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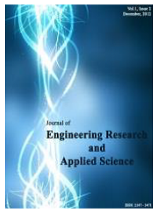

Hydrogen production from renewables: Biomass

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Abstract
The use of renewable energy sources is vital to secure the future of all humanity. Hydrogen energy produced from renewable energy sources has an important role in clean and sustainable energy production. One of the most important characteristics of hydrogen energy is that it does not leave any harmful residues that threaten nature and human life when burned. Hydrogen and renewable energy generation partnerships can provide some advantages to both technologies. Renewables can use hydrogen to storage overage production and supply energy on demand. Renewables can add reliability to the clean energy demands of hydrogen, providing that the production of hydrogen is in fact greenhouse gases emissions free and independent from fossil fuels. However, there are many subjects that need to be well-considered in determining the potential for this option. Some of those subjects are the cost of hydrogen generation from renewables, the suitability of hydrogen storage process, the efficiency of electricity generation from hydrogen, and the all efficiency of renewable energy and hydrogen system. There are also numerous different storage alternatives for renewables that show promise and may deserve more attention. This paper will analyze the present state of R&D for renewable-hydrogen integration from biomass in Turkey.

Keywords: renewable energy, hydrogen energy, biomass, gasification, Turkey.

1. Introduction

Hydrogen is not a primary energy source: it is an intermediate form of energy, or an energy carrier. Hydrogen does not exist in the earth as oil, coal and natural gas. The use of hydrogen in combination with renewable energy is intended to use it as an energy storage medium. Thus, the energy stored as hydrogen can then be used to produce the energy form needed. When dealing with hydrogen and renewable energy integration, both the generation of electricity from hydrogen and the acquisition of hydrogen should be considered [1-4]. There are some important properties that make hydrogen a good energy carrier and fuel. Hydrogen is transportable, is non-toxic, is lightweight, is storable could have a great energy density depending on its storage form, it produces non-toxic exhaust emissions (though it can generate NOx provided that air is used as an oxidant like in piston engines or gas turbines), it can be produced from many different energy sources and by various means, and it can be used in many sectors of the economy (thermal power, transportation and electrical power). Since hydrogen has a high energy density and it is flammable, it may pose risks to storage and also to safety [5-7].

2. Hydrogen as a clean energy carrier

Hydrogen is the lightest of the known elements and the most common in the universe. Hydrogen is not considered a primary source of energy in nature, since oxygen in water and in particular fossil fuels are combined with carbon and hydrogen. [3]. If hydrogen can be separated from its compounds to form molecular hydrogen, it becomes a very important and attractive fuel for the environment. [4]. It can be combined with oxygen and also burned in a fuel cell without forming carbon dioxide. It is a clean form of energy, such as electrical energy, and can only form explosive mixtures such as natural gas and butane when combined with air. [5-8].

Some advantages of hydrogen economy are as follows: [9-12]:

- *Security:* Vehicles using hydrogen as fuel reduce oil imports.
- *Sustainability:* Many renewable energy sources also have potentially abundant

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hydrogen.

- *The problem of climate change:* Carbon dioxide emissions of hydrogen powered vehicles are close to zero.
- *Air pollution in cities and districts:* Hydrogen can significantly reduce or completely eliminate exhaust emissions (GHG, hydrocarbons, NOx).
- *Economic:* The commercialization of hydrogen production and its use in fuel cells may play an important role in shaping global energy markets in the future.

In order for hydrogen energy to form an important vision for energy security in the future, considerable scientific and technical problems must be overcome. The hydrogen economy has considerable technical difficulties in terms of production, storage and handling. Innovations in the field of sciences and nanotechnology have shown a promising development to overcome many of the existing disabilities. Thermochemical pathways for conversion of biomass to biofuels are shown Figure 1 [2].

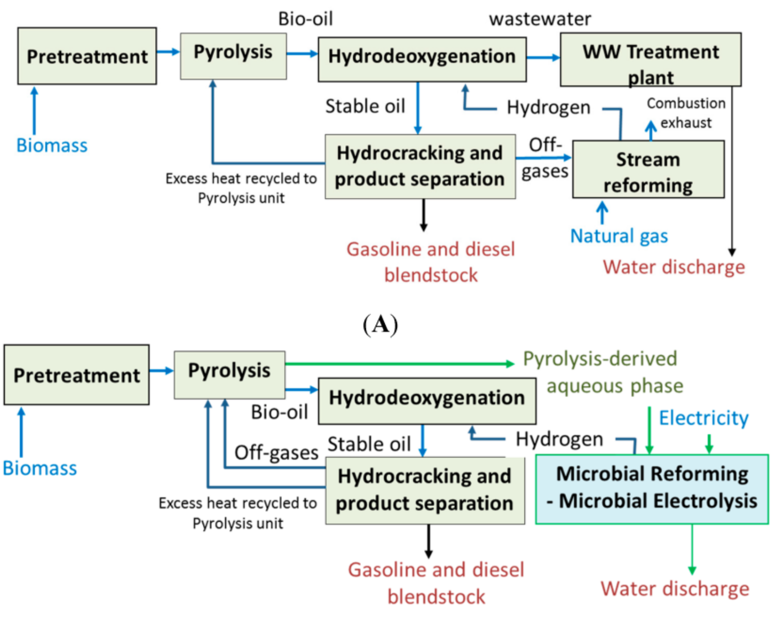


Figure 1. Thermochemical pathways for conversion of biomass to biofuels. (A) Conventional pathway using pyrolysis with natural gas as a source of hydrogen; (B) Alternate pathway integrating microbial electrolysis for hydrogen production [2].

3. Hydrogen production from biomass gasification

When biomass is formed, the carbon present in its structure is released into the air as carbon dioxide when burned, and the net carbon dioxide emission is zero. Therefore, it is very important for the environment to use biomass instead of fossil fuels to produce hydrogen [5].

Hydrogen can be produced from biomass sources such as agricultural residues, forestry and wood processing, urban waste, energy crops and animal waste [2, 3]. Today's technologies for converting biomass into molecular hydrogen generally include gasification or pyrolysis of biomass coupled following steam reforming. The essential conversion operations are oxygen-blown gasification, indirect heat gasification, and anaerobic fermentation [4, 5].

Innovative methods of converting biomass to hydrogen show that hydrogen cannot be produced at a competitive price, even when compared to hydrogen produced by natural gas. However, it can contribute to clean energy production and recovery from agricultural and domestic wastes the environmental effect of growing remarkable amount of biomass as energy crops including genetically engineered, high-yield crops, will most likely place important strains on natural resources and land availability. The cost of harvesting, collecting and transporting biomass is generally high. It would result in building quite lots of small biomass gasification factories without the economy of scale [6, 7].

3.1. Biomass gasification

Gasification is a chemical process that converts carbon-containing substances such as biomass into useful gaseous fuels and chemicals. Gasification is not only an energy conversion but also an important application in which some of the necessary chemical raw materials are produced in some industrial processes. Currently, gasification is not limited to solid hydrocarbons. Partial oxidation of methane gas is widely used in synthesis gas production. Recently, the gasification of heavy oil residues has gained popularity for the production of lighter hydrocarbons. Many large gasification facilities include coal or other hydrocarbons hydrogen and chemical raw materials are produced. Biomass pyrolysis to produce charcoal (tar) can be considered as the first large-scale gasification application. Gas mixtures obtained from the gasification process are as follows [5]:

18%–22% carbon monoxide (CO), 8%–12% hydrogen (H_2), 8%–12% carbon dioxide (CO_2), 2%–4% methane (CH_4) and 45%–50% nitrogen (N_2) making up the rest.

3.2. Gasification reactions

If the reactions that occur during the gasification process are examined under two main headings; the first is gas-solid reactions and the other is gas-phase reactions. It is also necessary to examine the Fischer-Tropsch synthesis reaction, an important method for the production of catalytic hydrocarbons from the synthesis gas.

3.2.1. Gas solid reactions

There are four main reactions in which solid carbon is converted to gas products and can be summarized in Table 1. The highly exothermic carbon-oxygen reaction is very important in providing energy to endothermic processes such as pyrolysis, drying and heating. The carbon-oxygen reaction also provides thermal energy to bonding and carbon-water reactions, which are important for gasification of charcoal to CO and H_2. Although the hydrogenation reaction is not as much as the carbon-oxygen reaction, it contributes energy to the endothermic H_2 production process.

Table 1. Gas-solid reactions

Carbon-oxygen reaction	$C + 1/2O_2 \leftrightarrow CO$	ΔH_R = - 110.5 MJ kmol^{-1}
Binding reaction	$C + CO_2 \leftrightarrow 2CO$	ΔH_R = 172 MJ kmol^{-1}
Carbon-water reaction	$C + H_2O \leftrightarrow H_2 + CO$	ΔH_R = 131.3 MJ kmol^{-1}
Hydrogenation reaction	$C + 2H_2 \leftrightarrow CH_4$	ΔH_R = -74.8 MJ kmol^{-1}

3.2.1. Gas phase reactions

Volatiles generated during pyrolysis are involved in gas-phase reactions to the extent that they are exposed to high temperatures. One of the two most important reactions to determine the final composition of gas products is the water-gas displacement reaction and the other is the methane formation reaction [5].

Water-gas displacement reaction:

$$CO + H_2O \leftrightarrow CO_2 + H_2 \quad \Delta H_R = -41.1 \text{MJ kmol}^{-1} \quad (1)$$

Methane formation reaction:

$$CO + 3H_2 \leftrightarrow CH_4 + H_2O \quad \Delta H_R = -206{,}1 \text{ MJ kmol}^{-1} \quad (2)$$

While water-gas bonding reactions increase the H_2 content in the synthesis gas, the methane formation reaction increases the amount of methane in the synthesis gas and contributes to the production of synthetic natural gas. Both reactions are exothermic and thermodynamically preferred at low temperatures.

3.2.3. Fischer-Tropsch Reactions

A series of hydrocarbons including diesel fuel can be synthesized by the Fischer-Tropsch reaction. Various dispersions of alkanes and paraffins are obtained in low-medium temperatures, high pressures and Fischer-Tropsch synthesis using transition metals as catalysts. Equation 3 shows the Fischer-Tropsch reaction;

$$(2n+1)H_2 + nCO \leftrightarrow C_nH_{(2n+2)} + nH_2O \quad (3)$$

3.2.4. Synthesis gas

The synthesis gas is essentially a mixture of carbon monoxide (CO) and hydrogen (H_2). In addition, the synthesis gas contains hydrocarbons such as carbon dioxide (CO_2), methane (CH_4), ethylene and ethane, other components from gasification such as propane and propylene, and nitrogen from gasification of the air. Synthesis gas is an important raw material for the chemical and energy industries. Many of hydrocarbons conventionally produced from oil can also be produced from synthesis gases [5-7].

The synthesis gas can be produced from gas coal, oil, biomass and various hydrocarbon derivatives. Synthetic gas produced from biomass is called biosynthesis gas in order to distinguish the synthesis gas produced from biomass and the synthesis gas produced from coal or oil. Gasification of biomass yields are hydrogen, water, carbon monoxide, carbon dioxide, methane, aliphatic hydrocarbons, benzene, toluene, small amounts of ammonia, hydrochloric acid and hydrogen sulfide [5]. To produce synthesis gas, carbon monoxide and hydrogen gas must be separated from this mixture. One of the important applications of the synthesis gas produced from biomass is hydrogen production in refineries. As natural gas prices are low, synthesis gas production is mostly made from natural gas today. However, since natural gas is also a consumable fossil fuel, the decrease in the amount of time will bring about price increase and synthesis gas production with gasification technology will gain the deserved importance again [2-7].

3.3. Advantages of biomass gasification technologies [6-8]

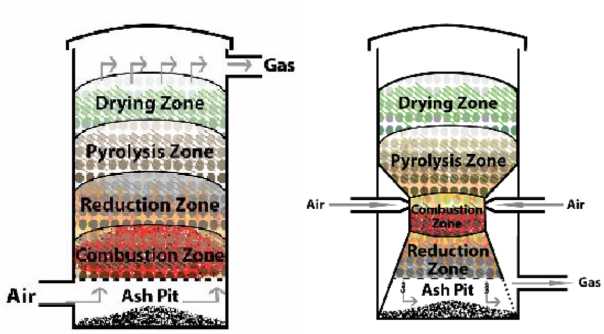
- Biomass gasification technology is open to development and can be designed to suit many designs and capacities as required.
- Gasification technology is also suitable and economical for applications smaller than megawatt.
- A gasification-based system, unlike wind and solar power systems, can generate electricity when required and also wherever required. Although large-scale thermal power plants and solar and wind systems are more site-specific, biomass gasification systems can be installed wherever biomass stock is available.
- In small-scale applications, production by gasification is more cost-effective than conventional diesel-based power generation**.**
- Socioeconomically biomass gasifier-based energy generation creates new jobs for the people of the region.
- Biomass is an energy source with a neutral emission of carbon dioxide. The use of biomass in gasification rather than fossil sources, especially for hydrogen production, is an appropriate method to reduce the adverse effects of climate change

3.4. Types of gasifiers

Three different gasifiers have been developed for fuels with different properties. These are downdraft, updraft and cross-draft gasifiers. The difference is related to the way the gas flows through the gasifier. In practice, the updraft type gasifier uses biomass with high moisture content. The gases obtained are suitable for incineration in a boiler, and the high it is not suitable for motor applications due to tar (5-10%). The rate of tar formed in the downdraft type gasifier is about 0.65-0.50%. The gasification of the biomass occurs in a closed, airtight system, at a slight suction or ambient pressure. The fuel column is fired at one point and the gas is vented from another point. Incomplete combustion of fuel with air biomass gasification is the beginning part. The process occurs in different regions. These include drying, distillation, reduction, ignition and ash zones [12,13].

3.4.1. Downdraft or co-current gasifiers

Downdraft gasifier, also known as co-current, is one of the most commonly used gasifier types. In downdraft gasifiers, the pyrolysis area is above the combustion area and the reduction area is below the combustion area. Gas flow and air move downward from the reduction and combustion zones. The term co-current is used because air moves downward in the same direction as the fuel. The downdraft gasifier is designed to pass through the area where the tar produced by pyrolysis is burned. As a result, the gas mixture at the outlet is relatively clean. Thus, the position of the combustion zone is a critical element in the downdrafts. The main advantage of this gasifiers being that it produces gas with a relatively low tar content suitable for gas engines. [12-15].



(a) (b)

Figure 2. a) Downdraft gasifier and b) Updraft gasifier

3.4.2. Updraft or counter-current gasifier

In updraft gasifiers (also known as counter-current), air enters from below the grate and flows upwards, whereas the fuel flows downwards. An updraft gasifier has distinctly defined zones for partial combustion, reduction, pyrolysis, and drying. The gas produced in the reduction zone leaves the gasifier reactor together with the products of pyrolysis from the pyrolysis zone and steam from the drying zone (see Figs. 2a-b). The resulting combustible producer gas is rich in hydrocarbons (tars) and, therefore, has a higher calorific value, which makes updraft gasifiers more suitable where heat is needed, for example in industrial furnaces. The producer gas needs to be thoroughly cleaned if it is to be used for generating electricity.

3.4.3. Cross-draft gasifier

In a cross-draft gasifier (Figure 3), air enters from one side of the gasifier reactor and leaves from the other. Cross-draft gasifiers have a few distinct advantages such as compact construction and low cleaning requirements. Also, cross-draft gasifiers do not need a grate; the ash falls to the bottom and does not come in the way of normal operation.

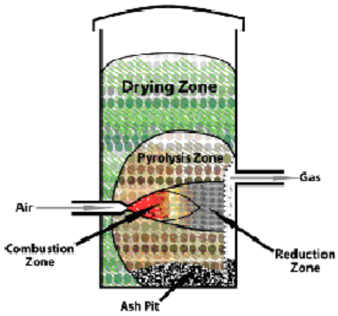


Figure 3. Cross-draft gasifier

4. Biomass energy potential in Turkey

Annual biomass potential of Turkey is approximately 32 Mtoe (million tons of oil equivalent). Total available bioenergy potential is estimated to be approximately 17.2 Mtoe. In 2017, Turkey's total biomass consumption was 4.8 Mtoe. According to the Republic of Turkey Ministry of Energy and Natural Resources "Biomass" report, Aegean, Black Sea, Central and Eastern Anatolia have good biomass potentials. However, the 2006 Corine land cover data show that land in Turkey consists of 42.35 % agricultural areas and 54.04 % forestry and semi-natural vegetation where almost 96%of the country's land can be defined as natural environment [16]. The increases in population, urbanization and industrialization have raised the use of non-intentional agricultural fields [17]. Figure 4 shows electricity capacity generation (MW) from crop residues in Turkey. As shown in these figure, there is a lot of biomass potential as a crop residues for electricity generation capacity in Turkey. In recently, the electricity generation from crop residues increased to 10 MW [2, 3, 18-20].

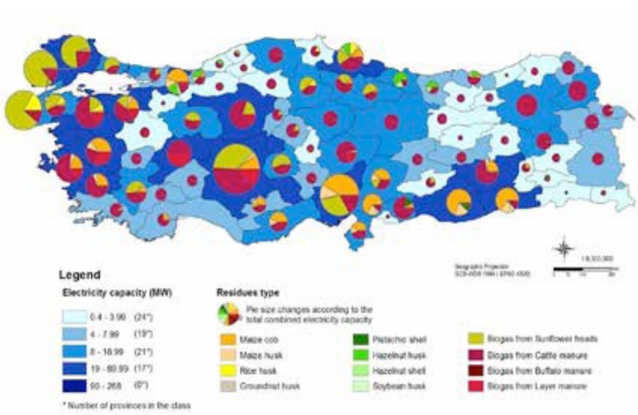


Figure 4. Electricity capacity generation (MW) from crop residues in Turkey [15].

5. Conclusions

Hydrogen appears to be a promising resource as an energy carrier. Hydrogen, which is produced from renewable energy sources, is considered as an environmentally friendly and clean energy source from production to usage. Besides, hydrogen develop the efficiency of renewable systems as a long-term energy storage and a high density energy carrier. However, some research and development is still required to improve hydrogen storage methods and to reduce production and storage costs. In addition, national and international policies should be developed and adopted to promote sustainable and renewable energy. Increasing climate changes and decreasing fossil fuel reserves require the adoption of the importance of new and renewable clean energy sources. Turkey has a very significant renewable energy potential and this potential has increased significantly over the last decade in particular. In this study, the importance of hydrogen energy production methods and the area of land available in Turkey has drawn attention to the suitability for production of hydrogen from biomass. Comparison and evaluation of micro and macro scale is considered to be very useful for hydrogen production methods peculiar to Turkey. Land cover classes change, though Turkey's biomass has a negative impact on the potential, the Turkish government is planning to increase the biomass production in Turkey and can make this biomass is a promising hydrogen feedstock. In addition to the presence of raw materials; technical, financial, environmental and social impact comparison, although it has a very low AP sorting, biomass gasification hydrogen production method shows that it is a very promising for Turkey.

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