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A Review on Production of Hydrogen from Renewable Sources and Applications for Fuel Cell Vehicles

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Abstract

Hydrogen gas is an energy carrier that has many advantages, including energy density for high mass and environmentally friendly. Hydrogen can be produced from various sources by numerous methods. Hydrogen production from renewable sources is interesting, due to the sustainable and inexpensive supply of the raw materials. Among the sources of renewable raw materials for hydrogen production are water and biomass with various production methods. It consists of the electrolysis of water with acidic and basic conditions, as well as thermochemical and biochemical biomass conversion.

Keywords

Biomass; Electrolyzer; Fuel cell vehicles; Hydrogen; Water electrolysis

1 Introduction

Transportation is a primary need to support human activity in the field of economic, social, and so on. The rapid growth in human population and activity have resulted in the increase of fuel needs [1]. All of the transportations modes need fuels that are commonly still using non-renewable fossil fuels. Moreover, the availability of fossil fuels will continue to deplete so that they cannot meet human needs [2]. On the other hand, fossil fuels also have a negative impact on the environment caused by exhaust emissions in vehicles in the form of CO_2 [1].

In recent years, the increase of greenhouse gases from the transportation industry has been raising concern from society. Greenhouse gas emissions are generated from the production, refining, transportation, and storage of crude oil and petroleum products that release various kinds of gases such as CO_2, CO, SO_x, NO_x, CH_4 and flying ash into the atmosphere. Hydrogen-powered vehicles do not produce exhaust emissions so they can reduce and eliminate CO_2 emissions and other greenhouse gases generated from vehicles on the streets. Hydrogen production and application will be zero pollution if hydrogen is produced from renewable sources [3, 4].

Hydrogen is much in demand for the hydrogenation process, power generation and transportation industries [4]. Hydrogen can be produced from a promising renewable energy source for transportation and domestic applications [2]. Tseng et al. (2005) reported that hydrogen-based energy could reduce carbon emissions if hydrogen is produced from renewable sources or technology [5].

2 The Characteristic of Hydrogen

Hydrogen is the lightest and simplest element on the periodic table, with density (in the form of gas) of 0.0899 kg/Nm^3, which is 15 times lighter than air. Hydrogen is a fuel with a wide range of inflammability, both in the air from 4-75%, and in oxygen from 4-95%. Hydrogen is also the highest energy fuel (per mass unit) with Higher Heating Value (HHV) of 3.54 kWh / Nm^3 (39.42 kWh / kg), where this value is 2.5 times higher than methane and 3 times higher than gasoline [6].

3 Production of Hydrogen

The production of hydrogen has various methods and sources. Hydrogen can be produced from both conventional sources and renewable sources. The conventional sources consist of coal, petroleum, and natural gas (from the methane reformation process),

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while renewable sources are including water through hydroelectric power, wind power systems and photovoltaic [7, 8]. Besides, hydrogen can also be produced from carbonized fossil fuels [8]. There are several pathways for the production of hydrogen, including biomass, biological and thermal separation of water, also electrolysis of water carried out with renewable primary energy sources [9]. In this paper, we will discuss the production of hydrogen from the renewable sources and methods (electrolysis process of water, glycerol and biomass), and its application to vehicle fuel.

3.1 Water electrolysis

The electrolysis process of water is a method used to separate water into two gases, hydrogen, and oxygen, which requires electrical energy with the electrochemical principle [10]. Water electrolysis is done by using an electrolyzer to split the water. The electrolyzer is a device that combines oxidation and reduction reactions, which is run using electricity, to produce hydrogen and oxygen gases [11]. Electrochemical water decomposition can produce hydrogen with a high purity of around > 99.999%. Electrolytic hydrogen production with carbon-free electricity sources is the only way to produce large amounts of hydrogen without emitting side products such as fossil fuels [12]. Water electrolysis reactions can be carried out using acidic or alkaline electrolytes. The performance chart of electrolysis reactions in the alkaline condition is presented in Figure 1.

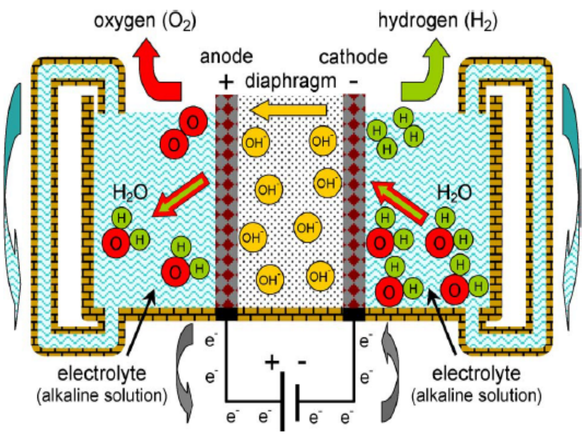

Figure 1 Performance chart of alkaline electrolyzer [13]

Two reactions that occur in alkaline solutions [14] can be written as follows:

Cathode: $4H_2O + 4e^- \rightarrow 2H_2 + 4OH^-$ (1)

Anode : $4OH^- \rightarrow O_2 + 2H_2O + 4e^-$ (2)

The overall reaction of electrolysis of water can be written as follows:

$$H_2O_{(^1/_g)} \rightarrow {^1/_2}\, O_2 + H_2 \quad (3)$$

Based on the electrolyte used, cell electrolysis is divided into 3 type [8, 9, 15]: alkaline electrolysis with liquid electrolytes; electrolysis of Polymer Electrolyte Membrane (PEM) with acid ionomer electrolytes - also known as Solid Polymer Electrolysis (SPE); and high temperature steam electrolysis, with solid electrolyte oxide. These three technologies have the same basic principle: water is fed into electrochemical cells which have been given a high enough voltage, one electrode is connected to the anode and another electrode to the cathode. Both of these electrodes are stored at the base of a multilevel tube to produce gas. So hydrogen is produced on the cathode side, and oxygen is produced on the anode side [8, 10].

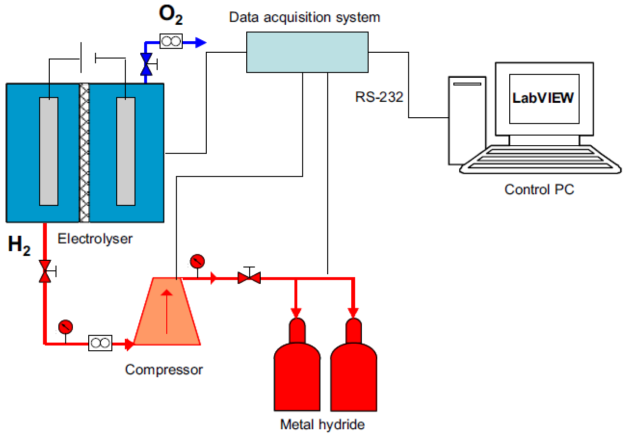

Figure 2 Experimental alkaline electrolyzer setting scheme [12]

Figure 2 shows an experimental setup scheme. This system consists of a 3 kW electrolyzer, a hydrogen compressor and four metal hydride tanks. Each cell contains two bipolar electrodes separated by a membrane, which prevents the hydrogen produced on the cathode side mixed with oxygen on the anode side. The electrolyte used is 30% NaOH in deionized water. Deionized water is fed automatically using a pump from the water tank to the electrolyzer [12].

Chakik et al. (2017) made the best comparison of Zinc alloy concentrations for hydrogen production using alkaline water electrolysis cells with NaOH solution as electrolytes, and various Zinc alloy mixtures of concentrations as cathodes. Variations in the composition of electrode types, electrolyte concentrations, variations in current and voltage were carried out. The results showed that the concentration of electrodes with alloy mixtures (Zn95%-Cr5%) and (Zn90%-Cr10%) produced more hydrogen than other alloys, with maximum efficiency of 99.13% and 97.66%, respectively [14].

3.2 Biomass conversion

Biomass is one of the most promising renewable energy sources in producing hydrogen. In recent years, reforms of biomaterials to produce hydrogen have been carried out [12, 13, 16]. In this process, hydrogen can be produced by pyrolysis, gasification, high-pressure water conversion, and fermentation from biomass [11].

The hydrogen formation reaction from biomass [3] is written as follows:

$$Solid\ waste + air \rightarrow CO + H_2 \quad (4)$$

$$Biomass + H_2O + air \rightarrow H_2 + CO_2 \quad (5)$$

$$Cellulose + H_2O + air \rightarrow H_2 + CO + CH_4 \quad (6)$$

There are two general categories of process in energy production from biomass, namely thermochemical and biological processes [10–12]. The thermochemical process consists of combustion, pyrolysis, liquefaction, and gasification.

Direct combustion of biomass in air converts chemical energy into heat, mechanical or electrical energy using equipment such as stoves, boilers, or steam turbines. In the other hand, combustion process produces pollutant emissions as a by-product and has low energy efficiency (10% – 30%), so the combustion process is considered inaccurate and less efficient for the hydrogen production process.

The biomass liquefaction process is done by heating biomass into water at a temperature of 525 K – 600 K under a pressure of 5 MPa – 20 MPa in a vacuum with the addition of a solvent or catalyst [17]. However, biomass liquefaction still has shortcomings such as the difficulty to achieve the proper operating conditions and the low production of hydrogen. Therefore, liquefaction is not efficient enough to produce hydrogen.

Pyrolysis is done by heating biomass at a temperature of 650 K – 800 K under a pressure of 0.1 MPa – 0.5 MPa without air so that the results are liquid oil, solid charcoal, and gas. Pyrolysis is divided into slow pyrolysis and fast pyrolysis. Slow pyrolysis is not considered for hydrogen production due to charcoal as the main product [17].

Fast pyrolysis is carried out at high operating temperatures to produce steam which will be condensed into a dark brown liquid. Biologics consist of direct biophotolysis, indirect biophotolysis, shifting reactions of biological gases, photo-fermentation, and dark fermentation. Other thermochemical processes such as pyrolysis and gasification, and biological processes such as biophotolysis, the shifting reactions of biological gases, and fermentation have received much attention. Many research has been done in the hydrogen production process in recent years [17]. Figure 3 shows some biomass pathways that can be done to produce hydrogen.

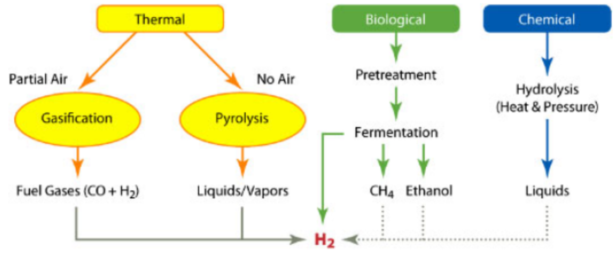

Figure 3 Biomass pathway to hydrogen [11]

3.3 Glycerol conversion

Glycerol can produce hydrogen through several processes including Steam Reforming (SR), Partial Oxidation (PO), Autothermal Reforming (ATR), Aqueous-phase Reforming (APR) and Supercritical Water reform (SCW) [18].

Steam reforming

Hydrogen production in the industrial world generally using the steam reforming method (7). The catalyst acts to speed up the reaction that occurs between steam and the substrate. This reaction produces hydrogen and also by-products in the form of carbon dioxide (CO_2) and carbon monoxide (CO) [18].

$$Substrate\ (C_nH_mO_p) + steam \rightarrow CO_2 + H_2 \quad (7)$$

The conversion process mainly involves the separation of hydrocarbons from the reaction of water and water gas displacement as shown in the following reaction:

$$C_nH_{2n+2} + nH_2O \rightarrow nCO + (2n+1)H_2 \quad (8)$$

$$CO + H_2O \rightarrow CO_2 + H_2 \quad (9)$$

The overall reaction of hydrogen production by reforming glycerol vapor ($C_3H_8O_3$) can be described as follows:

$$C_3H_8O_{3(g)} + 3H_2O_{(g)} \rightarrow 7H_{2(g)} + 3CO_{2(g)} \quad (10)$$

The process of reforming glycerol vapor is carried out using material such as Ce, Mg, Zr and La, to support the work of the alumina catalyst so that hydrogen selectivity can increase. The catalyst is needed to activate the steam, one of which is Ni [19]. The catalyst that shows the best performance in hydrogen production from glycerol is Ni/Al_2O_3 and $RH/CeO_2/Al_2O_3$ [20].

High concentration will result in higher stability and capacity to activate steam reformer [21].

Partial oxidation

Partial oxidation is carried out by reacting the substrate with oxygen and producing heat. The oxidation process on several substrates requires balancing the energy produced from the air supply. The substrate will be oxidized as a whole and produce carbon dioxide and water if the air supply is excessive. The process can be shown as follows:

$$Substrate\ (C_nH_mO_p) + air\ \rightarrow CO_2 + H_2 +\ N_2 \quad (11)$$

If CO_2 increases, the selectivity of hydrogen will increase. Temperature affects the selectivity of hydrogen. The decreasing temperature of heating selectivity to hydrogen will also decrease [22]. The reaction can take place without using a catalyst, examples of partial oxidation occur in the gasification process [23].

Reforming the autothermal

Unlike the partial oxidation method, the autothermal process is carried out using a catalyst. This process can be described as follows:

$$Substrate(C_nH_mO_p) + air + steam \rightarrow CO_2 + H_2 + N_2\ \Delta H = 0 \quad (12)$$

Ce/Al_2O_3 is a catalyst used in the autothermal process in producing hydrogen from glycerol. Addition of CO vapor and RH catalyst can increase hydrogen selectivity. In the process of autothermal the reaction takes no energy [22]. The autothermal steam reformation process produces a higher amount of hydrogen [24]. In 1 mole of crude glycerol can produce 4.4 moles of hydrogen, but deactivated and coke catalysts greatly affect the amount of production so that it needs special attention [25].

Aqueous-phase reforming

The Aqueous-phase reforming process is carried out at a relatively low temperature of 270 ^oC with a pressure of 60 bar in the liquid phase. One of the advantages of this method is that the CO produced is relatively less. Hydrogen selectivity can be achieved up to 51% in the use of $Pt/C\text{-}Al_2O_3$ catalyst with a pressure of 56 bar temperature 265 ^oC [26]. Selectivity will decrease with the presence of impurities. Severe deactivation which causes oxidation on Ni catalysts supported by alumina using promoters such as catalysts Ce, Mg, Zr, and La [21]. From the various catalysts used, the lanthanum catalyst gives the best results in converting glycerol to hydrogen reaching 37% [18].

Supercritical water reform

Supercritical water reformation is water produced by heating and compression under the critical temperature of 347 ^oC and pressure 22.1 MPa [27]. The catalyst used in supercritical water reform is Ru/Al_2O_3 to produce hydrogen from glycerol. Hydrogen can be produced from 1 mole of glycerol as much as 6.5 moles with the amount of glycerol fed as much as 5% in water at a temperature of 800 C and the temperature used is 241 bar [28].

Glycerol which is a by-product of biodiesel production can be used as a raw material in hydrogen production. Biodiesel has been widely used and sold commercially in several countries in the past two decades and it is estimated that its use will grow rapidly because of its renewable nature and can reduce carbon dioxide emissions which are quite large compared to fossil fuels. In biodiesel synthesis generally through transesterification of triglycerides with methanol, with by-products in the form of glycerol about 0.1-ton stoichiometry produced per ton of biodiesel [29].

Research on the conversion of glycerol to hydrogen aims to increase the usefulness of glycerol which is the main by-product in biodiesel production. Glycerol is one of the most widely used chemical raw materials and is massively applied, such as in the fields of pharmaceuticals, food, and cleaning. However, because the by-product glycerol transesterification of biodiesel still contains many impurities such as alcohol, fatty acids, salt and water, its use directly in applications that require high purity cannot be done. The glycerol reformation reacts glycerol with steam to produce synthesis gas (hydrogen and carbon monoxide) at atmospheric pressure and normal temperatures above 500°C. The next shifting reaction consists of the reaction of carbon monoxide with steam which produces more hydrogen and carbon dioxide. The shift in reactions that occur is exothermic, but the reform reaction is very endothermic [30].

4 Hydrogen Application as Fuel Cell Vehicle

Hydrogen can be used in vehicles in two ways as fuel for internal combustion engines and as energy carriers for fuel cells, which produces the energy needed to move the vehicle. However, in both cases, hydrogen must be stored in the vehicle [31].

Jain (2009) reports that various hydrogen applications in the future can be used as power plants, fuel for automobiles, hydrogen-powered industries, jet planes, hydrogen villages and for all domestic energy needs [32]. There are 3 ways to use hydrogen as a vehicle fuel. First, hydrogen is burned inside the engine like burning gasoline in a vehicle in general. The second, more efficient option is to use a fuel cell that results from the reaction between hydrogen and oxygen from the atmosphere to produce electrical power with very high efficiency. The electricity produced is used to drive the wheels. And the third option is Hybrid-Electric Vehicles (HEV), a technology that combines Internal Combustion Engines (ICE) with an electric motor to produce efficiency that is almost the same as a fuel cell but at a much lower cost [33]. To use hydrogen as fuel with an IC engine, the engine must be designed to avoid abnormal combustion [34]. Al-Baghdadi (2002) has conducted research on hydrogen-ethanol mixture as an alternative fuel in spark ignition engines [35, 36]. Ma (2003) reported that the hydrogen engine has a thermal efficiency in the range of 35-50%, this range is greater than a petrol or diesel engine [37].

The Proton Exchange Membrane Fuel Cell (PEMFC) are commonly used in transportation applications and other stationary applications. PEMFC is chosen because of its fast start up time and good power-to-weight ratio. PEM fuel cell is the right technology for passenger vehicles such as buses and cars [38].

The PEMFC as a fuel cell vehicle resource has zero emission advantages, no pollution, high efficiency, and low operating temperature, which is suitable for vehicle [39]. However, costs and durability are still the two main obstacles to large-scale manufacturing and the full commercialization of this technology. For example, the electrocatalyst is a major contributor to PEMFC's limited performance, high costs, and poor durability. At present, only Pt or Pt-based catalysts (e.g, Pt-Co) are practical for driving electrochemical reactions in PEMFC environments. Platinum consists of a large portion of PEMFC costs because of its high price and limited supply.

In the sophisticated PEMFC stack, account electrocatalyst for ca. 60% of the total cost, which is much higher than the costs of other single components, for example membrane proton polymer (PEM) (10%), bipolar plate (BPP) (10%), and gas diffusion layer (GDL) (10%). Furthermore, the stability of the catalyst is one of the main limitations on PEMFC durability, membrane exchange (PEM) (10%), bipolar plate (BPP) (10%), and gas diffusion layer (GDL) (10%). Furthermore, the stability of the catalyst is one of the main limitations of PEMFC durability, which is an important step in achieving PEMFC commercialization. Thus, developing high-performance, low-cost and highly durable catalysts is the main priority of PEMFC research [39]. PEMFC vehicles can survive for 5000 hours in various environmental conditions [40]. As a result, PEMFC is considered a very promising resource for emissions-free cars [7].

5 Conclusion

The production of hydrogen from renewable sources has several advantages both from sustainable supply and low emission levels. Meanwhile, the application of hydrogen for transportation has a very good prospect because it can reduce greenhouse gas pollution.

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