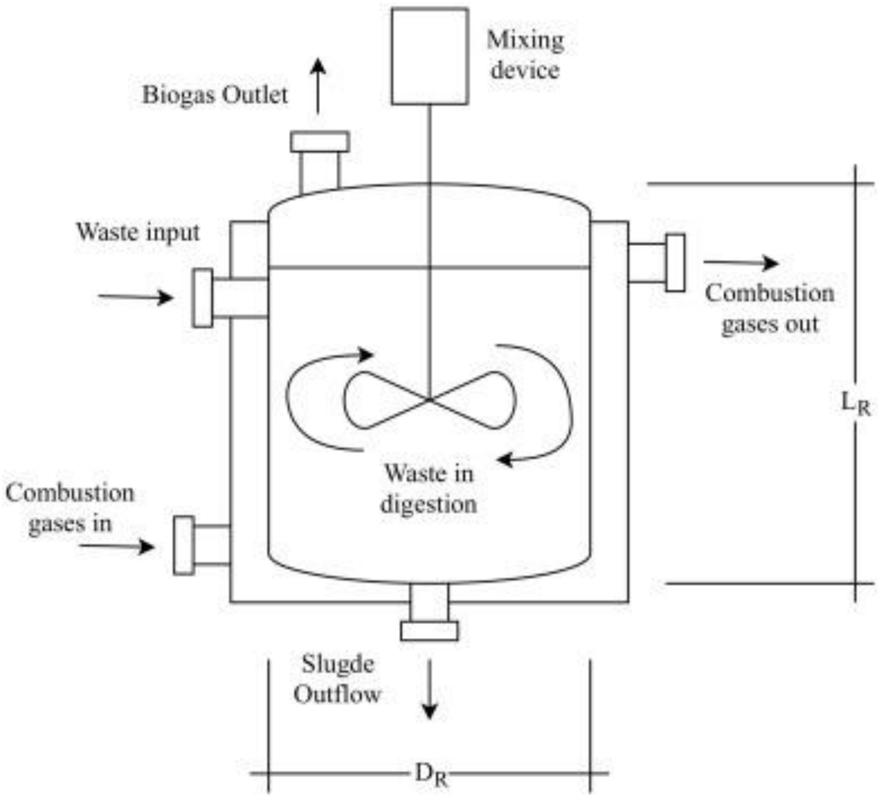
LECTURE-7

Barkip Anaerobic Digestion Plant

View of a working plant in Scotland



Simplest Sketch Diagram of an Anaerobic Digester

LECTURE-7

BIOCHEMICAL CONVERSION

➢ INTRODUCTION

- biochemical conversion processes involve the use of microbes (or the cells, such as plant and animal cells), modified form of the microbes (or the cells), part of the microbes, enzymes etc. to convert the raw materials (usually the substrates) to desired product(s) in order to achieve societal objectives with respect to energy, environment, food security and chemicals
- along with the understanding of biological sciences, engineering principles (such as chemical engineering) are used for attainment of the goal
- bioresources, such as 'biomass' may be one of the inspiring source to be used in biochemical conversion process
- involves the use of enzymes, bacteria or other microbes to break down biomass into liquids and gaseous feedstocks and includes anaerobic digestion, fermentation and composting
- feedstocks can be converted to energy, transportation fuels and renewable chemicals
- biochemical conversion is one among the few which provide environment-friendly direction for obtaining energy fuel from municipal solid waste (MSW)
- anaerobic digestion is helpful in lessening the load of solid waste and recover of energy
- biomass can be turned into different products, such as hydrogen, biogas, ethanol, acetone, butanol, organic acids (pyruvate, lactate, oxalic acid, levulinic acid, citric acid), 2,3-butanediol, 1,4-butanediol, isobutanol, xylitol, mannitol, and xanthan gum by selecting different microorganisms in the process of biochemical conversion
- on the one hand, such products can synthetize replacements of petroleum-based products
- on the other hand, the products can replace products derived from grains, such as ethanol
- compared with other conversion technologies, biochemical conversion technologies are moderate, pure, clean, and efficient
- moreover, biomass can be turned into various intermediates by screening different enzymes or microorganisms through biochemical conversion technologies
- provides many platforms for the conversion of renewable materials, fuels, and chemicals
- as a result, people pay much attention to biochemical conversion technologies of biomass. Overall view of the process is demonstrated by the **Figure-1**, below:

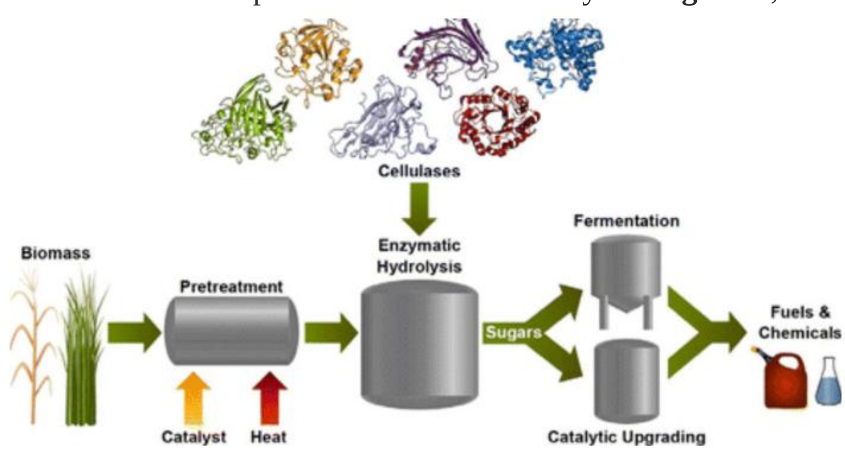


Figure-1:Overall view of a conventional biochemical conversion process to produce fuels and chemicals from lignocellulosic biomass.

➢ ANAEROBIC DIGESTION

- **What is Anaerobic Digestion?**
  - ✓ anaerobic digestion (AD) is the process by which organic materials in an enclosed vessel are broken down by micro-organisms, in the absence of oxygen (**Figure-2**)
  - ✓ AD produces biogas (consisting primarily of methane and carbon dioxide)
  - ✓ AD systems are also often referred to as “biogas systems.”
  - ✓ depending on the system design, biogas can be combusted to run a generator producing electricity and heat (called a co-generation system), burned as a fuel in a boiler or furnace, or cleaned and used as a natural gas replacement
  - ✓ AD process also produces a liquid effluent (called digestate) that contains all the water, all the minerals and approximately half of the carbon from the incoming materials
  - ✓ AD systems provide a valuable manure treatment option, since most other economically effective manure treatment systems (such as composting) require solid materials with dry matter greater than 30%
- **Potential Benefits of AD**
  - ✓ the main objective of anaerobic digestion (AD) is the degradation and destruction of organic substances, with consequent reduction of the odorous emissions and pathogens
  - ✓ reduce greenhouse gas production from a farmstead and other organic wastes
  - ✓ produce renewable energy
  - ✓ utilizes food byproducts, animal wastes, food wastes, kitchen wastes, municipal solid wastes, crop and crop residues, industrial sludge, and municipal sewage sludge etc and other organic waste materials
  - ✓ improve the fertilizer value of the manure
  - ✓ co-digestion system improves the biogas yields due to positives synergisms established in the digestion medium and the supply of missing nutrients

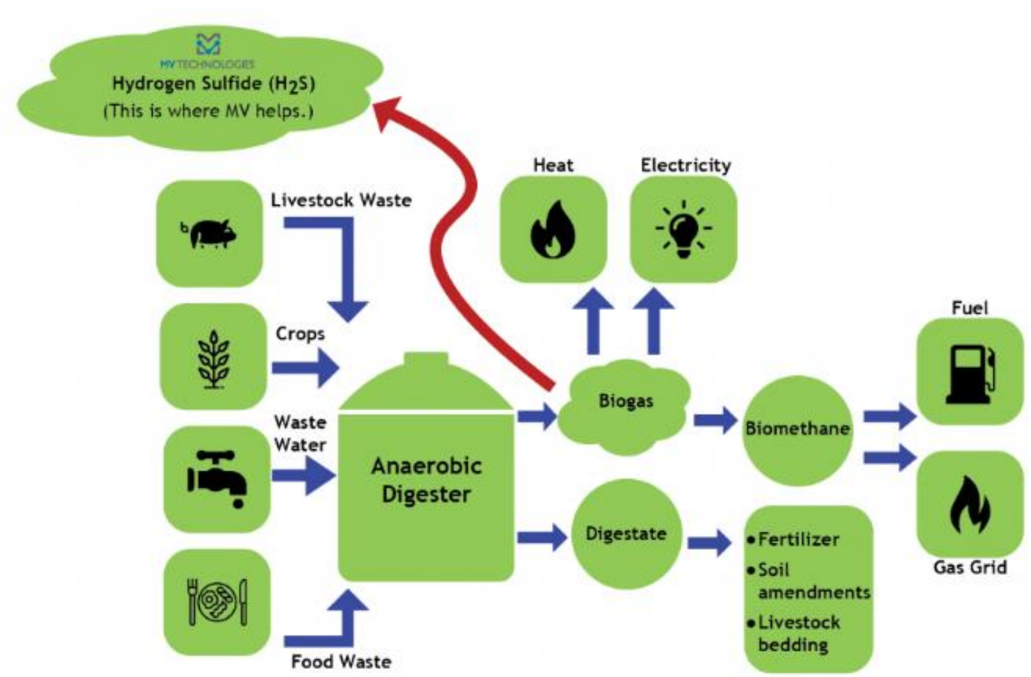


Figure-2:Anaerobic digestion.

- **Anaerobic Digestion Process (Principle of Anaerobic Digestion)**
  - ✓ it is the multi-step biological process during which organic material is converted to biogas and digestate in the absence of oxygen
  - ✓ anaerobic biodegradation of organic material proceeds in the absence of oxygen and in the presence of anaerobic microorganisms
  - ✓ it is the consequence of a series of metabolic interactions among various groups of microorganisms
  - ✓ it occurs in four stages, hydrolysis/liquefaction, acidogenesis, acetogenesis and methanogenesis
  - ✓ the various stages have been detailed below and shown in **Figure-3**

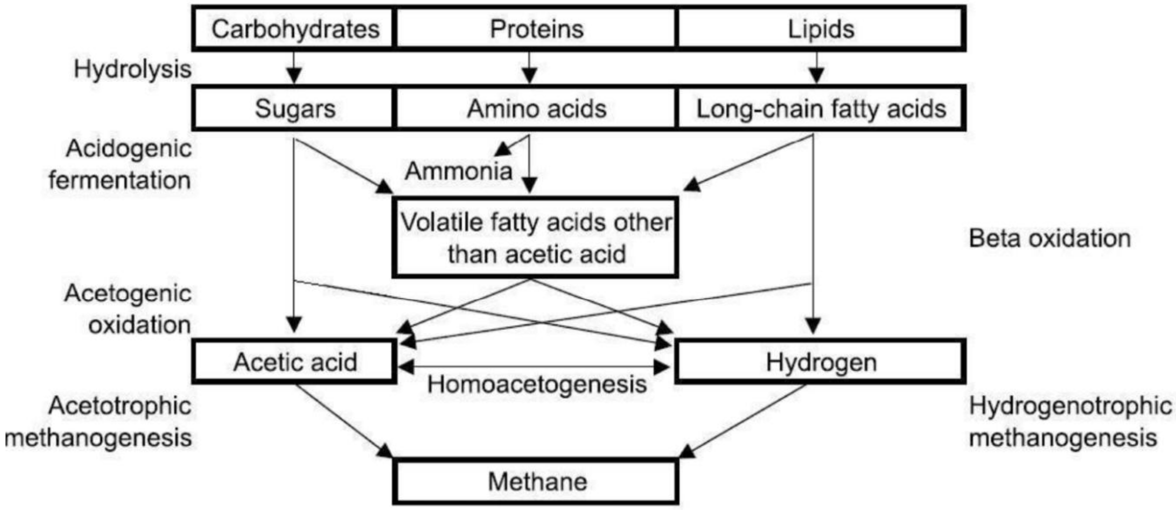


Figure-3: Anaerobic pathways in anaerobic degradation.

- **Hydrolysis/liquefaction**
  - this step is very important for the anaerobic digestion process since polymers cannot be directly utilized by the fermentative microorganisms
  - hydrolysis therefore renders the substrate accessible for the subsequent conversion steps
  - in this step insoluble complex organic matter is broken down into their backbone constituents in order to allow their transport through microbial cell membrane
  - hydrolysis is achieved through the action of hydrolytic enzymes
  - in the first stage of hydrolysis, or liquefaction, fermentative bacteria convert the insoluble complex organic matter, such as cellulose, into soluble molecules such as sugars, amino acids and fatty acids
  - proteases, secreted by proteolytic microbes, convert proteins into amino acids; celluloses and/or xylanases, produced by cellulytic and xylanolytic microbes, hydrolyze cellulose and xylose (both complex carbohydrates) into glucose and xylem
    (both sugars), respectively; finally lipases, created by lipolytic microbes, convert lipids (fats and oils) into long-chain fatty acids and glycerol
  - the hydrolytic activity is of significant importance in high organic waste and may become rate limiting

- some industrial operations overcome this limitation by the use of chemical reagents to enhance hydrolysis
- the application of chemicals to enhance the first step has been found to result in a shorter digestion time and provide a higher methane
- Hydrolysis/Liquefaction reactions: (1)

  Lipids → Fatty Acids

  Polysaccharides → Monosaccharides

  Protein → Amino Acids

  Nucleic Acids → Purines & Pyrimidines

- **Acidogenisis (Fermentations)**
  - fermentation involves the conversion of the sugars, amino acids and fatty acids to hydrogen, acetate, carbon dioxide, VFAs such as propionic, butyric and acetic acid, ketones, alcohols and lactic acid by facultative and anaerobic bacteria
  - even though a simple substrate such as glucose can be fermented, different products are produced by the diverse bacterial community
  - equations: 2, 3 and 4 show the conversion of glucose to acetate, ethanol and propionate, respectively.

    $$C_6H_{12}O_6 + 2H_2O \rightarrow 2CH_3COOH + 2CO_2 + 4H_2 \quad (2)$$

    $$C_6H_{12}O_6 \rightarrow 2CH_3CH_2OH + 2CO_2 \quad (3)$$

    $$C_6H_{12}O_6 + 2H_2 \rightarrow 2CH_3CH_2COOH + 2H_2O \quad (4)$$

  - in an equilibrated system, most of the organic matter is converted into readily available substrates for methanogenic microbes (acetate, hydrogen and carbon dioxide), but a significant part (approximately 30%) is transformed to short chain fatty acids or alcohols
  - degradable organic matter is removed in this stage
  - by-product of amino acids fermentation, ammonia and hydrogen sulphide are released that can be inhibitory for anaerobic digestion
- **Acetogenesis**
  - acetogenesis is the conversion of certain fermentation products such as volatile fatty acuds (VFAs) with more than two carbon atoms , alcohols and aromatic fatty acids into acetate and hydrogen by obligate hydrogen producing bacteria
  - in this stage, acetogenic bacteria, also known as acid formers, convert the products of the first phase to simple organic acids, carbon dioxide and hydrogen
  - the principal acids produced are acetic acid (CH_3COOH), propionic acid (CH_3CH_2COOH), butyric acid ($CH_3CH_2CH_2COOH$), and ethanol (C_2H_5OH)
  - the products formed during acetogenesis are due to a number of different microbes, e.g., syntrophobacter wolinii, a propionate decomposer and sytrophomonos wolfei, a butyrate decomposer
  - other acid formers are clostridium spp., peptococcus anerobus, lactobacillus, and actinomyces (www.biogasworks.com- Microbes in AD
  - while hydrogen-producing acetogenic bacteria produce acetate, H_2 and CO_2 from volatile fatty acids and alcohol, homoacetogenic bacteria create acetate from CO_2 and H_2
  - but most of the acetate is created by hydrogen-producing acetogenic bacteria
  - an acetogenesis reaction is shown as: $C_6H_{12}O_6 \rightarrow 2C_2H_5OH + 2CO_2$

- **Methanogenesis**
  - a variety of methane-forming bacteria is required in the anaerobic digestion system, since no single species can degrade all the available substrates
  - the methanogenic bacteria include methanobacterium, methanobacillus, methanococcus and methanosarcina
  - methanogenesis can also be divided into two groups: acetate and H_2/CO_2 consumers
  - methanosarcina spp. and methanothrix spp. (also, methanosaeta) are considered to be important in AD both as acetate and H_2/CO_2 consumers
  - approximately 70% of the methane is produced from acetate, while the remaining 30% is produced from the reduction of carbon dioxide by hydrogen and other electron donors
  - according to the type of substrate utilized by the methanogens,v methanogenesis is divided into two main types:
    a. hydrogenotrophic methanogenesis: hydrogen and carbon dioxide are converted into methane according to the reaction:
    $$CO_2+4H_2 \rightarrow CH_4+2H_2O \quad (5)$$
    b. acetotrophic or aceticlastic methanogenesis: methane is formed from the conversion of acetate through the reaction:
    $$CH_3COOH \rightarrow CH_4 + CO_2 \quad (6)$$

➢ IMPORTANT FACTORS AFFECTING ANAEROBIC DIGESTION

The growth rate of the microorganisms is highly significant in the AD process. The factors affecting the growth must be controlled in the digester in order to improve the microbial activities, and finally enhance the anaerobic degradation efficiency of the system. Some of these parameters are:

i. Waste Composition/Volatile Solids (VS)/
ii. Alkalinity
iii. pH Level
iv. Sulphate
v. Ammonia
vi. Temperature
vii. Carbon to Nitrogen Ratio (C/N)
viii. Nutrient
ix. Total solids content (TS)/Organic Loading Rate (OLR)
x. Feedstock
xi. Retention (or residence) Time
xii. Mixing
xiii. Compost

- **Waste composition/Volatile Solids (VS)**
  - ✓ wastes treated by AD may comprise a biodegradable organic fraction, a combustible and an inert fraction
  - ✓ biodegradable organic fraction includes kitchen waste, food waste, and garden waste
  - ✓ combustible fraction includes slowly degrading lignocellulosic organic matter containing coarser wood, paper, and cardboard

- as these lignocellulosic organic materials do not readily degrade under anaerobic conditions, they are better suited for waste-to-energy plants
- finally, the inert fraction contains stones, glass, sand, metal, etc.
- this fraction ideally should be removed, recycled or used as land fill
- the removal of inert fraction prior to digestion is important as otherwise it increases digester volume and wear of equipment
- the volatile solids (VS) in organic wastes are measured as total solids minus the ash content, as obtained by complete combustion of the feed wastes
- olatile solids comprise the biodegradable volatile solids (BVS) fraction and the refractory volatile solids (RVS)
- it is seen that knowledge of the BVS fraction of substrate helps in better estimation of the biodegradability of waste, of biogas generation, organic loading rate and C/N ratio
- lignin is a complex organic material that is not easily degraded by anaerobic bacteria and constitutes the refractory volatile solids (RVS) in organic matter
- waste characterized by high VS and low non-biodegradable matter, or RVS, is best suited to AD treatment

- **Alkalinity**
  - acid-neutralizing or buffering capacity of a digester is termed as alkalinity
  - it is attained with the help of number of substances and it is mostly described by the carbonate, bicarbonate and hydroxide content of the digester
  - at the neutral pH at which anaerobic digesters operate, the carbon dioxide-bicarbonate system is primarily responsible for controlling alkalinity, and therefore bicarbonate alkalinity is of the greatest importance
  - bicarbonate is also the main source of carbon for methane-forming bacteria
  - alkalinity is crucial in pH control and enhances digester stability
  - alkalinity is mainly present in the form of bicarbonates in equilibrium with carbon dioxide gas at a given pH
  - alkalinity in anaerobic digestion is also derived from the degradation of organic nitrogen containing compounds
  - such compounds are amino acids and proteins
  - during their degradation, amino groups are released which further leads to the production of ammonia
  - ammonia further reacts with CO_2, yielding alkalinity in the form of ammonium bicarbonate
  - additional alkalinity can be generated from the metabolism of the microorganisms in the anaerobic digester
  - this type of alkalinity consists of the release of cations during the degradation of organic compounds.
- **pH Level**
  - the pH requirements of the groups of microorganisms participating in anaerobic digesters differ
  - while acidogenic bacteria can perform well when the pH is above 5, methanogenic bacteria require a minimum pH value of 6.2
  - anaerobic bacteria, specially the methanogens, are sensitive to the acid concentration within the digester and their growth can be inhibited by acidic conditions
  - it has been determined that an optimum pH value for AD lies between 5.5 and 8.5

- ✓ during digestion, the two processes of acidification and methanogenesis require different pH levels for optimal process control
- ✓ the retention time of digestate affects the pH value and in a batch reactor acetogenesis occurs at a rapid pace
- ✓ acetogenesis can lead to accumulation of large amounts of organic acids resulting in pH below 5
- ✓ after gas production, pH is the best indicator of future digester instability
- ✓ initially, pH decreases as organic matter undergoes acetogenesis, but methanogens rapidly consume those acids increasing pH and stabilizing digester performance
- ✓ due to their sensitivity to acid conditions, excessive generation of acid can inhibit methanogens
- ✓ reduction in pH can be controlled by the addition of lime or recycled filtrate obtained during residue treatment

- **Sulphate**
  - ✓ in anaerobic digestion system, sulphate is reduced biologically under anaerobic conditions to sulfide, which may upset the biological process if the sulphide concentration exceeds 200 mg/l
  - ✓ some inhibitory compounds may equally affect all major microbial groups in the digester (e.g. LCFA and phthalate esters) while others may specifically impair some microbial species
- **Ammonia**
  - ✓ in anaerobic digestion ammonia originates from soluble ammonia in the influent, from protein degradation and other compounds such as urea
  - ✓ there are two forms of ammonia which depends upon the pH of the system: ammonium ion ($NH4^{+}$) and dissolved non-ionized form of ammonia (NH3)
  - ✓ it is generally accepted that it is the non-ionized form of ammonia that is responsible for inhibition
  - ✓ pH has a significant effect on the level of ammonia inhibition, as the pH value determine the degree of ionization
- **Temperature**
  - ✓ temperature is a principal environmental factor affecting performance
  - ✓ it affects the physical and physico-chemical properties of compounds present in the digester and the kinetics and thermodynamics of biological processes
  - ✓ there are mainly two temperature ranges that provide optimum digestion conditions for the production of methane – the mesophilic and thermophilic ranges
  - ✓ **mesophilic digestion** takes place optimally around 30 to 38°C, or at ambient temperatures between 20 and 45°C, where mesophilic are the primary microorganism present
  - ✓ **thermophilic digestion** takes place optimally around 49 to 57°C, or at elevated temperatures up to 70°C, where thermophilic are the primary microorganisms present
- **Carbon to Nitrogen Ratio (C/N)**
  - ✓ the relationship between the amount of carbon and nitrogen present in feedstock is represented by the C/N ratio
  - ✓ it is a very important process parameter
  - ✓ a low ratio can cause ammonia inhibition whereas a high ratio leads deficiency

- ✓ the adjustment of the ratio to be within the optimum range (25-30) can be achieved through the co-digestion of different waste streams
- ✓ optimum C/N ratios in anaerobic digesters are between 20 & 30
- ✓ a high C/N ratio is an indication of rapid consumption of nitrogen by methanogens and results in lower gas production
- ✓ on the other hand, a lower C/N ratio causes ammonia accumulation and pH values exceeding 8.5, which is toxic to methanogenic bacteria
- ✓ optimum C/N ratios of the digester materials can be achieved by mixing materials of high and low C/N ratios, such as organic solid waste mixed with animal manure or sewage

- **Nutrients**
  - ✓ methane forming bacteria have particular growth requirements
  - ✓ it has been demonstrated that specific metals such as nickel, cobalt, molybdenum and iron are necessary for optimal growth and methane production
  - ✓ trace metals play an important role to stimulate methanogenic activity
  - ✓ selenium, molybdenum, manganese, aluminum, and boron have been recommended as additional components in media
  - ✓ the recommended requirements for iron, cobalt, nickel, and zinc are 0.002, 0.004, 0.003 and 0.02mg/g acetate produced respectively
  - ✓ it is noted that a requirement for nickel is quite unusual for biological systems, and this requirement uniquely characterizes methanogenic bacteria
  - ✓ supplementation of anaerobic digesters with solutions of metal ions can improve the performance of the system
- **Total solids content (TS)/Organic Loading Rate (OLR)**
  - ✓ low solids (LS) AD systems contain less than 10 % TS, medium solids (MS) about 15-20% and high solids (HS) processes range from 22% to 40%
  - ✓ an increase in TS in the reactor results in a corresponding decrease in reactor volume
  - ✓ the organic loading rate (OLR) is the organic matter flowing into the digester per time, expressed as mass of organic matter over digester volume over time
  - ✓ typical values of OLR ranges between 0.5 and 3 kg VS/m3/d
  - ✓ organic loading rate (OLR) is also defined as measure of the biological conversion capacity of the AD system
  - ✓ feeding the system above its sustainable OLR results in low biogas yield due to accumulation of inhibiting substances such as fatty acids in the digester slurry
  - ✓ in such a case, the feeding rate to the system must be reduced
  - ✓ OLR is a particularly important control parameter in continuous systems
  - ✓ many plants have reported system failures due to overloading
- **Feedstock**
  - ✓ feedstock is defined to include any substrate that can be converted to methane by anaerobic bacteria
  - ✓ carbon, oxygen, nitrogen, hydrogen and phosphorus are the main components in organic wastes (feedstock**)**, and microbial cell material is approximately 50, 20, 12, 8 and 2 % of these elements, respectively
  - ✓ also sulphur is required to synthesize vital proteins in metabolic and anabolic pathways
  - ✓ feedstocks can range from readily degradable wastewater to complex high-solid waste

- ✓ a feedstock C/N ratio of 25:1 produces optimal gas production
- ✓ if the C/N ratio is low, too much nitrogen is present leading to ammonia (NH3) accumulation that causes either high pH values or methanogenic inhibition
- ✓ if the C/N ratio is high nitrogen is rapidly depleted and results lower gas production

- **Retention (or residence) Time**
  - ✓ HRT stands for hydraulic retention time while SRT stands for solid retention time
  - ✓ HRT is the time that the fluid element of the feed remains in the digester
  - ✓ SRT is the time that refers to the residence time of the bacteria (solids) in the reactor
  - ✓ the required retention time for completion of the AD reactions varies with differing technologies, process temperature, and waste composition
  - ✓ the retention time for wastes treated in mesophilic digester range from 10 to 40 days
  - ✓ lower retention times are required in digesters operated in the thermophilic range
  - ✓ a high solids reactor operating in the thermophilic range has a retention time of 14 days
  - ✓ anaerobic digestion retention times range from 14 and 30 days.
  - ✓ given the relatively long generation time of methanogens, SRT should be over 12 days in order to avoid microbial washout
  - ✓ short retention time will produce higher biogas per volume, but less organic matter will be degraded
  - ✓ although a short retention time is desired for reducing the digester volume, a balance must be made to achieve the desired operational conditions
- **Mixing**
  - ✓ the purpose of mixing in a digester is to blend the fresh material with digestate containing microbes
  - ✓ also mixing prevents scum formation and avoids temperature gradients within the digester
  - ✓ however excessive mixing can disrupt the microbes so slow mixing is preferred
  - ✓ the kind of mixing equipment and amount of mixing varies with the type of reactor and the solids content in the digester
  - ✓ the benefits of mixing include:

    1) eliminates or reduces scum buildup
    2) eliminates thermal stratification or localized pockets of depressed temperature
    3) Maintains digester sludge's chemical and physical uniformity throughout the tank
    4) stimulates the rapid dispersion of metabolic wastes produced during substrate digestion that could otherwise inhibit methane production
    5) Stimulates the rapid dispersion of any toxic material entering the tank (minimizing toxicity)
    6) Mixing also prevents deposition of grit
- **Compost**
  - ✓ when the digestion is complete, the residue slurry, also known as digestate, is removed, the water content is filtered out and re-circulated to the digester, and the filter cake is cured aerobically, usually in compost piles, to form compost
  - ✓ the compost product is screened for any undesirable materials, (such as glass shards, plastic pieces etc) and sold as soil amendment
  - ✓ the quality of compost is dependent on the waste composition. Some countries have prescribed standards for compost quality

- ✓ the U.S. Department of Agriculture has set standards for heavy metals in the compost
- ✓ these standards are for compost treated by the aerobic process but may also be applied to AD compost product

➢ PRODUCTS OF ANAEROBIC DIGESTION

The three principal products of anaerobic digestion are biogas, digestate, and wastewater.

- **Biogas**
  - ✓ biogas is the ultimate product of the anaerobic digestion and is mostly methane and carbon dioxide also with a small amount of hydrogen and trace of hydrogen sulfide
  - ✓ most of the biogas is produced during the middle of the digestion, after the bacterial population has grown, and tapers off as the putrescible material is exhausted
  - ✓ the gas is normally stored on top of the digester in an inflatable gas bubble or extracted and stored next to the facility in a gas holder
- **Wastewater**
  - ✓ the final output from anaerobic digestion systems is water and this water may be released from the dewatering of the digestate or may be implicitly separated from the digestate
  - ✓ the wastewater exiting the anaerobic digestion facility will typically have elevated levels of biochemical oxygen demand (BOD) and chemical oxygen demand (COD)
  - ✓ these measures of the reactivity of the effluent indicate it's an ability to pollute
- **Digestate**
  - ✓ digestate is the solid remnants of the original input material to the digesters that the microbes cannot use
  - ✓ it also consists of the mineralized remains of the dead bacteria from within the digesters
  - ✓ digestate can come in three forms: fibrous, liquor, or a sludge based combination of the two fractions
  - ✓ in two-stage systems, different forms of digestate come from different digestion tanks
  - ✓ in single-stage digestion systems, the two fractions will be combined and, if desired, separated by further processing

➢ ADVANTAGES AND DISADVANTAGES OF ANAEROBIC DIGESTION

- **Advantages**
  - ✓ generation of biogas and
  - ✓ reduction of greenhouse gas emissions through methane recovery
  - ✓ combined treatment of different organic waste and wastewaters
  - ✓ reduction of solids to be handled
  - ✓ good pathogen removal depending on temperature
  - ✓ process stability
- **Disadvantages**
  - ✓ small- and middle-scale anaerobic technology for the treatment of solid waste in middle- and low-income countries is still relatively new
  - ✓ experts are required for the design and construction, depending on scale may also for operation and maintenance
  - ✓ reuse of produced energy (e.g. transformation into, fire/light, heat and power) needs to be established
  - ✓ high sensitivity of methanogenic bacteria to a large number of chemical compounds
  - ✓ sulphurous compounds can lead to odour

ANAEROBIC CO-DIGESTION

Co-digestion is the simultaneous digestion of two or more organic waste feedstock. The anaerobic co-digestion process can be defined as the simultaneous treatment of two – or more – organic biodegradable waste streams. Anaerobic digestion offers great potential for the proper disposal of the organic fraction of solid waste coming from source or separate collection systems. This type of treatment offers the possibility of using existing anaerobic reactors in wastewater treatment plants, with minor modifications and some additional requirements. By bringing together the treatments of two problematic wastes i.e. organic part of municipal solid waste and paper pulp sludge higher yield in the production of biogas can be achieved. Traditionally, anaerobic digestion was a single substrate, single purpose treatment. Recently, it has been realized that AD as such became more stable when the variety of substrates applied at the same time is increased.

The most common situation is when a major amount of a main basic substrate (e.g. manure or sewage sludge) is mixed and digested together with minor amounts of a single, or a variety of additional substrate. The use of co-substrates usually improves the biogas yields from anaerobic digester due to positive synergisms established in the digestion medium and the supply of missing nutrients by the co-substrates.

- **Advantages and disadvantages of anaerobic Co-digestion**
  - ✓ **Advantages**
    - improved nutrient balance and digestion
    - additional biogas collection
    - possible gate fees for waste treatment
    - additional fertilizer i.e soil conditioner
    - renewable biomass disposable for digestion in agriculture
  - ✓ **Disadvantages**
    - increased digester effluent COD
    - additional pre-treatment requirement
    - increased mixing requirements
    - wastewater treatment requirement
    - hygienization requirements
    - restrictions of land use for digestate
    - economically critical dependent on crop