

## CHAPTER II

### LITERATURE REVIEW

#### 2.1 Background of Hydrogen and methane

The global demand for energy has risen inexorably in the last many years in step with industrial development and population growth. The global energy is supplied by coal, oil, petroleum and natural gas products- the fossil fuel that formed long ago from remain plant and animal. However, these are non-renewable sources that will one day be exhausted. Moreover, the overwhelming scientific evidence is that use of fossil fuels is causing the world's climate to change, with potential disastrous effect. Hydrogen and methane have been preserved as fossil energy. Hydrogen is one of two natural elements that combine to make water. Hydrogen is not an energy source, but an energy carrier because it takes a great deal of energy to extract it from water. It is useful as a compact energy source in fuel cells and batteries. Methane, also called marsh gas, colorless, odorless gas that occurs abundantly in nature and a product of the anaerobic bacterial decomposition of vegetable matter under water. The decomposition of sludge by anaerobic bacteria in sewage-treatment processes also produces a gas rich in methane. Since commercial natural gas is composed largely of methane, their uses may for all practical purposes be considered identical. Because of its abundance, low cost, ease of handling, and cleanliness, such gas is widely used as a fuel in homes, commercial establishments, and factories. Methane is an important source of hydrogen and some organic chemicals. Methane reacts with steam at high temperatures to yield carbon monoxide and hydrogen; the latter is used in the manufacture of ammonia for fertilizers and explosives. Other valuable chemicals derived from methane include methanol, chloroform, carbon tetrachloride, and nitromethane. The incomplete combustion of methane yields carbon black, which is widely used as a reinforcing agent in rubber used for automobile tires.

## 2.2 Advantage of Hydrogen and Methane

### 2.2.1 Availability.

Hydrogen is available in the entire universe and in abundant quantities. Also, it is a renewable source of energy and does not get depleted with time. Hydrogen is found in water, and the three parts of our planet is made up of water. So there is no question of depletion when it comes to hydrogen. For methane availability, There are a lot of methane production, but an alternative method of obtaining methane is via biogas generated by the fermentation of organic matter including manure, wastewater sludge, municipal solid waste (including landfills), or any other biodegradable feedstock, under anaerobic conditions. Rice fields also generate large amounts of methane during plant growth. Methane hydrates/clathrates (ice-like combinations of methane and water on the sea floor, found in vast quantities) are a potential future source of methane.

### 2.2.2 Efficiency

According to Columbia University research, hydrogen fuel cells are twice as efficient as regular internal combustion engines. its high energy content (122 kJ/g) which 2.8 times more energy than gasoline when compared with the same mass, and so produces more energy with less fuel. For methane efficiency, At about 891 kJ/mole, methane's heat of combustion is lower than any other hydrocarbon but the ratio of the heat of combustion (891 kJ/mole) to the molecular mass (16.0 g/mole, of which 12.0 g/mole is carbon) shows that methane, being the simplest hydrocarbon, produces more heat per mass unit (55.7 kJ/g) than other complex hydrocarbons.

### 2.2.3 Environmentally friendly

Conventional energy resources can significantly produce greenhouse gases, especially carbon dioxide, which is thought to be responsible for changes in global climate, but hydrogen burns in the air and leaves water vapor as residue. Water vapor has no environmental disadvantages as of now. So, hydrogen fuel can contribute to reducing greenhouse gas emissions and can reduce the production of many toxic pollutants. Although methane produced naturally at high levels from large-scale agricultural facilities and municipal landfills is greenhouse gas, it has been successfully utilized to generate electricity. The use of methane reduces green-

house gas emission. Moreover, when methane burn to create energy, it releases 20% that less of carbon dioxide in to the atmosphere than normal diesel or petrol vehicle

#### 2.2.4 Harmless fuel

Hydrogen is the safest of all fuels because it 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 while that other fuels take longer to disperse or may spill onto the ground. Methane is harmless gas by inhalation and it is not dangerous to touch unlike gas from petrol and diesel which can be very dangerous and even cause death. Additional, methane also doesn't harm soil or nearest environment

#### 2.2.5 Various sources.

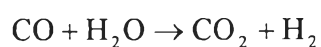
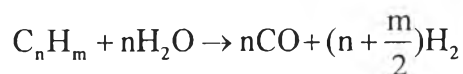
Advantage of hydrogen and methane are that there are many ways to produce it, using both renewable and traditional energy sources. The most common method of hydrogen production is by reforming fossil fuels, particularly natural gas. Electrolysis is another method of hydrogen production that uses electricity to split water into hydrogen and oxygen gases. One advantage of electrolysis is that one can perform electrolysis using renewable source so that the hydrogen produced is a renewable fuel. For methane production, methane is mainly produced by the process of methanogenesis which is a form of anaerobic respiration used by organisms that occupy landfill, ruminants (e.g., cattle), and the guts of termites. Methane could also be produced by a non-biological process called serpentinization involving water, carbon dioxide, and the mineral olivine

### 2.3 Hydrogen Production Processes

Hydrogen is produced mainly from fossil fuel, water and biomass. There are many methods for producing hydrogen.

#### 2.3.1 Steam reforming of natural gas

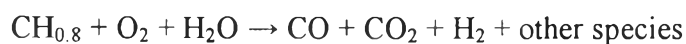
Steam reforming is a thermal process that consists of two reactions as show below



The first reaction is that natural gas is reacted with high temperature steam at in rang 700-1000 °C. The product is synthesis gas that is a mixture of carbon monoxide and hydrogen. After that carbon monoxide are convert to carbon dioxide and hydrogen though water-gas shit reaction (Kothari et al., 2004) shown in equation 2. Steam reforming of natural gas is the most basic and least expensive methods. At present, the most of hydrogen (approximately 80% of global hydrogen production) is produced from this process.

### 2.3.2 Coal gasification

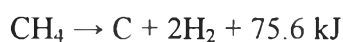
The gasification of coal is one method that can produce hydrogen. Coal with oxygen and steam under high pressures and temperatures to form synthesis gas, a mixture consisting primarily of carbon monoxide and hydrogen from the following reaction (unbalanced):



Impurities will be removed from the synthesis gas and then the carbon monoxide as a product in this reaction reacts with steam via the water-gas shift reaction to provide additional hydrogen and carbon dioxide. Then, hydrogen will be removed from other gas by a separation process.

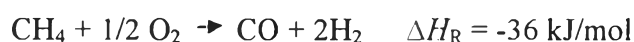
### 2.3.3 Thermal cracking of natural gas

Hydrogen is produced from decomposition of CH<sub>4</sub>. Methane is under high temperature, about 2,000 °C. This method is alternative production that more environmentally friendly than steam reforming process because of no carbon dioxide. The reaction is shown below:



### 2.3.4 Partial oxidation of methane (POX)

Partial oxidation that is the exothermic reaction so it is easy to operate when compared to other processes. This process is converting natural gas into carbon monoxide and hydrogen (syngas), which can be converted to higher alkanes or methanol (Deutschmann and Schmidt, 1998). The reaction of this process is:



### 2.3.5 Electrolysis

Electrolysis uses an electric current to split water into hydrogen at the cathode (+) and oxygen at the anode (-). If renewable energy is used to produce electricity, which is used to split the water into hydrogen and oxygen, the hydrogen will be an even cleaner form of energy. The efficiency of the electrolyzer is an important factor because the consumption of energy makes up 80-90 % of the production costs at an electrolysis plant. The chemical reaction of water electrolysis is:



Disadvantages of this method are that it needs to have a high temperature heat source at above 2,500 K for a reasonable degree of dissociation possibility, recombination of H<sub>2</sub> and O<sub>2</sub>, or end up with an explosion. H<sub>2</sub> from electrolysis is extremely pure, but expensive at the same time; being ten times more costly than from steam reforming of natural gas. Moreover, this method is not efficient when it comes to produce large amounts of hydrogen.

### 2.3.6 Hydrogen production from biomass

Biomass such as agricultural and domestic wastes (Argun et al., 2008), has been used as a carbon source which is a renewable sources for hydrogen production (Kapdan and Kargi, 2006). This process has been given attention due to operation under mild conditions. However, there are problems in biohydrogen production from wastes are the low rates and yields. Hydrogen production from biomass can be classified into two categories, which are thermochemical process and biological process

#### 2.3.6.1 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 oils, solid charcoal, and gaseous compounds. Pyrolysis can be further classified into slow and fast pyrolysis. Slow pyrolysis is normally not considered to produce hydrogen because charcoal is the main product. Fast pyrolysis is a high temperature process. In the absence of air, biomass is rapidly

heated to form vapor and afterwards condensed to a dark brown mobile bio-liquid as follows:



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

#### (2) Biomass gasification

Gasification of biomass under partial oxidation and high temperature (above 1,000 K) with steam and oxygen gives gas and charcoal. Finally, charcoal is reduced to  $\text{H}_2$ ,  $\text{CH}_4$ ,  $\text{CO}$ ,  $\text{CO}_2$ , and some hydrocarbons, as follow:



The problem of biomass gasification is the production of tar and ash; tar causes formation of tar aerosols and polymerization to more complex structures, but ash causes deposition, sintering, slagging, fouling, and agglomeration. If biomass has moisture content over than 35 %, the gasification can be done under the supercritical water condition with heating water to a temperature (674 K) and compressing it over its critical pressure (22 MPa). Then, the biomass is rapidly decomposed to small molecules and gases with no tar and ash formation.

#### 2.3.6.2 Biological process

Biological process for hydrogen production, also known as “biohydrogen production”, uses microorganisms to decompose complex organic compounds in waste or wastewater to simple end products, such as hydrogen, methane, carbon dioxide volatile fatty acids, and alcohols (Kapdan *et al.*, 2006). Most of biological processes are operated at an ambient temperature (30-40°C) and normal pressure, therefore, they are not energy intensive (Das et al, 2001). Moreover,

they are very inexpensive and very simple perspective method (Bartacek *et al.*, 2007). There are two types of biological processes:

#### (1) Photo-fermentation

Photo-fermentation is the process to decompose organic compounds to hydrogen as the product by photosynthetic bacteria. They undergo anoxygenic photosynthesis with organic compounds or reduced sulfur compounds as electron donors. Some non-sulfur photosynthetic bacteria are potent hydrogen producers, utilizing organic acids, such as lactic, succinic and butyric acids, or alcohols as electron donors. Hydrogen production by photosynthetic bacteria is mediated by nitrogenase activity, although hydrogenases may be active for both hydrogen production and hydrogen uptake under some conditions. Photosynthetic bacteria are the most promising microbial system for biohydrogen production because of their high theoretical conversion yields and lack of oxygen evolving activity, which causes problem of oxygen inactivation of different biological systems. Moreover, they have the ability to use wide spectrum of light and consume organic substrates derivable from wastes and wastewater treatment (Fascetti, 1998). If photosynthetic bacteria are combined with fermentative bacteria, the fermentative bacteria could produce the small organic acids, which the photosynthetic bacteria could then use.

#### (2) Dark fermentation

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

microorganisms to the production system (Das *et al.*, 2001). From these several advantages, hydrogen production by dark fermentation is feasible for industrial application (Das *et al.*, 2001).

## **2.4 Methane production process**

### **2.4.1 Biomass**

Methane can be produced from biomass through a process called anaerobic digestion. Anaerobic digestion involves using bacteria to decompose organic matter in the absence of oxygen. Vegetable solid wastes, leaves, grasses, woods, weeds, marine and freshwater biomass have been explored for their anaerobic digestion potential to methane (Gunaseelan, 1997). The first step, biomass are changed by acidogenesis bacterial to produced volatile fatty acid such as acetic acid, propionic acid and then they degrades by methanogenesis bacterial to methane in the second step that called methanogenesis step

## **2.5 Anaerobic Fermentation**

Anaerobic fermentation is a microbial process to converse carbonaceous compounds and soluble inorganic substances containing oxygen under the absence of dissolved oxygen. Anaerobic fermentation has three anaerobic decomposition processes. Three basic steps are involved in the overall anaerobic oxidation of a waste

### **2.5.1 Decomposition of carbonaceous compounds**

There are 3 main sequential steps.

#### **2.5.1.1 Hydrolysis**

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

#### **2.5.1.2 Acetogenesis**

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



### 2.5.1.3 Methanogenesis

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

## 2.6 Common parameters in wastewater

### 2.6.1 Total and suspended solid

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

### 2.6.2 Total volatile solids (TVS)

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

### 2.6.3 Total suspended solids (TSS)

Total suspended solids (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 dry suspended solids is weighed. The weight of suspended solids is equal to the difference between this weight and the original weight of the clean filter. The concentration of total suspended solids is the

weight of the dry solids divided by the volume of the sample and is usually expressed in milligrams per liter.

#### 2.6.4 Volatile suspended solids (VSS)

Volatile suspended solids (VSS) are determined by igniting the dry solids at  $550\pm 50^{\circ}\text{C}$  after placing the filter disk in a porcelain dish. The concentration of volatile suspended solids is the weight of dry solids minus the weight of fixed solids divided by the volume of the original liquid sample.

#### 2.6.5 Biochemical and chemical oxygen demand

##### 2.6.5.1 Biochemical oxygen demand

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

##### 2.6.5.2 Chemical oxygen demand

Chemical oxygen demand (COD) is a measure of the oxygen equivalent of the organic matter in wastewater that can be oxidized chemically using dichromate in an acid solution. The organic matter is converted into carbon dioxide and water. COD value presents both biodegradable and non-biodegradable organic matter in the sample.

#### 2.6.6 Hydraulic retention time

The hydraulic retention time (HRT) or  $\tau$  (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:

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

where  $\tau$  = Hydraulic retention time, h

$V$  = Volume of reactor,  $\text{m}^3$

$Q$  = Volumetric flow rate,  $\text{m}^3/\text{h}$

## 2.7 Two-Step Hydrogen and Methane Production

One of the significant problems in the fermentative hydrogen production process is that most of the organic fraction of the feeding wastewater

remains as soluble fermentation products. Thus, a complementary stage after fermentation would be necessary for COD elimination. It is well known that VFA formation during acidogenesis of the organic matter is actually the precursor to methanogenesis. Therefore, the hydrogen production process could be efficiently coupled with a subsequent anaerobic digestion step with the conversion of the remaining organic content to biogas (mainly methane and carbon dioxide). A two-stage anaerobic digestion process, in which acidogenesis and methanogenesis occur in separate reactors, may offer several advantages as shown in Table 2.1 in order to enhance hydrogen and methane production and achieve stabilization of the treated wastewater prior to disposal.

Two-stage anaerobic digestion is a process configuration using two separate reactors. The first reactor is acidogenic-stage, which is maintained at a low pH or alkalinity and develops a high CO<sub>2</sub> and low CH<sub>4</sub> content in the gaseous products. Acidifying organisms dominate in the first reactor, and the major biochemical reaction is enzymatic hydrolysis and fermentation. Another one is methanogenic-stage, which is maintained at pH around 7 and high alkalinity, resulting in high specific methanogenic activity.

**Table 2.1** The advantages of the two-stage system over the one-stage system when treating the same waste or wastewater

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

## **2.8 Related works on hydrogen and methane production from waste by using anaerobic fermentation**

Heguang Zhu (2006) studied hydrogen and methane co-production from potato waste by using two-stage process of anaerobic digestion. The hydrogen stage was operated in continuous flow under a pH 5.5 and a HRT of 6 h. The methane stage was operated in both continuous and semi-continuous flow under HRT 30 h and 90 h, respectively, with pH controlled at 7. This experiment result showed that the maximum gas production rate recorded from hydrogen reactor was 270 ml/h, which was observed on Day 17. The hydrogen concentration in the biogas was 45% on average. This result also found that hydrogen production strongly relied on the addition of fresh substrate because the hydrogen production was stopped completely within 1 h. after the feed was stopped. For methane production, the maximum methane production was 187 ml/h and the methane concentration in the gas production was 76% on average. The result indicated that the methane production was the main cause for the COD reduction due to the total COD removal rate was 62% in the reactor.

Wenlu Song (2009) investigated the cogeneration hydrogen and methane from protein-mixed food waste by two-phase anaerobic fermentation. The result showed that the co-fermentation of *Saccharomyces cerevisiae* with hydrogen bacterial promoted the hydrogen yield from 171.9 ml/g-TVS to 186 ml/g-TVS from DMP (defatted milk powder) feedstock because *S.cerevisiae* can quickly consume the trace amount of oxygen to create an absolute anaerobic environment for the growth of *Clostridium* which is the main hydrogen-producing bacteria. The residual solution from the first hydrogen producing stage was reutilized by methanogen community to produce methane. The residual solution from DMP with *S.cervisiae* give a methane yield 209.7 ml/g-TVS which lower than the methane yield in control condition without pretreatment methanogen community not only reutilizes the residual VFAs to produce methane, but also reutilizes the residual protein an polypeptides which barely exists in residual from DMP with *S.cervisiae*.

Yoshiyuki Ueno (2006) studied production of hydrogen and methane from organic solid wastewater by phase-separation of anaerobic process. Acidogenic process was operated emphasizing on either hydrogen production, or solubilizing efficiency of solid materials. In either effluent from hydrogenogenic, or solubilizing operation, maximum allowable organic loading rate achieved at methanogenesis was higher than the single methanogenic process. Hydrogenogenic operation was more suitable to combine methanogenic process due to retention time of hydrogenogenic operation was much shorter than the solubilizing operation. The combination of hydrogenogenic operation in acidogenic and methanogenic process produced approximately  $442 \text{ mmol l-reactor}^{-1} \text{ day}^{-1}$  of methane and  $199 \text{ mmol l-reactor}^{-1} \text{ day}^{-1}$  of hydrogen at 25 h of total retention indicating 82% of COD removal with 96% of VSS decomposition.

Mi Jung Park (2010) investigated production of hydrogen and methane from a cost-effective byproduct of food industrial, molasses, by two-stage anaerobic digestion process. In the first-stage hydrogenic reactor operated at pH 5.5 and  $35 \text{ }^{\circ}\text{C}$ . The experiment result showed that the HRT significantly affected the production rate and content of hydrogen from the hydrogenic reactor. As HRT was decreased from 24 h to 6 h, biogas production rate and hydrogen content in biogas increase. Thus, a HRT of 6 h was determined to be the optimum HRT condition for continuous production of hydrogen from molasses. The highest production rate of hydrogen was calculated as  $2.8 \text{ L-H}_2\text{/L-reactor/d}$ . In this study, the main VFAs of the first-stage process were found to be acetate, butyrate, lactate and propionate. At long HRT above 8 h, acetate and butyrate were the main components of VFA generated from acidogenesis of molasses. As the HRT was decreased from 24 h. to 5 h, lactate concentration increased more than 100 times. In the presence of acetate, lactate is known be further degraded to hydrogen by Clostridium species. Thus the high concentration of lactate in the first-stage process could be considered as an indicator of inefficient acidogenesis of molasses. COD removal efficiencies also decreased. Here, it should be noted that the aim of the first-stage process was to reduce bioenergy in the form of hydrogen without consideration of COD removal efficiency. For methane

production in the second-state methanogenic process, a short HRT of 6 h was the optimum condition for the second-stage process in this study since the main aim of the second-stage process was to reduce final discharge concentration of COD as more as possible. Overall Cod removal efficiency of two- stage process was 79.8% with production rate of 1.48 L-CH<sub>4</sub>/L-reactor/d at the HRT of 6 d.

Haijun Yang (2006) studied continuous biological production using wastewater from citric acid as raw materials. Upward flow anaerobic sludge blanket (UASB) reactor with a working volume 50 m<sup>3</sup> was used under the following condition: Temperature at 35-38° C, pH at 6.8-7.2. The optimum biogas production rate of 1.95 m<sup>3</sup>/m<sup>3</sup>reactor d and the optimum hydrogen production rate of 0.72 m<sup>3</sup>H<sub>2</sub>/m<sup>3</sup>reactor d were both obtained as 12 h of hydraulic retention time (HRT). While the HRT was less than 12 h, both parameter declined rapidly due to the large number of bacteria were washed out of the reactor and pH value decrease because of an increase in VFAs.