

Nitrogen and sulfur conversion during pressurized pyrolysis under CO₂ atmosphere in fluidized bed

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Abstract: Pressurized oxy-fuel combustion (POFC) is a promising technology for CO₂ capture from coal-fired power plants, offering both high efficiency and a low penalty. However, the high partial pressure of CO₂ in a POFC furnace has important impacts on fuel-N and fuel-S conversion during the coal pyrolysis process, and understanding this will help to achieve further control of SO_x/NO_x. In this study, coal pyrolysis experiments were conducted in a pressurized fluidized bed with the pressure range of 0.1-0.7MPa under N₂ and CO₂ atmosphere. The gaseous products were monitored by a Fourier transform infrared spectroscopy analyzer (FTIR) and the char residue was characterized by an X-ray photoelectron spectroscopy (XPS) analyzer in order to acquire the species information for S-containing and N-containing compounds. Results show that the enrichment of CO₂ in the local atmosphere enhances the fuel-N conversion to HCN in the pyrolysis process, which serves as a favorable precursor to N₂O. The generation of HCN and NH₃ increase simultaneously with the increase of overall pressure. SO₂ concentration in the gaseous product is relatively low, and as the pressure increases, the concentration decreases slightly due to CO reduction of SO₂ to COS. Sulfur content in the char decreases as the pressure goes from 0.1MPa to 0.7MPa indicating higher CO₂ pressure accelerates the decomposition of sulfur compounds in the coal, which is further confirmed by the XPS results.

Key words: pressurized oxy-fuel combustion; pyrolysis; CO₂ atmosphere; nitrogen conversion; sulfur speciation;

28

29 1. Introduction

30 Carbon capture and storage (CCS) technologies capture up to 90% of CO₂ emissions from a
31 power plant or industrial facility and store them in underground geologic formations. The
32 International Energy Agency (IEA) estimates that CCS can achieve 13% of the global greenhouse
33 gas emissions reductions needed by 2050 to limit global warming to 2°C [1]. Carbon capture has
34 been established for some industrial processes, but it is still a relatively expensive technology.
35 Much effort needs to be devoted to reducing the cost of CCS technologies in the near future.

36 Oxy-fuel technology, as one of the major coal-fired power plant CCS technologies, has
37 received much attention recently. In oxy-fuel technology, the process typically entails burning the
38 fuel in a mixture of recycled flue gas and O₂ instead of air as the primary oxidant. The high CO₂
39 concentration in the flue gas makes it conducive to CO₂ separation. Also, other gaseous pollutants
40 such as NO_x and SO_x can be simultaneously removed [2]. The biggest obstacle to the development
41 and application of oxy-fuel technology at present is the net efficiency penalty associated with the
42 high cost of the air separation unit (ASU) and compression purification unit (CPU). For a
43 conventional air-fired coal power plant, the net efficiency reduced by more than 10% when it is
44 converted to oxy-firing [3-5].

45 In the first generation oxy-fuel technology, the ASU and CPU run under pressure, while the
46 boiler is run at atmospheric pressure. Thus, the pressure fluctuation associated with the ASU,
47 boiler and CPU cause energy losses and a reduction of net efficiency. However, for second
48 generation oxy-fuel technology, or pressurized oxy-fuel combustion (POFC) technology, the
49 whole system runs under pressure, and hence the work losses due to the pressure fluctuations can
50 be substantially reduced. Together with this feature, many other advantages can also be achieved
51 by deploying POFC [6-8] including: (1) recovering latent heat from flue gas; (2) increasing the
52 convective heat transfer for a given mean velocity; (3) reducing the boiler size and equipment
53 costs; (4) avoiding air ingress, thus ensuring the production of high purity of CO₂ in the flue gas
54 and a relatively low purification cost; and (5) reducing the cost of flue gas recirculation fan and

55 the CPU system.

56 To date, many studies have contributed to the optimization of the POFC systems. Hong et al.
57 [9,10] analyzed the ISOTHERM[®] pressurized oxy-combustion system of ENEL [11], and found
58 the maximum efficiency could be achieved in the vicinity of the 1.0MPa operating pressure. The
59 net efficiency showed nearly 3% increment at 1.0MPa over atmospheric combustion. Gopan et al.
60 [12,13] introduced a staged pressurized oxy-combustion (SPOC) system with fuel staging and low
61 flue gas recycle rate. The simulation of thermal system showed the optimal pressure was around
62 1.6MPa and the SPOC process increased the net efficiency up to 6% over conventional
63 atmospheric oxy-combustion.

64 However, on the other hand, there are few experimental studies on the POFC. The only
65 reported work includes coal combustion on the pressurized thermo-gravimetric analyzer (PTGA)
66 [14-16] and fluidized bed [3,17]. Wang et al. [14] conducted the coal combustion experiments on
67 the PTGA and the results indicated the effects of pressure on coal ignition mode. With the
68 increase of pressure, the heterogeneous ignition at atmospheric pressure converted to
69 homogeneous ignition at low and medium pressures, and then converted back to heterogeneous
70 ignition at high pressure. Lasek et al. [3,17] investigated the effect of pressure on pollutant
71 emissions, using a laboratory scale fluidized bed with continuous-feeding and found that NO,
72 N₂O, SO₂ emission were reduced under higher pressures during oxy-combustion.

73 As the first step of coal combustion, pyrolysis has great impact on the subsequent reactions.
74 The conversion of N and S in the pyrolysis stage has an important influence on NO_x/SO_x emission
75 and the operation safety of CPU system [18,19]. CO₂ is a reactant in the char gasification reaction,
76 as well as one of the final product of coal pyrolysis, so the existence of high partial pressures of
77 CO₂ affects the yield of volatile and N/S conversion significantly. Li et al. [20-25] conducted a
78 series of studies on the pyrolysis characteristics of the Victorian brown coal, mainly focused on
79 the generation of NO_x precursors with different operating parameters like atmosphere and reactor
80 types. The experiments show that CO₂ atmosphere surrounding coal/char particles can greatly
81 affect the formation of NH₃ and HCN through its influence on the availability of H-radicals

82 [24,25]. The CO₂ atmosphere tends to reduce the formation of NH₃ and HCN if the thermal
83 cracking of char generates a significant amount of H-radicals. Many efforts have been made to
84 investigate the effects of other operation parameters like fuel type, temperature and heating rate on
85 the formation of NO_x precursor during coal pyrolysis under CO₂ atmosphere, and findings suggest
86 that the CO₂-C gasification rate and the opening of -CN bond greatly affect the formation of NH₃
87 and HCN [26,27]. However, these studies are limited to atmospheric pressure and there are still
88 few studies about the effects of pressure on N conversion during coal pyrolysis under pure CO₂
89 atmosphere.

90 Previous studies [28-30] have also revealed that the sulfur-containing gas and residual sulfur
91 content in char during CO₂ pyrolysis is highly depends on the minerals and sulfur forms in raw
92 coal. Experimental work shows the high CO₂ concentrations may promote the CO₂ reduction
93 reaction of pyrite and generate more Fe₃O₄, CO and SO₂ [31]. The results of pyrolysis experiment
94 of coal under N₂ and CO₂ atmosphere by Karaca [32] indicate that CO₂ atmosphere has more
95 effects on the organic sulfur removal at high temperatures. Carbonate in coal can promote the
96 decomposition of organic sulfur, and inhibit the decomposition of pyrite, while the silicate seems
97 to promote the conversion from easily removable organic sulfur compounds to thermal stable
98 organic sulfur compounds. At the same time, the effect of pressure on sulfur conversion during
99 pyrolysis has mostly focused on pressurized hydro-pyrolysis studies, which showed that the
100 increase of hydrogen pressure enhanced the removal of sulfur from coal [33,34].

101 Currently, information on N/S conversion of coal during pressurized pyrolysis under CO₂
102 atmosphere is still limited, and a more complete understanding of the pathway for fuel-N and
103 fuel-S conversion is important for future work on POFC technology, and in particular for gaseous
104 pollutant control and system optimization. This information will also help to build up a
105 comprehensive model of the PFOC by providing detailed reaction mechanisms. In this study,
106 experiments on a lab-scale pressurized fluidized-bed system have been done to help determine the
107 influence of pressure on the N/S conversion into both gaseous and solid products.

108 2. Experimental

109 2.1 Fuel and bed material

110 Table 1 shows the ultimate and proximate analysis of the bituminous coal used in the
111 experiment. The sulfur speciation in the raw coal was determined according to the Chinese
112 standard method (GB/T 215-2003), and is shown in Table 2. The particle size of coal ranged from
113 0.45 to 0.60mm. Silica sand (particle size: 0.25 to 0.35mm, true density: 2600kg/m³) was used as
114 bed material, giving a static bed height of 0.3m.

115 2.2 Apparatus and procedure

116 Experiments were conducted on a 20kW_{th} lab-scale pressurized fluidized bed system, as
117 shown in Fig. 1, which consists of a bubbling fluidized bed combustor, gas distribution, feeding
118 system, temperature and pressure controlling system, flue gas cooling system, and the gas
119 analyzers. The combustor was made of the stainless steel, with an inner diameter of 50mm and a
120 height of 1300mm. The combustor was placed in a pressure vessel, which was designed to
121 withstand a pressure of 2.0MPa at 200°C. The bottom of the windbox was open, permitting the
122 pressurized gas flowing into the riser to pass through it. During the experiments, the gas went into
123 the pressure vessel first, and was heated by the reactor wall and then flowed into the windbox.
124 However, because of this design, the pressure vessel is not operated at high temperature (<100°C).
125 The flue gas leaving the reactor was then cooled down to 200°C by the gas cooler before entering
126 the sampling line. A regulating valve was used at the outlet of the cooler to control the reaction
127 pressure in the riser. The gas sampling line was connected to the sampling port after the regulating
128 valve. The sampling line was electrically heated to control the temperature to around 165°C, to
129 avoid the gas condensation. A filter was used to remove fine particles larger than 0.1μm from the
130 flue gas. The Fourier transform infrared spectroscopy (FTIR) analyzer (Antaris IGS, Thermo
131 Fisher Scientific Inc, USA) was used to monitor the composition of flue gas. The measuring
132 accuracy of HCN/NH₃/SO₂ was 0.01ppm.

133 The coal pyrolysis characteristics under N₂ and CO₂ atmosphere were investigated with the
134 operation pressure ranging from 0.1 to 0.7MPa. The bed temperature in the dense zone was

135 controlled at 750°C, 800°C, 850°C and 900°C, respectively. Batch feeding was used in this
136 experiment to avoid the unstable coal feeding under high pressure operation. Typically, 3-9g coal
137 particles with the desired size were injected into the bottom zone of the reactor by the pressurized
138 carrier gas. The gas velocity in the riser was normally in the range of 0.7-1m/s to guarantee the
139 good fluidization of the silica sand bed material. Each test run was repeated 3-5 times to minimize
140 the uncertainty in experiments.

141 2.3 Analysis methods of char

142 After each test, bed material was drained and char was removed by hand. This was easy to do
143 since the colour of the coal char and sand are very different. The char produced at 850°C and CO₂
144 atmosphere was collected and analysed by a CTS5000B sulfur analyzer in order to obtain the
145 sulfur content in the char. An X-ray photoelectron spectroscopy (XPS) analyzer (Escalab250Xi,
146 Thermo Scientific Inc) was used to quantify the S form at the char surface. The XPS
147 measurements in this study were carried out with an unmonochromated AlK α (1486.6eV)
148 radiation. The step size was set as 0.1eV, and the internal standard calibration was set as C1s
149 (284.6eV). The spectral features of S2p peak were used for sulfur speciation analysis.

150 In XPS analysis, the peak-fitting method is often chosen to identify the sulfur forms. The
151 reliability of the peak data is highly dependent on the specific method and parameter setting of
152 peak-fitting, and the two most common methods are $2p_{3/2}/2p_{1/2}$ doublet fitting and $2p_{3/2}$ single
153 peak fitting.

154 Based on previous studies [35-37] and the XPS database of American National Institute of
155 Standards and Technology (NIST) [38], the S $2p_{3/2}$ binding energies are summarized in Table 3.
156 Each sulfur specie in Table 3 refers to a class of chemicals except pyrite. The binding energy of
157 pyrite and sulfide have overlapping parts. Pyrite is the main sulfide components in coal, followed
158 by marcasite, sphalerite and galena. In this paper, S content in coal is divided into five categories:
159 sulfide/pyrite, thiophene, sulfoxide, sulfone and sulfate. The S $2p_{3/2}$ peak of sulfide is classified as
160 pyrite. The XPS peakfit 4.1 software was used in the peak analysis and parameters setting is
161 mainly based on the following principles [39]: (i) a 2:1 relative area was separated by 1.18 eV; (ii)

162 the L-G% (Lorentzian-Gaussian%) was set as 0; and (iii) the full width at half-maximum
163 (FWHM) was set to the same value for each peak ranging from 0 to 2.

164 3. Results and Discussion

165 3.1 Fuel-nitrogen releasing during pyrolysis

166 Pyridines, pyrrole, and quaternary nitrogen are the three principal N-compounds in the coal.
167 Previous study shows that part of the pyridines and pyrrole nitrogen are converted to HCN during
168 pyrolysis process [40]. The formation of NH₃ has two main sources: one is the decomposition of
169 quaternary nitrogen, while the other is the secondary reaction of tar and char. Fig. 2 presents the
170 concentration of nitrogen-containing gases during coal pyrolysis under N₂ and CO₂ atmosphere at
171 0.5MPa and 850°C. NH₃ and HCN are the major nitrogen-containing gases during coal pyrolysis,
172 while NO and N₂O can also be detected in the gases produced. Because of the very low
173 concentration of NO and N₂O, their curves are not included in Fig. 2. The NH₃/HCN ratios under
174 both atmospheres are relatively low in this study, a result which is very different with that
175 previously reported [24]. This difference may be caused by the differences in quaternary nitrogen
176 content in various coals. Also from Fig. 2, the HCN concentration in CO₂ atmosphere is higher
177 than that in N₂ atmosphere, owing to strong C/CO₂ reaction in CO₂ atmosphere. The gasification
178 process breaks the stable -CN bonds and make it much easier to form HCN.

179 The HCN release profiles in different temperature at 0.5MPa and CO₂ atmosphere are shown
180 in Fig. 3. The peak value of HCN concentration curve increases as the pyrolysis temperature
181 increases. As mentioned above, most of the HCN originates from the thermal-stable pyridines and
182 pyrrole nitrogen in coal, and the higher temperature will increase their decomposition and generate
183 more HCN [41]. In terms of nitrogen conversion, the nitrogen converted to HCN in CO₂ and N₂
184 atmosphere is 5.45 and 3.01 times of that converted into NH₃ in N₂ atmosphere. The existence of
185 CO₂ during pyrolysis clearly enhances total nitrogen conversion rate of coal. In Fig. 3, the higher
186 pyrolysis temperature leads to a shorter time for HCN concentration to reach its peak value. This
187 also can be explained by the thermal-stability of pyridines and pyrrole nitrogen.

188 Fig. 4 and Fig. 5 show the N-containing gases release profiles of coal at different pressure

189 and atmospheres. For the NH₃ obtained in both atmospheres, with the increase of pressure the
190 peak value of NH₃ concentration shows a slight increase. The quaternary nitrogen is completely
191 decomposed over 800°C [40]. Therefore, the influence of the pressure on the quaternary nitrogen
192 decomposition at 850°C should be negligible. In addition, the direct hydrogenation of char-N by
193 H-radicals is another important source of NH₃ in the volatiles [22]. Higher pressure would slow
194 down the diffusion of volatile precursors out from inside the particle, leading to increases in the
195 residence time of volatile precursors inside the particles. This in turn intensify the thermal
196 cracking of volatile precursors to produce more radicals, including H-radicals, and allow more
197 time for the H-radical-laden volatile precursors to interact with the char-N to form NH₃.

198 From 0.1MPa to 0.7MPa the peak value of HCN concentration in N₂ and CO₂ atmosphere
199 experienced a gradual rise. Pyridines and pyrrole nitrogen have a high thermal-stability, and are
200 difficult to completely decompose even at 1000°C. However, high pressure is advantageous in
201 enhancing the degree of pyrolysis, and the strong C/CO₂ reaction in pressurized CO₂ atmosphere
202 breaks the stable -CN bonds of coal. And the exposed -CN sites encourage the formation of HCN
203 with H-radical. It can be concluded that higher pressures enhance the generation of NO_x
204 precursors.

205 Fig. 6 presents the conversion rate under different temperature and pressure. Raising the
206 temperature at each operating pressure will lead an increase to fuel-N conversion rate. At 0.1MPa,
207 the nitrogen conversion rate from 750°C to 900°C increased by 4.49%. While at 0.7MPa, this
208 increase is about 12.78%. Thus it is clear that increasing temperature and pressure jointly promote
209 the conversion of fuel-N to NO_x precursors.

210 3.2 Sulfur conversion during pressurized pyrolysis

211 H₂S and COS were not monitored in this study, however the sulfur content and sulfur
212 speciation in the char residue were carefully investigated to provide us with additional information
213 to better understand the sulfur chemistry under these conditions. During coal pyrolysis under CO₂
214 atmosphere, SO₂ concentration in the gaseous product was monitored and the curves of SO₂ under
215 different pressure are shown in Fig. 7. SO₂ concentration in the gaseous product is relatively low,

216 however as the pressure increases, this concentration has a slight decrease. Another interesting
217 result is that the elevation of pyrolysis pressure leads to a reduction in the amount of sulfur in the
218 char. The sulfur content in the char residue at 850°C is shown in Table 4. As the pressure
219 increases, the sulfur content in char decrease, indicating that more tar-S and volatile-S are
220 generated. As SO₂ also decrease with pressure, there may be more COS or H₂S formation. By
221 elevating the pyrolysis pressure, the high partial pressure of CO₂ enhances the formation of CO,
222 which can be seen from Fig. 8. CO also appears to enhance the decomposition of sulfur in coal.
223 This causes the drop of sulfur in char and creates more S-containing gases like H₂S and COS. The
224 high concentration of CO also enhances the conversion reaction from SO₂ to COS [28], as R1 and
225 R2 show:



226 However, this is only one possible route for the simultaneous reduction of SO₂ and char
227 residue sulfur as the pressure increases, and more experiments with accurate measurement of H₂S
228 and COS must be made to verify this explanation.

229 Fig. 9 shows the S2p_{3/2} and S2p_{1/2} doublet fitting results of raw coal and char obtained from
230 pyrolysis under different pressures. In XPS peak fitting, the percentage of each peak area in
231 relation to the total area is equated to the relative content of each sulfur form. Thus, based on the
232 curve fitting results in Fig. 9, the distribution proportion of different sulfur forms is summarized in
233 Table 5. The main sulfur forms in the raw coal surface is the sulfone (~37.32%) and thiophene
234 (~23.29%), while the sulfide/FeS₂ only accounts for 16.04% of the total sulfur content of raw coal.

235 Sulfur conversion during coal pyrolysis is very complex. Sulfur-containing functional groups
236 in coal decompose and release during pyrolysis process, and at the same time the interactions
237 between pyrite, sulfate and organic sulfur also affect the distribution and speciation of sulfur in the
238 final products. Zhang et al. [42] proposed a schematic of the sulfur conversion mechanisms during
239 coal pyrolysis, as shown in Fig. 10, to illustrate the complex series of reactions.

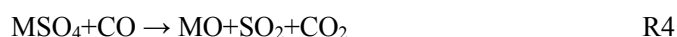
240 For coal pyrolysis under high pressure CO₂ atmosphere, the reaction mechanism in Fig. 10

241 still applies. However, with different pressure, the rate and extent of each reaction will be different.
242 Thus, for instance, the increase of pressure causes the pyrite content to generally decrease. In
243 reductive atmosphere, the decomposition reaction of FeS₂ is mainly controlled by the following
244 reaction:



245 The R3 reaction is one of the main sources of COS during coal pyrolysis. This reaction is
246 very slow at 800°C [28]. Given the pyrolysis temperature and short residence time of coal in the
247 fluidized bed, part of FeS₂ will be converted to FeS, and will resist further reaction. The elevation
248 of pressure enhances the reductive atmosphere through producing more CO, and accelerates the
249 consumption rate of pyrite, so the pyrite content decreases when pressure increases.

250 The main kinds of sulfate in coal are the mixtures of BaSO₄, CaSO₄·2H₂O, CaSO₄ and FeSO₄,
251 and these sulfates in the raw coal are typically only present at about 0.31% as shown in Table 2.
252 Fig. 9 and Table 5 show the change of sulfate content is not obvious under different pressure. Two
253 facts can be deduced about the influence of pressure on sulfate. One is that as the pressure
254 increases, the sulfur fixation ability of the coal ash is likely to be enhanced [43], given that
255 calcium, potassium and sodium in the ash can capture the SO₂ in the gas more efficiently. The
256 other is that as the pressure increase, higher concentration of CO will react with the sulfate to form
257 SO₂, as show below:



258 Here M represents an alkali or alkaline earth metal. In addition, the reaction rate increases as
259 the CO partial pressure increase. However, given that SO₂ levels were not shown to be high in this
260 study, we believe the first explanation is likely to be the more important one, and indeed we can
261 see the overall sulfate content under high pressure is higher than that in low pressure.

262 Thiophene, sulfoxide and sulfone are usually referred to as organic sulfur in coal. The
263 composition and structure of organic sulfur are very complex and with the total different thermal
264 stability. Thiophene is much more stable and difficult to decompose because sulfur in the
265 thiophene is aromatically bound [28]. The thiophene in coal can be generated from the two

266 reactions as shown in Fig. 10, one is S or H₂S react with the organic matter in coal; The other is
267 the pyrite reacts with small organic molecules like ethylene. When pyrolysis pressure increases,
268 the relative content of thiophene will also rise. High pressure CO₂ promotes the gasification of
269 coal and increases the concentration of small organic molecules, thus accelerating the generation
270 of thiophene. Moreover, the decomposition of pyrite and sulfone reduces the total amount of
271 sulfur in char under high pressure, so the relative content of thiophene which is thermal stable will
272 increase.

273 Compared with the S2 curves, the specific components of S3 and S4 curves are much more
274 complex and difficult to specify. The thermal stability of sulfoxide and sulfone is highly
275 dependent on the functional groups contacted with -SO₂- and -SO-. Previous study [44] shows the
276 thermal stability of sulfoxide and sulfone as follows: aliphatic sulfoxide < aromatic sulfoxide <
277 sulfone < 650°C. So sulfoxide and sulfone decompose at experimental condition (850°C). The
278 pyrolysis of coal makes the conversion of sulfoxide and sulfone into gaseous products, and the
279 removal rate of them increase with the increase of pressure and the degree of gasification.

280 In summary, the possible pathway of how the high pressure CO₂ atmosphere affects sulfur
281 conversion during pyrolysis appear to be as follows: (1) high pressure increases the sulfur
282 conversion rate, resulting in more gaseous products like COS; (2) high partial pressure of CO
283 accelerates the decomposition of pyrite; (3) the sulfur fixation ability of the ash is further
284 enhanced by high pressure; (4) high pressure increases the conversion from gaseous S and pyrite
285 to thiophene.

286 4. Conclusion

287 Experiments on pyrolysis of coal at CO₂ atmospheres were conducted in a lab-scale
288 pressurized fluidized bed system, and the influence of pressure on N and S conversion was
289 explored. Some general conclusions can be drawn as follow:

290 1) For the raw coal in this experiment, HCN is the major nitrogen-containing gaseous
291 product for coal pyrolysis at CO₂ atmosphere.

292 2) The generation of HCN and NH₃ increase simultaneously with the increase of overall
293 pressure. High pressure and the existence of high partial pressures of CO₂ enhance the fuel-N
294 conversion rate in pyrolysis process.

295 3) SO₂ concentration in gaseous product and sulfur content in char decrease simultaneously
296 with the increase of overall pressure, indicating that more COS and H₂S are generated during the
297 pyrolysis process.

298 4) The effects of high pressure CO₂ on the migration of sulfur during pyrolysis are mainly
299 due to the changes of volatile yield and the rate of sulfur conversion reactions. High pressure of
300 CO₂ accelerates the decomposition of pyrite and also intensifies the conversion from gaseous S
301 and pyrite to thiophene.

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304 **References**

- 305 [1] Carbon Capture and Storage: The solution for deep emissions reductions, IEA, 2015.
- 306 [2] Chen L, Yong S Z, Ghoniem A F. Oxy-fuel combustion of pulverized coal: Characterization,
307 fundamentals, stabilization and CFD modeling[J]. Progress in Energy and Combustion
308 Science, 2012,38(2):156-214.
- 309 [3] Lasek J A, Janusz M, Zuwała J, et al. Oxy-fuel combustion of selected solid fuels under
310 atmospheric and elevated pressures[J]. Energy, 2013,62:105-112.
- 311 [4] Escudero A I, Espatolero S, Romeo L M, et al. Minimization of CO₂ capture energy penalty
312 in second generation oxy-fuel power plants[J]. Applied Thermal Engineering,
313 2016,103:274-281.
- 314 [5] Darde A, Prabhakar R, Tranier J, et al. Air separation and flue gas compression and
315 purification units for oxy-coal combustion systems[J]. Energy Procedia, 2009,1(1):527-534.
- 316 [6] Xia F, Yang Z, Adeosun A, et al. Pressurized oxy-combustion with low flue gas recycle:

- 317 Computational fluid dynamic simulations of radiant boilers[J]. Fuel, 2016.
- 318 [7] Zebian H, Mitsos A. Pressurized OCC (oxy-coal combustion) process ideally flexible to the
319 thermal load[J]. Energy, 2014,73:416-429.
- 320 [8] Zebian H, Gazzino M, Mitsos A. Multi-variable optimization of pressurized oxy-coal
321 combustion[J]. Energy, 2012,38(1):37-57.
- 322 [9] Hong J, Chaudhry G, Brisson J G, et al. Analysis of oxy-fuel combustion power cycle
323 utilizing a pressurized coal combustor[J]. Energy, 2009, 34(9): 1332-1340.
- 324 [10] Hong J, Field R, Gazzino M, et al. Operating pressure dependence of the pressurized oxy-fuel
325 combustion power cycle[J]. Energy, 2010, 35(12): 5391-5399.
- 326 [11] Gazzino M, Benelli G. Pressurised oxy-coal combustion Rankine-cycle for future zero
327 emission power plants: process design and energy analysis[C]//ASME 2008 2nd International
328 Conference on Energy Sustainability collocated with the Heat Transfer, Fluids Engineering,
329 and 3rd Energy Nanotechnology Conferences. American Society of Mechanical Engineers,
330 2008: 269-278.
- 331 [12] Gopan A, Kumfer B M, Phillips J, et al. Process design and performance analysis of a Staged,
332 Pressurized Oxy-Combustion (SPOC) power plant for carbon capture[J]. Applied Energy,
333 2014, 125: 179-188.
- 334 [13] Gopan A, Kumfer B M, Axelbaum R L. Effect of operating pressure and fuel moisture on net
335 plant efficiency of a staged, pressurized oxy-combustion power plant[J]. International Journal
336 of Greenhouse Gas Control, 2015, 39: 390-396.
- 337 [14] Wang C, Lei M, Yan W, et al. Combustion characteristics and ash formation of pulverized
338 coal under pressurized oxy-fuel conditions[J]. Energy & Fuels, 2011, 25(10): 4333-4344.
- 339 [15] Lei M, Huang X, Wang C, et al. Investigation on SO₂, NO and NO₂ release characteristics of
340 Datong bituminous coal during pressurized oxy-fuel combustion [J]. Journal of Thermal
341 Analysis and Calorimetry, 2016. doi:10.1007/s10973-016-5652-y

- 342 [16] Ying Z, Zheng X, Cui G. Pressurized oxy-fuel combustion performance of pulverized coal
343 for CO₂ capture[J]. Applied Thermal Engineering, 2016, 99: 411-418.
- 344 [17] Lasek J A, Głód K, Janusz M, et al. Pressurized oxy-fuel combustion: A Study of selected
345 parameters[J]. Energy & Fuels, 2012, 26(11): 6492-6500.
- 346 [18] Pipitone G, Bolland O. Power generation with CO₂ capture: technology for CO₂
347 purification[J]. International journal of greenhouse gas control, 2009, 3(5): 528-534.
- 348 [19] Kim S, Ahn H, Choi S, et al. Impurity effects on the oxy-coal combustion power generation
349 system[J]. International Journal of Greenhouse Gas Control, 2012, 11: 262-270.
- 350 [20] Xie Z, Feng J, Zhao W, et al. Formation of NO_x and SO_x precursors during the pyrolysis of
351 coal and biomass. Part IV. Pyrolysis of a set of Australian and Chinese coals[J]. Fuel,
352 2001,80(15):2131-2138.
- 353 [21] Tan L L, Li C. Formation of NO_x and SO_x precursors during the pyrolysis of coal and
354 biomass. Part II. Effects of experimental conditions on the yields of NO_x and SO_x precursors
355 from the pyrolysis of a Victorian brown coal[J]. Fuel, 2000,79(15):1891-1897.
- 356 [22] Li C, Tan L L. Formation of NO_x and SO_x precursors during the pyrolysis of coal and
357 biomass. Part III. Further discussion on the formation of HCN and NH₃ during pyrolysis[J].
358 Fuel, 2000,79(15):1899-1906.
- 359 [23] Tan L L, Li C. Formation of NO_x and SO_x precursors during the pyrolysis of coal and
360 biomass. Part I. Effects of reactor configuration on the determined yields of HCN and NH₃
361 during pyrolysis[J]. Fuel, 2000,79(15):1883-1889.
- 362 [24] Jamil K, Hayashi J, Li C. Pyrolysis of a Victorian brown coal and gasification of nascent char
363 in CO₂ atmosphere in a wire-mesh reactor[J]. Fuel, 2004,83(7-8):833-843.
- 364 [25] Chang L, Xie Z, Xie K, et al. Formation of NO_x precursors during the pyrolysis of coal and
365 biomass. Part VI. Effects of gas atmosphere on the formation of NH₃ and HCN[J]. Fuel,
366 2003,82(10):1159-1166.

- 367 [26] Li X, Zhang S, Yang W, et al. Evolution of NO_x precursors during rapid pyrolysis of coals in
368 CO₂ atmosphere[J]. Energy & Fuels, 2015,29(11):7474-7482.
- 369 [27] Duan L, Zhao C, Zhou W, et al. Investigation on coal pyrolysis in CO₂ atmosphere[J].
370 Energy & Fuels, 2009, 23(7): 3826-3830.
- 371 [28] Attar A. Chemistry, thermodynamics and kinetics of reactions of sulphur in coal-gas
372 reactions: A review[J]. Fuel, 1978, 57(4): 201-212.
- 373 [29] Wang P, Jin L, Liu J, et al. Analysis of coal tar derived from pyrolysis at different
374 atmospheres[J]. Fuel, 2013,104:14-21.
- 375 [30] Hu H, Zhou Q, Zhu S, et al. Product distribution and sulfur behavior in coal pyrolysis[J].
376 Fuel Processing Technology, 2004,85(8-10):849-861.
- 377 [31] Huang F, Zhang L, Yi B, et al. Transformation pathway of excluded mineral pyrite
378 decomposition in CO₂ atmosphere[J]. Fuel Processing Technology, 2015,138:814-824.
- 379 [32] Karaca S. Desulfurization of a Turkish lignite at various gas atmospheres by pyrolysis. Effect
380 of mineral matter[J]. Fuel, 2003,82(12):1509-1516.
- 381 [33] Chen H, Li B, Zhang B. Decomposition of pyrite and the interaction of pyrite with coal
382 organic matrix in pyrolysis and hydrolyrolysis[J]. Fuel, 2000, 79(13): 1627-1631.
- 383 [34] Xu W C, Kumagai M. Sulfur transformation during rapid hydrolyrolysis of coal under high
384 pressure by using a continuous free fall pyrolyzer[J]. Fuel, 2003, 82(3): 245-254.
- 385 [35] Grzybek T, Pietrzak R, Wachowska H. X-ray photoelectron spectroscopy study of oxidized
386 coals with different sulphur content[J]. Fuel processing technology, 2002, 77: 1-7.
- 387 [36] Kozłowski M. XPS study of reductively and non-reductively modified coals[J]. Fuel, 2004,
388 83(3): 259-265.
- 389 [37] Marinov S P, Tyuliev G, Stefanova M, et al. Low rank coals sulphur functionality study by
390 AP-TPR/TPO coupled with MS and potentiometric detection and by XPS[J]. Fuel processing
391 technology, 2004, 85(4): 267-277.

- 392 [38] <http://srdata.nist.gov/xps/selectEnergyType.aspx>
- 393 [39] Wang Z, Li Q, Lin Z, et al. Transformation of nitrogen and sulphur impurities during
394 hydrothermal upgrading of low quality coals[J]. Fuel, 2016,164:254-261.
- 395 [40] Duan L, Zhao C, Ren Q, et al. NO_x precursors evolution during coal heating process in CO₂
396 atmosphere[J]. Fuel, 2011,90(4):1668-1673.
- 397 [41] Glarborg P. Fuel nitrogen conversion in solid fuel fired systems[J]. Progress in Energy and
398 Combustion Science, 2003,29(2):89-113.
- 399 [42] Zhang D, Yani S. Sulphur transformation during pyrolysis of an Australian lignite[J].
400 Proceedings of the Combustion Institute, 2011, 33(2): 1747-1753.
- 401 [43] Zakkay V, Clisset H, Ganesh A, et al. Sulfur retention of North Dakota (Beulah) lignite ash
402 in PFBC[C]//ASME 1984 International Gas Turbine Conference and Exhibit. American
403 Society of Mechanical Engineers, 1984: V003T05A014-V003T05A014.
- 404 [44] Van Aelst J, Yperman J, Franco D V, et al. Study of silica-immobilized sulfur model
405 compounds as calibrants for the AP-TPR study of oxidized coal samples[J]. Energy & fuels,
406 2000, 14(5): 1002-1008.

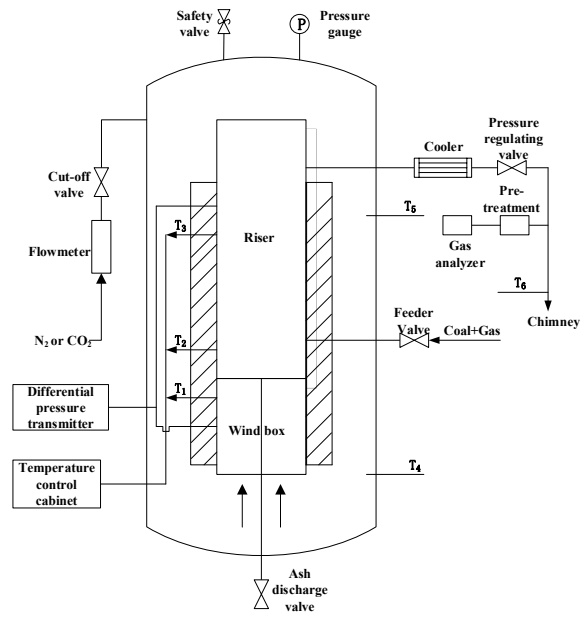


Fig. 1. Schematic diagram of pressurized fluidized bed system

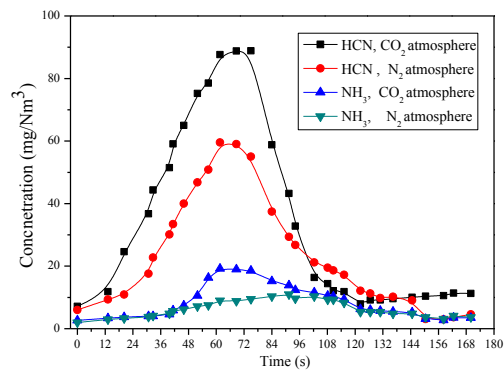


Fig. 2. Concentration of N-containing gases during coal pyrolysis at 0.5MPa and 850°C

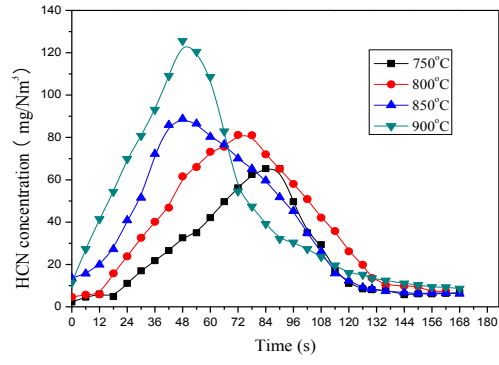


Fig. 3. HCN concentration curves of coal pyrolysis at 0.5MPa and CO₂ atmosphere

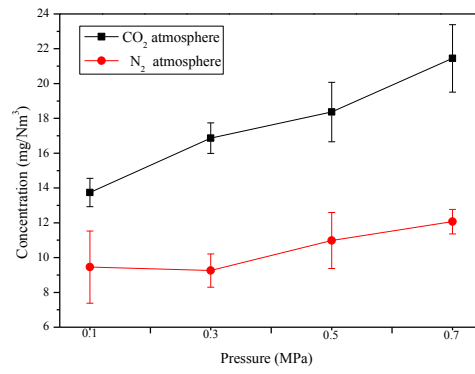
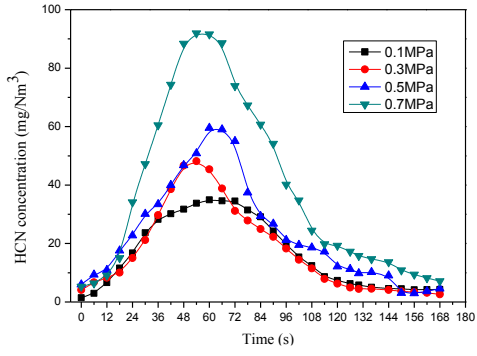
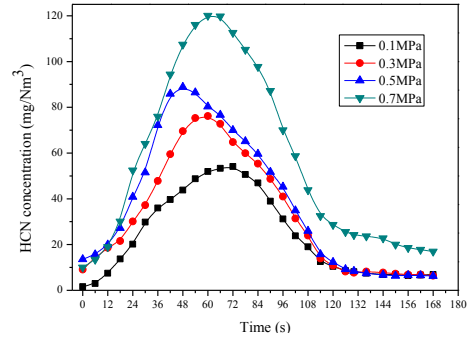


Fig. 4. NH₃ peak concentration at 850°C with different pressure



(a) N₂ atmosphere



(b) CO₂ atmosphere

Fig. 5. HCN release curves of coal pyrolysis at 850°C with different pressure

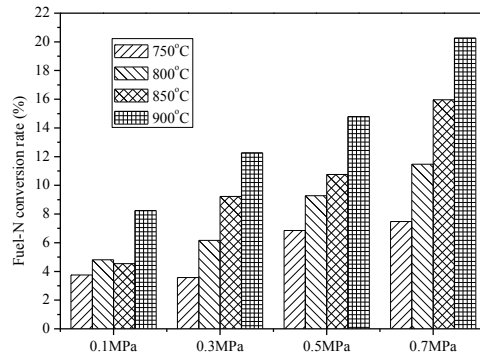


Fig. 6. Fuel-N conversion rate under CO₂ atmosphere at different temperature and pressure

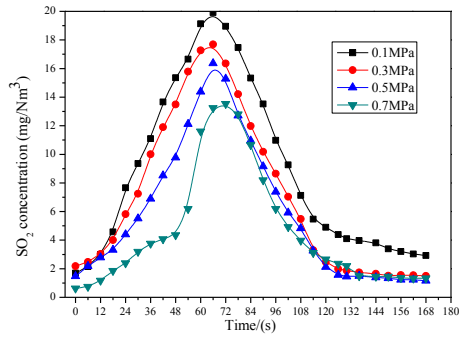


Fig. 7. SO₂ release curves of coal pyrolysis at 850°C and CO₂ atmosphere with different pressure

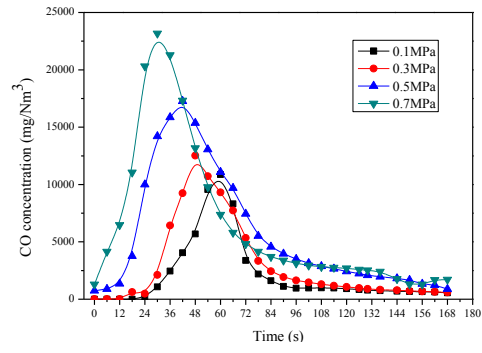
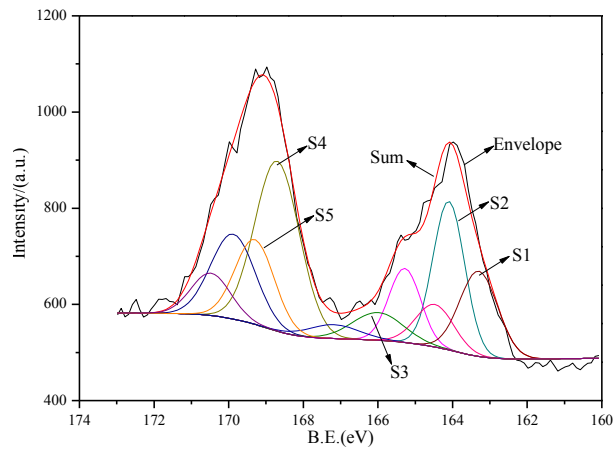
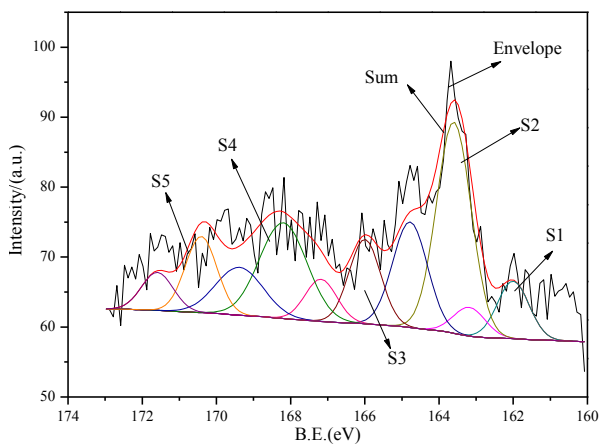


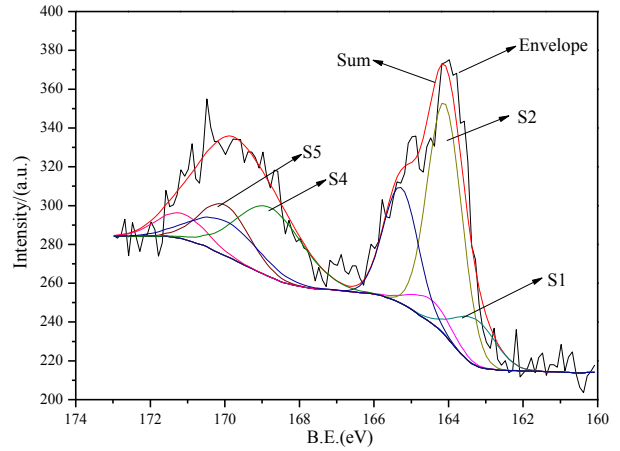
Fig. 8. CO release curves of coal pyrolysis at 850°C and CO₂ atmosphere with different pressure



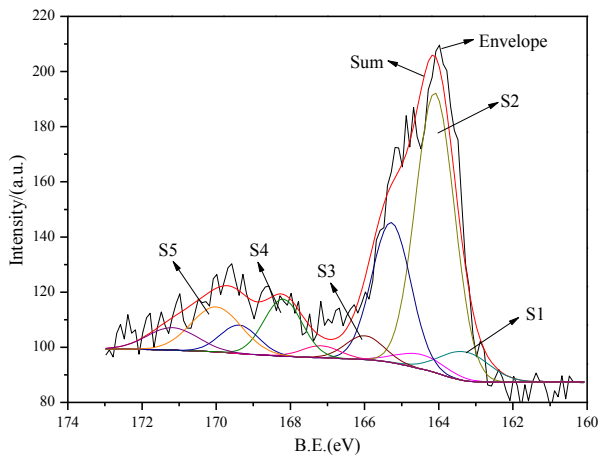
(a). Raw coal



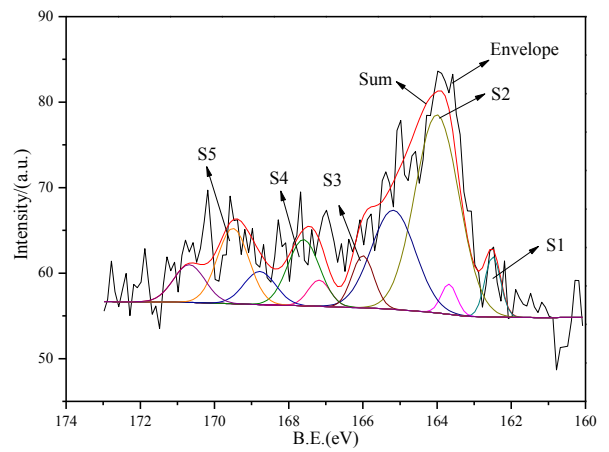
(b). Char under 0.1MPa



(c). Char under 0.3MPa



(d). Char under 0.5MPa



(e). Char under 0.7MPa

Fig. 9. Curve fitting results of raw coal and char

(S1-Pyrite peak; S2-Thiophene peak; S3-Sulfoxide peak; S4-Sulfone peak; S5-Sulfate peak)

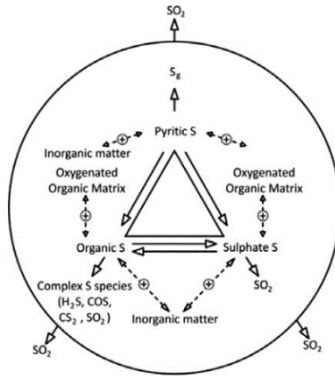


Fig. 10. A schematic of the mechanisms of sulfur conversion during coal pyrolysis [42]

Table 1. Ultimate and proximate analysis of raw coal / %

Coal samples	Ultimate analysis						Proximate analysis			Lower calorific value/ (MJ•kg ⁻¹)
	w(C _{ad})	w(H _{ad})	w(O _{ad})	w(N _{ad})	w(S _{ad})	w(M _{ad})	w(A _{ad})	w(V _{ad})	w(FC _{ad})	
Raw coal	67.42	4.14	8.31	1.04	2.72	6.52	9.85	35.34	48.29	26.66

*ad denotes air dried basis

Table 2. Forms of sulfur in raw coal / %

Total sulfur	Pyrite sulfur	Sulfate sulfur	Organic sulfur
2.72	0.51	0.31	1.90

Table 3. Binding energies of S2p_{3/2}

Sulfur species	Binding energy (eV)
Pyrite	162.3-162.9
Sulfide	162.1-163.6
Thiophene	164.0-164.4
Sulfoxide	165.0-166.0
Sulfone	167.0-168.3
Sulfate	> 168.4

Table 4. Sulfur content in char under various pressures

Pressure/MPa	0.1	0.3	0.5	0.7
w(Sulfur content)/%	2.37	1.93	1.75	1.64

Table 5. Distribution proportion of different sulfur forms after the curve fitting procedure

Sulfur species	Sulfur content w/%				
	Raw coal	Char under 0.1MPa	Char under 0.3MPa	Char under 0.5MPa	Char under 0.7MPa
Sulfide/Pyrite	16.04	12.20	11.14	8.07	6.36
Thiophene	23.29	38.13	46.98	62.26	58.10
Sulfoxide	6.93	9.68	0.00	5.18	8.11
Sulfone	37.32	28.17	27.25	11.46	11.55
Sulfate	16.42	11.82	14.63	13.03	15.88

Nitrogen and sulfur conversion during pressurized pyrolysis under CO₂ atmosphere in fluidized bed

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