



CHAPTER II

LITERATURE REVIEW

2.1 Background of Hydrogen

Lately the international community has shown an increasing interest in renewable energy sources. Microorganisms have the potential of converting biomass (Including wastes/wastewater) to valuable liquid or gaseous substances that can be used as energy sources and especially as fuels. Production of biofuels will help to cope with the overproduction of agricultural products and will further work for reduction of carbon dioxide emissions (Gavala *et al.*, 2006). From these reasons hydrogen is one of the renewable energy sources that have been focused.

2.1.1 Advantages of Hydrogen

2.1.1.1 *Hydrogen is Clean Fuel.*

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

2.1.1.2 *Hydrogen is Harmless Fuel.*

Hydrogen is the safest of all fuels, partly because of how light it is compared with other fuels. Gaseous hydrogen is fourteen times lighter than air and four times lighter than helium. In the event of an accidental release, it disperses rapidly upward into the atmosphere. Other fuels take longer to disperse or may spill onto the ground.

2.1.1.3 *Hydrogen is Environmentally Friendly.*

Conventional energy resources can significantly produce greenhouse gases, especially carbon dioxide, which is thought to be responsible for changes in global climate. The long-term environmental benefits of using hydrogen as a fuel are enormous. Hydrogen fuel produces few pollutants when burnt, and non

eat 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 Locally from Numerous Sources.

Hydrogen can be produced either centrally, and then distributed, or onsite where it will be used. Hydrogen gas can be produced from methane, gasoline, biomass, coal or water. Each of these sources brings with it different amounts of pollution, technical challenges, and energy requirements.

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 and oxygen, and most of hydrogen is bound as H_2O . Because of this, energy must be expended to separate these elements. To extract hydrogen from water, for example, about 2.3 gallons of water and 45 kilowatts-hours of electricity are needed to make enough hydrogen to have an energy content equivalent to a gallon of gasoline. Direct thermal dissociation of H_2O requires temperature more than $2,000^\circ C$ and temperature more than $900^\circ C$ with Pt/Ru catalyst.

2.1.1.7 If Hydrogen is Produced from Water We have a Sustainable Production System .

Electrolysis is the method of separating water into hydrogen and oxygen. Renewable energy can be used to power electrolyzers to produce the hydrogen from water. Using renewable energy provides a sustainable system that is independent of petroleum products and is nonpolluting. Some of the renewable

sources used to power electrolyzers are wind, hydro, solar and tidal energy. After the hydrogen is produced in an electrolyzer it can be used in a fuel cell to produce electricity. The byproducts of the fuel cell process are water and heat. If fuel cells operate at high temperatures the system can be set up as a co-generator, with the waste energy used for heating.

2.1.2 Hydrogen Production

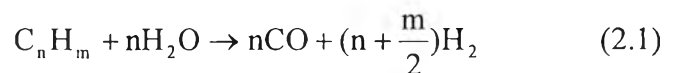
Nowadays, hydrogen can be produced mainly from fossil fuels, water, and biomass (organic wastes and wastewater).

2.1.2.1 *Fossil Fuels as a Source of Hydrogen Production*

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

2.1.2.1.1 *Steam Reforming of Natural Gas*

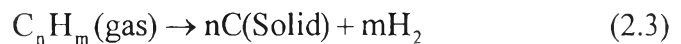
Steam reforming, which is a thermal process, consists of two reactions in a process:



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

2.1.2.1.2 Thermal Cracking of Natural Gas

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

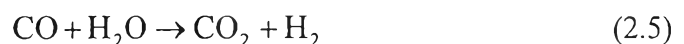
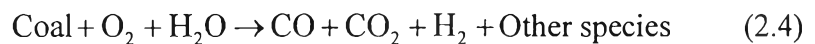


2.1.2.1.3 Partial Oxidation of Hydrocarbons Heavier than Naphtha

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

2.1.2.1.4 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 high temperature of 1330°C. The gaseous coal is treated with steam and controlled amount of oxygen to produce hydrogen, carbon monoxide, and carbon dioxide. And then, carbon monoxide is reacted with steam to produce more hydrogen and carbon dioxide in water gas shift reaction. The reactions are shown below as:



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

2.1.2.2 *Water as a Source of Hydrogen Production*

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

2.1.2.2.1 *Electrolysis*

Electrolysis is the process to split the water molecules into their basic elements of hydrogen and oxygen by passing an electric current between two electrodes (cathode and anode) through water. Hydrogen rises from the (negative) cathode, and oxygen is collected at the (positive) anode. This process is the most common method to produce hydrogen after steam reforming of natural gas. In addition, it is very well understood.

2.1.2.2.2 *Thermolysis or Direct Thermal Decomposition*

Thermolysis (or direct thermal decomposition) is a high temperature process for hydrogen production. When water is heated to a high temperature at 3000 K (2727°C), it can be decomposed into hydrogen and oxygen. This process has high efficiency, but it is normally not applied to produce hydrogen.

2.1.2.2.3 *Thermochemical Cycles*

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

2.1.2.2.4 *Photolysis*

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

1) *Biophotolysis Process*

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

2) *Photochemical Process*

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

3) *Photoelectrochemical Process*

Photoelectrochemical process uses sunlight and specialized semiconductors (photocatalyst) that is called photoelectrochemical materials to produce hydrogen from water. In the photoelectrochemical (PEC) system, the semiconductor can directly split water molecules into hydrogen and oxygen by using light energy. Different semiconductor materials work at particular wavelengths of light and energy.

2.1.2.3 *Biomass as a Source of Hydrogen Production*

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

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

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

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

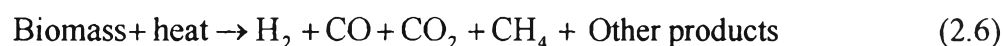
(iv) Industrial waste and wastewater, municipal waste and wastewater: municipal solid waste (MSW), sewage sludge and industry waste.

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

2.1.2.3.1 Thermochemical Process for Hydrogen Production

1) Biomass Pyrolysis

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

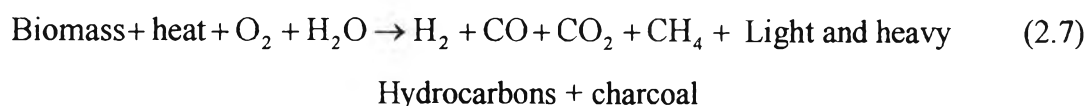


All solid, liquid, and gas phase can be found as the products of this process. Solid products consist of char, pure carbon, and other inert materials. Liquid products include tar and oils that remain in liquid form at room temperature. Gaseous products comprise hydrogen, methane, carbon monoxide, carbon dioxide, and others, depending on the organic nature of biomass. Methane and other hydrocarbon vapors produced can be steam-reformed for more hydrogen production. Moreover, water gas shift reaction can be applied to increase

the hydrogen production. Besides the gaseous products, the oily products can also be processed to produce hydrogen.

2) Biomass Gasification

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



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

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

2.1.2.3.2 Biological Process for Hydrogen Production

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:

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, 1998). If photosynthetic bacteria are combined with fermentative bacteria, the fermentative bacteria could produce the small organic acids, which the photosynthetic bacteria could then use.

2) *Dark Fermentation*

Hydrogen production via dark fermentation is a special type of anaerobic digestion process comprising only hydrolysis and acidogenesis (Bartacek *et al.*, 2007). Fermentative bacteria producing hydrogen, carbon dioxide, and some simple organic compounds, e.g. volatile fatty acid (VFA) and alcohols, in the dark may be cultivated in pure culture or occur in uncharacterized mixed cultures selected from natural sources, such as anaerobic digested sewage sludge and soil (Bartacek *et al.*, 2007 and Vijayaraghavan *et al.*, 2008). The advantages of dark fermentation are that fermentative bacteria are capable of high hydrogen generation rate, and hydrogen is produced throughout the day and night at a constant rate since it does not depend on energy provided by sunlight (Vijayaraghavan *et al.*, 2005). This decreases the energy demand, and the technology can be simpler (Bartacek *et al.*, 2007). In addition, fermentative bacteria can have good growth rate for supply of microorganisms to the production system (Das *et al.*, 2001). From these several advantages, hydrogen production by dark fermentation is feasible for industrial application (Das *et al.*, 2001).

2.2 Alcohol Wastewater

Alcohol wastewater which used as raw material is derived from Saphthip Lopburi Co., Ltd. The process is generated from cassava fermentation with enzyme. The products from fermentation process are fractionated by a distillation column. Then, the products, ethanol, and water are separated to product tank and wastewater treatment system. Saphthip Lopburi Co., Ltd. is an ethanol production plant in Thailand. The capacity is about 200,000 liters per day. The process of ethanol production is shown in Figure 2.1.

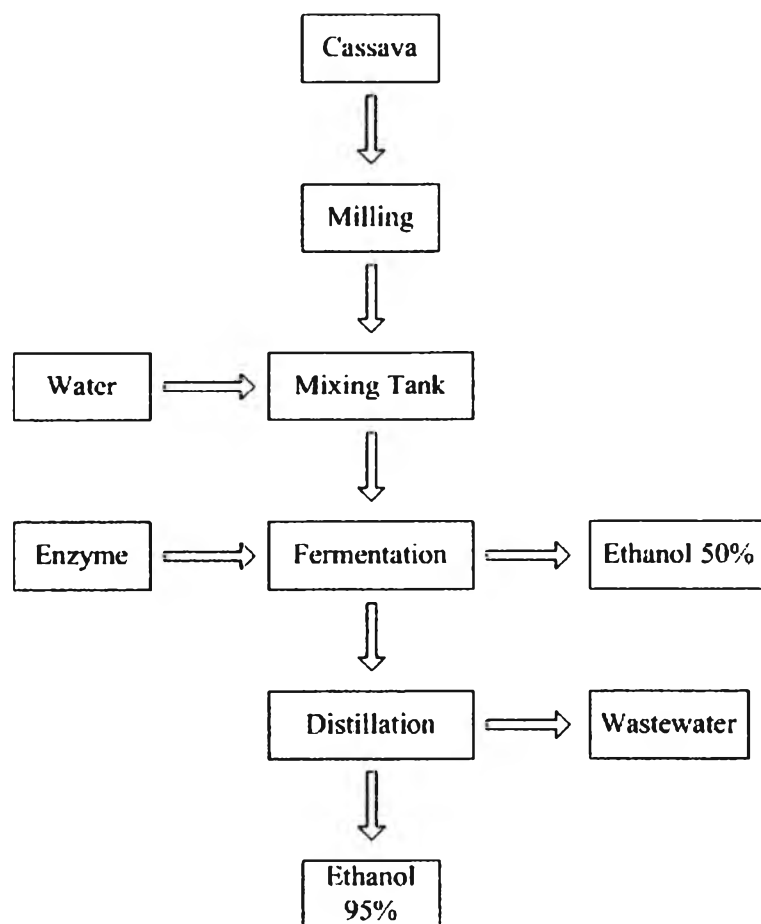


Figure 2.1 Flow diagram of alcohol production process at Saphthip Lopburi Co., Ltd.

2.3 Anaerobic Fermentation

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 (as shown in Figure 2.2)

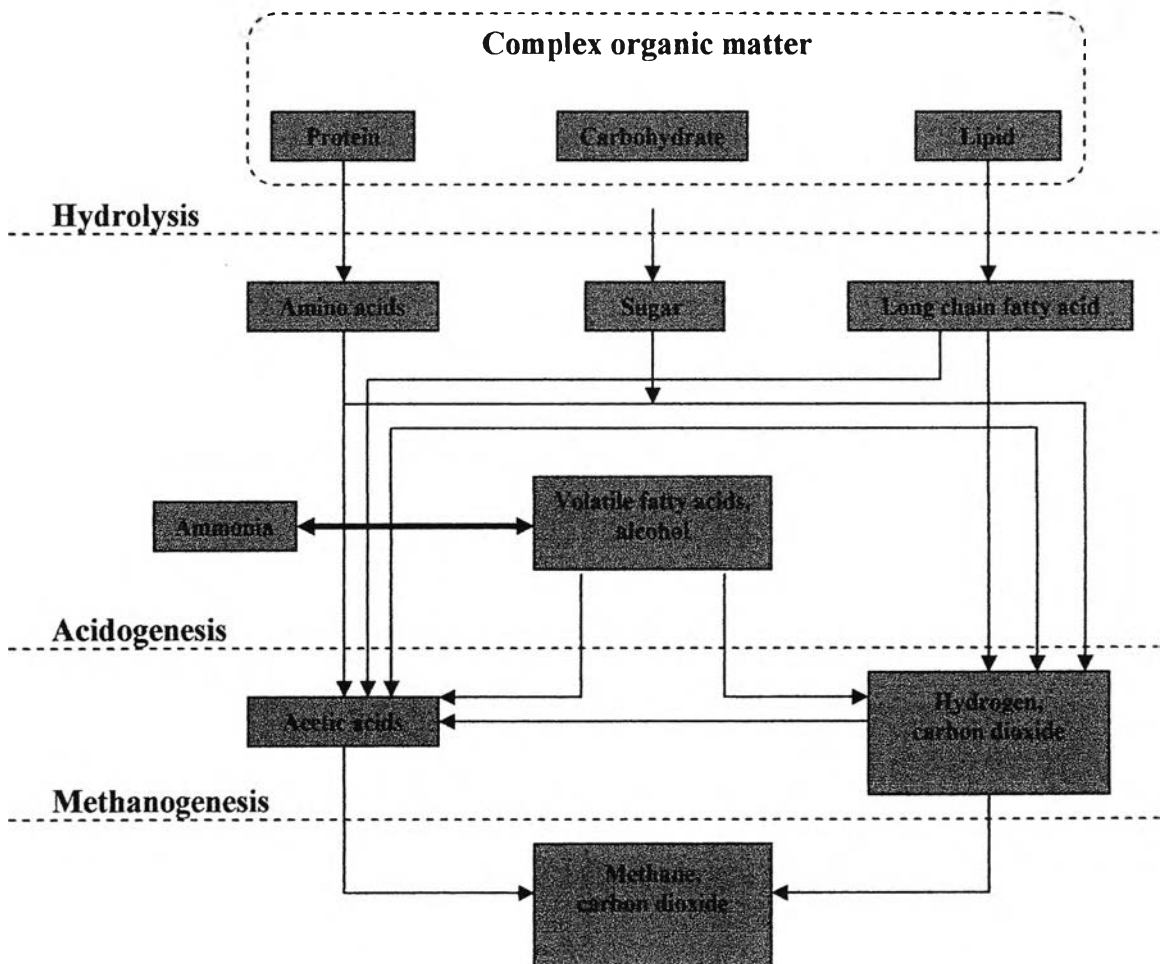


Figure 2.2 The schematic representation of anaerobic fermentation.

2.3.1 Decomposition of Carbonaceous Compounds

There are 3 main sequential steps:

2.3.1.1 *Hydrolysis*

Large organic molecules are hydrolyzed to simple molecule by external enzymes release by bacteria.

2.3.1.2 *Acidogenesis*

In this step, it will change soluble organics into organic acids (volatile fatty acid, VFA) e.g. butyrate, propionate, valerate, acetate. Some alcohol can be produced in this step. Moreover in this step can be produced hydrogen.

2.3.1.3 *Methanogenesis*

In this process, organic acids (volatile fatty acid, VFA) will change into methane. In this step can be produced about 70% of methane.

2.4. Wastewater Treatment

Wastewater treatment refers to the process of removing pollutants from water previously discharged to the environment or employed for industrial, agricultural, or municipal uses. The techniques used to remove the pollutants present in wastewater can be divided into biological, chemical, physical, and energetic ones. These different techniques are applied through many stages of wastewater treatment.

2.4.1 Classification of Wastewater Treatment

Wastewater treatment processes are often classified as preliminary treatment, primary treatment, advanced primary treatment, secondary treatment, tertiary treatment, advanced treatment, and sludge treatment, as shown in Figure 2.3.

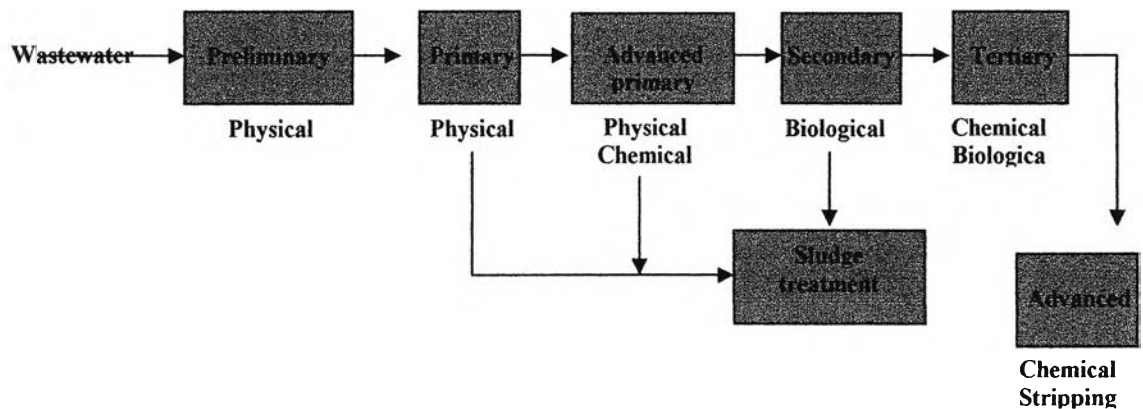


Figure 2.3 The flow diagram of wastewater treatment processes.

2.4.1.1 Preliminary Treatment

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

2.4.1.2 Primary Treatment

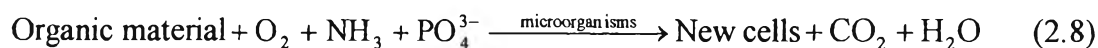
Primary treatment is a physical operation, usually sedimentation, is used to remove a portion of the suspended solids from the wastewater by settling or floating.

2.4.1.3 Advanced primary Treatment

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

2.4.1.4 Secondary Treatment

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



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

2.4.1.4.1 *Biological Treatment Options*

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

1) *Aerobic Biological Treatment*

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

2) *Anaerobic Biological Treatment*

Anaerobic biological treatment is similar to aerobic treatment, but anaerobic treatment 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

2.4.1.4.2 *Biological Treatment Processes*

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

1) Suspended Growth Process

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

2) Attached Growth Process

In attached growth or fixed film process, the microorganisms responsible for the conversion of organic material or nutrients are attached to a surface of inert packing material, the fixed film (or biofilm), which may be mobile or stationary with wastewater (liquid). The organic material and nutrients are removed from the wastewater during flowing past the surface/media. Packing material used in this process includes rock, gravel, slag, sand, redwood, and a wide range of plastic and other synthetic materials. This process can also be operated as aerobic or anaerobic processes. The packing can be submerged completely in liquid or not submerged, with air or gas space above the biofilm liquid layer.

2.4.1.5 Tertiary Treatment

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

2.4.1.6 Advanced Treatment

Advanced treatment is necessary in some treatment systems to remove nutrients from wastewater. Chemicals are sometimes added during the treatment process to help settle out or strip out phosphorus or nitrogen. Some examples of nutrient removal systems include coagulant addition for phosphorus removal and air stripping for ammonia removal.

2.4.1.7 Sludge Treatment

Wastewater treatment processes generate significant quantities of sludge from suspended solids in the feed, biomass generated by biological process, and precipitates from added chemicals, in which require the

processes to treat them. Sludge treatment is the process to stabilize the sludge, 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. The sludge is still largely water, as much as 97 percent. Settling the sludge and decanting off the separated liquid remove some of the water and reduce the sludge volume. Settling can result in sludge with about 92 to 96 percent water. More water can be removed from sludge by using sand drying beds, vacuum filters, filter presses, and centrifuges, resulting in sludge with between 50 to 80 percent water. This dried sludge is called a sludge cake. Aerobic and anaerobic digestions are used to decompose organic matter to reduce volume. Digestion also stabilizes the sludge to reduce odors. Caustic chemicals can be added to sludge, or it may be heat-treated to kill disease-causing organisms. Following treatment, liquid and cake sludge are usually spread on fields, returning organic matter and nutrients to the soil.

2.4.2 Common Parameters in Wastewater

2.4.2.1 *Total and Suspended Solids*

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

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

The term *Total Suspended Solids (TSS)* refers to the nonfilterable residue that is retained on a glass-fiber disk after filtration of a sample

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

Volatile Suspended Solids (VSS) are determined by igniting the dry solids at 550±50°C after placing the filter disk in a porcelain dish. The concentration of volatile suspended solids is the weight of dry solids minus the weight of fixed solids divided by the volume of the original liquid sample.

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

2.4.2.2 *Biochemical and Chemical Oxygen Demands*

2.4.2.2.1 *Biochemical Oxygen Demand*

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

2.4.2.2.2 *Chemical Oxygen Demand*

Chemical oxygen demand (COD) is a measure of the oxygen equivalent of the organic matter in wastewater that can be oxidized chemically using 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.

2.4.2.3 Total Organic Carbon

Total Organic Carbon (TOC) is the value used to indicate the concentration of organic matter in wastewater that can be used as a measure of the degree of water pollution. The test method for TOC utilizes heat and oxygen, ultraviolet radiation, chemical oxidants, or some combination of these methods to convert organic carbon to carbon dioxide, which is measured with an infrared analyzer or by other means. The TOC test is also gaining more interest because it takes only 5 to 10 minutes for complete analysis.

2.4.2.4 Hydraulic Retention Time

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

$$\tau = \frac{V}{Q} \quad (2.9)$$

Where;

- τ = Hydraulic retention time, h
- V = Volume of reactor, m³
- Q = Volumetric flow rate, m³/h

2.5 Anaerobic Bioreactors

Anaerobic fermentation is an excellent odor-reducing technique and also converts the degradable organic substrate to gas in a tank for use as a fuel. The organic substrates, such as glucose, sucrose, paper mill waste, municipal solid waste, food processing waste, rice winery and palm oil mill effluents, can be used for hydrogen production (Vijayaraghavan and Soom, 2006). The different types of substrate and bioreactor affect the amount of produced hydrogen. Metcalf and Eddy (2003) categorized anaerobic bioreactor into 3 groups: anaerobic suspended growth reactor, attached growth anaerobic reactor, and upflow anaerobic sludge blanket reactor.

2.5.1 Anaerobic Suspended Growth Treatment Processes

Anaerobic suspended growth processes are classified into three types:

2.5.1.1 *Complete-mix Process*

For the complete-mix anaerobic digester as shown in Figure 2.4(a), the solid retention time and hydraulic retention are equal. 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

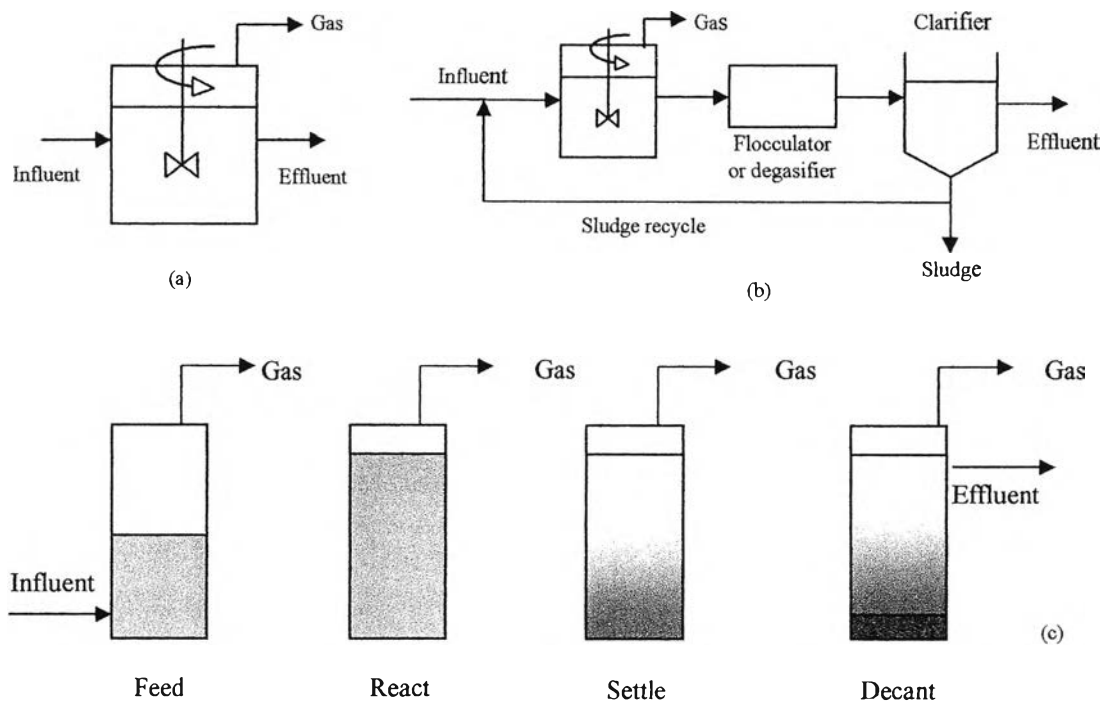


Figure 2.4 Anaerobic suspended growth processes: (a) complete-mix process, (b) anaerobic contact process, and (c) anaerobic sequencing batch reactor process.

2.5.1.2 Anaerobic Contact Process

This process, as shown in Figure 2.4(b), can overcome the disadvantages of a complete-mix process without recycle. Separated biomass is returned to the complete-mix 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 separating SRT and τ values. 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.

2.5.1.3 Anaerobic Sequencing Batch Reactor (ASBR)

This reactor, as shown in Figure 2.4(c), is typically operated under batch-mode comprising four different 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 solids.

2.5.2 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 all of these, the UASB process is the most commonly studied because of high rate of production, (Perez *et al.*, 2006), low energy requirement, and simple operation (Metcalf and Eddy, 2003).

2.5.2.1 Upflow Anaerobic Sludge Blanket (UASB)

The basic UASB reactor is shown in Figure 2.5(a). 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. Modifications to the basic UASB design include adding a settling tank, as shown in Figure 2.5(b), or the use of packing material at the top of the reactor, as shown in Figure 2.5(c). 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.

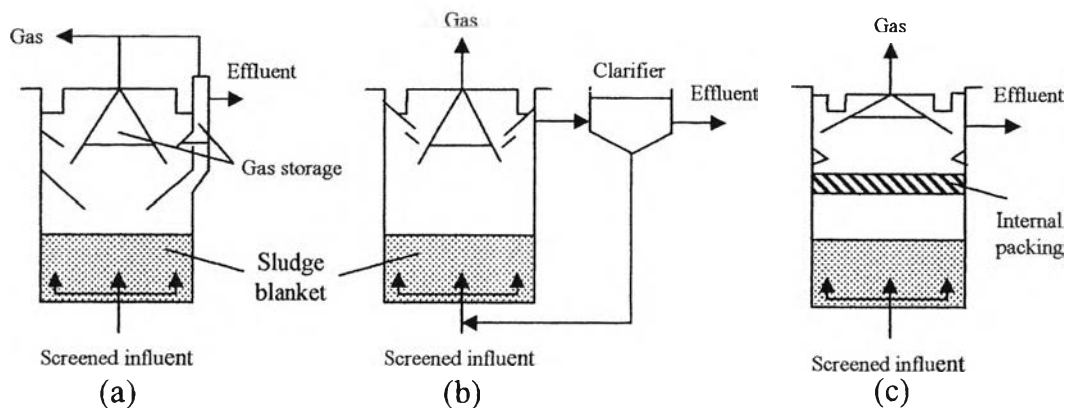


Figure 2.5 Schematic of the UASB process and some modifications: (a) original UASB process, (b) UASB reactor with sedimentation tank and sludge recycle, and (c) UASB reactor with internal packing for fixed-film attached growth, placed above the sludge blanket.

2.5.2.2 Anaerobic Baffled Reactor (ABR)

In the ABR process, as shown in Figure 2.6(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 is used to capture and return solids, or (3) packing is used in the upper portion of each chamber to capture solids.

Advantages for the ABR process include the following:

- Long solid retention time possible with low hydraulic retention time
- No special biomass characteristic required
- Compatible with various kinds of wastewaters with a wide variety of constituent characteristics.
- Stable to shock loads

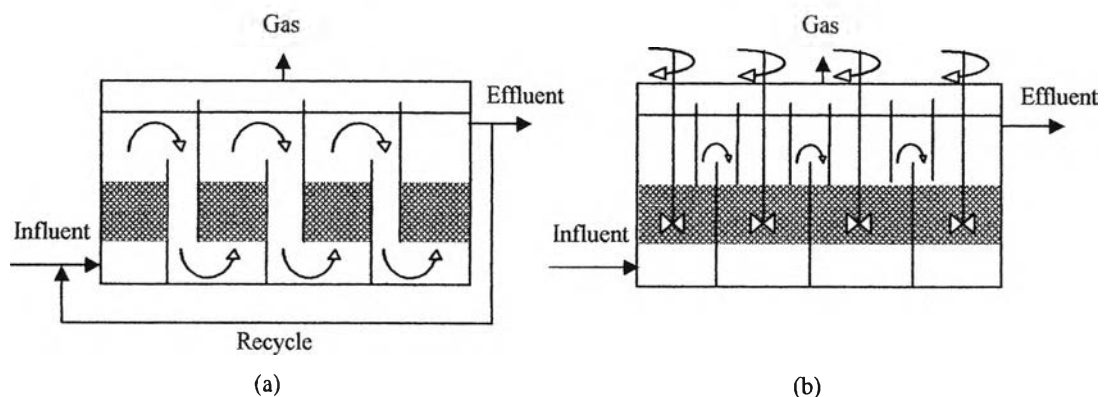


Figure 2.6 Schematic of alternative sludge blanket processes: (a) anaerobic baffled reactor (ABR) and (b) anaerobic migrating blanket reactor (AMBR).

2.5.2.3 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 2.6(b). In this 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.

2.5.3 Attached Growth Anaerobic Processes

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

2.5.3.1 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 2.7(a). 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 the washout of the biomass. Over time, solids and biomass will accumulate in the packing to cause plugging and flow short-circuiting. At this point, solids must be removed by flushing and draining the packing.

Advantages of upflow attached growth anaerobic reactors are the compatibility with 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.

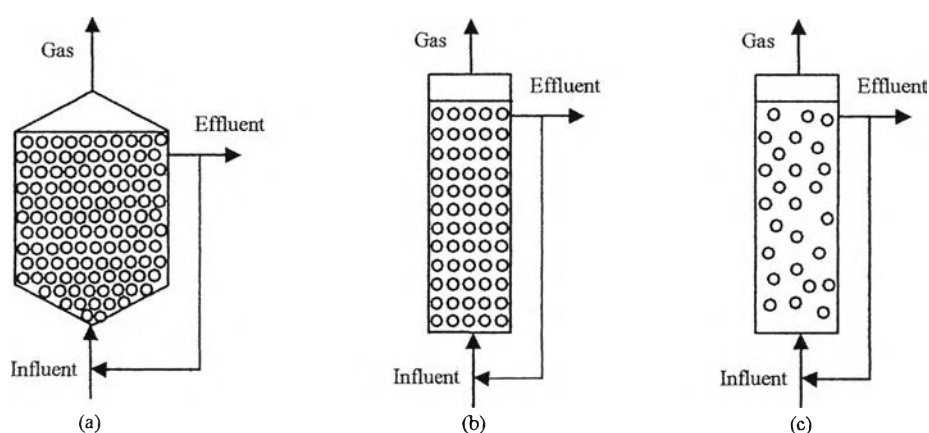


Figure 2.7 Upflow anaerobic attached growth treatment reactors: (a) anaerobic upflow packed-bed reactor, (b) anaerobic expanded-bed reactor, and (c) anaerobic fluidized-bed reactor.

2.5.3.2 Upflow Attached Growth Anaerobic Expanded-bed Reactor

The anaerobic expanded-bed reactor (AEBR), as shown in Figure 2.7(b), uses silica sand with a diameter in the range of 0.2 to 0.5 mm and specific gravity of 2.65 as the packing material to support biofilm growth. The smaller packing provides a greater surface area per unit volume. 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. Most applications for the AEBR treatment process have been for the treatment of domestic wastewater.

2.5.3.3 Attached Growth Anaerobic Fluidized-bed Reactor

The anaerobic fluidized-bed reactor (AFBR), as shown in Figure 2.7(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 percent bed expansion. Effluent recycle is used to provide sufficient upflow velocity.

The advantages for the AFBR process include the ability to provide high biomass concentrations and relatively high organic loading, high mass transfer characteristics, ability to handle shock loads due to its mixing and dilution with recycle, and minimal space requirements.

2.5.3.4 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, no plugging problem, and a simple operation.

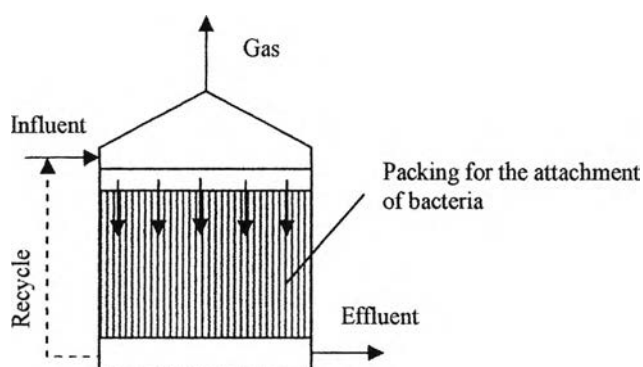


Figure 2.8 Downflow attached growth anaerobic treatment reactor.

2.6 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 as shown in Table 2.2 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 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. Another one is methanogenic-stage, which is maintained at pH around 7 and high alkalinity, resulting in high specific methanogenic activity.

Table 2.2 The advantages of the two-stage system over the one-stage system when treating the same waste or wastewater

<ul style="list-style-type: none"> • Have short hydraulic retention time for rapidly degradable waste
<ul style="list-style-type: none"> • Higher COD removal efficiency
<ul style="list-style-type: none"> • Higher methane concentration in the gaseous products because the specific activity of methanogenic bacteria increases.
<ul style="list-style-type: none"> • Better process reliability, resilience, and stability, especially with variable waste conditions and readily degradable waste, which causes unstable performance in one-stage system.
<ul style="list-style-type: none"> • Physical separation of the acidogenic and methanogenic bacteria for maximum hydrogen and methane production rate.
<ul style="list-style-type: none"> • The acid phase and methane phase can be started much more easily and quickly than in conventional, single-stage digesters.

2.7 Related Works on Biohydrogen Production from Wastewaters

2.7.1 Effect of pH on Hydrogen Production from Glucose by a Mixed Culture

The effect of pH on hydrogen production from glucose by a mixed culture was studied (Fang *et al.*, 2002). The pH was varied from 4 to 7 under 36°C.

Hydrogen yield reached the optimum condition at pH 5.5 and when they considered the gas content, the biogas comprised of mostly H₂ and CO₂. The CO₂ in biogas followed an opposite trend of H₂ and the biogas was free of methane at pH 5.5 or lower. This means that the appropriate pH for hydrogen production is 5.5.

2.7.2 Continuous Bio-Hydrogen Production from Citric Acid Wastewater via Facultative Anaerobic Bacteria.

In this study continuous biological hydrogen production using wastewater from citric acid factory as raw material was investigated (Yang *et al.*,

2006). For finding out the industrialized feasibility of continuous bio-hydrogen production, the ability of hydrogen production via facultative anaerobe and optimum hydraulic retention time (HRT) were also studied. They used an UASB reactor under mesophilic and pH 7. The optimum biogas that they found is $0.95 \text{ m}^3 / \text{m}^3 \text{ reactor d}$ and hydrogen production rate is $0.72 \text{ m}^3 / \text{m}^3 \text{ reactor d}$. Both of them got an optimum condition at 12 hours of HRT. From this result they concluded that the optimum condition is the highest point of hydrogen production and after the optimum condition it decrease due to toxicity from volatile fatty acids (VFAs).