Hydrogen Production from Biomass

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ABSTRACT

Nowadays, hydrogen plays a major role as a fuel and in future energy infrastructure for producing heat and power. Hydrogen is used as an energy source. Currently, about 50% of hydrogen is produced through thermo-catalytic and gasification processes using natural gas, heavy oils, naphtha, etc. Recently, much research has focused on sustainable energy production from biomass to replace non-renewable sources. For this purpose, H_2 production from biomass and biomass derivatives is a promising route. Biomass is an abundant, clean, and sustainable source and consumes atmospheric carbon dioxide during its growth. Biomass produces less CO_2 compared to fossil fuels during hydrogen production. Various processes are used for hydrogen manufacturing from biomass. Generally, H_2 is produced through thermochemical and biological methods. Thermochemical processes include pyrolysis, gasification, and supercritical water gasification, and they are widely popular for their high efficiency and low production cost. Biological processes are more environment friendly and less energy intensive than thermochemical processes. Biological processes mainly include Biophotolysis, Fermentation, Biological water gas shift, and Hybrid reactor systems. These H_2 production techniques, their future aspects, and their developments are mainly highlighted in this paper. The effect of the catalyst, different reaction conditions, and the analysis of different types of biomass are mentioned in this paper.

***Keywords:** Biomass; Hydrogen; Gasification; Pyrolysis; Biophotolysis; Fermentation*

Introduction

Nowadays, the whole world is completely dependent on non-renewable energy sources. In the 20th century, petroleum has become the primary source of energy for transportation. The increasing cost of petroleum, the limited source of fossil fuels, and concerns regarding the greenhouse effect, health hazards, and safety precautions are forcing us to search for new energy sources. For this purpose, continuous efforts have been made to find renewable energy sources. Increasing energy demand reduced the amount of fossil fuel.

For this purpose, hydrogen is a significant candidate. Hydrogen generates electrical power in a fuel cell, emitting only water vapor and warm air and nearing zero percent greenhouse gas emissions. H_2 has a higher energy yield (122 Kj/g) than hydrocarbon fuels. H_2 is a secondary energy source that has to be generated like electricity.

Research on biomass has recently received increasing attention because of the probable waste-to-energy application. Using biomass instead of fossil fuels to produce H_2 is a better

approach to reducing the net amount of CO_2 in the environment. H_2 is used as a fuel in electric vehicles and in many other applications. It holds promise as a dream fuel of the future with many social, economic, and environmental benefits.

Literature Review

Various Type of Biomass Sources for Energy Production:

Various types of biomasses can be used for producing energy. They can be divided into some general categories.

1. Energy Crops: Energy crops are low cost and low maintenance crops. They are grown only for renewable bio-energy production (not edible). Wood, sugar and starch crops, hydrocarbon producing crops are called energy crops.

2. **Agricultural Waste:** which are mostly left on the fields after harvesting such as rice straw, wheat straw, rice husk, crop waste and animal waste.

3. Forest Residues: These residues include mill wood waste, bark, logging residues, trees and shrub residues.

4. Industrial and Municipal Wastes: These are mainly including municipal solid waste (MSW), sewage sludge and waste materials of several industries.

Component of Biomass:

Biomass components have an important role in Bio-fuels production. Mainly, biomass consists of lignocellulose and a trace amount of minerals. Lignocellulose is composed of cellulose, hemicelluloses, lignin, and extractives. Cellulose [$(C_6H_{10}O_5)n$], hemicellulose ($(C_5H_8O_4)n$) and lignin have high molecular weights and contribute much mass, while extractives have small molecular sizes. Cellulose, hemicellulose, and extractives are more abundant in hardwoods (78.8%) than softwoods (70.3%), while lignin is more abundant in softwoods (29.2%) than hardwoods (21.7%). Generally, hardwoods consist of about 43% cellulose, 35% hemicellulose, and 22% lignin, while softwoods contain about 43% cellulose, 28% hemicellulose and 29% lignin (on an extractive-free basis) (Balat, 2008; Demirbas *et al.,* 2009a).

Cellulose is more abundant in the cell walls of plants. Cellulose is a high-molecular-weight (106 or more) linear polymer of *β*-1,4-linked D-glucose units in the 4C1 conformation. Glucose anhydride is formed by removing water from the glucose molecule. Glucose anhydrate units are linked through *β*-1,4 glycosidic bond. Cellulose contains nearly 5000-10,000 cellobiose units (glucose anhydride).

Hemicellulose is a heteropolymer consisting of various monoccharides such as glucose, mannose, galactose, xylose, arabinose, 4-O-methyl glucuronic acid, and galacturonic acid residues. Among these, Xylose is the major one. The number of repeating saccharide monomers is less in hemicellulose (~150) compared to the number in cellulose (5000-10,000).

Lignin is an aromatic polymer synthesized from phenylpropanoid precursors (Lignols). The lignin fraction consists of non-sugar molecules that are bonded via C-O and C-C bonds. It contains a variety of functional groups, such as hydroxyl, methoxyl, and carbonyl, which give a high polarity to the lignin polymer.

Hydrogen Production Routes from Biomass:

H_2 is mainly produced from biomass through Thermochemical and Biological methods. Thermochemical process further divided into some subdivision: pyrolysis, gasification and super critical water gasification and also biological process has four subdivisions: Bio photolysis, fermentation, biological water gas shift and hybrid reactor system. Hydrogen production from biomass by using thermochemical route has been considered as most promising route.

Basically, thermochemical routes have higher hydrogen production rate than biological process. In presence of heat, biomass molecules break down and produce Bio-H2.

Biological production of hydrogen from biomass is a new section of biotechnology that offers effective production of usable hydrogen. The biological process started receiving attention when the oil crisis broken out in 1970s. Most of the biological techniques are controlled by the hydrogen-producing enzymes such as hydrogenase and nitrogenase. Bio-hydrogen provides low pollution and high working efficiency. Currently, most of the hydrogen is produced through pyrolysis and gasification processes.

Thermochemical Process

Pyrolysis

The pyrolysis process is the thermal breakdown of substances at high temperatures in an inert atmosphere. In pyrolysis, solid (char), liquid (tar and other organic compounds), and gaseous (syngas) products are formed, which are used as alternative sources of energy. In biomass pyrolysis, approximately 650 -800 K is required. A hydrogen production strategy is shown in Figure 1.
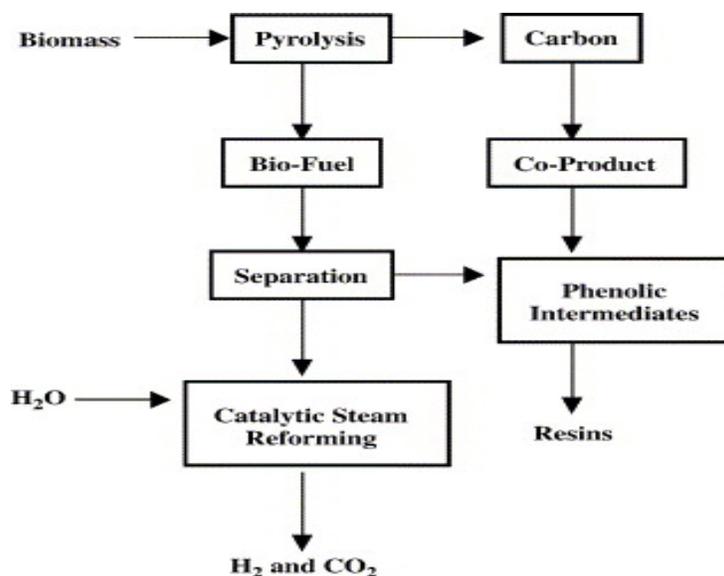
*Figure 1: Hydrogen Production Strategy from Biomass Pyrolysis (Ni et al., 2006)*

conventional (slow) pyrolysis, fast pyrolysis and flash pyrolysis are the subdivisions of pyrolysis process which are categorized based on working conditions.

In Slow pyrolysis heating rate is lower and charcoal is formed as major product. In the fast pyrolysis requires much faster heating rates (about $10\text{-}200^{\circ}Cs^{-1}$), it is associated with tar at low temperature (675-775K) and gas at high temperature. Fast pyrolysis is better than slow pyrolysis. Flash pyrolysis is an improved version of fast pyrolysis where the heating rate is very high (near about $>1000^{\circ}Cs^{-1}$) and the reaction is complete within few seconds.

currently fast or flash pyrolysis is widely used. The thermal break down of biomass species is represented by following reaction:

Biomass + Heat $\rightarrow$ H_2 + CO + CH_4 + other products

Steam reforming process is carried out on CH_4 and other hydrocarbon vapors to form CO and H_2.

CH_4 + H_2O $\rightarrow$ CO + $3H_2$
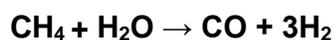
Water-gas shift reaction is applied as follows to increase the production of H_2:

CO + H_2O $\rightarrow$ CO_2 + H_2
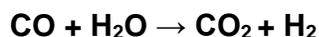
The pyrolysis of biomass is not an easy task. Some factors (types of biomass species, chemical and structural composition of biomass, particle size, temperature, heating rate, atmospheric conditions, etc.) affect the yield and the composition of the products. High temperatures and a high heating rate are required in hydrogen manufacturing. An experiment showed that the gaseous yield increases to around 40–50% at 1023 K, while the yield increases 30–35% at 773K based on dry biomass feedstock. Demirbas *et al.* (2009b) investigated the yield of H_2 rich gases obtained from biomass pyrolysis at different temperature ranges. He found that as the temperature increased, the gaseous yield also increased. Agricultural residues, peanut shell, post-consumer wastes such as plastics, trap grease, mixed biomass, and synthetic polymers have been widely tested for hydrogen production through pyrolysis. Pyrolysis of hazelnut shell, tea waste, and spruce wood showed that the percent of H_2 in gaseous products increased from 36.8% to 43.5%, 41.0% to 53.9%, and 40.0% to 51.5%, respectively, while the reaction temperature increased from 700-950K. Demirbas (2002) pyrolysed the olive husk, cotton cocoon shell, and tea waste at about 775-1025K temperature in the presence of $Zncl_2$. The highest yield of hydrogen rich gas has been obtained from olive husk by using about 13% $ZnCl_2$ at 1025K temperature. This study also examined how K_2CO_3 and Na_2CO_3 affect the yield of gaseous products obtained from different biomass species. In the experimental studies of Çağlar and Demirbas (2002), it was observed that Na_2CO_3 has greater catalytic power than $CaCO_3$ for the pyrolysis of rice straw.

On the other hand, it is also possible to get H_2 from various types of oily products by applying a catalytic steam reforming reaction. The pyrolysis of oil is classified into two sections based on water solubility. The water-soluble fraction can be used for hydrogen production. Hydrogen production from bio-oil is shown by the following reactions:

Bio-oil + $H_2O \rightarrow CO + H_2$

$CO + H_2O \rightarrow CO_2 + H_2$
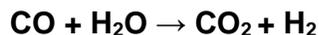
Chlorides, carbonates, and chromate salts have an advantageous effect on the pyrolysis reaction rate. Many other catalysts, such as Ni-based catalysts, Y-type zeolite, K_2CO_3, Na_2CO_3, $CaCO_3$, and various metal oxides, have also been explored, and it was found that the catalytic power of different catalysts was different based on feedstocks. Compared to other metal oxides, Al_2O_3 and Cr_2O_3 exhibit better catalytic action than others. Na_2CO_3 shows better catalytic action than K_2CO_3 and $CaCO_3$. Especially noble metals Ru and Rh are far more effective than Ni catalysts as they are less capable of forming carbon. These are more expensive than other catalysts; for this reason, they are not commonly used but are used in some special cases.

Duman and Yanik (2017) tested different char-based catalysts to evaluate the enhancement of hydrogen production from steam pyrolysis of olive pomace in a two-stage fixed-bed reactor system. Biomass char, nickel-loaded biomass char, coal char, nickel- or iron-loaded coal chars, and acid-washed biomass char were tested. The result showed that, in the absence of a catalyst, steam had no effect on hydrogen production. Increasing the catalyst bed temperature (500oC-700oC) increases hydrogen production in the presence of Ni-impregnated and non-impregnated biomass char. Ni-based biomass char exhibits the highest catalytic activity in hydrogen production.

Gasification

Gasification is a thermochemical process where organic matter or fossil fuel-based carbonaceous materials thermally decompose under certain reaction conditions and form gases. Gasification is a thermal treatment that produces gaseous products (producer gas) and small quantities of char, tar, and ash. Gasification is a form of pyrolysis that is carried out at high temperatures with a controlled oxygen supply that restricts the combustion of biomass. In general, gasification is carried out at a higher temperature range than pyrolysis, and the yield of hydrogen in gasification is also higher than that in pyrolysis.

The following reaction takes place in biomass gasification:

Biomass + O_2 (or H_2O) $\rightarrow CO$, CO_2, H_2, H_2O, CH_4 + other CHs + tar + char + ash

Biomass is gasified at a higher temperature and produces a gaseous mixture that contains CO, CO_2, CH_4 and 6-6.5% H_2. This gaseous mixture is called producer gas. The biomass particle undergoes partial oxidation and, as a result, produces gases, charcoal, and tar. The steam reforming process was conducted on the produced gases to produce hydrogen, and the process was further improved by the water-gas shift reaction to increase the yield of H_2. When biomass tar and synthetic gas are formed together, it becomes difficult to separate them and remove the tar using a simple physical dust removal method. The following techniques can be utilized to minimize tar formation:

(i) proper design of the gasifier; (ii) proper control and operation; and (iii) use of additives.

Some factors, such as gasification temperature, reactor type, etc., affect the product distribution and gas composition. Some well-known gasifiers are fixed beds (updraft, downdraft, and cross-draft fixed beds), fluidized beds (bubbling, circulating), and entrained flow gasifiers. The design of a gasifier depends on the type of fuel. Synthetic gas is a mixture of carbon monoxide and hydrogen ($CO + H_2$), which is also called as bio-syngas. Hydrogen can be easily produced using bio-syngas by non-catalytic, catalytic, and steam gasification processes. The steam reforming process which is also known as dry or CO_2 reforming occurs according to the following reactions, and specific catalysts are also used.

$C_nH_m + nH_2O \leftrightarrow nCO + (n + m/2) H_2$

$C_nH_m + nCO_2 \leftrightarrow (2n) CO + (m/2) H_2$

Syngas as well as H_2 production from biomass by steam gasification is not very easy because of the variability of raw materials. Biomasses have different compositions, structures, reactivity rates, physical properties, etc., and they also react under some severe conditions (temperature, residence time, heating rate, etc.). The yield of H_2 from steam gasification increases with an increasing water-to-sample (W/S) ratio.

Researchers tested different biomass under different operating conditions to improve the hydrogen production technology. Using a fluidized bed gasifier along with a suitable catalyst, hydrogen production can be achieved at about 60% volume. Gasification has become an attractive and impressive H_2 production alternative because of its high conversion efficiency.

The effect of catalysts on gasification products is very important. When some catalyst is used in the water-gas shift reaction, the H_2 yield is increased. Dolomite, Ni-based catalysts, and alkaline metal oxides are mostly used as gasification catalysts (Ni *et al.,* 2006). Lv *et al.* (2004) gasified the biomass in a fluidized-bed gasifier using dolomite and in a fixed-bed reactor downstream using nickel-based catalysts and noted the yield of hydrogen for both cases. They obtained a maximum hydrogen yield (130.28 g H_2/Kg biomass) over the temperature range 925-1125K. Xiao and Liu (2009) studied the effect of particle size on the gasification performance at different bed temperatures by the catalytic steam gasification of biomass. The analysis showed that with decreasing particle size, the dry gas yield, carbon conversion efficiency, and Hydrogen yield increased, while the content of char and tar decreased.

Hydrogen production from biomass is a major challenge because there is no proper technology demonstration. A novel gasification method was proposed by Lin *et al.* (2005). The name of the process is hydrogen production by reaction-integrated novel gasification (HyPr-RING). The HyPr-RING method is an integration of the water-hydrocarbon reaction, the water-gas shift reaction, and the absorption of CO_2 and other pollutants in a single reactor under both sub-critical and supercritical water conditions.

This reaction is exothermic and high yield of hydrogen can be obtained at relatively low temperature (923-973 K). The reaction of HyPr-RING method can be expressed as:

$C + 2H_2O + CaO \rightarrow CaCO_3 + 2H_2$ $\Delta H^0_{298} = -88$ KJ/mol
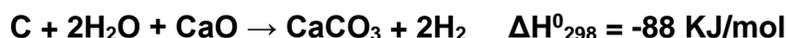
As compared with conventional gasification, the HyPr-RING process can be conducted in a much simpler manner as the reactions for hydrogen production and gas separation are carried out in one single reactor at a lower temperature. A comparison between conventional gasification and Hy-Pr-RING is shown in Figure 2.
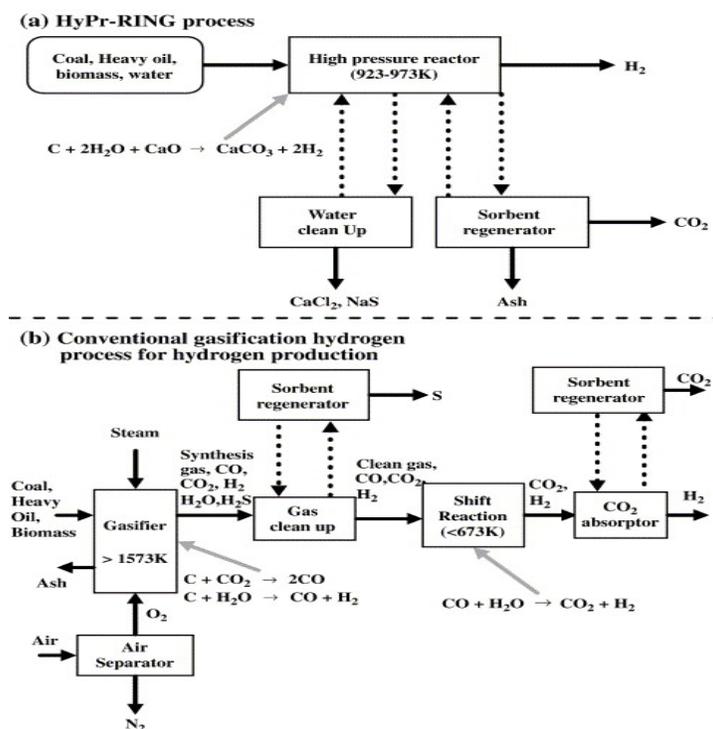

Figure 2: Comparison of HyPr-RING and Conventional Gasification Process of Hydrogen Production (Ni et al., 2006)

This innovative gasification technique has been examined theoretically and demonstrated experimentally in a very efficient way. Biomass gasification will become a dominant technology in future, it is the earliest and most favorable route for the renewable hydrogen production.

Supercritical Water Gasification:

When biomass has a high moisture content above 35%, it is likely to gasify in supercritical water conditions. SFE (supercritical fluid extraction) is a separation method that separates one component from another using a supercritical fluid solvent. Water is a supercritical fluid above 647.2K and 22.1 Mpa (Demirbas, 2004; 2009c). The dielectric constant and the number of hydrogen bonds are much lower in SCW, and their strength is weaker. As a result, at high temperatures, water behaves like organic solvents, so organic compounds are completely miscible with SCW, and gases are also miscible with SCW. Reactions under supercritical water conditions occur in a single phase, while in conventional methods they proceed via a multi-phase system.

The biomass gasification in SCW is a complex process, but the overall chemical conversion can be represented by the following reaction:

$CH_xO_y + (2-y) H_2O \rightarrow CO_2 + (2-y+x/2) H_2$
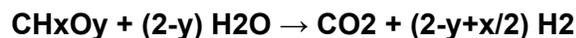
This reaction shows that H_2O is not only a solvent but also a reactant, and H_2 in the water is released by the gasification reaction. The Efficiency and final gas composition depend on the heating rate. The formation of dangerous chemicals such as tars, phenol, and furfural is prevented by a higher heating rate at a temperature over 500°C. Biomass gasification in supercritical water is useful because it reduces several processing steps needed by other thermochemical hydrogen formation methods. Hydrogen was formed by Alvarez et al. through the supercritical conversion of substrate (sawdust). 80 mole H_2/kg biomass were manufactured at 25 MPa and 600 °C, and this amount of H_2 was the maximum condition. H_2 production from cellulose through gasification in SCW using Ni catalysts was also investigated. 95% water-containing bio-fuel gives the most effective results in this process; 90 mole H_2/kg biomass (containing 95% water) produced at 25 MPa and 900 °C was studied by Lu *et al.* (2007). The yield of hydrogen decreased when the substrate contained a very low water content. A hydrogen yield of 12 mol/kg substrate was obtained during gasification of corncob, amended with sodium salt, in the presence of carboxyl methyl cellulose in a fluidized-bed reactor reported by Lu *et al.* (2008). When the raw material contained 3% corncob and 2% salt, it gave the highest H_2 yield at 60 seconds of reaction time. 32 to 36% H_2 was contained in the resultant gas while the reaction conditions were 25MPa pressure and 650°C temperature (Lu *et al.,* 2008).

Comparison between Several Chemical Processes:

Normally, gasification occurs at a higher temperature in the presence of a controlled amount of O_2 and pyrolysis occurs at a lower temperature in the absence of oxygen supply. The yield of H_2 is higher in gasification than in the pyrolysis method. Generally, pyrolysis produces heat, combustible liquids, and gases, while gasification produces heat and combustible gases only. In gasification, there is a major problem with tar (hazardous) formation that occurs during the process. Another problem with gasification is ash formation, which is fixed by fractionation and leaching. Demirbas (2006) studied the yield of H_2 through supercritical fluid extraction, pyrolysis, and steam gasification of wheat straw and olive waste at different temperatures. When pyrolysis and steam gasification occur on wheat straw, it gives the highest H_2 yield, while olive waste gives the lowest H_2 yield. SCW gasification has high efficiency at lower temperatures and can directly deal with wet biomass (Demirbas, 2006). Hydrogen production through SCW gasification reduces the feedstock drying cost and is a promising technology for making use of high moisture content biomass. Another advantage of this method is that the hydrogen produced at a higher pressure can be stored directly.

**Biological process:**

Fermentation:

There are several H_2 formation methods that use organic raw materials coming from organic effluent, such as farming effluent, food, paper industries, manure, and effluent. Most important is the bacterial fermentation described by many authors (Giang *et al.,* 2019; Zieliński *et al.*, 2017), and the other processes that play important roles in H_2 formation. These processes

are butanol fermentation, Bacillus sp., mixed acid fermentation, one kind of the genus Clostridium sp., and the family Enterobacteriaceae (Kapdan & Kargi, 2006).

Kumar and Das (2000) give a vast amount of information about the mechanism of H_2 formation through fermentation by Enterobacter cloacae at IIT-BT 08 using various organic raw materials, and sucrose and cellobiose used as raw materials gave a rate of H_2 formation of about 35.6 mmol H_2 /dm³.h. This formation rate was crossed by using various raw materials known from various studies with a formation rate 75.6mmol H_2 /dm³.h. In this case, the reactor was packed with lignocellulosic materials such as coconut coir, bagasse, and rice straw to create anaerobic bacteria, and the enhanced rate of this bacteria became highest in coconut coir. A coconut coir-based reactor forms more bacteria among those because the coir contains a higher cell density, leading to the greatest active surface area of the cells. Fermentation of swime manure containing glucose gave an H_2 formation rate of 2.25 dm³ /dm³.d and Wu, Yao and Zhu (2010) exanimated this. The optimum pH for fermentation, which is 5.0, leading to the highest performance, was investigated by the authors. That confirmed the stable hydrogen formation and density throughout the experiment (22d) using an ASBR system having a 98.5 to 99.6% $C_6H_{12}O_6$ humiliation capability range.

(a) Dark fermentation

H_2 formation is done, especially under dark conditions. Here, the fermentation is carried out by a few microalgae and anaerobic bacteria on carbohydrate-containing substrates at 30 to 80°C. The biophotolysis method only forms H_2 but H_2 and carbon dioxide merged with other gases such as H_2S and methane can be formed by dark fermentation. The ratio of gases except H_2 and CO_2 can be controlled by the reaction method and substrate. 4 mol H_2/mol glucose (used as the model substrate) is manufactured, leading to the maximum amount of H2 formation with the end of the acetic acid. The dark H_2 fermentation process was tested by Fang and Liu (2002) in a 3L reactor at a pH range 4.0-7.0A synthetic medium containing 7.0g/dm³ C6H12O6 was provided to a digester and the method achieved stability after 14 days by producing 90% degraded glucose. The amount of formed H_2 reached 2.1mol H_2 /mol glucose at optimum pH (5.5) containing 64% hydrogen content in the biogas (Fang & Lui, 2002). 128 cm³ hydrogen/ g COD remove was obtained by Kim *et al.* (2008). At pH 5.5and 40°C, fermentation of food waste was done by Clostridium beijerinckii KCTC 1785 (Kim *et al.,* 2008). Dark fermentation method was also done by taking cow dung compost to form 290.8 cm³ H_2/dm³ culture and the overall method was conducted by Song *et al.* (2012). At initial pH 7.0, the raw material provided into a system having the density of 10g/dm³ and the most useful hydrogen creator were Clostridium sp. and Enterobacter sp. (Song *et al.,* 2012). The reduction of protons is done by hydrogenase utilizing the donated electron of ferredoxin (donated electrons are transferred by ferredoxin) under anaerobic methods and the this is the biohydrogen formation mechanism. On going the degradation of glucose to pyruvate, electrons become free, and pyruvate is further oxidized to acetyl $-CO\,A$ and CO_2. By following Figure 3 it becomes easy to understand. Types of ingredients and criteria such as substrate density, hydrolytic retention time (HRT), pH, temperature, microbial strain control the formation of H_2 under dark fermentation conditions.
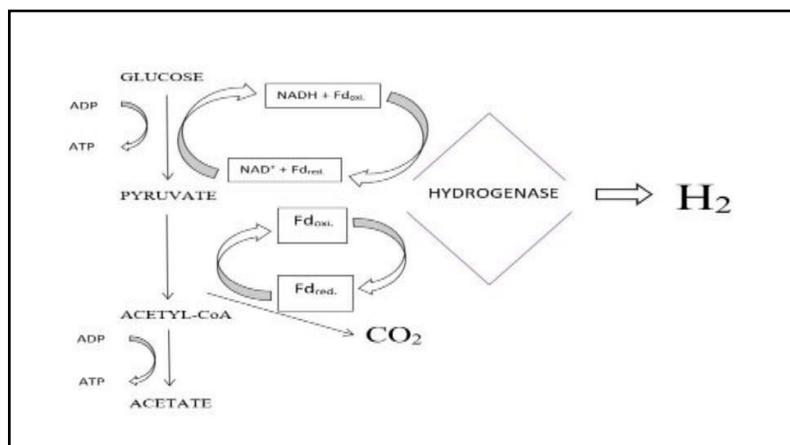
Figure 3: H₂ formation Using Clostridium sp.

Facultative anaerobes having better capacity to tolerate oxygen, including common Clostridium sp. and Enterobacter sp., are a suitable choice compared to restraint anaerobes because the activity of hydrogenase is hindered by the presence of a small amount of oxygen in the bioreactors. Lower pH has an effect on microbial metabolism, which shifts toward the chemical process. The optimum pH for hydrogen production is the pH range 5.0-6.0 and pH below 4.0 prevents microbial growth (Wu, Yao & Zhu, 2010). Methanogenic bacteria become active at high pH and with the help of this condition, they take hydrogen to produce methane. To remove the Methanogenic bacteria from the communities in anaerobic sludge, heat treatment at 80 to 104°C is used. This heat treatment gives the benefit of surviving the hydrogenous spores, creating microbes such as Clostridium sp. and Bacillus sp. Hydrogen producing microbes get competition from bacteria whose growth limits are fixed by short hydraulic retention times. Undissociated volatile fatty acids produced in the reactor disturb the H_2 fermentation efficiency. Gathered CH_3CH_2COOH and $CH_3CH_2CH_2COOH$ by the presence of excess hydrogen levels in the system reduce the hydrogen production together with a decrease in the partial pressure of hydrogen (Kisielewska, Dębowski & Zieliński, 2015). As a result, the performance of H_2 fermentation is enhanced by the increased concentration of hydrogen. At this time, other parameters, such as iron level and nitrogen level, are kept in a suitable amount.

(b) Photofermentation:

Green or purple Sulphur and non-Sulphur anaerobic bacteria are able to transform the organic acids into H_2 and carbon dioxide. These anaerobic bacteria take part in Photofermentationc. The primary fermentative enzyme that is able to catalyze its reaction in either direction is nitrogenase. Ammonia is formed by the reduction of N_2. Microbes that take electrons from ferredoxin in the presence of inhibitory N_2 use the electron to reduce N_2. Electrons can be transferred by nitrogenase in nitrogen-deficient environments, and oxygen, ammonia, and excess C or N decrease the activity of nitrogenase. The electrons that are transferred by ferredoxin are created during the degradation of organic substrates by ferredoxin, and the

electrons are taken by nitrogenase from ferredoxin to be utilized to reduce the protons into normal H_2. The required energy taken from the light source is used for the protein-mediated electron transfer and is realizable Figure 4 is given below.
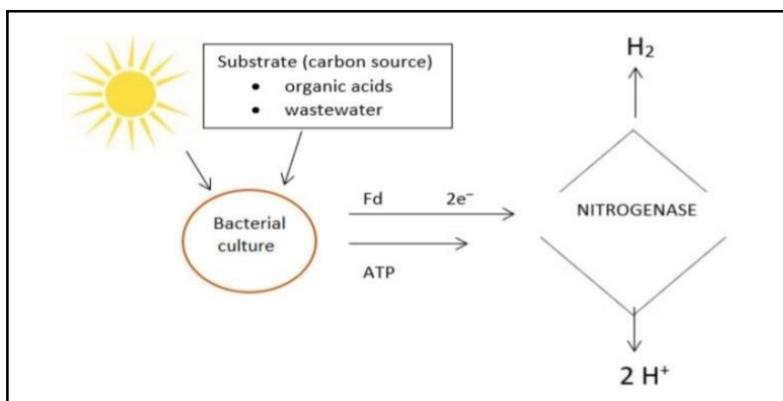

(Source: Dębowski et al., 2021)

Figure 4: H_2 Formation under Photo Fermentation Using Microbes

A source of bright light (400–1000 nm), a temperature between 30 and 36 °C, and a near neutral pH (6.8-7.5) must be satisfied to acquire suitable conditions for photo fermentation (Kim, Beak & Lee, 2006). Yields and H_2 formation rates are increased by optical illumination intensity. Alternating light-dark cycles are generally utilized instead to reduce the high running cost of such a solution. The amount of H_2 formed via photofermentation directly depends on various types and designs of bioreactors, and the most common are the tubular column and flat plate. To hinder staining, oxygen enterence, and the formation of competing microbial species, the units are compactly sealed and closed. Recently used bioreactors for photofermentation are very similar in design to microalgae production bioreactors. Rhodobactor sphaeroids O.U.001 utilizing sugar refinery wastewater as raw material gave 3.8cm³/dm³.h H_2 via photo fermentation H_2 formation method. Again, Rhodobactor sphaeroides O.U.001 with dilution of olive mill wastewater, produced hydrogen at about 13.9dm³ H_2/dm³.This was studied by Eroğlu et al. (2004). Rhodopseudomonas palustris P4 produced 2.4-2.8 mol H_2/mol CH3COOH under photofermentation, and that was studied by Oh et al. (2004). Photofermentation H_2 formation by Rhodobactor spaeroides-RV depends on different light sources and intensities. That was examined by Argun and Kargi (2010). H_2 formation efficacy was 781cm³ H_2/fatty acid. H_2 formation was done by using halogen lamps, where the raw material of fatty acid was used and the fatty acid was collected from ground wheat. The formation of 1037 cm^3 H_2/g fatty acid was done by using high-intensity light of about 5klux expressing the highest performance (Argun & Kargi, 2010). Photofermentative was also done by using Rhodobactor sphaeroides KKU-PS5. The operational parameters that were used in photofermentation were 30°C temperature, 6 klux light intensity, and 7.0 initial pH. Microorganisms used malic acid as a primary feedstock with a concentration of about 30 mmol/dm³. 1330 cm³ H_2/dm³, 3.80 mol H_2/mol malate, and11.08 cm³ H_2 /dm³·h were the yields and rate of H_2 formation.

Biophotolysis:

(a) Direct Biophotolysis:

Chemical energy in the form of H_2 comes from sun radiation by microphytes photosynthetic systems, and this direct biophotolysis method is useful for H_2 formation. The photosynthesis method involves two kinds of photosynthetic systems. The first system, or photosystem I (PSI), involves the formation of a reductant that is utilized to reduce carbon dioxide. PhotosystemII (PSII) also involves cleaving water and releasing oxygen. Two photons from water, which are generated in the biophotolysis method, are used by PSI to reduce carbon dioxide, or they are also used to form H_2 in the presence of hydrogenase. The green plant can only reduce carbon dioxide due to the absence of hydrogenase. Microalgae with hydrogenase, like green algae and cyanobacteria, can produce H_2. PSII, consuming solar radiation energy, forms electrons that are introduced at ferredoxin with the help of solar energy that is consumed by PSI. H_2 formation by hydrogenase that takes the electron from Fd is shown below in Figure 5.
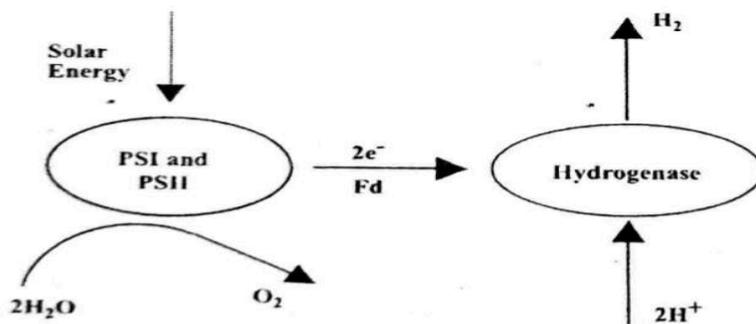
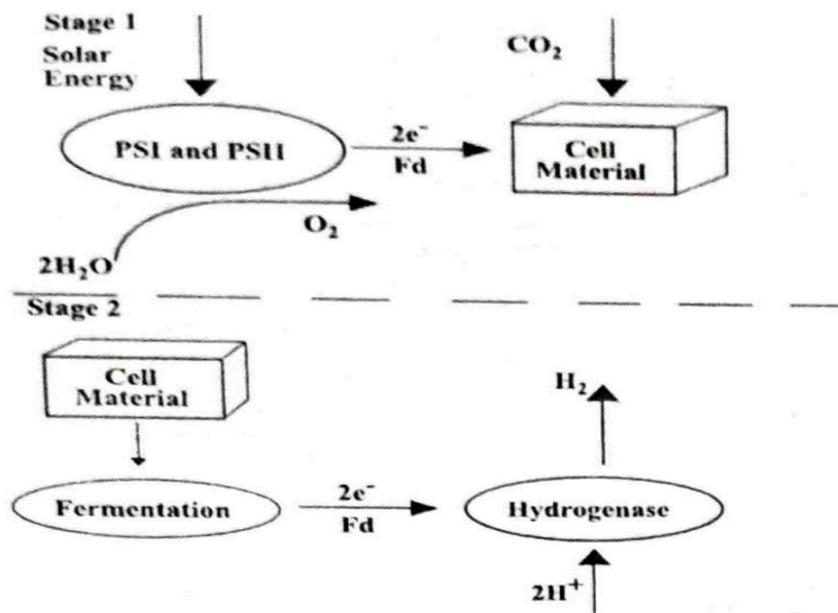*Figure 5: H_2 Formation Via Direct Biophotolysis (Ni et al., 2006)*

The working ability of hydrogenase is reduced by the presence of oxygen. That's why oxygen content stays at a very low level, about 0.1%. This situation is created by Chlamydomonas reinhardtii, which can destroy the oxygen content during oxidative respiration. Working ability is lower because, during this process, a sufficient amount of substrate is absorbed and breathed in. Mutants that can be produced from microphytes involve higher H_2 formation and a higher production rate. US$60/m² is the capital cost for an overall solar transformation efficiency of 10%, and that was assumed by Benemann after expressing a hydrogen formation value of $20GJ by himself. The capital cost of US$100/m^2 was assumed by Benemann and Hallenbeck with a similar estimation. They avoided gas isolation and maintenance.

(b) Indirect Biophotolysis:

This process contains four steps for H_2 formation. The steps are (I)photosynthesis production of biomass, (II)biomass density, (III)formation of 4mol H_2/mol glucose, along with 2mol acetate by aerobic dark fermentation in an algae cell,(IV) transformation of acetate to H_2. In the following reaction, Cyanobacteria involves to the hydrogen formation.

$$12H_2O + 6CO_2 \longrightarrow C_6H_{12}O_6 + 6O_2$$

$$C_6H_{12}O_6 + 12H_2O \longrightarrow 12H_2 + 6CO_2$$

In the first and second stages, at light intensities of 95–55 micromol-1 m2 and 170-180 micro mol-1 m-2 indirect biophotolysis was investigated. During this process, Cyanobacterium anabaena variables manifested at the above-mentioned light intensities. 12.5 mL/g cdw (cell dry weight) was the H_2 formation rate. Optimal H_2 was produced at a pH between 6.8 and 8.3. That was studied by Troshina *et al*. (2002) in the presence of Cyanobacterium gloeocapsa alpicola in indirect biophotolysis. H_2 formation increases twice with an increase in temperature from 30°C to 40°C. The H_2 formation rate by hydrogenase is comparable with the H_2 formation rate via indirect biophotolysis. Technological advancement can make a comfortable transformation to the estimated cost. Nowadays, the indirect biophotolysis method is under active research and enhancement. The above-mentioned four steps are below Figure 6.

Figure 6: H_2 Formation Via Indirect Biophotolysi (Ni et al., 2006)

Water Gas-shift Reaction:

WSG is the most valuable industrial mechanism for manufacturing of NH_3, hydrocarbon, methanol and mainly hydrogen. It is most important method to producing hydrogen gas from CO or another hydrocarbon. It also become an important source of fuel for current hydrogen economy. If H_2 is produced at low cost, then it would be significant step towards the sustainable energy. This reaction classified in two categories –

Conventional WGS Reaction

Biological WGS Reaction

(a) Conventional WGS Raction:

Mechanism: After long and extensive study, this reaction becomes simple but remains controversial and complicated because of the sensitivity of the catalyst for a very minor change.

The WGS reaction is mainly synthesized by two processes. 1. Redox pathway 2. Associative (Langmuir-Hinshelwoodmen).

The redox mechanism is an endothermic reaction where the adsorption of CO on the surface of the catalyst occurs and takes O_2 from metal oxide. As a result, a vacancy of O_2 is produced, and the vacancy is filled by the dissociation of H_2O molecules and the production of H and O atoms. Then H atoms combine to form hydrogen gas, and O_2 is captured by metal oxide, which is O_2 deficient in nature (Kim *et al.,* 2020).

The associative reaction happens at low temperatures. This reaction also occurs by adsorption of CO and H_2O on the surface of the catalyst to produce an intermediate that is reactive in nature and decomposes to form CO_2 and H_2 (Tenca *et al.,* 2011). Many catalysts are used in this reaction, such as Cu/ ZnO/Al_2O_3, Ru/C, transitional metal catalysts, graphitic oxides, PT nano particles with TiO_2, gold nano particles and Nobel gas.

Theoretically, it is proven from combined DFT calculations that the redox mechanism was the most appropriate mechanism for WGS from combined DFT calculation (micro-kinetic process on Au/TiO_2 catalyst) (Sun *et al.,* 2017). Ammal and Hayden (2017) also got the same result from their reaction on Pt/TiO_2.In this reaction, pt follow the redox mechanism. Hydrogen production by conventional water gas shift reactions is given below in Figure 7.
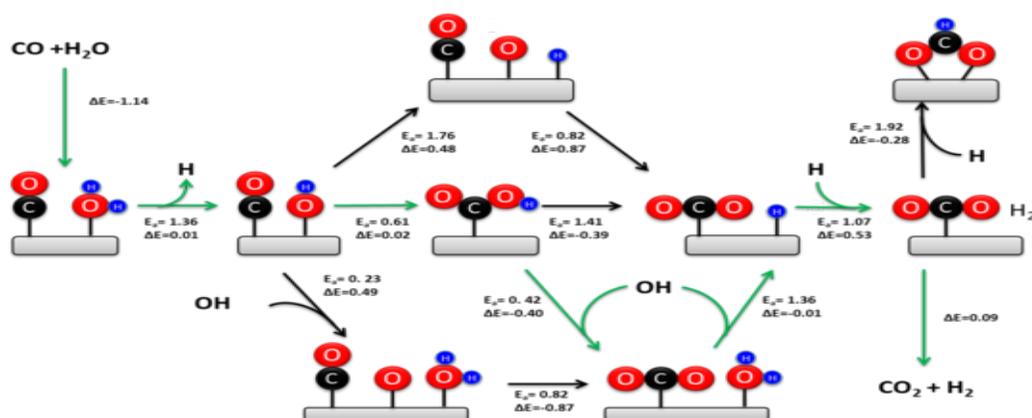
Figure 7: Associative and Redox Mechanism of the Water Gas Shift Reaction (Gokhale, Dumesic & Mavrikakis, 2008)

(b) Biological WGS Reaction:

It is an example of chemically synthesized procedure. Reaction is given below

$CO(g) + H_2O(v) \rightarrow CO_2(g) + H_2(g)$
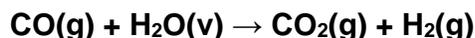
This reaction is an important industrial reaction. This reaction is used for the production of high-purity H_2. It is a very cost-effective technology.

For this reaction, photosynthetic bacteria are used.

In this reaction, CO is oxidized to CO_2 and H_2O is reduced to hydrogen. Rubrivivax gelatinosus is a purple photosynthetic bacteria that is mainly used in WGS reactions under an anaerobic pathway. This bacterium is a non-sulfate bacteria. The reaction also proceeds under atmospheric pressure and room temperature (25 degrees Celsius). Wolfrum *et al.* (2003) proved that the organism can proceed with reactions at pressures up to 4 atm. The organism obtains energy from the biological water-gas shift reaction to maintain metabolic processes for growth. Alternatively, the biological WSG reaction occurs in an anaerobic dark phase. This mechanism produces less energy than the photosynthetic or aerobic pathways for metabolism. As a result, the production of energy is lower, so the cellular growth rate is very slow. It reduces the production of waste cells, which are produced by the biological water gas shift reaction. In this case no expensive photobioreactor is required. In the biological water gas shift reaction, energy is obtained by giving electrons to CO and H_2O. The reaction is given below.

$CO + H_2O \rightarrow CO_2 + 2e + 2H^+$

$H^+ + 2e \rightarrow H_2$

$CO + H_2O \rightarrow CO_2 + H_2$

This reaction is exothermic in nature. It releases 4.46 kcal/mol. schemetic representation of hydrogen production is given below (Figure 8):
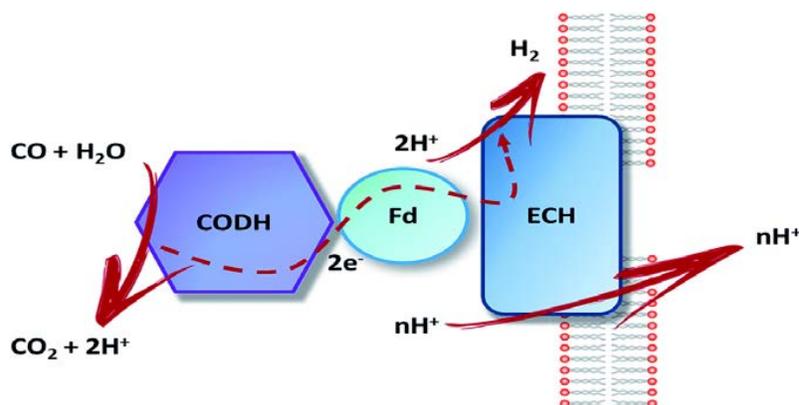
Figure 8: Schematic Representation of Hydrogen Production by Biological WGS **(Alfano & Cavazza, 2018)**

In this pathway, corpuscles growth is very important to proceed with this reaction. Most of the cells are used to convert the CO to H_2. Sometimes the cell is inoculated for higher growth.

Sometimes the food is provided to Rx. Gelatinous CBs form acetate, malate, or a low-cost sugar source, and well as oxygen to boost energy production.

But sometimes there are some drawbacks. If there are many organisms in the reactor, they use acetate and oxygen for their growing processes. If the growing process of another organism is faster than that of Rx. Gelatinous CBs then no H_2 is produced.

At the time of boosting cell growth, if there are many organisms and if they use acetate and O_2, As a result, other cells growth will be faster than Rx. Gelatinosus CBS, then no hydrogen would be produced. In this situation, the first step should be sterilization and re-inoculation to proceed with the reaction. In this case, a safer solution is to have the reaction proceed only in the presence of CO. Although it is a very time-consuming process, It is also proven that if the reactor has no problem, then the reaction will proceed continuously without any break.

Bio Energetics of the Biological WGS Reaction:

The appropriate metabolic pathway and enzymes that are involved in biological WGS reactions are not well known. The overall free energy helps determine the highest amount of energy the Rx gelatinosus could get from biological WGS performance. Approximately 60% energy is assumed for the biological process, and we came to know that cell production per gram of co-fed bacteria Rx gelatinosus produces 1.4 g of cells per 1 mol of CO. But when it is growing aerobically in O_2 and acetate, the cell production would be 2 g per mol of acetate.

From bioenergetic calculations, one can obtain information about the reaction environment, such as pH, temperature, and feed concentration, and come to know whether the reaction is more favorable or less favorable. When a reaction becomes more favorable, the production of energy is high for the organism. If a reaction is thermodynamically unfavorable, the reaction may shut down completely. Calculations of the effect of co concentration and pH, and concentration of H_2 were done by bio energetics of the biological WGS reaction.

Hydrogen Production by WGS Reaction (Packed Bed Reactor):

In this process, Rhodospirillum rubrum is used for the WGS reaction. In this pathway, scientists observed that high recirculation rates increase the rate of mass transfer in packed bubble columns. Kareem, Al-Obaidi and Mohammed (2013) used a triculture of R. rubrum, M. barkeri, and Methanobacterium formicicum to produce CH_4. Among these, R rubrum performed WGS to produce H_2 and CO. The reaction also proceeds at ambient temperature.

In this reaction, circulation rates are most important. When H_2O circulation rates are checked among 200, 400, 600, and 800 ml/min, In this pathway, the reaction rate increases with increasing water circulation. But it increases at certain times; it reaches up to 67% at a circulation rate of 800. This is the major drawback.

Comparison between Conventional and Biological Water Gas Shift Reaction:

Between two types of reactions conventional WGS reaction is less expensive than biological. So the process is more favorable. In the aspect of thermodynamics biological process is

favored than conventional WGS but kinetically less favored. Biological process is more expensive.

Most important advantage of using bacteria for biological process is that the reaction proceed at room or laboratory temperature and there is no equilibrium limitation. (25 degree centigrade $\sim 5\times 10^{4}$).

Hybrid Reactor System:

Hybrid reactor system is two stage process. These two processes are.

First one is dark fermentation in which light independent bacteria is used to produce hydrogen yield. In this reaction anaerobic fermentation of carbohydrate occurs. As a result, an intermediate is formed like as lower weighted molecular acid which transformed into hydrogen by photo fermentation using photosynthetic bacteria in second stage in a photo bio reactor.
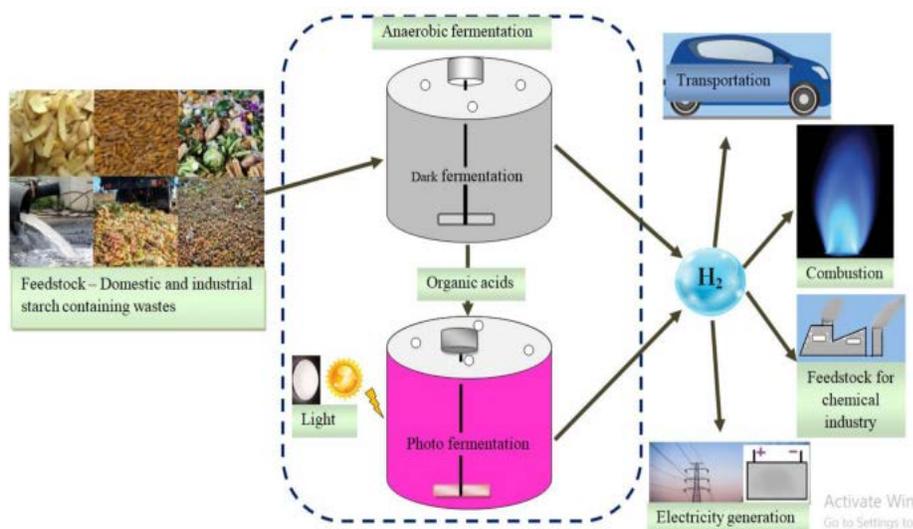
The reaction is given below (Figure 9)

First step:

In this reaction (facultative anaerobes)

$C_6H_{12}O_6 + 2H_2O \rightarrow 2CH_3COOH + 2CO_2 + 4H_2$

Second step:

Photo fermentation (photo -synthetic bacteria)

$2CH_3COOH + 4H_2O \rightarrow 8H_2 + 4CO_2$

Figure 9: Hybrid Reactor System (Das & Basak, 2021)

In anaerobic fermentation (dark condition) reaction acetic acid is main product and assumed that twelve hydrogens are produced from 1 mole of $C_6H_{12}O_6$. Lee *et al*. (2002) analyses that the combination of purple non-sulfur bacteria (photosynthetic) anaerobic bacteria is used to produce hydrogen from waste water. In this reaction three reactors of carbohydrate have

been used. In another case Kim *et al.* (2001) studied the combined procedure of dark and photo fermentation process to synthesis hydrogen from water which is full of waste and drainage water. Nath, Kumar and Das (2005) used glucose in dark fermentation. The result is same but he used anoxygenic phototrophic PNS bacteria to produce hydrogen.

Present Scenario and Future Prospectus:

H_2 can be a most useful alternative source of energy. Now a days H_2 is used in many states as a significant energy source which gives us a sustainable future in purpose of energy Hydrogen is not an original source of energy, it is unavailable in nature.

Hydrogen can be the product of many original energy sources by different technologies. Production of hydrogen is very costly. In this case of hydrogen gas, the most significant problem is that it is not available easily in nature. Now a days mostly used, and less expensive process is steam methane reforming process.

Presently nonrenewable sources like oil, natural gas and coal are involved to produce H_2. Also, thermocatalytic and gasification processes are also used for the half manufacture of H_2. For this pathway the starting materials can be heavy oils and naphtha the percentage ratio of H_2 production from H_2O using electricity and biomass respectively is 4%,1% and 95% H_2 is manufactured from fossil which is one type of fuel.

But fossil fuel is not eco-friendly in nature because of the production of CO_2 as a side product which is responsible for 'greenhouse effect'. As time passes returnable primary energy (wind, biomass and energy) becomes the source of H_2. For H_2 production biomass is used to reduce the releasing of CO_2.

Currently the range of total hydrogen consumption is about 400-500 billion Nm^3. But only 3% is used for energy consumption and it will grow up to 5-10% per year. At present hydrogen is accepted as a (chemical feedstock) for petrochemical, food, electronics and metallurgical industries. The global market of hydrogen is about US$40 billion per year. Mainly H_2 is used to produce NH_3, refine Petroleum and also produce methanol.

H_2 is only fuel (pollution free) which can be used as transportation. It can be used in automobiles also for a pollution free environment. It has a special property to use as transport fuel and it has also an effective octane number. It is nontoxic in nature. It has no sufficient properties to form ozone. From this it has greater flammability range in air than methane and gasoline.

Future of Hydrogen Gas:

In every country, mostly developing countries, the demand for energy has increased significantly, and in the future, the demand will increase continuously. Utilization of energy becomes the main reason for the sustainable development of developed or developing countries (Marechal, Favrat & Jochem, 2005). It is expected that energy demand will be in the range of 600-1000 EJ in 2050 (Miyake, Matsunaga & San Pietro, 2001). But in the present situation, 80% of sources of energy are fossil fuels, such as crude oil, natural gas, and coal (Evans, 2007).

Non-renewable energy sources are limited and reserved for specific places in the world, and the use of non-returnable energy sources reaches its peak. So that condition is very dangerous to us. It also increases the "greenhouse effect". For that, an alternative returnable energy source is required to minimize CO_2 in the environment (Lovley, 2006). Consequently, renewable energies play a major role in innovation in energy.

The main reason for the greenhouse gas effect as well as global warming is increasing CO_2. Most of the CO_2 is produced by commercial processes such as the cement industry and the disposal of natural gas. Globally, one fifth of CO_2 comes from transportation. As a result, other energy sources like ethanol, biodiesel, and H_2 are needed at a time when a great future is in sight.

According to many national environmental agencies around the world, H_2 is selected as a fuel for a feasible future.

Conclusion

Developed human living practices brought a dangerous situation to earth. Due to the sufficient use of fossil fuels or non-returnable energy, pollution and climate change occur. Excessive use of disposable products. Waste increases rapidly, and COVID-19 becomes a favorable condition. This condition has forced us to think about new, returnable energy. In that case, H_2 draws special attention. Biomass can be the source of H_2 production.

This project introduces all the processes for hydrogen production from biomass. This also introduced multiple pathways, such as thermochemical and biological technologies. Pyrolysis and gasification pathways are the most popular for their highest production yields and low costs. The biological process is eco-friendly, so its application has significantly increased.

In the present situation, natural gas produced via steam methane reforming produces H_2. But it is not sustainable. H_2 production from returnable primary energy sources such as solar, wind, and biomass gradually increases, while production of hydrogen from fossil fuels gradually decreases. Biomass is a major raw material for producing H_2 and that has drawn special attention in recent years. But the production technology is not sufficiently developed at present. The manufacture of H_2 from biomass becomes very costly. The process of hydrogen production is much more eco-friendly. So, the innovative thinking about the (automobile's fuel) fuel of vehicles will be advanced gradually.

Recently, gasification of biomass has been introduced to produce renewable H_2 in a beneficial manner. Through this process, biomass resources are successfully utilized. It helps to make an evaluation of the process of H_2 production. It helps to reduce dependence on non-returnable energy sources like fossil fuels and also to create a pollution-free world.

Acknowledgment

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