MODELING OF ASPHALT PYROLYSIS BASED ON CHEMICAL PERCOLATION DEVOLATILIZATION THEORY

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Highlights

- Developed chemical percolation theory to describe asphalt devolatilization.
- Modified chemical structure parameters with consideration of side chain detailed structure.
- Justified the necessity of distillation model and cross-linking model.

1. Introduction

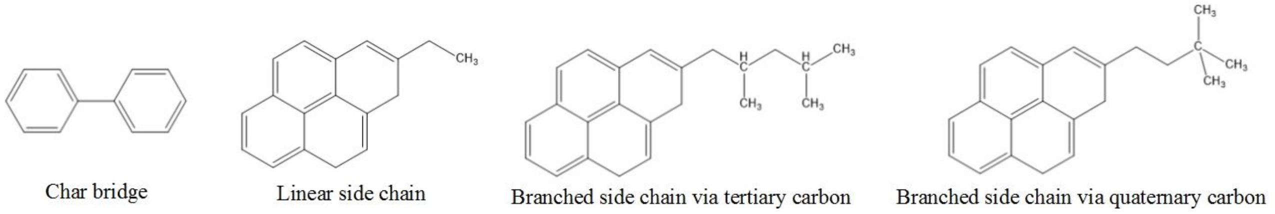
Asphalt is the semi-solid and bituminous fractions of crude oil, of which the pyrolysis has attracted much attention for its efficient utilization [1]. Various models were proposed to predict the pyrolysis of asphalt. However, those global models usually over-simplified the chemical features of raw materials, leading to insufficient understanding on the process. Chemical percolation devolatilization (CPD) model has been developed specially for coal devolatilization by Fletcher et al. in the 1990s [2], in which the chemical structure of the sample is directly associated with its devolatilization kinetics. In principle, it is capable of predicting the devolatilization of different carbonaceous substances, while the original algebraic approaches of CPD model need further modification when applied to substances other than coal.

In this work, we aim to develop the CPD modeling scheme to describe the devolatilization performance of an asphalt sample. Methods for acquiring two chemical structure parameters, i.e. initial intact bridge and char bridge fraction, are modified according to the sample property. Furthermore, two sub-models, i.e. the distillation model and the cross-linking model, are found to be indispensable.

2. Methods

Asphalt is a complex mixture of aromatic and heterocyclic clusters, attached by aliphatic side chains. During the pyrolysis, asphalt would release light gas and finite fragment(s), which would be either converted to the light gas through second-cracking or cross linked into the residue.

In Fletcher's work [3], when calculating the initial fraction of the intact bridge, methyl group and methoxy group were regarded as the aliphatic side chain in coal and subtracted from the possible bridge site. This is improper when applied to asphalt, as the fraction of terminal methyl group in the asphalt is no longer equal to that of side chain.



Char bridge   Linear side chain   Branched side chain via tertiary carbon   Branched side chain via quaternary carbon

Figure 1. Typical hypothetical bridge and chain structures of asphalt

For instance, in Figure 1, one side chain has only one terminal methyl group, while two or more methyl groups could be contained when the side chain has non-linear structure. Therefore, the algebraic approach for initial fraction of side chain should be modified when applied to asphalt. In the present work, the integral fraction from 50 to 40 ppm is regarded as the tertiary carbon in the side chains and therefore subtracted from the methyl group to modify the approach. In addition, methoxy group is neglected because the oxygen content is rather small and most oxygen would present in the ester groups. As a result, the modified initial fraction of the intact bridge is given as

$$p_0 = [f_a^p + f_a^s - (f_{al,CH_3} - f_{al,CH})]/(f_a^p + f_a^s) \qquad (1)$$

in which p_0 is the initial fraction of the intact bridge and f_a^P, f_a^S, $f_{a,CH3}$ and $f_{al,CH}$ are the fractions of phenolic carbon, alkylated aromatic carbon, methyl group and methine group, respectively.

Besides, direct connection of the phenyls is assumed as the major form of the char bridge, shown in Figure 1, and thus its initial fraction is determined as Eq. (2) rather than empirically determined in the literature work:

$$c_0 = f_C / (f_a^p + f_a^s) \qquad (2)$$

In Eq. (2), c_0 is the initial fraction of the char bridge, f_C is the fraction of multi-phenyls carbon.

3. Results and discussion

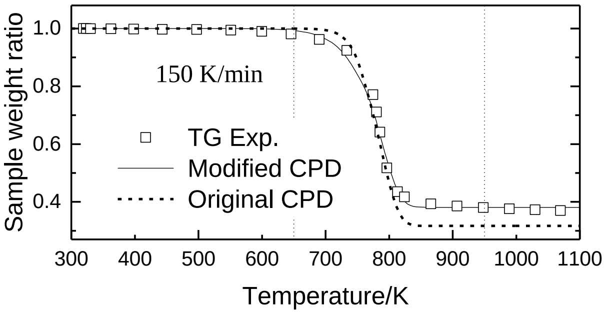


Figure 2. Comparison of model predictions with TG profiles under heating rate of 150 K/min

Figure 2 shows typical results of model predictions together with the TG curve at heating rate of 150 K/min. The predicted data are in good agreement with the experiments both on the devolatilization rate and the final conversion. The devolatilization process goes slowly before 700 K and accelerates in the range of 700 K ~ 800 K. It should be noticed that the simulated conversion with modified chemical structure parameters is consistent with the TG curve while satisfactory prediction could not be obtained with the original CPD model. These results provide acceptable certification on the modification of the two chemical structure parameters given in Eqs. (1) and (2).

In this work, two sub-models, i.e. the distillation model and the cross-linking model are taken into account to describe the two processes of finite clusters formed by the breaking of labile bridges. The simulation of cross-linked fraction, tar, light gas and the total volatile was conducted at three conditions: (1) case with both sub-models; (2) case with only distillation model; (3) case with only cross-linking model. It is found that both tar and light gas are formed before 650 K, and the amount of tar tends to be stable at 850 K or higher while light gas at 800 K or higher. The cross-linking process starts at 750 K, after the formation of light gas and tar. In case (2), more tar is formed, leading to the over estimation of volatiles. In case (3), however, no tar is formed, which is undoubtedly wrong. The predicted volatile yield agrees well with the experimental results only when the two sub-models are enabled, proving that both sub-models are indispensable.

4. Conclusions

CPD model is extended to study the devolatilization performance of asphalt. Two chemical structure parameters are modified, considering the structure features of the asphalt sample. And two sub-models, i.e. the distillation model and the cross-linking model, are found to be indispensable. This work is anticipated to build a cornerstone to theoretically characterize the asphalt pyrolysis based on its chemical structures.

References

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Keywords
Asphalt; pyrolysis; chemical percolation devolatilization (CPD); kinetics