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# Structure evolution of lignite char in step pyrolysis and its combustion reactivity

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## Abstract

Step pyrolysis was conducted in a laboratory-scale fixed bed reactor for char preparation. Characterization techniques such as volume solvent swelling, thermal gravimetric analysis (TGA), X-ray diffraction (XRD) and X-ray photoelectron spectroscopy (XPS) were applied to reveal char structure evolution during step pyrolysis. Combustion reactivities of the prepared chars were examined at a thermal gravimetric analyzer. Newly formed bond structures in char such as C<sub>al</sub>-C<sub>al</sub> and C<sub>ar</sub>-C<sub>al</sub>/O have been identified at the 1<sup>st</sup> stage of step pyrolysis, which evidences the occurrence of cross-linking reactions. As a result, step pyrolysis has higher char yield than direct pyrolysis. The char yield from step pyrolysis increases as the 1<sup>st</sup> stage pyrolysis temperature increases and reaches a maximum at 773 K. An index was put forward to assess the extent of cross-linking reactions during pyrolysis, which is well

25 correlated with char production. The char from step pyrolysis has relatively high  
26 graphitization degree than from direct pyrolysis, and thus has lower combustion  
27 reactivity. Step pyrolysis can suppress sulfur and nitrogen release in comparison with  
28 direct pyrolysis owing to the formation of more stable sulfur and nitrogen species in  
29 char. The difference in nitrogen release varies within 8 percentage points and for sulfur  
30 release, it is within 5 percentage points under the examined experimental conditions.

31

32 **Keyword:** step pyrolysis, crossing-linking reaction, lignite char, structure evolution

## 33 1 Introduction

34 Lignite has characteristics such as high moisture and oxygen contents, and low  
35 heating value[1]. These characteristics make lignite inefficient for direct combustion.  
36 Moreover, its high spontaneous combustion tendency increases fire risk during storage  
37 and transportation [2]. Pyrolysis is considered an effective method to improve the  
38 unfavored characteristics of lignite to combustion. The char derived from pyrolysis is a  
39 more environment-friendly fuel than its parent coal, with less emissions of pollutants  
40 in combustion such as sulfur, NO<sub>x</sub> and soot[3].

41 A variety of pyrolysis processes like Char Oil Energy Development (COED)  
42 process[4], Lurgi-Ruhrgas (L-R) process[5] and Dalian University of Technology (DG)  
43 process[6] have been developed to upgrade lignite into relatively “clean” coal,  
44 meanwhile producing tar and gas[7]. Tar and gas production is of help to the process  
45 economics. A multistage cyclone pyrolysis process has been put forward, recently by

46 our group[8]. In this process, millimeter sized particles experience low-and high-  
47 temperature stages in multistage cyclones. Tar is collected at low temperature stage to  
48 avoid high-temperature cracking. The solid continues to pass through high temperature  
49 stage cyclone, where the volatiles are further driven out to maximize gas production. In  
50 this way, tar and gas can be produced to the greatest extent possible. The produced char  
51 is used as domestic fuel or injection fuel of blast furnace. Thermal history has a strong  
52 effect on char structure evolution and thus combustion reactivity[9-12]. The char  
53 produced from the step pyrolysis may have quite different physiochemical properties  
54 from the one generated from normal direct pyrolysis. Understanding of the effect of  
55 step pyrolysis on derived char properties would be beneficial to subsequent thermal  
56 conversions.

57 In general, char has higher ignition and burnout temperatures than its parent coal.  
58 The combustion process is delayed towards high temperature region owing to less  
59 volatiles and structure changes. Pyrolysis conditions such as temperature, atmosphere,  
60 holding time and heating rate have strong effects on combustion reactivity and  
61 physiochemical structures of char[13-15]. Much research has been devoted to this  
62 aspect. High temperature and long holding time lead to high ignition and burnout  
63 temperatures of char due to less volatiles and higher ordering degree of carbonaceous  
64 structures[9, 14, 16]. Char combustion reactivity is to some extent related to char  
65 aromaticity. The char with high aromaticity is relatively inert. High temperature leads  
66 to high aromaticity of char[17]. The char derived from oxy-pyrolysis is more reactive

67 than the one under nitrogen atmosphere, attributed to relatively lower degree of  
68 graphitization and more porous structures[18]. The chemical occurrence forms of  
69 nitrogen and sulfur, and their quantities and distributions in char may also change with  
70 pyrolysis conditions, which significantly affect their releasing behaviors in subsequent  
71 thermal conversion[19-21]. Knowledge on these aspects is significant for reactor design  
72 and process development.

73 In this work, step pyrolysis was carried out in a fixed bed reactor with direct  
74 pyrolysis as a reference for comparison. A thermal gravimetric analyzer (TGA) was  
75 employed to evaluate the derived char combustion performance. Characterizations such  
76 as XRD, XPS and solvent swelling test were applied to examine structures of char  
77 samples generated from different pyrolysis conditions in attempt to reveal char structure  
78 evolution in step pyrolysis and the correlation with char reactivity. Transformations of  
79 sulfur and nitrogen during step pyrolysis were also discussed.

## 80 2 Experimental

### 81 2.1 Sample preparation

82 A lignite from Inner Mongolia was employed for char preparation. Its proximate  
83 and ultimate analyses are shown in Table 1. The char was produced in a fixed bed  
84 reactor under a nitrogen flow of 0.2 NL/min (shown in Figure 1). Prior to pyrolysis, the  
85 lignite was pulverized to pass through an 80-mesh sieve (0.2 mm). Then it was dried at  
86 105 °C for 4 hours. A stream of nitrogen was introduced from the top into the reactor.

87 After the reactor was electrically heated up to target temperature, 1.5 g of coal sample  
 88 was dropped into a quartz basket located in the middle of the reactor via feeding tube.  
 89 For step pyrolysis, the sample was pyrolyzed firstly at mild temperature. It was then  
 90 lowered to the quenching zone after a certain pyrolysis time. Waiting until the heating  
 91 zone temperature rises to a higher desired temperature, the sample was pulled back to  
 92 continue the pyrolysis. After pyrolysis, the sample was lower to the quenching zone and  
 93 purged with nitrogen.

94 Table1. Proximate and ultimate analyses of lignite

Proximate analysis (wt%)			Ultimate analysis (wt% dry base)				
A <sub>d</sub>	V <sub>daf</sub>	FC <sub>daf</sub>	C	H	N	S	O*
9.83	55.53	44.47	59.77	4.18	1.82	1.23	22.55

95 \*Calculated by difference.

## 96 2.2 Py-DTG analysis

97 Chemical structures of chars were analyzed with a simultaneous thermal analyzer  
 98 (Netzsch, Model STA-449C), based on the method developed by Shi and Liu et al. [22].  
 99 Lignite and char samples were heated to 1473 K at a heating rate of 10 K/min in  
 100 nitrogen. The mass loss during heating is attributed mainly to the cleavages of covalent  
 101 bonds in coal. The covalent bonds with different bonding energies are dissociated at  
 102 different temperatures. Accordingly, chemical structures of coal can be revealed by  
 103 resolving its DTG curve via peak fitting method. Figure 2 gives an example of a char  
 104 sample. Peak assignment is shown in Table 2. Five peaks are resulted from DTG curve  
 105 in this work, which is a little different from the result of 6 peaks in reference[22], since

106 water and carboxylic group are eliminated during char preparation. With respect to the  
 107 coal used, the peak of water and carboxylic group are found small and negligible, which  
 108 could be the result that it is dried for 4 hours at 105 °C prior to experimentation. No  
 109 obvious weight loss prior to 473 K consolidates this point.

110 Peak area represents the abundance of a certain bond structure in coal/char. With  
 111 the parent coal as a reference base, the abundance of a certain chemical bond structure  
 112 in char is expressed as:

$$113 \quad R_i = \frac{Y_{char} \cdot M_{i,char}}{M_{i,coal}} \quad \text{eq 1}$$

114 where  $M_{i,char}$  is the percentage of mass loss due to the cleavage of bond  $i$  in char.  $M_{i,coal}$   
 115 is the percentage of mass loss due to the cleavage of bond  $i$  in coal.  $M_{i,coal}$  and  $M_{i,char}$   
 116 can be obtained by calculating corresponding peak areas.  $Y_{char}$  is char yield.

117

118 Table 2. Assignment of peaks from DTG curve

Temperature K	Main origin of volatiles
629	O-C <sub>al</sub> breakage
703	C <sub>al</sub> -C <sub>al</sub> breakage
793	C <sub>ar</sub> - C <sub>al</sub> /O breakage
973	Carbonate's decomposition
1073	Aromatic structure condensation

### 119 2.3 XRD analysis

120 XRD technique (Model AXIOS, PANalytical B.V. , Netherlands) was applied to  
 121 analyze microcrystalline structure in char. It was operated in an omega/2theta ( $2\theta-\omega$ )  
 122 linkage symmetric scanning mode. The copper target was bombarded by high velocity  
 123 electrons at 40 kV and 30 mA. And the induced X-ray source of K $\alpha$ 1 was used to radiate  
 124 char sample in a step scan mode with 0.2° step<sup>-1</sup> over the angular  $2\theta$  range of 15°-70°.

125 Average stacking number  $N$  and average lateral size of crystallite  $L_a$  on a sample were  
126 calculated with Scherrer's equation[23].

#### 127 2.4 Solvent swelling test

128 Covalent cross-links density of char was analyzed in accordance with the solvent  
129 swelling method developed by Green et al. [24]. Pyridine was used to determine the  
130 swelling ratio of a char sample, defined as the ratio of the volume of swollen char in  
131 equilibrium in the solvent to its original volume.

#### 132 2.5 XPS analysis

133 XPS analyses were performed with a monochromatized Al-K $\alpha$  X-ray source  
134 operating at 150 W (ESCALAB 250Xi, Thermo Fisher Scientific Ltd) to identify the  
135 functionalities of nitrogen and sulfur on char. The calibration was carried out to the  
136 main C 1s peak at 284.6 eV. N 1s and S 2p curves were resolved into Gaussian bands  
137 according to previous research[25-28].

#### 138 2.6 Evaluation of char combustion performance

139 Char combustion performance was evaluated in a Simultaneous Thermal Analyzer  
140 (Netzsch, Model STA-449C). The experimental conditions were as follows: heating  
141 rate=20 K/min; air flow rate=5 0mL/min; char sample weight was about 15 mg. Char  
142 combustion reactivity was evaluated with  $R_w$ [29] given bellow:

$$143 \quad R_w = \frac{560}{T_i} + \frac{650}{T_{max}} + 0.27k_{max} \quad \text{eq1}$$

144 in which,  $T_i$  is ignition temperature, determined by the method proposed by Li et al[30];



145  $T_{max}$  is the temperature corresponding to the maximal mass loss rate,  $k_{max}$ .

## 146 3 Results and discussion

### 147 3.1 Char combustion reactivity

148 Figure 3 shows combustion reactivities of four chars, derived respectively from  
149 direct pyrolysis with different pyrolysis time, and from step pyrolysis. The pyrolysis  
150 conditions (pyrolysis temperature and holding time) can be found in Figure 3. D refers  
151 the char from direct pyrolysis. S stands for the one from step pyrolysis.

152 The higher is the  $R_w$ , the more reactive the char is. For direct pyrolysis, char  
153 combustion reactivity decreases with an increasing pyrolysis time. The influence of  
154 pyrolysis time on char combustion reactivity becomes weak as pyrolysis time increases.  
155 The reduction in combustion reactivity with the time can be attributed to less volatiles  
156 and more relatively inert aromatic structure and graphite formed in char as revealed by  
157 previous study[9, 14]. The char generated from direct pyrolysis has higher combustion  
158 reactivity than the step-pyrolysis char. Apparently, low temperature holding in pyrolysis  
159 (Char S) plays a significant role in decay of combustion reactivity. Even a reduction of  
160 holding time at high temperature cannot offset the low temperature holding effect by  
161 comparing Char S with Char D3.

162 Further, the effects of the temperature of the 1st stage in step pyrolysis were  
163 thoroughly examined shown in Figure 4. Group A and B both have the holding time of  
164 5 mins at first stage, and 0.5 mins and 5 mins respectively at a temperature of 1173K

165 (second stage). The determination on the duration of each stage is illustrated in  
166 supplementary material. Both groups include the char sample from direct pyrolysis as  
167 a reference, which were prepared at 1173 K, with the duration time as same as the  
168 second stage of step pyrolysis of each group, i.e. 0.5 mins corresponding to Group A  
169 and 5 mins corresponding to Group B. Significant drop in combustion reactivity is  
170 observed for both groups no matter how long the holding time at high temperature is.  
171 The effect of the 1<sup>st</sup> stage temperature seems more pronounced when the holding time  
172 at high temperature is longer.

## 173 3.2 Char yield

174 The yield of char derived from step pyrolysis is shown in Figure 5. Group A have  
175 higher char yields than Group B. It is reasonable since they have shorter pyrolysis  
176 holding times. It is worth noting that step pyrolysis is favorable to char production in  
177 comparison with direct pyrolysis. It increases with an increase of the 1<sup>st</sup> stage  
178 temperature. With the exception at 873K, it shows a slight decrease for both groups.  
179 These phenomena are resulted by low temperature cross-linking reactions during step  
180 pyrolysis, which suppress the release of volatiles (to be discussed later).

## 181 3.3 Char structure evolution

### 182 3.3.1 Variation of bond structures

183 The chars generated from the 1<sup>st</sup> stage of step pyrolysis are characterized with the  
184 DTG curve fitting method. The abundance of bond structure,  $R_i$  in the intermediate char

185 is shown in Figure 6. The O-C<sub>al</sub> bond in char has a significant drop as the pyrolysis  
186 temperature decreases. There is no O-C<sub>al</sub> for the chars derived at the temperatures  
187 higher than 573K. The C<sub>al</sub>-C<sub>al</sub> and C<sub>ar</sub>-C<sub>al</sub>/O have maximal values at 573 K and 673K,  
188 respectively, which are higher than those in the parent coal. It indicates that there are  
189 new formations of aliphatic structures, aromatic side chains and bridge structures in  
190 char during step pyrolysis, manifesting the occurrence of cross-linking reactions. The  
191 content of aromatic structures is relatively stable with the pyrolysis temperature since  
192 polymerization mainly occurs over 873K.

193 It is known that cross-linking reactions can suppress volatiles release[31], thus  
194 leading to more char production. For the chars from direct pyrolysis at a temperature of  
195 1173K (D in Figure 5), there is no chance of C<sub>al</sub>-C<sub>al</sub> and C<sub>ar</sub>-C<sub>al</sub>/O formation since all  
196 these structures have been destructed. In contrast, the chars derived from step pyrolysis  
197 have low temperature pyrolysis experience, fostering the formation of crosslink  
198 structures like C<sub>al</sub>-C<sub>al</sub> and C<sub>ar</sub>-C<sub>al</sub>/O that is most likely converted from the O-C<sub>al</sub>  
199 structures. These structures are solidified by condensation and polymerization into  
200 more stable aromatic structures at higher temperature. As a consequence, there is a  
201 higher char yield from step pyrolysis than from direct pyrolysis as observed in Figure  
202 5. The increasing char yield indicates the extent of cross-linking reactions to some  
203 extent. The loose structures like C<sub>al</sub>-C<sub>al</sub> and C<sub>ar</sub>-C<sub>al</sub>/O become unstable at 873K. Their  
204 abundance significantly drops as shown in Figure 6. Part of these structures are released  
205 as volatiles. The extent of cross-linking reactions is slightly lower. Thus, there is a

206 slight drop at 873K in char yield.

### 207 3.3.2 Swelling ratio and index to cross-linking reactions

208 Swelling ratio reflects the covalent crosslink density in char/coal. In order to  
209 measure the extent of crosslinking reactions during step pyrolysis, the volume swelling  
210 tests were performed with the chars derived from the 1<sup>st</sup> stage of step pyrolysis and their  
211 parent coal, shown in Figure 7. It is seen that the swelling ratio decreases with the  
212 increasing temperature, indicating a higher covalent crosslink density. Research has  
213 shown that the volume swelling is mainly contributed by loose covalent crosslink  
214 structures like functional groups, aliphatic structures and aromatic side chain  
215 structures[32]. These loose structures occupy very less (~10%) in coal, whose main  
216 body is three-dimensional macromolecular aromatic structure fastened by dense  
217 covalent crosslinks[33]. The volume swelling ratio reflect volume change as a whole,  
218 and cannot sensitively reflect the extent of crosslinking reactions (mainly occur in side  
219 chain structures) due to the large body of macromolecular phase. In consideration of  
220 this fact, the volume swelling change per unit of loose structures in coal/char is  
221 proposed in this work to measure the extent of crosslinking reactions, given as bellow.

$$222 \quad C_{link} = \frac{Q-1}{(M_{C_{al}-C_{al}} + M_{C_{ar}-C_{al}/O})} \quad \text{eq 2}$$

223 The O-Cal is not accounted for the loose structures since it disappears over 573 K. A  
224 higher  $C_{link}$  indicates a lower extent of cross-linking reactions in pyrolysis. It is found  
225 that the trend of  $C_{link}$  (shown in Figure 8) matches well with the trend of char yield in  
226 Figure 5. The correlation coefficient is over 0.97 as shown in Figure 9, indicating the

227  $C_{link}$  can well reflect the extent of cross-linking reactions.

### 228 3.3.3 XRD analysis

229 Table 3 shows graphite crystallite lateral size (La) and graphite crystallite stacking  
230 number (N) of the chars obtained by XRD characterization. La and N of the chars  
231 derived from direct pyrolysis are smaller than those from step pyrolysis. The increases  
232 of La and N indicate the growth of graphite crystallite on char. It means that the char  
233 from step pyrolysis has relatively higher graphitization degree in comparison with the  
234 one from direct pyrolysis. Cross-linking reactions could be an important factor  
235 promoting char graphitization. Good linear dependence of La and N with  $C_{link}$  indicate  
236 this point as shown in Figure 10. One possibility is that cross-linking structures formed  
237 during low temperature pyrolysis convert to graphite crystallites in subsequent high  
238 temperature pyrolysis stage. Another possibility could be that cross-linking structures  
239 can offer a favorable environment for the growth of graphite crystallites. H free radicals  
240 released by cross-linking reactions can promote the condensation of aromatic  
241 structure[34, 35]. However, it should be acknowledged that it is hard to quantify the  
242 contributions from the cross-linking structures conversion since the graphite formed  
243 during pyrolysis could be sourced either from the cross-linking structures or from the  
244 amorphous structures originally existing in coal.

245 Table 3. La and N from XRD analysis

Pyrolysis temperature K	N		La	
	Group A	Group B	Group A	Group B
D	7.74	12.95	3.89	4.87
S-573	8.14	13.91	4.11	4.99
S-673	8.47	14.81	4.23	5.19
S-773	9.13	15.94	4.42	5.38

246

247 Research has demonstrated that graphitization has a negative effect on char  
248 combustion reactivity [16, 36]. The trend of combustion reactivity shown in Figure 4 is  
249 well explained by the extent of char graphitization indicated by La and N in Table 4.

### 250 3.4 Release ratios of sulfur and nitrogen

251 Compared with direct pyrolysis, step pyrolysis has lower sulfur and nitrogen  
252 release ratios as shown in Figure 11. The results are far from our expectation in  
253 consideration of the fact that step pyrolysis has longer pyrolysis time than direct  
254 pyrolysis.

255 In order to explain the phenomena, XPS analysis was carried out to characterize  
256 the functionalities of nitrogen and sulfur on the chars generated from direct pyrolysis  
257 and step pyrolysis. Their speciation and distribution on char are given in Table 4 and 5  
258 (take Group A as an example). Nitrogen functionality on char can be classified into  
259 oxidized nitrogen (N-X,  $403 \pm 0.3$  eV), pyrrolic nitrogen (N-5,  $400.36 \pm 0.3$  eV),  
260 pyridinic nitrogen (N-6,  $398.76 \pm 0.3$  eV) and quaternary nitrogen (N-Q,  $401.46 \pm 0.5$   
261 eV). It is noteworthy that the step-pyrolysis char has higher contents of N-6 and N-Q  
262 and less N-5 and N-X in comparison with direct-pyrolysis char. It is known that N-6  
263 and N-Q are more stable than N-X and N-5[37, 38]. It is thus speculated that some N-  
264 X and N-5 have been converted into more stable functionalities of N-6 and N-Q during  
265 step pyrolysis. This could explain the fact that the step pyrolysis has lower nitrogen  
266 release. Similarity is found with the sulfur. There are four types of sulfur functionalities

267 (thiophene, sulfoxide, sulphone and sulfate) on char. More thiophene and sulphone are  
 268 observed on the step-pyrolysis char. The thiophene and sulphone are relatively stable  
 269 relative to the others[39]. Hence, relatively lower sulfur is released during step  
 270 pyrolysis.

271

272 Table 4 Speciation and distribution of sulfur functionalities on char (Group A)

Char sample	Sulfur functionalities, %			
	Thiophene	Sulfoxide	Sulphone	Sulfate
D	16.78	11.25	13.85	58.11
S-573K	21.02	7.84	17.82	53.32
S-673K	23.89	2.85	21.79	51.46
S-773K	26.38	0.00	20.30	53.32
S-873K	27.70	0.00	20.31	51.99

273

274 Table 5 Speciation and distribution of nitrogen functionalities on char (Group A)

Char sample	Nitrogen functionalities, %			
	N-6	N-5	N-Q	N-X
D	23.39	42.62	20.46	13.54
S-573K	25.37	41.21	21.27	12.16
S-673K	28.68	38.57	21.37	11.38
S-773K	28.02	37.31	23.48	11.19
S-873K	29.08	33.88	26.01	11.02

275

276

## 277 4 Conclusion

278 The following conclusions can be drawn from the present work.

- 279 (1) Step pyrolysis favors char production relative to direct pyrolysis. It is attributed to  
 280 cross-linking reactions at low temperature, evidenced by newly formed bond  
 281 structures characterized by TGA analysis.
- 282 (2) Compared with the volume swelling ratio, the volume swelling ratio change per unit  
 283 of loose structures is more sensitive to the cross-linking reactions, which has been

284 proposed to evaluate the extent of cross-linking reactions during pyrolysis. The  
285 results are well correlated with char yield.

286 (3) The char derived from step pyrolysis has more ordered structure than the one from  
287 direct pyrolysis, which leads to relatively lower combustion reactivity. Low-  
288 temperature cross-linking reactions occurred during step pyrolysis is considered the  
289 cause resulting in relatively high graphitization in char.

290 (4) Step pyrolysis inhibits nitrogen and sulfur releases by forming more stable  
291 functionalities of nitrogen and sulfur.

292 These conclusions give us a general rule on the pyrolysis process design and  
293 operation in future. That is: direct pyrolysis generally favors nitrogen and sulfur  
294 releases, and high reactive char production in comparison with step pyrolysis. Step  
295 pyrolysis could be a better choice for char production required with relatively inert  
296 nature in order to reduce the risks of explosion and spontaneous combustion in  
297 subsequent usage. Long duration and relatively high temperature (<873K) at the first  
298 stage are favorable conditions for step pyrolysis to produce char with relatively inert  
299 nature.

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307

## 308 References

- 309 [1] Si, C., J. Wu, Y. Wang, Y. Zhang, and X. Shang, *Drying of Low-Rank Coals: A*  
310 *Review of Fluidized Bed Technologies*. *Drying Technology*, 2015. **33**(3): p. 277-  
311 287.<https://doi.org/10.1080/07373937.2014.952382>
- 312 [2] Zhang, K. and C. You, *Effect of Upgraded Lignite Product Water Content on*  
313 *the Propensity for Spontaneous Ignition*. *Energy & Fuels*, 2013. **27**: p. 20-  
314 26.<https://doi.org/10.1021/ef301771r> | *Energy Fuels* 2013, 27, 20?26
- 315 [3] Li, Q., X. Li, J. Jiang, L. Duan, S. Ge, et al., *Semi-coke briquettes: towards*  
316 *reducing emissions of primary PM2.5, particulate carbon, and carbon*  
317 *monoxide from household coal combustion in China*. *Sci Rep*, 2016. **6**: p.  
318 19306.<https://doi.org/10.1038/srep19306>
- 319 [4] Jones, J.F., M.R. Schmid, M.E. Sacks, Y.-C. Chen, and C.A. Gray, *Char oil*  
320 *energy development. [Process for more effectively utilizing coal]*. 1967, FMC  
321 Corp., Princeton, N.J. (USA). Chemical Research and Development Center.
- 322 [5] DORING, H., H. SOMMERS, and R. RAMMLER, *GASEOUS AND LIQUID*  
323 *FUELS FROM COAL - PRODUCTION OF GAS, TAR AND OIL BY*  
324 *DEVOLATILIZATION OF COAL FOR POWER PLANTS(LURGI-RUHRGAS-*  
325 *PROCESS)*. *ERDOL & KOHLE ERDGAS PETROCHEMIE*, 1975. **28**(5): p.  
326 225-232
- 327 [6] Guo, S., C. Luo, and Z. Han, *Lignite Retorting Using Solid Heat Carrier*. *Fuel*  
328 *Science and Technology International*, 1990. **8**(1): p. 39-49.[https://doi.org/10.1](https://doi.org/10.1080/08843759008915912)  
329 [080/08843759008915912](https://doi.org/10.1080/08843759008915912)
- 330 [7] Xue, F., D. Li, Y. Guo, X. Liu, X. Zhang, et al., *Technical Progress and the*  
331 *Prospect of Low-Rank Coal Pyrolysis in China*. *Energy Technology*, 2017. **5**(11):  
332 p. 1897-1907.<https://doi.org/10.1002/ente.201700203>
- 333 [8] SONGGENG, L., S. WENLI, H. LIFANG, and F. CHUIGANG, *Pyrolysis*  
334 *apparatus and pyrolysis method for producing coke breeze and light tar*. 2017:  
335 China.
- 336 [9] Zhang, S.-Y., J.-F. Lu, J.-S. Zhang, and G.-X. Yue, *Effect of Pyrolysis Intensity*  
337 *on the Reactivity of Coal Char*. *Energy & Fuels*, 2008. **22**(5): p. 3213-  
338 3221.<https://doi.org/10.1021/ef800245z>
- 339 [10] Cai, H.Y., A.J. Güell, I.N. Chatzakis, J.Y. Lim, D.R. Dugwell, et al., *Combustion*  
340 *reactivity and morphological change in coal chars: Effect of pyrolysis*  
341 *temperature, heating rate and pressure*. *Fuel*, 1996. **75**(1): p. 15-  
342 24.[https://doi.org/10.1016/0016-2361\(94\)00192-8](https://doi.org/10.1016/0016-2361(94)00192-8)

- 343 [11] Jiménez, F., F. Mondragón, and D. López, *Structural changes in coal chars after*  
344 *pressurized pyrolysis*. Journal of Analytical and Applied Pyrolysis, 2012. **95**: p.  
345 164-170.<https://doi.org/10.1016/j.jaap.2012.02.003>
- 346 [12] Zhou, Q., T. Zou, M. Zhong, Y. Zhang, R. Wu, et al., *Lignite upgrading by multi-*  
347 *stage fluidized bed pyrolysis*. Fuel Processing Technology, 2013. **116**: p. 35-  
348 43.<https://doi.org/10.1016/j.fuproc.2013.04.022>
- 349 [13] Wedler, C., R. Span, and M. Richter, *Comparison of micro- and macropore*  
350 *evolution of coal char during pyrolysis*. Fuel, 2020.  
351 **275**.<https://doi.org/10.1016/j.fuel.2020.117845>
- 352 [14] Meng, D., C. Yue, T. Wang, and X. Chen, *Evolution of carbon structure and*  
353 *functional group during Shenmu lump coal pyrolysis*. Fuel, 2021.  
354 **287**.<https://doi.org/10.1016/j.fuel.2020.119538>
- 355 [15] Liu, H., T. Chen, and L. Fang, *Evolution of char structure during non-*  
356 *isothermal low temperature pyrolysis of ZhunDong coal by microwave heating:*  
357 *A comparative study with conventional heating*. Journal of the Energy Institute,  
358 2020. **93**(3): p. 1195-1206.<https://doi.org/10.1016/j.joei.2019.11.003>
- 359 [16] Feng, B., S.K. Bhatia, and J.C. Barry, *Structural ordering of coal char during*  
360 *heat treatment and its impact on reactivity*. Carbon, 2002. **40**(4): p. 481-  
361 496.[https://doi.org/10.1016/s0008-6223\(01\)00137-3](https://doi.org/10.1016/s0008-6223(01)00137-3)
- 362 [17] Zhu, Y., C.W. Kwong, P.J. van Eyk, R. de Nys, D. Wang, et al., *Pyrolysis*  
363 *Characteristics and Char Reactivity of Oedogonium sp. and Loy Yang Coal*.  
364 Energy & Fuels, 2015. **29**(8): p. 5047-  
365 5055.<https://doi.org/10.1021/acs.energyfuels.5b00642>
- 366 [18] Qi, J., C. Fan, and S. Li, *Characteristics of lignite char derived from oxy-*  
367 *pyrolysis*. Fuel, 2021. **291**.<https://doi.org/10.1016/j.fuel.2021.120261>
- 368 [19] Ma, J., X. Tian, C. Wang, H. Zhao, Z. Liu, et al., *Fate of fuel-nitrogen during in*  
369 *situ gasification chemical looping combustion of coal*. Fuel Processing  
370 Technology, 2021. **215**.<https://doi.org/10.1016/j.fuproc.2020.106710>
- 371 [20] Zhang, H. and T.H. Fletcher, *Nitrogen Transformations during Secondary Coal*  
372 *Pyrolysis*. Energy & Fuels, 2001. **15**(6): p. 1512-  
373 1522.<https://doi.org/10.1021/ef010118g>
- 374 [21] Xu, F., M. Chu, Z. Chang, Z. Gu, and X. Sun, *Sulfur release and transformation*  
375 *during the pyrolysis of lignite with different particle sizes*. Journal of Analytical  
376 and Applied Pyrolysis, 2021. **156**.<https://doi.org/10.1016/j.jaap.2021.105162>
- 377 [22] Shi, L., Q. Liu, X. Guo, W. Wu, and Z. Liu, *Pyrolysis behavior and bonding*  
378 *information of coal — A TGA study*. Fuel Processing Technology, 2013. **108**: p.  
379 125-132.<https://doi.org/10.1016/j.fuproc.2012.06.023>
- 380 [23] Feng, B., S.K. Bhatia, and J.C. Barry, *Variation of the Crystalline Structure of*  
381 *Coal Char during Gasification*. Energy & Fuels, 2003. **17**(3): p. 744-  
382 754.<https://doi.org/10.1021/ef0202541>
- 383 [24] Green, T.K., J. Kovac, and J.W. Larsen, *A rapid and convenient method for*  
384 *measuring the swelling of coals by solvents*. Fuel, 1984. **63**(7): p. 935-

- 385 938.[https://doi.org/10.1016/0016-2361\(84\)90313-2](https://doi.org/10.1016/0016-2361(84)90313-2)
- 386 [25] Schmiers, H., J. Friebel, P. Streubel, R. Hesse, and R. Köpsel, *Change of*  
387 *chemical bonding of nitrogen of polymeric N-heterocyclic compounds during*  
388 *pyrolysis*. Carbon, 1999. **37**(12): p. 1965-1978.[https://doi.org/10.1016/s0008-](https://doi.org/10.1016/s0008-6223(99)00071-8)  
389 [6223\(99\)00071-8](https://doi.org/10.1016/s0008-6223(99)00071-8)
- 390 [26] Kapteijn, F., J.A. Moulijn, S. Matzner, and H.P. Boehm, *The development of*  
391 *nitrogen functionality in model chars during gasification in CO<sub>2</sub> and O<sub>2</sub>*.  
392 Carbon, 1999. **37**(7): p. 1143-1150.[https://doi.org/10.1016/s0008-](https://doi.org/10.1016/s0008-6223(98)00312-1)  
393 [6223\(98\)00312-1](https://doi.org/10.1016/s0008-6223(98)00312-1)
- 394 [27] Grzybek, T., R. Pietrzak, and H. Wachowska, *X-ray photoelectron spectroscopy*  
395 *study of oxidized coals with different sulphur content*. Fuel Processing  
396 Technology, 2002. **77-78**: p. 1-7.[https://doi.org/10.1016/s0378-3820\(02\)00058-](https://doi.org/10.1016/s0378-3820(02)00058-9)  
397 [9](https://doi.org/10.1016/s0378-3820(02)00058-9)
- 398 [28] Chen, H., *Transformation of sulfur during pyrolysis and hydrolysis of coal*.  
399 Fuel, 1998. **77**(6): p. 487-493.[https://doi.org/10.1016/s0016-2361\(97\)00275-5](https://doi.org/10.1016/s0016-2361(97)00275-5)
- 400 [29] Janković, B. and V. Dodevski, *The combustion performances and thermo-*  
401 *oxidative degradation kinetics of plane tree seeds (PTS) (Platanus orientalis L.)*.  
402 Energy, 2018. **154**: p. 308-318.<https://doi.org/10.1016/j.energy.2018.04.149>
- 403 [30] Li, P.S., Q. Wang, Q. Xu, W. Yu, Y.N. Yue, et al., *Combustion reaction*  
404 *mechanism of four typical Chinese biomass by TG and DTG*. Asia-Pacific  
405 Journal of Chemical Engineering, 2012. **7**: p. S209-  
406 S215.<https://doi.org/10.1002/apj.616>
- 407 [31] Dong, P.-w., J.-r. Yue, S.-q. Gao, and G.-w. Xu, *Influence of thermal*  
408 *pretreatment on pyrolysis of lignite*. Journal of Fuel Chemistry and Technology,  
409 2012. **40**(8): p. 897-905.[https://doi.org/10.1016/s1872-5813\(12\)60033-4](https://doi.org/10.1016/s1872-5813(12)60033-4)
- 410 [32] Krzesińska, M., B. Pilawa, and S. Pusz, *The Physical Parameters of Different*  
411 *Rank Coals Related To Their Degree of Cross-Linking and the Caking Ability*.  
412 Energy & Fuels, 2006. **20**(3): p. 1103-1110.<https://doi.org/10.1021/ef050284e>
- 413 [33] Given, P.H., *The Distribution of Hydrogen in Coals and Its Relation To Coal*  
414 *Structure*. Fuel, 1960. **39**(2): p. 147-153
- 415 [34] Li, T., L. Zhang, L. Dong, and C.-Z. Li, *Effects of gasification atmosphere and*  
416 *temperature on char structural evolution during the gasification of Collie sub-*  
417 *bituminous coal*. Fuel, 2014. **117**: p. 1190-  
418 1195.<https://doi.org/10.1016/j.fuel.2013.08.040>
- 419 [35] Wang, S., L. Wu, X. Hu, L. Zhang, T. Li, et al., *Effects of the Particle Size and*  
420 *Gasification Atmosphere on the Changes in the Char Structure during the*  
421 *Gasification of Mallee Biomass*. Energy & Fuels, 2018. **32**(7): p. 7678-  
422 7684.<https://doi.org/10.1021/acs.energyfuels.8b01309>
- 423 [36] Liu, M., Q. He, J. Bai, J. Yu, L. Kong, et al., *Char reactivity and kinetics based*  
424 *on the dynamic char structure during gasification by CO<sub>2</sub>*. Fuel Processing  
425 Technology, 2021. **211**.<https://doi.org/10.1016/j.fuproc.2020.106583>
- 426 [37] Phiri, Z., R.C. Everson, H.W.J.P. Neomagus, and B.J. Wood, *Transformation of*

- 427 *nitrogen functional forms and the accompanying chemical-structural properties*  
428 *emanating from pyrolysis of bituminous coals.* Applied Energy, 2018. **216**: p.  
429 414-427. <https://doi.org/10.1016/j.apenergy.2018.02.107>
- 430 [38] Zhang, Y., J. Zhang, C. Sheng, J. Chen, Y. Liu, et al., *X-ray Photoelectron*  
431 *Spectroscopy (XPS) Investigation of Nitrogen Functionalities during Coal Char*  
432 *Combustion in O<sub>2</sub>/CO<sub>2</sub> and O<sub>2</sub>/Ar Atmospheres.* Energy & Fuels, 2011. **25**(1):  
433 p. 240-245. <https://doi.org/10.1021/ef101134a>
- 434 [39] Li, P.S., Y. Hu, W. Yu, Y.N. Yue, Q. Xu, et al., *Investigation of sulfur forms and*  
435 *transformation during the co-combustion of sewage sludge and coal using X-*  
436 *ray photoelectron spectroscopy.* J Hazard Mater, 2009. **167**(1-3): p. 1126-  
437 32. <https://doi.org/10.1016/j.jhazmat.2009.01.115>

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#### 440 Figure caption

441 Figure 1. Schematic diagram of a fixed-bed reactor

442 (1) Nitrogen (2) Mass flow controller (3) Coal container (4) Valve (5) Furnace temperature  
443 controller (6) Quartz basket (7) Electric furnace (8) Quartz tube (9) Tar trap (10) Gas bag

444

445 Figure 2. DTG curve and fitting curves of a char sample

446

447 Figure 3. Combustion reactivities of the chars derived from direct and step pyrolysis

448

449 Figure 4. Effect of the 1<sup>st</sup> stage temperature on char combustion reactivity

450

451 Figure 5. Char yield

452

453 Figure 6. Abundance of various bond structures in the chars from 1<sup>st</sup> stage of step  
454 pyrolysis

455

456 Figure 7. Swelling ratio of 1<sup>st</sup> stage char and its parent coal

457

458 Figure 8. Index of cross-linking reactions

459

460 Figure 9. Correlation between  $C_{link}$  of 1<sup>st</sup> stage char and char yield

461

462 Figure 10. Correlations of La and N with  $C_{link}$

463

464 Figure 11. Nitrogen and sulfur release ratio of two-stage pyrolysis char

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