

## CHAPTER II

### LITERATURE REVIEW

#### 2.1 Limitations of Conventional Hydrogen and Methane Production

Conventional hydrogen production technologies and limitations molecular hydrogen does not occur naturally in the Earth's crust. For practical applications, molecular hydrogen needs to be produced. At present, the total annual world hydrogen production is around 368 trillion cubic meters ([www.fsec.ucf.edu](http://www.fsec.ucf.edu)). Out of the total global production of hydrogen, 48% is produced from steam methane reforming, about 30% from oil/naphtha reforming from refinery/chemical industrial off-gases, 18% from coal gasification, 3.9% from water electrolysis, and 0.1% from other sources(Jeffrey *et al.*, 2010). These figures imply that globally 96% of the hydrogen production comes from fossils. However, these conventional processes are energy intensive and not always environmentally friendly. For example, methane steam reforming, coal gasification, and methane pyrolysis produce 0.25, 0.83, and 0.05 mol CO<sub>2</sub>mol<sup>-1</sup>H<sub>2</sub>, respectively(Abanades *et al.*, 2012).

Methane contributes to the enhanced greenhouse effect. Wetlands, including rice paddies, contribute between 15 and 45% of global methane emissions(Prather *et al.*, 1995). Methane emissions from wetlands show a large variation (Bartlett & Harris., 1993) which can only partly be described by correlations with environmental variables (Kettunen *et al.*, 1996). This limits the accuracy of estimates of both current and future global emissions, the latter being the result of possibly changed conditions due to a change in climate or changed soil management. Insight in the underlying processes could improve this situation.

## 2.2 Hydrogen and Methane Production Methods

### 2.2.1 Hydrogen Production Methods

At present hydrogen is produced mainly from fossil fuels, biomass and water. Among this method steam-reforming process alone produces nearly 90% of hydrogen (Das *et al.*, 2001).

#### 2.2.1.1 Method Adopted to Produce Hydrogen from Fossil Fuels

Method adopted to produce hydrogen from fossil fuels are based on the following, viz:

##### 2.2.1.1.1 *Steam Reforming of Natural Gas*

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<sub>2</sub>) and carbon monoxide (CO). This can be described by the following reaction.



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.



##### 2.2.1.1.2 *Thermal Cracking of Natural Gas*

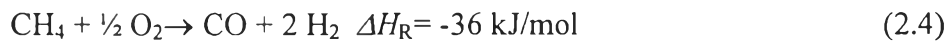
Thermal cracking of natural gas, such as methane, is a high temperature process, which can replace steam reforming process because of no carbon dioxide emission. It requires high temperature about 2,000°C to produce 60 % of hydrogen and 40 % of carbon black that is a pigment used in many dyeing processes (Kothari *et al.*, 2004). The reaction of this process is:



#### 2.2.1.1.3 *Partial oxidation of Heavier than Naphtha*

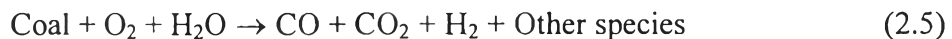
##### *Hydrocarbons*

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. 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:



#### 2.2.1.1.4 *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 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).

#### 2.2.1.2 *Method Adopted to Produce Hydrogen from Water*

Method adopted to produce hydrogen from water are based on the following, viz:

##### 2.2.1.2.1 *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:



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.

#### *2.2.1.2.2 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.

#### *2.2.1.2.3 Thermochemical Process*

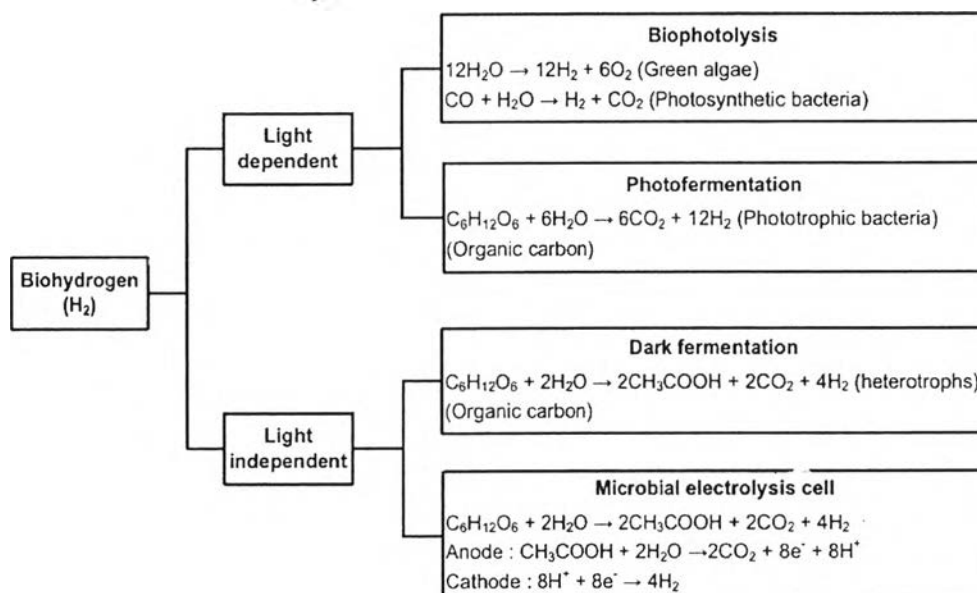
Thermochemical process is developed from thermolysis in order to mitigate the high temperature required. It uses solar energy to drive an endothermic reversible reaction that produces hydrogen (Meyerset al., 2001).

#### *2.2.1.2.4 Direct Thermal Decomposition or Thermaolysis*

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.

### 2.2.1.3 *Method Adopted to Produce Hydrogen from Biological*

#### *Methods*



**Figure 2.1** Biological pathways to produce hydrogen.

Method adopted to produce hydrogen from biological methods as shown in Figure 2.1 are based on the following, viz:

#### 2.2.1.3.1 *Biophotolysis of Water by Algae and Cyanobacteria*

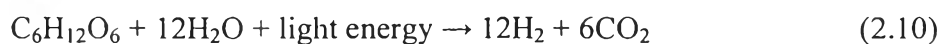
For direct biophotolysis by algae, this method is the same process as found in plants and algae photosynthesis. The solar energy as the light source is directly converted to hydrogen in a direct photosynthesis reaction, as follows:



This is an attractive process because solar energy is used to convert a readily available substrate, water, to oxygen and hydrogen. However, only under this condition, hydrogen production is possible by using

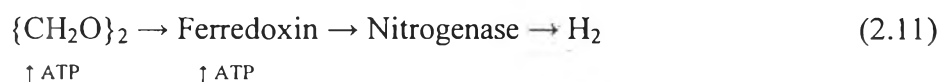
Fehydrogenase as an enzyme since the activity of this enzyme is extremely oxygensensitive.

For indirect biophotolysis by cyanobacteria, in indirect photolysis, the sensitivity of hydrogen processing problems is potentially circumvented by separating temporally oxygen and hydrogen evolution. Thus, indirect biophotolysis processes involve separation of the hydrogen and oxygen evolution reactions into separate stages, coupled through carbon dioxide fixation. Cyanobacteria or blue-green algae have the unique characteristics of using carbon dioxide in the air as a carbon source and solar energy as energy source (Equation 2.9). The cell takes up carbon dioxide first to produce cellular substrates, which are subsequently used for hydrogen production (Equation 2.10). The overall mechanism of hydrogen production in cyanobacteria can be represented as:

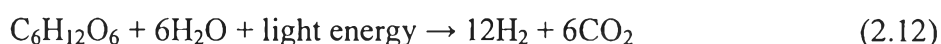


#### 2.2.1.3.2 Photodecomposition of Organic Compounds by Photosynthetic Bacteria.

Photosynthetic bacteria evolve molecular hydrogen catalyzed by nitrogenase under a lack of nitrogen conditions using light energy and reduced organic acids. These bacteria themselves are not powerful enough to split water. However, under anaerobic conditions, these bacteria are able to use simple organic acids, like acetic acid, as electron donors. These electrons are transported to the nitrogenase by ferredoxin using energy in the form of ATP. When nitrogen is not present, this nitrogenase enzyme can reduce proton into hydrogen gas again using extra energy in the form of ATP (Equation 2.11).



The overall reaction of hydrogen production can be given as Equation 2.12.

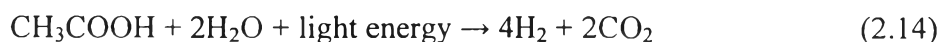


### 2.2.1.3.3 *Hybrid Systems using Photosynthetic and Fermentative Bacteria*

Hybrid system comprises on non-photosynthetic and photosynthetic bacteria. It can enhanced the hydrogen production. Variety of carbohydrates as substrates can be digested by fermentative bacteria to produce hydrogen with degradation of substrates without using light (Equation 2.13).



Resulting organic acids, like acetic acid, from dark-fermentation stage can be oxidized by photosynthetic bacteria with using light in the next stage to produce hydrogen (Equation 2.14).



The combination of the both kinds of bacteria not only reduces the light energy demand of photosynthetic bacteria but also increases hydrogen production.

### 2.2.1.3.4 *Fermentative Hydrogen Production from Organic Compounds*

It is well known that dark fermentation process is the highly potential method for hydrogen production. Carbohydrate-rich substrates are a suitable feedstock while protein, amino acid, and peptides are relatively less suitable for biohydrogen production from dark fermentation process. Many kinds of wastewaters have been used as substrate to produce hydrogen.

## 2.2.2 Methane Production Methods

### 2.2.2.1 Biological Method

Naturally occurring methane is mainly produced by the process of methanogenesis. This multistep process is used by microorganisms as an energy source. The net reaction is:



The final step in the process is catalyzed by the enzyme methyl-coenzyme M reductase. Methanogenesis is a form of anaerobic

respiration used by organisms that occupy landfill, ruminants (e.g., cattle), and the guts of termites.

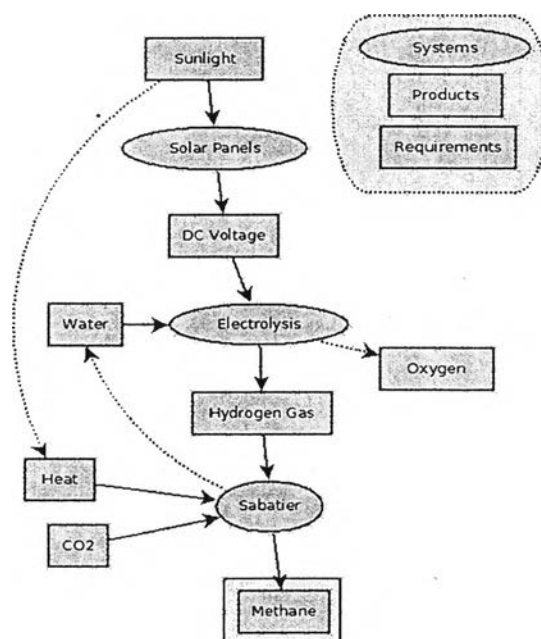
#### 2.2.2.2 *Serpentinization*

Methane could also be produced by a non-biological process called serpentinization involving water, carbon dioxide, and the mineral olivine, which is known to be common on Mars.

#### 2.2.2.3 *Industrial method*

Methane can be produced by hydrogenating carbon dioxide through the Sabatier process. Methane is also a side product of the hydrogenation of carbon monoxide in the Fischer-Tropsch process. This technology is practiced on a large scale to produce longer chain molecules than methane.

An adaptation of the Sabatier methanation as shown in Figure 2.2 may be used via a mixed catalyst bed and a reverse water gas shift in a single reactor to produce methane from the raw materials available on Mars, utilizing water from the Martian subsoil and carbon dioxide in the Martian atmosphere.



**Figure 2.2** A method for producing methane sustainably.



#### 2.2.2.4 Laboratory Synthesis

Methane can also be produced by the destructive distillation of acetic acid in the presence of soda lime or similar. Acetic acid is decarboxylated in this process. Methane can also be prepared by reaction of aluminium carbide with water or strong acids.

### 2.3 Anaerobic Hydrolysis and Microaeration

Complex wastewater has been proven to be degradable under anaerobic conditions. During the digestion process in the conversion of the complex organic molecules into mono- and dimmer components, also called the hydrolysis, is often the rate-limiting step. Design and optimization of the anaerobic conversion of complex waste (water) is essential (Sanders., 2001).

**Table 2.1** Advantages and disadvantages of various pretreatment processes for lignocellulosic materials (Balat., 2011)

Pretreatment process	Advantages	Disadvantages
<b>Mechanical comminution</b>	Reduces cellulose crystallinity	Power consumption usually higher than inherent biomass energy
<b>Steam explosion</b>	Causes hemicellulose degradation and lignin transformation; cost-effective	Incomplete disruption of the lignin-carbohydrate matrix; generation of compounds inhibitory to microorganisms
<b>CO<sub>2</sub> explosion</b>	Increases accessible surface area; cost-effective; does not cause formation of inhibitory compounds	Does not modify lignin or hemicelluloses
<b>Ozonolysis</b>	Reduces lignin content; does not produce toxic residues	Large amount of ozone required; expensive
<b>Acid hydrolysis</b>	Hydrolyzes hemicellulose to xylose	High cost; equipment corrosion;

	and other sugars; alters lignin structure	formation of toxic substances
<b>Alkaline hydrolysis</b>	Removes hemicelluloses and lignin; increases accessible surface area	Long residence times required; irrecoverable salts formed and incorporated into biomass
<b>Pyrolysis</b>	Produces gas and liquid products	High temperature; ash production
<b>Biological</b>	Simple equipment degrades lignin	Rate of hydrolysis is very low

Aerobic and anaerobic (including anoxic) digestion are the two major biological treatment methods for wastewater. Under aerobic conditions, organic components are oxidized to carbon dioxide and under anaerobic to carbon dioxide and methane. When comparing the two treatment methods with respect to sustainability, anaerobic digestion by far is the favorite because hardly if any energy input is needed, the methane produced can be used as a substitute for fossil fuels, and the production of excess sludge is much lower. Moreover, the technology of anaerobic treatment is much less complex, and anaerobic systems are applicable at any site and any size (Sanders et al., 2001).

Most of the substrate in complex waste (water) is present as particulate matter. Although less common, some of the complex waste (water) contains a significant amount of dissolved substrate requiring hydrolysis (Levine *et al.*, 1991).

The main intermediates and end-products of the anaerobic digestion process are volatile fatty acids, hydrogen, and biogas, respectively. Because the methanogenic bacteria are very sensitive to a drop in pH that could be caused by accumulation of volatile fatty acids, the digestion of complex waste obviously is a delicate balance between the rate of hydrolysis, acidogenesis, and methanogenesis (Sanders et al., 2001).

Veeken *et al.*, (2000) studied the anaerobic hydrolysis rate of organic solid waste at fixed volatile fatty acid (VFA) concentrations ranging from 3 to 30 g COD/L and fixed pH values between 5 and 7. For separate control of both VFA and pH, a special completely mixed reactor was designed. Results showed that hydrolysis of the organic solid waste followed first-order kinetics. Using a statistical analysis

found that the hydrolysis rate constant was pH dependent but was not related to the total VFA and undissociated VFA concentrations.

After that, Denise *et al.* (2012) studied the effect of pH control and hydraulic flush on hydrolysis and VFA production and profile in anaerobic leach bed reactors digesting a high solids content substrate. The results showed that buffering at pH~6.5 improved hydrolysis (volatile solid (VS) degradation) and VFA production by ~50%. Butyric and acetic acid were dominant, when reactors were buffered, while only butyric acid was produced at low pH. Hydraulic flush enhanced VS degradation and VFA production by ~15% and ~32%, respectively. Most Probable Number (MPN) of cellulolytic microorganisms indicated a wash out when hydraulic flush was applied, but pH control helped to counteract this. The highest VS degradation (~89%), VFA yield ( $0.84 \text{ kgCOD} \cdot \text{kg}^{-1} \text{VS}_{\text{added}}$ ) and theoretical methane potential ( $0.37 \text{ m}^3 \text{CH}_4 \cdot \text{kg}^{-1} \text{VS}_{\text{added}}$ ) were obtained when pH control and hydraulic flush were applied.

Jenicek (Jenicek et al., 2011) described microaerobic condition that it was a condition between aerobic and anaerobic systems such as aerobic system with low oxygen concentration and anaerobic system with limited  $\text{O}_2$  supply. Besides, he indicated the potential benefits and drawbacks of microaerobic conditions were as follows:

Potential benefits of microaerobic conditions;

- Augmentation of microbial species diversity
- Improvement of biogas composition (hydrogen sulfide removal)
- Detoxification of the digester (sulphide removal)
- Improvement of organic compounds biodegradability

Potential drawbacks of microaerobic conditions;

- Dilution of biogas by nitrogen if air is used
- Lower methane production (not in all cases)
- Lack of full scale experience
- Oxygenophobia of digester operators

Oxygen is considered as a potential toxic compound during anaerobic digestion, especially, for the end-of-food-chain microorganisms, the acetogens and principally

the methanogens, which are usually regarded as strict anaerobes. However, some previous studies showed that microaeration can be used in anaerobic digestion.

Jenicek et al. (2008) studied effects of microaerobic conditions for anaerobic digestion of solid wastes containing slowly biodegradable compounds or high level of sulphur compounds. Results showed that in the operation of microaerobic desulphurization in the anaerobic mesophilic digester, the efficiency of hydrogen sulfide removal from biogas was very good and stable – average of 99.0% is a realistic value at high initial concentration (4,000-8,000 mg/m<sup>3</sup>). The presence of the limited amount of oxygen in the digester does not destroy the digestion process even in the systems where the oxygen is not consumed by prompt sulphide oxidation. The VSS/TSS ratio of the digested sludge decreased due to the better efficiency in VSS degradation, including the decrease of the soluble COD concentration, ammonia, nitrogen, and phosphate concentration in the sludge liquor. Besides, the decrease of the relative methane content in biogas was caused by the presence of nitrogen remaining in the biogas from the dosed air. Therefore, microaerobic conditions (that means controlled dosing of small amount of air or oxygen into digester) was an efficient tool to increase the biodegradability of treated material and/or to increase the activity of methanogenic bacteria. After that, Jenicek et al. (2010) studied results of microaerobic experiments for anaerobic digestion at both high and low sulphide concentrations and showed that anaerobic bacteria including methanogens can be active also in this system. In a mixed culture, even strict anaerobes can survive without inhibition, if the facultative microorganisms are able to consume the present oxygen quickly and fully. Besides, the microaerobic conditions were predominantly used for hydrogen sulphide removal from biogas.

#### **2.4 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.

## 2.5 Important Parameters in Wastewater

### 2.5.1 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 ( $\text{mg}\cdot\text{L}^{-1}$ ).

### 2.5.2 Total Volatile Solids (TVS)

Total volatile solids (TVS) are determined by igniting the TS at  $550\pm 50$  °C in a furnace. The residue that remains after burning is called fixed solids, and the loss of weight upon ignition is referred to as 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.

### 2.5.3 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.

$$TSS = \frac{\left( \begin{array}{l} \text{weight of sample} \\ \text{after drying, g} \end{array} \right) - \left( \begin{array}{l} \text{tare weight of filter} \\ \text{before use, g} \end{array} \right)}{\text{volume of sample, L}} \quad (2.16)$$

### 2.5.4 Volatile Suspended Solids (VSS)

Volatile suspended solids (VSS) are represented by the undissolved organic fraction which is determined by calcining the filtered solid at  $550\pm 50$  °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.

### 2.5.5 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).

$$TDS = TS - TSS \quad (2.17)$$

### 2.5.6 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 consists 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.

### 2.5.7 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.

## 2.6 **Anaerobic Fermentation Process**

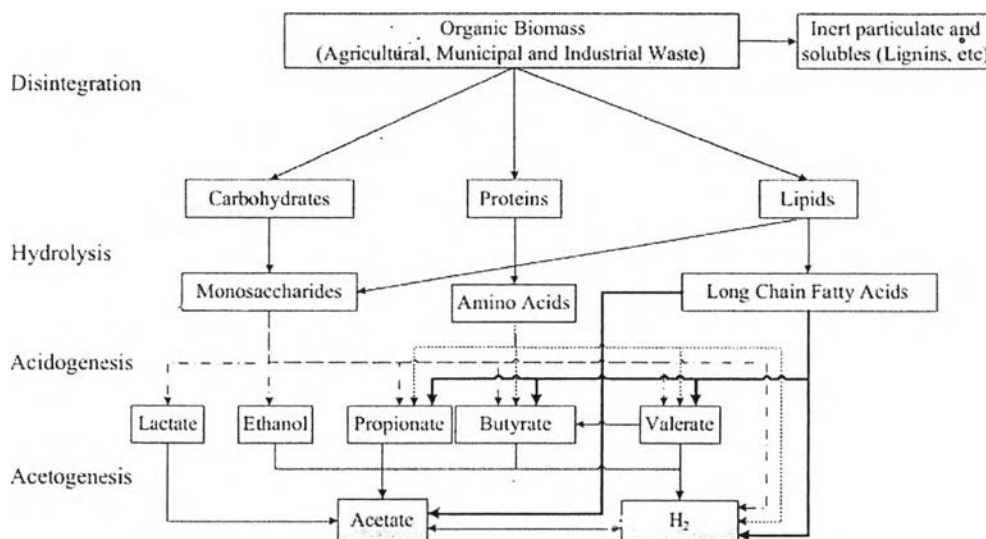
### 2.6.1 Principle of Anaerobic Fermentation Process

Anaerobic fermentation is a microbial process to convert carbonaceous compounds and soluble inorganic substances containing oxygen under the absence of dissolved oxygen. Anaerobic fermentation has three anaerobic decomposition processes. Three basic steps are involved in the overall anaerobic oxidation of a waste (Kim *et al.*, 2013), as illustrated in Figure 2.3.

#### 2.6.1.1 Hydrolysis

In the first step of hydrolysis, large, complex, and insoluble organics (protein, polysaccharides, and lipids) will be broken down enzymatically 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.



**Figure 2.3** Flow diagram of the anaerobic digestion process (Kim *et al.*, 2013).

#### 2.6.1.2 Acidogenesis

Acidogenesis is a second step. At this step, amino acids, sugars, and some fatty acids are degraded further, as shown in Figure 2.3. 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).

#### 2.6.1.3 Methanogenesis

This is the third step of anaerobic biological treatment, methanogenesis, carried out by methanogenic 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.

### 2.6.2 Reactor Configuration

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.

#### 2.6.2.1 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 2.4a, 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 2.2, as compared to anaerobic contact and anaerobic sequencing reactor processes.

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

Process	Volumetric organic loading, $\text{kg COD}\cdot\text{m}^{-3}\cdot\text{d}^{-1}$	Hydraulic retention time ( $\tau$ ), 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

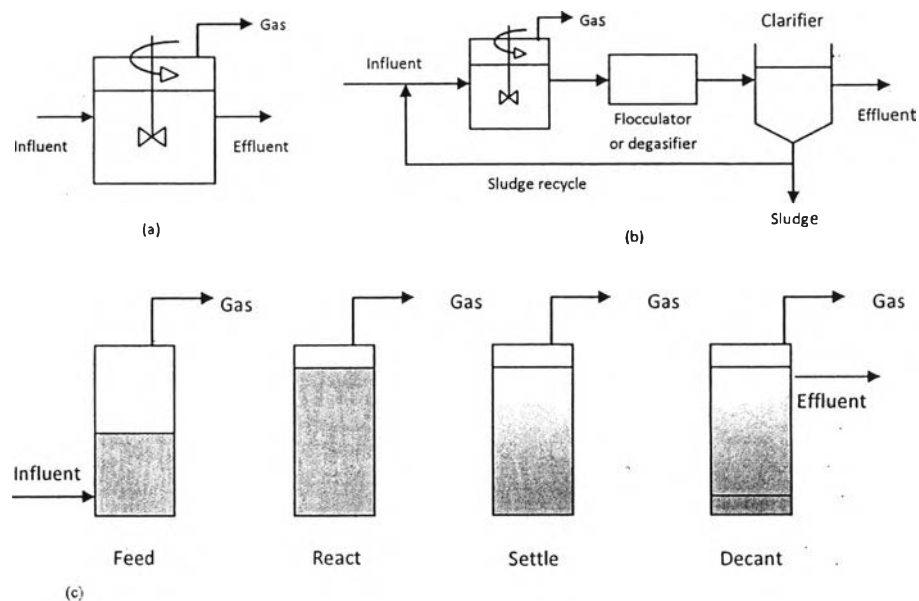


## (2) Anaerobic Contact Process

This process, as shown in Figure 2.4b, 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 ( $\tau$ ). This process can reduce the anaerobic reactor volume by increasing SRT with a short  $\tau$  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 Batch Reactor (ASBR)

This reactor, as shown in Figure 2.4c, 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 (Sreethawong *et al.*, 2010).



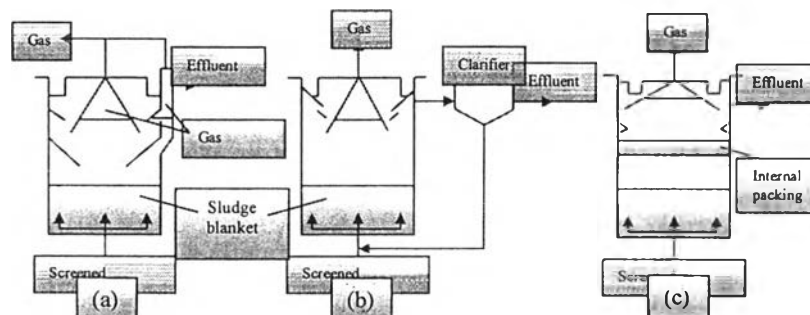
**Figure 2.4** Anaerobic suspended growth processes: (a) complete-mix process, (b) anaerobic contact process, and (c) anaerobic sequencing batch reactor process.

### 2.6.2.2 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 *et al.*, 2003).

#### (1) Upflow Anaerobic Sludge Blanket (UASB)

The basic UASB reactor is shown in Figure 2.5a. 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 2.5b, or the use of packing material at the top of the reactor, as shown in Figure 2.5c. 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 2.5** 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)

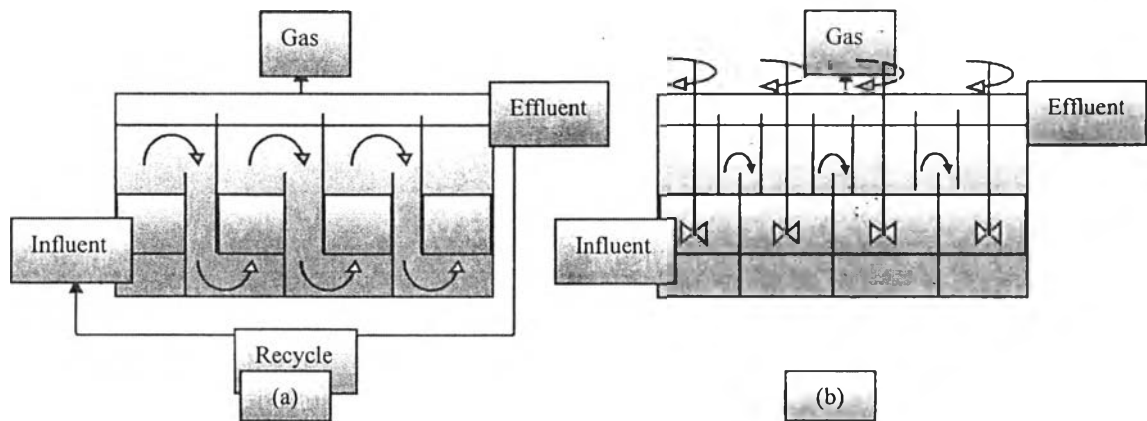
In the ABR process, as shown in Figure 2.6a, baffles are used to direct the flow of wastewater in an upflow mode through a series of sludge blanket reactors. The sludge in the reactor rises and falls with gas production and flows but moves through the reactor at a slow rate. Various modifications have 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 2.6b. 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 2.6** Schematic of alternative sludge blanket processes: (a) anaerobic baffled reactor (ABR) and (b) anaerobic migrating blanket reactor (AMBR).

### 2.6.2.3 *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 *et al.*, 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 2.7a. The most common packing materials are corrugated plastic crossflow or tubular 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.

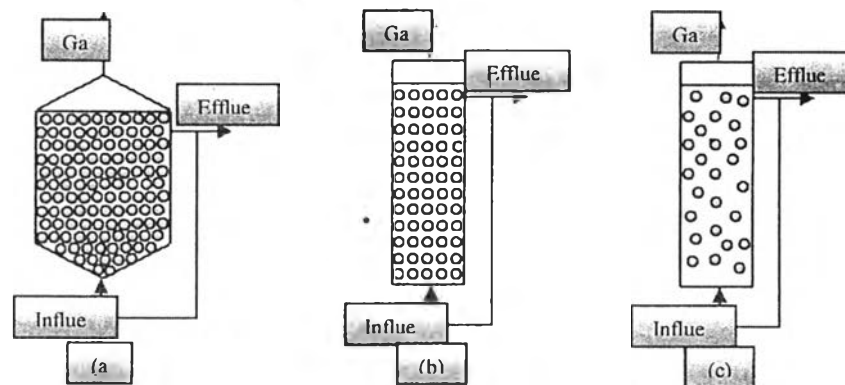
(2) Upflow Attached Growth Anaerobic Expanded-bed Reactor

The anaerobic expanded-bed reactor (AEBR), as shown in Figure 2.7b, 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 particlesize 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 2.7c, 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.



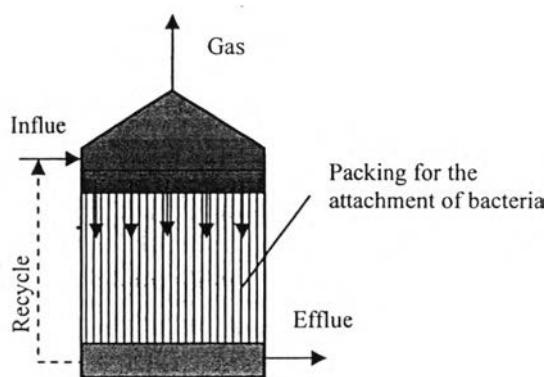
**Figure 2.7** Upflow anaerobic attached growth treatment reactors: (a) anaerobic upflow packed-bed reactor, (b) anaerobic expanded-bed reactor, and (c) anaerobic fluidized-bed reactor.

#### (4) Downflow Attached Growth Process

The downflow attached growth anaerobic processes, as illustrated in Figure 2.8, 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 2.8** Downflow attached growth anaerobic treatment reactor.

## 2.7 Two-Step Hydrogen and Methane Production

One of the significant problems in the fermentative hydrogen production process is that most of the organic fraction of the feeding wastewater remains as soluble fermentation products. Thus, 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, in which acidogenesis and methanogenesis occur in separate reactors, may offer several advantages in order to enhance hydrogen and methane production and achieve stabilization of the treated wastewater prior to disposal.

Two-stage anaerobic digestion is a process configuration using two separate reactors. The first reactor is acidogenic-stage, which is maintained at a low pH or alkalinity and develops a high  $\text{CO}_2$  and low  $\text{CH}_4$  content in the gaseous products. Acidifying organisms dominate in the first reactor, and the major biochemical reaction is enzymatic hydrolysis and fermentation. Another one is methanogenic-stage, which is maintained at pH around 7 and high alkalinity, resulting in high specific methanogenic activity.

The benefits of two-Step hydrogen and methane production including with having 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. Moreover, 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<sup>-3</sup>·d<sup>-1</sup> 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.

Keet *et al.* (2005) suggested that two-stage process achieves enhanced stability and higher loading capacities for the methanogenesis process compared with the traditional one stage process. In addition, it provided better process efficiencies overall.

Liu *et al.* (2006) worked on the two-stage process of both hydrogen and methane production and compared with the traditional one-stage process. It had been discovered that the methane production in two-stage process attained methane performances higher than in one-stage process. It is due to the fact that total VFA concentrations in the second-stage process was much less than in one-stage process. It means that more VFAs were converted to methane in two-stage process.