Fuel 230 (2018) 18–26

Contents lists available at ScienceDirect

Fuel

journal homepage: www.elsevier.com/locate/fuel

Full Length Article

The Boltzmann-Monte-Carlo-Percolation (BMCP) model on pyrolysis of coal: The volatiles' reactions

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ARTICLE INFO

Keywords:
Coal pyrolysis
Volatile reaction
Modeling
Boltzmann-Monte-Carlo
Percolation theory

ABSTRACT

It is well recognized that the reaction of volatiles generated from coal in pyrolysis is the main reaction determining the quality and quantity of the products such as the tar. Most of pyrolysis models reported however treat the volatiles' reaction by empirical correlations determined from a few experiments under limited conditions. This work studies the volatiles' reaction from a covalent bond view by adopting a bond "dissociation-coupling" mechanism that employs a Boltzmann-Monte-Carlo algorithm coupled with a products formation algorithm based on the percolation theory. The simulation results accord well with experimental data under a few assumptions on the "coupling" step. It shows that the method is promising to reasonably simulate the chemical nature of the volatiles' reaction. Furthermore, the bonds' "dissociation" step may be the rate-determining step in the "dissociation-coupling" mechanism of the volatiles' reaction.

1. Introduction

Tar is an important product of coal pyrolysis and has been studied extensively on its quantity and composition under many pyrolysis conditions. The early understanding considered tar as a direct product of pyrolysis [1], while the current understanding, with the aid of huge amounts of experimental data, recognizes the tar formation follow two steps [2], the primary generation of volatiles from coal structure and then the reaction of volatiles. These two steps are also frequently termed as primary pyrolysis and secondary pyrolysis of coal. In other words, coal is the reactant of the primary pyrolysis that yields volatiles and fixed carbon, while the volatiles are the reactants of the secondary pyrolysis that yields the final products, tar, gas and secondary coke or soot [3].

Under almost all the conditions, the volatiles generated from the cleavage of covalent bonds in coal in the primary pyrolysis transport to higher temperature environments during their diffusing out of the coal pores and through coal bed [4] and flowing through the gas phase in reactors [5]. The temperature gradient the volatiles experiencing is larger in fast pyrolysis than that in slow pyrolysis. For instance, in a fluidized-bed fast pyrolysis process the temperature of major volatiles generation could be 100 K lower than the temperature of the surface of coal particles [4] and more than 200 K lower than the temperature of other particles, such as ash or coke, in the bed [5]. Obviously, in the same reactor the primary pyrolysis and the volatiles' reaction occur at very different temperatures, and the much higher temperature of the volatiles' reaction greatly affects the quantity and composition of the tar and gas finally collected.

Coal is very complex in structure and composition, and it is not easy to determine its pyrolysis reaction network. Model compounds, therefore, were used to study the volatiles' reaction experimentally [6,7] and to develop reaction networks [8–10]. The models determined however were still empirical and largely reactor-dependent, involving little intrinsic reaction. To overcome the limitation of empirical models ReaxFF method was introduced to simulate the volatiles' reaction based on the universal force field and also on inverting atom matrix [11,12]. This method predicts the volatiles' reaction under various conditions without using empirical parameters but requires a huge computer power. Furthermore, the high reaction temperature (> 1500 K) and short residence time ($< 10^{-7}$ s) makes the simulation difficult to be compared with experimental data.

Our earlier work showed that pyrolysis of kraft lignin can be simulated roughly based on a Boltzmann-Monte-Carlo algorithm which involves dissociation of covalent bonds in kraft lignin and coupling of the radicals generated from the bonds dissociation [15]. Since the covalent bond distribution of coals can be determined from a matrix based on the ultimate analysis and NMR data of coals [13], and the volatiles' yield of coals in pyrolysis can be attributed to dissociation of 5

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https://doi.org/10.1016/j.fuel.2018.05.016
Received 28 November 2017; Received in revised form 8 March 2018; Accepted 3 May 2018
Available online 12 May 2018

Nomenclature

$BDE_{X\text{-}Y}$	bond dissociation energy of bond X-Y, J/mol
d	the diameter of the collision molecules, m
E	overall energy barrier of the reaction following Rice-Kossiakoff mechanism, J/mol
$F(p)$	the probability of the finite clusters, dimensionless
$F_n(p)$	the probability of the n sites clusters' formation, dimensionless
k	Boltzmann constant, 1.381×10^{-23} J/K
k_m	coefficient of proportionality in Monte-Carlo algorithm, dimensionless, 1 in this work
$n_{radical}$	the amounts of radicals in the system, mol
$m_{average}$	the geometric average molecular weight of the two radical fragments, kg/kmol
$m_{radical1}$	the molecular weights of the radical fragments in collision, kg/kmol
$m_{radical2}$	the molecular weights of the radical fragments in collision, kg/kmol
$MW_{Cal\cdot}$	the molecular weight of radical with the unpaired electron on aliphatic carbon, kg/kmol
$MW_{Car\cdot}$	the molecular weight of radical with the unpaired electron on aromatic carbon, kg/kmol
$MW_{H\cdot}$	the molecular weight of radical with the unpaired electron on proton, kg/kmol
$MW_{O\cdot}$	the molecular weight of radical with the unpaired electron on oxygen, kg/kmol
n	the site amounts in a cluster, dimensionless
nb_n	the distinct configuration of a cluster with n sites, dimensionless
n_{Cal}	the amounts of aliphatic carbon atoms, mol
n_{Car}	the amounts of aromatic carbon atoms, mol
n_O	the amounts of oxygen atoms, mol
n_{total}	the amounts of total atoms, mol
$n_{X\text{-}H}$	the amount of bonds connected with H except H—H, mol
$n_{X=O}$	the amount of unsaturated bond connected with unsaturated O except O═O, mol
$n_{X\text{-}Y}$	the amount of bonds except H—H, mol
p	the probability of a site being occupied, dimensionless
p^*	the solution of percolation equation, dimensionless
p'	the occupation probability of volatile's pyrolysis, dimensionless
R	ideal gas constant, 8.314 J/mol/K
s	the number of bridges in the n sites cluster, dimensionless
T	absolute temperature of pyrolysis, K
x_1	the dissociated portion of bond X-Y in a relaxation time, dimensionless
$X_{H3Cal\cdot}$	the portion of $H_3C_{al}O\cdot$ radical in $C_{al\cdot}$ radicals, dimensionless
$X_{H3CalO\cdot}$	the portion of $H_3C_{al}O\cdot$ radical in $C_{al\cdot}$ radicals, dimensionless
$X_{HO\cdot}$	the portion of HO· radical in O· radicals, dimensionless
$x_{R\text{-}K}$	the probability of reaction following Rice-Kossiakoff mechanism, dimensionless
$Z_{average}$	the average collision probability of two radicals in AI, dimensionless
$Z_{j\text{-}k}$	the relative yield of products with sites ranging from j to k, dimensionless
π	circular constant, dimensionless, 3.142
σ	the number of sites a site connecting with in the next layer, dimensionless
$\sigma_{average}$	the average σ of volatile during pyrolysis, dimensionless
τ	perimeter of the n sites cluster, dimensionless

major types of covalent bonds [14], it is possible to simulate coal pyrolysis and predict its products using the Boltzmann-Monte-Carlo algorithm.

It should be noted, however, that the Boltzmann-Monte-Carlo algorithm developed previously can only estimate population of different bonds but not the distribution of actual products. If the covalent bonds determined as the products in the simulation can be extended to structural lattices, the product distribution can be obtained by inverting the bond information to probabilities of clusters of different sizes using the percolation theory [16,17], while the clusters can be further transformed to different pyrolysis products such as the tar and gas.

Although numerical study [18], especially those with percolation theory [19–22], were adopted to coal pyrolysis, the study from chemical nature of pyrolysis, "dissociation" and "coupling", without empirical parameters has not been established and used before. This work combines the Boltzmann-Monte-Carlo algorithm, which simulates the evolution of bonds in pyrolysis, with the percolation theory, which provides generation probabilities of clusters with different sizes, to form a new method to simulate coal pyrolysis. The simulation results with various assumptions of the "coupling" step and a principal model of the volatiles' reactions are compared with experimental data in the literature.

2. Theory

2.1. Boltzmann-Monte Carlo model

It is generally recognized that the pyrolysis of coals and reactions of coal volatiles follow radical mechanism, which involves two major steps: dissociation or cracking of covalent bonds to generate free radical fragments ("dissociation" step) and reaction or combination of the free radical fragments to form products ("coupling" step) [23]. In a previous work [15], the Boltzmann distribution was introduced to describe the portion of the bonds dissociated while the Monte-Carlo algorithm was introduced to describe the bond formation through coupling or collision of radical fragments. Furthermore, different assumptions of the "dissociation" and "coupling" steps were considered [15] to analyze the importance of each step.

In the "dissociation" step the portion of the bond X-Y dissociated in a relaxation time is x_1 as shown by Eq. (1) [15].

$$x_1 = \frac{e^{-BDE_{X-Y}/RT}}{1 + e^{-BDE_{X-Y}/RT}} \tag{1}$$

Besides via Eq. (1), some covalent bonds may undergo consecutive cracking following the Rice-Kossiakoff mechanism to form unsaturated bonds [24] with the probability $x_{R\text{-}K}$ described in Eq. (2) in a relaxation time [15].

$$x_{R-K} = k_m \times \frac{e^{-E/RT}}{1 + e^{-E/RT}} \tag{2}$$

The radical fragments generated from the bond dissociation step can be grouped into 4 types, such as $C_{ar}\cdot$ (such as C_{ar}═$C_{ar}\cdot$ and C_{ar}—$C_{ar}\cdot$), $C_{al}\cdot$(such as C_{ar}—$C_{al}\cdot$ and $H_3C_{al}\cdot$), O· (such as HO· and $H_3C_{al}O\cdot$) and H·. These radical fragments may couple to form ten different bonds except the unstable O—O bond [15]. The "coupling" step may follow two mechanisms: complete random collision (termed Assumption Random, AR) and ideal gas collision (termed Assumption Ideal gas, AI). The AR assumes the equal collision probability for radical fragments of different molecular weight while the AI assumes the collision probability governed by the Maxwell-Boltzmann distribution described by the velocity of ideal gas. The average collision probability of two radicals in AI, $Z_{average}$, can be estimated by Eq. (3) [15].