Numerical investigation of reaction kinetics of coal volatiles with a detailed chemistry and its simplification

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Abstract
Reaction kinetics of coal volatile were numerically investigated based on analyses during reaction mechanism reduction procedure in detail in this paper. Computation on a closed homogeneous reactor model was performed to clarify important chemical species and their reaction pathways with evaluating the capability of prediction of ignition delay time and chemical species concentration under a wide range of equivalence ratios and temperatures. The kinetics of large hydrocarbons such as polycyclic aromatic hydrocarbons (PAH) that comprise a large portion of combustion features for complex hydrocarbon materials was focused on in a coal flame. The data computed here was analyzed through the combined process of the directed relation graph with error propagation and sensitivity analysis (DRGEP/SA) and the computational singular perturbation (CSP) that can evaluate the roles of each species and reaction pathway respectively in the chemical system. Results show that hydrocarbons such as aromatics, methyl and ethyl groups play important role in the ignition and flame propagation processes. Finally, the skeletal mechanism including 64 species and 150 reactions was derived from the detailed mechanism that consists of 257 species and 1107 reactions with in 30% error in the prediction of the ignition delay time and the mole fractions of major species in the propagating flame.

Key words : Coal combustion, Volatile matter, Reaction kinetics, Mechanism reduction, Skeletal mechanism

1. Introduction
Many experimental approaches have been performed to clarify the combustion physics in the coal flame (Makino and Kimoto, 1994; Yi-guo and Jian-ming, 2011; Moon et al., 2013; Hwang et al., 2005; Hayashi et al., 2013). Although the experimental researches have brought enormous advances in understanding the combustion field, our knowledge of the physics taking place within the system is limited due to the difficulties in the direct observation of this two-phase reacting flow. As an alternative, a numerical simulation is used to make up for the experiments (Kurose et al., 2007; Hashimoto et al., 2007; Watanabe et al., 2009b; Kurose et al., 2009; Muto et al., 2015; Franchetti et al., 2013). In general, a simple chemical kinetic mechanism namely a global reaction mechanism has been used in the simulation. Watanabe and cooperators have performed LES of a lab-scale burner and a semi-industrial-scale furnace with the CxHyOz postulate substance two-step global reaction mechanism (Watanabe et al., 2009b; Kurose et al., 2009; Muto et al., 2015). Franchetti et al. (2013) also employed the CxHyOz postulate substance mechanism to perform a LES of a pulverized coal jet flame. While these studies give us the detailed information of the coal flame rather than the experiments, it is still difficult to represent more complex physics such as ignition, formations of nitrogen oxide and sulfide, tar decomposition, polymerization and soot formation which are generally observed in the coal flame and are typically critical criteria to operate the coal-fire plants. The gas phase chemistry concerning devolatilized substances from coal particles that generally consist of light and heavy gases, tars and soot, should be paid attention to understand such complex physics.

Recently, especially with great progress of laser diagnostics, such complex physics in the coal flame has been gradually revealed. Hwang et al. (2005) applied LDV, SDPA and Mie scattering to clarify the particle dispersion in a
coal coaxial jet flame and discussed the flame structure with the OH-LIF data. Hayashi et al. (2013) investigated the soot formation characteristics in the coaxial jet flame with the simultaneous measurement of Mie scattering and LII signals. These findings encourage us to implement the detailed chemistry in the CFD in order to predict the detailed flame structure for the enhancement of CFD capability.

However, a direct application of a detailed chemical mechanism with hundreds of chemical species and thousands of elementary reactions on a large-scale simulation is too expensive in terms of the computational cost. Therefore, it should be useful to generate a reasonable downsized mechanism. Many research groups have performed reduction of detailed mechanism and proposed the simplified versions (Nagy and Turanyi, 2009; Luo et al., 2012; Lu and Law, 2008; An et al., 2014; Wang et al., 2013). However, the number of simplified mechanisms for the coal flame is very limited due to the wide range of equivalence ratio and the wide variation of volatiles composition generally appear in the coal flame and it is difficult to distinguish the important chemical species and reactions in the huge reaction system.

In the present study, important chemical species and crucial reaction pathways in combustion of coal volatiles whose composition is estimated in a typical rapid pyrolysis condition by a coal chemical structure analysis for a bituminous coal of fuel ratio 2.0 (Umemoto et al., 2012, Umemoto et al., 2013) are analyzed in terms of equivalence ratio and temperature using the detailed mechanism. To clarify the important chemical species and reaction pathways, the mechanism reduction techniques (Lu and Law, 2005; Pepiot-Desjardins and Pitsch, 2008; Niemeyer et al., 2010; Lu and Law, 2001; Lu and Law, 2006) are used and the prominent parts in the reaction system are discussed. Finally, a skeletal mechanism is generated as a result of the analysis.

2. Kinetic analysis and simulation

2.1 Detailed mechanism for reaction of coal volatile

In this study, a detailed chemical mechanism proposed by Richter and Howard (2002) that includes 257 chemical species and 1107 elemental reactions is employed. This mechanism was initially developed for benzene oxidation, and then extended to larger aromatic materials up to the coronene (C90H50) in atmospheric pressure condition. Since many researchers have computed coal volatile and syngas flames on the simplified 0D or 1D models and validated this mechanism in comparison with the experiment (Norinaga and Hayashi, 2010; Wijayanta et al., 2010; Wijayanta et al., 2012; Appari et al., 2015), it can be thought that it is appropriate to employ it as a reference mechanism in this study.

2.2 Kinetic analysis

A mechanism reduction technique should be a powerful tool to analyze the importance of each chemical species and reaction pathway in the entire reaction network. In the present study, the direct relation graph with error propagation and sensitivity analysis (DRGEPSA) and the computational singular perturbation (CSP) are used to identify the important chemical species and reaction pathways in the complex reaction system(Niemeyer et al., 2010; Lu and Law, 2001).

2.2.1 DRGEPSA

DRGEPSA proposed by Niemeyer et al. (2010) consists of two separated parts, DRGEP (Pepiot-Desjardins and Pitsch, 2008) and sensitivity analysis. DRGEP can classify effective species on the important reaction substances such as fuels and oxidant from all species in the detailed mechanism by quantifying the connection between two species as expressed in Eq. (1). For example, the connectivity of species B with species A is calculated as,

$$r_{AB} = \frac{[\nu_{A,j}^i \omega_{A,i}^i \delta_{A,i}^i]}{\max (P_A C_A)}$$

where $i$ is $i$th reaction and $N_r$ represents the total number of reactions. $\omega_{A,i}$ and $\nu_{A,j}$ mean the net reaction rate and the stoichiometric coefficient of species A in the $j$th reaction. $P_A$ and $C_A$ indicate production and consumption factors calculated and $\delta_{A,i}$ is the switch factor of species B. The connectivity between all species pairs is calculated by Eq. (1), then a graph searching begins to find out the effective species for the target species which are selected by operators using the revised depth-first-search (RDFS) algorithm proposed by Lu and Law (2006). This method searches all path-dependent values represents error propagation as below.
$$r_{AB,p} = \prod_{i=1}^{n-1} r_{Si|i+1},$$

where $n$ is the total species number between the target species A and a certain species B to calculate the $r_{AB}$ in the path $p$. $S_i$ and $S_{i+1}$ indicate the interaction value of species pairs located between the two species A and B. The final connectivity between species A and any species B can be defined as the maximum value among all path-dependent calculation results.

The sensitivity analysis is performed for further elimination of unimportant species from the DRGEP result. The sensitivity analysis is conducted using a special value evaluated by an error induced by the removal of each species from the detailed mechanism and the DRGEP result as presented in the Eq. (3) (Niemeyer et al., 2010).

$$\delta_S = |\delta_{S,ind} - \delta_{DRGEP}|,$$

where $\delta_{DRGEP}$ is the error of the first reduced mechanism when a species is removed temporarily from the first process, DRGEP. And the $\delta_{S,ind}$ is an error of the detailed mechanism induced by the elimination of a species S at a time. DRGEP-SA can be regarded as a chemical species-based analysis.

### 2.2.2 CSP

CSP proposed by Lu and Law (2001) is a powerful and efficient method to classify unneedful parts of reactions. This method separates redundant reactions that have limited effect on the reaction characteristics using an importance index, Eq. (4).

$$I_{k,i} = \frac{|v_{k,i}|}{\sum_{j=1,0}|v_{k,j}|}$$

where $I_{k,i}$ is the importance index of $i$th reaction to the production rate of the $k$th species, $v_{k,i}$ stoichiometric coefficient of the $k$th species in the $i$th reaction. $N$ is the number of reactions, and $\omega_i$ is the net rate of the $i$th reaction. The calculated value indicates the normalized contribution of a reaction to the production rate of a species. The importance of a certain reaction is calculated in all time steps for every species in the mechanism, then the maximum value is defined as the representative index for the reaction. CSP can be regarded as a reaction-based analysis.

### 2.2.3 Evaluation of error

Through the iterative calculation in a range of threshold values, the optimal condition will be selected as the representative error. Most cases have similar steps. The procedure is conducted with minimum considered threshold value, for instance $1.0 \times 10^{-5}$ in the DRGEP process, and generates a temporary skeletal mechanism. For the confirmation of the reliability of this mechanism, errors are calculated under all operating conditions, and the maximum value is defined as the representative error of this mechanism. Two errors are used for this process. First is the ignition delay time calculated by the following equation.

$$\delta_{skel} = \max_{k \in [0]} \frac{t^{k}_{det} - t^{k}_{skel}}{t^{k}_{det}},$$

In the above equation, $t^{k}_{det}$ and $t^{k}_{skel}$ are the ignition delay time of the detailed mechanism and the skeletal mechanism respectively under the condition, $k$. The second consideration is the error of the mole fractions of the target species supposed by Nagy and Turanyi (2009) as presented at the following equation.

$$\delta_{i}(t_j) = 2 \frac{e^{skel}(t_j) - e^{det}(t_j)}{e^{skel}(t_j) + e^{det}(t_j)},$$

where $\delta_i$ and $e_i$ mean the local error and the mole fraction of target species $i$ at the time $t_j$ respectively. The maximum value from all target species and times is defined as the error of mole fractions of this condition. The representative error of a skeletal mechanism is decided to the maximum value among the maximum error of the ignition delay time and the maximum error of mole fractions in all test conditions in a certain threshold value. If the maximum error is
lower than the allowed error, the next threshold value can be applied until the error of skeletal mechanism reaches the limit.

2.2.4 Computational details

The closed homogeneous reactor model of CHEMKIN-PRO is used to calculate a reaction of volatile matters in coal combustion. Table 1 shows the gas composition used as volatile matter that is referred from Umemoto et al. (2012; 2013). The composition is estimated in a process of rapid pyrolysis of a bituminous coal whose fuel ratio is 2.0 for a mean heating rate for a mean particle size by analyses of 13C-NMR and Curie point pyrolyzer. The composition of the gas mixture for the homogeneous model is volatiles/O_2/N_2 = 1.0/1.0/170. The chemical species in Table 1 are also the target species which should be defined prior to DRGEP and set on the top vertex in the graphs. The reaction time for all cases is set to 3 sec. The cases are in a wide range of conditions in which 0.5 ~ 1.5 in the equivalence ratio, 1,100 ~ 2,000 K in initial temperature, 1 ~ 2 atm in pressure, totally 126 conditions are examined. These conditions should cover most of all reacting conditions in an actual coal flame. The ignition delay time and the final composition of the product gas computed by the mechanism generated in each step are paid attention to be compared with the detailed mechanism to evaluate the error. The laminar flame speed is not focused in this study, because one of the major issues for a coal flame is the ignition behavior in various operating conditions and the burning velocity in an actual coal (non-premixed) flame, namely turbulent burning velocity, should differ from the laminar flame speed.

| Table 1. Gas composition examined. |
|-----------------------------------|
| Species | wt % |
| H_2O   | 6.5  |
| CO     | 26.9 |
| CO_2   | 9.7  |
| CH_4   | 14.0 |
| C_4H_6 | 5.7  |
| C_10H_8| 2.5  |
| C_14H_10| 34.7 |

3. Results and discussion
3.1 Chemical species-based analysis

Figure 1 shows the relationship between the number of species and the error of the ignition delay time and the mole fractions of target species with varying the threshold value set in DRGEP analysis. Here, the error in Fig. 1 represents the maximum error calculated under 126 test conditions with varying the equivalence ratio, temperature and pressure on each threshold value. 97 species are comfortably assorted into a redundant part from the first step at the threshold value of 1.0×10^{-5}. The number of species and the error maintain the level until the threshold value of 1.0×10^{-4}, and then, more species can be separated from the detailed mechanism with the same level of the error until 8.0×10^{-4}. During this procedure it is found that some isomers of high-carbon species such as polycyclic aromatic hydrocarbons (PAH) do not influence on the reaction field and the mole fractions of major species distribution very much. It is also revealed that some radicals which live in short time have limited effect on the ignition process. To clarify their role in the ignition process in detail, all ignition delay time and the mole fractions of the important species are checked. Table 2 shows the important reactions related to the four species. Especially, since ethynyl radical, C_2H which is frequently used as an indicator of carbon rich area, is connected with many highly reactive species, light hydro-carbons (e.g. acetylene oxidation pathway), it significantly affects energy distribution of the reaction field and the ignition delay time. Another species, cyclopropenylidene (C_6H_3) that is known as carbenes is in highly reactive class of organic molecules and also affects the ignition timing. It should be noted that the error in the ignition delay time is much larger and dominant than that in the concentrations of the important species. C_{16}H_{10} does not only have considerable effect on the ignition timing but also the concentration of
important species despite its single reaction path, because this reaction is an isomerized reaction (accumulated reaction).

![Graph showing the number of species and error with varying threshold value.](image)

**Fig. 1** The number of species and error with varying threshold value.

### Table 2 Species removed and related important reactions between threshold values of $8.0 \times 10^{-4}$ and $1.0 \times 10^{-3}$.

| Species | Reactions |
|---------|-----------|
| C$_2$H  | C$_2$H + O$_2$ = HCO + CO, CH$_3$OH + C$_2$H = CH$_2$OH + C$_2$H$_2$ |
| C$_3$H  | C$_3$H + O$_2$ = HCCO + O, C$_3$H + CH$_2$ = C$_2$H$_2$ + CH$_3$ |
| C$_4$H  | C$_4$H + OH = HCCO + H |
| C$_5$H  | C$_5$H + OH = HCCO + H |
| C$_6$H  | C$_6$H + OH = HCCO + H |
| C$_7$H  | C$_7$H + OH = HCCO + H |
| C$_8$H  | C$_8$H + OH = HCCO + H |
| C$_9$H  | C$_9$H + OH = HCCO + H |
| C$_{10}$H | C$_{10}$H (isomerized pyrene) = C$_{10}$H$_{10}$ (fluoranthene) |

Through the first analysis, the important part in the combustion of volatiles is defined with 118 species and 523 related reactions from the detailed mechanism. About 54% species and 53% reactions are removed within the acceptable accuracy loss. After the first investigation, a supplementary process is performed to find out redundant species by the sensitivity analysis. The sensitivity on the error is defined as the difference in the ignition delay time and the number of total reactions, the error in the sensitivity analysis and the error after sensitivity analysis. During the sensitivity analysis, it is found that the error reaches around 30% once when 16 species are removed. Some light hydrocarbons such as C$_2$H$_3$, C$_3$H$_5$, C$_4$H$_2$, and C$_6$H$_4$ are removed in this step. Some isomers of carbon-rich species also show a limited effect on the error, because their existing time is very short in the reaction field and the influence of their existence on important species is limited. One more crucial point is that the error goes down after this peak, and then it stays continuously under 30% until another 30 species are removed. During this step, the some carbon-rich species, higher number than four carbons, are removed which have higher influence on the concentrations of the target species in the product gas than the ignition timing. The error in the concentrations of the important species is up to 3-5%. And then, the error exceeds 30% when C$_4$H$_2$CH$_3$ that has only one reaction path, C$_4$H$_4$ + CH$_3$ = C$_3$H$_3$CH$_3$, is removed at the point where totally 47 species are removed. This reaction includes methyl group, CH$_3$ that should considerably affect the ignition timing. The effect of CH$_3$ will be discussed in the next section again.
The error of skeletal mechanisms generated via sensitivity analysis are evaluated in ignition delay time and mole fractions of interesting species under same testing conditions as the DRGEP process. As shown in the figure, the error of all tested conditions is less than 20% even over the last point. Of course, the two points in which the error reaches 30% are under 20%, so the more simplified mechanism is selected for next process.

![Figure 2: Number of total reactions, the error during the sensitivity analysis and the error of DRGEP-SA by the number of removed species.](image)

### 3.2 Reaction-based analysis

To clarify the importance of the reaction pathways, CSP method that is namely the reaction-based analysis is performed based on the selected mechanism from the DRGEP-SA in this section. The value of the importance index is determined by the maximum value among all sampling conditions. Figure 3 shows the induced error by eliminating the number of reactions with various threshold values. It is found that the error gradually increases as the threshold value increase and excesses 30% twice at the points where the threshold value reaches $6.0 \times 10^{-4}$ and $2.0 \times 10^{-2}$. Table 3 shows that the removed reactions at this two points. In the first point when the threshold value increases from $4.0 \times 10^{-4}$ to $6.0 \times 10^{-4}$, one oxidation reaction of carbon monoxide, two methyl groups and two polymerization reactions that affect the ignition timing and the concentrations of the target species in the product gas slightly. Consequently, the difference in the composed species causes the error. This phenomenon can be clearly observed in the second point. Since the important reactions related to carbon monoxide and dioxide, other methyl group reactions which involve highly reactive species are removed (See Table 3), the effect of the lack of these reactions is identified in the error. From this behavior, the threshold value of $1.0 \times 10^{-2}$ is selected that extracts 71 species and 154 reactions. Additionally, $C_{14}H_{10}$, $C_{10}H_{5}C_{1}H_{4}$, $C_{10}H_{5}$, and $C_{14}H_{10}$ are also removed because they are not included in any remained reactions. Therefore, the final mechanism generated here consists of 67 species and 154 reactions with less than 30% error in this step.
Thus, it is not sensible in the promotion of hydrocarbon oxidation in the ignition procedure. The species which have a lower mole fraction than a certain threshold value and related reactions are removed. This test is conducted iteratively with various threshold values to find out the optimized condition. Figure 4 shows that the relationship between the number of species and reactions, and the error for four threshold values. It is found that the 30% error is maintained until the threshold value is up to $1.0 \times 10^{-8}$ and then, the error drastically increases. To investigate this behavior in detail, the removed species and related reactions are listed in Table 4. It is found in the case with the threshold value of $1.0 \times 10^{-8}$ that naphthacene radical ($C_{18}H_{11}$) and anthracenyl radical ($C_{14}H_{8}$) have a restrictive effect on the ignition and the concentrations of the target species in the product gas, because the reactions including selected species relevant to PAH kinetics of chrysene and anthracene which have very slow reaction rates. Thus, it is not sensible in the promotion of hydrocarbon oxidation in the ignition procedure, and production or consumption of important species. However, in the case with $1.0 \times 10^{-7}$, ethyl radical ($C_{2}H_{5}$) is removed. The species connected with the ethyl group reactions which are highly reactive, and known as taking an important role in combustion chemistry. This brings a large error in this step, while this species has very low peak mole fraction. Pyrenyl radical ($C_{16}H_{10}$) is eliminated during the removing process of naphthacene radical because it has only one linked reaction with naphthacene in the mechanism. From this result, the final skeletal mechanism which consists of 64 species and 150 reactions is obtained.

\[
\begin{array}{llll}
\text{CO} + \text{O}_2 &= \text{CO}_2 + \text{O} & \text{HCO} + \text{O}_2 &= \text{CO}_2 + \text{OH} & \text{CH}_3 + \text{CH}_3 &= \text{C}_2\text{H}_4 + \text{H}_2 \\
\text{CH}_3 + \text{H} &= \text{HCH} + \text{H}_2 & \text{CO} + \text{O} + \text{M} &= \text{CO}_2 + \text{M} & \text{CH}_3\text{OH} + \text{M} &= \text{CH}_2\text{O} + \text{H} + \text{M} \\
\text{CH}_3\text{OH} + \text{O}_2 &= \text{CH}_2\text{OH} + \text{HO}_2 & \text{HCH} + \text{O} &= \text{CO} + \text{H}_2 & \text{CH}_3\text{OH} + \text{H} &= \text{CH}_3\text{OH} + \text{H}_2 \\
\text{C}_9\text{H}_8 + \text{C}_2\text{H}_3 &= \text{C}_{12}\text{H}_{18} + 2\text{H} & \text{CH}_3 + \text{H} + \text{M} &= \text{CH}_4 + \text{M} & \text{CH}_3\text{OH} + \text{H} &= \text{CH}_3\text{O} + \text{H}_2 \\
\text{C}_{18}\text{H}_{11} + \text{H} &= \text{C}_{18}\text{H}_{12} & \text{CH}_3 + \text{O}_2 &= \text{CH}_3\text{O} + \text{O} & \text{CH}_4 + \text{O}_2 &= \text{CH}_3 + \text{HO}_2 \\
& & \text{CH}_3 + \text{OH} &= \text{CH}_3\text{OH} & \text{CH}_4 + \text{H} &= \text{CH}_3 + \text{H}_2 \\
& & \text{CH}_3 + \text{OH} &= \text{CH}_3\text{OH} + \text{H} & \text{C}_{18}\text{H}_{12} + \text{H} &= \text{C}_{18}\text{H}_{11} + \text{H}_2 \\
\end{array}
\]
3.3 Skeletal mechanism

The skeletal mechanism is generated through the analyses in the previous sections. This mechanism involves much lower number of species and reactions than the detailed mechanism, and it expedites large-scale simulations. To validate the skeletal mechanism (SAP), the predicted combustion characteristics of coal volatile are calculated using 1D premixed model of CHEMKIN-PRO with measured temperature profiles and compared with the detailed mechanism (DAP) and the experiments. Figure 5 shows the comparison of ignition delay time with variation of major species in ignition delay time with change of initial temperature from 1,200 to 1,500K. It can be thought that the ignition delay time predicted by SAP at 1,500K has less error than 20%. In the lower temperature region, the error slightly increases again, but it still within maximum error appears at the high temperature region while the middle range of initial temperature from 1,200 to 1,500K has less error than 20%. In the lower temperature region, the error slightly increases again, but it still within 20%. It can be thought that the ignition delay time predicted by SAP is acceptable comparing to that by DAP. It is important on a numerical simulation of a coal flame because the ignition of coal volatile is one of the major issues to evaluate the characteristics of the coal type.

Figure 6 shows the comparison of mole fractions between the experimental data and the computations, (a) fuel rich ethylene-oxygen-argon flame with C/O = 0.76, 20 torr, 50 % argon and cold gas velocity = 62.5 cm s⁻¹ by Bhargava and Westmoreland (1998) and (b) benzene-oxygen-argon flame with C/O=0.71, 30 torr, 50 % argon and cold flow rate = 32.7 cm s⁻¹ by Yang et al. (2007). The profile predicted by DAP is also displayed to compare in each figure. It is found that the general feature of the variation of major species in Fig. 6 (a) can be precisely captured by SAP, while the increase in product gases by the ignition in the upstream region is slightly faster than that for the experiment and DAP. This should be due to the error of SAP comparing with DAP discussed in Fig. 5 and so on. The characteristics of the decomposition of aromatic hydrocarbon (benzene) is compared in Fig. 6 (b). The detailed mechanism for a low pressure condition (DLP) generated by Richter et al. (2005) that has 157 species and 872 reactions and the skeletal mechanisms derived from the detailed mechanism (SLP) by the same reduction procedure presented in this paper are also displayed that can be considered to be more appropriate to predict the combustion characteristics in the experiment because of its low pressure condition. To add brief explanation on the simplification process of SLP, the first temporary skeletal mechanism consists of 66 species and 304 reactions is prepared via DRGEPISA and the SLP has 66 species and 221 reactions is obtained through CSP within about 15% error. Here, the computation with DAP cannot be performed.

| Species                  | Reactions                                  | Species | Reactions                                  |
|--------------------------|--------------------------------------------|---------|--------------------------------------------|
| Naphthacene radical      | \( C_{12}H_6 + C_2H_2 = C_{13}H_{11} \)    | C\(_2\)H\(_3\) | \( C_2H_4 + H = C_2H_3 \)                 |
|                          | \( C_{14}H_{12} + H = C_{13}H_{11} + H_2 \)|         | \( C_2H_6 + CH_3 = C_2H_3 + CH_4 \)       |
|                          | \( C_{14}H_{12} + OH = C_{13}H_{11} + H_2O \)|         | \( C_2H_6 + H = C_2H_5 + H_2 \)           |
| Anthracenyl radical      | \( C_{12}H_7 + C_2H_2 = C_{14}H_9 \)       |         | \( C_2H_6 + O = C_2H_4 + OH \)            |
|                          | (C\(_4\)H\(_3\))                          |         | \( C_2H_6 + OH = C_2H_5 + H_2O \)        |

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due to the singularity, non-physical stiffness of the chemical system. This should be because it was generated for the atmospheric pressure condition. It is revealed that the profile of decomposition process of C₆H₆ is qualitatively captured by all of three mechanisms with a slight underestimation. For major species, SAP underestimates CO concentration and overestimates CO₂ concentration respectively, while DLP and SLP can capture the trends accurately. From this observation, it is found that the present reduction procedure can precisely reduce the number of species and reactions from the detailed mechanism and derive the skeletal mechanism, while it cannot cover the wide range of pressure condition. Since a coal flame targeted in this study is generally in atmospheric pressure, SAP generated in this paper should cover the entire range of the combustion condition taking place in a coal flame.

Fig. 5 Comparison of ignition timing between the detailed mechanism and the skeletal mechanism

Fig. 6 Comparison of mole fractions between experimental data and model predictions, (a) fuel-rich ethylene-oxygen-argon flame (symbols: experimental data, black lines: DAP, red lines: SAP), and (b) benzene-oxygen-argon flame (symbols: experimental data, black lines: SAP, red lines: DLP, blue lines: SLP)

4. Conclusion
The importance of chemical species and reactions are analyzed in detail under the wide range of equivalence ratio, initial temperature and pressure conditions to clarify the reaction kinetics of coal volatiles in a coal flame. The detailed mechanism is used to analyze with the mechanism reduction methods such as DRGEPSA and CSP. The major findings in this study are listed below.
• In the species-based analysis by DRGEP, it is found that the hydrocarbons which are related to the fast and sensitive reactions in the high temperature conditions play important role to provide thermal energy in the reaction zone during the ignition process. In addition, the sensitivity analysis reveals that the methyl group is key species to evaluate the ignition delay time. It is also revealed that they does not affect the final composition of the product gas very much.

• In the reaction-based analysis by CSP, the important reactions related to carbon monoxide and dioxide, and methyl group are extracted that significantly affect the ignition timing and the composition of the product gas. Moreover, it is revealed that the ethyl group known as highly reactive and affects the reaction field significantly still takes an important role even it has small concentration.

• Through the kinetic analysis with the mechanism reduction methods, the simplified skeletal mechanism that consists of 64 species and 150 reactions is generated. The skeletal mechanism is validated by the comparison of the ignition delay time and the distribution of the mole fractions of major and important chemical species in the premixed flame with the experiment and detailed mechanism. This should be an advantage in a large-scale numerical simulation and the applicability to a large-eddy simulation on an actual coal flame will be discussed in a future work.

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