CHAPTER II
LITERATURE REVIEW

2.1 Background of Hydrogen

Nowadays, global energy requirements are mostly dependent on fossil fuels (about 80% of the present world energy demand). This will eventually lead to the foreseeable depletion of limited fossil energy resources. Presently, the utilization of fossil fuels are causing global climate change mainly due to the emission of pollutants, including CO_x, NO_x, SO_x, C_xH_x, soot, ash, droplets of tars, and other organic compounds, which are released into the atmosphere as a result of their combustion. In order to remedy the depletion of fossil fuels and their environmental misdeeds, hydrogen has been suggested as the energy carrier of the future (Das *et al.*, 2001).

2.1.1 Advantages of Hydrogen Utilization

2.1.1.1 Hydrogen Can Be Totally Nonpolluting

When fuels such as coal, oil, natural gas, propane, and wood, burn, they create pollutants, including carbon monoxide, carbon dioxide, a variety of hydrocarbon chemicals, and quantities of particulate matter. This is because they are all carbon-based fuels. In contrast to hydrogen combustion, water is the only main product. Thus, hydrogen is regarded as a clean non-polluting fuel. As compared to other gaseous fuels, hydrogen is harmless to humans and the environment. Pure hydrogen produces only heat energy, water, and trace amounts of oxides of nitrogen when burned. Oxides of nitrogen and water are naturally present in earth's atmosphere. In fact, one pound of hydrogen combined with oxygen will make nine pounds of water. This means that a hydrogen power plant could make electricity and clean distilled water.

2.1.1.2 Hydrogen Can Help Prevent the Depletion of Fossil Fuel Reserves

The reason is that hydrogen can be produced in any country from a variety of energy sources, especially renewable resources such as water and biomass. Nowadays, hydrogen can be directly used to generate electricity through fuel cells. Automobile manufacturers in Europe, Asia, and North America are developing cars that run on hydrogen-based fuel cells. Global industry and governments are working to build the infrastructure needed to deliver hydrogen fuel to run the transportation sector. Hence, electricity can replace the energy generated from fossil fuel.

2.1.1.3 Hydrogen Is Among the Safest of all Fuels

Hydrogen is the safest of all fuels, partly because of how light it is compared to other fuels. Gaseous hydrogen is fourteen times lighter than air and four times lighter than helium. In the event of an accidental release, it disperses rapidly upward into the atmosphere. Other fuels take longer to disperse or may spill onto the ground. Some, such as gasoline, require specialized cleanup efforts and present toxic hazards to the nearby environment.

2.1.1.4 Hydrogen Is an Excellent Energy Carrier

Hydrogen holds more chemical energy pound for pound than any other fuels. Two pounds of hydrogen provide as much energy as a gallon of gasoline. The hydrogen contained in 2.2 gallons of water will replace one gallon of gasoline. It takes just under one-third of a gallon of gasoline to equal the energy in a gallon of liquid hydrogen.

2.1.1.5 Hydrogen Is the Most Abundant Element on the Earth

Hydrogen is also the most abundant element on the earth, but less than 1% in from of H_2. Hydrogen is typically chemically attached to other atoms such as carbon or oxygen, most of hydrogen is bound as H_2O. Because of this, energy must be expended to separate these elements. To extract hydrogen from water, for example, about 2.3 gallons of water and 45 kilowatts-hours of electricity are needed to make enough hydrogen to have an energy content equivalent to a gallon of gasoline. Direct thermal dissociation of H_2O requires temperature more than 2,000°C and temperature more than 900°C with Pt/Ru catalyst.

2.1.2 Hydrogen Productions

2.1.2.1 Steam Reforming of Natural Gas

Steam reforming of natural gas is currently the least expensive method for producing hydrogen and is used for about half of the world's production of hydrogen. Steam, at a temperature of 700-1,100°C is mixed with methane gas in a reactor with a catalyst at 3-25 bar pressure.

The formula for this process is:

$CH_4 + H_2O \Rightarrow CO + 3H_2$

It is usually followed by the shift reaction:

$CO + H_2O \Rightarrow CO_2 + H_2$

The percentage of hydrogen to water is 50%.

2.1.2.2 Thermal Cracking of Natural Gas

H_2 can be produced via thermal decomposition of CH_4. However, this method requires high reaction temperature about 2,000°C.

The reaction of this process is:

$CH_4\ (gas) \Rightarrow C\ (solid) + 2H_2$

2.1.2.3 Coal Gasification

Gasification of coal is the oldest method for production of hydrogen. Generally, coal is heated up to 900°C with a catalyst but without air. There are also more complex ways of gasifying coal. These techniques are similar to that by using steam and oxygen at temperatures over 1,400°C, in which carbon is changed into H_2, CO, and CO_2. In addition, these create some sulfur and nitrogen that must be treated. It is almost twice as expensive to produce hydrogen from coal as from natural gas.

2.1.2.4 Pyrolysis or Gasification of Biomass

Hydrogen can also be produced by thermal gasification of biomass, such as forestry waste products, straw, municipal solid wastes (MSW), and sewage (municipal waste). With applied extreme heat, biomass decomposes to gas. The gas consists mainly of H_2, CO, and CH_4 (methane). Steam is then applied to reform the methane into hydrogen and CO. The CO is then reinjected into the process to increase the yield of hydrogen. These processes produce a large amount of carbon monoxide (CO), and it is therefore necessary to go through a shift process to get an acceptable yield.

2.1.2.5 Electrolysis of Water

Electrolysis uses electrical current to split water into hydrogen at the cathode (+) and oxygen at the anode (-). If renewable energy is used to produce electricity, which is used to split the water into hydrogen and oxygen, the hydrogen will be an even cleaner form of energy. Efficiency of electrolyzer is an important factor because consumption of energy makes up 80-90% of the production costs at an electrolysis plant.

Disadvantages of this method are that it needs to have a high temperature heat source at above 2,500 K for reasonable degree of dissociation possibility of water into H_2 and O_2, therefore the risk of explosion is high. Although H_2 from electrolysis is extremely pure, it is expensive at the same time. H_2 from electrolysis has ten times costly as natural gas.

2.1.2.6 Photoelectrochemical Systems of Water

Photoelectrochemical systems use semi-conducting materials (like photovoltaics) to split water using sunlight. This is the cleanest way to produce hydrogen by using sunlight to directly split water into hydrogen and oxygen. Multijunction cell technology developed by the photovoltaic industry is being used for photoelectrochemical (PEC) light harvesting systems that generate sufficient voltage to split water and are stable in a water/electrolyte environment.

2.1.2.7 Fermentative Hydrogen Production from Organic Compounds

The fermentative hydrogen production is the biological process that uses bacteria to produce hydrogen and other valuable fatty acids from organic wastes. This process is dark anaerobic fermentation. The evolution of hydrogen by fermentation has several advantages for industrial production (Das *et al.,* 2001) such as:

1. Fermentative bacteria have very high evolution rate of hydrogen.
2. It can produce hydrogen constantly through day and night from organic substrates.
3. It can utilize different carbon sources, such as starch, sucrose, etc.

4. It can produce valuable components, such as butyric acid, acetic acid, etc. as by product.

5. It is anaerobic process, so there is no oxygen limitation problem.

2.2 Wastewater Treatment

Wastewater may be defined as a combination of the liquid or water-carried wastes discarded from residences, institutions, and commercial and industrial establishments, together with such groundwater, surface water, and storm water as may be present (Stafford *et al.*, 1980; Qasim, 2003).

2.2.1 Wastewater Treatment Methods

Wastewater treatment uses microbes to decompose organic matter in sewage. If too much untreated sewage or other organic matters is added to a lake or stream, dissolved oxygen levels will drop too low to support sensitive species of fish and other aquatic life. Wastewater treatment systems are designed to digest much of the organic matter before the wastewater is released so that this will not occur. Wastewater treatment systems can be classified into six treatment levels. Schematic for wastewater treatment methods is shown in Figure 2.1. These treatment systems use physical, chemical, and biological processes:

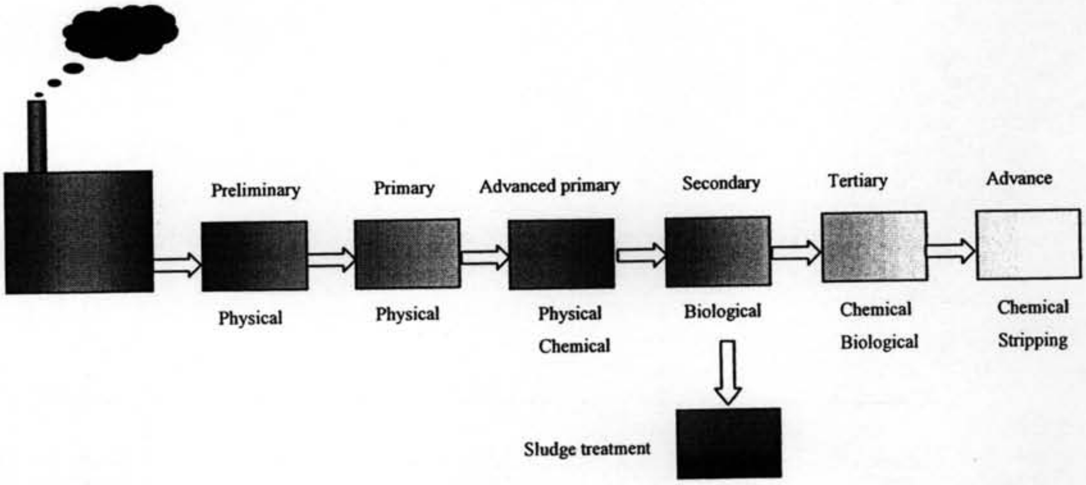


Figure 2.1 Schematic for wastewater treatment methods.

2.2.1.1 Preliminary Treatment

It is physically removal of wastewater constituents, such as rag, sticks, floatable grit, and grease, may cause maintenance or operational problems with the treatment operation, processes, and ancillary systems.

2.2.1.2 Primary Treatment

It is a physical operation, in which sedimentation is usually used to remove the floating and precipitate materials found in wastewater.

2.2.1.3 Advanced Primary Treatment

It is the enhanced removal of suspended solids and organic matter from the wastewater. Typically, this treatment is accomplished by chemical addition or filtration.

2.2.1.4 Secondary Treatment

It promotes growth of bacteria and other microbes that break down the organic wastes. These biodegradation processes also take place in streams, lakes, and oceans, but the purification systems in nature can easily be overloaded with input of too much organic waste. Secondary treatment prevents this type of pollution by degrading most of the organic matter before the water is released into the environment.

2.2.1.5 Tertiary Treatment

It is used only to protect the receiving waters from excess nutrients. In tertiary treatment, the concentrations of phosphorus or nitrogen are reduced through biological or chemical processes. Disinfection kills disease-causing organisms, most commonly through chlorination.

2.2.1.6 Advanced Treatment

It is necessary in some treatment systems to remove nutrients from wastewater. Chemicals are sometimes added during the treatment process to help settle out or strip out phosphorus or nitrogen. Some examples of nutrient removal systems include coagulant addition for phosphorus removal and air stripping for ammonia removal.

Sludge, the collection of solids that are removed during wastewater treatment, requires processing to reduce odor and water content.

Depending on the disposal method, the sludge also may undergo treatment to decompose organic matter or kill disease-causing organisms.

2.2.2 Some Important Parameters of Wastewater

2.2.2.1 Total solids (TS)

The residue remained after a wastewater sample has been evaporated and dried at a specified temperature (103 to 105°C).

2.2.2.2 Total volatile solids (TVS)

The solids that can be volatilized and burnt when the TS are ignited (about 500°C).

2.2.2.3 Total suspended solids (TSS)

Portion of the TS retained on a filter with a specific pore size, measured after being dried at a specific temperature (105°C). The filter has a nominal pore size of about 1.58 μm.

2.2.2.4 Volatile suspended solids (VSS)

The solids that can be volatilized and burnt when the TSS are ignited (about 500°C).

2.2.2.5 Total dissolved solids (TDS)

The solids that can pass through the filter and are then evaporated and dried at specific temperature. TDS=TS-TSS.

2.2.2.6 Biochemical oxygen demand (BOD)

This determination involves the measurement of the dissolved oxygen used by microorganisms in biochemical oxidation of organic matter. The limitations of the BOD test are as follows: (1) a high concentration of acclimated seed bacteria is required, (2) pretreatment is needed when dealing with toxic wastes, (3) only biodegradable organics are measured.

2.2.2.7 Chemical oxygen demand (COD)

COD is a method to determine the concentration of organic compounds present in a wastewater sample using chemical oxidation reaction with potassium dichromate under acidic condition. It presents both biodegradable and non-biodegradable organics in the sample.

2.2.2.8 Hydraulic retention time (τ)

The theoretical hydraulic retention time is defined as:

$$\tau = V/Q \qquad (1)$$

where τ = hydraulic retention time, h

V = volume of the reactor, m^3

Q = volumetric flowrate, m^3/h

2.2.3 Biological Wastewater Treatment

Biological treatments are generally part of secondary treatment systems. The microorganisms used are responsible for the degradation of the organic matter and the stabilization of organic wastes. With regard to the way in which they utilize oxygen, they can be classified into aerobic (require oxygen for their metabolism), anaerobic (grow in absence of oxygen), and facultative (can proliferate either in absence or presence of oxygen although using different metabolic processes).

2.2.3.1 Objectives of Biological Treatment

- To transform (i.e. oxidize) dissolved and particulate biodegradable constituents into acceptable end products.
- To capture and incorporate suspended and non-settling colloidal solids into biological flocculants or biofilm.
- To transform or remove nutrients, such as nitrogen and phosphorous.
- For industrial wastewater, the objective is to remove or reduce the concentration of organic and inorganic compounds because some of the constitutions and compounds found in industrial wastewater are toxic to microorganisms, and pretreatment may be required before the industrial wastewater can be discharged to municipal collection system.
- For agricultural irrigation return wastewater, the objective is to remove nutrients, specifically nitrogen and phosphorus, which are capable of stimulating the growth of aquatic plants.

2.2.3.2 *Types of Biological Processes for Wastewater Treatment*

- *Suspended-growth processes*. The most common suspended growth process used for municipal wastewater treatment is the activated-sludge process as shown in Figure 2.2.

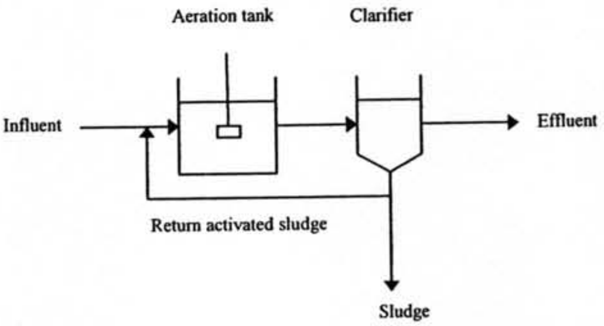


Figure 2.2 Suspended-growth process.

The activated sludge process is common name because it involves the production of an activated mass of microorganisms capable of stabilizing a waste under aerobic conditions. In the aeration tank, contact time is provided for mixing and aerating influent wastewater with microbial suspension generally referred to as the mixed liquor suspended solids (MLSS) or mixed liquor volatile suspended solids (MLVSS). Mechanical equipment is used to provide the mixing and transfer of oxygen into the process. The mixed liquor then flows to a clarifier where the microbial suspension is settled and thickened. The settled biomass, described as activated sludge because of the presence of active microorganisms, is returned to the aeration tank to continue biodegradation of the influence organic material. A portion of the thickened solids is removed daily or periodically as the process produces excess biomass that would accumulate along with the non-biodegradable solids contained in the influent wastewater. If the accumulated solids are not removed, they will eventually find their way to the system effluent.

- *Attached-growth processes*. The organic material and nutrients are removed from the wastewater flowing through a biofilm. Packing materials used in attached growth processes include rock, gravel, slag, sand, and wide range of plastic and other synthetic materials. Attached growth processes can also be operated as aerobic or anaerobic processes. The packing can be submerged completely in liquid or not submerged, with air or gas space above the biofilm liquid layer.

The most common aerobic attached growth process reactor is the trickling filter, in which wastewater is distributed over the top area of a vessel containing non-submerged packing material (see Figure 2.3).

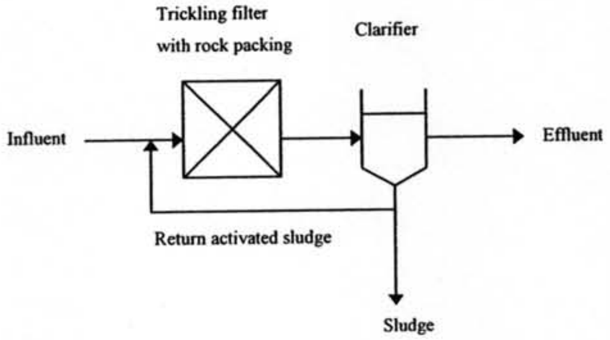


Figure 2.3 Attached-growth process.

2.2.3.3 Aerobic Process

In this process, the reactions occurring can be summarized as:

organic load + oxygen + more cells => $CO_2 + H_2O$

In wastewater treatment, the need for addition of nutrients (the most common being nitrogen and phosphorus) seldom appears, but an adequate provision of oxygen is essential for successful operation of the systems.

2.2.3.4 Anaerobic Process

Three basic steps are involved in the overall anaerobic oxidation of a waste: (1) hydrolysis, (2) fermentation (also known as acidogenesis), and (3) methanogenesis. These three steps are illustrated schematically in Figure 2.4. The starting point on the schematic for a particular application depends on the nature of the waste to be processed.

- *Hydrolysis*. The first step for most fermentation processes, in which particulate material is converted to soluble compounds that can then be hydrolyzed further to simple monomers that are used by bacteria that perform fermentation, is termed hydrolysis. For some industrial wastewater, fermentation may be the first step in the anaerobic process.

- *Fermentation.* The second step is fermentation (also referred to as acidogenesis). In the fermentation process, amino, acids, sugars, and some fatty acids are degraded further, as shown in Figure 2.4. The principle products of fermentation are acetate, hydrogen, CO_2, propionate, and butyrate. The propionate and butyrate are fermented further to produce hydrogen, $CO_{2,}$ and acetate. Thus, the final products of fermentation (acetate, hydrogen, and CO_2) are the precursors for methane formation (methanogenesis).

- *Methanogenesis.* The third step, methanogenesis, is carried out by group of organisms known collectively as methanogens. Two groups of methanogenic organisms are involved in methane production. One group, termed aceticlastic methanogens, splits acetate into methane and carbon dioxide. The second group, termed hydrogen-utilizing methanogens, uses hydrogen as electron donor and CO_2 as electron acceptor to produce methane. Bacteria within anaerobic processes, termed acetogens, are also able to use CO_2 to oxidize hydrogen and form acetic acid. However, the acetic acid will be converted to methane, so the impact of this reaction is minor. As shown in Figure 2.4, about 72 percent of the methane produced in anaerobic digestion is from acetate formation.

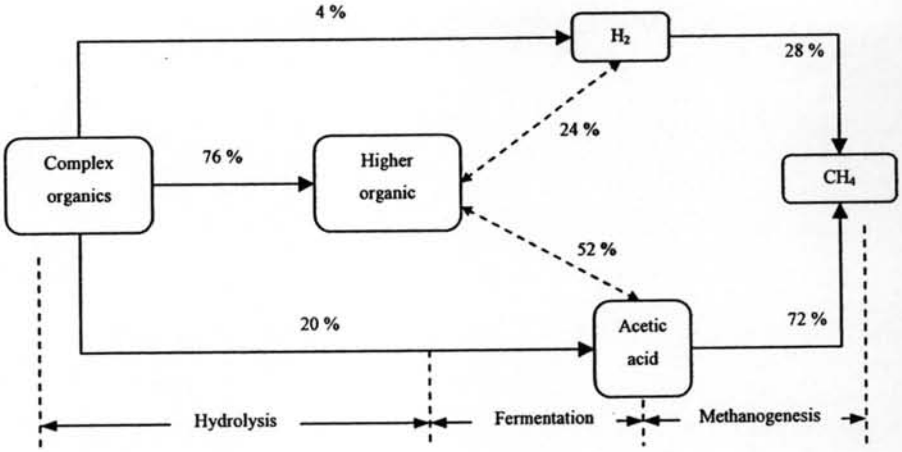


Figure 2.4 Carbon and hydrogen flow in anaerobic digestion process.

2.2.5 Anaerobic Treatment Process

2.2.5.1 Advantages of Anaerobic Treatment Process

- *Energy considerations*. Anaerobic processes may be net energy producers instead of energy users as in the case for aerobic processes. An energy balance comparison for a high-strength wastewater at 20°C is presented in Table 2.1.

Table 2.1 Comparison of energy balance for aerobic and anaerobic processes (Matcarf & Eddy, 2003).

	Value, kJ/d	
Energy	**Anaerobic**	**Aerobic**
Aeration		$-1.9\text{x}10^6$
Methane produced	$12.5\text{x}10^6$	
Increase wastewater temperature to 30^0C	$-2.1\text{x}10^6$	
Net energy, kJ/d	$10.4\text{x}10^6$	$-1.9\text{x}10^6$

- *Lower biomass yield.* Because the energy utilization of anaerobic processes results in lower biomass production by a factor of about 6 to 8 times, sludge processing and disposal costs are reduced greatly.

- *Fewer nutrients required.* Many industrial wastewaters lack sufficient nutrients to support aerobic growth. The cost for nutrient addition is much less for anaerobic processes because less biomass is produced.

- *Higher volumetric loading.* Anaerobic processes generally have higher volumetric organic loads than aerobic processes, so smaller reactor volumes and less space may be required for treatment.

2.2.5.2 *Disadvantages of Anaerobic Treatment Processes*

- *Operational considerations.* This major concern with anaerobic processes is their longer start-up time, their sensitivity to possible toxic compounds, operational stability, the potential for odor production, and corrosiveness of the digester gas.

- *Need for alkalinity addition.* Alkalinity concentrations of 2000 to 3000 mg/L as $CaCO_3$ may be needed in anaerobic processes to maintain an acceptable pH with the high gas phase CO_2 concentration.

- *Need for further treatment.* Anaerobic processes can also be followed by aerobic processes for effluent polishing to utilize the benefits of both processes. Series reactors of anaerobic-aerobic processes have been shown feasible for treating municipal wastewaters in warmer climates, resulting in lower energy requirements and less sludge production.

- *Summary assessment.* In general, for municipal wastewaters with low concentrations of biodegradable COD, lower temperatures, higher effluent quality needs, and nutrient removal requirements, aerobic processes are favored at present. For industrial wastewaters with much higher biodegradable COD concentrations and elevated temperatures, anaerobic processes may be more economical. In the future, as more is learned about anaerobic treatment processes, it is anticipated that their use will become more widespread in a variety of applications.

2.2.6 Types of Anaerobic Treatment Process

2.2.6.1 *Complete-Mix Process*

For the complete-mix anaerobic digester (see Figure 2.5a), the hydraulic retention time and solids retention times are equal (τ = SRT). The complete-mix digester without sludge recycle is more suitable for wastes with high concentrations of solids or extremely high dissolved organic concentrations, where thickening the effluent solids is difficult so that it is more practical to operate with τ equal to the SRT. Typical organic loading rates for the complete-mix process are presented in Table 2.2, along with comparative values for the anaerobic contact and anaerobic sequence reactor processes.

Table 2.2 Typical organic loading rates for anaerobic suspended growth processes at 30°C

Process	Volumetric organic loading, kg COD/m^3d	Hydraulic retention time (τ), d
Complete-mix	1.0-5.0	15-30
Anaerobic contact	1.0-8.0	0.5-5
Anaerobic sequential batch reactor	1.2-2.4	0.25-0.50

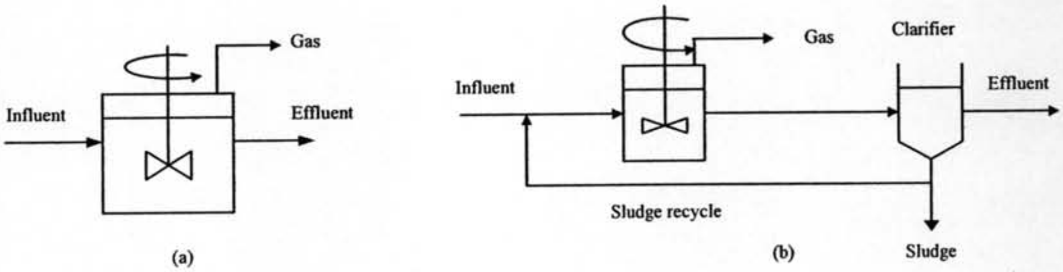


Figure 2.5 (a) Complete-mix reactor and (b) Anaerobic contact process.

2.2.6.2 Anaerobic Contact Process (AC)

The anaerobic contact process (see Figure 2.5b) overcomes the disadvantages of a complete-mix process without recycle. Biomass is separated and returned to the complete-mix or contact reactor so that the process SRT is longer than τ. By separating τ and SRT values, the anaerobic reactor volume can be reduced. Gravity separation is the most common approach for solids separation and thickening prior to sludge recycle.

Since the reactor sludge contains gas produced in the anaerobic process and gas production can continue in the separation process, solid-liquid separation can be inefficient and unpredictable.

2.2.6.3 Anaerobic Sequencing Batch Reactor (ASBR)

The anaerobic sequencing batch reactor (ASBR) process (see Figure 2.6) can be considered a suspended growth process with reaction and solid-liquid separation in the same vessel, much like that for aerobic sequencing batch reactor (SBR). The operation of ASBR consists of four steps: (1) feed, (2) react, (3) settle, and (4) decant. During the react period, intermittent mixing for a few minutes each hour is done to provide uniform distribution of substrate and solids. The organic loading of the process can be changed by selecting hydraulic retention times from 6.0 to 24 h at 25°C, and 92-98 percent COD removal was achieved at volumetric organic loading of 1.2 to 2.4 kg COD/m^{3}d.

A critical feature of the ASBR process is the setting velocity of the sludge during the settle period before decanting the effluent. Settling times used are about 30 min.

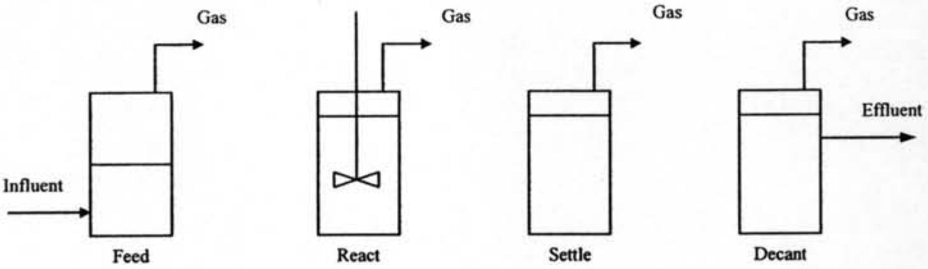
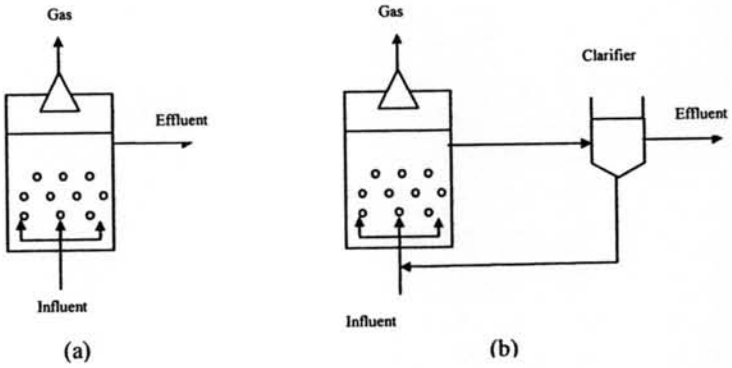


Figure 2.6 Anaerobic sequencing batch reactor (ASBR).

2.2.6.4 Upflow Anaerobic Sludge Blanket Process (UASB)

The basic UASB reactor is illustrated in Figure 2.7. The influent wastewater is distributed at bottom of the UASB reactor and travels in an upflow mode through the sludge blanket. Critical elements of the UASB reactor design are the influent distribution system, the gas-solids separator, and the effluent withdrawal design. Modifications to the basic UASB reactor design include adding a settling tank as shown in Figure 2.7b. Both modifications are intended to provide better solids capture in the system and to prevent the loss of large amounts of the UASB reactor solids due to process upsets or changes in the UASB sludge blanket characteristics and density.

The key feature of the UASB process that allows the use of high volumetric COD loadings compared to other anaerobic processes is the development of a dense granulated sludge.



(a)

(b)

Figure 2.7 (a) Original UASB process and (b) UASB with sedimentation tank.

2.2.6.5 Anaerobic Baffled Reactor Process (AFR)

In the anaerobic baffled reactor process (AFR), as shown in Figure 2.8, baffles are used to direct the flow of wastewater in an upflow mode through a series of sludge blanket reactors. The sludge in the reactor rises and falls with gas production and flows but moves through the reactor at a slow rate. Various modifications have been made to the ABR to improve performance. The modifications include: (1) changes to the baffle design, (2) hybrid reactors where a settler has been used to capture and return solids, and (3) packing has been used in the upper portion of each chamber to capture solids.

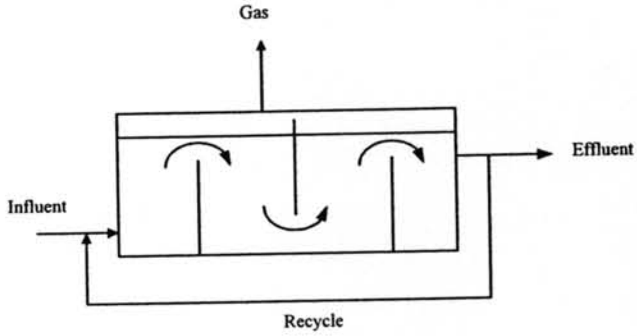


Figure 2.8 Anaerobic baffled reactor (ABR).

2.2.6.6 Upflow Packed-Bed Reactor

Full-scale upflow packed-bed anaerobic filters are used in cylindrical or rectangular tanks at widths and diameters ranging from 2 to 8 m and heights from 3 to 13 m, as shown in Figure 2.9a. Packing material placement may be in the entire depth or, for hybrid designs, only in the upper 50 to 70 percent.

A large portion of the biomass responsible for treatment in the upflow attached growth anaerobic processes is loosely held in the packing void spaces and not just attached to the packing material. Low upflow velocities are generally used to prevent washing out the biomass. Over time, solids and biomass will accumulate in the packing to cause plugging and flow short circuiting. At this point, solids must be removed by flushing and draining the packing.

Advantages of upflow attached growth anaerobic reactors are high COD loadings, relatively small reactor volumes, and operational simplicity. The main limitations are the cost of the packing material, operational problems, and maintenance associated with solids accumulation and possible packing plugging. The process is best suited for wastewaters with low suspended solid concentrations.

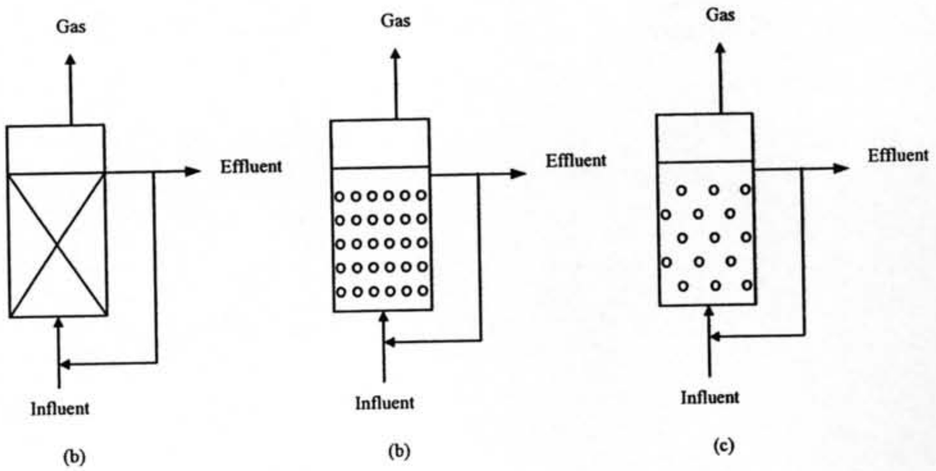


Figure 2.9 (a) Anaerobic upflow packed-bed reactor, (b) Anaerobic upflow expanded-bed reactor, and (c) Anaerobic upflow fluidized-bed reactor.

2.2.6.7 Upflow Anaerobic Expanded-Bed Reactor (AEBR)

In the upflow attached growth anaerobic expanded-bed reactor (AEBR) process, as shown in Figure 2.9b, the packing material is generally silica sand with a diameter in the range of 0.2 to 0.5 mm and specific gravity of 2.65. For operation with about 20 percent bed expansion, an upflow velocity of about 2 m/h is used. The smaller packing provides a greater surface area per unit volume, theoretically supporting a greater amount of biomass growth. The packing void fraction is about 50 percent when expanded. Because the expanded-bed system is not fully fluidized, some solids are trapped and some degree of solids degradation occurs.

2.2.6.8 Anaerobic Fluidized-Bed Reactor (AFBR)

The attached growth anaerobic fluidized-bed reactor (AFBR) (see Figure 2.9c) is similar in physical design to the upflow expanded-bed reactor. The packing size is similar to the expanded-bed reactor, but the AFBR is operated at higher upflow liquid velocities of about 20 m/h to provide about 100 percent bed expansion. Effluent recycle is used to provide sufficient upflow velocity.

2.3 Biohydrogen Production from Wastewater

The biological hydrogen production is part of anaerobic treatment processes, which can use organic compounds as substrate to produce hydrogen using bacteria. Conventional anaerobic treatment processes are used to produce biogas, which is methane and carbon dioxide in order to burn as fuel. The biological hydrogen production can be used to convert organic wastes to hydrogen at first stage. The by-product fermentation end products, which are chiefly acetic and butyric acids and residual organic compounds from the first stage, can be passed to methanogenic reactor in order to generate methane as well (Figure 2.10).

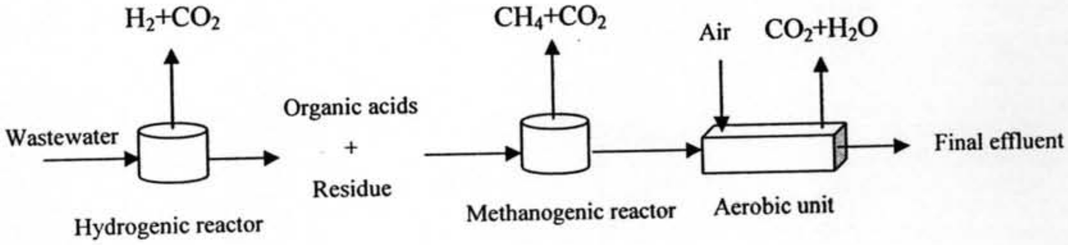


Figure 2.10 Schematic for H_2 production in secondary treatment.

In biological hydrogen production processes, various types of bioreactors have been used to produce hydrogen, including batch (Oh *et al.*, 2003, Morimoto *et al.*, 2004, Zhang *et al.*, 2003, Fan *et al.*, 2006, Ginkel *et al.*, 2005, Shin *et al.*, 2004, Kim *et al.*, 2004, Yu *et al.*, 2001), CSTR (Ueno *et al.*, 1996, Horiuchi *et al.*, 2002, Mizuno *et al.*, 2000, Gavala *et al.*, 2006, Lin *et al.*, Fang *et al.*, 2002), anaerobic contact filter (Vijayaraghavan *et al.*, 2006), fixed-bed (Chang *et al.*, 2002), UASB (Yu *et al.*, 2003, Yu *et al.*, 2002, Gavala *et al.*, 2006), unsaturated flow (Zhang *et al.*, 2006), and leaching bed (Han *et al.*, 2004).

For sustainable biohydrogen production, carbohydrates are the preferred organic carbon source for hydrogen-producing fermentations. Glucose in biomass and wastewater gives a maximum yield of 4 mole H_2 per 1 mole glucose when acetic is the by-product.

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

Half of this yield per glucose is obtained with butyric acid as the fermentation end product.

$$C_6H_{12}O_6 \rightarrow CH_3CH_2CH_2COOH + 2CO_2 + 2H_2 \qquad (3)$$

These two equations have shown that acetic and butyric acids are the main by-products (Hawkes *et al.*, 2002).

2.3.1 Batch Reactors

In batch tests, glucose was used as carbon source and *Citrobacter* sp. Y19, which was isolated from an anaerobic wastewater sludge digester, was used as microorganism to produce hydrogen (Oh *et al.*, 2003). It has been found that the maximum hydrogen yield was estimated to be 2.49 mole H_2 per mole of glucose. The optimal specific H_2 production activity, which was observed at 36°C and pH 6-7, was 32.3 mmol H_2/g cell·h. The natural anaerobic microorganisms, which were obtained from different sources, were used in biohydrogen production processes. The maximum yield of hydrogen per decomposed glucose was 2.1 mole per mole of glucose at 50°C obtained from sludge compost, and the conversion rate was 0.137 L/(L med·h) (Morimoto *et al.*, 2004). Few studies have been conducted to convert starch in wastewater into hydrogen under thermophilic condition of 55°C. The maximum hydrogen yield of 92 mL/g of starch added was found for wastewater at pH 6, but the maximum specific hydrogen production rate of 365 mL/(g·VSS·d) was found at pH 7.0 (Zhang *et al.*, 2003).

However, food waste, a carbohydrate-rich organic solid waste, was used as substrate for hydrogen production using the mesophilic and thermophilic acidogenic culture. The amount of hydrogen production from thermophilic condition was much higher than that from the mesophilic condition. The hydrogen yield was in the range of 0.9-1.8 mol H_2/mol hexose and peaked at 6 g VS/L (Shin *et al.*, 2004). The addition of sewage sludge on food waste up to 13-19% could enhance specific hydrogen production potential of 122.9 mL/g carbohydrate-COD at the ratio of food waste to sewage sludge of 87:13 and the VS concentration of 3.0%. The maximum H_2 production rate was 111.2 mL/(g VSS h) (Kim *et al.*, 2004).

In anaerobic treatment, complex organics, including polysaccharides, proteins, and lipids, are first hydrolyzed by enzymes to form sugars amino acids and fatty acids. These intermediate products are then degraded by acidogens, forming volatile fatty acids (VFA), carbon dioxide, and hydrogen (Matcarf & Eddy., 2003). The influence of daily wastewater, which contained complex organics on acidification, was investigated in batch experiments. The results showed that carbohydrate was preferentially acidified as compared to protein and lipid (Yu *et al.,* 2001). In China, cellulose was converted to hydrogen by cow dung composts. The maximum yield of H_2 68.6 ml H_2/g TVS was observed (Fan *et al.,* 2006).

2.3.2 Continuous Stirred Tank Reactors (CSTR)

Effect of pH on the continuous production of hydrogen was investigated by mixed culture. Glucose was used as the model substrate for carbohydrates. The results showed that the hydrogen production yield of 2.1 ± 0.1 mol H_2/ mol glucose and a specific production rate of 4.6 ± 0.4 L-H_2/(g-VSS d) at the optimal pH 5.5 were observed (Fang *et al.,* 2002). In addition, the hydrogen production in chemostat-type anaerobic reactor at ambient temperature (15-34°C) was examined. The maximum yield of hydrogen production of 1.42 mol-H_2/mole glucose was obtained at the shortest tested SRT of 0.25 days, and the organic loading rate was 416 mmol-glucose/L/day (Lin *et al*., 2004). Enhancement of hydrogen production is the one way to increase hydrogen production yield. Nitrogen gas sparging was used to enhance hydrogen yield. The hydrogen yield increased from 0.85 to 1.43 mol-H_2/mol-glucose, and also the specific hydrogen production rate increased from 1.446 to 3.131 mL-H_2/L/g biomass under sparging conditions (Mizuno *et al.,* 2000).

In contrast, Horiuchi *et al.* (2002) studied on the selective production of organic acids by pH control. The results showed that the main products were changed from butyric acid to acetic and propionic acids depending on the culture pH from 5.0 to 8.0, and the dilution rate did not affect this phenomenon.

Wastewater from a sugar factory was used to study the hydrogen production by anaerobic microflora. A maximum hydrogen production yield of hydrogen of 2.59 mol/mol hexose decomposed was obtained at an HRT of 0.5 days, but the maximum removal effiency of carbohydrates was approximately 97% at an HRT of 3 days (Ueno *et al.,* 1996).

Normally, most studies on biological fermentative hydrogen production from carbohydrates using mixed cultures have been conducted in conventional continuous stirred tank reactors (CSTR) under mesophilic conditions. Investigations on biohydrogen production in upflow anaerobic sludge blanket process in the thermophilic temperature range were studied and compared. From the CSTR experiments at 6 h retention time, the specific hydrogen production rate under thermophilic conditions was higher than that under mesophilic conditions. The specific hydrogen production rates under thermophilic and mesophilic were 104 and 12 mmol H_2/h/L/g VSS, respectively. On the other hand, the hydrogen production yield in the UASB was higher in the CSTR reactor at all HRTs tested (Gavala *et al.*, 2006).

2.3.3 Upflow Anaerobic Reactors

In all the studies concerning biohydrogen production, glucose or pure chemicals were used as substrate. Rice winery wastewater, a carbohydrate-rich waste, was selected as the substrate for hydrogen production. The experiment was conducted in upflow reactor. An optimum hydrogen production rate of 9.33 L-H_2/g VSS d was achieved at an HRT of 2 h, COD of 34 g/L, pH 5.5, and 55^0C. The hydrogen yield was in the range of 1.37-2.14 mol/mol-hexose (Yu *et al.,* 2002).

2.3.4 Other Anaerobic Reactors

Generally, most of biohydrogen production use anaerobic suspended growth processes to optimize the hydrogen yield and hydrogen production rate. Immobilized-cell systems have become common alternatives to suspened-cell systems in continuous operations, since they are more efficient in solid/liquid separation. Fixed-bed bioreactors were used to investigate the hydrogen production. Three porous materials, loofah sponge (LS), expanded clay (EC), and activated carbon (AC), were used as the support of hydrogen-producing bacteria in fixed-bed reactors. It was found that LS was inefficient for biomass immobilization. The EC reactor was able to produce H_2 at an optimal rate of 0.415 L-H_2/h/L at HRT of 2 h. In contrast, the AC reactor exhibited a better hydrogen production of 1.32 L-H_2/h/L at HRT of 1-3 h (Chang *et al.,* 2002). The leaching-bed reactor was used to investigate the hydrogen production of food waste. The highest fermentation efficiency of 58% was observed at initial dilution rate of 4.5 d^{-1}. The removed chemical oxygen demand (COD) was converted to hydrogen was about 10.1%. Moreover, the fermentation efficiency was improved from 58% to 70.8% by adjusting D from 4.5 to 2.3 d^{-1} (Han *et al.,* 2004).

In addition, the most common anaerobic attached growth processes were also used to investigate hydrogen production using *Clostridium acetobutylicum* as hydrogen-producing bacteria. The specific hydrogen production rates increased from 680 to 1270 mL/g glucose/L when influent glucose concentrations were varied from 1.0 to 10.5 g/L. The hydrogen yield was 15-27%, based on a theoretical limit by fermentation of 4 mole of H_2 from 1 mole of glucose (Zhang *et al.,* 2006). A novel method of anaerobic digestion using contact filter was also applied to treat solid waste generated from the jackfruit processing industry. The results showed that the biogas generation was found to be 0.72 L/g VS destroyed. The hydrogen content in the biogas was $55 \pm 2\%$. The highest volatile solids destruction efficiency of 50% was observed at HRT of 12 days (Vijayaraghavan *et al.,* 2006).