

## Investigation on Solubility of Hydrogen Sulfide in Molten Sulfur Using Iodometric Back Titration Method

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Received: Feb. 27, 2017 / Accepted: Apr. 29, 2017

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### Abstract

In order to conduct laboratory studies on composition and behavior of Claus-derived molten sulfur, the examined sulfur should contain dissolved  $H_2S$  and  $H_2S_x$  with a concentration of about 230-250ppmw. Here, by injecting hydrogen sulfide to sulfur, a method for synthesis of molten sulfur containing hydrogen sulfide and polysulfide as a proper sample for laboratory studies is developed. The molten sulfur as product was prepared by injecting the pressurized hydrogen sulfide on the surface of solid sulfur followed by further heat treatments during the time. According to the Iodometric Back Titration (IBT) analysis, final molten sulfur contained 500-1100ppmw of soluble hydrogen sulfide and polysulfide components based on the initial gas pressure.

**Keywords:** Molten sulfur, Gassing, Degassing, Iodometric Back Titration

## 1. Introduction

Claus units in refineries are used for processing the sour gas as the byproduct of gas sweetening process [1]. Passing through the combustion chamber, the sour gas components are converted to sulfur vapors and non-reacted gases. Then, after separation and condensation of sulfur in special condensers, the remained gases are moved to Claus catalytic beds, where catalytic reactions took place and collection of condensate sulfur continues [2].

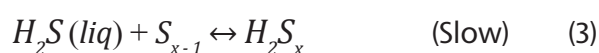
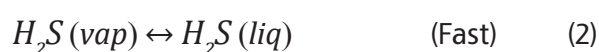
Usually, pure sulfur at atmospheric pressure and temperatures higher than its melting point (118°C) is available in the form of  $S_8$  with ring structure. At temperatures higher than 148°C, sulfur structure is converted to straight chains. According to Eq. 1 this phenomenon leads to generation of polymeric chains with different length and sometimes of thousands of units [3].

(1)



Formation of such polymeric chains in the condensers of Claus unit causes a complex physicochemical interaction between the dissolved hydrogen sulfide and molten sulfur. In fact there is an equilibrium relation between the hydrogen sulfide in the gas phase and hydrogen sulfide dissolved in the liquid phase, which is a kind of equilibrium solubility of gases dominant in liquid-gas systems. This relationship is reversible depending on the partial pressure of hydrogen sulfide in the gas phase and temperature of liquid sulfur.

Equilibrium exchange of hydrogen sulfide between gas and liquid phases is fast, while the dissolved hydrogen sulfide can react with the polymeric chains in molten sulfur and form polysulfide components [4-6]:



As mentioned before formation of polysulfide species in the solution is relatively fast, while decomposition of them is usually very slow. Finally, a mass of molten sulfur is collected in storage tanks containing hydrogen sulfide and hydrogen polysulfide with a concentration of about 250-350 ppmw. Since it is necessary to pass the product sulfur via granulation unit before sending to the market, existence of sulfide and polysulfide cause problems and risks at this step. Because high temperature of the process prevents the transfer of hydrogen sulfide from liquid phase to gas phase, but at lower temperatures (in storage tanks), polysulfide components are decomposed and release hydrogen sulfide. In fact, the equilibrium reactions of (3) and (2) are moved to left side, respectively and hydrogen sulfide is immediately moved to gas phase. In this condition, gas accumulation in enclosed space causes problems like poisoning and explosion. Hence, some methods are presented by scholars for reduction of hydrogen sulfide concentration in molten sulfur before entering the grading units aiming to break the polysulfide chains and reduce the concentration of hydrogen sulfide until the concentration of about 10ppmw [5-7].

The main problem in investigation of degassing methods in laboratory scale is lack of access to molten sulfur of the Claus unit, because transportation of such material is very difficult and dangerous, due to release of hydrogen sulfide.

In this regard, some methods are reported by the researchers to study the interaction of hydrogen sulfide and molten sulfur. For example, Fanelli [8] studied the solubility of hydrogen sulfide in molten sulfur by measuring the weight difference and concluded that solubility of hydrogen sulfide in molten sulfur is increased by increase of temperature. He also showed that solubility of hydrogen sulfide in molten sulfur changes the viscosity of molten sulfur and attributed it to formation of polysulfide species.

Then, Wiewiorowski and Touro [9] confirmed Fanelli's observations using Fourier Transform Infrared spectroscopy (FTIR) and attributed the different generated peaks to hydrogen sulfide and polysulfide.

Marriott et al. [10] also studied the solubility of hydrogen sulfide in molten sulfur using hydrogen sulfide gas flow diluted by nitrogen gas at the pressures lower than 1 bar and finally derived a correlation representing the ratio of hydrogen polysulfide to hydrogen sulfide species in the solution.

Ji et al. [11] used a laboratory system to investigate the solubility of hydrogen sulfide in molten sulfur and derived the diffusion coefficients of hydrogen sulfide in molten sulfur and rate constants of Eq. 3 at 130°C and 150°C. But because it took a long time to reach the equilibrium state, they applied a regression equation to predict the equilibrium pressure.

Here, we apply a method to investigate the equilibrium condition at pressures higher than 1bar to produce molten sulfur containing specific concentration of hydrogen sulfide and polysulfide which was then detected by IBT method. The prepared sample can be used for degassing operations at laboratory scale.

## 2. Experimental

### 2.1. Materials and Equipment

Pure sulfur (99%, Tehran refinery), hydrogen sulfide cylinder (99%, Roham Gas), cadmium acetate dehydrate (Merck), 0.05M iodine standard solution (Sigma Aldrich), sodium thiosulfate (Sigma Aldrich), starch solution, hydrochloric acid (Merck) were used as reagents. A 250mL jacketed steel reactor equipped with hot oil circulator, magnetic stirrer, pressure gauge (-1:10bar, Wika), hydrogen sulfide

analyzer (7H CiTiceL, UK) were also used to conduct the experiments.

### 2.2. Dissolution of H<sub>2</sub>S in Molten Sulfur

200g of solid sulfur with density of 2g/cm<sup>3</sup> was put into the reactor (Figure 1) and then reactor was evacuated until -0.9barg to remove excess air in the vessel. Hydrogen sulfide was injected to the reactor from a top valve until the total pressure reached to about 3barg. Reactor temperature was raised and fixed at 150°C using the hot oil circulator system. Then it was allowed to reach equilibrium under 200 rpm stirring followed by stabilization of system pressure. After reaching the equilibrium state, system was left for 24 hours in order to form polysulfide. After desired time, system pressure was lowered to atmospheric pressure and released content of hydrogen sulfide was trapped in a solution of cadmium acetate (step 1). The hydrogen sulfide existed on the surface of molten sulfur also was stripped by nitrogen gas and trapped in the absorbent solution, until the concentration of detected hydrogen sulfide in H<sub>2</sub>S analyzer became less than 1ppmw (step 2). Then, the absorbent solution was replaced by a fresh solution of cadmium acetate. Again, by sparging nitrogen gas into the molten sulfur, the color of trap solution was changed slowly to pale yellow and this process was continued for about 6-7 hours, as concentration of detected hydrogen sulfide in gas phase reached lower than 1ppmw (step 3). Trap solutions were analyzed by Iodometric Back Titration (IBT) for quantitative studies.

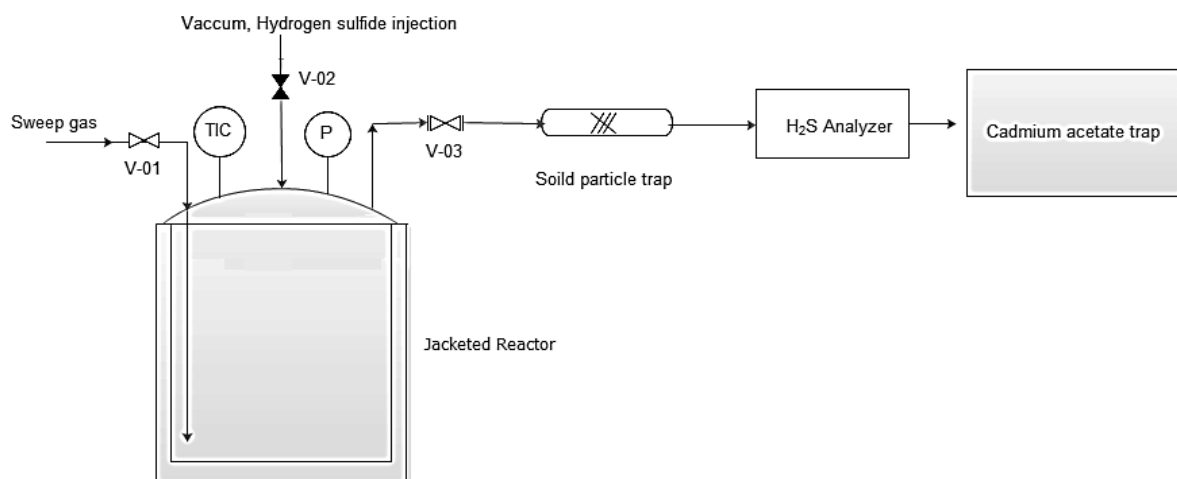


Figure.1. Molten sulfur gassing system

### 2.3. Iodometric Back Titration

For standardization, 25 ml of the 0.1N iodine solution was pipette to the flask. The solution was then titrated with 0.1N solution of sodium thiosulfate until a clear endpoint. Then, excess amounts of a mixture of 37% hydrochloric acid and 0.1N standard iodine solution were added to the trap. After adding a drop of starch solution to the mixture as indicator, resulting solution was titrated by 0.1N sodium thiosulfate solution until the colorless point. The used volume of sodium thiosulfate solution was read for further calculations.

## 3. Results and Discussions

### 3.1. IBT analysis

#### 3.1.1. Standardization

As mentioned above, concentration of hydrogen sulfide in each step was detected by analysis of cadmium acetate solution via Iodometric Back Titration (IBT) method based on interaction of hydrogen sulfide with excess iodine solution and titration by sodium thiosulfate. Before conducting the analysis, it is important to standardize the iodine and sodium thiosulfate solutions for accurate results. Accordingly:

$A = \text{normality of iodine solution} \times \text{volume used (ml)}$

$B = \text{normality of sodium thiosulfate solution} \times \text{volume used (ml)}$

$F = B/A$

If the F factor was within the limits of 0.95-1.05, solutions were prepared accurately and can be used in IBT analysis. Else, solutions should be prepared again until the F factor lays within the desired range. In this work, standard solutions were obtained after two runs. Results are shown in Table 1.

Table 1. Results of Standardization

Run	Volume of iodine solution (ml)	Volume of sodium thiosulfate solution (ml)	A	B	F=B/A
1	25	23.5	2.5	2.35	0.94
2	25	24	2.5	2.40	0.96

### 3.2.2. IBT calculations

First, absorption of hydrogen sulfide in cadmium acetate solution led to formation of yellow precipitates of cadmium sulfide, as shown in Eq.6:



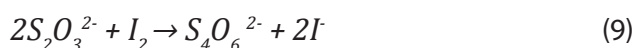
Since stoichiometric coefficients of hydrogen sulfide and cadmium sulfide are the same, the equal moles of cadmium sulfide would be generated.

Then, according to Eq. 7 and Eq. 8 addition of hydrochloric acid and excess iodine solution, led to liberation of hydrogen sulfide and generation of HI, respectively.



As shown above, addition of concentrated hydrochloric acid leads to liberation of hydrogen sulfide, which is immediately absorbed by iodine contents in the solution. Since iodine solution was used in excess values, some parts of non-reacted iodine ions remains in the environment. According to the literature [12], such excess values can be determined by titration of solution with sodium thiosulfate solution, which is standardized by iodine solution.

In continue, number of the excess iodine moles reacted with sodium thiosulfate solution (Eq. 9) was obtained by titration of solution in presence of starch solution [13].



The number of iodine moles reacted with hydrogen sulfide are calculated as the difference of initial iodine moles and remained moles which reacted with sodium thiosulfate. Hence, the content of hydrogen sulfide moles in each step can be determined.

### 3.1 Gassing

First, by putting solid sulfur in the reactor with the density of 2 g/cm<sup>3</sup>, 150 cm<sup>3</sup> of reactor space was remained for injection of hydrogen

sulfide. The initial number of hydrogen sulfide moles injected to the vessel was calculated according to Ideal gas law at 25°C and vessel pressure. So, this initial value should be equal to the sum of hydrogen sulfide moles in trap solutions of three steps, detected by Iodometric Back Titration (IBT).

As reported in literature [6-8], despite most of gas-liquid systems, solubility of hydrogen sulfide in molten sulfur increases with temperature. Such behavior may be attributed to formation of polysulfide species in liquid sulfur. In fact, since generation of polysulfide bonds is facilitated at higher temperatures, more hydrogen sulfide is dissolved in liquid sulfur. For further investigations, experiments were repeated at 2.5 bar and results are presented in Figure 2.

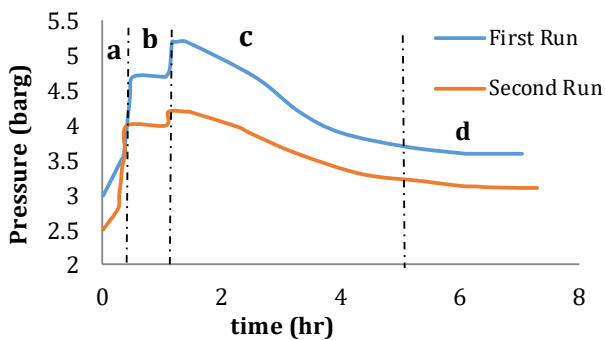


Figure 2. Pressure change rate of hydrogen sulfide in molten sulfur

According to Figure 2, in zone (a) gas pressure is increased due to of increase of system temperature. In zone (b), system pressure (and temperature) is fixed for a specific time, which indicates the phase change of solid sulfur to molten state. After complete melting of sulfur at about 120°C, system pressure was increased further until the temperature of whole system was fixed at 150°C (at the end of zone b). After reaching the maximum pressure and temperature, pressure decay process was initiated in zone (c), referring to dissolution of hydrogen sulfide in molten sulfur. Such trend was continued for a specific time and after reaching the equilibrium state ( $P_{eq}$ ), system pressure was stabilized in zone (d). In fact, when reactor temperature was fixed at the equilibrium condition, it was allowed to form

hydrogen polysulfide by interaction of sulfur free radicals with hydrogen sulfide dissolved in molten sulfur during 24 hours. According to Ji et al. [11] initial concentration of hydrogen sulfide in liquid sulfur can be derived by Eq. 5.

$$C = \frac{M(P_i - P_{eq})V_g}{RTm_s} \quad (5)$$

Where  $C$  is the concentration of hydrogen sulfide in molten sulfur,  $M$  is the molecular weight of hydrogen sulfide,  $P_i$  is the initial pressure of the vessel,  $P_{eq}$  is the vessel pressure at equilibrium condition,  $V_g$  is the gas injection volume,  $R$  is the gas constant,  $T$  is the vessel temperature and  $m_s$  is the weight of solid sulfur.

After reaching the equilibrium state, as mentioned above, un-reacted and excess hydrogen sulfide remained on the headspace of molten sulfur was discharged during steps 1&2. Such release was so fast and after some minutes, concentration of hydrogen sulfide in the stripper gas reached lower than 1ppmw, using  $H_2S$  analyzer. Regarding the fast release of gas from molten sulfur, it could be said that it was unbounded hydrogen sulfide. Hydrogen sulfide content released in these steps was trapped in cadmium acetate solution. Then, the orange trap solution containing cadmium sulfide was replaced by a fresh colorless solution of cadmium acetate. In continue, by sparge of nitrogen gas into the molten sulfur, gradual color change of trap solution was happened and continued for about 6-7 hours, where concentration of hydrogen sulfide detected by  $H_2S$  analyzer reached lower than 1ppmw (step 3). In this regard, despite steps 1&2, very slow rate of hydrogen sulfide release from solution can be attributed to decomposition of polysulfide species in the sample. The trap solutions of steps 1&2 and step 3 were analyzed by Iodometric Back Titration (IBT) method for determining the hydrogen sulfide content released in each step.

For more investigations, results obtained by Eq. 5 were compared to analytical results of Iodometric Back Titration (IBT) method, as shown in Table 2.

Table 2. Results of dissolution process

Run	Initial H <sub>2</sub> S pressure (bar)	Initial H <sub>2</sub> S (mol)	Maximum H <sub>2</sub> S pressure (bar)	Equilibrium H <sub>2</sub> S pressure (bar)	Un-bounded H <sub>2</sub> S in steps 1&2 (mol)	H <sub>2</sub> S in step 3	Calculated concentration of H <sub>2</sub> S in molten sulfur according to IBT analysis (ppmw)	C(ppmw) according to eq.5
1	3	0.018	5.21	3.4	0.0118	0.0062	991	1100
2	2.5	0.015	4.2	3.2	0.0115	0.0035	560	624

As shown in Table 2, initial injection pressure of H<sub>2</sub>S was used for estimation of initial (total) moles of hydrogen sulfide in the system. Maximum and equilibrium pressures of H<sub>2</sub>S were used for calculation of C (ppmw) according to eq. (5). H<sub>2</sub>S content in step 3 was determined by Iodometric Back Titration (IBT) analysis of the second trap solution and then was applied for determination of dissolved hydrogen sulfide and polysulfide concentration in molten sulfur.

Clearly, the initial mole of injected hydrogen sulfide was equal to sum of moles of unbonded and bounded hydrogen sulfide in steps 1&2 and 3. In addition, the concentrations (ppmw) obtained by eq. (5) and dissolved hydrogen sulfide content at step 3 were in a good agreement, while the difference of about 50-100ppmw was also reported by other researchers [11].

#### 4. Conclusions

Regarding the need to molten sulfur containing dissolved hydrogen sulfide and polysulfide in laboratories for studying different degassing methods, this article aims to investigate a gassing procedure at pressures higher than atmospheric. In this study, we applied pressures up to 3bars and allowed the system to reach equilibrium during the time. Outputs of system were analyzed by Iodometric Back Titration and compared with theoretical investigations. Results showed that there is a good agreement between results obtained via these two approaches. Therefore, we can conclude that molten sulfur containing dissolved hydrogen sulfide and hydrogen

polysulfide components can be produced via this method and be used for further processing of degassing methods in the laboratory.

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## بررسی حالیت هیدروژن سولفید در گوگرد مذاب با استفاده از روش تیتراسیون برگشتی یدومتری

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### چکیده

به منظور انجام بررسی های آزمایشگاهی بر روی ترکیب و رفتار گوگرد مذاب حاصل از واحد کلاوس، نیاز است که گوگرد مذاب حاوی ۲۵۰-۲۰۰ ppmw هیدروژن سولفید ( $H_2S$ ) و هیدروژن پلی سولفید ( $H_2S_x$ ) حل شده باشد. در این پژوهش تولید این محصول با استفاده از تزریق هیدروژن سولفید به گوگرد مذاب مطالعه شد و نمونه مناسبی جهت بررسی های آزمایشگاهی تولید گردید. محصول گوگرد مذاب حاصل در این روش توسط تزریق هیدروژن سولفید تحت فشار به سطح گوگرد جامد و عملیات حرارتی در طی زمان مناسب ایجاد شده است. همچنین طبق نتایج حاصل از آنالیز یدومتری برگشتی، نمونه گوگرد مذاب نهایی دارای ۵۰۰-۱۱۰۰ ppmw هیدروژن سولفید و هیدروژن پلی سولفید محلول بر اساس میزان فشار تزریقی بوده است.

واژگان کلیدی: گوگرد مذاب، گازدهی، گازدایی، تیتراسیون برگشتی یدومتری.