CHAPTER II
LITERATURE REVIEW

2.1 Background of Hydrogen and Methane

Nowadays, humans are associated with energy use such as transportation, residential, commercial, and industrial. Most of the energy source is fossil fuels. The rapid consumption of these fossil resources causes carbon dioxide (CO_2) emission which is the primary greenhouse. The resulting increase of the carbon dioxide concentration in the atmosphere is known as the major cause of the global warming (Intanoo *et al.*, 2012). Moreover, the combustion of fossil fuels at the high temperatures and pressures can produce other toxic emissions such as CO_x, NO_x, SO_x, and C_xH_y which cause acid rain problems when released into the atmosphere (Searmsirimongkol *et al.*, 2012). Another problem is the rise of fossil fuel price in the future. To keep away these problems, hydrogen and methane have been focused for an alternative energy resource because they are renewable and environmentally friendly.

2.2 Advantages of Hydrogen

Hydrogen is a clean energy source because when it is burned, the only emission it makes is water. (carbon dioxide is not produced.) Therefore, 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.

Conventional fuels 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 the reduction of greenhouse gas emissions and can reduce the production of many toxic pollutants.

The greatest advantage of hydrogen is that it can be produced by several production processes, 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.
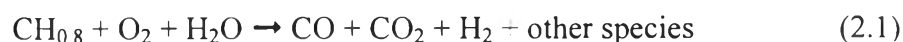
2.3 Advantages of Methane

Biomethane is one of a few alternative sources of energy which are not only renewable but are also environmentally friendly. It is produced from organic waste, sewage, and manure, which will never run out as long as there will be life on this planet. Another great advantage of biomethane over fossil fuels is the fact that it does not harm the environment in any way because it does not contribute to carbon dioxide emissions despite the fact that biomethane combustion produces this greenhouse gas as well. This is due to the fact that the utilization of biomethane is basically only utilization of energy which is released during the natural decomposition of organic matter. Carbon dioxide which is released into the atmosphere during biomethane combustion equals the amount of carbon dioxide that is emitted during natural decomposition of manure for instance.

2.4 Hydrogen Production Processes

To use hydrogen as a fuel, it is necessary to break up hydrogen bond in organic matter and in water. There are many methods for producing hydrogen, as shown below.

2.4.1 Coal Gasification

Coal gasification is a process to convert the coal in solid state to gaseous state at high temperature (1330 °C). The first reaction, 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.

$$CH_{0.8} + O_2 + H_2O \rightarrow CO + CO_2 + H_2 + \text{other species} \qquad (2.1)$$

$$CO + H_2O \rightarrow CO_2 + H_2 \qquad (2.2)$$

2.4.2 Thermal Cracking of Methane

Thermal cracking is a high temperature process about 2,000 °C and endothermic reaction. This is an alternative method to replace steam reforming process because of no carbon dioxide emission. The reaction is shown below:

$$CH_4 \rightarrow C + 2H_2 \qquad (2.3)$$

### 2.4.3 Partial Oxidation (POX)

Partial oxidation is the process producing hydrogen through the partial combustion of methane with oxygen gas to yield synthesis gas (carbon monoxide and hydrogen) (2.4). 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 (Riis *et al.*, 2006).

$$CH_4 + 1/2O_2 \rightarrow CO + 2H_2 \qquad (2.4)$$

2.4.4 Electrolysis

Electrolysis of water may be the cleanest technology for hydrogen gas production (Kapdan *et al.*, 2006). It is a process for producing hydrogen by applying electric current into water. When two metal plates are placed in water in the presence

of a catalyst and connected to a source of electricity, water is split into its chemical components (hydrogen and oxygen). 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. The chemical reaction of water electrolysis is:

$$2H_2O + energy \rightarrow 2H_2 + O_2 \tag{2.5}$$
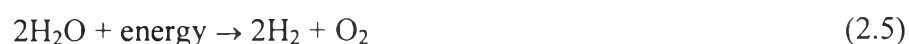
However, this method is not efficient when it comes to produce large amounts of hydrogen. This is because it is energy-intensive, and if using electricity generated from fossil fuels, carbon dioxide will be produced at an earlier stage in the process.

2.4.5 Biological Process

Biological process for hydrogen production, also known as "bio-hydrogen 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:

2.4.5.1 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 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.

2.4.5.2 Dark-fermentation

Hydrogen production via dark fermentation is a special type of anaerobic digestion process comprising only hydrolysis and acidogenesis. 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. 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. 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 *et al.*, 2001).

2.5 Cassava Production in Thailand

Cassava can be grown in most parts of Thailand, especially in the Northeastern region (Sangyoka, 2006). Nowadays, more and more cassava roots are utilized for production of starch, not only produced for domestic use but also for export. About 40 % of cassava starch is used domestically, mainly as chemically or physically modified starch, as sweeteners or as native starch in many industries. The remaining 60 % is exported, mainly in the form of native or modified starch. During the past ten years, exports of cassava starch and starch-derived products have increased dramatically (Poramacom *et al.*, 2013). Cassava is a lignocellulosic biomasss which mainly composed of carbohydrate polymers such as cellulose and

hemicellulose with a small of aromatic polymer (lignin). These carbohydrate polymers contain different sugar monomers (six and five carbon sugars) and they are tightly bound to lignin.

2.6 Cassava Wastewater

Cassava wastewater is a carbohydrate-rich waste which generated from washing and starch extraction processes. 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 (Ugwu *et al.*, 2012). Thus, there is a need to treat this effluent before being discharged into the environment.

2.7 Common Parameters in Wastewater

2.7.1 Total Solids (TS)

Analytically the total solids content of a wastewater is defined as the residual left after evaporation at 103 to 105 °C. Matter that has a significant vapor pressure at this temperature is lost during evaporation and is not defined as a solid. The concentration of total solids is the weight of dried solids divided by the volume of the sample, usually expressed in milligrams per liter (mg/l).

2.7.2 Total Volatile Solids (TVS)

Total volatile solids (TVS) are determined by ignited the TS at 550±50 °C in a furnace. The residue that remains after burning is called fixed solids, and the loss of weight upon ignition is referred to volatile solids. The concentration of total volatile solids is the weight of dried solids minus the weight of fixed solids divided by the volume of the original wastewater sample. Volatile solid content also can be expressed as a percentage of the dry solids in the sample.

2.7.3 Total Suspended Solids (TSS)

TSS is defined as the non-filterable residue that is retained on a glass-fiber disk after filtration of a sample of wastewater. The principle of TSS is that a well-mixed sample is filtered through a weighed standard glass fibre filter and the

residue which is retained on the filter is dried to a constant weight at 103-105 °C. The increase in the weight of the filter determines the total suspended solids.

$$TSS = \frac{\left(\begin{array}{c}weight\ of\ simple\\ after\ drying, g\end{array}\right) - \left(\begin{array}{c}tare\ weight\ of\ filter\\ before\ use, g\end{array}\right)}{voume\ of\ sample, L} \qquad (2.13)$$

2.7.4 Volatile Suspended Solids (VSS)

Volatile suspended solids (VSS) are represented the undissolved organic fraction which determined by calcided the filtered solid at 550±50 °C. The concentration of volatile suspended solids is the weight difference between the dried solids and the fixed solids, divided by the volume of the original liquid sample.

2.7.5 Total Dissolved Solids (TDS)

Dissolved solids are solids that are in dissolved state in solution. Total dissolved solids (TDS) are the difference in the weight of total solids and the total suspended solids expressed in the same units (Metcalf *et al.*, 2003).

$$TDS = TS - TSS \qquad (2.14)$$

2.7.6 Biochemical Oxygen Demand (BOD)

BOD is defined as the amount of oxygen required to oxidize organic matter in water by microorganisms under aerobic conditions. The BOD test is used to define the pollution load of wastewater, the degree of pollution and the efficiency of wastewater treatment methods. This method composes of filling the samples in airtight bottles of specified size and incubating them at specified temperature (20 °C) for 5 days. The BOD of the sample is determined as the difference in the dissolved oxygen measured initially and after incubation.

2.7.7 Chemical Oxygen Demand (COD)

Chemical oxygen demand (COD) is a method to measure the oxygen equivalent of the organic compounds that present in wastewater using chemical oxidation reaction with dichromate in an acid solution. The organic matter is

converted into carbon dioxide and water. COD value presents both biodegradable and non-biodegradable organic matter in the sample.

2.8 Anaerobic Fermentation Process

2.8.1 Fundamental of Anaerobic Fermentation Process

The overall conversion process of anaerobic or dark fermentation is often described as a three-stage process, which occurs simultaneously within anaerobic digesters: hydrolysis, acidogenesis, and methanogenesis (Metcalf *et al.*, 2003), as illustrated in Figure 2.1.
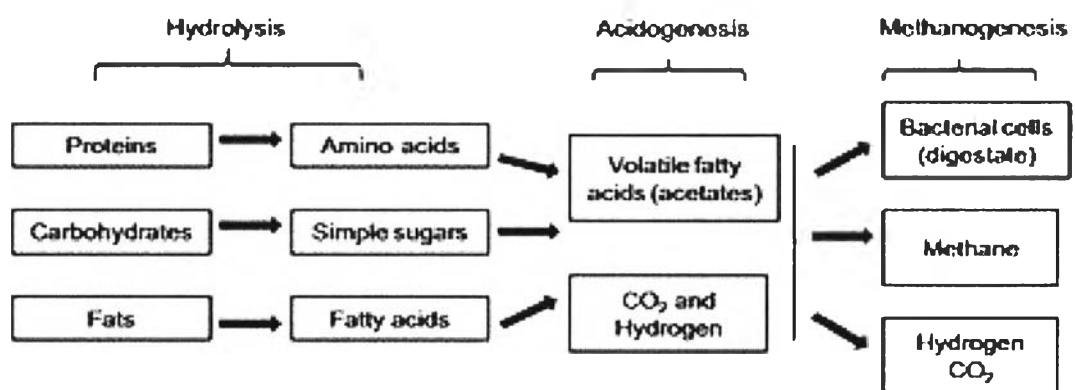
Figure 2.1 Flow diagram of the anaerobic digestion process.

2.8.1.1 Hydrolysis

In the first step of hydrolysis, large, complex, and insoluble organics (protein, polysaccharides, and lipids) will be broken down enzamatically into small molecules (amino acids, sugars, and fatty acids) that can be transported into the microbial cells, metabolized, and further used by bacteria that perform fermentation.

2.8.1.2 Acidogenesis

Acidogenesis is a second step. At this step, amino acids, sugars, and some fatty acids are degraded further, as shown in Figure 2.1. 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).

2.8.1.3 Methanogenesis

This is the third step of anaerobic biological treatment, methanogenesis, carried out by methanogens microorganisms. For methane production, there are two groups of methanogenic organisms involved. The first group is acetoclastic methanogens. It splits acetate into carbon dioxide and methane. The second group is hydrogen-utilizing methanogens. It uses hydrogen as the electron donor and carbon dioxide as the electron acceptor for producing of methane. Moreover, bacteria in terms of acetogens also use carbon dioxide to oxidize hydrogen and form acetic acid. However, the acetic acid will be converted to methane around 72 %, which has the negative impact to environment.

2.8.2 Types of Anaerobic Treatment Processes

Anaerobic treatment is an excellent odor-reducing technique. It will convert the degradable solids to gas in a tank for use as a fuel. If substantial portions of the solids are degraded in the digester, it will reduce odor in the digested liquid and solid effluent. There are several types of anaerobic treatment processes as follow.

2.8.2.1 Anaerobic Suspended Growth Treatment Processes

There are three basic types of anaerobic suspended growth treatment processes (Metcalf et al., 2003).

(1) Complete-mix Process

For the complete-mix anaerobic digester as shown in Figure 2.2a, the solid retention time and hydraulic retention time are equal, maybe in the range of 15 to 30 d. The complete-mix digester without sludge recycle is more suitable for wastes with high concentrations of solids or extremely high dissolved organic concentrations, where it is difficult for thickening the effluent solids. Organic loading rates for this process are present in Table 2.1, as compared to anaerobic contact and anaerobic sequencing reactor processes.

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 (τ), day
Complete-mix	1.0-5.0	15-30
Anaerobic contact	1.0-8.0	0.5-5
Anaerobic sequencing batch reactor	1.2-2.4	0.25-0.50

(2) Anaerobic Contact Process

This process, as shown in Figure 2.2b, can overcome the disadvantages of a complete-mix process without recycle. Separated biomass is returned to the complete-mixed or contact reactor, so the solid retention time (SRT) is longer than hydraulic retention time (τ). This process can reduce the anaerobic reactor volume by increasing SRT with a short τ value. Gravity separation is the most common approach for thickening and solid separation prior to sludge recycle. In some cases, gas flotation is used for solid separation by dissolving the process off-gas under pressure. 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 Bath Reactor (ASBR)

This reactor, as shown in Figure 2.2c, is typically operated under batch-mode feeding with four different sequencing phases, including feed, react, settle, and decant or effluent withdrawal. The completely mixed condition is only done during the react phase to provide uniform distribution of substrate and microbial cells.
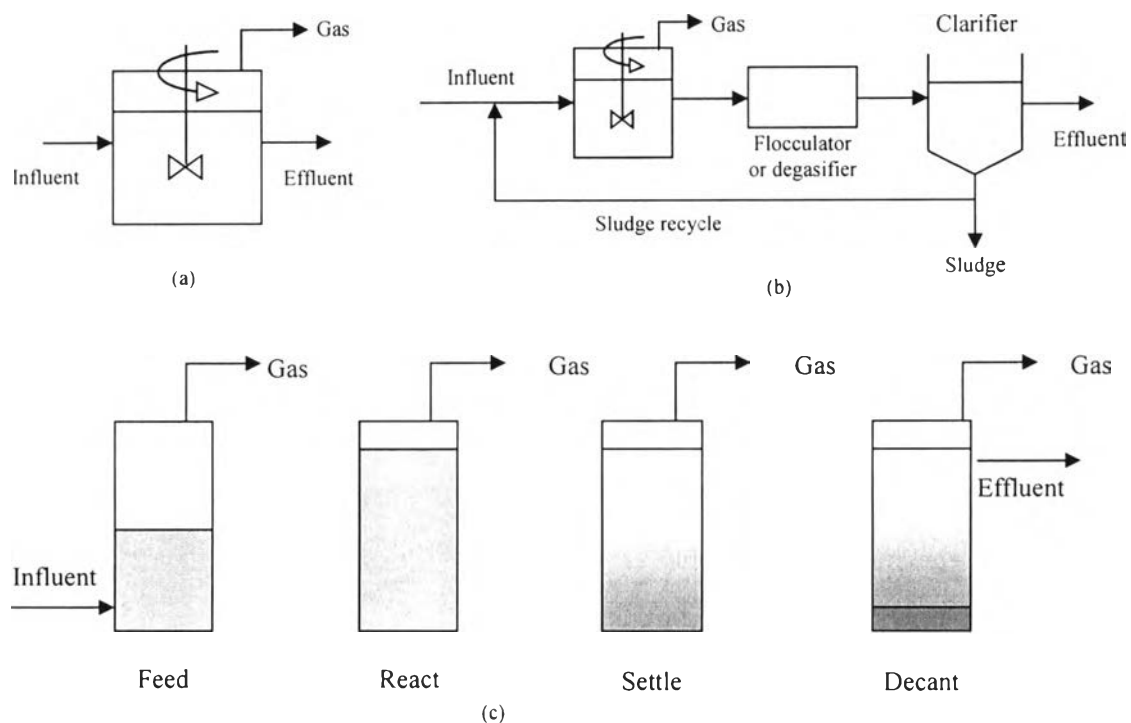
Figure 2.2 Anaerobic suspended growth processes: (a) complete-mix process, (b) anaerobic contact process, and (c) anaerobic sequencing batch reactor process.

2.8.2.2 Anaerobic Sludge Blanket Processes

These principal types of anaerobic sludge blanket processes include the original upflow anaerobic sludge blanket (UASB) process, anaerobic baffled reactor (ABR), and anaerobic migrating blanket reactor (AMBR). Among them, the UASB process is the most commonly used, with over 500 installations treating a wide range of industrial wastewaters (Metcalf and Eddy, 2003).

(1) Upflow Anaerobic Sludge Blanket (UASB)

The basic UASB reactor is shown in Figure 2.3a. The influent wastewater is distributed at the bottom of the reactor and travels in an upflow mode through the sludge blanket. The influent distribution system, the effluent withdrawal design, and the gas-solid separator are the critical elements of the UASB reactor design and operation. Modifications to the basic UASB design include adding a settling tank, as shown in Figure 2.3b, or the use of packing material at the top of the reactor, as shown in Figure 2.3c. The key feature of this process that

allows the use of high volumetric COD loadings compared with other anaerobic processes is the development of a dense granulated sludge depending on the proper design and operation, and the characteristic of wastewater.
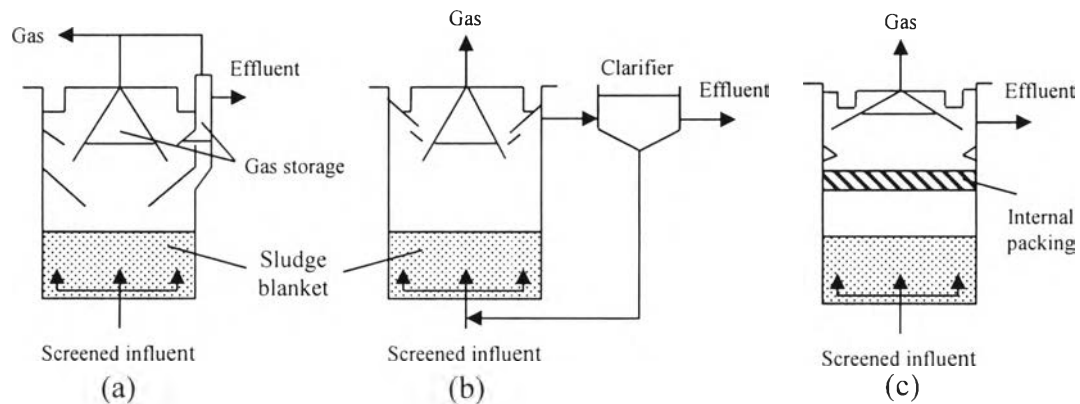
Figure 2.3 Schematic of the UASB process and some modifications: (a) original UASB process, (b) UASB reactor with sedimentation tank and sludge recycle, and (c) UASB reactor with internal packing for fixed-film attached growth, placed above the sludge blanket.
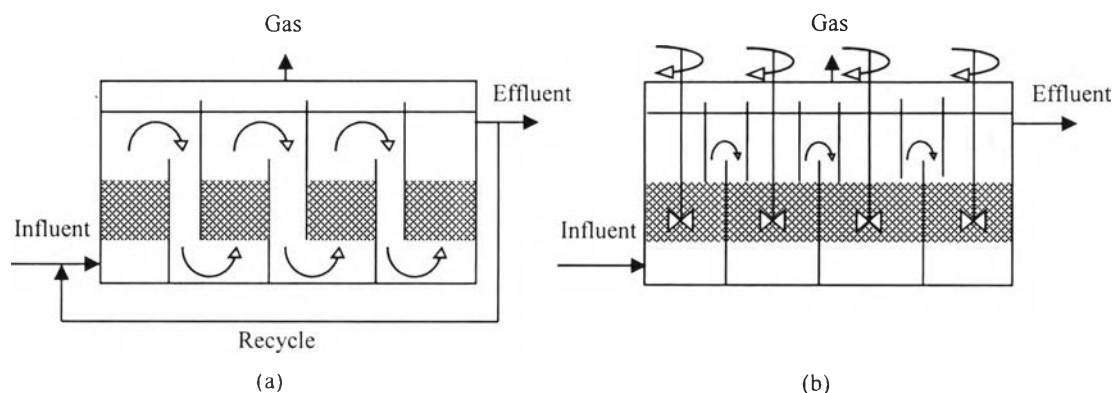
(2) Anaerobic Baffled Reactor (ABR)

In the ABR process, as shown in Figure 2.4a, 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.

Advantages of the ABR process include the following:

- Long solid retention time possible with a low hydraulic retention time
- No special biomass characteristics required
- Wastewaters with a wide variety of constituent characteristics can be treated
- Stable to shock loads

(3) Anaerobic Migrating Blanket Reactor (AMBR)

The 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 2.4b. In this process, the 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 2.4 Schematic of alternative sludge blanket processes: (a) anaerobic baffled reactor (ABR) and (b) anaerobic migrating blanket reactor (AMBR).

2.8.2.3 Attached Growth Anaerobic Processes

Upflow attached growth anaerobic treatment reactors differ by the type of packing media used and the degree of bed expansion. This attached growth can be classified as following details (Metcalf and Eddy, 2003).

(1) Upflow Packed-bed Attached Growth Reactor

Full-scale upflow packed-bed anaerobic filters are used in cylindrical or rectangular tanks at widths and diameters ranging from 2 to 8 m and heights from 3 to 13 m, as shown in Figure 2.5a. The most common packing materials are corrugated plastic crossflow or turbular modules and plastic pall rings. 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 void to cause plugging and flow short circuiting. At this point, solids must be removed by flushing with a high liquid velocity.

The 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.
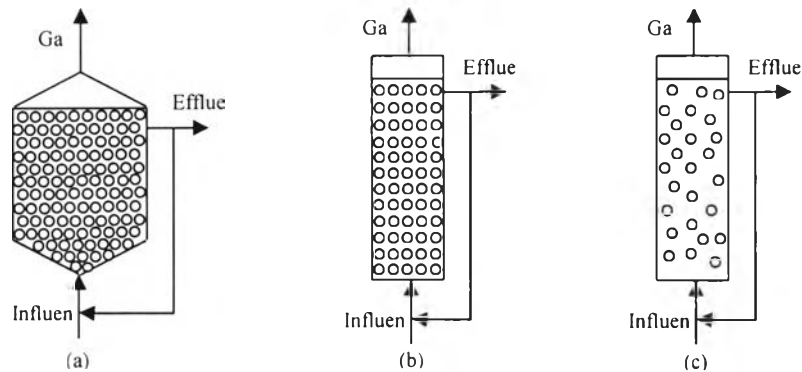
(2) Upflow Attached Growth Anaerobic Expanded-bed
    Reactor

The anaerobic expanded-bed reactor (AEBR), as shown in Figure 2.5b, uses silica sand with a diameter in the range of 0.2 to 0.5 mm and specific gravity of 2.65 as the support particle to provide biofilm growth. The smaller particle provides a greater surface area per unit volume. With such a small partickesize 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. Most applications for the AEBR treatment process have been for the treatment of domestic wastewater.

(3) Attached Growth Anaerobic Fluidized-bed Reactor

This anaerobic fluidized-bed reactor (AFBR), as shown in Figure 2.5c, is similar in physical design to the upflow expanded-bed reactor. The support particle 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. Effluent recycle is used to provide a sufficient upflow velocity.

The advantages of the AFBR process include the ability to provide a high biomass concentration with a relatively high organic loading rate, high mass transfer characteristics, the ability to handle shock loads and minimal space requirements because of its good mixing and the dilution with recycle.
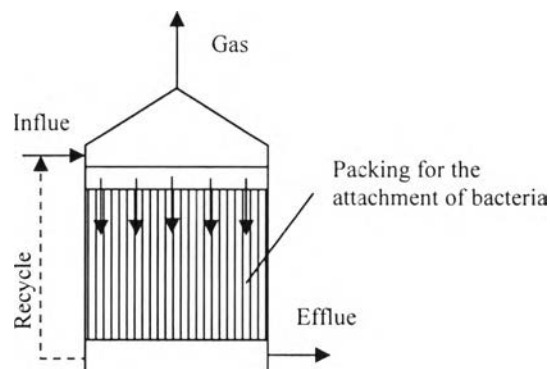
Figure 2.5 Upflow anaerobic attached growth treatment reactors: (a) anaerobic upflow packed-bed reactor, (b) anaerobic expanded-bed reactor, and (c) anaerobic fluidized-bed reactor.

(4) Downflow Attached Growth Process

The downflow attached growth anaerobic processes, as illustrated in Figure 2.6, 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.

The major advantages for the downflow attached growth process, where a higher void space packing material is used, are a simple inlet flow distribution design, a high COD loading rate, and a simple operation. However, the process has two main drawbacks of the high cost of packing media and clogging problem from the excessive growth.

Figure 2.6 Downflow attached growth anaerobic treatment reactor.

2.9 Two-Step Hydrogen and Methane Production

One of the significant problems in the dark hydrogen fermentation process is that most of the organic fraction of the feeding wastewater remains as soluble fermentation products. So, a complementary stage after fermentation would be necessary for COD elimination. It is well known that VFA formation during acidogenesis of the organic matter is actually the precursor to methanogenesis. Therefore, the hydrogen production process could be efficiently coupled with a subsequent anaerobic digestion step with the conversion of the remaining organic content to biogas (mainly methane and carbon dioxide). A two-stage anaerobic digestion process consists of acidogenesis and methanogenesis that occur in separate reactors. This process improves hydrogen and methane production and achieves stabilization of the treated wastewater prior to disposal.

Two-stage fermentation is a process that involves with using two separate reactors. The first reactor is acidogenic-stage, which is maintained at a low pH or alkalinity and develops a high CO_2 and low CH_4 content in the gaseous products. Acidifying organisms dominate in the first reactor, and the major biochemical reaction is enzymatic hydrolysis and fermentation. The second one is methanogenic-stage, which is maintained at pH around 7 and high alkalinity, resulting in high specific methanogenic activity.

As compared two-stage fermentation with conventional single-stage fermentation, two-stage fermentation exhibited more advantages:

- Have short hydraulic retention time for rapidly degradable waste.
- Higher COD removal efficiency.
- Higher methane concentration in the gaseous products because the specific activity of methanogenic bacteria increases.
- Better process reliability, resilience, and stability, especially with variable waste conditions and readily degradable waste, which causes unstable performance in one-stage system.
- Physical separation of the acidogenic and methanogenic bacteria for maximum hydrogen and methane production rate.

- The acid phase and methane phase can be started much more easily and quickly than in conventional, single-stage digesters.

Sarada *et al.* (1996) investigated the methane production performance of single and two stage processes from tomato processing waste. The results reported that under similar conditions (30°C, 24 days HRT and 4.5 kg/m^3/day loading rate), methane production efficiency of a two-stage anaerobic system gave a 50 % increase in the gas production rate and 40 % increase in the methane yield when compared with a single-stage process.

Ke *et al.* (2005) reported that two-stage process achieves enhanced stabitily and higher loading capacities for the methanogenesis process compared with the traditional one stage process. Moreover, it provided better process efficiencies overall.

Lui *et al.* (2006) studied on the two-stage process combining hydrogen and methane production and compared with the traditional one-stage process. It had been found that the methane production in two-stage process obtained methane higher than in one-stage process. This is because total VFA value in the second-stage process was much lower than in one-stage process. It shows that more VFAs were converted to methane in two-stage process.

Tahti *et al.* (2013) studied on hydrogen and methane production in extreme thermophilic (77 °C) conditions by using two-stage upflow anaerobic sludge blanket reactor. The hydrogen reactor was operated with hydraulic retention time (HRT) of 5 h and organic loading rate (OLR) of 25.1 kg COD/m^3/d. The hydrogen yield was 0.73 mol/mol glucose$_{added}$. For methane reactor, operated with HRT of 13 h and organic loading rate (OLR) of 7.8 kg COD/m^3/d, methane yield was 11.75 ml/g COD$_{added}$. The also reported that two stage process was more stable compared to one stage methane production.