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Integrated reduction of large chemical kinetic model of bio-butanol

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ABSTRACT

A 74-species reduced mechanism and a 94-species skeletal mechanism for bio-butanol oxidation were obtained from a 234-species detailed mechanism using an integrated reduction method involving directed relation graph (DRG), DRG-related and computational singular perturbation (CSP) + quasi-steady-state approximation (QSSA) methods. Firstly, the skeletal mechanism with 94 species and 497 reactions was derived by comparing the DRG and DRG-related methods. Then, 112 unimportant reactions were identified and eliminated through the CSP importance index method, and the final skeletal mechanism with 94 species and 385 reactions was generated. Finally, a reduced mechanism with 74 species and 70 step reactions was derived by using the CSP + QSSA method to identify and eliminate 20 QSS species. Simulation results of the 94-species skeletal mechanism and the 74-species reduced mechanism show good agreement with that of the detailed mechanism for different phenomena such as ignition, extinction, laminar flame speed and homogeneous charge compression ignition combustion.

Keywords: Bio-butanol; Integrated reduction; Reduced mechanism; Skeletal mechanism; Homogeneous charge compression ignition

1. Introduction

Fossil fuels widely used in the transport sector are non-renewable energy resources, and combustion exhaust products have caused global continuous environmental pollution [1]. To solve these problems, biofuels generated from biomass are receiving more attention. Thereby, bio-ethanol is widely used both as a gasoline additive and as fuel, it has many disadvantages such as low energy density, high water solubility, high volatility, etc. Bio-butanol has better physical and chemical properties than bio-ethanol, so it has been considered to be an alternative to bio-ethanol [2,3].

However, the effect of bio-butanol applied to traditional gasoline engines depends on the type and operating condition of the specific engine. Therefore, it is very important to understand the combustion process of bio-butanol. Accurate chemical kinetic mechanism plays a key role in calculating the combustion processes of bio-butanol. Moss et al. [4] first proposed a detailed bio-butanol mechanism containing 161 species and 1,256 reactions, which was later extensively quoted and improved. Black et al. [5] developed a detailed bio-butanol mechanism comprising 234 species and 1,399 reactions, which was confirmed by the following experiments: shock tube, jet-stirred reactor, and rapid compression machine. Zhang et al. [6] proposed a high-temperature bio-butanol mechanism involving 243 species and 1,475 reactions, which was obtained on the basis of the Black by updating the sub-mechanism of *n*-butanol.

The detailed mechanisms of bio-butanol with hundreds of species bring the following problems: prohibitively expensive memory and CPU time, stiffness and nonlinearity, which make it difficult to apply the detailed mechanisms to two-dimensional or three-dimensional combustion simulation. Therefore, in regard to fully reproduce the relevant combustion phenomena using as few species as possible under target conditions is important and urgent.

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Currently, the most widely used mechanism reduction approaches are skeletal reduction and timescale based reduction. In particular, the skeletal reduction mainly includes directed relation graph (DRG) and DRG-related methods [7–11], and the timescale based reduction mainly includes computational singular perturbation (CSP) [12], quasi-steady-state approximation (QSSA) [13], and intrinsic low dimensional manifold [14]. Indeed, it is difficult to obtain the smallest mechanism by using only one method, so several methods need to be tried to reduce the detailed mechanism.

In the present study, several approaches, for example, DRG, directed relation graph with error propagation, path flux analysis (PFA), directed relation graph with the maximum coefficient of all reactions (DRGMAX), CSP + QSSA, were used to obtain sufficiently small bio-butanol mechanisms from Black's mechanism. First, a skeletal mechanism with 94 species and 497 reactions was obtained base on DRG and DRG-related methods. Then, a skeletal mechanism with 94 species and 385 reactions was generated base on a CSP importance index method. Finally, a reduced mechanism with 74 species and 70 step reactions was derived by using the CSP + QSSA method.

2. Reduction strategy

2.1. Skeletal reduction

The skeletal mechanisms can be obtained through DRG and DRG-related methods, which eliminate the unimportant species and reactions of the detailed mechanism. The DRG and DRG-related methods require sampled reduction data and different threshold values to implement the reduction. The sampled reduction data were derived from auto-ignition [15–17]. The interval of auto-ignition sampling was as follows: pressure (1, 10, 20, 30, and 50 atm), initial temperature (800; 900; 1,000; 1,100; 1,200; 1,300; 1,400 and 1,500 K) and equivalence ratio (0.5, 1, 2).

Afterwards, on the premise that the error is less than 10%, different skeletal mechanisms were derived through DRG and DRG-related methods, as shown in Table 1.

Comparing these methods, the smallest size mechanism was obtained through the PFA approach, which can be further reduced by removing the unimportant reactions of the mechanism through through the CSP importance index method. The sampled reduction data were also derived from auto-ignition, and the parameter range for auto-ignition was the same as DRG and DRG-related methods. On the premise that the error is less than 5%, with the threshold value of 0.055, 112 unimportant reactions were identified and eliminated, and a final skeletal mechanism consisting of 94 species and 385 reactions was generated.

2.2. Time-scale reduction

The 94-species skeletal mechanism was then reduced through QSSA after identifying QSS species using the CSP method. The sampled reduction data were also derived from auto-ignition, and the parameter range for auto-ignition was same as DRG and DRG-related methods. On the premise that the error is less than 5%, with QSS species threshold value of 0.0132 and fast subspace Jacobian matrix eigenvalue threshold value of 1.0×10^{-6}, 20 QSS species, namely C_2H_5O, $C_3H_6OOH_{1-2}$, C_3H_6OH, $C_3H_6OOH_{2-1}O_2$, C_3H_5O, CH_3CO, C_3H_2, C_4H_8OH–3, SC_2H_4OH, $C_3H_6OOH_{1-3}$, CH_2CCH_2OH, CH_2OH, C_4H_8OH–2, C_4H_8OH–1, CH_2(S), $HOC_3H_6O_2$, $C_3H_6OOH_{1-2}O_2$, C_4H_8OH–4, HCO, $C_3H_6OOH_{1-3}O_2$, were identified and eliminated. Finally, a reduced mechanism with 74 species and 70 step reactions was obtained, which is about 3 times smaller than the original detailed mechanism. Using the reduced mechanism, simulation computation time, a quadratic function of the species number, can be reduced by 9 times.

In summary, the integrated reduction method can minimize the detailed mechanism. Fig. 1 shows the integrated reduction flow chart.

3. Validation of the 94-species skeletal mechanism and the 74-species

The 94-species skeletal mechanism and the 74-species reduced mechanism were first validated in constant pressure auto-ignition, from which the sampled reduction data were obtained. Fig. 2 reveals the ignition delay time of the skeletal mechanism, reduced mechanism and 234-species detailed mechanism in the closed homogeneous constant-pressure reactor with different pressure (1~50 atm), different equivalence ratio (0.5~1.5), and different initial temperature (850~1,550 K). It is indicated that the 94-species skeletal mechanism and the 74-species reduced mechanism have a good agreement with the detailed mechanism.

Moreover, Fig. 3 shows the temperature profiles with different equivalence ratios (0.5~1.5) in perfectly stirred reactor (PSR). The 94-species skeletal mechanism and the 74-species reduced mechanism relatively accurately reproduce the results from the 234-species detailed mechanism.

To further verify the validity of the 94-species skeletal mechanism and the 74-species reduced mechanism, the temperature profiles for constant-pressure auto-ignition under the initial temperatures of 850; 1,100 and 1,550 K, the

Table 1
Threshold value, maximum error, and mechanism size of different reduction methods

Method	Threshold value	Maximum error	Mechanism size
DRG	0.21	9.3%	100 species 591 reactions
DRGEP	0.0225	5.8%	106 species 617 reactions
PFA	0.45	6.8%	94 species 497 reactions
DRGMAX	0.77	9.9%	97 species 548 reactions

DRG – directed relation graph; DRGEP – directed relation graph with error propagation; PFA – path flux analysis.

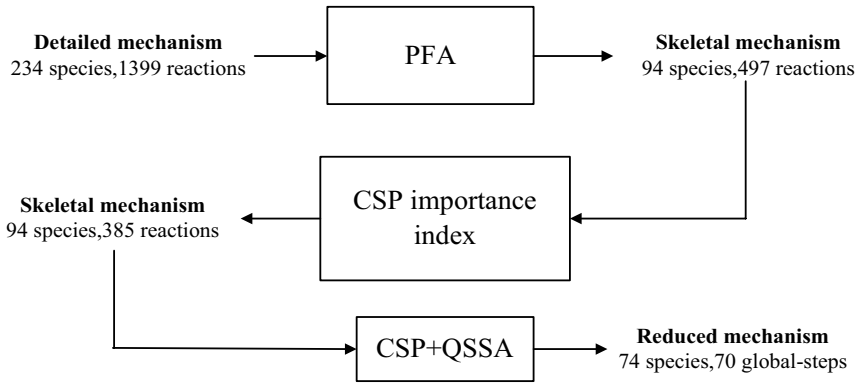

Fig. 1. Flow chart of the integrated reduction method.

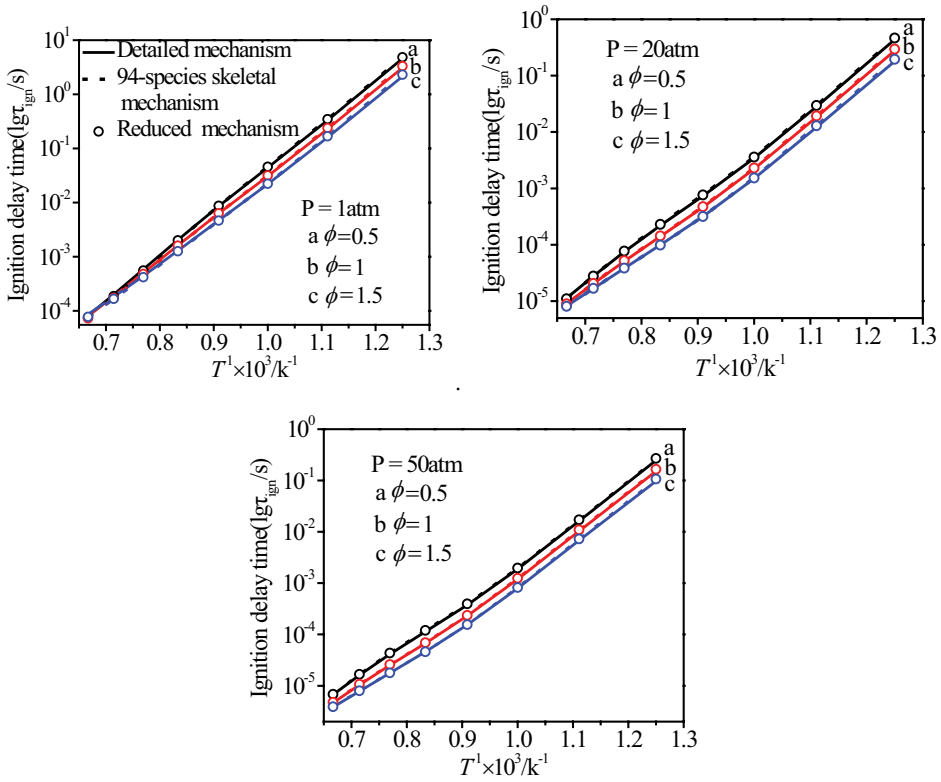

Fig. 2. Ignition delay time of the different bio-butanol mechanisms for constant-pressure auto-ignition.

pressures of 1, 5, 10 atm, and the equivalence ratios of 0.5, 1, 2, are plotted in Fig. 4. It is seen that the temperature results from the 94-species skeletal mechanism and the 74-species reduced mechanism are close to that of the 234-species detailed mechanism, with the observable temperature rise delay deviation under the initial temperatures of 850 K and the pressure of 10 atm.

In addition, Fig. 5 shows the mole fraction of selected species in the closed homogeneous constant-pressure reactor with the pressure of 1atm, the equivalence ratio of 1, and the initial temperature of 1,100 K. It is revealed that the simulation results of the 234-species detailed mechanism were perfectly reproduced by the 94-species skeletal mechanism and the 74-species reduced mechanism.

To examine the diffusive performance, the flame speeds of different mechanisms under different pressure are plotted in Fig. 6. It is seen that the flame speeds of the 94-species skeletal mechanism and the 74-species reduced mechanism are similar to that of the 234-species detailed mechanism, and the maximum deviation is less than 3.1 cm/s with the pressure of 1 atm, the equivalence ratio of 1.1.

Finally, to examine the homogeneous charge compression ignition (HCCI) combustion performance, the cylinder temperature and pressure profiles of different

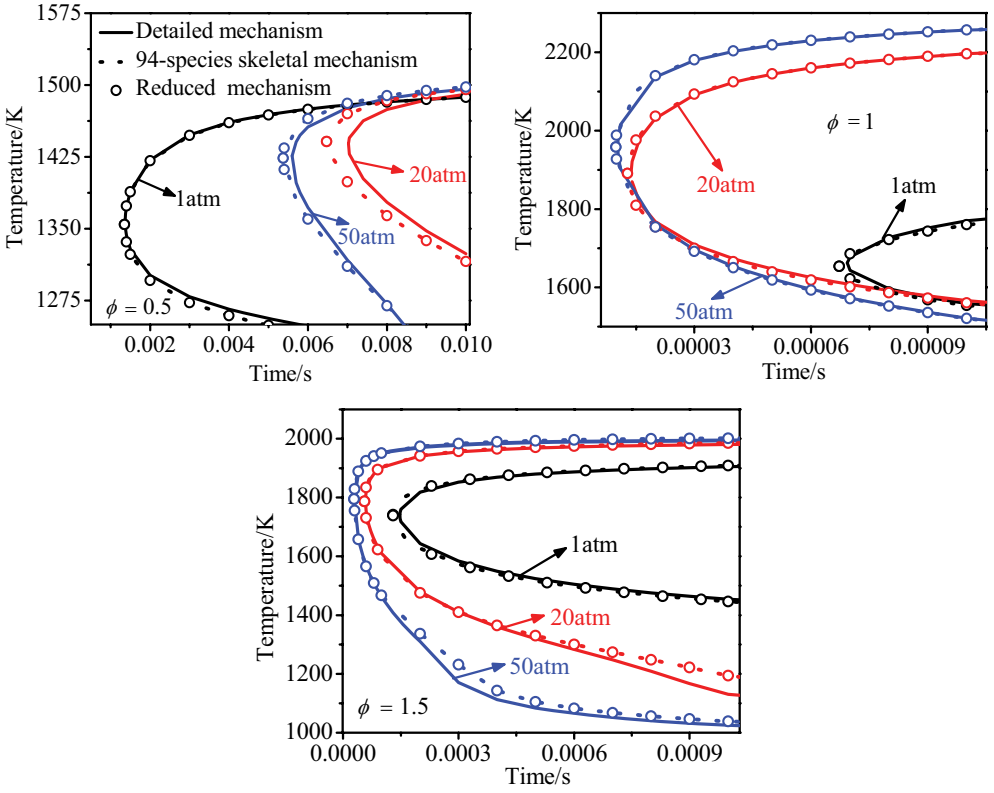

Fig. 3. Temperature profiles of the different bio-butanol mechanisms for extinction.

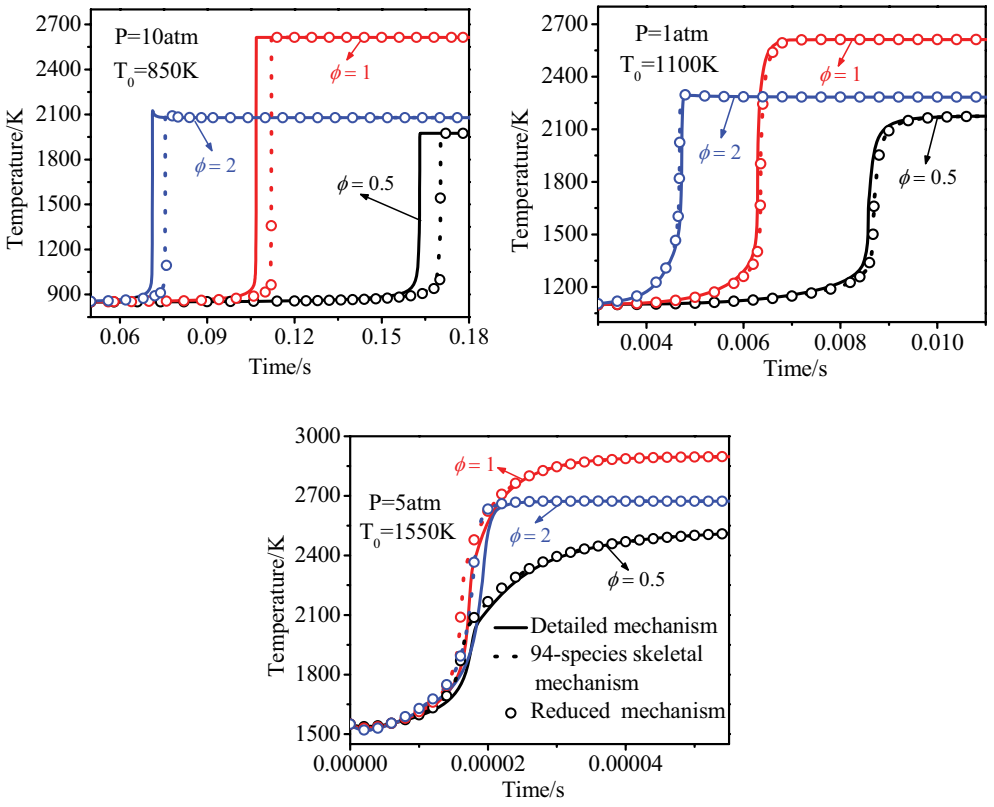

Fig. 4. Temperature profiles of the different bio-butanol mechanisms for constant-pressure auto-ignition.

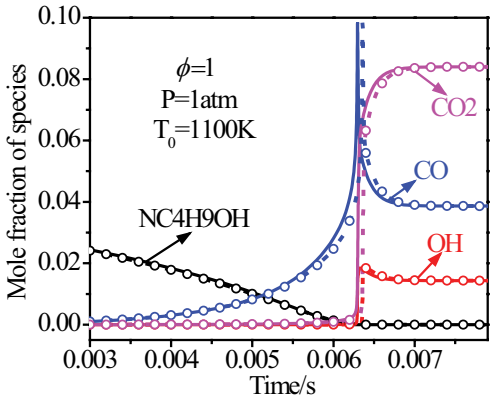

Fig. 5. Mole fraction of selected species of the different bio-butanol mechanisms under atmospheric pressure.

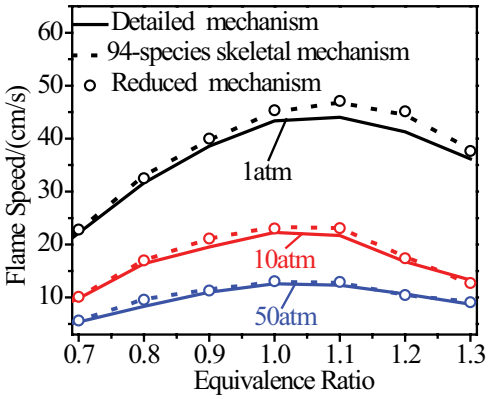

Fig. 6. Flame speeds of different mechanisms under different pressure.

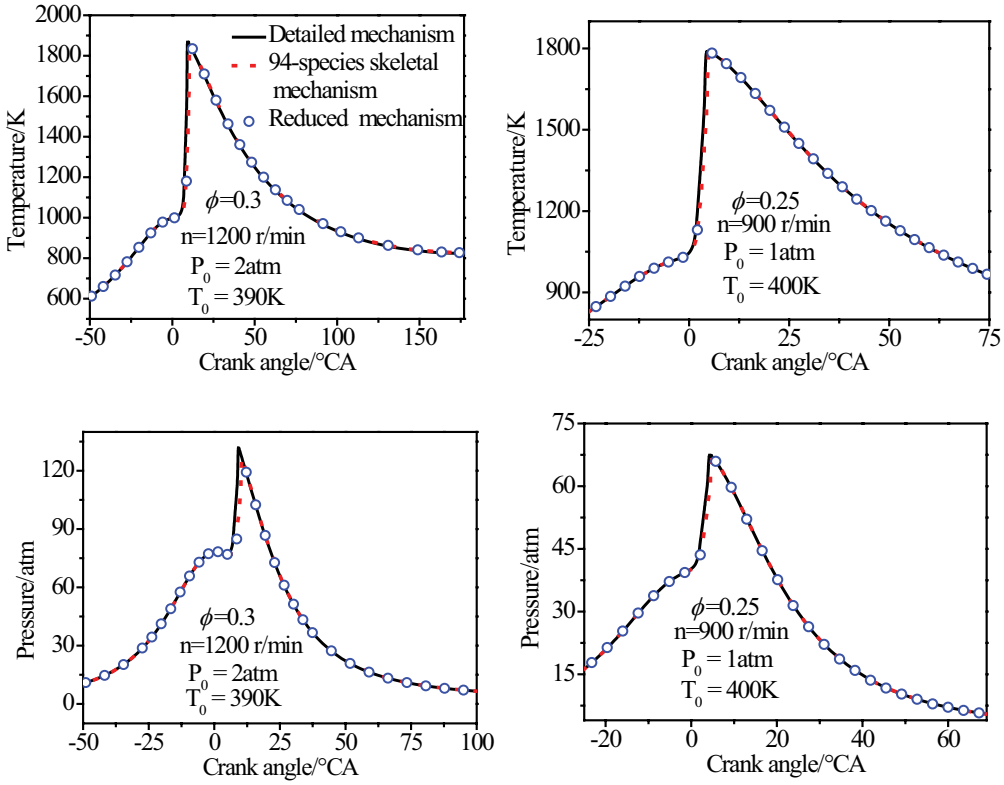

Fig. 7. Cylinder temperature and pressure profiles of different mechanisms for HCCI combustion.

mechanisms under different initial conditions are plotted in Fig. 7. The HCCI engine parameters are indicated in Table 2. Fig. 7 shows that the results calculated by the 94-species skeletal mechanism, the 74-species reduced mechanism and the 234-species detailed mechanism have a good agreement.

4. Conclusions

An integrated reduction method involving DRG, DRG-related, CSP importance index and CSP + QSSA methods were employed to reduce the bio-butanol detailed mechanism, resulting in a 94-species skeletal mechanism and a 74-species reduced mechanism. The 94-species skeletal mechanism was obtained from the 234 species detailed mechanism using the PFA method and CSP importance index method in turn. Then the 74-species reduced mechanism was obtained from the 94-species skeletal mechanism using the CSP + QSSA method. The simulation results of the 234 species detailed mechanism, the 94-species skeletal mechanism and the 74-species reduced mechanism in the closed homogeneous

Table 2
Engine parameters

Parameter	Value
Compression ratio	16.7
Bore	127 mm
Stroke	154 mm
Displacement	1,948.8 cc
Connecting rod	255 mm
Intake valve close	139°BTDC

constant-pressure reactor show good accuracy for both the ignition delay time and the temperature and mole fraction of selected species profiles over wide parameter ranges. It was further indicated that the 94-species skeletal mechanism and the 74-species reduced mechanism agree well with the 234 species detailed mechanism for extinction calculations in PSR. In addition, the flame speeds of the 94-species skeletal mechanism and the 74-species reduced mechanism also agree well with that of the 234 species detailed mechanism. Finally, our results of the present study concluded that the HCCI combustion performance calculated through the 94-species skeletal mechanism, the 74-species reduced mechanism and 234-species detailed mechanism has a good agreement.

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