Research article

Development and industrial application of catalyzer for low-temperature hydrogenation hydrolysis of Claus tail gas

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Abstract

With the implementation of more strict national environmental protection laws, energy conservation, emission reduction and clean production will present higher requirements for sulfur recovery tail gas processing techniques and catalyzers. As for Claus tail gas, conventional hydrogenation catalyzers are gradually being replaced by low-temperature hydrogenation catalyzers. This paper concentrates on the development of technologies for low-temperature hydrogenation hydrolysis catalyzers, preparation of such catalyzers and their industrial application. In view of the specific features of SO_2 hydrogenation and organic sulfur hydrolysis during low-temperature hydrogenation, a new technical process involving joint application of hydrogenation catalyzers and hydrolysis catalyzers was proposed. In addition, low-temperature hydrogenation catalyzers and low-temperature hydrolysis catalyzers suitable for low-temperature conditions were developed. Joint application of these two kinds of catalyzers may reduce the inlet temperatures in the conventional hydrogenation reactors from 280 °C to 220 °C, at the same time, hydrogenation conversion rates of SO_2 can be enhanced to over 99%. To further accelerate the hydrolysis rate of organic sulfur, the catalyzers for hydrolysis of low-temperature organic sulfur were developed. In lab tests, the volume ratio of the total sulfur content in tail gas can be as low as 131×10^{-6} when these two kinds of catalyzers were used in a proportion of 5:5 in volumes. Industrial application of these catalyzers was implemented in 17 sulfur recovery tail gas processing facilities of 15 companies. As a result, Sinopec Jinling Petrochemical Company had outstanding application performances with a tail gas discharging rate lower than 77.9 mg/m^3 and a total sulfur recovery of 99.97%.
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Keywords: High-sulfur natural gas; Claus; Tail gas; Low-temperature; Hydrogenation; Hydrolyzation; Catalyzer; Industrial application

1. Introduction

As the requirements in China on clean production, energy conservation and emission reduction, and environmental protection get higher, the requirement on SO_2 emission for refinery plants and natural gas purification plants becomes increasingly strict. Sulfur recovery and tail gas treatment are the primary technologies to treat sulfur acid gas. The reduction−absorption procedure widely used in large-scale facilities is the key technology to ensure SO_2 emission in tail gas to meet the standard [1].

Since the 1970s, a major progress has been made in reduction−absorption procedure for sulfur recovery and tail gas treatment, greatly reducing the SO_2 emission in tail gas. Traditional reduction−absorption procedure requires high inlet temperature of reactor, which can only be achieved by electric heating or online combustion. In order to meet the requirement of clean production and energy saving, the reactivity of catalyzers has been raised and the activity energy of catalyzers decreased to realize low-temperature hydrogenation reduction; the surplus medium-pressure steam in equipment is used for heat transfer to save energy [2,3].

Low-temperature hydrogenation catalyzer is the key to low-temperature hydrogenation reduction procedure. Co—Mo/γ-Al_2O_3 is the most widely used catalyzer in industrial application at present, which can simultaneously hydrogenate SO_2 and hydrolyze organic sulfur at the reactor inlet temperature of 230—250 °C. Therefore, the available low-temperature hydrogenation catalyzer is only a transitional catalyzer between high-temperature hydrogenation catalyzers and low-temperature hydrogenation catalyzers. The application of the catalyzer at low temperature could result in Claus side reaction, which will lead to the rapid decrease of organic sulfur hydrolyzing efficiency and the increase of SO_2 concentration in tail gas [4—7].

Based on the SO_2 hydrogenation and organic sulfur hydrolyzation in low-temperature hydrogenation reaction, a new procedure using hydrogenation and hydrolyzation catalyzer jointly is proposed in this study. Low-temperature hydrogenation and low-temperature hydrolyzation catalyzers applicable to low-temperature condition have been developed respectively, and the inlet temperature of traditional hydrogenation reactor was reduced from 280 °C to 220 °C by joint application of the two catalyzers. In addition, the hydrogenating and hydrolyzing efficiency has also been improved. The Sinopec Jinling Petrochemical Company is taken as an example to demonstrate the effect of the industrial application of the two catalyzers.

2. Laboratory experiment

2.1. Preparation of catalyzers

A low-temperature hydrogenation catalyzer and a low-temperature hydrolyzation catalyzer were developed respectively for hydrogenation and hydrolyzation reactions, hereinafter referred to as Catalyzer A and Catalyzer B. The preparation of Catalyzer A involves preparing a new carrier by band extrusion firstly, impregnating the new carrier with active components, and then drying and calcinating the new carrier to get the final product. The preparation of Catalyzer B involves impregnating spherical carrier γ-Al_2O_3 with active component, and then drying and calcinating to get the final catalyzer. In order to compare the reactivity of the catalyzers, a low-temperature hydrogenation catalyzer made by a foreign company (referred to as Catalyzer C) was selected to do comparison experiment.

2.2. Laboratory reactivity evaluation equipment

A fixed bed reactor was used to evaluate the reactivity of different catalyzers, and the specific process is shown in Fig. 1. H_2S, SO_2, H_2, CO_2 and N_2 were provided by gas steel cylinders, CS_2 and steam were carried by CO_2 and N_2 bubbling respectively.

2.3. Reactivity evaluation and characterization of catalyzers

The air speed and reaction temperature are 1500 m^3/h and 220 °C respectively in the catalyzer reactivity evaluation if not
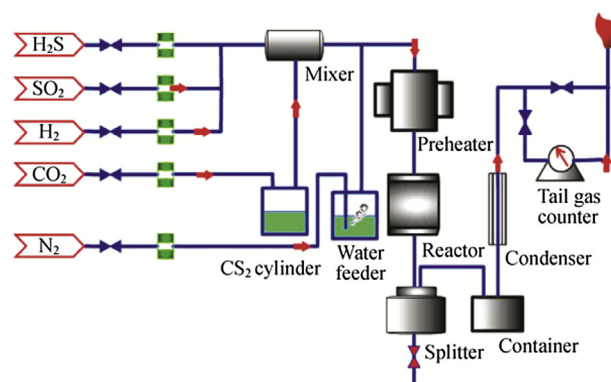

Fig. 1. Flow of laboratory catalyzer reactivity evaluation.

noted specifically. The gas composition used in evaluating catalyzer hydrogenating, hydrolyzing, and hydrogenating-hydrolyzing performances is listed in Table 1. The composition of feed gas and tail gas were tested by Agilent 7890 gas chromatography with TCD detector. The total sulfur content except H_2S (hereinafter referred to as total sulfur content of tail gas) was tested by trace sulfur analyzer.

Catalyzer bulk density, attrition rate, crush strength and specific surface area were tested according to the standards of GB/T 6286-1986, HG/T 2976-1999, HG/T 2782-1996 and GB/T 5816-1995. JEOL JSM6501 SEM was used in the catalyzer characterization.

3. Experimental results

3.1. Physico-chemical properties of catalyzers

Table 2 shows the physic-chemical properties of the catalyzers, including bulk density, attrition rate, crush strength and specific surface area. This indicates that the catalyzers are applicable to industrial application.

3.2. Evaluation of hydrogenation catalyzers

Fig. 2 shows the SO_2 hydrogenating performance of Catalyzer A and Catalyzer B at different reaction temperatures. This figure demonstrates that, when the reaction temperature is 280 °C, the SO_2 hydrogenating rate of Catalyzer A is 99.7%, which is slightly higher than that of Catalyzer C; SO_2 hydrogenating rate decreases with the decrease of reaction temperature, when the reaction temperature reduces to 210 °C, the SO_2 hydrogenating rate of Catalyzer A reduces to 98.3%. In contrast, the SO_2 hydrogenating rate of Catalyzer C couldn't be accurately tested due to the production of massive sulfur in tail gas as a result of Claus side reaction at this temperature.

Fig. 3 shows the SEM image of Catalyzer A and Catalyzer C. It can be seen from this figure that the crystals of Catalyzer A are smaller in size, allowing even distribution of active components on the catalyzer surface. In comparison, crystals on Catalyzer C are large in size (at micron scale), and

Table 1
Feed gas composition in laboratory reactivity evaluation.

Evaluation item	H_2S	SO_2	CS_2	H_2	CO_2	H_2O	N_2
Hydrogenating performance	2%	0.50%	0	3%	10%	30%	Allowance
Hydrolyzing performance	2%	0	0.14%	3%	10%	30%	Allowance
Hydrogenating-hydrolyzing performance	2%	0.50%	0.14%	3%	10%	30%	Allowance

unfavorable for the dispersion of active components. Catalyzer reactivity is closely related to the dispersibility of active components. Generally, with the increase of dispersibility, the number of catalyzer active centers increases, and the catalyzer reactivity also increases, which is why the reactivity of Catalyzer A using a new carrier is higher than that of Catalyzer C using γ-Al_2O_3 as a carrier.

Claus gas contains not only SO_2, but also a certain amount of organic sulfur in the forms of CS_2 and COS. In order to keep the total sulfur content of tail gas within emission standard, if only a hydrogenation catalyzer is loaded in the reactor, the catalyzer must have not only good SO_2 hydrogenating performance but also organic sulfur hydrolyzing performance. The evaluation of catalyzer hydrogenating (hydrolyzing) performance (Table 3) indicates that Catalyzer A works better in SO_2 hydrogenation, and the total sulfur content (volume ratio, the same below) of tail gas was only 56×10^{-6}, but the corresponding sulfur content rapidly increased to 753×10^{-6} when a certain amount of organic sulfur was added. The hydrolyzing performance evaluation of Catalyzer A demonstrates that the total sulfur content of tail gas was up to 662×10^{-6}, suggesting that Catalyzer A couldn't effectively promote the hydrolyzation of organic sulfur. The same phenomenon was found for Catalyzer C. The result demonstrates that Catalyzer A cannot promote complete hydrolyzation of organic sulfur, so it is unable to make the tail gas meet the emission standard.

3.3. Evaluation of hydrolyzation catalyzers

Fig. 4 shows the hydrolyzing rate of Catalyzer B under different reaction temperatures. It can be seen from this figure that the CS_2 hydrolyzing rate is only 90% at the reaction temperature of 180 °C. The CS_2 hydrolyzing rate increases with the increase of reaction temperature, and the CS_2 hydrolyzing rate is 99% at the reaction temperature of 260 °C. The inlet temperature of low-temperature hydrogenation reactor is generally 220 °C, and the CS_2 hydrolyzing rate of Catalyzer B is 96.5% at this temperature, which is higher than that of Catalyzer A and Catalyzer C.

Table 2
Physic-chemical properties of Catalyzer A and Catalyzer B.

Physic-chemical properties	Catalyzer A	Catalyzer B
Bulk density/(g·mL^{-1})	0.86	0.81
Attrition rate	0.65	0.70
Crush strength/(N·cm^{-1})	169	110
Specific surface area/(m^2·g^{-1})	249	207

Traditional low-temperature hydrolyzation catalyzers are generally prepared by loading alkali metal or alkaline-earth metal on γ-Al_2O_3 carrier. This kind of catalyzer is likely to become inactivated by sulfating when contacting with SO_2. There is also high content of SO_2 in the low-temperature hydrogenation reactor, therefore, it is necessary to evaluate the anti-SO_2 poisoning performance of Catalyzer B. The procedure is shown in Fig. 5. It can be seen that the stable CS_2 hydrolyzing rate of Catalyzer B is around 96.5% without adding SO_2 (the first 10 h), also that CS_2 hydrolyzing rate continuously decreases after adding 0.5% SO_2, and that the CS_2 hydrolyzing rate decreases to 30.6% at the reaction time of 20 h; the CS_2 hydrolyzing rate continuously increases after closing SO_2 and restores to the original level before adding SO_2 and becomes stable. This demonstrates that the anti-SO_2 poisoning of Catalyzer B is unsatisfactory, but the poisoning is recoverable.

3.4. Joint application of catalyzers

In order to take full advantage of Catalyzer A hydrogenating performance and Catalyzer B hydrolyzing performance, Catalyzer A and Catalyzer B must be applied jointly. Fig. 6 shows the effect of different packing modes on the performance of the catalyzers. The tail gas treating efficiency of packed Catalyzer A in the upper part is higher than that of both packed Catalyzer B in the upper part and the mixture of them. When Catalyzer B is packed in the upper part of the reactor, SO_2 concentration is relatively high in the upper part of it, and the reactivity of hydrogenation catalyzer will decrease due to long-time exposure to high concentration of SO_2, which will result in the failure to hydrolyze CS_2 and increase tail gas total sulfur content. When Catalyzer A is packed in the upper part
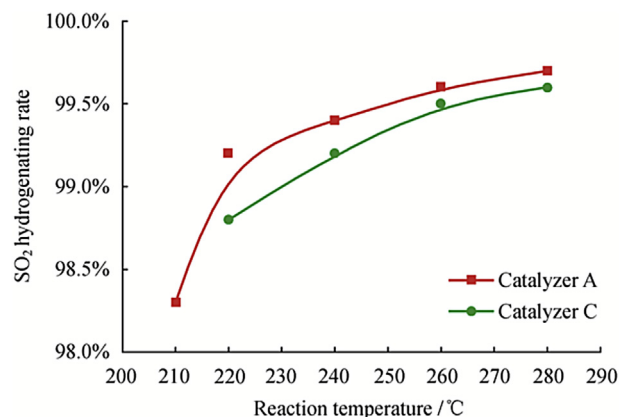

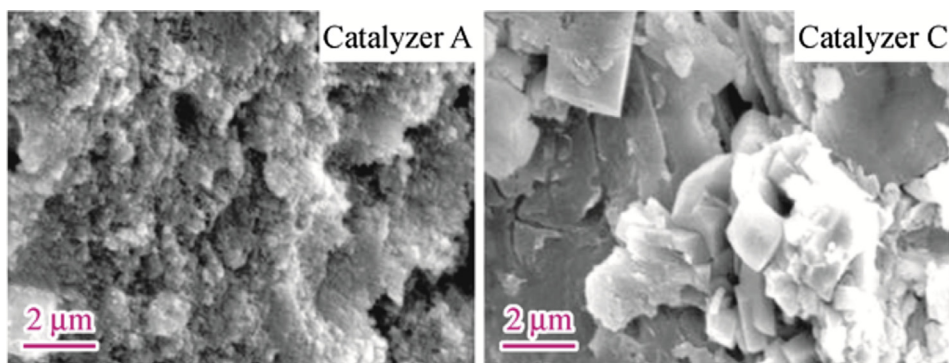Fig. 2. SO_2 hydrogenating performance of Catalyzer A and Catalyzer C.

Fig. 3. SEM image of Catalyzer A and Catalyzer C.

Table 3
Hydrogenating performance of different low-temperature hydrogenation catalyzers.

Catalyzer	Main gas component		Total sulfur content of tail gas
	SO_2	CS_2	
Catalyzer A	0.72%	/	56×10^{-6}
	/	0.14%	662×10^{-6}
	0.72%	0.14%	753×10^{-6}
Catalyzer C	0.72%	/	63×10^{-6}
	0.72%	0.14%	930×10^{-6}

of the reactor, SO_2 can be hydrogenated to produce H_2S by Catalyzer A, which could prevent Catalyzer B from being inactivated by long-time exposure to SO_2. Therefore, the only reasonable packing mode is to pack Catalyzer A in the upper part of the reactor and Catalyzer B in the lower part of the reactor.

Fig. 7 shows the effect of Catalyzer B volume on the total sulfur content of tail gas when the total volume of catalyzers keeps constant. Fig. 7 shows that the total sulfur content of tail gas is up to 753×10^{-6} when only Catalyzer A is packed.
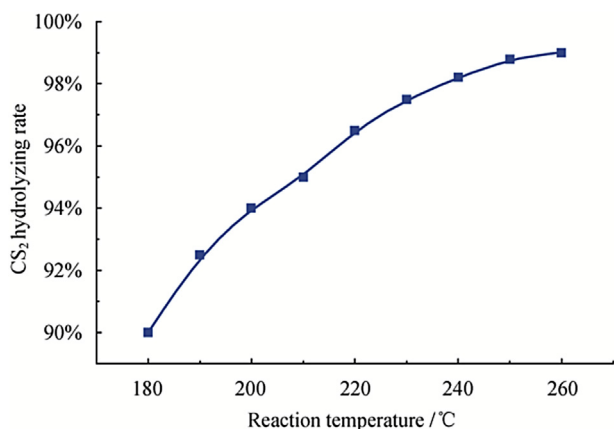

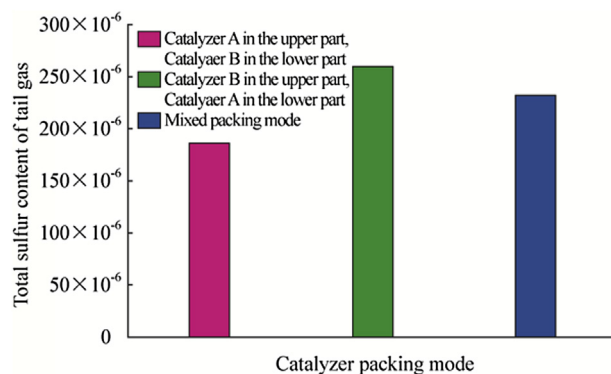Fig. 4. CS_2 hydrolyzing rates of Catalyzer B at different reaction temperatures.

Fig. 6. Effect of different packing modes on the performance of catalyzers (the volume ratio of Catalyzer A to Catalyzer B is 1:1).
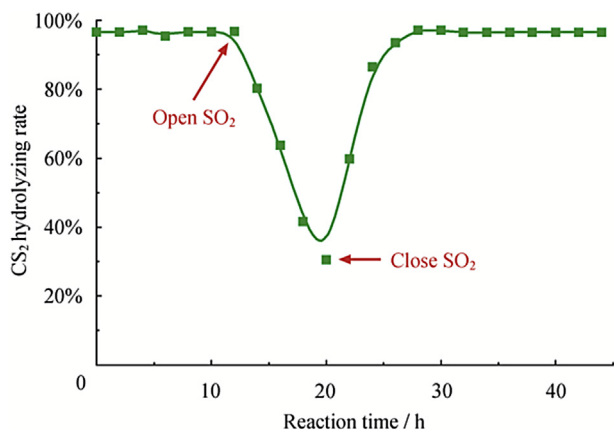

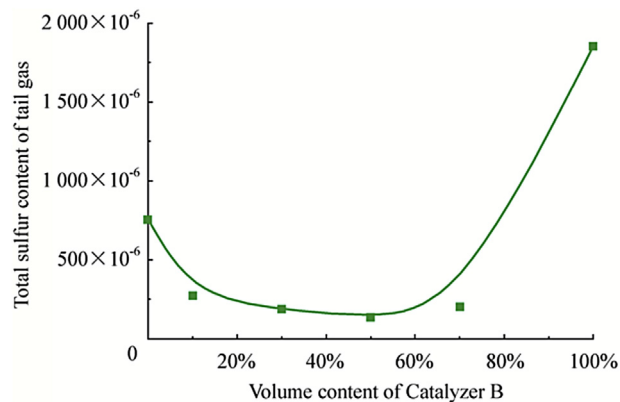Fig. 5. Anti-SO_2 poisoning evaluation of Catalyzer B.

Fig. 7. Relationship between the volume content of Catalyzer B and total sulfur content of tail gas.

When the volume content of Catalyzer B increases to 10%, the total sulfur content of tail gas rapidly reduces to 272×10^{-6}. The total sulfur content of tail gas continues to decrease with the increase of the Catalyzer B volume content. The minimum total sulfur content of tail gas is 131×10^{-6} when the volume content of Catalyzer B is 50%. Then the total sulfur content of tail gas increases when the volume content of Catalyzer B continues to increase; and the total sulfur content of tail gas reaches 1853×10^{-6} when the volume content of Catalyzer B increases to 100%.

4. Industrial application

4.1. Overview

Since the low-temperature hydrogenation and low-temperature hydrolyzation catalyzers were promoted in PetroChina Dushanzi Petrochemical Company in August 2011, the production and sales volume of the catalyzers have increased year by year. The annual sales volumes of 2011, 2012, 2013 and 2014 were 5 t, 29 t, 76 t and 115 t respectively, and the total sales volume exceeded 225 t. The two catalyzers have been applied in 17 sets of sulfur recovery tail gas treatment units in 15 companies, and the specific industrial applications are shown in Table 4. Sinopec Jinling Petrochemical Company is taken as an example to demonstrate the industrial application of these catalyzers.

4.2. Industrial application in Sinopec Jinling Petrochemical Company

4.2.1. Facility overview

Italian KTI technology has been introduced for the sulfur recovery facility with 10×10^4 t/a treating capacity in

Table 4
Outline of the application of catalyzers in different companies.

No.	Company	Unit treating capacity/(10^4t·a^{-1})
1	Fujian Refining & Petrochemical Company Limited	20
2	Sinopec Zhenhai Oil Refining Chemical Company	10×2
3	Sinopec Jinling Petrochemical Company	10
4	Sinopec Changling Refinery Company	6
5	PetroChina Guangxi Petrochemical Company	6
6	PetroChina Longgang Natural Gas Purification Plant	6
7	PetroChina Dushanzi Petrochemical Company	5 + 0.4
8	PetroChina Lanzhou Petrochemical Company	4
9	Sinopec Tahe Petrochemical Company	2
10	Chongqing XingFaJinGuan Chemical Co., Ltd.	3
11	Shenhua Coal Liquefaction Project (Erdos)	3
12	Taizhou Petrochemical Co., Ltd.	1
13	Xinjiang Tianye Chemical Co., Ltd.	1
14	PetroChina Ningxia Petrochemical Company	0.5
15	PetroChina Qinghai Oilfield Company Golmud Refinery	0.5

Sinopec Jinling Petrochemical Company oil quality upgrading project, and this facility includes three units, sulfur recovery, tail gas treatment and solvent regeneration. Claus unit uses partial combustion and an external two-stage conversion in sulfur-production, and RAR reduction–adsorption in tail gas treatment, with a designed recovery rate of more than 99.9%. Conventional alumina catalyzer and titanium-based sulfur recovery catalyzer were packed in the Claus reactor in this unit, and 20 t low-temperature hydrogenation-hydrolyzation catalyzer presented in this paper was packed in the hydrogenation reactor. The energy consumption of the facility during calibration was 119.039 kg (standard oil)/t, lower than that of designed value of 263.09 kg (standard oil)/t, which mainly results from insufficient 1 MPa steam production during calibration. When the 1 MPa steam production is sufficient, the unit energy consumption will increase by 33.3 kg (standard oil)/t, which is still lower than the designed value.

4.2.2. Facility evaluation

The facility and catalyzer were evaluated a month after commissioning in August 2012. Table 5 shows that the inlet temperature of hydrogenation reactor was 244–246 °C, slightly higher than the designed value, and the outlet temperature was 255–260 °C. Quench water pH was 7.5–7.6, which suggests that the SO_2 concentration at the hydrogenation reactor outlet was as low as being negligible, and the low-temperature hydrogenation hydrolyzation catalyzer has very good anti-SO_2 penetration performance.

Table 6 shows the hydrogenation reactor inlet gas composition and flue gas SO_2 emissions. It can be seen that the hydrogenation reactor inlet gas composition was relatively stable with a H_2S content of 0.34%–0.67%, and a SO_2 content of 0.11%–0.35%. The SO_2 emission concentration of flue gas was 31–77.9 mg/m^3, which is much lower than the relevant national environmental standard. The evaluation showed the facility had a total sulfur recovery rate of 99.97%, which is higher than the design value of 99.9%, indicating a good catalyzer performance.

5. Conclusions

A joint process of hydrogenation and hydrolyzation was proposed, a low-temperature hydrogenation catalyzer and a low-temperature hydrolyzation catalyzer were developed based on the reactions of SO_2 and organic sulfur in low-temperature hydrogenation reactor, which reduces the inlet temperature of low-temperature reactor from 280 °C to 220 °C. Laboratory experiments show that the minimum total sulfur content of tail gas is 31×10^{-6} when the volume ratio of the two catalyzers is 5:5. These catalyzers were applied in 17 sulfur recovery tail gas processing facilities of 15 companies. In Jinling Petrochemical Company, the SO_2 emission concentration of tail gas is lower than 77.9 mg/m^3 and the total sulfur recovery rate is up to 99.97%, which demonstrates good effect of the catalyzers.

Table 5
Inlet and outlet temperatures and quench water pH values at hydrogenation reactor beds during the calibration.

Temperature of hydrogenation reactor/°C				Quench water pH
Designed inlet temperature	Measured inlet temperature	Bed temperature	Measured outlet temperature	
240	244	257	255	7.6
	244	261	258	7.6
	245	259	260	7.6
	246	258	256	7.5

Table 6
Gas composition and flue gas SO_2 emissions at hydrogenation reactor inlet during the calibration.

Sampling position	Composition	Time (date)				
		15:00 (6 Aug., 2012)	9:00 (7 Aug., 2012)	15:00 (7 Aug., 2012)	9:00 (8 Aug., 2012)	9:00 (9 Aug., 2012)
Reactor inlet	H_2S	0.67%	0.46%	0.44%	0.34%	0.70%
	SO_2	0.12%	0.17%	0.18%	0.35%	0.11%
Chimney	$SO_2/(mg \cdot m^{-3})$	77.9	31	83	35	49

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