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INNOVATIVE EUROPEAN STUDIES on RENEWABLE ENERGY SYSTEMS

Energetic application of bioethanol from biomass

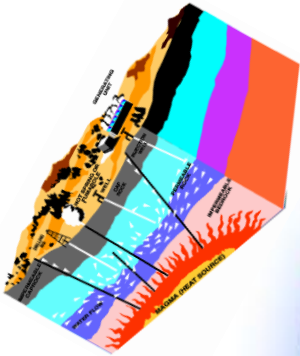
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Geologia
Università degli Studi di Perugia*

6th – 12st May 2018, Ankara

CURRENT ENERGY SITUATION:

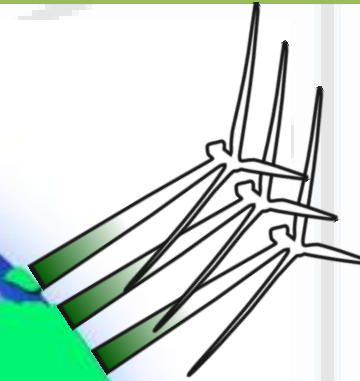
GEOHERMAL ENERGY



RENEWABLE ENERGIES:

“forms of energy derived from sources that due to intrinsic characteristics regenerate at least at the same rate at which they are consumed”

WIND POWER



BIOMASSES

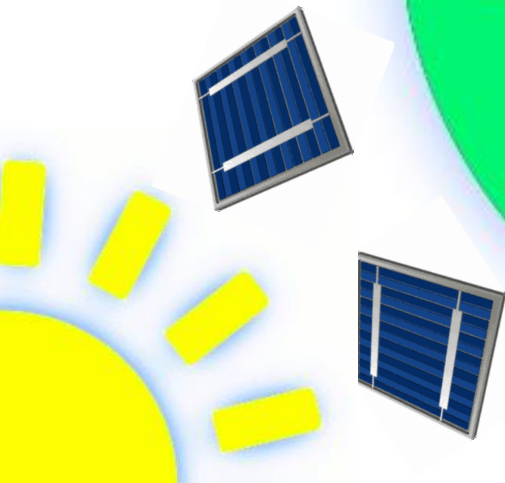
biofuels

Energy

HYDROPOWER



SOLAR ENERGY



European directives

- **The Renewables Energy Directive (2009/28/EC)**

The Directive addresses a number of issues relating to renewable energies within the EU including the legally binding share of renewable energy in gross final energy consumption. **Renewable Energy share of energy mix to rise to 20% by 2020.**

- By 1st February, 2011 all 27 Member States submitted a National Renewable Energy Plan (NREAP).
- The ECN (Energy Research Network of the Netherlands) has collected all data from the NREAP documents

Sustainability criteria of biofuels in the European Union

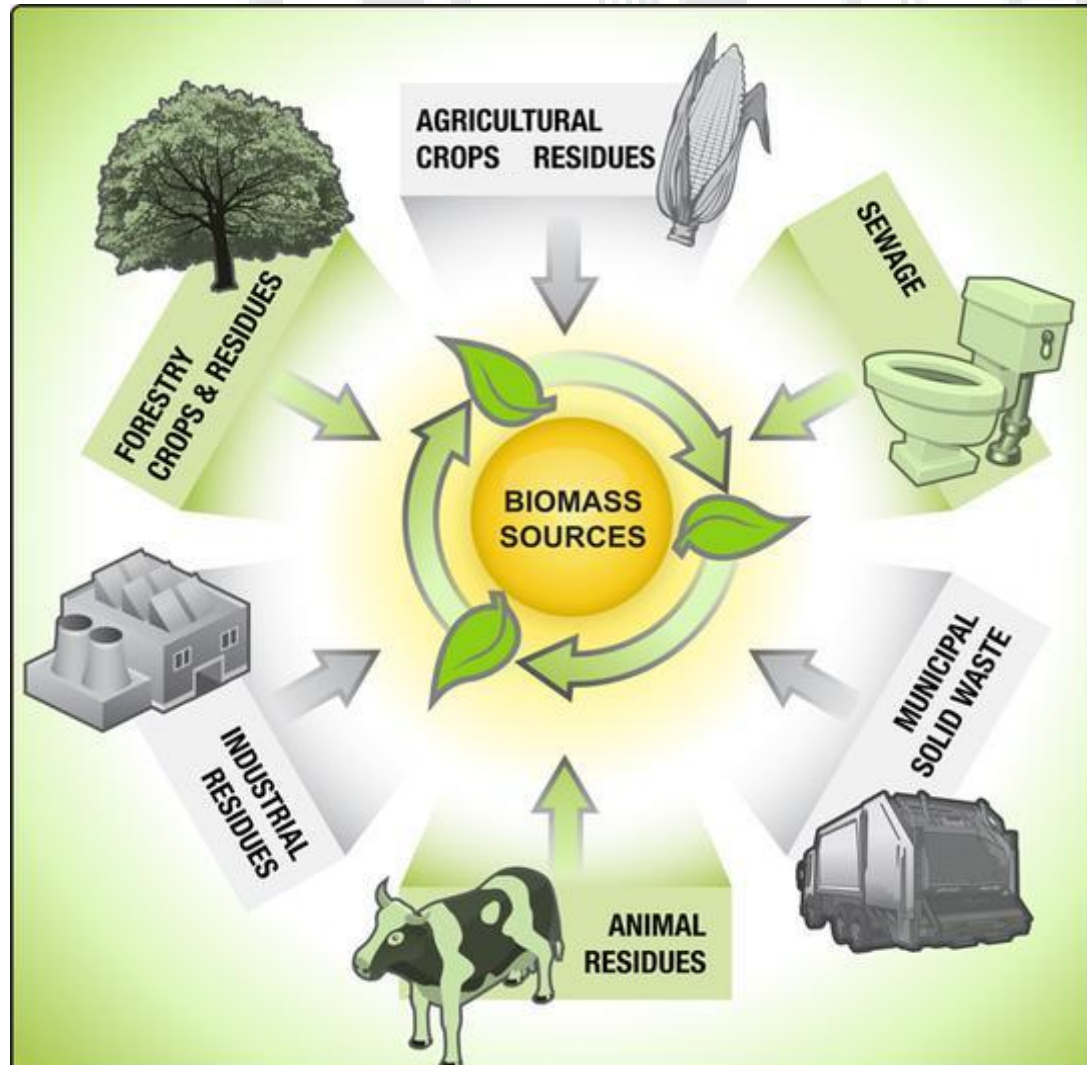
The European Union has adopted a very ambitious plan to increase the share of renewables in their energy consumption to 20% by 2020, **including a 10% goal for the use of renewables in transport alone.**

Article 17 of the Directive defines two sets of sustainability criteria for biofuels. The two main sets of criteria, which must be fulfilled cumulatively, are **greenhouse gas (GHG) emission savings and land-use requirements.**

Article 3.4 Each Member State shall ensure that the share of energy from renewable sources in all forms of transport in 2020 is at least **10 % of the final consumption of energy in transport** in that Member State

Some Definitions:

- Biomass is biological material derived from living, or recently living organisms.



- **Bioenergy** is energy of biological origin, derived from **biomass**, such as fuelwood, livestock manure, municipal waste, energy crops
- **Biofuels** are fuels produced from biomass, usually of agricultural origin:
 - Bioethanol
 - Biodiesel
 - Biogas

WHY PROMOTE BIOFUELS?

- Transport biofuels have risen to prominence in recent years. The main reasons for promoting biofuels are:
 - To contribute to the **reduction** of greenhouse gas **emissions**;
 - Reducing dependence of fossil fuels
 - To contribute to the **security of energy supply**;
 - To promote a greater use of **renewable energy**;
 - To diversify **agricultural economies** into new markets.



To promote the used of biofuels, many member states are relying on **fuel tax exemptions**.



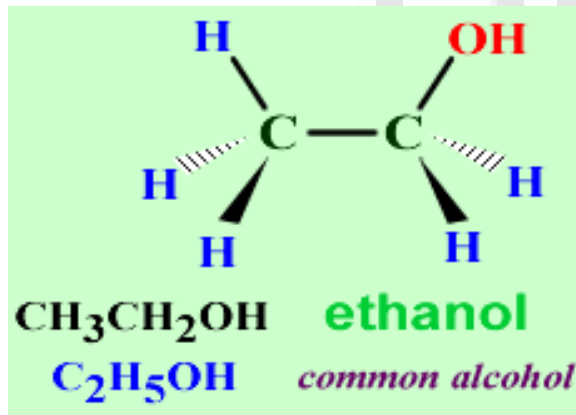
A - BIOETHANOL

What is Bioethanol?

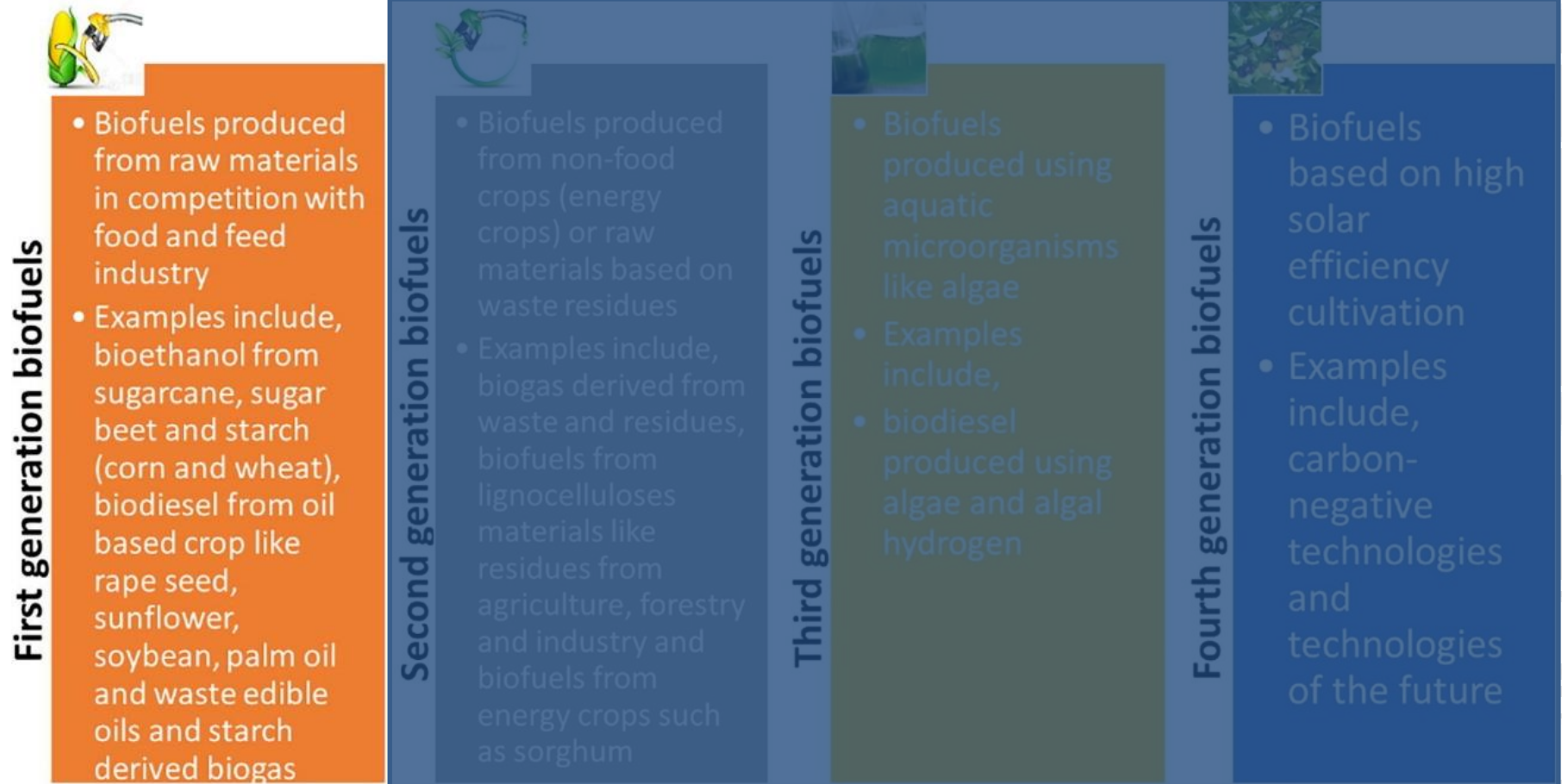
Bioethanol is ethanol (alcohol) that is derived exclusively from the fermentation of plant starches.

Bioethanol is the most widely used bio fuel today.

Molecular structure of ethanol:

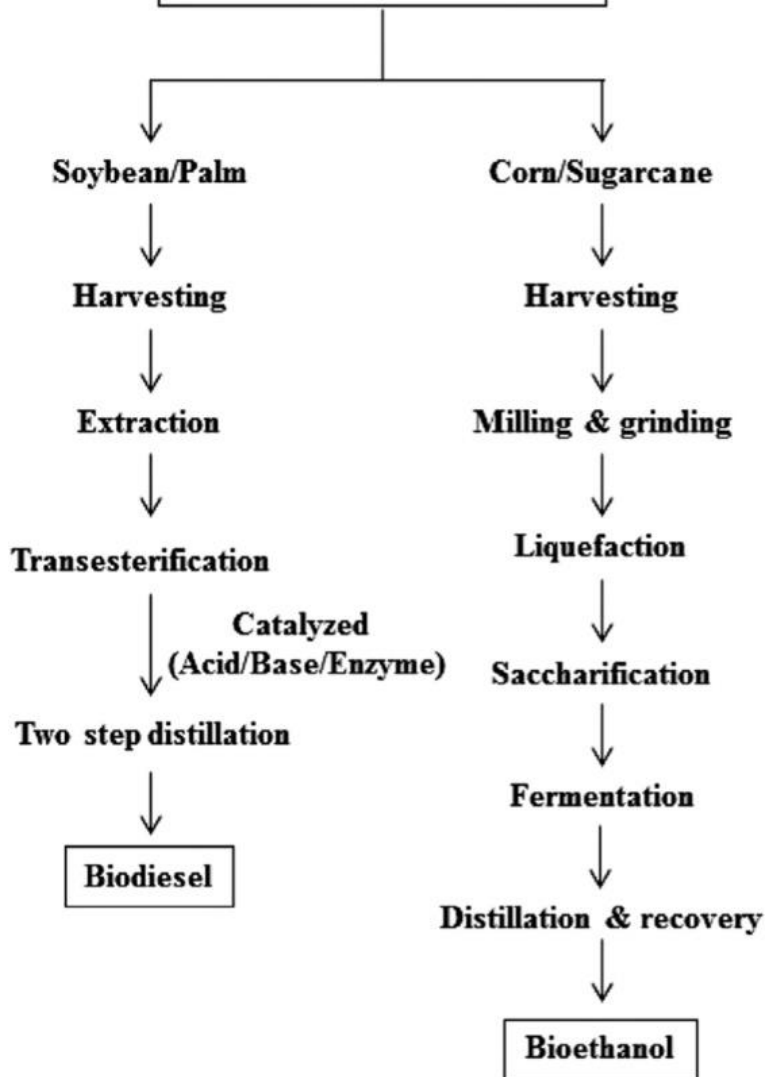


First generation Biofuels

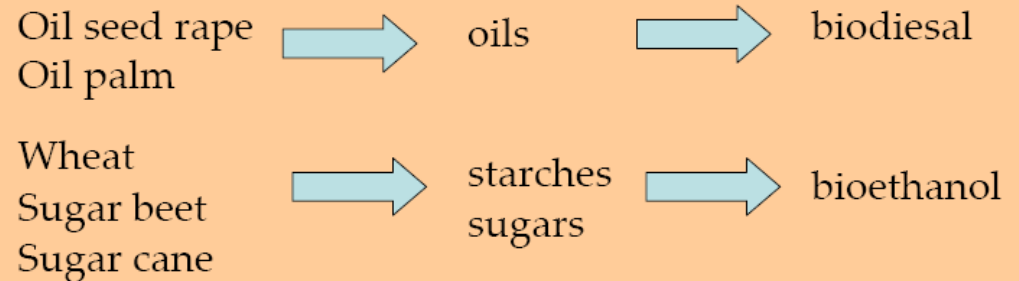


Depending on the raw materials or feedstocks, they are classified into first, second, third and fourth generation biorefineries

First Generation Biofuel

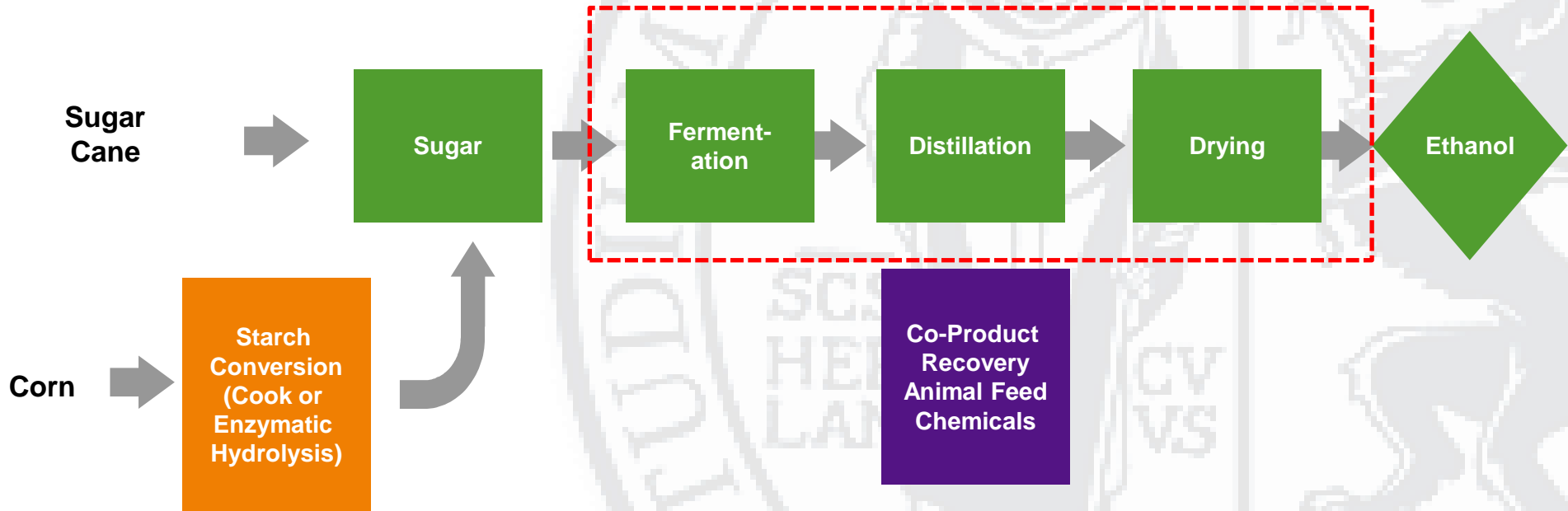


- Biofuel made from sugar, starchy crops, vegetable oil or animal fat using conventional technology.
- The starch from the basic feedstocks is fermented into bioethanol, or the vegetable oil through chemical process to biodiesel. .
- They don't seem to be more environment friendly than the fossil fuels.



First generation biofuels

Bioethanol production process diagram

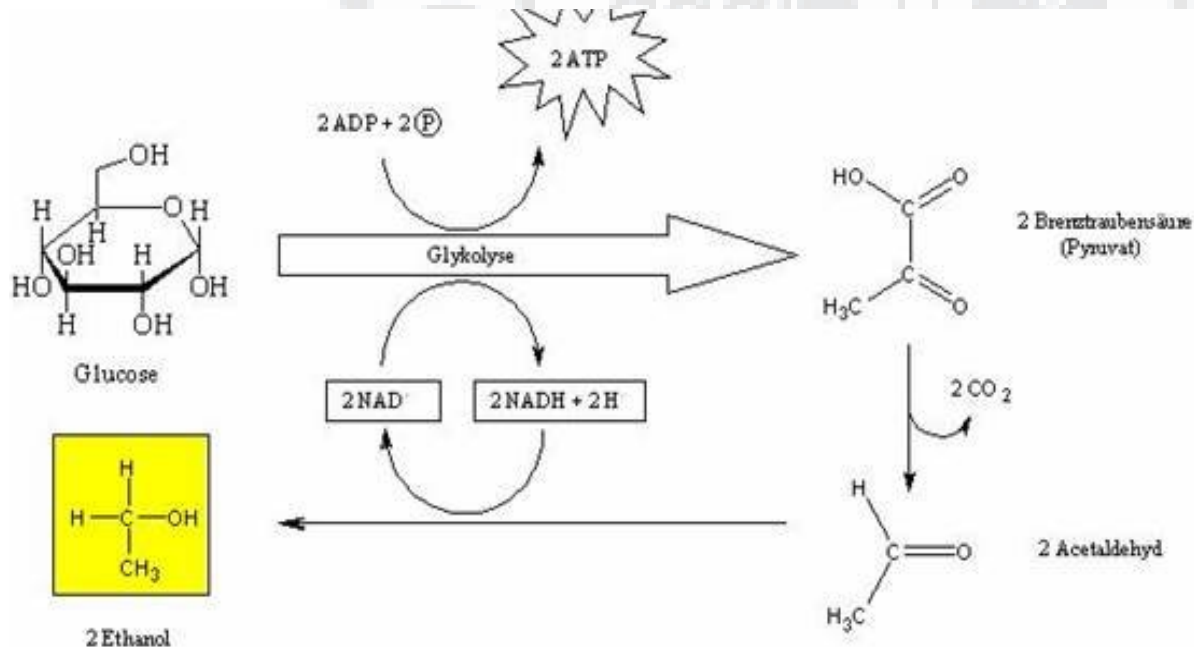


Principle of fermentation:

- Summarizing chemical equation for ethanol fermentation:



- One glucose molecule is converted into two ethanol molecules and two carbondioxide molecules.

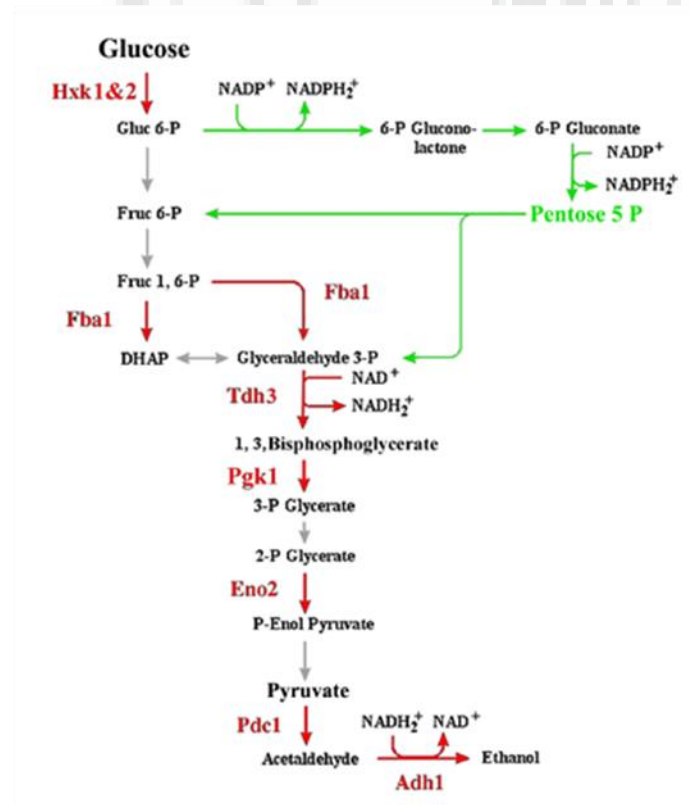
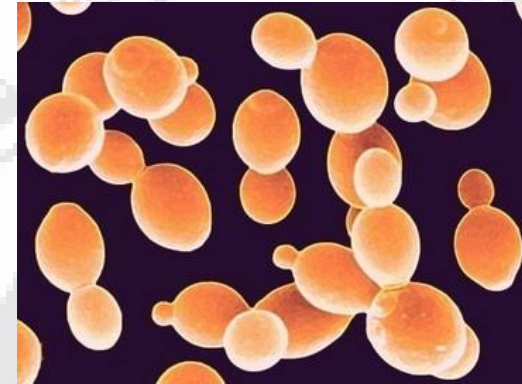


Fermentation Process

- Using yeast or bacteria
- In yeast fermentation, the glucose solution obtained from starch saccharification or cellulose hydrolysis is cooled to around 32°C.
- Yeast culture is added into the solution under aseptic condition
- Glucose in the solution penetrates into the yeast cells through a series of enzymatic reactions to eventually ethanol, CO₂ and energy.
- Both ethanol and CO₂ penetrate out of yeast cells.
- CO₂ readily dissolves in water, but can easily be saturated in fermentation broth.
- The length of initial stage depends on yeast inoculation ratio and the fermentation temperature.
- At normal inoculation ratio (5-10%), 30°C, it takes approximately 6-8 h.
- Then the yeast cells will tremendously increase to over 10⁸ cells/mL.
- The fermentation becomes very active, resulting in rapid ethanol, CO₂ and energy production, which is indicated by vigorous bubbling and heat production.
- At this time, cooling is required to maintain the fermentation temperature at 30°C.
- Active fermentation lasts about 12h, then the fermentation activity slows down because less glucose is available.
- During the slow fermentation period, the yeast cells do not grow anymore, the biochemical reactions are limited by the substrate (glucose) concentration

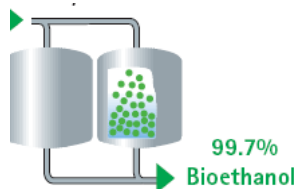
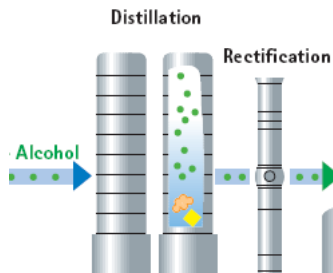
Principal Yeasts used

- *Saccharomyces cerevisiae*
- *Zymomonas mobilis*



After Fermentation

- Fermentation product is usually a dilute aqueous solution containing 3-12 wt% of ethanol
- Separation of ethanol from fermentation broth is an energy-intensive process



- **Distillation and Rectification:** That means concentration and cleaning the ethanol produced by the distillation by removing by-products.
 - **Definition of Distillation:** It is a thermal separation method that can be used to fractionate liquid mixtures. It utilises the different volatility of the components of the mixture to be separated.
- Dehydration:** drying (removing residual water) off the ethanol

A NEW DILEMMA IN FOOD SECURITY



LIMITED
NATURAL
RESOURCES

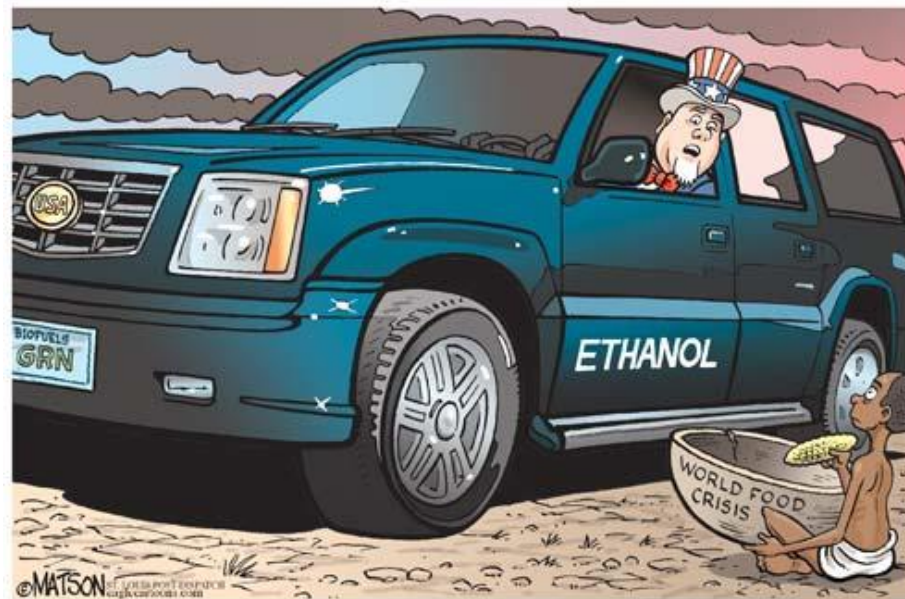


CROPS

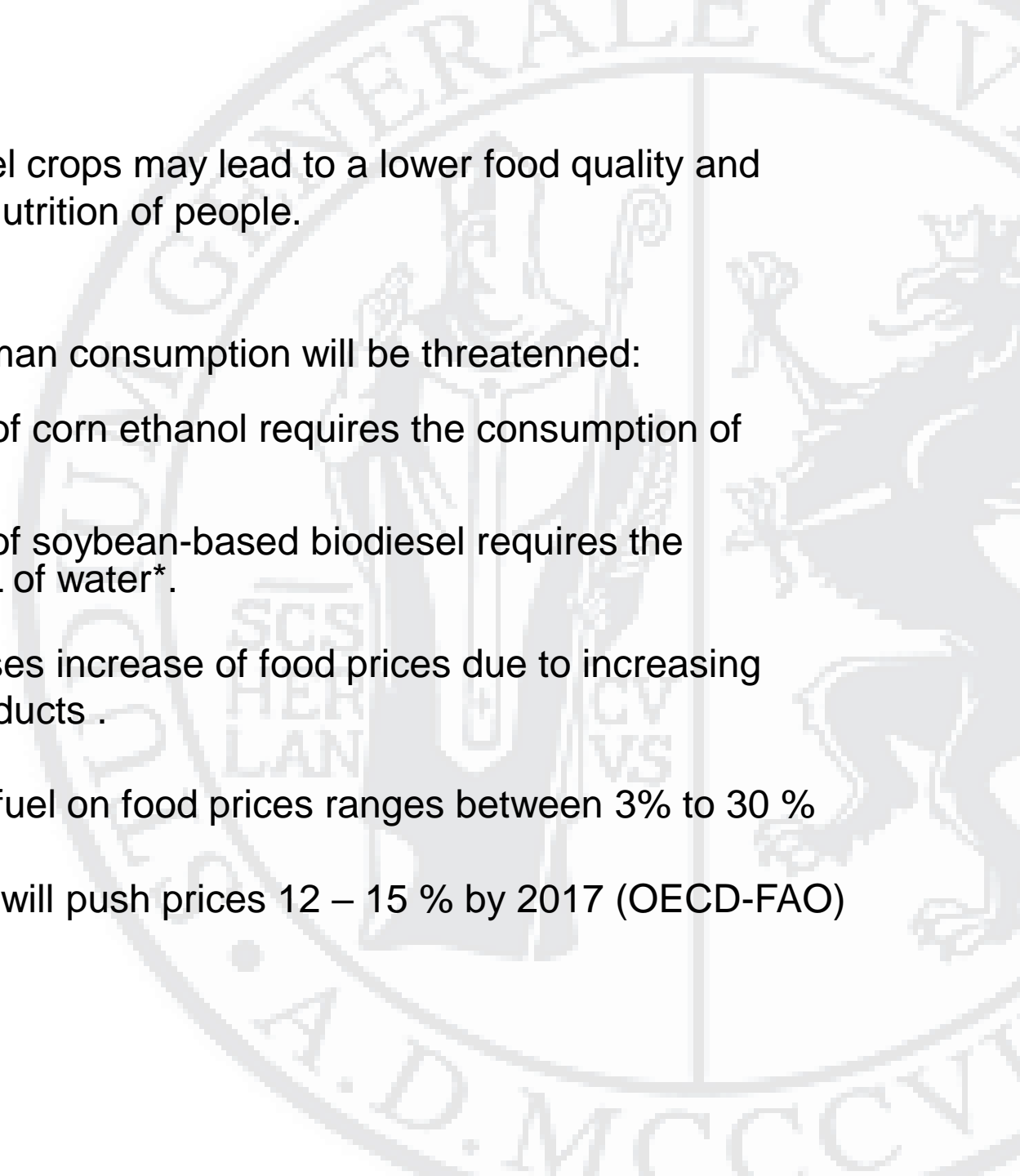
FOOD

**INCREASED
COMPETITION**

BIOFUELS



"YOU GONNA EAT THAT?"

- 
- Increase in demand of fuel crops may lead to a lower food quality and diversity, threatenning the nutrition of people.
 - Water availability for human consumption will be threatennd:
 - Producing one gallon of corn ethanol requires the consumption of 640 L of water*.
 - Producing one gallon of soybean-based biodiesel requires the consumption of 3400 L of water*.
 - Biofuels production causes increase of food prices due to increasing demand for agricultural products .
 - Current influence of biofuel on food prices ranges between 3% to 30 %
 - Future trend: biofuels will push prices 12 – 15 % by 2017 (OECD-FAO)

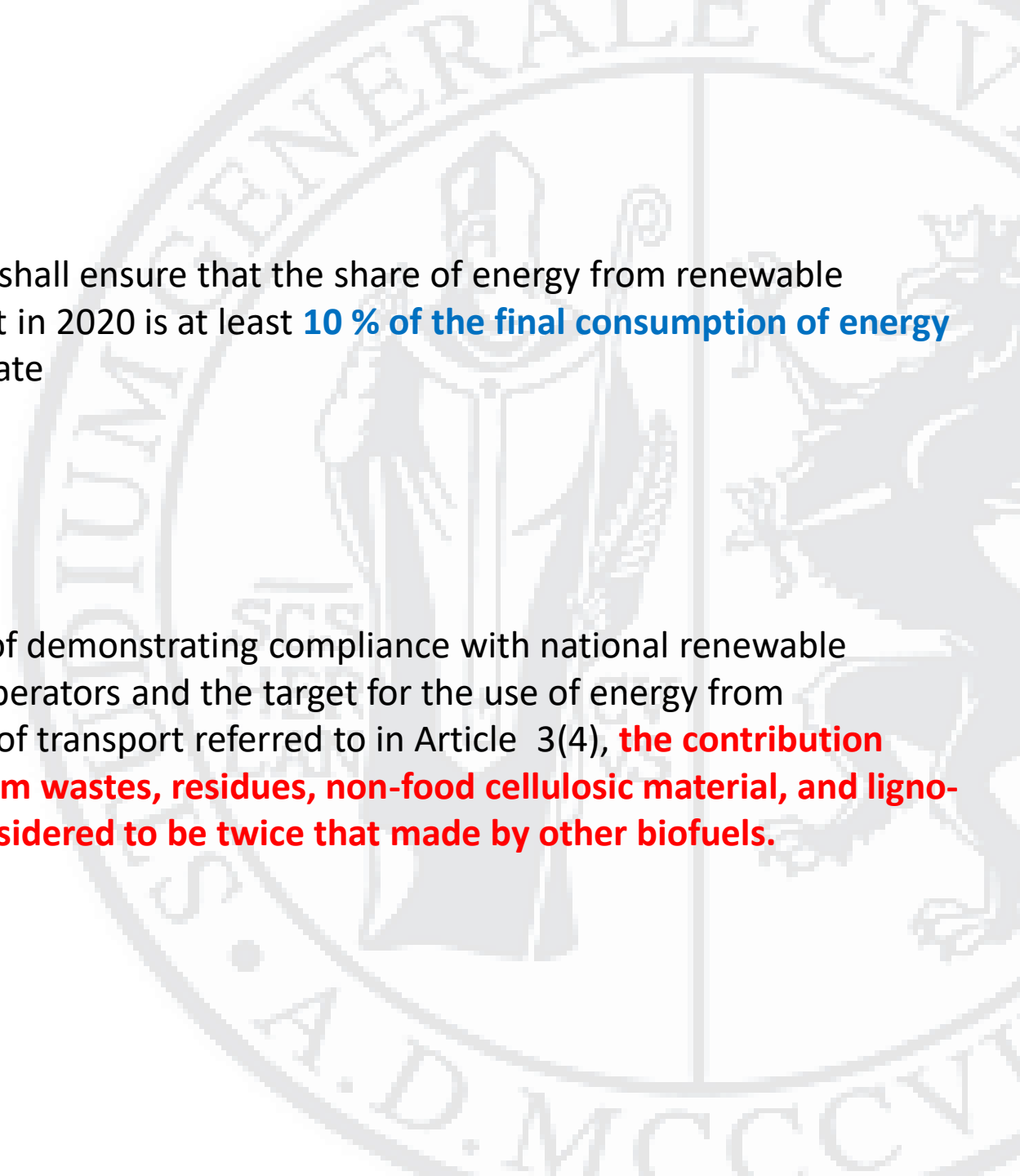
*www.energytribune.com

Land-use requirements **Article 17 (3)-(5) of the Directive 2009/28/EC** specifies three criteria for the land from which the feedstock for the biofuel originates.

First, biofuels shall not be made from raw material obtained from land with high biodiversity value, which includes primary forest and other wooded land, areas designated for nature protection or the protection of rare, threatened or endangered ecosystems or species, and highly biodiverse grasslands.

Second, biofuels shall not be made from raw material obtained from land with high carbon stock, namely wetlands, continuously forested areas, or land spanning more than one hectare with a certain minimum canopy cover.

Third, biofuels shall not be made from raw material obtained from peatland, unless evidence is provided that the cultivation and harvesting of that raw material does not involve drainage of previously undrained soil.



Article 3.4 Each Member State shall ensure that the share of energy from renewable sources in all forms of transport in 2020 is at least **10 % of the final consumption of energy in transport** in that Member State

Article 21.2. For the purposes of demonstrating compliance with national renewable energy obligations placed on operators and the target for the use of energy from renewable sources in all forms of transport referred to in Article 3(4), **the contribution made by biofuels produced from wastes, residues, non-food cellulosic material, and ligno-cellulosic material shall be considered to be twice that made by other biofuels.**

The EU perspective

“There has never been a better moment to push the case for biofuels. Crude oil prices remain high. We face stringent targets under the Kyoto Protocol. And the recent controversy over imports of Russian gas has underlined the importance of increasing Europe’s energy self-sufficiency. Raw materials for biofuel production also provide a potential new outlet for Europe’s farmers, who have been freed by CAP reform to become true entrepreneurs.”

**Mariann Fischer Boel, Commissioner for
Agriculture and Rural Development,
8 February 2006**

Source: Commission, Fact Sheet on Biofuels, 2006

Second generation Biofuels

First generation biofuels



- Biofuels produced from raw materials in competition with food and feed industry
- Examples include, bioethanol from sugarcane, sugar beet and starch (corn and wheat), biodiesel from oil based crop like rape seed, sunflower, soybean, palm oil and waste edible oils and starch derived biogas

Second generation biofuels



- Biofuels produced from non-food crops (energy crops) or raw materials based on waste residues
- Examples include, biogas derived from waste and residues, biofuels from lignocelluloses materials like residues from agriculture, forestry and industry and biofuels from energy crops such as sorghum

Third generation biofuels



- Biofuels produced using aquatic microorganisms like algae
- Examples include,
- biodiesel produced using algae and algal hydrogen

Fourth generation biofuels




- Biofuels based on high solar efficiency cultivation
- Examples include, carbon-negative technologies and technologies of the future



Municipal Waste

- Food waste
- Waste Cooking Oil
- Sewage
- Plastics
- Paper
- Cardboards
- Textile
- Leather
- Construction and Demolition waste



Animal Waste

- Fats
- Tallow
- Lard
- Intestine
- Blood
- Meat
- Processing waste
- Manure
- Swine waste



Forestry Waste

- Bark
- Sawdust
- Pulping liquors
- Fibres
- Dead trees
- Cutting and Logging waste
- Leaves
- Straws



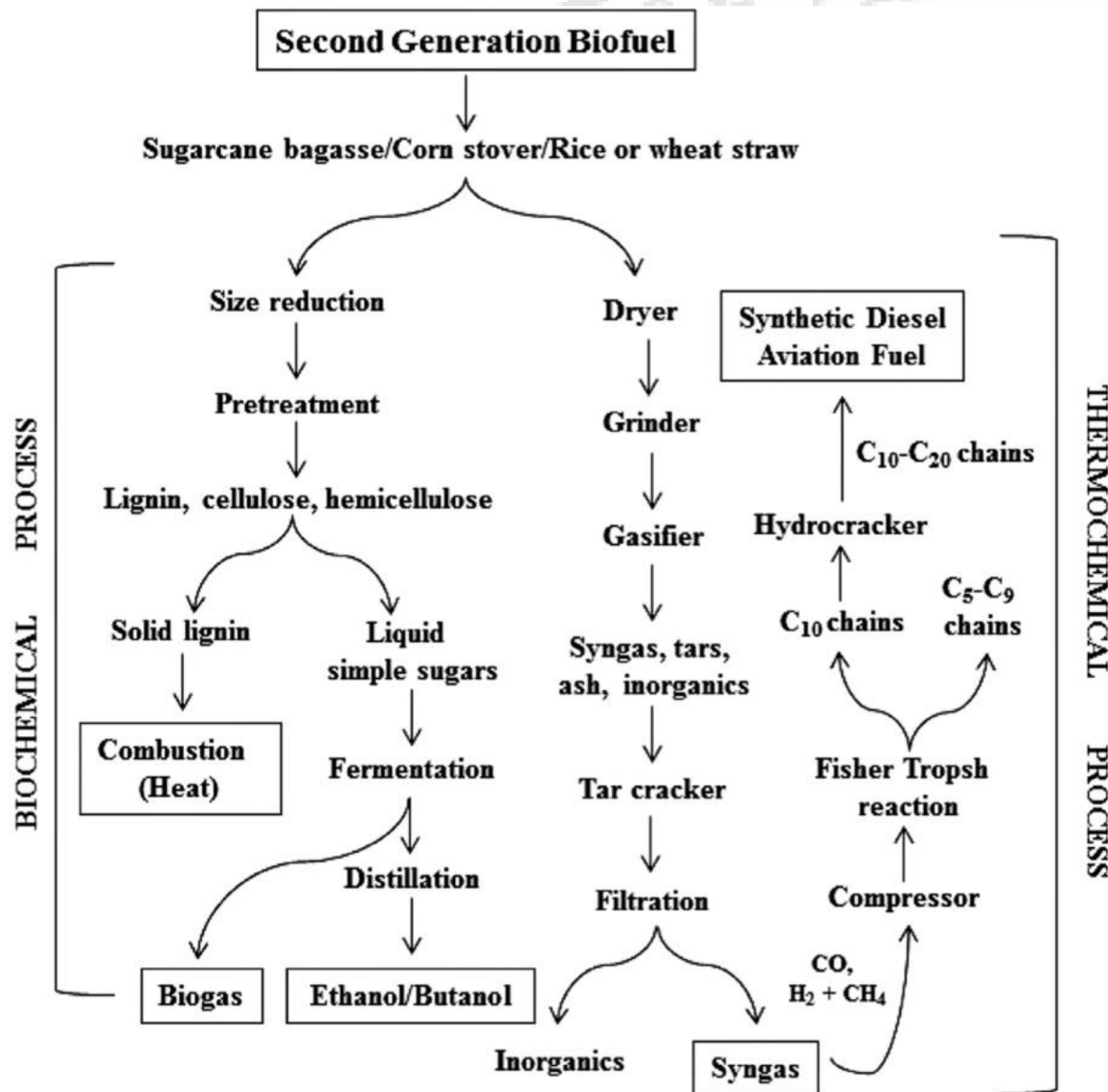
Agricultural Waste

- Crop waste
- Citrus waste
- Green waste
- Rice straw
- Wood chips
- Sawdust



Industrial Waste

- Olive
- Pulp and Paper industry waste
- Sugar and coffee industry waste





Produces inhibitory compounds:
Furfural,
Acetic acid,
HMF

Requires removal

Optimum temp **50-55°C**

Requires cooling

Normal yeast Strain
~ 30°C

Higher recovery cost to increase temperature

Conventional process

Lignocellulosic Material

Pre-treatment

Saccharification

Fermentation

Distillation

Ethanol

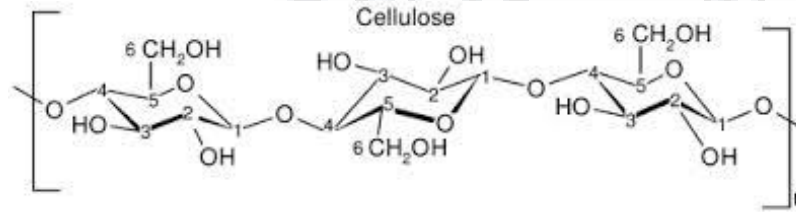
In the same tank

Simultaneous Saccharification & Fermentation

Usage of **tor** tolerant strain

Usage of heat tolerant strain

Basic structure of cellulose



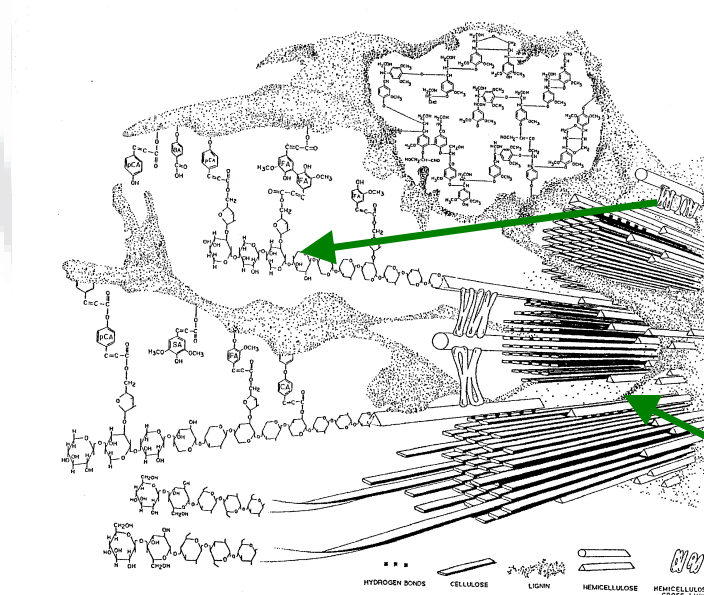
Cellulose is a long-chain homogeneous polysaccharide of D-glucose units, linked by β -1,4 glycosidic bonds.

It is composed of over 10,000 glucose units.

Lignocellulosic material can be degraded to fermentable sugars, but is more difficult to convert than starch derived raw materials

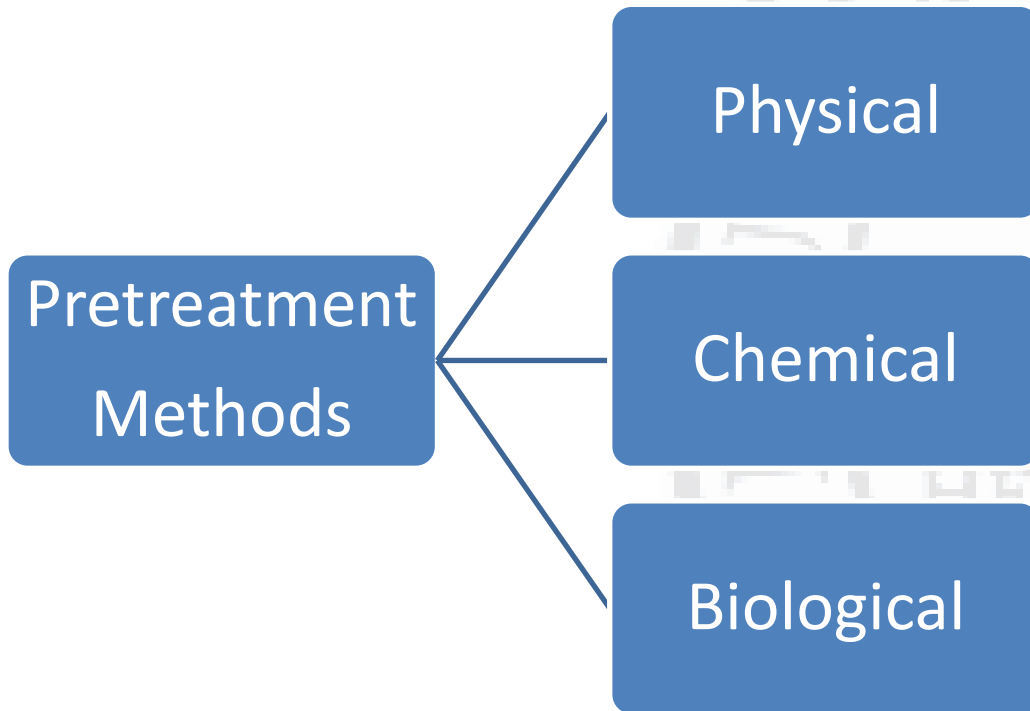
Purposes of pretreatment

- Helps in separation of main biomass components (cellulose, hemicellulose and lignin)
- Increase available surface area
- Reduce particle size
- Ideally pretreatment:
 - *Solubilizes hemicellulose*
 - *Increases enzymatic hydrolysis ability of cellulose*



Hemicellulose is degraded to mainly glucose, galactose, mannose, xylose and arabinose

Cellulose is hydrolysed to glucose units



Physical Pretreatments



Mechanical comminution

- By chipping, grinding, milling to reduce cellulose crystallinity.
- Size of material is usually 1 - 3 cm after chipping, and 0.2 – 2 mm after milling or grinding.
- Vibratory ball milling is more effective than the ordinary ball milling.

Steam explosion

- Most commonly used methods for lignocellulosic materials
- Chipped biomass is treated with high-pressure saturated steam and then the pressure is swiftly released, which makes the materials undergo an explosive decompression.
- Carried out at 160 – 260 °C (0.69 – 4.83 MPa)
- It causes hemicellulose degradation and lignin transformation due to high temperature, thus increases the potential of cellulose hydrolysis.
- Factors to consider during steam explosion pretreatment; residence time, temperature, chip size, moisture content
- Addition of H_2SO_4 (or SO_2) or CO_2 in steam explosion can improve enzymatic hydrolysis, decrease inhibitory compounds and lead to more complete removal of hemicellulose.

- Optimal conditions of steam explosion pretreatment for sugarcane bagasse: temperature, 220°C; residence time, 30 s; water-to-solid ratio, 2; H₂SO₄ dose, 1 g H₂SO₄ per 100 g dry bagasse. Based on this set condition, they got 65.1 g sugar/100 g starting bagasse after steam explosion pretreatment.
- Advantages of steam explosion pretreatment:
 - a) low energy requirement compared to mechanical comminution
 - b) no recycling or environmental costs associated with chemical pretreatment
 - c) the most cost-effective pretreatment processes for hardwoods and agricultural residues, but less effective for softwoods.
- Limitations of steam explosion:
 - a) destruction of a portion of xylan fraction
 - b) incomplete disruption of lignin-carbohydrate matrix
 - c) generation of inhibitory compounds in downstream processing

Ammonia fiber explosion (AFEX)

Carbon dioxide explosion

Pyrolysis

- Lignocellulosic materials are treated at temperature higher than 300°C.
- Cellulose would rapidly decompose to produce gaseous and tarry compounds.

Chemical Pretreatment



Ozonolysis

- Ozone is used to degrade lignin and hemicellulose, while cellulose is hardly affected.
- Advantages:
 - a) it effectively removes lignin
 - b) it does not produce toxic residues for the downstream processes
 - c) the reactions are carried out at room temperature and pressure.
- Disadvantage:

A large amount of ozone is required in the process, making the process expensive.

Acid Hydrolysis

- Using concentrated acids such as H_2SO_4 and HCl
- Dilute sulfuric acid pretreatment could achieve high reaction rates and significantly improve cellulose hydrolysis.
- There are two types of dilute acid pretreatment process:

High temperature ($T > 160^\circ\text{C}$), continuous-flow process for low solids loading (5%-10% [w/w])

Lower temperature ($T < 160^\circ\text{C}$), batch process for high solids loading (10%-40% [w/w])

- Cost is higher than steam explosion or AFEX.
- A neutralization of pH is necessary before enzymatic hydrolysis or fermentation process.

Alkaline Hydrolysis

- Alkaline pretreatment can disrupt lignin structure and decrease crystallinity of cellulose and degree of sugar polymerization.
- Compared with acid pretreatment, alkaline pretreatment has less sugar degradation and inhibitory compounds (furan derivatives) formation
- NaOH and lime can be recovered or regenerated.
- NaOH is very efficient in removing lignin from lignocellulosic materials at a temperature of 100°C for 15-30 min.
- Lime pretreatment of switchgrass at low temperature could significantly improve the sugar yield , but the time is longer (6 h).

Oxidative delignification

- Lignin biodegradation could be catalyzed by peroxidase enzyme with the presence of H_2O_2 .
- It was reported that about 50% lignin and most hemicellulose were solubilized by 2% H_2O_2 at 30°C within 8 h.

Organosolv Pretreatment

- An organic or aqueous organic solvent mixture with inorganic acid catalyst (HCl or H_2SO_4) is used to break the internal lignin and hemicellulose bonds.
- The organic solvents used include methanol, ethanol, acetone, ethylene glycol, triethylene glycol and tetrahydrofurfuryl alcohol.
- At high temperature ($T > 185^\circ\text{C}$), the addition of catalyst is unnecessary.
- Usually, a high yield of xylose can be obtained with the addition of acid.
- **Solvents used in the process need to be drained from the reactor, evaporated, condensed and recycled to reduce the cost.**
- **Removal of solvents from the system is necessary because the solvents may be inhibitory to the growth of organisms.**

Biological Pretreatment



Fungi pretreatment

- Microbes used: brown-, white-, and soft-rot fungi.
- Brown rots mainly attack cellulose.
- White and soft-rots attack both cellulose and lignin.
- White-rot fungi are the most effective basidiomycetes for biological pretreatment of lignocellulosic materials.
- The white-rot fungus *Phanerochaete chrysosporium* produces lignin-degrading enzymes, lignin peroxidases in response to carbon or nitrogen limitation.
- Advantages of biological pretreatment:
Low energy requirement and mild environmental conditions
- Disadvantage of biological pretreatment:
Rate of hydrolysis is very slow



White rot fungi

Disadvantages:

- More of these species can be invasive and have negative impacts on water resources, biodiversity and agriculture
- At the moment they are still more expensive than fossil fuels
- Still under research and development for a significant commercial scale

Third generation Biofuels

First generation biofuels



- Biofuels produced from raw materials in competition with food and feed industry
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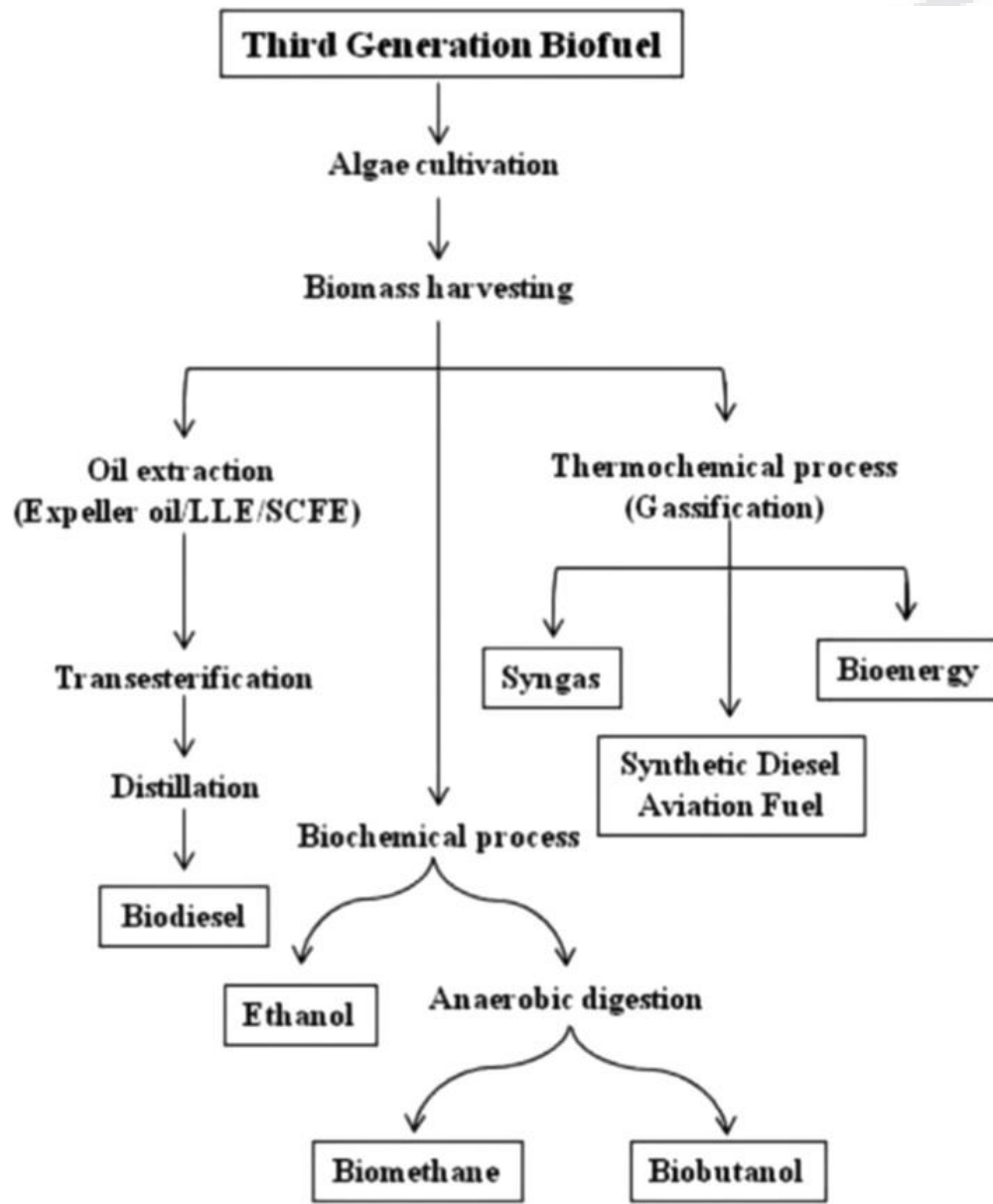


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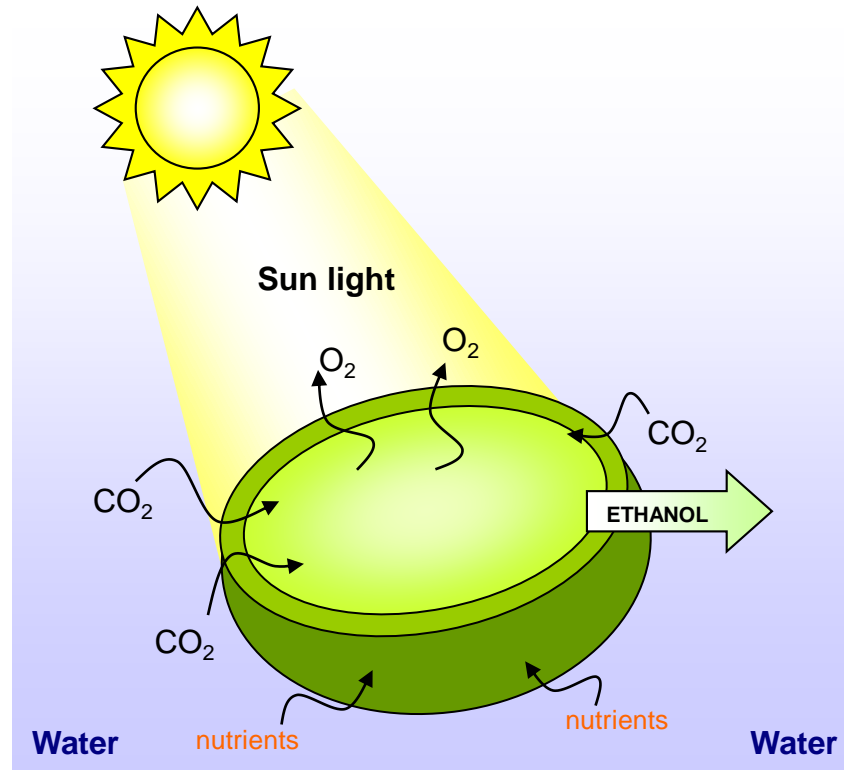
Fourth generation biofuels



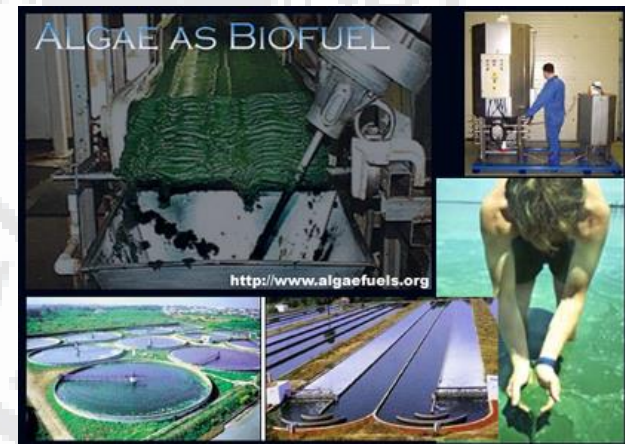
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- Examples include, carbon-negative technologies and technologies of the future



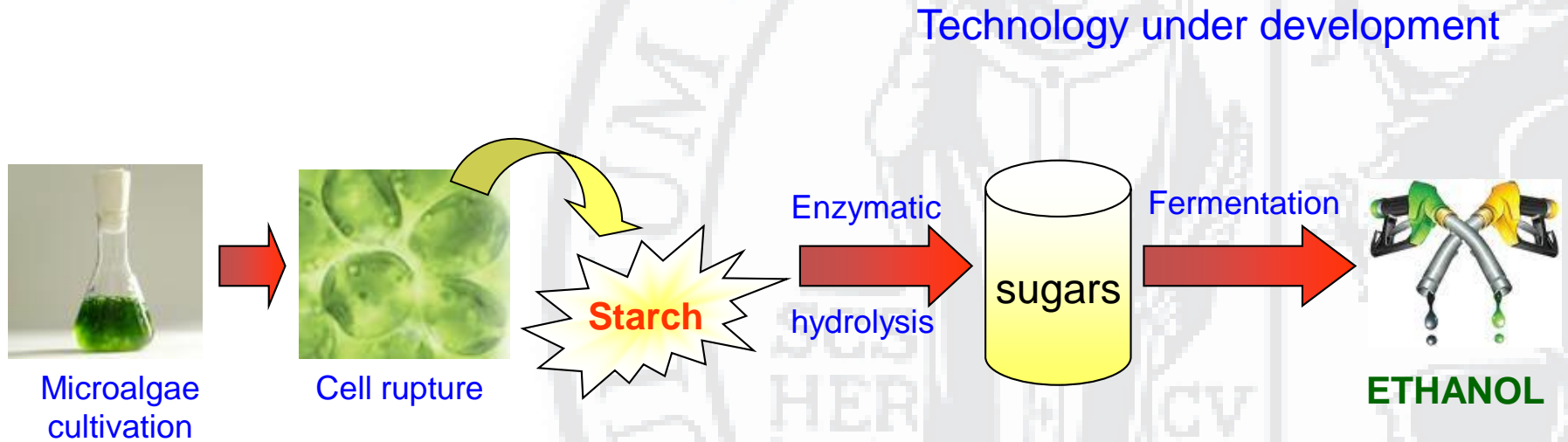
Microalgae as a feedstock for bioethanol production



*The microalgae *Chlorella vulgaris*, particularly, has been considered as a promising feedstock for bio-ethanol production*



Microalgae as a feedstock for bioethanol production



Some algal species are able to conduct self-fermentation

Bioethanol yield from different sources:

Source	Ethanol yield (L/hectare)
Corn stover	1,050-1,400
Wheat	2,590
Cassava	3,310
Sweet sorghum	3,050-4,070
Corn	3,460-4,020
Sugar beet	5,010-6,680
Sugarcane	6,190-7,500
Switch grass	10,760
Microalgae	46,760-140,290

Advantages of this process:

- ✓ microalgae can be harvested batch-wise nearly all-year-round
- ✓ they grow in aqueous media, but need less water than terrestrial crops, therefore reducing the load on freshwater sources
- ✓ the ability of microalgae to fix CO₂
- ✓ They are relatively easy to grow, but the algal oil is hard and expensive to extract

Fourth generation Biofuels

First generation biofuels



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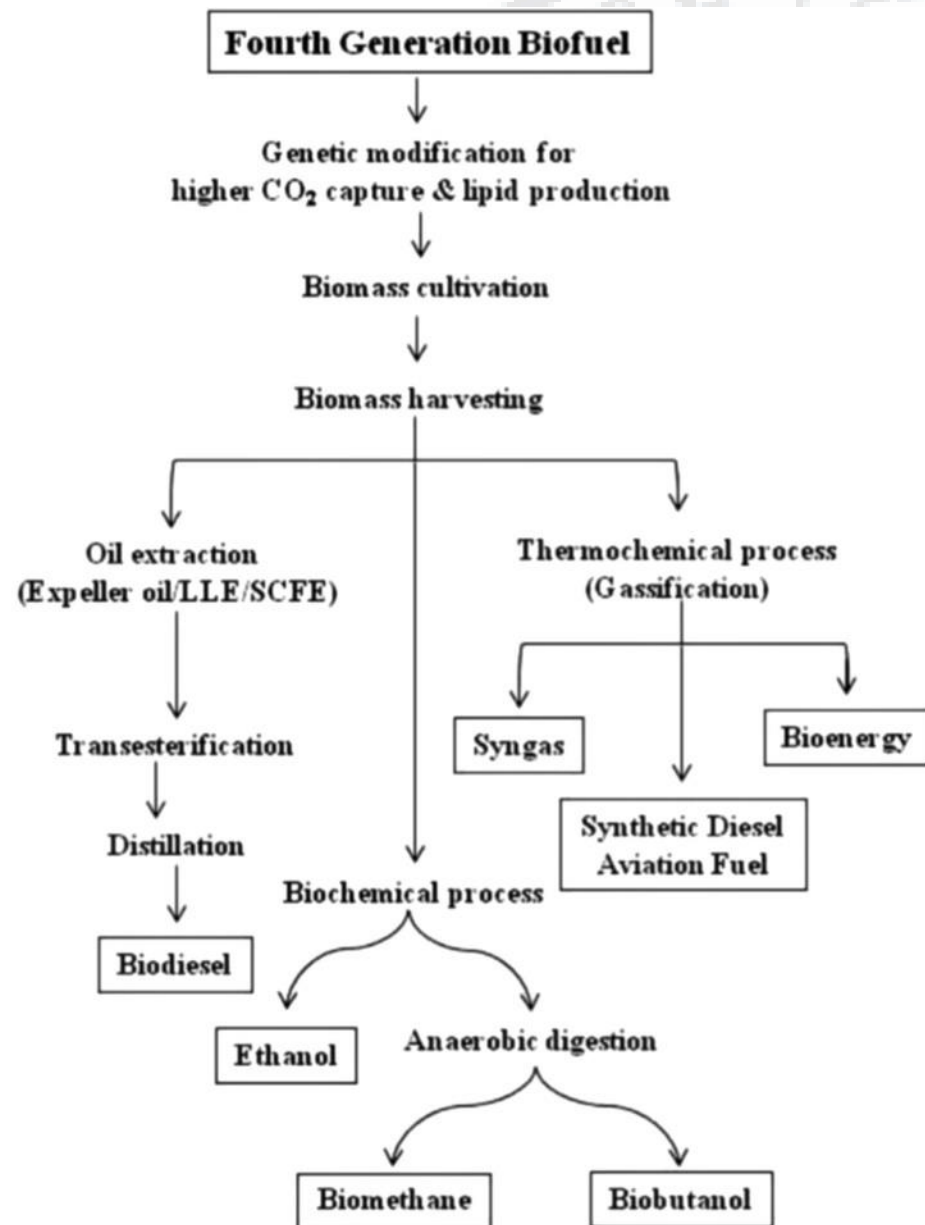


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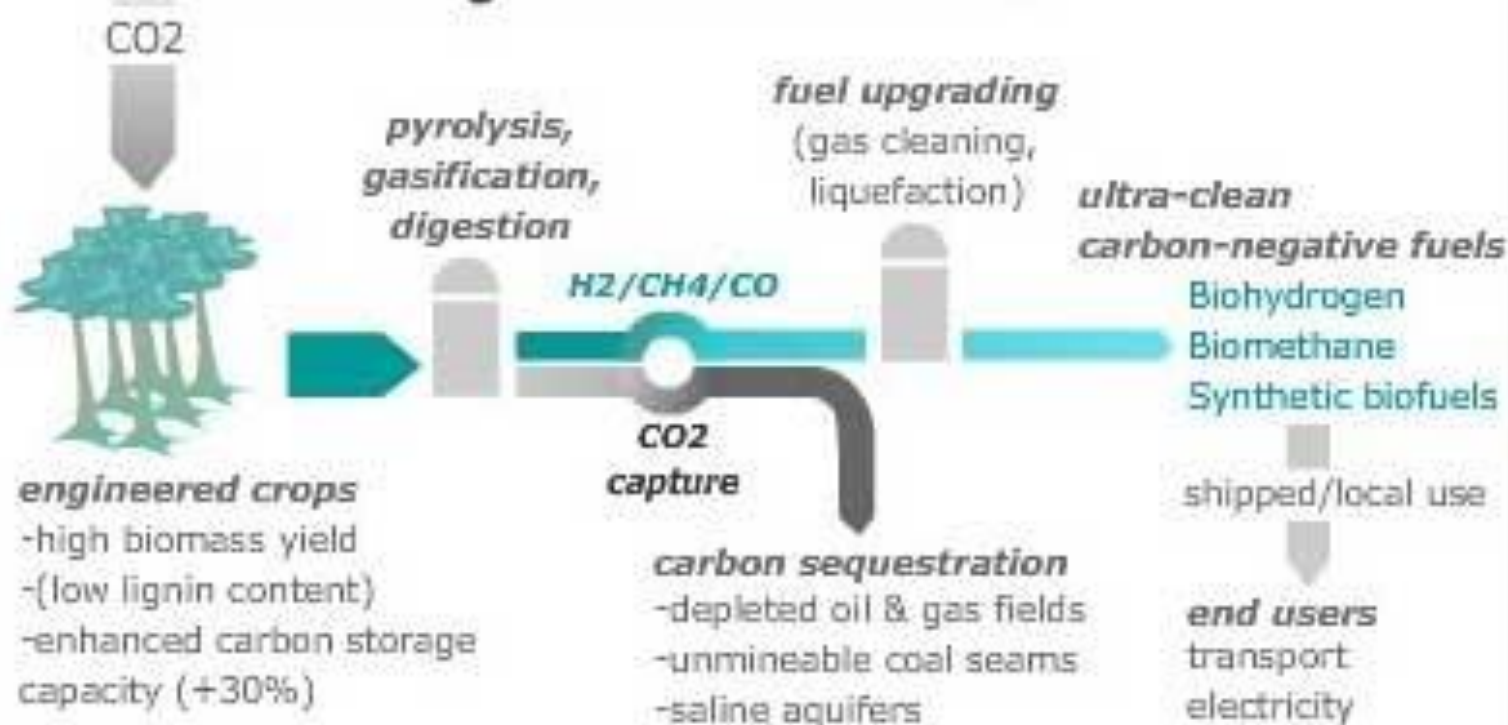
Fourth generation biofuels



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'Fourth generation' biofuels



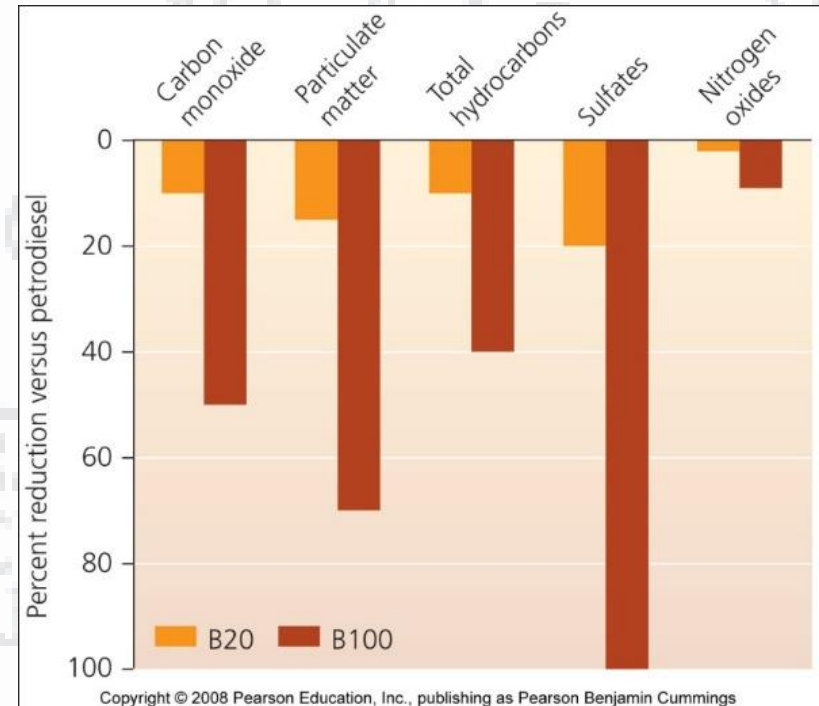
B - BIODIESEL

The Biodiesel Cycle



Biodiesel is produced from vegetable oil

- U.S. biodiesel producers use soybean oil
 - Animal fats, used grease, and cooking oil can also be used
 - Vehicles can run on 100% biodiesel, but the engine needs to be modified
 - Biodiesel cuts down on emissions; its fuel economy is almost as good and costs slightly more than gasoline



Biofuel uses

- Bioethanol
 - Used as neat ethanol (E95, blend of 95% ethanol and 5% water)
 - Used as E85 (85% volume ethanol with petrol) in flex-fuel vehicles
 - Used as blend smaller than 5% volume (E5) in ordinary petrol or as its derivative ETBE
- Biodiesel
 - Current maximum 5% in diesel blends, otherwise can only be used in modified diesel engines

E10

- Contains 10% ethanol, 90% gasoline
- Most common blend in U.S.
- EPA: “Substantially similar” to gasoline in all vehicles

E15

- Contains 15% ethanol, 85% gasoline
- EPA: “Substantially similar” to gasoline in MY2001 and newer vehicles

E85

- Contains 85% ethanol, 15% gasoline
- Alternative fuel under Energy Policy Act of 1992
- Used in flexible fuel vehicles (FFVs)
- Available in most states



Ethanol Steam Reforming



250-600°C

...An interesting alternative

- CO minimized
- Thermal duty reduced...
- No special steel alloys required

BUT

By-products (**coke**) more favoured

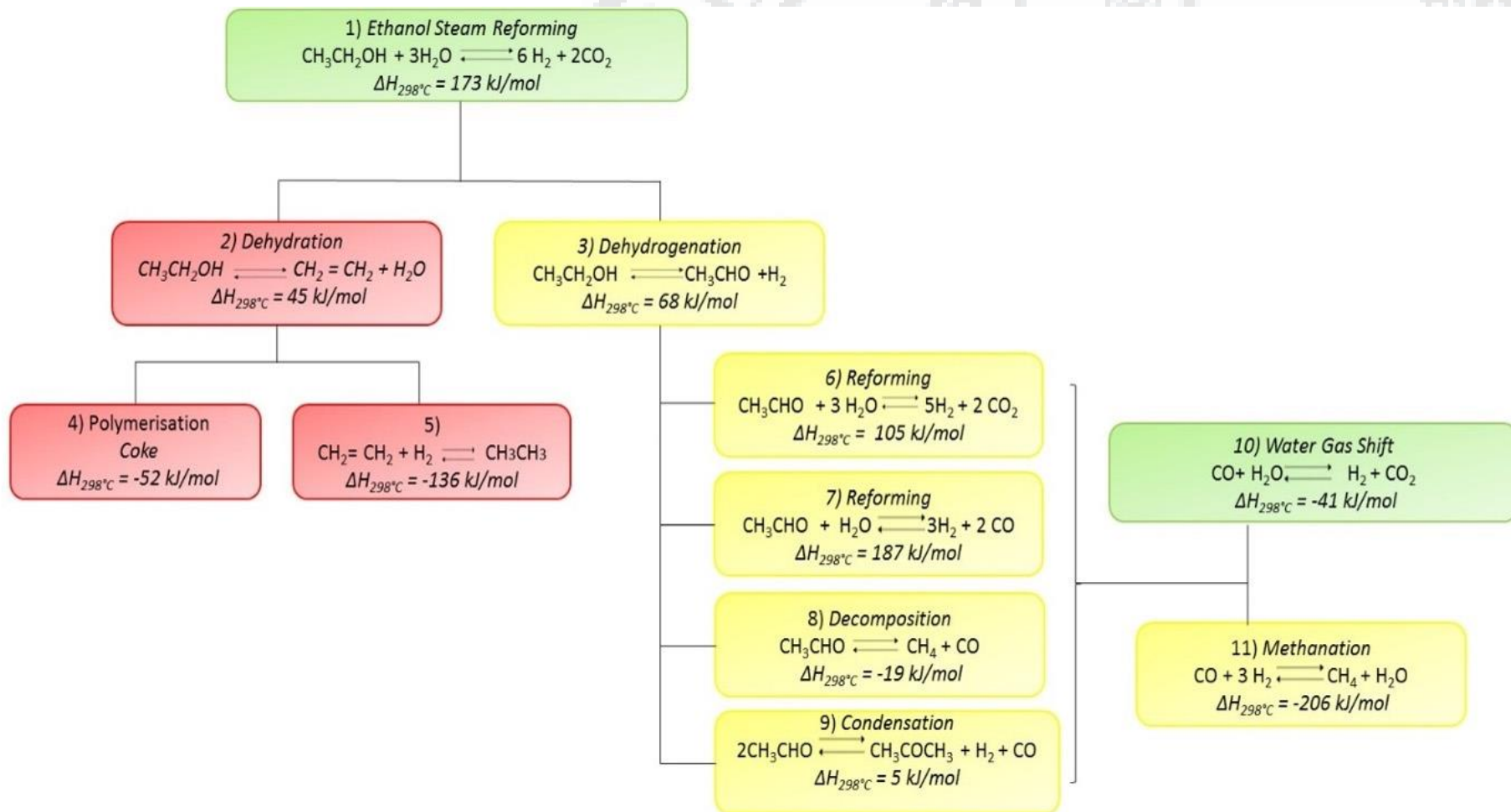
Catalyst deactivation

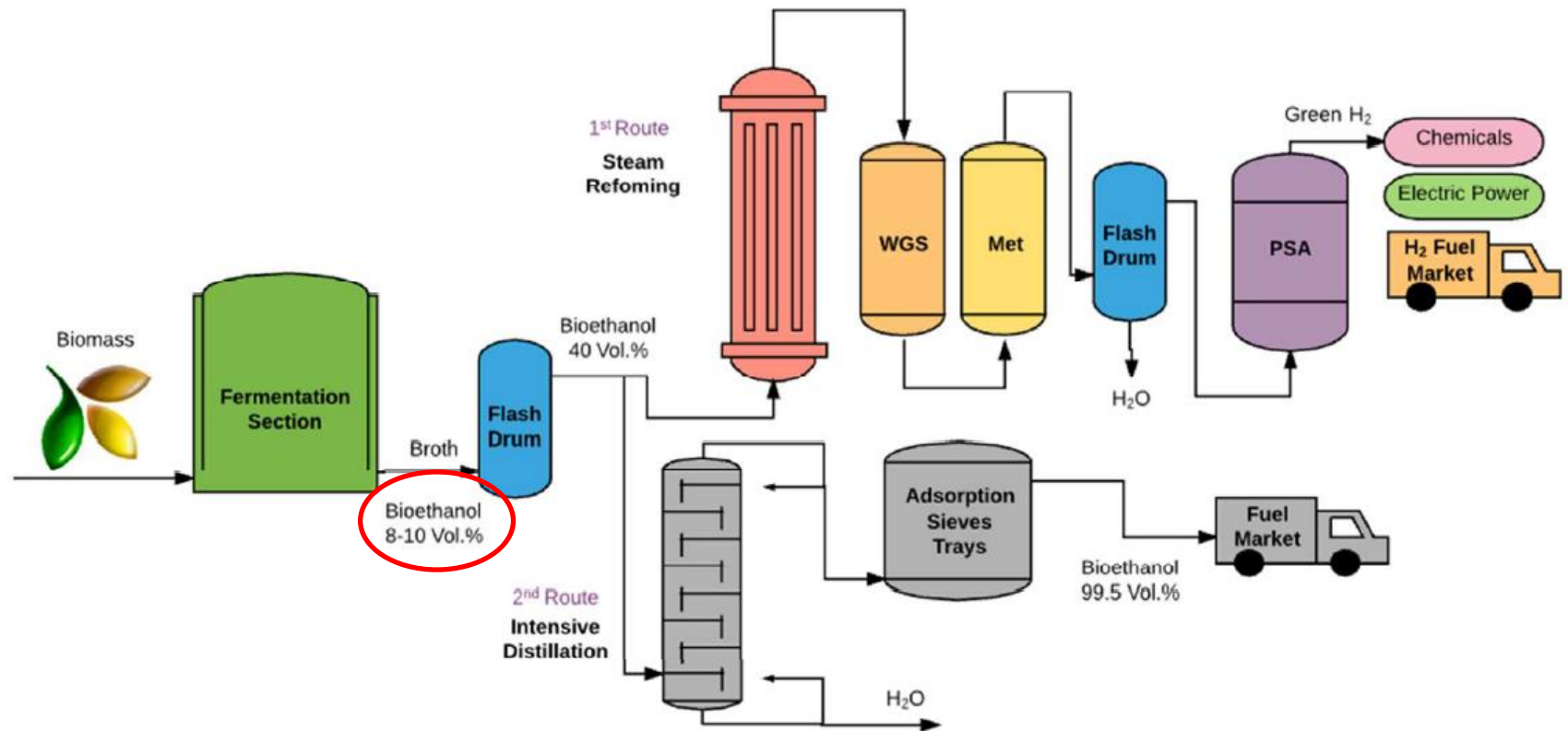
CATALYST Selection



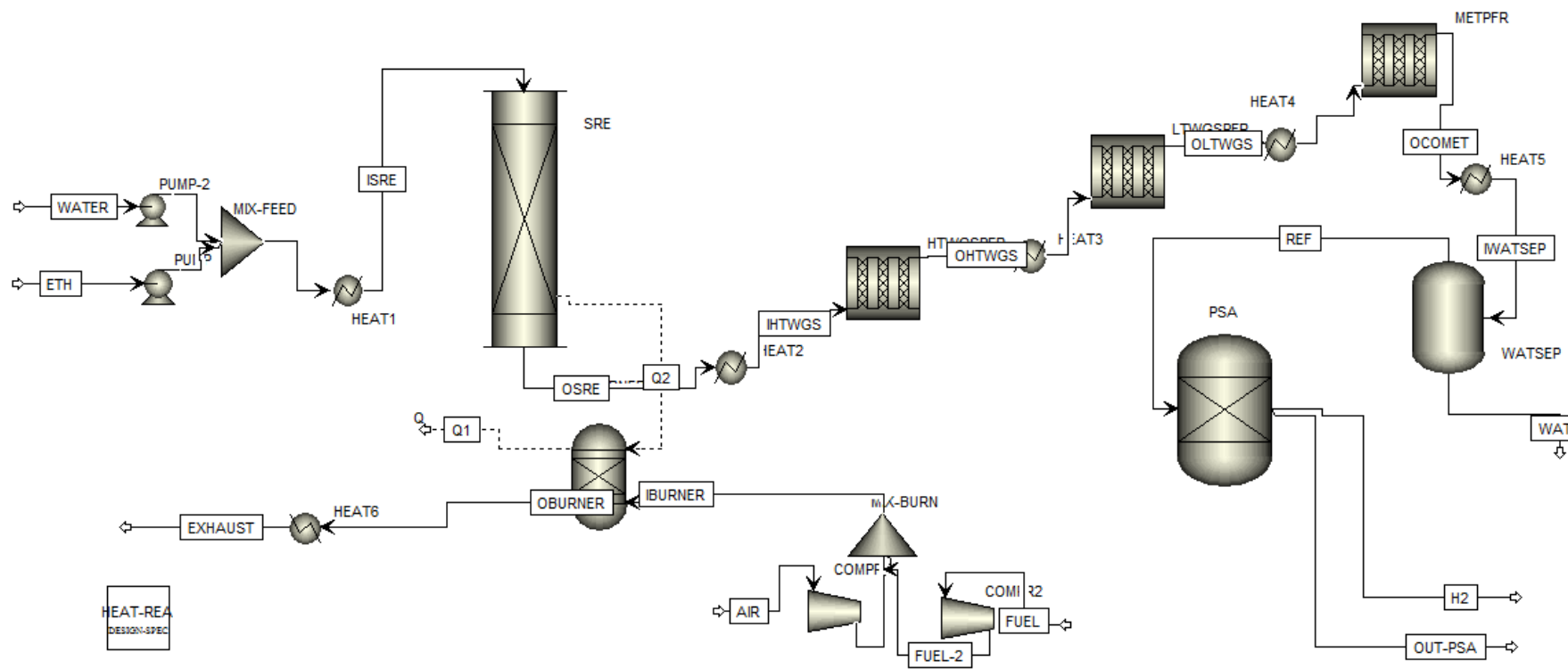
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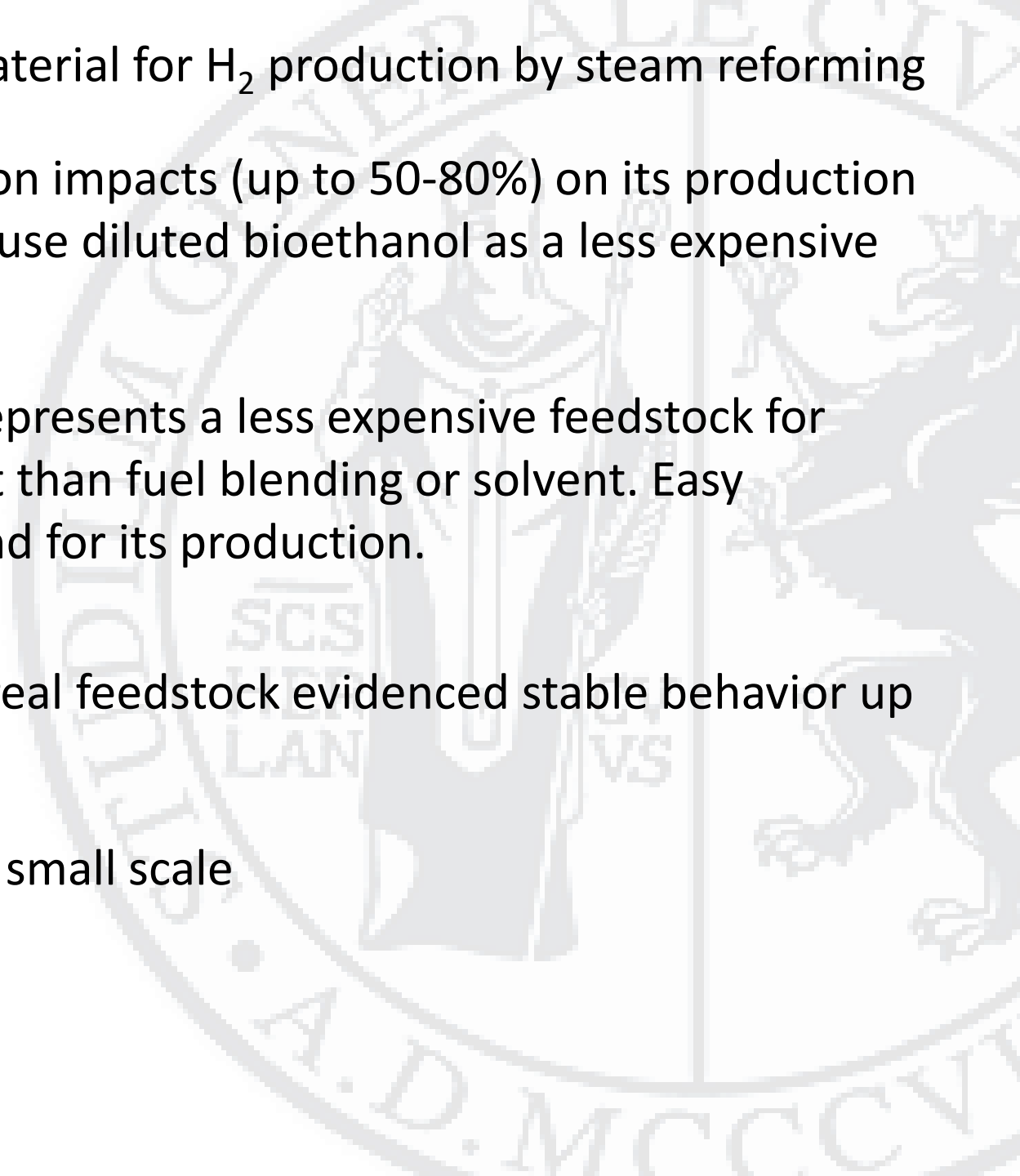






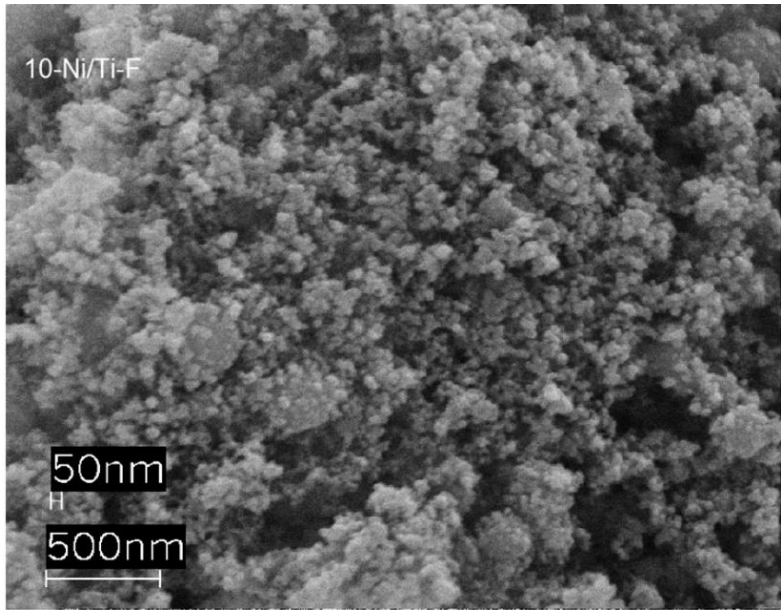
Fermentation product is usually a dilute aqueous solution containing 8-10 wt% of ethanol



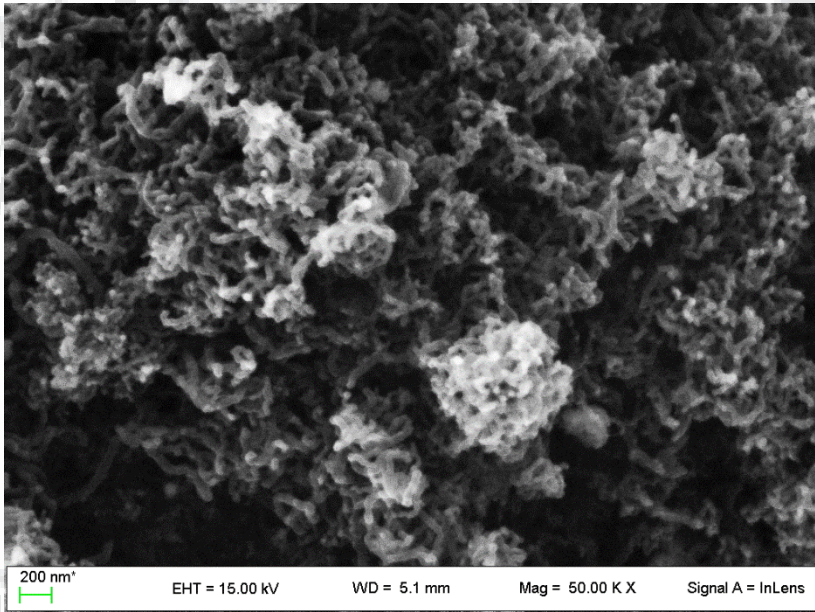
- 
- ✓ Bioethanol as raw material for H₂ production by steam reforming
 - ✓ Bioethanol purification impacts (up to 50-80%) on its production cost → possibility to use diluted bioethanol as a less expensive feedstock
 - ✓ Diluted bioethanol represents a less expensive feedstock for applications different than fuel blending or solvent. Easy solutions can be found for its production.
 - ✓ Testing less purified real feedstock evidenced stable behavior up to 100 h-on-stream.
 - ✓ Process feasible on a small scale

example

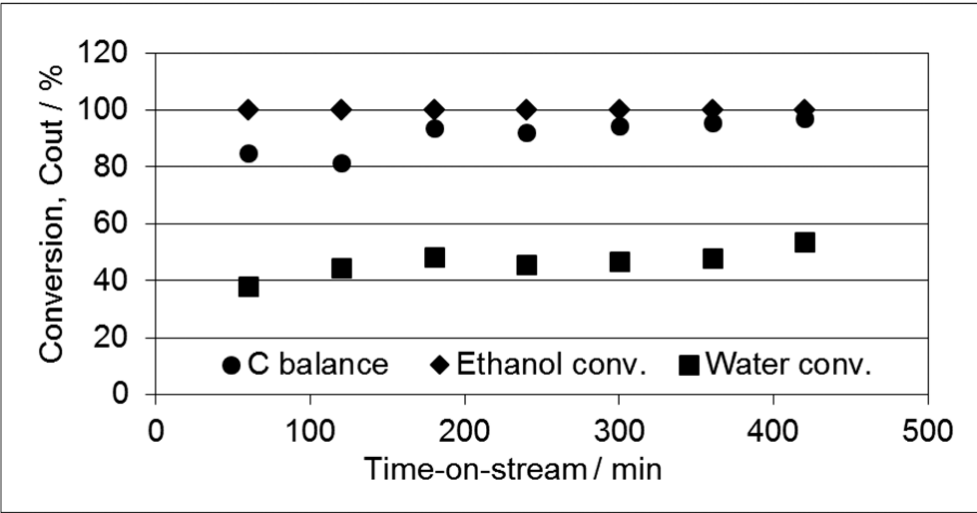
Ni/ZrO₂



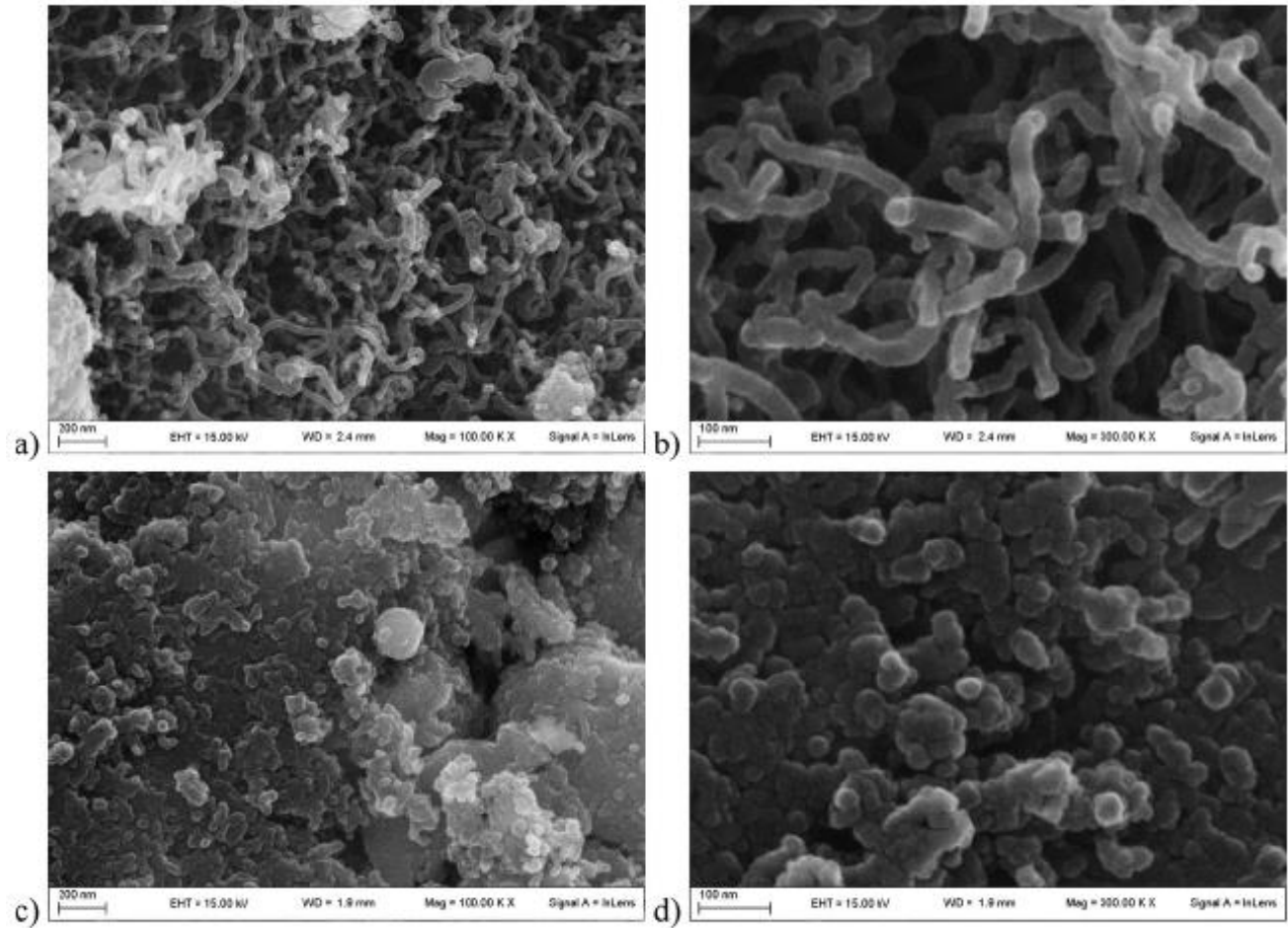
Before



After



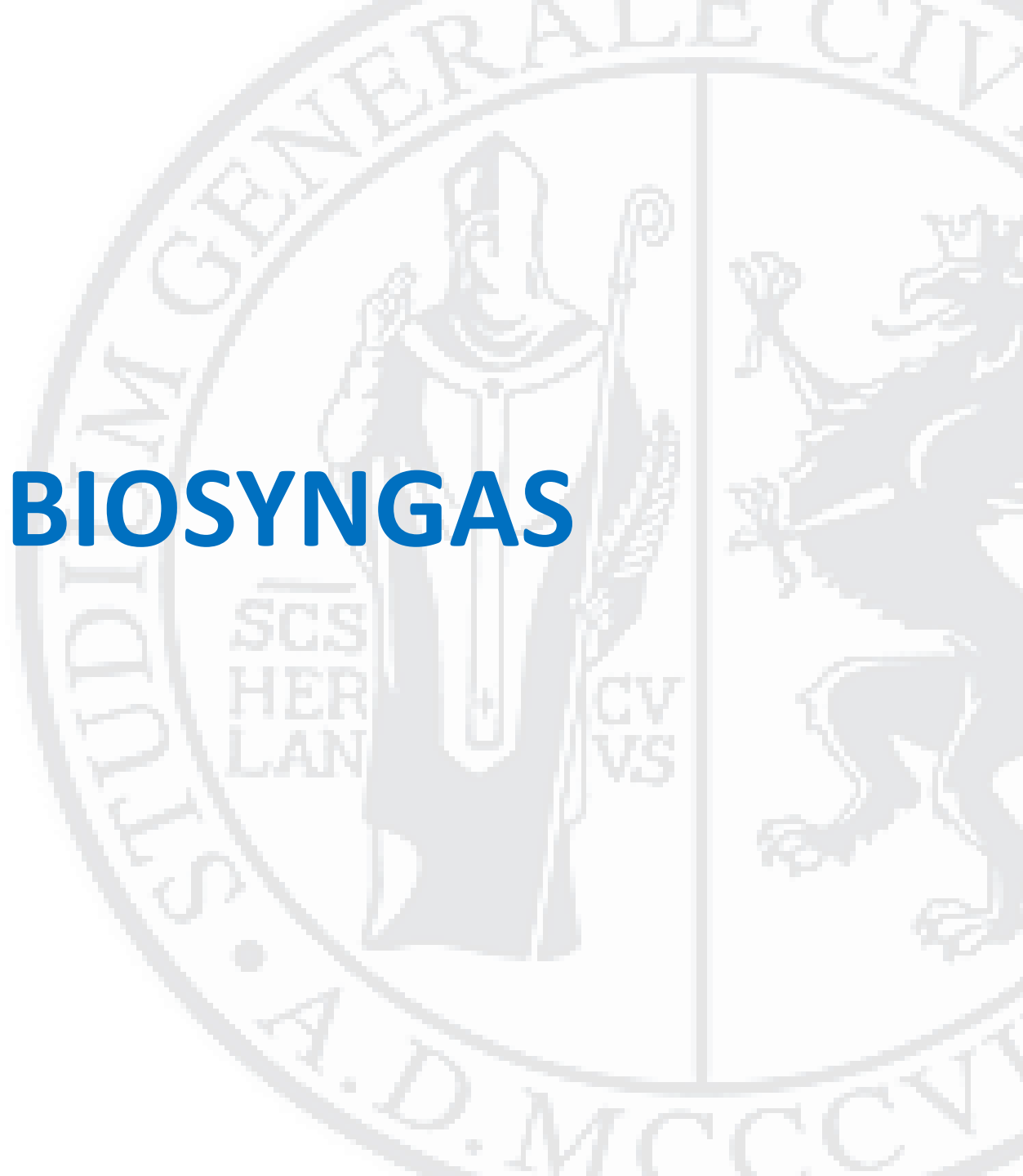
Ni/ZrO₂



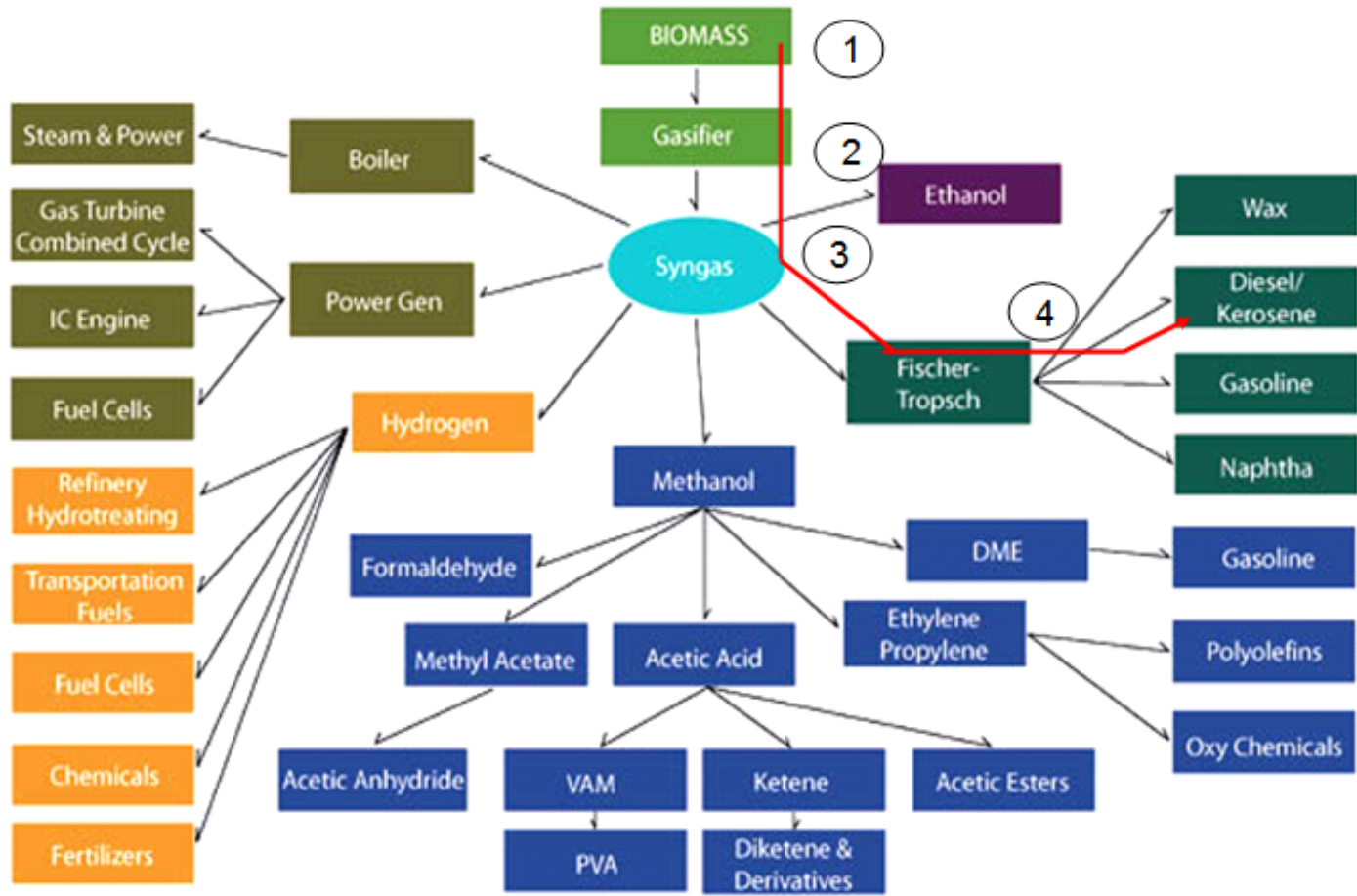
Ni-**Ca**/ZrO₂

Fig. 9. FE-SEM images of spent samples ZNi (a and b) and ZCa₉Ni (c and d).

C - BIOSYNGAS



What can be done with syngas?



Waste to Liquid Technologies
WTL

Application of Bioethanol for Fuel Cells

From biomass...



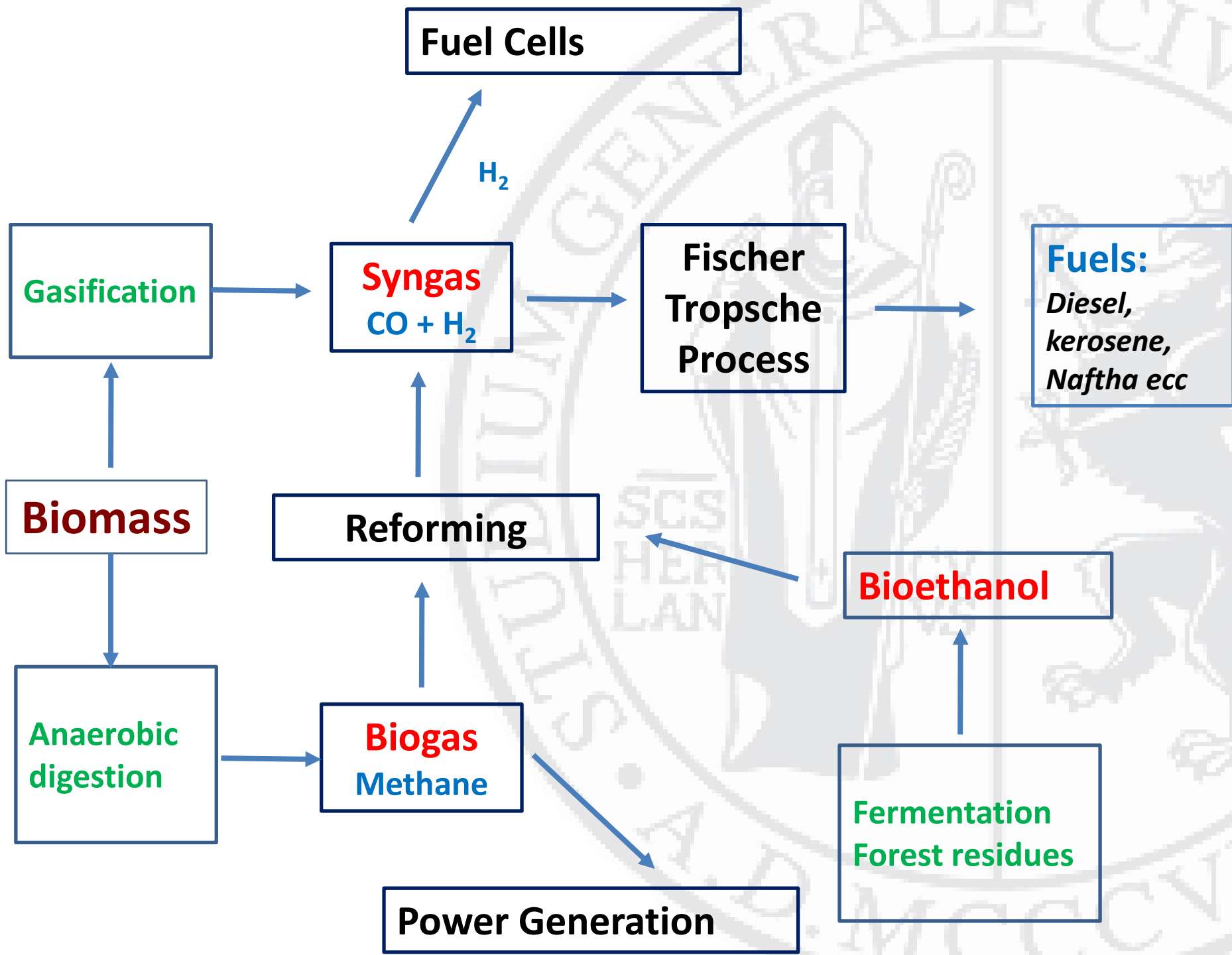
...to hydrogen!



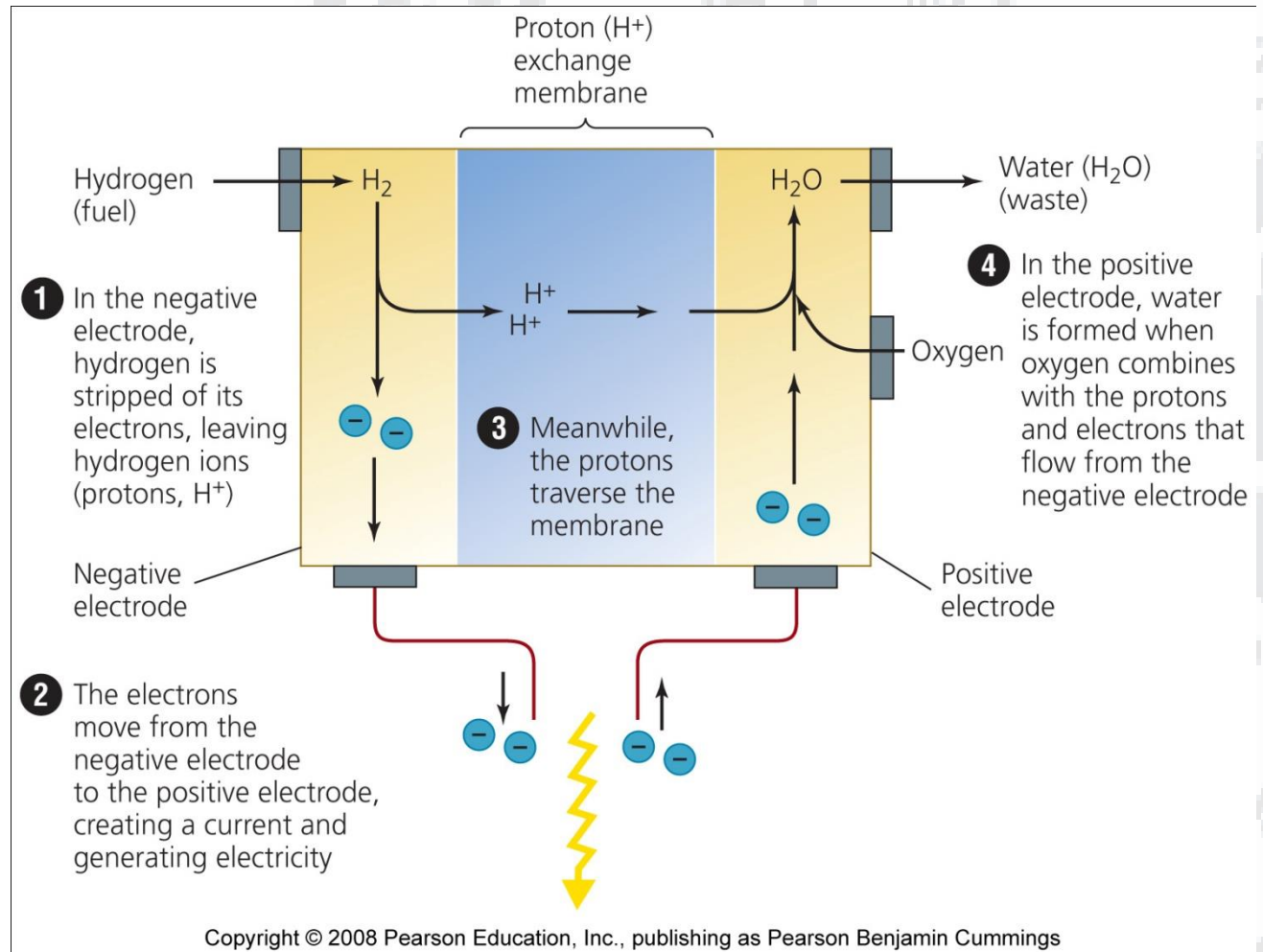
**Hydrogen is the
future energy vector**

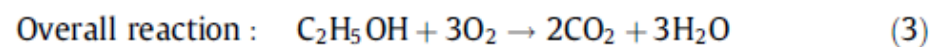
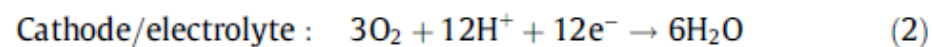
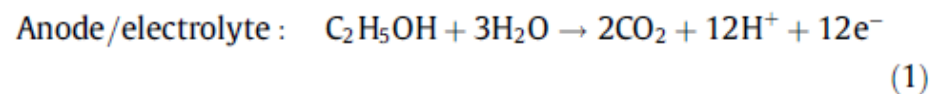
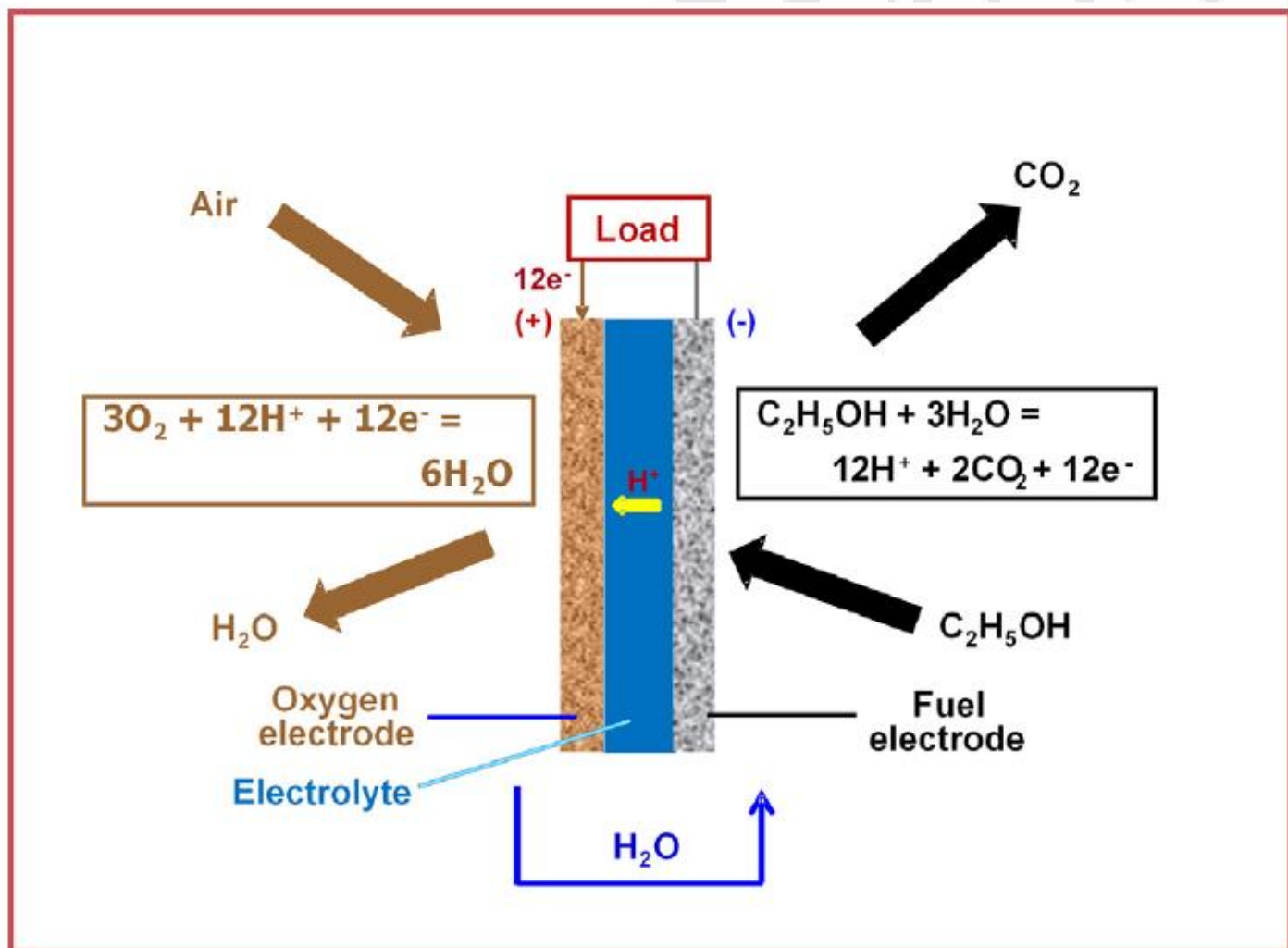


Clean
No CO₂ emissions
High efficiency
Direct use



A typical hydrogen fuel cell

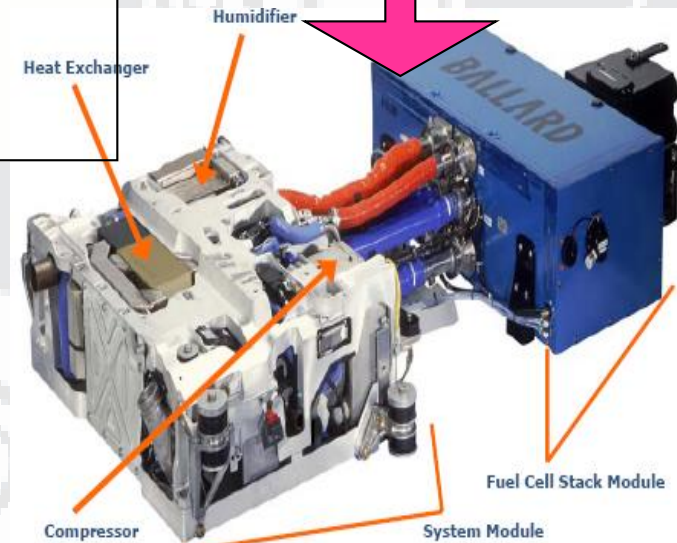
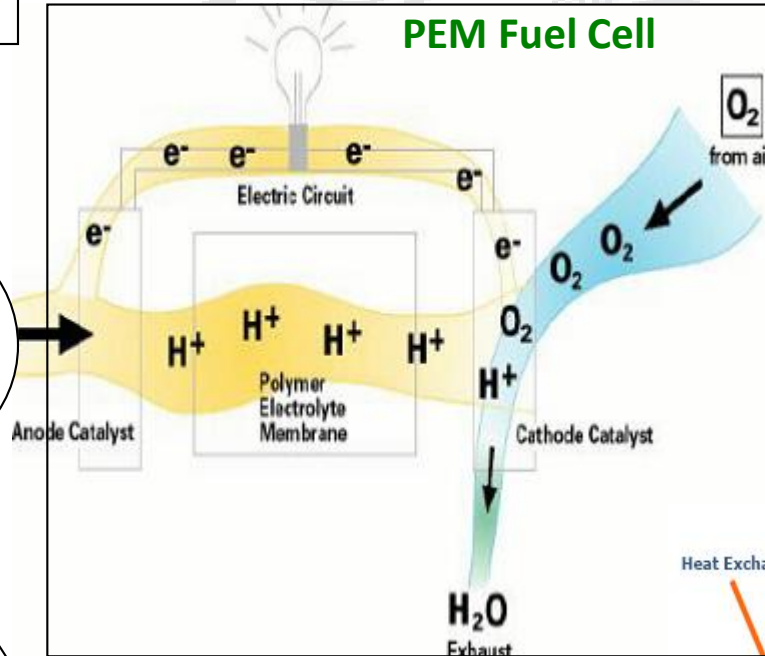




Pure H₂ Supply

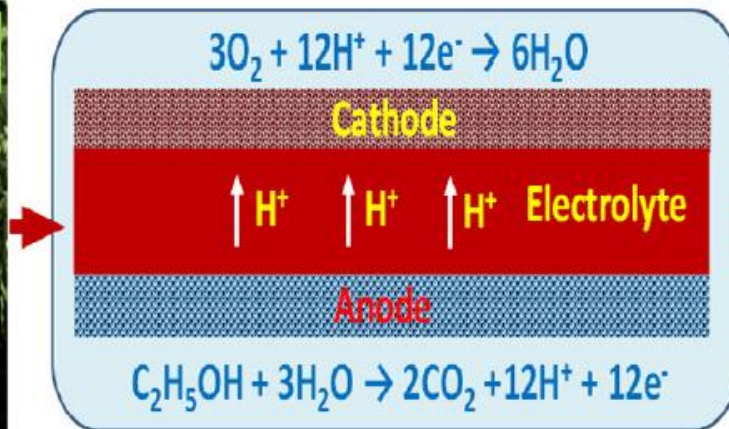
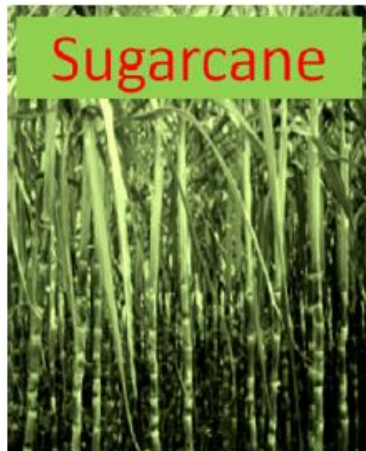
- Compressed H₂
- Liquid H₂
- H₂ Hydrid

**H₂
Fuel**



H₂ from Reformed liquid HC

- Methanol
- Ethanol
- DME



THANKS FOR YOUR ATTENTION

