CHAPTER II
LITERATURE REVIEW

2.1 Biodiesel Production and Crude Glycerol

Biodiesel is an alternative diesel fuel that are exponentially increasing because biodiesel has more favorable combustion emission profile than petroleum-based diesel in terms of low emission of sulphur, particulate matter, carbon monoxide, nontoxic, and easily biodegradable fuel. The biodiesel (≈ 68.7%) were produced in Germany, US, France, Argentina, and Brazil where are top five biodiesel production in the world and the market of biodiesel expected to be worth US$ 12.6 billion by 2014.

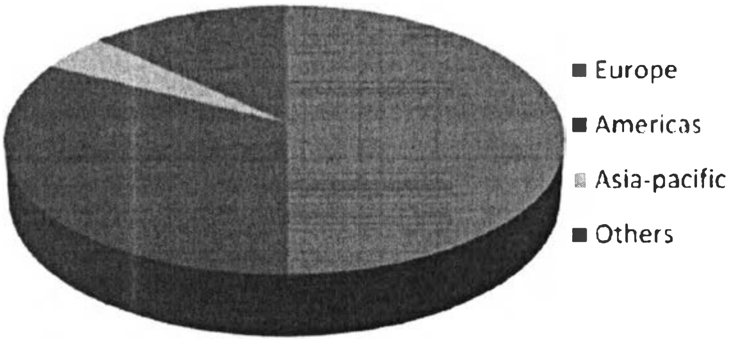

Figure 2.1 Global biodiesel production share of different geographic regions of the world till 2009 (Sarma *et al.*, 2012).

Moreover, biodiesel also has a relatively high flash point so that it low volatile and safe for transportation. Biodiesel has a lubricating properties that causes extend engine life (Encinar *et al.*, 2005). Therefore, there are various processes have been received more attention for improving or managing biodiesel production processes into high yield of biodiesel. Crude glycerol are produced during biodiesel process and they are an important raw material for food, pharmaceutical and cosmetic industry. Moreover, it can be converted into high valuable product such as biohydrogen and methane production. Biohydrogen from biodiesel manufacturing can be used as biofuel because it has high energy content as same as hydrogen from thermochemical and electrochemical process.

2.1.1 Feedstock for Biodiesel Production (Van Gerpen *et al*, 2004)

2.1.1.1 Reactant

- Vegetable oils, animal fats and recycled greases: they contain triglycerides, free fatty acids, and other contaminants depend on the degree of pretreatment.
- Primary alcohol: The most common primary alcohol is methanol but other alcohols can be used such as ethanol, isopropanol.

2.1.1.2 Catalyst: Catalysts can be used are base, acid, or enzyme materials but the most catalysts used are sodium hydroxide and potassium hydroxide.

2.1.1.3 Neutralizer: After the reaction, the catalyst must be neutralized with mineral acid.

2.1.2 Biodiesel Production Process

Biodiesel production is the production process of biofuel through chemical reaction tranesterification and esterification. Vegetable or animal fats and oils were reacted with short-chain alcohols like methanol or ethanol via tranesterification in reactor. Homogenous base-catalyzed such as sodium hydroxide or potassium hydroxide is added as catalyst of the reaction and the mixture is agitated under to the boiling point of alcohol that used from previous process. When the agitation stopped, the mixture separated into two phases. The upper layer is methyl ester of fatty acid or biodiesel and the lower layer is crude glycerol that contained many substrates such as salt, methanol, ethanol and solid substances in the raw material. The crude glycerol was produced as byproduct of biodiesel processes contaminated in released wastewater; thus, there are several processes separated glycerol from impurity and can be applied in many industries such as in cosmetic and pharmaceutical industry.

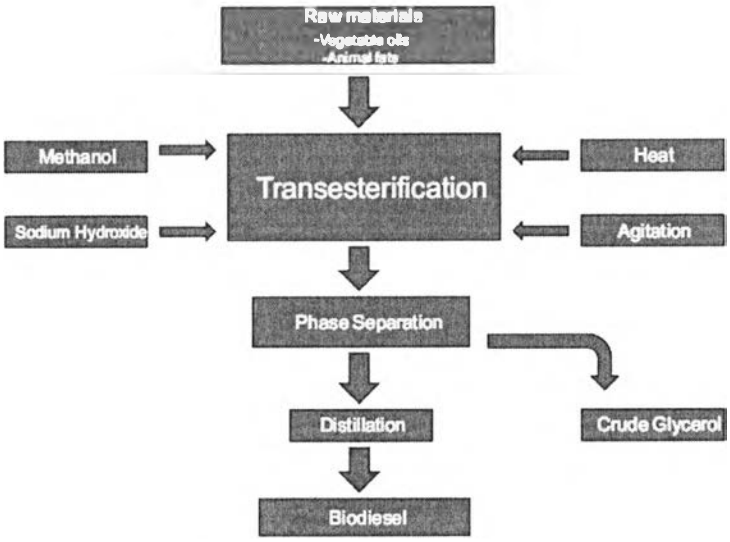

Figure 2.2 Schematic representation of a general biodiesel production process using tranesterification of vegetable oil and fats (Sarma *et al.*, 2012).

2.1.3 Reaction of Biodiesel Process

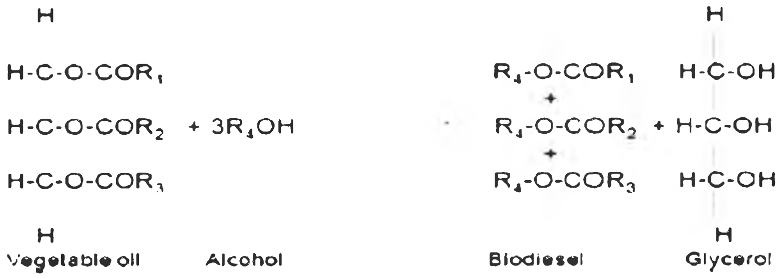

Figure 2.3 Equation showing tranesterification of large branched triglyceride molecule to biodiesel and glycerol (Sarma *et al.*, 2012).

2.1.4 Biodiesel Production Methods (Van Gerpen *et al*, 2004)

2.1.4.1 Batch Processing

Batch method under stirred tank reactor is the simplest method for biodiesel production under the ratio of alcohol to triglyceride ratios from 4:1 to 20:1 (mole:mole) with a 6:1 ratio most common reactor may be sealed or equipped with a reflux condenser. The temperature is usually operated 65°C or between 25°C to 85°C. The catalyst commonly used is sodium hydroxide and potassium hydroxide is used as well. Typical catalyst loadings range from 0.3 % to about 1.5%. The beginning of the reaction is necessary by taking the oil, catalyst and alcohol into intimate contact. When the end of the reaction, less mixing can help increase the extent of reaction by allowing the inhibitory product, glycerol, to phase separate from biodiesel. At high temperature and high alcohol:oil ratios can help to increase the percent completion and the reaction times is from 20 minutes to more than one hour.

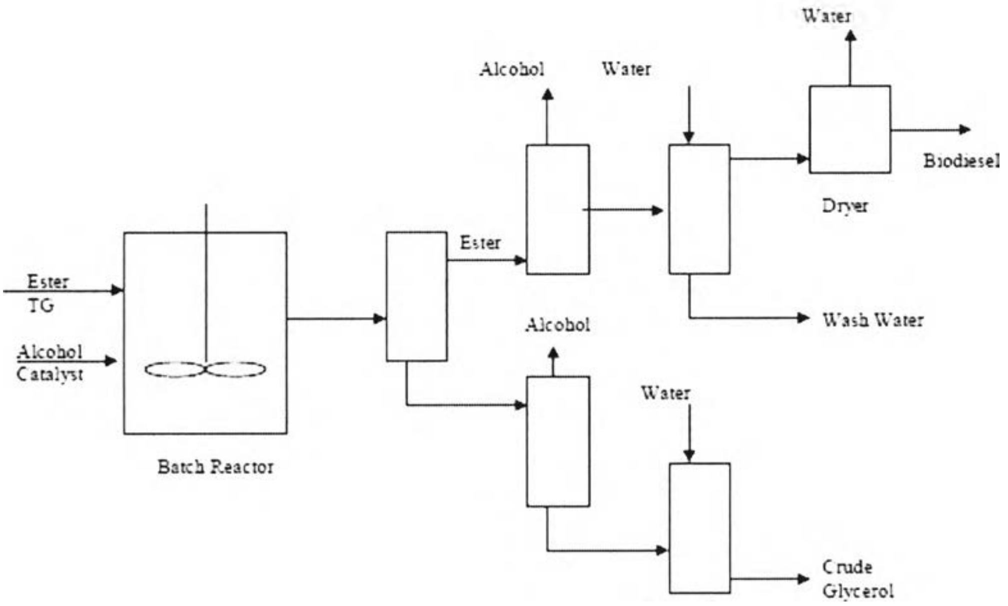

Figure 2.4 Schematic represent of batch reaction process.

2.1.4.2 Continuous Process Systems

Continuous stirred tank reactors (CSTRs) in series are very popular as same as batch process. For the longer residence time in CSTR1, CSTR can be varied the volume in order to achieve greater extent of reaction. After the initial product glycerol is decanted, the reaction in CSTR 2 is rather rapid, with 98+ completion not uncommon. The composition in reactor is constant so the essential element is added into the CSTR2 as a result the time required for phase separation is extended. The reactor is tubular or called a plug-flow reactor (PFR), behaves as if it were a series of small CSTRs chained together. It is requires shorter reaction time, as low as 6 to 10 minutes for near completion of the reaction. This type of reactor operates under high temperature and pressure in order to increase the reaction rate.

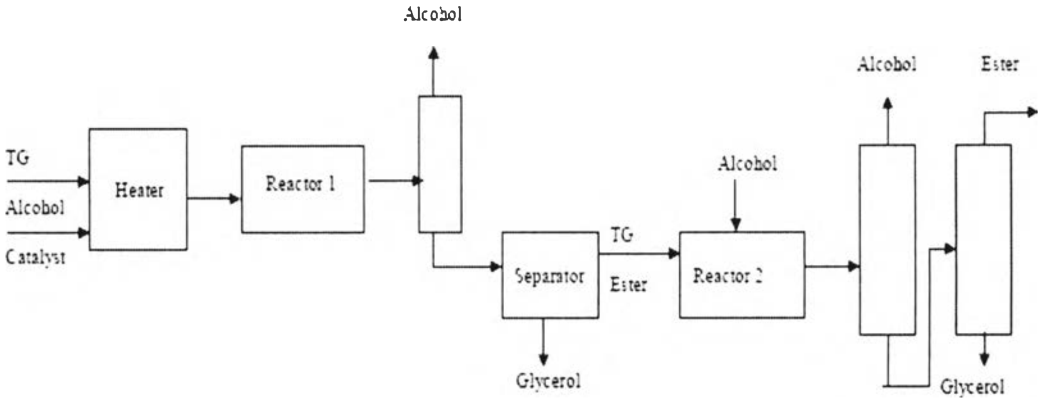

Figure 2.5 Schematic represent of plug flow reaction system.

2.1.4.3 High Free Fatty Acid Systems

This process is suitable for feedstock that has high free fatty acid(FFA) and cheap feedstock such as tallow or yellow grease that have high in free fatty acids (FFA) characteristic. FFA can be transformed into methyl esters using an acid esterification process. Because of in a base catalyzed system, high free fatty acid feedstock will react with the catalyst and form soap. Moreover, it has the amount of free fatty acid limitation as well. Also, this process can reduce operated cost for remove the access free fatty acid in feedstock. Direct acid esterification of a high free fatty acid feed requires water removal during the reaction, or the reaction will be quenched prematurely. Alcohol to FFA ratio usually requires between 20:1 and 40:1 and require larger amount of acid as well. The esterification reaction of FFAs with methanol produces waster as byproduct that must be removed. The water can be remove by setting, vaporization, or centrifugation as a methanol-water mixture. The initial catalyst has been used phosphoric acid, neutralize with an excess of KOH for the base step, and then neutralize with phosphoric acid. The insoluble potassium phosphate is recovered, washed, and dried for use as a fertilizer. The problem with this strategy is that the soap stock system contains a large amount of water that must be removed before the product esters can meet the biodiesel standard.

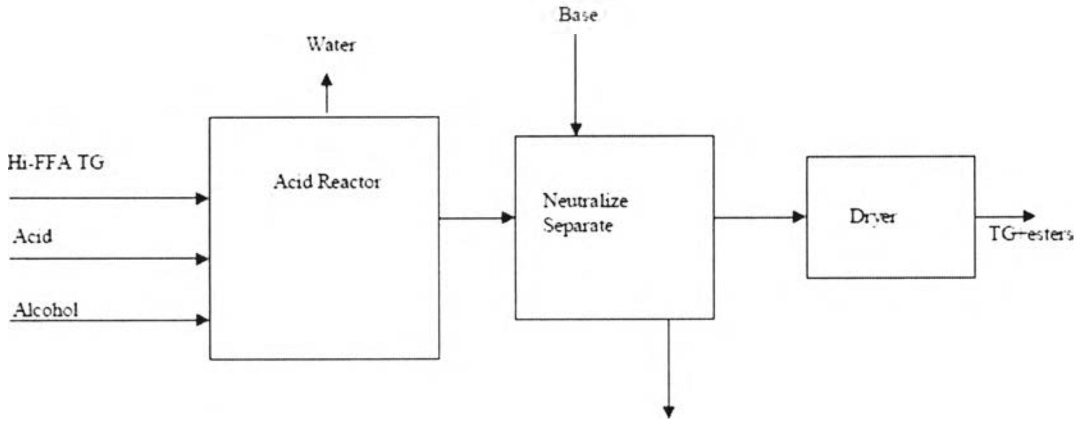

Figure 2.6 Schematic represent of acid catalyzed direct esterification process.

An alternative procedure for processing high FFA feeds is to hydrolyze the feedstock into pure FFA and glycerine. Typically this is done in a counter current reactor using sulfuric/sulfonic acids and steam. The output is pure free fatty acids and glycerin. Any contaminates in the feedstock partition mostly into the glycerin and some may leave with the steam/water effluent. Some contaminants continue with the FFA and can be removed or left in, depending on the processes and product specifications. The pure FFA is then acid esterified in another countercurrent reactor to transform them into methyl esters. The methyl esters are then neutralized and dried. Yields can exceed 99%. Equipment need to be acid resistant too.

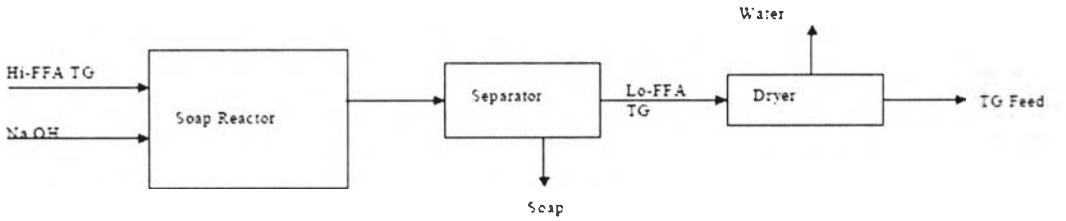

Figure 2.7 Schematic represent of preparation of soap stock from a high FFA feed.

For the base-catalyzed system keep away from high FFA problem is that using a fixed bed, insoluble base as shown in Figure 2.8. An example of this system, using calcium carbonate as the catalyst, has been demonstrated at the bench-scale.

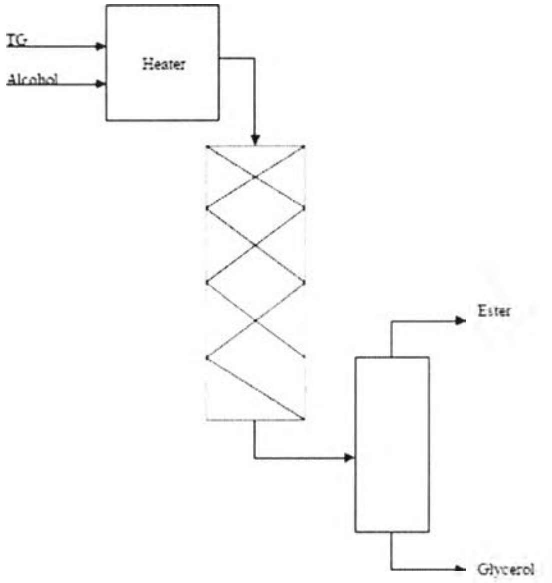

Figure 2.8 Schematic represent of fixed-bed, base catalyzed reactor system.

2.1.4.4 Non-Catalyzed Systems (Biox Process)

This process used co-solvent for increasing the dissolution of alcohol in the TG phase. One approach that is nearing commercialization is the Biox Process. These process commonly used tetrahydrofuran to solubilize the methanol because its boiling point very close to the metanol. The result is a fast reaction, on the order of 5 to 10 minutes, and no catalyst residues in either the ester or the glycerol phase. After the reaction is complete, the excess methanol and the tetrahydrofuran co-solvent are recovered in a single step. This system requires a rather low operating temperature, 30 °C. The ester-glycerol phase separation is clean and the final products are catalyst-free and water-free. The equipment volume has to be larger for the same quantity of final product because of the additional volume of the co-solvent. Moreover, another co-solvents is MTBE that have been investigated. Co-solvents is a hazardous subject so it have to be completely removed from the glycerin as well as the biodiesel. The schematic of Biox Co-Solvent Process was shown on figure 2.9

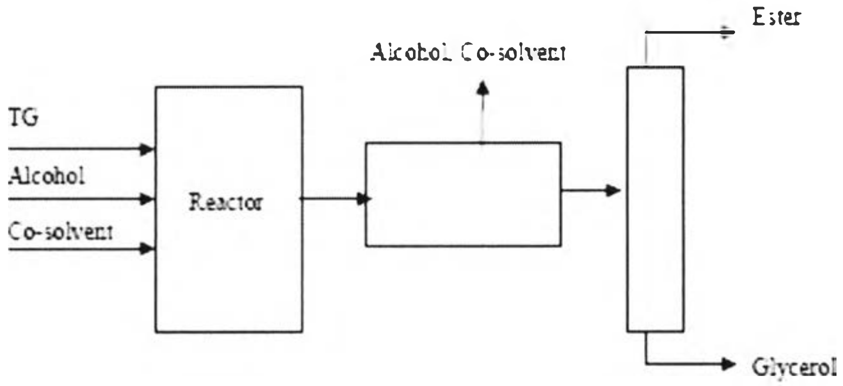

Figure 2.9 Schematic represent of biox co-solvent process.

2.1.4.5 Non-Catalyzed Systems (Supercritical Process)

Supercritical conditions in this process operated under temperature 250 to 400 °C and pressure more than 80 atm or 1200 psi so the reaction complete in about 4 minutes. When a fluid or gas is subjected to temperatures and pressures in excess of its critical point, there are a number of unusual properties exhibited or there are no different between liquid and vapor phase. A non-catalytic is using the high of alcohol to oil ratio (42:1) ratio. Because these process operated under high temperature and high pressure; thus, capital and operating costs can be more expensive, and energy consumption higher. An intriguing example of this process has been demonstrated in Japan, where oils in a very large excess of methanol have been subjected to very high temperatures and pressures for a short period of time. The result is a very fast (3 to 5 minute) reaction to form esters and glycerol. The reaction must be quenched very rapidly so that the products do not decompose. The reactor used in the work to date is a 5 ml cylinder that is dropped into a bath of molten metal, and then quenched in water. Clearly, while the results are very interesting, the scale-up to a useful process may be quite difficult. Although, it is a topic of great importance to the choice of biodiesel production process. Generally the quality of the glycerol produced and its value as a coproduct is an important economic variable. The typical glycerol produced by a biodiesel plant is

50% glycerol or less and contains water, salts, methanol, methyl esters, and unreacted glycerides, color and odor bodies, dimers, timers, and other minor compounds. This is commonly referred to as "biodiesel crude" and is generally worth less than 5 cents per pound. Removing the water and methanol and bringing the glycerol content up to 88% can generate a credit based on the value of crude glycerol. Salts, and particularly sulfur salts or potassium salts reduces the value of the crude glycerol produced.

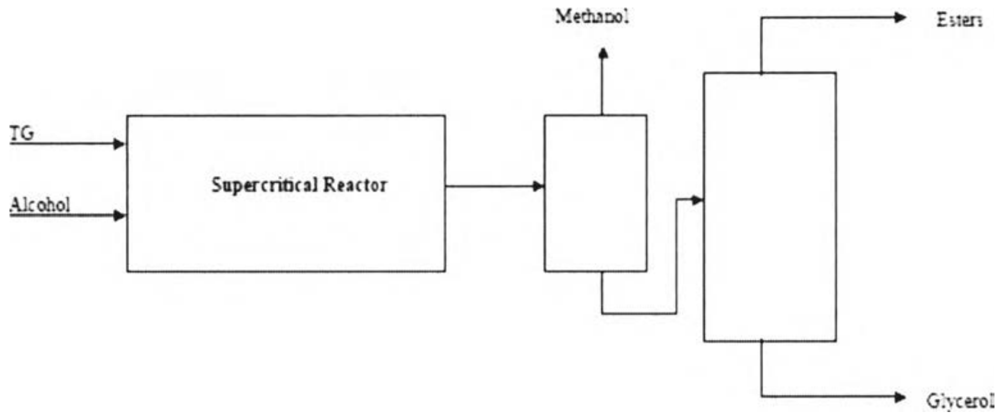

Figure 2.10 Schematic represent of supercritical esterification process.

2.1.5. Glycerol

Glycerol or glycerin has structure molecule as polyol. Its structure molecule is

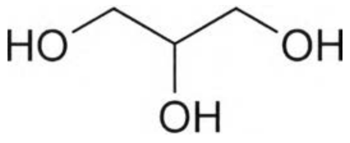

Figure 2.11 Structure molecule of glycerol.

Glycerol is liquid and chemical formula is $CH_2OHCHOHCH_2OH$. It is adorless, colorless, and sweet-tasting. The molecule of glycerol has hydrochloric 3 groups so it can be dissolved by water or called hydroscopic. Moreover, it can be dissolved by ethanol as well. The melting point is 17.8 °C and boiling point is 290 °C, it can be produced from propylene synthesis and sugar fermentation of sodium bisulfate. Besides, it has produced continuously as by-product of biodiesel process.

The demand of biodiesel extremely increased as renewable energy sources so that the amount of glycerol as by-product more produced. The glycerol was generated during biodiesel manufacturing process can be used a good carbon sources for dark fermentation of biohydrogen production (Sittijunda and Reungsang, 2012). The potential of using crude glycerol as a feedstock for hydrogen production was investigated by using microbial process, different technical constraints of crude glycerol bioconversion, various bioreactors for converted glycerol to high valuable product as hydrogen or methane (Sarma *et al.*, 2012). These possibility of converting crude glycerol into biohydrogen production has been carried out according to many researchers studied on biohydrogen from crude glycerol using biodiesel wastewater. For instance, Yuwa-anornpitak studied biohydrogen production by glycerol waste from biodiesel process. Anaerobic digested sludge obtained from milk industry wastewater plant by using Escherichia coli U5/41 (E. coli HB41). He determined the optimum condition for the highest hydrogen production at 2% glycerol concentration, pH 7, temperature 35 °C and NH_4Cl as nitrogen sources. The results show that hydrogen content amount of 84 % was produced within 12-36 h of batch process. This research showed that biodiesel wastewater which was pretreated by acid can be used as carbon source for hydrogen production. Ito *et al.* studied hydrogen and ethanol production from glycerol-containing from biodiesel wastewater by using *Enterobacteraerogenes HU-101*. They compared hydrogen and ethanol production from biodiesel wastes (contained glycerol 40% w/w, total organic carbon (TOC) 540 g/l, ash 8% w/v, methanol 25% w/w, and other impurities) with pure glycerol. The results showed that the hydrogen and ethanol production from biodiesel waste were lower than pure glycerol due to a high salt content in biodiesel waste. Synthetic medium were added in biodiesel waste to increase the rate of glycerol utilization and addition of yeast extract and tryptone to the synthetic medium accelerated the production of hydrogen and ethanol. Moreover, they investigated the maximum hydrogen production rate from biodiesel waste using porous ceramics as a support material to fix cells in the reactor was 63 mmol/l/h which higher than maximum hydrogen production rate using self-immobilized cells (30 mmol/l/h) because packed-bed reactor with support material prevented the efflux of cell flocs from the reactor. Glycerol was consumed completely at a dilution rates up to 1.2 h^{-1}.Sittijunda and Reungsang investigated media composition parameters affecting thermophilic production from waste glycerol by using response surface methodology (RSM) with central composition design (CCD) for converting waste glycerol into biohydrogen under anaerobic mixed cultures. These parameters were waste glycerol concentration, urea concentration, the amount of Endo-nutrient addition and the disodium hydrogen phosphate (Na_2HPO_4) concentration. They found that the optimal media composition were 20.33 g/L of waste glycerol, 0.16 g/l of urea. 3.97 g/l of Na_2HPO_4 and 0.20 ml/l of the amount of endo-nutrient addition which gave the maximum hydrogen production rate at 1,502.84 ml H_2/l. Moreover, the results from polymerase chain reaction-denaturing gradient gel electrophoresis (PCR-DGGE) analysis indicated that hydrogen producers in the fermentation broth was Thermoanaerobacterium sp. and the main metabolic products from the fermentation process were 1,3-propanediol (1,3-PD), ethanol, acetic, formic, lactic, butyric, and propionic acids.

However, different impurities present in crude glycerol also affected on biohydrogen production because they inhibited microbial growth. Hence, the suitable treatment of crude glycerol such as operation mode and engineering microorganism development have been investigated.

2.2 Foundation and Background of Hydrogen

Hydrogen is an element which is the most abundant in universe. It presents 75% of matter in many stars, nebulae, and sun. Hydrogen elements have easily structure, 1 nucleus in the center and 1 electron surrounding. Also, they are the lowest boiling and freezing point inferior to Helium element. Moreover, they are gas states at ambient condition, colorless, odorless, tasteless, only slightly soluble in water, great affinity for oxygen, powerful reduction agent, density much lower than air, high diffusely ability on different material including material that another gas could not spread through on its. Besides, hydrogen also has high energy content per unit mass of 122 kJ/g, which greater than 2.75 times of hydrocarbon fuels (Kapdan *et al.*, 2006) and could be easily flammable with high range of air(4-75% in air), in some range could be blast (15-59 % in air). When leaked out occurrence, they will rapidly spread out and may be harmful. However, hydrogen is a new renewable energy that being friendly with environmental. Thus, hydrogen is being a viable alternative fuels and cleanest energy carrier in the future which is considering as sustainable energy in the realm of fossil fuels.

2.2.1 Advantages of Hydrogen

2.2.1.1 Hydrogen is Clean Fuel.

The utilization of hydrogen is wildly use for hydrodesulfurization and hydrodenitrogenation of gasoline in refineries (Eastan and Gardner, 1983), cryogenics process (Miller and Stoecker, 2001), hydrogenation of fats and oils, fuel cell systems, and feedstock for the production of chemical. Because hydrogen is the cleanest energy with no CO_2 emissions and only water production (Das and Veziroglu, 2001), when it used as combustion fuels or converted to electricity. Thus, hydrogen is regarded as a clean non-polluting fuel. Pure hydrogen produces only heat energy, water, and trace amounts of oxides of nitrogen when burnt. When used in a fuel cell, hydrogen combines with oxygen to form water vapor. This reaction takes place at lower temperatures, and so the only waste product from a fuel cell is water vapor.

2.2.1.2 Hydrogen is Harmless Fuel.

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

2.2.1.3 Hydrogen is Environmentally Friendly.

Greenhouse gases have significant produced from conventional energy resource, especially carbon dioxide which have been affecting to global warming. 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.

2.2.1.4 Hydrogen can Prevent the Depletion of Fossil Fuels.

There are many applications for hydroden utilization such as for hydrodesulfurization and hydrodenitrogenation of gasoline in refineries, Cryogenics process, hydrogenation of fats and oils, fuel cell systems, and feedstock for the production of chemical, 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.

2.2.1.5 Hydrogen can be Produced from Various Sources.

There are several ways to produce hydrogen that have already been available such as stream reforming of natural gas(SRM), partial oxidation of fossil fuel(POX), combination of SRM and POX, electrolysis of water, gasificaton or pyrolysis of biomass , photocatalytic methods, nuclear power methods, and photo-electrochemical methods so that the hydrogen produced is a renewable fuel.

2.2.1.6 Hydrogen is the Most Abundant Element on Earth.

Hydrogen is also the most abundant element on earth, but less than 1 % in the 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 (kWh) 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 high than 900°C with Pt/Ru catalyst.

2.2.2 Hydrogen Production

There are many methods to generate hydrogen. They can be produced mainly from fossil fuels, water, and biomass (organic wastes and wastewater).

2.2.2.1 Hydrogen Production from Fossil Fuels

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

Steam-Methane Reforming (SMR)

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

The first reaction is *the reforming of natural gas.* Natural gas, such as methane, is reacted with steam at high temperatures (750-800°C) to produce synthesis gas (syngas), which contains hydrogen (H_2) and carbon monoxide (CO). This can be described by the following reaction.

$$CH_4 + H_2O\ (+\ \text{heat}) \longrightarrow CO + 3H_2 \qquad (2.1)$$

The second reaction is *the shift reaction (water gas shift).* In this step, carbon monoxide produced in the first reaction is reacted with high temperature steam to form hydrogen and carbon dioxide. This process occurs in two stages, consisting of a high temperature shift (HTS) at 350°C (662°F) and a low temperature shift (LTS) at 190 °C – 210 °C (374 °F – 410 °F). This can be described by the following reaction.

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

Partial Oxidation(POX) / Autothermal reforming of Methane

The partial oxidation process directly oxidized methane into a syngas mixture of CO and H_2 which can be converted to higher alkanes or methanol. Because this process is the exothermic reaction, it can generate its own heat that is used as energy supply in the process itself, following the reaction

$$CH_4 + \tfrac{1}{2} O_2 \longrightarrow CO + 2\,H_2 \quad \Delta H_R = -36\ \text{kJ/mol} \qquad (2.3)$$

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

Thermal Cracking of Methane

Thermal cracking of natural gas, such as methane, is a high temperature process, which can replace stream reforming process because of no carbon dioxide emission. It requires high temperature about 2,000°C to produce 60 % of hydrogen and 40 % of carbon black that is a pigment used in many dying processes. This can be described by the following reaction.

$$CH_4 \longrightarrow C + 2H_2 + 75.6\ \text{kJ} \qquad (2.4)$$

Coal Gasification

Gasification of coal is the oldest process to produce hydrogen gas. The coal feed stock in solid state is heated with high temperature (1,330 °C) and high pressure stream under the amount of oxygen control to produce hydrogen, carbon monoxide, and carbon dioxide. And then, carbon monoxide is reacted with steam to produce more hydrogen and carbon dioxide in the water gas shift reaction. This can be described by the following reaction.

$$\text{Coal} + O_2 + H_2O \longrightarrow CO + CO_2 + H_2 + \text{Other species} \qquad (2.5)$$

$$CO + H_2O \longrightarrow CO_2 + H_2O \qquad (2.6)$$

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

2.2.2.2 Hydrogen Production from Water

There are four types of process to hydrogen production from water

Electrolysis

Electrolysis of water suited for distributed power generation such as hydrogen in fuel cell and may be the cleanest technology for hydrogen gas production (IEA Energy Technology Essentials, 2013). They dissociated the molecule of water to hydrogen and oxygen by passing an electric current between two electrodes (cathode and anode) through water. Hydrogen bubbles will be collected on the negative plate (cathode) while oxygen bubbles gather on the positive plate (anode). There is no carbon dioxide given off during the process, and it can be results shown by the following chemical reaction

$$2H_2O + \text{energy} \longrightarrow 2H_2 + O_2 \qquad (2.7)$$

However, this method is not efficient when it comes to produce large amounts of hydrogen because it is energy intensive process and more expensive than stream reforming of natural gas.

Thermolysis or Direct Thermal Decomposition

Thermolysis (or direct thermal decomposition) is a process for hydrogen production under high temperature condition by used solar energy. When water is heated to a high temperature at 3,000 K (2,727°C), it can be decomposed into hydrogen and oxygen. This process has high efficiency, but it is normally not applied to produce hydrogen.

Thermochemical Process

Thermochemical process is *sulfur-iodine cycle* (S-I cycle) which developed from thermolysis in order to generate hydrogen from water. It has been hydrogen production efficiency higher than water splitting and suited to production by high-temperature nuclear reactor by concentrating solar power systems or CSP (IEA Energy Technology Essentials, 2007).

$$H_2O \longrightarrow H_2 + 0.5O_2 \qquad (2.8)$$

Photolysis

The molecule of water absorb sunlight and use the energy from it to separate water into hydrogen and oxygen in the presence of photocatalysts so it is called photolysis process. This process can be categorized into three types depend on photocatalyst kinds

(1) Biophotolysis Process

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

(2) Photochemical Process

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

(3) Photoelectrochemical Process

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

2.2.2.3 Hydrogen Production from Biomass

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

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

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

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

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

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

Thermochemical Process

(1) Biomass Pyrolysis

In this process, biomass is heated at a temperature and pressure of 650-800 K (377-527°C) and 0.1-0.5 MPa in the absence of oxygen (or air) to convert biomass into liquid, charcoal and non-condensable gases, acetic acid, acetone, and methanol. The main gaseous products from pyrolysis are hydrogen, carbon dioxide, carbon monoxide, and hydrocarbon gases. The reactions are shown below:

$$\text{Biomass} + \text{heat} \rightarrow H_2 + CO + CO_2 + CH_4 + \text{Other products} \qquad (2.9)$$

(2) Biomass Gasification

The basic process of biomass gasification is to gasify biomass at a high temperature (above 1,000 K). It is partially oxidized in the presence of oxygen (or air) to form gas and charcoal as follows:

$$\text{Biomass} + \text{heat} + O_2 + H_2O \longrightarrow H_2 + CO + CO_2 + CH_4 + \text{Light and heavy} + \text{hydrocarbons} + \text{charcoal} \quad (2.10)$$

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

As mentioned above, the product from pyrolysis aims to produce bio-oils and charcoal but the products from biomass gasification are mainly gases. Therefore, biomass gasification is more favorable for hydrogen production than pyrolysis (Richard L. Bain, 2010).

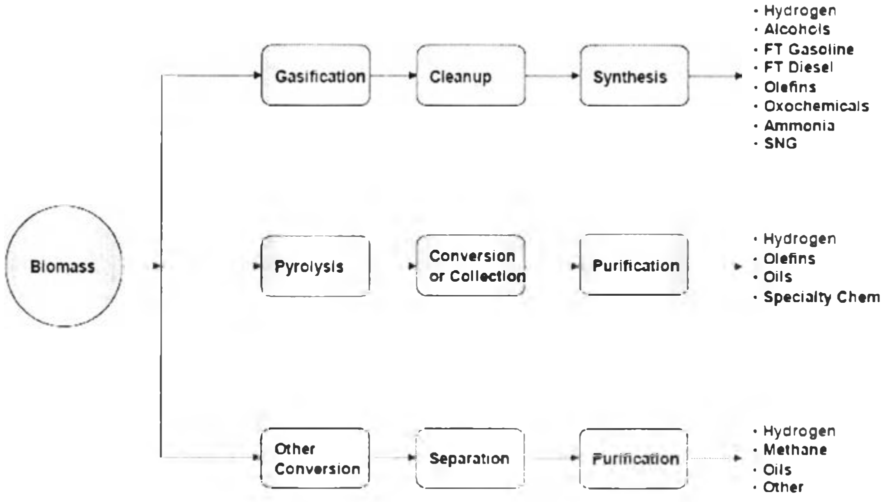

Figure 2.12 Schematic hydrogen production by gasification and pyrolysis (Richard L. Bain. ,2010).

Biological Process

An alternative method for hydrogen production and environmental friendly known as biological hydrogen production process or green technology (Kapdan and Kargi, 2006). This process uses microorganisms to decompose complex organic compounds in waste or wastewater, which are composed of carbohydrate-rich and non-toxic materials, to simple end-products, such as hydrogen, methane, carbon dioxide volatile fatty acids, and alcohols. Thus, hydrogen production by biological process is being considerable because they can be produced by less energy-intensive processes under mild condition and more environmental friendly, leading to reducing energy consumption and being to economical processes.

This process uses microorganisms to decompose complex organic compounds in waste or wastewater, which are composed of carbohydrate-rich and non-toxic materials, to simple end-products, such as hydrogen, methane, carbon dioxide volatile fatty acids, and alcohols. Most of biological processes are operated at an ambient temperature (30-40°C) and normal pressure; hence, they are less energy-intensive and environmentally friendly (Das and Veziroglu, 2001). There are two types of biological processes: photo fermentation and dark fermentation. The major bio-hydrogen processes are bio-photolysis of water by algae, photosynthesis condition (photo fermentation) and anaerobic condition (dark fermentation) of microorganisms using raw materials which containing carbohydrate and protein rich-biomass (Kapdan and Kargi, 2006).

(1) Bio-photolysis of water by algae

Hydrogen was produced by the molecule of water split to hydrogen ion and oxygen via photosynthesis. Hydrogen ion generation are converted into hydrogen gas by hydrogenise enzyme and operated under anaerobic condition, carbon dioxide is required for some cultures during hydrogen evolution phases. Now, the hydrogen production by algae is considerably lower than that obtained by dark or photo-fermentations. Nevertheless, the algae hydrogen production is sustainable and economical process in term of carbon dioxide consumption and water utilization but the oxygen generation from these processes are strong inhibition on hydrogenase enzyme. Inhibition of the hydrogenise enzyme by oxygen can be alleviated by cultivation of algae under sulfur deprivation for 2-3 days to provide anaerobic conditions in the light. Moreover, low hydrogen production and no waste utilization are disadvantage of this way (Kapdan and Kargi, 2006).

(2) Photo Fermentation

Photo fermentation is the process to decompose organic compounds to hydrogen as the product by photosynthetic bacteria. They undergo anoxygenic photosynthesis with organic compounds or reduced sulfur compounds as electron donors. Some non-sulfur photosynthetic bacteria are potent hydrogen producers, utilizing organic acids, such as lactic, succinic, and butyric acids, or alcohols as electron donors. Hydrogen production by photosynthetic bacteria is mediated by nitrogenase activity, although hydrogenases may be active for both hydrogen production and hydrogen uptake under some conditions. Photosynthetic bacteria are the most promising microbial system for biohydrogen production because of their high theoretical conversion yields and lack of oxygen-evolving activity, which causes problem of oxygen inactivation of different biological systems. Moreover, they have the ability to use wide light intensity and consume organic substrates derived from wastes and wastewaters (Kapdan and Kargi, 2006). If photosynthetic bacteria are combined with fermentative bacteria, the fermentative bacteria could produce the small organic acids, which the photosynthetic bacteria could then use.

(3) Dark Fermentation

Dark fermentation is a special type of anaerobic digestion process comprising only hydrolysis and acidogenesis. They converted organic compound into hydrogen, carbon dioxide, and some simple organic compounds, e.g. volatile fatty acid (VFA) and alcohols under anaerobic condition. The utilization of waste or wastewater has attended considerable in recent years especially in the dark fermentation process. In the dark may be cultivated in pure culture or occur in uncharacterized mixed cultures selected from natural sources. The advantages of dark fermentation are that fermentative bacteria are capable of high hydrogen generation rate, and hydrogen is produced throughout the day and night at a constant rate since it does not depend on energy provided by sunlight (Hallenbeck and Benemann, 2002). Moreover, the dark fermentation is more promising approach for hydrogen production than photo fermentation because of the light penetration and operation under ambient temperature and pressure condition (Kapdan and Kargi, 2006). In addition, biohydrogen from anaerobic condition is also more stable and higher hydrogen production rate than pho fermentation. Thus, anaerobic condition is favorable for biohydrogen production. From these several advantages, biohydrogen production by dark fermentation is feasible for industrial application and there are many researchers studied on biohydrogen production via dark fermentation under optimum condition

2.3 Wastewater Treatment

2.3.1 Fundamental of Wastewater Treatment

Nowaday, there are several industries are developing, the quantity of waste generated also increases. Thus, it is essential for remove the community's sewage from homes and industries. There are many techniques used to move away pollutants before being released to the environment such as biological, chemical, physical, and energetic ones. These different techniques are applied through many stages of wastewater treatment. Wastewater treatment is a multi-stage process to renovate wastewater before it return to water sources. The aim of wastewater treatment to reduce or remove organic matter, solid, nutrients, disease-causing organisms, and other pollutants from wastewater. Therefore, each sewage treatment plant must hold a permit listing the allowable levels of BOD, COD, suspended solid, coliform bacteria, and other pollutants. The overall scheme of wastewater treatment process show as Finger 2.13.

2.3.2 Wastewater Treatment Procedure

Wastewater treatment step consist of two major steps: primary treatment processes (physical removal of floatable and settle solids) and secondary treatment processes (biological removal of dissolved solids). These two steps can be divided to preliminary treatment, primary treatment, advanced primary treatment, secondary treatment, tertiary treatment, advanced treatment, and sludge treatment. The overall scheme of wastewater treatment process as shown in Finger 2.13.

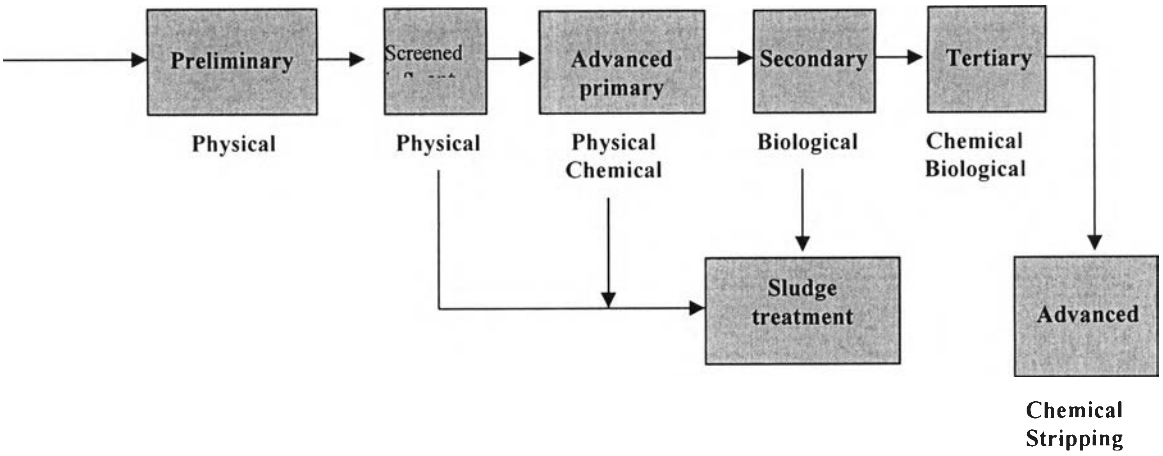

Figure 2.13 Flow diagram of wastewater treatment processes.

2.3.2.1 Preliminary Treatment

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

2.3.2.2 Primary Treatment

In primary treatment, it is the following step from preliminary step, which is physical operation. The incoming flow is slow in large tanks for remove a portion of the suspended solids from wastewater by floating or settling.

2.3.2.3 Advanced Primary Treatment

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

2.3.2.4 Secondary Treatment

Wastewater from primary treatment process has to remove or reduce contaminants, known as secondary treatment. Usually, biological treatment is used to treat wastewater in this step because it is the most effective type of treatment. The basic characteristic of this process is the use of bacteria and microorganisms to remove and stabilize contaminants from wastewater by assimilating them. Microorganisms are used to oxidize (i.e. convert) dissolved, suspended, and colloidal organic materials into simple end-products and additional biomass (stable solids and more microorganisms), as represented by the following equation for the aerobic biological oxidation of organic matter.

$$\text{Organic material} + O_2 + NH_3 + PO_4^{3-} \xrightarrow{\text{microorganism}} \text{New cells} + CO_2 + H_2O \quad (2.11)$$

From Equation (2.11), the organic materials serve as both an energy source and a source of carbon for cell synthesis under these circumstances.Oxygen(O_2),ammonia (NH_3), and phosphate(PO_4^{3-})are used to represent the nutrients needed for the conversion of organic matter to simple end-products (i.e. carbon dioxide (CO_2) and water). The term shown over the directional arrow is used to denote the fact that microorganisms are needed to carry out the oxidation process. The term new cells represent the biomass produced as a result of the oxidation of the organic matter.

2.3.2.5 Tertiary Treatment

After primary and secondary treatments process, wastewater will be sent to tertiary treatment process to remove disease-causing organisms from wastewater. Treated wastewater can be sterilized by adding chlorine or by using ultraviolet light. Moreover, this treatment process may include processes to remove nutrients, such as nitrogen and phosphorus, and carbon adsorption to remove chemicals.

2.3.2.6 Advanced Treatment

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

2.3.2.7 Sludge Treatment

Wastewater treatment processes generate significant quantities of sludge from suspended solids in the feed, biomass generated by biological process, and precipitates from added chemicals, which require the processes to treat them. Sludge treatment process is to stabilize the sludge and reduce order, remove some of water and reduce volume, decompose some of the organic matter and reduce volume, kill disease-causing organisms, and disinfect the sludge.

2.3.3 Wastewater Parameters

2.3.3.1 pH

Effluent standards for industrial waste discharge should be 5-9.

2.3.3.2 Organic Component

BOD (Biochemical Oxygen Demand)

It is a parameter which determine a concentration of biodegradable in water sample under controlled condition. BOD is the most parameter in both wastewater treatment and water pollution control. It is expressed as the amount of oxygen required by bacteria while stabilizing decomposable organic matters under aerobic condition. BOD has three methods to analyze: (1) BOD bottle technique

(2) Monometric BOD analyzer (3) Membrane method

COD (Chemical Oxygen Demand)

COD is the method to determine the concentration of organic compounds present in a wastewater sample using chemical oxidation reaction with potassium dichromate under acidic condition. The value of COD is calculated in term of oxygen required for this chemical oxidation reaction and it represents both biodegradable and non-biodegradable organics in the sample.

2.3.3.3 Inorganic and organic contents

Total Solids (TS)

Total solids (TS) represent total solid both soluble and insoluble forms of both organics and inorganics. The term total solids refer to the matter remained after a wastewater sample is evaporated and dried at a specified temperature (103 to 105°C). The weight of the dried sample is used to represent TS in mg/l.

$$TS = TSS + TDS \tag{2.12}$$

Total Volatile Solids (TVS)

Total volatile solids (TVS) represent the organic fraction of both soluble and insoluble forms. It can be measured by calcite or oxidize the dried sample at 550 °C in unit of mg/l.

$$TVS = TS - ash \tag{2.13}$$

Suspended Solids (SS)

It represent the total un-dissolved solids in both organic and inorganic forms by filter a dry sample with a 1 μm filter membrane and then dry at 105 °C in unit of mg/l.

Volatile Suspended Solids (VSS)

Volatile suspended solids (VSS) represent the un-dissolved organic fraction by calcite the filtered solids at 550 °C

Total Dissolved Solid (TDS)

It represent both soluble and insoluble of organic and inorganic compound according to

$$TDS = TS-SS \tag{2.14}$$

2.3.3.4 Hydraulic Retention Time

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

$$\tau = \frac{V}{Q} \tag{2.15}$$

Where τ = Hydraulic retention time, h

V = Volume of reactor, m^3

Q = Volumetric flow rate, m^3/h

2.3.4 Biological Treatment

Biological treatment is an important and integral part of any wastewater treatment plant. Normally, biological wastewater treatment is the second process of wastewater treatment. Sewage microorganisms are cultivated and added to the wastewater to transform dissolved and particulate biodegradable constitutes into acceptable end products. There are two basic categories of biological treatment: aerobic treatment process and anaerobic treatment process

2.3.4.1 Aerobic Treatment Process

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

2.3.4.2 Anaerobic Treatment Process

This process is similar to aerobic treatment, but microorganisms that do not required the addition of oxygen.

Table 2.1 Comparison between aerobic treatment process and anaerobic treatment process (Arun Mittal, 2011)

Parameter	**Aerobic treatment**	**Anaerobic treatment**
Process principal	- Microbial reactions take place in the presence of molecular/ free oxygen - Reactions products are carbon dioxide, water and excess biomass	- Microbial reactions take place in the absence of molecular/ free oxygen - Reactions products are carbon dioxide, methane and excess biomass
Applications	Wastewater with low to medium organic impurities (COD < 1000 ppm) and for wastewater that are difficult to biodegrade e.g. municipal sewage, refinery wastewater etc.	Wastewater with medium to high organic impurities (COD > 1000 ppm) and easily biodegradable wastewater e.g. food and beverage wastewater rich in starch/sugar/alcohol
Reaction Kinetic	Relatively fast	Relatively slow
Net Sludge Yield	Relatively high	Relatively low (generally one fifth to one tenth of aerobic treatment processes)
Post Treatment	Typically direct discharge or filtration/disinfection	Invariably followed by aerobic treatment
Capital Investment	Relatively high	Relatively low with pay back
Example Technologies	Activated Sludge e.g. Extended Aeration, Oxidation Ditch, MBR, Fixed Film Processes e.g. Trickling Filter/Biotower, BAF, MBBR or Hybrid Processes e.g. IFAS	Continuously stirred tank reactor/digester, Upflow Anaerobic sludge Blanket (UASB), Ultra High Rate Fluidized Bed reactors e.g. EGSBTM, ICTM etc.

Table 2.2 Advantage and disadvantages of anaerobic processes

Advantage	**Disadvantage**
• Less energy required	• May required alkalinity or specific ion addition
• Less biological sludge production	• Longer start-up time to develop necessary biomass inventory
• Fewer nutrients required	• May required further treatment with an aerobic treatment process to meet discharge requirements
• Elimination of off-gas air pollution	• Biological nitrogen and phosphorus removal is not possible
• Smaller reactor volume required	• Much more sensitive to the adverse effect of lower temperatures on reaction rates
• Rapid response to substrate addition after long periods without feeding	• May be more susceptible to upsets due to toxic substances
	• Potential for production of odors and corrosive gases

2.3.5 Anaerobic Fermentation

Anaerobic fermentation is a microbial process to convert carbonaceous compounds and soluble inorganic substances containing oxygen under the absence of dissolved oxygen. The microbiological will convert organic matter to methane, hydrogen and other organic compounds. The decomposition is caused by natural bacteria action in various stages. It takes place in a variety of natural anaerobic environment, including water sediment, water-logged soils, natural hot springs, ocean thermal vents, and the stomach of various animals.

2.3.5.1 Process Description

The main objective is to stabilize the sludge produced from mostly aerobic treatment plants of domestic wastewater and the digested sludge has a mass reduction of 50% of the original sludge and is free from odor problem when being disposed off on land.

Decomposition of Carbonaceous Compounds

Carbonaceous compounds are decomposed biologically by microorganisms and there are three main sequential step:

(1) Hydrolysis: Large organic molecules are hydrolyzed to simple molecules by external enzymes which released by bacteria. For example carbohydrates and starch are hydrolyzed to glucose, oils are hydrolyzed to fatty acids and proteins are hydrolyzed to amino acids. These simple organic molecules which are soluble can diffuse through the cell wall of bacteria. For some industrial wastewater, fermentation may be the first step in the anaerobic process

(2) Acidogenesis: These step converted soluble organics to organic acids such as butyrate, propionate, valerate, and acetate. Moreover, there are some alcohols can be produced. This group of bacteria called acidogens, acid formers or acidogenic bacteria. Amino acids, sugars, and some fatty acids are degraded further. 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).

(3) Methanogenesis: The third step, methanogenesis, is carried out by a group of organisms known collectively as methanogens. Two groups of methanogenic organisms are involved in methane production. The first group, aceticlastic methanogens, splits acetate into methane and carbon dioxide. The second group, hydrogen-utilizing methanogens, uses hydrogen as the electron donor and carbon dioxide as the electron acceptor to produce methane.

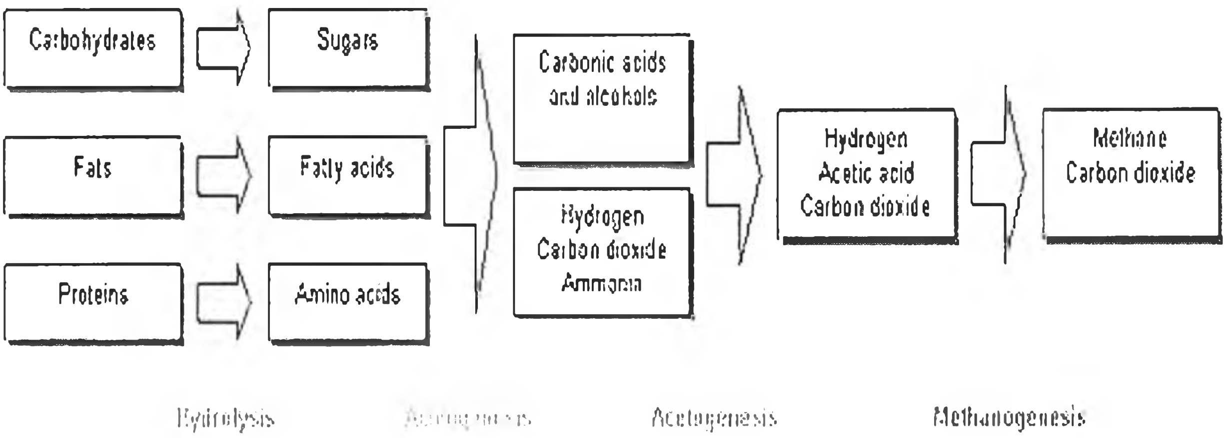

Figure 2.14 Overall anaerobic digestion process.

Sulphate Reduction

Sulphate can be reduced by sulphate-reducing bacteria under anaerobic conditions and it occur simultaneously with decomposition of carbonaceous compound according to below equation

$$SO_4^{2-} + 2H_2 \longrightarrow S + H_2O + 2OH^- \quad \Delta G = -154 \text{ kJ/mol} \quad (2.16)$$

$$SO_4^{2-} + CH_3COOH \longrightarrow H_2S + 2HCO_3^- \quad \Delta G = -43 \text{ kJ/mol} \quad (2.17)$$

Denitrification

Nitrate can be utilized by reduction reaction known as denitrification .It occurs when both of methanogenesis and sulphate reduction are almost completed. This can be described by the following reaction.

$$NO_3^- + 5/6CH_3OH \rightarrow 1/2N_2 + 5/6CO_2 + 7/6H_2O + OH^- + \text{energy} \quad (2.18)$$

2.3.5.2 Factors affecting anaerobic fermentation

Moisture or Water Content: Waste water should have water content higher than 99%.

Temperature: There are three ranges of temperature but two main temperature ranges is Mesophilic range and Thermophilic range

(1) Psychrophilic range between 5-15 °C

(2) Mesophilic range

Mesophilic process is the most commonly used for anaerobic biological treatment process, in particular waste sludge treatment. Decomposition of the volatile suspended solids (VSS) is around 40 % over a retention time of 15 to 40 day at a temperature of 30 to 40°C, which requires larger digestion tanks. It is usually more robust than the thermophilic process, but the biogas production tends to be less, and additional sanitization is usually required.

(3) Thermophilic range

Thermophilic process operates at a high temperature. The process is heated to 55°C and held for a period of 12 to 14 d. The microorganism rapidly breaks down organic matter and produces large volumes of biogas. The quick breakdown means that the digester volume can be smaller than in other systems. Thermophilic processes provide higher biogas production, but the technology is more expensive, more energy is needed, and it is necessary to have more refined control and instrumentation. Greater insulation is necessary to maintain the optimum temperature range. These processes may be more sensitive to upset due to temperature variations. However, these processes are more effective in pathogen removal

Table 2.3 Comparison of Mesophilic and Thermophilic digesters

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

pH:

(1) Methanogenic step the optimum pH about 7.0 but at pH< 5.5 destructed of methanogens.

(2) Acidogenic step the optimum pH about 7.0 but at pH< 4.5 destructed of acidogens.

Alkalinity: An ability of the system to resist the pH change when acid or VFA increase express in term of $CaCO_3$ in unit of mg/L

Volatile Fatty Acids (VFA): It is produced in acidogenic stage and express in term of acetic acid (mg/L) and increase VFA will reduce the system pH so it should not exceed 200 mg/L.

Nutrients: In anaerobic treatment BOD:N:P = 100:1:0.2 and COD:N:P = 100:2:0.4

Toxic Substance: Inorganic salts at high concentration become toxic.

Feeding Mode: There are 3 main types of feeding

(1) Batch (Landfill)

(2) Semi-continuous (Farm wastes)

(3) Continuous wastewater (farm wastes most industrials)

Mixing: There are 4 types of mixing

(1) Mechanical mixing: poor mixing, leakage problem and expensive

(2) Slurry recirculation: partial mixing

(3) Gas mixing: well mixing

(4) Intermittent mixing: low cost and popular in Upflow Anaerobic sludge Blanket (UASB)

2.3.5.3 Types of Anaerobic Treatment Process

Anaerobic Suspended Growth Process

There are anaerobic suspended growth process three types

(1) Complete-Mix Process

In the complete-mix anaerobic process, as shown in Figure 2.3(a), the hydraulic retention and solid retention times are equal (τ = SRT). Generally, hydraulic retention time may be in the range of 15 to 30 d to provide sufficient safety factors for operation and process stability. This process without sludge recycle is more suitable for wastes that have high concentrations of solids or extremely high dissolved organic concentrations, where thickening the effluent solids is difficult. Typical organic loading rates for this process are present in Table 2.1, compared with anaerobic contact and anaerobic sequencing reactor processes.

(2) Anaerobic Contact Process

The anaerobic contact process, as shown in Figure 2.3(b), overcomes the disadvantages of a complete-mix process without recycle. Biomass is separated and returned to the complete-mix or contact reactor so that the solid retention time (SRT) is longer than hydraulic retention time (τ). The anaerobic reactor volume can be reduced by separating τ and SRT values. Gravitational separation is the most common approach for solid separation and thickening prior to sludge recycle.In some cases, gas flotation is used for solid separation by dissolving the process off-gas under pressure, which has been used in place of gravitational separation. Since the reactor sludge contains gas produced in the anaerobic process and gas production can continue in the separation process, solid-liquid separation can be inefficient and unpredictable.

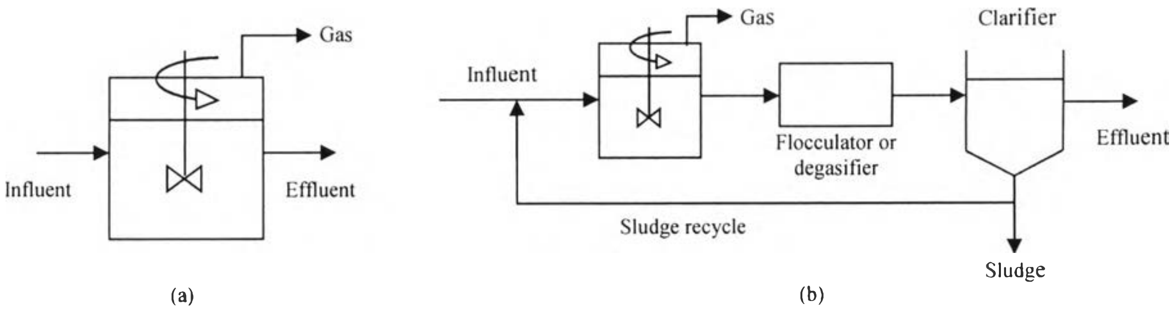

Figure 2.15 Anaerobic suspended growth processes: (a) complete-mix process, and (b) anaerobic contact process.

(3) Anaerobic Sequencing Batch Reactor Process

The anaerobic sequencing batch reactor process, as shown in Figure 2.4, can be considered a suspended growth process with reaction and solid-liquid separation in the same vessel, much like that for aerobic sequencing batch reactor (SBR). The operation of ASBR consists of four steps: (1) feeding, (2) reacting, (3) settling, and (4) decanting. During the reacting period, intermittent mixing for a few minutes each hour is done to provide uniform distribution of substrate and solids. The organic loading of the process can be changed by selecting hydraulic retention times from 6 to 24 h. At 25°C, 92 to 98 % COD removal can be achieved at volumetric organic loading of 1.2 to 2.4 kg COD/m^{3}d.

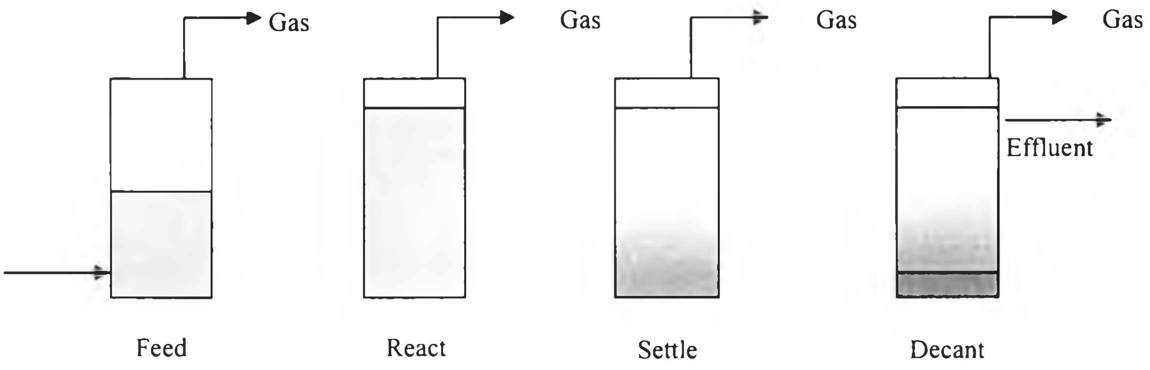

Figure 2.16 Anaerobic sequencing batch reactor process(ASBR).

Table 2.4 Typical organic loading rates for anaerobic suspended growth processes at 30°C

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

Anaerobic sludge blanket process

This process uses an anaerobic process, whilst forming a blanket of granular sludge and being suspended in the tank. The key feature of this process is that the anaerobic sludge inherently has superior flocculation and settling characteristics, which favorably provide the physical and chemical conditions for sludge flocculation. When these conditions are met, a high solid retention time (at high HRT loadings) can be achieved, with separation of the gas from the sludge. One of the most notable developments in anaerobic treatment process technology is the upflow anaerobic sludge blanket (UASB) reactor. The principal types of anaerobic sludge blanket processes include (1) the original UASB process and modification of the original design, (2) the anaerobic baffled reactor (ABR), and (3) the anaerobic migrating blanket reactor (AMBR). Of these sludge blanket processes, the UASB is the most common used process for treating a wide range of industrial wastewaters.

(1) Upflow Sludge Blanket Reactor Process

The basic UASB reactor is illustrated in Figure 2.4(a). The influent wastewater is distributed at bottom of the UASB reactor and travels in an upflow mode through the sludge blanket. Critical elements of the UASB reactor design are the influent distribution system, the gas-solid separator, and the effluent withdrawal 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). Both modifications are intended to provide better solid capture in the system and to prevent the loss of large amounts of the UASB reactor solid due to process upsets or changes in the UASB sludge blanket characteristics and density.

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

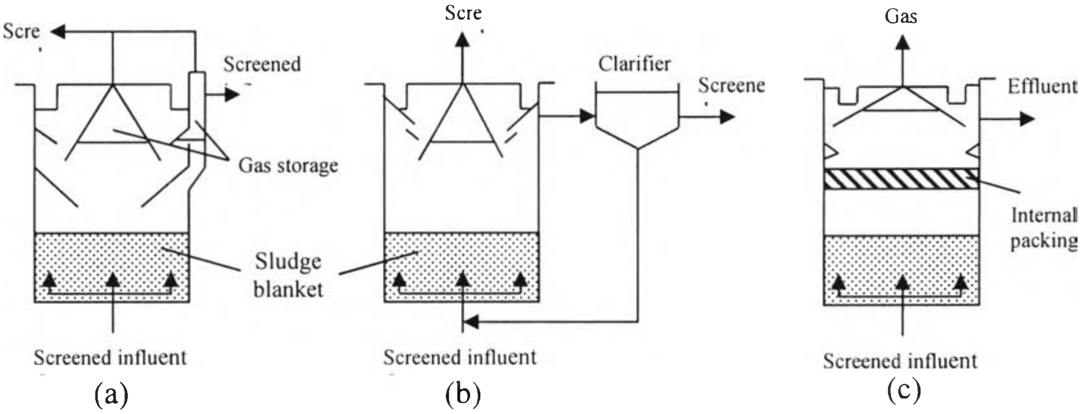

Figure 2.17 Schematic of the UASB process and some modifications: (a) original process, (b) UASB reactor with sedimentation tank and sludge recycle, and (c) UASB reactor with internal packing for fixed-film attached growth.

(2) Anaerobic Baffled Reactor Process

In the anaerobic baffled reactor process (ABR), 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.

(3) Anaerobic Migrating Blanket Reactor

The anaerobic migrating blanket reactor (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 the AMBR process, the influent feed point is changed periodically to the effluent side, and the effluent withdrawal point is also changed. In this way, the sludge blanket remains more uniform in the anaerobic reactor. The flow is reversed when a significant quantity of solids accumulates in the last stage.

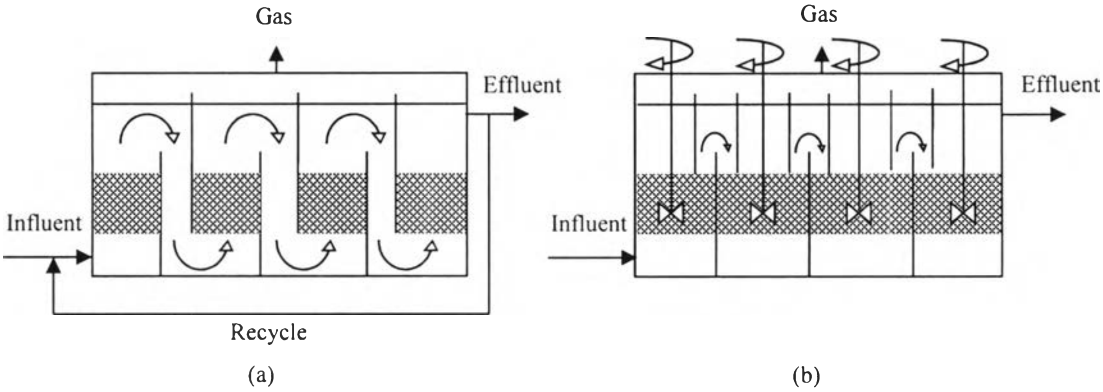

Figure 2.18 Schematic of alternative sludge blanket processes: (a) anaerobic baffled reactor (ABR) and (b) anaerobic migrating blanket reactor (AMBR).

Attached growth anaerobic processes

Attached growth anaerobic treatment reactors differ by the type of packing used and the degree of bed expansion. There are four types of attached growth processes

(1) Upflow Packed-Bed Reactor

In the upflow packed-bed reactor, as shown in Figure 2.6(a), the packing is fixed, and the wastewater flows up through the interstitial spaces between the packing and biogrowth. Effluent recycle is generally not used for the packed-bed reactor, except for high-strength wastewaters. While the first upflow anaerobic packed-bed processes contained rock, a variety of designs employing synthetic plastic packing is used currently. A large portion of the biomass responsible for treatment in the upflow attached growth anaerobic processes is loosely held in the packing void spaces and not just attached to the packing material. Low upflow velocities are generally used to prevent the washout of the biomass. Over time, solids and biomass will accumulate in the packing to cause plugging and flow short-circuiting. At this point, solids must be removed by flushing and draining the packing.

Advantages of upflow attached growth anaerobic reactors are 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. Recycle is used to provide upflow velocity, resulting in 20 % bed expansion. The smaller packing provides a greater surface area per unit volume, theoretically supporting a greater amount of biomass growth. The packing void fraction is about 50 % when expanded. With such a small packing and void volume, the expanded-bed operation is necessary to prevent plugging. Because the expanded-bed system is not fully fluidized, some solids are trapped, and some degree of solid degradation occurs.

(3) Attached Growth Anaerobic Fluidized-Bed Reactor

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. Both fluidization and mixing of the packing material occurs in fluidized-bed system. Effluent recycle is used to provide sufficient upflow velocity.

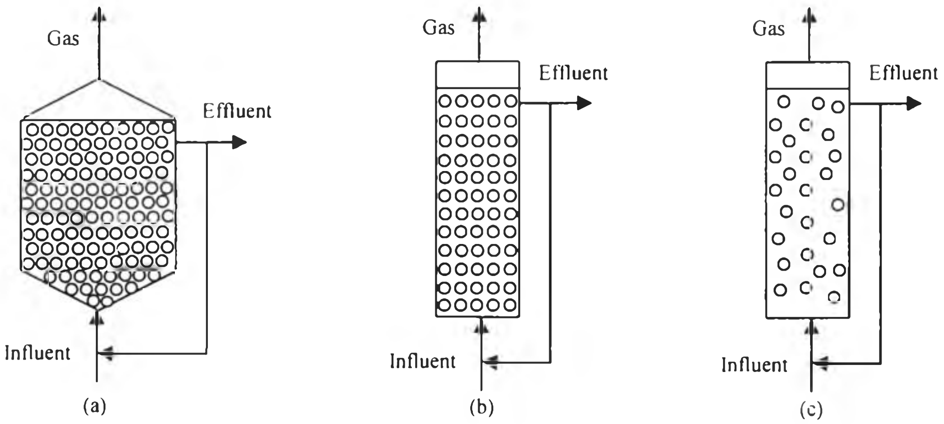

Figure 2.19 Upflow anaerobic attached growth treatment reactors: (a) anaerobic upflow packed-bed reactor, (b) anaerobic expanded-bed reactor, and (c) anaerobic fluidized-bed reactor.

The expanded-bed and fluidized-bed reactors have more surface area per reactor volume for biomass growth and better mass transfer than the upflow packed-bed reactor, but have lower solid capture.

(4) Down flow Attached Growth Process

The down flow attached growth anaerobic processes, as illustrated in Figure 2.20, have been applied for treatment of high-strength wastewaters using a variety of packing materials, including cinder block, random plastic, and tubular plastic. Systems are designed to allow recirculation of the reactor effluent.

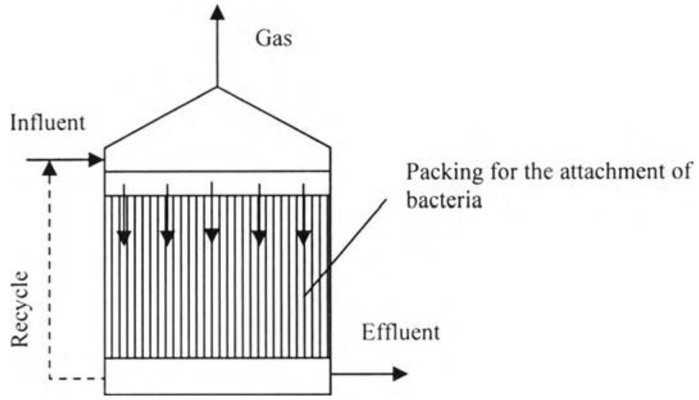

Figure 2.20 Down flow attached growth anaerobic treatment reactor.

2.3.5.4 Biohydrogen Production from Wastewater using Anaerobic Sequencing Batch Reactor Process (ASBR)

Raw materials for biohydrogen production

- Animal manures
- Municipal solid wastes(MSW) in only organic fraction
- Sludge from treatment plant
- Industrial wastewaters at high COD value
- Agricultural residues after utilization

The main raw material is substrate which contains mainly carbohydrate and protein - rich biomass because carbohydrate are the preferred organic carbon source for hydrogen-producing fermentation. Moreover, the effluent wastewater from brewery, dairy industry, olive mill, and baker's yeast could be used as raw material for bio-hydrogen production (Kapdan and Kargi, 2006). The main by-product are acetic acid and butyric acid following below equation.

$$C_6H_{12}O_6 + 2H_2O \longrightarrow 2CH_3COOH + 2CO_2 + 4H_2 \quad (2.19)$$

$$C_6H_{12}O_6 \longrightarrow 2CH_3CH_2CH_2COOH + 2CO_2 + 4H_2 \quad (2.20)$$

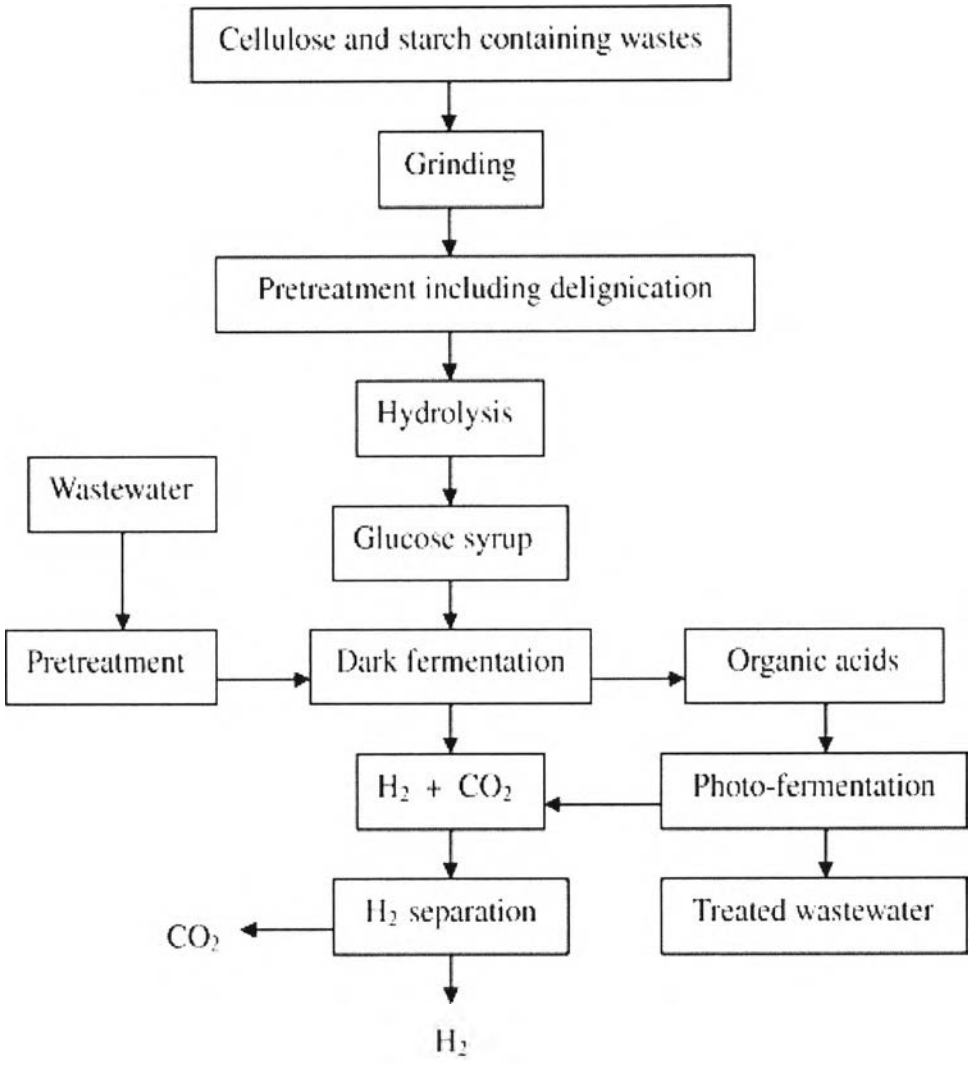

Figure 2.21 A schematic diagram for bio-hydrogen production from cellulose/starch (Kirtay, 2011).

There are many researchers studied on biohydrogen by various wastewater sources because not only approach to wastewater treatment but also the sustainable biohydrogen production. For example, Searmsirimongkol *et al.* studied the hydrogen production from alcohol distillery wastewater containing high potassium and sulfate using an anaerobic sequencing batch reactor. They investigated the feasibility of hydrogen production from alcohol distillery wastewater that containing high potassium and sulfate and seed sludge taken from anaerobic tank. They boiled the seed sludge about 15 minutes before being feed to the ASBR for get rid of the hygrogen-consuming bacterium and then operated under difference chemical oxygen demand and different COD loading. They controlled under the optimum condition for biohydrogen production such as control the temperature at mesophilic temperature (37 °C), pH at 5.5 and cycle time 6 cycles per day and only H_2 and CO_2 were found under these optimum condition. The result showed that the best condition for biohydrogen production was a feed COD of 40,000 mg/l or COD loading rate 60 mg/m^3 d and hydraulic retention time(HRT) 16 h that can be produced hydrogen yield of 172 ml H_2/g COD removed, the specific hydrogen production rate (SHPR) of 270 ml H_2/g MLVSS d (or 3310 ml H_2/l d). If feed exceeded 40,000 mg/l, the system was toxic by potassium and sulfate and resulted for lower biohydrogen production. Intanoo et al. investigated hydrogen production from alcohol wastewater by an anaerobic sequencing batch reactor (ASBR) under thermophilic operation and at a constant pH 5.5. They studied under optimum COD loading rate of 68 kg/m^3 d and the produced gas contained 43% H_2 without methane and the system provided a specific hydrogen production rate of 2100 ml H_2/l d and hydrogen yield of 130 ml H_2/g COD removed. The nutrient requirement in term of COD:N:P was found to be 100:6:0.5, nitrogen uptake was obtained from organic nitrogen. Moreover, the hydrogen production under thermophilic operation in this work require nutrient more than biogas production and hydrogen production under mesophilic operation. Sreethawong et al. studied hydrogen production from cassava wastewater using anaerobic sequencing batch reactor (ASBR) and determined the optimum number of cycle per day, Chemical oxygen demand (COD), loading rate, and COD:N ratio. In this work, they observed that the maximum hydrogen production performance show in terms of specific hydrogen production rate (SHPR) was 388 ml H_2/g VSS d or 3800 ml H_2/l d and hydrogen yield was 186 ml H_2/g COD removed under COD loading rate of 30 kg/m^3 d and 6 cycles per day. Besides, they added NH_4HCO_3 into the system under optimum condition (COD loading rate 30 kg/m^3 d and 6 cycles per day) and found that the COD:N ratio of 100:2.2 gave the maximum SHPR of 524 ml H_2/g VSS d (5680 ml H_2/l d) and hydrogen yield 438 ml H_2/ g COD removed. The COD: N ratio was excess nitrogen may affect higher organic acids and ethanol production as a result to decreased hydrogen production efficiency.