Production of Hydrogen from Lignocellulosic Biomass

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Hydrogen is considered one of the most important forms of energy for the future, as it can be generated from renewable sources and reduce CO_2 emissions.

hydrogen gasification liquefaction

1. Introduction

The growth in the world population generates significant increases in fossil fuel consumption, leading to an increase in anthropogenic emissions of greenhouse gases and global warming. According to the 2015 World Energy Statistical Review report, almost 85% of energy consumption mainly depends on these reserves, resulting in environmental problems, energy crises, and depletion of sources [1]. For these reasons, one of the main challenges today is to address the growing global demand for energy and discover ways to meet this demand through sustainable and environmentally friendly energy solutions [2]. To substitute fossil fuels, researchers are exploring new alternative sources of renewable fuels with environmental safety in mind [3]. Among the promising renewable energy resources are biodiesel, bioethanol, and hydrogen. According to Zhang et al., biodiesel is considered a stable, biodegradable, non-toxic, and environmentally friendly renewable energy source with excellent acid catalytic activity, ideal in the field of biorefinery [4]. It is also easy to store/transport and is technically and economically accessible [5][6]. It can be produced from fatty acids, various edible oils, and non-edible oils with small-chain alcohol by esterification/transesterification over an acid/base catalyst [7]. Biodiesel shows a similar combustion performance to fossil diesel [8]. There are also several studies related to the production of bioethanol; for instance, different biomasses have been evaluated, such as sorghum biomass, Delonix regia pods, waste date palm fruits, etc., to obtain bioethanol through enzymatic hydrolysis processes, using different biomasses and processes applying acid hydrolysis, followed by fermentation with yeasts [8][9][10][11]. In addition to studies on the production of biodiesel and bioethanol, there are several studies related to hydrogen, which is considered one of the most important forms of energy for the future due to its cleanliness and high calorific value. As a result, it has become a focus of renewed interest in many parts of the world [12]. It has been proposed as a high-yield potential energy vector—it has the highest energy density of all fuels and energy carriers with a yield of 122 $MJKg^{-1}$. It is believed to be an effective replacement for gasoline because 9.5 kg of hydrogen is enough to replace 25 kg of gasoline. Its properties of high energy density, fast burning, high octane number, and zero damage potential, will soon make it the fuel of choice [13]. Even when comparing hydrogen with electricity, which can also be produced by renewable sources, electricity has the disadvantages of transmission and heat losses caused by high voltages and electrical resistance, while hydrogen offers some advantages, such as high conversion efficiency of energy, abundant sources, ability to be created with zero emissions from water, and long-distance transportation [2]. As for the cons of hydrogen as a biofuel, its storage is challenging. As the lightest molecule, hydrogen gas has a very low density: 1 kg of hydrogen gas occupies more than 11 m^3 at room temperature and atmospheric pressure, and pure hydrogen has flammable and explosive characteristics [14]. Thus, for hydrogen storage to be economically viable, its storage density must be increased. Various storage methods are currently being investigated [15]. However, expensive equipment is required to liquefy hydrogen, as well as to transport the liquid hydrogen [16]. In addition, biomass conversion techniques (e.g., gasification and pyrolysis) have some limitations and are very energy intensive [17].

The predominant method for hydrogen production is based on natural gas or other fossil fuel sources that require abundant energy and result in the emission of a significant amount of CO_2 into the atmosphere [18]. An alternative to obtaining hydrogen is the use of biomass energy, which is considered a green source with almost zero carbon emissions. Unlike solar energy, biomass has no time limit. This energy source contains significant amounts of carbon and hydrogen, making it favorable for producing fuels and chemical products [19]. In addition, lignocellulosic biomass is broadly accessible as a low-cost renewable feedstock with a nonreactive nature [20]. It has a high potential for the production of bio-oil and other chemical products [21] and is considered the fourth largest energy source available [22]. Residues are obtained from forestry and agriculture, although biomass grown in Europe is significantly more expensive than biomass grown in Latin America [23]. Forestry residues generated by wood extraction operations have traditionally been considered products of low economic value [24].

Different methods of converting biomass into hydrogen have been developed, and thermochemical and biochemical conversion is the most recommended. Alongside biomass thermochemical conversion processes, other methods include gasification, pyrolysis, and liquefaction, with steam gasification considered the most promising to produce hydrogen-rich synthesis gas. In this route, the use of steam as a gasifying agent not only provides H_2-rich synthesis gas but also causes minimal environmental impact, especially preventing NO_x formation with low CO_2 generation, making the hydrogen obtained to be considered “green” [25][26]. However, the wide varieties of biomass have different physical characteristics and chemical compositions, which always result in different steam gasification efficiencies [27]. Biomass containing less sulfur in the fuel reduces acid rain. As a result, the use of biomass fuel instead of fossil fuel causes a decrease in GHG (greenhouse gas) emissions [28].

2. Hydrogen Production from Biomass

Based on the process of gas generation, the direct production of hydrogen from biomass can be achieved by two routes: thermochemical methods and biochemical processes using microorganisms. The former include gasification, pyrolysis, and liquefaction and are considered the most effective methods for producing hydrogen-rich gases from biomass. These processes define all biomass into liquid and gaseous biofuels, which are then synthesized into the required chemical. Otherwise, they can be used directly as a transportation fuel. Thermal gasification is a known thermochemical method, producing a temperature of 800 to 1000 °C and involving partial oxidation of biomass in the presence of gasifying agents, such as steam or oxygen and air that provide O_2 in amounts less than stoichiometric amounts [29]. In the case of gasification with air, energy for the process is produced by partial combustion of the fuel, whereas for gasification with steam, energy from an external source is required to generate steam and is, therefore, more challenging. Syngas (a mixture of CO and H_2) and biofuels are the main products of gasification and pyrolysis, respectively. Biofuels are also determined in the synthesis of gas through some specific conversion techniques, such as bio-oil reforming, bio-oil gasification, online pyrolysis reforming, etc. [30][31]. Pyrolysis or co-pyrolysis is another promising technique for hydrogen production. In this technique, the heating and gasification of organic matter take precedence in a temperature range of 500–900 °C at a pressure of 0.1–0.5 MPa. Although the pyrolysis process is considered the precursor to gasification, it differs significantly. The primary products of pyrolysis comprise condensable gases and solid carbon. Condensable gases can be further decomposed into CO, CO_2, H_2, and CH_4, liquid, and char through homogeneous gas-phase reactions and heterogeneous thermal gas–solid-phase reactions. In addition, non-condensable gases, such as H_2, CO, CO_2, and LHG (light hydrocarbon gas), are formed due to the cracking of condensable vapor through gas-phase reactions. Another thermochemical process is gas liquefaction, which is a highly complex process that consumes a lot of energy [32]. Liquid hydrogen is produced by cooling, purifying, converting ortho to hydrogen, expanding, and liquefying hydrogen feed gas from atmospheric temperature to approximately 20 K [33].

There are also several biohydrogen production routes that use the biochemical processes of microorganisms, such as, depending on the type of dark substrate and the microorganism, biophotolysis, indirect photolysis, fermentation, and photofermentation. The biophotolysis process is similar to the photosynthesis process in that a water molecule is used by the microbial photosynthesis mechanism to transfer solar energy to molecular hydrogen. Scenedesmus spp., Chlorococcum spp., and Chlorella spp are considered to be algal strains that produce inefficient hydrogen cells using this route of hydrogen production. At the end of biophotolysis, two protons are released from the water molecule. Hydrogen is formed by the presence of hydrogenase or by the reduction in CO_2 [34] Indirect photolysis is the process in which many cyanobacteria and microalgae can be used to produce hydrogen from starch or glycogen. Two steps are involved in indirect biophotolysis: the synthesis of carbohydrates using light energy and the production of hydrogen from the synthesized carbohydrate using the cell's metabolism under dark and photodecomposition conditions [20][34]. Dark fermentation is considered the most promising technique for biohydrogen generation through biomass conversion. It has a net energy ratio equivalent to 1.9, while for steam-reforming methane, it is only 0.64. Hydrogen production can be carried out by anaerobic bacteria, which is grown in a substrate rich in carbohydrates or a dark substrate. In this method, in addition to obtaining hydrogen, acetic, butyric, lactic, and propionic acids are produced, as well as solvents such as ethanol, methanol, and acetone. Photofermentation involves the production of hydrogen from the conversion of organic substrates by photosynthetic microorganisms. In this process, anoxygenic photosynthetic bacteria, especially purple bacteria without sulfur, are capable of reducing H^+ ions to gaseous H_2 by reducing the power obtained from the oxidation of organic compounds. It is estimated that the yield of H_2 is around 9–49 gKg^{-1} of raw material [35].

3. Technical and Economic Evaluations

Climate change and global warming have garnered a lot of interest due to the need to reduce anthropogenic emissions of greenhouse gases, which is why the low-carbon economy contributes to implementing new and profitable energy systems [36]. Therefore, renewable energy technologies, such as solar, wind, hydro, biomass, geothermal, and hydrogen, have been introduced to generate electricity to overcome the current environmental crisis [37]. An official report from the International Energy Agency (IEA) states that the demand for the use of fossil fuels to generate electricity has begun to decrease since 2019 [38]. Hydrogen is a very interesting energy carrier with an energy yield of 122 KJg^{-1}, which is 2.75 times more than the fossil fuels [39]. Solid biomass in the United States was estimated to be able to supply 48 million metric tons (MMT) of hydrogen per year [40].

Research shows that the cost of renewable energy has an indirect effect on attitudes towards the use of renewable energy through the associated impact on the perception of ease of use and perceived usefulness [38]. To optimize processes, biomass must be as cheap as possible according to Klein and Lepage, as conditions have a significant impact on cost, including energy to increase temperature and pressure, electricity used for equipment or reactions, and catalyst type and cost. Cost estimates are also affected by external factors, such as fluctuating fossil fuel prices, variations in a given country's biofuel policies, and emissions [41][42]. Biomass gasification represents an effective and promising conversion technology for different energy carriers/chemicals, it has promising potential to offer high energy-conversion efficiency (in the range of 57 to 59%), lower energy costs, and decarbonization penalties (around 2.2 to 3.5 net), and present negative carbon emissions [36]. One of the key characteristics of biomass-based sources is their potential renewability. The overall efficiency of power generation from biomass is low (15–30%) [43]. The gasification life cycle cost was 35% lower than a single gas system. For systems with large biomass gasification, the capital cost is considered to be around USD 700/kW of hydrogen. The results show that forestry-residue-derived hydrogen is economically competitive (USD 1.52–2.92/kg H_2) compared to fossil-derived hydrogen [44].

Studies on the techno-economics of the fast pyrolysis of corn stover to hydrogen production demonstrate a production cost of USD 2.1–3.09/kg of H_2 [45]. The cost of producing hydrogen gas should typically be near to USD 0.3/kg H_2, which is equivalent to the cost of gasoline (USD 2.5/GJ) [39]. The biogas production cost of these types of processes should be considered. These expenditures, therefore, cause the production cost of hydrogen using biomass materials to be in the range of USD 1.2–2.4/kg, while natural gas reforming can produce hydrogen with a cost of less than USD 0.8/kg [41].

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