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An intermediate heat exchanging–depressurizing loop for nuclear hydrogen production

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ABSTRACT

Sulfur–iodine (SI) cycle should overcome many engineering challenges to commercialize and prove its feasibilities to compete other thermo-chemical cycles. Some critical issues such as structural material, harsh operating condition and high capital costs were considered obstacles to be actualized. Operating SI cycle at low-pressure is one of the solutions to actualize the cycle. The flash operation with over-azeotropic HI at low pressure does not require temperature and pressure as high as those in the existing methods as well as heating for separation. The operation in low pressure reduces corrosion problems and enables us to use flexible selection of structural material. We devised an intermediate heat exchanging–depressurizing loop to eliminate high operating pressure in the hydrogen side as well as a large pressure difference between the reactor side and the hydrogen side. Molten salts are adequate candidates as working fluids under the high-temperature condition with homogeneous phase during pressure changing process. Using molten salts, 2.20–4.65 MW of pumping work is required to change the pressure from 1 bar to 7 MPa. We selected BeF_2-containing salts as the possible candidates based on preliminary economic and thermal hydraulic consideration.

1. Introduction

Growth of energy demand is rapidly increasing nowadays, however a shortage of fossil fuel and a limitation of release for greenhouse gases are critical issues that should be solved in near future. Hydrogen is an appropriate energy carrier which could be substituted for fossil fuel used in various ways of energy consumption. Paradoxically, fossil resources are taking charge of about 95% of hydrogen production. Water splitting, therefore, could be an inevitable method for the massive hydrogen production.

The sulfur–iodine (SI) cycle is considered one of the most feasible processes among the water splitting thermo-chemical process for the economically competitive hydrogen production. General Atomic Corp. (GA) suggested the SI cycle coupled with high temperature heat from nuclear reactors (Norman et al., 1981). The SI cycle is composed of three main sections. Lee et al. (2008) suggested an optimal operation window considering operational temperatures and excess material flow expressed as follows from (1) to (3).

$$(5\text{–}7)I_2 + SO_2 + (13\text{–}15)H_2O \leftrightarrow [H_2SO_4 + 5H_2O] + [2HI + (4\text{–}6)I_2 + (6\text{–}8)H_2O] \quad (1)$$

$$H_2SO_4 + 5H_2O \leftrightarrow SO_2 + 6H_2O + \tfrac{1}{2}O_2 \quad (2)$$

$$2HI + (4\text{–}6)I_2 + (6\text{–}8)H_2O \leftrightarrow H_2 + (5\text{–}7)I_2 + (6\text{–}8)H_2O \quad (3)$$

The water is split by sulfur dioxide (SO_2) and iodine (I_2) into sulfuric acid (H_2SO_4) and hydroiodic acid (HIx) phases, expressed in Eq. (1) which is called the Bunsen reaction. The each product is separated and fed to the next processes. The Bunsen reaction undergoes exothermically and spontaneously. Lee et al. (2008) proposed the optimum temperature of the Bunsen section at 330–350 K. The operating pressure is different from each major research group, i.e. 4–40 bar (Brown et al., 2003; Gilardi et al., 2006; Sakaba et al., 2007; Lee et al., 2009). The second section, expressed in Eq. (2), is sulfuric acid decomposition section. The H_2SO_4 decomposition process composed of mainly two stages. The sulfuric acid which is fed from the Bunsen section is concentrated about 95% by distillation and evaporated at the first stage. The sulfuric acid is decomposed into sulfuric dioxide (SO_2) and oxygen (O_2) at 1073–1173 K. The sulfuric dioxide is recycled and fed to Bunsen section. The HIx from Bunsen reaction is decomposed as hydrogen (H_2) and iodine (I_2) expressed in Eq. (3) at 473–973 K. Several decomposition methods are suggested in the HI decomposition such as reactive distillation and extractive distillation (GA), electro-electro dialysis (JAEA), membrane reactor system (KIER), etc (Hwang et al., 2003).

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Nomenclature

C_p	heat capacity (kJ/kg °C)
D	pipe diameter (m)
k	friction coefficient
$\dot{m}$	mass flow rate (kg/s)
P	pressure (bar)
ΔP	system pressure difference (bar)
P_{drop}	friction pressure drop (bar)
Q	heat from reactor (MW)
T	temperature (°C)
ΔT	system temperature difference (°C)
v	linear velocity (m/s)
W_{pump}	pumping work (MW)

Greek symbol

ρ	density (kg/m^3)

2. Engineering challenges

The reactants used in the SI cycle are highly corrosive acids and the operating conditions (e.g., over 700 °C and 50 bar) are very harsh compared to commercial chemical plants. High pressure at the hydrogen side is required to mitigate the pressure difference between primary side (heat source side) and secondary (hydrogen plant side). The coupling of high pressure and high temperature condition adopted in the extremely strong acid environment induces significant problem to the structural health of the material. Ceramics or glass materials such as silicon carbide (SiC) or alumina (Al_2O_3) are considered one of the candidates, but SiC still has major difficulties especially the brittle and pitting problems. Though ceramic has highly strong enough strength compared to the iron, the brittle characteristic is critical especially under the high pressure condition. The sealing problem between each components caused by using ceramic reactor is a serious challenge. Using metal gasket causes a serious corrosion problem and using plastic gasket (e.g., Teflon) is not allowable over 300 °C (Connolly et al., 2009). It seems that, therefore, using metal reactor is the only choice for the highly pressurized vessel in the highly corrosive condition. Among the metal candidates, novel metal alloys were most relevant candidates, but their costs were too expensive to construct.

Though numerous studies have been conducted across the world, the SI cycle is still an engineering challenge to be actualized, such as:

- To guarantee the process material operable at high temperature (over 850 °C) and high pressure (over 50 bar) under highly corrosive environment.
- To maintain pressure difference between primary and secondary side as small as possible.
- To depend from the increase of capital cost caused by the use of novel materials.

In this paper, the authors describe the material problem and pressure effect on the SI cycle and provide a possibility of breakthrough by introducing low-pressure operation in SI cycle, which is adapting intermediate heat exchanging–depressurizing loop.

3. Pressure effect on the SI cycle

Goldstein et al. (2005) proposed the optimum operating pressure of each section to obtain maximum efficiency. Each section has different optimum operating pressure because of its thermodynamic characteristics. Most research agencies are targeting high pressure (over 20 bar) as their operating pressure considering the global efficiency of the cycle. Few results, however, were published conducted in the high pressure, either the whole process or individual section. Some estimation was found in the literature which is produced by simulation or calculation. The pressure effect on sulfuric acid decomposition was published by KIST in 2007. Heat demand and feed amount were calculated according to the pressure change by PRO/II simulation. The kinetic simulation of HI decomposition was conducted by Zhang et al. (2008). They calculated the homogeneous process using CHEMKIN III.

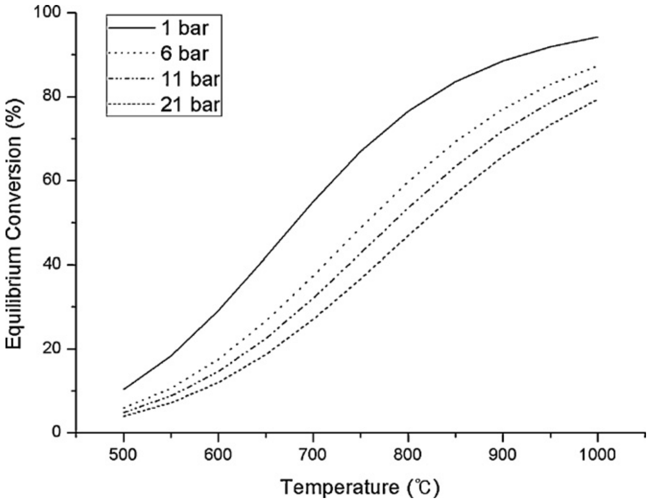

Fig. 1. Equilibrium conversion of SO_3 to SO_2 (Jeong et al., 2007).

3.1. Sulfuric acid decomposition section

The operating pressure of sulfuric acid decomposition is favorable in the lower pressure because the mole number of products is higher than feeds. The equilibrium conversion, therefore, is decreased as the system pressure is increased as shown in Fig. 1. For example, the conversion of SO_3 to SO_2 is changed from 55.03% at 1 bar to 27.03% at 21 bar at 700 °C condition. More feed, at the higher pressure, should be supplied to produce the same amount of product compared to the atmospheric condition. As shown in Fig. 2, at 21 bar, about 1.5 times more feed is needed at 21 bar compared to the 1 bar condition at 850 °C (Jeong et al., 2007). The reaction heat is independent of system pressure at the same temperature, but the heat which is required for heating and evaporating is increased

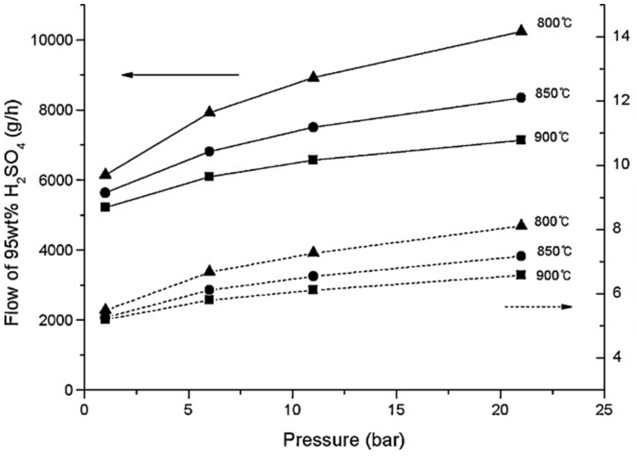

Fig. 2. Feed and heat required for H_2SO_4 decomposition to produce 1000 L/h H_2 (Jeong et al., 2007).