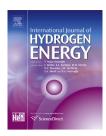


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Comparative assessment of various chlorine family thermochemical cycles for hydrogen production



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ARTICLE INFO

Article history:
Received 10 July 2015
Received in revised form
3 December 2015
Accepted 15 December 2015
Available online 25 March 2016

Keywords:

Cu-Cl

Mg-Cl

Fe-Cl

V–Cl Thermochemical

Hydrogen

ABSTRACT

This study deals with a comparative assessment of various chlorine family cycles, namely copper—chlorine (CuCl), magnesium—chlorine (MgCl), iron—chlorine (Fe—Cl) and vanadium—chlorine (V—Cl) cycles, which are driven by heat and/or electricity. Hydrogen production through thermochemical and/or hybrid cycles can play a significant role in reducing greenhouse gas emissions and hence offering opportunities for better environment and sustainability. In this paper, we conduct energy and exergy analyses of the VCl cycle and examine both energy and exergy efficiencies of the cycle. We also undertake a parametric study to investigate how the overall cycle performance is affected by changing the reference environment temperature and cycle operating conditions. The performance of VCl cycle are evaluated and compared with CuCl, MgCl and FeCl cycles. Furthermore, these cycles are discussed and compared with each other through their advantages and challenges. As a result, VCl cycle offers a good potential due to its high efficiency over 40% based on a complete reaction. In this regard, VCl cycle appears to be one of the most promising low temperature cycles. It may, therefore, compete with other low temperature cycles such as copper—chlorine.

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Introduction

Global increased utilization of fossil fuels for energy demand has resulted in critical environmental issues, such as acid rain, ozone depletion and global warming. In addition to these environmental issues, there are other significant concerns in the dimensions of energy, economics and politics. In this regard, research and development efforts on alternative forms of energy options have increase during the past a few

decades. The development of alternative energy options and fuels is nowadays top priority to ensure a sustainable energy outlook for future generations. Therefore, many scientists and researchers propose a large variety of solutions with the fact that one of the important solutions is implementing the hydrogen economy. Hydrogen economy offers a compelling vision of an energy future for the nation and the world that is at once abundant, clean, flexible and secure [1]. However, in today's hydrogen economy, hydrogen is mostly produced from fossil fuels (e.g., natural gas) through steam methane

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reforming (SMR), coal gasification and through electrolysis. Currently, SMR is the most widely used hydrogen production method, which is well developed and established for commercial use [2-4]. Also, it has some disadvantages, such as using extensive amount of electricity and releasing high levels of CO2. Therefore, it presents non-environmentally friendly solution to combat with these global problems [5,6]. Dincer has outlined the key technical and environmental issues of current hydrogen production technologies [7]. Hydrogen can be produced from several resources, including renewable resources. By developing hydrogen energy system, we can transfer energy consumption to the water cycle rather than the hydrocarbon-based cycle. It is important to highlight that hydrogen has substantial environmental benefits, if it is produced through renewable energy sources.

Many researchers undertake studies on new technologies for producing hydrogen in a sustainable way, which are more cost effective and efficient and release no/reduced greenhouse gas emissions. Alternatively, clean and efficient pathways for the production of pure hydrogen are water electrolysis and thermochemical water-splitting cycles, which are more sustainable than present hydrogen production processes. Numerous investigators [8-11] have published several reports and articles related to various proposed thermochemical cycles for hydrogen production over the past 40 years. Some of the authors [12,13] have investigated the specific aspects of thermochemical water decomposition processes and identified six low-temperature thermochemical and hybrid cycles. As a result of their studies, the copper-chlorine (CuCl) cycle appears to be the most promising cycle for thermochemical hydrogen production. Additionally, the authors discussed the low temperature magnesium chlorine (MgCl) cycle and they assessed its performance through energy and exergy analyses. They also concluded that the MgCl cycle can compete with the most-well known CuCl thermochemical cycle.

In recent years, various studies on hydrogen production through CuCl and MgCl cycles have been carried out by many researchers [12-18]. Many studies have been reported on hydrogen production through various thermochemical and hybrid cycles in the open literature. However, in the literature a few studies of them are discussed and compared each other. The main purposes of this paper, CuCl, MgCl, FeCl and VCl cycles are discussed and compared with each other for their pros and cons. Also, the performance of VCl cycle are evaluated and compared with CuCl, MgCl and Fe-Cl cycles.

Description of cycles

In the literature, most of the thermochemical cycles require process heat at temperatures of 1123-1173 K. Only a few cycles require process heat at below 1123 K. In this context, four low temperature chlorine family cycles are selected, can be coupled with renewable energy sources to produce clean and sustainable hydrogen.

The vanadium chlorine cycle (VCl)

The VCl cycle is a pure thermochemical cycle using only heat to produce hydrogen from water at a maximum process temperature of 925 °C. This cycle was initially studied by McRea and his team with the highest reported efficiency in the chlorine family cycles [10,19–21]. This cycle originally consists of one low-temperature, one moderate-temperature and two high-temperature reactions as follows:

$$\begin{split} &2VCl_2(s) + 2HCl(a) = > 2VCl_3(s) + H_2(g) \quad (298-393 \text{ K}) \\ &4VCl_3(s) = > 2VCl_4(g) + 2VCl_2(s) \quad (1023-1039 \text{ K}) \\ &2VCl_4(l) = > 2VCl_3 + Cl_2(g) \quad (473 \text{ K}) \end{split}$$

 $Cl_2(g) + H_2O(g) = > 2HCl(g) + \frac{1}{2}O_2(g)$ (1123–1198 K)

In literature, this cycle has several different chemical reactions to be performed successively to get a higher efficiency.

For example; Knoche and Schuster [20] and Knoche et al. [21] proposed the following two reactions for the last step of this cycle which is so-called: reverse Deacon reaction:

$$\label{eq:local_solution} \begin{split} 1/3 V_2 O_5(l) + C l_2(g) &= > 2/3 VOC l_3(g) + \frac{1}{2} O_2(g) \quad (1148 \ K) \\ \\ 2/3 VOC l_3(g) + H_2 O(g) &= > 1/3 V_2 O_5(l) + 2 HC l(g) \quad (398 \ K) \end{split}$$

The sum of above reactions is basically the last step of the VCl cycle. The Lewis and Masin [19] emphasized that the hydrogen production step of this cycle can be substituted with below reactions [20,21]:

$$\begin{split} 2VCl_2(s) + (2nH_2O + 2HCl)(l) &= > 2 \ (VCl_3 \cdot nH_2O)(s) \\ &+ H_2(g) \quad (393 \ K) \end{split}$$

2
$$(VCl_3 \cdot nH_2O)(s) = > 2VCl_3(s) + H_2O(g)$$
 (433 K)

In addition, Amendola [22] reported two variants of the cycle in his patent application. In his application, VCl3 is decomposed to VCl_2 and chlorine gas at about 798 K. In second step, chlorine gas from the first step is reacted with steam to produce oxygen and HCl. In the last step, HCl is reacted with VCl₂ to produce hydrogen and VCl₃. VCl₃ is ready to begin the cycle. The first one is the dry process which consists of three chemical reactions.

$$\begin{split} 2VCl_3(s) &= > 2VCl_2(s) + Cl_2(g) \quad (798 \ K) \\ \\ Cl_2(g) &+ H_2O(g) = > 2HCl(g) + \frac{1}{2}O_2(g) \ \, (\text{Co catalyst}) \quad (373 \ K) \\ \\ 2VCl_2(s) &+ 2HCl = > 2VCl_3(s) + H_2(g) \quad (573 \ K) \end{split}$$

The second one is the wet process which hydrogen is produced from an aqueous solution of HCl as given below.

$$\begin{split} &2VCl_3(s) = > 2VCl_2(s) + Cl_2(g) \quad (798 \ K) \\ &Cl_2(g) + H_2O(g) = > 2HCl(g) + \frac{1}{2}O_2(g) \ \, (\text{Co catalyst}) \quad (373 \ K) \\ &2VCl_2(s) + 2HCl(a) = > 2VCl_3(a) + H_2(g) \quad (303 \ K) \end{split}$$

The advantage of the wet process is that there is no need to remove HCl from O₂ since the products of the second step are

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