Circulating Fluidized Bed Gasification of Low Rank Coal: Influence of O-2/C Molar Ratio on Gasification Performance and Sulphur Transformation Postprint

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Abstract

To promote the utilization efficiency of coal resources, and to assist with the control of sulphur during gasification and/or downstream processes, it is essential to gain basic knowledge of sulphur transformation associated with gasification performance. In this research we investigated the influence of O-2/C molar ratio both on gasification performance and sulphur transformation of a low rank coal, and the sulphur transformation mechanism was also discussed. Experiments were performed in a circulating fluidized bed gasifier with O-2/C molar ratio ranging from 0.39 to 0.78 mol/mol. The results showed that increasing the O-2/C molar ratio from 0.39 to 0.78 mol/mol can increase carbon conversion from 57.65% to 91.92%, and increase sulphur release ratio from 29.66% to 63.11%. The increase of O-2/C molar ratio favors the formation of H2S, and also favors the retained sulphur transforming to more stable forms. Due to the reducing conditions of coal gasification, H2S is the main form of the released sulphur, which could be formed by decomposition of pyrite and by secondary reactions. Bottom char shows lower sulphur content than fly ash, and mainly exist as sulphates. X-ray photoelectron spectroscopy (XPS) measurements also show that the intensity of pyrite declines and the intensity of sulphates increases for fly ash and bottom char, and the change is more obvious for bottom char. During CFB gasification process, bigger char particles circulate in the system and have longer residence time for further reaction, which favors the release of sulphur species and can enhance the retained sulphur transforming to more stable forms.

Full Text

Preamble

Circulating Fluidized Bed Gasification of Low Rank Coal: Influence of O /C Molar Ratio on Gasification Performance and Sulphur Transformation

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To promote the utilization efficiency of coal resources and assist with sulphur control during gasification and/or downstream processes, it is essential to gain fundamental knowledge of sulphur transformation associated with gasification performance. This research investigated the influence of O /C molar ratio on both gasification performance and sulphur transformation of a low-rank coal, and the sulphur transformation mechanism was also discussed. Experiments were performed in a circulating fluidized bed gasifier with O /C molar ratio ranging from 0.39 to 0.78 mol/mol. The results showed that increasing the O /C molar ratio from 0.39 to 0.78 mol/mol increased carbon conversion from 57.65% to 91.92% and increased sulphur release ratio from 29.66% to 63.11%. The increase in O /C molar ratio favors H S formation and also promotes transformation of retained sulphur to more stable forms. Due to the reducing conditions of coal gasification, H S is the main form of released sulphur, which could be formed by decomposition of pyrite and by secondary reactions. Bottom char shows lower sulphur content than fly ash and exists mainly as sulphates. X-ray photoelectron spectroscopy (XPS) measurements also show that the intensity of pyrite declines and the intensity of sulphates increases for both fly ash and bottom char, with the change being more obvious for bottom char. During CFB gasification, larger char particles circulate in the system and have longer residence time for further reaction, which favors release of sulphur species and can enhance transformation of retained sulphur to more stable forms.

Keywords: gasification, circulating fluidized bed, sulphur transformation, O /C molar ratio

Introduction

Coal will remain one of the top energy resources for the foreseeable future. Gasification technology represents a promising and highly efficient way to utilize low-rank coal and has attracted considerable interest in recent years [1-3]. However, coal gasification is also associated with environmental and plant system problems [4-6].

Sulphur is one of the most important heteroatoms in coal and has a major impact on coal gasification, whether as fuel gas or as raw material for formation of different products [4]. Generally, both organic and inorganic sulphur compounds exist in coal, and the sulphur amount does not depend on coal rank but rather on the origin of the coal. During gasification, some sulphur present in coal might pass to the gas phase, and the environmental implications should be carefully evaluated because many countries impose emission limits to minimize environmental impact [7]. Moreover, sulphur in coal may cause formation of compounds in fuel gas that could lead to corrosion and deposition, thereby increasing maintenance costs [7,8]. Therefore, process and environmental control mechanisms of coal gasification are becoming increasingly important for providing cheap, clean, and reliable energy.

Sulphur transformation can be influenced by several parameters such as fuel properties, temperature, pressure, heating rate, and so on [5,7-11]. To date, some researchers have studied the effects of these parameters on sulphur transformation through experimental and theoretical methods with different feedstocks. Pinto et al. [7] and Khan et al. [12] reported that higher temperatures can increase sulphur release, though this trend is not always consistent for biomass gasification [9]. Bläsing et al. [8] found that release of sulphur species is greatly influenced by the amount of hydrogen and volatiles during devolatilization, with release amount being highly positively correlated with the sulphur content of the feedstock. However, Middleton et al. [10] stated that the sulphur release ratio is proportional to the conversion of coal into the gas phase during gasification.

Given the complicated nature of coal and some contradictory statements in the literature, several scientific problems remain directly connected to sulphur transformation during gasification.

Circulating fluidized bed (CFB) gasification is a promising technology that usually operates at moderate temperatures and can achieve desulphurization within the gasifier. In recent years, great attention has focused on either gasification performance of CFB or sulphur transformation properties [13-16], but rarely on both simultaneously. From perspectives of environmental protection and process optimization, it is essential to gain intimate knowledge of sulphur transformation associated with gasification performance. Moreover, sulphur transformation may be controlled during gasification by adjusting experimental conditions and/or by utilizing the advantages of CFB gasifiers.

The aim of this work is to study the influence of O /C molar ratio on gasification performance and sulphur transformation of a low-rank coal. Experiments were carried out in a lab-scale CFB gasifier with air as the gasifying agent. The sulphur forms and contents of raw coal and gasification residuals were analyzed by chemical analysis methods. X-ray photoelectron spectroscopy (XPS) was used for qualitative determination of the major sulphur forms in raw coal and gasification residuals, which is especially valuable for revealing transformation of various sulphur forms.

Experimental Section

Test Rig

The whole system consists of a CFB gasifier and an auxiliary system. The riser of the CFB gasifier is 100 mm in diameter and 4300 mm in height, which is connected with a cyclone and a loop seal to form a circulating route. Coal is supplied via a screw feeder from the hopper into the riser, with the coal feeding port approximately 400 mm above the blast cap. Air is supplied by an air compressor, and the flows for the riser and loop seal are individually controlled by mass flow controllers. Nitrogen is supplied by cylinders and used to cool the gasifier at the end of experiments. Temperature measuring ports and pressure drop measuring ports are placed along the height of the riser and fuel gas pipe. The test rig contains twelve thermocouples, five of which are in the riser at heights of 50, 250, 400, 2750, and 4300 mm individually. There are two gas sampling ports downstream of the second ash collection tank.

[Figure 1: see original paper]

Fig. 1 Schematic diagram of the test rig.

Experimental Materials

Shenmu coal from Shaanxi Province of China was used for the experiments. The diameter of coal particles is smaller than 1 mm, with a mean particle size d of 0.65 mm. The coal was analyzed according to Chinese standards GB/T212-2008, GB/T 214-2007, GB/T 476-2008, GB/T 19227-2008, and GB/T 213-2008, with proximate, ultimate, and net calorific value analysis results listed in Table 1 . The ash composition of Shenmu coal was analyzed according to Chinese standard GB/T 1574-2007, with results listed in Table 2 . Quartz sand with diameter ranging from 0.1-1 mm was used as bed material.

Table 1 Ultimate, proximate, and net calorific value analysis of Shenmu coal

Table 2 Ash composition of Shenmu coal

Experimental Procedure and Sample Characteristics

At the beginning of each experiment, quartz sand was added to the gasifier, air was supplied to fluidize the quartz sand, and the electric heating device was turned on to heat the system. When the temperature exceeded 500°C, coal was continuously fed to the riser. As the temperature reached the required level for coal gasification, the air flow and coal feeding rate were adjusted to achieve the desired oxygen/carbon (O /C) molar ratios.

All gasification experiments were performed with the same air flow rate of 22.32 Nm^3/h but with different coal feeding rates. The coal feeding rates used were 9, 8.3, 5.5, and 4.5 kg/h, corresponding to O /C molar ratios of 0.39, 0.42, 0.64, and 0.78 mol/mol, respectively. At least two runs were repeated at each experimental condition, and good reproducibility was obtained.

CFB gasification produces solid byproducts defined as gasification residuals. Larger char particles are recovered by the cyclone and transferred back to the riser via the loop seal for further reaction or heat transfer, while smaller particulate matter passes through the cyclone to the downstream. For each run, larger char samples were obtained from the loop seal (defined as bottom char), and smaller particulate samples were obtained from the first ash collection tank (defined as fly ash).

Sulphur contents of gasification residuals were determined according to GB/T 214-2007. Sulphur forms in Shenmu coal and gasification residuals were analyzed by classical wet chemical method according to GB/T 215-2013 and by XPS. XPS is a non-destructive method for studying surface composition that can determine several elements simultaneously [17,18]. In this study, XPS measurements were performed using a VG Scientific ESCALAB 250Xi spectrometer (Thermoelectricity Instruments, USA) with Al K X-ray as the light source. Spectra were smoothed and Shirley background was subtracted. Calibration was carried out using the main C 1s peak at 284.6 eV. Gas compositions were measured via gas chromatograph (Agilent GC 3000). Reproducibility was checked and good agreement was obtained, with experimental errors always lower than 5%. Each gas composition and sulphur content represents the average value of at least two trials.

Results and Discussion

Gasification Performance

O /C molar ratio is one of the most important operating variables affecting coal gasification performance. In this study, the O /C molar ratio was adjusted by changing coal feeding rates while maintaining constant air flow rate to minimize effects on residence time. The selected air flow rate ensured good bed fluidization even at the highest coal feeding rate.

[Figure 2: see original paper]

Fig. 2 Temperature profile of the CFB riser with different O /C molar ratio.

Figure 2 shows temperature profiles of the CFB riser for all experiments, representing average values during gasification. All profiles exhibit the same trend: temperature first increases then decreases with riser height, consistent with results reported by others [15,16]. This temperature variation can be explained by reactions occurring in the system, structural characteristics of the test rig, and system heat loss. The main reactions are listed in Table 3 [15,21]. At the riser bottom, air introduction forms a low-temperature zone due to relatively cool air temperature. However, due to intensified mixing and reactions, temperature reaches maximum value at 400 mm height (T). Where fresh coal is supplied and larger char particles are recirculated, exothermic reactions R1 and R2 predominate, contributing to temperature increase given elevated carbon and oxygen concentrations. In the upper riser section, temperature drops slightly along height, interpreted as resulting from heat loss and energy-consuming reactions such as R7, R8, as well as pyrolysis and gasification of entrained coal particles. With increasing O /C molar ratio, less coal is supplied and oxygen becomes more sufficient to enhance oxidation or partial oxidation of coal and produced flue gas, resulting in higher system temperature as illustrated in Fig. 2.

The influence of O /C molar ratio on gas composition and gas heating value is exhibited in Fig. 3 [Figure 3: see original paper]. The concentration of CO increases with O /C molar ratio, while CO, CH , H , and heating value decrease. Increased O /C molar ratio favors exothermic reactions R1 and CO oxidation reaction R3, leading to CO decrease and CO increase. Moreover, increased O /C molar ratio may cause a small portion of H and CH to be oxidized according to reactions R4, R5, and R6. These adverse effects predominate as O /C molar ratio rises, leading to lower fuel gas heating value. Particularly, rapid heating value decrease from 3.35 MJ/Nm³ to 1.92 MJ/Nm³ is observed when O /C molar ratio increases from 0.39 to 0.78 mol/mol. The gas heating value (Qgas,net) is calculated by:

Qgas,net = yH2 × 10.79 + yCO × 12.64 + yH2, yCO and yCH4 are the volumetric percentages of H2, CO and CH4 respectively in the fuel gas.

Results presented in Fig. 3 agree fairly well with literature reported by Chen et al. [19], even when different systems and feedstocks were studied. Coal gasification in an atmospheric fluidized bed also showed that CO, CH , H , and heating value clearly decreased when O /C molar ratio increased, explained by enhanced combustion reactions of coal and volatile matter [19]. These authors also observed increased H with bed temperature, while CO, CH , and heating value decreased, attributed to water-gas shift reaction and combustion of carbon or volatiles at higher bed temperature. However, results obtained by Liu et al. [15] studying coal gasification in a CFB gasifier with air, or by Pinto et al. [20] studying co-gasification of coal and wastes with air/steam, showed apparent optimum regions for gas composition and heating value, though optimal ratios differed. Different trends in Fig. 3 compared to literature [15,20] are mainly due to differences in systems studied and in equipment and operating variables.

[Figure 3: see original paper]

Fig. 3 Gas composition and heat value under different O /C molar ratio.

Figure 4 displays carbon conversion and cold gas efficiency versus O /C molar ratio. Carbon conversion (Xc) and cold gas efficiency (gas) are described as:

Xc = (Fair × 79%/ yN2 %/22.4 × (yCH4 + yCO + yCO2)% × 12)/ (Wc × Cc%) × 100% (2)

gas=(Fair × 79%/ yN2 % × Qgas,net)/(Wc×Qad,net) (3)

where Fair is air flow rate (Nm³/h), yCO, yCH , yCO , and yN are volumetric percentages of CO, CH , CO , and N respectively in fuel gas, Wc is coal feeding rate (kg/h), and Cc is mass percentage of carbon in coal ultimate analysis. Qad,net is net calorific value of coal (MJ/kg).

As shown in Fig. 4 [Figure 4: see original paper], carbon conversion continuously increases from 57.65% to 91.92% with O /C molar ratio increase from 0.39 to 0.78 mol/mol. Increased O /C molar ratio permits both combustion and gasification reactions, but mainly the former. At fixed air flow rate, rising O /C molar ratio means less coal reacts with oxygen, enabling conversion of more carbon to gaseous products through reactions R1 and R2. Figure 4 shows that cold gas efficiency changes non-monotonically with an apparent maximum region at O /C molar ratio of about 0.64 mol/mol, explained by changes in gas composition and heating value.

[Figure 4: see original paper]

Fig. 4 Carbon conversion and cold gas efficiency under different O /C molar ratio.

Sulphur Transformation Performance

During gasification, some sulphur releases to the gas phase. Figure 5(a) shows H S concentration for different O /C molar ratios. Sulphur release ratio (Sgas,t) and its distribution between H S and other gas forms (Sgas,H2S and Sgas,other forms) are also presented. These parameters are described by:

Sgas,t = (Wc × Sc% − Wchar × Schar% − Wash × Sash%) / (Wc × Sc%) × 100% (4)

Sgas,H2S = (Fair × 79%/yN2% × Cgas,H2S × 10-6) / (Wc×Sc%) × 100% (5)

where Sc, Schar, and Sash are mass percentages of total sulfur in coal, bottom char, and fly ash respectively. Wchar is mass of bottom char recovered for a specific experiment (kg/h). Wash is mass of fly ash (kg/h), calculated by ash balance. Cgas,H2S is H S concentration in flue gas (mg/Nm³).

As exhibited in Fig. 5(a) and 5(b) [Figure 5: see original paper], increasing O /C molar ratio leads to increased H S formation and increased sulphur release ratio in both H S and other gas forms. When O /C molar ratio increases from 0.39 to 0.78 mol/mol, H S concentration increases from 255 to 300 mg/Nm³, and sulphur release ratio increases from 29.66% to 63.11%. For each O /C molar ratio, more than 70% of released sulphur is in H S form, meaning H S is the main form of released sulphur, consistent with other studies [14,22].

Higher O /C molar ratio might be expected to favor char combustion and gasification reactions, leading to release of higher sulphur contents and formation of sulphur oxides such as SO . However, as shown in Fig. 5(b), the increase in H S amount is lower than that of other gas forms. Due to reducing conditions, released sulphur occurs mainly as H S in this study. Coal gasification by Sciazko et al. [23] in a fluidized bed gasifier showed sulphur oxides present in gas product, with increased air/coal molar ratio promoting H S formation. H S is the precursor of all sulphur pollutants [22] and could be formed by decomposition of pyrite and secondary reactions, discussed in detail in the possible mechanism section.

These results indicate that increasing O /C molar ratio enhances sulphur release, coherent with other studies using different fuels and gasifiers [7,10,12,23]. However, specific sulphur release ratios and H S concentrations may differ due to varying operating conditions, mineral matter compositions, or additives. Pinto et al. [7] reported that increasing gasification temperature from 850°C to 900°C increased H S formation by about 15%. Najjar et al. [24] stated that sulphur release ratio decreased significantly when iron compounds were added to coal ash due to formation of a new major oxysulphide phase in addition to the silicate phase. Sciazko et al. [23] showed about 60% of total sulphur released to gas phase, with higher release ratios attributed to different mineral matter composition.

In addition to sulphur release to gas phase, some sulphur may be retained in gasification residuals. Sulphur contents and forms in raw coal and gasification residuals were analyzed by classical wet chemical methods. As illustrated in Fig. 6(a) [Figure 6: see original paper], sulphur contents are enriched at higher O /C molar ratio for both bottom char and fly ash, indicating dependence of sulphur transformation on gasification progress. The reason is described later by investigating changes in surface sulphur forms. Figure 6(b) shows sulphur distribution among different forms under parity ash content. Organic sulphur is the main form in raw coal, accounting for 55% of total sulphur. Sulphide sulphur and sulphate sulphur are relatively less abundant at 37.5% and 7.50% respectively. At O /C ratio of 0.42 mol/mol, organic sulphur dramatically increases to 80.80% while sulphide sulphur significantly decreases to 1.33%, interpreted as decomposition of sulphide sulphur and conversion of sulphur compounds present in coal. Further increasing O /C ratio to 0.78 mol/mol causes obvious decreases in organic and sulphide sulphur but remarkable increase in sulphate sulphur, suggesting more stable sulphur species may form at higher O /C molar ratio during CFB gasification.

XPS measurements were used to examine functional forms of sulfur present in raw coal and gasification residuals. S 2p peaks at 162.5, 163.3±0.3, 164.1, 165.1±0.3, 167.9±0.4, and 169.5 eV are interpreted as pyrite, alkyl sulphides, thiophene, sulphoxides, sulphones, and sulphates according to literature [25,26]. Figure 7 [Figure 7: see original paper] compares spectral lines of raw coal and gasification residuals at O /C molar ratio of 0.78 mol/mol. Functional forms of sulphur in raw coal are mainly pyrite and organic sulphur (alkyl sulphides, thiophene, sulphoxides, and sulphones). The signal attributable to sulphates is very weak, likely due to low content confirmed by chemical analysis in Fig. 6(a). Compared with raw coal, signals for thiophene, sulphoxides, and sulphates in fly ash and bottom char increase obviously, indicating surface enrichment of sulphur after gasification. Gasification leads to carbon decrease, so apparent sulphur intensity increase may be caused by sulphur transformation or carbon content reduction [27]. No signals attributable to alkyl sulphides appear for fly ash and bottom char, mainly due to coal dealkylation during gasification. Additionally, no signals assigned to sulphones appear for fly ash and bottom char, likely due to their release or conversion to other forms.

It is worth mentioning that pyrite intensity declines for fly ash and almost disappears for bottom char, while sulphate intensity increases significantly for both, with more obvious change for bottom char. These opposite trends from XPS measurements are similar to chemical analysis results in Fig. 6(b). During CFB gasification, larger char particles circulate in the system with longer residence time for further reaction, which favors sulphur species release and can enhance transformation of retained sulphur to more stable forms.

[Figure 5: see original paper]

Fig. 5 Effects of O /C molar ratio on H S concentration and sulphur release properties.

[Figure 6: see original paper]

Fig. 6 (a) Sulphur content and (b) its distribution among different forms under parity ash content. (A) Shenmu coal, (B) fly ash and (C) bottom char with O /C ratio of 0.42 mol/mol, (D) fly ash and (E) bottom char with O /C ratio of 0.78 mol/mol.

[Figure 7: see original paper]

Fig. 7 S 2p peaks for (a) Shenmu coal, (b) fly ash, and (c) bottom char with O /C molar ratio of 0.78 mol/mol.

Possible Mechanism for Sulphur Transformation

Results strongly suggest that sulphur in coal, comprising inorganic and organic functionalities, evolves significantly during gasification. Decreased pyrite sulphur percentages in gasification residuals (Fig. 6(b)) and decreased pyrite signals (Fig. 7) could be attributed to pyrite decomposition and chemical reactions with other components. Reaction mechanisms are given in Eqs. (7)-(9) [8,28]:

Under gasification conditions, pyrite can decompose according to Eq. (7) or react directly with H or CO in fuel gas according to Eqs. (8)-(9), either of which can decrease pyrite amount. Moreover, FeS as pyrite decomposition product can also react with H , CO, or H O in fuel gas as given in Eqs. (10)-(12) [8,28], which can further enhance pyrite decomposition and correspondingly decrease pyrite amount.

As shown in Fig. 5(a), H S is the main sulphur form in gas phase, though other gas forms may also be formed during gasification. H S is the precursor of all sulphur pollutants and could be formed by Eqs. (8), (10), and (12) [8,28]. As fuel gas has certain residence time in the gasifier, some initially formed H S might be retained or destroyed afterward [22]. Some initially formed H S may react with mineral matter in coal ash, especially calcium or iron, to form metal sulphide according to Eq. (13) and remain inside the gasifier [22]. Alternatively, COS can be formed by reaction of CO with H S (Eq. 14) or by reaction of CO with H S (Eq. 15). Kinetics of these reactions are slow, and shifts would generally increase H S. Nevertheless, Bläsing et al. [8] and Yan et al. [29] emphasized that COS and H S release occurs simultaneously during gasification. Additionally, H S might react with H O or CO by Eq. (16) or (17) to form SO , as reported by Nichols et al. [30]. Beyond direct H S and COS formation, *SH radical can be released during thermal conversion of organic-bound sulphur and can undergo several secondary reactions with remaining char to form H S, COS, and sulphur-containing structures in char [8,29]. Enhanced intensities of more stable sulphur in gasification residuals (Fig. 7) can be interpreted by transformation of sulphur compounds present in coal and by secondary reactions. Some active sulphur can react readily with inorganic impurities to form stable sulphur forms retained in gasification residuals [23,24,31].

Figures 2-6 clearly indicate that O /C molar ratio is an important factor influencing gasification performance and sulphur transformation. Higher carbon conversion and higher sulphur release ratio correspond to higher O /C molar ratio. Results obtained in this work are in relatively satisfactory agreement with literature considering different feedstocks and gasifiers were used [10].

From perspectives of CFB gasification commercial application and environmental protection, it is essential to achieve higher carbon conversion with tolerable sulphur content in fuel gas. Generally, sulphur can be effectively removed by moderate-temperature gasification, suggesting a viable solution for sulphur removal during gasification to avoid or alleviate sulphur problems. Considering the long residence time of coal particles in CFB gasifiers and tunable gasifier geometry, CFB gasifiers might be optimal reactors.

Conclusions

This study investigated the influence of O /C molar ratio on gasification performance and sulphur transformation in a lab-scale CFB gasifier with Shenmu coal as feedstock. The following conclusions can be drawn:

Increasing O /C molar ratio from 0.39 to 0.78 mol/mol continuously increased carbon conversion from 57.65% to 91.92% and sulphur release ratio from 29.66% to 63.11%, while decreasing gas heating value from 3.35 to 1.92 MJ/Nm^3. An apparent optimum region for cold gas efficiency exists at O /C molar ratio of about 0.64 mol/mol.

Sulphur evolved significantly during gasification. When O /C molar ratio increased from 0.39 to 0.78 mol/mol, H S concentration increased from 255 to 300 mg/Nm^3, and sulphur release ratio in both H S and other gas forms increased obviously. Due to reducing conditions of coal gasification, H S is the main form of released sulphur, formed by pyrite decomposition and secondary reactions.

Bottom char shows lower sulphur content than fly ash and exists mainly as sulphate sulphur. XPS measurements show that pyrite intensity declines and sulphate intensity increases significantly for both fly ash and bottom char, with more obvious change for bottom char. During CFB gasification, larger char particles circulate in the system with longer residence time for further reaction, which favors sulphur species release and can enhance transformation of retained sulphur to more stable forms.

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Note: Figure translations are in progress. See original paper for figures.

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