CHAPTER II
LITERATURE REVIEW

2.1 Background of Hydrogen

Energy is one of the most important factors in the world. The current world's energy requirement is based on fossil fuels (about 80% of the world energy demand) (Das and Veziroglu, 2001). Fossil fuels have served as energy for transport and industry. However, the combustion of fossil fuels has negative effects on environment. When these fuels are burnt, their carbon recombines with oxygen from the air to form carbon dioxide (CO_2), and carbon dioxide emission into the atmosphere 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 has been focused for an alternative energy resource.

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 with air. 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 among all fuels, partly because of how light it is as 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 to prevent the depletion of fossil fuels.

Hydrogen can be used in any applications, in which fossil fuels are being used, such as a fuel in furnaces, internal combustion engines, turbines and jet engines, automobiles, buses, and airplanes. Nowadays, hydrogen can be directly used to generate electricity through fuel cells, which are mostly used in transportation section. Moreover, hydrogen and fuel cell technology have the potential to strengthen our national energy security by reducing our dependence on foreign oil.

2.1.1.5 Hydrogen can be produced from various sources.

The greatest advantage of hydrogen is that there are many production processes, using both renewable and traditional energy sources. The most common method of hydrogen production is by reforming fossil fuels, particularly natural gas. Electrolysis is another method of hydrogen production that uses electricity to split water into hydrogen and oxygen gases. One advantage of electrolysis is that one can perform electrolysis using renewable source so that the hydrogen produced is a renewable fuel.

2.1.1.6 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 °C and temperature more than 900 °C with Pt/Ru catalyst.

2.1.2 Hydrogen Production Processes

Hydrogen is found on the earth almost only in combination with other elements, such as oxygen, carbon, and nitrogen. In order to use hydrogen, it must be separated from these elements. There are many methods for producing hydrogen. The main sources for hydrogen production are fossil fuels, water, and biomass.

2.1.2.1 Hydrogen production from fossil fuels

(1) Steam-methane reforming (SMR)

This process consists of the following two steps.

Reforming of natural gas: methane is reacted with steam at 750–800 °C (1380–1470 °F) to produce a synthesis gas (syngas), a mixture primarily made up of hydrogen (H_2) and carbon monoxide (CO), which is described by the following reaction:

$$CH_4 + H_2O \text{ (+heat)} \rightarrow CO + 3H_2 \qquad (2.1)$$
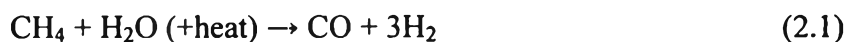
Shift reaction known as a water gas shift (WGS) reaction: the carbon monoxide produced in the first reaction is reacted with steam over a catalyst to form hydrogen and carbon dioxide (CO_2). This process occurs in two stages, consisting of a high temperature shift (HTS) at 350 °C (662 °F) and a low temperature shift (LTS) at 190–210 °C (374–410 °F) (http://www.getenergysmart. org/Files/HydrogenEducation/6HydrogenProductionSteamMethaneReforming.pdf), which is described by the following reaction:

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

(2) Coal gasification

The gasification of coal is one method that can produce hydrogen. First, reaction of coal with oxygen and steam occurs under high pressures and temperatures to form synthesis gas, a mixture consisting primarily of carbon monoxide and hydrogen from the following reaction (unbalanced):

$$CH_{0.8} + O_2 + H_2O \rightarrow CO + CO_2 + H_2 + \text{other species} \qquad (2.3)$$
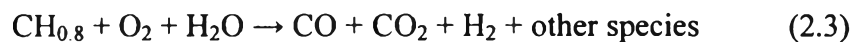
After the impurities are removed from the synthesis gas, the carbon monoxide in the gas mixture is reacted with steam via the water-gas shift reaction to produce additional hydrogen and carbon dioxide. Then, hydrogen will be removed by a separation process.

(3) Partial oxidation of methane (POX)

Partial oxidation is a process for converting natural gas into carbon dioxide and hydrogen (syngas), which can be converted to higher alkanes or methanol (Deutschmann and Schmidt, 1998). The reaction of this process is:

$$CH_4 + 1/2\,O_2 \rightarrow CO + 2H_2 \qquad \Delta H_R = -36\ kJ/mol \qquad (2.4)$$
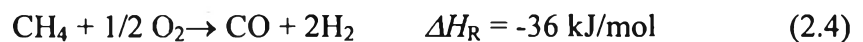
This process is the exothermic reaction so it is easy to operate as compared to other processes.

(4) Thermal cracking of methane

This is an alternative method to replace steam reforming process because of no carbon dioxide emission. This method requires high reaction temperature about 2,000 °C to produce hydrogen. The reaction is shown below:

$$CH_4 \rightarrow C + 2H_2 + 75.6\ kJ \qquad (2.5)$$

2.1.2.2 Hydrogen production from water

(1) Electrolysis

Electrolysis of water may be the cleanest technology for hydrogen gas production (Kapdan and Kargi, 2006). It is a process for producing hydrogen by applying electric current into water. When two metal plates are placed in water in the presence of a catalyst and connected to a source of electricity, water is split into its chemical components - hydrogen and oxygen. Hydrogen bubbles will be collected on the negative plate (cathode) while oxygen bubbles gather on the positive

plate (anode). There is no carbon dioxide given off during the process. The chemical reaction of water electrolysis is:

$$2H_2O + energy \rightarrow 2H_2 + O_2 \tag{2.6}$$

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

(2) Thermochemical process

The promising thermochemical process uses solar energy to heat water to around 1000 °C. Heat from high temperature solar process is used for driving an endothermic reversible reaction to produce hydrogen (Meyers, 2001).

$$H_2O \rightarrow H_2 + 0.5O_2 \tag{2.7}$$

(3) Thermolysis process

Thermolysis uses solar energy to heat water to more than 2000 °C, causing the water to break down directly to hydrogen and oxygen (http://www.science.org.au/nova/111/111key.htm).

2.1.2.3 Hydrogen production from biomass

Biomass can be used as renewable sources for hydrogen production (Kapdan and Kargi, 2006). Hydrogen production from biomass has been given attention due to operation under mild conditions. Biomass wastes, such as agricultural and domestic wastes, can be major sources for bio-hydrogen production (Argun *et al.*, 2008). Hydrogen production from biomass can be classified into two categories, which are thermochemical process and biological process.

(1) Thermochemical process

- Biomass gasification

Biomass gasification involves heating biomass, such as crop waste, wood, and newspapers, with steam and oxygen to produce hydrogen under pressure and a controlled amount of oxygen (in a unit called a gasifier) to biomass (http://www.science.org.au/nova/111/111key.htm). The biomass is broken apart chemically by the gasifier's heat, steam, and oxygen, setting into chemical reactions that produce a synthesis gas, or "syngas"—a mixture of primarily hydrogen and carbon monoxide. The carbon monoxide then reacts with water to form carbon

dioxide and more hydrogen (water-gas shift reaction). Then, adsorbers or special membranes are used to separate the hydrogen from this gas stream. The produced carbon dioxide will be taken by the plants while they are alive, so the overall effect on greenhouse gas release is reduced, as shown in the following reaction:

$$C_6H_{12}O_6 + O_2 + H_2O \rightarrow CO + CO_2 + H_2 + \text{other species} \qquad (2.8)$$
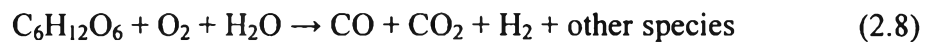
- Pyrolysis

This is the thermochemical process that converts biomass into liquid, charcoal, and non-condensable gases, i.e. acetic acid, acetone, and methanol, by heating the biomass to about 400 °C in the absence of air. The main gaseous products from pyrolysis are hydrogen, carbon dioxide, carbon monoxide, and hydrocarbon gases.

(2) Biological processes

Biological hydrogen production is an alternative method for hydrogen gas production. It is also known as "green technology" (Kapdan and Kargi, 2006), using anaerobic and photosynthetic microorganisms to degrade carbohydrate-rich and non-toxic raw materials, such as starch, into end products, i.e. volatile fatty acid, hydrogen, and carbon dioxide. These biological hydrogen production processes are operated at ambient temperatures and pressures, less-energy intensive, and environmentally friendly. There are two types of bio-hydrogen production: photosynthetic and dark fermentation (Vijayaraghavan and Soom, 2004).

- Bio-photolysis of water by algae

This is a direct method for producing hydrogen. It involves the absorption of light by two distinct photosynthetic systems operating in series: a water splitting and oxygen evolving system, and a second photosystem, which generates the reductant used for carbon dioxide reduction. In this coupled process, two photons (one per photosystem) are used for each electron removed from water and used in carbon dioxide reduction or hydrogen formation (Das and Veziroglu, 2001). Green and bluegreen algae will split water molecules to hydrogen ion and oxygen via photosynthesis. Then, the generated hydrogen ions are converted into hydrogen gas by hydrogenase enzyme (Kapdan and Kargi, 2006). However, hydrogen production by this process is low since it produces oxygen, which inhibits the hydrogenase enzyme activity. Thus, during light reaction, hydrogen evolution

ceases due to an accumulation of oxygen (Vijayaraghavan and Soom, 2004). Moreover, no waste is utilized in this process. Therefore, dark fermentation is considered to be more advantageous due to the utilization of waste materials and hydrogen gas production.

- Dark fermentation process

Hydrogen production through dark fermentation or anaerobic digestion process is considered as a sustainable hydrogen production method because it is pollution-free and less energy-intensive (Lee et al., 2008). This process is carried out by anaerobic acidogenic bacteria with low cost substrates, which may be cultivated in pure cultures or occur in uncharacterized mixed cultures selected from natural sources, such as anaerobically digested sewage sludge or soil (Vijayaraghavan and Soom, 2004). The dominant cultures for hydrogen production and elimination of methanogens were obtained by heat treatment of biological sludge. Much of waste is in water and is a product of food processing usually having high COD values and high carbohydrate content (Arooj et al., 2008). The major products are acetic, butyric, and propionic acids. Hydrogen is produced as a by-product during conversion of organic waste into organic acids, which are then used for methane generation (Kapdan and Kargi, 2006). Among the biohydrogen production methods, dark fermentation seems more feasible for commercial processes due to attaining much higher hydrogen production rate than other bio-hydrogenation systems (Lee et al., 2008).

2.2 Wastewater Treatment

Since industrial development increases, the quantity of waste generated also increases. These wastes make serious threat to public health when they are not readily disposed off. Wastewater comes from many sources, including home, business, industry, and stormwater. It contains 99 percent water, plus solid and dissolved material that are poured or flushed down the drain. The use of domestic wastewater for irrigation is advantageous for many reasons, including water conservation, ease of disposal, nutrient utilization, and avoidance of surface water pollution. Nevertheless, it must be realized that although the soil is an excellent

adsorbent for most soluble pollutants, domestic wastewater must be treated before it can be returned to the environment, lake, or streams to prevent the risk to both the public and environment.

2.2.1 Processing of wastewater treatment plant

Wastewater treatment plant can be divided into two major types: primary treatment plant (physical removal of floatable and settleable solids) and secondary treatment plant (biological removal of dissolved solids). The overall processes of wastewater treatment are shown in Figure 2.1.
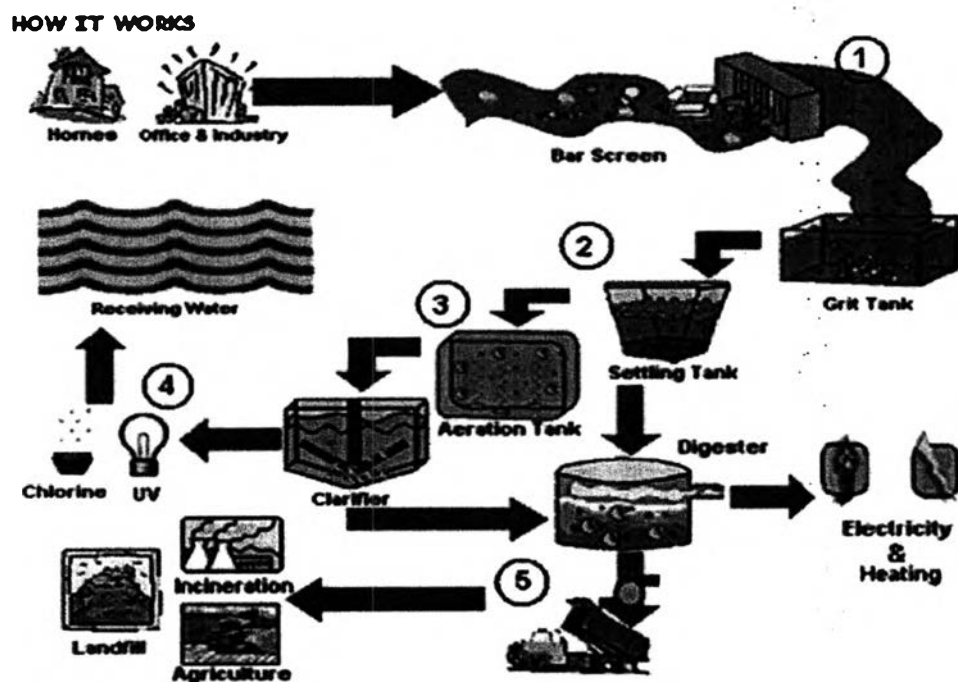

Figure 2.1 Wastewater treatment process.

2.2.1.1 Preliminary treatment

This is the first step for wastewater treatment plant. Wastewater is sent through a bar screen, which removes large solid objects, such as stones or sticks and rags, that could plug lines or block tank inlets. After that, the wastewater will slowly flow down into the grit tank. This allows sand, gravel, and other heavy materials that are not small enough to be caught by the bar screen to settle at the bottom. All the collected debris from the grit tank and bar screen are disposed of at a sanitary landfill or recycled.

2.2.1.2 Primary treatment

Primary treatment is the second step in wastewater treatment. It is the physical operation that aims for the separation of solids and greases from the wastewater. The wastewater from the preliminary treatment flows into a primary settling tank where it is held for several hours. This allows solid particles to settle to the bottom of the tank, and oils and greases to float to the top.

2.2.1.3 Secondary treatment

Secondary treatment is a biological treatment process that removes dissolved organic material from wastewater by bacterial and microorganism. The partially treated wastewater from the settling tank flows by gravity into an aeration tank. Here, it is mixed with solids containing microorganisms that use oxygen to consume the remaining organic matter in the wastewater as their food supply. Excessive biological growth washes out and is collected in the secondary clarifier. Secondary treatment prevents pollution from wastewater by degrading most of the organic matters before disposed to the environment. There are three processes involved:

(1) Activated sludge process: The used microorganisms in the treatment process will break down organic material with aeration and agitation, then allows solids to settle out. Bacteria-containing "activated sludge" is continually recirculated back to the aeration basin to increase the rate of organic decomposition.

(2) Trickling filters: It is composed of stone or plastic media (3–10 ft deep) to support microbial films. Wastewater is sprayed into the air (aeration), then allowed to trickle through the media, which contain microorganisms. Microorganisms break down organic material in the wastewater. Trickling filters drain at the bottom; the wastewater is collected and then undergoes sedimentation.

(3) Lagoons: This is the simple method, which is slow, cheap, and relatively inefficient, but can be used for various types of wastewater. Wastewater is hold for several months to allow the natural degradation. They rely on the interaction of sunlight, algae, microorganisms, and oxygen.

2.2.1.4 Tertiary treatment

The treated wastewater that remains infected has been treated before being released into receiving waters. There are many methods available to kill

these microorganisms; chlorine and ultraviolet disinfections are the most widely used. Dechlorination occurs in the final wastewater treatment step. A solution of sodium bisulfite is added to the chlorinated effluent to remove residual chlorine. So, the treated wastewater (now called final effluent) can be returned to the environment.

2.2.1.5 Sludge treatment

The convectional processes concentrate the waste organics into a volume of sludge less than the quantity of treated wastewater. However, disposal of the accumulated waste sludge is a major economic factor in wastewater treatment. Primary solids from the primary settling tank and secondary solids from the clarifier are sent to the digester. During this process, microorganisms use the organic material present in the solids as a food source and convert it to by-products, such as methane gas and water. This sludge treatment can reduce 90% of pathogens and produce a wet soil-like material called "biosolids" that contain 95–97% water. To remove some of this water and reduce the volume, mechanical equipments, such as filter presses and centrifuges, are used to squeeze water from the biosolids. The biosolids are then sent to landfills, incinerated, or beneficially used as a fertilizer or soil amendment.

2.2.1.6 Advanced treatment

Advanced wastewater treatment refers to methods and processes that remove more contaminants from wastewater that cannot be taken out by convectional processes (primary, secondary, and tertiary treatment). In some cases, the wastewater contains nutrients. It is necessary for advanced treatment 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.

2.2.2 Parameters about wastewater

2.2.2.1 Total solids (TS)

The term "total solids" refer to the residual left in a drying dish after evaporation of a sample 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.

2.2.2.2 Total volatile solids (TVS)

Total volatile solids are determined when the TS are ignited at 550±50 °C in a furnace. The residue remaining after burning is referred to as fixed solids, and the loss of weight upon 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 solid content also can be expressed as a percentage of the dry solids in the sample.

2.2.2.3 Total suspended solids (TSS)

It refers to the non-filterable 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 (mg/L).

$$TSS = \frac{\left(\begin{array}{c}residual\ of\ simple\\ after\ drying, g\end{array}\right) - \left(\begin{array}{c}tare\ mass\ filter\\ after\ drying, g\end{array}\right)}{voume\ of\ sample, L} \qquad (2.9)$$

2.2.2.4 Volatile suspended solids (VSS)

VSS are determined by igniting the TSS 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.

2.2.2.5 Dissolved solids (DS)

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. Volatile dissolved solids (VDS) equal total volatile solids minus volatile suspended solid (Metcalf and Eddy, 2003).

$$TDS = TS - TSS \tag{2.10}$$

$$VDS = TVS - VSS \tag{2.11}$$

2.2.2.6 Biochemical oxygen demand (BOD)

BOD is the quantity of oxygen used by microorganisms in the aerobic stabilization of wastewaters and polluted waters. The standard 5-day BOD value is commonly used to define the strength of municipal wastewaters, to evaluate the efficiency of treatment by measuring oxygen demand remaining in the effluent, and to determine the amount of organic pollution in surface water.

2.2.2.7 Chemical oxygen demand (COD)

COD is a parameter for measuring oxygen demand of organic compound in wastewater. Nearly all organic compounds can be fully oxidized to carbon dioxide with a strong oxidizing agent under acidic conditions. There are many oxidizing agents that have been used, such as ceric sulfate, potassium iodate, and potassium dichromate. However, potassium dichromate is shown to be the most effective. It is relatively cheap, easy to purify, and is able to nearly completely oxidize almost all organic compounds. In these methods, a fixed volume with a known excess amount of the oxidant is added to a sample of the solution being analyzed. After a refluxing digestion step, the initial concentration of organic substances in the sample is calculated from a titrimetric or spectrophotometric determination. The measured COD value is expressed in mg/L, which indicates the mass of oxygen consumed per liter of solution.

2.2.2.8 Hydraulic retention time

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

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

where   τ = Hydraulic retention time, h

V = Volume of reactor, m^3

Q = Volumetric flow rate, m^3/h

2.3 Biological Wastewater Treatment

Biological processes are the most important unit operations in wastewater treatment that rely on mixed biological culture to break down organic wastes and remove organic matters from solution. There are two processes involved: aerobic and anaerobic treatment processes.

(i) Aerobic treatment process

Aerobic treatment is accomplished by microorganisms using oxygen supplied through aeration to break down and assimilate wastewater.

(ii) Anaerobic treatment process

The anaerobic process is the degradation of organic substrates in the absence of oxygen to carbon dioxide and methane with only a small amount of bacterial growth. This process is typically used to treat strong organic wastewater.

2.4 Review of Anaerobic Fermentation Process

2.4.1 Fundamental of anaerobic fermentation process

The overall conversion process of anaerobic or dark fermentation is often described as a three-stage process, which occurs simultaneously within the anaerobic digester: hydrolysis, fermentation (also known as acidogenesis), and methanogenesis (Metcalf and Eddy, 2003), as illustrated in Figure 2.2.
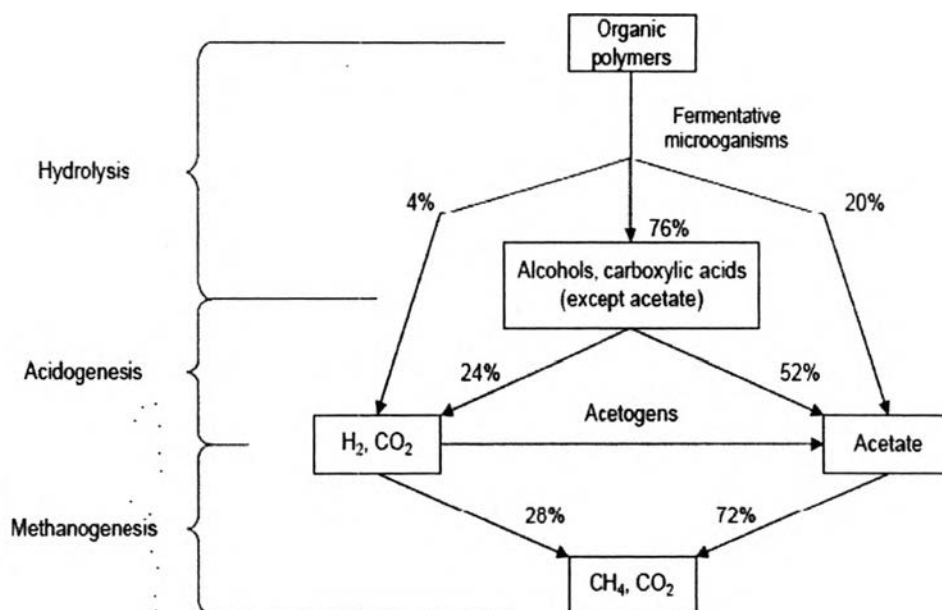
Figure 2.2 Overall process of anaerobic decomposition of organic matter (Zehnder, 1982).

2.4.1.1 Hydrolysis

This is the first step for most fermentation processes. Large, complex, and insoluble organics (protein, polysaccharides, and lipids) will be broken down into small molecules (amino acid, sugars, and fatty acids) that can be transported into the microbial cells, metabolized, and further used by bacteria that perform fermentation.

2.4.1.2 Fermentation

Fermentation (also referred to as acidogenesis) is the second step. At this step, amino acids, sugars, and some fatty acids are degraded further, as shown in Figure 2.2. Organic substrates serve as both the electron donors and acceptors. The principal products of this process are acetate, hydrogen, carbon dioxide, propionate, and butyrate. The propionate and butyrate are further fermented to produce hydrogen, carbon dioxide, and acetate. Thus, the final products of fermentation (acetate, hydrogen, and carbon dioxide) are the precursors of methane formation (methanogenesis).

2.4.1.3 Methanogenesis

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

2.4.2 Characteristics of wastewater

Anaerobic fermentation process is especially suitable for high strength and warm temperature wastewater because aeration is not required, thus saving energy cost and generating the low amount of solid. The wastewater can have COD concentrations ranging from 3,000 to 30,000 mg/L.

2.4.2.1 Advantages and disadvantages

(1) Advantages of anaerobic treatment

- Less energy required

- Low production of biosolid typically 1/3 or 1/5 of aerobic process

- Fewer nutrients required

- Smaller reactor volume required

- Elimination of off-gas air pollution

- Energy production instead of energy consumption

- Higher volumetric loading

- Increased resistance to organic shock loads

(2) Disadvantages of anaerobic treatment

- May require further treatment with an aerobic treatment process to meet discharge requirements

- Not possible for biological nitrogen and phosphorus removal

- May require alkalinity addition

- Longer start-up time to develop necessary biomass inventory

- May be more susceptible to upsets due to toxic substances

- Much more sensitive to the adverse effect of lower temperatures on reaction rates

2.4.3 Type of anaerobic treatment process

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

2.4.3.1 Anaerobic suspended growth treatment processes

There are three types of anaerobic suspended growth treatment processes (Metcalf and Eddy, 2003).

(1) Complete-mix process

For the complete-mix anaerobic digester as shown in Figure 2.3(a), the solid retention time and hydraulic retention time are equal, maybe in the range of 15 to 30 d. The complete-mix digester without sludge recycle is more suitable for wastes with high concentrations of solids or extremely high dissolved organic concentrations, where it is difficult for thickening the effluent solids. Organic loading rates for this process are present in Table 2.1, as compared to anaerobic contact and anaerobic sequencing reactor processes.

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

Process	Volumetric organic loading, kg COD/m^{3}d	Hydraulic retention time (τ), day
Complete-mix	1.0-5.0	15-30
Anaerobic contact	1.0-8.0	0.5-5
Anaerobic sequencing batch reactor	1.2-2.4	0.25-0.50

(2) Anaerobic contact process

This process, as shown in Figure 2.3(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.

(3) Anaerobic sequencing bath reactor (ASBR)

This reactor, as shown in Figure 2.3(c), is typically operated under batch-mode feeding with 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.
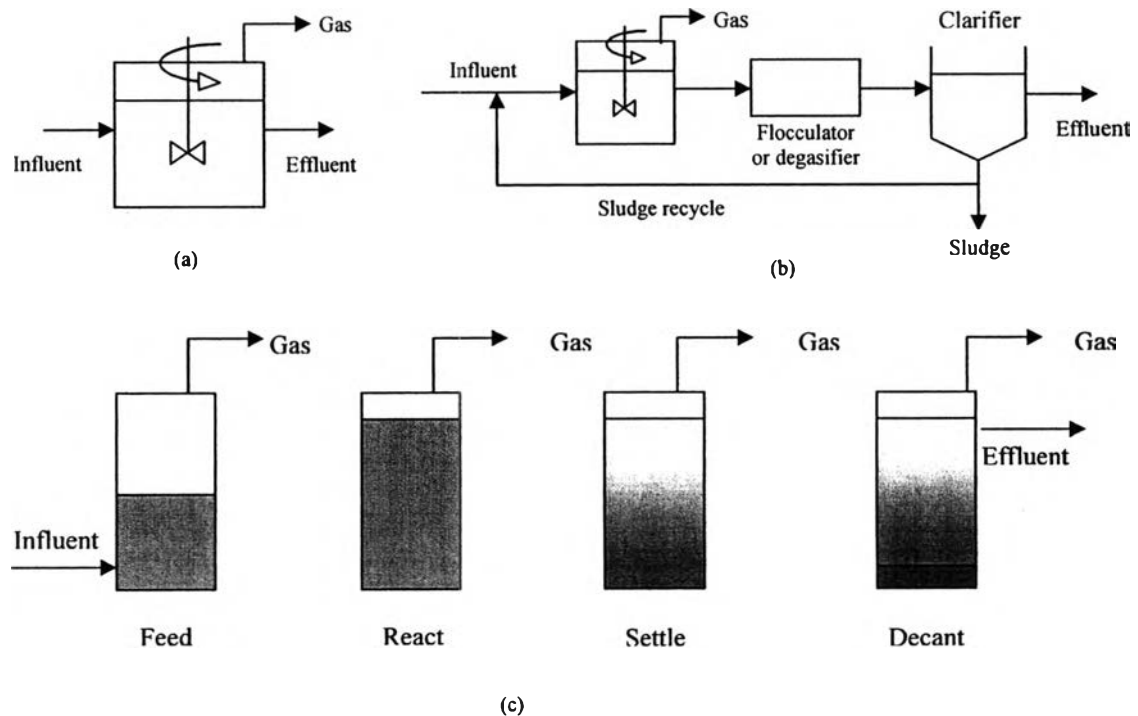
Figure 2.3 Anaerobic suspended growth processes: (a) complete-mix process, (b) anaerobic contact process, and (c) anaerobic sequencing batch reactor process.

20

2.4.3.2 Anaerobic sludge blanket processes

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

(1) Upflow anaerobic sludge blanket (UASB)

The basic UASB reactor is shown in Figure 2.4(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 2.4(b), or the use of packing material at the top of the reactor, as shown in Figure 2.4(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.
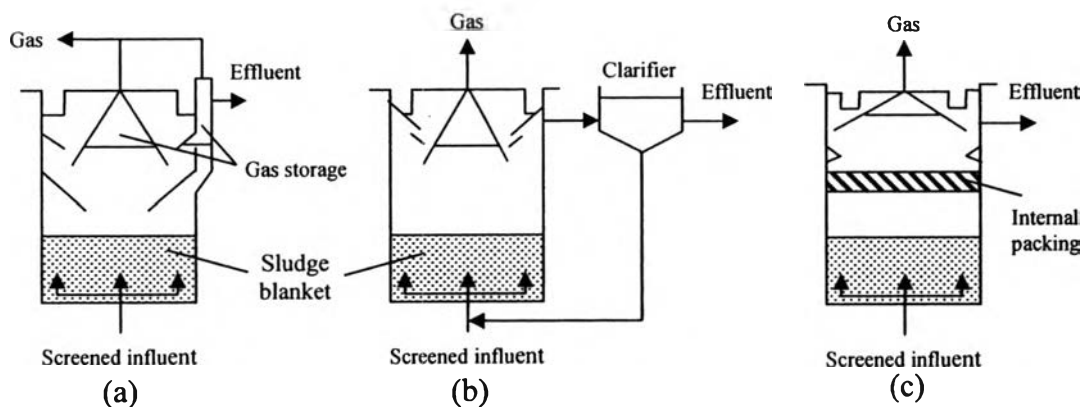

Figure 2.4 Schematic of the UASB process and some modifications: (a) original UASB process, (b) UASB reactor with sedimentation tank and sludge recycle, and (c) UASB reactor with internal packing for fixed-film attached growth, placed above the sludge blanket.

(2) Anaerobic baffled reactor (ABR)

In the ABR process, as shown in Figure 2.5(a), baffles are used to direct the flow of wastewater in an upflow mode through a series of sludge blanket reactors. The sludge in the reactor rises and falls with gas production and flows but moves through the reactor at a slow rate. Various modifications have been made to the ABR to improve performance. The modifications include: (1) changes of the baffle design, (2) hybrid reactors where a settler is used to capture and return solids, or (3) packing is used in the upper portion of each chamber to capture solids.

Advantages of the ABR process include the following:

- Long solid retention time possible with low hydraulic retention time

- No special biomass characteristic required

- Wastewaters with a wide variety of constituent characteristics can be treated

- Stable to shock loads

(3) Anaerobic migrating blanket reactor (AMBR)

The AMBR process is similar to the ABR with the added features of mechanical mixing in each stage and an operating approach to maintain the sludge in the system without resorting to packing or settlers for additional solid capture, as shown in Figure 2.5(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.
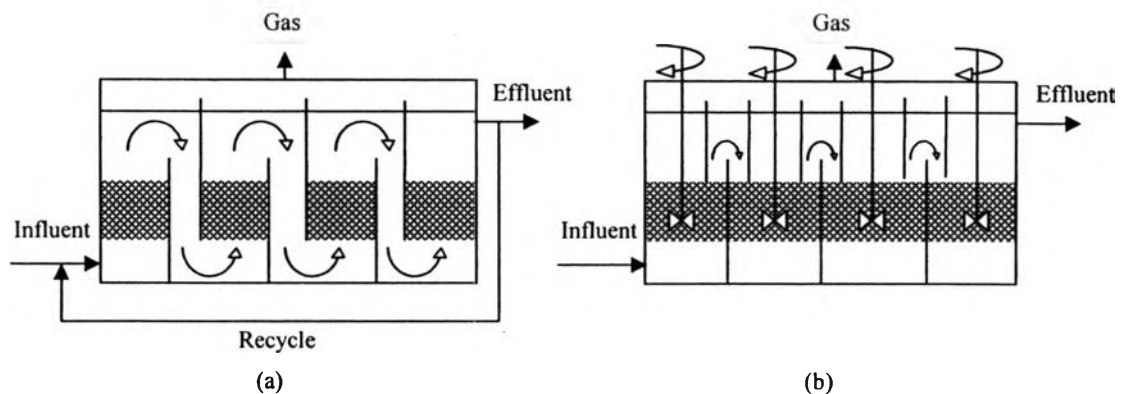
Gas

Effluent

Influent

Recycle

(a)

Gas

Effluent

Influent

(b)

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

2.4.3.3 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 can be classified as following details (Metcalf and Eddy, 2003).

(1) Upflow packed-bed attached growth reactor

Full-scale upflow packed-bed anaerobic filters are used in cylindrical or rectangular tanks at widths and diameters ranging from 2 to 8 m and heights from 3 to 13 m, as shown in Figure 2.6(a). The most common packing materials are corrugated plastic crossflow or turbular modules and plastic pall rings. A large portion of the biomass responsible for treatment in the upflow attached growth anaerobic processes is loosely held in the packing void spaces and not just attached to the packing material. Low upflow velocities are generally used to prevent washing out the biomass. Over time, solids and biomass will accumulate in the packing 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.

(2) Upflow attached growth anaerobic expanded-bed reactor

The anaerobic expanded-bed reactor (AEBR), as shown in Figure 2.6(b), uses silica sand with a diameter in the range of 0.2 to 0.5 mm and specific gravity of 2.65 as the packing material to support biofilm growth. 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.

(3) Attached growth anaerobic fluidized-bed reactor

This anaerobic fluidized-bed reactor (AFBR), as shown in Figure 2.6(c), is similar in physical design to the upflow expanded-bed reactor. The packing size is similar to the expanded-bed reactor, but the AFBR is operated at higher upflow liquid velocities of about 20 m/h to provide about 100% bed expansion. Effluent recycle is used to provide sufficient upflow velocity.

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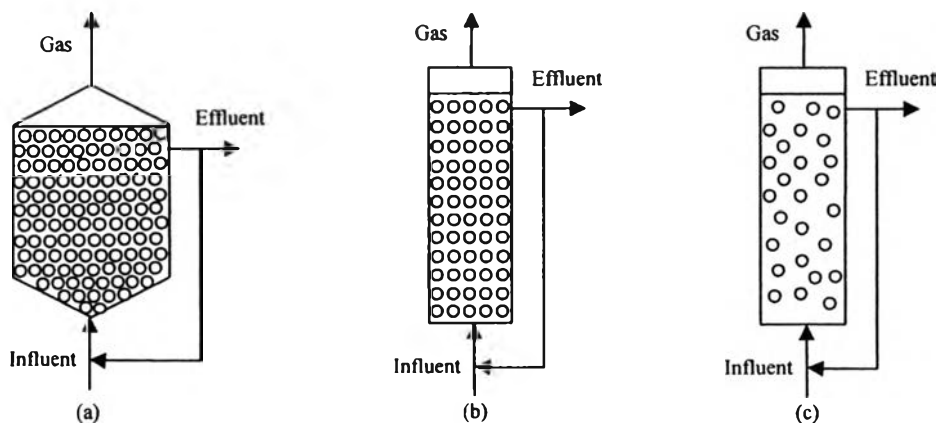

Figure 2.6 Upflow anaerobic attached growth treatment reactors: (a) anaerobic upflow packed-bed reactor, (b) anaerobic expanded-bed reactor, and (c) anaerobic fluidized-bed reactor.

(4) Downflow attached growth process

The downflow attached growth anaerobic processes, as illustrated in Figure 2.7, have been applied for treatment of high-strength wastewaters using a variety of packing materials, including cinder block, random plastic, and tubular plastic. Systems are designed to allow recirculation of the reactor effluent.

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.
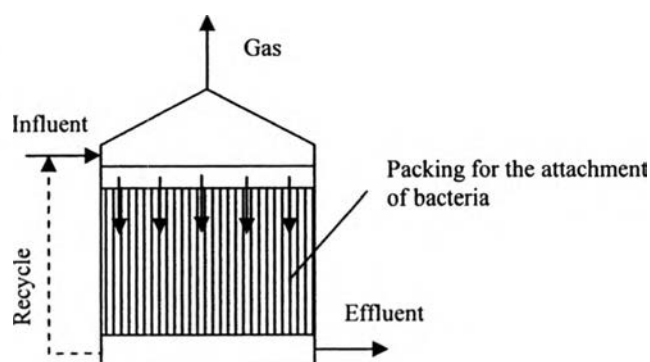
Figure 2.7 Downflow attached growth anaerobic treatment reactor.

2.5 Bio-ethanol

Ethanol or ethyl alcohol, CH_3CH_2OH, is a volatile, clear, colorless, and flammable liquid that is the intoxicating agent in liquors and is also used as a fuel or solvent. Ethanol is the most important member of a large group of organic compounds, which are called alcohol. The hydrogen atom of the hydroxyl group can be replaced by an active metal, such as sodium, potassium, and calcium, to form a metal ethoxide (ethylate) with the evolution of hydrogen gas.

Ethanol is one of the renewable fuels used for reduction of negative environmental impact. Bio-ethanol, derived from biomass, can be used in various methods as a transportation fuel. It can be used directly in vehicles or blended with

gasoline. Adding bio-ethanol in gasoline is an effective way to reduce the petroleum used and also to reduce the emission of greenhouse gas. However, the method for bio-ethanol production is relatively complicated.

2.5.1 Bio-ethanol feedstock

Bio-ethanol can be produced from agricultural raw materials. It is necessary to find out the cheapest carbohydrate sources for bio-ethanol production. There are different raw materials that have been used in the manufacture of ethanol via fermentation processes, which can be divided into three major groups: (1) sucrose-containing feedstocks, (2) starchy materials, and (3) lignocellulosic biomass. The main feedstocks for bio-ethanol production are sugars and starch. However, these feedstocks are likely to be expensive. Lignocellulosic biomass is an interesting due to its low cost and high availability.

2.5.1.1 Sucrose-containing feedstocks

Sugar cane, sugar beet, sweet sorghum, and fruits are the most important feedstocks for production of bio-ethanol. The conversion of sucrose to ethanol is easier than starchy materials because disaccharide can be broken down into ethanol directly, so previous hydrolysis of sugar is not required.

2.5.1.2 Starchy materials

Corn, wheat, rice, potatoes, cassava, sweet potatoes, and barley are the high yield feedstocks for bio-ethanol production, especially corn and wheat. In order to produce ethanol, hydrolysis is required to break down carbohydrate chain into glucose syrup (simple fermentable sugars), which is then converted to ethanol by yeast with fermentation process.

2.5.1.3 Lignocellulosic biomass

Biomasses, such as wood, straw, and grasses, are attractive to produce bio-ethanol. Lignocellulosic biomass consists of cellulose, hemicellulose, lignin, extractives, ash, and other components. Because the structure of lignocellulose is complex, pretreatment step is important. In the hydrolysis step, cellulose will be enzymetically degraded to obtain glucose that is fermented further by microorganism to form ethanol. Because this method is more complex than using cane beet or corn as feedstock, this cause leads to higher ethanol production cost. However, lignocellulosic materials come from agricultural or domestic waste. These

The hydrolysis processes of lignocellulosic biomass can be classified into two groups:

(1) Enzymatic hydrolysis

(2) Acid hydrolysis, which is the old method for converting lignocellulosic biomass into sugars. Moreover, acid hydrolysis can be divided into two basic types: dilute and concentrated acid hydrolysis.

As shown in Figure 2.8, pre-hydrolysis is the first step for bio-ethanol production. Dilute sulfuric acid is used for hydrolyzing hemicellulose to cellulose, lignin, and xylose sugar. After that, cellulose will be hydrolyzed by concentrated acid process to glucose and solid lignin. The obtained xylose sugar and glucose will be fermented in fermentation processes by microorganisms, such as yeast. The overall reaction in the fermentation process is shown as follows:

$$C_6H_{12}O_6 \rightarrow 2C_2H_5OH + 2CO_2 \qquad (2.13)$$
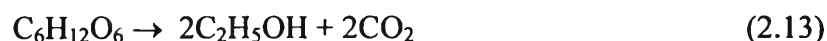
Theoretically, 1 kg of glucose will produce 0.51 kg of bio-ethanol and 0.49 kg of carbon dioxide. Practically, the actual yield is less than 100% because the part of glucose is used by microorganisms for growth (Balat and Balat, 2009).

2.5.2.2 Ethanol fermentation from molasses

Molasses is an inexpensive raw material for ethanol production. It is a mixture of monosaccharides and disaccharides containing about 50% of sugar, which can be classified into many types as follows:

- Cane molasses is a by-product of the manufacture or refining of sucrose from sugar cane.

- Beet molasses is a by-product of the sucrose production from sugar beets.

- Citrus molasses is the partially dehydrated juices obtained from the manufacture of dried citrus pulp.

- Starch molasses is a by-product of dextrose manufacture from starch derived from corn or grain sorghums, where the starch is hydrolyzed by enzymes and/or acid.
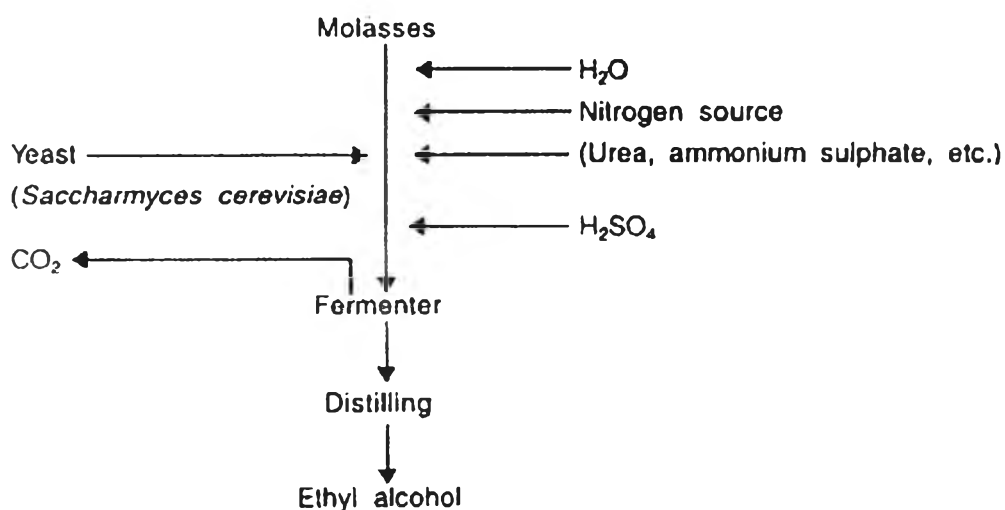
Molasses

Yeast ───────────────►│ ◄─────── H₂O
                       │ ◄─────── Nitrogen source
(Saccharmyces cerevisiae) ◄─────── (Urea, ammonium sulphate, etc.)

                          ◄─────── H₂SO₄

CO₂ ◄──────────────┐
                   │ ▼
              Fermenter

                   │
                   ▼
              Distilling

                   │
                   ▼
              Ethyl alcohol

Figure 2.9 Ethanol production from molasses.

In the ethanol production process shown in Figure 2.9, molasses is diluted with water to reach a suitable sugar concentration around 15–16%. A small quantity of nitrogen sources, such as urea, ammonium phosphate, and ammonium sulphate, is added as the nutrient supplement for microorganism growth. It is concerned that microorganism used for ethanol production must have a high tolerance for produced alcohol and must produce high amount of ethanol. Yeasts, particularly _Saccharomyces cerevisiae_, which represent the best microorganism used in the production of ethanol, are then added. Yeast has two enzymes for converting the saccharides to ethanol. Firstly, invertase will convert dissacharides (sucrose) to monosaccharides by catalytic hydrolysis reaction, and then glucose and fructose are converted to ethanol and carbon dioxide by the zymase enzyme. The pH is maintained at about 5.0. The fermentation starts and is allowed to proceed for about 24–40 h at about 25–30 °C.

2.6 Alcohol Distillation Process

Distillery slop or alcohol distillery wastewater is the wastewater from distillation of fermented mash column used both as industrial alcohol and for human consumption. This process uses sugar cane molasses as raw material and consists of four main steps, which are feed preparation, fermentation, distillation and packaging (Satyawali *et al.*, 2008), as shown in Figure 2.10. In general, the wastewater from this process is considered to be one of the most polluting wastewaters. It has high biochemical and chemical oxygen demands (BOD, COD), and suspended solid (SS). It has the temperature in the range of 70–80 °C, dark brown color, and high acid content (Mohana *et al.*, 2009). Moreover, it contains potassium, phosphates, and sulphates in high concentrations, as well as calcium, nitrogen, iron, sodium and chlorides including other trace elements (Nandy *et al.*, 2002). So, this alcohol distillery wastewater is considered to cause the problems in the treatment and disposal into environment.
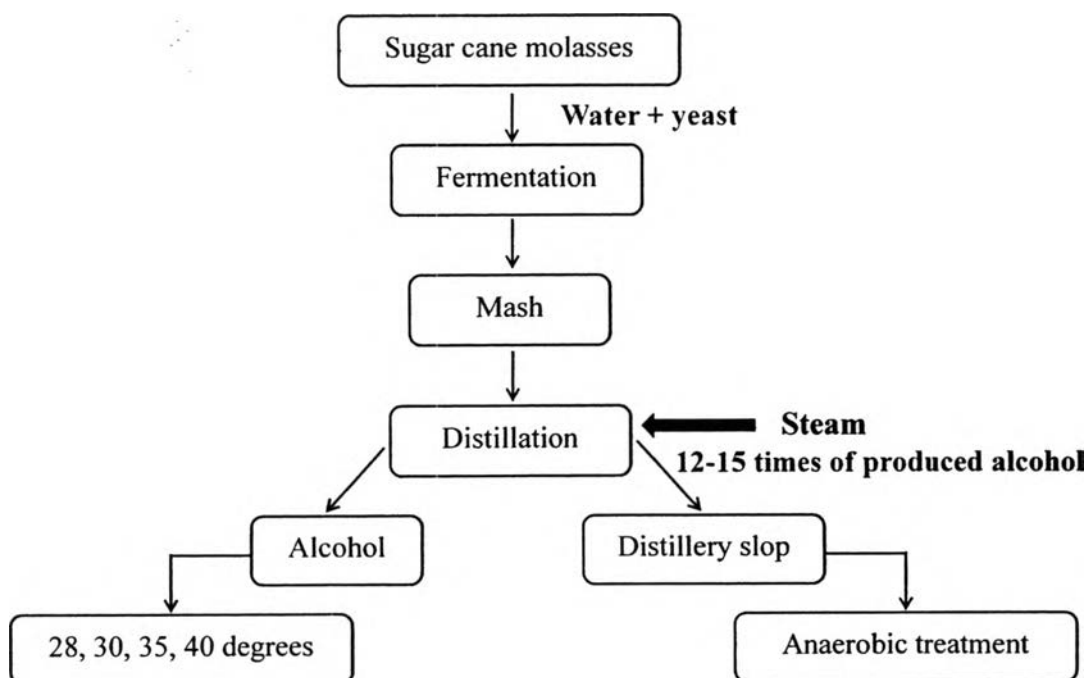

Figure 2.10 Alcohol distillation process.

2.7 Related Works on Biohydrogen Production from Wastewaters

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

2.7.1 Biohydrogen production from rice winery wastewater

High-strength rice winery wastewater was used as a substrate (Yu *et al.*, 2002). The experiment was conducted in an upflow reactor to study the effects of hydraulic retention time (HRT) (2–24 h), chemical oxygen demand (COD) concentration in wastewater (14–36 g COD/l), pH (4.5–6.0), and temperature (20–55 °C) on bio-hydrogen production from the wastewater.

- Effect of substrate concentration

The hydrogen yield slightly decreased when the wastewater concentration decreased. This means that wastewater concentration has a negative impact on hydrogen yield.

- Effect of pH

A pH value of 5.5 showed the maximum hydrogen yield, but hydrogen yield decreased with increasing pH value.

- Effect of temperature

It was found that both hydrogen yield and specific hydrogen production rate increased with temperature. Higher temperature took a benefit for hydrogen generation from rice winery wastewater.

Optimum conditions for producing hydrogen were achieved at HRT of 2 h, COD concentration of 34 g/L, pH 5.5, and temperature of 55 °C. Hydrogen production rate under these conditions was 9.33 L H_2/g VSS d. The hydrogen yield was in the range of 1.37–2.14 mol/mol-hexose.

2.7.2 Biohydrogen production from beer lees waste

The batch experiment was carried out in order to investigate hydrogen production from beer lees waste (Fan *et al.*, 2006). The effects pretreatment of substrate, substrate concentration, and pH value were studied.

- Effect of pretreatment

The experiment results showed that HCl pretreatment in the range of 0.04–0.2% played a key role in order to convert the beer lees waste into biohydrogen gas by the cow dung composts.

- Effect of substrate concentration

Hydrogen yield increased with increasing substrate concentration from 5 to 20 g/l, but gradually decreased with further increasing substrate concentration. This is because higher substrate concentration is favorable for VFAs production, which inhibits the hydrogen-producing bacteria and subsequently leads to lower hydrogen production yield.

- Effect of pH value

Cumulative hydrogen yield increased from 0.25 to 68.6 ml H_2/g TVS while the initial pH value increased from 4.5 to 6.5. It was observed that the initial pH of 5.5–7.5 may be the optimum ranges for hydrogen production.

The maximum hydrogen yield of 68.6 ml H_2/g TVS was observed at pH of 7.0 and substrate concentration of 20 g/l. The hydrogen percentage in the biogas was more than 45%, and there was no methane observed in the batch experiments. During the conversion of beer lees waste into hydrogen, the alcohols (e.g. ethanol, propanol, and butanol), acetate, and butyrate were the main by-products in the metabolism of hydrogen fermentation, but there was no significant propionate observed.

2.7.3 Biohydrogen production from cheese processing wastewater

Hydrogen production from cheese processing wastewater via anaerobic fermentation was conducted in batch experiment under mesophilic conditions (Yang *et al.*, 2007). The optimum hydrogen yields of 8 and 10 mM/g COD were observed at food-to-microorganism ratios of 1.0 and 1.5, respectively. Butyric, acetic, propionic, and valeric acids were the main by-products in this fermentation process.

2.7.4 Biohydrogen production from chemical wastewater

The effect of organic loading rate on hydrogen production by fermentation process in anaerobic sequencing batch reactor was investigated (Bhaskar et $al.$, 2008). The highest hydrogen production rate of 13.44 mol H_2/kg COD was observed at 6.3 kg COD/m^3d. An increase in organic loading rate resulted in decreases in hydrogen generation and COD removal efficiency. This may be due to the increase in recalcitrant nature of wastewater at studied organic loading rate.

2.7.5 Biohydrogen production from starch

Cassava starch could also be used as a substrate (Lee et $al.$, 2008). The experiment was carried out in batch fermentation mode using mixed anaerobic microflora. The effects of temperature, pH, and substrate concentration were investigated.

- Effect of temperature

The mesoplilic (37 °C) and thermophilic (55 °C) temperatures were studied. The results showed that hydrogen production at 37 °C was more effective than that at 55 °C. This indicated that H_2-producing bacteria in this literature was mainly mesophilic microorganism.

- Effect of pH

The operating pH of 5.5–6.0 showed the better hydrogen production performance than pH value of 6.5–7.0. It could be suggested that pH in the range of 5.5–6.0 was the effective range for microorganism that use starch for their growth.

- Effect of substrate concentration

The different initial substrate concentrations in the range of 8–32 g COD/L were investigated. The cumulative hydrogen and hydrogen yield increased with increasing initial substrate concentration to 16 g COD/l, but decreased at higher substrate concentrations. The optimum conditions in this literature were obtained at 37 °C, pH 6.0, and initial substrate concentration of 24 g COD/l with 9.47 mmol H_2/g starch.

2.7.6 Biohydrogen production from cassava starch

Hydrogen production from cassava wastewater using anaerobic sequencing batch reactors (ASBR) was investigated to determine the optimum number of cycles per day, chemical oxygen demand (COD) loading rate, and COD:N ratio (Sreethawong *et al.*, 2010).

- Effect of COD loading rate and cycle time

The system operated at a COD loading rate of 30 kg/m^{3}d and 6 cycles per day provided maximum hydrogen production performance in terms of specific hydrogen production rate (SHPR) (388 ml H$_2$/g VSS d or 3800 ml H$_2$/l d) and hydrogen yield (186 ml H$_2$/g COD removed).

- Effect of nitrogen supplementation

NH$_4$HCO$_3$ was added into the system at the COD:N ratios of 100:2.2, 100:3.3, and 100:4.4 under the COD loading rate of 30 kg/m^{3}d and 6 cycles per day. The maximum SHPR and hydrogen yield of 524 ml H$_2$/g VSS d (5680 ml H$_2$/l d) and 438 ml H$_2$/g COD removed, respectively, were obtained at the stoichiometric COD:N ratio of 100:2.2. Moreover, an excess nitrogen was found to promote the productions of higher organic acids and ethanol, resulting in lowering hydrogen production efficiency.

2.7.7 Biohydrogen production from Glucose-Containing Wastewater

The process performance of an anaerobic sequencing batch reactor (ASBR) for the hydrogen production from glucose-containing wastewater was investigated (Sreethawong *et al.*, 2010). The ASBR process was operated at a temperature of 37°C, a hydraulic reaction time (HRT) of 24 h, and different chemical oxygen demand (COD) loading rates from 10 to 50 kg/m^{3}d without and with pH control at 5.5. The results showed that at the optimum COD loading rate of 40 kg/m^{3}d and pH 5.5, the produced gas was found to contain 44% H$_2$ and 56% CO$_2$, and no methane in the produced gas was detected at all operating conditions.