

CHAPTER II

LITERATURE REVIEW

2.1 Background of Hydrogen

The current world's energy supplies are mainly 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), resulting in the carbon dioxide emission into the atmosphere, regarding the primary greenhouse gas that causes global warming. Furthermore, the combustion of fossil fuels at high temperatures and pressures of both internal combustion engines and electric power plants produces NO_x . Carbon monoxide, volatile organic chemicals, and fine particulates are also found to occur under uncomplete combustion. When being 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 further drive the current economy toward alternative energy sources.

2.1.1 Advantages of Hydrogen

Hydrogen is the cleanest fuel. When being 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 being 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.

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.

Conventional fuels significantly produce greenhouse gases, especially carbon dioxide, which is thought to be responsible for changes in global climate. The long-term environmental benefits of using hydrogen as a fuel are enormous. Hydrogen fuel produces few pollutants when burnt, and none at all when used in a fuel cell. Hydrogen is a carbon-free fuel, and when being produced using renewable energy, the whole energy system can become carbon-neutral, or even carbon-free. So, hydrogen fuel can contribute to the reduction of greenhouse gas emissions and can reduce the production of many toxic pollutants.

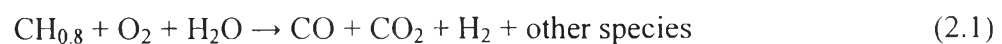
The greatest advantage of hydrogen is that it can be produced by several production processes, using both renewable and traditional energy sources. The most common method of hydrogen production is by reforming fossil fuels, particularly natural gas. Electrolysis is another method of hydrogen production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

2.1.2 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 compounds. There are many methods for producing hydrogen, as shown below.

2.1.2.1 *Coal Gasification*

The gasification of coal is one method that can produce hydrogen. First, the 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):



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.

2.1.2.2 Partial Oxidation of Methane (POX)

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



This process is the exothermic reaction so it is easy to operate as compared to other processes as well as has a lower production cost.

2.1.2.3 Thermal Cracking of Methane

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



2.1.2.4 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:



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.

2.1.2.5 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).



2.1.2.6 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>).

2.1.2.7 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:



2.1.2.8 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.

2.1.2.9 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, leading to be 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 and oxygen ions via photosynthesis. Then, the generated hydrogen ions are converted into hydrogen gas by hydrogenase enzyme (Kapdan and Kargi, 2006). However, the efficiency of hydrogen production by this process is low since the produced oxygen can inhibit the hydrogenase enzyme activity. Thus, during the light reaction, hydrogen evolution ceases due to an accumulation of oxygen (Vijayaraghavan and Soom, 2004).

- 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 acidogenic bacteria with low cost substrates, which may be cultivated in pure cultures or can 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. Most of wastewaters especially from of food processing usually have high COD values with high carbohydrate contents and so they can be used for hydrogen production economically (Arooj *et al.*, 2008). The major products are acetic, butyric, and propionic acids. Hydrogen is produced as an intermediate product during conversion of organic waste into organic acids, which are then used for methane generation (Kapdan and Kargi, 2006). Among the biohydrogen production techniques, dark fermentation seems more feasible commercially due to attaining a much higher hydrogen production rate with a much lower production cost than other bio-hydrogenation systems if high organic strength wastewaters are (Lee *et al.*, 2008).

2.2 Ethanol Production in Thailand

Nowadays, fossil fuels have been imported to Thailand more than 200,000,000 Baht per year. Moreover, the price of fossil fuels including crude oil tends to increase. Therefore, ethanol industry is currently promoted in Thailand in order to reduce the amount of import crude oil. Ethanol can be produced from various materials including cassava, molasses, corn, and sugar cane. In addition, ethanol production can also help increasing the prices of these mentioned agricultural products. In Thailand, cassava is one of the most economical raw material for producing ethanol because a large quantity of cassava is produced (4,000,000 ton per year), which can yield ethanol approximately 2,000,000 ton per year (<http://www.teenet.chula.ac.th/forum/allmsg.asp?ID=901>).

2.3 Ethanol Wastewater

Sapthip Lopburi Co., Ltd. is an ethanol production plant in Thailand. The capacity is about 200,000 liters per day. The process of ethanol production of the factory is shown in Figure 2.1. First, cassava roots or cassava chips are ground before mixing with water. The mixing solution is then hydrolyzed enzymatically before fermentation. After that, the fermentation solution is fed into a distillation column to

separate ethanol. The wastewater coming out at the bottom distillation column still contains high organic compound both in soluble and insoluble forms which is needed to be treated before discharging into the environment.

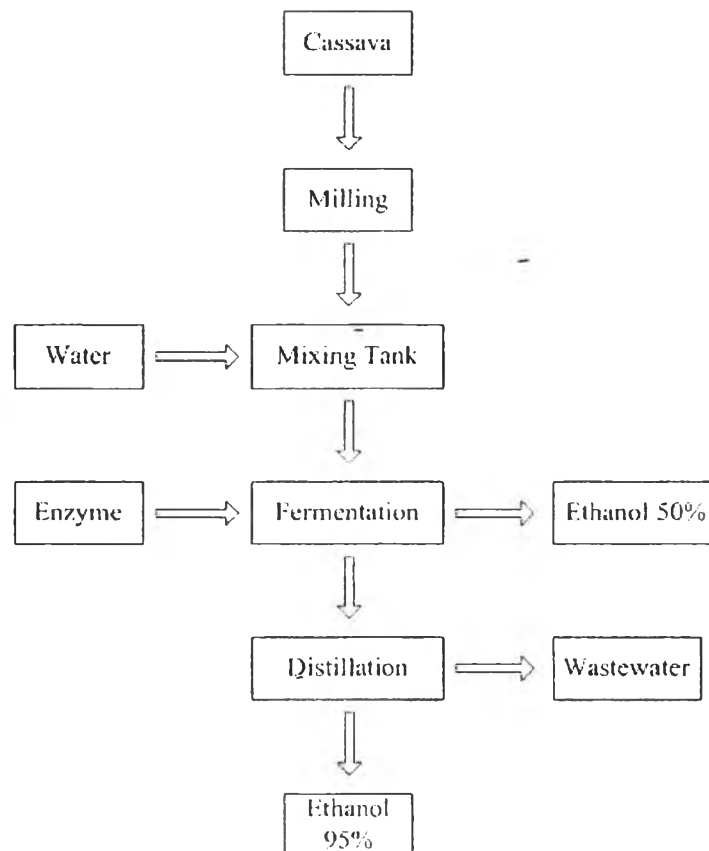


Figure 2.1 Flow diagram of ethanol production process from cassava at Sapthip Lopburi Co., Ltd.

2.4 Wastewater Treatment

Wastewaters come from many sources including home, business, industry, and stormwater. They generally contain up to 99 percent water, plus solids and dissolved materials which are mostly biodegradable. The use of domestic wastewater for irrigation is greatly 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. Moreover, most industrial wastewaters basically contain much higher both organic and inorganic substances as compared to domestic wastewater. It is a must to treat them before being discharge into any nearby public waterway.

2.4.1 Fundamental of Wastewater Treatment

To treat domestic wastewater or industrial wastewater containing low organic concentration, a wastewater treatment system basically consists of two sequential steps of primary treatment (physical removal of floatable and settleable solids) and secondary treatment (biological removal of dissolved organic compounds). The overall process of wastewater treatment is shown in Figure 2.2. For the mentioned two-step treatment processes, a preliminary treatment is normally employed in order to solve the damage problems to pumps derived from large sizes of solid object.

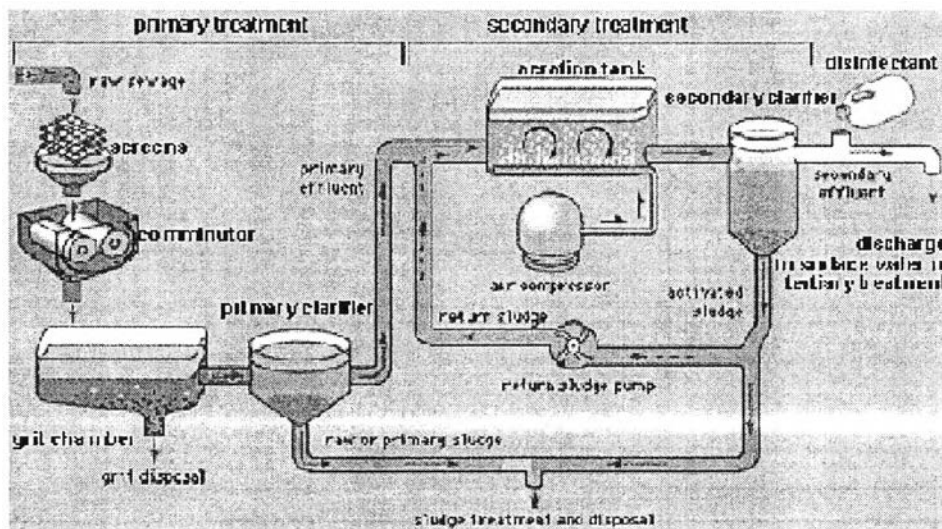


Figure 2.2 Wastewater treatment process (www.water.me.vccs.edu).

2.4.1.1 Preliminary Treatment

The first step of preliminary treatment is designed to remove mostly floatable and settleable solid of both organic and inorganic compounds. Firstly,

wastewater is sent through a bar screen, which removes large solid objects, such as stones, sticks, wooden objects, cans, and plastic containers that can plug lines or block tank inlets. After that, the wastewater will slowly flow down into a grit tank. This allows sand, gravel, and other heavy material particles that are too small 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.

2.4.1.2 Primary Treatment

Primary treatment is a second step in wastewater treatment. It is the physical operation that aims for the separation of solids and greases from wastewater. The wastewater from the preliminary treatment flows into an oil-trape chamber and a primary settling tank where it is held for a few hours. This allows oil and grease to float and solid particles to settle to the bottom of the sedimentation tank, respectively.

2.4.1.3 Secondary Treatment

Secondary treatment basically is a biological treatment process that the dissolved organic materials in wastewater are removal anaerobically by microorganisms. The partially treated wastewater from the settling tank flows by gravity into an aeration tank. Here, it is well mixed with the microorganisms to achieve both mixing and oxygen supply by aerators. Excessive biological growth washes out and is collected in a secondary clarifier. The settled sludge is returned to the aeration tank in order to keep a high microbial concentration in the system. There are basic three aerobic treatment processes as follows:

(1) Activated Sludge Process: The microorganisms in the aeration tank will break down organic materials under sufficient oxygen supply. After that, all microorganisms are settled in a sedimentation tank. Then the settled solids “activated sludge” are 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 over the media with microbial films. The microorganisms will break down the organic materials in

flowing-down wastewater. The treated wastewater will drain out at the bottom and is collected and then undergoes sedimentation.

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

2.4.1.4 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 safely returned to the environment.

2.4.1.5 Sludge Treatment

One of the major problems of anaerobic treatment processes is to generate a large volume of sludge. To reduce the disposal cost, the reduction of sludge volume has to be done. Both the settled sludge from the primary settling tank and secondary sedimentation tank are concentrated before fed into a digester. In the digestion step, the concentrated sludge is further decomposed either aerobically or anaerobically. 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 of the digester sludge, mechanical equipments, such as a filter press, centrifuge, and belt press 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.

2.4.1.6 Advanced Treatment

Advanced wastewater treatment refers to methods and processes that can remove more contaminants from wastewater that cannot be taken out by convectional processes (primary, and secondary treatments). In some cases, advanced treatment is also referred to remove nutrient removal 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.

2.4.2 Industrial Wastewater Treatment

Industrial wastewater usually contains pollutants both biodegradable and non-biodegradable materials as well as inorganic compounds with high concentrations as compared to domestic wastewater. Thus, the industrial wastewater treatment can be divided into 2 major types.

2.4.2.1 Physical/Chemical Treatment

Physical/chemical treatment is used to treat the non-biodegradable compounds present in wastewater. Physical process or usually removes suspended solids, rather than dissolved solids. It can be divided into two processes, passive and mechanically aided. For the passive process, it allows suspended pollutants to settle down or float to the top, depending on the density of suspended pollutants. On the other hand, the mechanically aided process may be used with flocculation, flotation, and/or filtration techniques. Chemical processes usually transform dissolvable metal or toxic pollutants into solid or harmless compounds, respectively. Dissolved metal pollutants can be precipitated in settleable forms by adding an alkaline solution with an organic coagulant aid, like electrolytes, to help flocculate and settle the precipitated metals hydroxides. Highly toxic pollutants can be converted into harmless compounds by oxidizing them with chloride or using ozone to destroy organic chemicals.

2.4.2.2 Biological Treatment

Biological treatment is commonly used to treat domestic or combined domestic and industrial wastewater. The process keeps wastewater under controlled conditions, so that the cleansing reaction is completed before being discharged into the environment. Biological treatment can be divided into 2 types;

2.4.2.2.1 Aerobic Biological Treatment

Aerobic treatment systems require oxygen for microorganisms to decompose the organic compounds in wastewater to harmless components. Sometimes, a wastewater is pretreated before it enters the aerobic unit. Regarding the economical point view and to meet the effluent standards, aerobic

treatment processes are applied for treating domestic wastewater and several industrial wastewaters having dilute organic contents.

2.4.2.2.2 Anaerobic Biological Treatment

In anaerobic treatment, the biological decomposition of organic compounds present in wastewater is undergone under the absence of dissolved oxygen. The anaerobic treatment of wastewater has now emerged as an energy saving wastewater treatment technology. Organic compounds are degraded to produce biogas. Due to increasing energy cost in the aerobic treatment, the technique of anaerobic wastewater treatment has gained substantial importance. However, the anaerobic treatment is limited to concentrated organic wastewater.

The comparison of aerobic and anaerobic biological wastewater treatments is shown in Table 2.1.

Table 2.1 Comparison of aerobic and anaerobic biological wastewater treatments

	Aerobic treatment	Anaerobic treatment
Start up	- Short start-up period	- Long start-up period
Process	<ul style="list-style-type: none"> - Integrated nitrogen and phosphorus removal possible - Production of high excess sludge quantities - Small reactor volume necessary - High nutrient requirements 	<ul style="list-style-type: none"> - No significant nitrogen or phosphorus removal, nutrients removal done via post treatment - Very little excess sludge (5-20%) - Large reactor volume - Low nutrient requirements
Carbon balance	- 50-60% incorporated into CO ₂ ; 40-50% incorporated into biomass	- 95% converted to biogas; 5% incorporated into microbial biomass
Energy balance	- 60% of available energy is used in new biomass; 40% lost as process heat	- 90% retained as CH ₄ , 3-5% is lost as heat, and 5-7% is used in new biomass formation
Residuals	<ul style="list-style-type: none"> - Excess sludge production - No need for post-treatment 	<ul style="list-style-type: none"> - Biogas, and nitrogen mineralized to ammonia. - Post-treatment required for removal of remaining organic matter and malodorous compounds
Costs	<ul style="list-style-type: none"> - Low investment costs - High operating costs for aeration, additional nutrient and sludge removal, and maintenance 	<ul style="list-style-type: none"> - Moderate or high investment - Low operating costs due to low power consumption - Additional nutrients hardly required
State of development	- Established technology	- Still under development for specific applications

2.4.3 Parameters Used in Wastewater Treatment

2.4.3.1 Total Solids (TS)

The term of “total solids (TS)” refers to the residual left in a drying dish after evaporation of a sample and subsequent drying in an oven. After a measured volume of wastewater sample 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 dried solids) is equal to the weight difference between the dish with the wastewater sample after drying and the empty dish. The concentration of total solids is the weight of dried solids divided by the volume of the sample, usually expressed in milligrams per liter (mg/l).

2.4.3.2 Total Volatile Solids (TVS)

Total volatile solids (TVS) are determined when the TS are further 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 dried solids minus the weight of fixed solids divided by the volume of the original wastewater sample. Volatile solid content also can be expressed as a percentage of the dry solids in the sample.

2.4.3.3 Total Suspended Solids (TSS)

TSS refer 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 dried 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).

$$TSS = \frac{\left(\begin{array}{l} \text{weight of sample} \\ \text{after drying, g} \end{array} \right) - \left(\begin{array}{l} \text{tare weight of filter} \\ \text{before use, g} \end{array} \right)}{\text{volume of sample, L}} \quad (2.7)$$

2.4.3.4 Volatile Suspended Solids (VSS)

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

2.4.3.5 Total Dissolved Solids (TDS)

TDS are the solids that pass through the glass-fiber filters and are calculated from the weight difference between the total and suspended solids analyses. Total dissolved solids (TDS) equal total solids (TS) minus total suspended solids (TSS) (Metcalf and Eddy, 2003).

$$TDS = TS - TSS \quad (2.8)$$

2.4.3.6 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.

2.4.3.7 Chemical Oxygen Demand (COD)

COD is a parameter for measuring oxygen demand for oxidation of organic compounds in a wastewater sample. 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.

2.5 Review of Anaerobic Fermentation Process

2.5.1 Fundamental of Anaerobic Fermentation Process

The overall conversion process of anaerobic or dark fermentation is often described as a three-stage process, which occurs simultaneously within anaerobic digesters: hydrolysis, acidogenesis, and methanogenesis (Metcalf and Eddy, 2003), as illustrated in Figure 2.2.

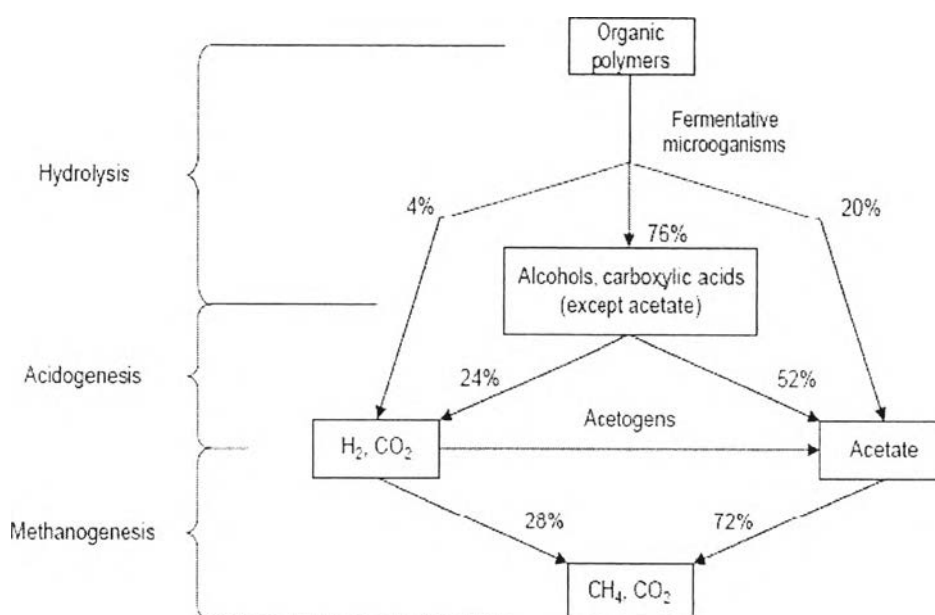


Figure 2.3 Overall process of anaerobic decomposition of organic matter (Zehnder, 1982).

2.5.1.1 Hydrolysis

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

2.5.1.2 Acidogenesis

Acidogenesis is a second step. At this step, amino acids, sugars, and some fatty acids are degraded further, as shown in Figure 2.2. 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).

2.5.1.3 Methanogenesis

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

2.5.2 Characteristics of Wastewater

Anaerobic fermentation process is especially suitable for high strength and warm temperature wastewater to produce both hydrogen and methane economically. Because aeration is not required, it can offer cost saving and a low amount of produced sludge for disposal as compared to all aerobic treatment processes. Any wastewaters having COD concentrations approximately higher than 3,000 mg/L can basically considered to be feasible economically for anaerobic treatment.

2.5.2.1 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
- Generally 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

2.5.3 Types of Anaerobic Treatment Processes

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

2.5.3.1 Anaerobic Suspended Growth Treatment Processes

There are three basic 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 2.4(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 2.2, as compared to anaerobic contact and anaerobic sequencing reactor processes.

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

Process	Volumetric organic loading, 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 2.4(b), can overcome the disadvantages of a complete-mix process without recycle. Separated biomass is returned to the complete-mixed or contact reactor, so the solid retention time (SRT) is much longer than hydraulic retention time (τ). This process can reduce the anaerobic reactor volume by increasing SRT with a short τ value. Gravity separation is the most common approach for thickening and solid separation prior to sludge recycle. In some cases, gas flotation is used for solid separation by dissolving the process off-gas under pressure. Since the reactor sludge contains gas produced in the anaerobic process and gas production can continue in the separation process, solid-liquid separation can be inefficient and unpredictable.

(3) Anaerobic sequencing bath reactor (ASBR)

This reactor, as shown in Figure 2.3(c), is typically operated under batch-mode feeding with four different sequencing phases, including feed, react, settle, and decant or effluent withdrawal. The completely mixed condition is only done during the react phase to provide uniform distribution of substrate and microbial cells.

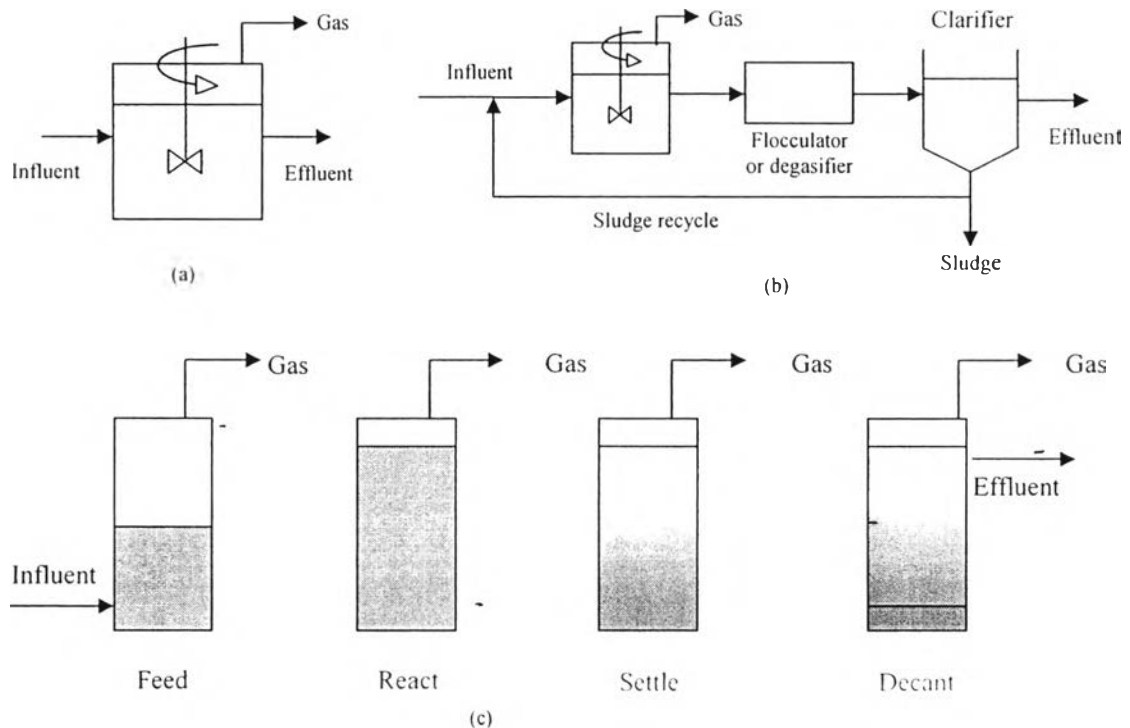


Figure 2.4 Anaerobic suspended growth processes: (a) complete-mix process, (b) anaerobic contact process, and (c) anaerobic sequencing batch reactor process.

2.5.3.2 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 wastewaters (Metcalf and Eddy, 2003).

(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 and operation. 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, depending on the proper design and operation, and the characteristic of wastewater.

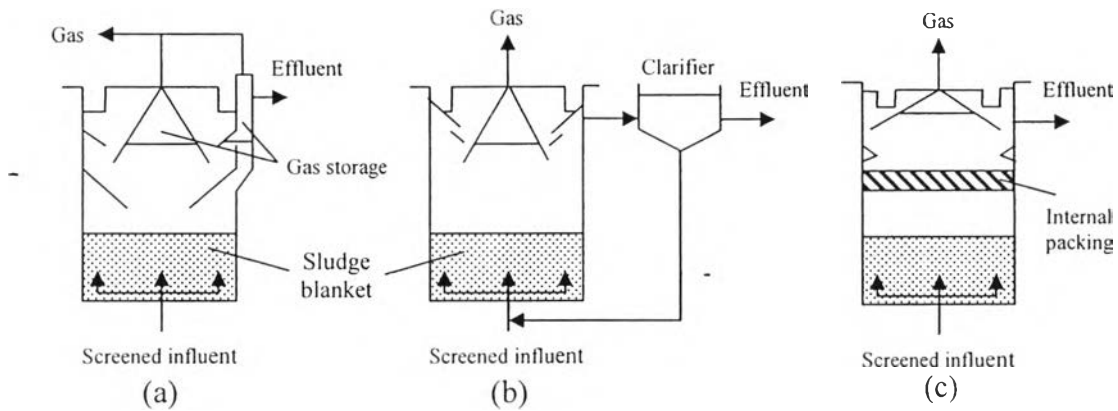


Figure 2.5 Schematic of the UASB process and some modifications: (a) original UASB process, (b) UASB reactor with sedimentation tank and sludge recycle, and (c) UASB reactor with internal packing for fixed-film attached growth, placed above the sludge blanket.

(2) Anaerobic baffled reactor (ABR)

In the ABR process, as shown in Figure 2.6(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 of the baffle design, (2) hybrid reactors where a settler is used to capture and return solids, or (3) packing is used in the upper portion of each chamber to capture solids.

Advantages of the ABR process include the following:

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

(3) Anaerobic migrating blanket reactor (AMBR)

The AMBR process is similar to the ABR with the added features of mechanical mixing in each stage and an operating approach to maintain the sludge in the system without resorting to packing or settlers for additional solid capture, as shown in Figure 2.6(b). In this process, the feed point is changed periodically to the effluent side, and the effluent withdrawal point is also changed. In this way, the sludge blanket remains more uniform in the anaerobic reactor. The flow is reversed when a significant quantity of solids accumulates in the last stage.

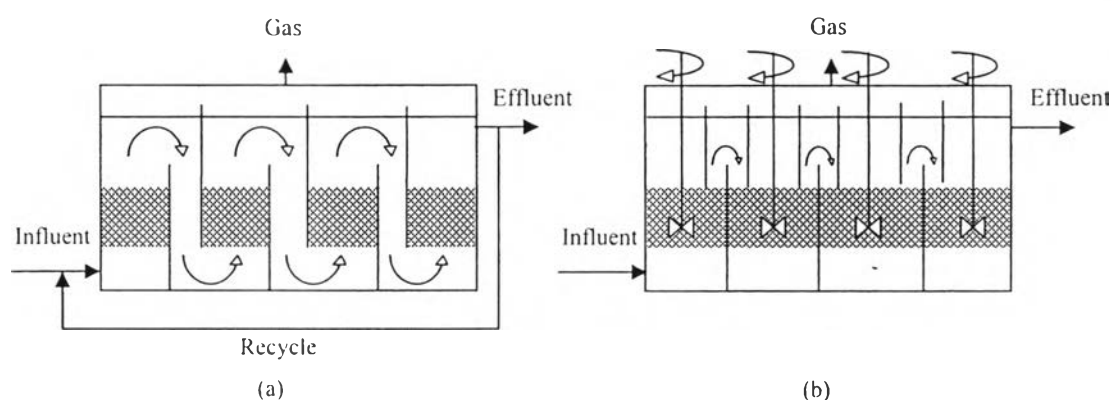


Figure 2.6 Schematic of alternative sludge blanket processes: (a) anaerobic baffled reactor (ABR) and (b) anaerobic migrating blanket reactor (AMBR).

2.5.3.3 Attached Growth Anaerobic Processes

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

(1) Upflow packed-bed attached growth reactor

Full-scale upflow packed-bed anaerobic filters are used in cylindrical or rectangular tanks at widths and diameters ranging from 2 to 8 m and heights from 3 to 13 m, as shown in Figure 2.7(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

washing out the biomass. Over time, solids and biomass will accumulate in the packing void to cause plugging and flow short circuiting. At this point, solids must be removed by flushing with a high liquid velocity.

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

(2) Upflow attached growth anaerobic expanded-bed reactor

The anaerobic expanded-bed reactor (AEBR), as shown in Figure 2.7(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 support particle to provide biofilm growth. The smaller particle provides a greater surface area per unit volume. With such a small particle size 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 2.7(c), is similar in physical design to the upflow expanded-bed reactor. The support particle size is similar to the expanded-bed reactor, but the AFBR is operated at higher upflow liquid velocities of about 20 m/h to provide about 100% bed expansion. Effluent recycle is used to provide a sufficient upflow velocity.

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

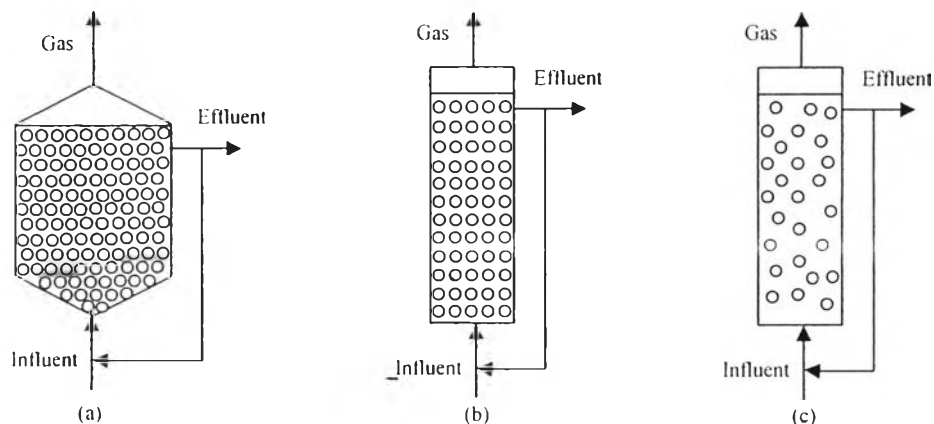


Figure 2.7 Upflow anaerobic attached growth treatment reactors: (a) anaerobic upflow packed-bed reactor, (b) anaerobic expanded-bed reactor, and (c) anaerobic fluidized-bed reactor.

(4) Downflow attached growth process

The downflow attached growth anaerobic processes, as illustrated in Figure 2.8, have been applied for treatment of high-strength wastewaters using a variety of packing materials, including cinder block, random plastic, and tubular plastic. Systems are designed to allow recirculation of the reactor effluent.

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

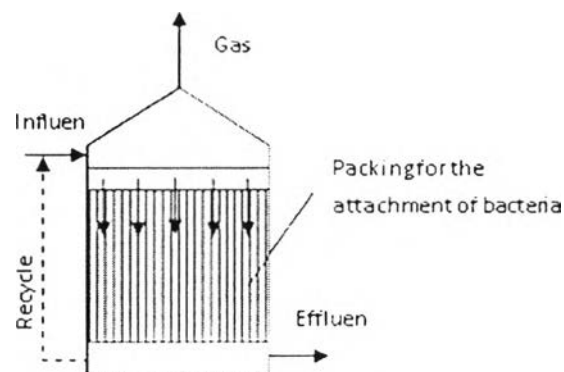


Figure 2.8 Downflow attached growth anaerobic treatment reactor.

2.6 Bio-ethanol Production

Ethanol or ethyl alcohol, $\text{CH}_3\text{CH}_2\text{OH}$, 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.

2.6.1 Bio-ethanol Feedstock

Bio-ethanol can be produced from several 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. Based on economical point view, the main feedstocks for bio-ethanol production are currently sugars and starch. However, these feedstocks are likely to be

expensive and also can disturb the food prices. Lignocellulosic biomass is an interesting raw material due to its low cost and high availability and believed to be an ideal raw material for bio-ethanol production in the future.

2.6.1.1 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 the hydrolysis of sugar is not required.

2.6.1.2 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.

2.6.1.3 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 needed. In the hydrolysis step, cellulose is enzymatically degraded to obtain glucose that is fermented further by yeast to form ethanol. Because this method is more complex than using cane beet or corn as feedstock, it leads to a higher ethanol production cost. However, lignocellulosic materials come from agricultural or domestic wastes. These offer high possibility for bio-ethanol production in large scale. So, it is considered that lignocellulosic biomass will become a main bio-ethanol feedstock for ethanol production in the future.

2.6.2 Bio-ethanol Production

Ethanol is a product of fermentation process by yeast. Fermentation is a sequence of reactions, which release energy from organic molecules in the absence of oxygen. In this application of fermentation, energy is obtained when sugar is changed to ethanol and carbon dioxide. All beverage alcohols and more than half of industrial ethanol are made by this process.

2.6.2.1 Bio-chemical Production of Ethanol by Biomass

This bio-ethanol process consists of four major units: (1) pretreatment, (2) hydrolysis, (3) fermentation, and (4) product separation or distillation (Balat and Balat, 2009), as shown in Figure 2.8.

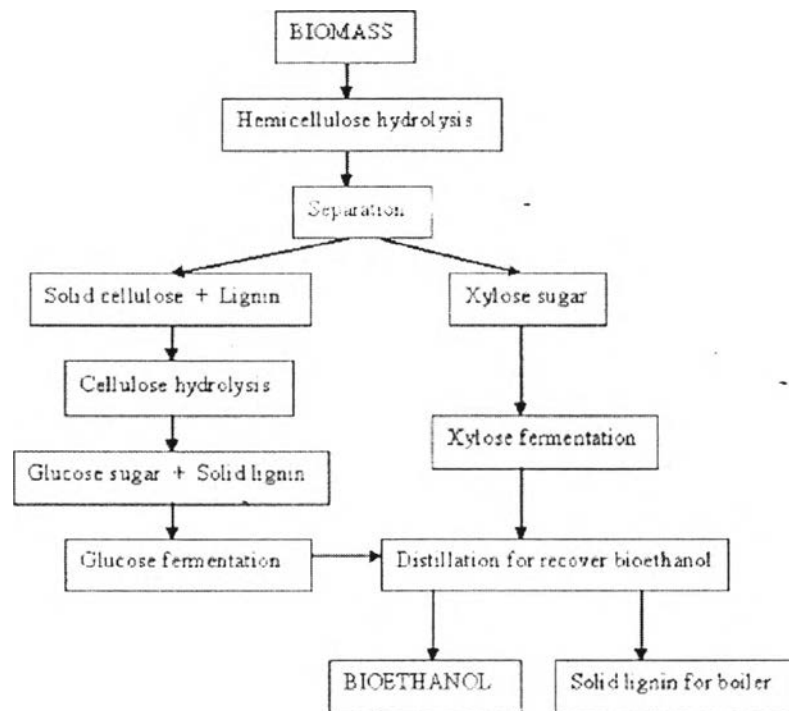


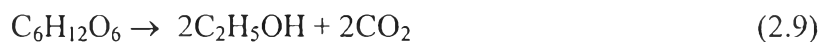
Figure 2.9 Flow chart for the production of bio-ethanol from lignocellulosic biomass (Balat and Balat, 2009).

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 2.9, pre-hydrolysis is the first step for bio-ethanol production. A dilute sulfuric acid is used for hydrolyzing hemicellulose to xylose sugar. Meanwhile, cellulose is hydrolyzed to glucose. The obtained xylose

sugar and glucose will be further fermented in fermentation step by microorganisms, such as yeast. The overall reaction in the fermentation process is shown as follows:



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).

2.6.2.2 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.

In the ethanol production process, as shown in Figure 2.10, 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 a 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 disaccharides (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.

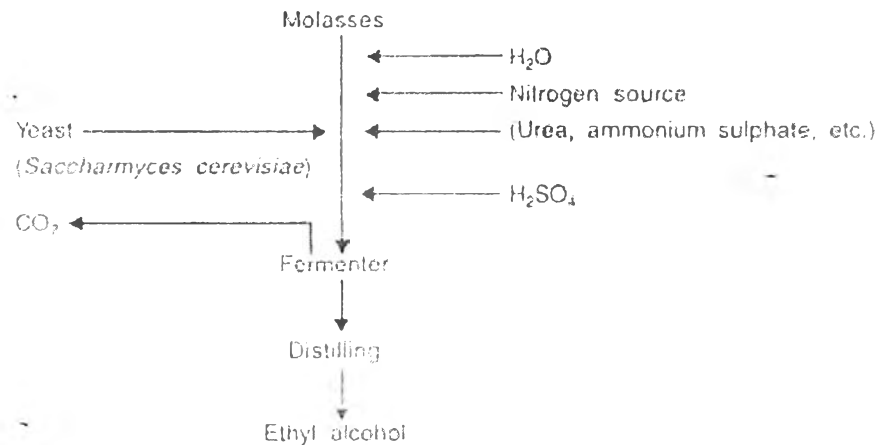


Figure 2.10 Ethanol production from molasses.

2.7 Alcohol Distillation Process

Distillery slop or alcohol distillery wastewater is the wastewater from the distillation column of fermented solution used both as industrial alcohol and for human consumption. This process mostly 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 2.11. 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). Interestingly, the distillery wastewater 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.

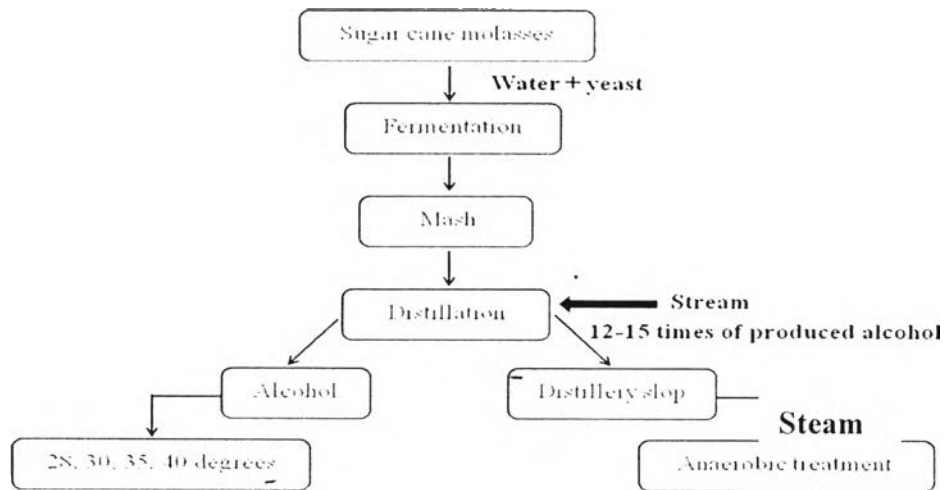


Figure 2.11 Alcohol distillation process.

2.8 Objectives of Study

◆ To investigate the hydrogen production from alcohol wastewater using an anaerobic sequencing batch reactor (ASBR) under thermophilic operation and at a constant pH of 5.5. Both nitrogen and phosphate uptakes transformation was also studied.

◆ To investigate the enhancement of hydrogen production from alcohol wastewater by adding fermentation residue using an anaerobic sequencing batch reactor (ASBR) under thermophilic operation (55 °C) and at a constant pH of 5.5. The digestibility of the added fermentation residue was also evaluated.

◆ To investigate the spontaneous hydrogen and methane production from cassava wastewater by using a two stage upflow anaerobic sludge blanket reactors (UASB) system under thermophilic operation (55 °C). The recycle ratio of the effluent from the methane bioreactor-to-the feed flow rate was fixed at 1:1 and the pH of the hydrogen UASB unit was maintained constant at 5.5