Nuclear Engineering and Design 256 (2013) 67–74

Contents lists available at SciVerse ScienceDirect

Nuclear Engineering and Design

journal homepage: www.elsevier.com/locate/nucengdes

Demonstration of the HI decomposition section embedded with electrodialysis stack in the sulfur–iodine thermochemical cycle for hydrogen production

Kyoung-Soo Kang, Chang-Hee Kim, Won-Chol Cho, Seong-Uk Jeong, Chu-Sik Park, Ki-Kwang Bae*

Hydrogen Energy Research Center, Korea Institute of Energy Research, 71-2 Jang-dong, Yuseong-gu, Daejeon 305-343, Republic of Korea

HIGHLIGHTS

- A HI decomposition section of SI process was constructed and operated.
- The electrodialysis cell achieved an effective level of HI concentration.
- Hydrogen production was approximately 10 L/h at pressurized conditions.

ARTICLE INFO

Article history:
Received 5 September 2012
Received in revised form
10 December 2012
Accepted 11 December 2012

ABSTRACT

Demonstration of the HI decomposition section (SEC3) embedded with electrodialysis stack in the SI (sulfur–iodine) process for hydrogen production was conducted in the pressurized conditions. The goal of the experiments was to verify that the SEC3 composed of the electrodialysis (ED), distillation and HI decomposition reactor can be operated properly and show the continuous hydrogen production. The ED embedded SEC3 operation at a pressurized condition was not yet disclosed. The automated process control and commercially available engineered components were used for constructing SEC3 prior to building fully integrated skids which will be composed of the Bunsen Section (SEC1), the H_2SO_4 decomposition section (SEC2) and SEC3. An electrodialysis stack was installed to concentrate HI in HIx solution and overcome the H_2O–HI azeotrope. A packed distillation column was used to obtain the concentrated HI gas. A Pt/SiO_2 catalyst was used to decompose the HI gas. The electrodialysis stack was able to concentrate HI over azeotrope composition effectively. The H_2O/HI molar ratio of the exit stream of the electrodialysis stack was approximately 4.2, which overcome the azeotropic composition of 5.2. These experiments demonstrated that hydrogen can be produced from a pressurized SEC3 of SI process, using an electrodialysis stack and engineered components. The hydrogen production rate was approximately 10 L/h at approximately 4.0 bar(g).

1. Introduction

The SI process could be an effective means of using nuclear heat or solar heat to produce hydrogen from water. The process is scientifically sound and technically feasible, with potentially attractive than other thermochemical cycles (Cho et al., 2009; Vitart et al., 2006, 2008; Murphy and O'Connell, 2012). General Atomics has advanced the Ispra Mark16 known as "GA process" from mid 1970s through the mid-1980s (O'Keefe et al., 1982; Funk, 2001). They provided important theoretical and experimental results which provide a firm basis for the process feasibility. Japan Atomic Energy Agency (JAEA) started the R&D activity on the SI process in the mid-1980s and verified that hydrogen and oxygen could be produced from water by operating a bench-scale SI process involving glassware at atmospheric pressure (Kubo et al., 2004; Xinxin and Onuki, 2005). JAEA also proposed an ED cell for exceeding the HI–H_2O azeotropic composition (Onuki et al., 2000). HYTHEC project was conducted in EU (Duigou et al., 2007). The objective of the project was to investigate the effective potential for massive hydrogen production of the SI cycle. In the project, flowsheeting, efficiency estimation, scale-up, safety and solar receiver study for sulfuric acid decomposition were conducted. SI research is also being carried out in China (Zhang et al., 2010a). INET (Institute of Nuclear and New Energy Technology) of Tsinghua University completed a demonstration of an ED cell embedded atmospheric pressure SI process (IS-10) in 2009. The ED cell exhibited stable operation, concentrating HI in the ED cell but the HI concentration did not go beyond the azeotropic composition (Zhang et al., 2010b). The hydrogen production rate reached 10 NL/h, while the oxygen rate kept at 5 NL/h. INET's work showed that the SI process was feasible

* Corresponding author. Tel.: +82 42 860 3445; fax: +82 42 860 3428.
E-mail address: kkbae@kier.re.kr (K.-K. Bae).

0029-5493/$ – see front matter © 2012 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.nucengdes.2012.12.005

and could be controlled. General Atomics, CEA and Sandia National Lab performed demonstrations of an integrated laboratory scale SI process involving engineered materials under pressurized conditions. Their research proved that the SI process could be constructed and operated with the commercially available components. In their study, the H_2PO_4 extraction process was adapted to concentrate HI (Moore et al., 2008).

Korea Institute of Energy Research (KIER) have also worked on the development of the SI process (Cho et al., 2009; Hur et al., 2011). In 2006, an integrated SI process experiment was conducted, confirming that hydrogen could be produced at atmospheric pressure from water. In 2008, a demonstration of an ED embedded SEC3 of the SI process was conducted and hydrogen was produced at a rate of 3.5 L/h. The HI feed rate into the ED cell was 10 cc/min with a $HI:I_2:H_2O$ molar ratio of 1:0.3:5.8. The cathode chamber of the ED cell successfully broke the azeotrope, with a H_2O/HI molar ratio in the outlet stream of approximately 4.6:1. Concentrated HI was fed into a HI distillation column; the HI vapor from the top of the column was in turn introduced into a HI decomposer filled with the Pt/Al_2O_3 catalyst showing a 21% conversion rate. Hydrogen was produced at a rate of 3.5 L/h at atmospheric pressure for approximately 5 h. Most of the apparatus was constructed of quartz with process line 1/4 inch. tubing.

In the SI process, three processes to overcome azeotrope are considered. Extractive distillation, electrodialysis and reactive distillation are the options for the HI decomposition section. Among them, the SEC3 integrated with an electrodialysis stack, a pressurized distillation column and HI decomposer was not yet demonstrated. The efficiency of the ED stack embedded SI cycle was evaluated by other researchers (Kasahara et al., 2004; Shin et al., 2012). The reactive distillation could be an alternative technology. HIx is distillated and decomposed at the same time to obtain hydrogen. The kinetics for reactive distillation is still relatively unknown (Richards et al., 2006). Moreover, the operating temperature of the reactive distillation column is around 300 °C which is relatively low temperature for HI decomposition. And the difference of HI conversion between the experiment data and theoretical value became wider as the temperature decreased (Shindo et al., 1984). The experimental data on the reactive distillation have not been disclosed. From the flowsheet analysis, the reactive distillation required 237–454 kJ/mol H_2 (Goldstein et al., 2005; Roth and Knoche, 1989; Brown et al., 2002). The ED embedded SEC3 required 103.5–584.8 kJ/mol H_2 (Kasahara et al., 2004). The energy requirement can vary with the thermodynamic models, heat recovery schemes and flow scenario. To delete the uncertainty of SI process, it will be meaningful to investigate the process feasibility by demonstrating the operation of the candidate process.

In this study, a simplified SEC3 was constructed and operated. The main units of the simplified SEC3 are ED cell, HI distillation column and HI decomposer. The HI concentration achieved by the ED cell, the HI decomposition catalyst, the distillation column, instruments and system control were tested before integrated operation of SEC1, SEC2 and SEC3. The results show that the ED cell successfully concentrated HI in the cathode and that H_2 gas was produced at a rate of 10 L/h under pressurized conditions. Minor changes in the pressure control, distillation column design and gasket selection are needed to ensure stable system operation.

2. Process description

Fig. 1 is a process diagram of the HI decomposition section, which will be integrated with the other sections of the SI cycle. The heavy phase from a Bunsen section is supplied to the cathode of the electrodialysis cell to concentrate HI. The concentrated HIx solution, which containing HI, I_2 and water, enters the distillation column at a concentration in excess of the azeotropic concentration. A HI decomposer, containing a platinum catalyst, decomposes HI gas to hydrogen and iodine. In the gas–liquid separator, hydrogen and HIx solution are separated, and a portion of the HIx solution is returned to the HIx decomposer. The remainder of the HIx solution is supplied to the anode of the ED cell, along with the raffinate of the distillation column. Iodine-rich HIx solution from the anode of the ED cell is returned to the Bunsen reactor. The preliminary flowsheet of an electrodialysis cell and membrane reactor embedded SI process can be found in the recent study (Shin et al., 2012). The thermal efficiency of the process was predicted as 39.4%. In the process diagram of SEC3 (Fig. 1) for demonstration, the membrane reactor for HI decomposition was replaced with a catalytic reactor. There has been a several works on the flowsheet of SEC3 (Kasahara et al., 2004; Shin et al., 2012; Guo et al., 2012). Recently, Guo et al. (2012) compared the 4 circuit designs in the HI decomposition section. They proposed a good flow scenario on SEC3 but more optimization study will be necessary for the more efficient process.

The HI decomposition process in this study has a simplified process design with low I_2 concentration in the HIx solution and no recycle stream (Fig. 2). The objective of testing of the simplified HI decomposition section was to demonstrate H2 production with commercially available engineered components, prior to building a fully integrated skids (SEC1, SEC2 and SEC3). The feature of the process was simplicity which facilitate easy operation and fast steady-state.

Consequently, we have used a HIx solution with relatively low iodine content for the demonstration of the simplified HI decomposition section. If an iodine recovery process is installed between the Bunsen section and the HI decomposition section, iodine content would be approximately 22–29 mol%. The iodine recovery process would be a melt crystallizer, solidifying the iodine in the HIx solution by cooling the solution. The solidified iodine would need to be melted before being returned to the Bunsen reactor. Table 1 shows the material balance for the simplified SEC3. In the material balance, the ratio of permeated quantities of water to H^+ was assumed to be 2.5 and concentration in EDC was assumed to be 30 mol HI/h. HI conversion in the HI decomposer was assumed to be 20% at 450 °C. The number of 2.5 for the ratio of permeated quantities of water to H^+ is a reasonable number in case of using Nafion 117 as membrane and atmospheric temperature operation. The concentration of HI in cathode outlet is also a reasonable value which can be achieved in previous researches (Chen et al., 2012; Yoshida et al., 2008; Kim, 2006; Hwang et al., 2003).

3. Demonstration set-up and operation

The SEC3 feed tank is made of glass lined carbon steel, and contains HIx solution at a $HI:I_2:H_2O$ molar ratio of 1:0.5:5.4. This HIx solution is fed to the anode and the cathode of the ED cell. The ED cell cathode effluent is sent to a glass buffer tank, while the anode effluent is sent to the Bunsen return tank. The stack consisted of 10 cells with 830 cm^2 (25.7 cm × 32.4 cm) active area per cell. Flow field plates were made of graphite. Electrode was activated carbon cloth. Au coated Cu plate was used for the current collector. Nafion 117 and PTFE were used as membrane and gasket respectively. A schematic diagram of the ED stack was illustrated in Fig. 3.

A diaphragm pump pressurizes the HIx solution up to 4 bar(g) and delivers the solution to the distillation tower. The distillation tower is 50 mm in diameter and 2.2 m long. The tower is made of solid tantalum with 2.5 wt.% tungsten and contains 6 mm diameter glass ring packing. The distillation tower consist of 4 parts: a reboiler (600 mm), a rectifying section (500 mm), a stripping section (600 mm) and a condenser (500 mm). The distillate from the