An overview of hydrogen-rich gas production from biomass by using thermal technologies

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Abstract. Studies on the production of hydrogen energy are at the forefront of reducing the dependence on fossil fuel energy. This work is a brief summary of hydrogen production systems especially in a supercritical water environment. Hydrogen production by the gasification of organic wastes in a supercritical water environment has been preferred more than other methods in recent years. In this study, the common biomass resources used for the hydrogen production have been explored, evaluating their properties. Moreover, catalysts which are used for the gasification of biomass have been presented in details. Therefore, a review of hydrogen production system by supercritical water gasification is summarized with the remarkable features.

1. Introduction
Energy is one of the indispensable elements of social and economic development and it has more important place in human life day by day. In parallel with the increase in the human population and technological developments, the need for energy is increasing rapidly, yet the reserves of fossil fuels, the most used energy source, are decreasing. Also, fossil fuel consumption causes air pollution, greenhouse gas effect, global warming problems and climate changes. Thus, it has been replaced by the search for alternative energy sources because renewable energy sources have not supplied the energy needs. From this point of view, hydrogen energy appears as an important alternative energy sources in solving these problems. Hydrogen energy, one of the most alternative energy resources, compared to other energy sources are; it is expressed as not being harmful to the environment, being able to produce the desired level of energy, and being scientifically developable with technological developments [1].

It is seen in Fig. 1, while alternative energy sources occupied 0.2% place among primary energy sources in 1973, today this rate has increased up to 2.2%. The use of fossil-based fuels has decreased to 36% in recent years, and the use of natural gas and alternative energy sources has increased compared to previous years.

The use of hydrogen-based energy sources meets three basic needs; (i) ensuring that hydrogen production processes are effective and cheaper, (ii) ensuring that new generation hydrogen storage systems are used in vehicles and other applications (iii) meets fuel cells and hydrogen-based systems to more reasonable prices [2].
2. Hydrogen Production Techniques
Hydrogen energy is an energy source that has the highest energy density among alternative energy sources and does not cause environmental pollution. The most important factors that distinguish hydrogen energy from other energy sources are that no harmful substances are released to the environment during production, it is light and it can be produced in a higher amount than renewable energy sources. Hydrogen is known as a chemical substance with a market where 40 Mt annual production corresponds to 50 trillion US dollars and it is mostly used in oil refineries. In the following years, the areas of use of hydrogen will expand and the need for their use in the automotive industry as fuel and other fertilizers and chemicals will increase due to the depletion of fossil fuels [3].

![Diagram of Hydrogen Production Process]

Figure 2 shows the processing of gas, liquid and solid fuels for hydrogen production [4]. Hydrogen production processes can be classified as follows:

**a) Fuel processes:** Hydrogen currently consists of fuel processing technologies. In fuel processing technologies; a hydrogen-containing chemical is converted into a hydrogen-rich vapor, such as ammonia or methanol. Sulphur, which is found in small amounts in most of the hydrocarbon fuels, causes the catalyst in the fuel process to fail operation. This problem is one of the biggest problems in the fuel process. For this reason, desulphurization methods are very important in fuel processes.
b) Hydrocarbon reformation: There are three basic techniques used to produce hydrogen from hydrocarbon fuels. These; vapor reformation is partial oxidation and autothermal reform. In hydrocarbon reformation processes, mostly hydrogen, carbon monoxide and carbon dioxide gases are produced. The endothermic vapor reformation process of hydrocarbons requires an external heat source. Steam reform does not require oxygen and has a lower operating temperature than partial oxidation and autothermal reformation. Hydrocarbon reformation produces 3:1 H/CO hydrogen, but this is the process with the highest emission among the three processes.

c) Steam reformation technique: The steam reformation method involves the catalytic conversion of hydrocarbon and steam to hydrogen and carbon oxides. Vapour gas reformation consists of synthesis gas production, methane water-gas cycle or gas purification steps. Impurified states of methane, natural gas and other methane-containing gases; can contain many hydrocarbons including ethane, propane, butane, and pentane. To produce purified hydrogen and prevent coking on the catalyst surface; the reaction should be carried out at 3:5 steam-carbon ratio at pressures up to 3.5 MPa at high temperatures [5].

d) Autothermal regeneration method: In the autothermal reforming method, exothermic partial oxidation method is used to increase hydrogen production and provide heat and endothermic vapor reformation. Basically, steam, oxygen or air is injected into the transducer. This situation leads to reformation and randomization of oxidation reactions [6].

e) Electrolysis: Electrolysis of water is the most important industrial process still used for hydrogen production today. It is estimated that the use of electrolysis will increase further in the future. Electrolysis of water is carried out based on the movement of electrons with an external cycle [7]. Catalysts are used to increase the current density and the electrolysis reaction rate. It is applied to the surface of platinum electrodes, one of the most used heterogeneous catalysts. Homogeneous catalysts are also used as electro-catalysts. Homogeneous catalysts are also more cost-effective than heterogeneous catalysts [8].

f) Plasma arc decomposition: Plasma is positively and negatively charged particles of an electron containing substance. Plasma also has the potential to be used to release high voltage electric current thanks to positively and negatively charged particles. The result of thermal plasma activity, methane gas converted into hydrogen and carbon black. While carbon black stays at the bottom, hydrogen in the gas phase accumulated at the top is collected [9]. Thermal plasma reactors have three electrodes connected to three phase voltages. Plasma gas is supplied to two of the three electrodes, while methane gas is supplied over the reactor. In this way, 100% pure hydrogen is produced with zero CO2 emission. Plasma arc decomposition can be categorized as “high temperature pyrolysis” [9]. In general, traditional hydrogen production methods and deficiencies can be classified as follows:
(I) Electrolysis of water, production cost is very high.
(II) Water photolysis and proper reactor construction are very difficult.
(III) Hydrogen production by thermal pyrolysis, moisture content should be limited, so dehydration is necessary for the pre-treatment of wet feeding.
(III) Hydrogen production reaction rate is slow and conversion efficiency is low by methane microorganism [10]. Therefore, hydrogen production systems that do not have harmful effects on the environment and at a low cost should be developed. In recent years, waste or lignocellulosic biomass has been used in potential hydrogen production to meet increasing energy demands. In addition, CO2 released from the combustion of fuels derived from waste biomass is used by plants during photosynthesis, which indicates a clean fuel system. Also, the use of lignocellulosic biomass may be a suitable option for producing H2 by gasification technologies. The European Directive 2009/28/EC are explained biomass as “biodegradable industrial and municipalities with biodegradable fraction of biologically sourced parts, waste and wastes from related industries, including agriculture (including plant and animal ingredients), forestry and fisheries and aquaculture defines them as waste” [11].
3. Hydrogen Production by Biomass Gasification

Gasification is a procedure that transforms organic or fossil fuels into carbon monoxide, hydrogen and carbon dioxide. This can be achieved by supplying oxygen to the system in a suitable stoichiometry proportional to the amount of carbon in the biomass at temperatures above 900 degrees.

Gasification of biomass, one of the renewable energy sources, ensures the syngas (H₂/CO) is released. The produced syngas is used as an intermediate in the production of ammonia and methanol as well as reducing energy transmission losses and reducing carbon emissions in commercial areas. Gasification also reduces landfill volume and converts it to energy [12].

Turn et al. discussed of hydrogen production from biomass using bed gasifier. Experiments were carried out to determine biomass ratio varies with the reactor temperature equivalence rate and steam parameters. In the research, characterisation of gas composition and efficiency were applied to measure hydrogen gas production rate by evaporating hydrocarbons. It was revealed that hydrogen yield potential was most sensitive to the equivalence ratio, from 0.37 to 62 g H₂ kg⁻¹ dry-ash-free biomass. It was obtained from dry and ash-free biomass at the rate of 0.0 equivalent to 128 g H₂ kg⁻¹. The highest yield was obtained as 165 g H₂ kg⁻¹ from dry biomass [13].

As shown in Table 1, the average total solid (TS) amount of crude domestic solid waste is in the range of 35.1 ± 2.1% (w/w), essential fatty acids (FA) in the range of 49.8 ± 2.2 mM, and pH ± 5.2 ± 0.1 [14].

| Features                        | Range         |
|---------------------------------|---------------|
| Total solids amount (% w/w)     | 35.1 ± 2.1%   |
| Volatile Solid (w/w)            | 26.1 ± 1.3%   |
| pH                              | 5.2 ± 0.1     |
| Total Volatile Fatty Acids (mM) | 49.8 ± 2.2    |
| Total N (gN/kg waste)           | 6.5 ± 0.46    |
| NH₄⁺ –N (gN/kg waste)           | 1.5 ± 0.1     |
| Fat (g/kg waste)                | 120 ± 13      |
| Carbohydrate (g/kg waste)       | 56.6 ± 5.7    |

The main challenging and limiting issue to perform gasification efficiently and improve its productivity is the release of tar. Tar is one of the most critical components and its removal is essential for synthesis gas (syngas: H₂ + CO) application. Recently, several researchers published the results from their experimental investigations on tar removal/reduction from syngas obtained in the result of gasification of biomass, municipal/household solid waste, plastics, etc. [15-22]. According to Tursunov et al., reduction or elimination of tars in the product gas after gasification (although necessary to achieve the gas purity required by its downstream processing) amplifies operation costs and reduces the energetic efficiency of the gasification process, because tars retain a significant share of the energy of the feedstock [16, 17, 19, 21]. Thereby, in order to improve thermal efficiency of biomass gasification system and controllability, it is important to convert tars into lighter gases during gasification process.

4. Supercritical Water Gasification

The high temperature water can be defined as where water exceeds the boiling point, specifically in the supercritical state. Also, supercritical water (SCW) provides more ions than water at ambient temperature. In SCW, high concentrations of H⁺ and OH⁻ ions can be attained and a suitable environment can be supplied for the reaction catalysed by acid or base. Water has a significant effect not only as a reactive reactant but also as a catalyst on the SCW reaction. Hence, the lightening of water in the SCW reaction is crucial for explaining catalytic mechanisms [23].

a) Catalysts: The catalyst is used to accelerate the reaction by decreasing the activation energy of the reaction. If the catalysts in solid, liquid and gas form are in the same phase as the reaction medium,
they are called homogeneous catalyst if they are in a different phase, they are called heterogeneous catalyst [24]. Nanocatalysts offer better conversion opportunities for biogas-converting reactions from biomass as they contain both metal nanoparticles and nanomaterials support to the challenges facing homogeneous and heterogeneous catalysts.

The transition of biomass into H2, CO, CO2 and CH4 via high-temperature (>700 °C) reactions with enough of oxygen and steam is defined as gasification. Supercritical water gasification (SCWG) is conducted at 374 °C and 22.1 MPa reaction environment. Hence, the major variation between SCWG and other thermochemical gasification systems are gasification environments, supercritical water or inert gas. Because of the supercritical water environment may act as ion provider. H+ and OH− ions may be produced in higher amount at supercritical conditions which in parallel ensures hydrolysis and pyrolysis reactions in better [25]. Regardless of the moisture content, the production of H2 by SCWG biomass makes it superior to other traditional thermochemical pathways.

While the biomass is gasified, in the first step, pyrolysis takes place in which the volatile matter and the wastes are removed. Subsequently, secondary reactions take place with volatile substances removing and in the last step, gasification is achieved [26]. Lignocellulosic wastes contain sugar cane and residues of sweet sorghum meal, rice husk, corn stalk, paper and cardboard. Thanks to the treatment of these wastes, the high hydrogen in it can be revealed. Hydrogen production by gasification of these wastes is much easier than fermenting. Because these wastes do not contain free sugar that can be easily fermented, they contain complex carbohydrate polymers (cellulose and hemicellulose) due to their structure. Therefore, hydrogen conversion of lignocellulosic residues is not easy in many cases. Therefore, the release of cellulosic and hemicellulose structures in lignocellulosic wastes can be accomplished with gasification, and the release of sugars in it, and thus the release of hydrogen easily [27].

Since cellulosic in the lignocellulosic biomass forms a complex and strong structure with hemicellulose and lignin, pretreatment is required to increase cellulose accessibility [28]. The liquid hot water (LHW) process is one of the pretreatment processes required to facilitate enzymatic hydrolysis of cellulose to glucose before ethanol fermentation. While LHW can remove hemicelluloses from the lignocellulosic structure, the addition of H2SO4 was more effective in the removal of hemicellulose [29, 30].

Glucose is a source of carbon that is easily biodegradable, found in most household waste, and can be obtained in abundance from agricultural waste. Theoretically, biological conversion of 1 mole of glucose yields 12 moles of hydrogen gas (H2). According to reaction stoichiometry, converting 1 mole of glucose to acetate gives 4 moles of H2/mol glucose, but only 2 moles of H2/mol glucose occurs when the butyrate is the final product. The highest hydrogen yield from glucose is around 2.0-2.4 mol/mol and this yield can be achieved through the gasification of wastes [31]. Singh et al produced hydrogen gas from potato starch, sugar cane, juice and whey. They found the hydrogen among the three substrates, 30 mL/mg of potato juice, 25 mL/mg of whey, and maximum hydrogen production of sugar cane juice as 45 mL/mg [32].

In another study related to how much acid used (HCl) increases hydrogen production; A maximum yield of 149.69 ml g−1 H2 at pH 7.0 and substrate concentration 15 gL−1 was obtained, which was found to be about 46 times higher than for raw corn waste. The reaction also conducted without acid, maximum hydrogen production was 7.6 mlg−1 H2 [33].

Lu et al. compared the catalytic performances of different oxide-supported Ni-based catalysts for SCWG of glucose at 400 °C and 23.5 MPa. They have shown that the efficiency of H2 production decreases in order for different catalyst supports: CeO2/Al2O3 > La2O3/Al2O3 > MgO/Al2O3 > Al2O3 > ZrO2/Al2O3 [34].

Waldner et al., conducted the study on the catalytic effect of Ni for woody biomass SCWG at 300-410 °C and 12-34 MPa operating conditions, and they revealed that the catalyst surface can be coated with some carbon deposit while full gassing is achieved [35].

Liu et al. modified the Ni/ZrO2 catalyst with MgO for glycerol reform supercritical water and stated that MgO addition to the catalyst significantly increased hydrogen production [36].
al. [37] discussed hydrogen production by supercritical water gasification of bioethanol with Ni/Al₂O₃ and Ni/CeZrO₂/Al₂O₃ catalysts (500 °C, 25 MPa) and revealed that hydrogen production improved 3-4 times compared to the catalyst-free environment. After the CeZrO₂ modification, the catalytic activity was drastically increased, and gassing was achieved completely without tar formation. CeZrO₂ not only induces the water-gas shift reaction, but also improves the hydrothermal stability of Al₂O₃ to achieve lower carbon monoxide production and higher hydrogen yield [37].

The effects of catalysts on hydrogen yield were explored in the study by Yan et al. In their study, the effects of operating conditions were examined with the reactor, the temperature range (420-500 °C), residence time (20-60 minutes) and feed stock amounts (2-10% by weight). The optimum H₂ yield was 13.34 mol/kg under optimum conditions, from non-catalytic experiments at 500 °C, 2% by weight feed stock and 60 minutes residence time. FeCl₃, K₂CO₃, activated carbon and KOH were used to study the catalytic effect of chemicals. The result showed that the highest hydrogen yield was obtained with a selectivity of 113.19% H₂ was 20.37 mol/kg and a total yield of 38.36 mol/kg with the addition of 5% by weight KOH. This shows that the addition of 5% KOH increases hydrogen yield by 58% [38].

5. Conclusion
In this study, a succinct review of hydrogen production technologies was presented. Biomass gasification process is one of the most important hydrogen production technologies, and can be improved gradually, resulting in higher hydrogen production. Also, supercritical water gasification of biomass offers a useful design in developing the catalyst complex for commercial operation. Hence, higher hydrogen production amounts can be achieved at lower cost, temperatures, and pressures by using different catalysts in supercritical water gasification of biomass in the future.

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