CHAPTER II
LITERATURE REVIEW

2.1 Background of Hydrogen

Energy is one of the basic needs for global prosperity. Global energy consumption is mostly dependent on fossil fuels (about 80% of the present world energy demand). Conventional petroleum-based fuels like gasoline or diesel, as well as natural gas and coal, all contain carbon. When these fuels are burnt, their carbon recombines with oxygen from the air to form carbon dioxide (CO_2), which is the primary greenhouse gas that causes global warming. Furthermore, the combustion of fossil fuels at the high temperatures and pressures inside an internal combustion engine or in an electric power plant produces other toxic gases such as carbon monoxide, nitrous oxide, volatile organic compounds (VOCs), and fine particulates. When released into the atmosphere, many of these compounds cause acid rain or react with sunlight to create ground-level smog. Moreover, the recent rise in oil and natural gas prices may drive the current economy toward alternative energy sources. Hydrogen has been received increasing attention to be used as an alternative energy.

2.1.1 Advantages of Hydrogen

2.1.1.1 Hydrogen as Clean Fuel

Hydrogen is the cleanest fuel. When used in a combustion engine, hydrogen burns to produce only water. Thus, hydrogen is regarded as a clean non-polluting fuel. Pure hydrogen produces only heat energy, water, and trace amounts of oxides of nitrogen when burnt. When used in a fuel cell, hydrogen combines with oxygen to form water vapor. This reaction takes place at lower temperatures, and so the only end-product from a fuel cell is water vapor.

2.1.1.2 Hydrogen as Harmless Fuel

Hydrogen is the safest of all 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.

2.1.1.3 Hydrogen as Environmentally Friendly Fuel

All conventional fuels mainly produce carbon dioxide, which is thought to be responsible for the global climate change. The long-term environmental benefits of using hydrogen as a fuel are enormous. Hydrogen fuel produces few pollutants when burnt, and none at all when used in a fuel cell. Hydrogen is a carbon-free fuel, and when produced using renewable energy, the whole energy system can become carbon-neutral, or even carbon-free. So, hydrogen fuel can contribute to the reduction of greenhouse gas emissions and can reduce the production of many toxic pollutants.

2.1.1.4 Hydrogen as an Alternative to Fossil Fuels

Hydrogen can be used in several applications, in which fossil fuels are being used, such as a fuel in furnaces, internal combustion engines, turbines and jet engines, automobiles, buses, and airplanes. Nowadays, hydrogen can be directly used to generate electricity through fuel cells, which are mostly used in transportation section. Moreover, hydrogen and fuel cell technology have the potential to strengthen our national energy security by reducing our dependence on foreign oil.

2.1.1.5 Hydrogen as be Produced from Various Sources

The greatest advantage of hydrogen utilization is that there are many ways to produce it, using both renewable and traditional energy sources. The most common method of hydrogen production is by reforming fossil fuels, particularly natural gas. Electrolysis is another method of hydrogen production that uses electricity to split water into hydrogen and oxygen gases. One advantage of electrolysis is that one can perform electrolysis using renewable source so that the hydrogen produced is a renewable fuel.

2.1.1.6 Hydrogen as 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 and oxygen, and most of hydrogen is bound as H_2O. Because of this, energy must be used to separate these elements. To extract hydrogen from water, for example, about 2.3 gallons of water and 45 kWh 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 a high temperature more than 2,000°C and more than 900°C with a Pt/Ru catalyst.

### 2.1.2 Hydrogen Production Processes

Nowadays, hydrogen can be produced mainly from fossil fuels, water, and biomass (organic wastes and wastewaters).

2.1.2.1 Fossil Fuels as a Source of Hydrogen Production

Hydrogen is currently derived from natural gas, petroleum, and coal by various production processes:

(1) Steam reforming of natural gas

Steam reforming, which is a thermal process, consists of two reactions in a process:

$$C_nH_m + nH_2O \rightarrow nCO + (n + \frac{m}{2})H_2 \qquad (2.1)$$

$$CO + H_2O \rightarrow CO_2 + H_2 \qquad (2.2)$$
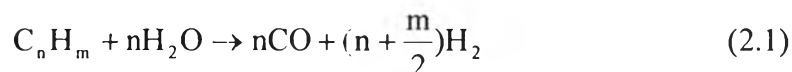
The first reaction is the reforming of natural gas. Natural gas (for example methane, ethane, or propane) is reacted with high temperature steam (700-1000°C) to break the bonds of natural gas in the presence of a catalyst. The product from this step is synthesis gas (or syngas) that is a mixture of carbon monoxide and hydrogen. In the second reaction, carbon monoxide and high temperature steam are converted to hydrogen and carbon dioxide. This step is called a water gas shift (Kothari et al., 2004). Steam reforming of natural gas is the most basic method to produce hydrogen commercially. It is also one of the best understood and least expensive methods. At present, the most of hydrogen (approximately 80% of global hydrogen production) is produced commercially from this process.

(2) Thermal cracking of natural gas

Thermal cracking of natural gas (e.g. methane, ethane, and propane) is a high temperature process. It requires a temperature about 2000°C to produce 60% of hydrogen and 40% of carbon black that is a pigment used in many dying processes (Kothari et al., 2004). The reaction of this process is:

$$C_nH_m (gas) \rightarrow nC(Solid) + mH_2 \qquad (2.3)$$

(3) Partial oxidation of hydrocarbons heavier than naphtha

Partial oxidation is a common process to convert hydrocarbons into a synthesis gas. Hydrocarbons are partially combusted with oxygen in air to produce hydrogen and carbon monoxide rather than fully oxidized to produce carbon dioxide and water. The advantage of this process is that it is the exothermic reaction rather than endothermic reaction. Therefore, it can generate its own heat that is used as energy supply in the process itself.

(4) Coal gasification

Coal gasification is the oldest technology to produce hydrogen. It is a process to convert the coal in solid state to gaseous state at a high temperature of 1330°C. The gaseous coal is treated with steam and controlled amount of oxygen to produce hydrogen, carbon monoxide, and carbon dioxide. And then, carbon monoxide is reacted with steam to produce more hydrogen and carbon dioxide in water gas shift reaction. The reactions are shown below as:

$$Coal + O_2 + H_2O \rightarrow CO + CO_2 + H_2 + Other\ species \quad (2.4)$$
$$CO + H_2O \rightarrow CO_2 + H_2 \quad (2.5)$$
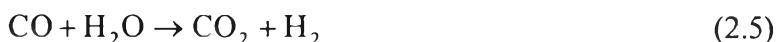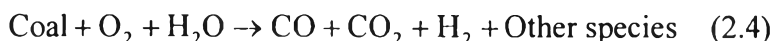
The coal gasification process is expensive to produce hydrogen as almost twice as that from natural gas because of the ratio of hydrogen to carbon that is 4:1 in natural gas and 0.8:1 in carbon (or coal).

2.1.2.2 Water as a source of hydrogen production

Hydrogen can be produced from water by four different techniques:

(1) Electrolysis

Electrolysis is the process to split the water molecules into their basic elements of hydrogen and oxygen by passing an electric current between two electrodes (cathode and anode) through water. Hydrogen rises from the (negative) cathode, and oxygen is collected at the (positive) anode. This electrolysis to produce hydrogen is rarely used because of its high electricity cost.

(2) Thermolysis or direct thermal decomposition

Thermolysis (or direct thermal decomposition) is a high temperature process for hydrogen production. When water is heated to a high

temperature at 3000 K (2727°C), it can be decomposed into hydrogen and oxygen. This process has high efficiency, but it is normally not applied to produce hydrogen because of its extremely high energy consumption.

(3) Thermochemical cycles

Thermochemical cycles are developed from thermolysis in order to mitigate the high temperature required. One or many intermediate is added into the water and then is heated to a lower temperature ranging from 900 to 1200 K (627-927°C). After experiencing variable reaction stage, the water is finally decomposed to hydrogen and oxygen with the help of intermediate. When reactions are completed, intermediate is not converted during reactions. Also, it can be recycled in the process. The efficiency of water decomposition ranges from 17.5 to 75%.

(4) Photolysis

Photolysis process occurs when water molecules absorb the sunlight and use the energy from it to separate water into hydrogen and oxygen in the presence of photocatalysts. This process can be divided into three kinds that are dependent on photocatalysts.

(i) Biophotolysis process

In biophotolysis process, hydrogen is produced from water by using sunlight and specialized microorganisms (photocatalyst), such as green algae and cyanobacteria. These microorganisms consume water and then produce hydrogen as a by-product of their natural metabolic processes, just like plants produce oxygen during photosynthesis.

(ii) Photochemical process

Photochemical process is similar to that of thermochemical cycles, which is to add a kind of photosensitive matter as activator to increase the absorption of wave energy in sunlight. Hydrogen is produced by photochemical reaction.

(iii) Photoelectrochemical process

Photoelectrochemical process uses sunlight and specialized semiconductors (photocatalyst) that is called photoelectrochemical materials to produce hydrogen from water. In the photoelectrochemical (PEC)

system, the semiconductor can directly split water molecules into hydrogen and oxygen by using light energy. Different semiconductor materials work at particular wavelengths of light and energy.

2.1.2.3 Biomass as a Source of Hydrogen Production

Biomass is one of the most abundant renewable resources. It is formed by fixing and consuming carbon dioxide in the atmosphere during the process of plant photosynthesis (Ni et al., 2006). It can also be used as a carbon source, which facilitates waste recycling (Manish et al., 2007). In hydrogen production processes, carbon dioxide is produced as by-product, which means that they result in a near-zero net release of greenhouse gas. Moreover, biomass is carbon neutral in its life cycle. At present, about 12% of today's world energy supply comes from biomass. A diverse array of biomass resources can be used to convert to energy (e.g. hydrogen, ethanol, and methane/biogas). They can be divided into four general categories:

(i) Energy crops: agricultural crops, industrial crops, herbaceous energy crops, woody energy crops, and aquatic crops.

(ii) Forestry waste and residues: trees and shrub residues, logging residues, and mill wood waste.

(iii) Agricultural waste, wastewater, and residues: crop waste, animal waste, and wastewater from animal confinements.

(iv) Industrial waste and wastewater, municipal waste and wastewater: municipal solid waste (MSW), sewage sludge and industry waste.

The available hydrogen production processes from biomass have two general categories: thermochemical and biological processes. Thermochemical processes can be divided into two types that are pyrolysis and gasification. For biological processes are photo-fermentation and dark fermentation.

(1) Thermochemical process for hydrogen production

- Biomass pyrolysis

In this pyrolysis process, biomass is converted under both high at a temperature and pressure of 650-800 K (377-527°C) and 0.1-0.5 MPa in the absence of oxygen (or air) into liquid oils, solid charcoal, and gaseous compounds. Pyrolysis can be further classified into slow and fast pyrolysis. Slow
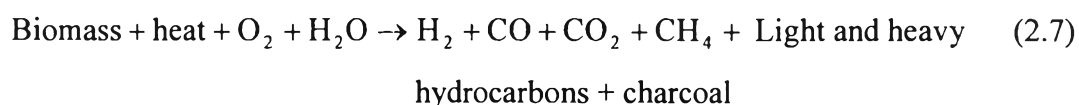
pyrolysis is normally not considered to produce hydrogen because charcoal is the main product. Fast pyrolysis is a high temperature process. In the absence of air, biomass is rapidly heated to form vapor and afterwards condensed to a dark brown mobile bio-liquid as follows:

$$\text{Biomass} + \text{heat} \to H_2 + CO + CO_2 + CH_4 + \text{Other products} \qquad (2.6)$$
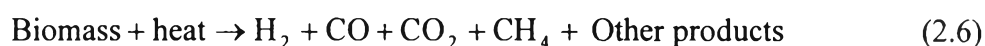
All solid, liquid, and gas phases can be found as the products of this process. Solid products consist of char, pure carbon, and other inert materials. Liquid products include tar and oils that remain in liquid form at room temperature. Gaseous products comprise hydrogen, methane, carbon monoxide, carbon dioxide, and others, depending on the organic nature of biomass. Methane and other hydrocarbon vapors produced can be steam-reformed for more hydrogen production. Moreover, water gas shift reaction can be applied to increase the hydrogen production. Besides the gaseous products, the oily products can also be processed to produce hydrogen.

- Biomass gasification

The basic process of biomass gasification is to gasify biomass at high temperatures (above 1000 K). It is partially oxidized in the presence of oxygen (or air) to form gas and charcoal as follows:

$$\text{Biomass} + \text{heat} + O_2 + H_2O \to H_2 + CO + CO_2 + CH_4 + \text{Light and heavy} \qquad (2.7)$$
$$\text{hydrocarbons} + \text{charcoal}$$

The gas and hydrocarbons products can be further converted into more hydrogen by steam reforming, and this process can be further improved by water gas shift reaction. Biomass gasification is available for biomass that has moisture content less than 35%.

As mentioned above, the products from biomass gasification are mainly gases while pyrolysis aims to produce bio-oils and charcoal. Also, biomass gasification is more favorable for hydrogen production than pyrolysis (Ni et al., 2006).

(2) Biological processes for hydrogen production

Biological process for hydrogen production, also known as "biohydrogen production", uses microorganisms to decompose complex organic

compounds in waste or wastewater to simple end products, such as hydrogen, methane, carbon dioxide volatile fatty acids, and alcohols (Kapdan *et al.*, 2006). Most of biological processes are operated at an ambient temperature (30-40°C) and normal pressure, therefore, they are not energy intensive (Das *et al.*, 2001). Moreover, they are very inexpensive and very simple perspective method (Bartacek *et al.*, 2007). There are two types of biological processes:

- Photo-fermentation

Photo-fermentation is the process to decompose organic compounds to hydrogen as the product by photosynthetic bacteria. They undergo anoxygenic photosynthesis with organic compounds or reduced sulfur compounds as electron donors. Some non-sulfur photosynthetic bacteria are potent hydrogen producers, utilizing organic acids, such as lactic, succinic and butyric acids, or alcohols as electron donors. Hydrogen production by photosynthetic bacteria is mediated by nitrogenase activity, although hydrogenases may be active for both hydrogen production and hydrogen uptake under some conditions. Photosynthetic bacteria is of interest for hydrogen production because of their high theoretical conversion yields and lack of oxygen evolving activity, which causes problem of oxygen inactivation of different biological systems. Moreover, they have the ability to use wide spectrum of light and consume organic substrates derivable from wastes and wastewater treatment (Fascetti *et al.*, 1998). If photosynthetic bacteria are combined with fermentative bacteria, the fermentative bacteria could produce the small organic acids, which the photosynthetic bacteria could then use.

- Dark fermentation

Hydrogen production via dark fermentation is a special type of anaerobic digestion process comprising only hydrolysis and acidogenesis (Bartacek *et al.*, 2007). Fermentative bacteria producing hydrogen, carbon dioxide, and some simple organic compounds, e.g. volatile fatty acid (VFA) and alcohols, in the dark may be cultivated in pure culture or occur in uncharacterized mixed cultures selected from natural sources, such as anaerobic digested sewage sludges and soils (Bartacek *et al.*, 2007). The advantages of dark fermentation are that fermentative bacteria have a high hydrogen generation rate, and can produce hydrogen throughout the day and night at a constant rate since it does not depend on solar energy

(Vijayaraghavan *et al.*, 2005). This decreases the energy demand, and the technology can be simpler (Bartacek *et al.*, 2007). In addition, fermentative bacteria have a high growth rate which can be maintained at a high microbial concentration in the system (Das *et al.*, 2001). From these several advantages, hydrogen production by dark fermentation is feasible for industrial application (Das *et al.*, 2001).

2.2 Wastewater Treatment

Wastewater treatment refers to the process of removing pollutants from wastewater to meet the effluent standards in order to prevent the environment impact. The techniques used to remove the pollutants present in wastewater can be divided into biological, chemical, and physical treatment. These different techniques are applied through many stages of wastewater treatment.

2.2.1 Classification of Wastewater Treatment

Wastewater treatment processes are often classified as preliminary treatment, primary treatment, advanced primary treatment, secondary treatment, tertiary treatment, advanced treatment, and sludge treatment, as shown in Figure 2.1.
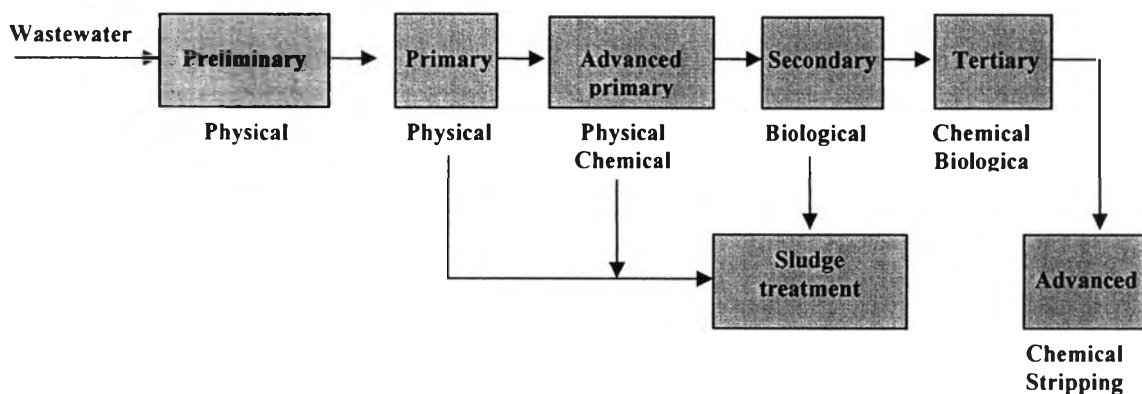

Figure 2.1 The flow diagram of wastewater treatment processes (Neramitsuk, 2007).

2.2.1.1 Preliminary Treatment

Preliminary treatment is the first stage in wastewater treatment process. Gross solids, such as large objects, rags, sticks, floatable, grit, and grease, in wastewater are physically removed since they may cause maintenance or operational problems with the treatment operations, processes, and ancillary systems.

2.2.1.2 Primary Treatment

Primary treatment is a physical operation, usually sedimentation, is used to remove a portion of the suspended solids from the wastewater by settling or floating.

2.2.1.3 Advanced Primary Treatment

In advanced primary treatment, chemicals are added in wastewater to enhance the removal of suspended solids and, to a lesser extent, dissolved solids.

2.2.1.4 Secondary Treatment

Biological treatment process is most commonly used for secondary treatment. The basic characteristic of this process is the use of bacteria and microorganisms (mainly bacteria) to remove and stabilize organic contaminants in wastewater by assimilating them. Microorganisms are used to oxidize (i.e. convert) dissolved, suspended, and colloidal organic materials into simple end products and additional biomass (stable solids and more microorganisms), as represented by the following equation for the aerobic biological oxidation of organic matter.

$$\text{Organic material} + O_2 + NH_3 + PO_4^{3-} \xrightarrow{\text{microorganisms}} \text{New cells} + CO_2 + H_2O \quad (2.8)$$
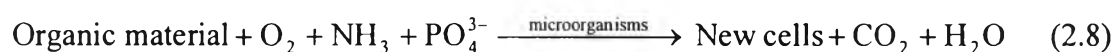
In equation (2.8), the organic materials serve as both an energy source and a source of carbon for cell synthesis under these circumstances. Oxygen (O_2), ammonia (NH_3), and phosphate (PO_4^{3-}) are used to represent the nutrients needed for the conversion of organic matter to simple end products (i.e. carbon dioxide (CO_2) and water). The term shown over the directional arrow is used to denote the fact that microorganisms are needed to carry out the oxidation process. The term new cells represents the biomass produced as a result of the oxidation of the organic matter.

(1) Biological treatment options

The principal processes used for the biological treatment of wastewater can be classified with respect to their metabolic function as aerobic processes and anaerobic processes:

- Aerobic treatment

Aerobic treatment, which may follow some form of pretreatment, involves contacting wastewater with microorganisms and oxygen in a reactor to optimize the growth and efficiency of the biomass. The microorganisms act to catalyze the oxidation of biodegradable organics and other contaminants, such as ammonia, generating innocuous by-products, such as carbon dioxide, water, and excess biomass (sludge).

- Anaerobic treatment

Anaerobic treatment is similar to aerobic treatment, but anaerobic treatment uses microorganisms that do not require oxygen in form of dissolved oxygen. These microorganisms use the compounds other than oxygen to catalyze the oxidation of biodegradable organics and other contaminants, resulting in innocuous by-products (Schultz, 2005).

(2) Biological treatment processes

The principal biological processes used for wastewater treatment can be divided into two main categories:

- Suspended growth process

In suspended growth processes, the microorganisms, which are responsible for the conversion of the organic matters or other constituents to gases and cell tissue, are maintained and freely suspended in wastewater. They are mixed together by appropriate mixing methods. Moreover, they can be aerated by a variety of devices that transfer oxygen to the bioreactor contents.

- Attached growth process

In attached growth or fixed film processes, the microorganisms responsible for the conversion of organic material or nutrients are attached to a surface of inert packing material, the fixed film (or biofilm), which may be mobile or stationary within wastewater (liquid). The organic materials and nutrients are removed from the wastewater during flowing past the surface/media.

Packing materials used in these processes include rock, gravel, slag, sand, redwood, and a wide range of plastic and other synthetic materials. These processes can also be operated as aerobic or anaerobic conditions. The packing materials can be submerged completely in liquid or not submerged, with air or gas space above the biofilm liquid layer.

2.2.1.5 Tertiary Treatment

Tertiary treatment is the removal of disease-causing organisms from wastewater. Treated wastewater can be disinfected by adding chlorine or by using ultraviolet light. High levels of chlorine may be harmful to aquatic life in receiving streams. Treatment systems often add a chlorine-neutralizing chemical to the treated wastewater before stream discharge.

2.2.1.6 Advanced Treatment

Advanced treatment 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.

2.2.1.7 Sludge Treatment

Wastewater treatment processes generate significant quantities of sludge from suspended solids in the feed, biomass generated by biological process, and precipitates from added chemicals, in which require the processes to treat them. Sludge treatment is a step to stabilize the sludge, reduce odors, remove some of the water in order to reduce volume, decompose some of the organic matters and reduce volume, kill disease-causing organisms, and disinfect the sludge. The sludge still contains largely water, as much as 97 percent. Settling the sludge and decanting off the separated liquid remove some of the water and reduce the sludge volume. Settling can result in sludge with about 92 to 96 percent of water content. More water can be removed from sludge by using sand drying beds, vacuum filters, filter presses, and centrifuges, resulting in sludge with between 50 to 80 percent of water content. This dried sludge is called a sludge cake. Aerobic and anaerobic digestions are used to decompose organic sludge in order to stabilize the sludge. Caustic chemicals can be added to sludge, or it may be heat-treated to kill

disease-causing organisms. Following treatment, liquid and cake sludge are usually spread on fields, returning organic matter and nutrients to the soil.

2.2.2 Treatment Parameters

2.2.2.1 Total and Suspened Solids

The term *total solids (TS)* refers to the residue left in a drying dish after evaporation of a wastewater sample and subsequent drying in an oven. After a measured volume is placed in a porcelain dish, the water is evaporated from the dish on a steam bath. The dish is then transferred to an oven and dried to a constant weight at 103-105°C. The total residue (or dry solids) is equal to the difference between the cooled weight of the dish and the original weight of the empty dish. The concentration of total solids is the weight of dry solids divided by the volume of the sample, usually expressed in milligrams per liter.

Total volatile solids (TVS) are determined by igniting the dry solids at 550±50°C in a furnace. The residue remaining after burning is referred to as fixed solids, and the loss of weight on ignition is reported as volatile solids. The concentration of total volatile solids is the weight of dry solids minus the weight of fixed solids divided by the volume of the original liquid sample. Volatile solids content also can be expressed as a percentage of the dry solids in the sample.

The term of *total suspended solids (TSS)* or *suspended solids (SS)* refers to the nonfilterable residue that is retained on a glass-fiber disk after filtration of a sample of wastewater. A measured portion of a sample is drawn through a glass-fiber filter but retained in a funnel, by applying a vacuum to the suction flask under the filter. The filter with damp suspended solids adhering to the surface is transferred from the filtration apparatus to an aluminum or stainless steel planchet as a support. After drying at 103-105°C in an oven, the filter with the dry suspended solids is weighed. The weight of suspended solids is equal to the difference between this weight and the original weight of the clean filter. The concentration of total suspended solids is the weight of the dry solids divided by the volume of the sample and is usually expressed in milligrams per liter.

Volatile suspended solids (VSS) are determined by igniting the dry solids at 550±50°C after placing the filter disk in a porcelain dish. The

concentration of volatile suspended solids is the weight of dry solids minus the weight of fixed solids divided by the volume of the original liquid sample.

Dissolved solids (DS) are the solids that pass through the glass-fiber filters and are calculated from total and suspended solids analyses. *Total dissolved solids (TDS)* equal total solids minus total suspended solids (TDS=TS-TSS). *Volatile dissolved solids (VDS)* equal total volatile solids minus volatile suspended solids (VDS=TVS-VSS).

2.2.2.2 Biochemical and Chemical Oxygen Demands

(1) Biochemical oxygen demand

Biochemical oxygen demand (BOD) is a measure of the amount of oxygen that is required to oxidize the organic matter in a sample, through the action of microorganisms contained in the sample during the biological reaction.

(2) Chemical oxygen demand

Chemical oxygen demand (COD) is a measure of the oxygen equivalent of the organic matter in a wastewater sample that can be oxidized chemically using dichromate in an acid solution. The organic matter is converted into carbon dioxide and water. The COD value presents both biodegradable and non-biodegradable organic matters in the sample.

2.2.2.3 Hydraulic Retention Time

The hydraulic retention time (HRT) or τ (tau) is a measure of the average length of time that a soluble compound remains in a bioreactor. The theoretical hydraulic retention time is defined as:

$$\tau = \frac{V}{Q} \tag{2.9}$$

where τ = Hydraulic retention time, h

   V = Volume of reactor, m^3

   Q = Volumetric flow rate, m^3/h

2.3 Anaerobic Biological Treatment

Anaerobic biological treatment (or anaerobic fermentation) is a process, in which microorganisms derive energy and grow by metabolizing organic materials in an oxygen-free environment, resulting in the simple end products.

2.3.1 Process Description

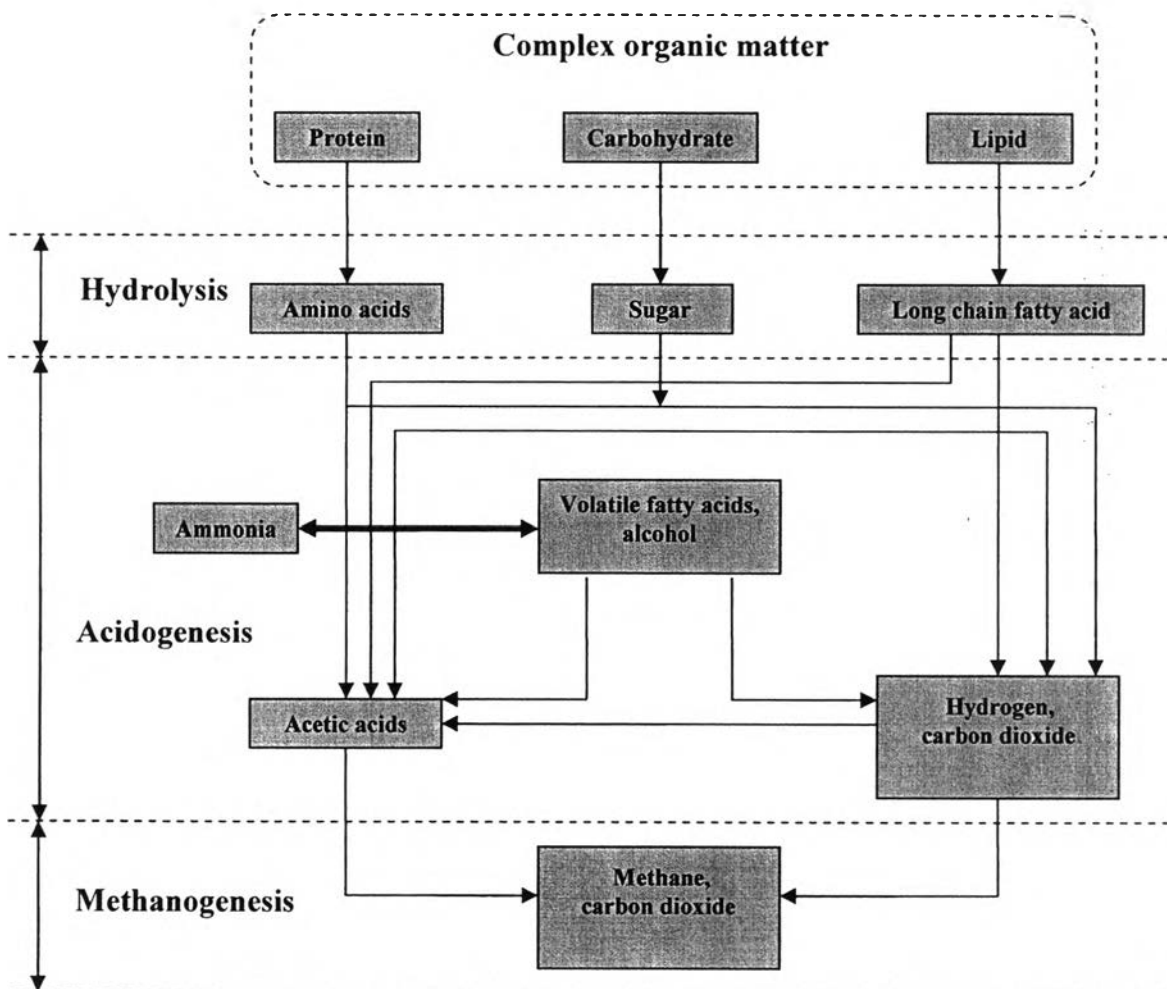Three basic steps are involved in the overall anaerobic decomposition of organic compounds, as shown in Figure 2.2.

Figure 2.2 The schematic representation of anaerobic biological treatment (Reith, 2003).

2.3.1.1 Hydrolysis

Hydrolysis is the first step for most fermentation processes, in which particulate materials are converted to soluble compounds that can then be hydrolyzed further to simple monomers that are used by bacteria that perform fermentation.

2.3.1.2 Acidogenesis

The second step is acidogenesis (also referred to as fermentation). In the acidogenic step, amino acids, sugars, and some fatty acids are degraded further. Organic substrates serve as both the electron donors and acceptors. The principal products of this process are acetate, hydrogen, carbon dioxide, propionate, and butyrate. The propionate and butyrate are further fermented to produce hydrogen, carbon dioxide, and acetate. Thus, the final products of the step (acetate, hydrogen, and carbon dioxide) are the precursors of methane formation (methanogenesis).

2.3.1.3 Methanogenesis

The third step, methanogenesis, is carried out by a group of organisms known collectively as methanogens. Two groups of methanogenic organisms are involved in methane production. The first group, aceticlastic methanogens, splits acetate into methane and carbon dioxide. The second group, hydrogen-utilizing methanogens, uses hydrogen as the electron donor and carbon dioxide as the electron acceptor to produce methane.

2.3.2 Advantages and Disadvantages of Anaerobic Treatment

2.3.2.1 Advantages of Anaerobic Biological Treatment

Advantages of anaerobic treatment are numerous and can be summarized as follows:

- This process generally consumes little energy. At ambient temperature, the energy requirements are in the range 0.05-0.1 kWh/m^3 (0.18-0.36 MJ/m3), depending on the need for pumping and recycling effluent.

  - Less biological sludge production

  - Fewer nutrients required

  - Provision of energy source through methane recovery

- Elimination of off-gas air pollution

- Rapid response to substrate addition after long periods without feed

- Raw waste stabilization

- Relatively odor-free end-products

- Modern anaerobic treatment can handle very high loads, exceeding values of 30 g COD/L d at 30°C and up to 50 g COD/L d at 40°C for medium strength, mainly soluble wastewater.

- The space requirements of this process are lower than conventional systems.

During anaerobic biological treatment, biodegradable compounds are effectively removed, leaving a number of reduced compounds in the effluents, as well as ammonium, organic N-compounds, sulphide, organic P-compounds, and pathogens. Depending on the further use, a subsequential treatment step is needed.

2.3.2.2 Disadvantages of Anaerobic Treatment Process

The disadvantages of anaerobic treatment are summarized below:

- Longer start-up time to develop necessary biomass inventory

- May require alkalinity addition

- May require further treatment with an aerobic treatment process to meet discharge requirements

- Biological nitrogen and phosphorus removal is not possible.

- Much more sensitive to the adverse effect of lower temperatures on reaction rates

- May be more susceptible to upsets due to toxic substances

- Potential for production of odors and corrosive gases

2.3.3 Anaerobic Treatment Processes

Anaerobic treatment processes include anaerobic suspended growth, anaerobic sludge blanket, and attached growth anaerobic processes.

2.3.3.1 Anaerobic Suspended Growth Processes

Anaerobic suspended growth processes are classified in three types:

(1) Complete-mix process

In the complete-mix anaerobic process, as shown in Figure 2.3(a), the hydraulic retention and solid retention times are equal (τ = SRT). Generally, hydraulic retention time may be in the range of 15 to 30 days to provide sufficient safety factors for operation and process stability. This process without sludge recycle is more suitable for wastes that have high concentrations of solids or extremely high dissolved organic concentrations, where thickening the effluent solids is difficult. Typical organic loading rates for this process are present in Table 2.1, compared with anaerobic contact and anaerobic sequencing reactor processes.

Table 2.1 Typical organic loading rates for anaerobic suspended growth processes at 30°C (Metcalf & Eddy, 2003)

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

(2) Anaerobic contact process

The anaerobic contact process, as shown in Figure 2.3(b), overcomes the disadvantages of a complete-mix process without recycle. Biomass is separated and returned to reactor so that the solid retention time (SRT) is much longer than the hydraulic retention time (τ). The anaerobic reactor volume can

be reduced by separating τ and SRT values. Gravity separation is the most common approach for solid separation and thickening prior to the sludge recycle. In some cases, gas flotation is used for solid separation by dissolving the process off-gas under pressure, which has been used in place of gravity separation. 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.

(3) Anaerobic sequencing batch reactor process

The anaerobic sequencing batch reactor process, as shown in Figure 2.3(c), 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) feeding, (2) reacting, (3) settling, and (4) decanting. During the reacting 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 to 24 h. At 25°C, 92 to 98 percent COD removal can be achieved at a volumetric organic loading in the range of 1.2 to 2.4 kg COD/m^{3}d.
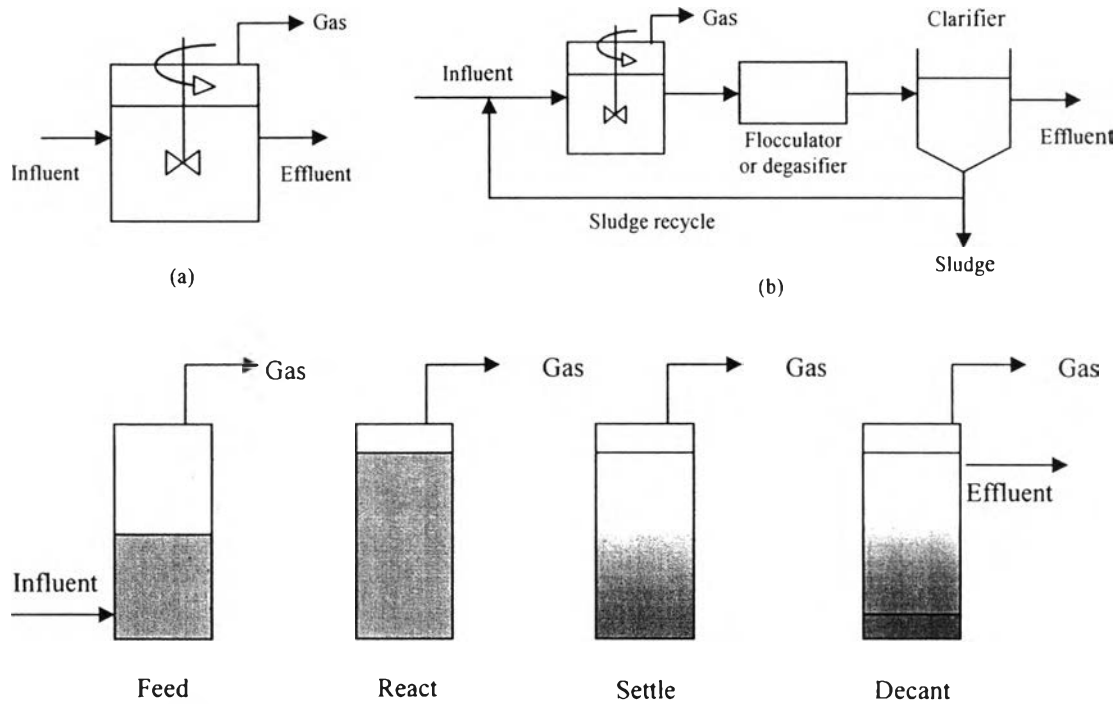
Figure 2.3 Anaerobic suspended growth processes (a) complete-mix process, (b) anaerobic contact process, (c) anaerobic sequencing batch reactor process (Metcalf & Eddy, 2003).

2.3.3.2 Anaerobic Sludge Blanket Processes

Anaerobic sludge blanket is an anaerobic process, whilst forming a blanket of granular sludge and being suspended in the tank. The key feature of this process is that the anaerobic sludge inherently has superior flocculation and settling characteristics, which favorably provide the physical and chemical conditions for sludge flocculation. When these conditions are met, a high solid retention time (at high HRT loadings) can be achieved, with separation of the gas from the sludge. One of the most notable developments in anaerobic treatment process technology is the upflow anaerobic sludge blanket (UASB) reactor. The principal types of anaerobic sludge blanket processes include (1) the original UASB process and modification of the original design, (2) the anaerobic baffled reactor (ABR), and (3) the anaerobic migrating blanket reactor (AMBR). Of these sludge blanket processes, the UASB is the most common used process for treating a wide range of industrial wastewaters.

(1) Upflow sludge blanket reactor (UASB) process

The basic UASB reactor is illustrated in Figure 2.4(a). 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-solid separator, and the effluent withdrawal design. Modifications to the basic UASB design include adding a settling tank, as shown in Figure 2.4(b), or the use of packing material at the top of the reactor, as shown in Figure 2.4(c). Both modifications are intended to provide better solid capture in the system and to prevent the loss of large amounts of the UASB reactor solid 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 with other anaerobic processes is the development of a dense granulated sludge.
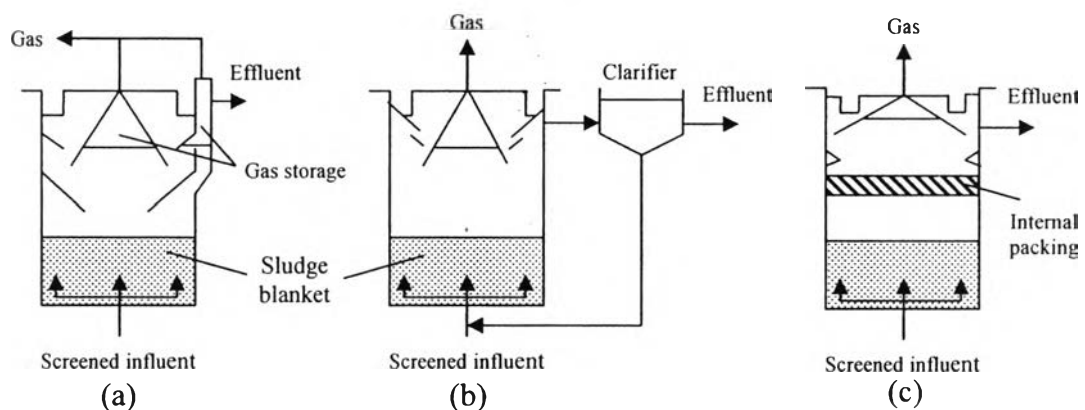

Figure 2.4 Schematic of the UASB process and some modifications: (a) original process, (b) UASB reactor with sedimentation tank and sludge recycle, and (c) UASB reactor with internal packing for fixed-film attached growth (Metcalf & Eddy, 2003).

(2) Anaerobic baffled reactor process

In the anaerobic baffled reactor process (ABR), as shown in Figure 2.5(a), 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, or (3) packing has been used in the upper portion of each chamber to capture solids.

(3) Anaerobic migrating blanket reactor

The anaerobic migrating blanket reactor (AMBR) process is similar to the ABR with the added features of mechanical mixing in each stage and an operating approach to maintain the sludge in the system without resorting to packing or settlers for additional solid capture, as shown in Figure 2.5(b). In the AMBR process, the influent feed point is changed periodically to the effluent side, and the effluent withdrawal point is also changed. In this way, the sludge blanket remains more uniform in the anaerobic reactor. The flow is reversed when a significant quantity of solids accumulates in the last stage.
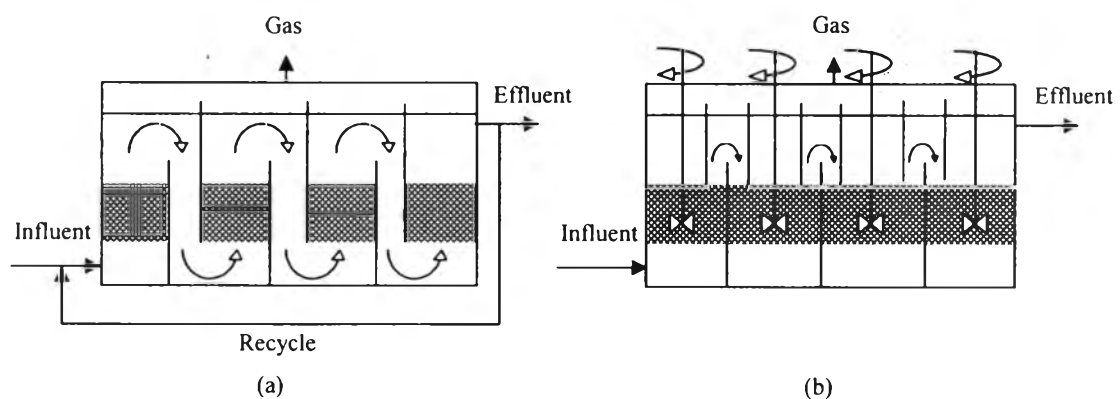

Figure 2.5 Schematic views of alternative sludge blanket processes: (a) anaerobic baffled reactor (ABR) and (b) anaerobic migrating blanket reactor (AMBR) (Metcalf & Eddy, 2003).

2.3.3.3 Attached Growth Anaerobic Processes

Attached-growth anaerobic treatment reactors differ by the type of packing media used and the degree of bed expansion. There are three types of attached growth processes as described below:

(1) Upflow packed-bed reactor

In the upflow packed-bed reactor, as shown in Figure 2.6(a), the packing is fixed, and the wastewater flows up through the interstitial spaces between the packing media with biogrowth. Effluent recycle is generally not used for the packed-bed reactor except for high-strength wastewaters. While the first upflow anaerobic packed-bed processes contained rock, a variety of designs employing synthetic plastic packing is used currently. 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 solid accumulation and possible packing plugging. The process is best suited for wastewaters with low suspended solid concentrations.

(2) Anaerobic expanded-bed reactor

The anaerobic expanded-bed reactor (AEBR), as shown in Figure 2.6(b), uses silica sand with a diameter in the range of 0.2 to 0.5 mm with specific gravity of 2.65 as the packing material to support biofilm growth. Recycle is used to provide sufficient upflow velocity, resulting in 20 percent bed expansion. The smaller size of media provides a greater surface area per unit volume, resulting in theoretically having a greater amount of biomass growth. The void fraction is about 50% when expanded. With such a small packing and void volume, the expanded-bed operation is necessary to prevent plugging. Because the expanded-bed

system is not fully fluidized, some solids are trapped, and some degree of solid degradation occurs.

(3) Attached growth anaerobic fluidized-bed reactor

Anaerobic fluidized-bed reactor (AFBR), as shown in Figure 2.6(c), is similar in physical design to the upflow expanded bed reactor. The media particles are 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% bed expansion. Both fluidization and mixing of the packing material occurs in fluidized-bed system. Effluent recycle is used to provide sufficient upflow velocity.
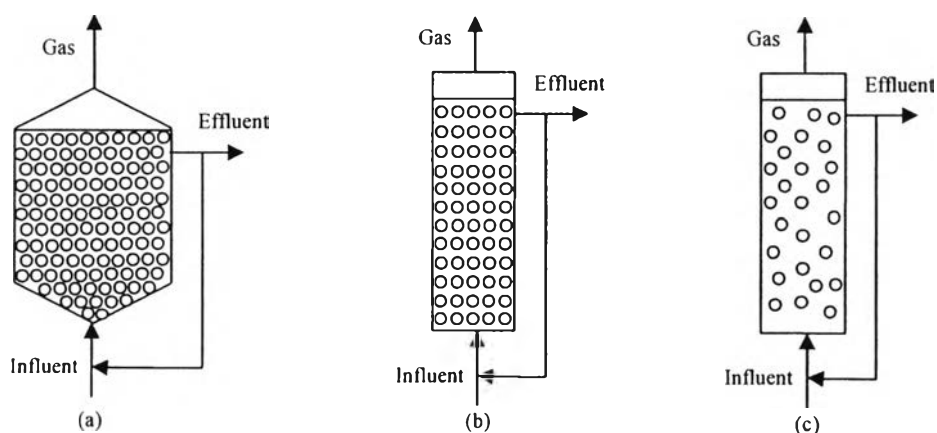

Figure 2.6 Upflow anaerobic attached growth treatment reactors: (a) anaerobic upflow packed-bed reactor, (b) anaerobic expanded-bed reactor, and (c) anaerobic fluidized-bed reactor (Metcalf & Eddy, 2003).

The expanded and fluidized-bed reactors have more surface area per reactor volume for biomass growth and better mass transfer than the upflow packed-bed reactor, but have lower solid capture.

(4) Downflow attached growth process

The downflow attached growth anaerobic processes, as illustrated in Figure 2.7, have been applied for treatment of high-strength wastewaters using a variety of packing materials, including cinder block, random plastic, and tubular plastic. Systems are designed to allow recirculation of the reactor effluent.
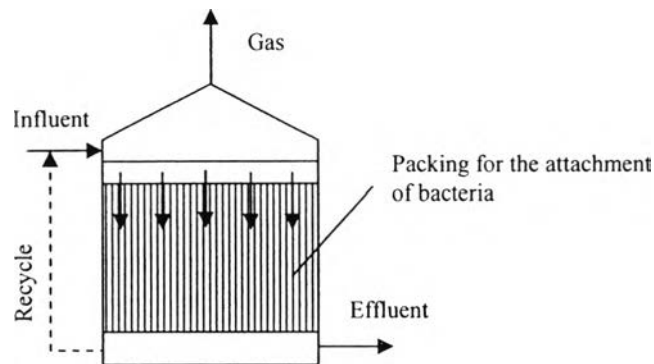
Figure 2.7 Downflow attached growth anaerobic treatment reactor (Metcalf & Eddy, 2003) .

2.4 Biohydrogen Production from Cassava Wastewater by Dark Fermentation

Thailand is the world's largest exporter of cassava products (tapioca), contributing to about 80% of total world exports (Food and Agricultural Organization of United Nations, 2000). Cassava can be grown in most parts of Thailand, especially in the Northeastern region (Sangyoka, 2006). It is a major source of starch, and about 18 million tons of starch is processed annually from cassava (International Starch Institute, 1999). Starch is recovered from cassava roots by wet processing, which generates a large volume of high strength liquid stream that is considered as end strength organic wastewater. One kilogram of fresh cassava roots yields about 0.2 kg of starch, 0.4-0.9 kg of cake, and about 5-7 L of wastewater in the starch production process (Plevin and Donnelly, 2004). Cassava wastewater is a subject of environmental concern because it has a very high chemical oxygen demand (COD), biochemical oxygen demand (BOD), and total solid, as shown in Table 2.2 (Sriroth, 2005). Thus, there is a need to treat this effluent before being discharged into the environment.

Table 2.2 Important characteristics of wastewater from cassava starch factories (Sriroth, 2005)

Component	Content
Total COD	13,000-19,500 mg/L
Soluble COD	6,500-13,600 mg/L
Total BOD	6,500-12,600 mg/L
Total solids	12,500-20,000 mg/L
Total soluble solids	5,800-8,000 mg/L

Cassava wastewater has already been proved to be feasible for hydrogen production. It could be conducted in batch, repeated-batch, upflow anaerobic sludge blanket (UASB), or anaerobic contact process by dark fermentation (Sangyoka, 2006 and Thailand Institute of Scientific and Technological Research, 1988):

2.4.1 Batch and Repeated-Batch Reactors

A series of batch tests were conducted to investigate the biohydrogen production potential from cassava starch manufacturing wastewater at 20,000 mg COD/L using anaerobic sludge (Sangyoka, 2006). The maximum specific hydrogen production of 1,511 ml H_2/g-VSS and the maximum hydrogen yield of 251 mL/g-COD fed were obtained at thermophilic temperature (55°C) and initial pH 5.0. In addition, heat-treated UASB granule was used in a 10 L bioreactor with a working volume of 8 L at room temperature and pH 6.0 by batch and repeated-batch fermentation. The specific hydrogen production potential, hydrogen yield, and maximum hydrogen production rate of 39,304.81 mL, 0.22 mL/mg COD, and 851.84 mL/h, respectively, were obtained in a batch reactor. A repeated-batch was conducted when the glucose concentration in fermentative broth was depleted to 150-250 mg/L which equivalent to 10-15% of initial glucose concentration. Repeated-batch reactor was operated at 3 different feed-in/feed-out rates, i.e. 25%, 50%, and 75%. From the experimental results, a suitable feed-in/feed-out rate for production of hydrogen from cassava wastewater was at 75%. This was indicated by the highest hydrogen yield, the highest potential maximum amount of hydrogen produced, a relatively high maximum hydrogen production rate, and a relatively high maximum

specific hydrogen production rate of 0.0094 mL/mg COD, 12,532.80 mL, 540.46 mL/h, and 3.5 mL/g VSS h, respectively.

2.4.2 Upflow Anaerobic Sludge Blanket (UASB)

Sustainable hydrogen production from cassava wastewater was conducted in upflow anaerobic sludge blanket (UASB) reactor (Sangyoka, 2006). Inoculum used to form UASB granule was anaerobic sludge obtained from the alcoholic wastewater treatment plant. Prior to granule formation, anaerobic sludge was heat-treated in boiling water for 30 minutes. A pH of the substrate in the UASB reactor was maintained at pH 6-6.5 by adding $NaHCO_3$. Heat shock treatment and pH control were conducted to inhibit methanogenic activity. The 9.4-L UASB reactor was operated for 7 months at 5 different hydraulic retention times (HRT), i.e. 4.8, 8.4, 12, 18, and 24 h, with concentrations of cassava wastewater and inoculum of approximately 10,000 mg COD/L and 10,000 mg/L, respectively. The results revealed that an optimum HRT was 12 h for hydrogen production from cassava wastewater. The hydrogen yield of 46 mL H_2/g COD and the hydrogen production rate of 16.1 L/d were obtained. Each gram of biomass produces 0.89 mL H_2/day with evolved gas mixture of 46% hydrogen, 40% carbon dioxide, and less than 2% methane. The effluent volatile suspended solid was 235 mg/L. During the efficient hydrogen production stage, a major soluble metabolite was butyric acid, followed by acetic acid and propionic acid.

2.4.3 Anaerobic Contact Process

Anaerobic contact process was also used to determine the optimum conditions for volatile fatty acid (VFA) production from the cassava wastewater at COD 10,000 mg/L both without nutrient supplementation and with 22,000 mg/L nutrient supplementation (Thailand Institute of Scientific and Technological Research, 1988). The fermenter in this process had the volume of 25 L and was carried out at 37°C with pH control. The cassava wastewater was fed continuously, and settled sludge was recycled back into the fermentor. The results indicated that the wastewater containing a high COD of 22,000 mg/L with nutrient supplementation was the optimum condition for producing VFA from cassava wastewater because it gave the high values of both VFA production rate and the VFA yield. Moreover, it had the minimum values of both the methane production

and methane yield. At this condition, the process had the optimum hydraulic retention time of 1 day. However, pH control was not necessary for operating the system under this optimum condition. Under this optimum condition and without pH control, the system gave the effluent VFA concentration of 5,800 mg/L as acetic acid (HAc), the VFA production rate of 4.67 kg HAc/m^{3}d, and the VFA yield of 0.4 kg HAc produced/kg organic removed.