

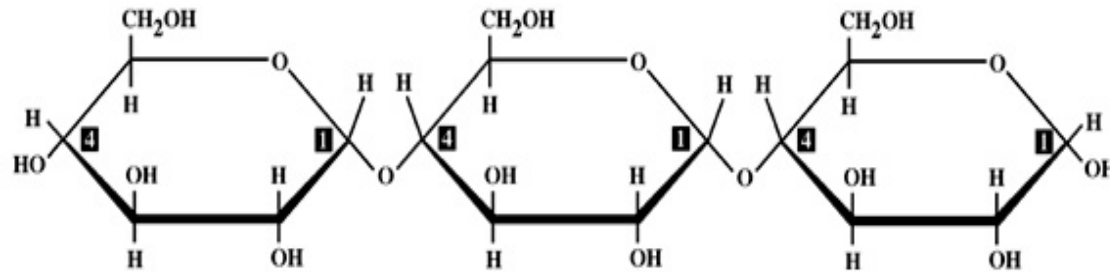
BIOMASS CONVERSION COURSE

Doctoral School
EPFL

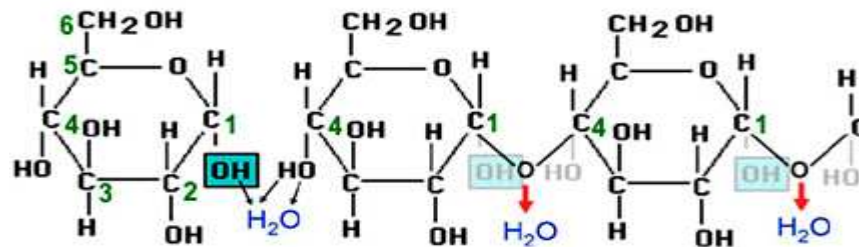
Bioethanol – Part 2

Starch Bioethanol Industry

- Starch is a polysaccharide carbohydrate, which consists of a large number of D-glucose-monomers



- Hydrolysis is required to breakdown this structure, making glucose available for fermentation

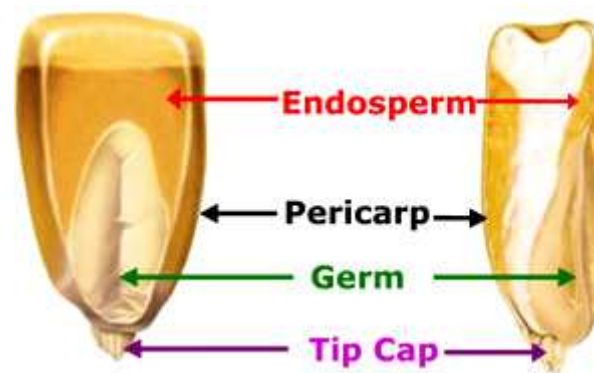


Starch Bioethanol Industry

- Two types of hydrolysis are known: **enzymatic hydrolysis** and **acid hydrolysis**.
- The enzymatic hydrolysis of starch is done by amylases enzymes.
- Important factors include: substrates, enzyme activity and reaction conditions (e.g. temperature, pH).
- Starchy materials have to be cooked at high temperatures (413-453 K) in order to obtain high bioethanol yields.

Corn Bioethanol Industry

- Starchy materials (e.g. wheat, corn and barley,...)
- Corn is the main source of starch for fuels

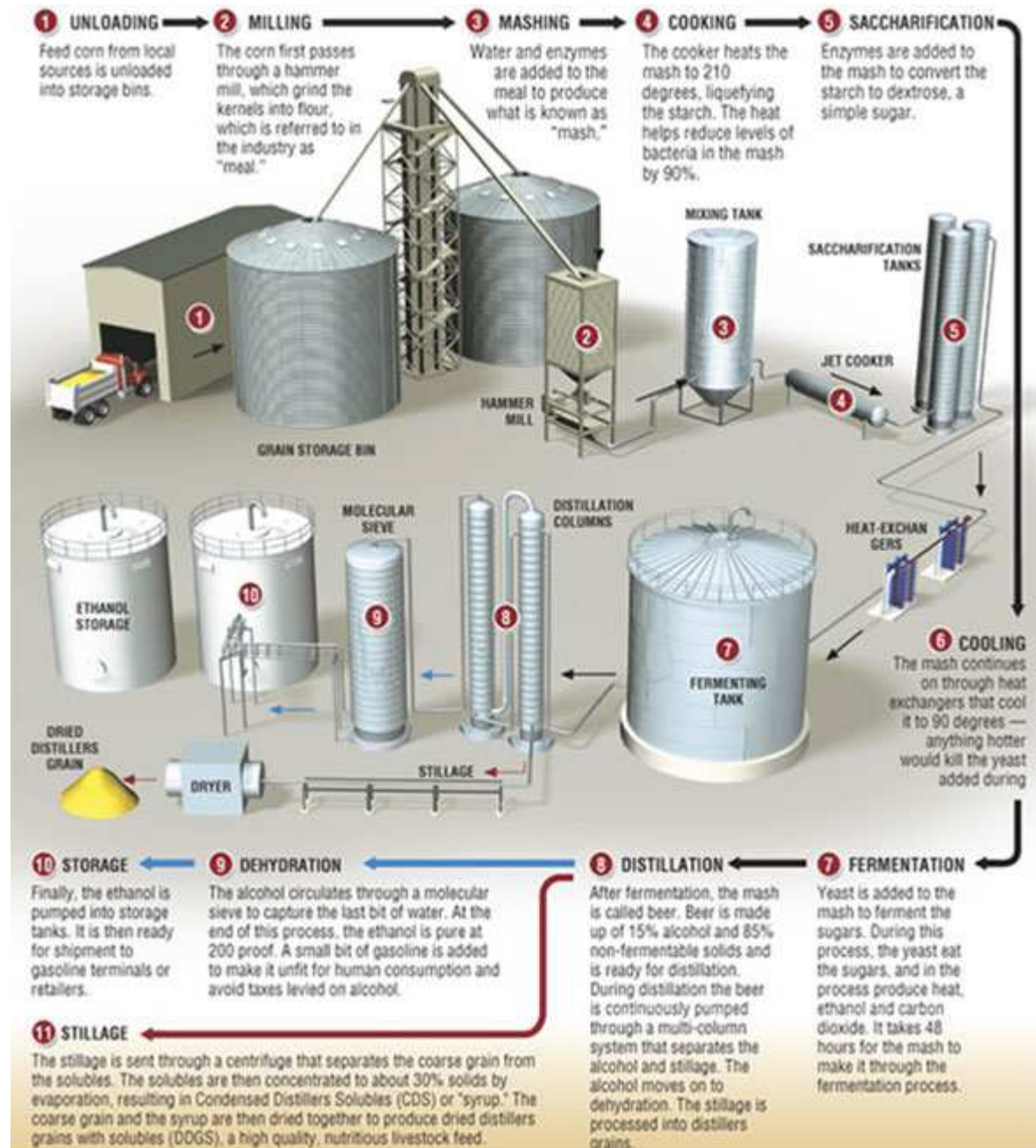


Source: <http://www.responsiblebusiness.eu/display/rebwp7/Starchy+feedstocks>



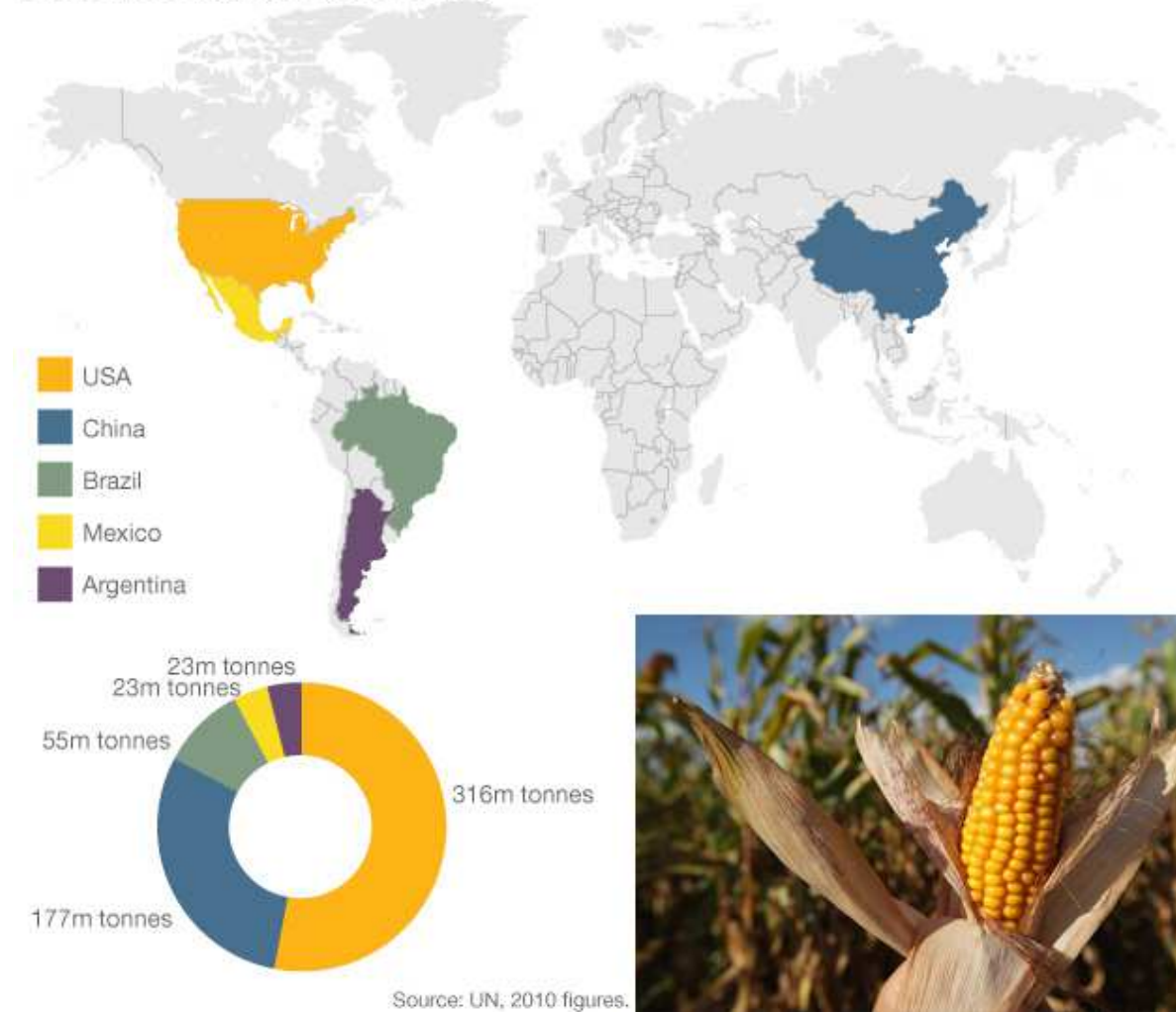
Kernel part		Percent of kernel	Starch	Oil	Protein	Ash	Sugar
Endosperm	Mean Range	82.9 81.8 - 83.5	97.6 86.4 - 88.9	0.8 0.7 - 1.0	8.0 6.9 - 10.4	0.3 0.2 - 0.5	0.62 0.5 - 0.8
Germ	Mean Range	11.1 10.2 - 11.9	8.3 5.1 - 10.0	33.2 31.1 - 35.1	18.4 17.3 - 19.0	10.5 9.9 - 11.3	10.8 10.0 - 12.5
Pericarp	Mean Range	5.3 5.1 - 5.7	7.3 3.5 - 10.4	1.0 0.7 - 1.2	3.7 2.9 - 3.9	0.8 0.4 - 1.0	0.34 0.2 - 0.4
Tip cap	Mean Range	0.8 0.8 - 1.1	5.3 NA	3.8 3.7 - 3.9	9.1 9.1 - 10.7	1.6 1.4 - 2.0	1.6 NA
Entire kernel	Mean Range	100	73.4 67.8 - 74.0	4.4 3.9 - 5.8	9.1 8.1 - 11.5	1.4 1.37 - 1.5	1.9 1.61 - 2.22

Corn Bioethanol Industry



Corn Production

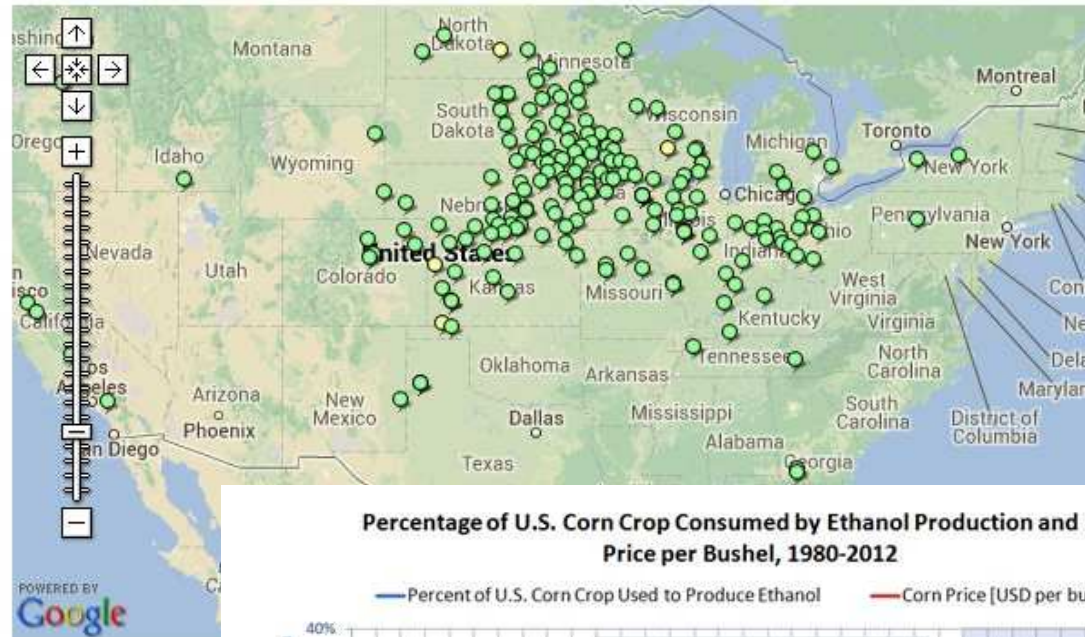
The world's top producers: Maize



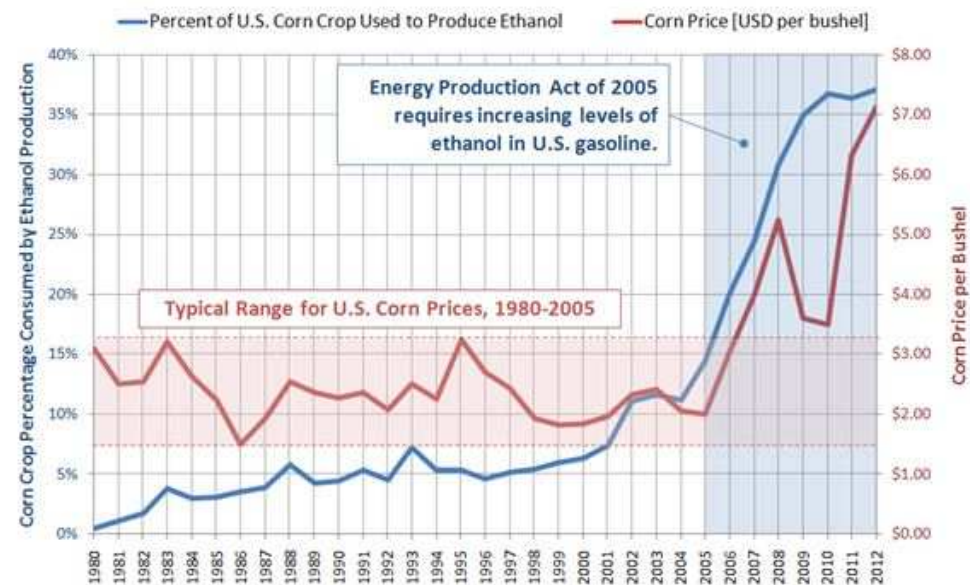
Corn Bioethanol Industry

- Installed plants <http://www.ethanolrfa.org/bio-refinery-locations/>

Biorefinery Locations

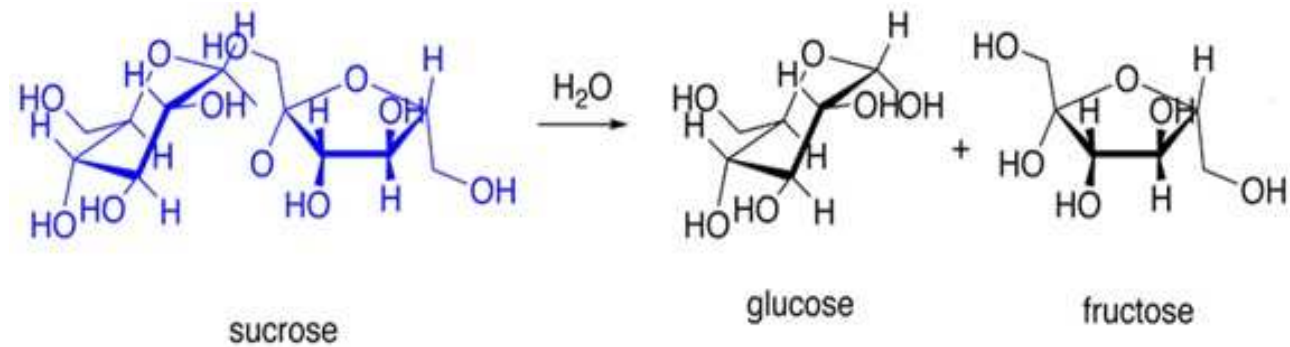


Percentage of U.S. Corn Crop Consumed by Ethanol Production and Corn Price per Bushel, 1980-2012

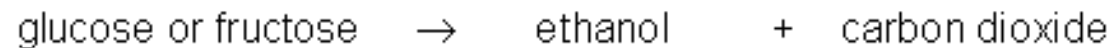
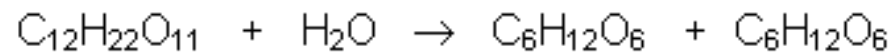
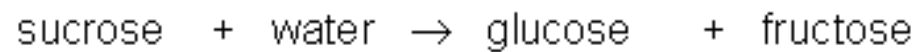


Source: USDA, National Agricultural Statistics Service, Agricultural Marketing Service, Ethanol from Corn: Production & Price Balance Sheet and U.S. D.A. Agricultural Prices

Fermentation of Sucrose

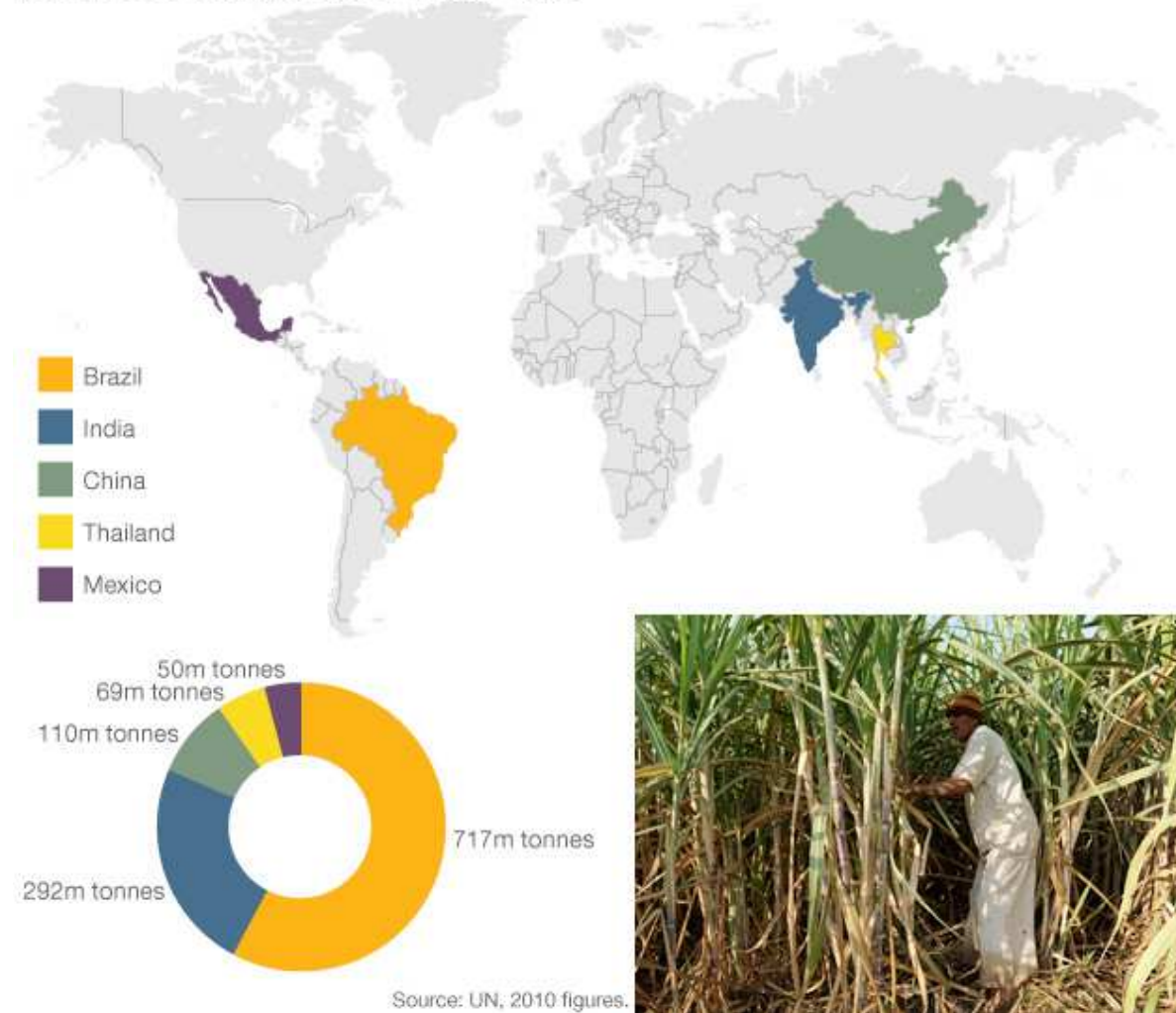


- Sucrose is a disaccharide and must be hydrolyzed to be fermented



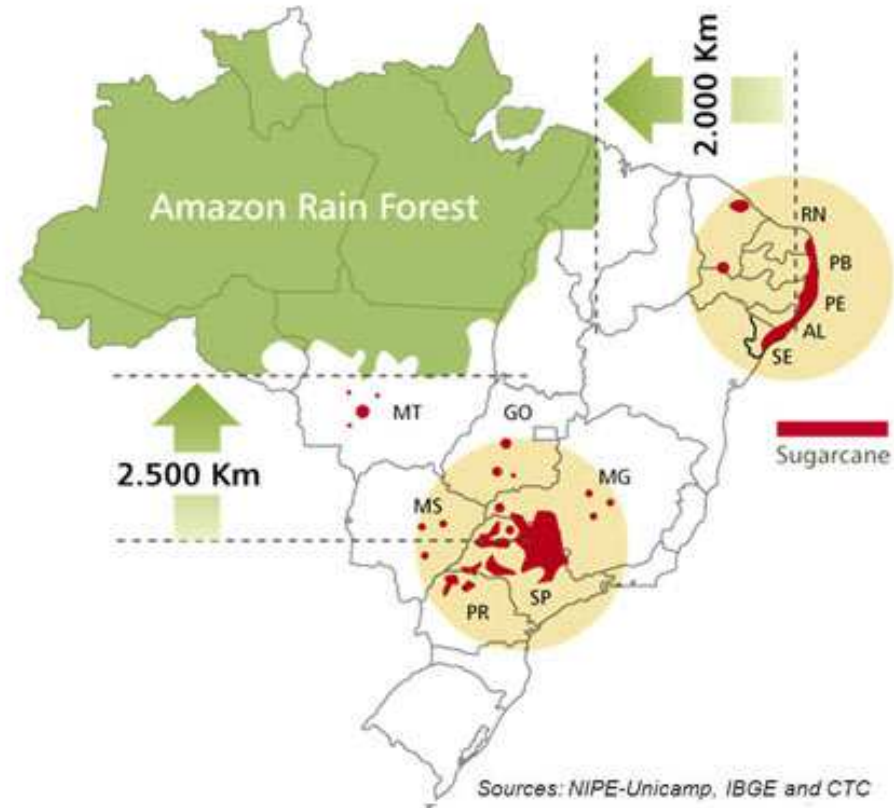
Sugarcane Production

The world's top producers: Sugar Cane



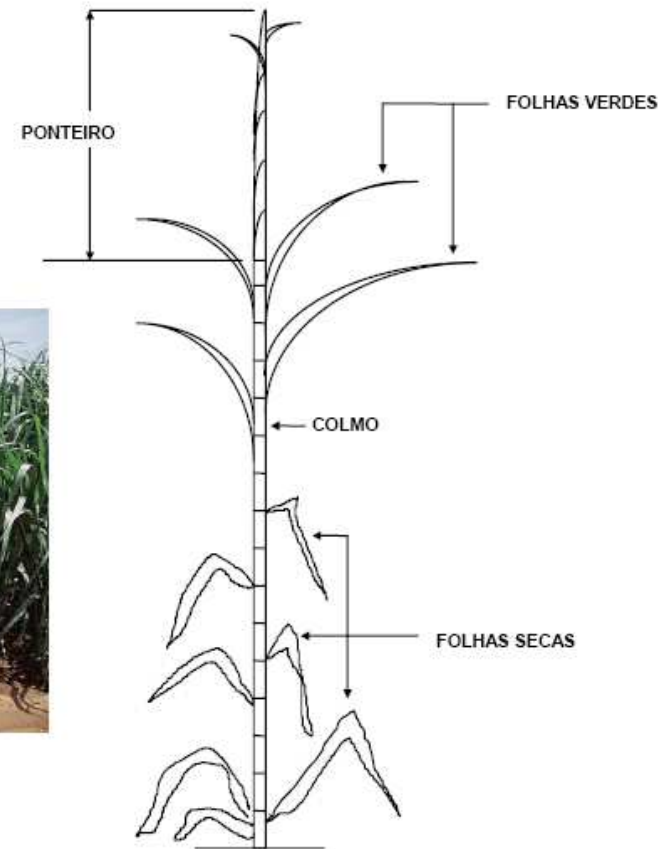
Sugarcane Production

Sugarcane producing regions in Brazil



Sugarcane Bioethanol

CANA DE AÇÚCAR





Sugarcane Bioethanol



Bagaço de cana

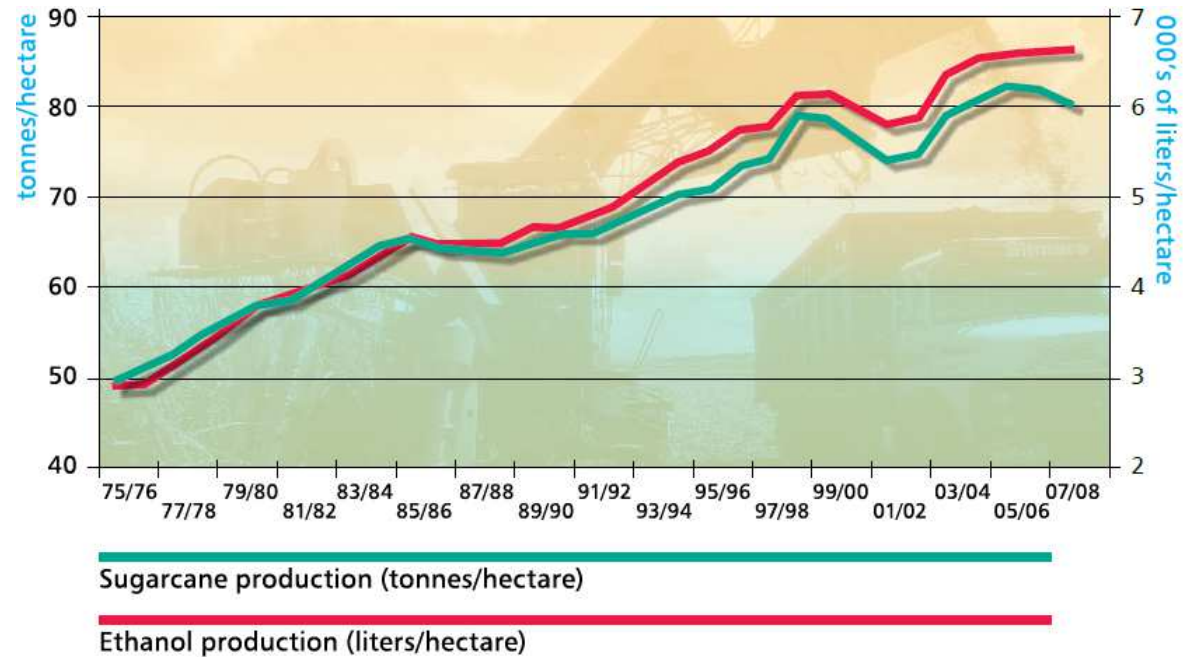


fibra



Pó (pith)

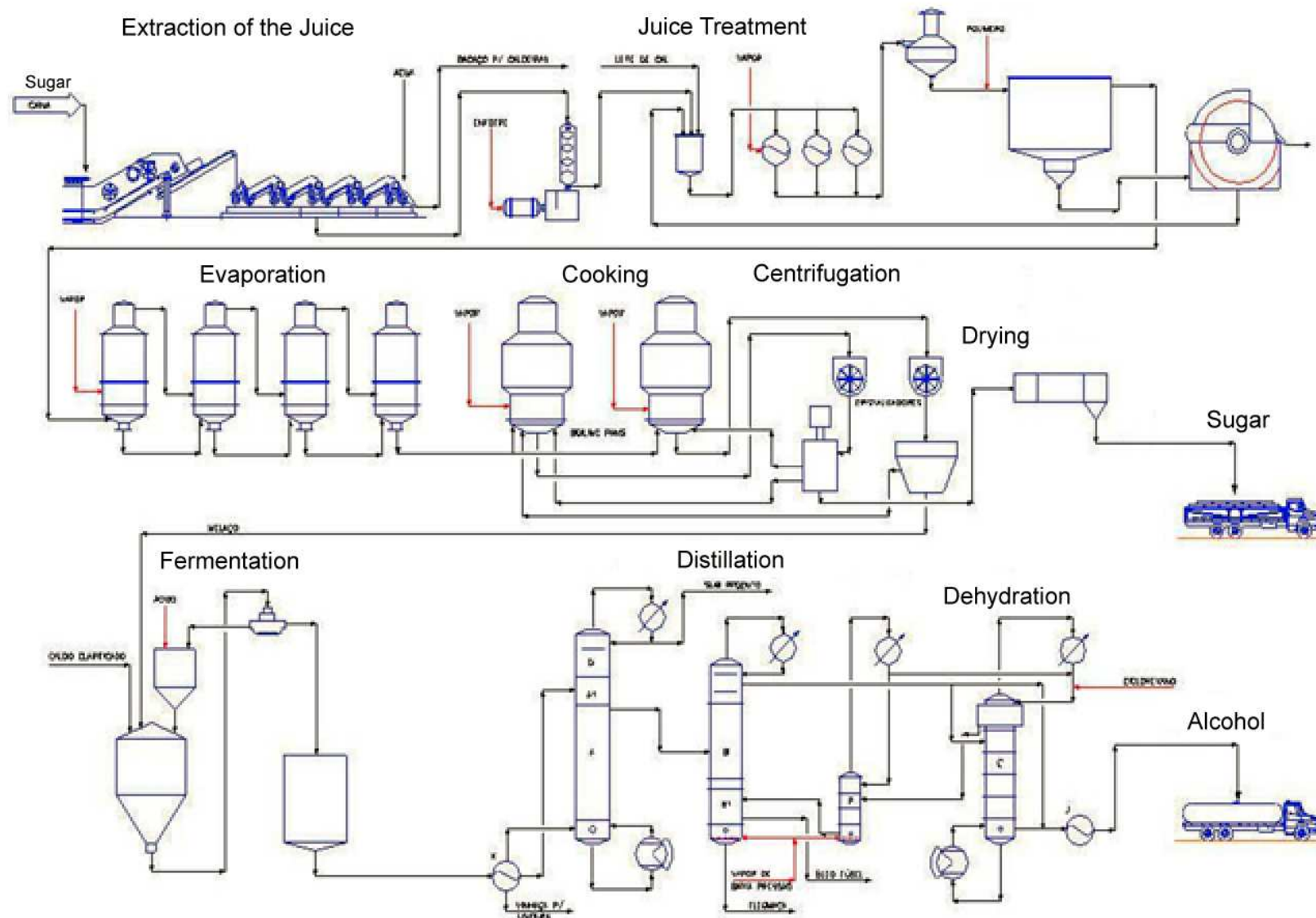
Sugarcane Bioethanol Cultivation Cycle



Source: Unica

Harvesting





Juice extraction



	Unit	Lower value	Upper value
Brix	°	15.7	23.1
Sucrose	wt%	11.93	16.68
Glucose	wt%	0.34	1.50
Fructose	wt%	0.38	1.57
pH		4.94	5.72

Fermentation

- Glucose conversion - Theoretical yield



M (g/mol)	180	46	44
Mass (g)	180	92	88

$$\text{Yield} = 92/180 = 0.511 \text{ g EtOH/Glucose}$$

Maximum conversion rate (Pasteur yield):
95%

Industrial conversion rate: 90%

Fermentation

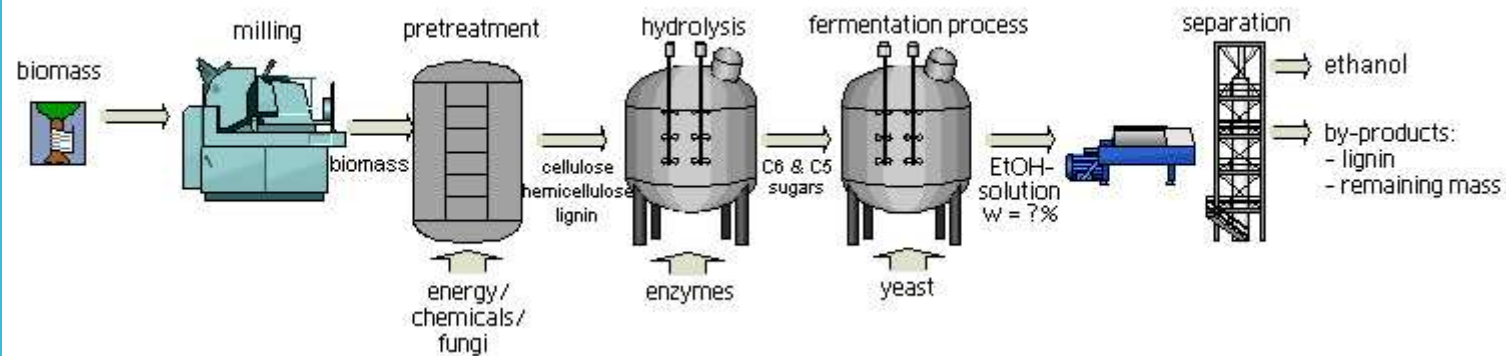
Product	Fraction of total reduced sugars - wt % (86-92% conversion)
Bioethanol	40-47
CO ₂	41-45
Yeast (biomass)	1-5
Glycerol	2-9
Succinic acid	0.3-1.2
Acetic acid	0.1-0.7
Fusel oil	0.2-0.6

Fusel oil - mixture of alcohols (propanol, butanol, isoamyl, etc.)

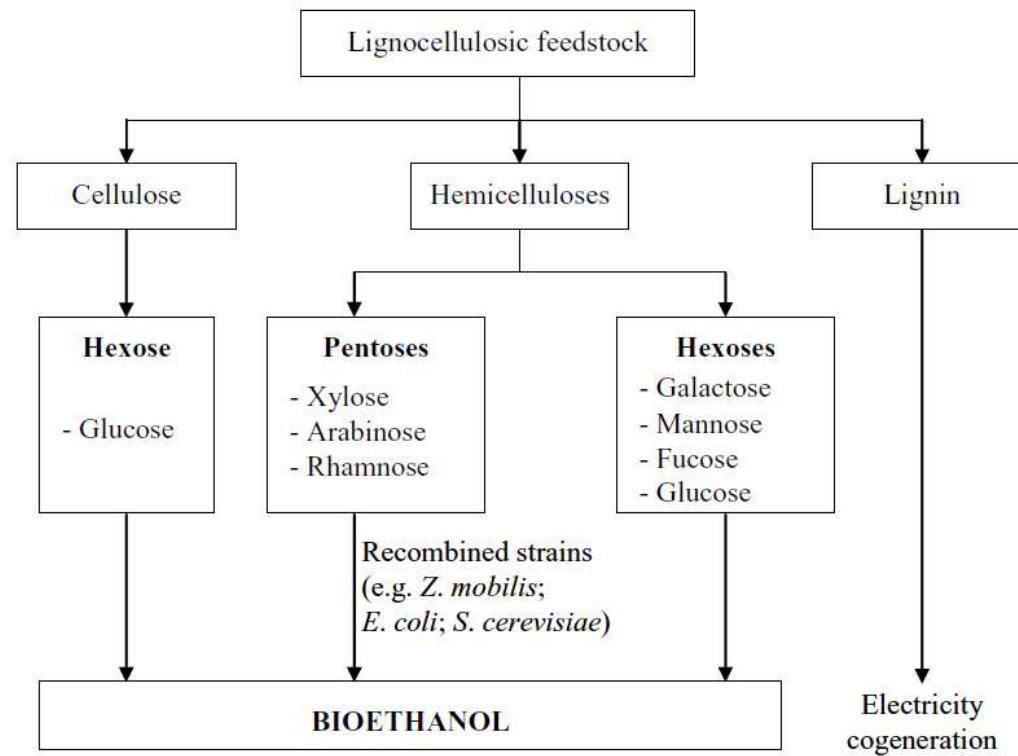
By-products derived from bacterial contamination, secondary fermentation, degradation of proteins in the must ,etc.

Lignocellulosic bioethanol

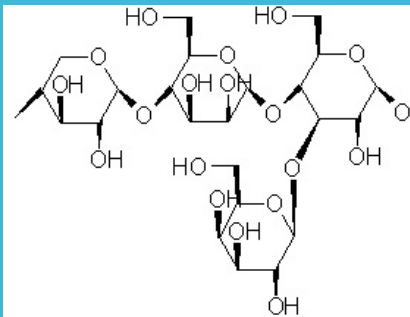
Biochemical Conversion



Lignocellulosic bioethanol



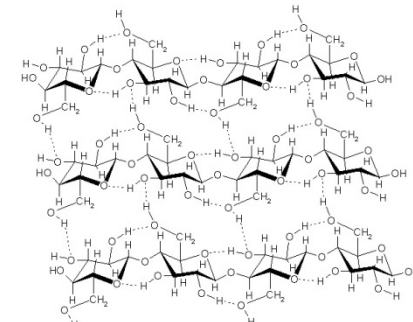
Lignocellulosic bioethanol



- Xylose - $\beta(1,4)$ - Mannose - $\beta(1,4)$ - Glucose -
- $\alpha(1,3)$ - Galactose

Hemicellulose

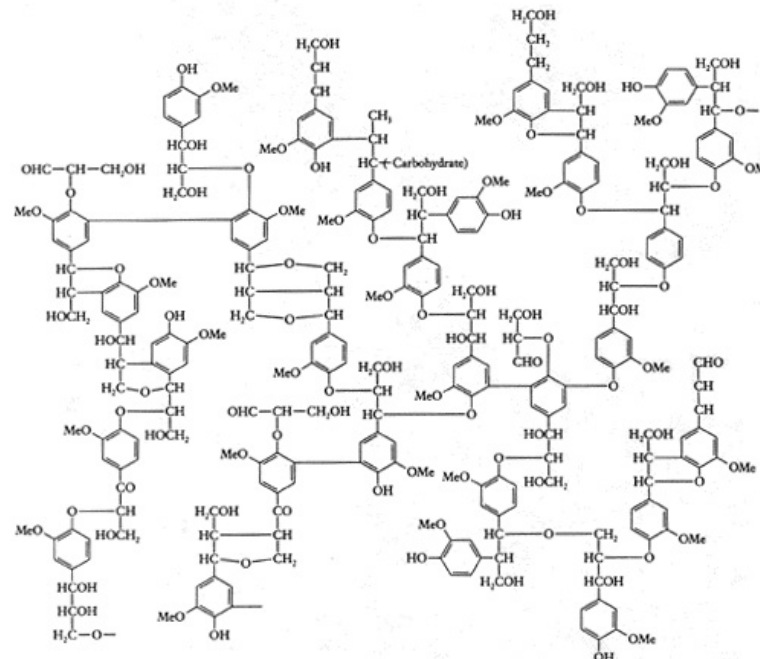
- Cellulose consists of approximately 40 – 50 wt% of dry and provides biomass strength.



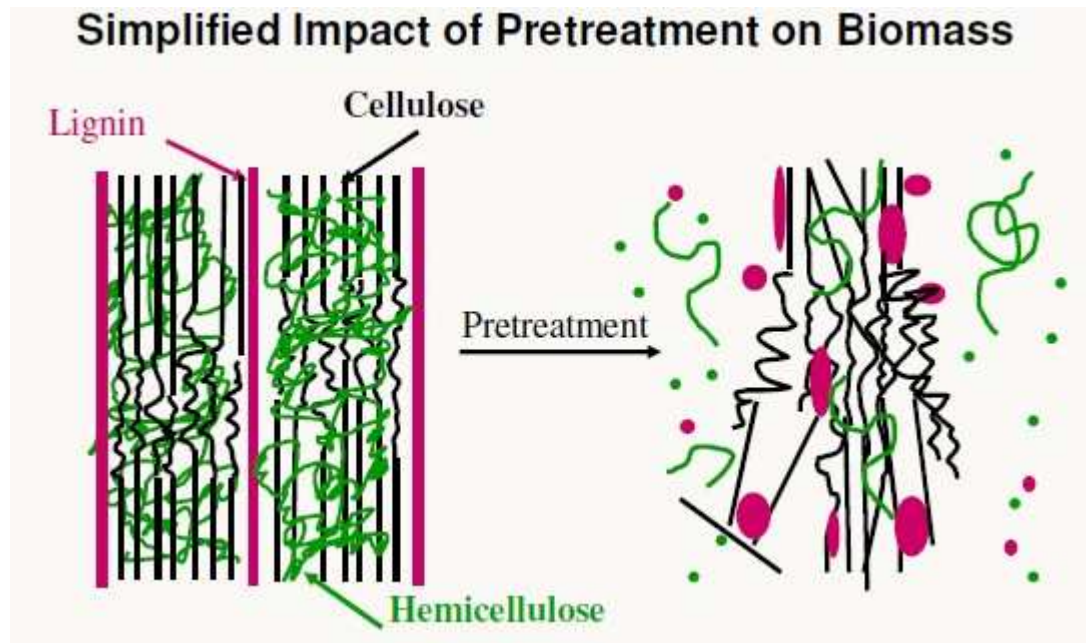
- Hemicellulose – also known as polyose – accounts for 25 – 35 % of the dry mass.
- Hemicellulose is a composition of numerous polymerized monosaccharides (e.g. glucose, mannose, galactose, xylose, arabinose, 4-*O*-methyl glucuronic acid and galacturonic acid residues).
- Xylose is the predominant included pentose sugar (C5-sugar).

Lignocellulosic bioethanol

- Lignin is a highly branched, substituted, mononuclear aromatic polymer in the cell walls of certain biomass, which is often bound to adjacent cellulose fibers, forming a lignocellulosic complex.
- This complex – and also lignin alone – are mostly resistant to conversion, using microorganisms, as well as chemical reagents.



Pre-treatments



- Formation of sugars and/or the ability to form sugars in the hydrolysis process
- Prevention of degradation or loss of carbohydrates
- Avoidance of by-products-formation, which may be prejudicial to hydrolysis and fermentation process
- Improvement of cost effectiveness

Pre-treatments

Pre-treatment method	Chemicals	Temperature/ Pressure	Reaction time (min)	Xylose yield (%)	Downstream enzymatic effect	Costs	Availability
Dilute acid hydrolysis	Acid	> 433 K	2 – 10	75 – 90	< 85 %	+	Now
Alkaline hydrolysis	Base			60 – 75	55 %	++	Now
Uncatalyzed steam explosion	-	433 – 533 K	2	45 – 65	90 %	-	2 – 5 year
Acid catalyzed steam explosion	Acid	433 – 493 K			88 % (2 steps)	-	2 – 5 year
Ammonia fiber explosion	Ammonia	363 K	30		50 – 90 % (2 steps)		
CO ₂ explosion	CO ₂	56.2 bar			75 % (2 steps)		

Lignocellulosic bioethanol

