Sulfur Dioxide Separation and Recovery with Ionic Liquid Absorbents

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ABSTRACT

In Sulfur-Iodine and Hybrid Sulfur cycles, sulfur dioxide (SO_2) as a product of sulfuric acid decomposition at high temperature needs to be separated from gaseous mixtures and recycle to the next process. Depending on the hydrogen production cycles, pure sulfur dioxide is recycled into Bunsen reaction or electrolysis after oxygen separation. Absorption process with ionic liquids was suggested and studied to confirm the feasibility of continuous SO_2 separation process without an absorbent loss during absorption and desorption. High SO_2 solubility by ionic liquids were examined and [EMIm]$EtSO_4$ was tested as a candidate. Cyclic absorption and desorption by temperature swing was confirmed without any loss of solubility of 0.95 gmol SO_2/gmol IL at various desorption temperatures. Lab-scale SO2/O2 separation process was realized and resulted in pure sulfur dioxide recycle into following process was confirmed with preliminary data.

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INTRODUCTION

Hydrogen is a promising game changer to replace fossil fuels which have been used for over 2 centuries leading to industrial development in spite of environmental problems and global warming issues. Hydrogen should be produced from environment-friendly resources to avoid hydrogen being regarded as pollution site shift from fossil fuel at power generation site to fossil fuel at the hydrogen production sites. To be completely naive to environment, hydrogen should be produced from water with clean energy resources.

These days in order to produce hydrogen from water without emitting any carbon dioxide during production process, nuclear hydrogen energy was suggested as a heat source for the hydrogen

production cycle such as Sulfur-Iodine thermochemical cycle and Hybrid Sulfur cycle [1-4]. In Fig.1 Sulfur-Iodine and Hybrid Sulfur cycles are illustrated with sulfuric acid decomposition in common. During whole cycle, water is supplied and decomposed into hydrogen and oxygen in a closed loop.

To complete a full closed loop, the sulfur dioxide decomposed from sulfuric acid should be separated and recycled into next process without loss. Moreover, pure sulfur dioxide after separation process is required for the next process such as electrolysis and Bunsen reaction. In this study, an absorption process with novel absorbents is suggested to satisfy two requirements of complete SO_2 recovery with high purity.

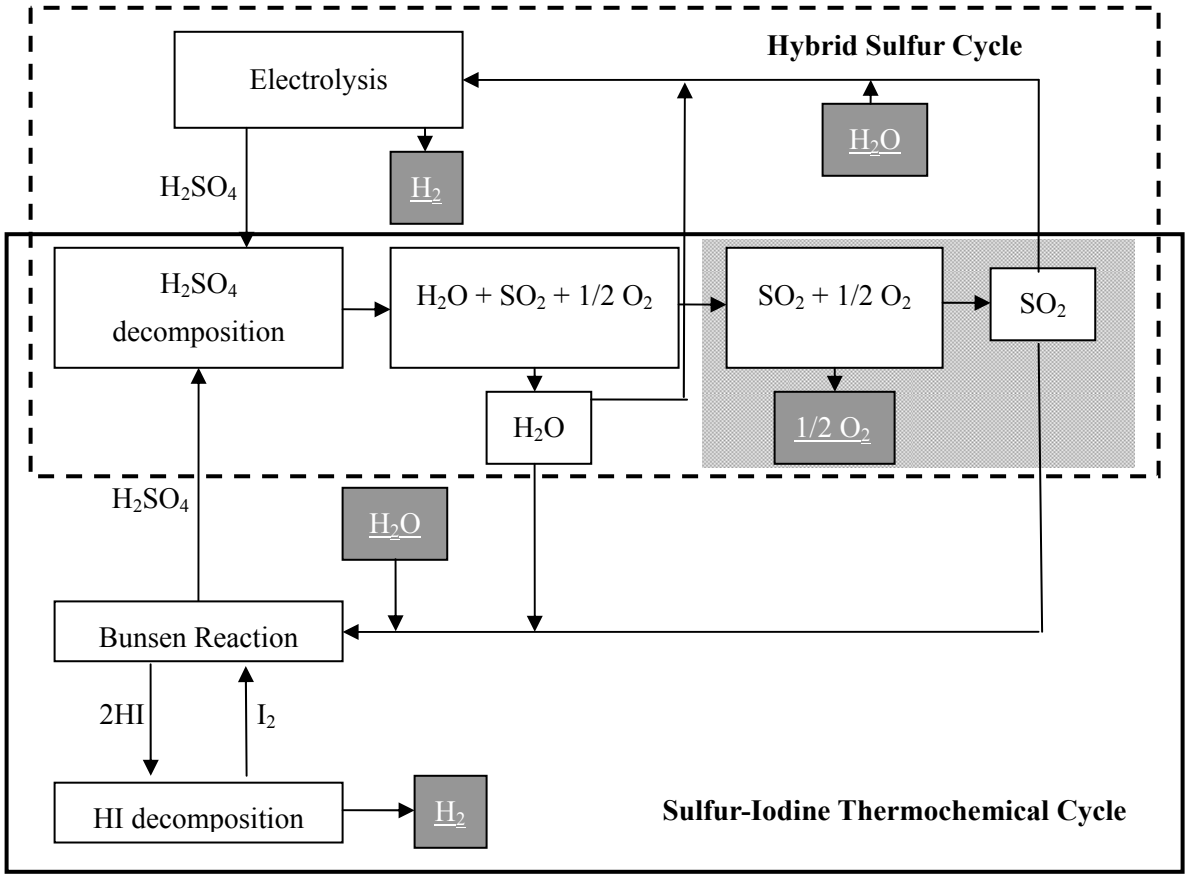

Figure 1. SO_2/O_2 separation process in Sulfur-Iodine Thermochemical Cycle and Hybrid Sulfur cycle

NOVEL ABSORBENTS

Ionic liquids are characterized as room temperature liquids with extremely low vapor pressures, high thermal and chemical stability. These characteristics are the most appropriate for SO_2 separation

and recovery due to low vapor pressure to high SO_2 purity as well as high thermal and chemical stability for temperature swing absorption process. The only requirement to be confirmed is high SO_2 absorbing capability and reversible absorption during temperature swing. From various candidating ionic liquids, after screening process with criteria of thermal stability, cost, and absorption capability [EMIm]$EtSO_4$ was selected and examined in detail.

In Fig.2 reversibly SO_2 absorption and high SO_2 solubility by [EMIm]$EtSO_4$ was verified even with different desorption temperatures. At 50 ^oC, [EMIm]EtSO4 absorbed 0.95 gmol SO_2 per gmol IL and desorbed SO_2 fully at high temperature. Depending on desorption temperature, the desorption speed is changed while full desorption was observed.

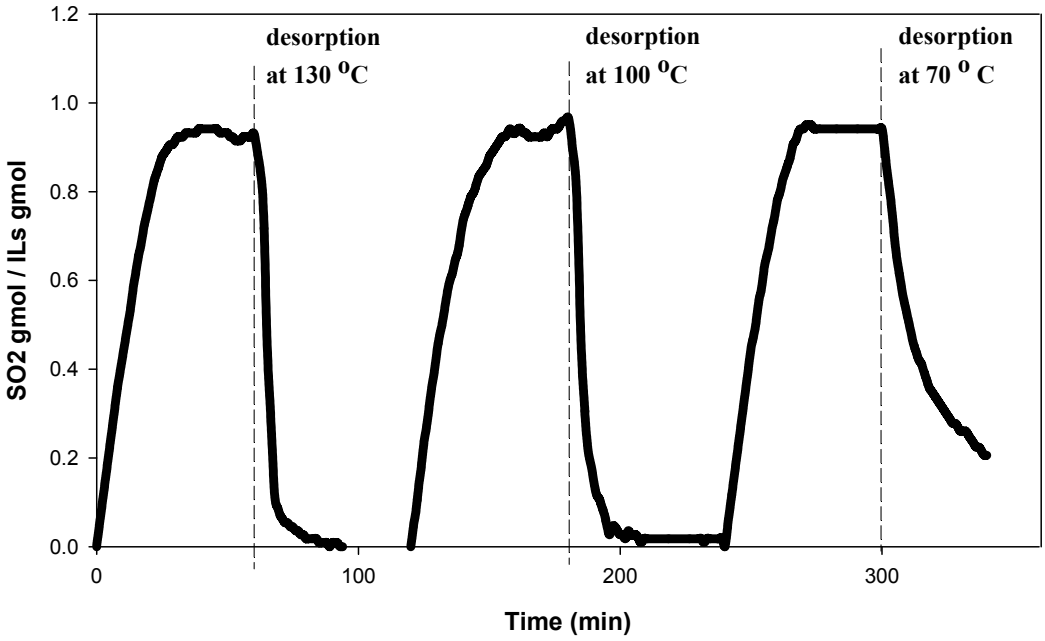

Figure 2 Cycle test of SO_2 absorption with [EMIm]$EtSO_4$ absorbed at 50 ^oC and 0.7 atm.

CONTINUOUS SO_2 SEPARATION FROM SO_2/O_2 MIXTURE

Additional requirement for SO_2 separating absorbents is the inertness with oxygen including negligible absorption and no reaction even at high temperature. To verify additional requirement and continuous process, bench-scale SO_2/O_2 separation apparatus was set up and operated. In Fig.3, the operation results were reported based on preliminary data. Absorption tower was operated at room temperature and temperature rise was observed from the heat of absorption reported as temperature range 20~40 ^oC.

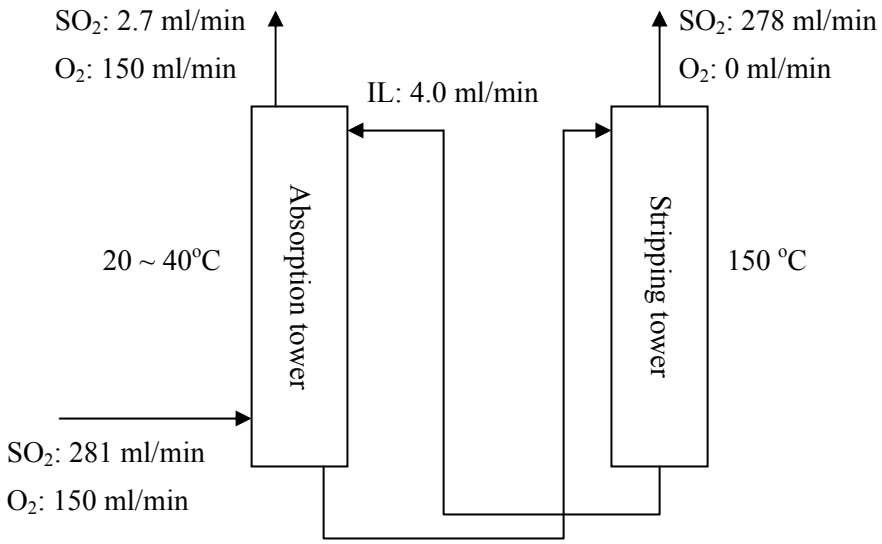

Figure 3 Lab-scale continuous SO_2/O_2 separation process with ionic liquid

After titration of gaseous outlet in the absorption and stripping towers, 278 ml/min SO_2 can be recovered even with 4.0 ml/min ionic liquid flow rate at 150 °C. During collecting stripped gas for titration, negligible oxygen content could be concluded from the observation of no bubble in the titration trap. Continuous SO_2/O_2 separation was demonstrated for a couple of hours without any disruption in the operation.

CONCLUSIONS

Novel absorbent for SO_2/O_2 separation process was evaluated from material properties to bench-scale process operation. Ionic liquids were appropriate SO_2 absorbents to satisfy pure SO_2 recovery for Sulfur-Iodide Cycle and Hybrid Sulfur Cycle which are suggested for hydrogen production by water splitting. From the absorption and desorption test, $[EMIm]EtSO_4$ was applicable to SO_2 separation process in that it is stable during temperature swing with constant SO_2 absorption capability. In bench-scale continuous process, 278 ml/min SO_2 could be separated and recovered in high purity with 4.0 ml/min ionic liquid flow rate. Moreover, the inertness of $[EMIm]EtSO_4$ with oxygen even at high temperature was confirmed from constant SO_2 separation capability.

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