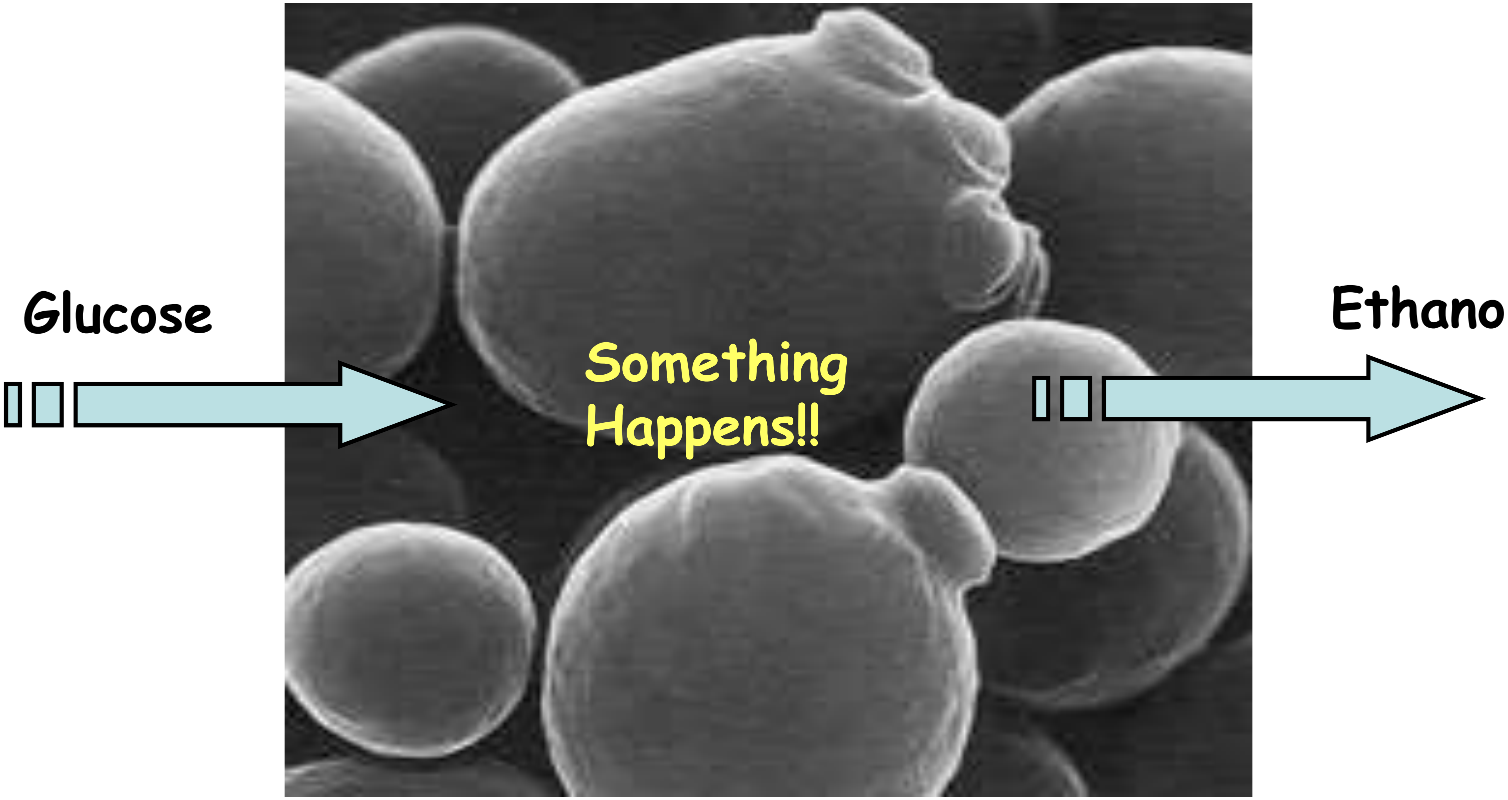
Topic Five
Starch Ethanol Production

Lecture Nine-Ten

Starch Ethanol Production

Summary of Topic Four



Engineers' view of yeast

Summary of Topic Four

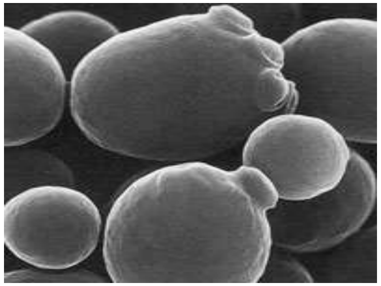
Six categories of enzymes

1. Oxidoreductases
2. Transferases
3. Hydrolases
4. Lyases
5. Isomerases
6. Ligases (synthases)

Summary of Topic Four

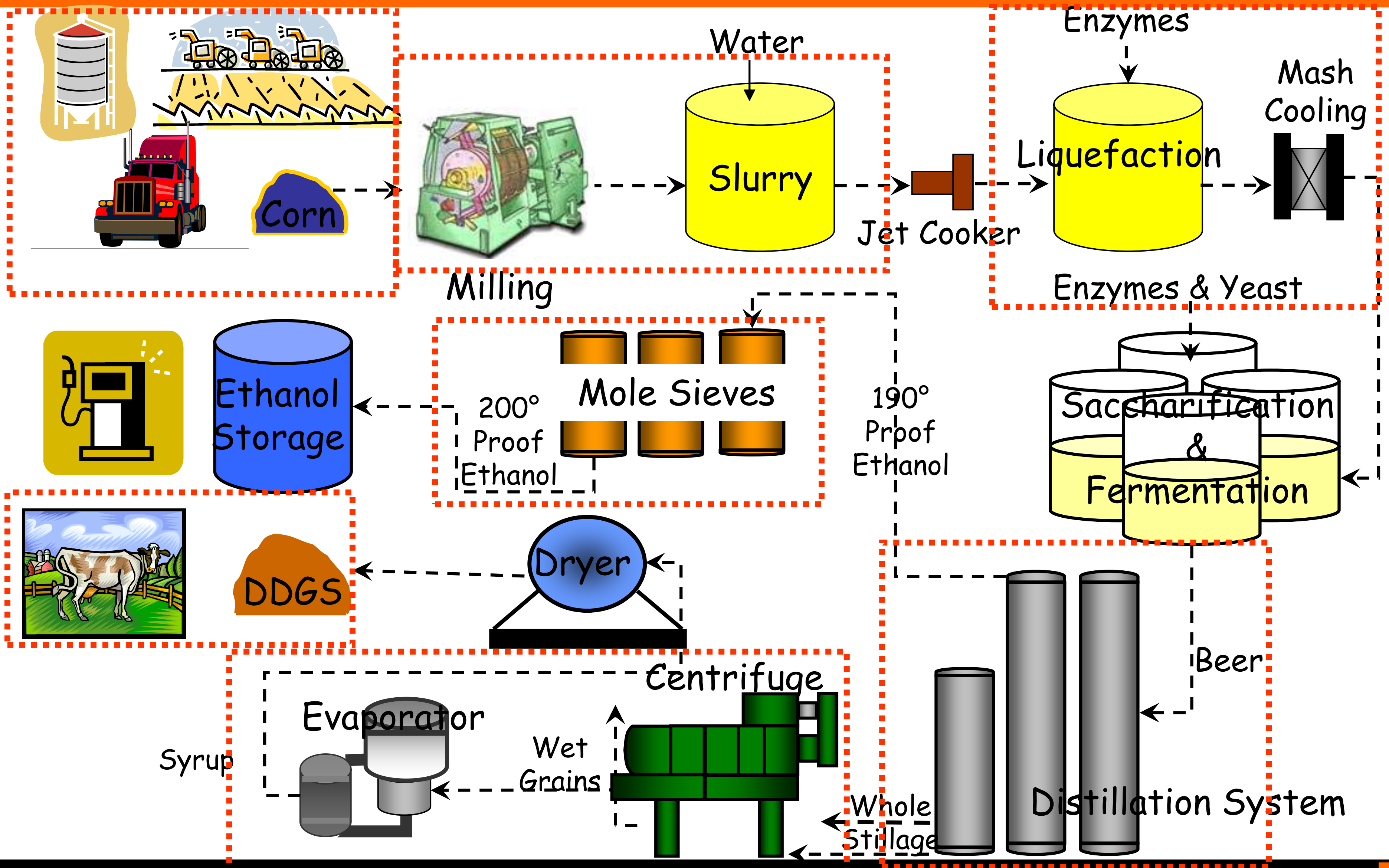
What are some of the important parameters in fermentations process?

- Particle size distribution of feedstock.
- Moisture content of feedstock.
- Presence of toxin producing fungi (ex. *Aspergillus niger*)
- Temperature and pH



- Sugar composition of feedstock (Starch, cellulose and hemicellulose).
- Enzyme activity and stability.
- Yeast cell numbers, viability, vitality.
- Sugars, alcohols (primarily ethanol and glycerol), organic acids
- Protein and lipid content of feedstock and coproducts.
- Dextrose Equivalent

Dry Grind Corn Process



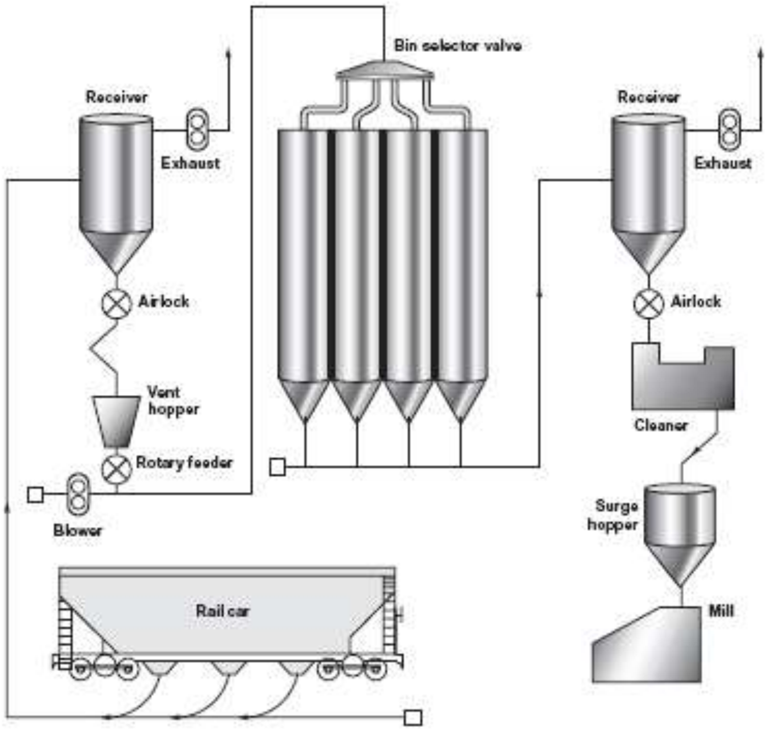
Dry Grind Corn Process

Grain Receiving

Importance: Quality testing, cleaning and preparation of corn for further unit operations. Size reduction increases surface area and aids in enzymatic hydrolysis.

Most of the corn is received by trucks and to a limited extent by rail road.

Corn is classified into 5 grades depending on its test weight (lb/bu), broken corn and foreign material (BCFM), damaged kernels, insects and presence of rodent droppings.



Ref: Alcohol Textbook; http://www.gipsa.usda.gov/GIPSA/documents/GIPSA_Documents/corninspection.pdf

Corn Grading Process

Grade	Minimum test weight per bushel (pounds)	Maximum limits of: Damaged kernels: Heat damaged kernels (percent)	Maximum limits of: Damaged kernels: Total (percent)	Maximum limits of: Broken corn and foreign material (percent)
U.S. No. 1	56.0	0.1	3.0	2.0
U.S. No. 2	54.0	0.2	5.0	3.0
U.S. No. 3	52.0	0.5	7.0	4.0
U.S. No. 4	49.0	1.0	10.0	5.0
U.S. No. 5	46.0	3.0	15.0	7.0

U.S. Sample Grade

U.S. Sample grade is corn that:

(a) Does not meet the requirements for the grades U.S. Nos. 1, 2, 3, 4, or 5; or

(b) Contains stones with an aggregate weight in excess of 0.1 percent of the sample weight, 2 or more pieces of glass, 3 or more crotalaria seeds (*Crotalaria* spp.), 2 or more castor beans (*Ricinus communis* L.), 4 or more particles of an unknown foreign substance(s) or a commonly recognized harmful or toxic substance(s), 8 or more cocklebурs (*Xanthium* spp.), or similar seeds singly or in combination, or animal filth in excess of 0.20 percent in 1,000 grams; or

(c) Has a musty, sour, or commercially objectionable foreign odor; or

(d) Is heating or otherwise of distinctly low quality.

Ref: http://archive.gipsa.usda.gov/reference-library/standards/810corn.pdf

Dry Grind Corn Process

Pretreatment in dry grind corn process involves quality testing, storage, cleaning, removal of stones and metal debris.

Importance: Incoming corn is tested for presence of fungi (*Aspergillus niger*) using black light. Fungal mycelia fluoresce when illuminated by black light.

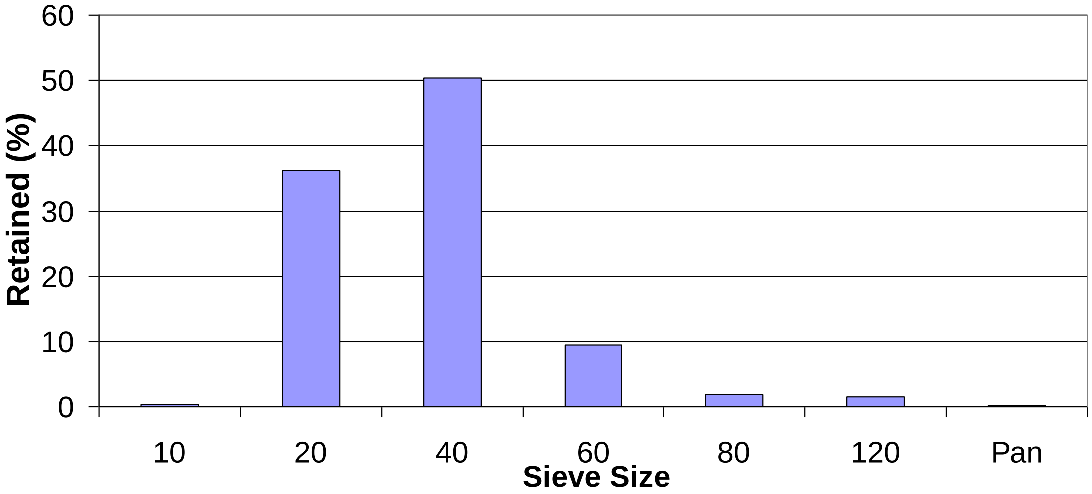
UV (Black) Light

Ref: Kellemax, Wikipedia.org

Dry Grind Corn Process

Pretreatment in dry grind corn process involves quality testing, storage, cleaning, removal of stones and metal debris.

- Clean corn is milled in hammer mills. Corn milling exposes starch granules inside the corn endosperm by splitting and removing pericarp fiber and disintegrating corn kernel.



Particle size distribution

Hammer Mill

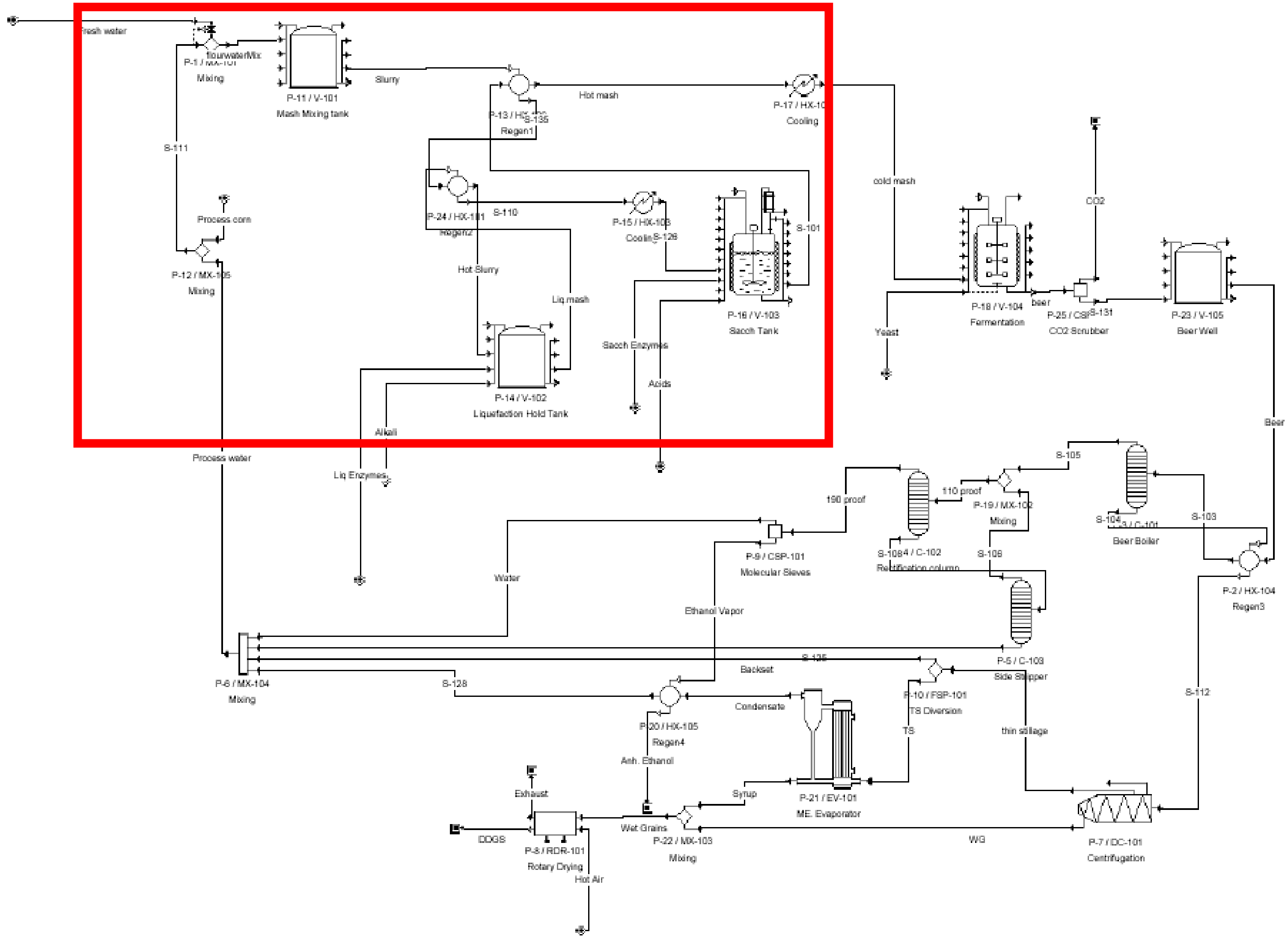
Dry Grind Corn Process

No of particles	1	10	1000
Dimension	1.00	0.01	0.001
S.A	1.00	4.64	10.00
Vol.	1.00	1.00	1.00

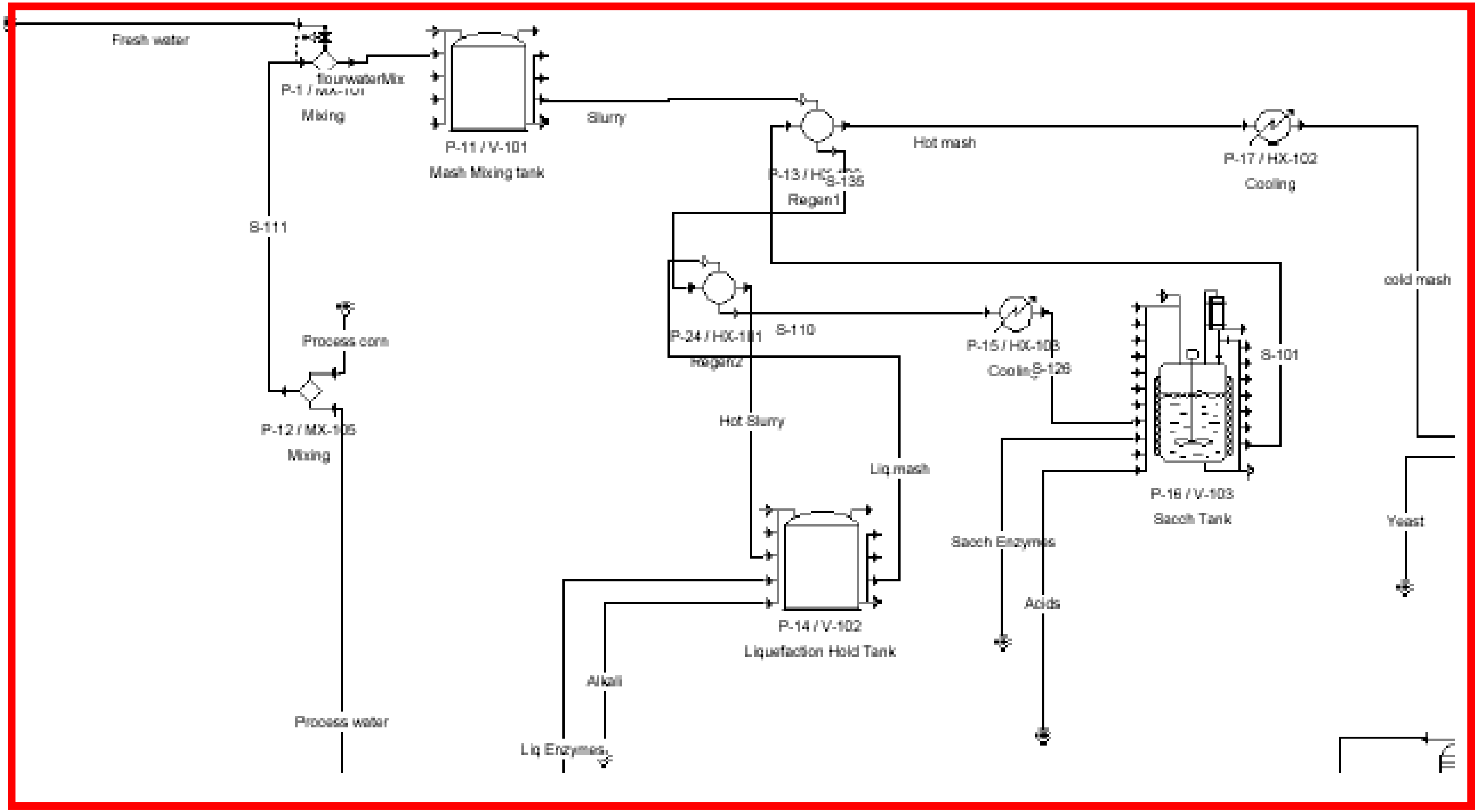
Industrial Scale Hammer Mill

Ref:http://news.thomasnet.com/images/large/503/503663.jpg

Dry Grind Corn Process



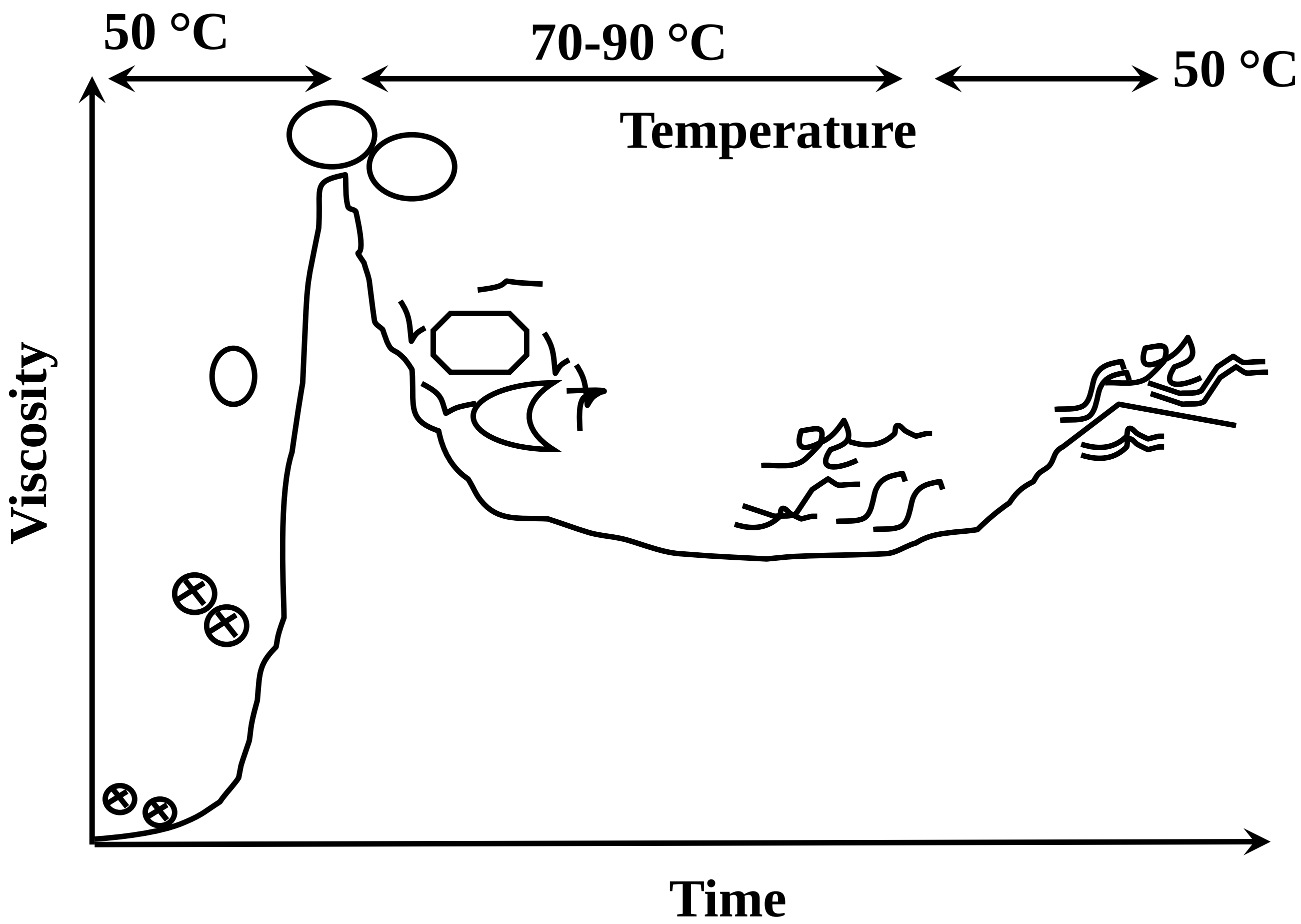
Feed Handling, Liquefaction and Saccharification



Dry Grind Corn Process

Liquefaction in dry grind corn process involves breakdown of starch into dextrins.

<u>Importance:</u> Gelatinization and breakdown of starch into dextrins.



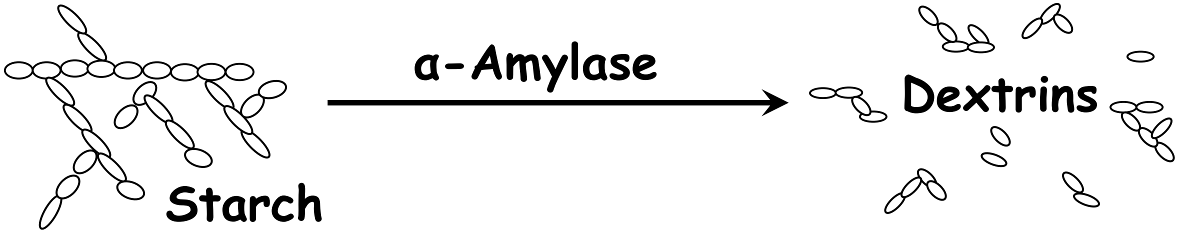
Dry Grind Corn Process

Liquefaction in dry grind corn process involves breakdown of starch into dextrins.

Enzymes: Alpha amylase breaks down starch into dextrins.

Operating Conditions: 90°C, 5.5-6.0 pH and high shear.

- At the end of liquefaction
  - The dextrose equivalent of corn mash is about 12-22.
  - Mash does not turn blue when iodine solution is added.
  - Starch granules lose their shape.
- Viscosity of the mash is lowered and hence it can be easily pumped in the plant.



Ref: www.q-jet.com/mixing-jet.htm

Jet cooker

Dry Grind Corn Process

Saccharification in dry grind corn process involves conversion of dextrins into mono saccharides (primarily) and disaccharides.

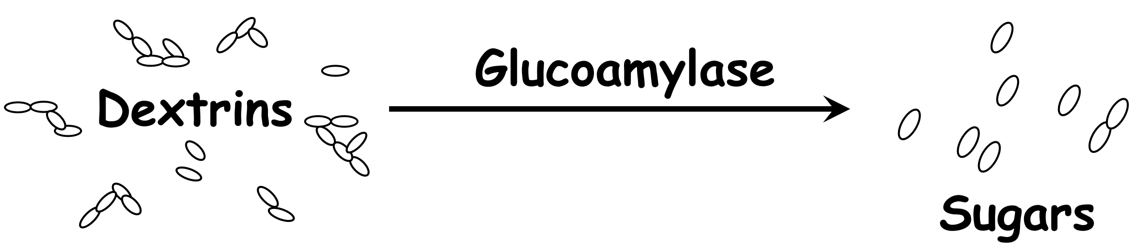
Importance: Yeast can only ferment mono- and disaccharides. Hence it is important to hydrolyze dextrins into glucose.

Enzymes: Gluco amylase breaks down dextrins into glucose.

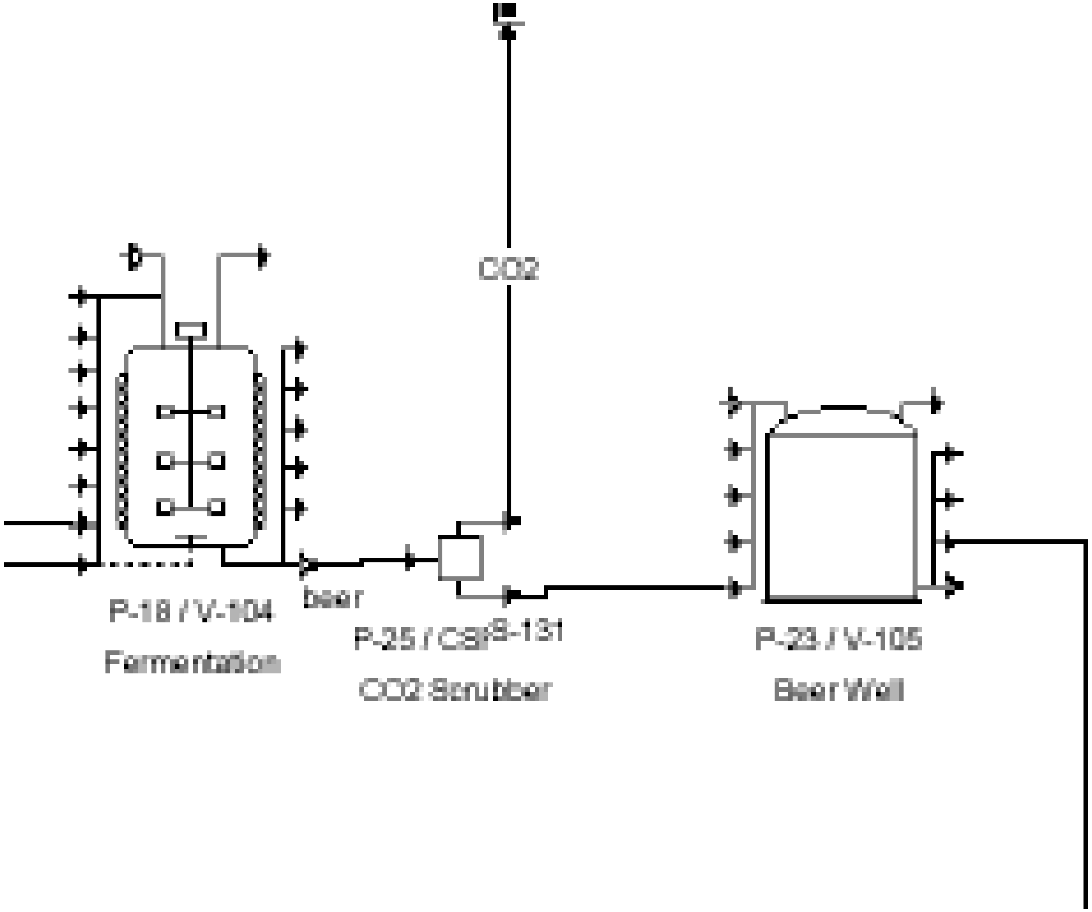
Operating Conditions: 60°C (2 hr) or 30°C (48 hr), 4.5-5.0 pH.

At the end of Saccharification

- The dextrose equivalent of corn mash is >70.
- Mash does not turn blue when iodine solution is added.
- Mash primarily consists of glucose sugar.



Fermentation



Dry Grind Corn Process

Fermentation in dry grind corn process involves anaerobic respiration of yeast consuming glucose and producing ethanol as a byproduct.

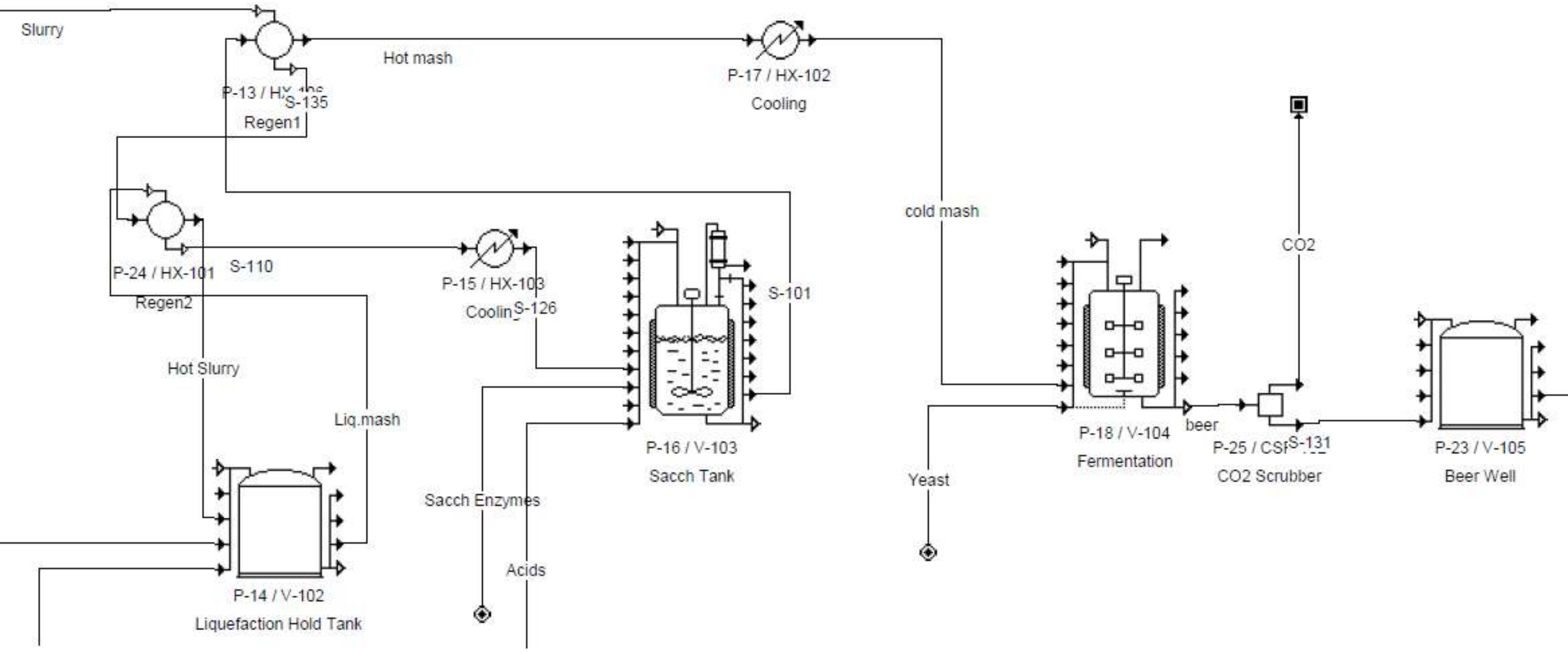
Importance: This is the heart of the corn ethanol process. Yeast consume sugars produced by starch hydrolysis and produce ethanol as a byproduct of anaerobic respiration.

Operating Conditions: 30°C (48-60 hr), 4.0-4.5 pH.

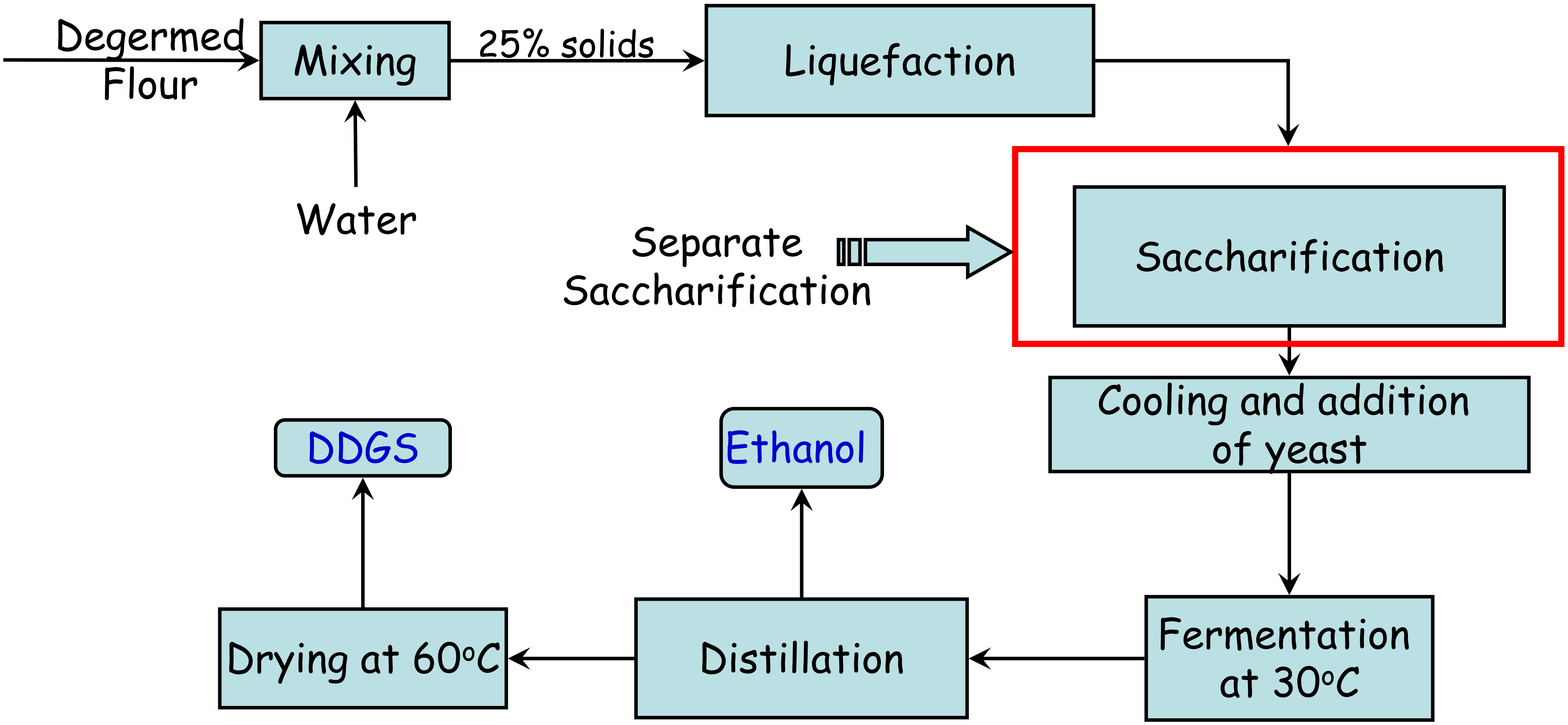
At the end of fermentation

- Glucose is consumed by yeast and ethanol is produced.
- The fermented mash is now known as ‘beer’.
- Depending on the solids content final ethanol concentration can vary. For example for 34% solids (w/w), final ethanol concentration is ~17.5% (v/v)

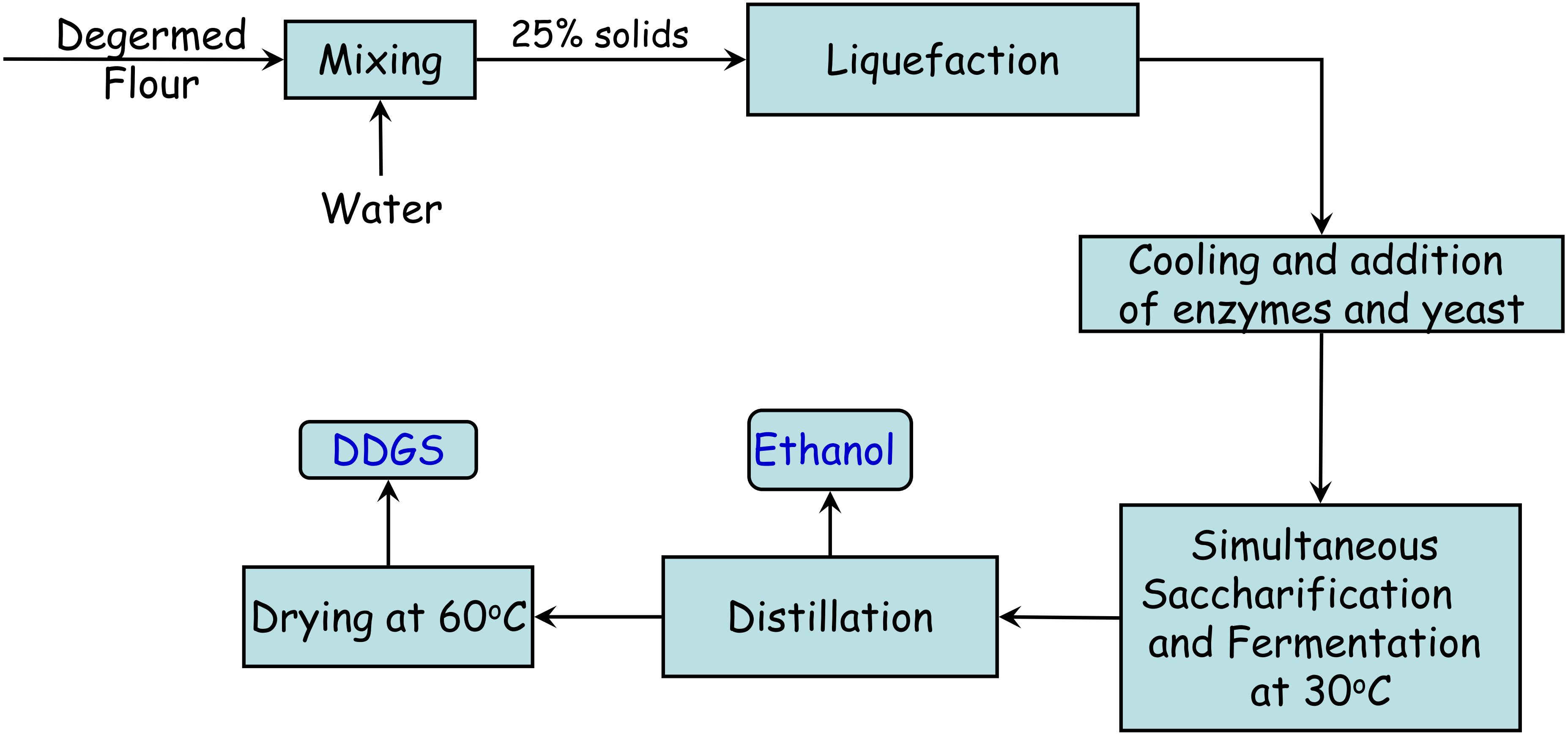
Liquefaction, Saccharification and Fermentation



(Separate Saccharification and Fermentation)



(Simultaneous Saccharification and Fermentation)



Dry Grind Corn Process

Fermentation in dry grind corn process involves anaerobic respiration of yeast consuming glucose and producing ethanol as a byproduct.

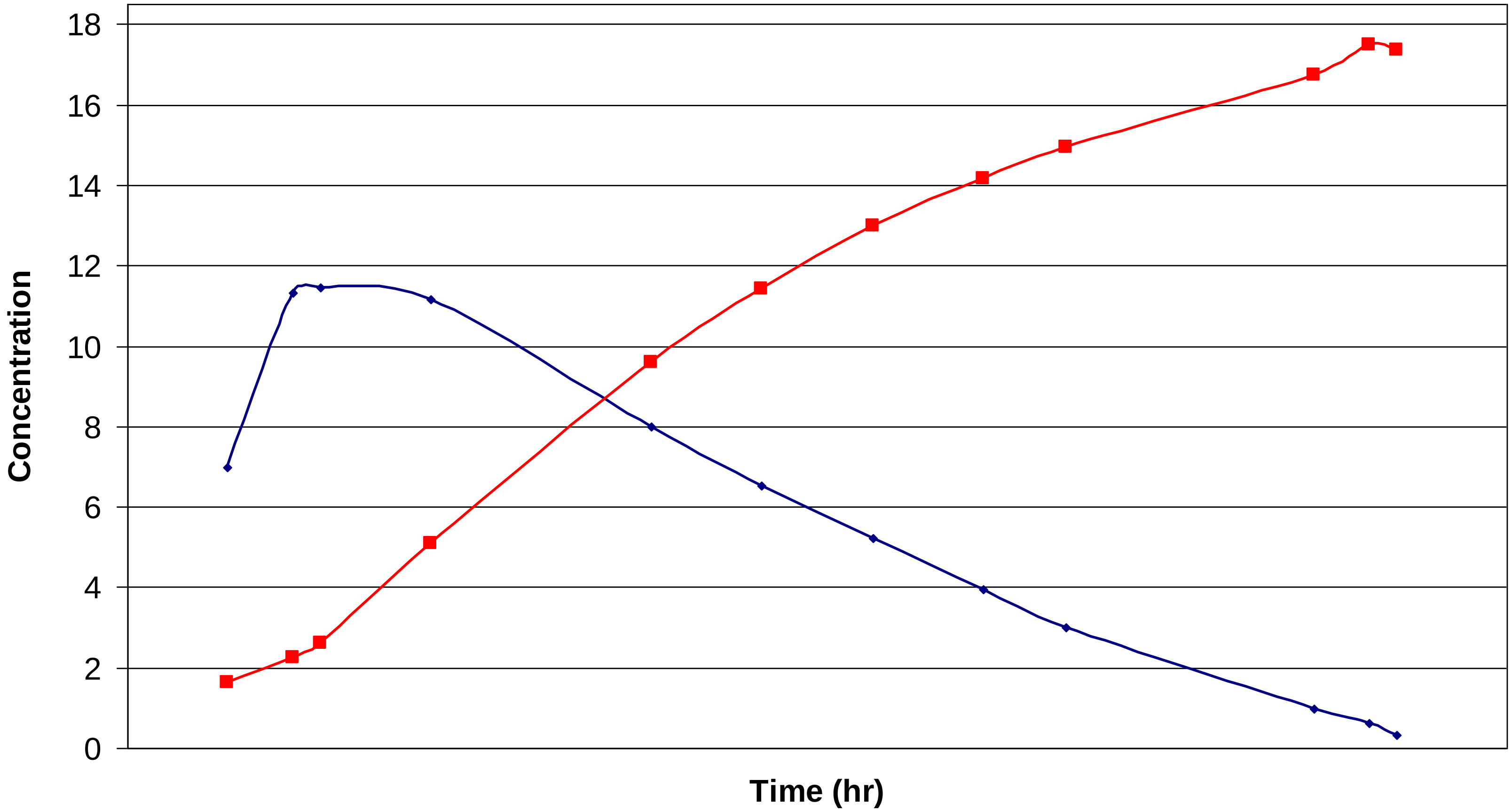
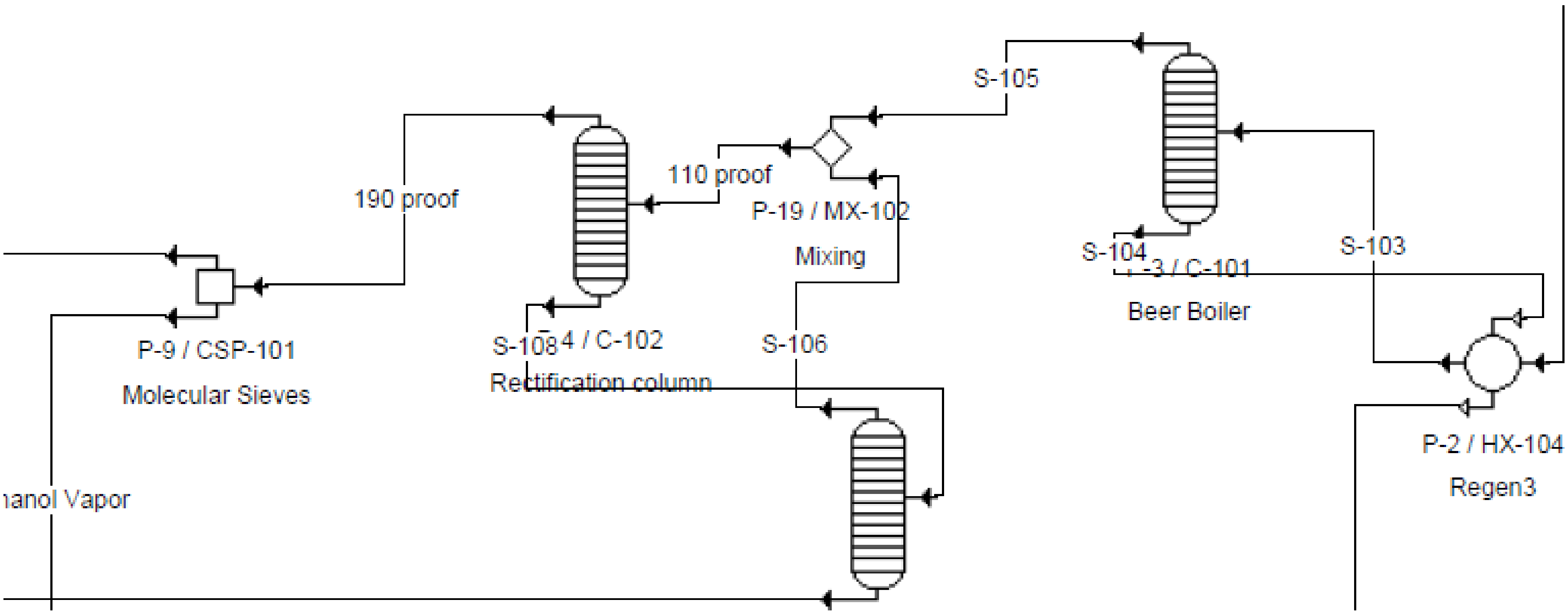


Fig. Typical fermentation profile in industrial scale fermentations

Ethanol Recovery



Dry Grind Corn Process

Distillation in dry grind corn process involves heating fermented mash and stripping the ethanol of water using molecular sieves to obtain anhydrous ethanol.

Importance: Distillation process is the most important process after fermentation. This step determines the total productivity of dry grind corn process.

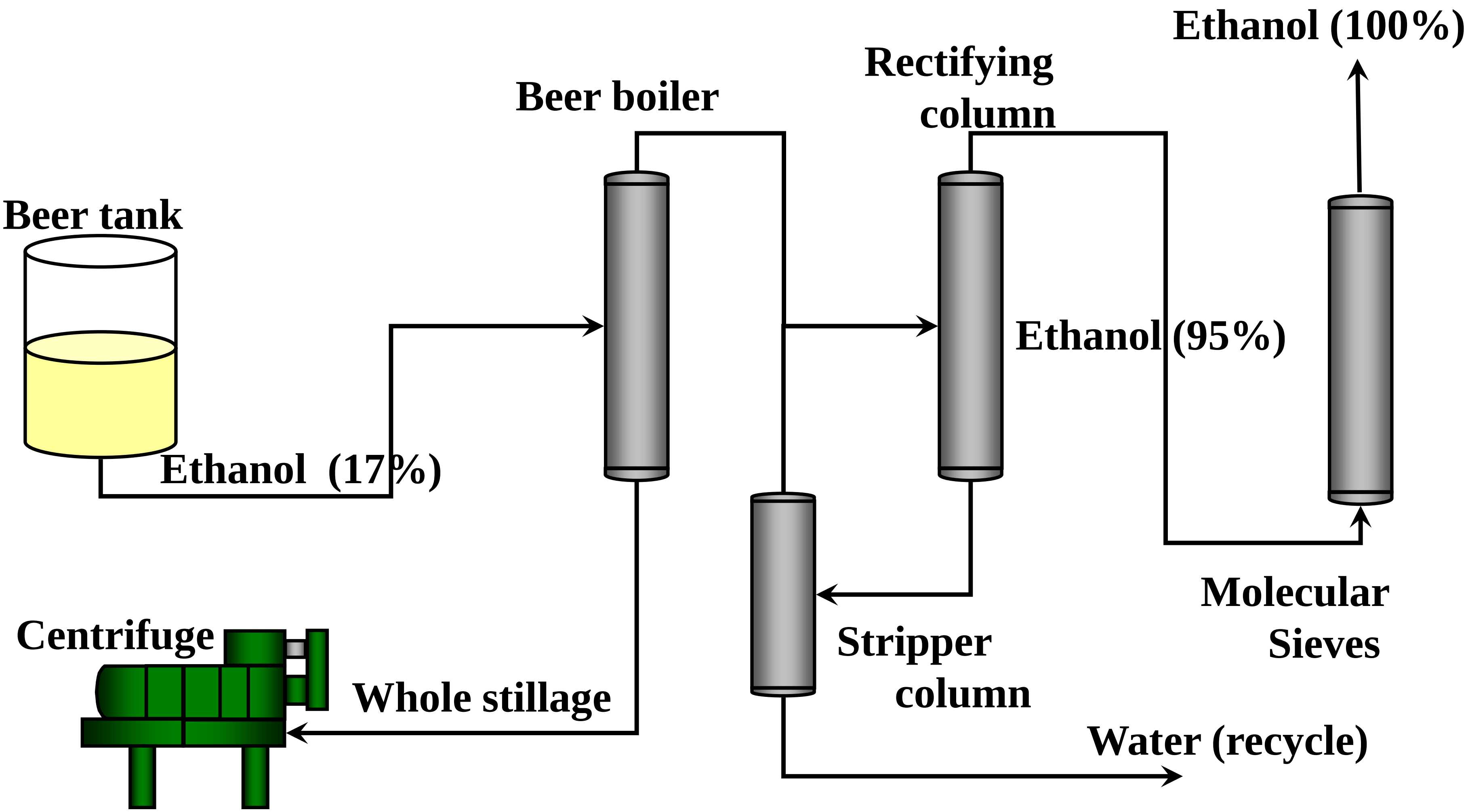
A simple distillation process cannot be used to completely separate water and ethanol because, water and ethanol form an 'azeotrope'.

Azeotrope is a mixture of two or more compounds having a characteristic boiling point such that the composition of mixture cannot be changed by simple distillation.

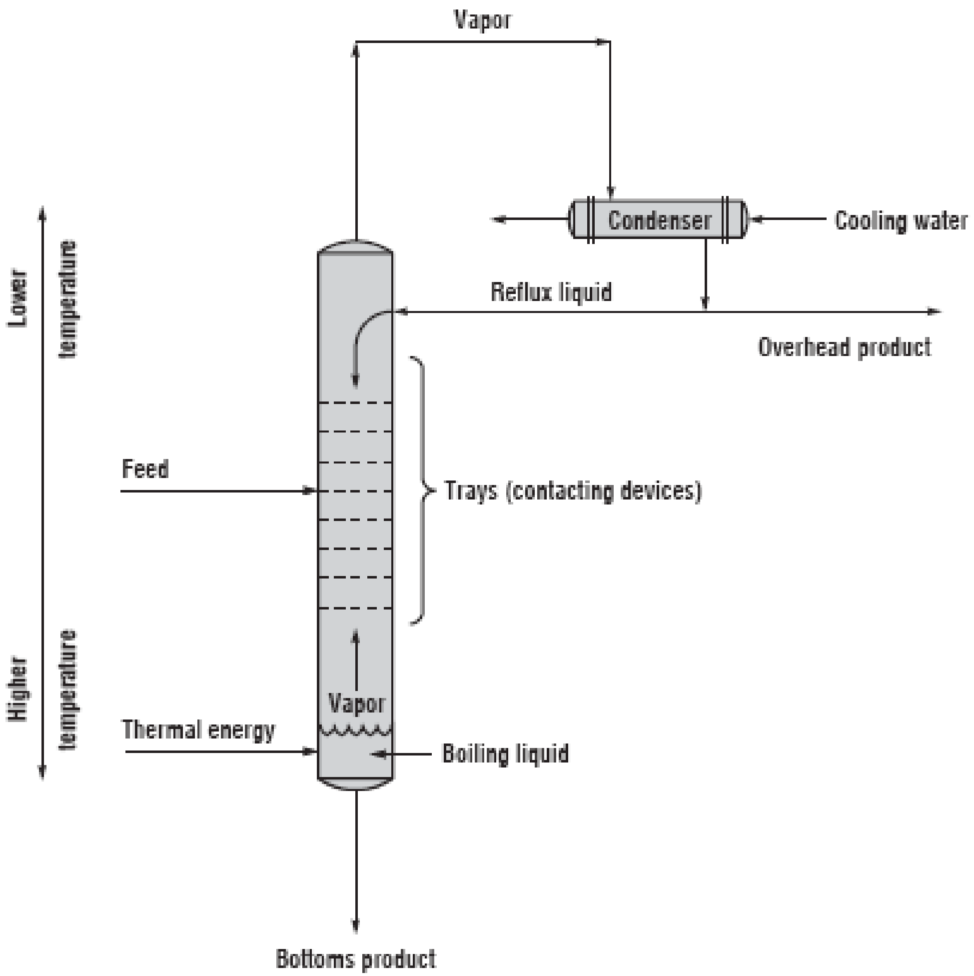
Water (95.63% w/w) and ethanol (4.67 % w/w) form an 'azeotrope'. Azeotrope is a mixture of two or more compounds having a characteristic boiling point such that the composition of mixture cannot be changed by simple distillation.

Dry Grind Corn Process

Distillation:



Dry Grind Corn Process

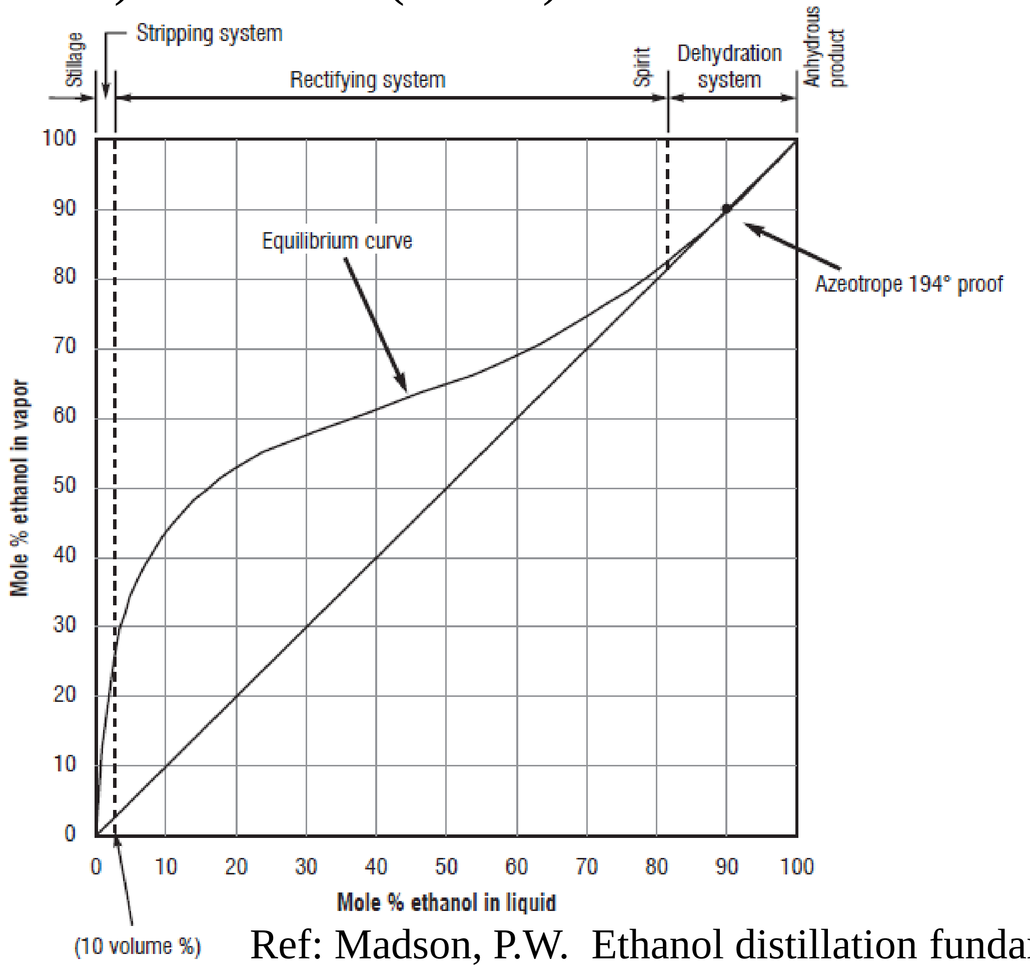


Ref: Madson, P.W. Ethanol distillation fundamentals in Alcohol textbook

Dry Grind Corn Process

Water and ethanol form a ‘positive azeotrope’ or minimal boiling mixture.

Pure ethanol (78.4°C) Pure water (100°C) Water-ethanol azeotrope (78.1°C)



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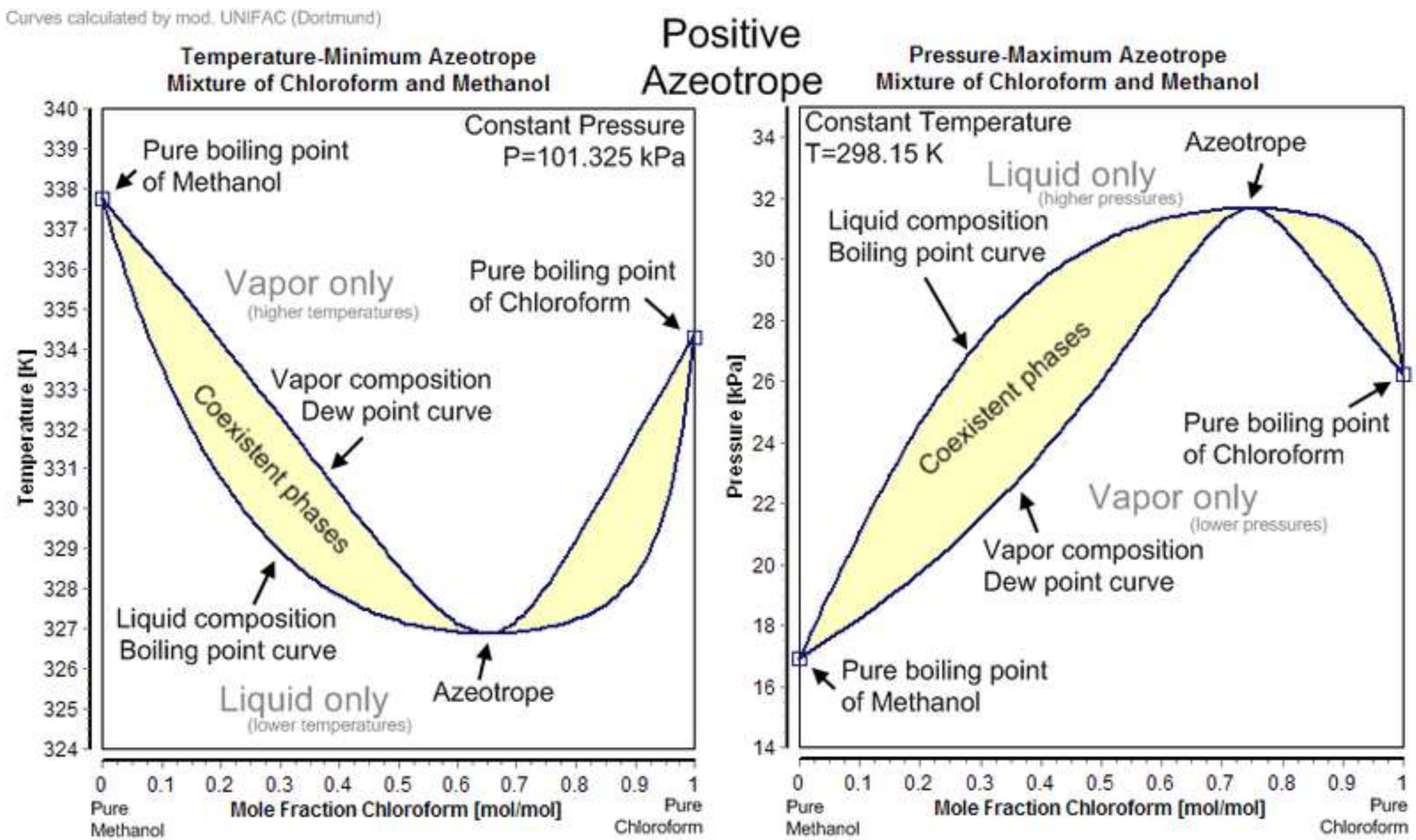
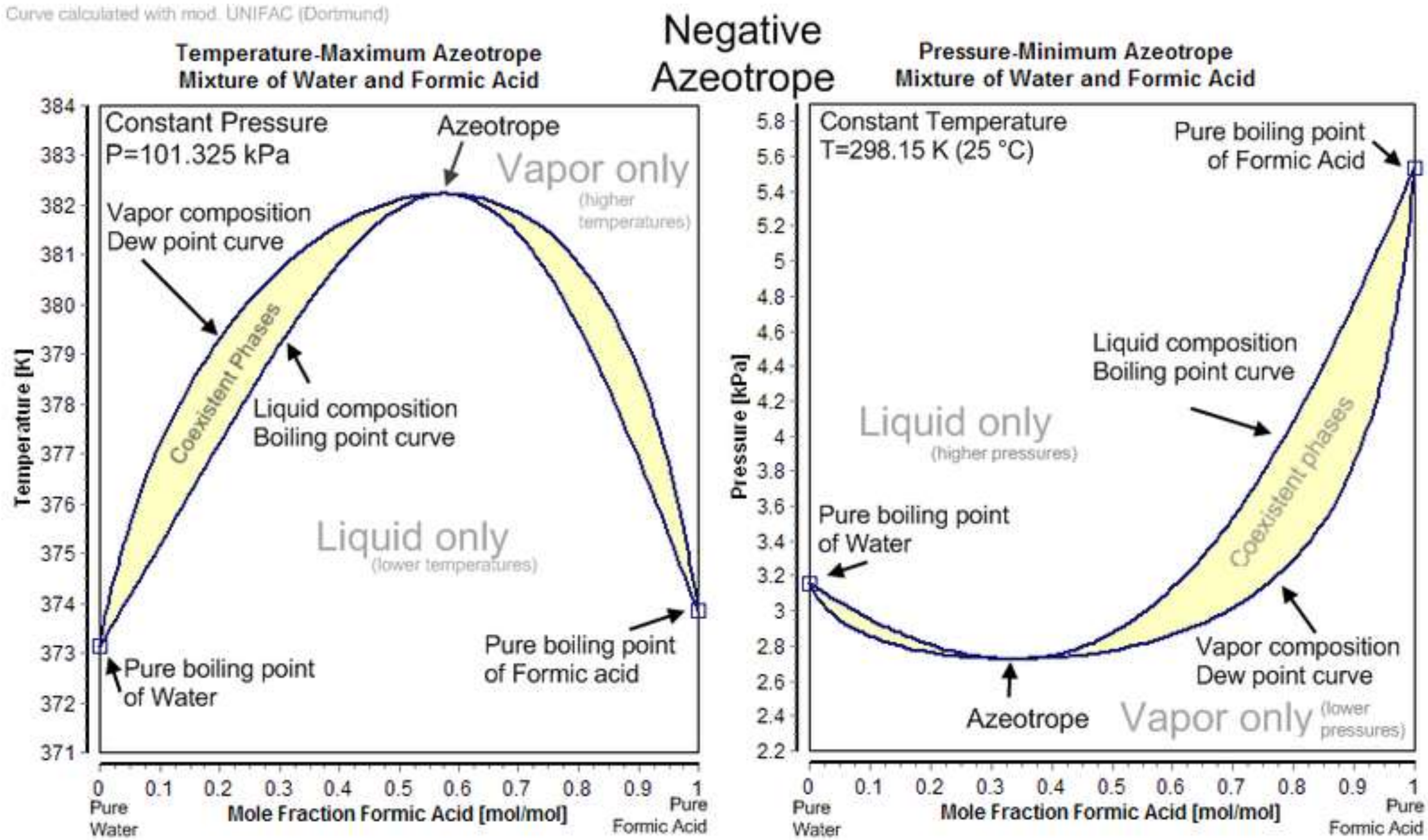
Dry Grind Corn Process



Ref: http://en.wikipedia.org/wiki/Azeotrope

Dry Grind Corn Process



Ref: http://en.wikipedia.org/wiki/Azeotrope

Dry Grind Corn Process

Molecular sieves are used to produce anhydrous ethanol.

Importance: Fuel grade ethanol must not have any water. Hence removal of traces of water from the azeotrope mixture is important.

Molecular sieve technology has largely replaced older technology using benzene to break the ethanol-water azeotrope. Molecular sieves are made of three dimensional network of silica and alumina. During the process to remove the water of hydration, they form cavities that selectively adsorb molecules.

Regeneration:

Molecular sieves are regenerated by circulating a heated carrier gas.

Ref: http://www.molecularsieve.org/Molecular_Sieve.htm

Dry Grind Corn Process

Molecular sieves are used to produce anhydrous ethanol.

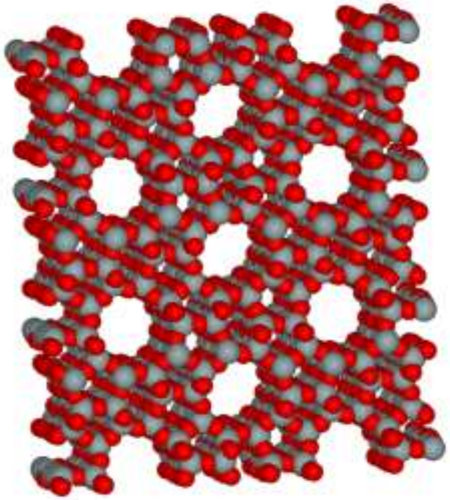
Importance: Fuel grade ethanol must not have any water. Hence removal of traces of water from the azeotrope mixture is important.

Commercial molecular sieve used in ethanol dehydration has pores of 3Å size (water molecule 2.8Å, ethanol 4.4Å). It is made by partial substitution of sodium ions with potassium ions in zeolite.

Zeolite

←Mineral

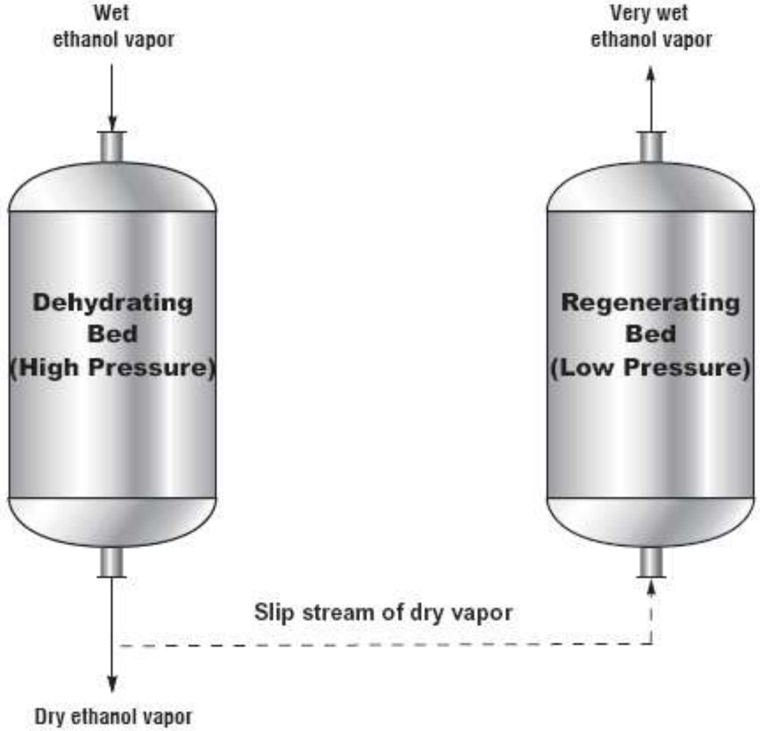
Structure→



Ref: http://www.molecularsieve.org/Molecular_Sieve.htm; http://en.wikipedia.org/wiki/Zeolite

Molecular Sieves

Molecular sieves adsorb more moisture at higher pressure. Using this effect (Pressure swing process), one of the beds is maintained at high pressure (operating/dehydrating) bed while the other is maintained at relatively low pressure and purged with pure ethanol vapors to regenerate the molecular sieves.



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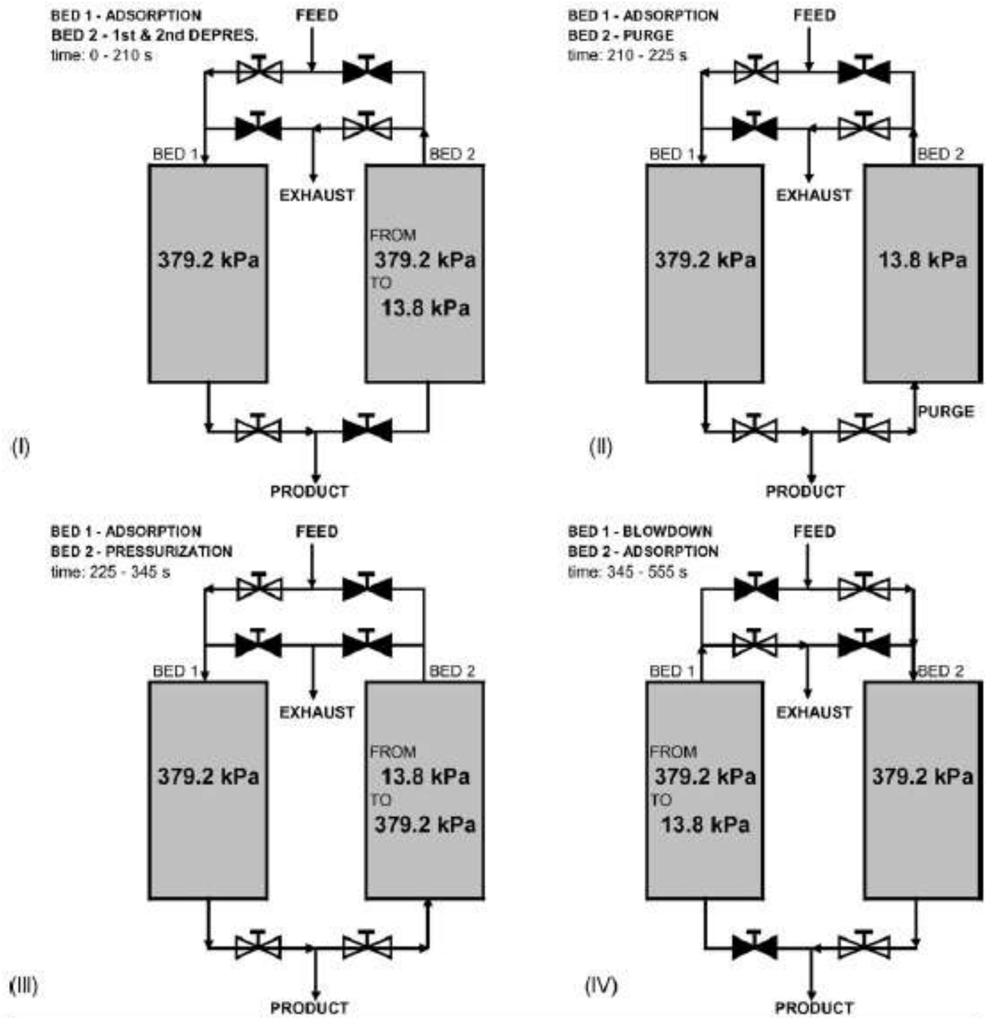
Molecular Sieves

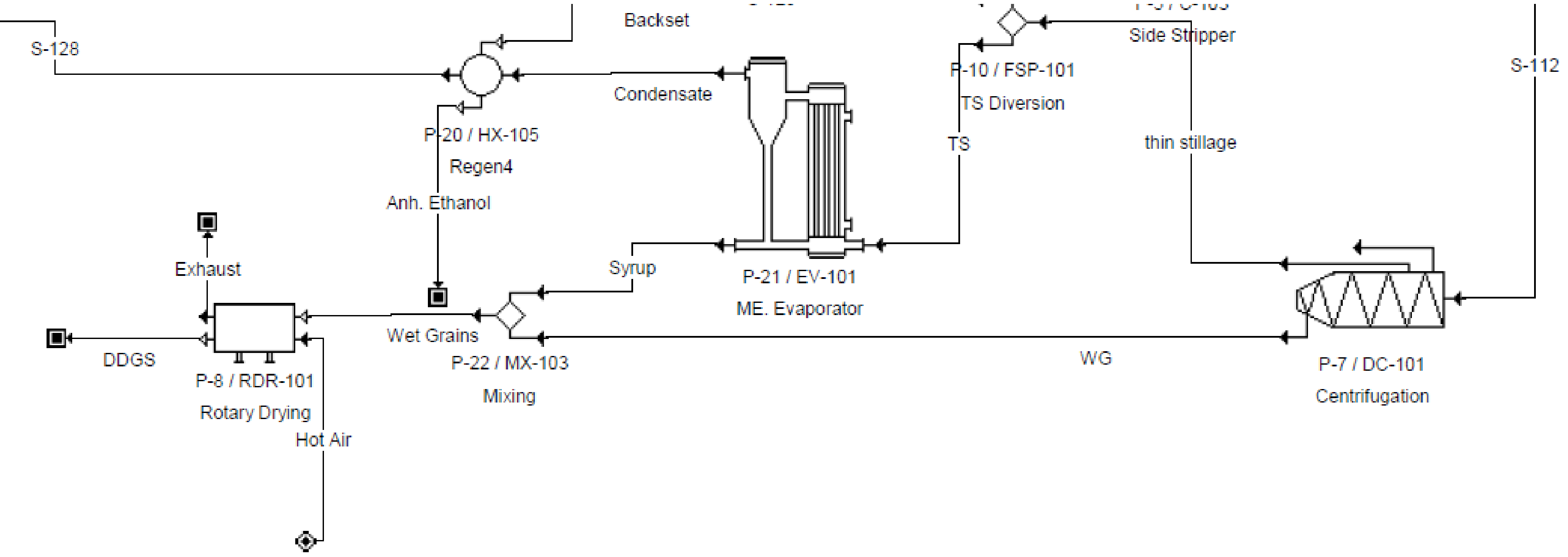


FEED: 92 wt% ethanol, 8wt% water, T_F=440K, F_F=20410 kg/hr

PRODUCT: ≥99.5 wt% ethanol, ≤0.5 wt% water

Ref: Simo et al. 2008

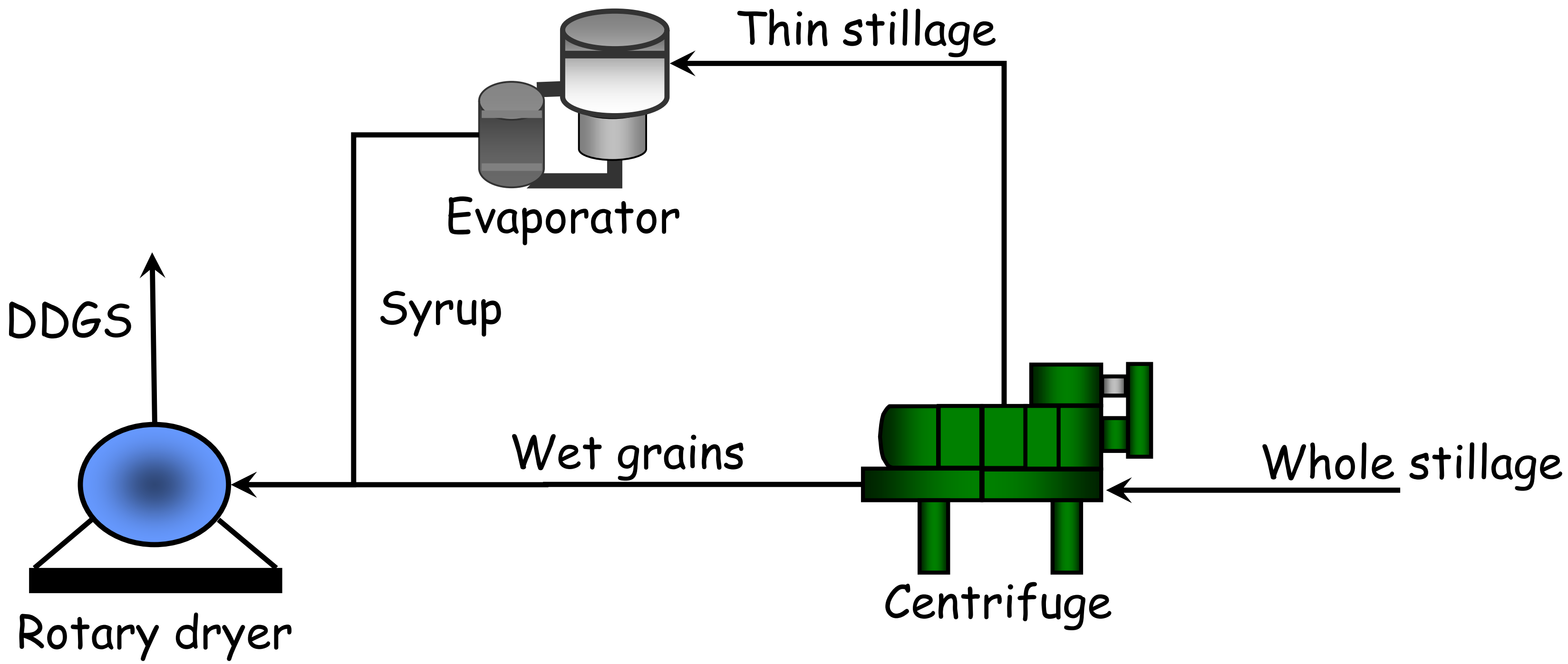
DDGS Processing



Dry Grind Corn Process

Centrifugation and Coproduct (DDGS) recovery

<u>Importance:</u> Coproducts contribute ~15% of the plant revenues.



Distillers dried grains with solubles (DDGS)

Ref: Kim et al. 2008

Dry Grind Corn Process

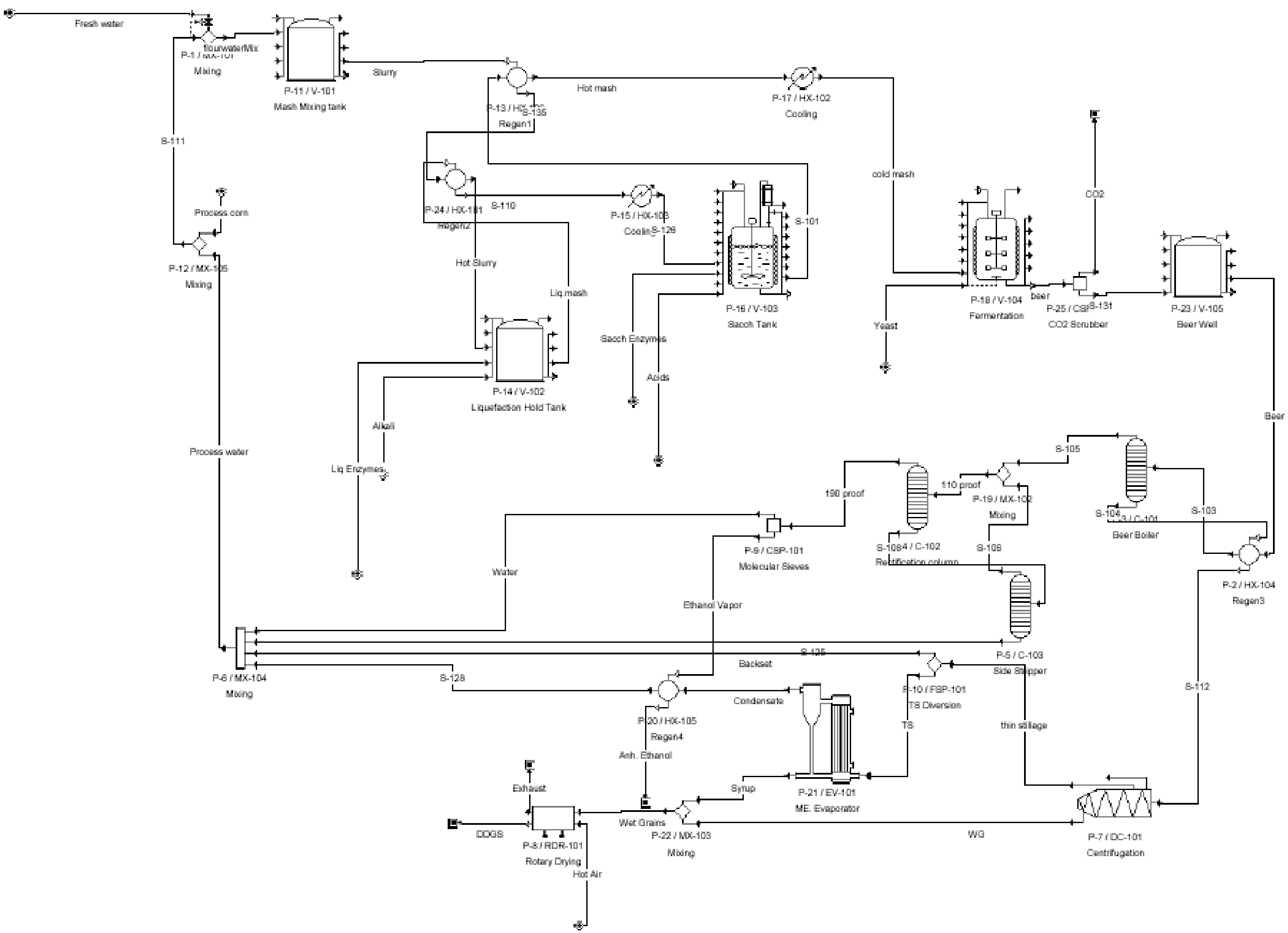
Ethanol denaturation, storage and shipping in dry grind corn process prepare ethanol for delivery.

Importance: Ethanol denaturation is a process of rendering the ethanol unsuitable for human consumption. Denatured ethanol has a lower tax liability than beverage alcohol.

Ethanol is denatured by adding 1-5% gasoline before storage in tanks.

Most of grain ethanol produced in US is shipped using railroad network.

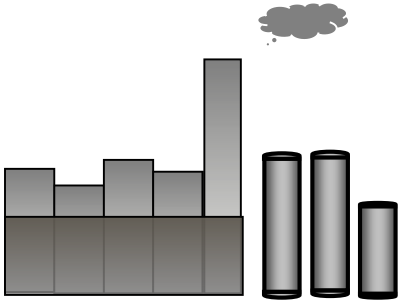
Dry Grind Corn Process



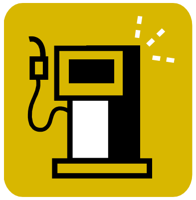
Dry Grind Corn Process

One bushel corn
(56 lb /25.4 Kg)

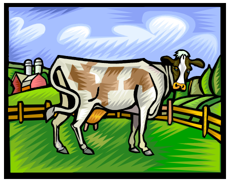
CO_2 18 lb
(8.2 Kg)



Ethanol 2.7 gal
(10.2 L)



	Corn	DDGS
Crude Protein	**9.10**	**31.3**
Starch	**71.4**	**5.1**
Oil	**4.21**	**11.9**
Ash	**nd**	**5.8**
Fiber	**nd**	**10.2**



DDGS 18 lb
(8.2 Kg)

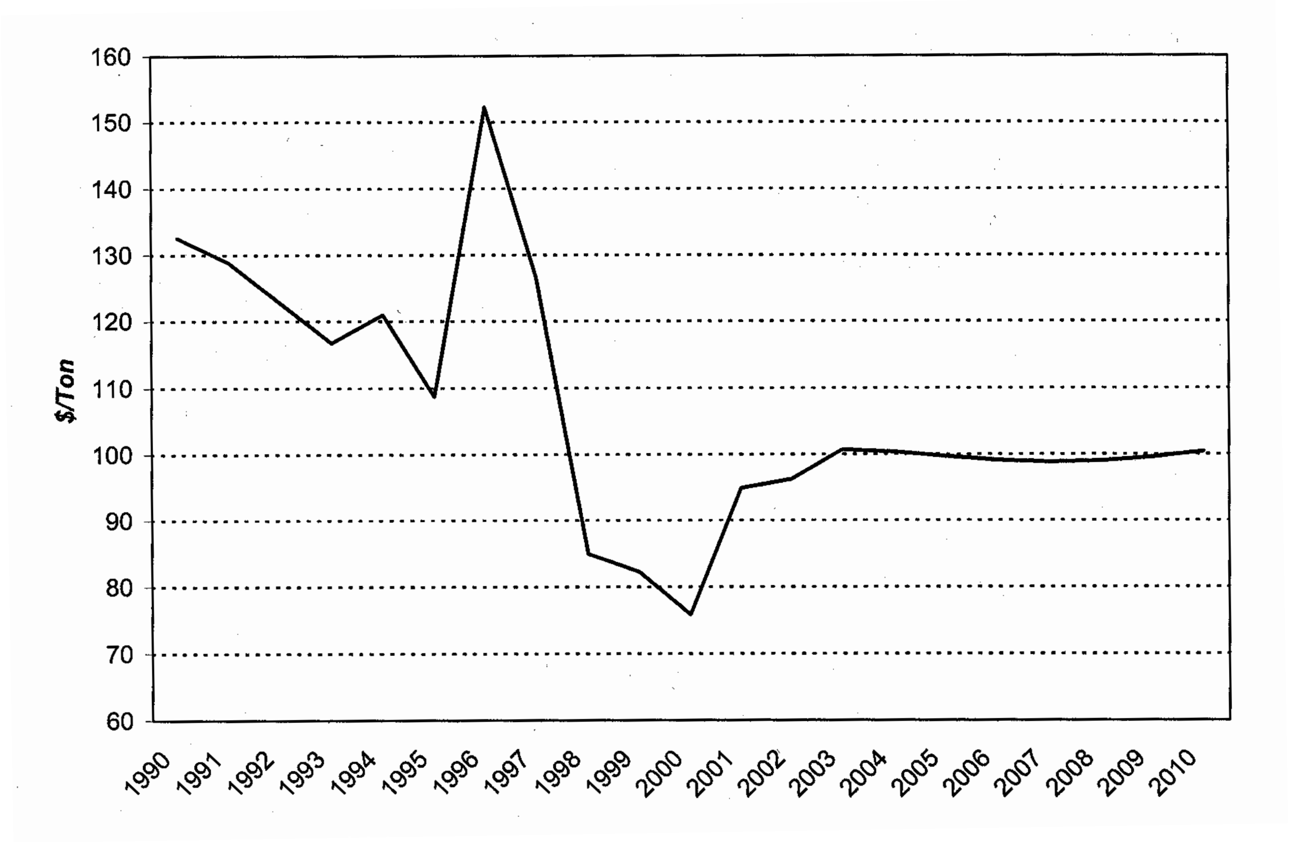
Ref: Belyea et al. 2004 and http://www.ddgs.umn.edu/

Challenges Ahead

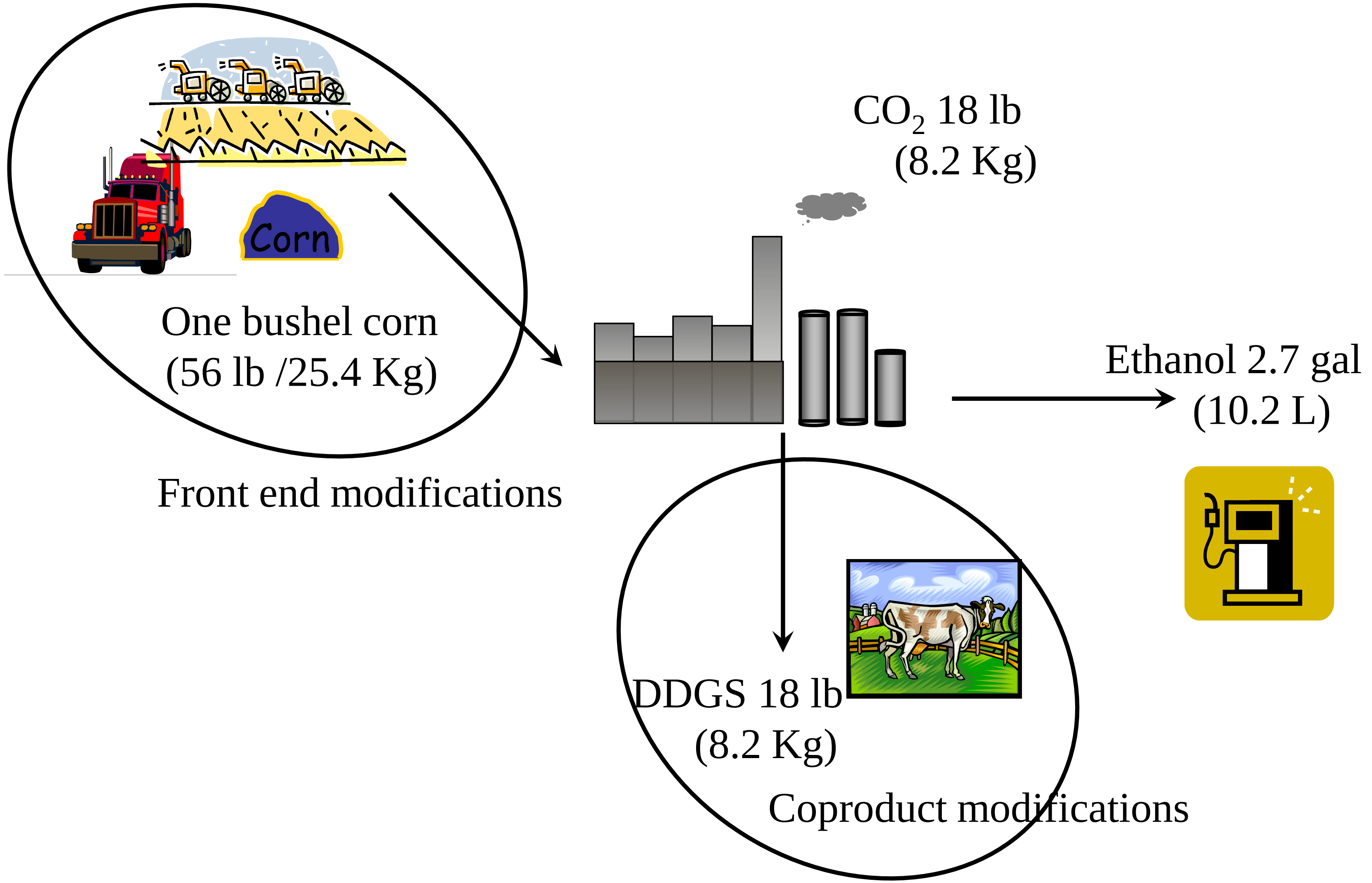
- One bushel of corn (25.4 kg or 56 lb) produces
  - 10.6 L (2.8 gal) ethanol
  - 7.2 kg (17 lb) DDGS
- DDGS has 3-6% of residual/unconverted starch
- DDGS is mainly fed to ruminants due to high fiber content
- DDGS markets will be saturated due to limited markets and increased production. There is a necessity to reduce DDGS volume

Modification of Conventional Dry Grind Process: Drivers

- Low value of coproducts
- Market saturation of DDGS

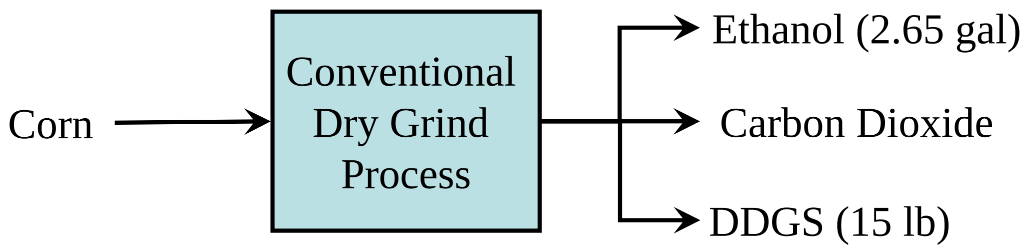


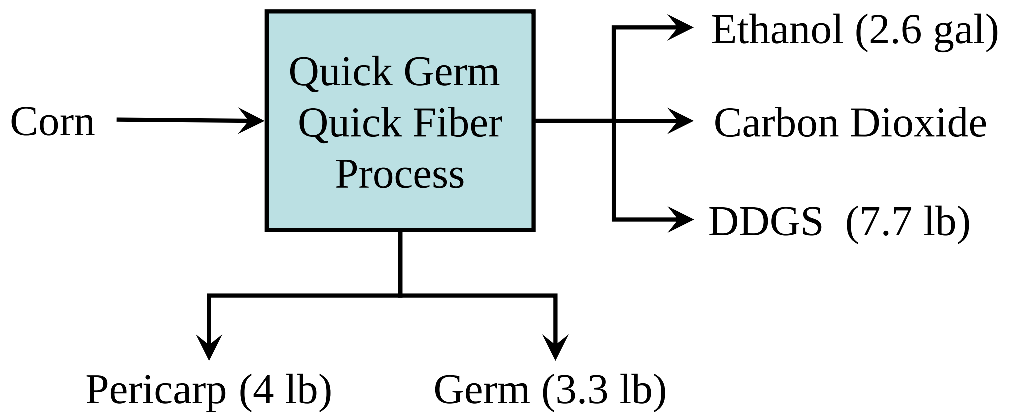
Dry Grind Processes



Modified Dry Grind Processes

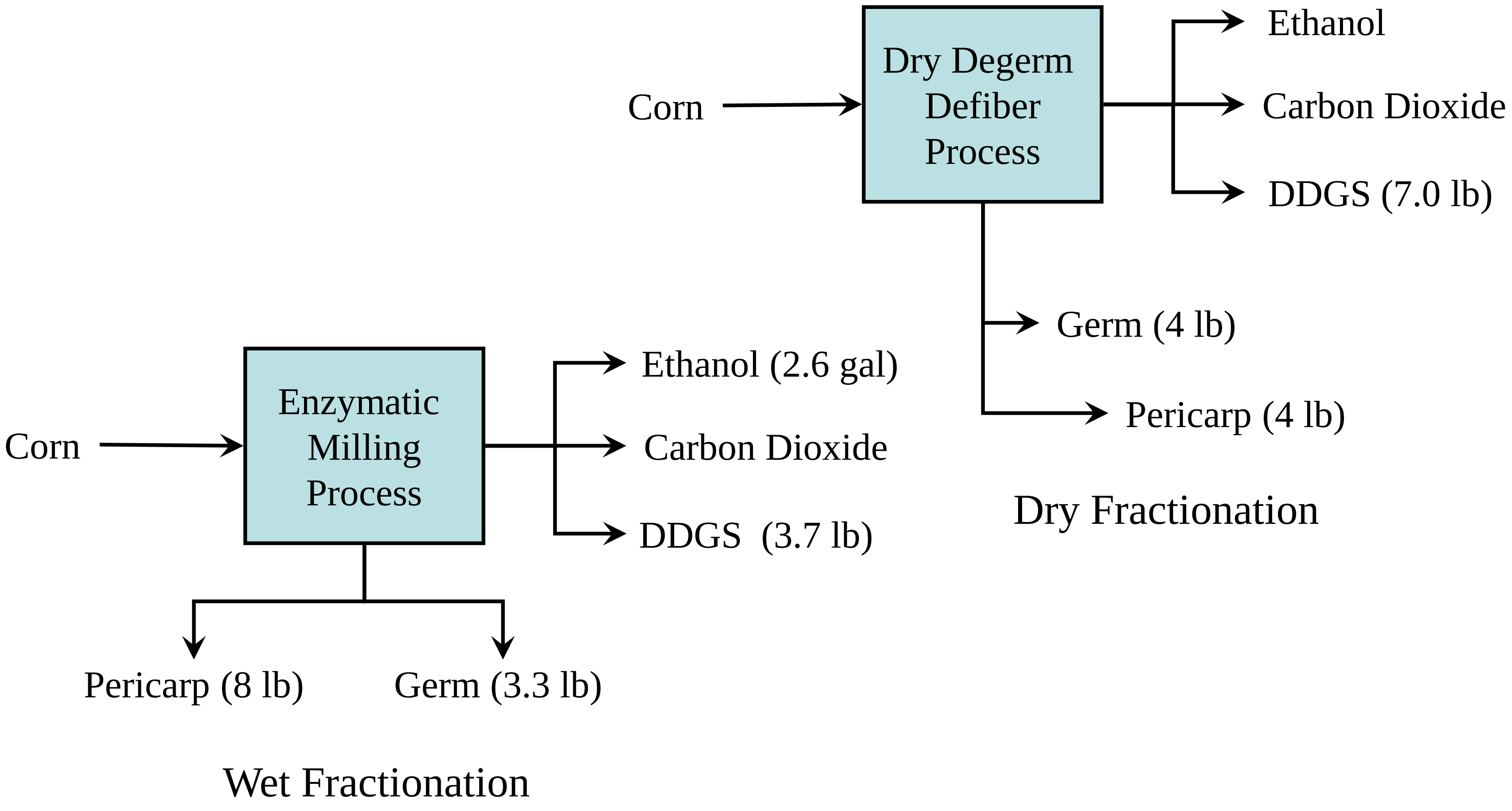
Conventional Dry Grind Corn



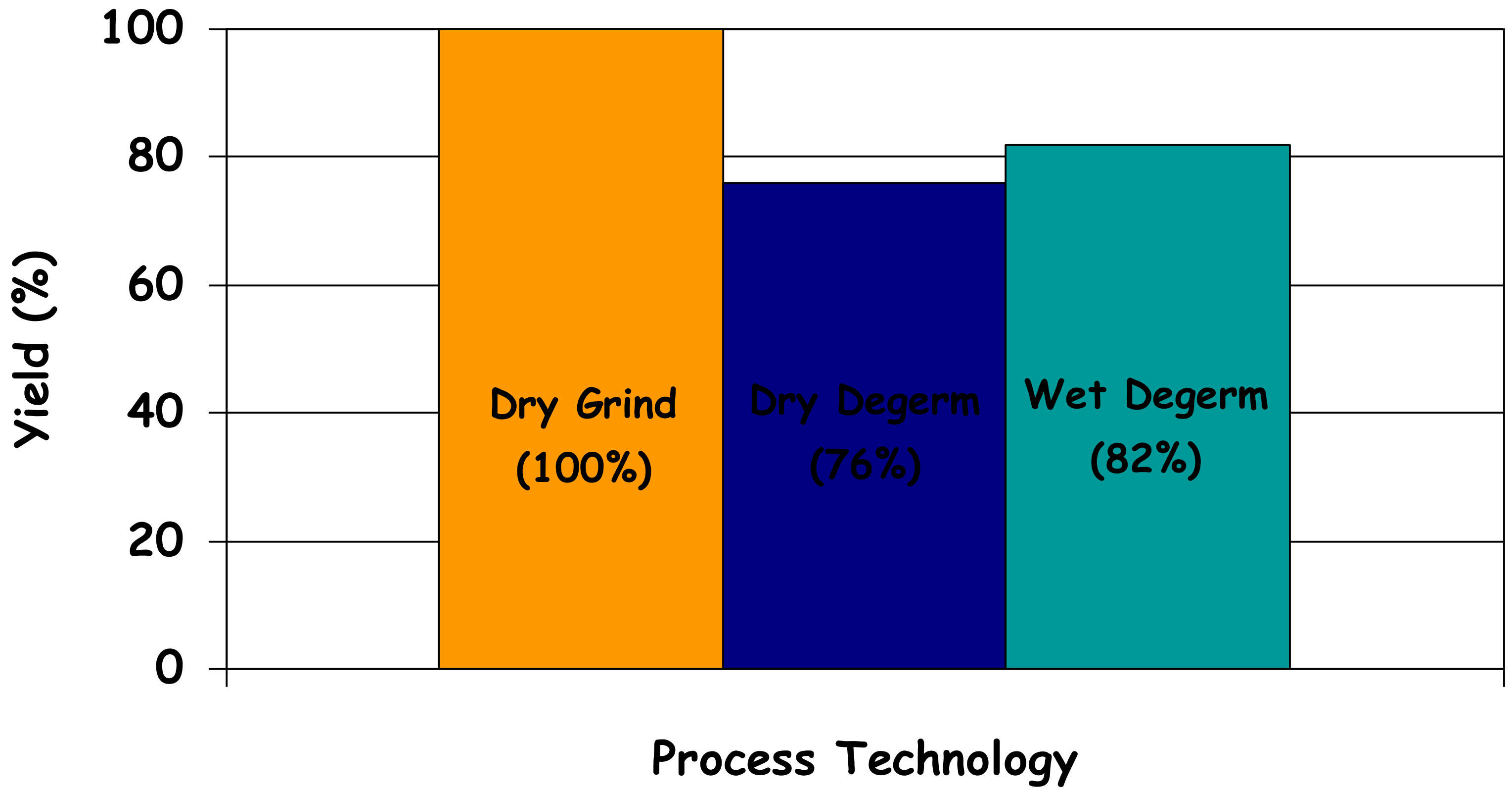


Wet Fractionation

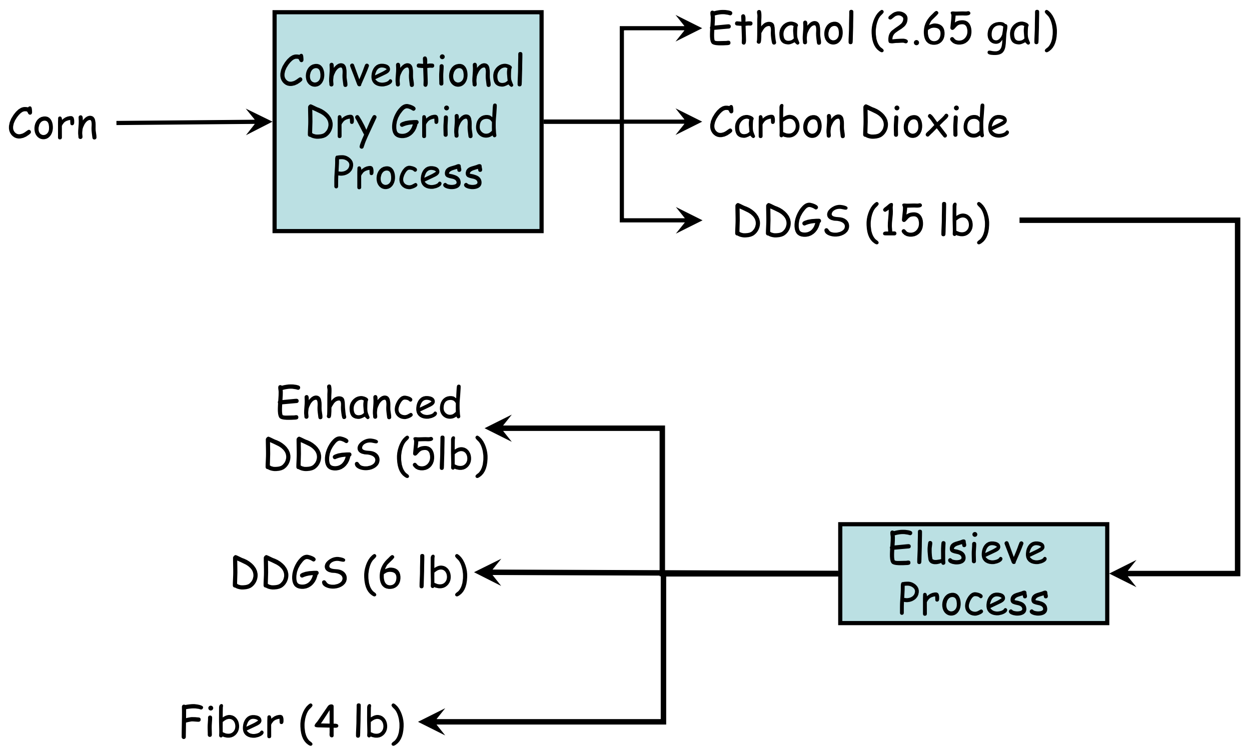
Modified Dry Grind Processes



Comparison of Modified Dry Grind Processes



Modified Dry Grind Processes



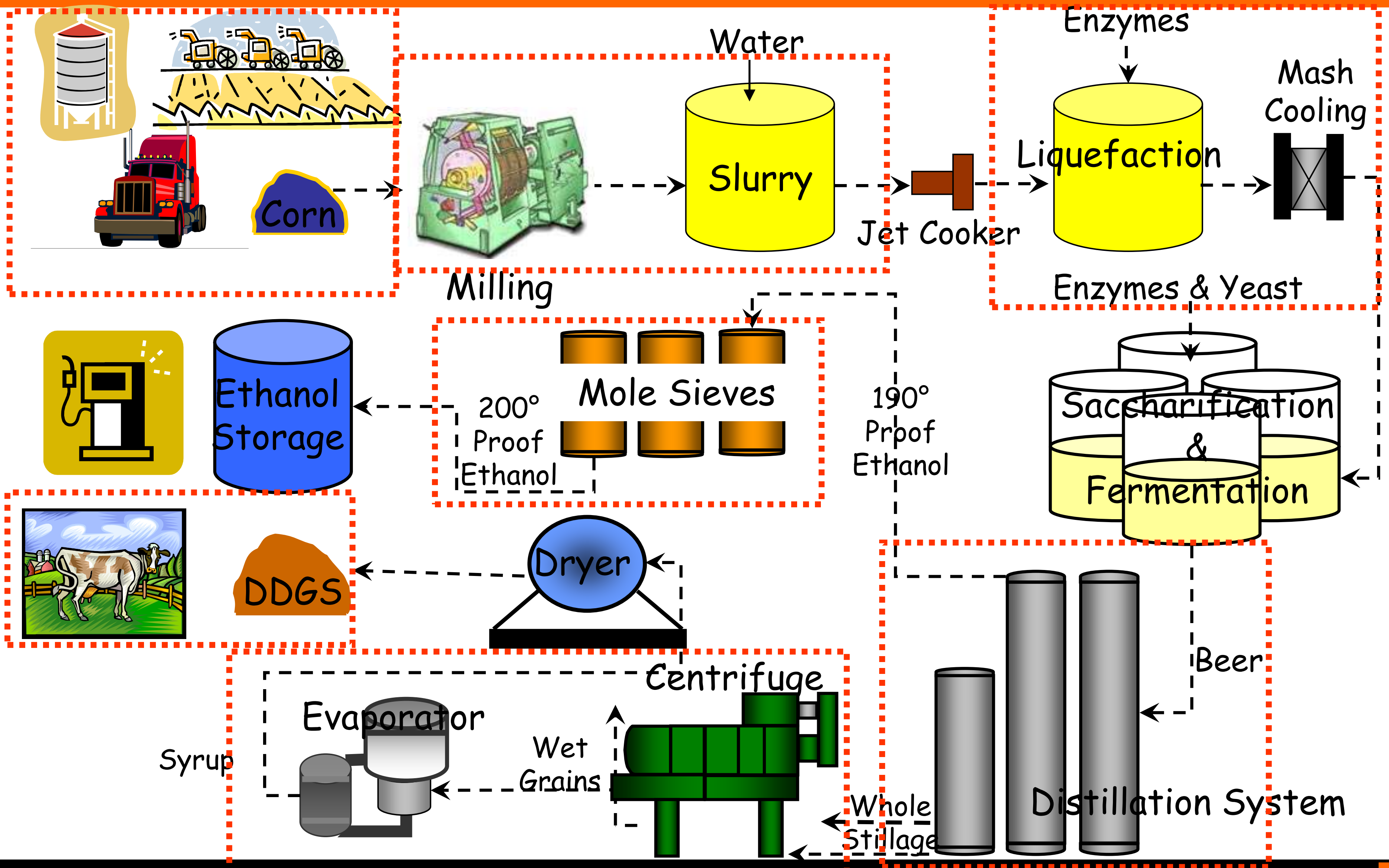
Coproduct modification

Thank you

Lecture Eleven

Process Calculations for Starch Ethanol Production

Summary of Lecture Ten



Ethanol Production: Process Calculations

Starch hydrolysis

$$[C_6H_{10}O_5]_n + (n\text{-}1)\ H_2O \rightarrow n\ [C_6H_{12}O_6]$$

Hydrolytic gain:

Molecular wt. of Glucose : 12x6+1 x12 + 16 x 6 = 180

Avg. Monomer weight of starch/ cellulose :

12x6+1 x10 + 16 x 5=162

Mol. Wt of Water: 18

Hydrolytic gain = (n 180)/ (n 162+18) ~ 1.11 (when n is large>100)

For every glucose monomer, one molecule of water is added during hydrolysis and therefore results in increased substrate weight during starch/cellulose hydrolysis. This increase is referred to as **Hydrolytic gain**.

Ethanol Production: Process Calculations

Starch hydrolysis

$$[C_6H_{10}O_5]_n + (n\text{-}1)\ H_2O \rightarrow n\ [C_6H_{12}O_6]$$

Efficiency of hydrolysis process is determined by many factors including composition, pretreatment, enzyme concentration and operating conditions.

Efficiency of enzymatic starch hydrolysis (70-95%) is dependent on amylose/amylopectin ratio and resistant starch.

Ethanol Production: Process Calculations

Fermentation

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

Fermenting one mole glucose, results in 2 moles of ethanol and 2 moles of carbon dioxide.

On a weight basis:

180 g of glucose → 92 g ethanol and 88 g Carbon dioxide

i.e. Ethanol = 0.51 glucose (w/w);

Carbon dioxide=0.49 glucose(w/w)

Efficiency of well controlled fermentation is very high (>95% conversion efficiency).

Ethanol Production: Process Calculations

Ethanol yield calculation example:

What is the yield of corn ethanol (gal per bushel) in a conventional dry grind process ?

Basis: Corn (10% moisture, 70% starch, 7% protein, 6% oil, 5% fiber, 2% ash)

Assume:

- Resistant starch is 3% of total starch
- Efficiency of hydrolysis is 90%.
- Efficiency of fermentation is 98%.
- DDGS moisture content as 12% (wb)

Ethanol Production: Process Calculations

Ethanol yield calculation example:

Calculations: One bushel =56 lb

Total starch= 56 x 0.70 = 39.2 lb

Resistant starch = 0.03 x 39.2 = 1.18 lb

Hydrolysable starch = 39.2 -1.18 = (1.0 -0.03) x 39.2 = 38.02 lb

Glucose produced = 0.9 x 1.11 x 38.02 = 37.98 lb

Ethanol produced = 0.98 x 0.51 x 37.98= 18.98 lb

Gal of ethanol = 18.98 x (0.454) /(0.789 x 3.79) = 2.88

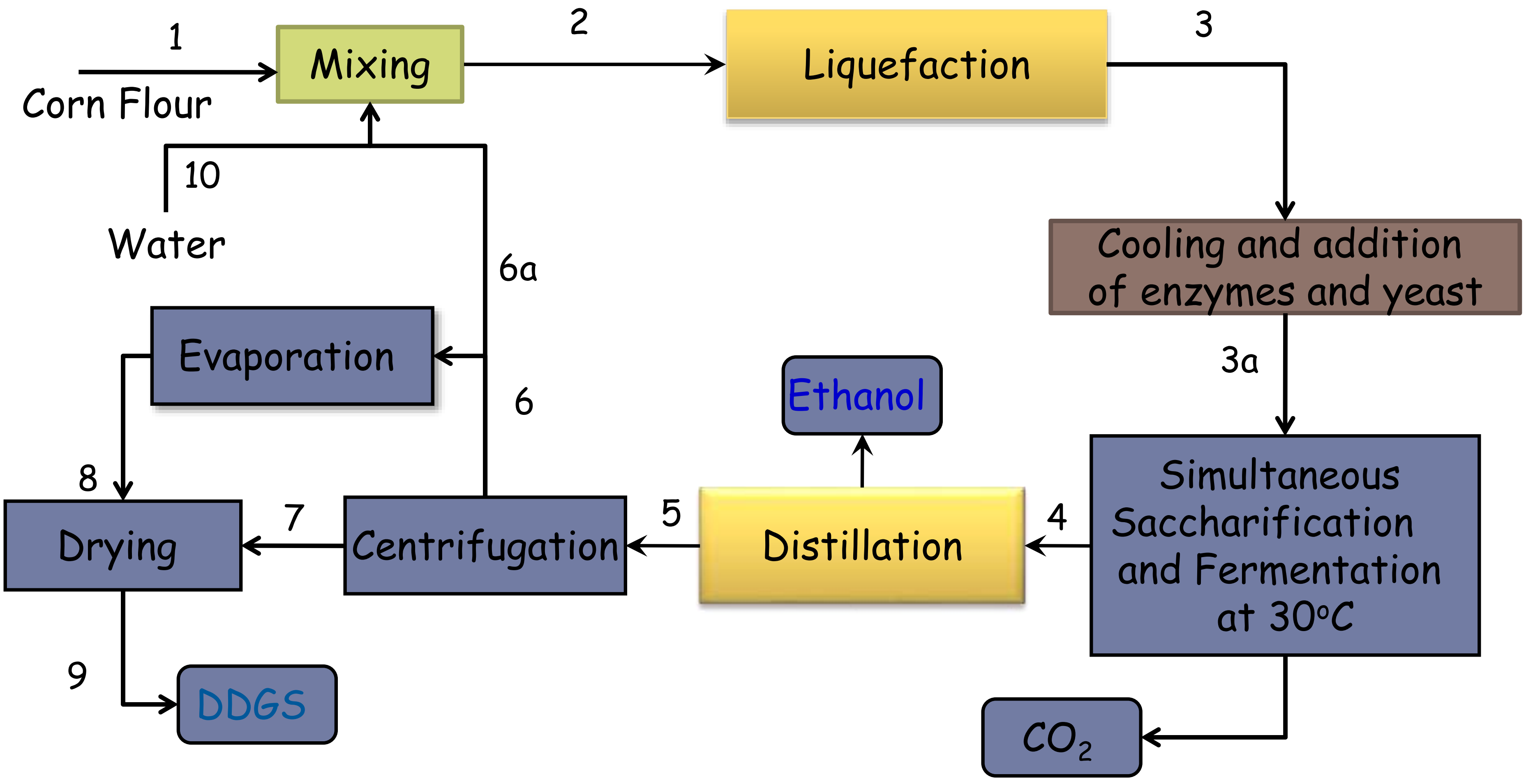
DDGS (dry weight) = 56 x (0.07+0.06+0.05+0.02) +Resistant starch + residual starch =11.2+1.18+38.02 x 0.1=16.2 lb

DDGS (Assuming 12% moisture) = 1.12 x 16.2 =18.12

Ethanol Yield = 2.88 Gal/ bu

Overall process efficiency = 0.9 x 0.98 = 0.882

Ethanol Production: Process Flow Calculations



Ethanol Production: Process Flow Calculations

Ethanol Process flow calculation example:

What are the process flows in the a conventional dry grind process ?

Basis: 100 kg of Corn (10% moisture, 67% starch, 9% protein, 8% fiber, 4.2 % oil, 1.8% ash)

Assume:

- Resistant starch is 3% of total starch
- Efficiency of hydrolysis (liquefaction and saccharification) is 95%.
- Efficiency of fermentation is 98%.
- DDGS moisture content as 12% (wb)
- Mash solids content is 34%
- Syrup has 35% solids
- Thin stillage has 5% suspended solids and 90% soluble solids.
- Thin stillage recycle:
  - 0% of thin stillage is recycled.
  - 30% of thin stillage is recycled.

First Generation Fuels: Challenges and Path Ahead

- Food vs. Fuel debate
- Limited capacity to meet the fuel needs
- Intensive use of agricultural inputs
- Relatively low Net Energy Balance
- Impact on environment
- Need for Arable lands
- Need for fresh water

Second generation biofuels such as ethanol from cellulosic feedstocks and third generation fuels such as algae biofuels address some of these concerns.

Thank you