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Characteristics of volatile release rate and fuel nitrogen conversion for three typical coals under high temperature fast pyrolysis

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Abstract. Drop Tube Furnace experiments were carried out to investigate the fast pyrolysis characteristics of three typical coals. The process of fast pyrolysis was simulated by a one-step pyrolysis model as well as a Chemical Percolation Devolatilization (CPD) model. The results indicate that coal rank, reaction temperature and residence time have complex influences on volatile release and nitrogen conversion. Both activation energy and frequency factor, which decrease with increasing coal rank, show obvious differences for the three considered coals. The volatile release coefficient Q_R is relative to coal rank and heating rate which fluctuates from 1.02 to 1.72. Predictions of volatile release and coal nitrogen conversion obtained from CPD model agree well with experiments. In addition, the one-step pyrolysis model could predict the volatile release of low-rank coal, whose precision is related to coal rank.

1. Introduction

As one of the primary processes in coal combustion, coal pyrolysis has a considerable influence on the ignition behavior [1], pollutant emissions [2] and the flame stability [3]. With the increasing of environment regulations on industrial, the focus of coal research has shifted to control pollutant such as nitrogen oxides (NO_x).

Fletcher et al. [4] presented a coal nitrogen distribution model which revealed that the coal nitrogen is being released in two stages during coal combustion. During the first stage ($T < 1050\text{K}$), nitrogen releases with tar and light gas called tar nitrogen (N_T). During the second stage ($T > 1050\text{K}$), additional nitrogen is released as HCN and NH₃ which is known as volatile nitrogen (N_V), residues in the char is char nitrogen (N_C). Staged combustion technology has achieved moderate success in reducing the amount of volatile nitrogen which is converted to NO_x. As a result, char nitrogen become the dominant factor of controlling the amount of NO_x emission.

In the last decade, some network devolatilization models based on the coal chemical structure have been developed, such as the one-step model [5], two-step model [6] and Chemical percolation devolatilization (CPD) model [4]. The one-step model has been widely use in experimental investigation and engineering applications due to its simplified formulation, CPD model represents the coal as a two-dimensional Bethe lattice of aromatic clusters linked by aliphatic bridges via the NMR spectroscopy technology. CPD model is widely used in CFD technology for improving predicted accuracy of pollutant emissions during coal combustion. Many researchers have conducted both experimental and numerical studies to better understand the characteristics of coal devolatilization



during fast pyrolysis [7-10]. They revealed that devolatilization is affected by many factors with complex interactions. On the other hand, useful studies dealing with different coal types have been performed on the coal nitrogen conversion and NO_x emissions [11-14], particularly for high volatile coals [15, 16]. However, little work has been done on the low volatile coal behavior under pyrolysis, and the comparison of pyrolysis characteristics for different coal rank has not been done. To authors' best knowledge, the investigation on comparison between fast pyrolysis experiments and CPD model prediction has not been addressed in literature.

The main purpose of this study is to provide fast pyrolysis characteristics of three typical Chinese coals in a Drop Tube Furnace (DTF), in terms of the influence of coal rank, residence time, reaction temperature on the volatile yields and conversion of coal nitrogen to char nitrogen. A ratio coefficient Q_D is established to improve predicting accuracy and to expand engineering applications range. The kinetics parameters are measured under fast pyrolysis conditions. The experimental results are compared with numerical simulations by using one-step equation and CPD models to discuss the model predicting accuracy.

2. Materials and methods

2.1. Coal samples preparations

The coal samples used in this study were three typical Chinese coals: XY meager-lean coal, QTH bituminous coal and ZD sub-bituminous coal. The raw coals were crushed and then sieved to obtain average 75 μm coal particles. The ultimate and proximate analyses of the three coal samples are presented in Table 1.

Table 1. Ultimate analysis and proximate analysis of raw coal samples.

sample	Ultimate Analysis (dry and ash free, %)					Proximate analysis (as received, %)			
	C	H	O	N	S	moisture	volatile	fixed carbon	ash
XY coal	90.09	4.32	1.69	0.92	2.14	1.33	10.11	61.83	26.74
QTH coal	92.81	5.95	0.56	0.80	0.18	2.15	23.19	45.39	29.27
ZD coal	79.45	4.28	0.51	0.56	0.67	6.94	25.90	62.51	4.65

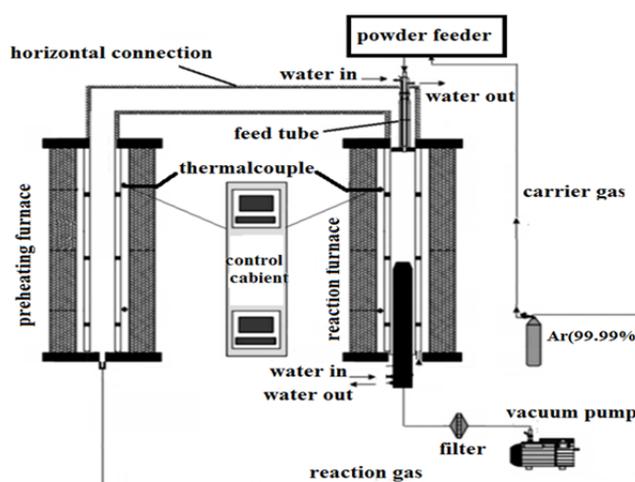


Figure 1. Schematic diagram of the DTF system.

2.2. Drop Tube Furnace experiments

The high-temperature devolatilization reactions were performed in a DTF, whose scheme is shown in Figure 1.

The DTF is an alumina tube having an internal diameter of 40 mm heated by six MoSi₂ heating elements wrapped around the tube. Before the experiments, the DTF was heated electrically to the reaction temperature. A uniform feed rate of 0.3 g/min was achieved by use of a mechanical vibrator and by partial fluidization of the coal particles in the feeder. The narrow stream emerging from the feeder was rapidly heated by the surrounding preheated argon stream and by radiation from the walls. Before being introduced into the reaction zone, the reaction gas flow was preheated to reaction temperature through preheating furnace, which has the similar construction and heating power as the reaction furnace. The particle stream was withdrawn at various distances from the feeder through a water cooled stainless steel filter in which the char residue was collected.

Table 2. Experimental conditions and parameters.

	unit	parameters
Sample		XY, QTH, ZD
Residence time	ms	20,30,40,50,60,70,80
Reaction temperature	K	1223,1373,1523
Heating rate	K/s	10 ⁴
Coal feed rate	g/min	0.3
Carrier gas(N ₂)	L/min	1.58,1.42,1.28
Reaction gas(N ₂)	L/min	7.50,7.17,6.33

For this pyrolysis experimental study, the reaction gas consisted of Ar with high purity(99.999%), and the reaction temperatures were set to 1223, 1373 and 1523 K. The temperature field of the DTF was measured by a B-type thermocouple, and a 700 mm long constant temperature zone was maintained, as shown in Figure 1. Therefore, assuming the difference in relative velocities between the gas and char particles is zero, the residence time can be controlled from 0.02 to 0.08 s with an interval of 0.01s. The main parameters are listed in Table 2. For this study, the residence time is defined as follows:

$$t = \frac{2L}{\frac{Q_1}{A_1} + \frac{Q_2}{A_2}} \quad (1)$$

where L is the heating length, Q_1 and Q_2 are the flux of carrier gas and reaction gas, A_1 and A_2 are the flow area of carrier gas and reaction gas.

3. Numerical model

3.1. Basic assumptions.

Because of highly heating rate and low sample particles loading, the reactions in DTF were approximately considered as isothermal. So the particle temperature T_p supposed to be as constant and equal to the reaction temperature.

3.2. Devolatilization model

In this paper, the volatile yields of coal V during pyrolysis reaction were obtained with ash tracer method, expressed as:

$$V = [1 - (\frac{A_0}{100 - A_0} \times \frac{100 - A_1}{A_1})] \times 100 \quad (2)$$

where A_0 and A_1 are the fractions of ash under dry basis of raw coal and residual char respectively. The fraction of coal nitrogen converted to char nitrogen N_{char} can be modeled by

$$N_{char} = \frac{[A_0 + \frac{(100 - A_0) \times (100 - V)}{100}] \times N_1}{N_0} \times 100 \quad (3)$$

where N_0 and N_1 presented the fractions of nitrogen under dry basis of raw coal and residual char respectively.

From mass balance we have the fraction of volatile nitrogen in coal N_{vol} :

$$N_{vol} = 100 - N_{char} \tag{4}$$

3.3. One-step model

In the DTF experimental study secondary reactions of pyrolysis product will not be considered as well as the mass transfer and heat transfer during mass diffusion. The variation of volatiles with time during fast pyrolysis is given as one-step model:

$$\frac{dV}{dt} = K(V_m - V) \tag{5}$$

where K is the reaction rate constant, V_m is the maximal volatile yields during reaction, usually reaction rate constant and reaction temperature T_p can be expressed in Arrhenius form:

$$K = A_r \exp\left(-\frac{E_r}{RT_p}\right) \tag{6}$$

where A_r is the frequency factor and E_r is the activation energy for pyrolysis, R is the universal gas constant equal to 8.314, and T_p is the particle temperature (equal to the reaction temperature as mentioned before). Substituting K from Eq. (6) into Eq. (5) and taking the logarithm, we have the correlation of $\ln(A_r)$ and $1/T_p$, from which A_r and E_r can be determined using the least square method.

4. Results and discussions

4.1. Volatile release rate V

Figure 2 presents the variations of volatile release rate V with respect to the residence time t for three different coals and different pyrolysis temperatures.

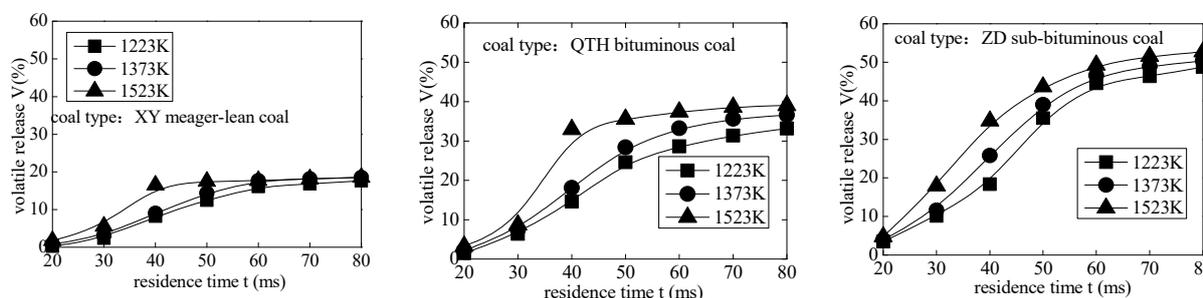


Figure 2. Variation of volatile release rate with residence time for different coals.

Comparison of the three coals, it is observed that V highly increases with the increase of t for each coal whatever the temperature and quickly reaches an almost steady-state regime. V highly increases with residence time until 60 ms while it slowly increases for residence time higher than 60ms. It is also noticed that for the three coals, volatile yields increase with the increase of reaction temperature T when both coal rank and residence time are constant. Slight declines of V can be seen when T varies from 1223K to 1373K while the relatively slow decline of V is corresponding to the heating temperature as 1523K. It indicates that the coal devolatilization is considered as thermal decomposition of plenty functional groups which require different energies, as a result, the quantity of pyrolysis yields increases with the increases of T .

Comparisons between the three cases show that V is the lowest for XY meager-lean coal and the highest for ZD sub-bituminous coal. ZD coal prefers to decompose as gaseous under fast heated condition owing to the worst stability of function group. In addition, the activation energy of ZD coal for pyrolysis maybe the lowest among the three coals. Notably, for all three coals, the volatile yields by using proximate analysis V_{daf} (dry and ash free) are less than the experimental results by using DTF. Surprisingly, there is a similar variation trend of volatile yields between proximate analysis and

experimental results ($V_{ZD,daf} > V_{QTH,daf} > V_{XY,daf}$), that is to say, the proximate analysis can be used to qualitatively distinguish volatile yield of different rank coal for some engineering applications.

Furthermore, there is obvious difference of volatile release rate (dV/dt) of the three coals for a constant temperature T . dV/dt for ZD sub-bituminous coal is almost the highest and XY meager-lean coal has the lowest dV/dt under the same conditions. Comparing the influence of temperature and coal rank, the latter has a stronger influence on coal devolatilization illustrating the volatile yields are complexly affected by coal rank, reaction temperature and residence time.

4.2. Determination of ratio coefficient Q_R

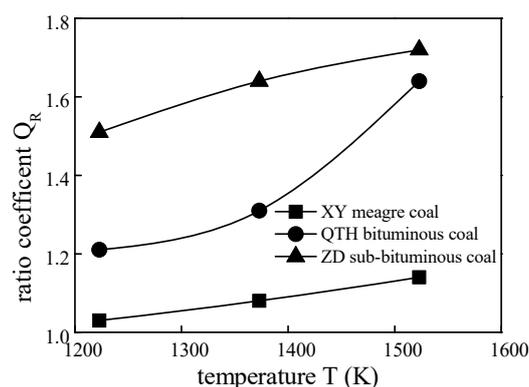


Figure 3. Ratio coefficient Q_R for different coals.

As mentioned above, the one-step and CPD models have been widely used in engineering and numerical simulations to explore the characteristics of pyrolysis. However, the one-step model is based on empirical results, leading to critical that calculation precision limited to the experimental conditions [17,18]. On the contrary, CPD model is not limited to coal rank and can be used with better generality. As unexpected, this model needs many input parameters and longly time of calculation. Besides, both models regard proximate analysis results as input parameters, and give as result, the predicting precision of models which is affected by reaction condition as lower heating rate and longer heating period than that in pulverized coal. Vascellari et al. [17] have built a coefficient Q_R to modify the initial input parameters of FLUENT software, which determine the ratio of numerical results from models (as CPD, FG-DVC, FLASHCHAIN) to proximate analysis results. As expected, the numerical results are in good agreement with experimental results. Similarly, a new coefficient Q_R is proposed to improve the predicted precision of pyrolysis model and to expand the application range. The details of Q_R varying with coal rank and temperature is presented in Figure 3 and the expression is shown as follow:

$$Q_R = V_{cjl} / V_{daf} \quad (7)$$

where V_{cjl} and V_{daf} present the volatile yields of DTF experiments and proximate analysis respectively.

From this figure, it can be found that V_{cjl} is higher than V_{daf} for all cases and Q_R varies from 1.02 to 1.72. It can be interpreted as follows: coal particle is polydisperse suspended and exposed in DTF furnace which can absorb a great amount of radiant heat. Conversely, coal particles obscured each other under fixed stacking state of the proximate analysis based on Chinese standard for coal analysis (GB/T212-2008) which results in obvious difference between V_{cjl} and V_{daf} .

4.3. Conversion of coal nitrogen

Figure 4 presents the variation of volatile nitrogen N_{vol} with residence time t for different reaction temperature T and the three coals used in this paper. Similarly, the variation of char nitrogen N_{char} with residence time t for different reaction temperature T is shown in Figure 5.

Generally, volatile nitrogen Nvol increases with the increase of residence time. It maybe the consequence of the increasing residence time t which leads to the increment of temperature and enhancing the functional group decomposition forced caused by the temperature difference. It is noticed that the notable variation can be seen when t varies from 0 to 60ms, while the relatively stable variation is corresponding to the residence time i.e., from 60ms to 80ms.

Comparing the three coals, volatile nitrogen Nvol increases with the increase of temperature T , while char nitrogen Nchar presents an opposite variation. Furthermore, there are notable differences in the variation gradient of three coals, the curves of XY meager-lean coal have the smallest gradients while the curves of ZD bituminous coal have the largest gradients. It reveals that char nitrogen can mainly be regarded as heterocyclic nitrogen with high stability, which release characteristics are affected by both temperature and coal rank.

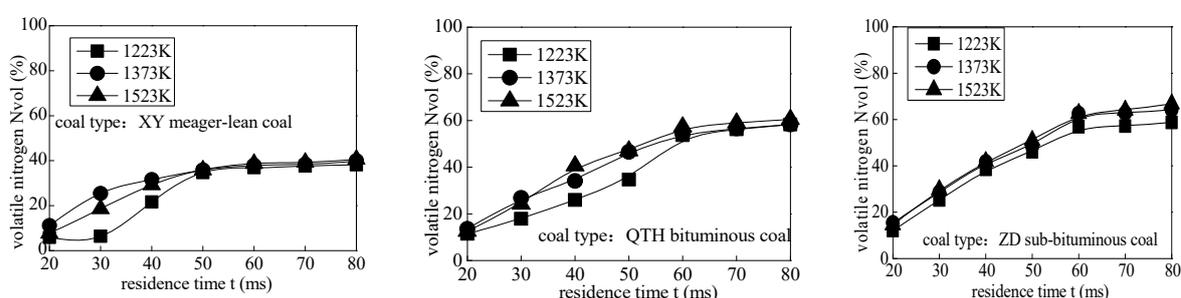


Figure 4. Variation of volatile nitrogen Nvol with residence time for different coals.

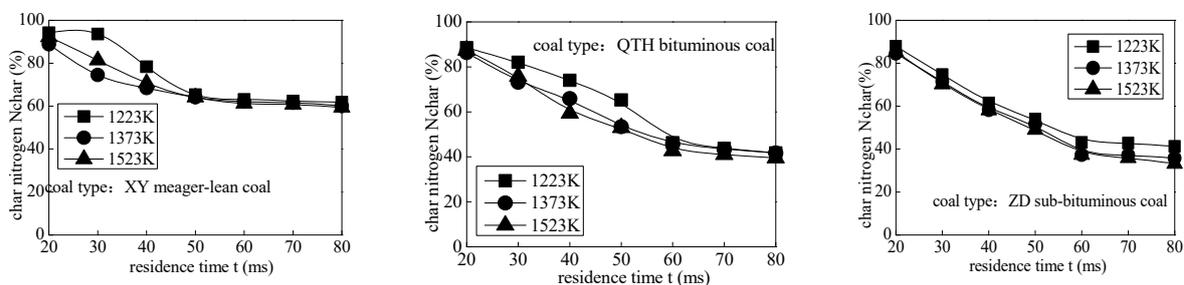


Figure 5. Variation of char nitrogen Nchar with residence time for different coals.

4.4. Variation of activation energy and frequency factor

Table 3 presents the reaction rate coefficient B calculated by Eq.6, which concerns with residence time t , temperature T , and coals rank.

In order to obtain the average activation energy E_r and frequency factor A_r for different coals, Figure 6 shows the relationship between reaction temperature and the intrinsic reaction rate measured by DTF. As expected, there is an excellent linear correlation between $\ln B$ and $1/T_p$. Besides, the correlation increases with the increase of volatile yields of coal. The predicting accuracy of one-step model is limited to experimental conditions. Surprisingly, the results are precise for the coal devolatilization process combined fast pyrolysis condition of DTF system with one-step model, especially for high volatile coal rank. Table 4 presents the calculated data of activation energy E_r , frequency factor A_r and kinetic equation of fast pyrolysis based on the correlation of $\ln B$ and $1/T_p$. Comparisons among the three coals show that E_r is the highest for XY meager-lean and is the lowest for ZD sub-bituminous coal which is reasonable. Because the portion unsteady construction of crow coal molecules increases with the increase of volatile yields, less energy is needed for process of devolatilization. Furthermore,

frequency factor A_r decreases with activation energy E_r as a consequence of a function of a compensation effect.

Table 3. Results of reaction rate coefficient B.

sample	Temperature $T(K)$	LnB1	LnB2	LnB3	LnB4	LnB5	LnB6	LnB7	LnB
XY coal	1223	0.37	1.53	2.71	3.13	3.56	3.6	3.56	2.64
	1373	0.81	1.79	2.81	3.38	3.89	3.94	4.04	2.95
	1523	1.59	2.46	3.96	3.97	4.02	4.11	4.22	3.48
QTH coal	1223	0.73	1.84	2.51	3.07	3.19	3.27	3.31	2.56
	1373	1.08	1.97	2.76	3.29	3.50	3.62	3.64	2.84
	1523	1.47	2.11	3.80	3.82	3.70	3.98	4.00	3.27
ZD coal	1223	0.90	1.61	2.26	3.11	3.59	3.42	3.47	2.62
	1373	1.36	2.11	2.82	3.29	3.57	3.61	3.63	2.91
	1523	1.52	2.59	3.24	3.48	4.06	3.69	3.73	3.19

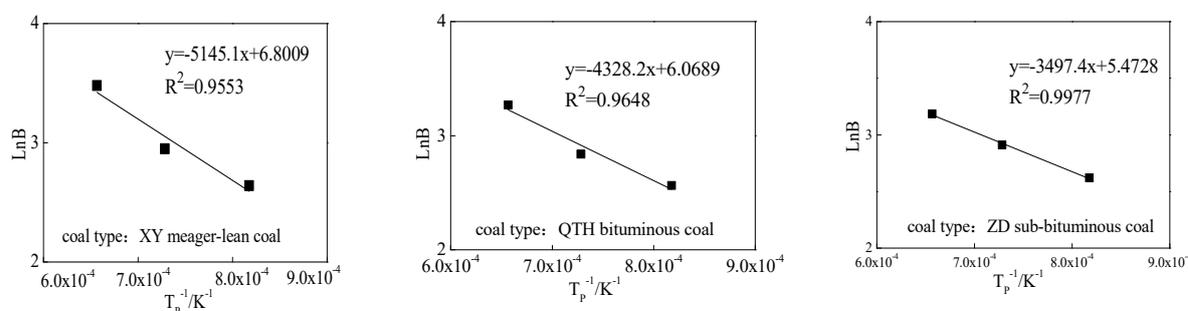


Figure 6. Arrhenius plots of different coals.

Table 4. Parameters and equations of devolatilization.

sample	activation energy E_r (J/mol)	frequency factor A_r (1/S)	correlation coefficient R^2	devolatilization equation
XY coal	42776.36	898.66	0.9553	$dV/dt = 898.66 \exp(5145.10/T_p)(V_m - V)$
QTH coal	35984.65	432.20	0.9648	$dV/dt = 432.2 \exp(4328.20/T_p)(V_m - V)$
ZD coal	29077.38	238.13	0.9977	$dV/dt = 238.13 \exp(3497.40/T_p)(V_m - V)$

5. Comparison of experimental results and devolatilization model prediction

In CPD model, coal is considered as a macromolecular array whose building blocks are clusters of fused aromatic rings of various sizes and types, including heteroaromatic systems with both nitrogen and oxygen atoms. These aromatic clusters are interconnected by a variety of chemical bridges, some of which are labile bonds that break readily during coal pyrolysis, while others are stable at a given temperature [19]. Four parameters derived from ^{13}C NMR experiments that describe the structure of the parent coal are used directly as input parameters to the CPD model [20,21], as shown in Table 5. This includes M_{cl} (the average molecular weight per aromatic cluster), M_{δ} (the average side-chain molecular weight), $\sigma + 1$ (the average number of attachments per cluster), and P_0 (the fraction of intact bridges). Dominic [22] has proposed an advanced model based on the five parameters mentioned above which received from large amount of experiments by using ^{13}C NMR technology, which can predict

volatile yields and char nitrogen conversion by means of Monte Carlo method. Table 5 presents the input parameters for CPD model as well as the structure parameters of coal used in this study are shown in Table 6.

Table 5. Structural parameters of coals used in correlation.

sample	M_δ	$\sigma+I$	P_0	C_0	Mcl
XY meagre coal	13	4.48	0.778	0.360	252
QTH bituminous coal	22	3.48	0.529	0.36	340
ZD sub-bituminous coal	32	5.26	0.683	0.034	300

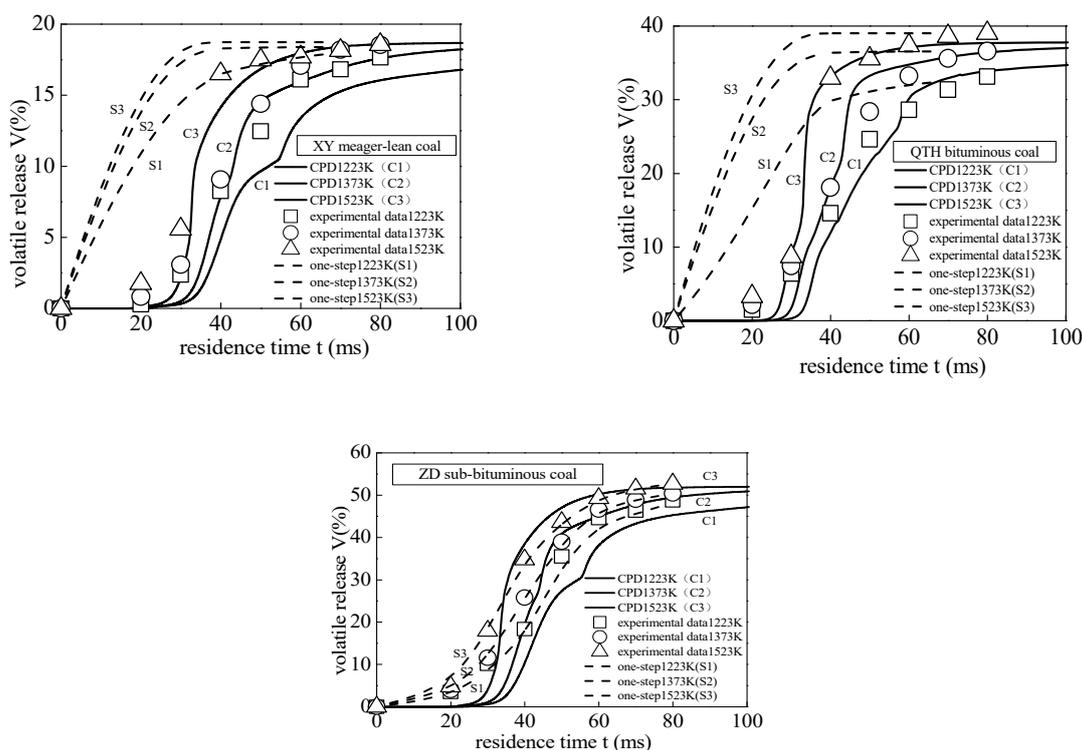


Figure 7. Experimental and numerical results of volatile yields by using different models.

Table 6. Input parameters for CPD model.

Parameters	unit	data	description
E_b	Cal/mol	55400	activation energy for bridge scission
A_b	1/s	2.6×10^{15}	frequency factor
σ_b	Cal/mol	1800	standard deviation from E_b
E_g	Cal/mol	69000	activation energy for gas releasing
A_g	1/s	3.0×10^{15}	frequency factor
σ_g	Cal/mol	8100	standard deviation from E_g
ρ	/	0.9	composite rate constant

Figure 7 shows volatile yields along the DTF obtained by one-step modeling, CPD modeling and experimental measurements during coal devolatilization under high-temperature entrained flow

conditions. In addition, nitrogen conversion received by CPD modeling and experimental results are presented in Figure 8.

5.1. Volatile yields

Figure 7 presents the variation of volatile release with residence time t under different by using CPD model and one-step model.

Comparing the prediction precision of CPD and one-step model, numerical results of CPD model are in better agreement with the experiment results, especially for XY meager-lean and QTH bituminous coals. However, errors exist at the beginning of the devolatilization process which may be due to multiple reactions of different function groups considered in CPD model, and the heating rate of CPD model is higher than experimental condition, leading to lower volatile yields predicted by CPD model than experiment results. As expected, the particle temperature increases with the increment of residence time t , while the influence of heating rate on volatile yields decrease with increasing reaction time. It is remarkable that comparing with CPD model, one-step model has a better prediction for ZD sub-bituminous coal but not for the other two coals, which indicates that the kinetic parameters come from one-step model are appropriate for low rank coal similarly with ZD sub-bituminous coal.

5.2. Nitrogen conversion

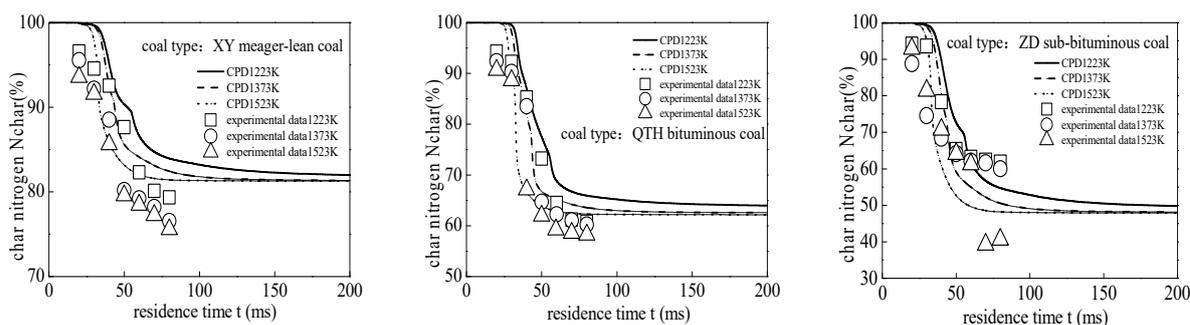


Figure 8. Experimental and CPD modelling results of volatile yields.

Figure 8 presents the char nitrogen conversion along DTF obtained by experimental measurements and CPD model results. As unexpected, the prediction of char nitrogen conversion by the one-step model cannot be obtained due to the limitation of calculation method. Generally, it is seen that volatile yields have a strong effect on char nitrogen matter, and N_{char} decreases significantly with the increase of volatile yields. Comparisons among the three coals show that N_{char} is the lowest for ZD sub-bituminous coal and is the lowest for XY meager-lean coal, indicating CPD model has an appropriate prediction for char nitrogen conversion of coal of high temperature fast pyrolysis.

6. Conclusions

The characteristics of fast high temperature pyrolysis of three Chinese typical coals in DTF were explored under different temperatures. The volatile release and coal nitrogen conversion were predicted by numerical modeling. The main findings are as follows:

(1) Both volatile release and char nitrogen conversion were affected by coal rank, reaction temperature, and residence time. For the given T and t , volatile nitrogen conversion N_v and V decrease with the increase of coal rank. For all coal rank in the experiment, N_v and V have obviously increments with the increasing of t , while N_c decreases with the increments of residence time. For a given t , V and N_v increase with the increasing of T . Oppositely, N_c obviously declines with increasing reaction temperature.

(2) The volatile yields obtained from DTF experiments are superior to that from proximate analysis under the same condition. The prediction precision of proximate analysis for high temperature pyrolysis can be improved by using ratio coefficient Q_R . In addition, Q_R varies significantly among different coals.

(3) The activation energy and frequency factor were affected by coal rank several. E_r and A_r increase with the increasing coal rank for a given condition.

(4) One-step model is usually used in predicting volatile yields of low rank coal with high volatile matters, whose precision is significantly related to the coal rank. Comparing with the one-step model, the CPD model is widely used and has better prediction accuracy for fast pyrolysis of different coal rank.

Acknowledgement

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