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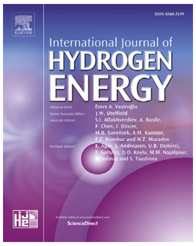

Na–O–H thermochemical water splitting cycle: A new approach in hydrogen production based on sodium cooled fast reactor

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Currently, the main energy options employed to maintain essential living standards, such as electricity, hot water and refrigeration, come from fossil fuels whose burning contributes to high environmental impacts like global warming. Then, the development of clean fuels is an important step towards sustainability. Hydrogen (H_2) can achieve such goal because its combustion mainly releases water. It can be obtained in different ways, including thermochemical cycles that consist of a sequence of chemical reactions to split water molecules into hydrogen and oxygen through a heat source at specific temperature conditions. Some traditional thermochemical processes available in the literature, like the cycles S-I (sulfur-iodine) and Cu-Cl (copper-chlorine) require temperature limits near to 900 °C and 550 °C, respectively. Additionally, the Mg-Cl (magnesium-chlorine) cycle can operate at temperatures about 450 °C while the U-Eu-Br (uranium-europium-bromium) cycle has its maximum operational temperature of 300 °C. In contrast to Cu-Cl, Mg-Cl and U-Eu-Br processes, which have relatively low and viable temperature ranges, there are thermochemical cycles that demand temperatures higher than 1000 °C. The low temperature requirement of a thermochemical process facilitates hydrogen production because it allows the use of many different heat sources like solar, nuclear and waste heat. In this line of reason, in a past work, it was proposed a new set of chemical reactions able to produce hydrogen, as a thermochemical process, which basic elements are sodium (Na), oxygen (O) and hydrogen (H). This system is named in this work as Na–O–H cycle and has potential to operate at temperatures about 400–500 °C or even below 400 °C. So, the aim of the paper is to present and evaluate a theoretical hydrogen production plant based on the Na–O–H cycle considering a Sodium Cooled Fast Reactor (SFR) as the heat source. The system was modeled in the Engineering Equation Solver (EES) software according to mass balances in addition to the first and second laws of thermodynamics. In this way, it was possible, for the first time, to estimate the amount of hydrogen obtained in this process. According to the results, the system can produce 1.321 kg/s of H_2, equivalent to 114 ton/day. This is a theoretical maximized value, because some aproximations were considered in the calculations. Additionally, the Na–O–H system has the potential for improvements through more research because it is in the initial stage of development.

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Introduction

Energy certainly is one of the most relevant issues nowadays. It covers several sectors of modern society like environment, resources, economics, decision making and international relations [1]. Besides that, energy is an indispensable resource to maintain some basic living standards such as electricity, hot water, air conditioning, food refrigeration and even different chemical products like those ones used as fertilizer and medicine [2].

Currently, the main energy resources employed to maintain these living standards come from fossil fuels such as coal, natural gas and oil. Despite all the benefits they can provide, fossil fuels are a natural resource and they will exhaust in some moment unless they are preserved. Besides that, burning fossil fuels to produce energy, in the form of heat or electricity, releases carbon dioxide (CO_2), a greenhouse gas that contributes to the global warming, a crucial environmental matter worldwide. In this way, the development of cleaner fuels and energy systems that do not require fossil resources are important steps towards sustainability. Additionally, it could be possible to reduce the economic dependency of nations on fossil fuels exporting countries [3]. One possible candidate able to achieve such goal is the hydrogen (H_2).

Hydrogen is the simplest and the most abundant chemical element in the universe [4]. It normally occurs aggregate with other elements like oxygen in the water, carbon in hydrocarbons, nitrogen in ammonia and other elements in biomass [5]. Because of that, hydrogen is not a primary source of energy unless it is splitted from these elements, in the form of H_2 gas, through an energy source, such as heat or electricity [4]. Such gas has many important applications including ammonia production (fertilizers), fuel cells to drive automobiles, a refining agent in metals processing, radiopharmacus and even fuel in power plants.

Moreover, hydrogen has some physical properties that make it an interesting fuel. They are [6]: easily flammable even in the presence of excessively air mixture; very low ignition energy; high ignition temperature; high diffusivity that facilitate the formation of a uniform mixture of hydrogen and air and if the fuel leaks, it rapidly disperses on air reducing unsafe atmosphere. Additionally, hydrogen has more energy content per kg than any other fuel. In contrast to these properties, hydrogen has very low density what demands a very large volume to provide the energy required, what reduces its energy per volume [6]. Besides that, hydrogen has some important environmental and economic advantages like [4]: energy safety due to reducing the consumption and importation of fossil fuels; less pollution and better air quality because burning H_2 produces water and near-zero carbon and nitroxides emissions (NO_x).

There are different processes or technologies to produce hydrogen described in the literature [4–9]. Each one of them is more suitable according to the type of energy available and the hydrogen source employed. Among them are steam reforming, partial oxidation and gasification that produce hydrogen by consuming natural gas, oil and coal, respectively [6], three non-renewable fossil resources. These technologies represent the majority of all hydrogen produced nowadays [10]. In contrast, hydrogen can also be obtained without using fossil fuels through thermochemical cycles or processes.

Thermochemical water splitting (TWS) or thermochemical water decomposition (TWD) cycles consist in a sequence of chemical reactions to crack water into hydrogen and oxygen using a heat source, including low-carbon energy options such as renewables and nuclear power plants (NPPs). Besides that, all the chemicals (reactants and products) involved in these processes can be recycled in a closed loop, except water which is the source of hydrogen [11]. Water is an abundant and renewable substance that can be obtained from many ways, including desalination processes. Because of these characteristics and the fact that they do not require fossil fuels, thermochemical cycles can be considered as a viable and environmental friendly route to produce hydrogen.

There are many thermochemical cycles under study in the literature [12,13], each one of them is more indicated according to the heat source or energy system available. Among the most recurrent and studied thermochemical processes are: S-I (sulfur-iodine) [14–21], Cu-Cl (copper-chlorine) [2,10,22–28] and Mg-Cl (magnesium–chlorine) [1,29–37]. Each cycle is composed by a well-defined number of steps represented by a single chemical reaction that occurs at specific conditions of pressure and temperature with chemical compounds of sulfur-iodine, copper-chlorine and magnesium–chlorine in its respective cycle. A same thermochemical process can have different configurations. The three-step or the four-step of the Cu-Cl cycle represent different forms of this process to achieve hydrogen production [5,28]. Thermochemical cycles can be evaluated according to many aspects such as economics, environment, safety, theoretical models and experimental analysis, as described in the following literature review related to different thermochemical cycles.

In relation to the S-I cycle, Bertrand et al. [14] evaluated safety aspects when a Very High Temperature Reactor (VHTR) is coupled to a thermochemical hydrogen production unit. The authors simulated some accidents like the rupture of pipes using the CATHARE2 code. Among the results, it was concluded that 100 m is a safety distance to avoid the effects of a hydrogen explosion against the nuclear reactor. On the other hand, Giraldi et al. [15] conducted a LCA (Life Cycle Analysis) study to determine how greenhouse gas (GHGs) emissions related to the life cycle of a hydrogen plant are affected by the different energy resources employed. The results show that nuclear power has potential to supply hydrogen in a sustainable way due to mitigation in GHGs. Zhou et al. [16] studied the absorption behavior, under different temperature and pressure conditions, when SO_2 (sulfur dioxide) reacts with hydriodic acid (HI) solution in a specific step of the sulfur-iodine cycle. Based on experimental results, the authors concluded that the absorption of SO_2 in HI rises as SO_2 partial pressure increases. Additionally, Park et al. [17] performed both energy and exergy analyses about the H_2SO_4 (sulfuric acid) decomposition reaction in the S-I cycle considering different pressure and temperature conditions. The results indicate that the exergy efficiency of the chemical reaction improves by increasing its temperature or reducing its pressure.

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