BTV3333 Biobased Fuels and Alternative Energy Applications

CHAPTER 1

INTRODUCTION TO BIOFUELS AND THE PROSPECT DEMANDS OF BIOFUELS

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Biomass

- Any organic material derived directly or indirectly from the photosynthesis process.
- A mixture of naturally derived materials (i.e. cellulose, hemicellulose, lignin, chitin, chitosan, etc.) extracted from plants (i.e. shrubs, crops), algae (i.e. macro and micro algae), and other organic materials.
- It is different in physical and chemical properties due to its diverse origin and species.
- A renewable and relatively clean feedstock for producing modern energy carriers such as transportation fuels and electricity.
- A key challenge is to develop efficient conversion technologies which could compete with fossil fuels.

Biomass (Con’t)

- Main source
  - Farm
  - Forestry residue
  - Woodworking wastes (i.e. shavings, sawdust)
  - Animal residues (livestock farms)
  - Wages
  - Aquatic plants
  - Municipal solid waste (MSW)

Biofuels

- Substitute conventional fossil fuels.
- Alternative green and renewable energy.
- It is produced from various biomass sources.
- Can reduce green house gases (GHG) emissions and atmospheric pollution.

Types of Biofuels

Biodiesel

- Comprises of fatty acid methyl ester (FAME)
- Produce by the conversion of biomass by transesterification reaction with methanol and with the aid of catalyst
- A suitable substitute for petroleum diesel because it has similar properties with conventional diesel

Bioethanol

- An ethanol (C_2H_5OH) made from biomass
- It is made by fermentation process of sugar from carbohydrate in biomass
- Used as a fuel in internal combustion engines (ICEs)
- Used as a gasoline improver

Biogas

- A mixture of mostly methane (CH_4) and carbon dioxide (CO_2), with several other gases
- It is convert from biomass by anaerobic digestion method
- Used for generation of heat or electricity

Generation of Biofuels

1st generation

- Edible crops such as wheat, soybean, potato, coconut, rapeseed, barley, almond, walnut, pistachio, sugarcane, sunflower oil, corn oil, palm oil.
- It can be used without blending or can be improvised by blending.
- However, it is interfere with food security and social conflicts (Competition for land and water used for food production).

Generation of Biofuels (Con’t)

2nd generation

- An assured alternative to 1st generation because of the source being non-food biomass.
- Non edible crops such as jojoba, jatropha and sea mango, forest residues and vegetative grasses, by-products of food processing industry like sugarcane bagasse, stalks of corn and wheat constitute, by product from wooden factories include inedible parts such as dry wood, municipal solid wastes, used oils such as used cooking oil, used frying oil food waste and animal fats.
- Pilot scale demonstration facilities are needed to ensure its compatibility and performance.
- Requires expensive and sophisticated technologies.

Generation of Biofuels (Con’t)

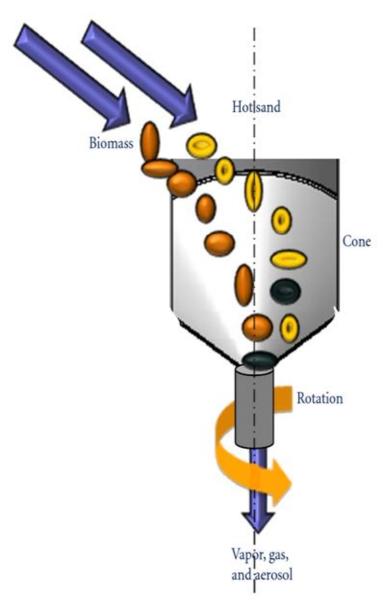
3rd generation

- Photosynthetic organisms which grow in aquatic environments in both marine and freshwater.
- Microalgae.
- Its contains high lipid content.
- Less generation time.
- High growth rate.

Biomass to Biofuels Conversion Method

- Thermochemical
  - Combustion
  - Gasification
  - Pyrolysis
  - Transesterification

- Biochemical
  - Fermentation
  - Anaerobic digestion



Thermochemical Method

Conversion Method

Combustion

- Most widely used method
- Contributes to over 97% of bio-energy production in the world
- Burn feedstocks directly
- Feasible only for biomass with moisturize content less < 50%
- Convert biomass into heat then electricity with output production of hot gases at temperature around 800 – 1000 °C

Conversion Method (Con't)

Gasification

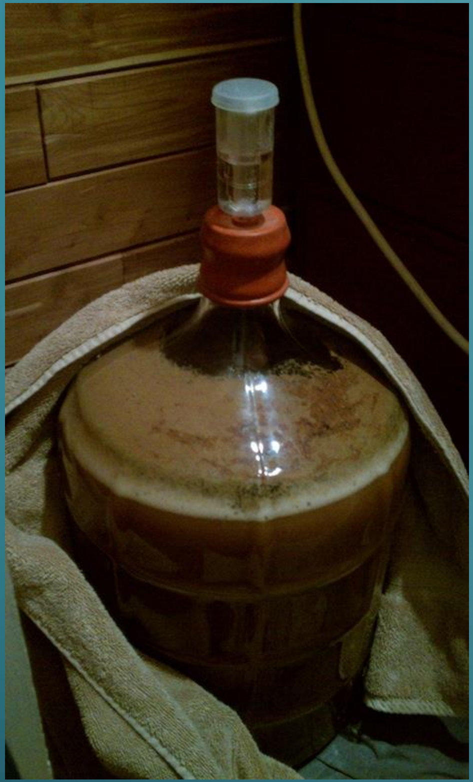
- Biomass is broken down into combustible gas, volatiles and ash
- Partial oxidation process using air or oxygen or steam at 500 to 1600 °C of operating temperature
- Produces gases include hydrogen (H_2) and carbon monoxide (CO) as well as other particular matter and ash

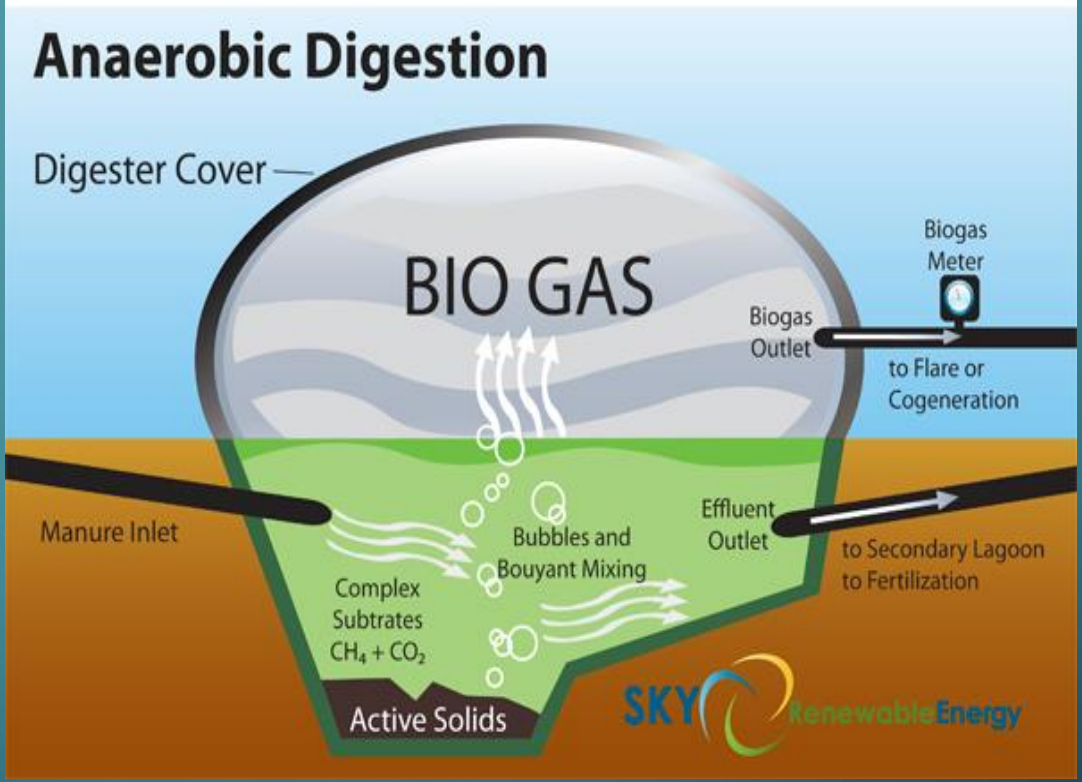
Conversion Method (Con’t)

Pyrolysis	Process of heating the biomass in the complete or limited absence of air or oxygen at a maximum reaction temperature (250 – 700 °C)
	Process start with the breakdown of bulk and large-sized molecules into various types of small-sized molecules
	Product of non-condensable gases (carbon monoxide, carbon dioxide, hydrogen, methane, etc), solid char, and liquid product
	The distribution of products depends on the reaction temperature

Conversion Method (Con’t)

Transesterification	A chemical reaction process involving triglycerides (in biomass) and alcohol in the presence or without the presence of a catalyst to form fatty acid alkyl esters (FAAE) and glycerol
	Different types of alcohols such as methanol, ethanol, propanol and butanol can be used to produce biofuel (biodiesel). However, methanol and ethanol are the most widely used
	Commonly, basic and acid types for both homogeneous and heterogeneous catalysts being used during the reaction
	The optimum reaction temperature is 65 to 110 °C





Biochemical Method

Conversion Method (Con’t)

Fermentation

- A metabolic conversion activity of substrate into biofuels (bioethanol/biohydrogen) and other by-products in the presence of fermentative microorganism in supporting conditions namely temperature and pH range
- A specific fermentation agent such as yeast and bacteria is commonly used in the fermentation process. These fermentative microorganisms including *S. cerevisiae, P. stipitis, Clostridium, E. coli,* and *Z. mobilis*.

Conversion Method (Con’t)

Anaerobic digestion

- Converting all the degradable components (carbohydrates, proteins and lipids) in the biomass to produce biogas.
- A process involving the degradation of organic matter by bacteria in the absence of oxygen.
- The products are mainly gases (methane (CH_3), carbon dioxide (CO_2), hydrogen (H_2), hydrogen sulphide (H_2S), ammonia (NH_3)).
- Anaerobic digestion occurs in four steps:
  - Hydrolysis - Organic polymers, namely carbohydrates, proteins and lipids are broken down into basic compounds such as amino acids, fatty acids, and simple sugars.
  - Acidogenesis - Bacteria breaks them down into organic acids (volatile fatty acids).
  - Acetogenesis – Acetogens (bacteria) work on the basic compounds and organic acids to produce acetic acid along with hydrogen (H_2), carbon dioxide (CO_2), ammonium (NH_4), as well as trace amounts of other by-products.
  - Methanogenesis - Methanogens (bacteria) produce methane from the final products (acetic acid and hydrogen (H2)) of acetogenesis step.
- Temperatures of about 35°C to 40°C are needed for standard *mosphilic* digestion to take place. The faster *thermophilic* digestion method requires temperatures of about 50°C to 55°C.

Advantages of Biofuels

Produced from high availability of feedstock

- Depends on the origin of the feedstock
- Variety of feedstock species/types

Sustainable alternative

- Renewable sources
- Eliminate the depending on only one feedstock

Generally it does not pollute the atmosphere as much as oil and coal (Environmental friendly)

- Reduce the emission of NOx, SOx
- Eliminates the greenhouse effect

Challenges of Biofuels

Lack of strongly implemented policy framework

- Need to increase the perception of the potential and commercial viability of biofuels

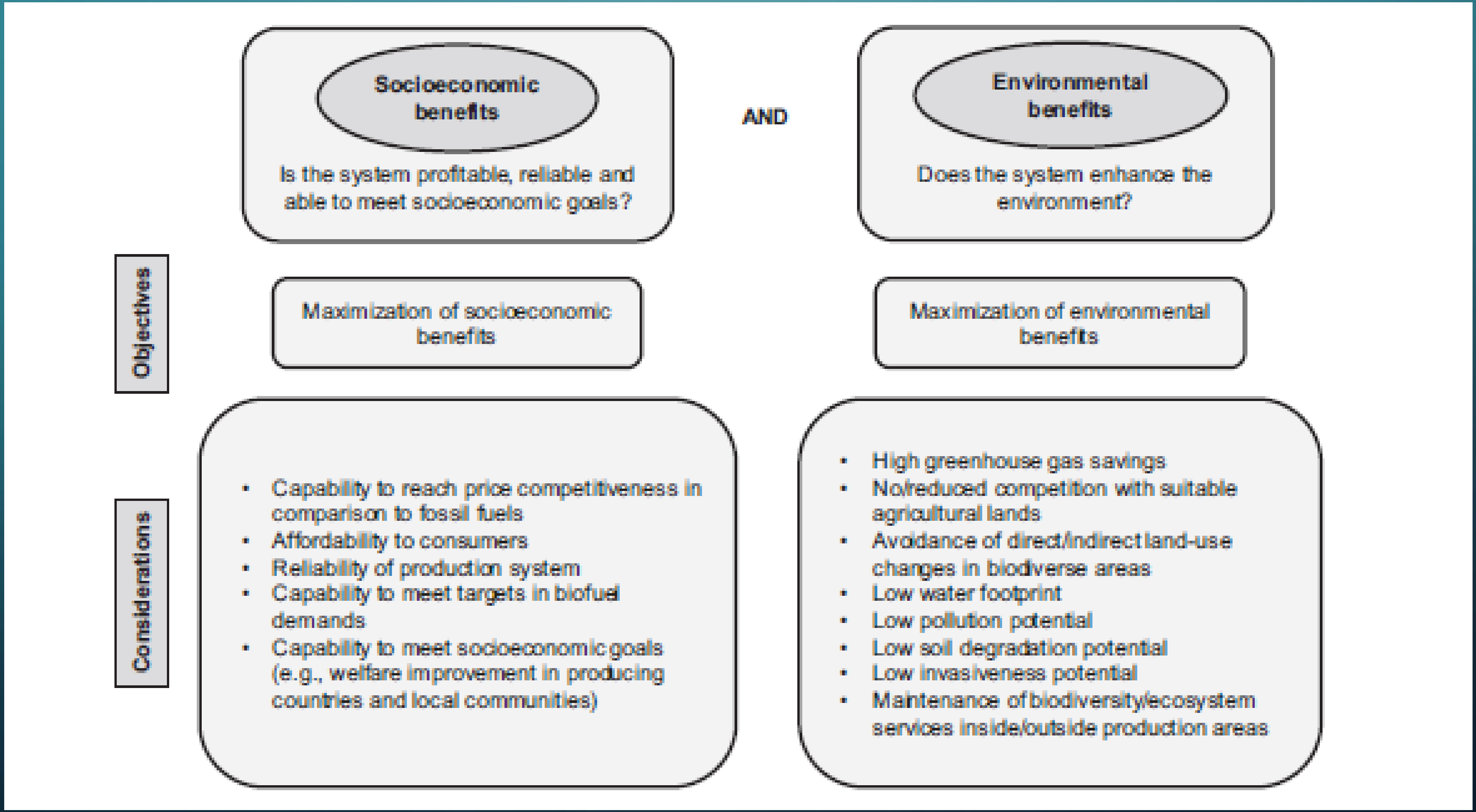
Lack of financial support

- Need to increase the interest from commercial investors

Lack of expertise in efficient handling equipment

- Need to increase the technical knowledge by providing a training through knowledge transfer from researcher to industry

Economic Benefits and Environmental Effects



Socioeconomic benefits

Is the system profitable, reliable and able to meet socioeconomic goals?

AND

Environmental benefits

Does the system enhance the environment?

Objectives

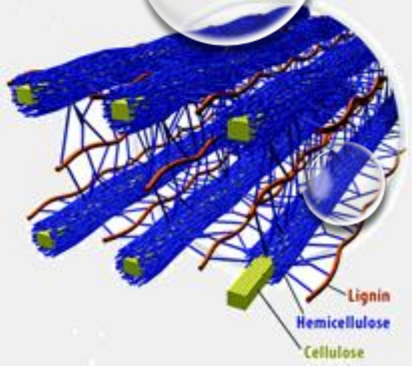
Maximization of socioeconomic benefits

Maximization of environmental benefits

Considerations

- Capability to reach price competitiveness in comparison to fossil fuels
- Affordability to consumers
- Reliability of production system
- Capability to meet targets in biofuel demands
- Capability to meet socioeconomic goals (e.g., welfare improvement in producing countries and local communities)

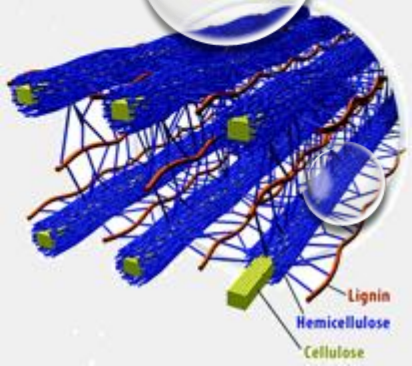
- High greenhouse gas savings
- No/reduced competition with suitable agricultural lands
- Avoidance of direct/indirect land-use changes in biodiverse areas
- Low water footprint
- Low pollution potential
- Low soil degradation potential
- Low invasiveness potential
- Maintenance of biodiversity/ecosystem services inside/outside production areas



Chapter 2

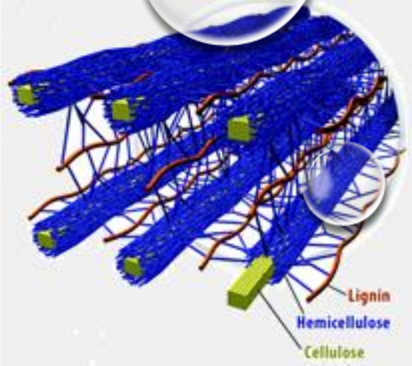
Lignocellulosic Biomass Pretreatment

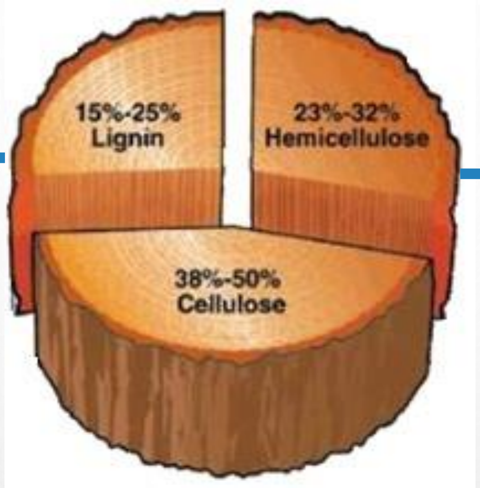
Lignocellulosic Biomass

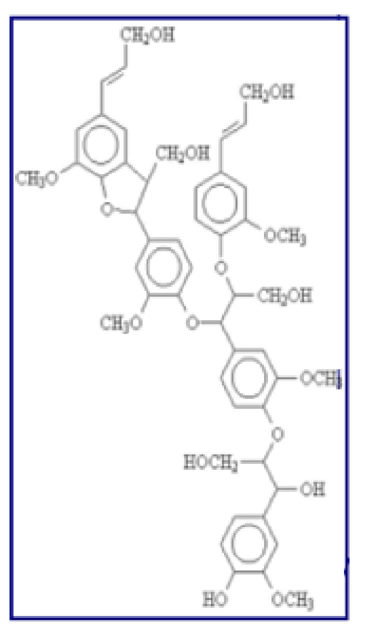


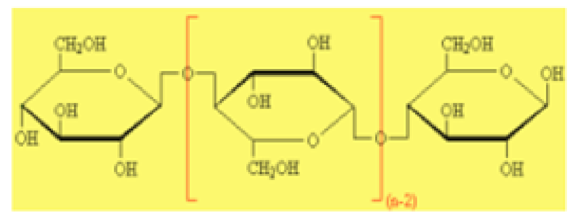
- Can be grown on barren uncultivable land
- Need less amount of water to grow
- Does not interfere with food chain
- Available in ample amount
- Mixture of lignocellulosic biomass avoid the problem of round the year biomass availability
- Higher yields per acre, either by using fast-growing lignocellulosic plants

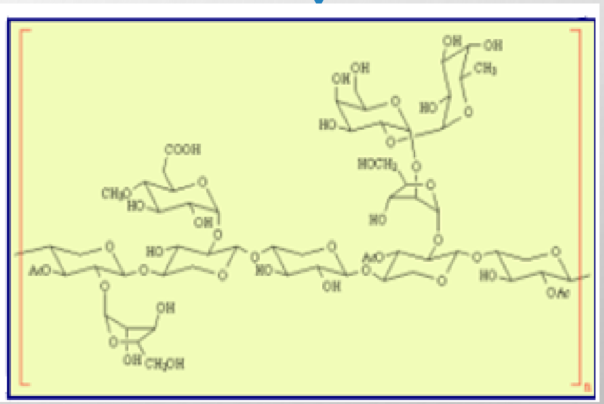
Composition of Lignocellulosic Biomass



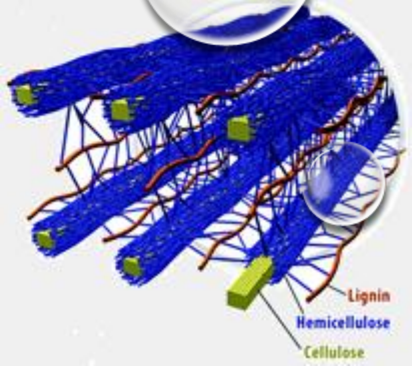


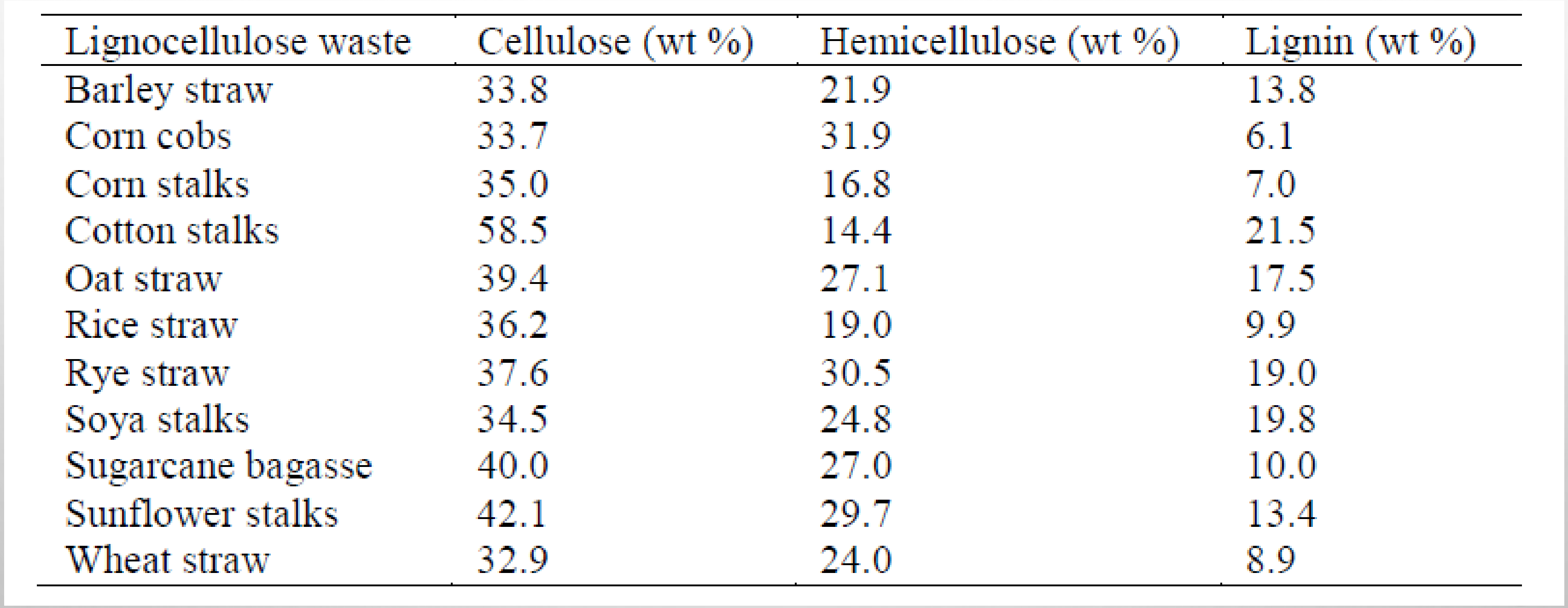






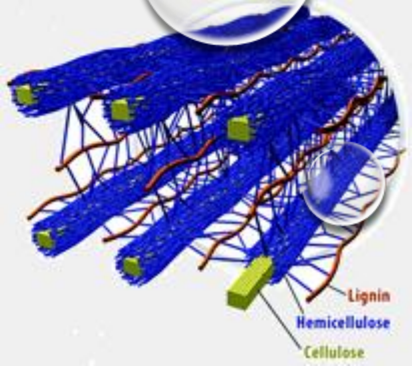
Type of lignocellulosic waste with its composition

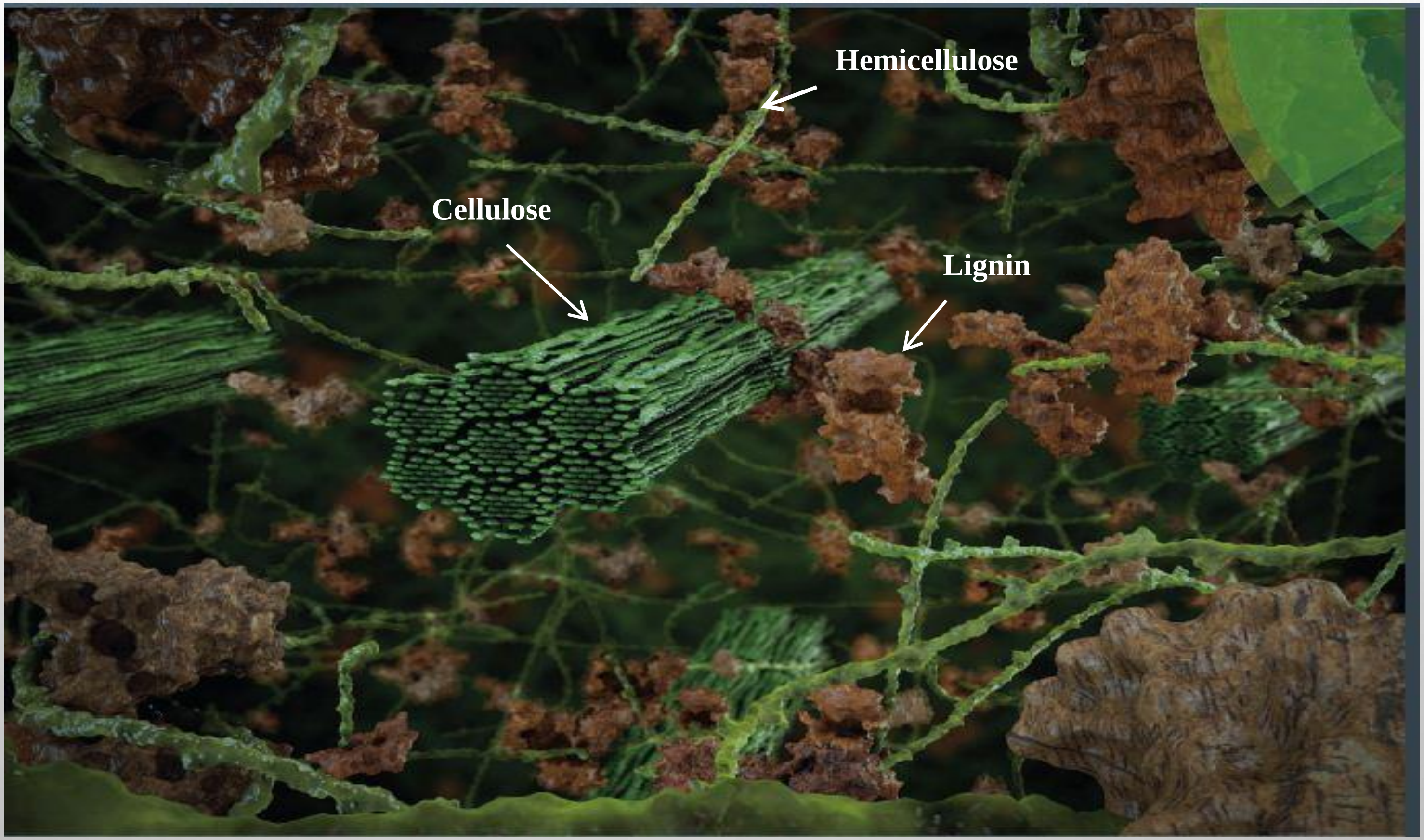


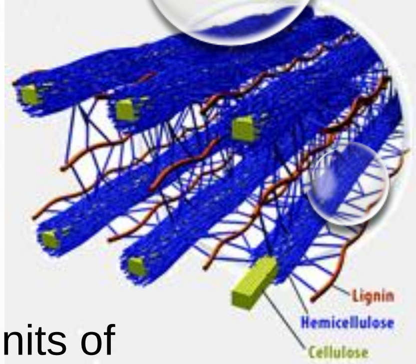


Lignocellulose waste	Cellulose (wt %)	Hemicellulose (wt %)	Lignin (wt %)
Barley straw	33.8	21.9	13.8
Corn cobs	33.7	31.9	6.1
Corn stalks	35.0	16.8	7.0
Cotton stalks	58.5	14.4	21.5
Oat straw	39.4	27.1	17.5
Rice straw	36.2	19.0	9.9
Rye straw	37.6	30.5	19.0
Soya stalks	34.5	24.8	19.8
Sugarcane bagasse	40.0	27.0	10.0
Sunflower stalks	42.1	29.7	13.4
Wheat straw	32.9	24.0	8.9

Ultra-structural view of lignocellulosics





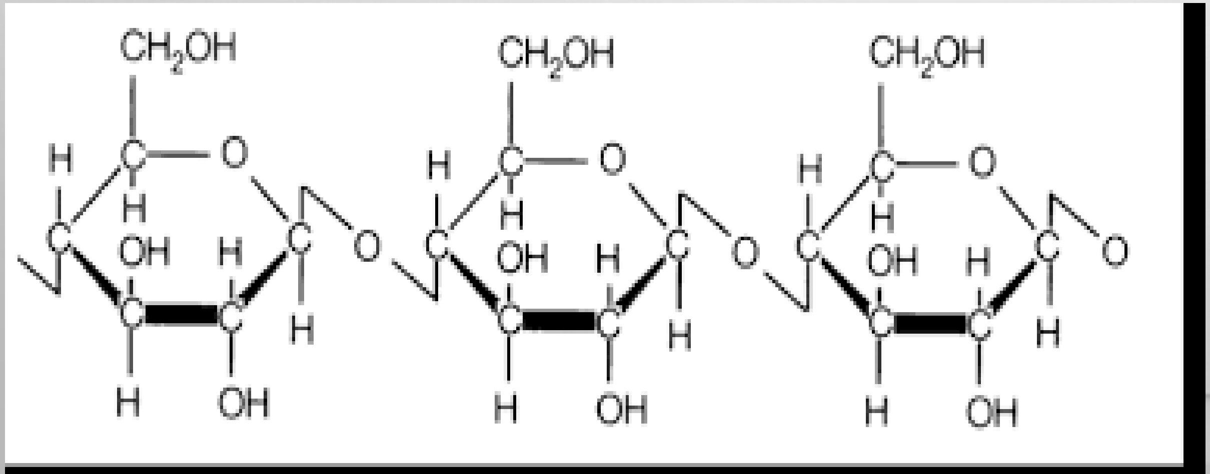


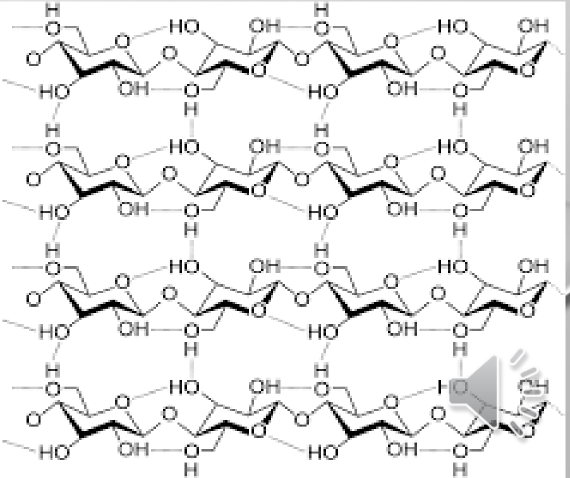
Cellulose

Cellulose is a high molecular weight linear homopolymer of repeated units of cellobiose (two anhydrous glucose rings joined via a β-1,4 glycosidic linkage).

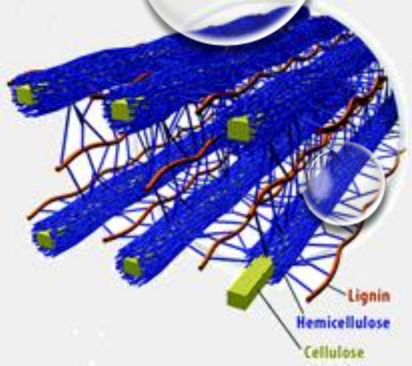
The long-chain cellulose polymers are linked together by hydrogen and Van der Walls bonds, which cause the cellulose to be packed into microfibrils.

By forming these hydrogen bonds, the chains tend to arrange in parallel and form a crystalline structure. Therefore, **cellulose microfibrils** have both **highly crystalline** regions (around 2/3 of the total cellulose) and **less-ordered amorphous** regions. More ordered or crystalline cellulose is **less soluble and less degradable.**

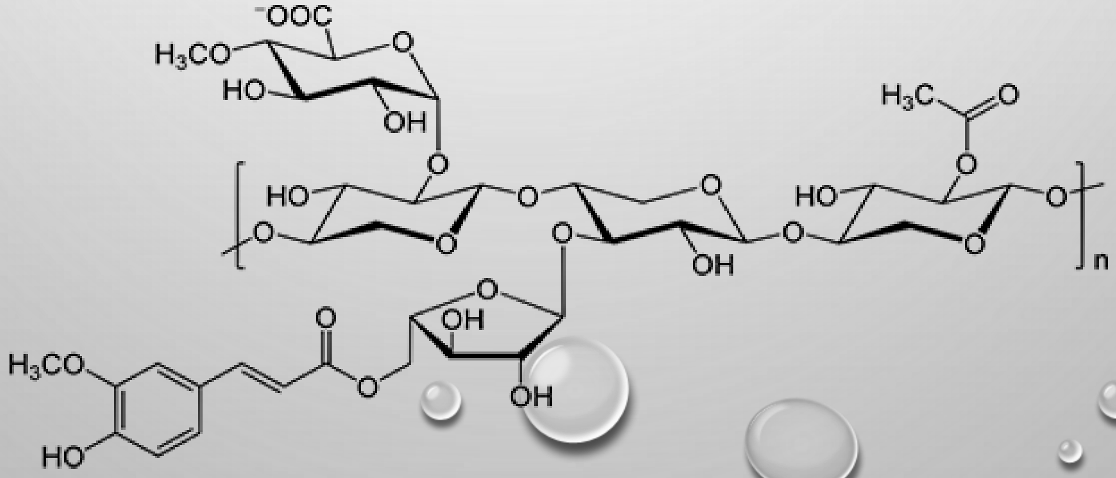




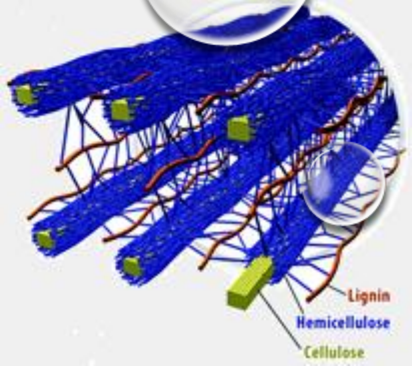
Hemicellulose



- Hemicellulose is a linear and branched heterogeneous polymer.
- Made up of five different sugars:
  L-arabinose, D-galactose, D-glucose, D-mannose, and D-xylose
- The backbone of the chains of hemicelluloses can be a homopolymer (generally consisting of single sugar repeat unit) or a heteropolymer (mixture of different sugars).
- Hemicellulose has different classifications e.g., xylans, mannans, glucans.



Cellulose vs. Hemicellulose

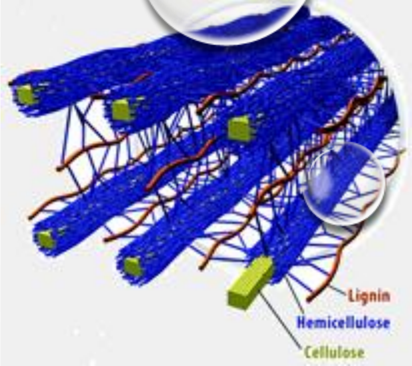


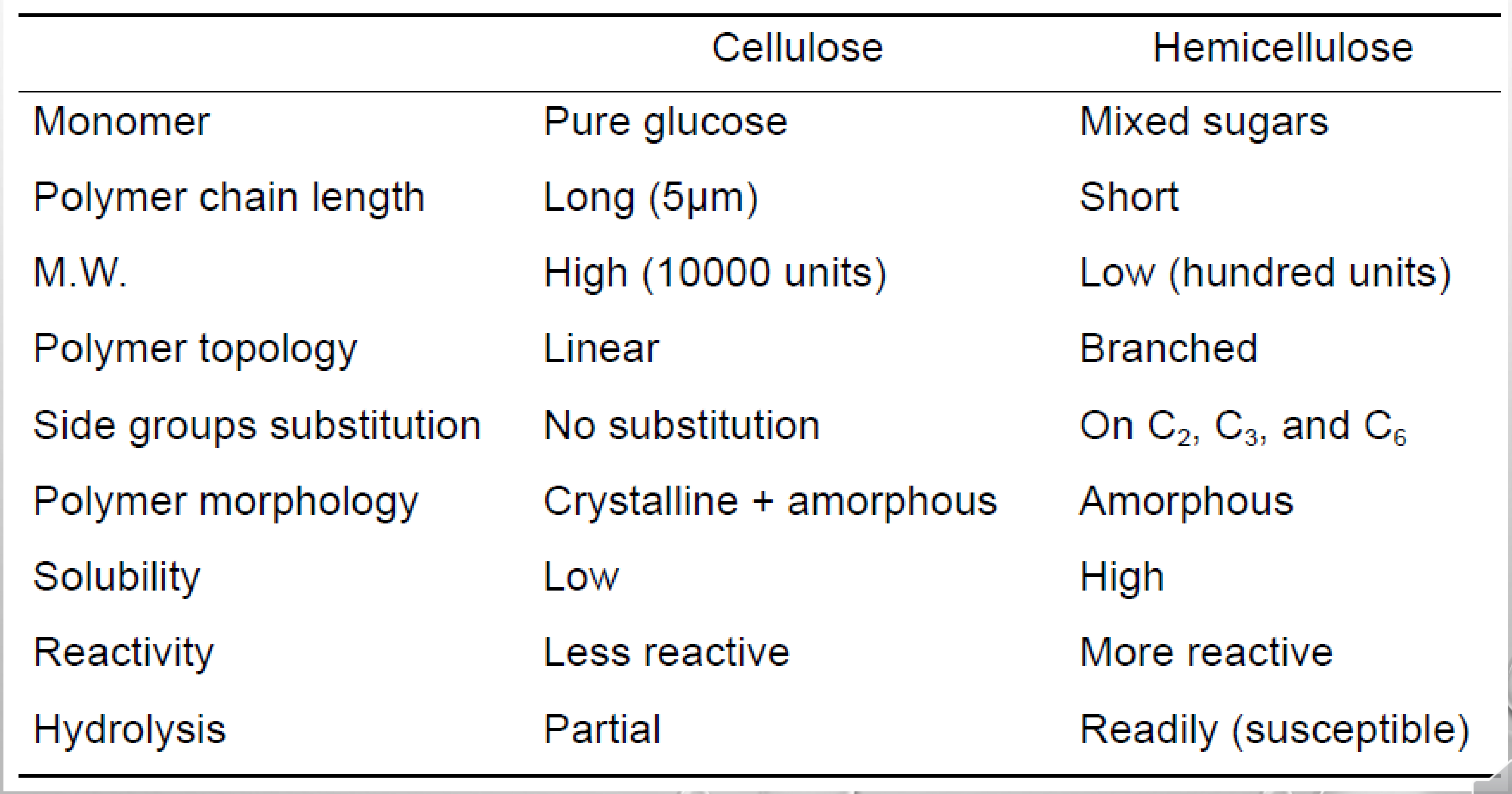
Compared to cellulose, **hemicelluloses** differ by

- composition of sugar units,
- presence of shorter chains,
- a branching of main chain molecules, and
- be amorphous

Thus made its structure **easier to hydrolyze** than cellulose.

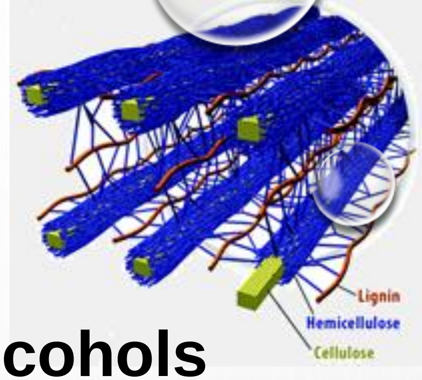
Cellulose vs. Hemicellulose



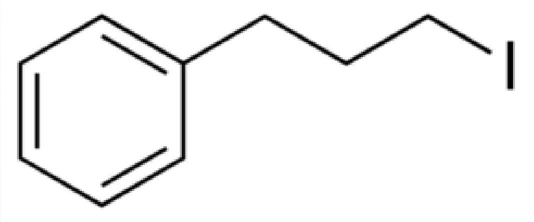


	Cellulose	Hemicellulose
Monomer	Pure glucose	Mixed sugars
Polymer chain length	Long (5μm)	Short
M.W.	High (10000 units)	Low (hundred units)
Polymer topology	Linear	Branched
Side groups substitution	No substitution	On C_2, C_3, and C_6
Polymer morphology	Crystalline + amorphous	Amorphous
Solubility	Low	High
Reactivity	Less reactive	More reactive
Hydrolysis	Partial	Readily (susceptible)

Lignin



Lignin is a very complex molecule of **aromatic alcohols** constructed of **phenyl propane** units linked in a large three-dimensional structure.



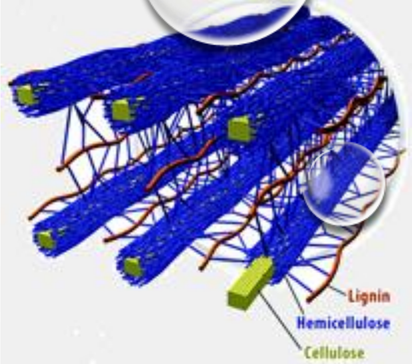
Three phenyl propionic alcohols exist as monomers of lignin: p-coumaryl alcohol, coniferyl alcohol and sinapyl alcohol.

p-Coumaryl alcohol

Coniferyl alcohol

Sinapyl alcohol

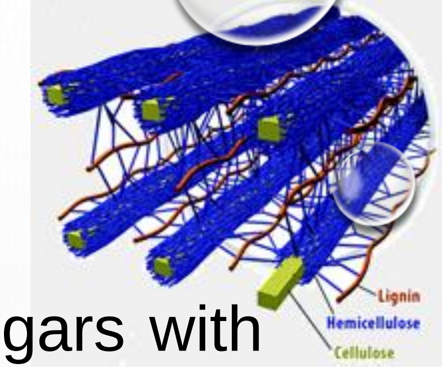
Lignin (cont.)



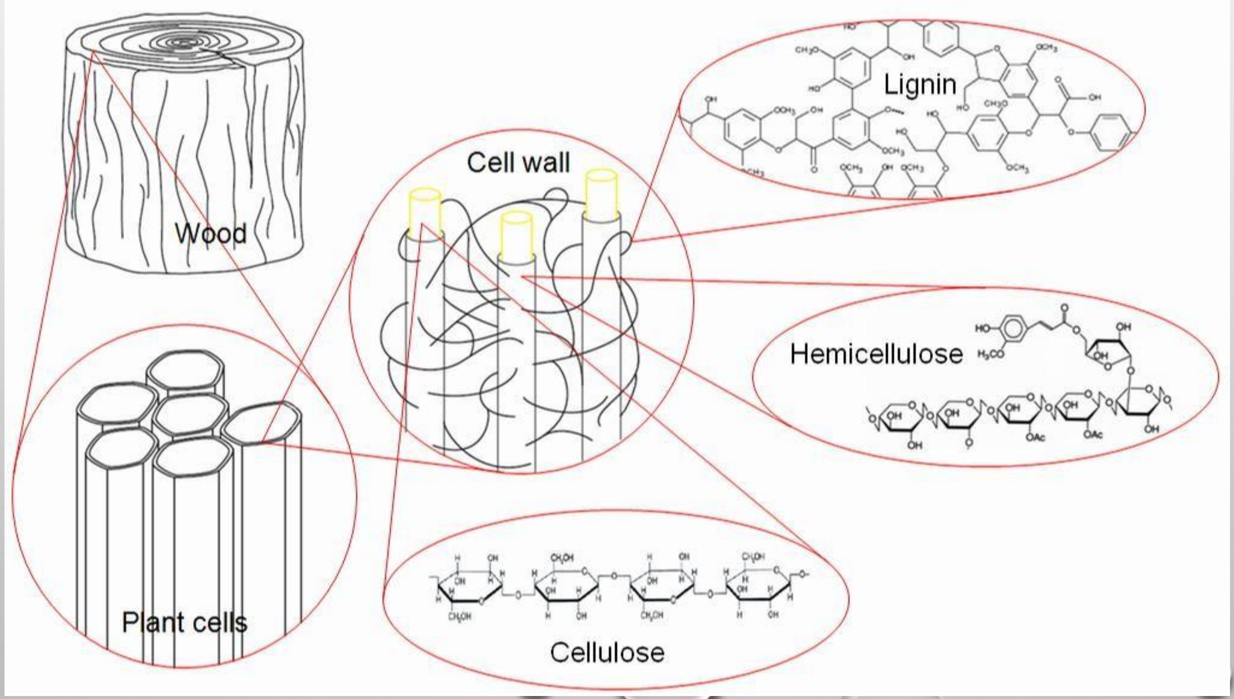
- closely bound to cellulose and hemicellulose,
- its function is to provide rigidity and cohesion to the material cell wall,
- allow water impermeability to xylem vessels, and
- form a physic–chemical barrier against microbial attack.

Due to its molecular configuration, lignins are **extremely resistant** to chemical and enzymatic degradation.

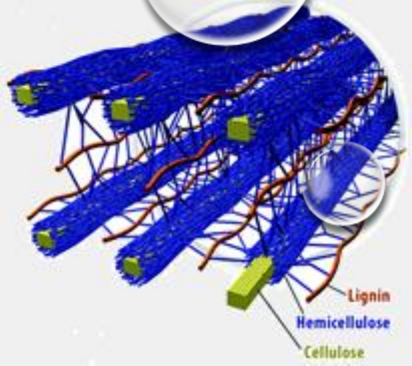
Cellulose, Hemicellulose and Lignin



Hemicellulose, a chain of five and six carbon sugars with xylose as the sugar backbone, form a protective barrier around the microfibrils of cellulose and are held in place by a glue-like material know as lignin.

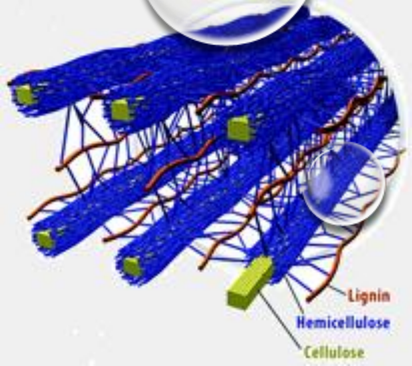


Summary



- **Lignocellulose** refers to plant dry matter (**biomass**).
- It is the most abundantly available raw material on the earth for the production of biofuels, mainly bioethanol.
- It is composed of carbohydrate polymers (cellulose, hemicellulose), and an aromatic polymer (lignin).
- **Cellulose** and **hemicellulose** are a potential source of fermentable sugars.
- **Lignin** can be converted into solid biofuel or higher added-value products.

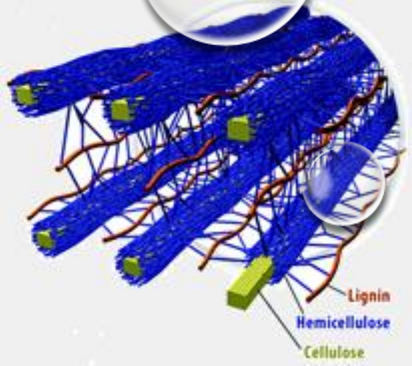
Goals of Pretreatment



The main objective of pretreatment is to prepare the biomass for efficient downstream processing.

- Maximize the **yields** of both c-5 and c-6 sugars for downstream processing with minimal degradation of produced sugars.
- Facilitate the **recovery of lignin** as a high- value product.
- Minimize the formation of **inhibitory** soluble chemicals including hydroxymethyfurfural, organic acids and phenolic compounds.
- Utilize **low-cost chemicals** with minimal generation of waste streams.
- Utilize **less energy** and have low capital and operating costs.

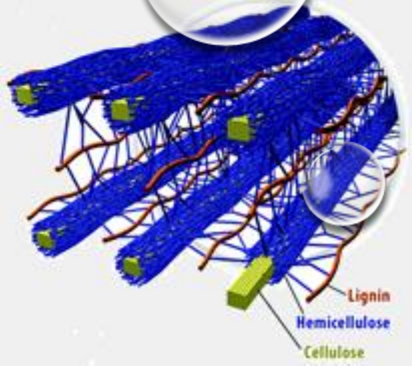
Goals of Pretreatment (cont.)



There are several key factors which affect the rate of biological degradation of lignocelluloses. The accessible **surface area** for enzymatic attack is related to:

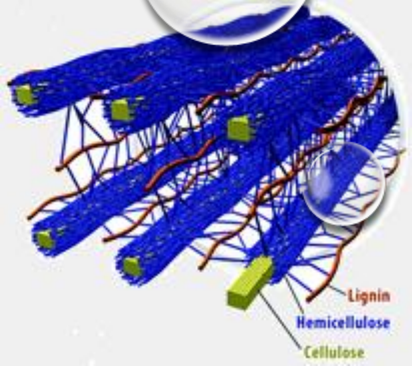
- cellulose crystallinity
- hemicellulose content
- lignin

Goals of Pretreatment
What is accessible Surface Area?



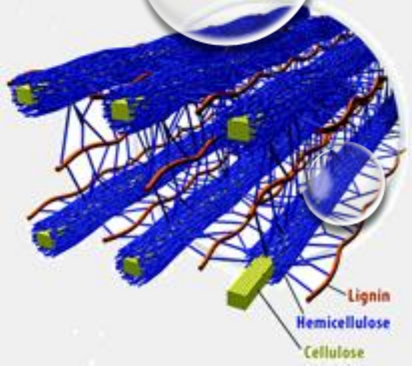
- There is a good correlation between the pore volumes (accessible surface area for cellulase and hemicellulase) and the enzymatic digestibility of lignocellulosic materials.
- Lignocellulosic biomass has two types of surface area: external and internal.
  - The external surface area is related to the particle size and shape.
  - The internal surface area depends on the capillary structure of cellulosic fibers.

Cellulose Crystallinity



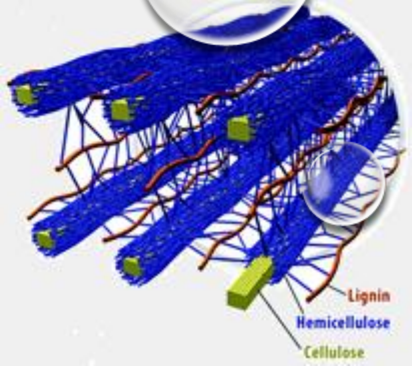
- The cellulose microfibrils have both crystalline and amorphous regions.
- Cellulose crystallinity is one of the important factors in determining the hydrolysis rates of cellulosic substrates.
- 2/3 of the total cellulose is in the crystalline form.
- Enzyme is not so effective in degrading the crystalline portion. Therefore, decreasing the crystallinity will increase the digestibility of lignocelluloses.

Effect of Hemicellulose & Lignin



- **Hemicellulose** is a physical barrier which covers the cellulose fibers and the removal of hemicellulose increases the mean pore size of the substrate and, therefore increases the cellulose hydrolysis yield.
- **Degree of acetylation in the hemicellulose** is another important factor as lignin and acetyl groups are attached to the hemicellulose matrix and may hinder polysaccharide breakdown.
- The cellulose and hemicellulose are covered by **lignin**. The presence of lignin hinders the access of enzymes to cellulose and hemicelluloses.
- Efficient **delignification** processes can improve the rate and extent of enzymatic hydrolysis.

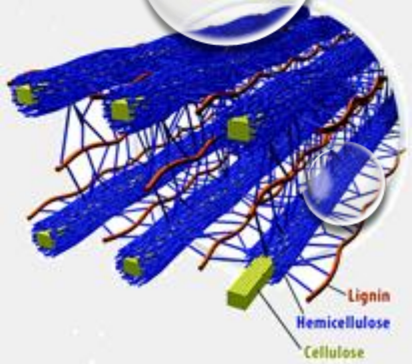
Pretreatment and Hemicellulose



Methods usually employed for Hemicellulose hydrolysis:

1. Dilute acid hydrolysis,
2. Steam explosion and
3. Biological hydrolysis

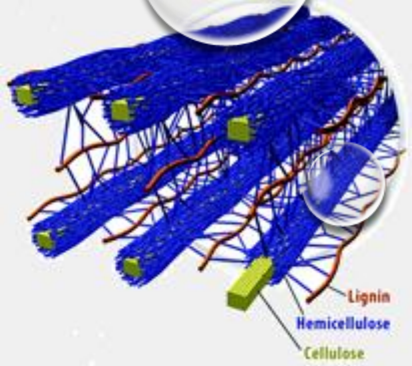
Pretreatment and Hemicellulose (cont.)



Dilute acid hydrolysis is the most employed technique for the hemicellulose breakdown.

- In this process, the use of diluted acids (1-4%), under moderate temperatures (120 to 170 °C), has proven for hemicellulose hydrolysis, with little sugar decomposition.
- H_2SO_4 is the usual acid employed although HCl, HNO_3, and H_3PO_4 are also used.
- The mechanism: acid catalyzes the breakdown of long hemicellulose chains to form shorter chain oligomers and then to sugar monomers.
- **Advantages** are the generation of lower degradation products as well much less corrosion problems in hydrolysis tanks.

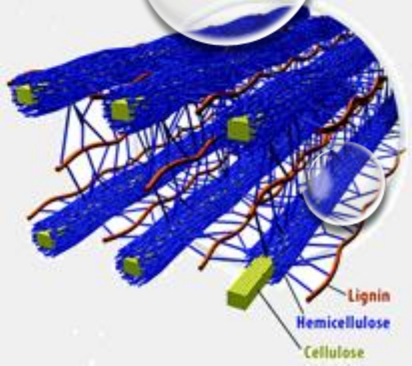
Pretreatment and Hemicellulose (cont.)



Steam explosion:

- The biomass is heated using high-pressure saturated steam (0.69-4.83 MPa, 160-260 ℃) for a short period (from seconds to few minutes). Steam condenses under high pressure, thereby wetting the material, and then the pressure is suddenly reduced, which makes the material undergo an explosive decompression.
- Combination of acetic acid with sudden depressurization, promote the hemicellulose hydrolysis and solubilization. Although avoiding acid catalysts is stated as an advantage of this method, addition of an acid catalyst improves hemicellulose hydrolysis and decreases production of degradation compounds.
- **Limitations** of steam explosion include an incomplete disruption of the lignin– carbohydrate matrix, and generation of compounds that may be inhibitory to microorganisms.

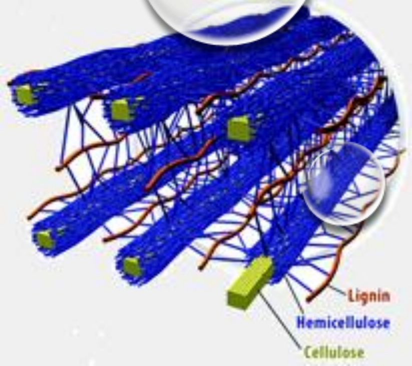
Pretreatment and Hemicellulose (cont.)



Biological treatment uses specific **microorganisms** or a suitable cocktail of enzymes known as **hemicellulases** can also promote the hemicellulose hydrolysis.

- **Hemicellulases** are produced by many species of **bacteria** and **fungi**, as well as by several **plants**. A number of hemicellulases, including xylanases and mannanases, have been identified.
- Today, most commercial hemicellulase preparations are produced by genetically modified *Trichoderma* or *Aspergillus* strains.
- Biological treatments have some **advantages** such as the high specificity, low energy consumption, no chemical requirement, and mild environmental conditions thus avoiding sugar degradation and resulting in high sugar yields.

Pretreatment and Lignin

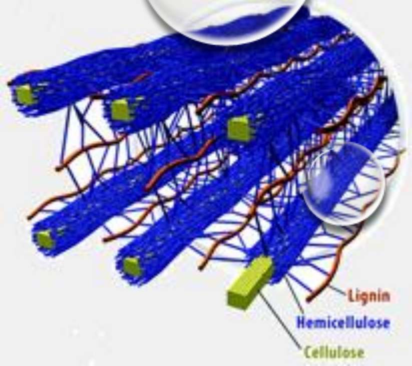


Methods usually employed for **Delignification** (lignin removal):

1. Alkaline,
2. Ozonolysis,
3. Peroxide
4. Organosolv treatments

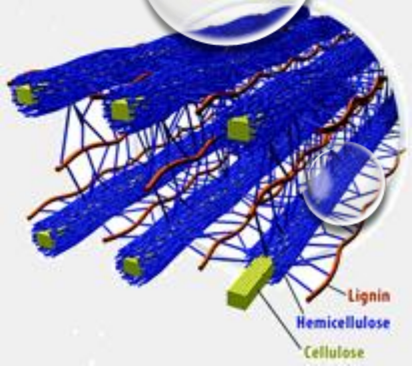
These methods are effective for lignin solubilization but part of the hemicellulose is also hydrolyzed.

Alkaline Pretreatment and Lignin



- The application of alkaline solutions such as NaOH, $Ca(OH)_2$ or ammonia.
- Treatment with NaOH is one of the most used for delignification of agricultural residues.
- The alkali treatment causes swelling, leading to an increase in internal surface area, a **decrease in the degree of polymerization**, a **decrease in crystallinity**, separation of structural linkages between lignin and carbohydrates, and disruption of the lignin structure.
- As a consequence, the lignin is separated in the form of a liquor rich in phenolic compounds.
- The inconvenient of this technique is that it also degrades part of the hemicellulose.

H_2O_2 Pretreatment and Lignin



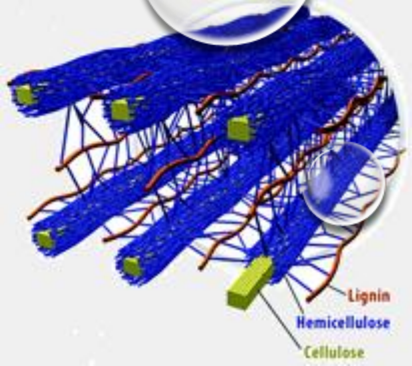
- Hydrogen peroxide treatment utilizes alkaline solutions at temperatures higher than 100 ºC, which promote a fast decomposition of H_2O_2. As a consequence, more reactive radicals such as hydroxyl radicals (HO) and superoxide anions (O_2^-) are produced, which are responsible for lignin degradation.

- This technique is **commonly used in paper and pulp industries** for bleaching and delignification purposes.

- Delignification by this process on a large scale can be costly.

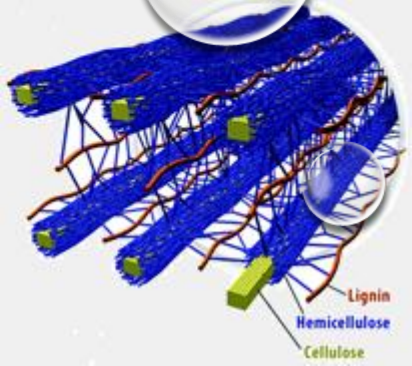
- During the lignin solubilization by hydrogen peroxide part of the hemicellulose is also removed from the material structure.

Organosolv Pretreatment and Lignin

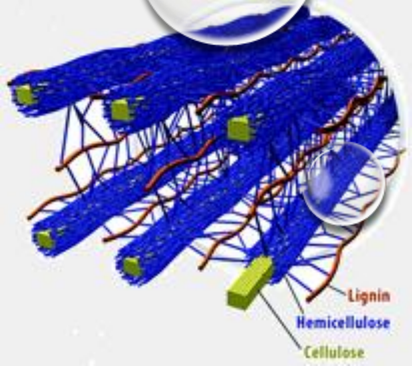


- Treatment with organosolvents involves the use of an organic liquid (eg: methanol, ethanol, acetone, ethylene glycol or triethylene glycol) and water, with or without addition of catalysts such as oxalic, salicylic, and acetylsalicylic acid.
- This mixture hydrolyzes lignin bonds and lignin-carbohydrate bonds, but many of the carbohydrate bonds in the hemicellulose components are also broken.
- Lignin is dissolved as a result of the solvent action and the cellulose remains in the residual solid material.

Ozone Pretreatment and Lignin

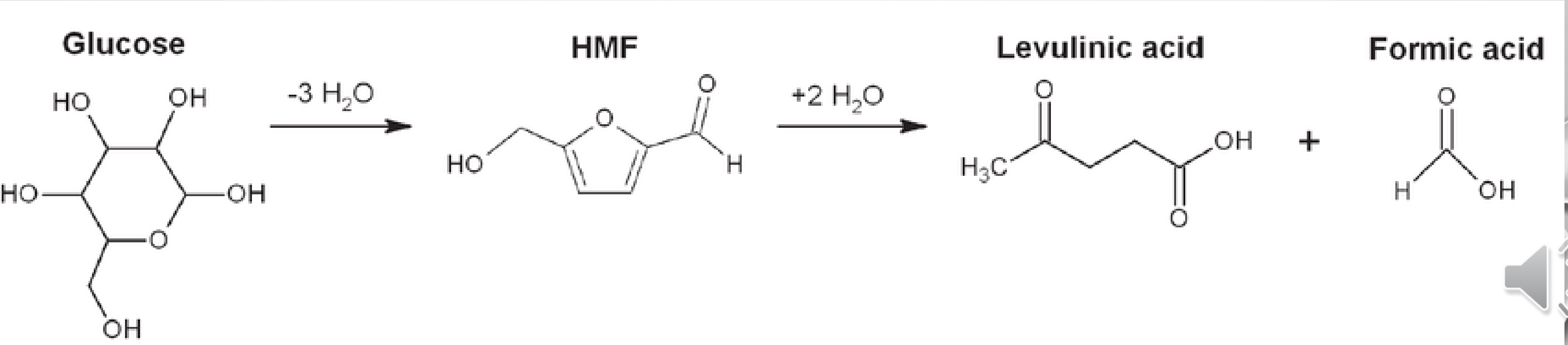


- Lignin attacks as a scavenger during this pre-treatment because it consumes most of ozone during the degradation of the carbohydrate content. Therefore, low ozone amounts are available for cellulose degradation.
- However, this treatment may also attacks the cellulose and hemicellulose components besides the lignin molecule.
- Cellulose degradation has been attributed partly to a direct reaction of ozone with the glycosidic linkage and partly to a free radical mediated oxidation of hydroxyl groups in glucose.
- Some advantages of this treatment are that ozonolysis are carried out at **room temperature and normal pressure**. Furthermore, since ozone can be easily decomposed by using a catalytic bed or increasing the temperature, this process can be designed to **minimize environmental pollution**.

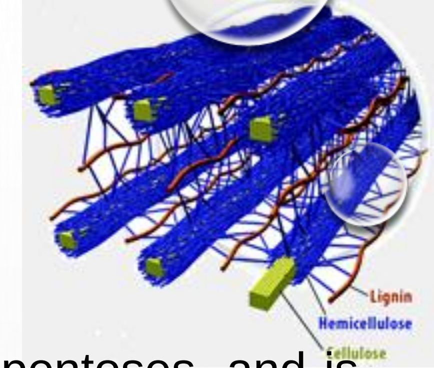


Inhibitory Compounds

Hydroxymethylfurfural: 5-hydroxymethyfufural (HMF) is a fermentation inhibitory compound that is generated by the degradation of six-carbon sugars like glucose, under severe pretreatment conditions such as high temperatures, pressures, holding time, and concentration of chemicals. Such pretreatment conditions promote three dehydration reactions of the hexose forming the phenolic HMF compound. An increase in the severity of pretreatment conditions can be further degrade HMF into **levulinic acid** and **formic acid**. It has been proposed that these weak acid have the ability to penetrate into microorganisms and inhibits cellular growth.



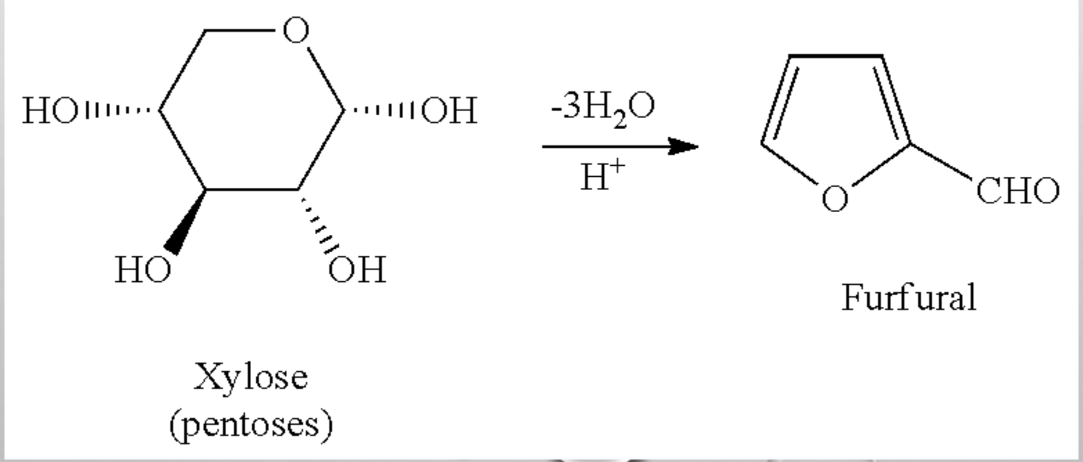
Inhibitory Compounds (cont.)

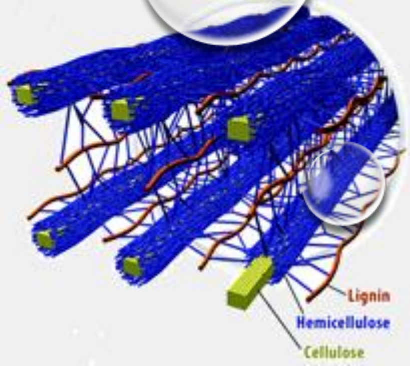


Furfural: is a degradation product formed by the dehydration of pentoses, and is produced exclusively from lignocellulosic biomass.

Under severe pretreatment conditions, furfural can be further degraded into formic acid. Furfural is reduced by *Saccharomyces cerevisiae* into furfuryl alcohols under aerobic, anaerobic, and oxygen limited condition.

It was proposed that furfural inhibits cell growth by outcompeting normal compound during metabolism: **namely that furfural inactivates cellular replication**.





THANK YOU

CHAPTER 4

BIOGAS PRODUCTION

TOPICS

Definition of biogas

Feedstock of biogas

Anaerobic digestion (AD)

Anaerobic digestion (AD) steps

Parameter and operational conditions of anaerobic digestion (AD)

BIOGAS

A mixture of different gases produced by breakdown of organic matter in absence of oxygen.

Primarily, it consists of methane (CH_4) and carbon dioxide (CO_2). Typically the gas mixture will also contain hydrogen (H_2), hydrogen sulphide (H_2S) and ammonia (NH_3).

Syngas is differ from biogas in terms of its product as the main product is the hydrogen (H_2) and carbon monoxide (CO). While, the particulate matter, hydrogen sulphide (H_2S) and tars are the by product of syngas.

Besides that, both biogas and syngas is differ in terms of the conversion method where biogas is convert by biochemical method whereas syngas is convert by thermochemical method.

FEEDSTOCKS OF BIOGAS

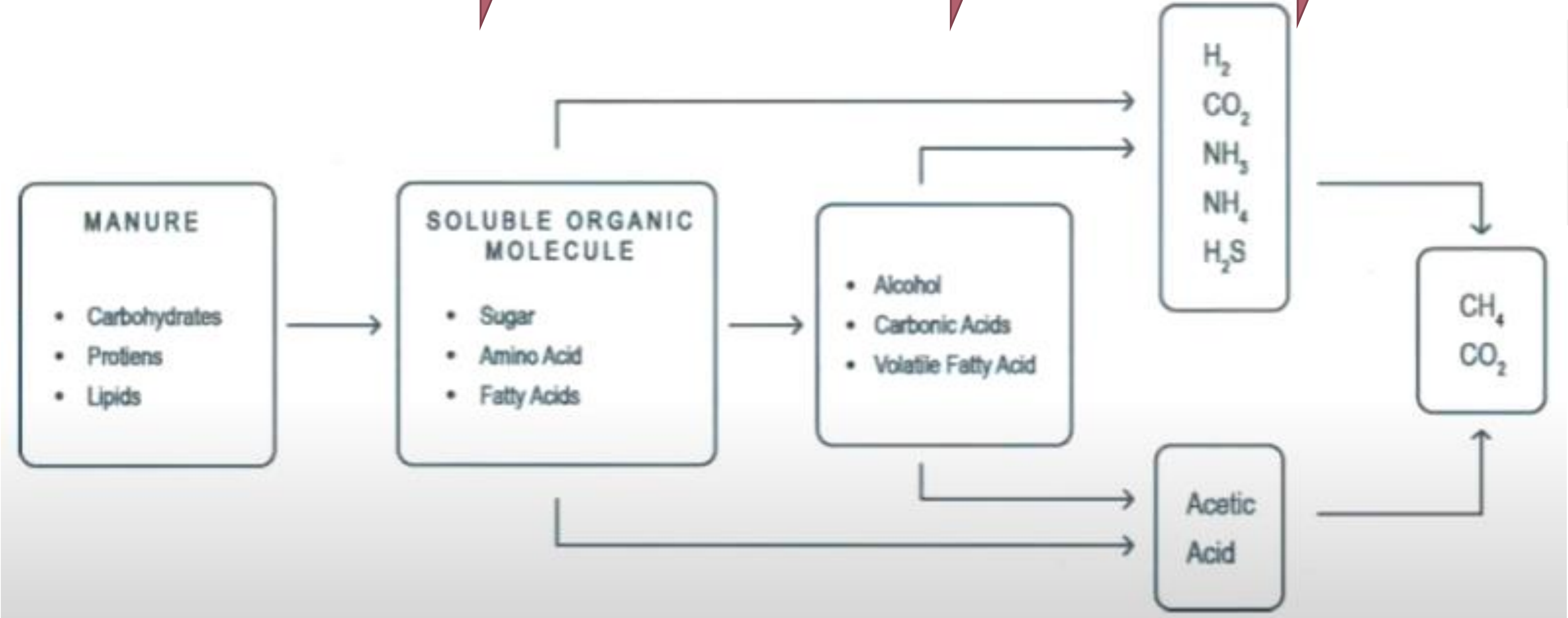
- Sewage sludge
- Agricultural wastes
- Food wastes
- Industry wastes
- Animal by-products
- Municipal solid waste

ANAEROBIC DIGESTION (AD)

A series of biological process in which microorganism breakdown biodegradable materials in the absence of oxygen.

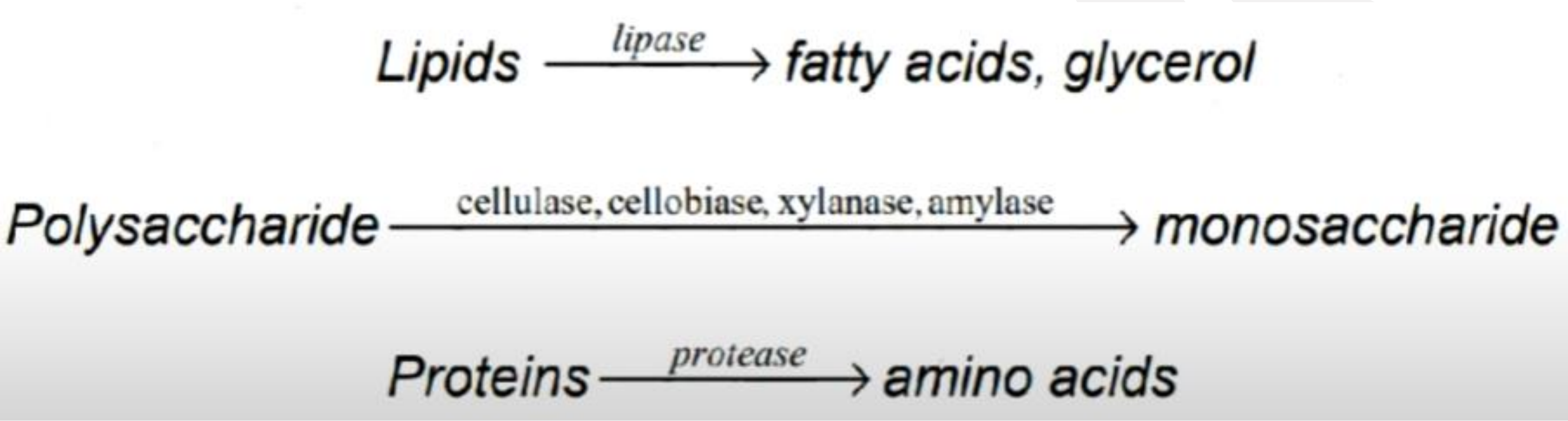
ANAEROBIC DIGESTION (AD) STEPS

HYDROLISIS → ACEDOGENESIS → ACETOGENESIS → METHANOGENESIS



There are 4 steps in anaerobic digestion (AD) which each step being performed by different group of bacteria (anaerobic bacteria).

HYDROLYSIS



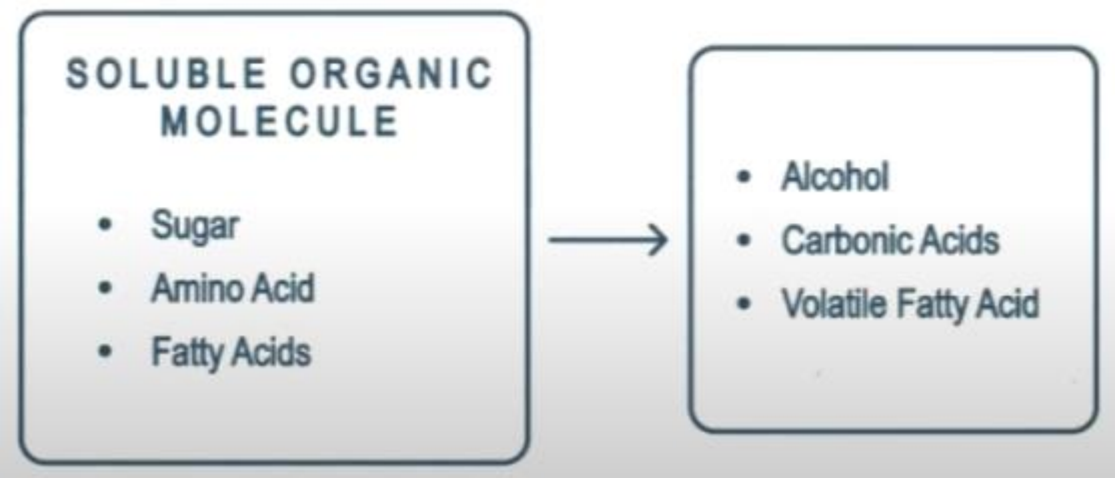
$$\text{Lipids} \xrightarrow{\textit{lipase}} \text{fatty acids, glycerol}$$

$$\text{Polysaccharide} \xrightarrow{\text{cellulase, cellobiase, xylanase, amylase}} \text{monosaccharide}$$

$$\text{Proteins} \xrightarrow{\textit{protease}} \text{amino acids}$$

Large organic polymers such as carbohydrates, fats and proteins are broken down into smaller elements like simple sugars, amino acids and fatty acids using water to split the chemical bonds between the substances.

ACEDOGENESIS



SOLUBLE ORGANIC MOLECULE

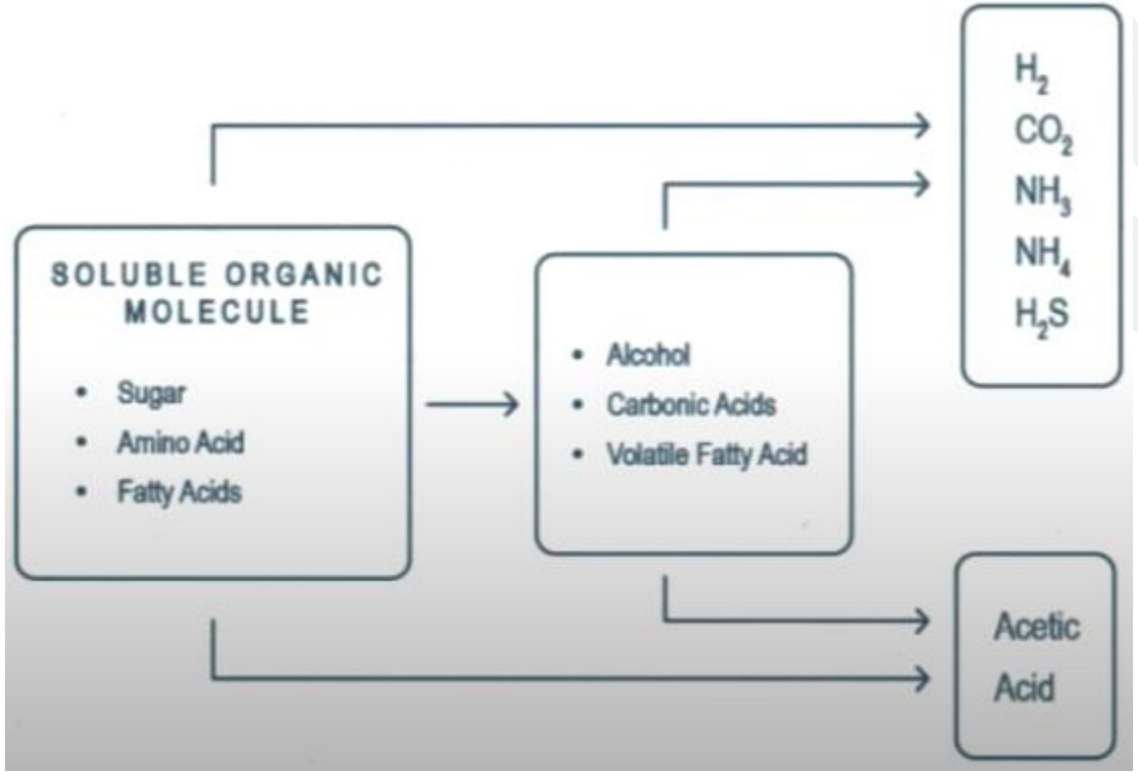
- Sugar
- Amino Acid
- Fatty Acids

→

- Alcohol
- Carbonic Acids
- Volatile Fatty Acid

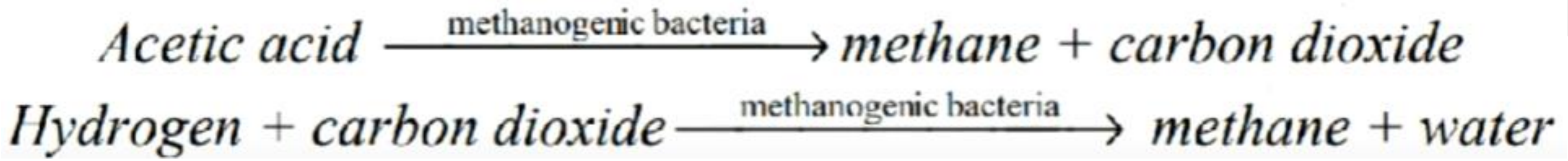
A further breakdown of the remaining components starts. It is done by the acidogenic bacteria which transform the materials into short-chained fatty acids, alcohols, CO_2, H_2 and NH_3.

ACETOGENESIS



In this phase, organic acids are formed. They are intermediary products needed for the subsequent methanogenesis phase. The bacteria responsible for the third phase is acetogens which are highly delicate to temperature variations.

METHANOGENESIS



$$\text{Acetic acid} \xrightarrow{\text{methanogenic bacteria}} \text{methane} + \text{carbon dioxide}$$

$$\text{Hydrogen} + \text{carbon dioxide} \xrightarrow{\text{methanogenic bacteria}} \text{methane} + \text{water}$$

The final stage of digestion results in methane formation. Also CO_2 is produced along with small proportions of some trace gases like H_2, H_2S and NH_3..

PARAMETER AND OPERATIONAL CONDITIONS OF ANAEROBIC DIGESTION (AD)

FEEDSTOCKS

Depending on the type of feedstock, namely dry or wet, it will convert to different amount of biogas yield.

Combination of agricultural wastes and food wastes is called ‘Co-digestion’.

pH

In acetogenic phase the pH is lower. However in methanogenic phase the pH is higher.

Adjust the pH range of the feedstock to around 6.5 to 7.5. Add lime, caustic soda, sodium hydroxide or dilute the feedstock to bring the pH within the desired limit if the pH is highly acidic or alkaline.

PARAMETER AND OPERATIONAL CONDITIONS OF ANAEROBIC DIGESTION (AD)

TEMPERATURE

Temperature below 15 ℃ is not ideal. The microorganism will slow down the reactivity.

Two common anaerobic temperature can be applied which in range of mesophilic zone and thermophilic zone.

Mesophilic zone range from 30 to 40 ℃. The microorganism degradation activity is slow in this temperature zone, therefore, the degradation time is high compare to thermophilic zone.

Thermophilic zone range from 45 to 60 ℃. The operation in this zone is more stable compare to mesophilic zone.

HYDRAULIC RETENTION TIME (HRT)

The time where feedstock stays in the reactor (days).

The ideal HRT is between 10 to 40 days.

PARAMETER AND OPERATIONAL CONDITIONS OF ANAEROBIC DIGESTION (AD)

PARTICLE SIZE

Reduce the particle size and create a homogeneous material by using crushers or shredding machines.

If the feedstock is delivered in the liquid or slurry form, removed the impurities in which particles of heavy materials such as gravel and bones. Settle at the bottom and those of lighter ones, such as plastics, float on the surface where they can be removed.

PROBLEM BASED CALCULATION

EXAMPLE 1

A small scale anaerobic digester is found to weigh 5.76 g more when filled with air at 25 ^{o}C and 1 atm (101.3 kPa) pressure than when it is evacuated. What is the volume of the digester? (Consider air to be 20% oxygen and 80% nitrogen by volume).

1) Air is 20% oxygen and 80% nitrogen by volume, and therefore 20% oxygen and 80% nitrogen by moles.
(Gases expand to uniformly fill their container, so the number of moles of any gas in a given volume is directly proportional to the volume, provided the temperature is unchanged.) Molecular weight of oxygen is 32 g/mol and nitrogen is 28 g/mol.

2) Let total number of moles present $= \mathrm{n} = \mathrm{mol\ O_2} + \mathrm{mol\ N_2}$, Therefore,

$$mol\ O_2 = 20\% \times 32\frac{g}{mol} \times n\ mol = 6.4n\ \mathrm{g}$$

$$mol\ \mathrm{N_2} = 80\% \times 28\frac{g}{mol} \times n\ mol = 22.4n\ \mathrm{g}$$

3) $Total\ mass = mass\ O_2 + \mathrm{mass}\ N_2\ (mass = mol \times molar\ mass)$

$$5.76 = 6.4n + 22.4\mathrm{n}$$

$$n = 0.2\ \ moles$$

4) Use the ideal gas equation to calculate V: PV = nRT

$$V = \frac{nRT}{P} = \frac{(0.2\ mol)(8.314\ J\ mol^{-1}K^{-1})(25℃ + 273\ K)}{101.3\ kPa} = \mathbf{4.89\ L}$$

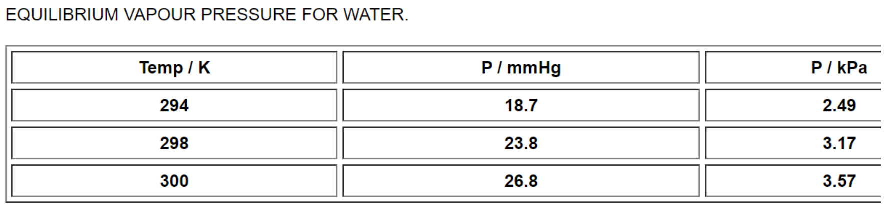
(Note that V will be in L if P is in kPa and R = 8.314 J K^{-1} mol^{-1})

EXAMPLE 2

Biogas gas is collected over water in a measuring cylinder, the level of water being the same inside and outside the cylinder. The volume of biogas collected was 120 mL, the temperature was read as 21°C. Barometric pressure inside the cylinder was observed to be 750.1 mmHg. Calculate the volume of dry biogas obtained at 298 K and 101.3 kPa.

1) Gases collected over water are saturated with water vapour. Therefore $P_{total} = P_{biogas} + P_{water}$
The partial pressure of water in the mixture, P_{water}, is the equilibrium vapour pressure of water at the temperature specified.

2) At 294 K (21 °C), from the data in the side Table , P_{water} = 2.49 kPa.
The pressure inside the container is the same as that outside = 750.1 mmHg
= (750.1/760.0) x 101.3 kPa = 100.0 kPa. (101.3 kPa = 760 mm Hg, 1 atm



EQUILIBRIUM VAPOUR PRESSURE FOR WATER.

Temp / K	P / mmHg	P / kPa
294	18.7	2.49
298	23.8	3.17
300	26.8	3.57

3) 100.0 kPa = P_{Biogas} + 2.49 kPa
Therefore, P_{Biogas} = 100.0 - 2.49 = 97.5 kPa.

4) The combined Boyle's and Charles's Laws can then be used to calculate the volume of dry biogas at 298 K and 101.3 kPa.

$$\left(\frac{P_1V_1}{T_1}\right)_{\text{inside cylinder}} = \left(\frac{P_2V_2}{T_2}\right)_{\text{outside cylinder}}$$

$$\left(\frac{97.5\ kPa \times 120\ mL}{294\ K}\right) = \left(\frac{101.3\ kPa \times V_2}{298\ K}\right)$$

$$V_2 = \frac{97.5 \times 120 \times 298}{294 \times 101.3}$$

Final answer, $\boldsymbol{V_2} = \mathbf{117\ mL\ of\ dry\ biogas\ at\ 298\ K\ and\ 101.3\ kPa}$

TUTORIAL

Table 1 shows the biofuel produced inside a vessel. A 500 L vessel was filled with 25 kg biomass to produce 242.2 g biofuels. Calculate the headspace volume of the vessel. Assume the temperature inside the vessel is 37 ℃ and pressure is 2 atm, while outside condition is 37 ℃ and 1 atm. Take the molecular weight for the biofuel as CH_4 16 g/mol, CO_2 44 g/mol, H_2 2 g/mol, NH_3 17 g/mol, CO 28 g/mol and H_2S 34 g/mol.

Table 1

Lignocellulosic biomass	**Biofuel composition (%)**						
	CH_4	**CO_2**	**H_2**	**NH_3**	**CO**	**H_2S**	**Total**
Rice straw	67	20	5.6	6.4	-	1	100

THANK YOU

Chapter 5

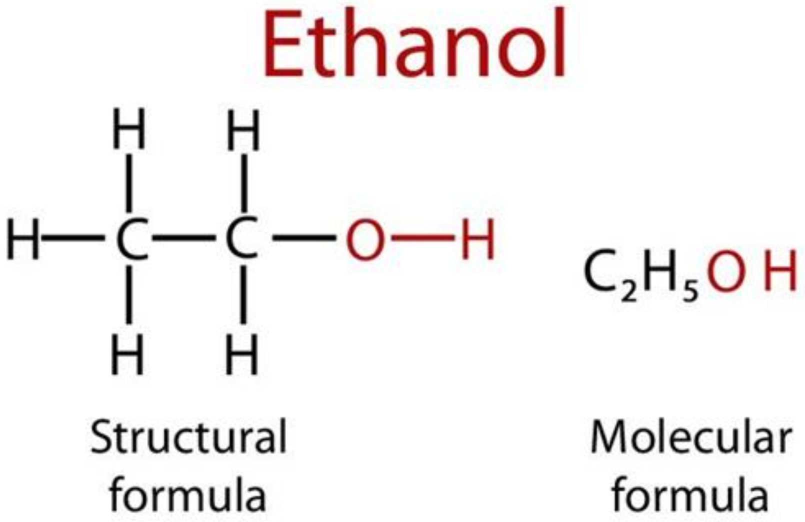
Bioethanol Production

TOPICS

- Introduction of bioethanol
- Sources of bioethanol
- Bioethanol production
  - Sugar
  - Starch
  - Lignocellulosic biomass
- Advantages
- Disadvantages

INTRODUCTION TO BIOETHANOL

- Bioethanol
  - An alcohol made by fermentation, mostly from carbohydrates produced in sugar, starch crops or lignocellulosic biomass

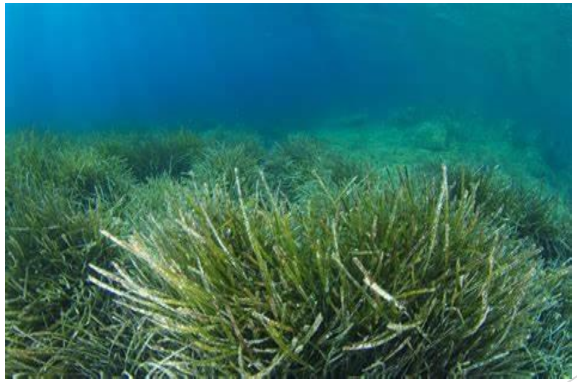


INTRODUCTION TO BIOETHANOL (CON'T)

- Applications of bioethanol
  - Transport fuel to replace gasoline
  - Fuel for power generation by thermal combustion
  - Fuel for fuel cells by thermochemical reaction
  - Fuel in cogeneration systems
  - Feedstock in the chemicals industry

SOURCES OF BIOETHANOL

- Agricultural Corps
  - Sugar crops: Sugar beet, Sugarcane, Sorghum
  - Starch crops: Corn, Sweet potato
- Marine
  - Algae: Seaweeds
  - Seagrasses


SOURCES OF BIOETHANOL (CON'T)

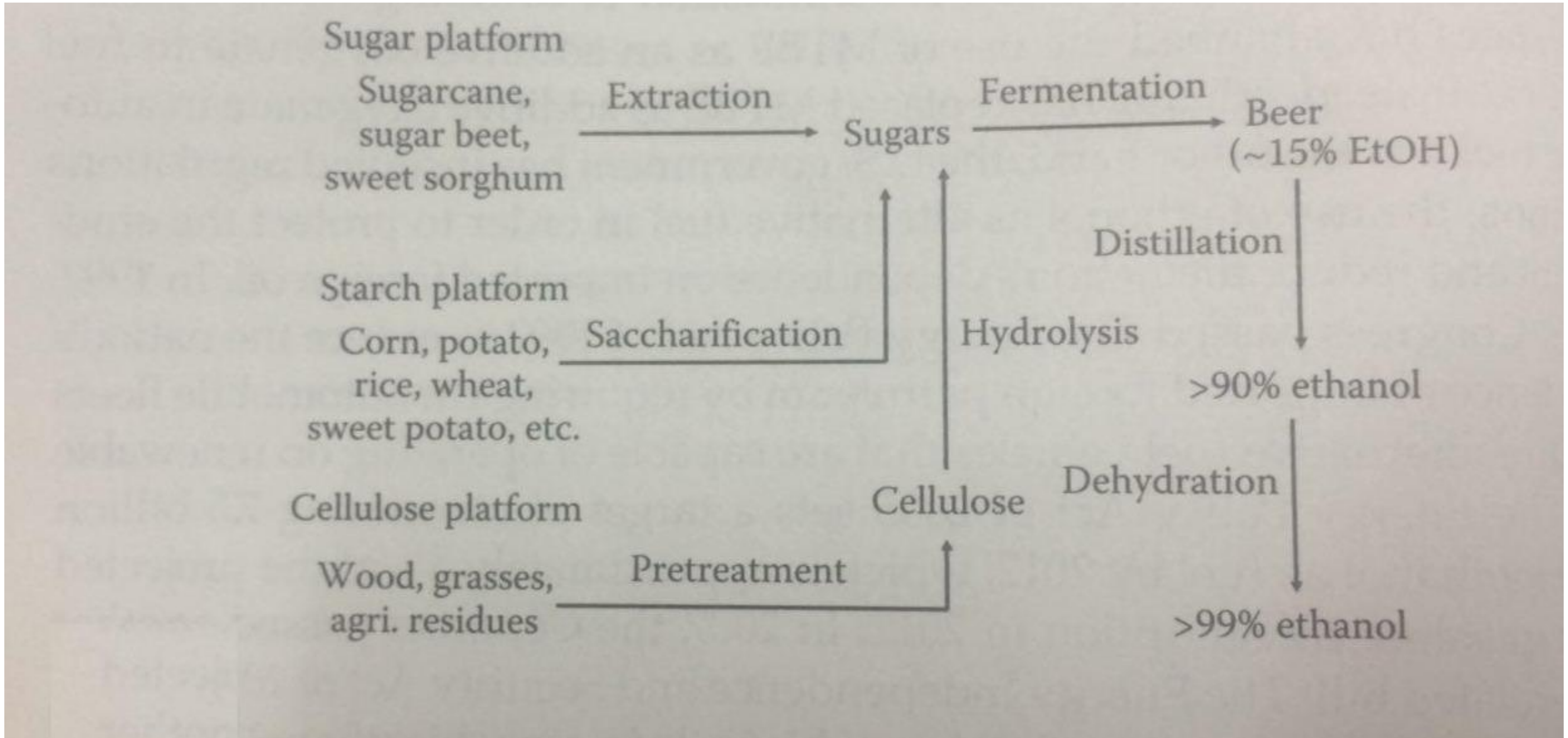


- Lignocellulosic biomass
  - Woody: Poplar tree, Willow tree, Pine tree, Cedar tree
  - Herbaceous: Miscanthus, Switchgrass, Alfaalfa



- Agricultural & Industrial waste:
  - Sugarcane bagasse
  - Rice straw
  - Wheat straw & bran
  - Corn stover
  - Paper sludge & paper waste


BIOETHANOL PRODUCTION



Biological processes for bioethanol production from different renewable materials.

BIOETHANOL PRODUCTION FROM SUGAR

- The yeast Saccharomyces cerevisiae is the universal organism for ethanol production.
- The production is carried out via the glycolytic pathway (also known as the Embden-Myerhof-Parnas (EMP) pathways).
- Zymomonas mobilis is considered the most effective bacteria for production of bioethanol, although it is not currently used commercially.
- It can produce ethanol at much faster than Saccharomyces cerevisiae.
- The production is carried out via the Enter-Doudoroff (ED) pathway.

BIOETHANOL PRODUCTION FROM STARCH

- Bioethanol is produced by either the dry milling or wet milling process

BIOETHANOL PRODUCTION FROM STARCH (CON’T)

- Dry milling process
  - Cleaning
    - By using sieves
  - Milling
    - Crush to small particles or powder
  - Mashing
    - Mixed with water, heated to 60 °C then starch dissolve in water for 5-10 min

BIOETHANOL PRODUCTION FROM STARCH (CON’T)

- Liquefaction
  - α- amylase is added, temperature is increased to 70 - 80 °C for 2 hours
  - Indication of complete process is a dramatic drop in viscosity
  - Starch → oligosaccharides & dextrin

BIOETHANOL PRODUCTION FROM STARCH (CON'T)

- Saccharification
  - Glucoamylase is added, temperature is 60 - 65 °C for 30 min
  - Iodine test used to complete the process
  - Oligosaccharides & dextrin ⟶ Glucose

BIOETHANOL PRODUCTION FROM STARCH (CON'T)

- Fermentation: Ethanol Conc. 10 - 15 % (w/w)
- Distillation : Ethanol Conc. 90% (w/w)
- Dehydration: Ethanol Conc. 99% (w/w)

BIOETHANOL PRODUCTION FROM STARCH (CON'T)

- Wet milling process
    - Cleaning
    - Steeping
        - In water to expand the structure
    - Degermination
        - Oil & germ meal are extracted and removed
    - Defiber
        - Fiber is separated from starch
    - Gluten separation

BIOETHANOL PRODUCTION FROM STARCH (CON'T)

- Mashing
- Liquefaction
- Saccharification
- Fermentation
    - Yeast is added to produce ethanol. 60 - 72 h process. CO_2 is a by-product
- Distillation & dehydration

BIOETHANOL PRODUCTION FROM STARCH (CON'T)

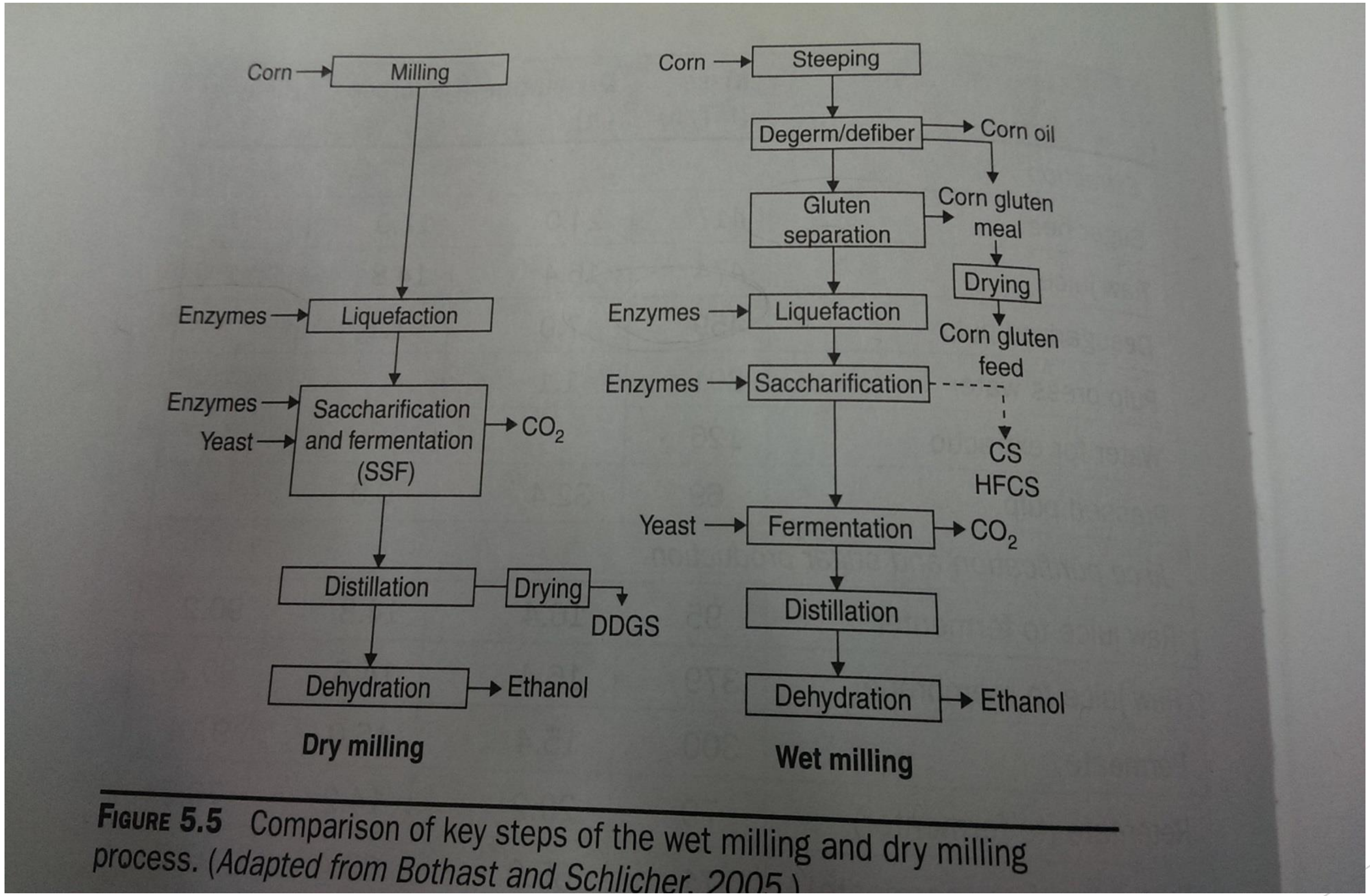


FIGURE 5.5 Comparison of key steps of the wet milling and dry milling process. (*Adapted from Bothast and Schlicher, 2005.*)

BIOETHANOL PRODUCTION FROM LIGNOCELLULOSIC BIOMASS

- The production comprises the following main steps:
  - Hydrolysis of cellulose and hemicellulose
  - Sugar fermentation
  - Separation of lignin residue
  - Recovery and purifying the ethanol to meet fuel specifications

ADVANTAGES OF BIOETHANOL

- Exhaust gases of ethanol are much cleaner
  - It burns more cleanly as a result of more complete combustion
- Greenhouse gases reduce
  - Ethanol-blended fuels such as E85 (85% ethanol and 15% gasoline) reduce up to 37.1% of GHGs
- Positive energy balance, depending on the type of raw stock
  - Output of energy during the production is more than the input
- Any plant can be use for production of bioethanol
  - It only has to contain sugar and starch

ADVANTAGES OF BIOETHANOL (CON'T)

- Decrease in ozone formation
  - The emissions produced by burning ethanol are less reactive with sunlight than those produced by burning gasoline, which results in a lower potential for forming ozone
- Renewable energy resource
  - Result of conversion of the sun's energy into usable energy
  - Photosynthesis -> feedstock grow -> processed into ethanol

ADVANTAGES OF BIOETHANOL (CON'T)

- Energy security
  - Especially countries that do not have access to crude oil resources
- Reduces the amount of high-octane additives
- Fuel spills are more easily biodegraded or diluted to non toxic concentrations

DISADVANTAGES OF BIOETHANOL

- Biodiversity
  - A large amount of arable land is required to grow crops, natural habitats would be destroyed
- Food vs. fuel debate
  - Due to the lucrative prices of bioethanol some farmers may sacrifice food crops for biofuel production which will increase food prices around the world

DISADVANTAGES OF BIOETHANOL (CON'T)

- Transportation
  - Ethanol is hygroscopic, it absorbs water from the air and thus has high corrosion aggressiveness
- Many older cars unequipped to handle even 10% ethanol

Chapter 6 Biodiesel Production

Topics

- Biodiesel
- Physical and chemical properties
- Quality standard
- Feedstocks
- Production process or method
- Transesterification reaction

Biodiesel

A mixture of fatty acids methyl ester (FAME) (C12–C24) synthesized from biomass

Physical and chemical properties

Physical appearance

A clear liquid with a light to dark-yellow colour

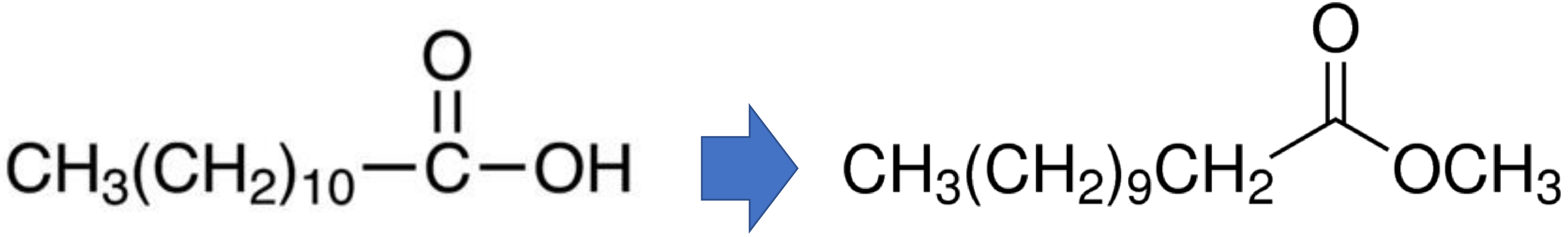
Insoluble in water

Has a light musty or soapy odour

Has stable reactivity except towards strong oxidizing agents

Chemical properties

- The chemical properties of biodiesel are determined by the amount of each fatty acid that are present in the feedstock (biomass).
- The fatty acids vary in their carbon chain length and in the number of unsaturated bonds they contain in the feedstock.

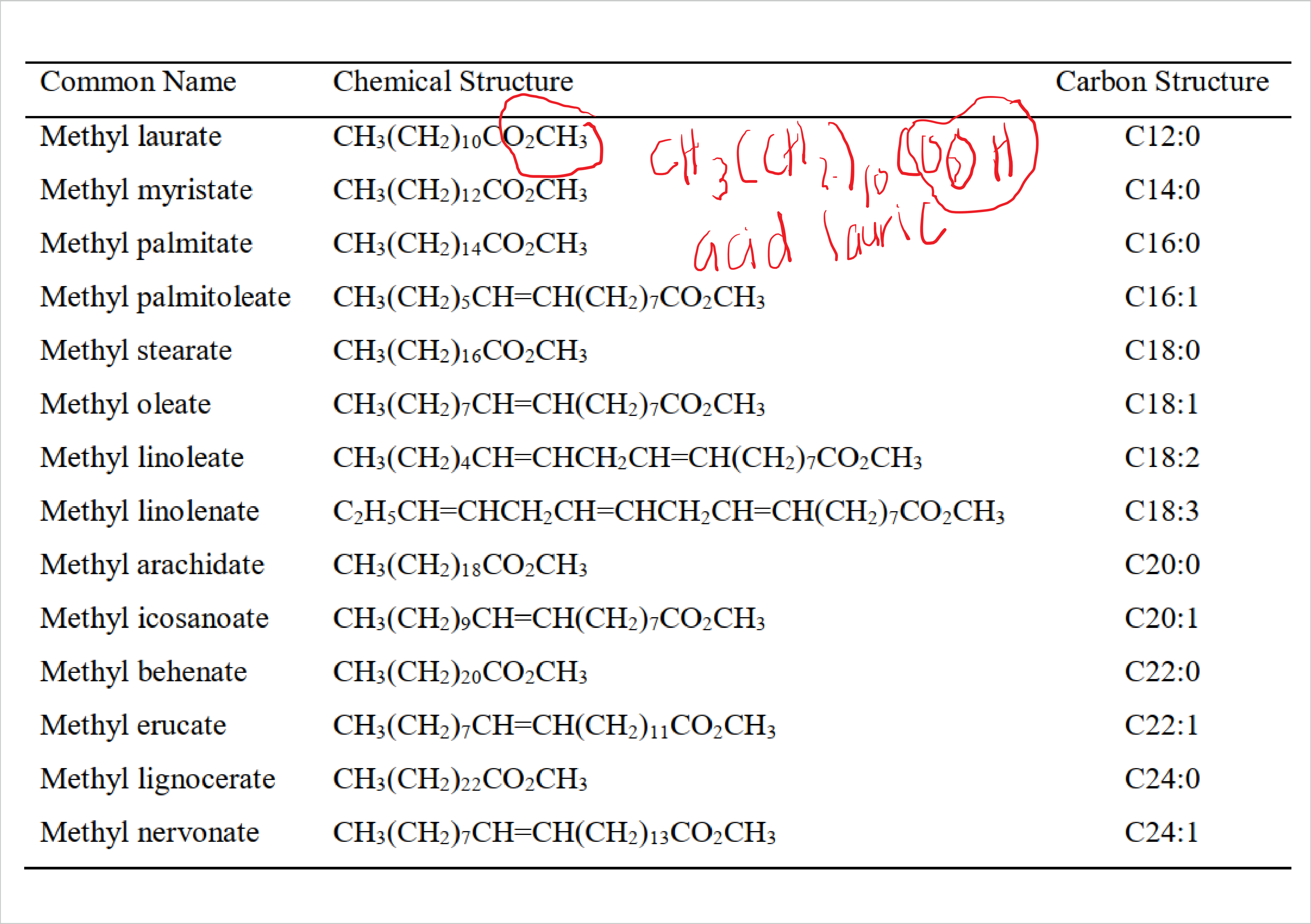


$$\mathrm{CH_3(CH_2)_{10}-\overset{\overset{O}{\|}}{C}-OH} \Rightarrow \mathrm{CH_3(CH_2)_9CH_2\overset{\overset{O}{\|}}{C}OCH_3}$$

Lauric Acid

Methyl laureate

Chemical compositions



Common Name	Chemical Structure	Carbon Structure
Methyl laurate	$CH_3(CH_2)_{10}CO_2CH_3$	C12:0
Methyl myristate	$CH_3(CH_2)_{12}CO_2CH_3$	C14:0
Methyl palmitate	$CH_3(CH_2)_{14}CO_2CH_3$	C16:0
Methyl palmitoleate	$CH_3(CH_2)_5CH{=}CH(CH_2)_7CO_2CH_3$	C16:1
Methyl stearate	$CH_3(CH_2)_{16}CO_2CH_3$	C18:0
Methyl oleate	$CH_3(CH_2)_7CH{=}CH(CH_2)_7CO_2CH_3$	C18:1
Methyl linoleate	$CH_3(CH_2)_4CH{=}CHCH_2CH{=}CH(CH_2)_7CO_2CH_3$	C18:2
Methyl linolenate	$C_2H_5CH{=}CHCH_2CH{=}CHCH_2CH{=}CH(CH_2)_7CO_2CH_3$	C18:3
Methyl arachidate	$CH_3(CH_2)_{18}CO_2CH_3$	C20:0
Methyl icosanoate	$CH_3(CH_2)_9CH{=}CH(CH_2)_7CO_2CH_3$	C20:1
Methyl behenate	$CH_3(CH_2)_{20}CO_2CH_3$	C22:0
Methyl erucate	$CH_3(CH_2)_7CH{=}CH(CH_2)_{11}CO_2CH_3$	C22:1
Methyl lignocerate	$CH_3(CH_2)_{22}CO_2CH_3$	C24:0
Methyl nervonate	$CH_3(CH_2)_7CH{=}CH(CH_2)_{13}CO_2CH_3$	C24:1

$CH_3(CH_2)_{10}COOH$

acid lauric

Example

- Give the name of the fatty acid of each fatty acid methyl ester (FAME).

(9 Marks)

a) Methyl palmitate

Fatty acid : Palmitic acid

b) Methyl stearate

Fatty acid: Stearic acid

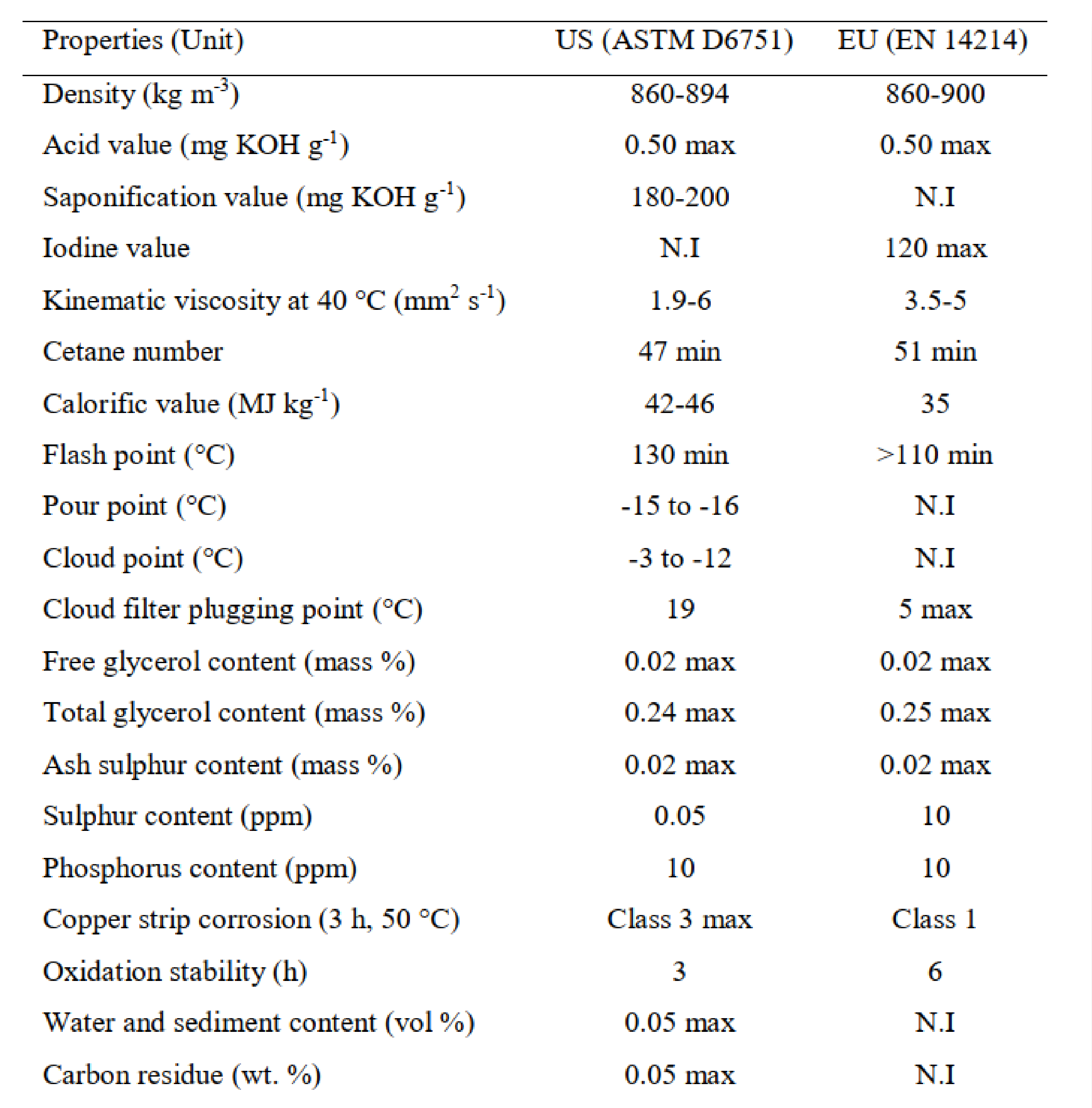
c) Methyl oleate

Fatty acid: Oleic acid

Quality standard

- Policies and standards for biodiesel have been set by different countries around the world to ensure the quality of fuel and also to meet the consumers' expectation.
- Countries such as the EU, USA, Australia, India, Japan, South Africa, Brazil, etc. have their specific biodiesel standards.
- Malaysia has decided to refers to ASTM D6751 (American Society for Testing and Materials) and EN 14214 (European Committee for Standardization) as the quality standard for biodiesel product.

Quality standard (Cont’)



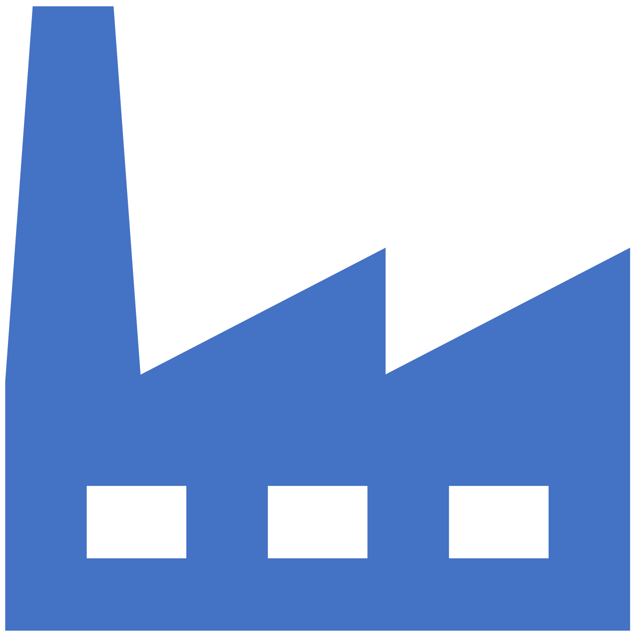
Properties (Unit)	US (ASTM D6751)	EU (EN 14214)
Density (kg m^{-3})	860-894	860-900
Acid value (mg KOH g^{-1})	0.50 max	0.50 max
Saponification value (mg KOH g^{-1})	180-200	N.I
Iodine value	N.I	120 max
Kinematic viscosity at 40 °C (mm^2 s^{-1})	1.9-6	3.5-5
Cetane number	47 min	51 min
Calorific value (MJ kg^{-1})	42-46	35
Flash point (°C)	130 min	>110 min
Pour point (°C)	-15 to -16	N.I
Cloud point (°C)	-3 to -12	N.I
Cloud filter plugging point (°C)	19	5 max
Free glycerol content (mass %)	0.02 max	0.02 max
Total glycerol content (mass %)	0.24 max	0.25 max
Ash sulphur content (mass %)	0.02 max	0.02 max
Sulphur content (ppm)	0.05	10
Phosphorus content (ppm)	10	10
Copper strip corrosion (3 h, 50 °C)	Class 3 max	Class 1
Oxidation stability (h)	3	6
Water and sediment content (vol %)	0.05 max	N.I
Carbon residue (wt. %)	0.05 max	N.I

Feedstocks

- There are a wide range of available feedstocks for biodiesel production.
- It can be different from one country to another depending on their geographical locations and agricultural practices.
- Selecting the best feedstock is essential to ensure a low production cost because feedstocks covers more than 75 % of the overall production cost.

Feedstocks (Con’t)

- Five types of feedstocks:
  - Edible oils (such as rapeseed, soybean, sunflower, palm and coconut oil)
  - Non-edible oils (such as jatropha, karanja, sea mango)
  - Microalgae
  - Animal fats (for example tallow, yellow grease, chicken fat and by-products from fish oil)
  - Used or recycled oil

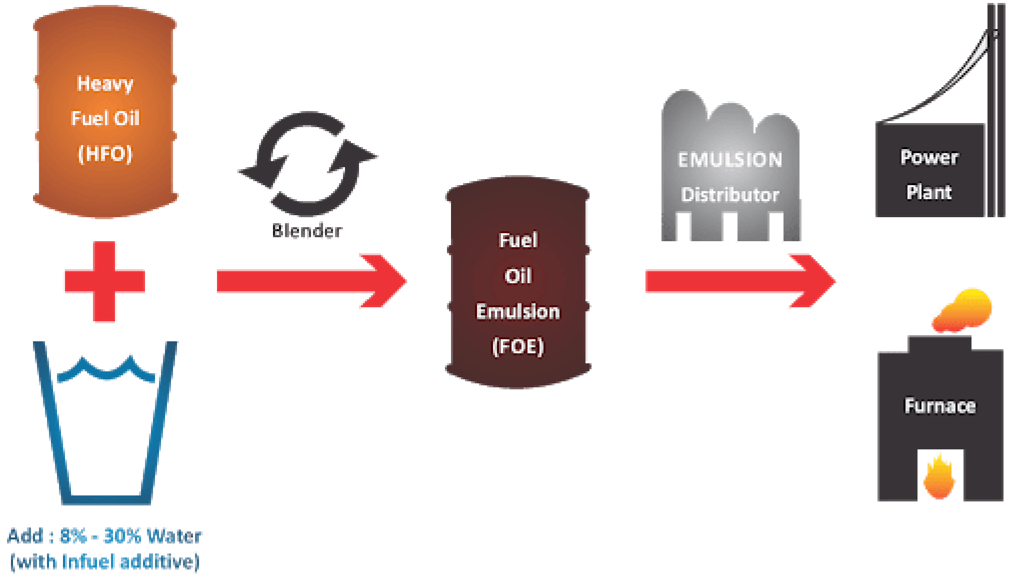


Production process/method

- There are four common technologies that have been well established for the production of biodiesel include:
  - Direct use and blending
  - Micro-emulsification
  - Pyrolysis
  - Transesterification

Direct use and blending

- Crude vegetable oils are mixed directly or diluted with diesel fuel and/or ethanol.
- This is to reduce the high viscosity of pure vegetable oils.
- Direct used of pure vegetable oils with high viscosities will led to the compression ignition engines problem.
- However, this method is generally been considered to be not satisfactory and impractical for both direct and indirect diesel engines.
- The use of this method to produce biodiesel for diesel engines requires significant engine modifications, otherwise engine running times are decreased and the danger of engine failure is increased.

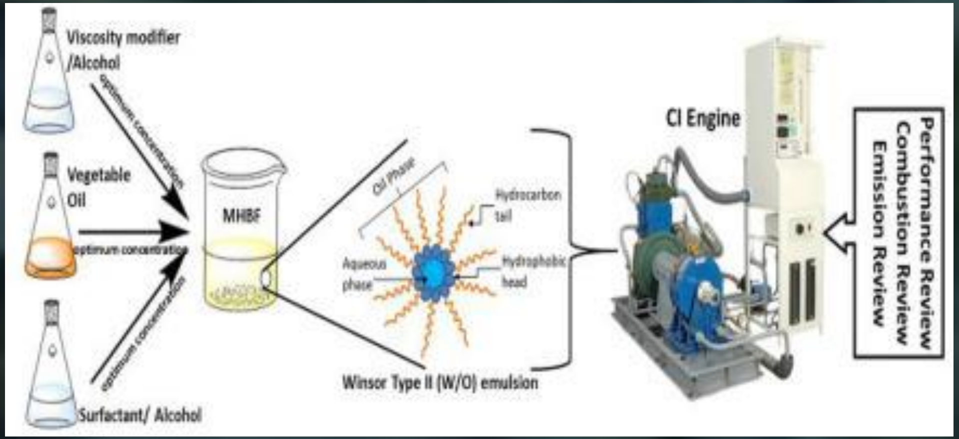


Micro-emulsification

Micro-emulsions of solvents were used to overcome the issue of straight vegetable oil high viscosity.

In this method, co-solvent, alcohol, cetane improver and surfactant are added into the oil.

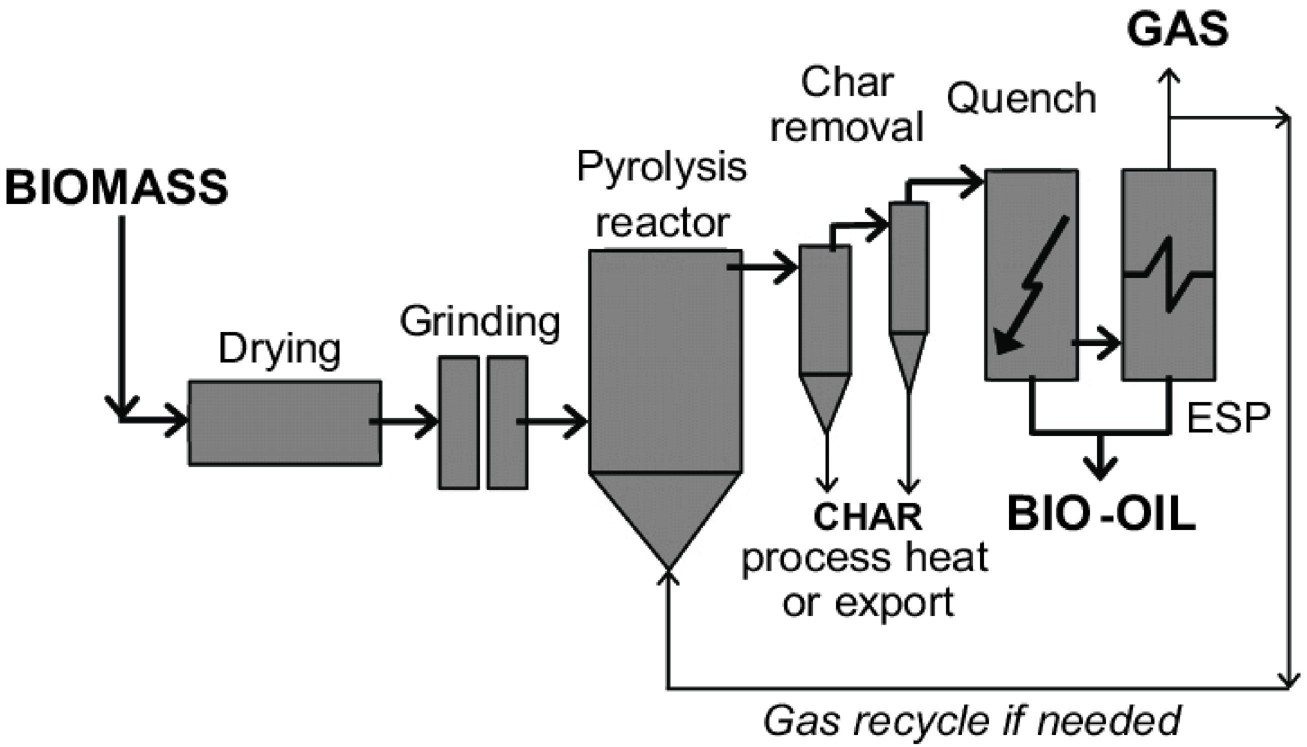
The process of micro-emulsion is easy.



Modifications of the original engine design, special and sophisticated equipment and such are not necessary.

However, it deals with issues of less volatility and stability.

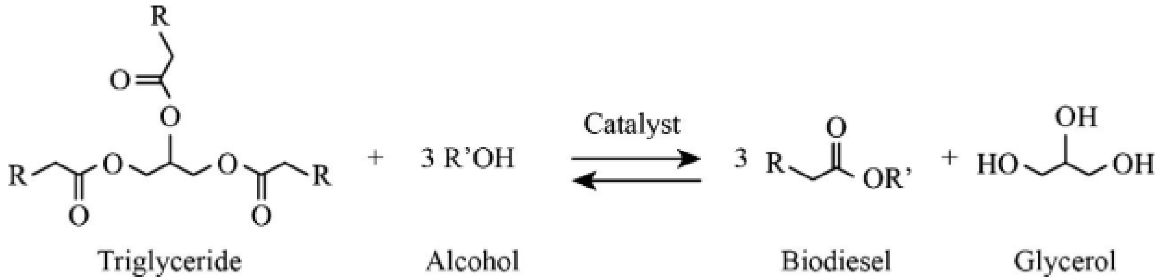
Pyrolysis



- The method of conversion of raw oil into biodiesel with heat or with the help of a catalyst is thermal cracking.
- No air or oxygen is required during the heating process.
- The temperature range for thermal cracking process is 400 - 600 °C.
- On the basis of the rate of pyrolysis; char, biodiesel, and gases are produced.
- The biodiesel obtained from this process has comparable properties with diesel fuel.
- The major drawback of this process is the high temperature required during the process makes it expensive.
- The absence of oxygen during the process of thermal cracking also reduces the amount of oxygen content in the fuel.

Transesterification reaction

- Transesterification reaction or also known as alcoholysis (due to reaction of free fatty acid with alcohol) is a favorable process for commercial biodiesel production.
- It is a reversible reaction between 1 mole of triglyceride with 3 moles of alcohol to produced 3 moles of fatty acid methyl esters (FAMEs) and 1 mole of glycerol with a presence of catalyst.
- Excess alcohol is used to shift the equilibrium toward the product because of reversible nature of reaction.
- A catalyst is usually used to improve the reaction rate and yield.
- Generally, methanol is the most common alcohol used during the transesterification reaction.
- The end products of transesterification process are separated, biodiesel settles on the top and due to high weight glycerol settles down.



Transesterification reaction (Cont’)

Procedure (Pilot scale)

- Transesterification reaction is carried out in a three-neck round bottom glass flask (250 mL) equipped with a reflux condenser, a thermometer and a digital hot plate with a magnetic stirrer as shown in Figure 1(a).
- Firstly, 3 mol of methanol is added to 1 mol of heated oil (65 °C).
- Then, a desired amount of catalyst is added and continue to heat (temperature maintain at 65 °C) until certain optimum period of time.
- The mixture is heated and mixed with vigorous stirring in a silicone oil bath to minimize the limitation of mass transfer.
- After a completion of the reaction, the heating is stopped and the used catalyst is separated from the reaction medium by filtration media.
- Then, the mixture is moved to the separating funnel and left for 24 h. In this stage, the liquid containing biodiesel and glycerol were allowed to separate.
- The biodiesel yield is calculated by using equation:

$$\text{Percentage of Volume yield} = \frac{\text{Volume of product}}{\text{Volume of feed}} \times 100$$

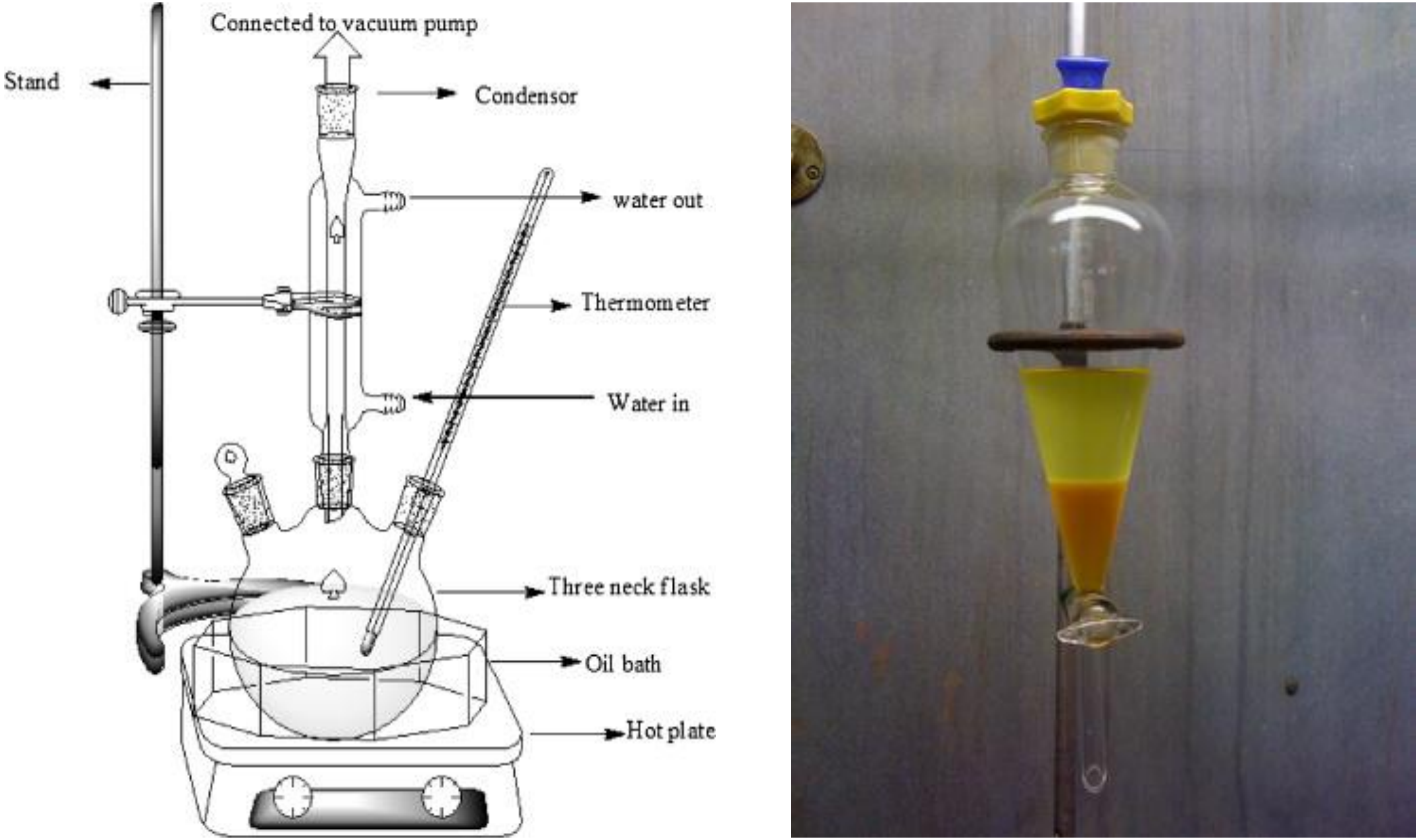


Figure 1: a) Schematic diagram of transesterification reaction b) Biodiesel separation layer

Transesterification reaction (Cont')

- The catalysts used for the transesterification reaction can be classified as:
  - Homogeneous catalyst which further could be subdivided into two categories:
    - Homogeneous acid catalysts (HCl, H_2SO_4)
    - Homogeneous base catalysts (NaOH, KOH)

  - Heterogeneous catalyst which further could be subdivided into three categories:
    - Heterogeneous acid catalysts (SiO_2, Fe_2O_3)
    - Heterogeneous basic catalysts (CaO, MgO)
    - Heterogeneous acid-base bi-functional catalysts (Na_2SiO_3, $CaTiO_3$)

Transesterification reaction (Cont’)

- Main parameters affecting transesterification reaction:
  - Effect of methanol to oil molar ratio
    - Various alcohols such as methanol, ethanol, butanol and isopropanol can be applied for transesterification of oils.
    - Among them, lower alcohols, i.e. , methanol and ethanol, are the most common alcohol used in this process.
    - Other alcohols are hardly applied because they are expensive and have no economic justification.
    - Methanol is advantageous over other alcohols, mainly due to its specific chemical and physical characteristics. For instance, it has the capability to react quickly with triglyceride.
    - Generally, it is supposed that high methanol to oil molar ratios facilitates the triglycerides conversion into monoglycerides and accelerates the transesterification process.
    - Stoichiometrically, the alcohol to oil molar ratio must be 3:1, however, in a real reaction system a higher molar ratio is needed to raise the possibility of their contact for improving the final product yield (to eliminate the mass transfer problem).
    - In practice, a feed mole ratio is employed (6:1, 9:1, 12:1, 15:1) to shift the transesterification reaction to the desired product.

Transesterification reaction (Cont’)

- Effect of catalyst loading
  - Catalyst influences the reaction by providing active surface sites for it to occur.
  - The increase of catalyst amount would increase the available catalytic sites.
  - The ideal amount of catalyst loading will accelerate the reaction.
  - However, an excess amount of catalyst loading is found to form emulsions reflecting on higher viscosity thereby making the recovery of biodiesel difficult.
  - Besides, it can create catalyst accumulation on the wall of the reactor.
  - The amount of catalyst loading is expressed in the form of weight percentage (wt. %) based on the weight of the feedstock used (1 wt.%, 3 wt. %, 5 wt.%, 7 wt. %).

Transesterification reaction (Cont')

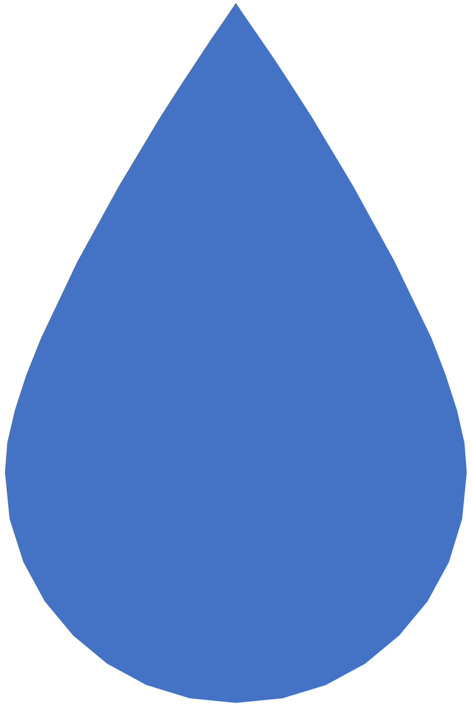
- Effect of reaction time
  - Reaction time is defined as the time that chemical species expend in the reactor till the reaction is completed or stopped (mixture is subjected to downstream processing, i.e., separation, feed recycling and washing).
  - The required residence time is directly dependent on other parameters that enhance the rate of transesterification reaction.
  - Appropriate reaction time would allow sufficient contact time between the reactants and the catalyst surface to achieve high catalytic performance.
  - The transesterification rate will be diminished and finally reached equilibrium as the optimum time has been reached.

Transesterification reaction (Cont')

- Effect of reaction temperature
  - Operational temperature is considered by many as an important factor for proper production of biodiesel.
  - The reaction temperature must be less than the boiling point of alcohol to ensure minimum vaporization.
  - Usually, the ideal reaction temperature is ranges from 60 °C to 65 °C (if methanol is used as the alcohol).
  - The application of temperatures lower than the melting point of oil, for example, 50 °C would not be practical due to elevated viscosity.
  - However, in several cases, high temperature is more favorable as increase in temperature is found to speed up the reaction and more yield is achieved which may be due to reduction of viscosity of oil on increasing the temperature resulting in better mixing of oil with alcohol and shorten the reaction time as well as faster the separation of glycerol from biodiesel.

Transesterification reaction (Cont’)

- Effect of water content
  - All materials involved in the transesterification process should be waterless as water leads to hydrolysis of triglycerides and FAME which simultaneously contributes to the formation of soap
  - This will makes the separation process difficult



Thank you

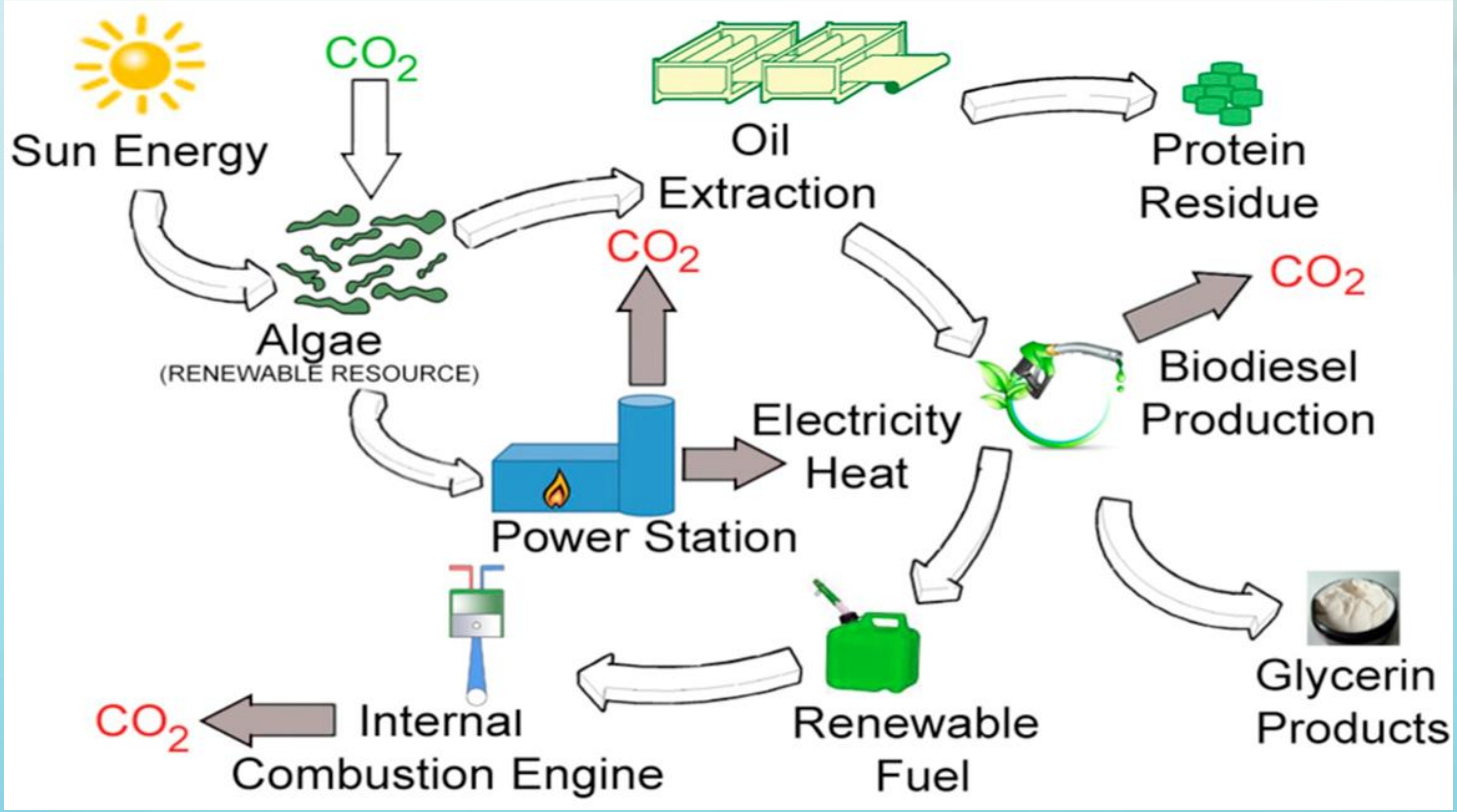
CHAPTER 5: MIROALGAE BIODIESEL PRODUCTION

Topics

- Introduction to microalgae
- Cultivation of microalgae
- Microalgae cultivation technology
- Lipid extraction method from microalgae
- Production of biodiesel from microalgae

Introduction to microalgae

- A large and diverse group of simple, usually autotrophic organisms that can have either unicellular or multicellular forms
- Microorganisms which are photosynthetic
- Considered as a viable alternative resource for first and second-generation biodiesel feedstock as it overcomes the disadvantages incurred from producing both generation of biodiesel
- It possess higher growth tendencies and biomass production because it can accumulate large cell lipid content of over 20–77%
- Its cultivation has no compulsory requirement of any chemicals like pesticides or herbicides
- It have a higher tolerance to CO_2 which helps to utilize and sequent CO_2 from various sources
- They can also be grown in any medium like coastal seawater and brackish water which usually affects any older generation biodiesel feedstock cultivation. Consequently, this eliminates the restrictions on growth conditions such as climate and water conditions
- The rate of water consumption is minimal in microalgae cultivation, also, they have a high growth rate when compared with other sources


Sun Energy
CO_2
Oil Extraction
Protein Residue
CO_2
CO_2
Algae
(RENEWABLE RESOURCE)
Biodiesel Production
Electricity Heat
Power Station
Glycerin Products
CO_2
Internal Combustion Engine
Renewable Fuel

Cultivation of microalgae

- Microalgae species are cultivated under controlled conditions to ensure effective end products from the feedstock
- The idea is to ensure organized photosynthesis so that the cells within the microalgae accumulate maximum lipid content
- The most critical parameters regulating microalgae growth are:
  - Light
  - Carbon dioxide
  - Temperature
  - pH

Most critical parameters regulating microalgae growth

Light

- Transform light energy into chemical energy received from the sunlight to help in converting carbon dioxide (CO_2) and water into complex carbohydrates through photosynthesis
- Wavelength of light has a noticeable effect on the microalgae growth rates
- Biomass production in most microalgae increases under higher light intensity

Carbon dioxide

- It is important role in photosynthesis, as water reacts with CO_2 in presence of light to produce complex organic molecules for lipid production

Temperature

- The temperature impact on the growth of microalgae in terms of its growth rate which increases with temperature rise until it reaches the optimal temperature

pH

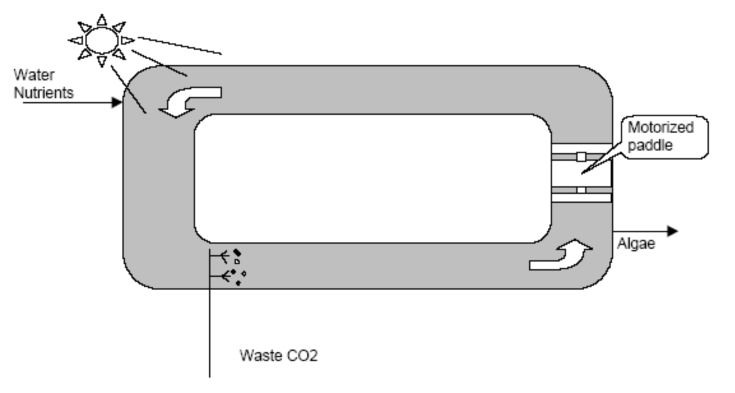
- Affects many biological mechanisms related to the growth of cells, metabolism and ion intake
- pH determines the availability and solubility of CO_2 including some of the essential nutrients, intracellular activities and cell wall associated enzymes

Microalgae cultivation technology

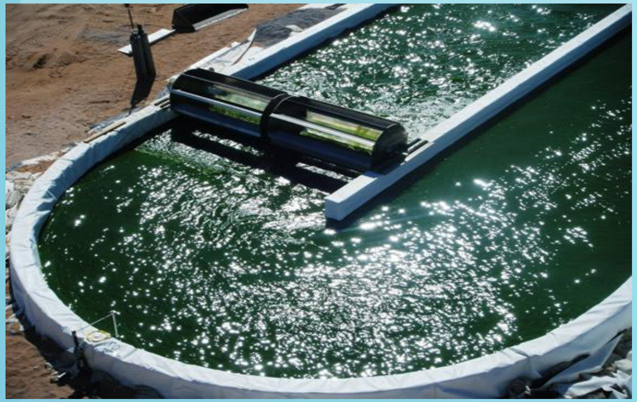
Open system

- Open Pond
  - Microalgae can growth in hot, sunny areas to get maximum production
  - Relatively cheap
  - Drawbacks:
    - Bad weather can stunt algae growth
    - Contamination from strains of bacteria or other outside organisms
    - The water in which the algae grow also has to be kept at a certain temperature, which can be difficult to maintain

Microalgae cultivation technology



Close system



- Race Pond
  - They utilized raceway ponds which allowed for “paddle wheels” to be applied that served to circulate the contents of the pond
  - This allowed for the better distribution of the nutrients that were added to allowed for the better distribution of the nutrients that were added to the pond
  - Drawbacks:
    - Little control of culture conditions, poor light utilization, use of a large land area, limited species of algae and low mass transfer rates

Microalgae cultivation technology

Close system

- Bioreactor
  - Vertical or slanted clear pipes and hanging bags were used to allow for the controlled circulation of the water and the mixing of the nutrients, plus the introduction of the CO_2 which is a necessary component of the feeding process for the algae
  - Drawback:
    - Capital costs relatively more expensive

Microalgae cultivation technology

Close system

- Photobioreactor
  - Horizontal, closed, full flood tubes connected together to form a photobioreactor
  - It could limit the contaminates that could enter into the microalgae being cultured
  - It controlled circulation in a continuous racetrack configuration, with some allowance for the injection of nutrients and CO_2

Lipid extraction method from microalgae

- Pressing Oil
- Chemical Lipid Extraction
- Super Critical Lipid Extraction
- Microwave Lipid Extraction

Pressing Oil

- Dry the microalgae and press the oil from it.
- Can retrieve up to 70% of the oil.
- While drying must prevent the microalgae from becoming contaminated.
- Cheapest and simplest method.

Chemical Lipid Extraction

- Use hexane solvents to extract the lipid.
- Hexane is a neurotoxin.
- Must be careful when using.
- Removes lipid out of almost all things.

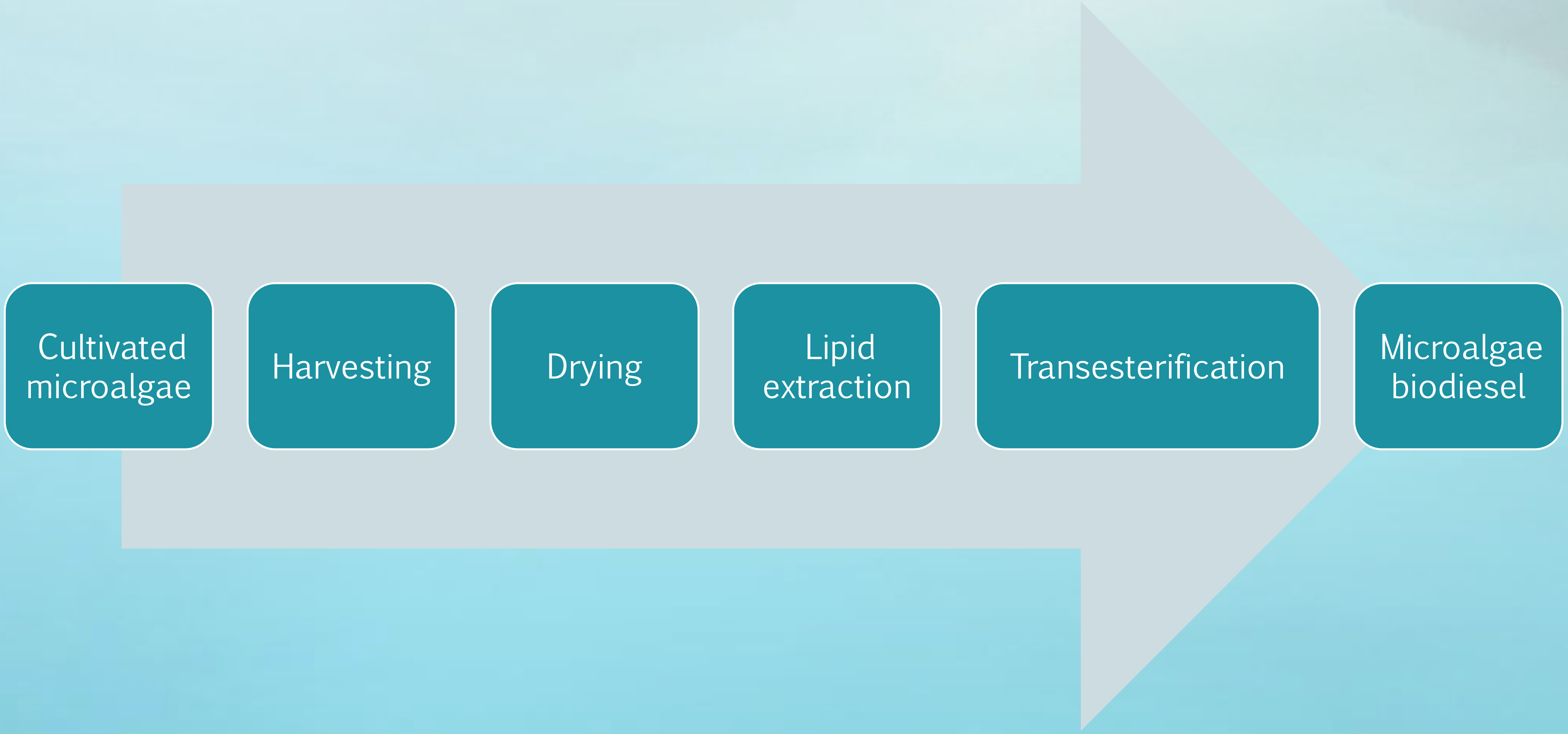
Super Critical Lipid Extraction

- Most efficient method.
- Uses carbon dioxide at critical pressure and temperature (CO_2 is almost a liquid).
- Rapid diffusion of the lipid.
- Very expensive process.
- Can retrieve up to 85% of the lipid.

Microwave Lipid Extraction

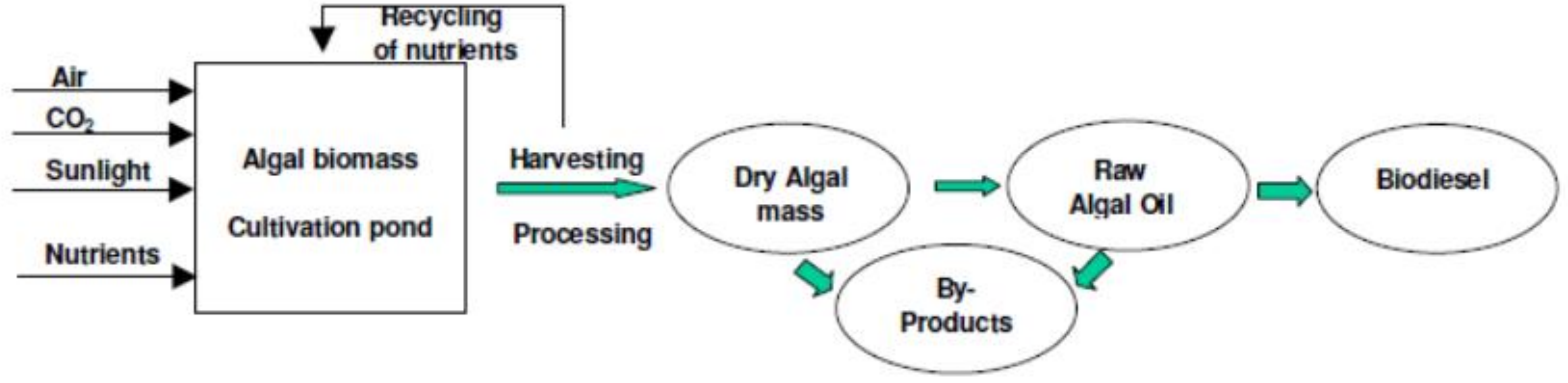
- Now recognized as efficient extraction techniques.
- Dramatically cut down working times.
- Increasing yields and often the quality of the extract.
- Can retrieve close to 100% of the lipid.

Production of biodiesel from microalgae



- Cultivated microalgae
- Harvesting
- Drying
- Lipid extraction
- Transesterification
- Microalgae biodiesel

Production of biodiesel from microalgae

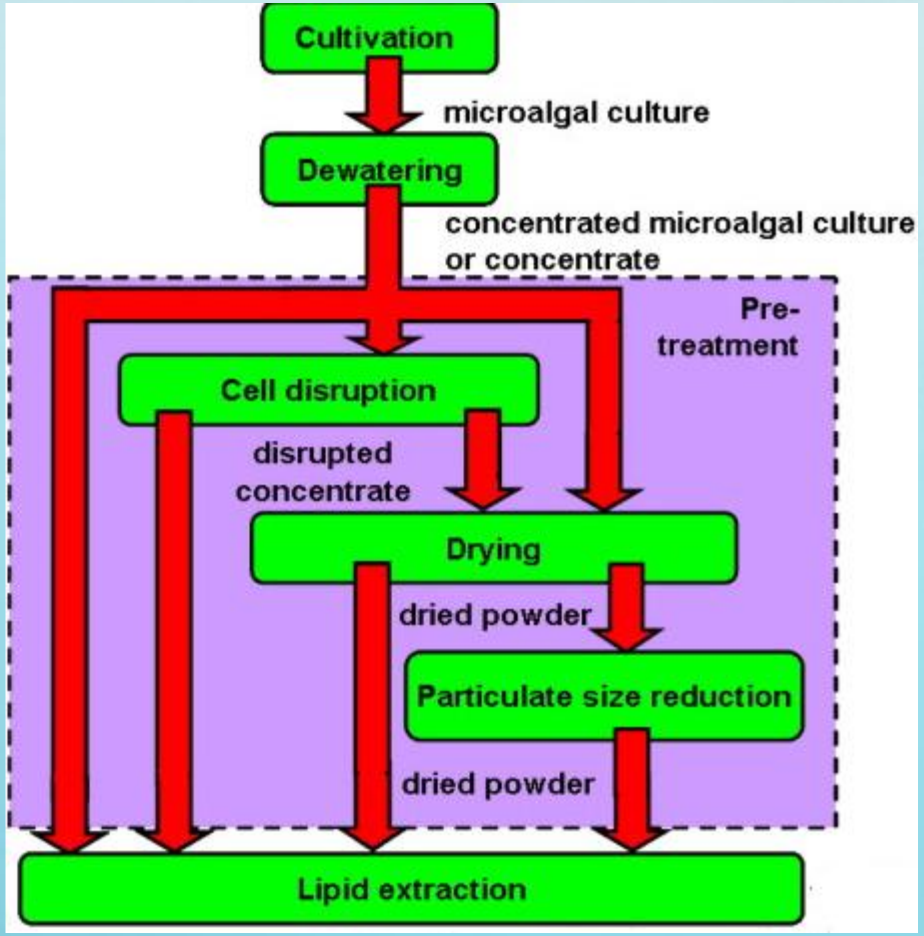


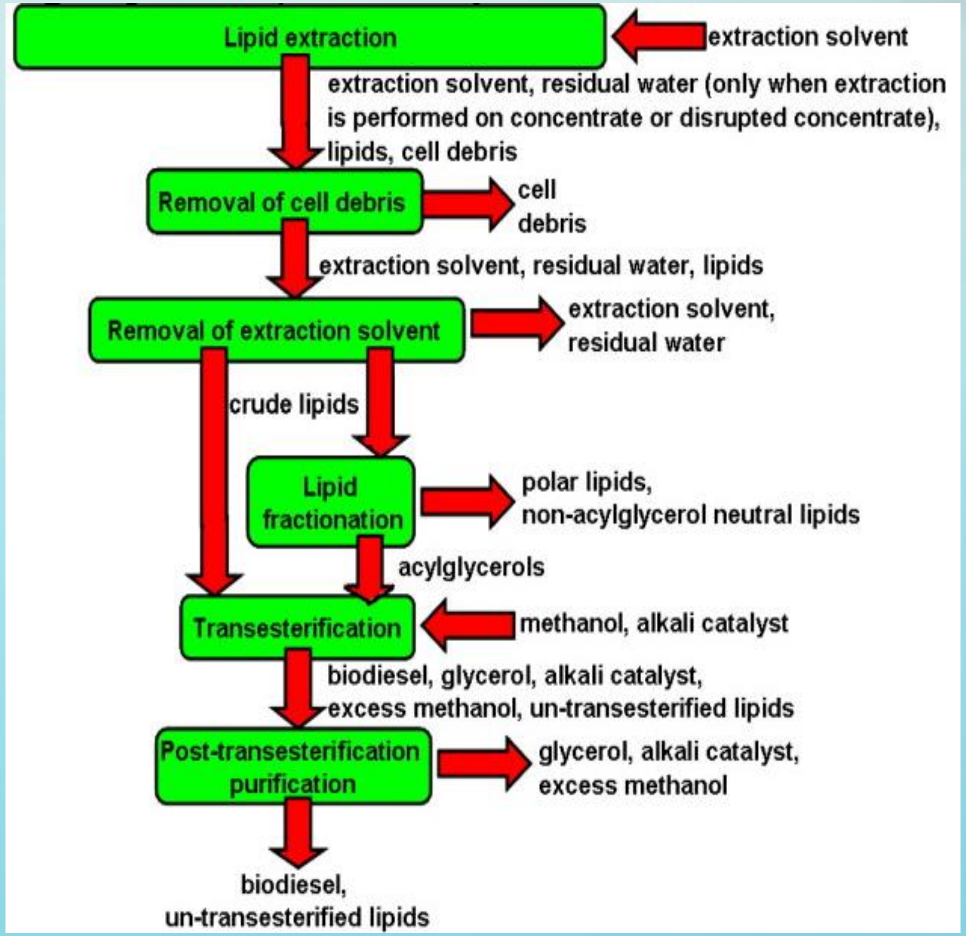
Different stages and process involved in Algal biomass production for biodesel

Optimum Growth Condition:

Temperature: 25-30ºC, CO_2: 1 to 2%; pH: 6.5-7.5 and Light: 1.2 Klux

Process flow diagram on the production of biodiesel from microalgae





Best microalgae strain for biodiesel production

Chlamydomonas reinhardtii (Green yeast)

The green microalga C. reinhardtii is the best-developed unicellular green microalgae with sophisticated genetic tools. C. reinhardtii is often called 'the green yeast' due to the power of its genetics. It has a short doubling time (8 hr). (Oil content: 21% dry weight)

***Scenedesmus bijugatus* (Turpin)**

Oil content: 16 to 40%   Biomass Yield (Dry weight): 450 kg/ha/day

***Chlorococcum humicolo* (Naegeli)**

Oil content: 14 to 22 %   Biomass Yield (Dry weight): 210 kg/ha/day

Chlorella vulgaris

Oil content: up to 46%   Biomass Yield: 8200 L/ha/day

Nannochloropsis

Oil content: up to 50%   Biomass Yield: 23000-34000 L/ha/day

Advantages of microalgae over other feedstocks

- Synthesis and accumulate large quantities of neutral lipids (20 to 77 % of dry cell weight).
- Multiply at higher rate (1-3 doubling time in a day).
- Sequester CO_2 from flue gases, thereby reducing emission of major green house gas.
- Microalgae biodiesel contains no sulfur, is non-toxic and highly biodegradable.
- Grow in suitable culture vessels throughout the year with an annual biomass productivity, on an area basis exceeding that of terrestrial plants by approximately tenfold.