

Development of a pilot-scale acid gas removal system for coal syngas

Seung Jong Lee[†], Soung Hyoun Kim, Kyoung Hoon Kang, Young Don Yoo and Yongseung Yun

Institute for Advanced Engineering, 633-2, Goan-ri, Baegam-myeon, Cheoin-Gu, Yongin-si, Gyeonggi-do 449-863, Korea

(Received 31 August 2006 • accepted 2 April 2007)

Abstract—The Korean pilot-scale gasification facility consists of a coal gasifier, hot gas filtering system, and acid gas removal (AGR) system. The syngas stream from the coal gasification at the rate of 100-120 Nm³/hr included pollutants such as fly ash, H₂S, COS, etc. The acid gas, such as H₂S and COS, is removed in the AGR system before generating electricity by gas engine and producing chemicals like Di-methyl Ether (DME) in the catalytic reactor. A hydrolysis system was installed to hydrolyze COS into H₂S. The designed operation temperature and pressure of the COS hydrolysis system are 150 °C and 8 kg/cm². After the hydrolysis system, COS was reduced below 1 ppm at the normal operating condition. The normal designed operation temperature and pressure of the AGR system are below 40 °C and 8 kg/cm². Fe-chelate was used as an absorbent. H₂S was removed below 0.5 ppm in the AGR system when the maximum concentration of H₂S was 900 ppm. A small scale COS adsorber was also installed and tested to remove COS below 0.5 ppm. COS was removed below 0.1 ppm after the COS adsorbents such as the activated carbon and ion exchange resin.

Key words: Gasification, Syngas, COS Hydrolysis, Acid Gas Removal, Absorbent, Fe-chelate

INTRODUCTION

Gasification technology has developed in the energy and environmental fields with many advantages to convert low-grade fuels such as coal, biomass, wastes, residual oil, natural gas, etc., into syngas with near-zero pollutant emissions. Syngas is primarily CO and H₂ (more than 85% by volume) and smaller quantities of CO₂, CH₄, NH₃, H₂S, COS etc., before the syngas purification. After purification, syngas can be variously used in energy and environment fields to produce electricity, hydrogen and synthetic fuels such as Fischer-Tropsch (FT) diesels, Di-methyl Ether (DME) and methanol after pollutants are removed.

Because of high prices for crude oil and regulations due to climate change, many countries including Korea have been interested in developing gasification technology and its applications. Korea imports almost all energy resources from abroad and thus must utilize abundant coal resources. For Korea, coal is an inevitable feedstock to cover at least 30% of the total electricity during the next 30-50 years, and the gasification technology will be the most environmentally suitable technology for coal utilization in Korea, unless there is a revolutionary discovery in energy conversion technologies.

In Korea, the pilot-scale entrained-bed coal gasifier has been operated since 1994. The gasifier has a maximum capacity of 3 tons/day (T/D) at maximum 30 bar and 1,550 °C. This gasification facility consists of the coal gasifier, the hot gas filtering system and the cold gas cleanup system to remove sulfur-containing trace gases. And from 2004, a process development facility in converting coal syngas into chemical feedstock has been operated.

It is inevitable to remove acid gases such as H₂S and COS before

converting syngas to chemicals for protecting catalysts from surface poisoning. This paper illustrates the design conditions and the operation results of the COS hydrolysis system and the AGR (acid gas removal) system.

EXPERIMENTAL

Fig. 1 illustrates a schematic block diagram of the pilot-scale coal gasification system. Sub-bituminous (or bituminous) coal is pulverized and dried in the pulverizing system and then moved into the injection system. The pulverized coal is then transported by N₂ to the gasifier. In the gasifier, coal powder mixes with O₂, steam and then produces syngas by the gasification reactions. On the top right-hand side, the particulate filtering and acid gas removal system are shown. Syngas containing small particulates flows into the metal or ceramic filters to remove particulates at 250-400 °C. The COS component included in the particulate-free syngas is converted into H₂S in the COS hydrolysis system [1]. After water scrubbing, the hydrolyzed syngas flows into the low-temperature AGR system to remove H₂S. The clean syngas is then used for generating electricity in the gas engine or producing DME in the catalyst reactor. For the gasification part, more details are published elsewhere [2].

The H₂S and COS removal system consist of three parts: the COS hydrolysis system, the AGR system (the H₂S removal system) and a small-scale COS absorber to test the COS removal in the slip-stream of syngas. Fig. 2 shows a schematic diagram of the H₂S and COS removal system installed in the pilot-scale gasification system.

The design condition of COS hydrolysis system is shown in Table 1. The operation temperature and pressure of the COS hydrolysis reactor are 150 °C and 8 kg/cm². The loading amount of catalysts made by BASF is 20 kg to hydrolyze about 50 ppm of COS included in 120 Nm³/hr of syngas. COS is converted to H₂S in the hydrolysis system [1]. The COS hydrolysis reaction is as follows:

[†]To whom correspondence should be addressed.

E-mail: sjlee@iae.re.kr

^{*}This work was presented at the 6th Korea-China Workshop on Clean Energy Technology held at Busan, Korea, July 4-7, 2006.

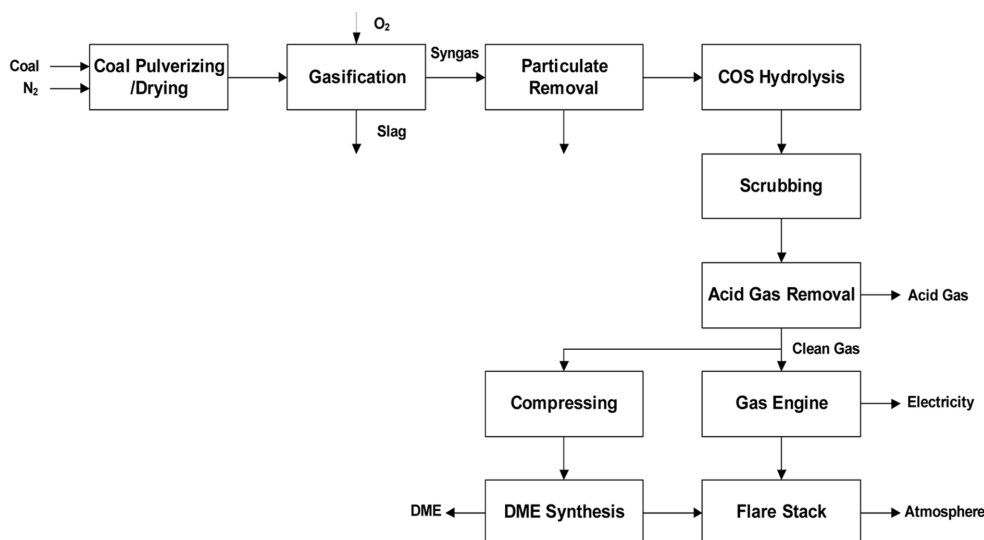


Fig. 1. Process flow block diagram of the pilot-scale coal gasification system.

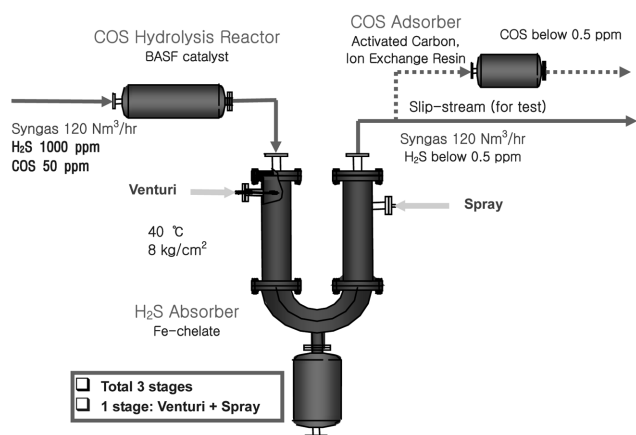
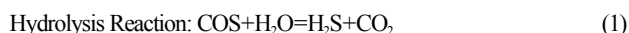


Fig. 2. A schematic diagram of the COS hydrolysis system and the AGR system installed in the pilot-scale coal gasification system.

Table 1. Design condition of the COS hydrolysis system

Item	Design condition	Remark
Operating pressure	8-10 kg/cm ²	Max. 25 kg/cm ²
Operating temperature	150 °C	Max. 500 °C
Syngas flow rate	100-120 Nm ³ /h	Max. 200 Nm ³ /h
Amount of catalyst loading	20 kg	BASF catalyst D 10-10
COS inlet concentration	50 ppm	Max. 70 ppm
COS outlet concentration	Below 2 ppm	

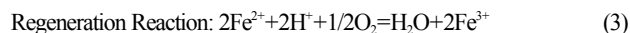
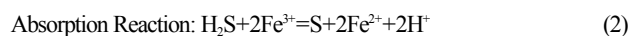


The design conditions of the low-temperature AGR system are shown in Table 2. The operation temperature and pressure of the AGR system are 40 °C and 8 kg/cm². About 1,000 ppm of H₂S included in the syngas of 120 Nm³/hr can be removed to below 0.5 ppm in the AGR system by using Fe-chelate. The AGR system consists of three stages. Each stage has one venturi nozzle and one spray

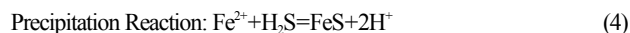
Table 2. Design condition of the low-temperature AGR system

Item	Design condition	Remark
Operating pressure	8-10 kg/cm ²	Max. 25 kg/cm ²
Operating temperature	30-40 °C	Max. 50 °C
Syngas flow rate	100-120 Nm ³ /h	Max. 200 Nm ³ /h
H ₂ S inlet concentration	250 ppm	Max. 1,000 ppm
H ₂ S outlet concentration	Below 0.5 ppm	
Dimension of AGR system (mm)	2,900×3,100×5,100	
Syngas residence time (sec)	120	

nozzle. Fe³⁺ converts Fe²⁺ to remove H₂S and then Fe²⁺ is regenerated to Fe³⁺ by the air in the regenerator [3]. The reactions in the AGR system are as follows:



It is important to maintain the pH of Fe-chelate solution between 8 and 9 for a suitable operating condition [3]. If the absorption reaction and the regeneration reaction proceed ideally, there is no change in the Fe-chelate concentration. However, if the regeneration reaction does not proceed sufficiently, Fe²⁺ may react with H₂S to produce FeS as follows:



Therefore, if a precipitation reaction occurs, the concentration and the pH of Fe-chelate solution would be reduced.

In order to test the COS removal to below 0.5 ppm, a small scale COS adsorber was installed in the slip-stream of syngas. The adsorbents used in this study are the activated carbon and ion exchange resin.

Gas chromatography (GC) and the on-line GC were used for the analysis of H₂S and COS. In the on-line GC, the H₂S and COS were directly injected through the sampling line to be analyzed in real

Table 3. Specifications of GC and on-line GC

Item	GC	On-line GC
Detector	Flame photometric	Flame photometric
Column	Varian CP 7685	60/80 Carboxpack B
Carrier gas	He	H ₂
Carrier gas flow rate	0.08 l/min	0.17 l/min
Isothermal temperature	40 °C	80 °C
Detection limit	1.0 (normal) 0.1 (calibrated experimentally)	0.1 (for low concentration) 1.0 (for high concentration)

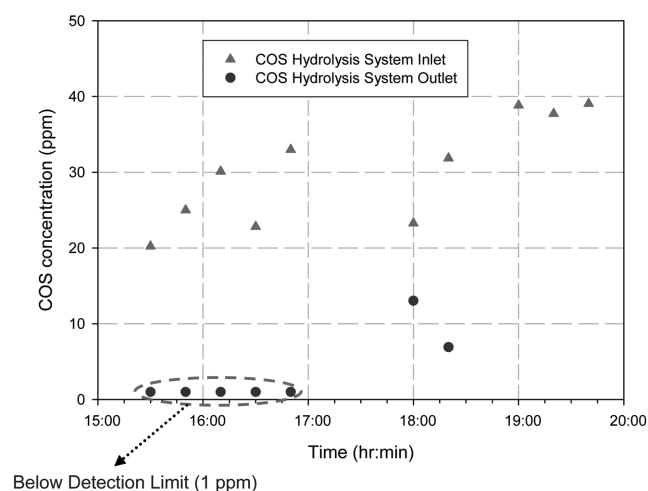
time. In the GC, the H₂S and COS were analyzed by using the sampling bag. The specifications of the GC and the on-line GC used in this study are shown in Table 3. The normal detection limit of GC is 1.0 ppm. After the calibration of GC was performed experimentally for more detailed analysis, the detection limit of GC was 0.1 ppm. The on-line GC can be used for two different concentration ranges of H₂S and COS. One is for analyzing high concentration gas (0–50 ppm) and the other is for analyzing low concentration gas (0–1 ppm). The detection limit of the on-line GC is 1.0 ppm for detecting high concentration of H₂S and COS and 0.1 ppm for detecting low concentration of H₂S and COS.

The AGR system was used to test four different conditions for the applications of the AGR system to the gasification system using different coals:

- 1) Partial regeneration of Fe-chelate solution in Kideco sub-bituminous coal gasification.
- 2) Full regeneration of Fe-chelate solution in Kideco sub-bituminous coal gasification.
- 3) Full regeneration of Fe-chelate solution in Roto sub-bituminous coal gasification.
- 4) Full regeneration of Fe-chelate solution in Shenhua sub-bituminous coal gasification.

RESULTS AND DISCUSSION

1. COS Hydrolysis System Operation

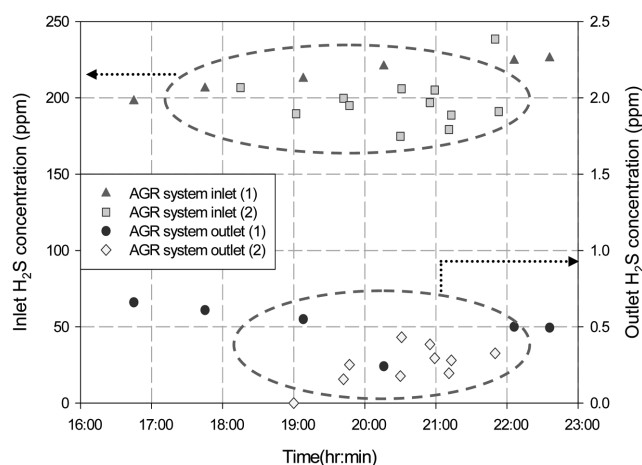
**Fig. 3. The operation results of the COS hydrolysis system.**

The operation results of the COS hydrolysis system are shown in Fig. 3 in Roto sub-bituminous coal gasification. The concentration of COS from the gasification system was maintained at 20–40 ppm. COS was reduced to below 1 ppm after the COS hydrolysis system when the operating temperature was maintained over 120 °C. However, when the operating temperature was below 120 °C, COS was increased to 10 ppm. Thus, it is important to maintain the operating temperature of the COS hydrolysis reactor. We are going to develop the operating method of the COS hydrolysis reactor for maintaining a stable operation temperature above 150 °C.

2. AGR System Operation

The operation results of the AGR system are shown in Figs. 4–6. Fig. 4 and Fig. 5 show the operation results of the AGR system when Kideco and Roto sub-bituminous coals were used. When Shenhua sub-bituminous coal was used for gasification, the operation result of the AGR system is shown in Fig. 6.

Two different operation condition results are shown in Fig. 4. One (No. 1) is the operation result of the partial regeneration of the Fe-chelate solution and the other (No. 2) is the operation result of the full regeneration of the Fe-chelate solution in Kideco sub-bituminous coal gasification. In the case of No. 1, H₂S was removed below 1 ppm, but not enough for the design condition (below 0.5 ppm). A considerable amount of the reduced Fe²⁺ might be reacted with H₂S to produce FeS because of the partial regeneration condition, and thus a reduction of the Fe-chelate concentration occurred. After the operation conditions to the full regeneration system of the Fe-

**Fig. 4. The operation results of the AGR system for the syngas from Indonesian Kideco coal.**

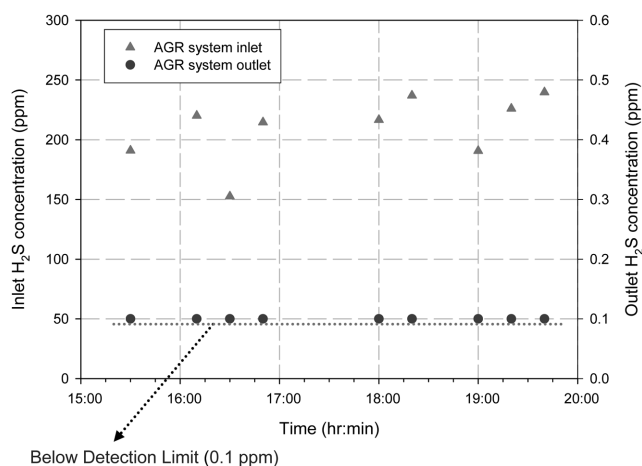


Fig. 5. The operation results of the AGR system for the syngas from Indonesian Roto coal.

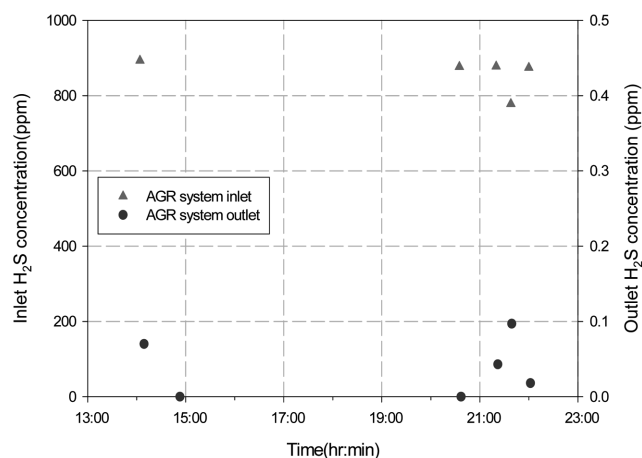


Fig. 6. The operation results of the AGR system for the syngas from Chinese Shenhua coal.

chelate solution (No. 2) were changed, H_2S could be removed below 0.5 ppm.

Fig. 5 shows the operation results of the AGR system detected by the on-line GC when Roto sub-bituminous coal was used for gasification. When the AGR system was stably operated, H_2S was removed to below the detection limit of the on-line GC which was below 0.1 ppm.

Because Kideco and Roto sub-bituminous coal could produce H_2S below 150–250 ppm in the gasification system not enough for testing the design condition of the AGR system, another coal was needed to produce high concentration of H_2S . Shenhua sub-bituminous coal was adopted to produce high concentration of H_2S in the gasification system. When H_2S was maintained at 800–900 ppm by the gasification with Shenhua sub-bituminous coal, H_2S was also stably removed to below 0.1 ppm in the AGR system that was detected by GC as shown in Fig. 6.

The operation temperature and pH of the AGR system are shown in Fig. 7 when Roto sub-bituminous coal was used. It is important to maintain the pH of Fe-chelate to remove H_2S effectively. Fig. 7 shows that the pH of Fe-chelate solution in each stage was main-

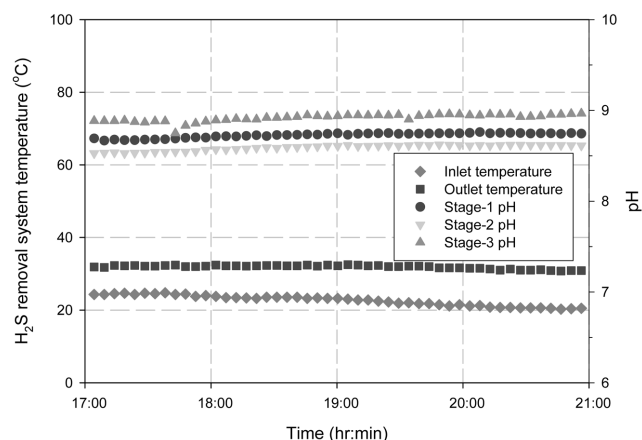


Fig. 7. Variations of the temperature and the pH of Fe-chelate during the operation of AGR system.

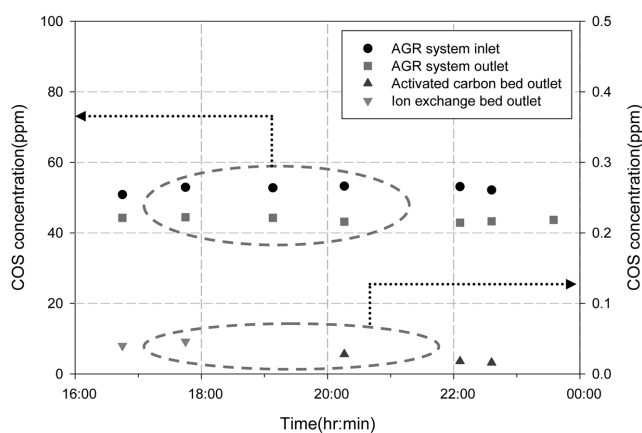


Fig. 8. The operation results of the COS adsorber.

tained between 8.5 and 9.0 stably. It also shows that the temperature of the AGR system was maintained at 20–40 °C and the temperature increased about 10 °C in the AGR system.

3. Small-scale COS Absorber Operation

Fig. 8 shows the analysis of COS concentration after the COS adsorbents. The adsorbents tested in this study were the activated carbon and the ion exchange resin. When the concentration of COS from the gasification system was maintained at 50 ppm, about 10 ppm of COS was removed in the AGR system even without COS adsorbents. In contrast, COS was removed below 0.1 ppm after the adsorbents.

CONCLUSIONS

In order to remove acid gases such as H_2S and COS from coal syngas, a hydrolysis system and AGR system were designed and installed. The designed operation temperature and pressure of the COS hydrolysis system were 150 °C and 8 kg/cm². The amount of the catalysts loaded in the hydrolysis reactor was 20 kg to treat 120 Nm³/hr of syngas. After the hydrolysis system, COS was reduced below 1 ppm and converted to H_2S at the normal operating condition. COS was also removed below 0.1 ppm in the small scale activated carbon and the ion exchange resin adsorbents tested through

the slip-stream of syngas.

The designed operation temperature and pressure of the AGR system were below 40 °C and 8 kg/cm². Fe-chelate was used as an absorbent. H₂S from three different kinds of coals was tested. H₂S was removed below 0.1 ppm in the AGR system when the maximum concentration of H₂S was 900 ppm. The temperature increased about 10 °C after passing the AGR system. The pH of the Fe-chelate was well maintained between 8.5 and 9.0 during the stable operation.

From the operation experience of the low-temperature desulfurization for coal syngas, it was confirmed that an economical desulfurization system at the pilot-scale level is possible without resorting to commercially available systems.

ACKNOWLEDGMENT

This work was supported by New & Renewable Energy Center, in Korea Energy Management Corporation (KEMCO), Korea with the research title of 'Development of Conversion Technology from Syngas to Chemicals in Coal Gasification'.

REFERENCES

1. B. P. Williams, N. C. Young, J. West, C. Rhodes and G. J. Hutchings, *Catalysis Today*, **49**, 99 (1999).
2. Y. Yun and Y. D. Yoo, *Korean J. Chem. Eng.*, **18**, 679 (2001).
3. S. G. Jin, J. M. Cha, I. W. Lee, S. J. Yoon and S. W. Kim, *J. of Korean Ind. & Eng. Chemistry*, **7**, 177 (1996).