Electronic Supplementary Information

Ionic Liquids-Mediated Claus Reaction: Highly Efficient Capture and Conversion of Hydrogen Sulfide

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Experimental Details

Materials: H_2S (99.99mol%) and SO_2 (99.99mol%) were supplied from Nanjing Messer Gas Co. Ltd.. Diglycol monomethylether (DGM) (99wt%) was purchased from Aladdin Chemical Reagent. 1-Butyl-3-methylimidazolium tetrafluoroborate ([bmim][BF_4]), 1-hexyl-3-methylimidazolium tetrafluoroborate ([hmim][BF_4]), 1-hexyl-3-methylimidazolium trifluoroacetate ([hmim][TfA]), 1-hexyl-3-methylimidazolium hexafluorophosphate ([hmim][PF_6]), 1-ethyl-3-methylimidazolium bis(trifluoromethane)sulfonimide ([emim][Tf_2N]), 1-butyl-3-methylimidazolium trifluoromethanesulfonate ([bmim][TfO]), 1-hexyl-3-methylimidazolium chloride ([hmim][Cl]) and 1-ethyl-3-methylimidazolium acetate ([emim][Ac]) were all obtained from Shanghai Chengjie Chemical Co. Ltd. with a purity of 99wt%. The ILs were dried and degassed at 80°C in vacuum for 48 h before use.

Procedure for the Claus reaction in ILs: The reaction of H_2S with SO_2 in ILs was performed in a 316 L stainless steel chamber (47.073 mL) which is equipped with a magnetic stirrer. The temperature of the reaction system was controlled by a water bath with an uncertainty of ±0.1°C. A known mass of IL was loaded in the reaction chamber and the air in the chamber was evacuated. 2 mmol of SO_2 was first injected into the reaction chamber. After the absorption of SO_2 in IL reached equilibrium, 4 mmol of H_2S was then injected into the reaction chamber and the pressure in the chamber was recorded online using a pressure transducer (Wideplus Precision Instruments Co. Ltd.) with an uncertainty of ±0.001 bar. The reaction lasted for 60 min. After the completion of reaction, the gas remained in the reaction chamber was swept by N_2 and introduced to aqueous solution of NaOH in case of leaking to the atmosphere. The conversion ratio of H_2S could be calculated from the residual gas pressure in the reaction chamber. Resulted solid sulfur was separated by centrifugation and filtration. The collected sulfur was rinsed with cold water, and then dried and weighed to calculate the recovery ratio of sulfur. XRD spectra was recorded on a Shimadzu XRD-6000 Instrument to confirm the structure of produced sulfur and melting point was measured using a Yice WRS-2 Instrument to evaluate the purity of produced sulfur. IL was dried under vacuum for at least 48 h and recycled for the next use.

Determination of gas solubility: Apparatus for measuring gas solubility is the same as that in our previous work (see the references of 14f~h in the main text). The whole device consists of two 316L stainless steel chambers whose volumes are 121.025 cm^3 (V_1) and 47.073 cm^3 (V_2), respectively. The bigger chamber, named as Gas Reservior, isolates gas before it contacts with the IL samples in the smaller chamber. The smaller chamber used as Equilibrium Cell is equipped with a magnetic stirrer. The temperatures (T) of both chambers are controlled by a water bath with an uncertainty of ±0.1°C. The pressures in the two chambers are monitored using two pressure transducers (Wideplus Precision Instruments Co. Ltd.) with an uncertainty of ±0.001 bar. In a typical run, a known mass (w) of IL sample was placed into the Equilibrium Cell and the air in the two chambers was evacuated. The pressure in the Equilibrium Cell was recorded to be P_0. Acidic gas from its gas cylinder was then fed into the Gas Reservior to a pressure of P_1. The needle valve between the two chambers was turned on to let the acidic gas be introduced to the Equilibrium Cell. Absorption equilibrium was thought to be reached when the pressures of the two chambers remained constant for at least 2 hours. The equilibrium pressures were denoted as P_2 for the Equilibrium cell and P'_1 for the Gas Reservior. The acidic gas partial pressure in the Equilibrium Cell was P_S=P_2-P_0. The acidic gas uptake, $n(P_S)$, can thus be calculated using the following equation:

$$n(P_S)=\rho_g(P_1,T)V_1-\rho_g(P'_1,T)V_1-\rho_g(P_S,T)(V_2-w/\rho_{IL})$$

where $\rho_g(P_i,T)$ represents the density of acidic gas in mol/cm^3 at P_i (i=1,S) and T. ρ_{IL} is the density of IL in g/cm^3 at T. V_1 and V_2 represent the volumes in cm^3 of the two chambers, respectively. Continual determinations of solubility data at elevated pressures were performed by introducing more acidic gas into the Equilibrium Cell to reach new equilibrium. After determinations, the gas left in the chambers should be introduced to an Off-gas Absorber containing aqueous solution of NaOH in case of the acidic gas leaking into the atmosphere.

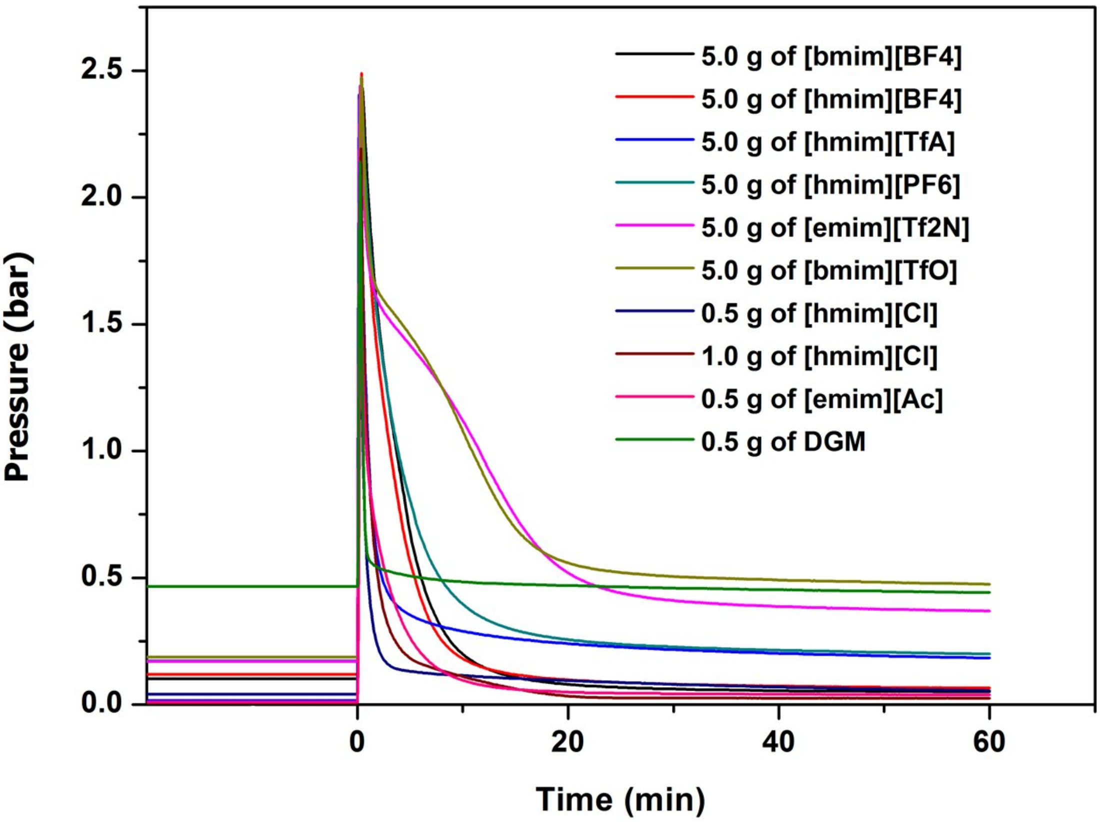

Figure S1. Pressure-time profiles of the reaction of H_2S with SO_2 in different ILs at 40°C. (Reaction conditions: 2 mmol of H_2S and 4 mmol of SO_2)

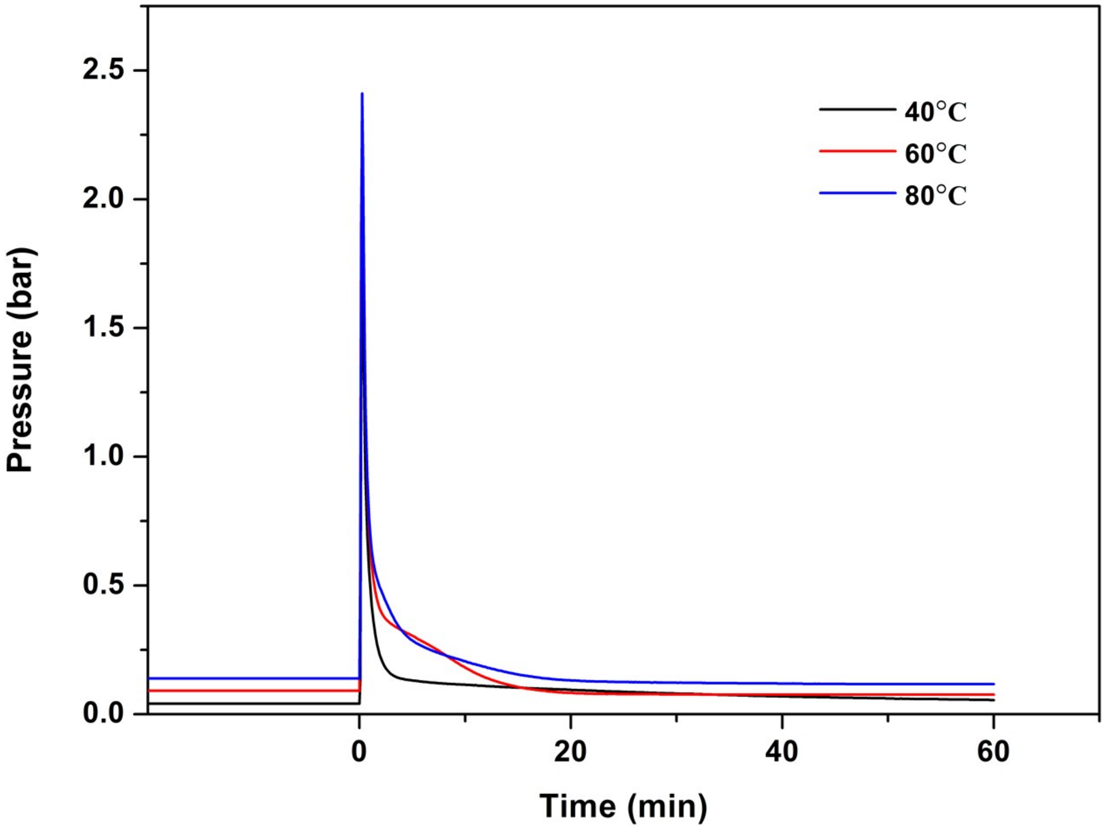

Figure S2. Pressure-time profile of the reaction of H_2S with SO_2 in [hmim][Cl] at different temperatures. (Reaction conditions: 0.5 g of IL, 2 mmol of H_2S and 4 mmol of SO_2)

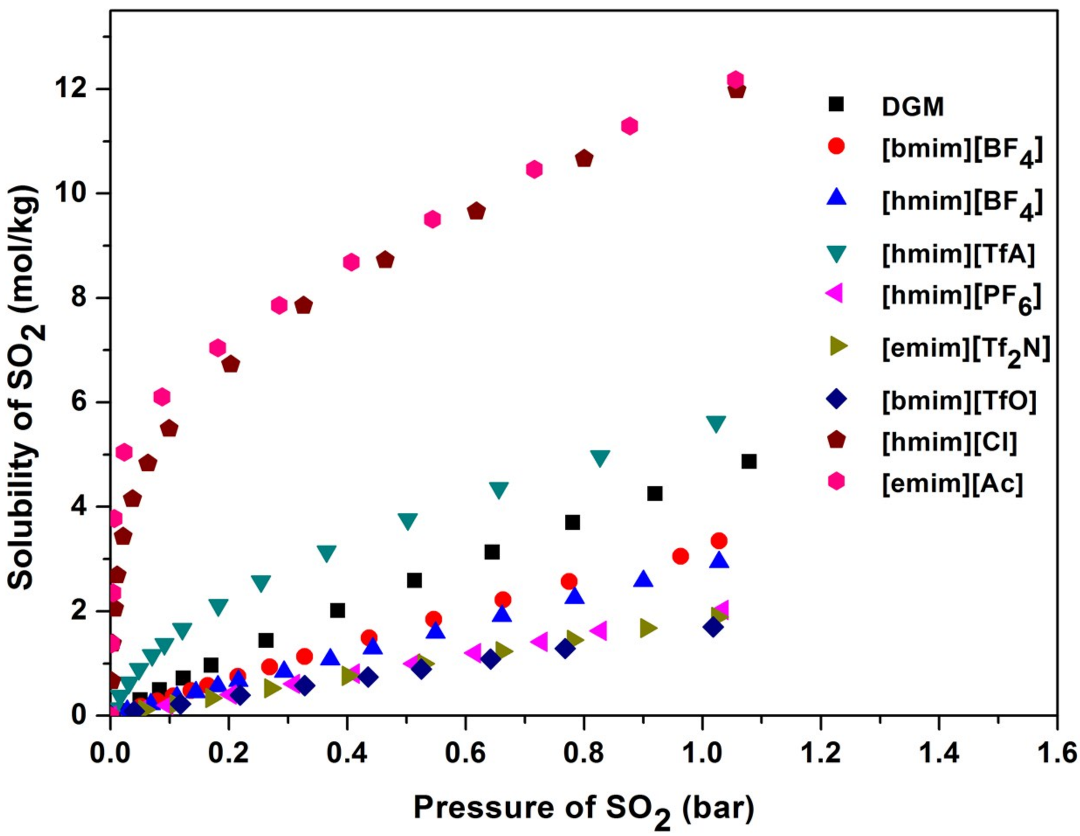

Figure S3. Solubility of SO_2 in different ILs at 40°C.

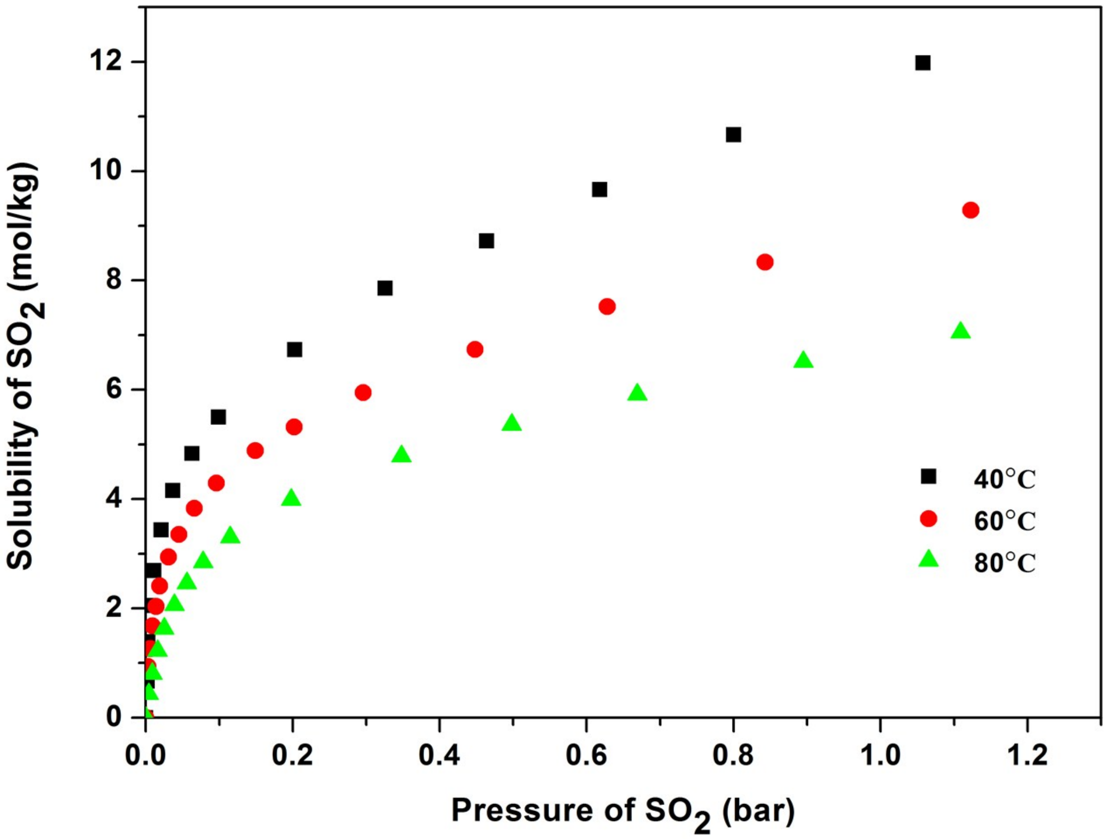

Figure S4. Solubility of SO_2 in [hmim][Cl] at different temperatures.

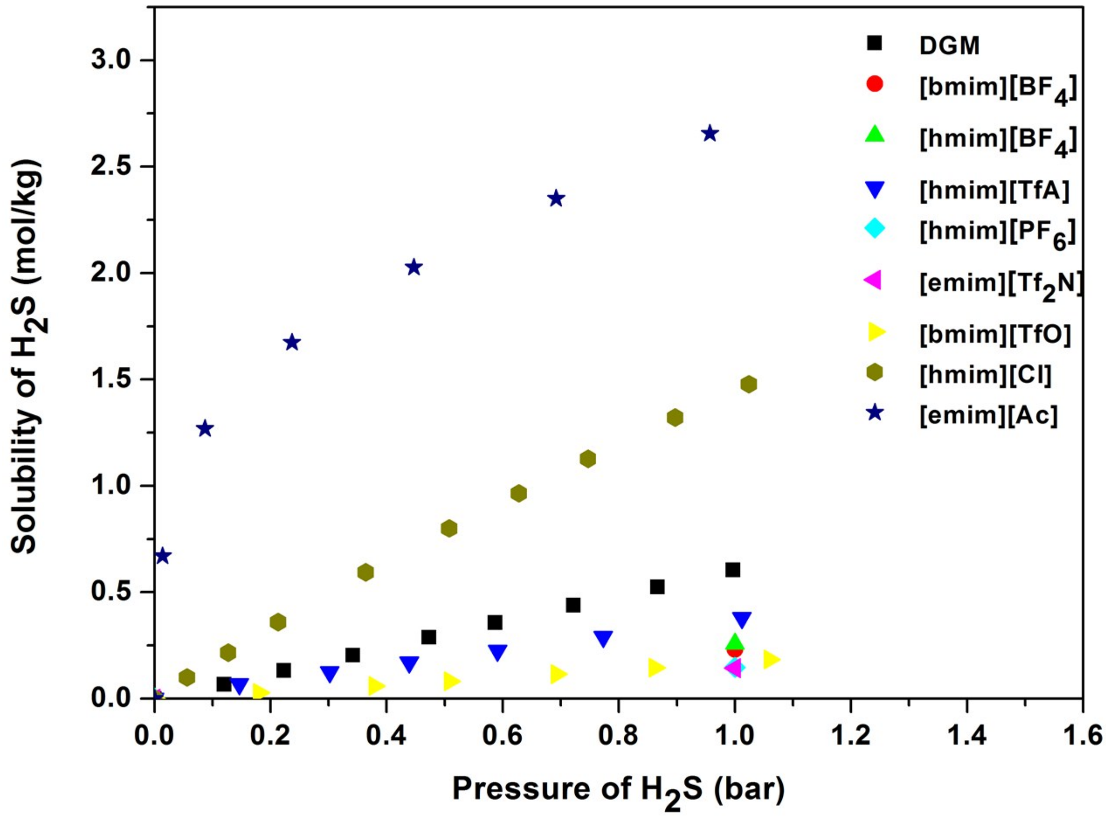

Figure S5. Solubility of H_2S in different ILs at 40°C. (The solubility of H_2S in [bmim][BF_4], [hmim][BF_4], [hmim][PF_6], [emim][Tf_2N] and [emim][Ac] were cited from references [14a], [14b], [14b], [14d] and [14f], respecitvely.)

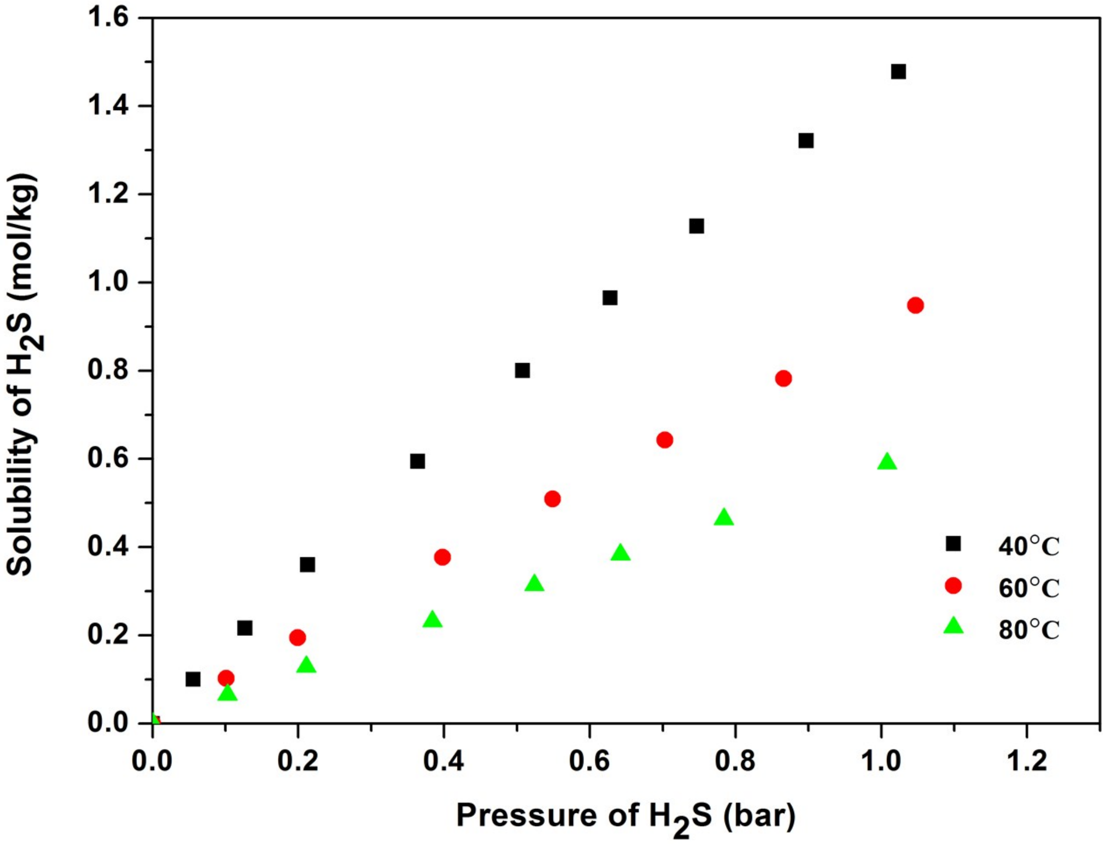

Figure S6. Solubility of H_2S in [hmim][Cl] at different temperatures.

Method for the calculation of conversion ratio of H_2S:

Assuming the residual gas pressure in reaction chamber is P after the completion of Claus reaction. The partial pressure of H_2S and SO_2 in gas phase are P_1 and P_2, respectively.

$$P=P_1+P_2 \qquad \text{(S1)}$$

Therefore, the amounts of H_2S and SO_2 in gas phase are:

$$n_{\mathrm{H_2S,g}} = \frac{P_1 V_\mathrm{g}}{RT} \qquad \text{(S2)}$$

$$n_{\mathrm{SO_2,g}} = \frac{P_2 V_\mathrm{g}}{RT} \qquad \text{(S3)}$$

where V_g is the gas phase volume.

If the effect of resulted sulfur and water on the solubility of H_2S and SO_2 in ILs is neglected, the amounts of H_2S and SO_2 in liquid phase are:

$$n_{\mathrm{H_2S,l}} = f_1(P_1) m_\mathrm{IL} \qquad \text{(S4)}$$

$$n_{\mathrm{SO_2,l}} = f_2(P_2) m_\mathrm{IL} \qquad \text{(S5)}$$

where f_1 and f_2 are the relationship between gas solubility (molality) and gas partial pressure. The expressions of f_1 and f_2 can be derived by correlating the solubility data in Figures S3~S6 using the dual-site Langmuir-Freundlich model. m_IL is the mass of IL.

The molar ratio of H_2S/SO_2 must follow the stoichiometric relationship (2:1), as a result:

$$n_{\mathrm{H_2S,g}} + n_{\mathrm{H_2S,l}} = 2(n_{\mathrm{SO_2,g}} + n_{\mathrm{SO_2,l}}) \qquad \text{(S6)}$$

Combining Equations S1~S6 would result in the total amount of H_2S remaining in the reaction chamber ($n_{\mathrm{H_2S,g}} + n_{\mathrm{H_2S,l}}$) after the completion of Claus reation. Therefore, the conversion ratio of H_2S (α_{H2S}) is:

$$\alpha_{\mathrm{H_2S}} = \frac{n_{\mathrm{H_2S,g}} + n_{\mathrm{H_2S,l}}}{n_{\mathrm{H_2S,0}}} \qquad \text{(S7)}$$

where $n_{\mathrm{H_2S,0}}$ is the initial amount of H_2S injected into the reaction chamber (4 mmol).