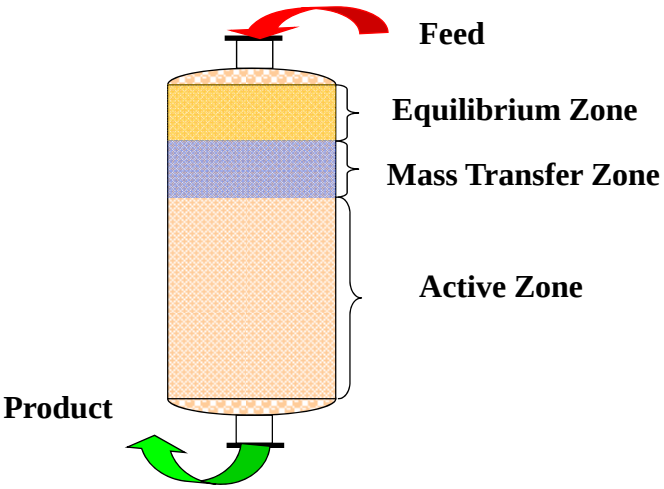
- At the start of Adsorption, bed is fully active –Active Zone
- As Ethanol-Water vapors enter the bed, water gets adsorbed on comparatively thin layer of bed called as Mass Transfer Zone
- In a short time, this layer gets saturated with water and it becomes in equilibrium with entering vapors called as Equilibrium Zone
- Mass Transfer Zone keeps shifting from entrance to exit and then bed is taken for regeneration

Molecular Sieve Bed

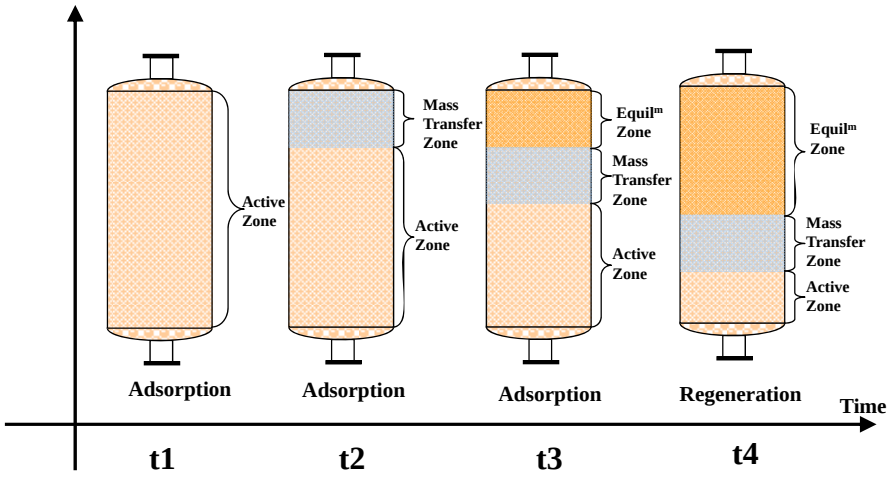


Mole Sieves

Mechanism of Adsorption



Mechanism of Adsorption

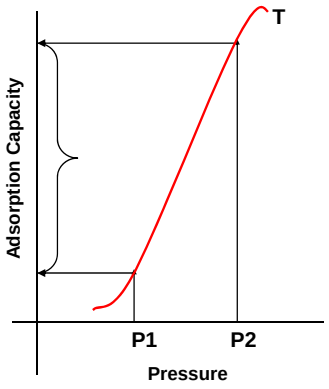


Pressure Swing Adsorption (PSA)

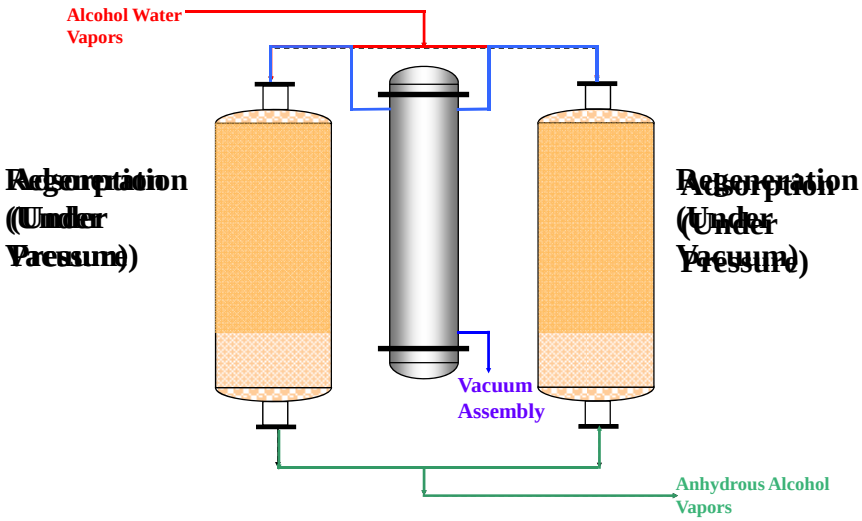
- Adsorption Capacity is a function of operating pressure.

  Adsorption: Under Pressure

  Regeneration : Under Vacuum This is called Pressure Swing adsorption
- This requires Short pressurizing and regeneration times which leads to Smaller bed Size



Ethanol Dehydration Using PSA



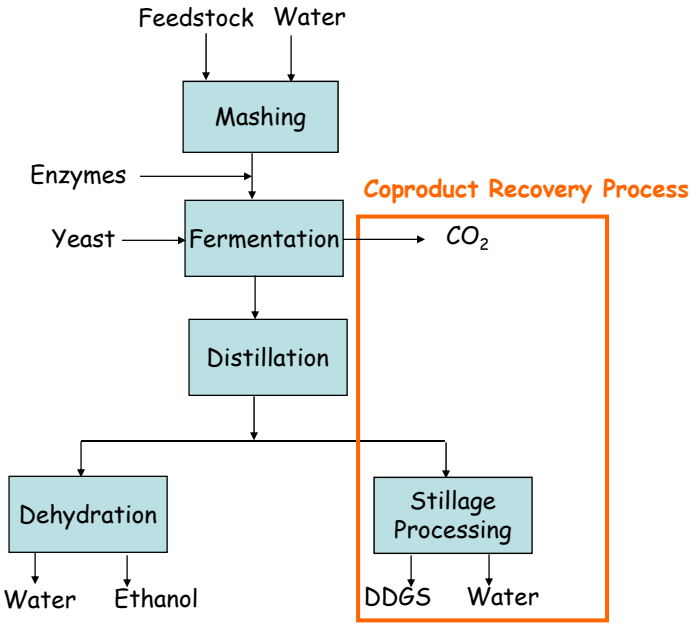
Design Considerations

- Feed Concentration
- Dehydration Pressure
- Regeneration Conditions
- Uniformity of Pore Size

Coproduct Recovery:Topics of Discussion

- Coproduct Recovery Process
- Conventional Coproducts
  - DDGS
  - CO_2
- Potential New Coproducts
  - Nutraceuticals
  - Gums
  - Other food, feed and industrial products

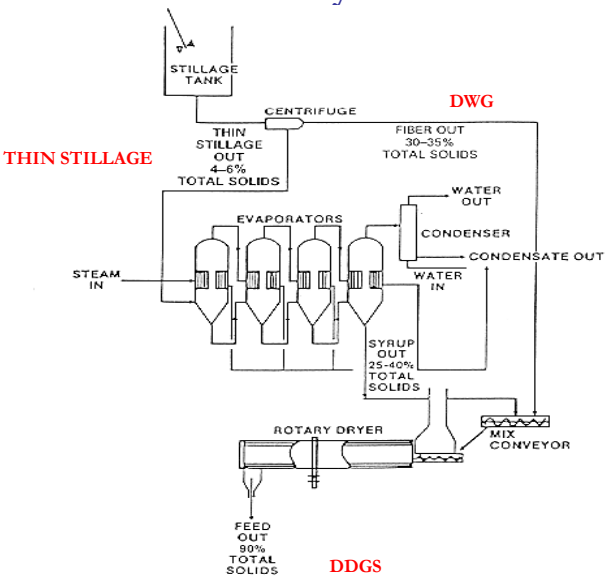
Ethanol Production Process



Whole Stillage

- Whole stillage is typically 6-10% total dry solids (TDS)
- TDS depends upon
  - Type of grain used
  - Water-to-grain ratio
  - Quantity and type of backset stillage used
  - Fermentation process used
  - Efficiency of sugar utilization during fermentation
- Approximate Whole stillage TDS analysis
  - 5.5% suspended solids
  - 2.5% dissolved solids
  - 92% moisture content

Distiller Dried Grains with Solubles (DDGS) Recovery Process



Composition of Distiller Dried Grains with Solubles Compared to Corn

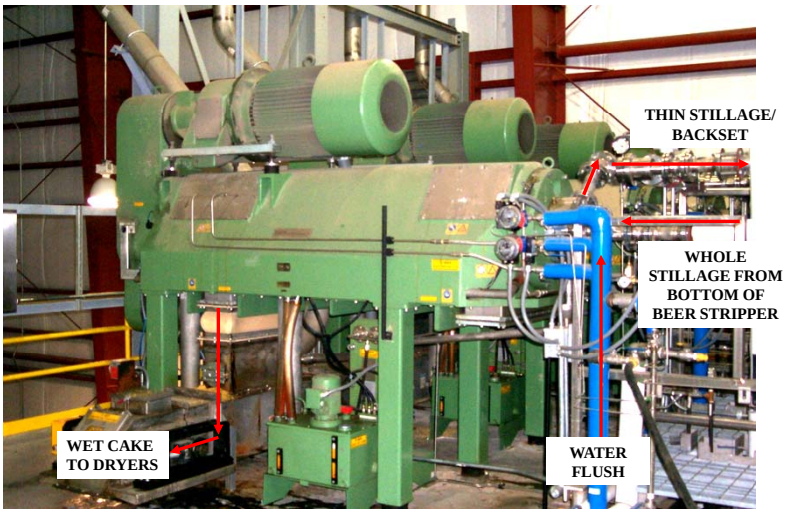
Feed	Dry Matter (%)	Crude Protein (%)	Crude Fat (%)	Crude Fiber(%)
Distiller Dried Grains with Solubles	92.5	27	8	8.5
Corn	88	8.9	3.5	2.9

Distiller Wet Grains (DWG)

- Approximately 30-35% solids
- Equipment normally used to make DWG from whole stillage
  - Screens
    - Vibrating, curved type, approximately 50 mesh
  - Presses
    - Screw and screen type
  - Centrifuges (most common)
    - Decanter centrifuges, disc or nozzle type

Wet Distiller Grains (DWG or Wet Cake)

Centrifuges

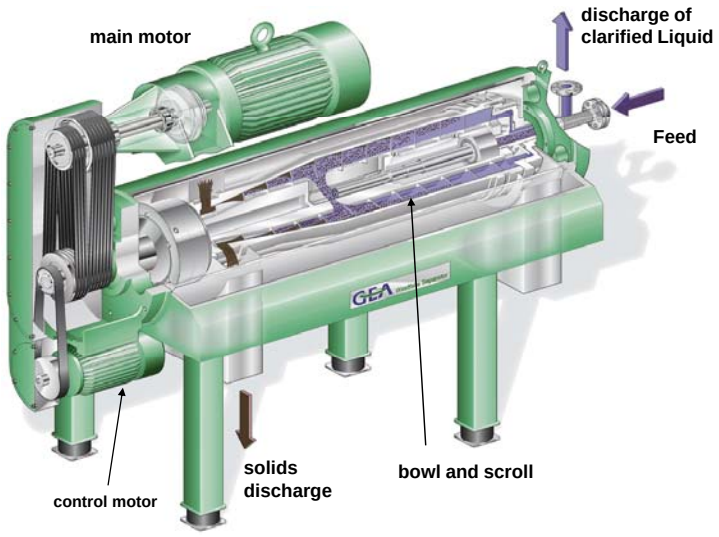


Stoke's Law

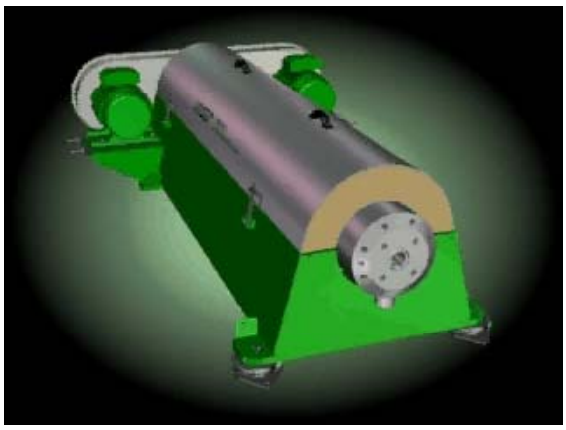
$$V_c = \frac{d^2(\rho_w - \rho_o)}{18\eta} r\omega^2$$

V_c	d^2	ρ_w	ρ_o	η	$r\omega^2$
centrifugal settling velocity (m/s)	particle size (mm Ø)	heavy phase density (kg/m^3)	light phase density (kg/m^3)	continuous phase viscosity (kg/ms)	centrifugal acceleration (m/s^2)

Decanter Centrifuge



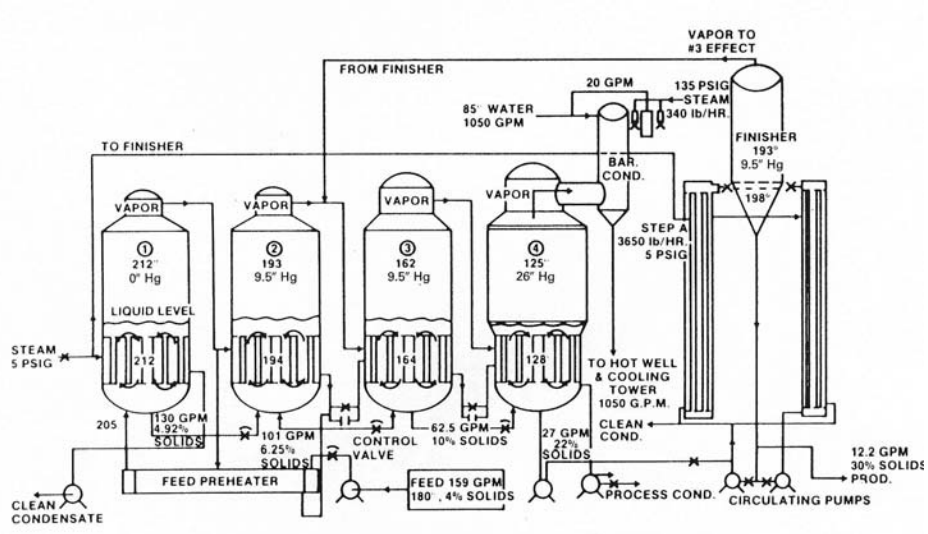
Whole Stillage Centrifuge



Thin Stillage (TS)

- Approximately 4-6% solids
- This stillage is concentrated to 25-30% solids by evaporation
- Concentrated thin stillage is also known as syrup
- Suspended solids less than 1% in TS

Typical Quadruple-Effect Evaporator with Finisher



Thin Stillage Evaporation

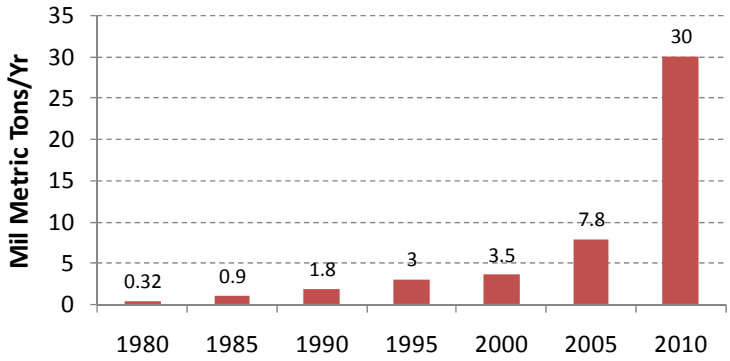
Distiller Dried Grains with Solubles

- Approximate Composition
  - 27% protein
  - 9% crude fat
  - 13% crude fiber
- Approximate Cost
  - $80-120/ton

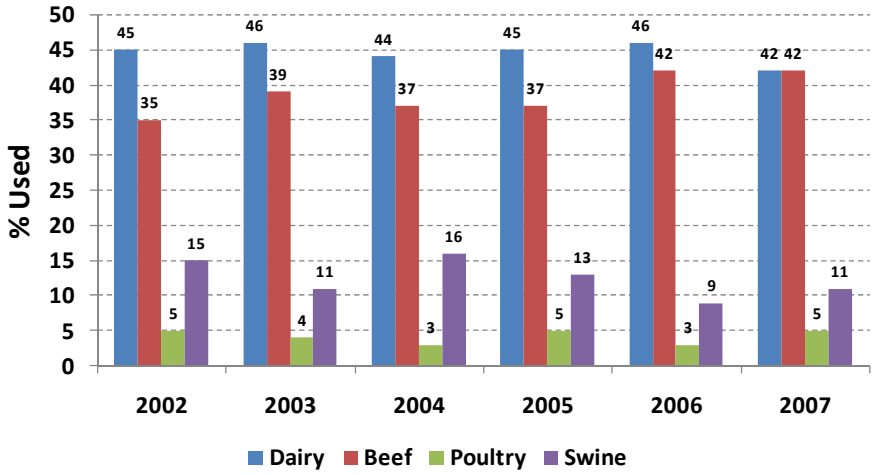
Use of DDGS

DDGS Production in the US

- DDGS production is increasing with ethanol production

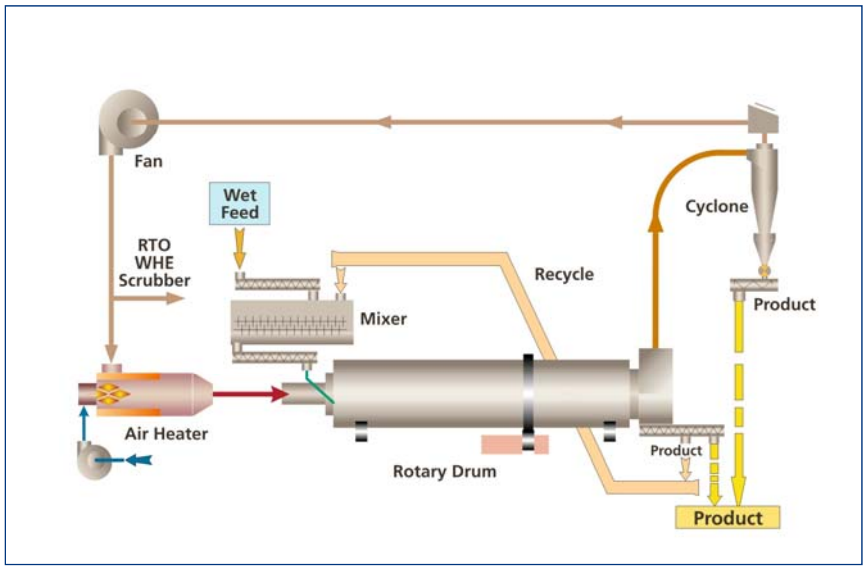


DDGS Utilization

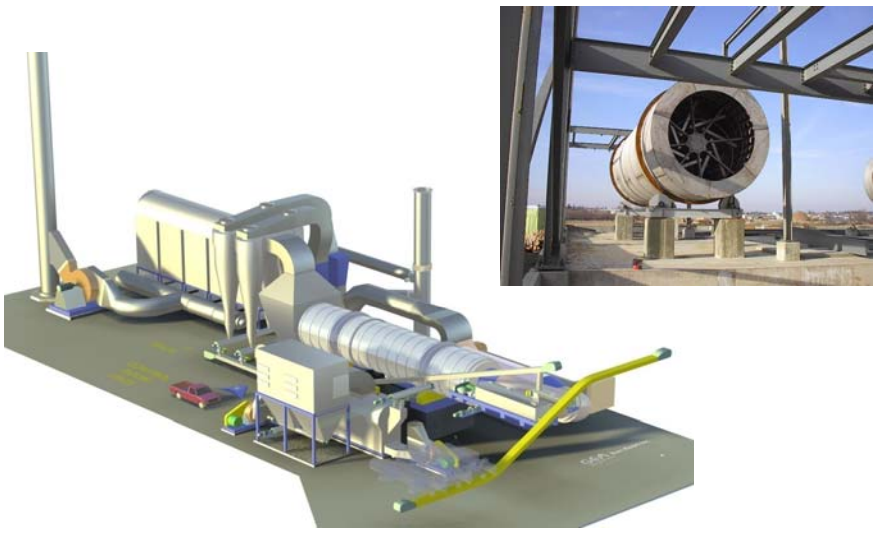


DDGS Dryers Industry Overview

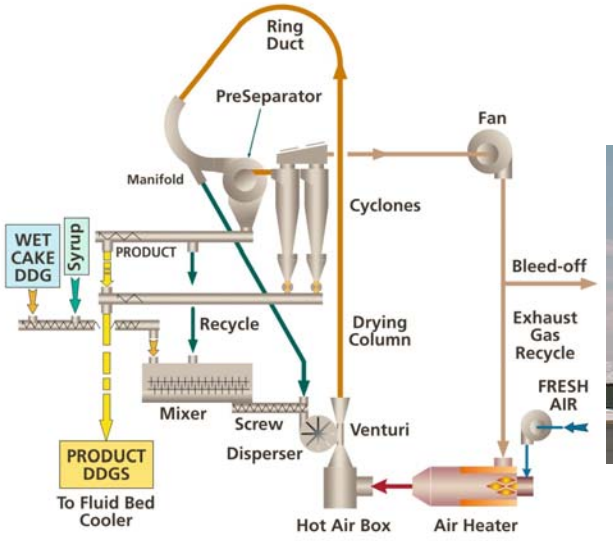
Partial Gas Recycle Rotary Dryer for DDGS



Single Rotary Dryer for DDGS
15 ft dia. by 69 ft long



Partially Closed Circuit Ring Dryer for DDGS

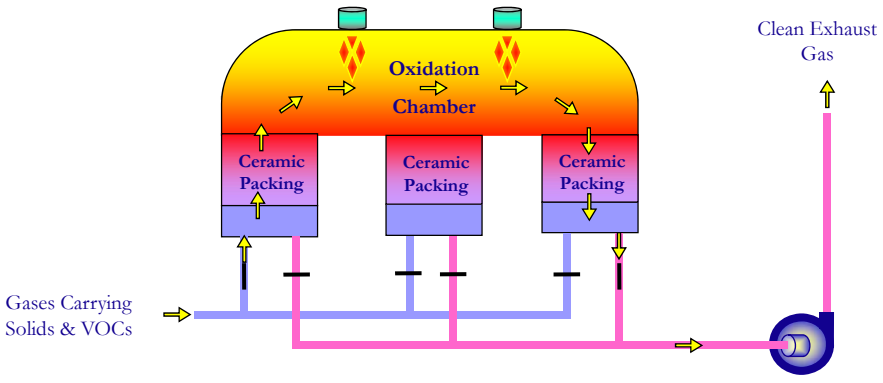


DDGS Dried in Rotary and Ring Dryer

Pollution Control

- **Main Pollutants From DDGS Dryer**
  - Volatile Organic Compounds (VOC)
  - Carbon Monoxide (CO)
  - Nitrogen oxides (NOx)
  - Particulate Matter
  - Odor
  - Opacity (Blue Haze)

Regenerative Thermal Oxidizer



Regenerative Thermal Oxidizer

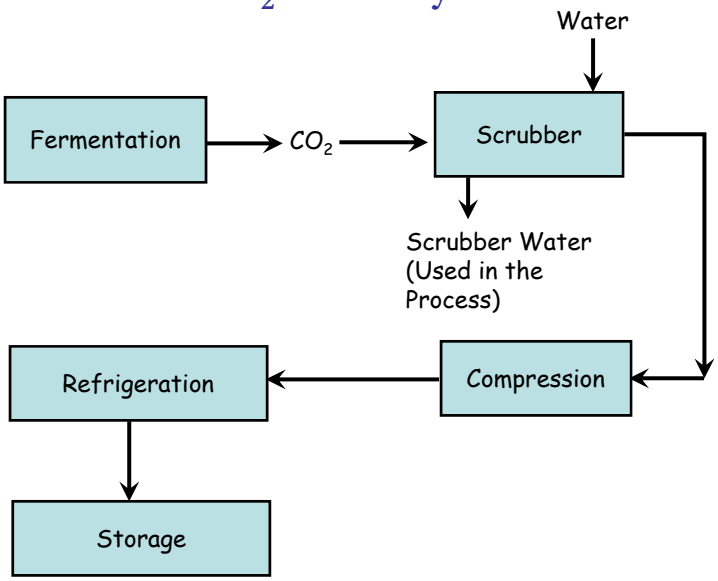
DDGS Storage

DDGS Loadout

Research on DDGS

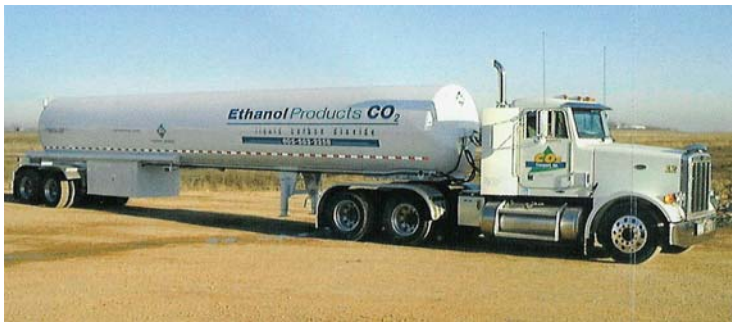
- Need to reduce the volume of DDGS
- Diversify markets utilization for DDGS
- Improve the quality of DDGS

CO_2 Recovery



Use of CO_2

- Carbonation of beverages
- Quick cooling of meats
- Refrigeration (Dry Ice)
- Biggest demand during summer time
- Approximate Cost??



CO_2 Facility

CO_2 Storage