



## Research article

## ReaxFF molecular dynamics simulation of pyrolysis and combustion of pyridine



LiuJia, GuoXin\*

State Key Laboratory of Coal Combustion, School of Energy and Power Engineering, Huazhong University of Science and Technology, Wuhan 430074, China

## ARTICLE INFO

## Article history:

Received 12 July 2016

Received in revised form 1 March 2017

Accepted 14 March 2017

Available online 20 March 2017

## Keywords:

ReaxFF

Pyridine

Pyrolysis

Combustion

## ABSTRACT

The reactive molecular dynamics (ReaxFF MD) simulation was applied to investigate the initial reaction mechanism of pyrolysis and combustion of pyridine. By analyzing the dynamic change with time of intermediates and products formed during the simulation process, the underlying detailed chemical reactions of pyrolysis and combustion of pyridine for a variety of reaction conditions (temperature, pressure/density and heating rate) were revealed. We found that a raise in temperature, pressure/density and heating rate shortens the initiation time and accelerates the pyrolysis of pyridines, producing more species and numbers of products. Specifically, the free radicals of H and pyridyl were generated from the pyridine molecules at the early stage of pyrolysis simulation, and prominent products observed during these decompositions were H<sub>2</sub>, C<sub>2</sub>H<sub>2</sub> and HCN, indicating the pyrolysis of pyridine is a chain process initiated principally by C–H bond fission. And we investigated the dynamic transformation pathways of nitrogen during the pyrolysis process. As the pyrolysis temperature and pressure/density increase, the nitrogen transformation process from HCN and CN to NH<sub>3</sub> and N<sub>2</sub> will be promoted. In addition, for the simulation of the oxidation of pyridines, we found that increasing temperature promotes the combustion of pyridine but only has a limited effect on the oxidation process when it reached a higher range, and the initiation of oxidation is the unimolecular C–H bond fission and bimolecular reaction with O<sub>2</sub> to form the pyridyl radical, which can further react with oxygenated species to form the pyridoxy radical. The simulation results agreed reasonably well with previous experimental studies, implying that this paper offers a new and promising approach to systematically study the detailed and dynamic chemical reactions of thermal decomposition of nitrogen compounds.

© 2017 Elsevier B.V. All rights reserved.

## 1. Introduction

The emission of oxides of nitrogen (NO<sub>x</sub>) from power generation using coal contributes to the formation of acid rain and photochemical smog, in addition to the direct effects on human health, which has been and will continue to be a major environmental concern [1]. Significant amount of nitrogen in coal is in the form of aromatic heterocyclic structures containing pyridine ring systems [2]. These heterocycles may form nitrogen precursors of NO<sub>x</sub> during pyrolysis and combustion process so that the product formation from representative nitrogen compounds will determine NO<sub>x</sub> formation in the combustion of coal. To further improve the control of NO<sub>x</sub> from coal utilization, the fundamental studies on the formation and transformation mechanism of the main nitrogen compounds in coal such as pyridine are of importance and essence.

Intensive researches and development efforts have been carried out on the pyrolysis of pyridine compounds. Hurd and Simon [3] investigated the pyrolysis of pyridine in continuous flow pyrolysis system with the temperature ranging from 1098 to 1123 K and the major products they observed were C<sub>3</sub>H<sub>3</sub>N, C<sub>2</sub>H<sub>3</sub>N, C<sub>7</sub>H<sub>5</sub>N and C<sub>9</sub>H<sub>7</sub>N and they claimed the initiation reaction of pyridine pyrolysis is opening ring. Based on the experimental results of Hurd, Axworthy and his co-workers [4] increased the pyrolysis temperature range to 1337 K and found that the principle intermediate in the formation of fuel nitric oxide is hydrogen cyanide, which was formed during the initial pre-flame stages of combustion from 1300 K to 2400 K. Mackie and co-workers investigated the pyrolysis of pyridine in a single-pulse shock-tube reactor [5] and they analyzed the products with capillary column GC along with GC/MS and FTIR spectroscopy, revealing that the thermal decomposition of pyridine was a chain process initiated principally by C–H bond fission, which is more easily to break than C–C bond demonstrated by Houser's study [6]. Then presumably followed by a rapid dissociation of the pyridyl radical, HCN and more species of nitriles have been found as the main N-containing products and many types of radicals such as H,

\* Corresponding author.

E-mail address: [guoxin@mail.hust.edu.cn](mailto:guoxin@mail.hust.edu.cn) (X. Guo).

$\text{CH}_3$  and other hydrocarbon radicals are involved in the chain reactions. Recently, Memon et al. [7] confirmed the nature of pyridine decomposition proposed by Mackie. They also proposed that all the C—H bonds undergo fission, but the C—H bond adjacent to that of the nitrogen atom is weaker and dissociation may dominate.

In addition, Houser and his co-workers studied the rate of oxidation of pyridine and the nitrogen-containing products formed during the oxidation in the temperature range of 675–775 °C using a Vycor, stirred-flow reactor [8]. And oxidation of pyridine has been studied behind reflected shock waves in a single-pulse shock tube by Ikeda et al. [9]. They found that CO was the principal product of oxidation at the lowest temperature and the oxidation is initiated both by unimolecular C—H bond fission and bimolecular reaction with  $\text{O}_2$  to generate the ortho-pyridyl radical which will further react with oxygenated species to form the pyridoxy radical.

However, reactions in pyrolysis and combustion processes take place because of the free radical initiations at high temperature in an extremely short period of time, which are hard to detect and replicate in the laboratory. Due to the limits of the available measurement methods, only limited pyrolysis species can be analyzed accurately and rather limited information about the intermediates or free radicals formed during the pyrolysis and combustion process can be obtained in the previous literature. It should be also pointed out that all the experimental techniques were not able to directly monitor the time evolution of a specific product during the reaction process. As a result, it's difficult to elucidate the detailed chemical mechanisms and the dominant reaction pathways for the pyrolysis and oxidation of pyridine.

It is imperative to apply computational approaches to understand the true nature of the reaction pathways. In principle, quantum mechanical (QM) calculations can provide accurate transition states and reaction rate constants for chemical kinetic modeling. Martropawiro and his co-workers applied the ab initio quantum chemical techniques to investigate the kinetics of pyrolysis of pyrrole theoretically [10]. However, these methods are too computationally expensive in

providing a detailed, dynamic description of the complex reactions during pyrolysis and combustion for a large-scale system exposed to a variety of temperature and pressure transients. On the other hand, molecular dynamics (MD) simulation can be used to tackle this problem. With conventional force fields, they can provide reasonable results of geometries, conformational information, and thermodynamic properties of large system, but they fail to describe the processes of bond breaking and bond formation in the chemical reactions. Historically, Brenner and his co-workers once developed a force field for hydrocarbons that can describe chemical bond breaking [11], which is based on the bond order/bond distance relationship introduced by Tersoff. However, the van der Waals and Coulombic interactions are not included in this force field, which limits the method to give a full description of breaking and forming bonds during complex chemical reactions. Recently van Duin and co-workers developed a reactive force field (ReaxFF) which includes van der Waals and Coulombic interactions explicitly at each iteration during the MD simulation [12]. The parameters in the force field are derived from an extensive training set of geometrical and energetic data that were calculated from QM calculations. As a result, the ReaxFF force field has good transferability and can be used to describe complex chemical reactions in a wide range of systems including reactions of energetic materials [13], thermal decompositions of polymers [14], coal [15,16], catalysis [17–19] and so on. Particularly, ReaxFF simulations have been reported to be applied successfully for studying reactive processes of nitrogen-containing compounds, including RDX [20] and condensed-phase nitromethane [21]. With ReaxFF MD, the time evolution tendency of products and intermediates from chemical process can be observed directly, and analysis of trajectories from simulations showed that pathways predicted by ReaxFF were in agreement with QM results and available experimental data. However, to the best of our knowledge, no reported investigations have addressed the effect of the pyrolysis and combustion conditions on the nitrogen transformation kinetics by using ReaxFF MD.

In this paper, we aim to uncover the effects of different factors (temperature, density/pressure, heating rate and oxygen ratio) on the

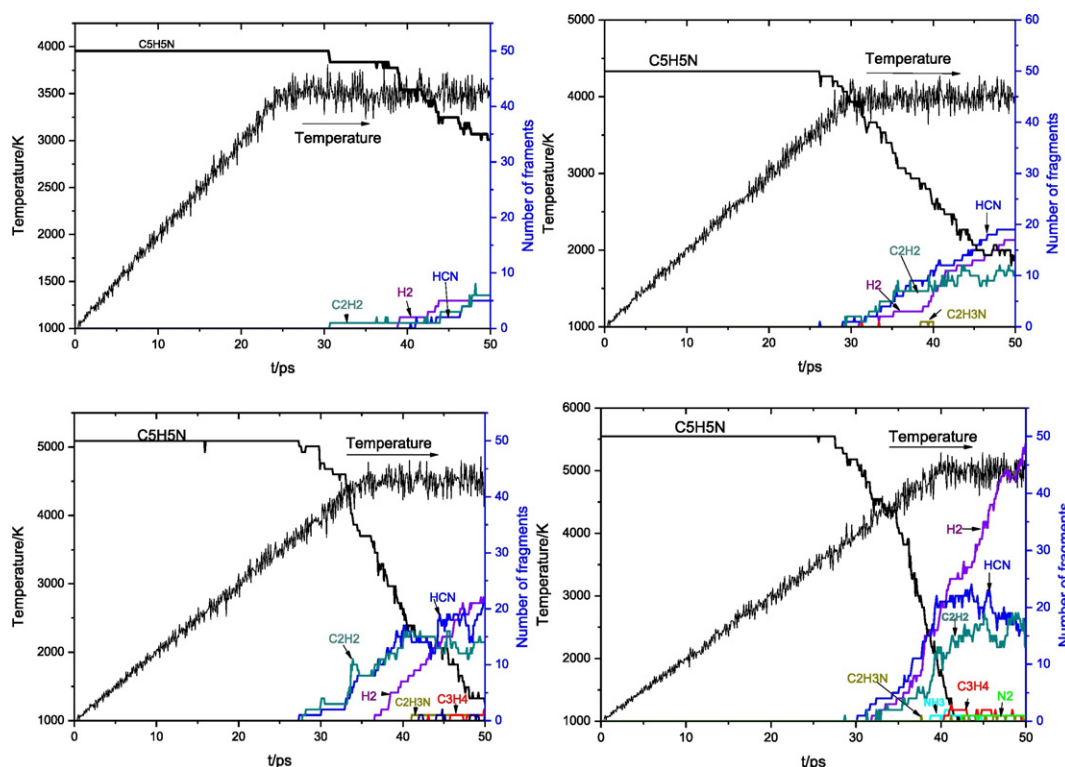


Fig. 1. Time evolution of main compounds at different final temperatures.

Download English Version:

<https://daneshyari.com/en/article/6476478>

Download Persian Version:

<https://daneshyari.com/article/6476478>

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