# CHAPTER II
# THEORETICAL BACKGROUND AND LITERATURE REVIEW

## 2.1 Background of Hydrogen

The world's energy requirements are essentially dependent on fossil fuels (about 80 % of the present world energy demand), which are limited (Das and Veziroglu, 2001). Fossil fuels are not only the depleting energy source, but also their combustion releases many pollutants that have negative effects to the environment. Because fossil fuels contain carbon, their carbon will recombine with oxygen from the air to form carbon dioxide ($CO_2$), which is the primary greenhouse gas that causes global warming, when they are burnt. Furthermore, combustion of fossil fuels at the high temperatures and pressures reached inside an internal combustion engine or in an electric power plant produces other toxic emissions. Carbon monoxide, nitrous oxide, volatile organic chemicals, and fine particulates are all components of air pollution attributable to the refining and combustion of fossil fuels. 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. To keep away from these problems, hydrogen has received an increasing attention to be used as an alternative energy.

### 2.1.1 Advantages of Hydrogen

#### 2.1.1.1 Hydrogen is 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 waste product from a fuel cell is water vapor.

### 2.1.1.2 Hydrogen is Harmless Fuel.

Hydrogen is the safest of all fuels, partly because of how light it is compared with 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.

### 2.1.1.3 Hydrogen is Environmentally Friendly.

Conventional energy resources can significantly produce greenhouse gases, especially carbon dioxide, which is thought to be responsible for changes in global climate. 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 reducing greenhouse gas emissions and can reduce the production of many toxic pollutants.

### 2.1.1.4 Hydrogen can Help Prevent the Depletion of Fossil Fuels.

Hydrogen can be used in any 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 can be Produced from Various Sources.

The greatest advantage of hydrogen 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 is the Most Abundant Element on Earth.

Hydrogen is also the most abundant element on earth, but less than 1 % in the form 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 expended to separate these elements. To extract hydrogen from water, for example, about 2.3 gallons of water and 45 kilowatts-hours (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 temperature more than 2,000°C and temperature high than 900°C with Pt/Ru catalyst.

### 2.1.2 Hydrogen Production Processes

There are many methods to generate hydrogen. They can be produced mainly from fossil fuels, water, and biomass (organic wastes and wastewater).

### 2.1.2.1 Hydrogen Production from Fossil Fuels

Hydrogen is presently derived from natural gas, petroleum, and coal by various ways:

- ### Steam-Methane Reforming (SMR)

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

The first reaction is *the reforming of natural gas*. Natural gas, such as methane, is reacted with steam at high temperatures (750-800°C) to produce synthesis gas (syngas), which contains hydrogen ($H_2$) and carbon monoxide (CO). This can be described by the following reaction.

$$CH_4 + H_2O \text{ (+ heat)} \rightarrow CO + 3\ H_2 \qquad (2.1)$$
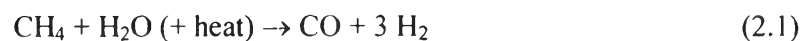
The second reaction is *the shift reaction (water gas shift)*. In this step, carbon monoxide produced in the first reaction is reacted with high temperature steam to form hydrogen and carbon dioxide. This process occurs in two stages, consisting of a high temperature shift (HTS) at 350°C (662°F) and a low

temperature shift (LTS) at 190-210°C (374-410°F). This can be described by the following reaction.

$$CO + H_2O \rightarrow CO_2 + H_2 \text{ (+ small amount of heat)} \qquad (2.2)$$

- *Thermal Cracking of Methane*

Thermal cracking of natural gas, such as methane, is a high temperature process, which can replace stream reforming process because of no carbon dioxide emission. It requires high temperature about 2,000°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:
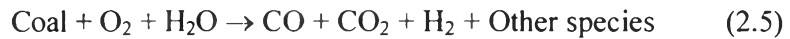
$$CH_4 \rightarrow C + 2H_2 + 75.6 \text{ kJ} \qquad (2.3)$$

- *Partial Oxidation of Methane (POX)*

Partial oxidation is a common process to convert natural gas into a synthesis gas (carbon dioxide and hydrogen), which can be converted to higher alkanes or methanol (Deutschmann and Schmidt, 1998). Because this process is the exothermic reaction, it can generate its own heat that is used as energy supply in the process itself. The reaction of this process is:

$$CH_4 + \tfrac{1}{2} O_2 \rightarrow CO + 2 H_2 \qquad \Delta H_R = -36 \text{ kJ/mol} \qquad (2.4)$$

- *Coal Gasification*

Coal gasification is the oldest method to produce hydrogen. It is a process to convert the coal in solid state to gaseous state at 1,330°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 the water gas shift reaction. The reactions are shown below as:

$$Coal + O_2 + H_2O \rightarrow CO + CO_2 + H_2 + \text{Other species} \qquad (2.5)$$

$$CO + H_2O \rightarrow CO_2 + H_2O \qquad (2.6)$$

Coal gasification is expensive to produce hydrogen from coal as almost twice as from natural gas because of the low ratio of hydrogen to carbon; that is 4:1 in natural gas and 0.8:1 in carbon (or coal).

### 2.1.2.2 Hydrogen Production from Water

Hydrogen can be produced from water by four types of process:

- _Electrolysis_

Electrolysis of water may be the cleanest technology for hydrogen gas production (Kapdan and Kargi, 2006). It is the process to separate 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 bubbles will be collected on the negative plate (cathode) while oxygen bubbles gather on the positive plate (anode). There is no carbon dioxide given off during the process, and it can be results shown by the following chemical reaction:

$$2H_2O + \text{energy} \rightarrow 2H_2 + O_2 \qquad (2.7)$$

However, this method is not efficient when it comes to produce large amounts of hydrogen because it is energy-intensive and if using electricity generated from fossil fuels, carbon dioxide will be produced at an earlier stage in the process.

- _Thermolysis or Direct Thermal Decomposition_

Thermolysis (or direct thermal decomposition) is a high temperature process for hydrogen production by uses solar energy. When water is heated to a high temperature at 3,000 K (2,727°C), it can be decomposed into hydrogen and oxygen. This process has high efficiency, but it is normally not applied to produce hydrogen.

- *Thermochemical Process*

Thermochemical process is developed from thermolysis in order to mitigate the high temperature required. It uses solar energy to drive an endothermic reversible reaction that produces hydrogen (Meyers, 2001).

$$H_2O \rightarrow H_2 + 0.5O_2 \qquad (2.8)$$

- *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 photocatalyst type.

(1) 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.

(2) Photochemical Process

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

(3) Photoelectrochemical Process

Photoelectrochemical process uses sunlight and specialized semiconductors (photocatalyst) that are 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 Hydrogen Production from Biomass

Biomass is one of the most abundant renewable sources. 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 and Banerjee, 2007). In hydrogen production processes, carbon dioxide is produced as a 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. Photo-fermentation and dark fermentation are the two types of biological processes.
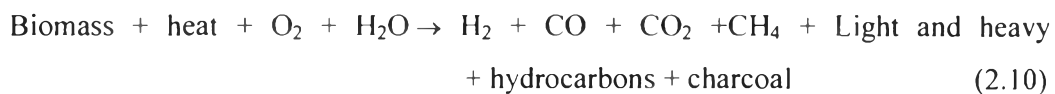
- *Thermochemical Process*

(1) Biomass Pyrolysis

In this process, biomass is heated 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) to convert biomass into liquid, charcoal and non-condensable gases, acetic acid, acetone, and methanol. The main gaseous products from pyrolysis are hydrogen, carbon dioxide, carbon monoxide, and hydrocarbon gases. The reactions are shown below:

$$\text{Biomass} + \text{heat} \rightarrow H_2 + CO + CO_2 + CH_4 + \text{Other products} \qquad (2.9)$$
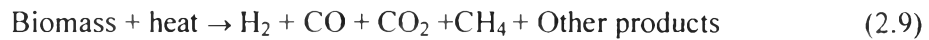
(2) Biomass Gasification

The basic process of biomass gasification is to gasify biomass at a high temperature (above 1,000 K). It is partially oxidized in the presence of oxygen (or air) to form gas and charcoal as follows:

$$\text{Biomass} + \text{heat} + O_2 + H_2O \rightarrow H_2 + CO + CO_2 + CH_4 + \text{Light and heavy} \\ + \text{hydrocarbons} + \text{charcoal} \qquad (2.10)$$

The gas and hydrocarbons products can be 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).

- *Biological Process*

Biological hydrogen production process is an alternative method for hydrogen gas production, also known as "green technology" (Kapdan and Kargi, 2006). This process uses microorganisms to decompose complex organic compounds in waste or wastewater, which are composed of carbohydrate-rich and non-toxic materials, to simple end-products. such as hydrogen, methane, carbon dioxide volatile fatty acids, and alcohols. Most of biological processes are operated at an ambient temperature (30-40°C) and normal pressure; hence. they are less energy-intensive and environmentally friendly (Das and Veziroglu, 2001). There are two types of biological processes: photo-fermentation and dark fermentation.

(1) 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 are the most promising microbial system for biohydrogen 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 derived from wastes and wastewaters (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.

(2)  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 sludge and soil (Bartacek *et al.*, 2007 and Vijayaraghavan and Soom, 2008). The advantages of dark fermentation are that fermentative bacteria are capable of high hydrogen generation rate. and hydrogen is produced throughout the day and night at a constant rate since it does not depend on energy provided by sunlight (Vijayaraghavan *et al.*, 2005). This decreases the energy demand, and the technology can be simpler (Bartacek *et al.*, 2007). In addition. fermentative bacteria can have good growth rate for supply of microorganisms to the production system. From these several advantages, hydrogen production by dark fermentation is feasible for industrial application (Das and Veziroglu, 2001).

## 2.2 Wastewater Treatment

Because several industries are developing in everyday, the quantity of waste generated also increases. Thus, they must remove pollutants before being released to the environment. The techniques used to remove the pollutants present in wastewater can be divided into biological, chemical, physical, and energetic ones. These different techniques are applied through many stages of wastewater treatment.

### 2.2.1 Classification of Wastewater Treatment

Wastewater treatment processes consist of two major steps: primary treatment processes (physical removal of floatable and settleable solids) and secondary treatment processes (biological removal of dissolved solids). These two steps can be divided to preliminary treatment, primary treatment, advanced primary treatment, secondary treatment, tertiary treatment, advanced treatment, and sludge treatment, as shown in Figure 2.1.
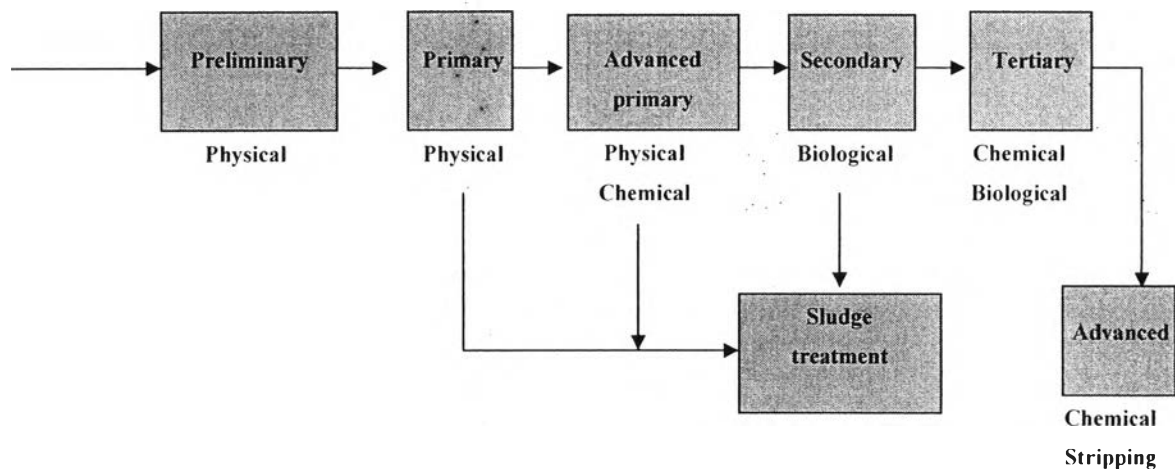


**Figure 2.1** Flow diagram of wastewater treatment processes.

*2.2.1.1 Preliminary Treatment*

Preliminary treatment is the first step 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 helping systems.

### 2.2.1.2 Primary Treatment

This is the following step from preliminary step, which is physical operation, usually sedimentation. It 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

The secondary treatment is the process for removing or reducing contaminants or growths that are left in the wastewater from the primary treatment process. Usually, biological treatment is used to treat wastewater in this step because it is the most effective type of treatment. The basic characteristic of this process is the use of bacteria and microorganisms to remove and stabilize contaminants from 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.

$$\text{Organic material} + O_2 + NH_3 + PO_4^{3-} \xrightarrow{\text{microorganism}} \text{New cells} + CO_2 + H_2O \quad (2.11)$$
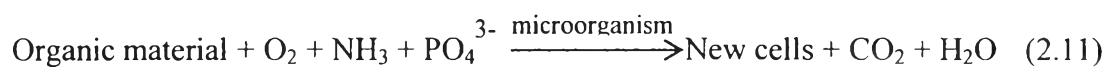
From Equation (2.11), the organic materials serve as both an energy source and a source of carbon for cell synthesis under these circumstances. Oxygen ($O_2$), ammonia ($NH_3$), and phosphate $(PO_4^{3-})$ are used to represent the nutrients needed for the conversion of organic matter to simple end-products (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 represent the biomass produced as a result of the oxidation of the organic matter.

### 2.2.1.5 Tertiary Treatment

After primary and secondary treatments process, wastewater will be sent to tertiary treatment process to remove disease-causing organisms from wastewater. Treated wastewater can be sterilized by adding chlorine or by using ultraviolet light. Moreover, this treatment process may include processes to remove nutrients, such as nitrogen and phosphorus, and carbon adsorption to remove chemicals.

### 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, which require the processes to treat them. Sludge treatment process is to stabilize the sludge and reduce order, remove some of water and reduce volume, decompose some of the organic matter and reduce volume, kill disease-causing organisms, and disinfect the sludge.

## 2.2.2 Parameters about Wastewater

### 2.2.2.1 Total Solids (TS)

The term total solids refer to the matter remained after a wastewater sample is evaporated and dried at a specified temperature (103 to 105°C). Total solids consist of suspended solids and dissolved solid.

$$TS = TSS + TDS \qquad (2.12)$$

### 2.2.2.2 Total Suspended Solids (TSS)

It refers to the nonfilterable residue retained on a glass fiber filter, with a specific pore size, after filtration of a sample of wastewater at a specific temperature (103 to 105°C).

### 2.2.2.3 Dissolved Solids (DS)

The solids that can pass through the filter with a pore size of 2.0 micron or smaller. Then, the filtrate is evaporated and dried at specific temperature (103 to 105°C).

### 2.2.2.4 Total Volatile Solids (TVS)

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

$$TVS = TS - ash \hspace{4cm} (2.13)$$

### 2.2.2.5 Volatile Suspended Solids (VSS)

VSS are determined by igniting the TSS at $550 \pm 50°C$ after placing the filter disk in a porcelain dish.

### 2.2.2.6 Biochemical Oxygen Demand (BOD)

BOD is a measuring parameter to determine the quantity of oxygen used by microorganisms in the aerobic stabilization of wastewaters and polluted waters. 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 waste, (3) only biodegradable organics are measured.

### 2.2.2.7 Chemical Oxygen Demand (COD)

COD is a method for measuring the concentration of organic compounds present in a wastewater sample using chemical oxidation reaction with potassium dichromate under acidic condition. The value of COD is calculated in terms of oxygen required for this chemical oxidation reaction. It presents both biodegradable and non-biodegradable organics in the sample.

*2.2.2.8 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:

$$\tau = \frac{V}{Q}$$ (2.12)

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 the process that digests the organic substrate by microorganisms. They derive energy and grow by metabolizing organic material in an absence of oxygen environment. The products of this process are the simple end-products, e.g. carbon dioxide and methane.

### 2.3.1 Process Description

There are three basic steps involved in this process:

*2.3.1.1 Hydrolysis*

Hydrolysis is the first step for most fermentation processes, in which particular material is 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 fermentation process, 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

fermentation (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. The process is shown in Figure 2.2.
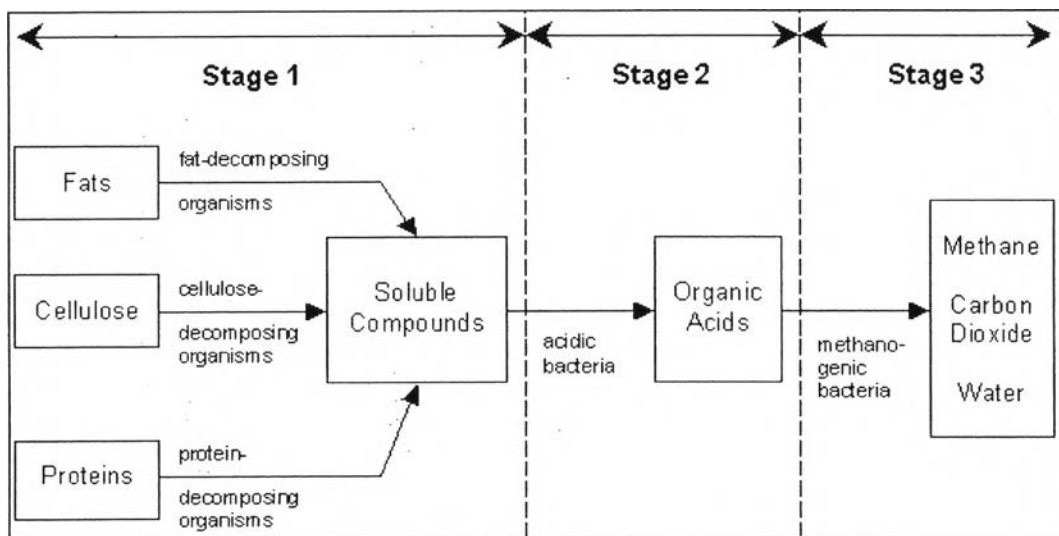


**Figure 2.2** Schematic representation of anaerobic biological treatment.

2.3.2 Effects of Temperature

One of the important factors controlling the anaerobic biological treatment process is temperature. Substrate degradation, $H_2$ production, product distribution, and bacteria growth are all affected by temperature.

There are two main temperature ranges for anaerobic biological treatment process.

- Mesophilic process is the most commonly used for anaerobic biological treatment process, in particular waste sludge treatment. Decomposition of the volatile suspended solids (VSS) is around 40 % over a retention time of 15 to 40 d at a temperature of 30 to 40°C, which requires larger digestion tanks. It is usually more robust than the thermophilic process, but the biogas production tends to be less, and additional sanitization is usually required.

- Thermophilic process operates at a high temperature. The process is heated to 55°C and held for a period of 12 to 14 d. The microorganism rapidly breaks down organic matter and produces large volumes of biogas. The quick breakdown means that the digester volume can be smaller than in other systems. Thermophilic processes provide higher biogas production, but the technology is more expensive, more energy is needed, and it is necessary to have more refined control and instrumentation. Greater insulation is necessary to maintain the optimum temperature range. These processes may be more sensitive to upset due to temperature variations. However, these processes are more effective in pathogen removal.

### 2.3.3 Advantages and Disadvantages of Anaerobic Biological Treatment

*2.3.3.1 Advantages of Anaerobic Biological Treatment*

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

• 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/m$^3$), depending on the need for pumping and recycling effluent.

• Less biological sludge production

• Fewer nutrients required

• Provision of energy source through methane recovery

• Smaller reactor volume required

• 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 construction costs are relatively low.

- 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 complementary treatment step is needed.

### 2.3.3.2 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 upset due to toxic substances

- Potential for production of odors and corrosive gases

### 2.3.4 Anaerobic Treatment Processes

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

*2.3.4.1 Anaerobic Suspended Growth Processes*

Anaerobic suspended growth processes are classified in three types:

• *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 ($\tau$ = SRT). Generally, hydraulic retention time may be in the range of 15 to 30 d 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.
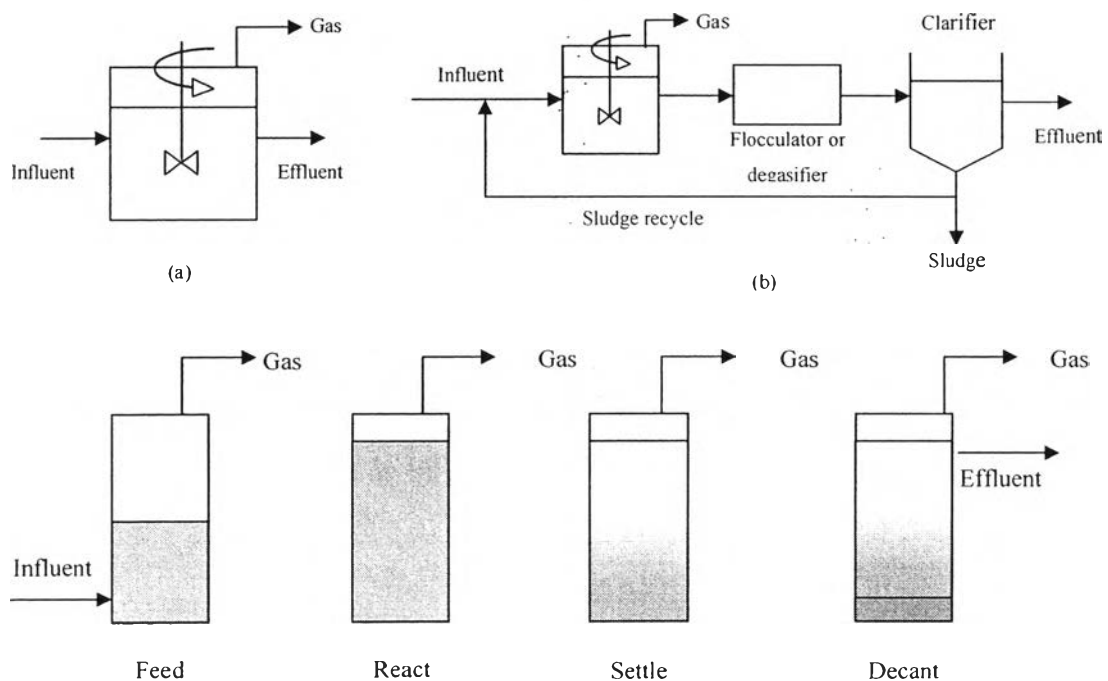


Figure 2.3 Anaerobic suspended growth processes: (a) complete-mix process, (b) anaerobic contact process, and (c) anaerobic sequencing batch reactor process.

**Table 2.1** Typical organic loading rates for anaerobic suspended growth processes at 30°C

| Process | Volumetric organic loading, kg COD/m$^3$d | Hydraulic retention time $\tau$, 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 |

- *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 the complete-mix or contact reactor so that the solid retention time (SRT) is longer than hydraulic retention time ($\tau$). The anaerobic reactor volume can be reduced by separating $\tau$ and SRT values. Gravitational separation is the most common approach for solid separation and thickening prior to 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 gravitational 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.

- *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 % COD removal can be achieved at volumetric organic loading of 1.2 to 2.4 kg $COD/m^3d$.

### 2.3.4.2 Anaerobic Sludge Blanket Processes

This process uses 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.

- *Upflow Sludge Blanket Reactor 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.
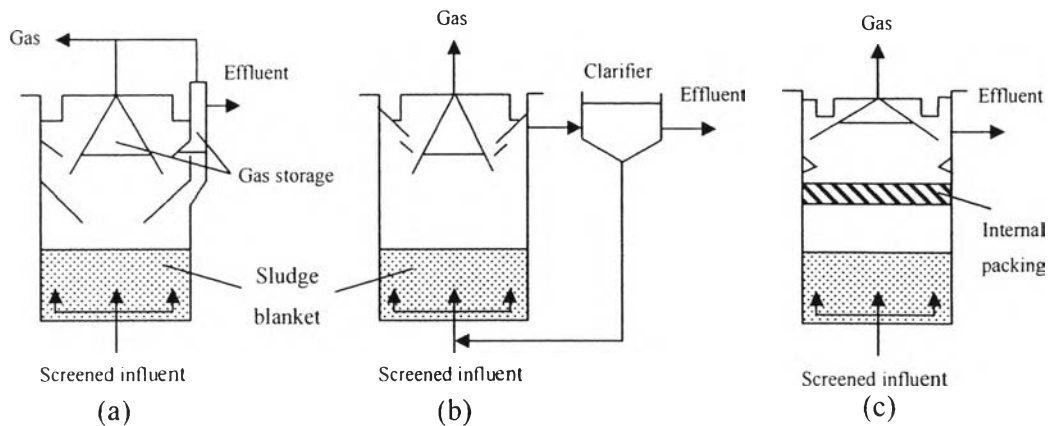
**Figure 2.4** Schematic of the UASB process and some modifications: (a) original process, (b) UASB reactor with sedimentation tank and sludge recycle, and (c) UASB reactor with internal packing for fixed-film attached growth.

- *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 of the baffle design, (2) hybrid reactors, where a settler is used to capture and return solids, or (3) packing is used in the upper portion of each chamber to capture solids.

- *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.
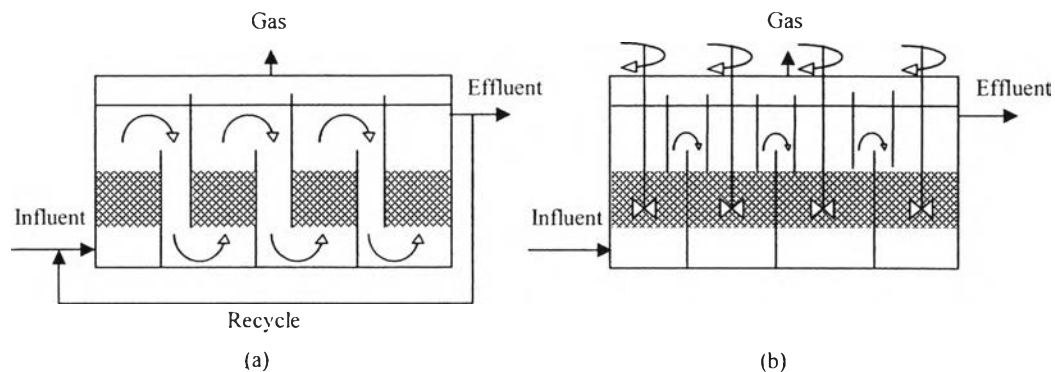
**Figure 2.5** Schematic of alternative sludge blanket processes: (a) anaerobic baffled reactor (ABR) and (b) anaerobic migrating blanket reactor (AMBR).

### 2.3.4.3  Attached Growth Anaerobic Processes

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

- *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 and 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 the washout of 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.

- *Upflow Attached Growth 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 and specific gravity of 2.65 as the packing material to support biofilm growth. Recycle is used to provide upflow velocity, resulting in 20 % bed expansion. 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 % 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.

- *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 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 % bed expansion. Both fluidization and mixing of the packing material occurs in fluidized-bed system. Effluent recycle is used to provide sufficient upflow velocity.
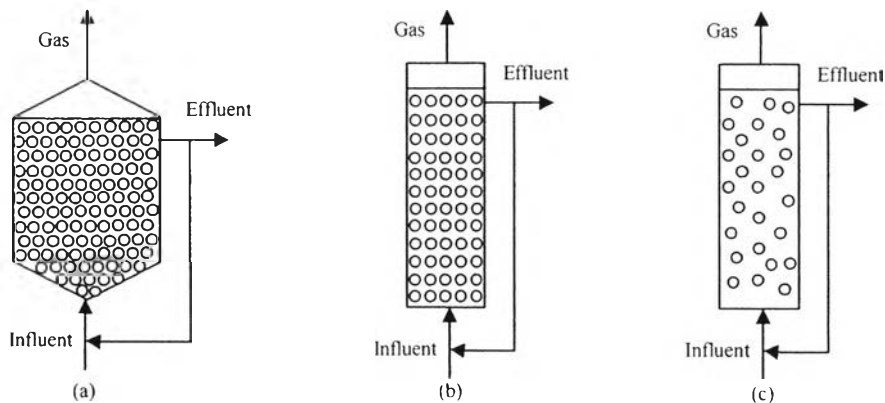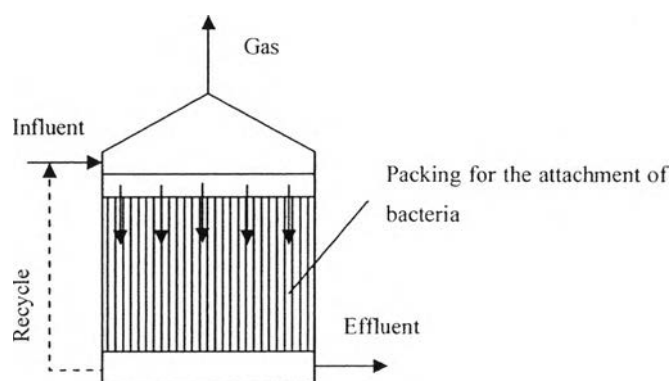
**Figure 2.6** Upflow anaerobic attached growth treatment reactors: (a) anaerobic upflow packed-bed reactor, (b) anaerobic expanded-bed reactor, and (c) anaerobic fluidized-bed reactor.

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.

• *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.

## 2.4 Hydrogen Production from Wastewaters by Using Anaerobic Sequencing Batch Reactor

The industrial production of several carbohydrate-containing products results in the discharge of large quantities of high-strength liquid wastes. These wastes not only have a high organic content, but also they are carbohydrate-rich. Hence, they are suitable to be feedstock for biohydrogen production by an anaerobic treatment process. Many wastewaters have been treated by an anaerobic sequencing batch reactor.

- Wastewater from olive mills, which had an average COD:N:P ratio of about 900:5:17, was treated by using an anaerobic sequencing batch reactor. COD removal more than 80 % was achieved at 3 d hydraulic retention time and at an organic load about 5.3 kg $COD/m^3/d$ (Bashaar, 2005).

- High-strength slaughterhouse wastewater, which contained between 30 and 53 % of its chemical oxygen demand (COD) as suspended solids (SS), was treated in an anaerobic sequencing batch reactor operated at 30, 25, and 20°C. The total COD was reduced by over 92 %, while average SS removal varied between 80 and 96 % (Masse and Masse, 2001).

- The biohydrogen production from dairy wastewater treatment in sequencing batch reactor (AnSBR) was found to be dependent on the organic loading rate applied. The optimum conditions for effective $H_2$ yield were acidophilic at pH 6. The results showed that COD removal efficiency was more than 50 % at operating organic loading rate less than 4.7 kg $COD/m^3/d$ (Mohan *et al.*, 2007).

- An anaerobic sequencing batch reactor was used for the hydrogen production from a glucose-containing wastewater operated at 37°C, a hydraulic reaction time (HRT) of 24 h, and different chemical oxygen demand (COD) loading rates from 10 to 50 kg $m^{-3}d^{-1}$ without and with pH control at 5.5. The results showed that the optimum COD loading rate of 40 kg $m^{-3}d^{-1}$ and pH 5.5 were found to provide 44 % $H_2$ and 56 % $CO_2$ (Sreethawong *et al.*, 2010b).

- The hydrogen production from a cassava wastewater using anaerobic sequencing batch reactors (ASBR) was studied. It was found that the operation at a COD loading rate of 30 kg/m$^3$d and 6 cycles per day provided maximum hydrogen production performance in terms of specific hydrogen production rate (SHPR) and hydrogen yield (Sreethawong *et al.*, 2010a).