Ethanol Production and Safety

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Outline

- Introduction of bioenergy
- Ethanol production
  - Feedstocks (starch, cellulosic materials)
  - Fermentation
  - Starch-based ethanol production
  - Lignocellulosic ethanol production
  - Safety issues

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Introduction
Bioenergy/Bioproducts

Feedstocks

- Trees
- Grasses
- Agricultural Crops
- Agricultural Residues
- Animal Wastes
- Municipal Solid Waste
- Food Processing

Conversion Processes

- Acid/enzymatic hydrolysis
- Fermentation
- Bioconversion
- Chemical Conversion
- Gasification or Pyrolysis
- Anaerobic Digestion

Bio-products

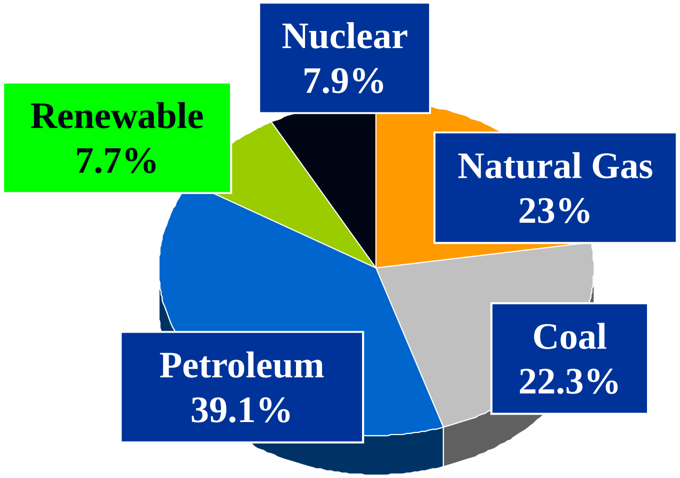
Energy products:

- Ethanol
- Renewable Diesel
- Power
- Electricity or Heat

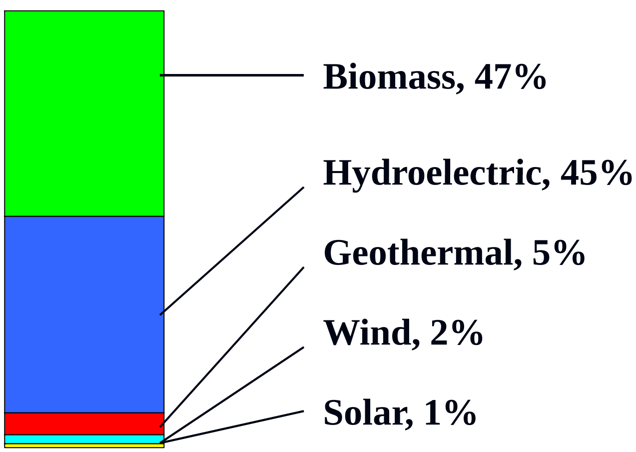
Chemicals:

- Plastics, resins, foams
- Phenolic resins
- Solvents, cleaning fluids
- Chemical Intermediates
- Adhesives
- Fatty acids
- Carbon blocks
- Paints, coatings
- Dyes, Pigments, and Ink
- Detergents
- Hydraulic fluids, etc.

Introduction
Facts of U.S. Energy Use*



Energy Sources



Renewable Energy Sources

Energy Use

- U.S. energy use: 97 Quads/year
- Population: 300 million
- Energy use/Capita: 324 million Btu

*: from USDA/DOE Billion Ton Study

Energy Facts

- 60% of oil reserves are in sensitive regions
- 75% of total CO_2 emissions are from fossil fuel
- 10k to 20k jobs per every billion gallons of ethanol production will be created

*: from DOE's Road Map to the Energy Future

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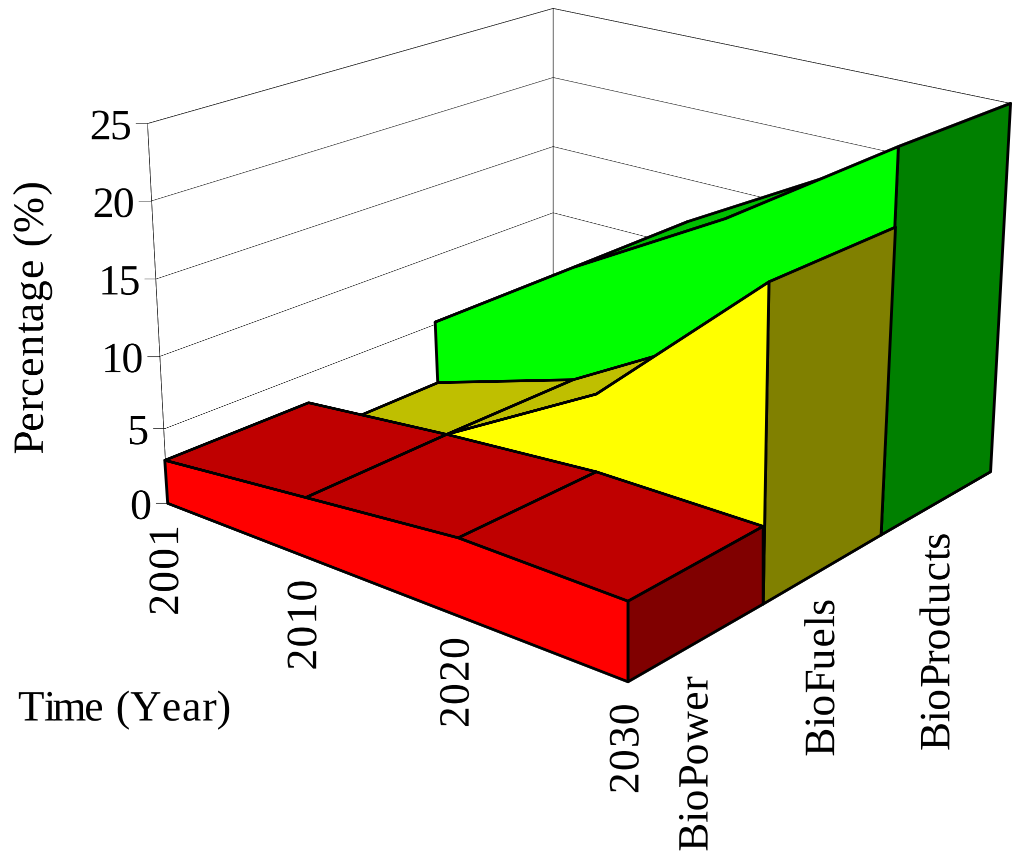
Introduction
Drivers for Bioenergy/Bioproducts

- **Energy security**
- **Environmental benefits**
- **Economic development - additional revenue for the communities and new job opportunities**

Introduction

U.S. DOE Vision for Bioenergy/Bioproducts*



BioPower - Biomass share of electricity & heat demand in utilities and industry
BioFuels - Biomass share of demand for transportation fuels
BioProducts - Share of target chemicals that are biobased

*: From Annual Report to Congress on the Biomass Research and Development (USDA-DOE)

Introduction

Michigan Agriculture and Forestry

General*:

- Agriculture: No.2 industry in the state
- Agricultural residents: 1 million
- Farms: 53,000
- Gross production: $ 60 billion
- Export value of agricultural products: $ 919 million

Crops*:

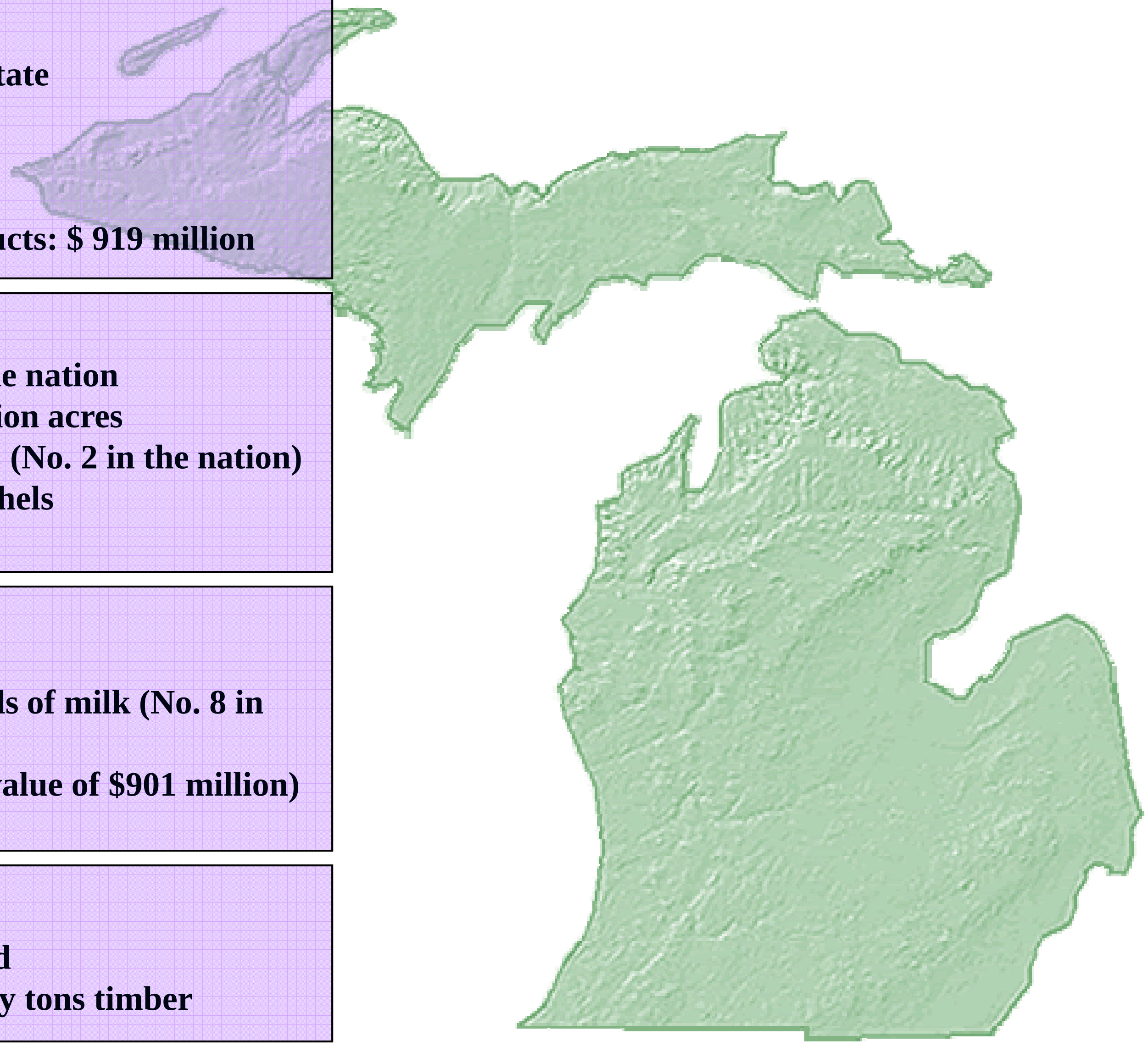
- Tart cherry production: No. 1 in the nation
- Land for corn production: 2.2 million acres
- Land for soybeans: 2 million acres (No. 2 in the nation)
- Apple production: 840 million bushels
- … etc.

Animals*:

- Dairy cows: 307,000
- Milk production: 6.3 billion pounds of milk (No. 8 in the nation)
- Cattle: 1 million head (estimated value of $901 million)
- … etc.

Forest biomass*:

- Area: 19 MM acres of forested land
- Supply: Approximately 23 MM dry tons timber



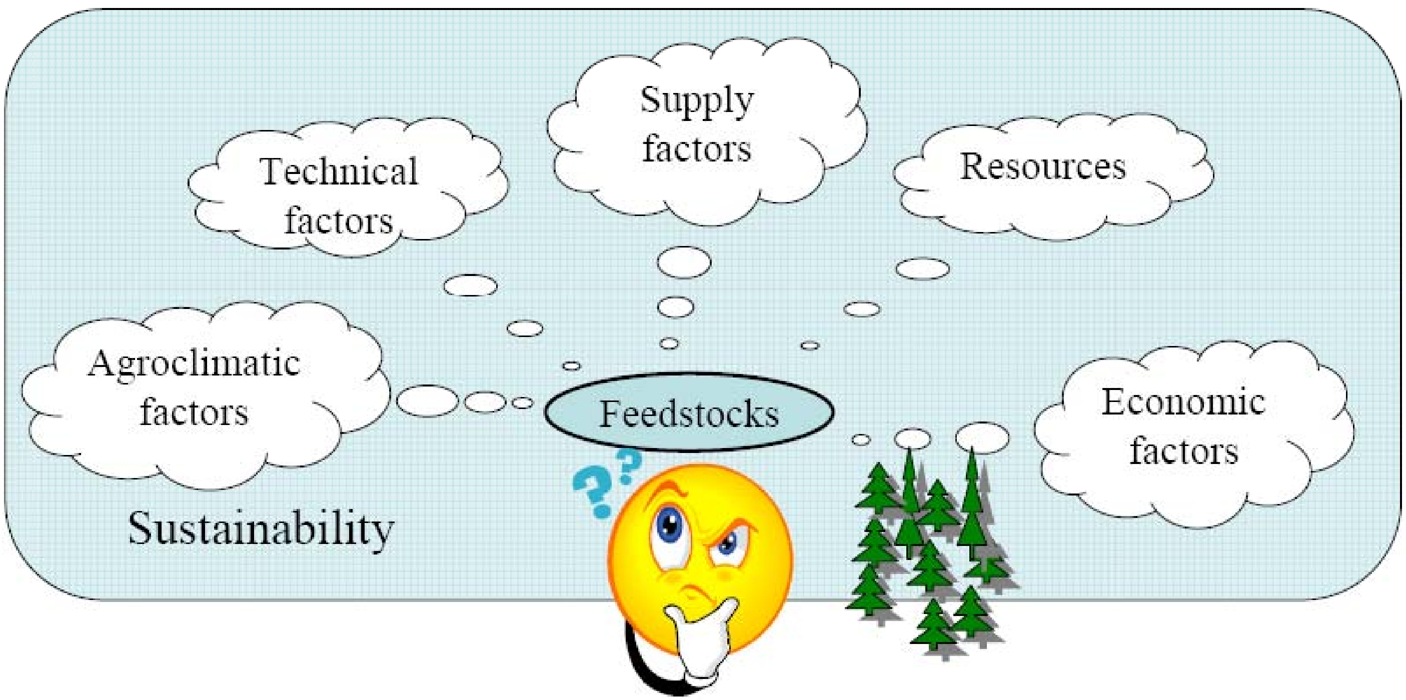
*: from: www.agclassroom.org/mi

Feedstocks

Critical factors of evaluating feedstocks

Technical factors:
- Chemical and physical properties of feedstocks
- Conversion processes technologies
- Scale of operation issues

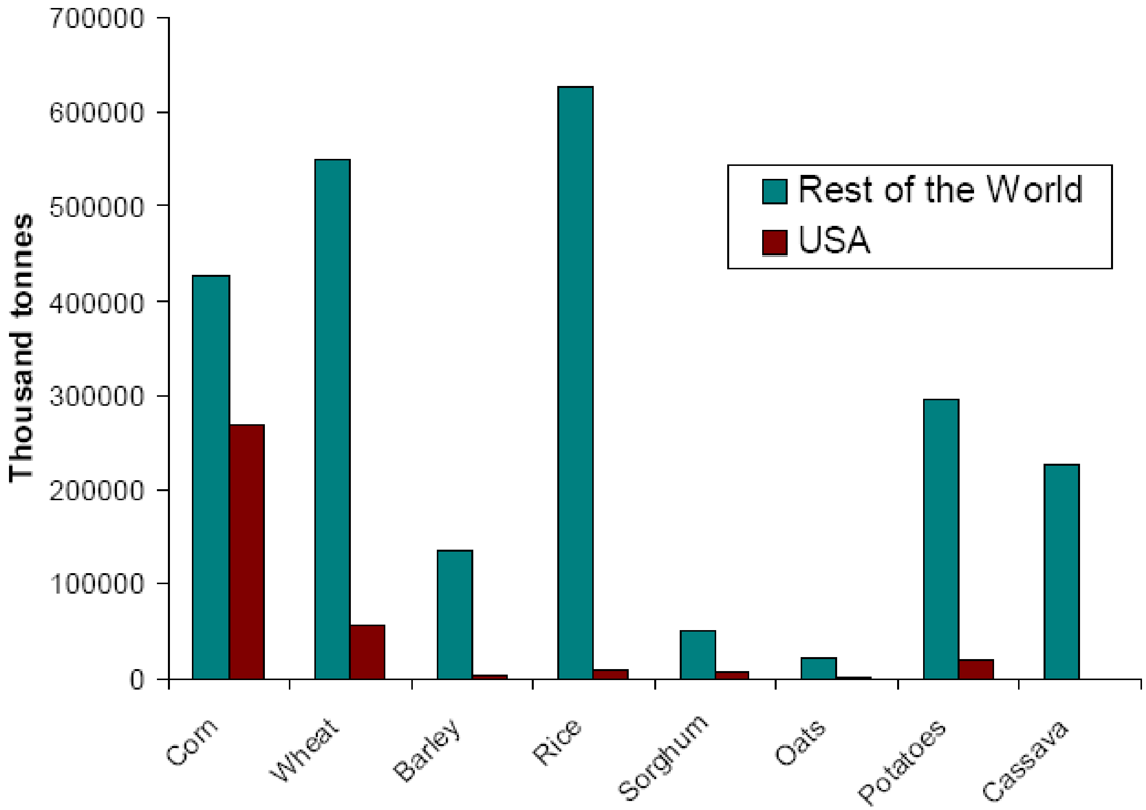
Supply factors:
- Recent availability and future forecast
- Geographical distribution



Feedstocks -- Starch

Major sources of starch in the world

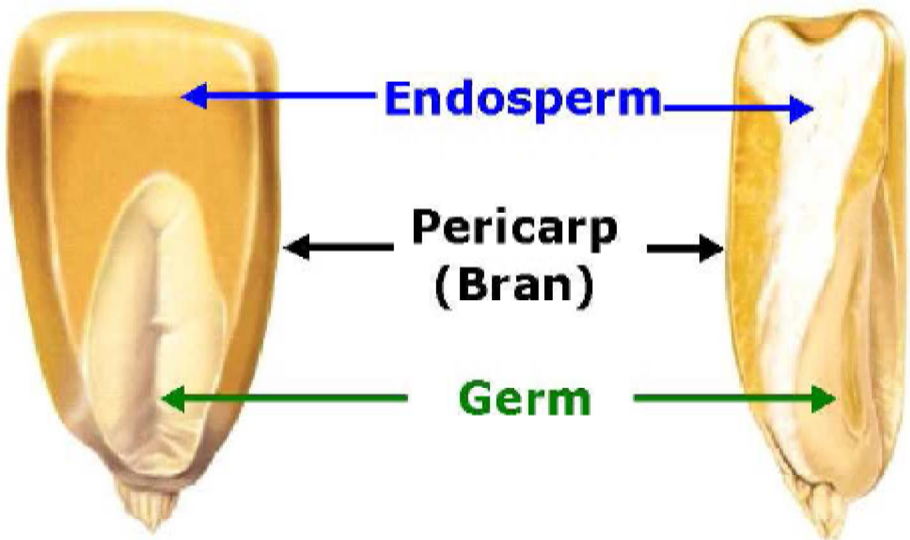
- Cereals: Wheat, corn, rice, barley, oats, sorghum
- Minor grains: Millets, rye, triticale
- Tubers and roots: Potatoes, sweet potatoes, cassava

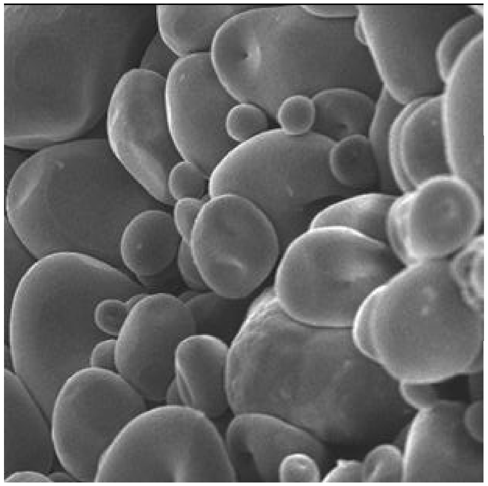


Ref: http://faostat.fao.org/site/567/DesktopDefault.aspx?PageID=567

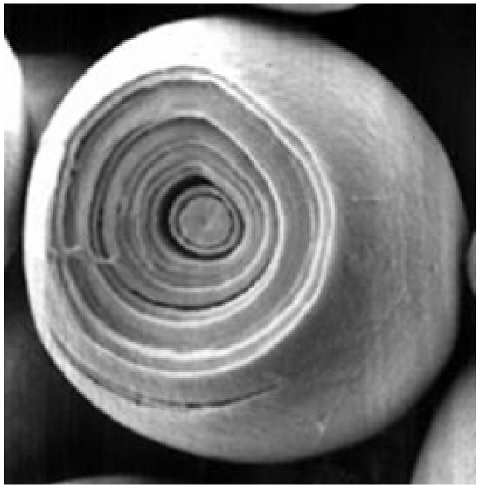
Feedstocks -- Starch

Corn Kernel Structure





Starch granule



Growth rings in a starch granule

Feedstocks – Cellulosic Material

Major source of cellulosic material

- Agricultural residue:
  Corn stover, wheat, rice, barley, oats, sorghum, rye and grass straw

- Forestry residue:
  Logging, forest slash, mill waste, pulp liquor

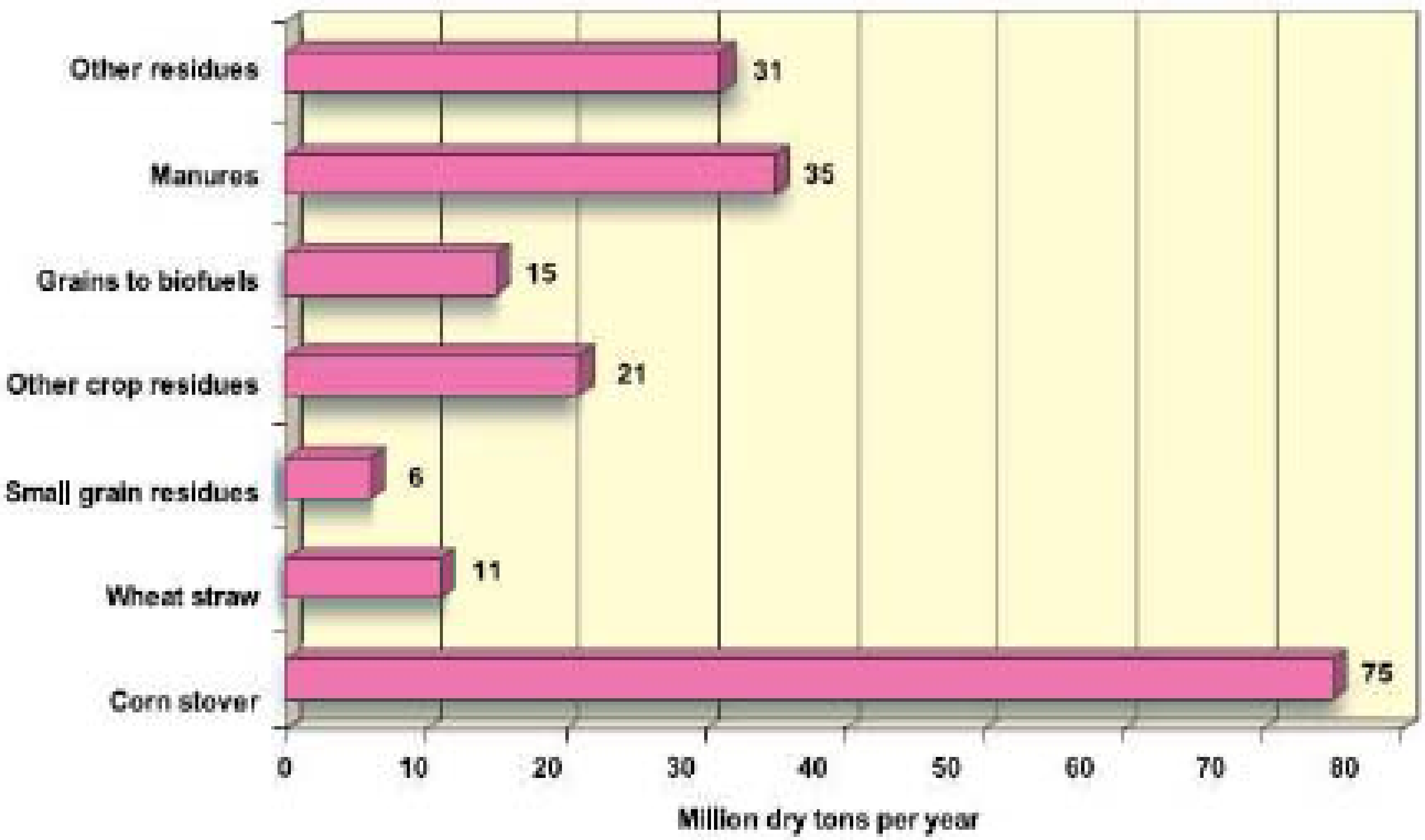
- Herbaceous crops:
  Perennial grasses such as switchgrass, rye grass, miscanthus, and giant reed
  Legumes such as alfalfa, lespediza, clover

- Short rotation woody crops:
  Poplar, silver maple, sweet gum, willow and black locust

- Municipal/Urban residue:
  Garden waste, construction debris

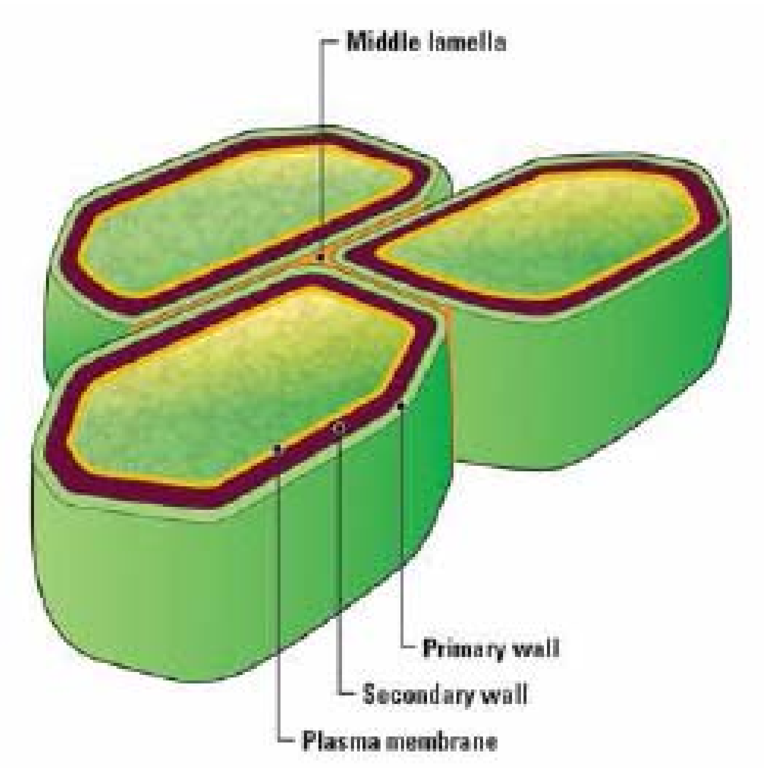
Ethanol Production

Feedstocks – Cellulosic Material

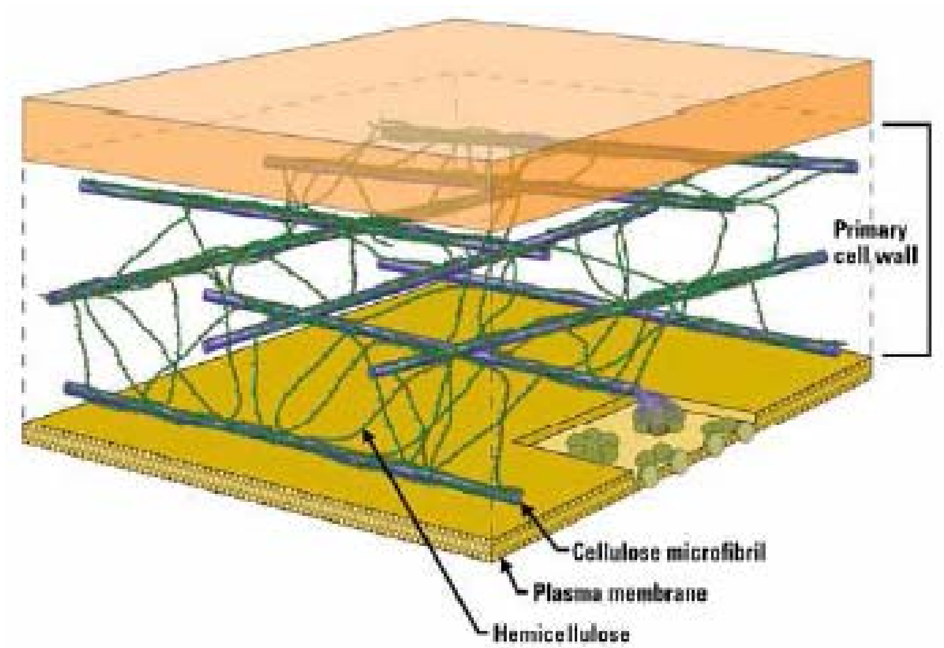


Ref: Wright et al .(2005) (Commonly referred to as Billion Ton study)

Feedstocks – Cellulosic Material



Plant cell wall

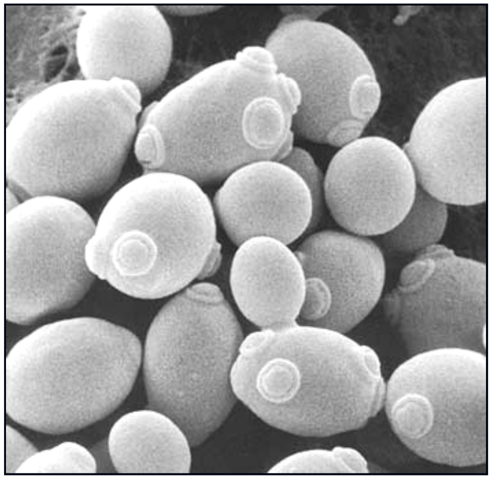


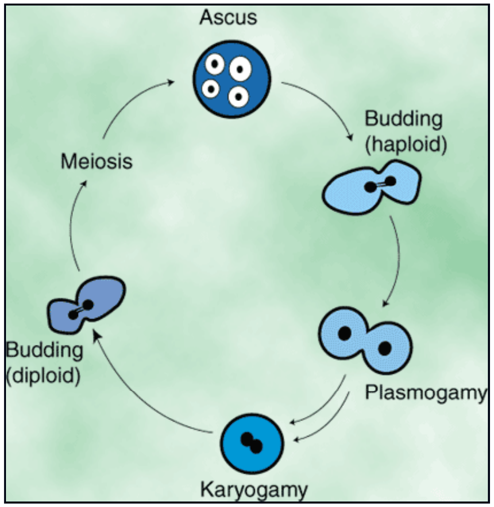
A simplified model of plant cell wall

Ref: http://genomicsgtl.energy.gov/biofuels/.

Ethanol producer – Yeast

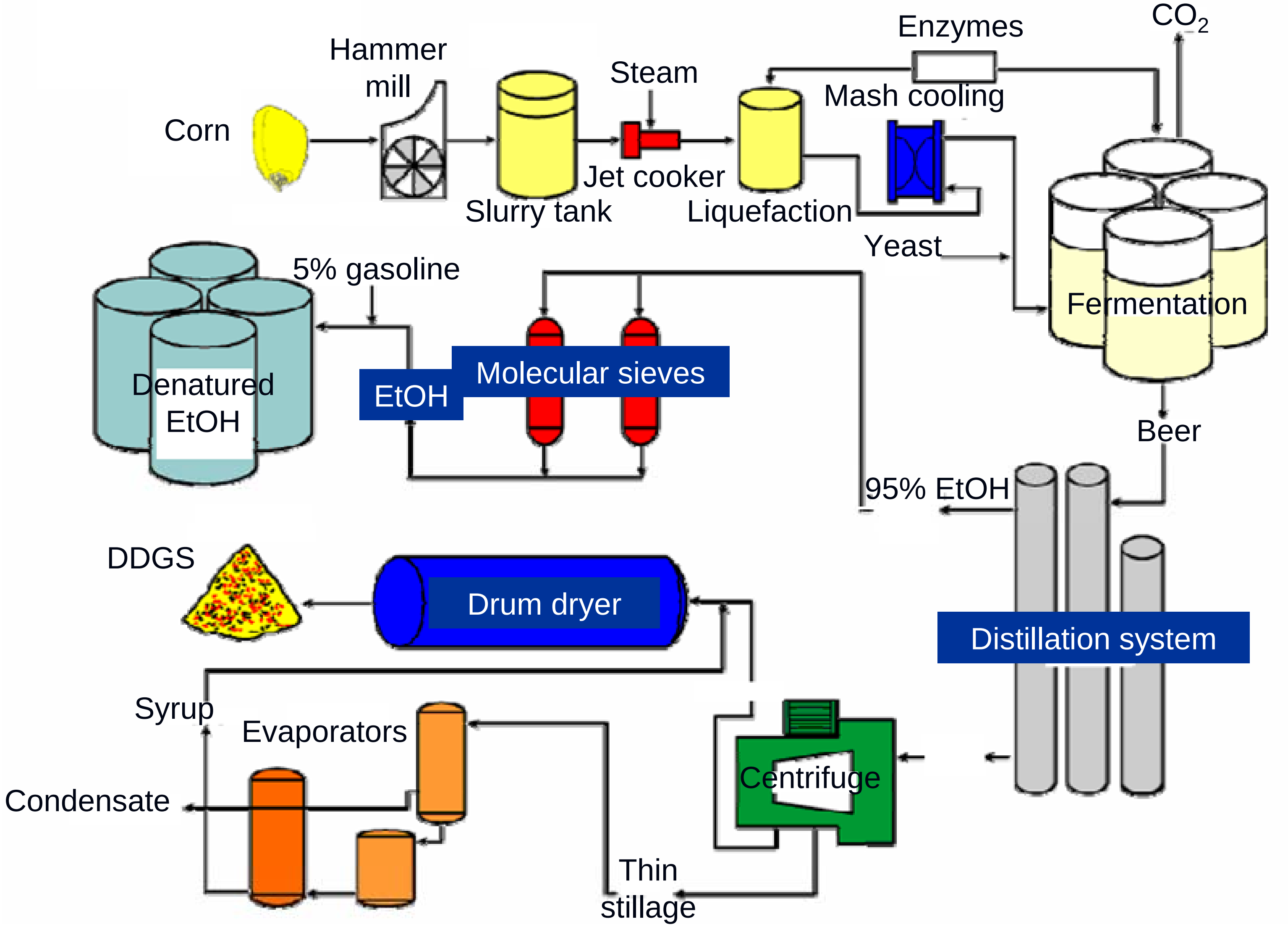
- Yeast are eukaryotic single celled fungi. Saccharomyces cerevisae is the most common yeast used in ethanol fermentations
- They have the capability to shift from completely aerobic to anaerobic metabolism
- yeast will switch to anaerobic fermentation regardless of oxygen concentration in the medium at high glucose concentrations (Crabtree effect)
- Preferentially utilize sugars in the medium (Diauxic shift)
- Cell divide 10-33 times before entering the senescent phase (Hayflick limit)
- Require carbon, nitrogen, lipids/oxygen, vitamin and other micronutrients for growth
- Viability and Vitality are important indicators of yeast health.
- Responses to changes in temperature, pH and nutrient limitation





Starch-based Ethanol Production

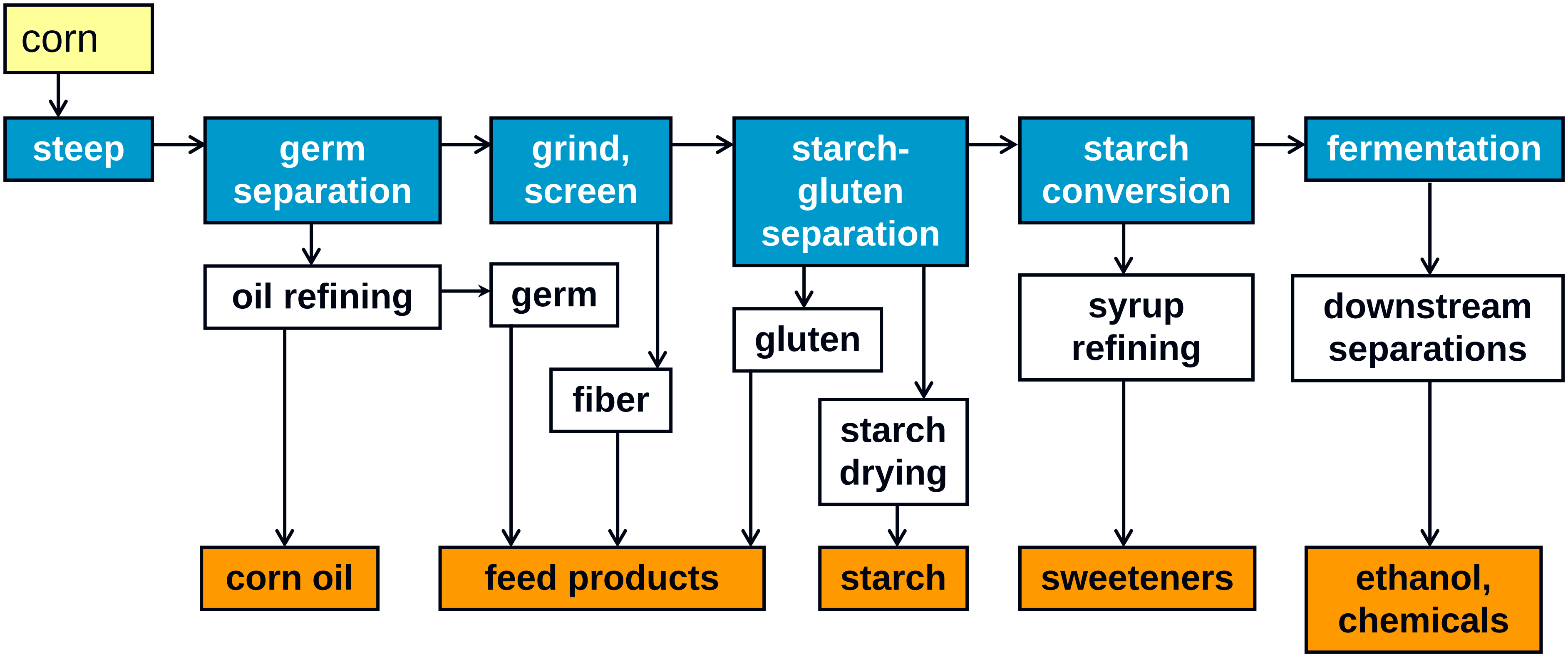
Dry mill process flow diagram



Adapted from: Renewable Fuels Association

Starch-based Ethanol Production

Wet mill process flow diagram

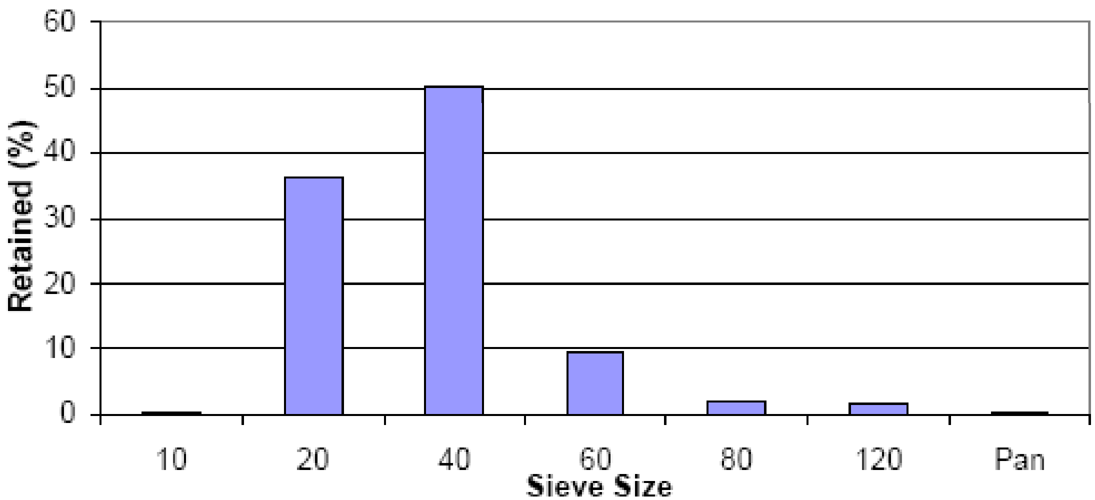


Adapted from: Corn Refiners Association of America, www.corn.org

Starch-based Ethanol Production

Pretreatment

- Pretreatment in dry grind corn process involves quality testing, storage, cleaning, removal of stones and metal debris.
- Incoming corn is tested for moisture content, presence of insects, broken kernels and presence of fungi (Aspergillus niger).
- 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.



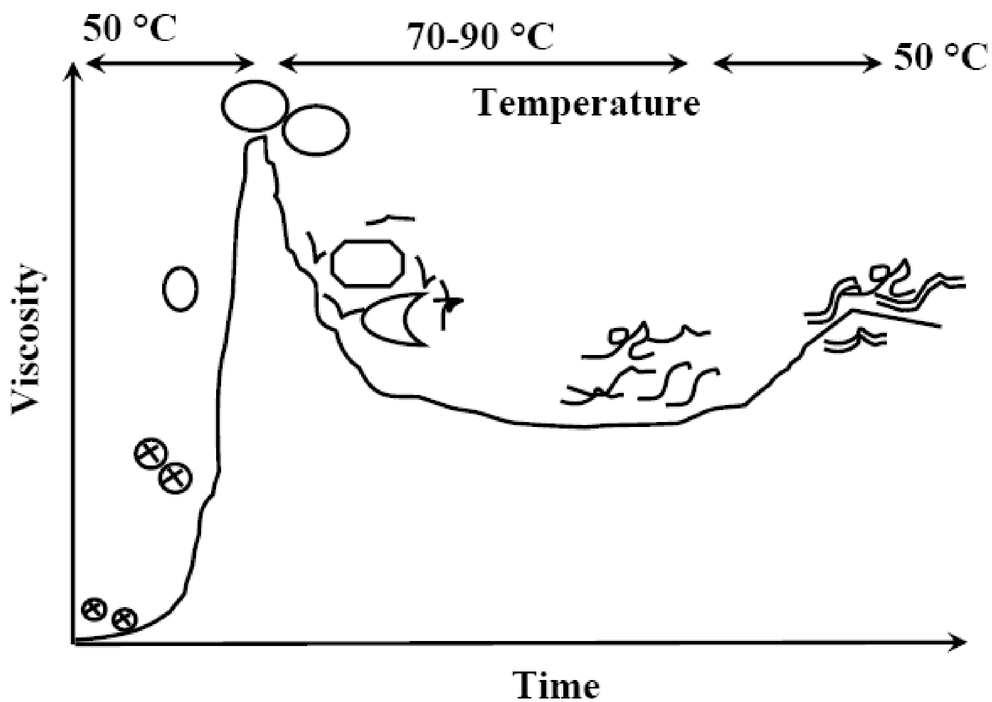
Particle size distribution

Hammer mill

Starch-based Ethanol Production

Liquefaction

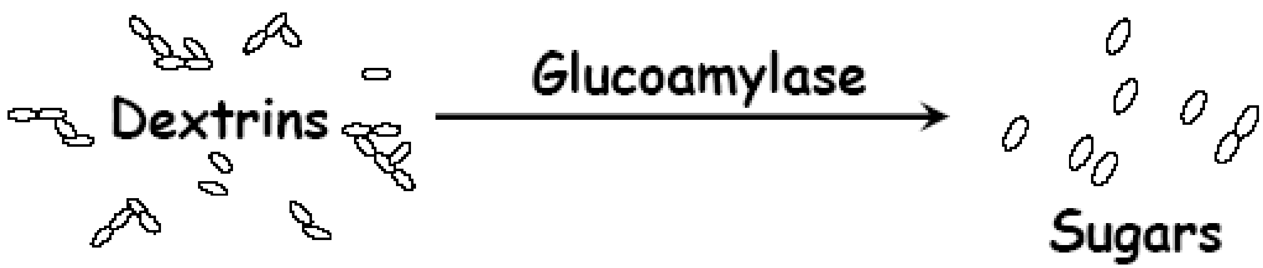
- Liquefaction in dry grind corn process involves breakdown of starch into dextrins
- Alpha amylase breaks down starch into dextrins at 90°C, 5.5-6.0 pH with high shear
- Starch granules lose their shape
- The dextrose equivalent of corn mash is about 12-22
- Mash does not turn blue when iodine solution is added
- Viscosity of the mash is lowered and hence it can be easily pumped in the plant



Starch-based Ethanol Production

Saccharification

- Saccharification in dry grind corn process involves conversion of dextrins into mono saccharides (primarily) and disaccharides.
- Gluco-amylase breaks down dextrins into glucose at 60°C (2 hr) or 30°C (48 hr), 4.5-5.0 pH
- The dextrose equivalent of corn mash is >70
- Mash does not turn blue when iodine solution is added
- Mash primarily consists of glucose sugar



Starch-based Ethanol Production

Fermentation

- Fermentation in dry grind corn process involves anaerobic respiration of yeast consuming glucose and producing ethanol as a byproduct.
- Yeast consume sugars produced by starch hydrolysis and produce ethanol as a byproduct of anaerobic respiration at 30°C (48-60 hr), 4.0-4.5 pH.
- 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)

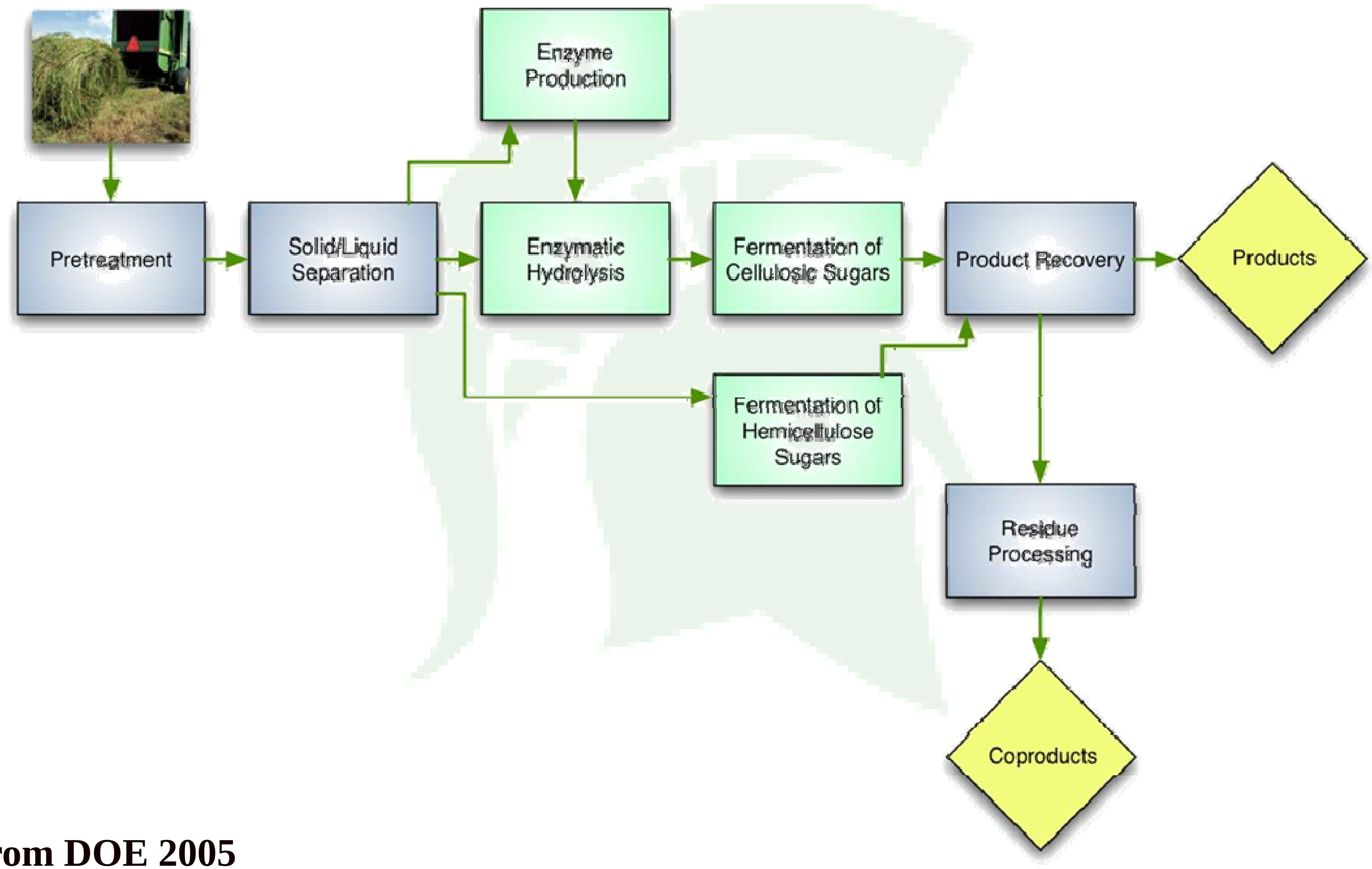
Starch-based Ethanol Production

Ethanol conversion rates

Corn – dry mill	**= 2.75 gallons/bu**	**=**	**98.21 gal/ton**
(4.2 T/ac. = 150 bu./ac. = 410 gal./ac.)			
Corn – wet mill	**= 2.65 gallons/bu**	**=**	**94.64 gal/ton**
Grain sorghum	= 2.70 gallons/bu	=	96.43 gal/ton
Wheat	= 2.80 gallons/bu	=	93.33 gal/ton
Barley	= 1.40 gallons/bu	=	58.33 gal/ton
Sugarcane		=	19.50 gal/ton
(35 T/ac. = 680 gal./ac.)			
Sugar beets		=	24.80 gal/ton
Molasses		=	69.40 gal/ton
Raw sugar		=	135.40 gal/ton
Refined sugar		=	141.00 gal/ton

Cellulose-based Ethanol Production

Cellulosic biorefinery

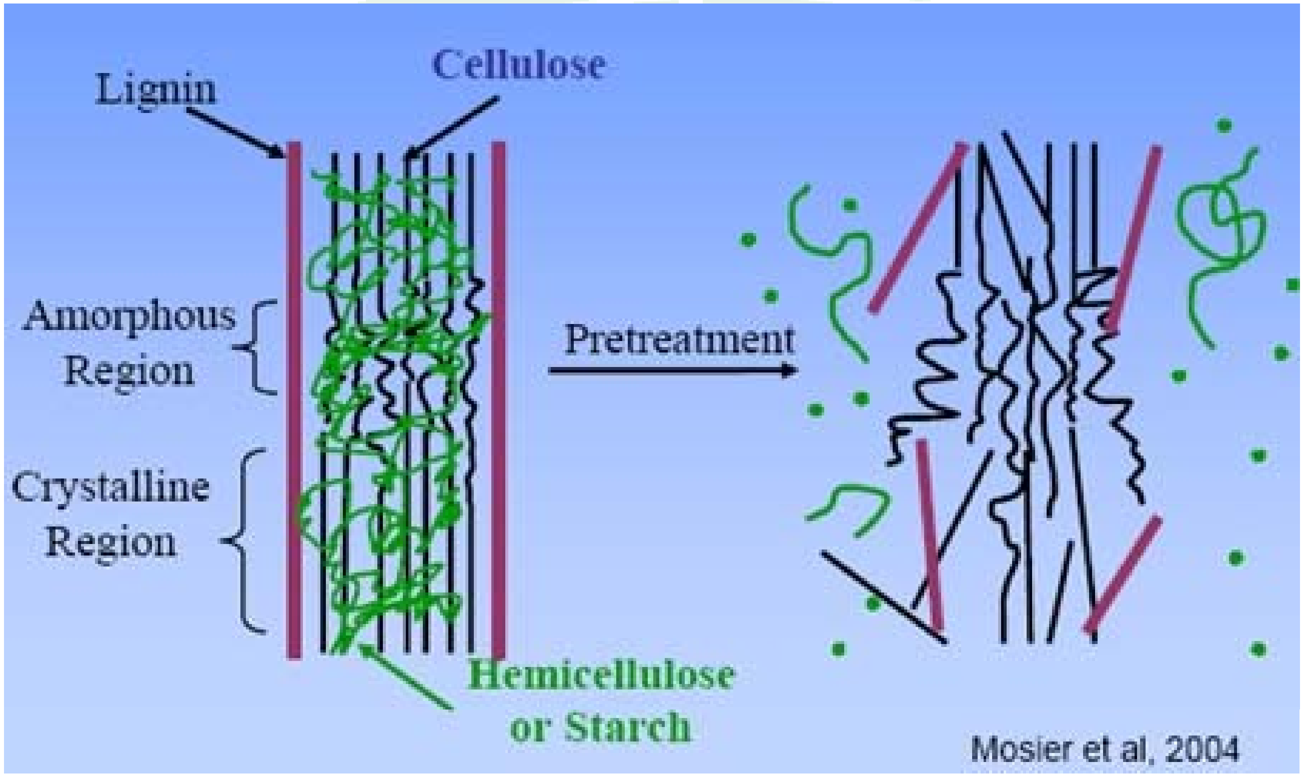


From DOE 2005

Cellulose-based Ethanol Production

Pretreatment

Primary goal of any pretreatment process is to facilitate enzyme action by making the substrate available. Pretreatment processes are critically dependent on type of feedstock



Ethanol Process Calculation

Ethanol conversion rates and extents

- Fermentation

  $C_6H_{12}O_6 \rightarrow 2C_2H_5OH + 2CO_2$ + 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).

Safety

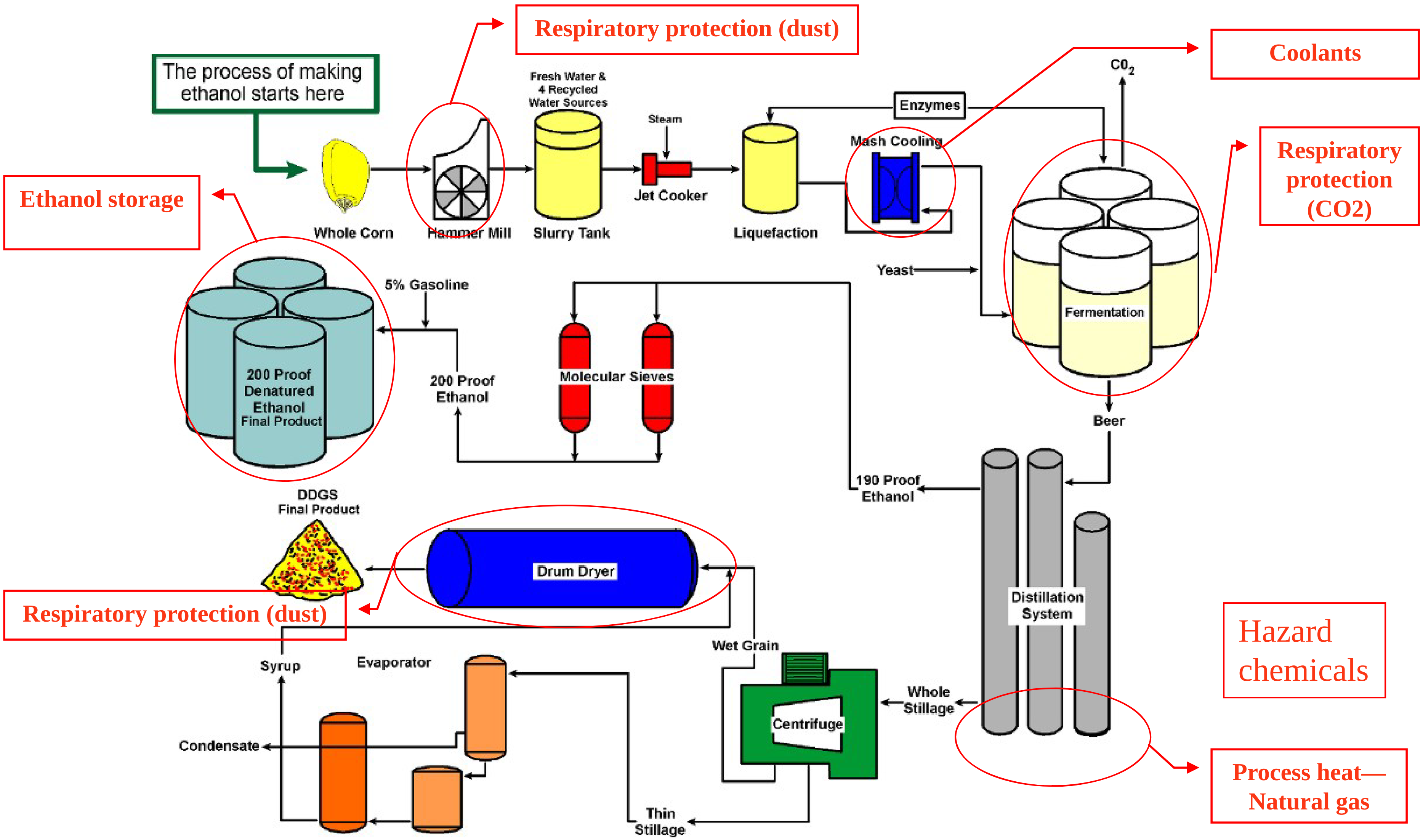
- Required and recommended plans (core plans from OSHA):
  - Hazard communication,
  - Lockout/tag-out,
  - Emergency action plan,
  - Fire prevention,
  - Personal protective equipment,
  - Hearing conservation,
  - Respiratory protection and others.

- Other safety plans common to ethanol plant operations:
  - Boiler safety,
  - Grain handling safety,
  - Specific chemical safety (chlorine, ammonia, CO2 etc.),
  - Injury prevention and first aid,
  - Confined space,
  - Fall protection and others

Ethanol Production

Safety

Main safety concerns



Safety

1. Pressurized tank

- Pressurized tanks: fermentation vessel, CO2 tank
- Device to control overpressurization: Pressure Relief Valves (PRV), Rupture Disks (RD)
  - PRV: cleanable, reusable device, often release pressure at 15 psi
  - RD: pan shaped object that is inserted between pipe flanges
- Most tanks are protected with both PRV and RD
- Record tank pressure using a pressure gauge: avoiding tank failure

PRV

RD

Pressure gauge

2. Coolants

Coolants for small-scale ethanol production:

- glycol product to keep fermenters cool
  - Glycol is moderately toxic (ingestion) and is slippery
- Ammonia and freon for heat exchanger
  - Expensive due to surcharges related with freon's role as an ozone depleting chemical
- Propane coolants
  - Flammable liquid and vapor

Ethanol Production
Safety

3. Respiratory protection

Substances	Respirator Type(s)
Nuisance Dusts/Mists • grain dust • diatomaceous earth	***Air Purifying Respirator (APR)*** HEPA dust/mist/fume specification • Cartridge type • Disposable type
Organic Vapors • solvents, thinners • paints	***Air Purifying Respirator (APR)*** organic vapor specification (activated carbon) • Cartridge type • Disposable type
Asphyxiating Atmospheres • high carbon dioxide conc. • high nitrogen concentrations	***Supplied Air Respirator (SAR)*** • SCBA (self contained breathing apparatus) • Airline respirator w/ escape cylinder • In either case, compliance with OSHA confined space requirements is likely

Safety

4. Ethanol storage

Properties of ethanol:

- Clear and colorless
- Hygroscopic, i.e. absorbs moisture from the air
- Heat of combustion = -1368 kJ/gmol
- Boiling point temperature = 78.3°C
- Vapor pressure = 60 mmHg at 25°C
- Liquid density = 0.79 g / cm^3
- Flash point temperature = 17°C
    - Defined as the lowest temperature that an ignitable mixture can be formed with air
- Toxicity = read MSDS

Storage tank fire at an ethanol plant

Ethanol tank explosion-- Tank roof blew off and fell on top of fire control systems rendering them inoperative

Safety

5. Ethanol ignition

Typical ignition sources:

- open flames
- lightning
- hot surfaces
- radiant heat
- smoking
- cutting and welding
- spontaneous ignition
- frictional heat or sparks
- static electricity
- electrical sparks
- stray currents
- ovens, furnaces, heating equipment

6. Hazard chemicals

- HAZCOM (Hazard communication program): workplace notices, container labels, material safety data sheets (MSDSs), training, and protective equipment
- Notices: states a “right to know” about chemical hazards in the workplace
- Labels: Identity of the chemicals; warning statements; contact information
- MSDSs: following OSHA’s specification
- Chemical inventory/Hazard assessment

Hazard	Examples
Corrosive	caustic cleaners, acid washes
Ignitable/Explosive	natural gas, propane, cleaning solvents, paint related materials, grain dust
Reactive/Poisonous	oxime, chlorine dioxide, iodine, kitchen sanitizers, insecticides and rodenticides
Asphyxiating	carbon dioxide, nitrogen
Slippery	caustic cleaners, glycol refrigerant, quaternary disinfectants, detergents, floor spills of any kind
Nuisance dusts	grain dust, diatomaceous earth

Thank You!