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Kinetic model of hydropyrolysis based on the CPD model

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HIGHLIGHTS

- A kinetic model of hydropyrolysis based on the CPD model was developed.
- Hydrogenation reactions of reactive intermediates with hydrogen were considered.
- The model was validated against published experimental data.
- The influence of coal type, final temperature, and pressure was shown.

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ABSTRACT

A kinetic model of hydropyrolysis was developed based on the Chemical Percolation Devolatilization (CPD) network devolatilization model, considering the hydrogenation reactions of active species and fragments produced during the decomposition of the coal structure with hydrogen. Light gas compositions were calculated and the yields of oxygen-containing species were corrected. The calculation results show that the model well predicts the yields of volatile matter and methane for the coals that are in the scope of application of the correlation of the chemical structure parameters, with the value of β ranging from 0.0035 to 0.004 atm^{-1}, where β is a coefficient related to the ratio of the reaction rate of hydrogenation to that of crosslinking. The model successfully predicts the influence of coal type, final temperature and pressure on the hydropyrolysis yield and gas compositions. Further studies are needed to validate the model and determine the value and influencing factors of β.

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1. Introduction

Hydropyrolysis, especially flash hydropyrolysis, is the main process for producing substitute natural gas and light aromatics (BTX and PCX) from coal [1,2]. Kinetic study of hydropyrolysis is important for optimal design of the reaction process. Many kinetic models of hydropyrolysis have been proposed to calculate the overall coal mass [3–5] or gaseous products [6] during hydropyrolysis. The single kinetic rate hydropyrolysis model [3] is the most widely used empirical model which assumes that the reaction rate is proportional to the mass of the unreacted coal and the hydrogen partial pressure. The Distributed Activation Energy Model (DAEM) [4] assumes that the thermal decomposition of coal consists of a large number of parallel and mutually independent elementary reactions, and the activation energy of these reactions follow a Gaussian distribution or a uniform distribution. The active species model [5] successfully predicts the rapid methane formation process during the hydropyrolysis of coal by assuming the formation of active but intermediate species. Johnson and Tran [6] proposed a kinetic model to predict the kinetics of volatile components including H_2O, CO_2, CO, CH_4, other hydrocarbon gases, and tar. However, the parameters in the above models should usually be derived from complicated experiments, and in most cases these models could not be applied to circumstances where the reaction conditions are greatly different from that of the experiments.

As the understanding of coal structure and devolatilization deepens, more sophisticated network devolatilization models based on the chemical structure of coal have been proposed since 1980s, such as the FG-DVC model [7], CPD model [8,9], and FLASHCHAIN model [10]. Compared to the above empirical kinetic models, the network devolatilization models have been successful in predicting volatile yields and tar yields for various types of coal at different temperatures, pressures and heating rates [11]. However, the influence of hydrogen on devolatilization is not considered in these network devolatilization models, while in the hydrogen atmosphere, the ultimate yields and the product distribution of devolatilization are different from those in the inert atmosphere [12]. Therefore, these network devolatilization models could not be directly applied to hydropyrolysis. It is expected that

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the fundamental feature of the network devolatilization model would enable improvements to account for the influence of hydrogen while preserving the predictive capability for various cases. Recently, the FLASHCHAIN model was further developed to interpret hydropyrolysis data by incorporating the effects of hydrogenation of labile bridges and suppression of bimolecular recombinations, which well depicts the joint dependence of hydropyrolysis yield on heating rate and hydrogen pressure [13,14].

In this paper, we proposed a kinetic model of hydropyrolysis based on the CPD network model, by considering the hydrogenation reactions of the reactive intermediates and molecular fragments with hydrogen. The empirical light gas submodel of the CPD model was used to calculate the gaseous products of coal hydropyrolysis, and the methane produced by the hydrogenation reactions was added to the gaseous products of coal hydropyrolysis. The ultimate yields of oxygen-containing species were corrected to obtain better agreements with the experimental data in hydropyrolysis conditions. The model predictions were compared with published experimental data of hydropyrolysis in wire-mesh reactors, and the influence of coal type, final temperature of hydropyrolysis, and pressure on overall yields and yields of gaseous products was analyzed.

2. Kinetic model of hydropyrolysis

2.1. CPD model

In the CPD model, coal is represented as a macromolecular array linking by aromatic clusters, aliphatic bridges, side chains and rings. The decomposition of coal and the consequent production of light gas, tar and char starts with the scission of bridges in the macromolecular array. The bridge scission mechanism is illustrated in Fig. 1(a). When heated, a labile bridge of the coal array, £, decomposes to form an unstable bridge intermediate, £*, which is highly reactive and rapidly consumed by two competing reaction paths. The bridge intermediate can be either stabilized by forming a charred bridge, *c*, with simultaneous release of light gases, g_2, or cleaved by forming two side chains, δ, which are eventually converted into light gases, g_1, with slower kinetics. The bridge involved reactions in Fig. 1(a) are modeled by first-order kinetics with distributed activation energies, and a constant value of 0.9 is assumed and assigned to the ratio of reaction rate of the two competing reactions, k_δ/k_c [8,9].

As the scission of bridges proceeds, a portion of the aromatic clusters are detached from the coal array forming finite fragments of different fragment sizes, i.e., monomers, dimers, trimers, etc. These finite fragments remain in the condensed phase as metaplast. The production and molecular weight distribution of the metaplast are calculated using percolation lattice statistics. The metaplast can vaporize from the condensed phase at a given temperature to form tar vapor and escape from the coal structure. Thus the tar is modeled as a collection of these finite fragments in the gas phase. The remaining metaplast undergoes reattachment to the infinite coal array by crosslinking, as shown in Fig. 1(b). A gas–liquid equilibrium is assumed in the vaporization process of tar, and a vapor pressure correlation is used. The crosslinking process is depicted by a sing-rate kinetic model [8,9].

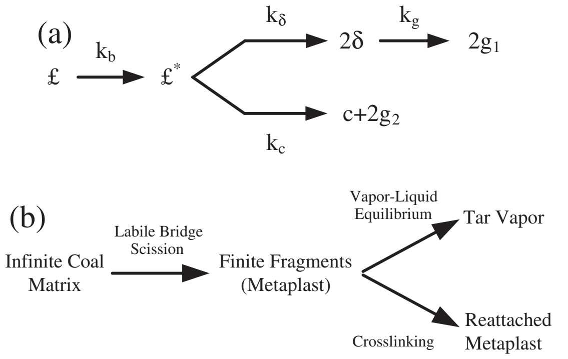

Fig. 1. CPD model: (a) bridge scission mechanism and (b) tar formation mechanism [8].

The CPD model requires as inputs five chemical structure parameters, including the average molecular weight of an aromatic cluster, M_{cl}, the average molecular weight of a side chain, M_δ, the initial number of intact labile bridges, L_0, the coordination number, $\sigma + 1$, and the initial number of char bridges, c_0. These chemical structure parameters can be derived from ^{13}C NMR experiments. In addition, a correlation, in the form of Eq. (1), was proposed by Genetti et al. [15].

$$y = f(\mathrm{C_{daf}},\ \mathrm{H_{daf}},\ \mathrm{O_{daf}},\ \mathrm{VM_{daf}}) \tag{1}$$

where *y* represents one of the above chemical structure parameters. The correlation uses the ultimate and proximate analysis data of coal to calculate the chemical structure parameters, which avoids the expensive and time-consuming ^{13}C NMR analysis. The correlation is based on the data set of ^{13}C NMR analysis for the coals which are in the range [15]: 66.6–95.4% for C_{daf}, 1.38–5.84% for H_{daf}, 1.40–24.16% for O_{daf}, 0.84–3.42% for N_{daf}, 0.37–6.29% for S_{daf}, and 3.92–78.67% for VM_{daf}.

2.2. Hydropyrolysis model

As the coal structure thermally decomposes, a large number of reactive intermediates and molecular fragments are produced, some of which combine with each other to form large macromolecular compounds and are trapped in the coal structure. Whereas in the hydrogen atmosphere, the reactive intermediates and molecular fragments produced can react with hydrogen to form small stable compounds, which are easy to escape from the coal structure [12]. It is assumed in this model that the metaplast is one of the reactive fragments and undergoes two competing reactions: crosslinking and hydrogenation. Since broken bridges and edges of the fragments can be active sites for both reattachment (leading to crosslinking) and hydrogen invasion (leading to hydrogenation), it is assumed that crosslinking and hydrogenation share the same active sites of the metaplast. Moreover, it is assumed that the activation of these active sites is the limiting step during the reaction of the metaplast. Thus the overall consumption rate of the metaplast in hydropyrolysis (i.e., the sum of the reaction rate of crosslinking and hydrogenation), is assumed to be the same as the reaction rate of crosslinking in pyrolysis, as calculated in Eq. (2):

$$R_{hyd} + R_{cross} = -dm_{meta}/dt = A\exp(-E/RT)m_{meta} \tag{2}$$

where R_{hyd} and R_{cross} is the reaction rate of hydrogenation and crosslinking, respectively; m_{meta} is the mass of the metaplast; *A* and *E* are kinetic parameters of the crosslinking reaction in pyrolysis [9]: $A = 3 \times 10^{15}\ \mathrm{s^{-1}}$, $E = 272\ \mathrm{kJ \cdot mol^{-1}}$.

The ratio of the metaplast consumed by hydrogenation to that by crosslinking is proportional to the hydrogen partial pressure, as illustrated in Eq. (3):

$$R_{hyd}/R_{cross} = \beta p_{H_2} \tag{3}$$

where p_{H2} is the partial pressure of hydrogen. β represents the tendency of the reactive intermediates and molecular fragments to combine with hydrogen, which is related to the property of the reactive intermediates and molecular fragments. Thus, β is a coal-dependent coefficient. Since no further information about β is available, it is used to fit the experimental data in this paper. Although there is no theoretical basis for the above assumptions,

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