A review of thermochemical water splitting cycles

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Abstract

This paper presents the review of solar thermochemical technologies. Solar thermochemical processes are the most efficient alternative of the fossil fuel. It has been observed that the solar thermochemical cycles are the best way of hydrogen and syngas production out of all five thermochemical processes. Further, the classification and advancement of solar thermochemical cycles also have been discussed. This paper also compares the various solar thermochemical cycles in different aspect to project the most efficient cycle for the solar thermochemical fuel production.

Keywords: Thermochemical cycles, water splitting.

1 Introduction

We are living in a time when 80% primary energy demand of the world has been covered by the fossil fuels, in which petroleum oil covers the major part up to 32% [1]. Even though fossil fuel are the best possible and easily available (currently) option for energy, might not be very good idea in near future due to its close and heavy impact on environment. International energy agency (IEA) report states that to limit the global temperature by 2°C, the CO_2 emission (industrial and energy) has be dropped by 60% [2]. Thus the situation demand to implement the ideas such as carbon capture and development of more efficient non-renewable sources of energy to reduce the factors causing the harm to environment. It has been evident that the hydrogen can be the alternative fuel option for sustainable environment [3]. Hydrogen is the fuel of future because of its high energy density and it comes without harmful emissions. Further it also can be converted into hydrocarbon fuel and electricity.

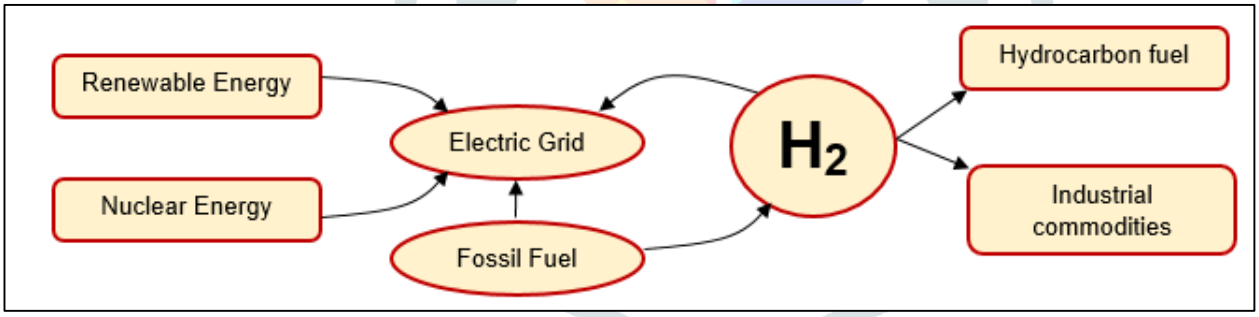

Figure 1: Hydrogen and its integration *[5]*

Hydrogen is the main element in the energy production chain as shown in the Figure *1* and it is also used for the production of industrial commodities such as ammonia, lime and ethanol [4]. Hydrogen is the integrating factor between all the industrial sectors and improve its electricity grid performance. Hydrogen can be produced from biomass and solar thermochemical processes as shown in the figure 2 and can be efficiently converted into electricity. The report of Hydrogen Council [5] states that by the year 2050, hydrogen energy can fulfil the 18% (78 EJ) of global energy demand.

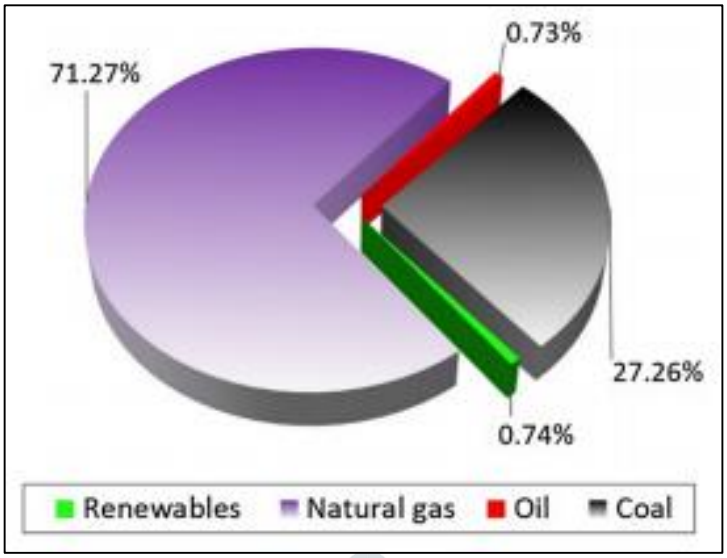

Figure 2: Global status of hydrogen production [6]

Figure 2 shows the current global status of hydrogen production. The record states that the most of the hydrogen is produced from the fossil fuel and just even less than 1% is being produced from the renewable resources [7]. It is worth noticing that the dedicated hydrogen production facilities produce the 85% of the hydrogen as primary product and 15% is produced as by product.

The development of solar thermochemical hydrogen production is sustainable and green fuel production model which will be beneficial for the environment in the long run. Thus to establish the hydrogen production technologies on the pilot scale and its integration with other technologies can lead to a better future. This review article presents an insight into the concepts, method and technologies of hydrogen production. It also slightly explores the economic condition of hydrogen production.

2 Hydrogen production

There are two way in which the hydrogen production methods have been classified known as material type and process type [8]. The material type segment contains the type of material used for the hydrogen production and process type segment describes the process which drives the energy. It has been suggested that the fossil based hydrogen production methods needs to be explored widely for the production of clean hydrogen fuel. The energy type used in the hydrogen production can be thermal, biological, mechanical, electrical or photonic.

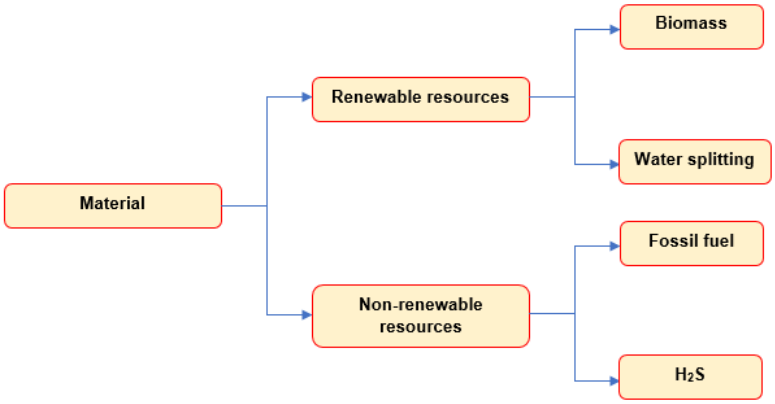

Figure 3: Materials based hydrogen production process classification

2.1 H_2 from biomass

In the biomass based hydrogen production, biomass is used as material source and falls in to the category of thermochemical process of hydrogen production. It has been seen that the water gasification process of hydrogen production poses significant advantages over other thermochemical methods of hydrogen production

due to its requirement of low operating temperature [9]. In this process occurs in the presence of water at the temperature of 374 °C and hydrogen is produced [10], [11]. Zhang et al [12] explored the biomass based hydrogen production and proposed a novel two-step process of hydrolysis-oxidation at the temperature of 160 °C and 85 °C respectively. This process gives the hydrogen as main product and methane and carbon mono-oxide as by products. It was observed that the conversion of hydrogen from biomass is mainly dependent on the catalysts thus the exploration of suitable catalysts in the reaction is high priority. The advancement of biomass based hydrogen production and the cost effectiveness of hydrogen and its application in the other technologies such as fuel cells is important. Archer and Steinberger-Wilckens[13] also contributed in the hydrogen production from biomass and their application in fuel cell technology. Since the biomass based process produced high pressure based syngas thus its integration with concentrated solar energy is recommended.

2.2 H_2 from H_2O splitting

H_2O (water) consist of two hydrogen molecules and one oxygen molecule thus high temperature based water splitting process are the best candidate for hydrogen production. There are five major categories for the water splitting based hydrogen production known as solar thermolysis, solar gasification, solar thermochemical cycles, solar cracking, solar methane reforming. Even though all of these technologies can produce hydrogen but the thermochemical cycles are the best candidate for hydrogen production. Here water is used as material input and solar concentrated energy is used as energy input and the process takes place in two or three step for hydrogen production. There are some other methods of water splitting such as electrolysis, sonochmical, photoysis[9]. Electrolysis is the simplest kind of process where the electric energy is converted into chemical energy by means of anode and cathode and produces the hydrogen [15]. The electrolysis can be performed at two temperature levels known as low temperature based (70–90 °C) and high temperature based (700–1000 °C). The high temperature based does not have any harmful emission thus presents to be better than low temperature based electrolysis [5].

3 Thermochemical cycles

Thermochemical Water-splitting are based on the concept of splitting water molecules into hydrogen and oxygen using intermediate reactions [15]. These processes are not dependent on the catalysts. The advantages of TWSCs are,

1. O2-H2 separation is not required
2. Operational temperature range is 500–1800 °C
3. No input electricity

Thermochemical cycles are divided into two parts, pure thermochemical cycles which are driven by thermal energy only and hybrid thermochemical cycles which are driven by thermal and one other form of energy such as electric or photonic energy. In hybrid TWSCs, heat (concentrated solar plants or nuclear reactors) and electricity and water are given as input and hydrogen is obtained as output in just one step [16]. Single step thermochemical cycles require very high temperature thus two or more steps cycles have been proposed which require lower temperature (2000 °C) [17].

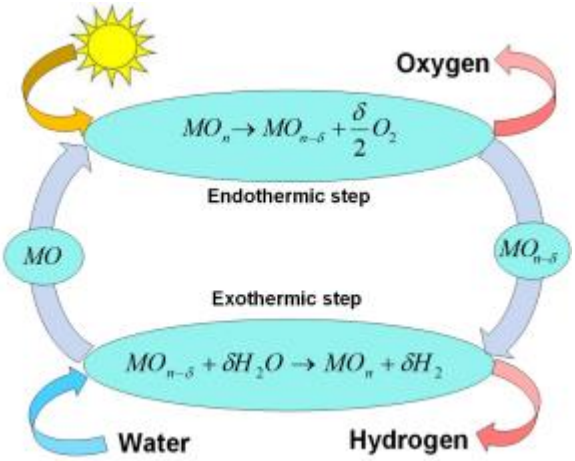

Figure 4: Two step thermochemical cycle

3.1 Two-step thermochemical cycles

Two-step thermochemical cycles first undergo reduction at high temperature and produce valance metal oxide. The operational temperature should be maintained at 1700–3000 K. Figure 4 shows the two-step thermochemical cycle where the metal oxide is reduced in endothermic step and then water is introduced to carry out oxidization in exothermic step to produce hydrogen. Many two-step thermochemical cycles are based on volatile and non-volatile metal oxides redox pair such as ZnO/Zn, Fe3O4/Fe, SnO2/SnO, CeO2/Ce2O3, Mn2O3/MnO, Co3O4/CoO, CdO/Cd, GeO2/GeO[18], [19]. It has been seen that the zinc based TWSCs have the thermodynamic superiority [20]. However, the ZnO/Zn have been tested on pilot scale yet due to some challenges such as slow kinetic reaction, back reactions and oxygen separation from zinc [21].

3.2 Three step thermochemical cycles

A three step cycle just two step cycle having the reduction reaction being replaced with two step reaction. This reduces the overall temperature of the cycle. The chemical reactions for three step thermochemical cycle are written as [22]:

$$H_2O + A \rightarrow 0.5O_2 + AH_2$$
$$AH_2 + B \rightarrow 0.5H_2 + AB$$
$$AB \rightarrow A + B$$

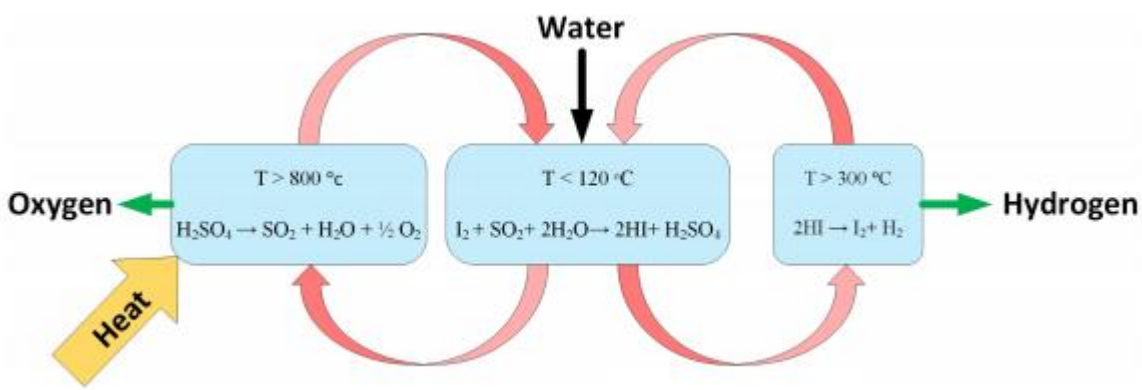

Figure 5: three step thermochemical cycle

The Sulphur-Iodine (S-I) cycle is the most common three step thermochemical cycle. Japan and Sandia National Laboratory (SNL) have widely explored the S-I thermochemical cycle[23] . The cycle efficiency was reported to be 52% upon integration with nuclear reactor. China tested the S-I cycle and produced 10 litr per hour of hydrogen in 2009 [24]. This process have three steps known as 1) Bunsen reaction, 2) sulfuric acid decomposition and 3) hydriodic acid (HI) decomposition. This cycle have some issues such as the operational temperature above 800 °C needed, corrosive reactions, Separation of HI from H2SO4.

4 Comparison of thermochemical cycles

The thermochemical cycles are in the development stage since past 50 years and yet have not been completed yet. These cycles are seen as the long term solution to the fossil fuel and environment problems.

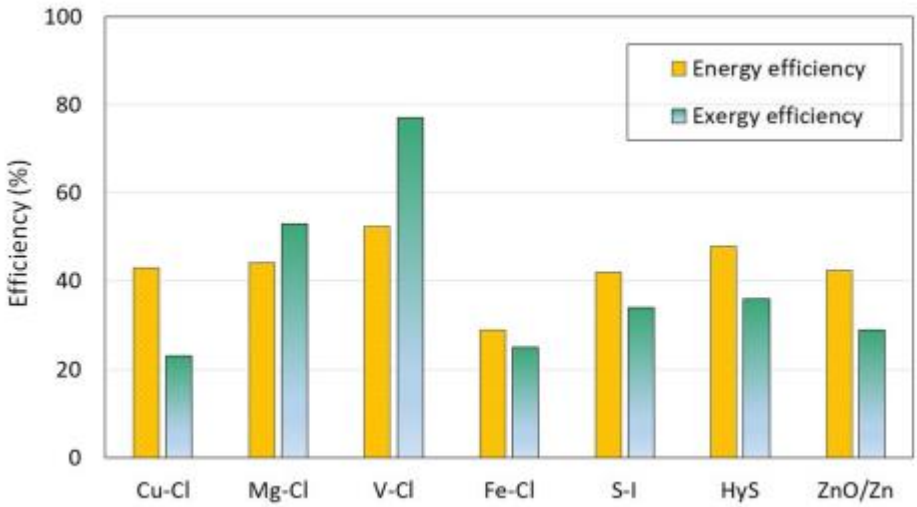

Figure 6: efficiency comparison [6]

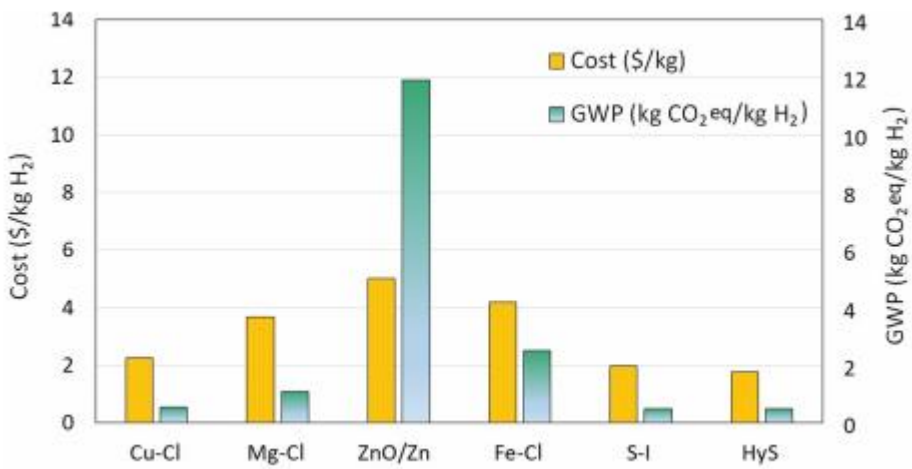

Figure 7: cost comparison[7]

Figure 6 shows the comparative evaluation of shown thermochemical cycles in terms of their efficiency. It can be seen that the V-Cl cycle has the higher exergy efficiency and e-Cl has the lowest. Figure 7 Shows the comparative evaluation of hydrogen production cost where ZnO/Zn cycle has the high hydrogen production cost of 12$ kg and the sulfurine based cycles have the lowest cost of 2$/kg H2.

5 Conclusions

The production of hydrogen is increasing slowly and it will reach its peak in time and it is expected that when that happens our reliability on the fossil fuel will decrease. Researchers around the world are investigating the thermochemical cycles and developing them. The efficiency of the thermochemical are being improved through efforts and the pilot scale testing of many cycles have been demonstrated. It has been seen that the V-Cl cycle has the high efficiency but hindered with some technical issues. Cu-Cl and Mg-Cl cycles are the promising in the field in terms of cost and efficiency.

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