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Comparison of thermochemical, electrolytic, photoelectrolytic and photochemical solar-to-hydrogen production technologies

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ABSTRACT

Hydrogen produced from solar energy is one of the most promising solar energy technologies that can significantly contribute to a sustainable energy supply in the future. This paper discusses the unique advantages of using solar energy over other forms of energy to produce hydrogen. Then it examines the latest research and development progress of various solar-to-hydrogen production technologies based on thermal, electrical, and photon energy. Comparisons are made to include water splitting methods, solar energy forms, energy efficiency, basic components needed by the processes, and engineering systems, among others. The definitions of overall solar-to-hydrogen production efficiencies and the categorization criteria for various methods are examined and discussed. The examined methods include thermochemical water splitting, water electrolysis, photoelectrochemical, and photochemical methods, among others. It is concluded that large production scales are more suitable for thermochemical cycles in order to minimize the energy losses caused by high temperature requirements or multiple chemical reactions and auxiliary processes. Water electrolysis powered by solar generated electricity is currently more mature than other technologies. The solar-to-electricity conversion efficiency is the main limitation in the improvement of the overall hydrogen production efficiency. By comparison, solar powered electrolysis, photoelectrochemical and photochemical technologies can be more advantageous for hydrogen fueling stations because fewer processes are needed, external power sources can be avoided, and extra hydrogen distribution systems can be avoided as well. The narrow wavelength ranges of photosensitive materials limit the efficiencies of solar photovoltaic panels, photoelectrodes, and photocatalysts, hence limit the solar-to-hydrogen efficiencies of solar based water electrolysis, photoelectrochemical and photochemical technologies. Extension of the working wavelength of the materials is an important future research direction to improve the solar-to-hydrogen efficiency.

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Nomenclature

A	area, m^2
C_{OX}	catalyst for oxidization reaction
C_R	catalyst for reduction reaction
I_S	total incident solar irradiance of the solar spectrum, Js^{-1}
h	Planck constant, 6.626×10^{-34} J s
L_I	local terrestrial solar irradiance flux, $J s^{-1} m^{-2}$
m_P	hydrogen production per unit time, mole s^{-1}
S	sensitizer
T	temperature, K
Greek	
η	efficiency
γ	photon frequency, Hz

1. Introduction

As the world's fossil fuel supply continues to diminish, the question of what will be the substitute is becoming more urgent. According to estimates by the World Coal Institute, coal, natural gas and petroleum may run out in 130, 60 and 42 years, respectively, at the present rate of consumption [1]. In addition, the usage of fossil fuels emits greenhouse gases and other pollutants that are worsening our environment and causing diseases. Therefore, cleaner energy systems must be developed and utilized. Nuclear, hydroelectric, geothermal and solar energy are all cleaner options. Nuclear fission energy has been well proven and is a fairly mature technology. But nuclear waste disposal challenges and unpredictable accidents such as Three Mile Island, Cheynobyl, and Fukushima are often cited by the public [2–5]. As to hydroelectric power, it is limited by the availability of waterways. River dams may also cause unpredictable influences on the aquatic ecosystems, fisheries, and river transport. Regarding geothermal, the usable energy is often located kilometres below the surface and there are concerns about seismic impacts. In comparison, solar energy is a safe, clean and unlimited resource [6]. However, the availability of sunlight on the earth's surface is intermittent because it is not available at nights and on rainy and cloudy days. The energy illuminated on various areas may differ significantly. Therefore, if the solar energy captured at daytime or in regions rich in sunlight can be stored, then the intermittency issue will be resolved. Storing solar energy in the form of hydrogen is a good option because hydrogen has a much higher energy density than most current fossil fuels [7–9]. The only product of hydrogen combustion is water, which can be recycled to produce hydrogen with solar energy. It was reported that the efficiency of a hydrogen internal combustion engine could be 10–40% higher than a gasoline engine. The hybrid electric motor and fuel cell vehicle could even be 2–3 times more efficient than an internal gasoline combustion engine [10]. Therefore, the solar plus hydrogen production from water route is widely viewed as a very promising option for a sustainable future.

Even in the conventional fossil fuel industry, hydrogen has an irreplaceable role in the upgrading of petroleum products. Also, hydrogen is a necessity for the production of fertilizers in the agricultural industry. Currently, oil upgrading and fertilizer production account for about 50% and 40% of the hydrogen consumption, respectively [11–13]. The fast rising need of hydrogen by modern agriculture and petroleum products will strongly advance the hydrogen economy [14,15]. However, the major hydrogen production methods of today are not clean because more than 95% of the global hydrogen is produced from fossil fuels, i.e., 48% from steam methane reforming (SMR), 30% from refinery/chemical off-gases, and 18% from coal gasification [16,17]. Water electrolysis accounts for less than 4%. Even this 4% is not fully clean because the electricity used for the hydrogen production is not fully generated from clean fuels. The usage of fossil fuels to produce hydrogen generates large amounts of greenhouse gases. Therefore, the future hydrogen production pathway from solar powered water splitting is a promising solution.

Engineers and scientists have developed numerous methods for hydrogen production from water splitting with solar energy, such as thermolysis, thermochemical, water electrolysis, photoelectrolysis, photoelectrochemical, photochemical, photodissociation, photodecomposition, photolysis, photodegradation, photocatalytic, photobiological, and hybrid methods. For conventional hydrogen production methods, such as steam methane reforming and coal gasification, there are also some investigations on supplying heat from solar energy rather than from burning of methane and coal, so as to decrease the greenhouse emissions. In this paper, only hydrogen production from water splitting is examined, i.e., the only feedstock to the hydrogen production plant is water and the products are hydrogen and oxygen. Since the input of many photobiological technologies is not water, e.g., acetic acid, photobiological hydrogen production will not be discussed in this paper. An objective of this paper is to review and compare the major water splitting technologies and categorize them according to the reaction mechanisms and engineering approaches. As there are many solar-to-hydrogen technologies and terminologies, and some of these terms are often used with no significant differentiation in public media, especially in non-academic publications such as newspapers, TV, and promotional pamphlets. To avoid ambiguity and confusion, this paper will examine and suggest some criteria to categorize the technologies when they are described and compared in the following sections. The criteria will address them from engineering and equipment perspectives rather than chemical reaction mechanisms viewed from the molecular level, so as to provide the key information for the industrialization of the technologies. The engineering approaches would be the focus for categorizing and comparing them from the aspects of apparatus, components, materials, equipment and layout of processes.