Proceedings of the 2nd International Conference on Green Energy, Environment and Sustainable Development (GEESD2021), D. Dobrotă and C. Cheng (Eds.)

doi:10.3233/ATDE210320

Thermogravimetric Analysis and Kinetic Calculation on the Combustion Characteristics of Two Typical Shenhua Chars

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Abstract. Recently, a new ultra-low nitrogen combustion technology, pyrolysis and gasification coupling combustion, was proposed. The dependence on SCR or SNCR was reduced measurably with this technology. However, given the lower content of volatile matter in semi-chars, the burn-up ratio and combustion efficiency seemed to become lower. Thus, in this study, the combustion characteristics of the Shenhun and Carboniferous char were investigated under combustion conditions with the thermogravimetric method; meantime, kinetic calculation on the combustion characteristics were evaluated with Coats–Redfern method. Experiments indicated that Shenhun char showed good ignition and burnout characteristics when the pyrolysis temperature ranged from 973.15 K to1073.15 K; meanwhile, Carboniferous char showed good ignition and burnout characteristics when the pyrolysis temperature ranged from 873.15 K to 973.15 K. Besides, both the calculations and experiments indicated that Shenhun char showed better combustion characteristics than Carboniferous char.

Keywords. Thermogravimetric analysis, kinetic calculation, combustion characteristics, semi-chars

1. Introduction

With the increasingly serious environmental problems and deepening understanding of sustainable development, the domestic environmental regulatory policies have been developed rapidly in China [1]. In order to meet the increasingly stringent environmental requirements, high-efficient flue gas denitrification technologies (e.g., SNCR, SCR) have been widely used in recent years. However, with the NOx emission decreasing, the ammonia slip increased [2]. Various damages, including catalyst deactivation, fouling, corrosion, insufficient output at high load, could be caused [3-5]. The ammonia slip has become the urgent problem for coal-fired power plants. To reduce the dependence on SCR and SNCR, a new ultra-low nitrogen combustion

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technology, pyrolysis and gasification coupling combustion, was proposed [6-7]. In this technology, a certain percentage of pulverized coal was heated to the appropriate temperature in a precombustion chamber under considerably lower than the stoichiometric ratio. Consequently, a large amount of volatile matter, including the reductive components (e.g., CH_4, H_2, CO, etc.) and nitrogen-containing precursors (e. g., NH_3, HCN, etc.), was released under such a condition. Then, the high temperature semi-chars were carried to the primary combustion zone by pneumatic conveying after separated, and burned with air staging combustion [8-10]. Given the lower content of volatile matter in semi-chars, the burn-up ratio and combustion efficiency were likely to be affected. However, the combustion characteristics of semi-chars under ultro-low nitrogen combustion are still seldom reported in previous researches to date.

To better understand pyrolysis and gasification coupling combustion technology, the thermal characteristics of Shenhun and Carboniferous char under combustion conditions were evaluated by the non-isothermal thermogravimetric method (TGA) and kinetic calculation respectively in this work, providing a theory foundation for the application of the pyrolysis and gasification coupling combustion technology in the semi-char combustion field.

2. Experimental Bench

2.1. Experimental

With thermal analysis as a reference, the combustion characteristics of Shenhun and Carboniferous chars shown in table 1 were studied in air combustion atmosphere using a Netzsch STA449F5 analyser with Non-isothermal TG/DTG module in this work. To minimize mass transfer limitations and heat transfer effects, a small amount of sample (e.g., 5 mg) and a moderate heating rate (40 K/min) were used in the experiments. Table 2 provided the ultimate and proximate analysis of Shenhun and Carboniferous chars.

Table 1. Shenhun and Carboniferous char making conditions.

	Shenhun char					Carboniferous char						
	1	2	3	4	5	6	7	8	9	10	11	12
Particle size distribution (μm)	75-97	38-61	75-97	106-125	150-200	75-97	75-97	38-61	75-97	106-125	150-200	75-97
Char-making temperature (°C)	700	800	800	800	800	900	600	700	700	700	700	800

Table 2. The ultimate and proximate analysis of Shenhun and Carboniferous chars.

	Proximate analysis (wt.%)				Ultimate analysis (wt.%)				
	V_{ar}	A_{ar}	M_{ar}	FC_{ar}	C_{ar}	H_{ar}	O_{ar}	N_{ar}	S_{ar}
Shenhun char	6.36	29.31	0.91	65.35	62.29	1.54	5.35	0.94	0.57
Carboniferous char	7.29	39.49	0.71	55.44	51.85	1.73	5.47	1.11	0.35

2.2. Experimental Results

To date, a series of methods for determining the burnout temperature (T_b) and ignition temperature (T_i) have been reported in previous researches [11-16]. The method in reference to TG and DTG profiles is one of the most popular and reliable determination methods [11, 14, 16]. Thus, as shown in figure 1, the burnout and ignition temperatures could be defined as following [11, 14, 16]: firstly, a vertical line, through the DTG peak (point A), was made upwards to meet the TG curve (point B); secondly, through the point B, a tangent line to TG curve was made and met the extended TG initial level line (point C); thirdly, through the point C, the other vertical line was made downwards to meet the temperature coordinate axis (point D). Subsequently, the temperature of point D could be defined as the ignition temperature, and the burnout temperature could be defined as the corresponding temperature of point E, which was the boundary point between the maximum mass loss-rate peak and the decomposition peak of minerals. Thus, with reference to the aforementioned methods, the ignition temperatures and burnout temperatures of the pulverized semi-char samples listed in table 1 were determined in reference to the TG and DTG profiles shown in figures 2-5.

Figures 2-3 indicated the ignition temperatures of Shenhun char were lower than those of Carboniferous char at 1073.15 K, moreover, a significantly lower trend was observed at 973.15 K (referred to pyrolysis temperature, same to below) when the particle size ranged from 75 μm to 97 μm. The burnout temperatures of Shenhun char were dramatically lower than those of Carboniferous char at 1073.15 K, however, a briefly higher trend was observed at 973.15 K when the particle size ranged from 75 μm to 97 μm, as shown in figures 4-5.

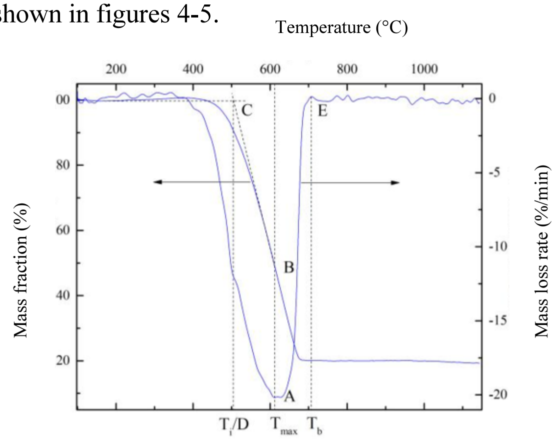

Figure 1. The combustion characteristic temperatures definition sketch.

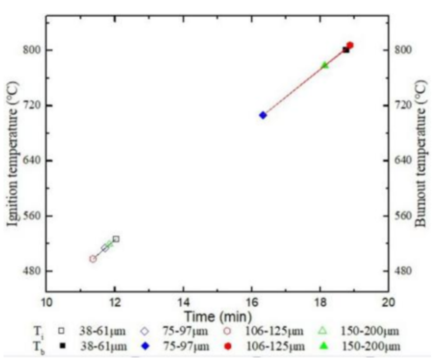

Figure 2. The burnout and ignition temperatures of Shenhun chars at 1073.15 K.

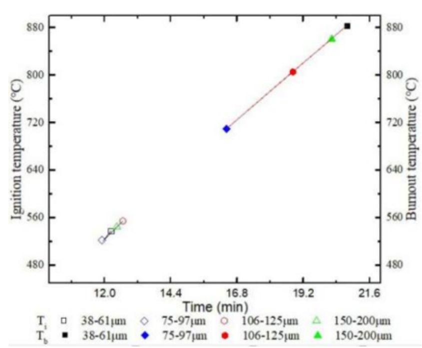

Figure 3. The ignition and burnout temperatures of Carboniferous chars at 973.15 K.

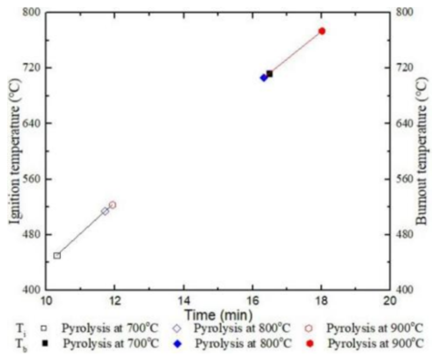

Figure 4. The ignition and burnout temperatures of Shenhun chars when the particle diameter ranged from 75μm to 97μm.

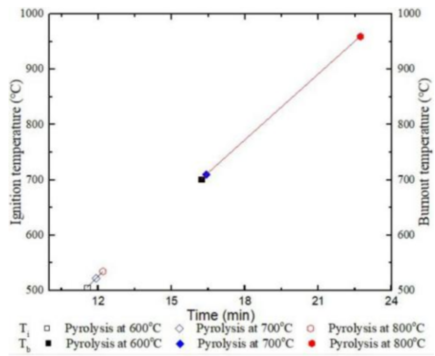

Figure 5. The ignition and burnout temperatures of Carboniferous chars when the particle diameter ranged from 75μm to 97μm.

3. Kinetic Calculation

3.1. Approach

The Arrhenius equation is one of the most common methods used to evaluate the kinetics during pyrolysis of coal, coke and semi-char [14-23]. Then, with Arrhenius equation as reference, the kinetic parameters of Shenhun and Carboniferous chars shown in table 1 were studied. The kinetic equation of heterogeneous solid-state thermal transformation studied by TG could be described with the following formula [14-23].

$$\frac{d\alpha}{dt} = f(\alpha)k(T) \tag{1}$$

where t is the time, min, T is the temperature, K, and α, the degree of combustion, %, can be determined as the following formula

$$\alpha = \frac{m_o - m}{m_o - m_f} \tag{2}$$

where m_o and m_f are the mass of the sample at the beginning and at the end of the mass loss reaction respectively, mg, and m is the mass of the sample at time t or temperature T, mg. f(α), the reaction model, is the functional relation between the rate and degree of combustion. k(T), the rate constant, can be formulated using Arrhenius equation:

$$k(T) = A\exp(-\frac{E}{RT}) \tag{3}$$

where A is the pre-exponential factor, min^{-1}, E is the activation energy, kJ/mol, and R is the ideal gas constant, J/(mol·K). As the heating rate is constant, the following equation can be obtained under such a condition:

$$\beta = \frac{\mathrm{d}T}{\mathrm{d}t} \tag{4}$$

where β is the heating rate, K/min. Submitting equations (3)-(4) to equation (1) and separating the variables, thus equation (1) can be integrated as

$$\frac{\mathrm{d}\alpha}{\mathrm{f}(\alpha)} = \frac{1}{\beta} A \exp(-\frac{E}{RT}) \mathrm{d}T \tag{5}$$

Due to the negligible reaction rate at the starting temperature, the starting temperature can be set as T = 0 K [20]. The variables can then be separated and equation (5) can be integrated as

$$\int_0^\alpha \frac{\mathrm{d}\alpha}{\mathrm{f}(\alpha)} = \frac{1}{\beta} A \int_0^T \exp(-\frac{E}{RT}) \mathrm{d}T \tag{6}$$

To date, a series of model-fitting methods for evaluating kinetic parameters have been reported in previous studies [20]. Compared to other model-fitting methods considering single thermoanalytical curve for investigating kinetic triplet (i. e., f(α), A and E), the Coats-Redfern method was more desirable [14]. Thus, with reference to Coats-Redfern method, the reaction mechanism function can be formulated as the following equation:

$$\mathrm{f}(\alpha) = (1-\alpha)^n \tag{7}$$

where n is the reaction order. However, it can be considered as a first order reaction for coal combustion reported in previous research results [19-20]. Thus, by submitting equation (7) into equation (6), there is

$$\int_0^\alpha \frac{\mathrm{d}\alpha}{(1\text{-}\alpha)} = \frac{1}{\beta} A \int_0^T \exp(-\frac{E}{RT}) \mathrm{d}T \tag{8}$$

Rearranging and integrating equation (8), there is

$$\ln\left[\frac{-\ln(1-\alpha)}{T^2}\right] = \ln\left[\frac{AR}{\beta E}(1-\frac{2RT}{E})\right] - \frac{E}{RT} \tag{9}$$

In reference to most values of E investigated previously, the $RT/E \ll 1$ in equation (9) and then the $(1\text{-}2RT/E) \approx 1$ under approximative assumptions [20]. Then, the integrated kinetic equation could be formulated as

$$\ln\left[\frac{-\ln(1-\alpha)}{T^2}\right] = \ln\frac{AR}{\beta E} - \frac{E}{RT} \tag{10}$$

Consequently, the plots of $\ln[-\ln(1\text{-}\alpha)/T^2]$ versus $1/T$ acquired from the experiments could be a line at certain temperatures, and E can be obtained from the slope (i.e., $-E/R$), whereas A can be acquired from the intercept [20].

3.2. Results and Discussion

Figures 6-9 provided the plots of ln[−ln(1−α)/T^2] versus 1/T of Shenhun and Carboniferous chars listed in table 1 when the pyrolysis temperature ranged from 973.15 K to 1173.15 K and from 873.15 K to 1073.15 K, respectively. As shown in figures 6-9, the combustion process can be described by three consecutive first order reactions corresponding to three consecutive temperature ranges, and the good correlation coefficients indicated that the calculations obtained by the corresponding first-order reaction models agreed well with the experiments. Consequently, the conversion α of each stage can be formulated separately. By applying Equation 10 to each of the aforementioned stages separately, the values of E and A under different stages can be obtained from the slope and intercept, respectively. Table 3 showed the kinetic parameters of the pulverized semi-char samples listed in table 1. E values of Shenhun char are dramatically lower than those of Carboniferous char when the particle size ranged from 75μm to 97μm at 973.15 K; meantime, A values of Shenhun char were dramatically higher than those of Carboniferous char when the particle size ranged from 75μm to 97μm at 973.15 K, as shown in table 3. With the activation increasing, the ignition temperature decreased; in the meantime, the combustion showed more vigorously with the pre-exponential factor increasing. Thus, it can be concluded that Shenhun char is more easily ignitable than Shenhun char with the aforementioned particle size distributions and at aforementioned pyrolysis temperatures, which is consistent with the experiments in this work well.

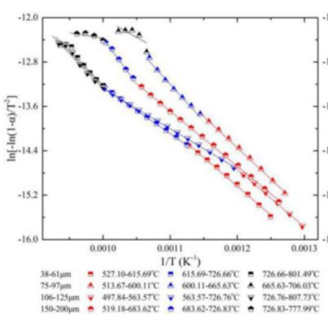

Figure 6. The plots of ln(-ln(1-α)/T^2) vs 1/T of Shenhun chars at 1073.15 K.

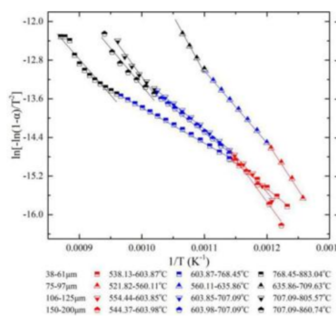

Figure 7. The plots of ln(-ln(1-α)/T^2) vs 1/T of Carboniferous chars at 973.15 K.

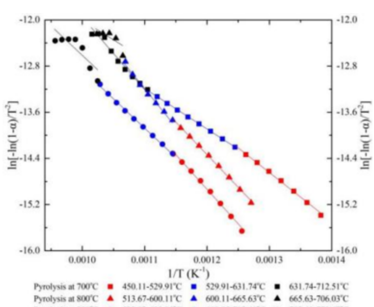

Figure 8. The plots of ln(-ln(1-α)/T^2) vs 1/T of Shenhun chars when the particle diameter ranged from 75μm to 97μm.

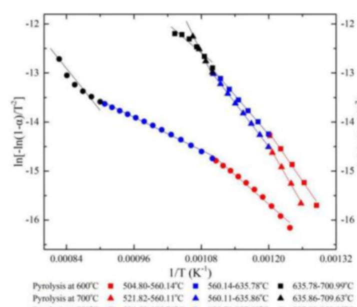

Figure 9. The plots of ln(-ln(1-α)/T^2) vs 1/T of Carboniferous chars when the particle diameter ranged from 75μm to 97μm.

Table 3. The kinetic parameters of Shenhun and Carboniferous chars.

Items	Temperature (°C)	Conversion range (%)	E (kJ·mol^{-1})	A (min^{-1})	R^2
	450.11-529.91	10.3017-35.3414	104.3460	9.1098×10^{5}	0.9788
No.1	529.91-631.74	35.3414-77.7387	58.2461	1.1629×10^{3}	0.9997
	631.74-712.51	77.7387-99.0515	70.7869	9.5202×10^{3}	0.9982
	527.10-615.69	10.3123-38.8249	86.1349	3.0851×10^{4}	0.9973
No.2	615.69-726.66	38.8249-83.5502	69.7362	2.6089×10^{3}	0.9997
	726.66-801.49	83.5502-98.5741	103.7733	2.3987×10^{5}	0.9489
	513.67-600.11	14.7618-56.0451	93.8351	2.0447×10^{5}	0.9986
No.3	600.11-665.63	56.0451-94.4380	110.6528	2.2646×10^{6}	0.9895
	665.63-706.03	94.4380-98.9760	55.8390	1.3474×10^{3}	0.6043
	497.84-563.57	8.1852-25.0142	86.3808	4.3435×10^{4}	0.9976
No.4	563.57-726.76	25.0142-82.7692	59.9471	6.7178×10^{2}	0.9996
	726.76-807.73	82.7692-98.8430	104.5229	2.5115×10^{5}	0.9652
	519.18-683.62	13.0054-84.8553	82.5880	2.5429×10^{4}	0.9994
No.5	683.62-726.83	84.8553-98.2914	134.8181	3.0349×10^{7}	0.9957
	726.83-777.99	98.2914-99.2850	15.6941	2.1337×10^{0}	0.5718
	523.02-600.05	9.5457-36.9364	99.6356	2.7541×10^{5}	0.9968
No.6	600.05-702.41	36.9364-86.7268	84.3955	3.4542×10^{4}	0.7176
	702.41-773.67	86.7268-99.0466	84.3718	2.6903×10^{4}	0.9982
	504.80-560.14	8.7729-36.2214	138.6503	2.2301×10^{8}	0.9960
No.7	560.14-635.78	36.2214-87.3228	110.5412	2.9069×10^{6}	0.9994
	635.78-700.99	87.3228-99.1681	81.8643	5.5716×10^{4}	0.9201
	538.13-603.87	8.4017-23.9875	88.1347	2.7668×10^{4}	0.9964
No.8	603.87-768.45	23.9875-77.3824	61.0068	4.6936×10^{2}	0.9987
	768.45-883.04	77.3824-99.7530	123.0347	1.0240×10^{6}	0.9524
	521.82-560.11	9.4971-29.1687	165.2329	9.3108×10^{9}	0.9972
No.9	560.11-635.86	29.1687-84.8406	124.0862	1.8014×10^{7}	0.9998
	635.86-709.63	84.8406-100	196.7242	4.0958×10^{11}	0.9712
	554.44-603.85	9.8861-27.9131	125.0958	7.5609×10^{6}	0.9928
No.10	603.85-707.09	27.9131-77.1765	87.9117	3.1731×10^{4}	0.9996
	707.09-805.57	77.1765-100	147.4782	7.0759×10^{7}	0.9267
	544.37-603.98	5.8349-26.3972	147.2077	1.7748×10^{8}	0.9900
No.11	603.98-707.09	26.3972-73.2483	84.8089	1.8954×10^{4}	0.9980
	707.09-860.74	73.2483-100	128.8702	5.5038×10^{6}	0.9426
	534.53-635.76	6.0783-27.8146	83.0257	9.9337×10^{3}	0.9900
No.12	635.76-837.88	27.8146-78.8284	46.7304	4.5391×10^{1}	0.9967
	837.88-959.32	78.8284-99.9933	118.3249	2.1896×10^{5}	0.8383

4. Conclusions

In this study, the ignition and burnout characteristics of Shenhun and Carboniferous char under combustion conditions were evaluated with the non-isothermal thermogravimetric method and kinetic calculation respectively. Furthermore, kinetic calculation on the combustion characteristics were evaluated with Coats–Redfern method. Experiments indicated that Shenhun char showed good ignition and burnout characteristics when pyrolysis temperature ranged from 973.15 K to1073.15 K; however, Carboniferous char presented good ignition and burnout characteristics when pyrolysis temperature ranged from 873.15 K to 973.15 K. Both the calculations and experiments indicated that Shenhun char showed better combustion characteristics than Carboniferous char. In addition, the burnout characteristics became worse with the increase of particle size. Thus, to provide a theory foundation for the application of the pyrolysis and gasification coupling combustion technology in the semi-char combustion field, the particle size below 125 μm and pyrolysis temperature ranged from 873.15 K to1073.15 K were recommended.

Acknowledgements

The financial support provided by the National Key R&D Program of China (No. 2018YFB0604203) is gratefully acknowledged.

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