

Detailed Reaction Mechanisms of Coal Volatile Combustion: Comparison between Without Soot and Soot Models

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New advance in instruments, computers and numerical methods have greatly increased in order to conduct the research efforts in coals. For numerical research work, Computational Fluid Dynamics (CFD) plays a key role to explain these developments of different coal chemistry steps including devolatilisation, volatile combustion and reforming, char oxidation and char gasification. In this research work, the authors investigate numerically the primary reactions of coal volatiles including the soot formation mechanism. Comparison between detailed mechanism without soot and soot model is provided. The effects of O₂/CO₂ concentration for the soot model for O₂/CO₂ gasification are also reported.

1. Introduction

The substantial worldwide attention is being focused on cleaner and more efficient use of coals. Coal gasification process, in particular, allows an efficient use of this energy source with a low environmental impact.

The volatile components of the coal diffuse into the gas stream when coal heats up. Volatiles generally are composed of H₂, H₂O, CO, CO₂, hydrocarbon gases, hydrocarbon liquids, and polycyclic aromatic hydrocarbons (PAHs). Most of the compounds will continue to react to produce successively lighter gases as the more complex molecules decompose, eventually forming CO₂ and H₂O provides if the sufficient oxygen is available. PAHs are products of primary pyrolysis and PAHs are precursors of soot in secondary pyrolysis. The conversion of PAHs into soot during secondary pyrolysis is accompanied by release of CO and H₂.

In the previous work¹⁾, the detailed reaction mechanism of coal volatiles without soot formation that consists of 255 chemical species and 1095 elementary reactions has already validated with the experimental results. In this research work, the authors investigate numerically the detailed reactions of coal volatiles including the soot formation under condition for thermal decomposition/pyrolysis, partial oxidation and O₂/CO₂ gasification. Comparison between detailed mechanism without soot and soot models is provided. We focus the further discussion for only condition of O₂/CO₂ gasification since coal combustion with O₂/CO₂ is one of several promising new technologies associated with CO₂ reduction in the atmosphere. The effects of O₂/CO₂ concentration for the soot model to analyze the combustion components are investigated and also reported in this paper.

2. Mathematical Model

A plug flow reaction model for reaction of coal volatiles is developed for pyrolysis, partial oxidation and O₂/CO₂ gasification with input of major species in the Table 1. Simulation is conducted inside the reactor of 28 mm in diameter and 1200 mm in length. The plug flow reactor model can be used to model multiple reactions as well

as reactions involving changing temperatures, pressures and densities of the flow. In the ideal tubular reactor, which is called the plug flow reactor, there is assumed to be complete mixing perpendicular to the direction of flow (i.e. the radial direction) and no mixing in the direction of flow. In the plug flow, the residence time in the reactor is the same for all elements of fluid. It means that the reaction proceeds as the reactants in a plug progress along the reactor tube. There is ideally no back-mixing in the reactor and there exists a uniform temperature, pressure and velocity profile across the radius.

Table 1 Input data for major species in mass fraction

| | Pyrolysis | Partial Oxidation | O ₂ /CO ₂ Gasification |
|-----------------|-----------|-------------------|--|
| H ₂ | 0.0005026 | 0.0005022 | 0.0004984 |
| CO | 0.002849 | 0.002846 | 0.002825 |
| CH ₄ | 0.002132 | 0.00213 | 0.002114 |
| O ₂ | 0 | 0.007354 | 0.007299 |
| CO ₂ | 0.002239 | 0.002237 | 0.02241 |

All the gas phase and surface phase reactions are considered in this mathematical model are as follows:



The lower case letters (*a*, *b*, *c* and *d*) represent stoichiometric coefficients, while the capital letters represent the reactants (*A* and *B*) and the products (*C* and *D*). *k* is the proportionality constant called the specific rate coefficient for the above reaction and follows the Arrhenius equation.

$$k = A_f T^\alpha \exp \frac{-E}{RT} \quad (2)$$

where *A_f* is a frequency factor (mole-m-sec-K), *T* is temperature (K), *α* is temperature exponent, *E* is activation energy (J/mole) and *R* is the gas constant (J K⁻¹ mole⁻¹).

2.1 Without soot formation

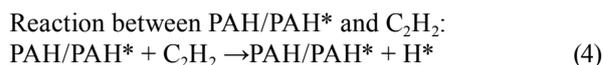
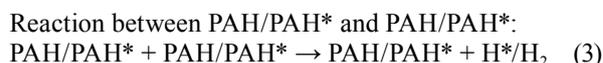
The kinetic mechanism of formation PAHs and their radicals in premixed flames that consists 255 chemical species and 1095 elementary reactions²⁾ is considered to carry out the numerical simulation. There is no particle species and surface reaction in the detailed mechanism without soot formation. Only gas phase reactions are considered to this mechanism.

2.2 Soot model

Nucleation is the process of forming new condensed-phase particles from a continuous phase, such as gas and vapor. Particle nucleation is the most important step in soot formation and results in generation of the solid particles. It is irreversible and all reactants must be gas phase species. The PAH molecules first grow into planar molecules while simultaneously reacting with the gas phase species and colliding with other PAH molecules to form large molecules. The PAH compounds having large molecular mass about 2000 is considered soot and the reaction mechanism is described from benzene to coronene (C₂₄H₁₂). Then, considering the concentration of H₂, CO, CO₂ and soot in the outlet of the reactor the authors define which model has significant regarding energy and environmental issues.

This soot model consists of the following principal processes: initial aromatic ring formation during small hydrocarbon oxidation, formation of larger PAH, particle nucleation/inception through coalescence of PAHs, particle growth and particle oxidation. Particle oxidation produces the lower PAHs. The reaction mechanism

developed in this model consists of 276 species, 2158 conventional gas phase reactions and 1635 surface phase reactions⁴⁾. Based on the detection of compounds containing more than 160 carbon atoms is considered as a particle⁵⁾, the remaining all aromatic compounds are considered as PAHs in this soot model. The main typical reactions considered in this model are:



where * indicates a radical entity.

3. Results and Discussion

Both mechanisms have been simulated for three different environments of pyrolysis, partial oxidation (O₂) and O₂/CO₂ gasification at a temperature of 1273K and a pressure of 0.1MPa in a plug flow reactor. Fig. 1 shows the comparisons of the relative value of outlet concentration for some species of the experiment and simulation results. The simulation shows a good agreement with the experiment, although the each result also provides the deviation. PAHs are defined as all aromatics from benzene (C₆H₆) to soot particles. Since soot particles are the large PAHs, total of PAHs for soot

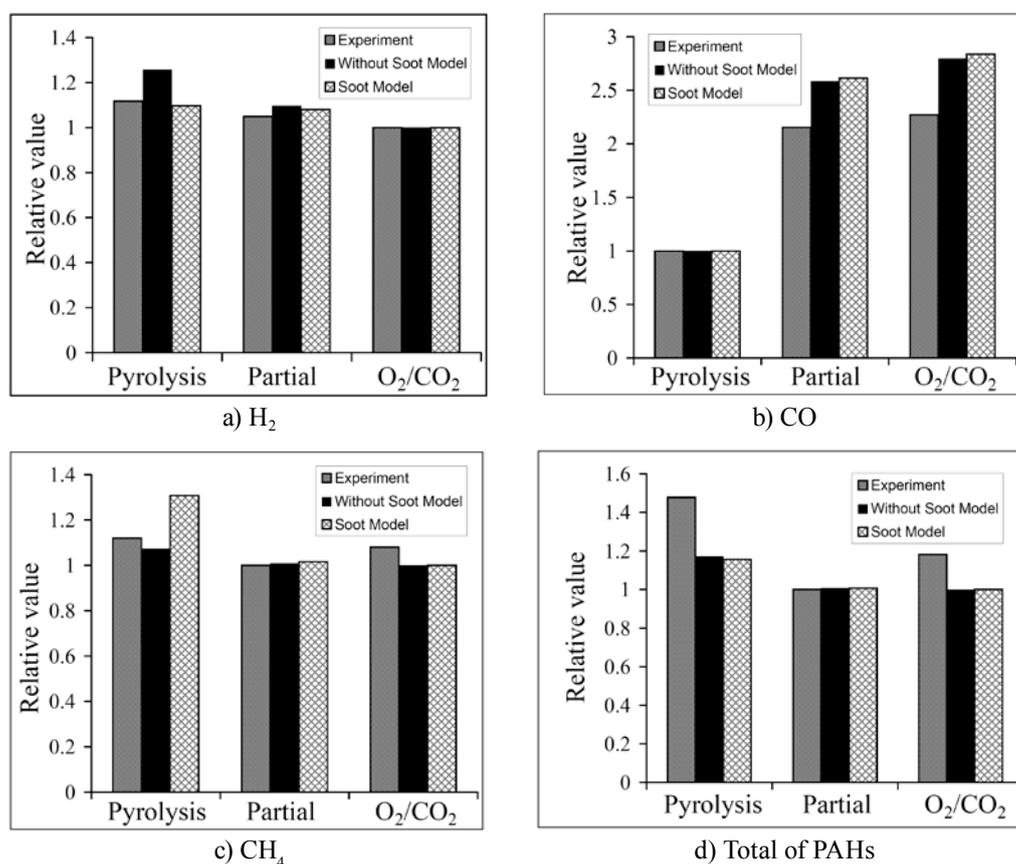


Fig. 1 Comparison of product concentrations between experiment and models.

model explained in the figure includes soot particles.

Fig. 2 shows the comparison of concentration profiles of the major combustion species for the mechanism with soot and without soot at 1273K, 0.1 MPa for O₂/CO₂ gasification. It is seen in Fig. 2-a that the both soot and without soot models provide different concentration profiles for all major combustion species. The concentration of CH₄ decreases for soot model since it is a source of PAHs in order to form the soot. The increase in concentrations of H₂ and CO in the soot model is due to the formation of CO and H₂ from the oxidation of soot. As illustrated in the Fig. 2-b, the significant difference

of PAH concentration is occurred for between the soot and without soot models. PAHs increase in the without soot model due to reactions of smaller hydrocarbons/aromatics that produce larger aromatics. Contrarily, the PAHs concentration for the soot model decreases since a number of PAHs produce the soot. Because of soot oxidation, the soot is almost zero but some PAHs appear at this condition.

Fig. 3 depicts the concentrations at higher temperature 1473K and pressure of 0.1MPa for comparison of soot model and without soot formation for O₂/CO₂ gasification. O₂/CO₂ gasification enables to provide more CO₂. The

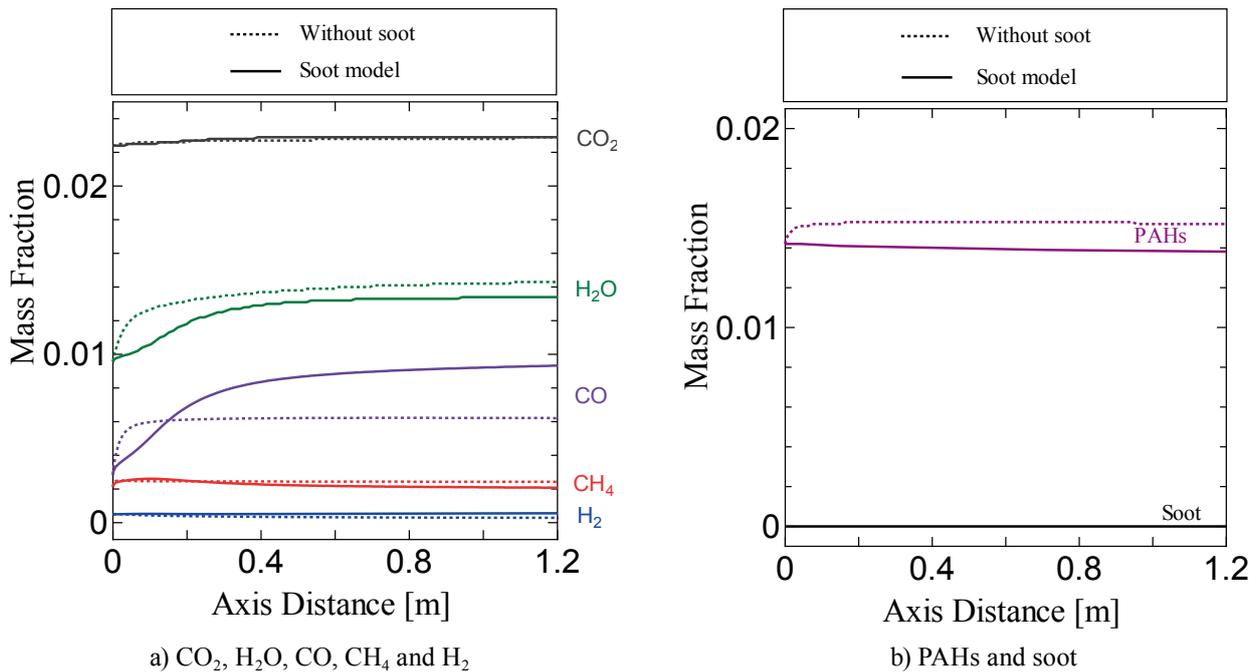


Fig. 2 Comparison between the mechanism without soot and soot models at 1273K, 0.1 MPa.

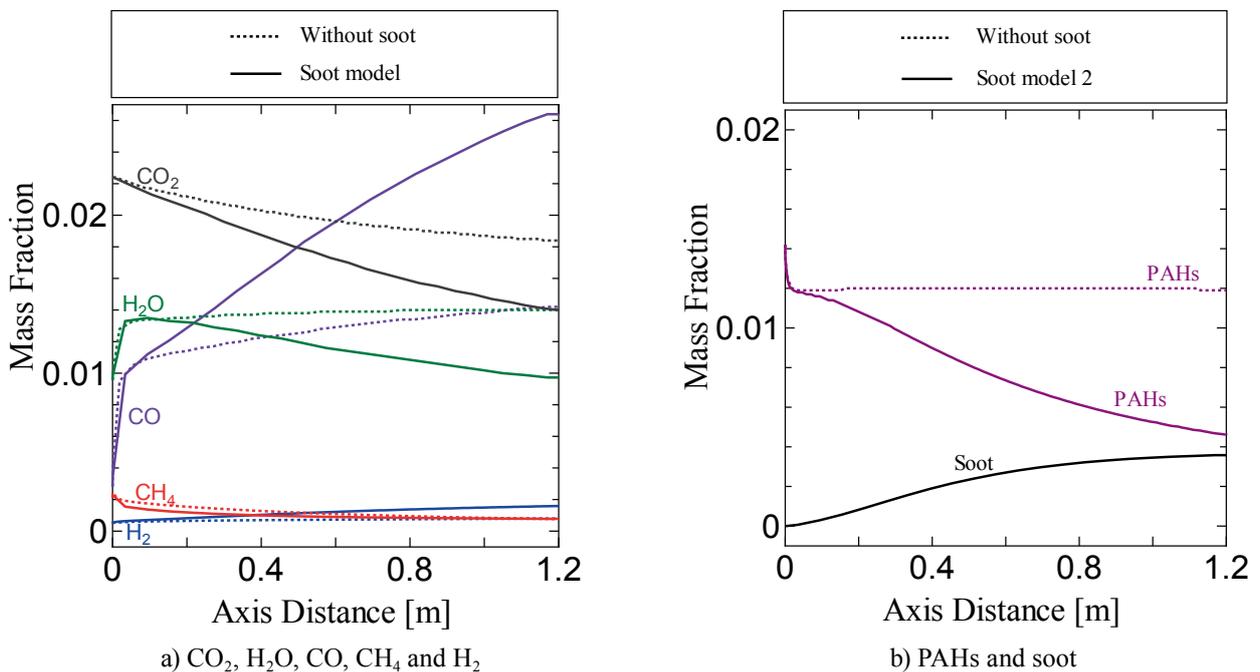


Fig. 3 Comparison between the mechanism without soot and soot models at 1473K, 0.1 MPa.

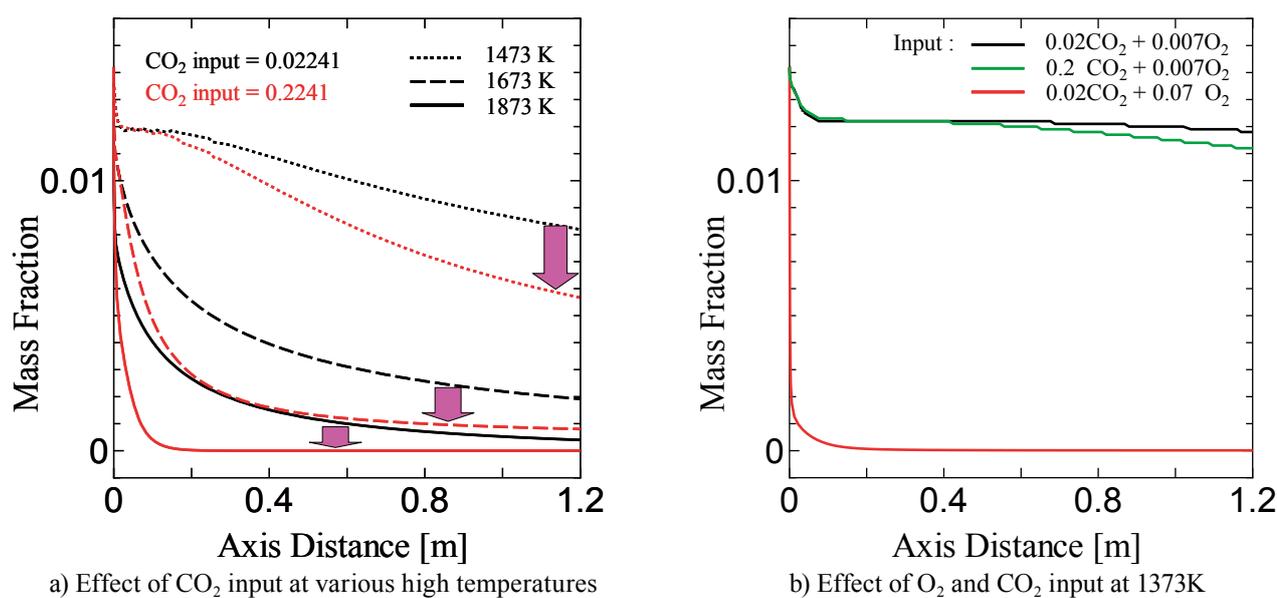


Fig. 4 Concentration profiles of total of PAHs and soot compound at 0.1 MPa for soot model.

concentration of CO increases intensively for soot model at higher temperature due to CO₂ decomposition to CO and oxygen radicals. Moreover, as also presented in the Fig. 3-a, the soot model provides the increase in H₂ significantly at this condition. As illustrated in the Fig. 3-b, the soot model also provides the less concentration of PAHs and soot due to particle oxidation.

Considering the advantages of the increasing in CO, H₂ and the decreasing in soot, the previous research work has reported that the soot model provides the significant effect at high temperatures and high pressures²⁾. Under the environment of O₂/CO₂ gasification, we investigate effect of CO₂ inputs in total of PAHs and soot compound at various high temperatures for soot model.

Fig. 4-a shows effect of CO₂ input at various high temperatures of 1473K to 1873K for soot model under O₂/CO₂ gasification. At high temperature, the increase of CO₂ input for 10 times of the default concentration provides significant effect to reduce the total PAHs and soot. The more availability of CO₂ at high temperature enables the following reactions to occur.



As a result, the particle oxidation in the equation 5 continues in order to reduce the total PAHs and soot. It means that it is necessary to maintain high temperature if CO₂ concentration increases. Higher temperature provides an advantage of PAHs and soot reduction (see again Figs. 2 and 3).

Fig. 4-b presents the effect of CO₂ and O₂ inputs at lower temperature of 1373K for soot model under O₂/CO₂ gasification. At the temperature, it has been found that the increase of O₂ input for 10 times of the default concentration can completely reduce the total of PAHs and soot. But, the increase of CO₂ input cannot do it. At that temperature, it is due to the domination of smaller

hydrocarbon addition with PAHs/soot rather than the PAHs/soot oxidation. Also, the oxidizing species of O* or OH* are insufficient at low temperature.

4. Conclusions

The detailed mechanism of coal volatile combustion has been investigated numerically. The simulation shows a good agreement with the experiment. The mechanisms without soot formation and soot models in environment of O₂/CO₂ gasification have been compared to analyze the major combustion species. Considering the advantages of the increasing in CO, H₂ and the decreasing in PAHs/soot, CO₂ concentration input has large effect on PAHs/soot reduction at higher temperatures, but O₂ can provide the significant effect of PAHs/soot reduction at low temperature.

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