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A comparative overview of hydrogen production processes

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ABSTRACT

Climate change and fossil fuel depletion are the main reasons leading to hydrogen technology. There are many processes for hydrogen production from both conventional and alternative energy resources such as natural gas, coal, nuclear, biomass, solar and wind. In this work, a comparative overview of the major hydrogen production methods is carried out. The process descriptions along with the technical and economic aspects of 14 different production methods are discussed. An overall comparison is carried out, and the results regarding both the conventional and renewable methods are presented. The thermochemical pyrolysis and gasification are economically viable approaches providing the highest potential to become competitive on a large scale in the near future while conventional methods retain their dominant role in H_2 production with costs in the range of 1.34–2.27 $/kg. Biological methods appear to be a promising pathway but further research studies are needed to improve their production rates, while the low conversion efficiencies in combination with the high investment costs are the key restrictions for water-splitting technologies to compete with conventional methods. However, further development of these technologies along with significant innovations concerning H_2 storage, transportation and utilization, implies the decrease of the national dependence on fossil fuel imports and green hydrogen will dominate over the traditional energy resources.

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1. Introduction

The introduction of greenhouse gases (GHG) into the atmosphere due to the continuous burning of fossil fuels, pose a serious threat to the global environment and consequent climate change [1]. In addition, the growing energy demand has imposed the increase of conventional fuel prices which are declining, exposing national economies which are dependent on their import. For the long-term treatment to climate change along with the reduction of the dependence on oil imports, future energy sources must meet the requirements of being carbon-free and renewable [2–5].

The expansion of the amount of renewable sources in the supply system is restricted by their intermittent and unpredictable nature. The increase in the contribution of renewable energy sources (RES), with simultaneous adaptation of production to demand, would not be feasible without the use of energy storage systems [6–8]. The major challenge for a storage device is to maintain the energy stored as long as needed and, when required, to be able to supply it as soon as possible. For this purpose, several studies in their effort to provide a clean and reliable alternative to traditional fossil fuels, which enjoy this particular feature, were led to hydrogen technology.

Unlike fossil fuels, hydrogen is not readily available in nature. It can be however produced from any primary energy source and to be then used as the fuel either for direct combustion in an internal combustion engine or in a fuel cell, only producing water as a byproduct [9–12]. As the only carbon-free and possessing the highest energy content compared to any known fuel (Table 1), hydrogen is globally accepted as an environmentally benign secondary form of renewable energy, alternative to fossil fuels [13–15]. A further advantage is that, supported by appropriate storage technologies, hydrogen can be utilized for domestic consumption as it can be safely transported through conventional means [16–19], and in order to be fed to stationary fuel cells, it can be stored as compressed gas, cryogenic liquid or solid hydride [20–22]. Currently the annual production of hydrogen is about 0.1 GT which is mainly consumed on-site, in refining and treating metals [23,24]. A small fraction is already used to fuel driving cars while in the near future applications including power generation and heating in residential and industrial sectors are expected [23,25,26].

The major problem in utilization of hydrogen gas as a fuel is its unavailability in nature and the need for inexpensive production methods [27]. A wide variety of processes are available for H_2 production which according to the raw materials used could be divided into two major categories namely, conventional and renewable technologies. The first category processes fossil fuels and includes the methods of hydrocarbon reforming and pyrolysis. In hydrocarbon reforming process, the participating chemical techniques are steam reforming, partial oxidation and autothermal steam reforming.

The second category accommodates the methods which produce hydrogen from renewable resources, either from biomass or water. Utilizing biomass as a feedstock, these methods can be subdivided into two general subcategories namely, thermochemical and biological processes. Thermochemical technology mainly involves pyrolysis, gasification, combustion and liquefaction, whereas the major biological processes are direct and indirect bio-photolysis, dark fermentation, photo-fermentation and sequential dark and photo-fermentation. The second class of renewable technologies regards the methods, which can produce H_2 through water-splitting processes such as electrolysis, thermolysis and photo-electrolysis, utilizing water as the only material input. The various pathways for hydrogen production are shown in Fig. 1.

Based on the extensive literature review, there has not yet been a comprehensive discussion, assessment and comparison of the operating principles along with the cost components relating to both H_2 production, storage, transportation and utilization. In this work a comparative overview of the major hydrogen production methods is carried out. The operating principles together with the technical features of the systems that comprise each technology are analyzed. Also, the raw materials used and the energy requirements relating to each method are reviewed. Finally, the associated production costs are provided and a qualitative comparison between the various production processes is undertaken, in order to evaluate the feasibility of such systems and their future contribution in the development of sustainable hydrogen economy.

In Section 2 the methods which produce hydrogen from fossil fuels are presented and discussed in detail, whereas Section 3 deals with renewable technologies. In Section 4, an overall comparison of the technical and economic aspects relating to each method is carried out and the issues concerning hydrogen storage, transportation and utilization are mentioned in Section 5. The conclusions are summarized in Section 6.

Table 1
Higher and lower heating values for various fuels (adapted from [104]).

Fuel	State at ambient temperature and pressure	HHV (MJ/kg)	LHV (MJ/kg)
Hydrogen	Gas	141.9	119.9
Methane	Gas	55.5	50
Ethane	Gas	51.9	47.8
Gasoline	Liquid	47.5	44.5
Diesel	Liquid	44.8	42.5
Methanol	Liquid	20	18.1

2. H_2 production from fossil fuels

There are several technologies of producing hydrogen from fossil fuels, the main of which are hydrocarbon reforming and pyrolysis. These methods are the most developed and commonly used, meeting almost the entire hydrogen demand. Specifically, up to date hydrogen was produced 48% from natural gas, 30% from heavy oils and naphtha, and 18% from coal [28–30]. Presently, fossil fuels retain their dominant role in the world hydrogen supply as the production costs are strongly correlated to fuel prices which are still kept to acceptable levels.

As in many fields of chemical and biochemical industries, membrane reactors also constitute new schemes for H_2 production from conventional fuels. A membrane is a structure which allows mass transfer under a gradient of driving forces (concentration, pressure, temperature, electric potential, etc) and is usually laterally much greater than its thickness [31]. In Fig. 2, the types of ideal continuous flows used in membrane-based separations are presented. Depending on the separation regime, membranes are classified into dense, porous and ion exchange. Based on their nature, the two major categories are biological and synthetic membranes, with the latter being distinguished in organic (polymer) and inorganic (ceramic or metallic). A suitable for H_2-production membrane should possess high selectivity for hydrogen, high permeability to operate with high flows and limited surfaces, and good chemical and structural stability. Therefore, a suitable (porous) support allowing the gases crossing, in combination with a barrier restricting the inter-diffusion in the metallic support are necessary parts for a composite membrane [32]. The common geometries of planar and tubular membranes are shown in Fig. 3.

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