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Performance investigation of magnesium–chloride hybrid thermochemical cycle for hydrogen production

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ABSTRACT

In this paper, we study the yields of reactants in hydrolysis and chlorination chemical processes of the low temperature Mg–Cl hybrid thermochemical cycle to investigate the requirements of temperature, pressure and product ratios for individual reactors of the cycle. A simulation of both hydrolysis and chlorination processes is conducted using the Aspen Plus software. A Mg–Cl cycle is developed by considering the results obtained from the present simulations. Both energy and exergy efficiencies of Mg–Cl cycle are comparatively evaluated under varying system and environmental parameters, and an efficiency comparison of the cycle with other promising thermochemical water splitting cycles is conducted. The results show that, compared to other cycles, lower pressure, higher temperature and higher steam to magnesium–chloride ratio are required for full conversion of reactants in the hydrolysis step; and hence, lower temperature, higher pressure and higher chlorine to magnesium oxide ratio is required for full conversion in chlorination reactor. The efficiency results show that Mg–Cl cycle can compete with other low temperature thermochemical water splitting cycles and under influence of various internal and external parameters.

1. Introduction

The present energy need is met mainly by the conventional fossil fuels and their derivatives, and thus it results in many environmental issues such as acid rain, ozone depletion and global warming [1,2]. Some potential fuel production methods have been considered as an option to meet the energy demand in long term, however, extraction of unconventional fuels such as synthetic Fischer–Tropsch fuel from coal, biofuels or alternative options for transportation sector such as fully or partially battery-powered vehicles are either very energy intensive during production or bear high environmental impact [3]. A drastic reduction of emissions requires partly or fully phase-out of fossil fuels and switch to renewable based energy production. Hydrogen appears to be a potential candidate to replace hydrocarbon fuels, and solar energy is the most sustainable resource for producing clean energy.

Among above proposed potential/alternative options, hydrogen is the most promising option as secondary carrier of energy just like electricity which can be produced from any primary energy source. Hydrogen is the most abundant element in the universe, representing 90% of the universe by

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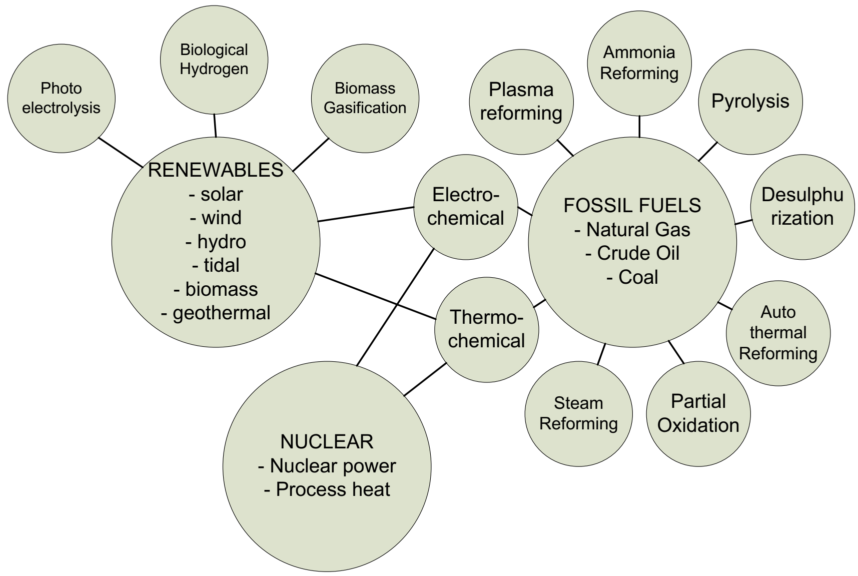

Fig. 1 – Hydrogen production methods based on energy sources (Modified from Ref. [6]).

weight, and the third most abundant in our planet. It is colorless, odorless, tasteless, and non-toxic under normal conditions and the lightest element with a density of 0.8988 g/l. Hydrogen can be produced by using conventional fuels and renewable. Hydrogen production from fossil fuels is a temporary option for cleaner production and utilization of energy. Cleanest way of producing hydrogen from fossil fuels is with CO_2 capture and storage which is possible with some novel system integration to conventional fossil fuel burning power plants. Integrated gasification combined cycles (IGCC) produce cleaner syngas which is eligible to produce hydrogen after some steps of chemical reactions at specific conditions such as chemical looping combustion and chemical looping hydrogen generations systems. These systems are expensive and still under research to validate long term performance. Production of hydrogen from renewable and waste heat from nuclear power plants is the cleanest and sustainable option with nearly zero emissions and offer reducing fossil fuel dependence in long terms [4].

Sustainable energy production is based on clean, non-polluting resources. Main energy sources for sustainable and clean energy production are mainly solar, hydro, ocean thermal, tidal, wind, biomass and geothermal. These resources can be used for clean energy production as well as hydrogen. Hydrogen production methods can also be separated into five main methods, namely electrochemical, thermochemical, hybrid, biochemical, radiochemical and photochemical [5]. Thermochemical water splitting method is the most promising among all other green methods for hydrogen production, since water is the most abundant natural resource containing hydrogen and can be succeeded in lower temperatures than that of direct splitting of water.

Hydrogen can be produced from both primary and secondary energy sources. Commercially applied methods generally consist of fuel processing and the required energy is provided from primary energy sources. Natural gas reforming and coal gasification are commercially available and still under research to improve efficiency of existing plants. Biomass based hydrogen production is still under development and not commercially available yet. Hydrogen production from secondary energy resources are exclusively by water electrolysis using electricity. Renewable based electrolytic or thermochemical hydrogen production is the most sustainable way which is clean, non-polluting and a promising alternative for fossil fuels. Renewable based hydrogen production is still under research [6]. Fig. 1 shows methods for hydrogen production based on primary, secondary and renewable energy resources.

In 1960s an interest in utilizing nuclear waste heat (up to 1573 K) for useful purposes like hydrogen production was developed, and more than 70 cycles were over time proposed [7]. The first multi-step process having a 50% efficiency was proposed by Marchetti and Beni, called Marc-1 [8] and a large number of other cycles (more than 280) were screened and proposed in Ref. [9]. Funk [10] discussed thermochemical water splitting processes for hydrogen production and a comparison of this methodology with fossil fuel based hydrogen production technologies. It is concluded that further studies are needed to be done in the future for a better interpretation of capital costs, thermal efficiencies and irreversibilities of such systems.

There are many known multi-step thermochemical water splitting cycles, however, only Sulfur–Iodine (S–I), copper–chlorine (Cu–Cl) and UT-3 cycles are under detailed research and development considering pure thermochemical water splitting processes. S–I cycle is a pure thermochemical process requires input temperature of 800–1000 °C to generate hydrogen. The cycle comprises three steps from which the first one is the Bunsen reaction producing two acids (HI and H_2SO_4) and separable with physical methods. Second reaction is HI decomposition to evolve hydrogen and the last reaction is H_2SO_4 decomposition producing SO_2, H_2O and O_2 requiring a solid catalyst [11]. S–I cycle steps take place at moderate temperature which can be obtained from nuclear waste heat