

Article

Investigation on the Cause of the SO₂ Generation during Hot Gas Desulfurization (HGD) Process

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Abstract: In the integrated gasification combined cycle (IGCC) process, the sulfur compounds present in coal are converted to hydrogen sulfide (H₂S) when the coal is gasified. Due to its harmful effects on sorbent/solvent and environmental regulations, H₂S needs to be removed from the product gas stream. To simulate the H₂S removal process, desulfurization was carried out using a dry sorbent as a fluidizing material within a bubbling, high-temperature fluidized bed reactor. The ZnO-based sorbent showed not only an excellent capacity of H₂S removal but also long-term stability. However, unexpected SO₂ gas at a concentration of several hundred ppm was detected during the desulfurization reaction. Thus, we determined that there is an unknown source that supplies oxygen to ZnS, and identified the oxygen supplier through three possibilities: oxygen by reactant (fresh sorbent, ZnO), byproduct (ZnSO₄), and product (H₂O). From the experiment results, we found that the H₂O produced from the reaction reacts with ZnS, resulting in SO₂ gas being generated during desulfurization. The unknown oxygen source during desulfurization was deduced to be oxygen from H₂O produced during desulfurization. That is, the oxygen from produced H₂O reacts with ZnS, leading to SO₂ generation at high temperature.

Keywords: hot gas desulfurization; hydrogen sulfide; sulfur dioxide; zinc oxide; H₂O



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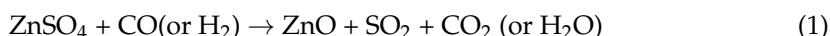


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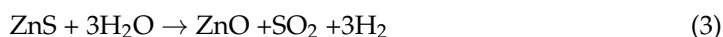
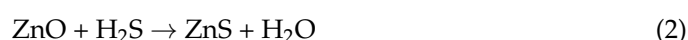
1. Introduction

The coal integrated gasification combined cycle (IGCC) emits sulfur in the form of hydrogen sulfide (H₂S) in the product gas [1–4]. It is necessary to clean the coal-derived H₂S gas in order to prevent gas turbine corrosion and to follow the strict regulations regarding pollutant emission. Recently, the research on power generation using natural gas, biogas, and reforming, etc. has been focused on the reduction of greenhouse gas emissions. These gases usually consist of several acidic pollutants, such as CO₂ and H₂S [5–8]. Generally, a typical chemical plant uses a wet desulfurization method, utilising amines as a sorbent at low temperatures, even though the wastewater treatment after the absorption process is a major problem. On the other hand, hot gas desulfurization (HGD) is regarded as a clean technology that scrubs the concentration of sulfur compounds to one-tenth of the original levels and improves the power generation efficiency at the same time, due to the sulfur compound removal. Various dry desulfurization sorbents (including Zn, Ca, Mn, Fe, Cu, and Ni-based sorbents) have been studied for high removal efficiency over HGD [9–17]. In recent years, most studies have mainly focused on the regenerability and durability of desulfurization sorbents. Additionally, many efforts have been made to find the cause of sulfate formation and zinc volatilization during desulfurization. Although numerous studies on desulfurization are being conducted, there are few studies

on SO₂ generation during desulfurization. In addition, the reason for SO₂ generation is still unknown [18–20]. There are some studies reporting that the formation of SO₂ is due to the reaction between the side products (ZnSO₄) of the desulfurization and H₂O [21–27]. Park et al. [25,26] also observed SO₂ during desulfurization over the reaction between the reducing gases (CO and H₂) and ZnSO₄, which was produced during the regeneration of sorbent under conditions of a low regeneration temperature and an excessive O₂ injection. The reaction is shown in Equation (1).



Sasaoka et al. [23,24] studied the effect of H₂O on ZnS formation during desulfurization using a temperature-programmed reduction (TPR), reporting that the formation of SO₂ was caused by the reaction of formed ZnS with H₂O at temperatures above 450 °C, as shown in Equations (2) and (3).



Even though there are a few studies that identified the presence of SO₂ during desulfurization, the exact cause of SO₂ gas generation has not yet been investigated.

In this study, experimental investigation was performed to find the reason for the SO₂ generation problems during the desulfurization, as well as the formation of ZnSO₄, a side reaction product. First, the effect of the presence of H₂O and reducing gases on the SO₂ generation during desulfurization was investigated under both the N₂ and reducing syngas in a fluidized bed reactor. In addition, the effect of the presence of H₂O only was investigated to identify the detailed HGD reaction mechanism. Based on the experimental works, a more scientific understanding for the SO₂ generation during desulfurization was obtained.

2. Results and Discussion

Figure 1 shows the result of desulfurization and SO₂ generation over fresh sorbent (ZnO) with H₂S gas (4000 ppm) at temperatures from 500 °C to 650 °C. As shown in Figure 1, no SO₂ gas was produced at below 500 °C, whereas SO₂ gas was formed above 550 °C, even though the removal rate of H₂S was 100%. This is possibly because SO₂ gas was generated over the oxidation of sulfur compound with an unknown source of oxygen when the ZnS was converted to Zn or ZnO. The SO₂ production rate increased as the operating temperature increased. Even in the absence of oxygen, the SO₂ generation phenomenon indicates that there were other causes of SO₂ generation during ZnS regeneration. To determine the unknown source of oxygen and the conditions for SO₂ generation, experiments were conducted under various conditions.

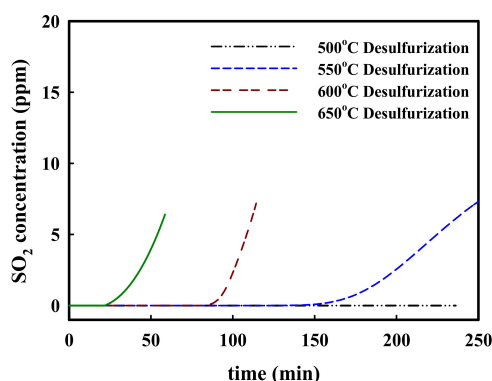


Figure 1. Effect of temperature on SO₂ generation of fresh sorbent in the desulfurization process with 4000 ppm H₂S.

During the desulfurization, the possible oxygen sources were from (1) oxygen contained in sorbent (ZnO), (2) oxygen from a side product (ZnSO_4) during desulfurization, and (3) oxygen from H_2O generated during desulfurization. Experiments were carried out to investigate the sources of oxygen.

First, an experiment was conducted to check whether the oxygen was from the ZnO sorbent, as shown in Figure 2. The sulfided sorbent (ZnS) and fresh sorbent (ZnO) were mixed at a ratio of 1:1, and then we evaluated whether SO_2 gas was generated at 550 °C with N_2 atmosphere. The presence of SO_2 gas would indicate that ZnS was regenerated by ZnO, resulting in the generation of SO_2 . We confirmed that no SO_2 gas was generated at 550 °C for 100 min under the N_2 condition. SO_2 gas was detected following regeneration under 3 vol. % O_2 at 650 °C, but no SO_2 gas was produced at 550 °C under N_2 atmosphere. From this result, we concluded that the ZnO was not an oxygen supplier for the generation of SO_2 because the SO_2 gas was not detected after holding ZnS with ZnO at the high temperature of 550 °C.

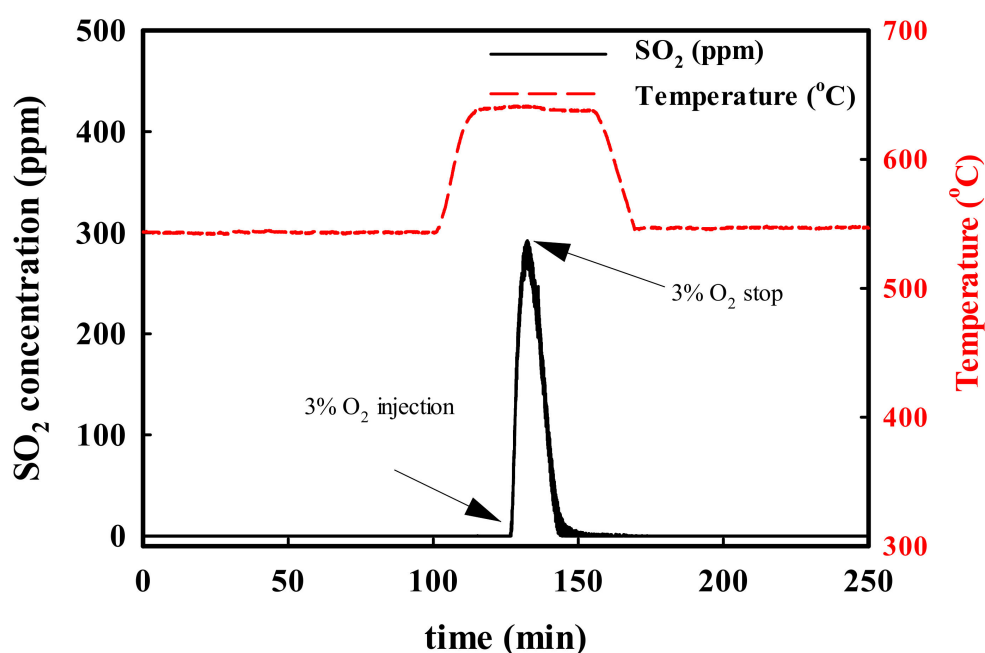


Figure 2. Effect of oxygen in the sorbent itself on the SO_2 generation.

Secondly, the formation of ZnSO_4 was analyzed using X-ray diffraction (XRD) to determine whether the SO_2 generation was from a side reaction of the desulfurization. Figure 3 shows the XRD patterns of the sorbents (SC-229TD, before and after the first desulfurization, after the first regeneration, and after the second desulfurization). The desulfurization was conducted at 550 °C and 4000 ppm H_2S . Then, the sorbent was regenerated at 650 °C under a 3% O_2 condition. As shown in the XRD patterns, the ZnO peak was mainly assigned in the fresh sorbent, and some NiO peak was found. Al- or Si-based compounds used as support were not detected. In the case of the sulfided sorbent, unreacted ZnO, sulfided ZnS, and NiS were found in the XRD patterns. The SiO_2 peaks identified in the XRD patterns were the inert material (sand) mixed with sorbent. In the sorbent after regeneration, the ZnS and NiS peaks disappeared as they existed as ZnO and NiO, which were in the same phase as before the desulfurization reaction. From these results, it can be concluded that the ZnSO_4 phase was not produced by side reactions during the desulfurization and regeneration, which leads to the conclusion that the generation of SO_2 gas was not by ZnSO_4 .

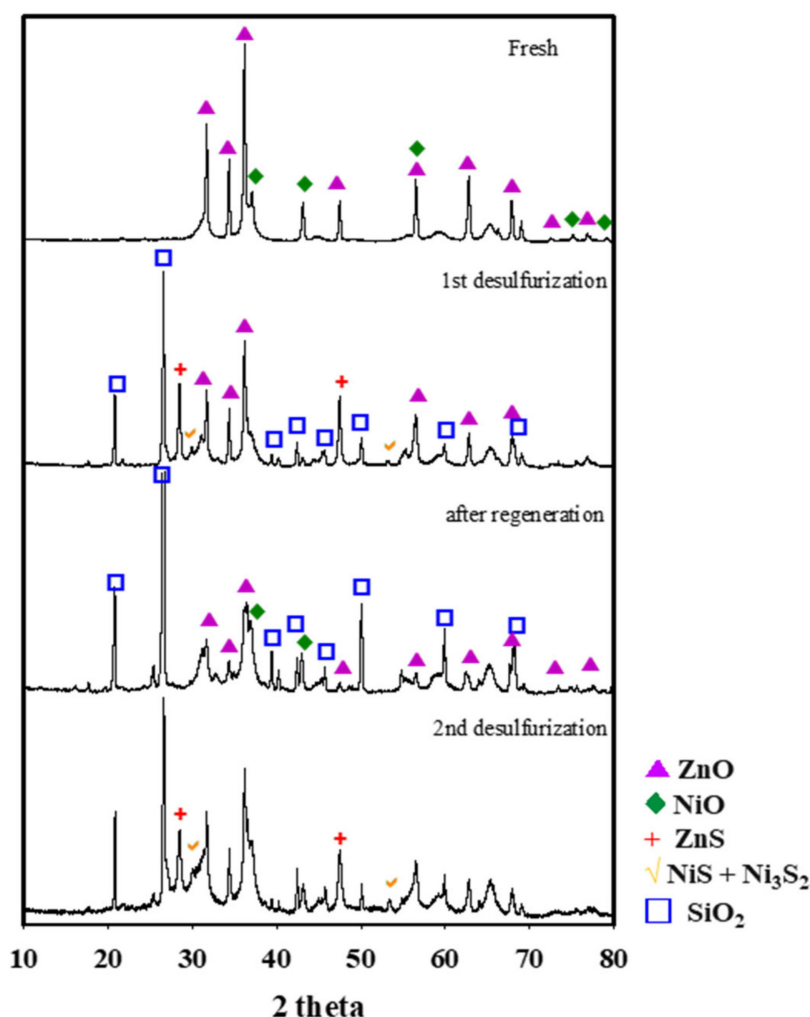


Figure 3. XRD patterns of the fresh, sulfurized, and regenerated sorbents (SC-229TD) in the repeated desulfurization and regeneration processes.

Thirdly, an experiment was carried out by injecting H_2O using a water pump to investigate the effect of H_2O on the SO_2 production. Figure 4 shows the results of SO_2 generation over the sulfided sorbent with the temperature range from 475 °C to 650 °C with 20% H_2O (N_2 balance). The maximum concentrations of SO_2 were 20 ppm at 550 °C, 100 ppm at 600 °C, and 200 ppm at 650 °C. An increase in temperature shortened the initial time of SO_2 generation and increased the concentration of SO_2 with the presence of water vapor. The sulfided sorbent emitted SO_2 at 550 °C and above, although oxygen gas was not present. The formation of SO_2 was due to the reaction between the ZnS and injected H_2O , which led to the regeneration of ZnS to ZnO . A previous work reported that the presence of water vapor can prevent the formation of ZnSO_4 because it promotes the conversion of sulfate (SO_4^{2-}) to sulfite (SO_3^{2-}), which is easier to be decomposed or removed from the surface of sorbent than sulfate species [28]. Figure 5 shows the effect of temperature on the consumption of reactant, and the generation of products during the regeneration by H_2O , using Outokumpu HSC 5.1 software. The concentrations of ZnS and H_2O decreased from about 450 °C, and the product SO_2 gas was also produced without oxygen during the regeneration. The desulfurization was thermodynamically favorable at the lower temperature. The activity of the reaction gradually decreased above 450 °C. Although the temperature was set for desulfurization, the regeneration over H_2O started from 450 °C. The concentration of products (SO_2 , H_2 , ZnO , and H_2S) increased as the temperature increased. These results indicate that the regeneration of ZnS

is thermodynamically possible, even at the desulfurization temperature, when water is present. Additionally, the results gained using the HSC 5.1 software are consistent with the results shown in Figure 4. From these results, it can be concluded that the H_2O produced from desulfurization was the major oxygen supplier, which is reactive with ZnS , leading to SO_2 generation during desulfurization.

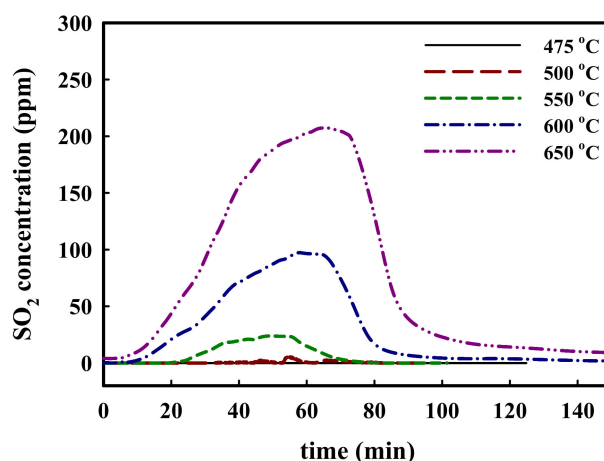


Figure 4. Effect of temperature on the SO_2 generation in HGD process with 20% H_2O balanced by N_2 .

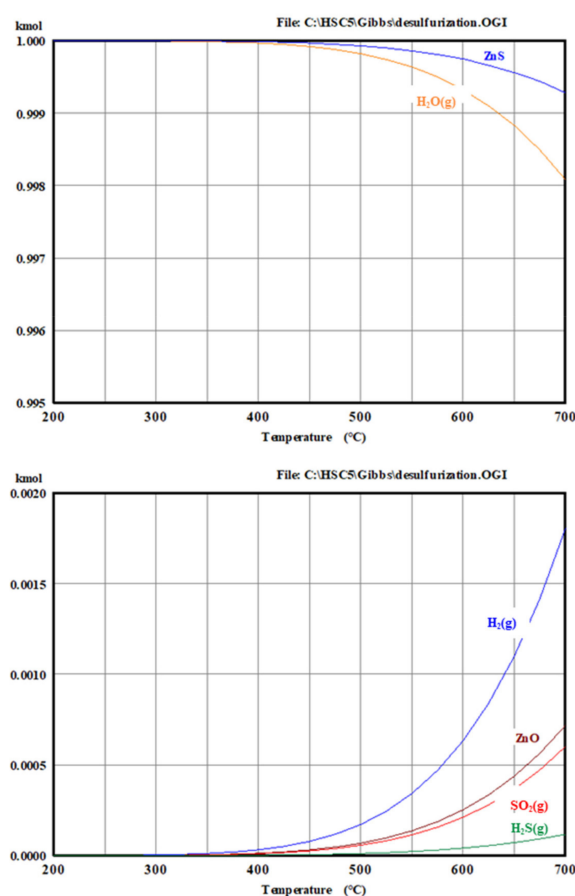


Figure 5. Effect of temperature on the consumption of reactant and generation of products in regeneration by H_2O , using Outokumpu HSC 5.1 software.

An additional experiment was carried out to confirm SO_2 generation under the condition of actual reducing gases (CO and H_2), as shown in Figure 6. The desulfurization of

3600 ppm H₂S was conducted at 550 °C under the reducing gas mixture (6.5% CO, 2.95% H₂, 0.15% CO₂, and N₂ balance). In the absence of reducing gases, ZnS was regenerated to ZnO by H₂O produced during desulfurization. Additionally, SO₂ gas was generated, as shown in Figure 5, whereas the ZnS was not regenerated during desulfurization in the presence of reducing gases.

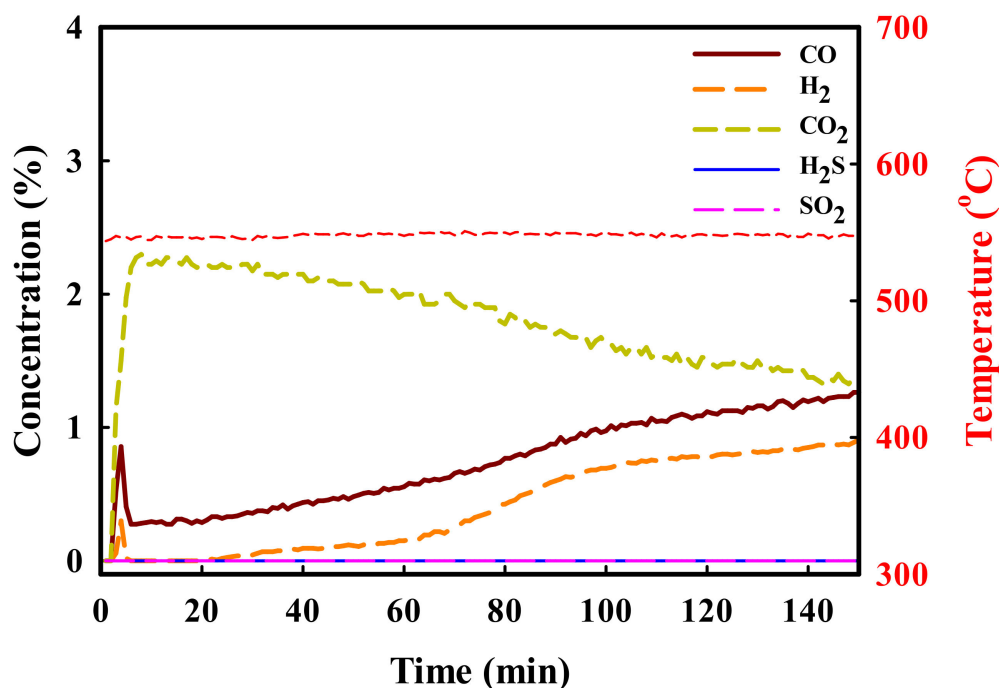


Figure 6. Variation in gas composition in the desulfurization process using 3600 ppm H₂S containing reducing gas (6.5% CO, 2.95% H₂, 0.15% CO₂ balanced by N₂).

It is expected that the H₂O generated during desulfurization can be formed over the water gas shift (WGS) reaction with reducing gases as shown in Equation (4).



However, the production of H₂ through the WGS reaction was very low, as the amount of H₂O (the reactant term) was already at a very low concentration due to a low concentration of H₂S for desulfurization (3600 ppm). As shown in Figure 6, the concentrations of CO and H₂ were detected as being as low as below 1% at the beginning of the reaction. The CO₂, injected at a concentration of 0.15%, increased to 2%. Due to the lower reduction temperature of NiO than ZnO, NiO can be partially reduced to Ni metal over the reducing gases of CO and H₂ by producing CO₂ gas (4). Additionally, as shown in Equations (5)–(8), the ZnS does not produce SO₂ because it is reduced by CO or H₂ [28–31].



Various possibilities were considered for the reason behind SO₂ generation during the desulfurization of H₂S. It is clear that ZnS was able to be regenerated by H₂O, resulting in the production of SO₂ in the N₂ atmosphere. However, in the reducing gas stream, H₂O can actively participate in the WGS reaction. Additionally, the metal oxide sorbent can be reduced by CO and H₂. Thus, the SO₂ gas was not produced under the simulated syngas

stream. Further study is needed to check whether the desulfurization sorbent affects the reduction gas composition beside the H_2S removal.

3. Materials and Methods

SC-229TD sorbent, manufactured by Korea Electric Power Corporation Research Institute (KEPCO RI) was used as a high-temperature desulfurization sorbent. The major components of the sorbent are active materials (40~50 wt% ZnO , 5~10% NiO) and support (Al_2O_3 , SiO_2). The SC-229TD sorbent was sieved to have a controlled particle size from 106 to 212 μm . The bulk density was 1001.64 kg/m^3 . The sorbent or mixture of sorbent and sand (weight ratio, 1:9) were filled to the height of 0.4 m in a fluidized bed reactor. Air was injected at 400 $^\circ\text{C}$ for 1 h to remove moisture and impurities before the desulfurization. The desulfurization experiment was started when no gases were detected, except for the balance gas of N_2 . The detailed conditions of the experiment are shown in Table 1.

Table 1. Experimental conditions of desulfurization.

	H_2S Desulfurization	Regeneration
Temperature ($^\circ\text{C}$)	450–650	650
Pressure	ambient	ambient
Flow rate (mL/min)	2000	2000
Gas composition (Vol.%)	H_2S : 0.4, or	O_2 : 3, N_2 : balance
	H_2S : 0.36	
	CO : 6.5,	
	H_2 : 2.95, CO_2 : 0.15, N_2 : balance	

Figure 7 shows the batch fluidized bed reactor used in this study. The fluidized bed reactor consists of a main reactor, a gas and water injection system, an electric furnace for maintaining the reactor temperature, and an on-line gas analyzer for analyzing the concentration of exhaust gas. The main reactor is made of stainless steel (SUS 310) with an inner diameter of 0.05 m, a thickness of 0.003 m, and a height of 0.7 m. The temperature of the reactor was controlled based on the internal temperature of the reactor (K-type thermocouple), by using an electric furnace temperature with a temperature indicator. The temperature was measured at a height of 0.2 m from the bottom of the reactor. The differential pressure of the fluidized bed was measured by installing a differential pressure transducer and pressure indicator at a height of 0.01 m and 0.58 m from the reactor bottom. The H_2S gas was supplied to the reactor using a mass flow controller (MFC) for desulfurization. The operating temperature range was from 450 $^\circ\text{C}$ to 650 $^\circ\text{C}$. For the sorbent regeneration, O_2 gas (3 vol.%) was used. The outlet gases from the reactor were automatically analyzed in real time with an on-line gas analyzer (Hartmann & Braun Co., Advance Optima) [32]. In addition, thermodynamic equilibrium data were calculated using the HSC 5.1 program. The ratio of ZnS and H_2O was assumed to be 1:1, and was calculated on the basis of 1 bar from 200 to 700 $^\circ\text{C}$.

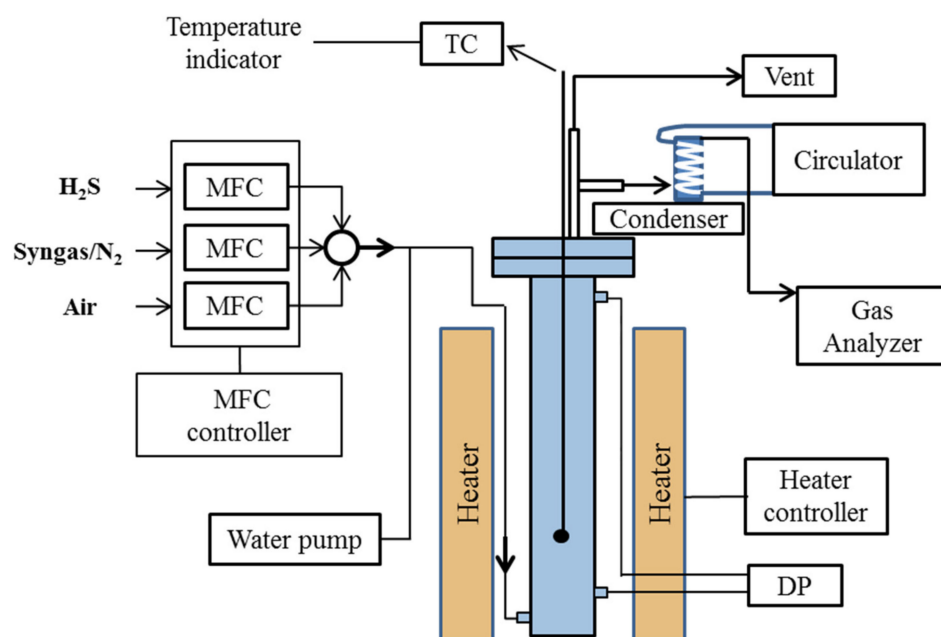


Figure 7. Schematic diagram of the experimental setup used with a batch type fluidized bed reactor for the HGD process.

4. Conclusions

In the integrated gasification combined cycle (IGCC) process, the sulfur compounds present in coal are converted to hydrogen sulfide (H_2S) when the coal is gasified. Due to the corrosive properties of H_2S , it deactivates the sorbent/solvent for CO_2 capture, due to its harmful effects; its release to the environment is also subject to environmental regulations. Thus, H_2S needs to be removed from the produced gas stream. To simulate the H_2S removal process, the desulfurization reaction was carried out using dry sorbent in a fluidized bed reactor at high temperatures. The ZnO -based sorbent used in this work showed not only an excellent capacity, but also long-term stability. However, SO_2 gas at a concentration of several hundred ppm was measured during the desulfurization process, where it was found that SO_2 gas was generated when the desulfurized ZnS was converted to Zn or ZnO by reacting with an unknown source of oxygen during desulfurization. The unknown oxygen source during desulfurization was deduced to be oxygen from H_2O produced during desulfurization. That is, the oxygen produced from H_2O reacted with ZnS , leading to SO_2 generation at a high temperature.

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Data Availability Statement: All relevant data are contained in the present manuscript. Other inherent data are available on request from the corresponding author.

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Conflicts of Interest: The authors declare no conflict of interest.

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