

# Application of coal gasification technology as a flue gas pre-conditioning step for the catalytic reduction of acid gases

Ming Fang<sup>a</sup>, Jianxin Ma<sup>b</sup>, Ngai T. Lau<sup>a,\*</sup>, Lei Wang<sup>b</sup>, Shaosong Qian<sup>b</sup>, King L. To<sup>a</sup>

<sup>a</sup> Institute for Environment and Sustainable Development, Hong Kong University of Science and Technology, Clearwater Bay, Hong Kong, Hong Kong

<sup>b</sup> Institute of Industrial Catalysis, East China University of Science and Technology, Shanghai, China

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## Abstract

Typical flue gas contains an excess amount of oxygen, which can deactivate the reduction catalyst for NO<sub>x</sub> and SO<sub>2</sub>, such as the lanthanum oxysulfide-based catalyst. The reductant available in a flue gas stream rich in oxygen is usually scarce and not sufficient for the reduction. Coal gasification was applied to pre-condition the flue gas to remove the excessive oxygen and co-generate carbon monoxide for the reduction of NO<sub>x</sub> and SO<sub>2</sub> in this study. Coal was carbonized to porous semi-coke to prevent clogging caused by the condensation of volatiles before being gasified. The reactivity of the semi-coke with simulated flue gas was found to be the same as activated carbon. The semi-coke samples prepared from various coal sources proved to be effective in removing O<sub>2</sub> (over 90%) from the flue gas and a sufficient amount of CO was co-generated for the conversion of NO and SO<sub>2</sub> over a supported lanthanum oxysulfide catalyst in a subsequent reduction reactor. NO and SO<sub>2</sub> in the flue gas were also reduced in the gasification process, contributing to the overall denitrification and desulfurization efficiency. An overall NO and SO<sub>2</sub> removal efficiency of over 96% was achieved for a sequential coal gasification and catalytic reduction process, and the selectivity to elemental sulfur was as high as 98%.

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**Keywords:** Coal gasification; Flue gas; Lanthanum oxysulfide; Sulfur dioxide; Nitric oxide

## 1. Introduction

Fang and Ma [1] and Ma et al. [2] showed that sulfur dioxide and nitric oxide can be reduced simultaneously to elemental sulfur and nitrogen by carbon monoxide over lanthanum oxysulfide-based catalysts. The conversion can be over 95% with high sulfur selectivity [1–3] and the catalyst can maintain its activity for at least 1000 h [4]. This reduction technology can be applied to the emission control of flue gas. However, flue gas usually contains a substantial amount of water vapor and residual oxygen, which can deactivate the catalysts [3]. At the same time, the amount of carbon monoxide left in the oxygen-rich flue gas is usually minimal and cannot meet the demand for the reductant.

In this study, a coal gasification technology is applied to reduce the oxygen content in the flue gas and to co-generate sufficient carbon monoxide for the reduction of sulfur dioxide and nitric oxide. This technique may not be the best solution because of the additional consumption of coal and emission of carbon dioxide; however, it does provide an

engineering option to the oxygen deactivation and the supply of the reducing agent issues.

Coal gasification is a well-developed technology in which coal is partially oxidized to a mixture of carbon dioxide, carbon monoxide and some light hydrocarbons by air or pure oxygen at high temperatures. Water may also be added to help reform the gas. The composition of the resulting gas products depends on the properties of the coal and the gasification conditions. The latter includes feed composition, temperature and pressure. Coal is usually carbonized to remove volatile matter at temperatures <973 K (low-temperature process) or ≥1173 K (high-temperature process) [5] before being gasified, and the low-temperature coal carbonization is known to yield substantial devolatilized yet sufficiently reactive semi-coke [6].

Semi-coke is different from activated carbon in that semi-coke contains mineral matter which can constitute as high as 35% by weight of the raw coal [6]. This mineral matter is made up of silicate, carbonate, oxide, sulfate and sulfide of various metals including alkali, alkaline and transition elements and is possibly influential to both the gasification and the catalytic reduction of sulfur dioxide and nitric oxide. Martinez-Alonso and Tascon [7] showed that mineral

\* Corresponding author. Tel.: +852-2358-6935; fax: +852-2719-6710.  
E-mail address: ntlau@ust.hk (N.T. Lau).

matter modified the reactivity of chars by a direct catalytic effect and an indirect effect to modify the chars' physical and chemical structures. Typical coal contains 1–43 ppm cobalt, 5–61 ppm copper, 3–80 ppm nickel and 0.06–3.78% iron [6]. These transition metals have enormous implications to the water-gas shift reaction [8,9] and the reduction of sulfur dioxide and nitric oxide [2,9–11]. The synergistic effect of transition metals, which has been elaborated with the reduction of sulfur dioxide over cobalt sulfides and lanthanum oxysulfide [11], promotes the catalytic reduction reactions.

## 2. Experimental

### 2.1. Carbon material

Four coal samples were tested. Three were obtained from a local power company (CC-1, CC-2, CC-3). The last one was a coal commonly used in the boiler plants in China (CC-4). Their properties are listed in Table 1. The data were either provided on manifests obtained from the coal suppliers or derived from thermal analysis (Netzsch, STA 409C) and carbonization experiments. The surface area was measured using BET method (Micromeritics, ASAP2000). In addition, three activated carbon samples from Supelco, Norit and Riedel-deHaën (AC-1, AC-2 and AC-3) were selected as reference carbon materials for comparison purposes.

All the coal samples were carbonized in ultra-high purity (UHP) nitrogen at 923 K for 2 h to remove volatile matter before they were used in the gasification experiment. The

Table 1  
Properties of coal samples

	Coal sample			
	CC-1	CC-2	CC-3	CC-4
Air-dry loss <sup>a,b</sup> (%)	8.1	6.5	6.6	–
Residual moisture <sup>b,c</sup> (%)	2.6	2.7	6.9	–
Total moisture <sup>a,b</sup> (%)	10.4	9.0	13.1	–
Gross calorific value <sup>b,d</sup> (kcal kg <sup>-1</sup> )	6993.4	6980.0	5960.0	–
Volatile matter <sup>b,d</sup> (%)	42.6	27.3	28.2	–
Volatile matter (thermogravimetry) (%)	39.5	24.5	34.0	27.5
Weight loss on carbonization (%)	40.9	25.5	29.9	23.7
Total sulfur content <sup>b,d</sup> (%)	0.97	0.20	0.60	–
Ash content <sup>b,d</sup> (%)	12.7	13.6	22.3	–
Ash content (thermogravimetry) (%)	12.5	13.0	14.0	28.0
Total acid-extractable iron <sup>a</sup> (%)	0.31	1.87	0.49	0.64
BET surface area <sup>e</sup> (m <sup>2</sup> g <sup>-1</sup> )	8.5	7.2	46.8	10.3

<sup>a</sup> As received.

<sup>b</sup> Data provided on certificates from coal suppliers.

<sup>c</sup> As analyzed.

<sup>d</sup> Dry basis.

<sup>e</sup> Data obtained from direct measurement made on the semi-coke samples.

weight loss during this carbonization pretreatment is comparable to the volatile matter content measured using standard methods such as ASTM D 3175.

Amongst the metals contained in coal, iron is a major constituent and its concentration usually reflects the total metal content of the coal. The iron content of the coal samples was determined as the total acid-extractable iron according to ISO 157. This result includes the hydrochloric acid-extractable iron and nitric acid-extractable pyritic iron. The iron concentration of the extracted solution was measured colorimetrically using a visible light spectrophotometer (Beckman, DU650) after the addition of 1,10-phenanthroline monohydrate.

### 2.2. Catalyst preparation

Monolith-supported lanthanum oxysulfide catalyst was used in this study. A ceramic honeycomb substrate of 400 cells in.<sup>-2</sup> was machined to fit the reactor (Ø1.4 cm × 3 cm) and coated with a washcoat of  $\gamma$ -alumina (washcoat: substrate = 0.25 by weight). The substrate was then impregnated with an aqueous solution of lanthanum nitrate. The amount of the active component (in the form of La<sub>2</sub>O<sub>3</sub>) was 20 wt.% after the catalyst was dried at 393 K for 4 h and calcined in air at 1123 K for 8 h. The supported catalyst was activated in situ in the reactor according to the sulfidization procedure described by Ma et al. [12].

### 2.3. Experimental setup

The schematic of the flow system used in the experiment is shown in Fig. 1. This study used two continuous-flow tubular fixed-bed reactors. One was used for gasification and carbonization and the other for catalytic reduction. A three-way valve was installed between the two reactors to switch either the feed or the effluent of the reactors to the gas analyzers, which included a process mass spectrometer (Extrel, MS250) and two non-dispersive NDIR gas analyzers (Horiba, VIA 510). The reactors were approximately 50 cm long fabricated with 2 cm diameter quartz tube. The quartz reactors were heated electrically from the outside.

UHP N<sub>2</sub> was used to carbonize the coal samples while a simulated flue gas mixture of SO<sub>2</sub>, NO, O<sub>2</sub>, H<sub>2</sub>O and N<sub>2</sub> was used to gasify the coal. The typical gasification feed contained 0.5% SO<sub>2</sub>, 0.2% NO, 3% O<sub>2</sub>, 10% H<sub>2</sub>O and balanced with N<sub>2</sub>. The flow rate of the dry feed was 200 ml min<sup>-1</sup>. Water vapor was introduced to the flow by pumping de-ionized water continuously to the preheating zone of the gasification reactor through a quartz capillary of 0.2 mm internal diameter with a syringe pump. The gasified stream was cooled and dried in an ice-bath trap before entering the reduction reactor.

### 2.4. Carbonization, gasification, desulfurization and denitrification

The initial coal bed had a volume of 10 ml and was carbonized by heating to 923 K within 0.5 h and held for 2 h.

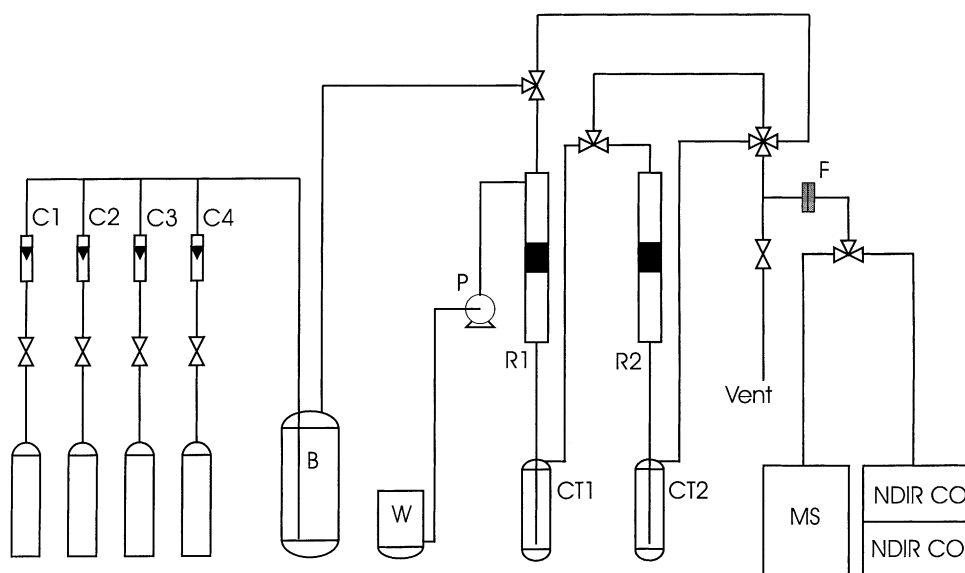


Fig. 1. Schematic diagram of apparatus used in the experiments—B: gas buffer; C1–C4: gas streams (1:  $\text{SO}_2/\text{N}_2$ , 2:  $\text{NO}/\text{N}_2$ , 3:  $\text{O}_2/\text{N}_2$ , 4:  $\text{N}_2$ ); CTs: ice bath traps; F: filter ( $2\ \mu\text{m}$ ); MS: mass spectrometer (EXTREL, MS250); NDIR: gas analyzers (Horiba, VIA310); P: syringe pump; R1: gasification reactor; R2: reduction reactor; W: water tank.

The sample was then cooled down in  $\text{N}_2$  and ready for the gasification experiment. The gasification experiment was performed in 50 K steps between 523 and 873 K. A detailed temperature dependence study was performed from 573 to 1073 K using the activated carbon sample AC-1. It took approximately 30 min for the gasification reaction to reach pseudo-steady-state in each step. The conversion efficiency of the combined gasification and simultaneous catalytic desulfurization and denitrification over the supported lanthanum oxysulfide catalyst was measured between 773 and 873 K for gasification, and between 873 and 923 K for reduction.

### 3. Results and discussions

#### 3.1. Coal carbonization

The volatile matter content of the coal samples is listed in Table 1. The volatile matter contents measured by weight difference before and after carbonization and by thermogravimetry in a nitrogen stream are close to the figures provided by the suppliers. All the four coal samples can be classified as bituminous [5].

The total sulfur content of the three coal samples from a local power company ranged from 0.2 to 0.97%. The total sulfur content of the coal sample from China was unknown and was not determined. It has been reported that the average sulfur content of coal sold in the market in China was about 1.1% [13]. This sulfur would increase the sulfur dioxide loading of flue gas conditioned by gasification.

The ash content of the samples ranged from 12.5 to 28%. The ash content measured by thermogravimetry in air stream

is not significantly different from the data provided by the coal suppliers. The maximum difference between the thermogravimetric and suppliers' figures is 37%. Most of the ash was retained in the gasification reactor instead of being entrained with the flue gas. It is expected that the dominant portion of the ash transported out of the gasification reactor, if any, would be deposited on the cool interconnecting tubing between the gasification and reduction reactors. There should be no significant deposition of ash on the reduction catalyst within the typical combined gasification and reduction experiment.

The total acid-extractable iron varied between 0.3 and 1.87%, providing rough estimates of the total mineral matter in the coal samples. Iron is known to be influential to the water-shift gasification reaction [8,9] and most of the iron was probably retained in the gasification reactor with the ash. Carbonization made the coal porous but did not change the volume significantly. The BET area of the carbonized coal samples or semi-cokes varied widely from  $7.2\ \text{m}^2\ \text{g}^{-1}$  (CC-2) to  $46.8\ \text{m}^2\ \text{g}^{-1}$  (CC-3).

#### 3.2. Gasification with flue gas

The main objective of the gasification reaction is to reduce the oxygen in the flue gas to a level that it will not deactivate the reduction catalyst, and to generate sufficient CO to reduce the  $\text{SO}_2$  and NO. It was found that the gasification reaction not only scavenges  $\text{O}_2$  but also reduces  $\text{SO}_2$  and NO, thus reduces the load for the reduction reactor.

The activated carbon AC-1 was examined over a wider temperature range for the effect of temperature on gasification. The  $\text{O}_2$  consumption, the production of CO and  $\text{CO}_2$  and the reaction of  $\text{SO}_2$  and NO are illustrated in Fig. 2.

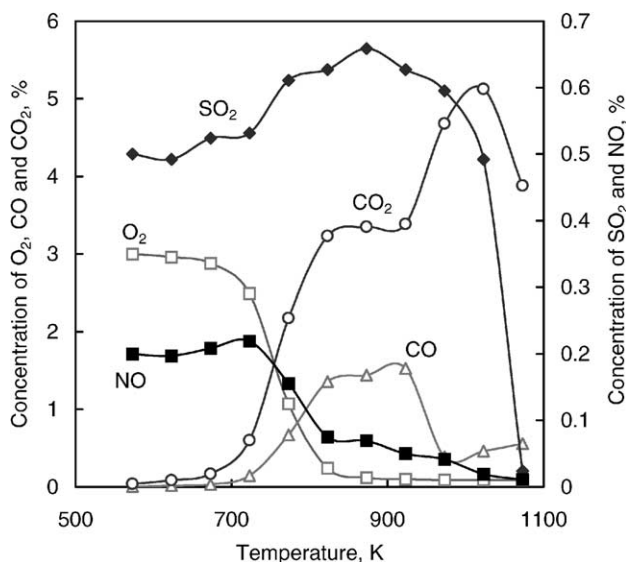


Fig. 2. Change in the concentration of  $\text{SO}_2$  (solid rhombus),  $\text{NO}$  (solid square),  $\text{O}_2$  (open square),  $\text{CO}_2$  (open circle) and  $\text{CO}$  (open triangle) in the gasification of activated charcoal AC-1 using simulated flue gas between 573 and 1073 K.

The concentration of  $\text{O}_2$  decreased rapidly with temperature from 723 K onwards. Almost all the  $\text{O}_2$  was consumed above 823 K. The production of  $\text{CO}$  increased with temperature, except in the range between 923 and 973 K.  $\text{CO}_2$  followed the same trend as  $\text{CO}$  at temperatures below 923 K and became the opposite at higher temperatures.  $\text{SO}_2$  increased in concentration from 623 to 873 K while  $\text{NO}$  increased in concentration between 623 and 723 K, and then steadily dropped. The increase could be partly attributed to the oxidation of the sulfur and nitrogen in the semi-coke samples and the desorption of the previously adsorbed  $\text{SO}_2$  and  $\text{NO}$  at low-temperature before gasification started. Additional  $\text{NO}_x$  might have been produced by the oxidation of  $\text{N}_2$  in the flue gas during the gasification. As the temperature increased sufficiently, the gases reacted with the semi-cokes and their outlet concentration decreased. The

minimum temperature of the reaction for  $\text{NO}$  ( $\sim 723$  K) was much lower than that of  $\text{SO}_2$  ( $\sim 873$  K).

Table 2 shows the major reactions involved in the coal gasification process [6]. The dominant reactions below 923 K are the oxidation and partial oxidation of carbon. The water-gas shift reaction becomes important between 923 and 1023 K. When the temperature increases further above 1023 K, the effect of the Boudouard reaction becomes prominent. Although an enormous amount of heat was released by the exothermic oxidation reactions, no thermal runaway was recorded. It was because the oxidation reactions were restricted by the limited supply of  $\text{O}_2$  and the overall amount of heat generated was regulated by the endothermic water-gas shift reactions and Boudouard reaction.

The residence time of the gasification reaction decreased as the sample was gradually consumed. The gasification reaction was more limited by the supply of  $\text{O}_2$  than the residence time, as the conversion was high throughout the experiment with nearly all the  $\text{O}_2$  consumed once gasification started.

### 3.3. Gasification—removal of $\text{O}_2$ with $\text{CO}$ co-generation

The four carbonized coal or semi-coke samples were all effective in removing  $\text{O}_2$  from the flue gas (Figs. 3–6). Their results are comparable to the activated carbons (AC-1 and AC-2) as shown in Figs. 7 and 8. A significant removal of  $\text{O}_2$  started at about 623 K and the  $\text{O}_2$  removal rate reached a maximum at  $\sim 673$  K. At 773 K, over 98% of  $\text{O}_2$  was removed. In comparison to the two activated carbon samples, the coal samples were more effective in removing  $\text{O}_2$ . No significant  $\text{O}_2$  removal was identified until 673 K for the activated carbon samples. It is noted that the concentration of the residual  $\text{O}_2$  is sufficiently low at 773 K to minimize  $\text{O}_2$  deactivation for a downstream reducing catalyst.

$\text{CO}$  and  $\text{CO}_2$  were produced above 523 K. The formation of  $\text{CO}$  increased monotonically between 573 and 873 K, with the exception of AC-2. For all the semi-cokes, the ratio of

Table 2

Reactions involved in coal gasification. The enthalpy and Gibbs free energy of formation, and the standard entropy are obtained from Lide [14]

	$\Delta H^\circ$ at 298.15 K (kJ mol <sup>-1</sup> )	$\Delta G^\circ$ at 298.15 K (kJ mol <sup>-1</sup> )	$S^\circ$ at 298.15 K (J mol <sup>-1</sup> K <sup>-1</sup> )
$\text{C(s)} + \text{O}_2(\text{g}) = \text{CO}_2(\text{g})$ (oxidation)	-393.5	-394.4	213.8
$\text{C(s)} + 0.5\text{O}_2(\text{g}) = \text{CO(g)}$ (partial oxidation)	-110.5	-137.2	197.7
$\text{H}_2(\text{g}) + 0.5\text{O}_2(\text{g}) = \text{H}_2\text{O(l)}$	-285.8	-237.1	70.0
$\text{H}_2(\text{g}) + 0.5\text{O}_2(\text{g}) = \text{H}_2\text{O(g)}$	-241.8	-228.6	188.8
$\text{C(s)} + 2\text{H}_2(\text{g}) = \text{CH}_4(\text{g})$	-74.4	-50.3	196.3
$2\text{C(s)} + \text{H}_2(\text{g}) = \text{C}_2\text{H}_2(\text{g})$	228.2	210.7	200.9
$\text{C(s)} + \text{CO}_2(\text{g}) = 2\text{CO(g)}$ (Boudouard reaction)	172.5	120.0	-
$\text{CO(g)} + 2\text{H}_2(\text{g}) = \text{CH}_3\text{OH(g)}$	-91.0	-64.3	-
$\text{CO(g)} + 3\text{H}_2(\text{g}) = \text{CH}_4(\text{g}) + \text{H}_2\text{O(g)}$	-205.7	-141.7	-
$\text{CO}_2(\text{g}) + 4\text{H}_2(\text{g}) = \text{CH}_4(\text{g}) + 2\text{H}_2\text{O(g)}$	-164.5	-113.1	-
$\text{C(s)} + \text{H}_2\text{O(g)} = \text{CO(g)} + \text{H}_2(\text{g})$	131.3	91.4	-
$\text{C(s)} + 2\text{H}_2\text{O(g)} = \text{CO}_2(\text{g}) + 2\text{H}_2(\text{g})$	90.1	62.8	-
$\text{CO(g)} + \text{H}_2\text{O(g)} = \text{CO}_2(\text{g}) + \text{H}_2(\text{g})$ (shift reaction)	-41.2	-28.6	-

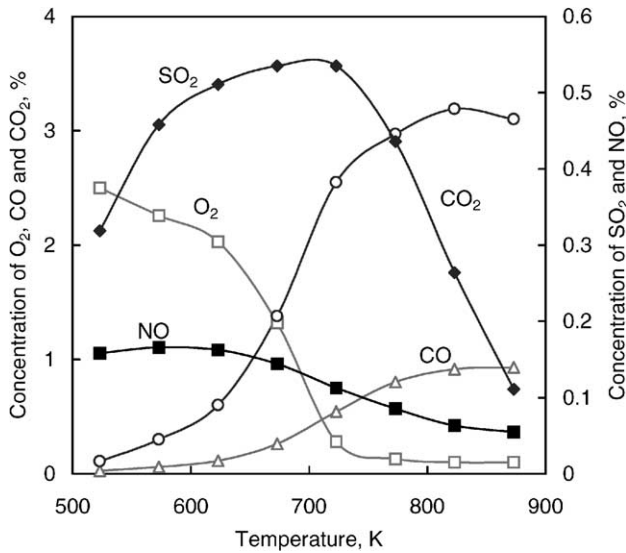


Fig. 3. Change in the concentration of SO<sub>2</sub> (solid rhombus), NO (solid square), O<sub>2</sub> (open square), CO<sub>2</sub> (open circle) and CO (open triangle) in the gasification of semi-coke CC-1 using simulated flue gas.

CO to CO<sub>2</sub> increased slightly with temperature, and the ratio at temperatures above 723 K followed the order: CC-4 > CC-2 > CC-1 > CC-3.

The most important product of the coal gasification is CO, which is paramount to the subsequent reduction of SO<sub>2</sub> and NO. The concentration of CO that could be produced at various temperatures is presented and compared in Table 3. Between 773 and 873 K, the average CO concentration increased in the order: CC-2 > CC-4 > CC-1 > CC-3. The change in the CO concentration for the two activated carbons (AC-1 and AC-2) was different. The CO produced by AC-1

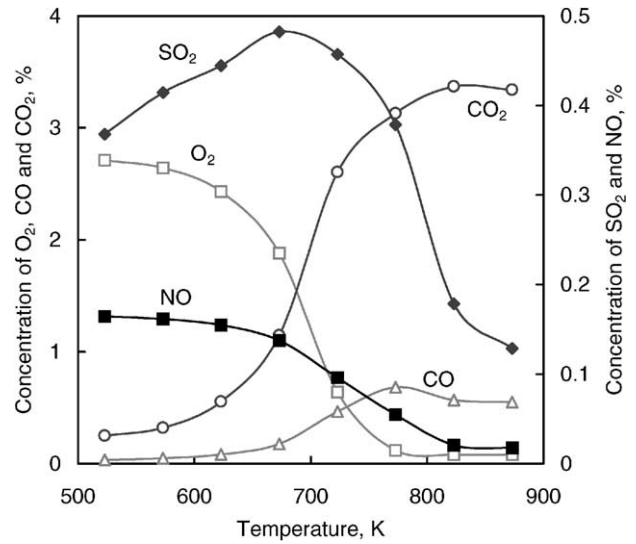


Fig. 5. Change in the concentration of SO<sub>2</sub> (solid rhombus), NO (solid square), O<sub>2</sub> (open square), CO<sub>2</sub> (open circle) and CO (open triangle) in the gasification of semi-coke CC-3 using simulated flue gas.

exceeded 1% and was higher than that of the semi-cokes. On the other hand, the CO produced by AC-2 was never over 0.8% and the maximum amount of CO was produced at 773 K.

### 3.4. Gasification—effect of NO and SO<sub>2</sub>

Both NO and SO<sub>2</sub> were consumed when the flue gas was passed over the semi-cokes and activated carbons. The outlet NO concentration decreased more rapidly as temperature reached 623–673 K. The decrease in the NO concentration was almost 50% at 723 K and reached 80–90% at 873 K.

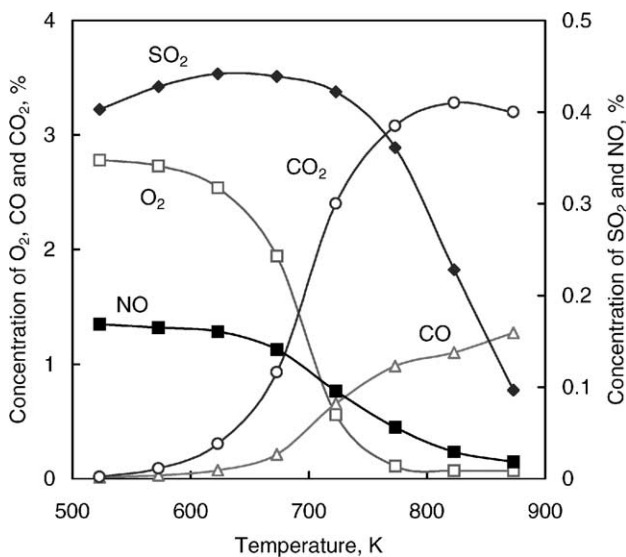


Fig. 4. Change in the concentration of SO<sub>2</sub> (solid rhombus), NO (solid square), O<sub>2</sub> (open square), CO<sub>2</sub> (open circle) and CO (open triangle) in the gasification of semi-coke CC-2 using simulated flue gas.

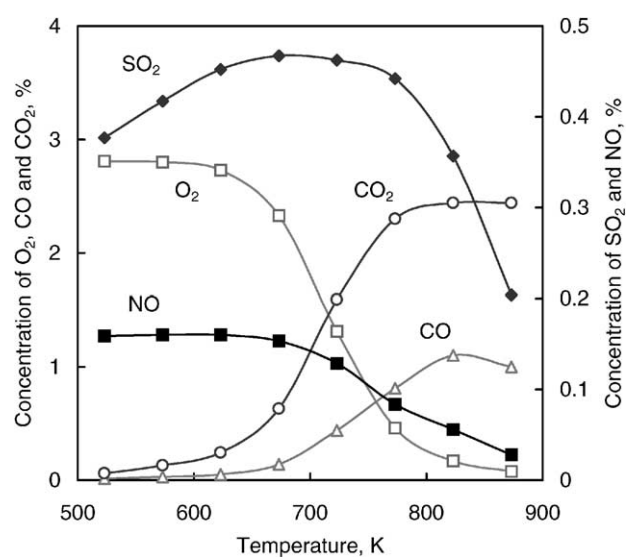


Fig. 6. Change in the concentration of SO<sub>2</sub> (solid rhombus), NO (solid square), O<sub>2</sub> (open square), CO<sub>2</sub> (open circle) and CO (open triangle) in the gasification of semi-coke CC-4 using simulated flue gas.

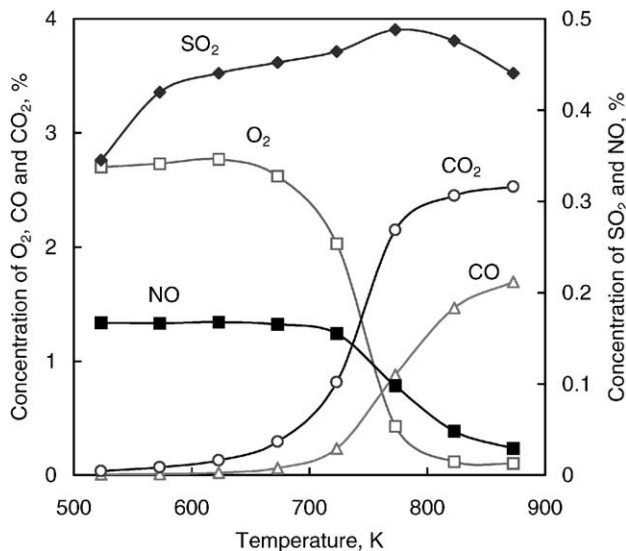


Fig. 7. Change in the concentration of SO<sub>2</sub> (solid rhombus), NO (solid square), O<sub>2</sub> (open square), CO<sub>2</sub> (open circle) and CO (open triangle) in the gasification of activated charcoal AC-1 using simulated flue gas.

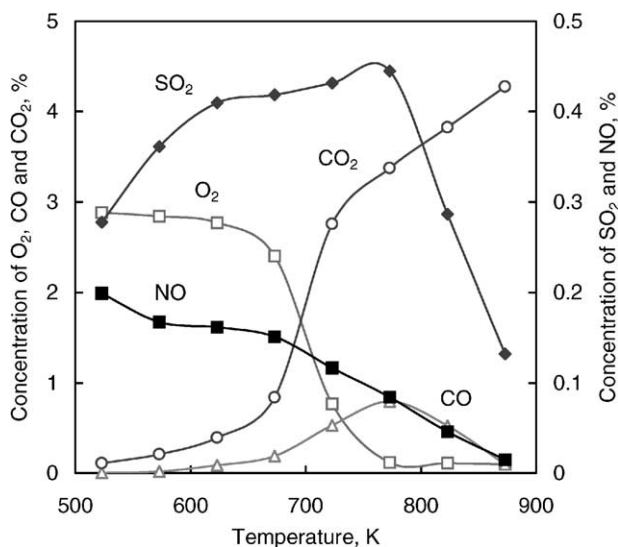


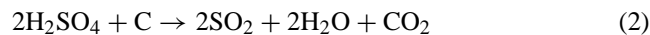
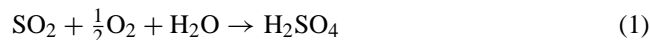
Fig. 8. Change in the concentration of SO<sub>2</sub> (solid rhombus), NO (solid square), O<sub>2</sub> (open square), CO<sub>2</sub> (open circle) and CO (open triangle) in the gasification of activated charcoal AC-2 using simulated flue gas.

Table 3  
Concentrations of CO generated at different temperatures in mol%

Temperature (K)	CC-1	CC-2	CC-3	CC-4	AC-1	AC-2
523	0.028	0.014	0.035	0.015	0.006	0.007
573	0.061	0.030	0.047	0.029	0.011	0.020
623	0.115	0.074	0.083	0.053	0.022	0.089
673	0.262	0.213	0.176	0.140	0.062	0.191
723	0.542	0.657	0.465	0.438	0.234	0.531
773	0.803	0.984	0.683	0.810	0.880	0.795
823	0.916	1.102	0.568	1.100	1.466	0.525
873	0.930	1.275	0.550	0.998	1.696	0.098
Average <sub>773–873</sub>	0.883	1.120	0.600	0.969	1.347	0.473

This decrease can be attributed to the chemisorption and reduction of NO in the semi-coke bed. Illán-Gómez et al. [15], who studied the reduction of NO in flue gas using carbon, reported a similar phenomenon that NO was chemisorbed at low-temperature and reduced at high temperatures.

A similar interaction was observed among the semi-cokes and the activated carbon samples, except the outlet concentration of SO<sub>2</sub> rapidly increased when the gasification temperature was not high enough to initiate the reduction of SO<sub>2</sub>. The increase could be attributed to both the oxidation of sulfur in the semi-cokes and the desorption of previously adsorbed SO<sub>2</sub> when the temperature was low. SO<sub>2</sub> started to react with the semi-cokes at about 723 K and with the activated carbons at about 773 K. The conversion of SO<sub>2</sub> was very different amongst these samples. The removal of SO<sub>2</sub> using activated carbon has been investigated extensively. It is believed that carbon particles catalyze the oxidation of SO<sub>2</sub> to SO<sub>3</sub> [6], which then reacts with water vapor to form sulfuric acid. The acid is then captured in the pores of the carbon and can be reduced in inert gas by the carbon to release concentrated SO<sub>2</sub>:



The overall reaction is the oxidation of carbon to CO<sub>2</sub>, which facilitates the removal of O<sub>2</sub>. As the SO<sub>2</sub> concentration decreased at temperatures above 723 K, elemental sulfur was observed in the exit of the gasification reactor. The change indicated the possible reduction of SO<sub>2</sub> by carbon to sulfur:



### 3.5. Gasification—effect of H<sub>2</sub>O

The effect of water vapor on gasification is illustrated in Fig. 9 using the activated carbon AC-3 sample. The gasification temperature was limited to 873 K at which the water-gas shift is subordinate and the influence of water vapor on the product distribution would be insignificant. However, it is likely that water vapor suppressed the formation of CO at temperatures above 773 K.

The presence of water vapor complicated the measurement of the gas composition and the rate of the reaction. First, SO<sub>2</sub>–SO<sub>3</sub> and NO<sub>x</sub> react with water to form H<sub>2</sub>SO<sub>3</sub>, H<sub>2</sub>SO<sub>4</sub> and HNO<sub>x+1</sub>. These compounds dissolve in the water condensate in the cold trap and thus the measured concentration of these acid gases will be smaller. In a reductive environment where most of the oxygen has been consumed and plenty of carbon monoxide is present, the more soluble SO<sub>3</sub> and NO<sub>2</sub> would be absent. On the other hand, SO<sub>2</sub> and NO are the more favorable forms in the reductive environment and they are far less soluble in water. Thus, the presence of water vapor would not make us underestimate the concentration of sulfur and nitrogen oxides significantly by gas measurement alone. Second, COS could be produced by the reaction between SO<sub>2</sub> and CO in the presence of suitable

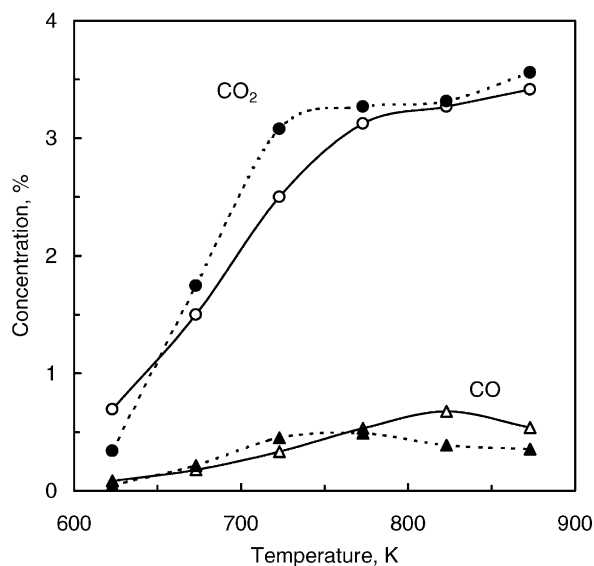


Fig. 9. Influence of water vapor on CO (triangles) and CO<sub>2</sub> (circles) formation. Solid lines: without water vapor; dashed lines: with water vapor.

catalyst in the gasification reactor, such as copper [9] in coal. COS was found in the effluent from the gasification reactor (effluent 1 measurements in Table 4) and the feed to the gasification reactor contained no COS. The water-gas shift reaction could further transform COS to H<sub>2</sub>S [3,9]. These reducing sulfur gases were ready to react with SO<sub>2</sub> under suitable conditions.

### 3.6. Simultaneous removal of SO<sub>2</sub> and NO from O<sub>2</sub>-rich flue gas

Table 4 shows the efficiency of the four samples in the removal of SO<sub>2</sub> and NO from O<sub>2</sub>-rich flue gas using the

combined coal gasification and catalytic reduction of SO<sub>2</sub> and NO by CO over lanthanum oxysulfide catalyst. Each experiment lasted for about 8 h until the samples were almost burned off. Solid yellow sulfur deposit was collected at the exit of the reduction reactor. With gasification temperatures at or above 773 K, over 90% of O<sub>2</sub> in the feed could be removed with a concomitant production of CO at about 0.9%. The total removal efficiency for both SO<sub>2</sub> and NO was over 96%. The conversions of SO<sub>2</sub> and NO in the gasification reactor were 17–35 and 67–81%. Even higher conversions were obtained in the reduction reactor, with SO<sub>2</sub> being 94–96% and NO 85–90%. The conversion figures are comparable to the published results on the reduction of SO<sub>2</sub> and NO by CO in the absence of O<sub>2</sub> over the same kind of catalytic material.

The mineral matter in the coal can deactivate or promote the activity of the La<sub>2</sub>O<sub>2</sub>S catalyst depending on the composition. Transition metals, such as cobalt and iron, usually promote the catalytic reaction [11] and they represent quite a portion of the minerals [6]. However, it is still desirable to remove the fly-ash from the deoxygenated gas stream before feeding into the reduction reactor to avoid the possible blockage of the catalyst bed and coverage of the catalyst.

We want to point out several limitations on the application of this flue gas conditioning method. First, this method needs additional fuel. To remove 2% O<sub>2</sub> from the flue gas is equivalent to consuming an extra 10% coal. The method may not be economically feasible if the O<sub>2</sub> content is high. Second, the ratios of CO to SO<sub>2</sub> and NO<sub>x</sub> should be kept close to the stoichiometric ratios for optimal conversion and selectivity. As illustrated in the gasification study, the production of CO depends on many variables including and not limited to the temperature and flue gas composition as well as the coal itself. Third, any unreacted CO left in the reduction reactor is not only a waste of valuable resource but also presents environment and health hazards. Control measures

Table 4  
Simultaneous reduction of SO<sub>2</sub> and NO cascaded to coal gasification for O<sub>2</sub> removal and CO generation

Reactor temperature (K)		Concentration (%)						Conversion (%)			Analysis point
Gasification	Reduction	SO <sub>2</sub>	NO	O <sub>2</sub>	CO	CO <sub>2</sub>	COS	SO <sub>2</sub>	NO	O <sub>2</sub>	
–	–	0.546	0.216	3.00	–	–	–	–	–	–	Feed <sup>a</sup>
773	–	0.454	0.072	0.168	0.920	2.42	0.000	17	68	94	Effluent 1
798	–	0.400	0.060	0.093	0.901	2.44	0.002	27	72	97	Effluent 1
798	873	0.200	0.016	–	0.215	3.55	0.008	63	93	–	Effluent 2
798	923	0.068	0.009	–	0.038	3.94	0.013	88	96	–	Effluent 2
823	923	0.017	0.008	–	0.049	3.70	0.022	97	96	–	Effluent 2
798	923	0.019	0.008	–	0.014	3.77	0.037	97	96	–	Effluent 2
798	873	0.018	0.008	–	0.013	3.89	0.036	97	97	–	Effluent 2
773	873	0.018	0.007	–	0.019	3.52	0.035	97	97	–	Effluent 2
773	–	0.356	0.062	0.324	0.892	2.47	0.003	35	71	90	Effluent 1
823	873	0.021	0.007	–	0.017	3.94	0.021	96	97	–	Effluent 2
848	873	0.023	0.006	–	0.018	4.11	0.025	96	97	–	Effluent 2
848	–	0.432	0.041	0.074	0.900	2.54	0.003	21	81	98	Effluent 1
873	873	0.024	0.006	–	0.019	3.91	0.022	96	97	–	Effluent 2
823	873	0.019	0.006	–	0.082	3.51	0.009	97	97	–	Effluent 2

<sup>a</sup> With 10% water vapor in the feed.

such as using lower than stoichiometric amount of CO with conversion penalty or catalytic incineration of CO can be used to regulate the emission of unwarranted CO. Fourth, although water participates in the coal gasification, its concentration in the flue gas should be minimized. Excessive water not only deactivates the lanthanum oxysulfide catalyst [3] but also shifts the selectivity of the reduction of sulfur dioxide from sulfur to H<sub>2</sub>S [3].

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