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Tar distribution prediction for rapid pyrolysis based on modified CPD Model under upgrading of coal with low-carbon emissions

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ABSTRACT

Rapid pyrolysis of pulverized coal is an essential procedure of the coal upgrading process, but still faced with the problem of high content of heavy components in the tar. The CPD model is a kinetic model that can effectively predict the distribution of coal pyrolysis gas-liquid-solid products, but incapable of achieving a detailed description of the specific composition of the tar. Therefore, based on the fundamental assumptions of the molecular structure of coal in original CPD model, a more detailed tar cutting method is carried out. For the tar component only contains one aromatic unit, the aromatic core is divided as 2 types and the yield of tar with less molecular weight can be calculated. By adopting the modifications above, a more accurate prediction of the tar product distribution can be achieved. This study can provide theoretical guidance for the intensification of the pyrolysis process.

Keywords: CPD model, coal structure, distillation cutting

NONMENCLATURE

Abbreviations	
CPD	Chemical Percolation Devolatilization
AI	Analyze Indicators
FT	Final Temperature
P	Pressure
LO	Light Oil
PO	Phenolic Oil
NO	Naphthalene Oil
WO	Washed Oil
AO	Anthracene Oil

1. INTRODUCTION

Coal pyrolysis is an efficient and clean technology that can realize low-rank coal's grading conversion. The simulation of its product distribution can save a lot of investment costs. Among various kinetic models describing fast coal pyrolysis, the CPD model can provide better theoretical guidance for predicting pyrolysis product distribution owing to its simple molecular structure assumptions, intuitive and clear reaction path construction, and wide applicability. CPD model is a typical lattice model. It starts from the structure of coal molecular network, considers the specific reaction process during the coal pyrolysis, quantitatively reveals the relationship between coal structure and reaction, and predicts the yield variation of three phases products for different coal types under various operating conditions (final temperature, heating rate, pressure, etc.)[1] The CPD model specifically simplifies the complex coal molecular structure to a Bethe lattice structure, i.e., a reticulation of aromatic core units connected by aliphatic bridge bonds in a certain ratio. Among the final products of pyrolysis, light gas molecules are formed by the conversion of broken side chains; tar molecules consist of fragments containing at least one aromatic core; and coke corresponds to the residual reticular structure after the small molecules fall off[2]. However, in the traditional CPD model, the division of the structure is too coarse and averaging, and the number of carbon atoms contained in one aromatic core is relatively large, which makes the calculation results of final tar product distribution of little application value.

Therefore, this paper further classifies the aromatic core units based on the CPD model's basic structural assumptions. The tar molecules containing an aromatic core, i.e., the typical key light components, could be cut in more detail to improve the predictive capacity of the CPD model.

2. MATERIAL AND MODEL

2.1 Acquisition and Regression of coal structural parameters

2.1.1 *Acquisition of coal structural parameters*

The acquisition of key structural parameters in the CPD model is based on ^{13}C solid-state NMR. The skeletal carbon information of the coal material is obtained by the combination of three sets of NMR experiments[3].

Figure 1 lists the classification of different types of carbon.

In fact, in the specific kinetic calculation, five structural parameters are involved, namely, the average coordination number $\sigma+1$, the average cluster molecular weight $M_{cluster}$, the average side chain mass m_{del}, the initial ratio of connecting bridge bonds p_0 and the initial ratio of stable char bridge bonds c_0. Only the first four can be derived from the NMR data (the

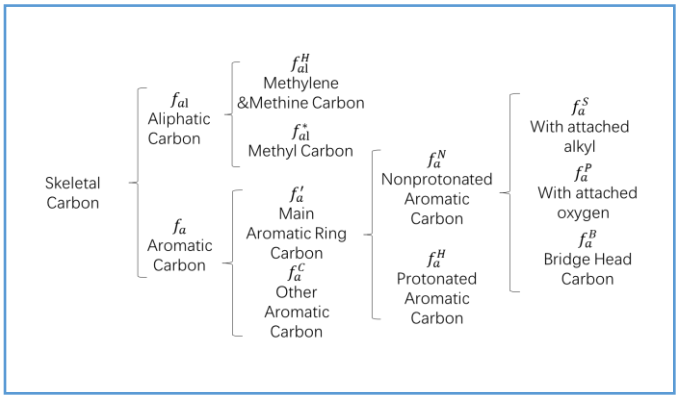

Fig. 1 Classification of skeletal carbon in coal

calculation formula is shown below). The ratio of stable bridge bonds is generally estimated with the elemental analysis data by empirical formula.

$$\sigma+1=\frac{(f_a^S+f_a^P)C}{f_a'} \quad (2.1)$$

$$p=\frac{f_a^S+f_a^P-f_a^*}{f_a^S+f_a^P} \quad (2.2)$$

$$M_{cluster}=\frac{12C}{f_a'Carbon\%} \quad (2.3)$$

$$m_{del}=\frac{M_{cluster}-13C\frac{f_a^H}{f_a'}-12C\frac{f_a^N}{f_a'}}{\sigma+1} \quad (2.4)$$

where C is the number of carbon atoms contained in the aromatic core unit, which is deducted inversely by the ratio of the bridgehead aromatic carbon. Polycyclic aromatic hydrocarbons can be divided into two types: linear type and circular type. For linear aromatic ring compounds, the bridgehead aromatic carbon ratio is:

$$\chi_b'=\frac{1}{2}-\frac{3}{C} \quad (2.5)$$

For linear aromatic ring compounds, the bridgehead aromatic carbon ratio is:

$$\chi_b''=1-\frac{\sqrt{6}}{\sqrt{C}} \quad (2.6)$$

The bridgehead aromatic carbon ratio of the overall aromatic core units is given by the following fitting equation[4]:

$$\chi_b=\frac{1}{2}\{[1-\tanh(\frac{C-C_0}{m})]\chi_b'+[1+\tanh(\frac{C-C_0}{m})]\chi_b''\} \quad (2.7)$$

The constants in Eq.(2.7) are $C_0=19.57, m=4.15$.

2.1.2 *Regression of structural parameters*

Based on the NMR data of 30 different types of coal samples and their approximate and industrial analysis data, the CPD model fitted a series of linear regression equations[5]. Although the fitting accuracy is relatively low, the equations can provide a preliminary estimation of the structural parameters of coal molecules in the absence of NMR data. Considering the limitations and difficulties in the implementation of the solid-state NMR technique, the CPD model also established correlation equations between the above four structural parameters and the approximate and industrial analysis data.

2.2 Assumptions on the products molecular structure

The CPD model allows the calculation of molecular weights and ratios of light gas, tar, and coke at each time point. The molecular weight of the light gas is always constant as the molecular weight of the side chain m_{del}; the molecular weight of the tar is calculated by the following equation[6].

$$m_{tar,n}(t)=nm_a+2(n-1)m_{del}\frac{1}{p}+\frac{\tau m_{del}\delta}{2(1-p)} \quad (2.8)$$

Where n is the number of aromatic core units contained in the tar molecule, and m_a is the molecular weight of the aromatic core units.

In fact, the molecular weight of tar with the number of aromatic core units equal to or greater than 2 is already quite large and can be considered as asphaltene in tar. Therefore, the component only containing 1 aromatic core unit is the lighter proportion of tar with higher added value. However, the original CPD model can no longer cut this part. Therefore, a new hypothesis will be proposed in the following to further classify the tar fraction containing 1 aromatic core unit.

2.3 Modified CPD model for tar fraction cutting

2.3.1 Aromatic unit division

Firstly, based on the known approximate and industrial analysis data of coal samples, combined with the existing linear regression equations, 4 key structural parameters can be estimated. From the average cluster molecular weight $M_{cluster}$, the average side chain mass m_{del} and the average coordination number $\sigma+1$, the average aromatic core molecular weight m_a can be calculated as follows:

$$m_a=M_{cluster}-(\sigma+1)m_{del}=(12+\frac{f_a^H}{f_a'})C \quad (3.1)$$

Assuming that the protonated aromatic carbon ratio $\frac{f_a^H}{f_a'}=0.5$, an average number of carbon atoms in an aromatic unit $C=\frac{m_a}{12.5}$. From the average carbon atoms quantity C, the average bridged aromatic carbon ratio χ_b can also be calculated.

In general, for low-order coals, parameter C is between 10 and 20. Considering the division of aromatic unit into single-ring and multiple-ring types, the number of carbon atoms in single-ring aromatic unit $C_{single} = 6$ and $C_{multi} = C + 2$ for multiple-ring aromatic unit. For single-ring aromatic unit, only a linear type exists, so there is only one bridgehead aromatic carbon ratio $\chi_{b,single}$. However, for multiple-ring aromatic unit, both linear and cirrcular types exist, so there are two bridgehead aromatic carbon ratios $\chi'_{b,multi}, \chi''_{b,multi}$. An equation group can be constructed:

$$\begin{cases} C_{single}x_{single} + C_{multi}x'_{multi} + C_{multi}x''_{multi} = C \\ \chi_{b,single}x_{single} + \chi'_{b,multi}x'_{multi} + \chi''_{b,multi}x''_{multi} = \chi_b \\ x_{single} + x'_{multi} + x''_{multi} = 1 \end{cases} \quad (3.2)$$

By solving the above equation group, the proportion of single-ring and multiple-ring aromatic unit can be obtained.After the division of the aromatic unit, due to the change of average carbon atoms number, and the average coordination number of the different aromatic units changes accordingly. Since the average coordination number is proportional to the number of carbon atoms, the new coordination number can be estimated as follows:

$$\sigma_{single} + 1 = (\sigma + 1)\frac{C_{single}}{C} \quad (3.3)$$

$$\sigma_{multi} + 1 = (\sigma + 1)\frac{C_{multi}}{C} \quad (3.4)$$

2.3.2 Tar fraction cutting

The generation of the tar product in the CPD model is achieved by the continuous accumulation of fragment molecules flashing, so in addition to the mass of the fragment molecules, the existence probability of different structured fragment molecules is also critical, which both determine the initial content and composition of the flash mixture. The existence probability of a fragment molecule containing n aromatic unit is:

$$Q_n(p) = b_n p^{n-1}(1-p)^{n(\sigma-1)+2} \quad (3.5)$$

The mass fraction of fragment molecules containing n aromatic units at time t is:

$$f_n(t) = \frac{Q_n(p)m_{tar,n}(t)}{mtot} \quad (3.6)$$

m_{tot} is the initial total mass of coal molecule (per aromatic unit), and its expression is:

$$m_{tot} = m_a + 2m_{del}(1-c_0)(\sigma+1) \quad (3.7)$$

For the tar component containing only 1 aromatic unit, its existence probability is:

$$Q_1(p) = (1-p)^{(\sigma+1)} \quad (3.8)$$

The mass fraction of the fragment molecule containing 1 aromatic unit at moment t is:

$$f_1(t) = \frac{Q_1(p)m_{tar,1}(t)}{mtot} = f_{1,single}(t) + f_{1,multi}(t) \quad (3.9)$$

Although the aromatic units have been classified in the above procedures, considering the complexity of the permutations and the fact that all multi-aromatic tar molecules can be defined as asphaltenes, the subsequent calculations only cut the tar molecules containing one aromatic unit, i.e., the structures of other tar molecules are still based on the original CPD assumptions. To ensure the consistency of the previous and subsequent calculations, the initial overall content of the tar molecules containing only one aromatic unit is also calculated based on the original assumption($\sigma + 1$,C), but the specific proportion of which is extrapolated with the newly proposed structural parameters：

$$\frac{f_{1,single}(t)}{f_{1,multi}(t)} = \frac{x_{single}(1-p)^{(\sigma_{single}+1)}(12.5C_{single} + \frac{(\sigma_{single}+1)m_{del}\delta}{2(1-p)})}{x_{multi}(1-p)^{(\sigma_{multi}+1)}(12.5C_{multi} + \frac{(\sigma_{multi}+1)m_{del}\delta}{2(1-p)})} \quad (3.10)$$

Referring to a widely used coal pyrolysis tar fraction cutting method[7], tar molecules containing one single-ring aromatic core correspond to light oil and phenolic oil; tar molecules containing one multiple-ring aromatic core correspond to naphthalene oil, washed oil and anthracene oil; tar molecules containing two or more aromatic cores are classified as asphaltene.

2.4 Coal sample

A basic set of analytical data of coal sample is shown as Table 1.

Table. 1 Analytical data of the coal sample(daf, wt%)

AI	C	H	O	VM
Value	75.57	5.32	17.34	45.29

Using the existing linear regression equations in CPD model to estimate the material structure parameters. The material structure parameters estimated by the linear regression equation in CPD model are shown in Table 2.

Table. 2 Structure parameters of the coal sample

Structure Parameters	$\sigma+1$	p_0	c_0	$M_{cluster}$	m_{del}
Value	4.98	0.54	0.068	358.77	34.55

3. RESULTS AND DISSCUSSION

Using the hypothesis proposed in this paper to divide the aromatic core unit as shown in Table. 3.

Table. 3 Aromatic unit structural parameters by new division

	C	$\sigma+1$	x
Average	15.34	4.98	1
Single	6	1.95	0.176
Multi	17.34	5.63	0.824

The tar distribution under different operating conditions is calculated and analyzed using the aromatic unit structure parameters and ratios obtained above.

3.1 *Distribution at varying final temperatures*

The pyrolysis temperature was simulated by using the programmed temperature rise, fixing other operating parameters constant and operating pressure of 1 atm, and only changing the final temperature of pyrolysis for calculation.

Table. 4 Tar distribution at different final temperature

	Tar Distribution			
FT/K	LO+PO	NO+ WO + AO	Asphalt	Tar Proportion
900	0.155	0.491	0.354	0.175
1000	0.141	0.446	0.413	0.190
1100	0.136	0.428	0.436	0.198

Analysis of the simulation data shows in Table. 4 that the tar yield increases with the increase of the final pyrolysis temperature, while the content of lighter components in the tar decreases.

3.2 Tar distribution under varying operating pressures

The pyrolysis temperature was simulated by using the programmed temperature rise, fixing the other operating parameters and the final pyrolysis temperature at 1000 K. Only the pyrolysis pressure was changed for the calculation.

Table. 5 Tar distribution under different pressure

	Tar Distribution			
P/atm	LO+PO	NO+ WO + AO	Asphalt	Tar Proportion
0.1	0.125	0.395	0.480	0.215
1	0.141	0.446	0.413	0.190
10	0.174	0.548	0.278	0.155

According to the simulation data in Table. 5, with the increase of pyrolysis pressure, the total yield of tar decreases, but the proportion of light components in tar increases, which is consistent with the trend of experimental data reported in the literature[8].

4. CONCLUSION

Using the new tar-cutting method to modify the original CPD model, a more concrete tar distribution can be calculated. The simulation results under different pyrolysis conditions show the same tendency with the experiment results reported in the literature, prove the validity of this new division method.

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