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Hydrogen – The Future Fuel

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Abstract

Hydrogen is notable for its unique properties making it the most viable alternative fuel for electricity generation and engine power. This element is highly abundant and is being used in numerous applications industrially. But hydrogen can be an important source of fuel and with the proper knowledge of its different technologies, innovations for hydrogen fuel production can then be addressed. Steam reforming of natural gas is the widely used hydrogen production technology. But environmentally safe production had been a pressing issue. Hence, a shift to a cleaner and more sustainable primary energy source is very essential. This paper gives brief background of the different hydrogen production techniques using two primary energy resources as well as the developments, the gaps, and the further improvements needed to be made. Note however, that comprehensive R&D details should be sought in specialist papers for a more thorough background. The sustainability of hydrogen production technology lies from where it is produced, thus this paper also aims to highlight the hydrogen fuel production from biomass citing its developments and its potential for high hydrogen yield.

Keywords: Hydrogen; Fuel; Economy; Biomass

Introduction

The world had been dependent on oil as the pillar of its economy [1] with fossil fuels leading as the world's primary energy supply. Member countries of the Organization of the Petroleum Exporting Countries (OPEC) are the major oil exporters in the world and depending on the supply and demand they control the price and supply of oil to its consumers. This dependence in oil was seen during the 1973 oil embargo which struck the economies of the industrialized countries for months. Countries with the highest energy consumptions are notably China followed by United States, and India in 2013 [5]. Since the advent of industrial revolution, the use of oil for electricity and other industrial applications had become inevitable. The driving force of a civilization will always be energy accessibility. But with the uncertainty of the oil reserves due to failed forecasting and underestimated oil reserves along with the increasing energy demand of the growing population, the necessity to develop alternatives for fossil fuel had been the focus of the century.

According to the 2014 World Energy Outlook of the International Energy Agency (IEA), 60% of the total global energy demand is concentrated in Asia today. The growth of world primary energy demand will continue to increase and is projected to be 37% higher in 2040 where at the same time coal and oil will be reaching its plateau. At this time, it is also said that the world energy supply will divide into four almost equal parts: low carbon sources (nuclear and renewables), oil, natural gas, and coal.

On the other hand, the environmental implications of using fossil fuel as energy due to its greenhouse gas emissions causing climate change had also been a growing concern urging countries to shift to a more sustainable and clean energy conversion chains. Electric power and transportation sectors had the highest CO_2 emissions amounting to 2,039 and 1,815 million metric tons in 2012, respectively [18]. While industrial and transportation sectors had the highest usage of energy accounting to 30.54 and 26.77 quadrillion Btu in 2012, respectively [18]. Mostly were derived from fossil fuels contributing to almost half of the greenhouse gas emissions due to the combustion of hydrocarbon fuels.

With the possible fossil fuel depletion and climate change impacts, the challenge at hand is to have a sustainable energy in the future. Industrialized countries has led us to the development of our primary energy fuel from renewable resources such as solar energy, wind energy, geothermal energy, biomass energy, hydropower, ocean energy and secondary energy source such as hydrogen energy. Technologies from these resources are important and are significantly growing. Conversion technologies from these resources are being developed in such a way that it is safe, secure, and compatible backed up with regulation laws and support from governments [15]. However, the precondition for the acceptance of these energies is the availability of marketable technologies for the production, distribution, and usage. Among these technologies, hydrogen energy is starting to build its hydrogen economy paving its way to the energy market. This paper will be discussing the energy capability of hydrogen by discussing its important properties and its viability to become the fuel for the future.

What makes Hydrogen Unique?

Hydrogen is the lightest and the most abundant element in the universe. But the hydrogen atom is chemically very reactive and due to its lightweight it easily escapes from Earth's gravity [14,18]. Hence, it is not found chemically free in nature with its availability on earth only in compounds [8]. Since it does not readily exist as pure hydrogen gas, it is considered as secondary energy source. As of today, electricity is still the leading secondary energy carrier in the world deriving its energy primarily from fossil fuels. Hydrogen is also a high quality energy carrier which can store and deliver usable form of energy similar to electricity that is produced from a variety of resources and as byproduct of chemical processes. Hydrogen can not only be used in fuel cells to generate electricity but it can also be used to fuel internal combustion engines to replace petrochemicals such as diesel.

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Considering the idea that it can replace petroleum as fuel, it is necessary that it possesses certain key criteria for an ideal fuel. As an ideal fuel it has to be identified by its inexhaustibility, cleanliness, convenience, and independence from foreign control [8]. Hydrogen is one of the most plentiful gas in the universe with the sun and stars comprising of hydrogen and helium gas. The unlikelihood of its exhaustion seemed unquestionable as compared with the possibility of fossil fuel of its impending depletion. Some of the important properties of hydrogen are compared with methane (as main constituent of natural gas) and iso-octane (representative of gasoline fuel) in Table 1. The unique properties of hydrogen enables it to become highly efficient and produces zero to near zero emissions at point of use.

Based on Table 1, the low density of hydrogen pose challenges for storing sufficient amount of fuel for hydrogen powered vehicles. On a weight basis hydrogen has the highest energy content among the three but in terms of its volume it is relatively low in energy; researches on storing and transporting hydrogen is highly adequate to achieve cost-effective and efficient utilization of its energy. In terms of its combustion property, it is easier to ignite compared to the other two as suggested by its low minimum ignition energy. The wide range of its flammability limits allowing stable operations even at highly dilute conditions which makes it an ideal fuel for lean burn combustion engines [8]. This type of engine would mean that excess air is introduced alongside with fuel. In effect, it lowers combustion temperature significantly reducing pollutants such as NO_X in the exhaust. Moreover, stoichiometric hydrogen-air mixtures have short combustion durations indicated by its high laminar flame speed enabling it to approach thermodynamic engine cycle [19] allowing it to be highly efficient. Technical review has been made by Sandia National Laboratories, Combustion Research Facility in 2006 regarding the development of hydrogen powered engines with increased power density, NO_X emissions, and thermal efficiency of the engine.

Another use of hydrogen as fuel is its application in fuel cells (FC). The revival of interest in hydrogen production came about due to fuel cell technology. With the continuous price hike of oil over the years, this technology efficiently utilizes hydrogen energy to provide cheap, clean and renewable electricity. Fuel cells is an electrochemical conversion device to convert hydrogen and oxygen into water while in the process also produces electricity. The difference of a fuel cell to a typical battery is that it can never go dead as long as there are chemicals constantly flowing into the cell. The type of fuel cells are classified by the operating temperature and electrolyte used. One of this is the polymer exchange membrane fuel cell (PEMFC) which is more suitable for transportation applications having high power density and low operating temperature. Developments on polymer electrolyte membranes were reviewed by Zhang and Shen based on improvements in membrane performances such as excellent chemical and electrochemical stabilities and better proton conductivity. Neelakandan et al. found that surface modified blended membranes comprised of sulfonated poly phenylene ether ether sulfone (SPEES) by charged surface modifying macromolecules (cSMMs) exhibits excellent thermal stability and acceptable dimension stability in 80°C is a promising material for PEMFC. In increasing the rate of oxidation at the anode at lower temperature, catalysts are used. The catalysts used for PEM and some other cells is very expensive; the usual catalyst used in these fuel cells is platinum catalyst which is not only expensive but also extremely sensitive. Hence, making the fabrication and use of FC cost inefficient inhibiting its mass production. Cost effective production remains a challenge; the technical and economic feasibility of advanced materials being developed for proton exchange membrane fuel cells must be satisfied [10] as well as the use of potential catalysts at reduced costs.

Property	*Hydrogen*	*Methane*	*Iso-octane*
Molecular Weight (g/mol)	2.016	16.043	114.236
Density gaseous (kg/m^3)	0.08	0.65	-
Density liquefied (kg/m^3)	71	430-470	692
Minimum Ignition energy (mJ)	0.02	0.28	0.28
Minimum quenching distance (mm)	0.64	2.03	3.5
Lower heating value (MJ/kg)	120	50	44.3
Stoichiometric air/ fuel ratio (kg/kg)	34.2	17.1	15
Flammability limits in air (vol %)	4-75	5-15	1.1-6
Flammability limits (λ*)(-)	10-0.14	2-0.6	1.51-0.26
Flammability limits (φ[1])(-)	0.1-7.1	0.5-1.67	0.66-3.85
[2]Diffusion Coefficient in air (cm^2/s)	0.61	0.16	-
[2]Self-Ignition Temp (°C)	585	540	-

*relative air/fuel ratio

[1]Fuel/air equivalence ratio

Source: [1]*Adapted from Verhelst, S. et. al. (2013)*, [2]*Adapted from Gupta, R.B. (2009)*

Table 1: Comparison of the fuel properties of hydrogen compared to methane and iso-octane.

Hydrogen Production Technologies

Aside from being used as fuel for ICE and FC, hydrogen is also an important raw material for several industries. One of its industrial applications is to process crude oil into refined fuels such as gasoline and diesel by removing its contaminants. It is also an important feedstock for ammonia production for use in fertilizer, semiconductor production, glass industry, hydrogenation of fats and oils, methanol production, production of HCl, plastics recycling, rocket fuel, and welding and cutting [6]. Hydrogen extraction methods are source-specific and can be produced using a variety of feedstock.

The research on hydrogen driven technologies are now focused on overcoming the problems associated with hydrogen production. Some of these technologies will be presented for the purpose of understanding the challenges on the different processes. There are various ways in order to utilize hydrogen from different resources. Hydrogen for industrial applications are currently being produced by cracking carbonaceous fossil fuel (e.g. methane) via steam reforming and partial oxidation but there are also developments on methods using renewable resources such as biomass through gasification. On the other hand, there are also ways to utilize hydrogen by water cracking wherein electrolysis is being employed. The high cost of electricity for production through electrolysis is a major setback hence, high temperature thermal cracking from nuclear reactors and photovoltaic cells are done instead to reduce electricity consumption.

Several technologies have been available for the production of hydrogen fuel, one of which is the production from fossil fuels that is natural gas. The feedstock, natural gas is purified by removing sulfur and chlorine by hydrogenation, and reaction with Zinc Oxide (ZnO) bed. After the removal of impurities, the remaining methane through endothermic condition is reacted with steam at 750-800°C at 3-25 bar pressure in the presence of catalysts, hence called steam reforming producing carbon monoxide (CO) and hydrogen (H2) as syngas. The resulting CO from the syngas was further reacted for high temperature water gas shift reaction and for high temperature water gas shift reaction and for low temperature water gas shift reaction at 350-190°C [6,17]. Afterwards, other impurities are removed by the Pressure-Swing Absorption (PSA) leaving essentially hydrogen as the product, and the impurities are moved back to the steam reformer to allow more production of hydrogen gas. The same water gas shift reaction process applies to the partial oxidation method the difference is that certain amount of methane will initially be oxidized by allowing it to react with a stoichiometric amount of oxygen yielding CO and H_2. Auto-thermal reforming on the other hand, is the combination of both steam reforming and partial oxidation to produce syngas. It operates at 950-1100°C at 10 MPa with about 80-90% efficiency.

Another abundant source of hydrogen on earth constitutes 70% of the Earth itself – water. As said earlier in this article that hydrogen exist on Earth in compounds, hence water splitting must be done to dissociate water into hydrogen and oxygen. Water splitting can be employed through the application of electrical energy in an electrolytic cell. An electrolyte, e.g. aqueous potassium hydroxide (KOH) solution or a polymer electrolyte membrane, is used to circulate to an electrolytic cell with an anode and a cathode [17]. In high temperature electrolysis method, water in the form of steam (using external heat source, e.g. solar or nuclear) is fed in the cathode of an electrolysis cell decomposing water. Oxygen conductive electrolyte in the anode separates the oxygen from hydrogen to prevent recombining. Mixture of hydrogen gas and steam are passed through a condenser leaving pure hydrogen as product. This cycle can provide up to 60% efficiency [6]. Solar energy from photovoltaic systems coupled to electrolyzer uses light to directly split water into hydrogen and oxygen is called photolysis. The latter method reduces overall electric energy costs however, the development of a photo-electrolytic cell with higher solar to hydrogen conversion efficiency and corrosion resistant material remains a challenge.

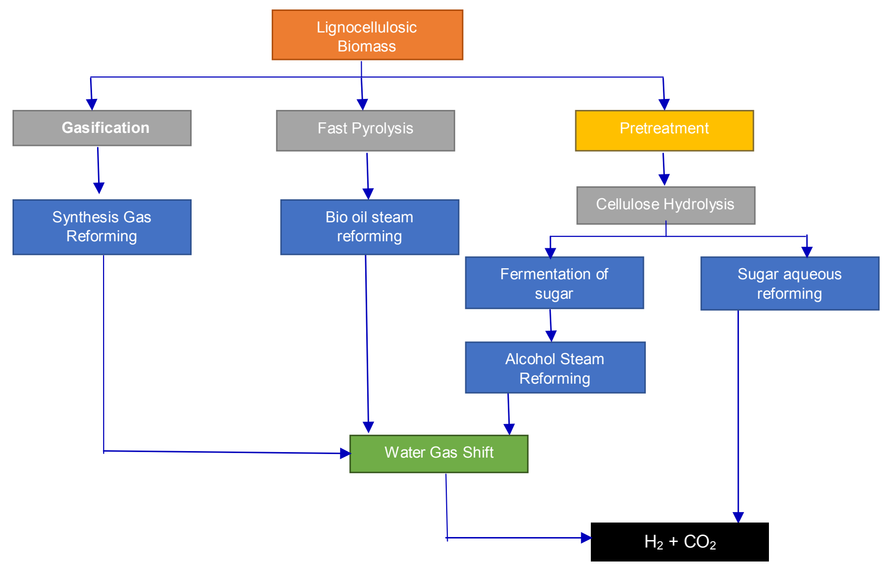
Water decomposition are done to dissociate hydrogen and oxygen however this method requires 4,027°C at 1 bar pressure for complete dissociation [6]. The problem lies with the vast amount of energy needed to achieve that certain temperature and the materials that can withstand such temperature during decomposition. Other processes for water decomposition at reduced temperatures has been suggested one of which is thermo chemical cycle wherein a series of chemical reactions at high temperatures is applied to decompose water [17]. Sulfur-Iodine cycle and Copper-Chlorine cycle are one of the examples of thermo chemical reactions but causes severe corrosion on materials during reactions.

The mentioned sources of hydrogen presents sustainability challenges as well as being highly energy intensive for its production. With these problems at hand, renewable resource in the form of biomass are the most advantageous and sustainable. These raw materials, biomass, are abundant, easily available, diverse, easier to transport, and improves CO_2 balance. Having renewable materials as hydrogen source, oil import dependence can be minimized and price level more stabilized compared to fossil fuels that are somehow dictated by the major oil exporters [12]. Biomass derived hydrogen the most attractive alternative feedstock for sustainable future fuel since it realizes the full environmental benefit of H_2 as a clean energy carrier [11,12].

Hydrogen from Biomass Conversion

Biomass is the most versatile among the renewable resources because gas can be harvested in liquid or gaseous form. Energy obtained from biomass in the world can be derived from wood wastes, municipal solid wastes, agricultural waste, and forestry wastes. Wood wastes are lingo cellulosic materials comprising of three polymers: cellulose, hemicellulose and lignin. Cellulose is 40-50% of the biomass wherein the most abundant functional group is hydroxyl groups consequently having hydrogen bonding as the main cohesive force of the polymer. Biomass chemical composition through ultimate analysis on the other hand identifies the amount of hydrogen which may be extracted from woody biomass. According to [8] the order of abundance in decreasing order of the most common elements in biomass are the following: C, O, H, N, Ca, K, Si, Mg, Al, S, Fe, P, Cl, Na, Mn, and Ti. Based on the ultimate analysis (dry basis) of some biomass [2], most common woods are made up of roughly 50 ± 3% Carbon, 40 ± 3% Oxygen and 6 ± 1% Hydrogen with the rest having relatively miniscule amounts of other elements and inorganic ash. Having relatively low H_2 content will also give H_2 low yield hence, the focus was turned into improving product gas composition, minimizing tar, and enhancing carbon conversion [11].

Extraction of H_2 from biomass may be direct or from biomass derived chemicals through either biological or thermo chemical processes. For this article, the conversion technologies presented will focus on thermo chemical route of H_2 synthesis. Figure 1 shows the



Source: *Adapted from Li, H., Yang, J., De, C. (2013)*

Figure 1: Schematic thermo chemical conversion route for H_2 production.

thermo chemical conversion route of lingo cellulosic feedstock (Figure 1).

The figure above shows that in enhancing H_2 production water gas shift (WGS) reaction was incorporated in the process. At this process, the gasifying agent steam is introduced resulting to steam reforming of produced hydrocarbons especially methane (CH_4). In the gas shift reaction, H_2 production is increased in the expense of carbon monoxide. The selection of the processes for biomass derived H_2 is dependent on biomass-derived chemicals and the property of the feedstock [11]. Different chemical, physical, and thermal pretreatments may be applied to the biomass in order to optimize the amount of hydrogen which may be extracted during the processes [12].

In the pyrolysis process, biomass is heated in the total absence of oxygen at the maximum temperature at a certain residence time. Fast pyrolysis is the type of pyrolysis with the highest yield of bio-oil where it heats the biomass at approximately 350-550°C in atmospheric pressure for less than two seconds of residence time [12]. The water soluble fraction of the bio-oil then undergoes catalytic steam reforming process coupled with WGS for hydrogen production. Czernick and French investigated the auto-thermal reforming of fast pyrolysis bio-oil using three different biomass. They used a noble metal catalyst at a reformer temperature of 800-850°C, a steam-to-carbon ratio of 2.8-4.0 and oxygen-to-carbon ratio of 0.9-1.1 producing 9.11 grams of hydrogen per 100g of fast pyrolysis bio-oil. It was found that there was significant impact on yield of hydrogen to the composition of bio-oil, and bio-oil carbon to gas conversion ranging from 70-89% [4]. The challenge, however, with pyrolysis followed by steam reforming is the quality of hydrogen gas produced and the emissions.

Hydrocarbons and oxygenates reacts with water molecules in aqueous phase during the aqueous phase reforming (APR) process at low temperature and elevated pressure [11]. Dehydrogenation then occurs forming CO and H_2 from C-C bond cleavage of biomass-derived polyols and sugars with C/O ratio of 1:1 (e.g. methanol, ethylene glycol, glycerol, glucose, and sorbitol) [12]. The CO adsorbed in the catalyst surface undergoes WGS yielding CO_2 and H_2. This technique is promising since it does not require energy intensive drying for the feedstock. It requires however, optimization of using catalyst in APR to reduce energy consumption, minimize side reactions and increase productivity in order to have impact in the production of hydrogen [3].

Gasification process is the conversion of liquid or solid feedstock by introducing a gasifying medium like steam, air or oxygen to rearrange molecular structure of feedstock packing energy into chemical bonds in the product gas [2]. Carbonaceous residue is partially oxidized in an exothermic condition producing H_2 and CO as it moves about the pyrolysis zone and then the gasification zone following a series of chemical reactions. Typical composition of the product gas is presented in Table 2 depending on the MC of the feedstock.

Component	Wood Gas (%vol)	Charcoal (%vol)
Nitrogen	50-54	55-65
Carbon Monoxide	17-22	28-32
Carbon Dioxide	9-15	1-3
Hydrogen	12-20	4-10
Methane	2-3	0-2
Gas Heating Value (kJ/m^3)	5000-5900	4500-5600

Source: Food and Agriculture Organization of the United Nations – FAO (1986). Wood gas as engine fuel. FAO Forestry Paper 72, Chapter 2. Retrieved March 8, 2015 at http://www.fao.org/docrep/t0512e/t0512e09.htm

Table 2. Composition of gas from commercial wood and charcoal gasifiers (Wood=20%MC, Charcoal=7% MC).

As seen from the table, 12-20% volume of hydrogen can be produced from wood gas. Addition of steam as gasifying agent results in steam reforming of hydrocarbons especially methane CH_4. The chemical reaction is presented in equation 1. This process is usually aided with the presence of a nickel based catalyst at 700-900°C [2]. Nowadays, gasification coupled with WGS is the widely used process for the production of hydrogen starting from biomass operating at 600-1000°C [12]. It further adds hydrogen into the product by stripping off carbon producing gases with higher hydrogen-to-carbon ratio. During the water gas shift reaction process, hydrogen is produced in expense of carbon monoxide [2] thereby increasing the yield of H_2 gas. The WGS reaction is presented in chemical equation 2.

$$CH_4 + H_2O \leftrightarrow CO + 3H_2 + 206\ \text{kJ/mol} \quad (1)$$

$$CO + H_2O \leftrightarrow CO_2 + H_2 - 41.2\ \text{kJ/mol} \quad (2)$$

Traces of any impurities in the product gas are removed using a pressure swing absorption (PSA) similar to steam reforming of natural gas. The issue with biomass gasification is the formation of tar and very high operating temperatures but new method may be developed to overcome this. Jaojaruek [9] studied two stage downdraft gasification with improved gasification rate by 30% compared to single stage gasification method as well as increased combustible gas from 25% to 40% with H_2 gas doubled. There was also a significant decrease in tar formation producing less than 50 mg/m^3 after producer gas was premixed with air.

Gasification using supercritical water, SW, ($T_C \geq 374$°C, $P_C \geq 22.1$ MPa) as gasifying medium on the other hand, had also been increasingly popular in this field of research. It is seen as safe, readily available, suitable and environmentally friendly medium [7]. By having low dielectric constant, consequently it can dissolve at certain conditions organic compounds such as tar precursors which may be directly reformed into H_2 and CO_2 [12]. Though being the most suitable medium for wet biomass gasification because of its physicochemical properties, problems arise because of its high activation energy, violent reaction condition, and high cost. These however, may be overcome through the use of appropriate catalysts; summary of investigations on SW gasification has been reviewed by Guo et.al in 2010.

Conclusion

Hydrogen, a secondary energy resource, is capable of generating power as well as fuel source. As discussed in this paper, it may be produced from a variety of feedstock. However, in building hydrogen economy for the future, the reliability of hydrogen production and its long term effects must be thoroughly considered. Reliability would mean a more sustainable hydrogen energy derivation consequently producing less emissions that can be harmful to the environment. Today, the most established hydrogen production is from fossil fuels through steam reforming process. But the limitation of this primary resource is an impending crisis, hence, stronger R&D areas should be considered in producing H_2 from renewable resources instead. Biological and thermo chemical process from biomass resources are rather cost-efficient compared to electrolysis in terms of its technological aspects. Biomass on the other hand, is considered as an erratic fuel feedstock lacking homogeneity and inconsistent quality contributing to poor technological innovations over the years. It is still the most promising feedstock with gasification and pyrolysis as the most favorable leading technology for H_2 commercialization. To realize this, there should be higher H_2 yield from thermo chemical processes. As seen from the presented processes, a lot of work still needs to be done one of which is improving the conversion technologies through reforming at lower temperatures, enhance suitability of feedstock, and increasing conversion efficiency. Furthermore, for a more stable hydrogen production the development of the economic and marketability of the fuel aspects in the future must be well established.

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