



Modeling of kraft lignin pyrolysis based on bond dissociation and fragments coupling



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ABSTRACT

It is generally recognized that pyrolysis of biomass involves two steps: dissociation of covalent bonds to generate free radical fragments and coupling of the free radical fragments to form products. Experiments and simulations on biomass pyrolysis in the literature, however, ignored the role of each step and provided only the overall results of the two steps. Based on the two-step mechanism, this work simulates pyrolysis of a structural unit of kraft lignin. The first step is assumed to be governed by Boltzmann distribution of each bond in the unit at a given temperature and time, while the second step is assumed to follow Monte-Carlo algorithm. The Boltzmann–Monte Carlo pyrolysis model built is analyzed with the aid of basic and secondary assumptions. The mode is further validated by simulating pyrolysis of kraft lignin and comparing the results with experimental data in the literature. It is found that the model simulates the pyrolysis behavior reasonably well, in terms of changes in bonds' population and amounts of radicals formed versus temperature and time.

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1. Introduction

It is generally recognized that pyrolysis of organic matters (including biomass, coal, and heavy petroleum fractions) involves two main 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) [1–4]. These two-step reactions are complex because that any of the feed stocks is composed of bonds of different dissociation energy and the products of the coupling step may crack further.

Lignin has been studied for pyrolysis by many because it is a main component of woody biomass and is relatively simple in structure. It is a three dimensional macromolecule network constructed by basic structure units and ether linkages such as β -O-4 and α -O-4 [5,6]. Kraft lignin obtained from kraft pulping is a small lignin [7] and has been taken as a model to understand mechanism of lignin pyrolysis. However, due to limitations in experimentation, these pyrolysis studies still could not distinguish the contribution of the individual pyrolysis steps, and simulation studies focused only on description of experimental data and yielded only overall kinetics [8].

Since the overall kinetic simulations on pyrolysis of kraft lignin and lignin reported in 1970s, many kinetic models has been proposed

[9], including the simplest first-order reaction model [10], Distributed Activation Energy Model (DAEM) [11], and reaction networks with a few reactions [12] to dozens reactions [13]. The conditions used in the modeling very from decomposition reactions at low temperatures (around 450 K) for a short time [14] to complex reactions such as generation of poly aromatic hydrocarbons (PAH) at high temperatures (around 1000 K) for a long time [15]. Although progresses have been made in the modeling, the bases of the models were similar: they all followed empirical reaction pathways and addressed mainly the changes in group composition to fit experimental data. A notable change in modeling strategy occurred in 2009 when Salmon et al. proposed an Empirical Force Field Model [16], which considered an empirical but relatively accurate micro-scale mechanism of lignin pyrolysis. However, due to requirement of a huge amount of computing time, this simulation was able to simulate pyrolysis at extremely high temperatures (higher than 1500 K) in a very short time (less than 10^{-7} s), which made comparison of the results with experimental data difficult.

It is noted that the complex behavior of lignin pyrolysis may be simplified by considering only the changes in covalent bonds since it is the core of any chemical reaction and there are only a few types of covalent bonds in lignin. This idea was practiced in pyrolysis of complex matters such as that reported by Lewan et al., they analyzed changes in products' aromaticity during pyrolysis of type II Kerogen based on changes in C-S and S-S bonds [17]. It was also practiced recently by Shi et al., they decoupled differential thermal gravimetric (DTG) data obtained from pyrolysis of 34 coals to 5 sub-curves representing the major types of covalent bonds in coals [18]. Successes of these

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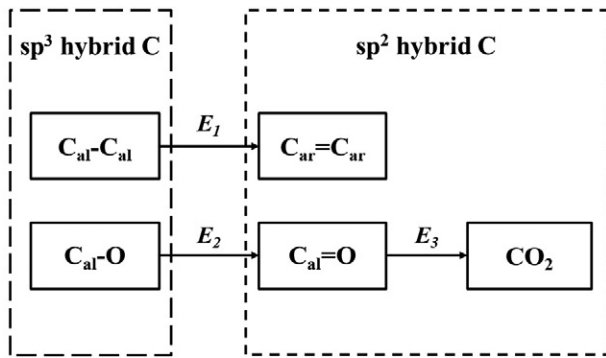


Fig. 1. Reactions follow “dissociation-dissociation-coupling” process.

works suggest that modeling of kraft lignin pyrolysis from the point of view of changes in bonds may be a reasonable and manageable approach.

This work analyzes the types and distribution of covalent bonds in kraft lignin and simulates its pyrolysis by two types of reactions, i.e. dissociation of covalent bonds to generate radical fragments and coupling of the radical fragments to form products. Assumptions

necessary for the modeling are discussed and modeling results are analyzed and compared with experimental data to understand the validity of the model.

2. Model and parameters

2.1. Model construction

In order to describe the “dissociation” and the “coupling” steps, it is necessary to define rate equations of the two steps and assumptions needed.

2.1.1. Principle formulations of model

2.1.1.1. “Dissociation” step. Dissociation of a bond is caused by vibration. Since vibration of a bond cannot be described by the law of mass action, it is necessary to introduce equilibrium distribution in thermodynamics to describe the behaviors of vibration and dissociation of a bond.

A pyrolysis system is usually considered as a canonical ensemble in molecular simulation [19]. Statistical thermodynamics indicates that the numbers of particles in different energy states follow Gibbs distribution [20]. For a system in which interactions between molecules are not strong, Gibbs distribution can be approximated by Boltzmann distribution [20]. According to the local equilibrium assumptions [20], a non-equilibrium pyrolysis process can be considered as a series of sub-processes in equilibrium. Therefore it

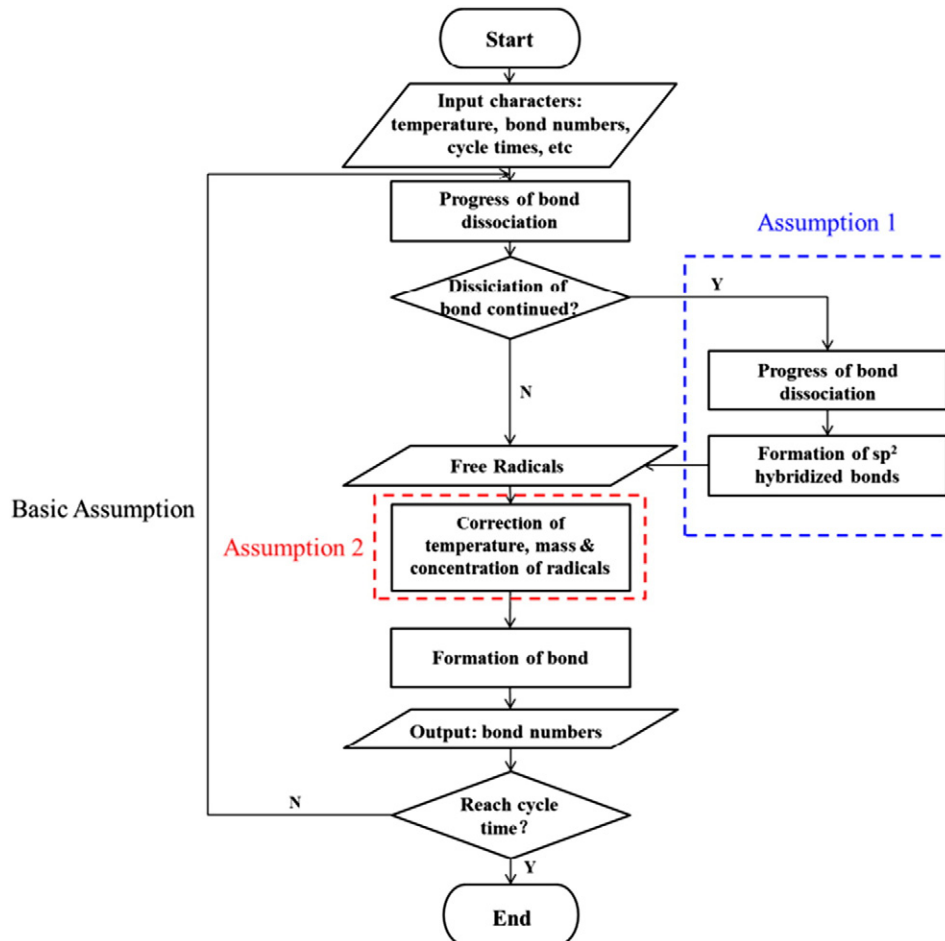


Fig. 2. Flowsheet of simulation programs.

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