



## CHAPTER II

### LITERATURE REVIEW

#### 2.1 Background of Hydrogen

Energy is one of the most important factors to global prosperity. Global energy requirements are mostly dependent on fossil fuels (about 80% of the present world energy demand). Conventional petroleum-based fuels like gasoline or diesel, as well as natural gas and coal, all contain carbon. When these fuels are burned, their carbon recombines with oxygen from the air to form carbon dioxide (CO<sub>2</sub>), which is the primary greenhouse gas that causes global warming. 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 avoid these problems, hydrogen is used as an alternative energy.

##### 2.1.1 Advantage 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 to other fuels. Gaseous hydrogen is fourteen times lighter than air and four times lighter than helium. In the event of an accidental release, it disperses

rapidly upward into the atmosphere. Other fuels take longer to disperse or may spill onto the ground.

#### *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 fuel.*

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 electricity so that the hydrogen produced is a renewable fuel.

#### *2.1.1.6 Hydrogen is the most abundant element on the earth.*

Hydrogen is also the most abundant element on the earth, but less than 1% in form of  $H_2$ . Hydrogen is typically chemically attached to other atoms, such as carbon or 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 kW.h of electricity are needed to make enough hydrogen to have an energy content equivalent to a gallon of gasoline. Direct thermal dissociation of H<sub>2</sub>O requires temperature more than 2,000°C and temperature more than 900°C with Pt/Ru catalyst.

## 2.1.2 Hydrogen production processes

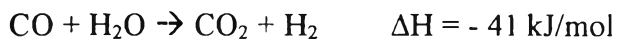
### 2.1.2.1 *Steam methane reforming*

Steam methane reforming is an old technology and tends to be the cheapest method. In this method, methane is first catalytically reformed at elevated temperature (700–850°C) and pressure (3-25 bar) to produce a syngas mixture of H<sub>2</sub> and CO.

The reforming step is described by the following reaction:

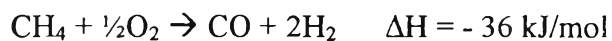


Second step in the process is the conversion of syngas to the desired H<sub>2</sub> product (water-gas shift reaction), following the reaction:



### 2.1.2.2 *Partial oxidation / autothermal reforming of methane*

The partial oxidation process directly oxidizes methane in a one step reaction. This process produces a syngas mixture of CO and H<sub>2</sub>, following the reaction:

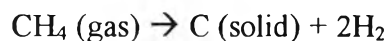


Autothermal reforming process is a combination of both steam reforming process and partial oxidation process. The outlet temperature from the reactor is in the range of 950 to 1,100°C, and the gas pressure can be as high as 100 bar.

### 2.1.2.3 *Thermal cracking of methane*

H<sub>2</sub> can be produced via thermal decomposition of CH<sub>4</sub>. However, this method requires high reaction temperature about 2,000°C.

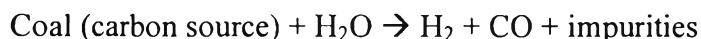
The reaction of this process is:



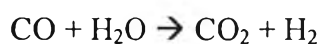
#### 2.1.2.4 Coal gasification

Gasification of coal is the oldest method for production of hydrogen. First, coal feedstock is heated with high temperature (1,330°C) and high pressure steam to produce raw synthesis gas.

The reaction of this process is:



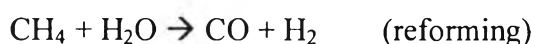
In the second step, the syngas passes through a shift reactor converting a portion of the carbon monoxide to carbon dioxide, as shown in the reaction below:



The last step, hydrogen product is purified to remove impurities that occur in second step, such as CH<sub>4</sub>, O<sub>2</sub>, N<sub>2</sub>, and H<sub>2</sub>S.

#### 2.1.2.5 Pyrolysis or gasification of biomass

Hydrogen can also be produced by thermal gasification of biomass, such as forestry waste products, straw, municipal solid wastes (MSW), and sewage (municipal waste). Biomass is treated with high temperature steam to produce a gas mixture composed of hydrogen, CO, CO<sub>2</sub>, water vapor, CH<sub>4</sub>, and tar. Next, methane is steam-reformed at 750–850°C, followed by a water gas shift reaction to convert CO to CO<sub>2</sub>. The reactions describing the process are:



#### 2.1.2.6 Electrolysis of water

Electrolysis processes are newer technology and tend to be more expensive than fossil fuel processes, but do not produce harmful emissions. Electrolysis uses electricity to split water into diatomic molecules of H<sub>2</sub> and O<sub>2</sub>. An electric potential is applied across a cell with two inert electrodes, where electrons are absorbed and released to form hydrogen at the cathode and oxygen at the anode.

The theoretical voltage for this decomposition of water at atmospheric pressure and 77°F is 1.23 volts (V). At this voltage, reaction rates are very slow. In practice, higher voltages are applied to increase the reaction rates. However, this results in increased heat losses to the surroundings, decreasing energy

efficiency. Although hydrogen from electrolysis is extremely pure, it is expensive at the same time. Hydrogen from electrolysis has ten times costly as natural gas.

#### 2.1.2.7 Photoelectrolysis

Photoelectrolysis of water is the process whereby light is used to split water directly into hydrogen and oxygen. Multijunction cell technology developed by the photovoltaic industry is being used for photoelectrochemical (PEC) light harvesting systems that generate sufficient voltage to split water and are stable in a water/electrolyte environment.

#### 2.1.2.8 Fermentation of organic compounds

This method is the biological process, which uses bacteria to produce hydrogen and volatile fatty acids from organic wastes. Biological hydrogen production is an environmentally benign and less energy-intensive process (Das and Veziroglu, 2001; Levin *et al.*, 2004). This process is dark anaerobic fermentation. The evolution of hydrogen by fermentation has several advantages for industrial production (Das *et al.*, 2001).

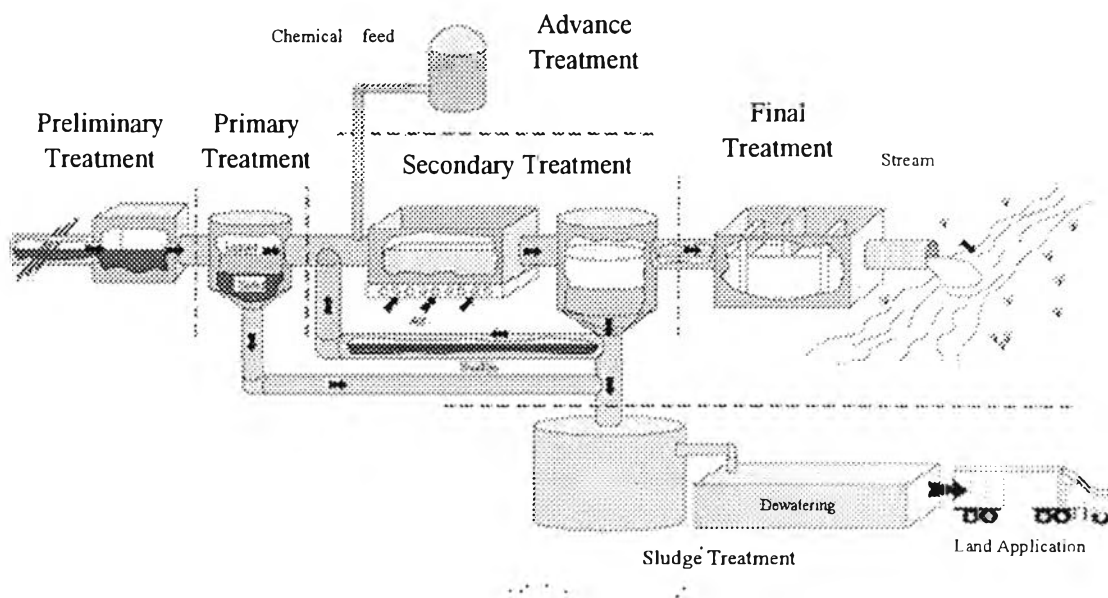
Galore microbial species, belonging to the genera *Enterobacter*, *Bacillus*, and *Clostridium*, are reported to produce hydrogen (Nandi and Sengupta, 1998). Apart from pure cultures, various mixed microflora and co-cultures have also been explored for hydrogen production from carbohydrates (Haruhiko *et al.*, 1998; Nandi and Sengupta, 1998; Das and Veziroglu, 2001). Sewage sludge has been reported to be the most proven and potent source of hydrogen producers.

## 2.2 Wastewater Treatment

### 2.2.1 Fundamental of wastewater treatment

Wastewater treatment is a multi-stage process to renovate wastewater before it re-enters to water sources. The goal of waste treatment is to reduce or remove organic matter, solids, nutrients, disease-causing organisms, and other pollutants from wastewater. Each water source has limits to the amount of pollutants it can receive without degradation. Therefore, each sewage treatment plant must hold a permit listing the allowable levels of BOD, COD, suspended solids, coliform

bacteria, and other pollutants. The overall processes of wastewater treatment are shown in Figure 2.1.



**Figure 2.1** Wastewater treatment process.

### 2.2.1.1 Preliminary treatment

Preliminary treatment is the first step in wastewater treatment. It is a physical process to screen out, grind up, or separate debris. Large objects, such as stones or sticks, that could plug lines or block tank inlets are removed at this stage to protect the pumping and other equipment in the treatment plant. Treatment equipment, such as bar screens, comminutors (a large version of a garbage disposal), and grit chambers, are used to slow down the flow to allow grit to fall out. The collected debris is usually disposed of in a landfill.

### 2.2.1.2 Primary treatment

Primary treatment is the second step in treatment and separates suspended solids and greases from wastewater. Wastewater is held in a sedimentation tank for several hours, allowing the particles to settle to the bottom and the greases to float to the top. The solids drawn off the bottom and skimmed off the top receive further treatment as sludge. The clarified wastewater flows on to the

next stage of wastewater treatment. Clarifiers and septic tanks are usually used to provide primary treatment.

### 2.2.1.3 Secondary treatment

Secondary treatment is a biological treatment process to remove dissolved organic matter from wastewater. Sewage microorganisms are cultivated and added to the wastewater. The microorganisms absorb organic matter from sewage as their food supply. These biodegradation processes also take place in streams, lakes, and oceans, but the purification systems in nature can easily be overloaded with input of too much organic waste. Secondary treatment prevents this type of pollution by degrading most of the organic matter before the water is released into the environment. Three approaches are used to accomplish secondary treatment; fixed film, suspended film, and lagoon systems.

- *Fixed film systems* grow microorganisms on substrates, such as rocks, sand, and plastic. The wastewater is spreaded over the substrate, allowing the wastewater to flow passing the film of microorganisms fixed to the substrate. As organic matter and nutrients are absorbed from the wastewater, the film of microorganisms grows and thickens. Trickling filters, rotating biological contactors, and sand filters are examples of fixed film systems.

- *Suspended film systems* stir and suspend microorganisms in wastewater. As the microorganisms absorb organic matter and nutrients from the wastewater, they grow in size and number. After the microorganisms have been suspended in the wastewater for several hours, they are settled out as sludge. Some of the sludge is pumped back into the incoming wastewater to provide "seed" microorganisms. The remainder is wasted and sent on to a sludge treatment process. Activated sludge, extended aeration, oxidation ditch, and sequential batch reactor systems are all examples of suspended film systems.

- *Lagoon systems* are shallow basins, which hold the wastewater for several months to allow the natural degradation of sewage. These systems take advantage of natural aeration and microorganisms in the wastewater to renovate sewage. These systems are slow, cheap, and relatively inefficient, but can be used for various types of wastewater. They rely on the interaction of sunlight, algae, microorganisms, and oxygen.

### 2.2.1.3 Tertiary treatment

After primary and secondary treatments, municipal wastewater is usually disinfected using chlorine or other disinfecting compounds, or occasionally ozone or ultraviolet light. An increasing number of wastewater facilities also employ tertiary treatment, often using advanced treatment methods. Tertiary treatment may include processes to remove nutrients, such as nitrogen and phosphorus, and carbon adsorption to remove chemicals. These processes can be physical, biological, or chemical.

### 2.2.1.4 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.

### 2.2.1.5 Sludge treatment

Sludge is generated through the sewage treatment process. Primary sludge, material that settles out during primary treatment, often has a strong odor and requires treatment prior to disposal. Secondary sludge is the extra microorganisms from the biological treatment processes. The goals of sludge treatment are to stabilize the sludge and reduce odors, remove some of the 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 of wastewater

### 2.2.2.1 Total solids (TS)

The matter remained after a wastewater sample is evaporated and dried at a specified temperature (103-105°C). Total solids compose of suspended solids and dissolved solid.

$$TS = TSS + TDS$$

### 2.2.2.2 Total suspended solids (TSS)

The nonfiltrable residue retained on a glass fiber filter with a specific pore size, measured after being dried at a specific temperature (103-105°C).



#### 2.2.2.3 *Total dissolved solids (TDS)*

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

#### 2.2.2.4 *Total volatile solids (TVS)*

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

$$\text{TVS} = \text{TS} - \text{ash}$$

#### 2.2.2.5 *Volatile suspended solids (VSS)*

The solids that can be volatilized and burnt when the TSS are ignited at 500°C. They are useful to the treatment plant operator because they give a rough approximation of the amount of organic matter present in the solid fraction of wastewater, activated sludge, and industrial wastes.

#### 2.2.2.6 *Biochemical oxygen demand (BOD)*

BOD is a measuring parameter to determine a concentration of biodegradable organics. It is defined as the amount of oxygen used by microorganisms in biochemical oxidation of organic matter under aerobic conditions. The limitations of the BOD test are as follows: (1) a high concentration of acclimated seed bacteria is required, (2) pretreatment is needed when dealing with toxic wastes, and (3) only biodegradable organics are measured.

#### 2.2.2.7 *Chemical oxygen demand (COD)*

COD is a method to determine the concentration of organic compounds present in a wastewater sample using chemical oxidation reaction with potassium dichromate under acidic condition. 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 ( $\tau$ )*

The hydraulic retention time (HRT) or  $\tau$  (tau) is a measure of the average length of time that a soluble compound remains in a constructed bioreactor.

The theoretical hydraulic retention time is defined as:

$$\tau = V/Q \quad (2.1)$$

where  $\tau$  = hydraulic retention time, h  
 $V$  = volume of the reactor, m<sup>3</sup>  
 $Q$  = volumetric flowrate, m<sup>3</sup>/h

### 2.2.3 Biological wastewater treatment

Normally, biological wastewater treatment is the second process of wastewater treatment. Sewage microorganisms are cultivated and added to the wastewater to transform dissolved and particulate biodegradable constituents into acceptable end products.

There are two basic categories of biological treatment: aerobic treatment process and anaerobic treatment process.

#### *Aerobic treatment process*

This process involves contacting wastewater with microbes and oxygen in a reactor to optimize the growth and efficiency of the biomass. The microorganisms act to catalyze the oxidation of biodegradable organics and other contaminants, such as ammonia, generating innocuous by-products, such as carbon dioxide, water, and excess biomass (sludge).

#### *Anaerobic treatment process*

This process is similar to aerobic treatment, but uses microorganisms that do not require the addition of oxygen. These microorganisms use the compounds other than oxygen to catalyze the oxidation of biodegradable organics and other contaminants, resulting in innocuous by-products.

The principal advantages and disadvantages of anaerobic treatment are listed in Table 2.1.

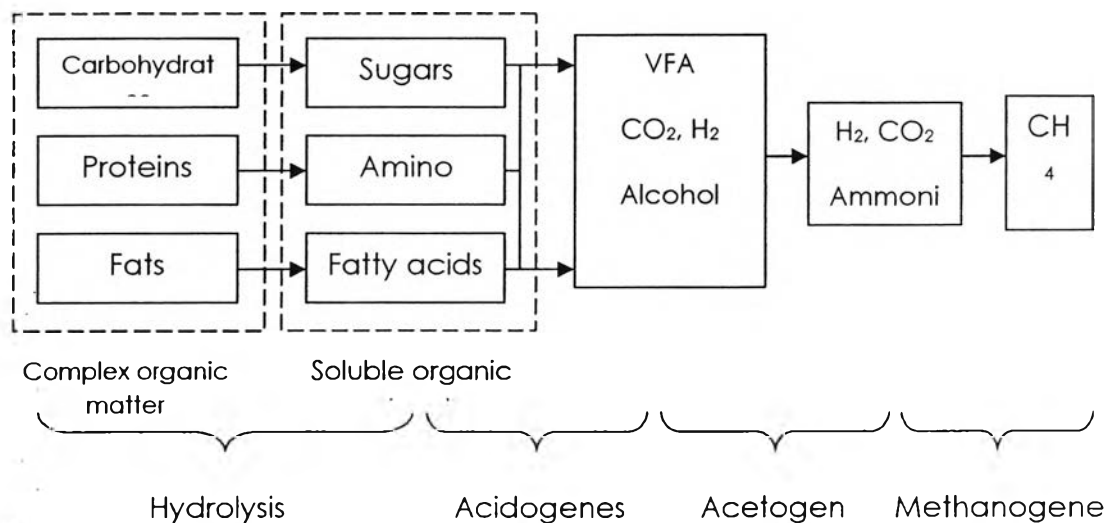
**Table 2.1** Advantages and disadvantages of anaerobic processes

Advantage	<ul style="list-style-type: none"> <li>- Less energy required</li> <li>- Less biological sludge production</li> <li>- Fewer nutrients required</li> <li>- Methane production, a potential energy source</li> <li>- Smaller reactor volume required</li> <li>- Elimination of off-gas air pollution</li> <li>- Rapid response to substrate addition after long periods without feeding</li> </ul>
Disadvantage	<ul style="list-style-type: none"> <li>- Longer start-up time to develop necessary biomass inventory</li> <li>- May require alkalinity or specific ion addition</li> <li>- May require further treatment with an aerobic treatment process to meet discharge requirements</li> <li>- Biological nitrogen and phosphorus removal is not possible</li> <li>- Much more sensitive to the adverse effect of lower temperatures on reaction rates</li> <li>- May be more susceptible to upsets due to toxic substances</li> <li>- Potential for production of odors and corrosive gases</li> </ul>

### 2.3 Background of Anaerobic Treatment Process

Anaerobic process or dark fermentation is a natural process and is the microbiological conversion of organic matter to methane in the absence of oxygen. The decomposition is caused by natural bacterial action in various stages. It takes place in a variety of natural anaerobic environments, including water sediment, water-logged soils, natural hot springs, ocean thermal vents, and the stomach of various animals. The digested organic matter resulting from the anaerobic digestion process is usually called digestate. During the process, a gas principally composed of methane (CH<sub>4</sub>) and carbon dioxide (CO<sub>2</sub>), otherwise known as biogas, is produced.

The amount of gas produced varies with the amount of organic waste fed to the digester, and temperature influences the rate of decomposition (and gas production).



**Figure 2.2** Overall anaerobic digestion process.

Anaerobic digestion occurs in four steps: (1) hydrolysis, (2) fermentation (also known as acidogenesis), (3) acetogenesis, and (4) methanogenesis, as shown in Figure 2.2.

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

- *Fermentation*: The second step is fermentation (also referred to as acidogenesis). In the fermentation process, amino acids, sugars, and some fatty acids are degraded further, as shown in Figure 2.2. The principal products of fermentation are acetate, hydrogen, CO<sub>2</sub>, propionate, and butyrate. The propionate and butyrate are fermented further to produce hydrogen, CO<sub>2</sub>, and acetate. Thus, the final products of fermentation (acetate, hydrogen, and CO<sub>2</sub>) are the precursors for methane formation (methanogenesis).

- *Acetogenesis*: The third step is acetogenesis. It is a process, through which volatile fatty acids (VFA) are converted into acetic acid, carbon dioxide, and hydrogen by acetogenic bacteria.

- *Methanogenesis*: The fourth step, methanogenesis, is carried out by group of organisms known collectively as methanogens. Two groups of methanogenic organisms are involved in methane production. One group, termed acetoclastic methanogens, splits acetate into methane and carbon dioxide. The second group, termed hydrogen-utilizing methanogens, uses hydrogen as electron donor and  $\text{CO}_2$  as electron acceptor to produce methane. Bacteria within anaerobic processes, termed acetogens, are also able to use  $\text{CO}_2$  to oxidize hydrogen and form acetic acid. However, the acetic acid will be converted to methane, so the impact of this reaction is minor. About 72% of the methane produced in anaerobic digestion is from acetate formation.

### 2.3.1 Temperature ranges

Temperature is one of the important factors influencing the biological  $\text{H}_2$  fermentation process. Substrate degradation,  $\text{H}_2$  production, product distribution, and bacterial growth are all affected by temperature.

There are two main temperature ranges for anaerobic digestion systems.

- Mesophilic digestion is the most commonly used process for anaerobic digestion, in particular waste sludge treatment. Decomposition of the volatile suspended solids (VSS) is around 40% over a retention time of 15 to 40 days 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 digestion operates at a high temperature. The digester is heated to 55°C and held for a period of 12 to 14 days. The microorganisms rapidly break down organic matter and produce large volumes of biogas. The quick breakdown means that the digester volume can be smaller than in other systems. Thermophilic digestion systems provide higher biogas production, but the technology is more expensive, more energy is needed, and it is necessary to have

more sophisticated control and instrumentation. Greater insulation is necessary to maintain the optimum temperature range. These systems may be more sensitive to upset due to temperature variations. However, these systems are more effective in pathogen removal.

Reported studies on fermentative H<sub>2</sub> production were operated in a mesophilic range, i.e. 30–37°C (Haruhiko *et al.*, 1998; Kim *et al.*, 2004; Lin and Chang, 2004; Cai and Liu, 2005), whereas some experiments were conducted in a thermophilic range, i.e. 50–60°C (Yeonghee *et al.*, 2005). H<sub>2</sub> production and substrate degradation rate can be increased through elevating operating temperature. However, operation at high temperatures is not favorable for energy recovery. Therefore, for a balance between H<sub>2</sub> production and energy recovery, it seems to be reasonable to operate biological H<sub>2</sub> producing reactors in the mesophilic range (Fabiano and Perego, 2002) The comparison of mesophilic and thermophilic digesters is shown in Table 2.2.

**Table 2.2** Comparison of mesophilic and thermophilic digesters

Feature	Mesophilic digester	Thermophilic digester
Loading rates	Lower	Higher
Destruction of pathogens	Lower	Higher
Sensitivity to toxicants	Lower	Higher
Operational costs	Lower	Higher
Temperature control	Less difficult	More difficult

### 2.3.2 Wastewater characteristics

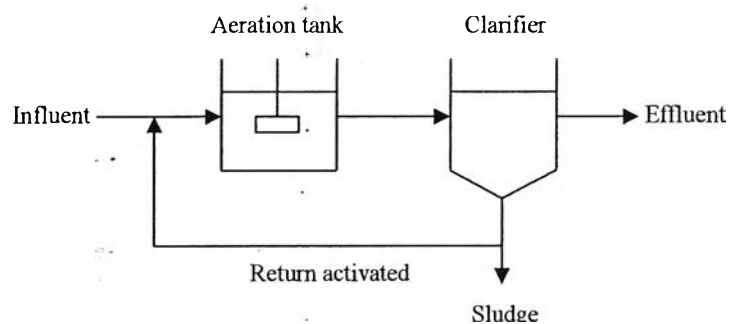
The proper wastewater for anaerobic treatment should have COD higher than 1500 mg L<sup>-1</sup> and temperature around 25-35°C. If the COD is lower than 1500 mg L<sup>-1</sup>, aerobic treatment is more preferred (Metcalf and Eddy, 2003).

### 2.3.3 Type of anaerobic treatment process

#### 2.3.3.1 Anaerobic suspended growth processes

Suspended growth processes freely suspend microorganisms in water. In these processes, microorganisms convert the organic matter or other constituents in the wastewater into gases and cell tissue. Suspended growth technologies are conventional activated sludge treatment systems that use various process modes, ranging from conventional, extended aeration, contact stabilization, sequencing batch, and single sludge, which are available for polishing anaerobically treated effluents.

Under optimum conditions, the organisms break down material in the water and improve the water quality. Natural suspended growth treatment systems, such as wastewater biological treatment, can be used for organic wastewaters, such as municipal sewage, and tend to be lower in cost for operation and maintenance. The most common suspended growth process used for municipal wastewater treatment is the activated-sludge process, as shown in Figure 2.3.



**Figure 2.3** Anaerobic suspended growth processes.

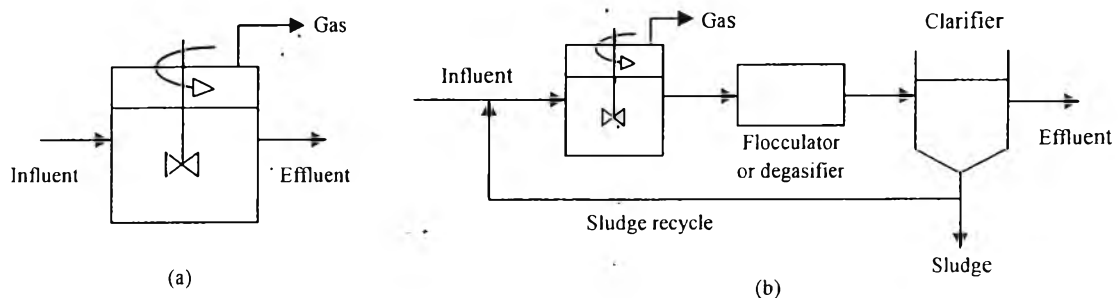
Three types of anaerobic suspended growth treatment processes are:

- *Complete-Mix Process*: For the complete-mix anaerobic digester, the hydraulic retention and solid retention times are equal ( $\tau = \text{SRT}$ ). The complete-mix digester without sludge recycle (see Figure 2.4(a)) is more suitable for wastes with high concentrations of solids or extremely high dissolved organic concentrations, where thickening the effluent solids is difficult so that it is more practical to operate

with  $\tau$  equal to the SRT. Typical organic loading rates for the complete-mix process are presented in Table 2.3, along with comparative values for the anaerobic contact and anaerobic sequence reactor processes.

**Table 2.3** Typical organic loading rates for anaerobic suspended growth processes at 30°C

Process	Volumetric organic loading, kg COD/m <sup>3</sup> d	Hydraulic retention time ( $\tau$ ), d
Complete-mix	1.0-5.0	15-30
Anaerobic contact	1.0-8.0	0.5-5
Anaerobic sequencing batch reactor (ASBR)	1.2-2.4	0.25-0.50



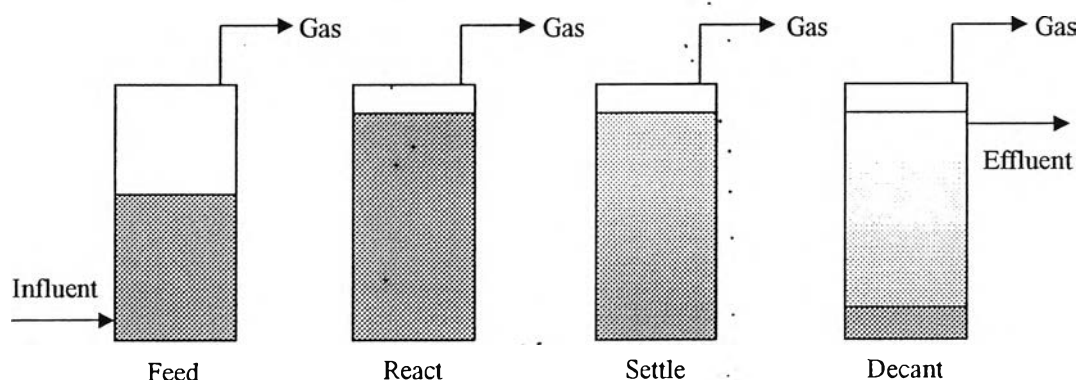
**Figure 2.4** (a) Complete-mix process and (b) Anaerobic contact process.

- *Anaerobic Contact Process*: The anaerobic contact process (see Figure 2.4(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 process SRT is longer than  $\tau$ . By separating  $\tau$  and SRT values, the anaerobic reactor volume can be reduced. Gravity 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 gravity separation. Since the reactor sludge contains gas



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

- *Anaerobic Sequencing Batch Reactor (ASBR)*: The anaerobic sequencing batch reactor process (see Figure 2.5) 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 react period, intermittent mixing for a few minutes each hour is done to provide uniform distribution of substrate and solids. The organic loading of the process can be changed by selecting hydraulic retention times from 6 to 24 h at 25°C, and 92-98% COD removal can be achieved at volumetric organic loading of 1.2 to 2.4 kg COD/m<sup>3</sup>d.



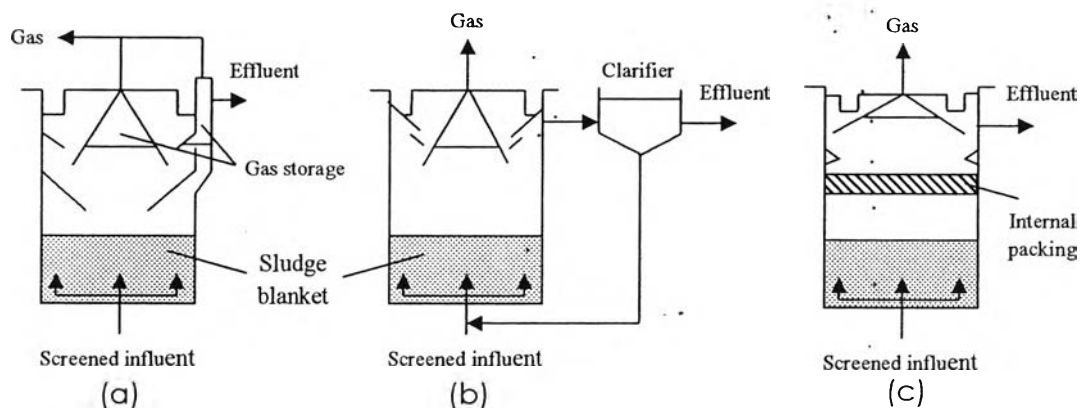
**Figure 2.5** Anaerobic sequencing batch reactor (ASBR).

### 2.3.3.2 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 that is 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. In this process, the UASB process is used most commonly.

- *Upflow Anaerobic Sludge Blanket Process (UASB)*: The basic UASB reactor is illustrated in Figure 2.6(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 separation, and the effluent withdrawal design. Modifications to the basic UASB design include adding a settling tank, as shown in Figure 2.6(b), or the use of packing material at the top of the reactor, as shown in Figure 2.6(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 solids due to process upsets or changes in the UASB sludge blanket characteristics and density.

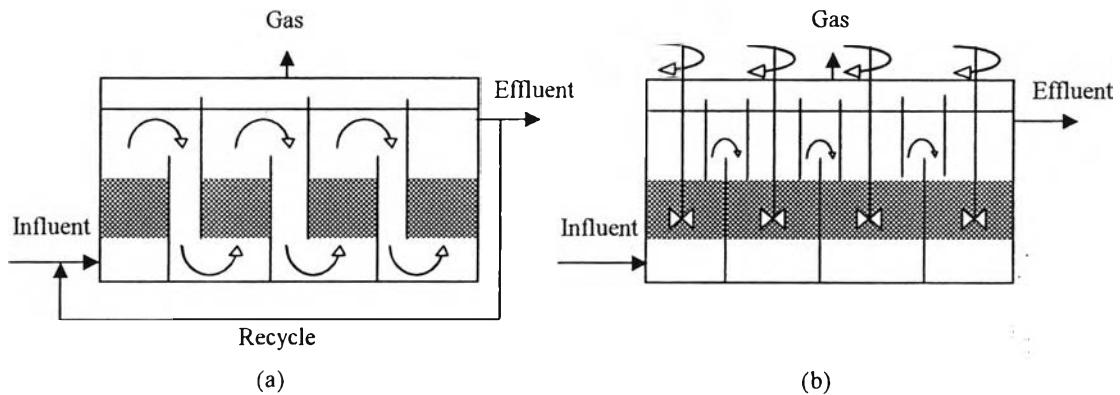
The key feature of the UASB process that allows the use of high volumetric COD loadings compared to other anaerobic processes is the development of a dense granulated sludge.



**Figure 2.6** (a) Original USAB process, (b) USAB reactor with sedimentation tank and sludge recycle, and (c) UASB reactor with internal packing for fixed-film attached growth.

- *Anaerobic Baffled Reactor Process (ABR)*: In the anaerobic baffled reactor process (ABR), as shown in Figure 2.7(a), baffles are used to direct the flow of wastewater in an upflow mode through a series of sludge blanket reactors. The sludge in the reactor rises and falls with gas production and flows but moves through the reactor at a slow rate. Various modifications have been made to the ABR to improve performance. The modifications include: (1) changes to the

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



**Figure 2.7** (a) Anaerobic baffled reactor (ABR) and (b) Anaerobic migrating blanket reactor (AMBR).

- *Anaerobic Migrating Blanket Reactor (AMBR)*: The anaerobic migrating blanket reactor 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 2.7(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.

### 2.3.3.3 Attached growth anaerobic processes

In these processes, microorganisms are held on a surface, the fixed film, which may be mobile or stationary with wastewater flowing past the surface. The packing can be submerged completely in liquid or not submerged, with air or gas space above the biofilm liquid layer. These processes are designed to actively contact the biofilm with the wastewater.

Attached-growth anaerobic treatment reactors differ by the type of packing used and the degree of bed expansion. Packing materials used in attached growth processes include rock, gravel, slag, sand, and wide range of plastic

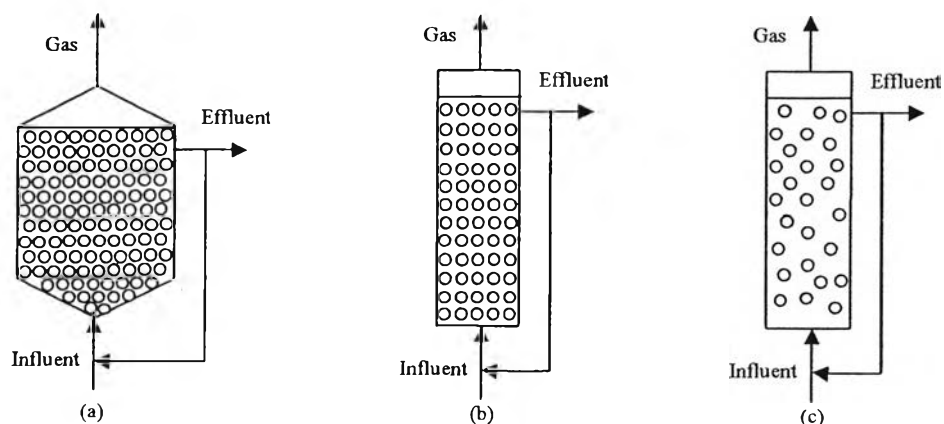
and other synthetic materials. Attached growth processes can also be operated as aerobic or anaerobic processes.

Four types of attached growth anaerobic treatment processes are:

- *Upflow Packed-Bed Reactor*: Full-scale upflow packed-bed anaerobic filters are used in cylindrical or rectangular tanks at widths and diameters ranging from 2 to 8 m and heights from 3 to 13 m, as shown in Figure 2.8(a). Packing material placement may be in the entire depth or, for hybrid designs, only in the upper 50 to 70%. The most common packing materials are corrugated plastic cross-flow or tubular modules.

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

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

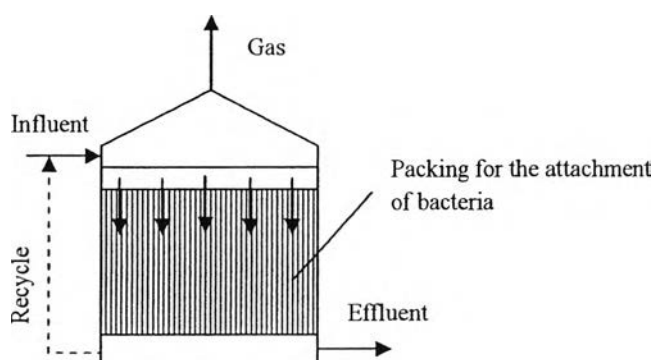


**Figure 2.8** (a) Anaerobic upflow packed-bed reactor, (b) Anaerobic expanded-bed reactor, and (c) Anaerobic fluidized-bed reactor.

- *Upflow Anaerobic Expanded-Bed Reactor (AEBR)*: In the upflow attached growth anaerobic expanded-bed reactor process as shown in Figure 2.8(b), the packing material is generally silica sand with a diameter in the range of 0.2 to 0.5 mm and specific gravity of 2.65. For operation with about 20% bed expansion, an upflow velocity of about 2 m/h is used. The smaller packing provides a greater surface area per unit volume, theoretically supporting a greater amount of biomass growth. The packing void fraction is about 50% 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.

- *Anaerobic Fluidized-Bed Reactor (AFBR)*: The anaerobic fluidized-bed reactor (see Figure 2.8(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. Effluent recycle is used to provide sufficient upflow velocity.

- *Downflow Attached Growth Processes*: The downflow attached growth anaerobic processes, as illustrated on Figure 2.9, 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.



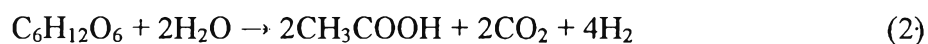
**Figure 2.9** Downflow attached growth anaerobic treatment reactor.

## 2.4 Biohydrogen Production by Fermentative Process

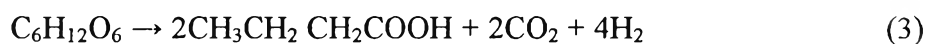
Biological hydrogen production is a process of applying biological fermentation method to produce hydrogen from organic wastes. Normally, the dark fermentation process for biohydrogen production is operated under anaerobic conditions. Under anaerobic condition at a very high organic loading, organics will be degraded anaerobically to produce hydrogen and organic acids as main products, as shown in Figure 2.10.

### 2.4.1 Feedstock for biohydrogen production

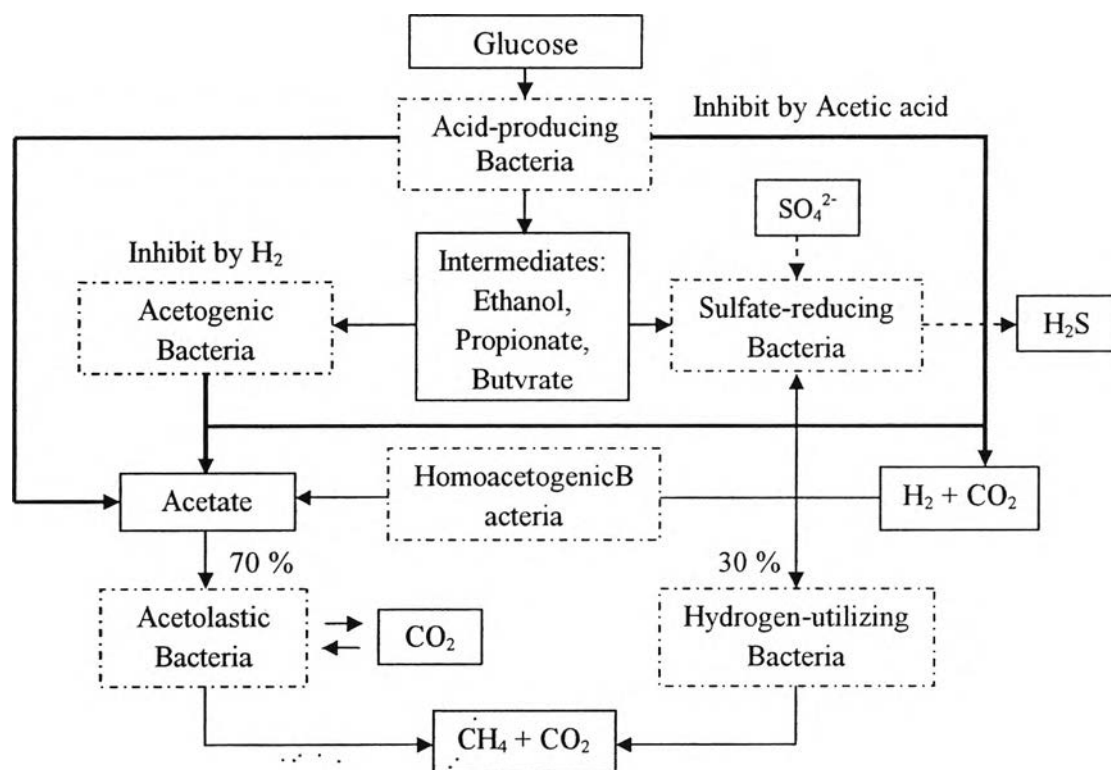
For sustainable biohydrogen production, carbohydrates are the preferred organic carbon source for hydrogen-producing fermentations. Glucose in biomass and wastewater gives a maximum yield of 4 mol of H<sub>2</sub> per 1 mol of glucose when acetic acid is the by-product.



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



These two equations have shown that acetic and butyric acids are the main by-products (Hawkes *et al.*, 2002; Han and Shin, 2004).



**Figure 2.10** Glucose fermentation.

Recently, many kinds of feedstock are used as a model substrate for carbohydrates to study the hydrogen production efficiency:

- Rice winery wastewater was used as a model substrate to investigate the individual effects of operating parameters on the hydrogen production by using mixed acidogenic cultures. From the results, the optimum hydrogen production rate of  $9.33 \text{ l H}_2 \text{ g}^{-1} \text{ VSS day}^{-1}$  was achieved at HRT of 2 h, COD of  $34 \text{ g L}^{-1}$ , pH 5.5, and  $55^\circ\text{C}$ . The hydrogen yield was in the range of  $1.37\text{-}2.14 \text{ mol H}_2/\text{mol hexose}$  contained in the waste water (Yu *et al.*, 2002).

- Beer lees wastes, the cellulose biomass, was converted to hydrogen by cow dung compost. The maximum hydrogen yield of  $68.6 \text{ ml H}_2 \text{ g}^{-1} \text{ TVS}$  was observed at the fixed initial pH of 7.0. The alcohols (ethanol, propanol, butanol), acetate, and butyrate were main by-products in the metabolism of hydrogen fermentation (Fan *et al.*, 2006).

- Biological hydrogen production from sucrose using anaerobic sequencing batch reactor (ASBR) was studied. From the results, at HRT of 8 h,

reaction period/settling period (R/S) ratio of 5.6, and an organic loading rate of 0.23 mol sucrose  $\text{dm}^{-3} \text{ day}^{-1}$ , each mole of sucrose in the mesophilic hydrogenic reactor yielded 2.6 mole of hydrogen (Lin and Jo, 2003).

- Starch in wastewater is converted to hydrogen under thermophilic condition of 55°C. The maximum hydrogen yield of 92 mL  $\text{g}^{-1}$  of starch added was found for wastewater at pH 6, but the maximum specific hydrogen production rate of 365 mL  $\text{g}^{-1} \text{ VSS day}^{-1}$  was found at pH 7.0 (Zhang *et al.*, 2003).

#### 2.4.2 Effect of operational parameter

The fermentative  $\text{H}_2$ -producing process is greatly influenced by many factors, such as pH, temperature, oxidation–reduction potential, and nutritional requirements (Das and Veziroglu, 2001; Levin *et al.*, 2004; Kim *et al.*, 2004; Lin and Lay, 2005).

Many effects of operational parameter on hydrogen production have been reported:

- The effect of  $\text{N}_2$  sparging on hydrogen yield was investigated using a hydrogen-producing mixed culture previously enriched from soya bean meal. The results showed that the hydrogen production yields of 0.85 and 1.43 mol  $\text{H}_2 \text{ mol}^{-1}$  glucose were obtained under non-sparging and sparging conditions, respectively; sparging with nitrogen resulted in a 68% increase in hydrogen yield (Mizuno *et al.*, 2000).

- The effect of pH on the conversion of glucose to hydrogen by a mixed culture of fermentative bacteria was evaluated. Over 90% of glucose was degraded at pH range of 4.0-7.0. At the optimum pH of 5.5, the hydrogen production yield of  $2.1 \pm 0.1 \text{ mol H}_2 \text{ mol}^{-1}$  glucose and a specific production rate of  $4.6 \pm 0.4 \text{ mol H}_2 \text{ g}^{-1} \text{ VSS day}^{-1}$  were observed (Fang and Liu, 2002).

- The effects of pH and volatile solid (VS) on hydrogen production from food waste, a carbohydrate-rich organic solid waste, by the mesophilic and thermophilic acidogenic culture were evaluated. The amount of hydrogen production from thermophilic condition was much higher than that from the mesophilic condition at all tested pHs, and when the VS concentration increased from 3 to 10 g  $\text{VS L}^{-1}$ , the quantity and quality of hydrogen increased. The hydrogen yield was in



the range of 0.9-1.8 mol H<sub>2</sub> mol<sup>-1</sup> hexose and peaked at 6 g VS L<sup>-1</sup> (Shin *et al.*, 2004).

- The selective production of organic acids with pH control was investigated using a chemostat culture. The results showed that pH control was effective for selective production of various organic acids from organic wastes. The main products were changed from butyric acid to acetic and propionic acids when pH was shifted from 5.0 to 8.0 (Horiuchi *et al.*, 2002).

- The addition of sewage sludge on food waste up to 13-19% could enhance specific hydrogen production potential of 122.9 mL g<sup>-1</sup> carbohydrate-COD at the ratio of food waste to sewage sludge of 87:13 and the VS concentration of 3.0%. The maximum H<sub>2</sub> production rate was 111.2 mL g<sup>-1</sup> VSS h<sup>-1</sup> (Kim *et al.*, 2004).

- The effect of nutrient supplementation on hydrogen production from palm oil mill effluent (POME) was studied: Thermophilic microflora was used a seed sludge. The results showed that nutrient supplementation could increase the hydrogen production yield from 1.6±0.1 to 2.24±0.03 mol H<sub>2</sub> mol<sup>-1</sup> hexose and hydrogen production rate from 4.4±0.38 to 6.1±0.03 L H<sub>2</sub> L<sup>-1</sup> POME day<sup>-1</sup> (O-Thong *et al.*, 2007).

- The effects of C/N and C/P ratios on hydrogen yield and specific production rate were investigated in dark fermentation of wheat powder solution (WPS) by external addition N and P since the wheat powder was N and P deficient. The results showed that hydrogen yield increased with increasing C/N and C/P ratios. Low nitrogen concentrations required low phosphorous contents for high hydrogen yields. A C/N ratio of 200 and C/P ratio of 1,000 yielded the highest hydrogen yield of 281 ml H<sub>2</sub> g<sup>-1</sup> starch at STP. Specific hydrogen production rate also increased with increasing C/N and C/P ratios and reached the maximum at 98 ml H<sub>2</sub> g<sup>-1</sup> biomass h<sup>-1</sup>. (Argun *et al.*, 2008)

**Table 2.4** The summary of operational conditions from literature review

<b>Feed stock</b>	<b>Reactor type</b>	<b>Studied parameter</b>	<b>Reference</b>
soya bean meal	CSTR	N <sub>2</sub> sparging	Mizuno <i>et al.</i> , 2000
glucose	CSTR	pH	Fang and Liu, 2002
glucose	CSTR	pH	Horiuchi <i>et al.</i> , 2002
rice winery wastewater	upflow anaerobic reactor	HRT, COD loading rate, pH, temperature	Yu <i>et al.</i> , 2002
sucrose	ASBR	HRT, react/settle ratio, organic loading rate	Lin and Jo, 2003
starch wastewater	batch reactor	pH, substrate concentration	Zhang <i>et al.</i> , 2003
food waste	batch reactor	volatile solids, mixing ratios of substrates	Kim <i>et al.</i> , 2004
food waste	batch reactor	bacteria species, pH, volatile solid	Shin <i>et al.</i> , 2004
beer lees wastes	batch reactor	pretreatment substrate, substrate concentration, pH	Fan <i>et al.</i> , 2006
palm oil mill effluent	ASBR	nutrient supplementation	Ó-Thong <i>et al.</i> , 2007
wheat powder solution	batch reactor	C/N, C/P ratio	Argun et al., 2008