



Research article

Extension of the chemical percolation devolatilization model for predicting formation of tar compounds as soot precursor in coal gasification



Satoshi Umemoto ^{a,b,*}, Shiro Kajitani ^a, Kouichi Miura ^c, Hiroaki Watanabe ^{a,d}, Motoaki Kawase ^b

^a Energy Engineering Research Laboratory, Central Research Institute of Electric Power Industry (CRIEPI), 2-6-1 Nagasaka, Yokosuka, Kanagawa 240-0196, Japan

^b Department of Chemical Engineering, Kyoto University, Kyoto-Daigaku Katsura, Nishikyo-ku, Kyoto 615-8510, Japan

^c Institute of Advanced Energy, Kyoto University, Gokasyo, Uji, Kyoto 611-0011, Japan

^d Department of Mechanical Engineering, Kyushu University, 744 Motooka, Nishi-ku, Fukuoka, Fukuoka 819-0395, Japan

ARTICLE INFO

Article history:

Received 31 October 2016

Received in revised form 19 January 2017

Accepted 20 January 2017

Available online 3 February 2017

Keywords:

Coal gasification

Pyrolysis model

Soot

PAH

CPD model

ABSTRACT

This paper proposed and validated a new coal devolatilization model that can predict yields of respective gas and tar components, and be directly coupled with an elementary step-like reaction model. The new model was an extension of the chemical percolation devolatilization (CPD) model. The CPD model is one of the existing primary pyrolysis models that consider the coal chemical structure. The mole fraction of labile bridges, cross links, peripheral groups, and average molecular weight of monomer in coals examined in this study were determined by a ¹³C NMR analysis. The aromatic ring clusters size distribution was determined by a coal pyrolysis test using a Curie point pyrolyzer. The thermal decomposition process of the coal chemical structure was expressed by nine elementary reactions. From the above, the extended CPD model can predict gas and tar components as respective chemical species (H₂O, CO₂, CO, CH₄, benzene, naphthalene and phenanthrene) and consequently capture the secondary decomposition and polymerization in gas phase by coupling the detailed gas-phase chemistry. The proposed model was validated by comparing with experiments using a pressurized drop tube furnace (PDTF). The results showed that the trend of light gases and soot yield in the experiments could be successfully reproduced by the extended CPD model.

© 2017 Elsevier B.V. All rights reserved.

1. Introduction

Coal pyrolysis (including primary pyrolysis or devolatilization, and secondary gas-phase decomposition) is an important reaction that has a significant influence on coal combustion and gasification. Lately, the authors have been focusing on the soot formation behavior in gasification conditions, because soot formation decreases carbon conversion efficiency [1]. Soot forms mainly through the primary pyrolysis, the gas-phase reaction, and the chemical deposition of volatile matters [2]. The primary pyrolysis is important as the first step of soot formation.

In addition, to predict the soot formation by a numerical approach, the behavior of soot precursors (volatile matters) should be estimated. Watanabe et al. [3] successfully captured the characteristics of soot formation in a spray flame by coupling a primary pyrolysis model with a gas-phase reaction model in order to estimate the formation of soot precursors. However, the number of researches to predict the soot

formation in coal gasification is very limited, because of the lack of a model that can predict yields of respective gases and tars, and can be directly coupled with a gas-phase reaction model [4,5]. This is because the complicated nature of the decomposition of coal chemical structure to determine the yields of the respective chemical species has been impeding the establishment of modeling methods.

Although the chemical structure of coal is very complex, it must be considered in order to achieve a reasonable modeling of the primary pyrolysis. In the 1980s, several primary coal pyrolysis models considering coal chemical structure were proposed: the FLASHCHAIN model [6–12], the functional group-depolymerization-vaporization-cross-linking (FG-DVC) model [13,14], and the chemical percolation devolatilization (CPD) model [15–18]. These models assume that coals consist of aromatic ring clusters, links, and peripheral groups. The links are divided into the labile bridges and the cross links. These models have been successfully utilized for predicting yields of gas, tar and char in coal primary pyrolysis and recently modified to predict light gas components [19–22]. However, these models assumed tar to be abstract “tar”, rather than specific components.

On the other hand, elementary step reaction models or their simplified models (elementary step-like reaction models) have been

* Corresponding author at: Energy Engineering Research Laboratory, Central Research Institute of Electric Power Industry (CRIEPI), 2-6-1 Nagasaka, Yokosuka, Kanagawa 240-0196, Japan.

E-mail address: umemoto@criepi.denken.or.jp (S. Umemoto).

Nomenclature

$A_{a,b}$	Pre-exponential factor of char gasification reaction [s^{-1}]
A_i	Pre-exponential factor of link or peripheral-group reaction [s^{-1}]
C_1	Fraction of cross link or direct connection between aromatic carbons [mol/mol-bond]
C_N	Number of cluster in a tar component [—]
dV_{gas}/dt	Total generation rate of light gas which has higher vapor pressure than total pressure [s^{-1}]
$dV_{n,m}/dt$	Vaporization rate of a molecule whose molecular weight is $M_{n,m}$ [s^{-1}]
$E_{a,b}$	Activation energy of char gasification reaction [kJ/mol]
E_i	Activation energy of link or peripheral-group reaction [kJ/mol]
F_n	Amount of n -mer [mol/mol-cluster]
f_x	Mole fraction of carbon which is included in x structure (details are listed in Table 2) [mol-C/mol-C]
H_1	Fraction of substituted hydrogen [mol/mol-bond]
k_i	Kinetic constant of link or peripheral-group reaction [s^{-1}]
L_1	Fraction of labile ethyl bridge [mol/mol-bond]
L_2	Fraction of labile ether bridge [mol/mol-bond]
M_a	Averaged molecular weight of aromatic ring cluster [g/mol]
M_b	Averaged molecular weight of bonds [kg/mol]
MW	Averaged molecular weight of monomers [kg/mol]
N_C	Number of carbon in a tar component [—]
n_{max}	Maximum size of molecules which are considered to be vaporized (or considered as metaplasts) [—]
p	Probability of bonds which remain intact (the ratio of bonds which are included in links to total bonds) [—]
PA	Peak area of gas chromatography signal
$P_{s,n,m}$	Saturated vapor pressure of a molecule whose molecular weight is $M_{n,m}$ [Pa]
P_t	Total pressure [Pa]
$P_{v,n,m}$	Vapor pressure of a molecule whose molecular weight is $M_{n,m}$ [Pa]
q_i	Amount of i -ring in a molecule [mol/mol-molecule]
$Q_{i,n}$	Amount of i -ring cluster which are included in n -mer [mol/mol-cluster]
R	Gas constant, 8.314×10^{-3} kJ/mol K^{-1}
$r_{a,b}$	Reaction rate of char gasification reaction with gasifying agent, a in temperature range, b [s^{-1}]
r_i	Reaction rate of link or peripheral-group reaction [s^{-1}]
SI	Similarity index of a component which was detected in gas chromatography [%]
T	Temperature [K]
W_{carbon}	Carbon fraction in the coal [kg/kg-coal, d.a.f.]
x_c	Conversion of char [—]
$Y_{i,n}$	Fraction of i -ring in n -mer [mol/mol]
Y_{i-ring}	Mole fraction of i -ring cluster [mol/mol-cluster]
α_s	Pre-exponential factor of vapor pressure equation (Eq. (6)) [Pa]
β_s	Activation energy-like factor of vapor pressure equation (Eq. (6)) [$g^{-\gamma_s} mol^{\gamma_s} K$]
γ_s	Molecular weight order of vapor pressure equation (Eq. (6)) [—]
δ_1	Fraction of carboxyl group [mol/mol-bond]
δ_2	Fraction of hydroxyl group [mol/mol-bond]
δ_3	Fraction of methyl group [mol/mol-bond]
$\sigma + 1$	Coordination number [—]

χ_b	Fraction of aromatic bridgehead carbons [mol/mol-aromatic carbon]
Ψ_a	Structure parameter in random pore model equation (Eq. (9)) [—]

developed to predict hydrocarbon polymerization to form polycyclic aromatic hydrocarbon (PAH) or carbon mainly in the chemical engineering field, such as chemical vapor deposition [23], the fossil fuel combustion field [24], and the oil cracking field [25]. These models are also used for predicting formation of polycyclic aromatic hydrocarbons (PAHs), which is the precursor of soot. Therefore, for examining soot formation behavior in coal gasification, it is necessary to identify respective volatile matter components in primary pyrolysis product in order to predict PAH formation behavior utilizing an elementary step-like reaction model.

For coupling a primary pyrolysis model with an elementary step-like reaction model, the primary pyrolysis model should be upgraded to predict specific volatile matter components. The benefit of the FLASHCHAIN model is that the model needs only the proximate analysis and ultimate analysis data of coal, while the FG-DVC model and the CPD model need ^{13}C NMR data. The feature, however, does not seem to be suitable for improvement to predict complex volatile matter components. The FG-DVC model is relatively similar to the complex chemical structure of coal, but the model is too complicated for further upgrades. The CPD model assumes that coal is composed of Bethe pseudo lattice molecules. This model can consider any size of molecules, that is, from monomer to unlimitedly large molecule in coal structures by relatively simple equation using a percolation theory. The extension of models necessarily complicates the model. Therefore, we chose the simplest model during the three famous models for the extension. In this study, the CPD model was extended so as to predict respective gas and tar components in primary pyrolysis. Then, the extended CPD model (Ex-CPD model) was used with an elementary step-like reaction model to predict PAH formation behavior. The PAH yields calculated by these models were compared with experimental results of coal gasification tests using a drop tube furnace (DTF).

2. Experimentation

2.1. Coal samples

Properties of coals used in the experiments [1] whose data were compared with the calculation results in this study are listed in Table 1.

^{13}C NMR data of these coals are listed in Table 2. ^{13}C NMR provides important information about the chemical structure model [26,27]. The ^{13}C NMR analysis was carried out with CMX-300 Infinity (Chemagnetics) operating at the carbon frequency of 75.2 MHz. A coal structure was determined by two tests. The first was CP/MAS (PD = 5 s) for identification, and the second was DD/MAS (PD = 200 s) for quantification. Other conditions were as follows: The test atmosphere was dried air, the temperature was room temperature (~ 295 K), the internal reference was a silicone rubber, the sweep width was 30.0 kHz, the 90° pulse width was 4.2 μs , the acquisition time was 0.0341 s, the contact time was 2 ms, and the sample rotation rate was 10.5 kHz.

2.2. Coal primary pyrolysis test to determine the aromatic ring size distribution

Coal primary pyrolysis tests with a Curie point pyrolyzer (JAI, JHP-5) were conducted to determine the aromatic ring size distribution in coals. The pyrolysis conditions were 1313 K, ambient pressure, and 100 vol% He. The produced gas composition was analyzed by GC-MS: (Shimadzu, QP-2010) and GC-FID (Shimadzu, GC-2010). The gas analysis conditions were as follows: The column was TC-5HT (GL Sciences),

Download English Version:

<https://daneshyari.com/en/article/4914363>

Download Persian Version:

<https://daneshyari.com/article/4914363>

[Daneshyari.com](https://daneshyari.com)