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Hydrogen Production Technologies with Specific Reference to Biomass

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Abstract- Consequences of environmental threat to our planet are reflected in the form of global warming. Transportation is one of the sectors for release of high carbon dioxide. Efforts are now concentrated on the use of hydrogen as a fuel. The present paper discusses the technologies for hydrogen production (from biomass) with some of the merits and demerits.

Keywords- Hydrogen, Biomass, Glycerol, Fuel processing technologies

1. Introduction

One of the environmental threats our planets is facing today is the long term changes in the earth's temperature and climatic pattern known as Global Climate Change. The emissions of the six green house gases i.e. Carbon dioxide, Methane, Nitrous Oxide, Hydrofluoro carbons (HCFs), Perflouro carbons (PFCs), Sulfur Hexaflouride (SF_6) from human activities have influenced the global climate. In the transportation sector light vehicles are responsible for the release of significant amount of carbon dioxide, volatile organic compound (VOC), carbon monoxide and nitrogen oxide (NOx) Thus efforts are made to diversify our energy supply particularly for the transportation sector and to find cleaner fuels. Hydrogen can be considered as a potential source of unlimited clean fuel but as of today it is not a primary energy source but is considered an energy carrier. Hence it must be manufactured before it is used as a fuel. Recently there has been international attention on the development of new hydrogen technologies as a potential solution to the current fears of global warming. Fuel processing technologies convert a hydrogen containing material such as gasoline, ammonia, or methanol into a hydrogen rich stream. There are many processes for hydrogen production. Hydrogen can be produced from carbonaceous materials mainly hydrocarbons and/or water by application of chemical, electrical or thermal energy. It can also be produced by the partial oxidation of hydrocarbons, steam-iron process, water-gas and producer-gas processes. Biomass can also become an important source of hydrogen. Biomass as a product of photosynthesis is a renewable resource that can be used for sustainable production of hydrogen. Except for very low cost feedstock and plants like switch grass direct production of hydrogen from biomass by gasification/water-gas shift technology is economically unfavorable. Alternatively it can be produced by a two-stage process: fast pyrolysis of biomass to generate bio-oil; and subsequently catalytic steam reforming of the oil or its fractions to produce hydrogen. Also in the production of biodiesel from biomass by the transesterification process, glycerol is the main biomass-derived product. Now a days the worldwide trend of increasing production of bio-fuels results in an overproduction of glycerol. The hydrogen production from glycerol by the aqueous-phase reforming process at low temperatures and high pressures has been tried on various supported catalysts including Pt/Al2O3, Pd/ Al2O3. Hydrogen can also be produced by the Aqueous Phase Reforming (APR) process which generates hydrogen-rich gas streams from biomass-derived compounds such as glycerol, sugars, and sugar alcohols. The reaction of these oxygenated compounds takes place in a single step reactor process compared to the three or more reaction steps required for hydrogen generation conventionally carried out by non-renewable fossil fuels. The reforming of these reactions takes place in the liquid phase. Hence attempts are made to produce hydrogen through various techniques all across the globe to achieve economically viable process. This paper reviews the technologies related to hydrogen production from renewable biomass resources including reforming (steam, partial oxidation, auto thermal` plasma, and aqueous phase) and pyrolysis.

2. Hydrogen from Biomass

In the near future, biomass is the most likely renewable organic substitute to petroleum [1] Biomass is available from a wide range of sources such as animal wastes, municipal solid wastes, crop residues, short rotation woody crops, agricultural wastes, sawdust, aquatic plants, short rotation herbaceous species (i.e. switch grass), waste paper, corn, and many more [2-10] For hydrogen generation, the current biomass technologies include: gasification, pyrolysis, conversion to liquid fuels by supercritical extraction, liquefaction, hydrolysis, etc. followed in some cases by reformation, and biological hydrogen production [11].

3. Biomass Gasification

Gasification of biomass coupled with water gas shift reaction is the most, common and mature technology used for hydrogen production. It is the conversion, by partial oxidation at high temperature, of a carbonaceous feedstock into a gaseous fuel as shown in figure 1. The heating value of the resulting gas generally ranges from about one-tenth to half that of natural gas, depending on the gasification process used. The product gas can be reformed to produce fuels such as methanol and hydrogen, which could then be used in fuel cells.

In a gasifier, by applying heat under pressure in the presence of steam and a controlled amount of oxygen, biomass is converted into primarily a gaseous mixture of hydrogen, carbon monoxide, carbon dioxide, and known as synthesis gas, or "syngas". The carbon monoxide then reacts with water to form carbon dioxide and more hydrogen (water-gas shift reaction). Absorbers or special membranes can separate the hydrogen from this gas stream. However, the gasifiers need to include significant gas conditioning along with the removal of tars and inorganic impurities and the subsequent conversion of CO to H_2 by water gas shift reaction

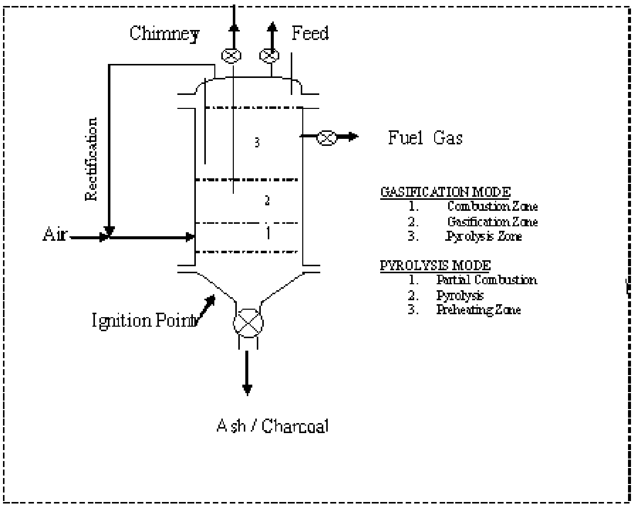

Fig. 1. Fluidized gasifier for the production of Hydrogen

3.1. Simplified Example Reaction

$$C_6H_{12}O_6 + O_2 + H_2O \rightarrow CO + CO_2 + H_2 + \text{others} \quad (1)$$

In the above reaction glucose is used as a reactant. However actual biomass has highly variable composition and complexity with cellulose as one major component.

3.2. Water-Gas Shift Reaction

$$CO + H_2O \rightarrow CO_2 + H_2 \text{ (+small amount of heat)} \quad (2)$$

The gasification process has a disadvantage of low thermal efficiency since moisture contained in the biomass must also be vaporized. The reactor used can be either fixed bed or fluidized bed with or without a catalyst. The performance of the fluidized bed reactor yields better results. Superheated steam (900°C) has been used to reform dried biomass to achieve high hydrogen yields .If gasification, is carried at high temperatures of 800-1000°C, it produces a significant amount of tar in the product gas. Hence several processes have been proposed to decrease the amount of tar produced in the gasification reactor like the use of catalysts like $Rh/CeO_2/M$ ($M = SiO_2$, Al_2O_3, and ZrO_2) [12]. Much cheaper catalysts would be required to make such an approach viable. The typical gasification reactors are built on a large scale and require massive amounts of biomass to be continuously fed to them. Pilot-scale experiments in the steam gasification of charred cellulosic waste material have been discussed by some researchers.[13] It is observed that some inorganic salts like chlorides, carbonates and chromates have a positive effect on this reaction. The problem with this technology is that a tremendous amount of resources must be used to supply large amounts of biomass to the central processing plant. Currently the high logistics costs typically limit the gasification plants to be located near the processing plant. Development of smaller efficient distributed gasification plants may be required for this technology for cost effective hydrogen production.

4. Fast Pyrolysis Followed by Reforming of Carbohydrate Fraction of Bio-Oil

This method produces hydrogen in two stages: the first stage is the fast pyrolysis of biomass to generate bio-oil followed by the catalytic steam reforming of the bio-oil to hydrogen and carbon dioxide.

$$\text{Biomass} + \text{Energy} \longrightarrow \text{Bio-oil} + \text{Char} + \text{Gas} \quad (3)$$

This is an endothermic reaction. This is followed by the second step which is the catalytic. Steam reforming of bio-oil at 750-850°C over a nickel-based catalyst is a two-step process that includes the shift reaction.

$$\text{Bio-oil} + H_2O \longrightarrow CO + H_2 \quad (4)$$

$$CO + H_2O \longrightarrow CO_2 + H_2 \quad (5)$$

The maximum yield of hydrogen obtained is 0.172 g H_2/g bio-oil and overall stoichiometry gives a 11.2% of hydrogen based on wood.

$$CH_{1.9}\,O_{0.7} + 1.26\,H_2O \qquad CO_2 + 2.21\,H_2 \qquad (6)$$

This concept has several advantages over the traditional gasification technology. First, bio-oil being liquid is much easier to transport than solid biomass hence pyrolysis and reforming can be carried out at locations which are economically viable. The second advantage is the potential for production and recovery of higher-value co-products from bio-oil that could significantly influence the economics of the entire process. The lignin-derived fraction can be separated from bio-oil and be used as a phenol substitute in phenol formaldehyde adhesives or can be converted to cyclohexyl ethers (fuel additives). The carbohydrate-derived fraction is catalytically steam reformed to produce hydrogen [14]

5. Direct Solar Gasification

The experiments on using solar process heat for the gasification of organic solid wastes and the production of hydrogen were also carried out A detailed review with many references of the technology describes solar gasification of carbonaceous materials to produce a syngas quality intermediate for production of hydrogen and other fuels [15]. Shahbazov and Usupov have shown good yield of hydrogen from agricultural wastes using a parabolic mirror reflector [16]. The use of a palladium diaphragm in this respect is reported to achieve solar-assisted hydrogen [17].

6. Hydrogen Production by Aqueous-Phase Reforming of Glycerol on Supported Metal Catalysts

First the esterification of biomass is carried out in which an alcohol (Ethanol/Methanol) in presence of a catalyst (NaOH/KOH) converts fatty acids into methyl or ethyl esters. From the chemical point of view it means taking a molecule from triglyceride or a complex fatty acid to neutralize the free fatty acids and produce glycerin and an ester [18]. The fats and oils required for the process can be obtained by extraction or pressing of seeds

$$\begin{array}{lll}
CH_2-O-COR_1 & R_1-COOCH_3 & CH_2OH \\
| & + & | \\
CH-O-COR_2+3CH_3OH \xrightarrow[Catalyst]{Heat} & R_2-COOCH_3 & +\ CHOH \\
|\qquad Methanol & + & | \\
CH_2-O-COR_3 & R_3-COOCH_3 & CH_2OH \\
Triglyceride & Fatty\ acid\ methyl\ ester & Glycerol
\end{array} \qquad (7)$$

The environmental benefit of power generation from hydrogen fuel cells can only be achieved if hydrogen is produced from sustainable resources such as biomass. Glycerol is the main biomass-derived product formed by the esterification process during bio-diesel production. Nowadays the worldwide trend of increasing production of bio-fuels results in an overproduction of glycerol. The hydrogen production from glycerol by the aqueous-phase reforming process at low temperatures and high pressures on various supported catalysts including Pt/Al_2O_3, Pd/Al_2O_3, Ni/Al_2O_3, Ru/Al_2O_3 and Rh/Al_2O_3, has been studied.[19].

5. Aqueous Phase Reforming

Aqueous phase reforming (APR) is under development to process oxygenated hydrocarbons or carbohydrates to produce hydrogen. These reactors often operate at pressures up to 25-30 MPa and temperatures ranging from 220 to 270 0 C. The reforming reactions are complex which are followed by the Water Gas Shift reaction [20]. Most reactions have been focused on supported Group VIII catalysts, and Pt-containing catalysts are found to have the highest activity. A lot of research has also been carried out on nickel based catalysts, in spite of their low activity since nickel is a low cost catalyst. The advantages of APR reactors include elimination of the need to vaporize water and feedstock and also fuels that cannot be vaporized such as glucose can be processed without the need to degrade them. APR occurs at low temperatures which favors Water Gas Shift reaction to increase the hydrogen yield and at the same time suppresses the formation of CO. Thus the reforming and Water Gas Shift reaction occur in a single step eliminating multiple reactors. This technology has the advantage that it can efficiently and selectively convert biomass feedstock to hydrogen.

7. Plasma Reforming

In plasma reforming, energy and free radicals used for conventional reforming reaction are provided by a plasma, typically generated with electricity or heat [21-23].When water or steam is injected with the fuel, H, OH, and O radicals in addition to electrons are formed, thus creating conditions for both reductive and oxidative reactions to occur [24]. Plasma reforming overcomes many limitations of conventional techniques such as cost and deterioration of the catalysts, size and weight requirements, sluggish response, and limitations on hydrogen production from heavy hydrocarbons. This technique can be used at lower temperatures than traditional reforming. The main reported disadvantages include the electrical requirements and high electrode erosion at elevated pressures [25].

8. Supercritical Conversion of Biomass

Many researchers have investigated the aqueous conversion of whole biomass to hydrogen under low temperature and in supercritical conditions. No solid residue or char is produced by this method and hydrogen gas concentration up to 18% (v/v) is reported.

9. Comparative Analysis of Various Techniques

When comparison of various techniques to produce hydrogen from biomass is done, it is seen that all the techniques are associated with some merits and demerits which is highlighted in Table-1.

Table 1. Merits and Demerits of Producing Hydrogen By Various Technologies

Process	Merits	Demerits
Thermo chemical gasification	Maximum conversion is carried out	Low thermal efficiency Large amount of tar is produced Resources required is high
2. Fast Pyrolysis	1. Production and recovery of value added co-products 2.Transportation cost of bio-oil is low.	Chances of catalyst deactivation is high
3. Solar gasification	Hydrogen yield is high	Effective collector plates are required
4 Aqueous phase reforming	1. All types of fuels can be used. 2.Reforming and water gas shift reaction takes place in a single step	1 .Tars and inorganic impurities are produced. 2. Reforming reactions are complex.
5.Plasma reforming	1. Low cost and deterioration of catalyst is less. 2 Can produce hydrogen from even heavy hydrocarbons.	1.Electrical requirement is high 2. High electrode erosion at elevated pressure..
6.Supercritical conversion	No solid residue or char is produced.	Selection of supercritical medium

10. Conclusion

This paper has presented various technologies which can be considered for the generation of hydrogen from biomass. In today's market, it is unlikely that the techniques currently used (the steam reforming of hydrocarbons, and the partial oxidation of heavy hydrocarbons) will be displaced by other technologies. However since biomass is a renewable source of energy, active research is being carried out to make the production of hydrogen from biomass an economically viable process.

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