



## Full Length Article

# Prediction of ethylene and propylene release during coal pyrolysis with modified CPD model

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## ABSTRACT

The well-known CPD model (chemical percolation model for devolatilization) is further developed to simulate typical volatile organic compounds (ethylene and propylene) release during coal pyrolysis. A look-up table of ethylene corresponding to the extent of light gas release is constructed and added to the light gas sub-model. With the updated CPD model, the mass fractions of the released ethylene from the flash pyrolysis experiments in a Currie Point pyrolyzer are successfully predicted for a set of coals under different pyrolysis temperatures. The results suggest that, the predicted ethylene yields are accurate when the coal is located in the vicinity of the reference coal in the interpolation mesh and the secondary reactions are insignificant. The predicted release of ethylene during the pyrolysis of an anthracite coal and a bituminous coal using a tube furnace also compares well with the available experimental data. It reveals that as long as the temperatures of coal/char particles are estimated accurately, the prediction of the ethylene mass fraction can be applied to a wider range of heating rates. In addition, the propylene is estimated based on the time-resolved profiles obtained from an online single-photon ionization time-of-flight mass spectrometry (SPI-TOFMS) and the main pyrolysis products acquired from an offline gas chromatograph/mass spectrometry (GC/MS). Accordingly, the prediction of propylene is carried out. The consistent yields of ethylene and/or propylene at identical pyrolysis temperatures, regardless of coal types, indicate that the evolution of these light gases is insensitive to coal type. When the ratio of the final mass fraction between ethylene and propylene is fixed to be 1.1, the predicted release profiles of these compounds correlate well with the published experimental data, indicating the effectiveness of the modified CPD model.

## 1. Introduction

Coal is likely to remain as a dominant energy and power supply worldwide for at least another decade [1]. Coal combustion produces a range of pollutants, including SO<sub>2</sub>, NO<sub>x</sub>, particulate matter (PM), mercury (Hg) and volatile organic compounds (VOCs). While extensive research has been done on the formation mechanisms and control strategies of other pollutants [2–8], little has been conducted on VOCs, which have significantly adverse impacts on human health and environment [9]. VOCs refer to the organic compounds that have vapor pressures higher than 0.01 kPa under room temperature and can participate in atmospheric photochemical reactions, including aliphatic and aromatic hydrocarbons, and oxygenates. They are produced from coal pyrolysis and mostly oxidized during combustion process. However, some VOCs may still emit to the atmosphere because of poor mixing of coal and air during the combustion process. In particular, the commonly-employed deep low NO<sub>x</sub> combustion technology, which uses lower stoichiometric ratio in the main combustion zone to depress NO<sub>x</sub>

formation, favors the emission of VOCs [10].

Pyrolysis (devolatilization) is the first stage of coal combustion. It is a process that the bridges linking the aromatic clusters of coal matrix break, forming light gases, heavy gases and char [11]. The light gases include water, carbon dioxide, carbon monoxide, methane, ethylene, ammonia, SO<sub>2</sub> and COS [12–16]. The heavy gases, also named as tar, are large molecules, which are normally condensable at room temperature. The VOCs released during coal pyrolysis consist of some organic light gases as well as some light tar such as benzene, toluene and xylene. The pyrolysis process is strongly dependent on temperature, pressure, heating rate, coal type, and particle size. To develop technologies for eliminating or reducing VOC emissions, a thorough understanding of the formation mechanism of VOCs is essential.

To accomplish this, modeling work is essential, for the reason that it is relatively inexpensive and less time-consuming compared to experimental work. It is also important for accurately predicting coal combustion in a computational fluid dynamic (CFD) framework. Current coal pyrolysis models, including the relatively mature CPD (chemical

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percolation devolatilization) model we used, are able to predict the yields of total light gases, tar and char, as well as their dependence on coal type and pyrolysis conditions based on the chemical structure of coal. However, they are unable to predict the release process of individual organic gases other than methane (See Section 2.1 for details).

Thus, this paper aims to predict the production of ethylene and propylene, as typical VOCs, via a modified CPD model by using the previously proposed interpolation method [17]. A look-up table of ethylene corresponding to the extent of light gas release was first constructed and then added to the light gas sub-model based on the existing experimental data [12,15]. The modified model was well validated against another set of experimental data on the pyrolysis of coals of different ranks at different temperatures, using a Currie Point pyrolyzer and our previous measurements on the pyrolysis of anthracite and bituminous coals in a tube furnace, using both the online single-photon ionization time-of-flight mass spectrometry (SPI-TOFMS) and the offline gas chromatograph-mass spectrometry (GC/MS) [18].

## 2. Methods

### 2.1. Coal pyrolysis models

Instead of the early pyrolysis models which were purely empirical and were not able to predict the species of the pyrolysis products [11,19,20], the currently used pyrolysis models, including the FG-DVC (group-depolymerization, vaporization and cross-linking) model [14,21], the FLASHCHAIN (distributed-energy chain) model [22–24], and the CPD (chemical percolation devolatilization) model [25–27], are all based on the knowledge of the coal chemical structure and use a statistical network model to represent the highly non-linear relationship between bridge scission and tar release. Therefore, these models are capable of predicting the light gases and tar yield as well as their dependence on the temperature, pressure, heating rate, residence time, coal type and particle size [11]. For example, in the CPD model developed by Grant et al. [25], the chemical structure of coal is expressed by clusters of aromatic rings connected by labile (breakable) bridges, such as ether bond, sulfur bond, thioether bond and aliphatic bridges/rings. Five parameters derived from solid state nuclear magnetic resonance ( $^{13}\text{C}$  NMR) measurements are used to describe the unique chemical structure of each coal type, which are the average molecular weight of each aromatic group ( $M_{cl}$ , including bridges and side chains), the average molecular weight of each bridge or side chain ( $m_\delta$ ), the coordination number ( $\sigma + 1$ ), the initial proportion of intact bridges ( $p_0$ , it is the ratio of the number of bridges to the number of bridges and side chains), and the initial proportion of char (unbreakable) bridges ( $c_0$ ). A set of parameters are used to simplify the pyrolysis process to a series of bond-breaking processes (see Fig. 1). The rate constants of this series of reactions are independent of coal type, thus by entering the coal structural parameters, the kinetic parameters and the particle time–temperature profile, similar differential equations can be established for different coals. And the changes of labile bridge ( $L$ ), char bridge ( $c$ ), side chain ( $\delta$ ), light gas ( $g_1, g_2$ ) and the mass fractions of the pyrolysis products, including light gas ( $f_{gas}$ ), tar ( $f_{tar}$ ) and char ( $f_{char}$ ) can be achieved easily by applying the steady-state approximation to the bridge intermediate ( $L^*$ ) and solving the differential equations. The

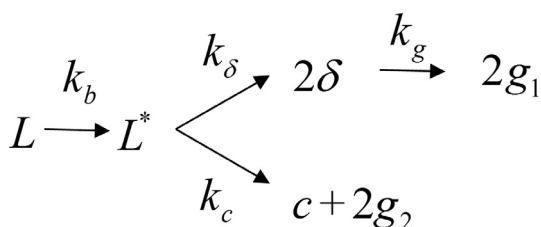


Fig. 1. Reaction scheme of the CPD model.

percolation lattice statistics is used to determine the non-linear relationship between the bridge scission and tar release. Both vapor–liquid and cross-linking mechanisms are used to determine the distribution of liberated fragments. Fragments with low molecular weight can vaporize as tar, while heavy components defined as metaplast may not vaporize and may be reattached to the char matrix in solid phase, which is based on molecular weight and temperature and calculated with an empirical vapor pressure formula [27].

Although the model is excellent to predict the yields of total light gases, tar and char, as well as their dependence on coal type and pyrolysis conditions, it is unable to directly predict the yields of individual VOCs. To overcome this issue, Zhao et al. [17] proposed an interpolation method using O/C and H/C molar ratios as rank indicators, which was attached to the FG-DVC model to calculate the mass fraction of some light gas components including  $\text{H}_2\text{O}$ ,  $\text{CO}_2$ ,  $\text{CO}$  and  $\text{CH}_4$ . This method was also adopted by Genetti [28] to enable the CPD model to predict the yields of the four aforementioned light gases. However, the yields of the other VOCs such as light olefins and light tar are not considered, although some of them are at least equivalently important as methane.

### 2.2. CPD model modification

In this work, the interpolation method proposed by Zhao et al. [17] was adopted to calculate the release of ethylene based on the CPD model. The core of this approach is to establish a complete database of the reference coals for ethylene release. Previous studies [17,28] suggest that the composition of light gases appears to correlate well with coal type and the extent of total light gas release. Thus, a look-up table was created accordingly based on the experimental data [12,15] on the pyrolysis of 12 coals, as shown in Table 1. Each row of Table 1 represents a reference coal, while each column from 1 to 12 denotes the mass fraction of ethylene in total light gas at various extents of total light gas release. The value between columns can be calculated through linear interpolation. These coals were used as reference coals because their  $^{13}\text{C}$  NMR structural parameters are available and the yields of ethylene from pyrolysis were reported. Their proximate and ultimate analyses are compiled in Table 2 and their positions in the interpolation mesh of van Krevelen diagram are presented in Fig. 2 by black dots.

The mass fraction of  $\text{C}_2\text{H}_4$  in total light gas for a test coal (coals used for validating the prediction of ethylene) was calculated from Table 1 by the interpolation method. As shown in Fig. 2, the method used the O/C and H/C molar ratios of a set of reference coals to form a triangular mesh on a diagram referred to as Van Krevelen diagram. For an unknown coal, its position in the diagram can be determined by its elemental molar ratios. If the coal is located within a triangle of the reference coals, its parameters are determined by interpolation from the corresponding parameters of the adjacent three reference coals as well as the area of the triangle. Otherwise, the parameters of this coal are estimated from the corresponding parameters of the nearest reference coal by extrapolation.

Updating the light gas sub-model by adding the calculation of ethylene enables the CPD model to predict the mass fractions of ethylene in total light gas produced from pyrolysis of any coal, expressed as g of ethylene per g of total light gas, and thus the mass fraction of ethylene in the original coal, expressed as g of ethylene per g of coal (daf). The prediction was validated using the experimental data on the pyrolysis of a set of coals under various pyrolysis temperatures in a Currie Point pyrolyzer [29,30] (Sections 3.1 and 3.2), and our previous work on the pyrolysis of an anthracite and a bituminous coal under different pyrolysis temperatures in a tube furnace [18] (Section 3.3). The proximate and ultimate analyses of test coals are listed in Table 2, with their O/C and H/C molar ratios marked in Fig. 2 as orange triangle symbols.

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