Construction of Simple Reaction Mechanisms for C_3H_8/air Mixtures Considering Five Combustion Properties

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1 Introduction

For accurate predictions of combustion phenomena in various combustion devices such as reciprocating engines and gas turbines, various detailed reaction mechanisms [1–4] have been developed actively for a couple of decades. However, computational fluid dynamics (CFD) with detailed reaction mechanisms in practical combustion devices at realistic conditions is still a challenging task due to huge computational costs. Therefore, a large number of studies on chemical mechanism reductions [5–7] were conducted to date. On the other hand, much simpler reaction mechanisms with only several species and reactions are of use for capturing essential physics of target combustion phenomena. Here, we made an attempt to construct simple reaction mechanisms with improved prediction capability on the basis of phenomenological approach.

In this study, simple reaction mechanisms for propane/air mixtures, which contain one of the commonly used fuels, are constructed based on five kinds of combustion properties: dependences of the laminar burning velocity on the initial gas temperature, equivalence ratio and pressure (SLT, SLE, SLP); dependence of the ignition delay time on the initial gas temperature (IGT); and the intermediate profile in a laminar flame represented by CO (I-CO). The purpose of this study is to construct simple reaction mechanisms which are able to reproduce these five combustion properties simultaneously for propane/air mixtures.

2 Construction of Simple Reaction Mechanisms

In this study, five combustion properties (SLT, SLE, SLP, IGT and I-CO) were used as the indexes for the construction of simple reaction mechanisms. All computations were conducted for propane/air mixtures. Table 1 shows the computational conditions of the combustion properties. SLT was considered for an initial temperature range of 300–700 K. SLE was considered for an equivalence ratio range of 0.6–1.5. SLP was considered for a pressure range of 1–100 atm. IGT was considered in an initial temperature range of 800–1200 K. As one of the intermediate species, CO mole fraction distribution in an 1-D planar adiabatic freely

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Table 1: Computational conditions.

Combustion properties	Computational conditions			Calculation code
	P [atm]	ϕ [-]	T_0 [K]	
SLT	1.0	1.0	300 – 700	PREMIX[8]
SLE	1.0	0.6 – 1.5	300	
SLP	1.0 – 100	1.0	300	
I-CO	1.0	1.0	300	
IGT	1.0	1.0	800 – 1200	AURORA[9]

propagating flame was used to consider the index of I-CO.

A rate constant of each reaction is expressed by the Arrhenius equation:

$$k = A\exp\left(-\frac{E}{RT}\right) \quad (1)$$

Here *A, E, T,* and *R* are frequency factor, activation energy, temperature and gas constant. To simplify the construction method of the simple reaction mechanism, reaction order of each chemical species was set to be 1. The simple reaction mechanisms were constructed by setting and adjusting *A* and *E* to fit the above-mentioned combustion properties.

3 Computational Method

CHEMKIN-PRO package was used to get the computational results with all reaction mechanisms. For calculating SLT, SLE, SLP and I-CO, the 1-D steady combustion code PREMIX [8] was used. For calculating IGT, the 0-D unsteady combustion code AURORA [9] was used. The above five combustion properties obtained by a detailed reaction mechanism, Natural gas III (NgIII) [2] (293 species, 1593 reactions), were regarded as target values for constructing simple reaction mechanisms in this study. Thermodynamic data of NgIII and transport data of AramcoMech 1.3 [3] were used for all the computations.

4 Results and Discussion

4.1 Overall One-step Reaction Mechanisms

Table 2 shows the values of the parameters for the constructed overall one-step reaction mechanisms. 1-STEP-SLT and 1-STEP-IGT are overall one-step reaction mechanisms constructed based on SLT and IGT, respectively.

Figure 1 shows the computational results of the overall one-step reaction mechanisms. 1-STEP-SLT

Table 2: Parameters of overall one-step reaction mechanisms.

in cm^3-mol-cal-sec units

Symbol	Reaction	A	E
1-STEP-IGT	(R1) $C_3H_8 + 5O_2 \rightarrow 3CO_2 + 4H_2O$	9.00E+13	40000
1-STEP-SLT		1.30E+16	44100

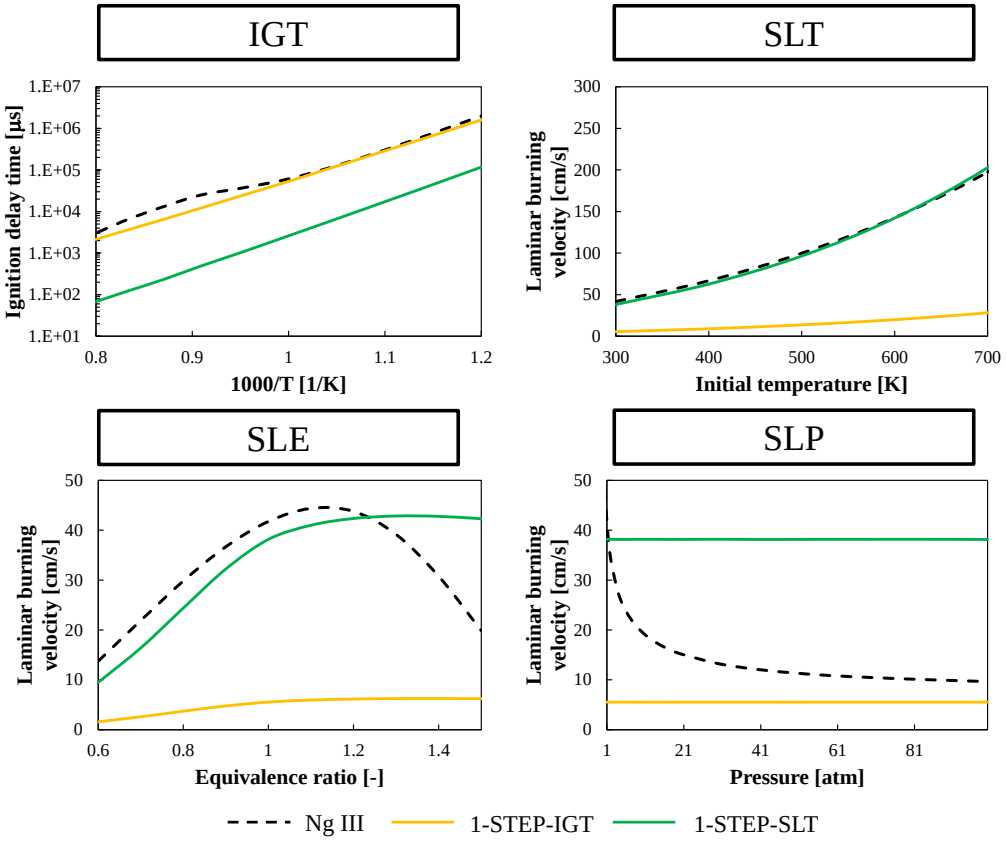

Figure 1. Computational results of overall one-step reaction mechanisms.

which reproduces SLT underestimates ignition delay times and 1-STEP-IGT which reproduces IGT underestimates laminar burning velocities. Because reaction time scale of deflagration is different from that of ignition, it is practically impossible for an identical overall one-step reaction mechanism to reproduce both deflagration and ignition properties. Therefore, multi-step reaction mechanisms are needed to reproduce multiple combustion properties simultaneously. Moreover, laminar burning velocities of the overall one-step mechanisms are almost constant with an increase of equivalence ratio in the fuel rich condition and with an increase of pressure. These results coincide with earlier studies [10, 11].

4.2 Multi-Step Reaction Mechanisms

Four-step mechanism which reproduced IGT and SLT, seven-step mechanism which reproduced IGT, SLT and SLE and eight-step mechanism which reproduced IGT, SLT, SLE and I-CO were constructed. Finally, ten steps were necessary to reproduce all the above five combustion properties. The ten-step mechanism was named 10-STEP. Due to the limitations of space, 10-STEP will only be explained in this manuscript.

Table 3 shows parameters for 10-STEP and Figure 2 shows the reaction path of 10-STEP. An oxidation reaction from propane to CO was introduced for the mechanism construction to reproduce IGT. To model the overall reactivity enhanced by radical diffusion from the reaction sheet in propagating flames, a branching cycle consisting of chain branching [12] and chain carrier reactions was introduced. The OH radical was selected as a representative of diffusing radicals in propagating flames. The chain branching cycle was modelled to proceed only in flame propagation by introducing CO_2 in the burned gas as a third-

Table 3: Parameters of 10-STEP.

in cm^3-mol-cal-sec units

Symbol	Reaction		*A*	*E*
10-STEP	(R1) $C_3H_8 + 5O_2 \rightarrow 3CO + 6OH + H_2O$		3.50E+14	41000
	(R2) $C_3H_8 + 4OH \rightarrow 3CH_2O + H_2O + 2H_2$		3.00E+21	50000
	(R3) $CH_2O + O_2 \rightarrow CO + H_2 + O_2$		6.00E+18	44100
	(R4) $2CH_2O + C_3H_8 \rightarrow C_2H_4 + 2O + C_3H_8$		2.30E+19	44100
	(R5) $C_2H_4 + 2O \rightarrow 2CO + 2H_2$		8.00E+14	44100
	(R6) $O_2 + H_2 + CO_2 \rightarrow 2OH + CO_2$		2.10E+34	90000
	(R7) $2OH \rightarrow H_2O_2$	PLOG /1	1.50E+04	9000
		PLOG /4	4.00E+07	10000
		PLOG/20	6.00E+08	10000
		PLOG/100	1.40E+09	10000
	(R8) $H_2O_2 \rightarrow 2OH$	PLOG /1	1.00E+04	9000
		PLOG /4	1.30E+07	10000
		PLOG/20	4.50E+07	10000
	(R9) $CO + 2OH \rightarrow CO_2 + H_2O$		2.00E+10	2000
	(R10) $CO_2 + H_2O \rightarrow CO + 2OH$		4.00E+08	9000

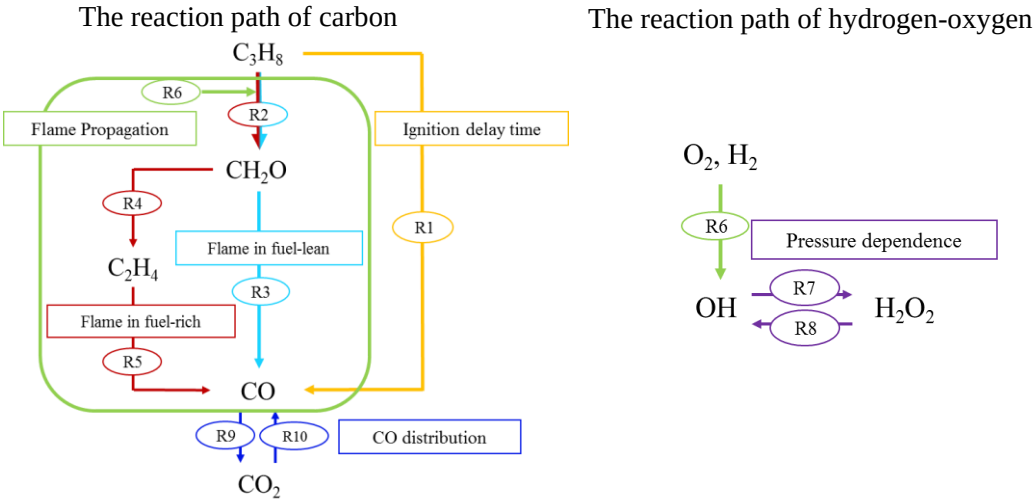

Figure 2. Computational results of 10-STEP.

body. To express laminar burning velocities in lean and rich conditions, two decomposition paths of CH_2O, which is one of the representative intermediates, were employed. The dominant decomposition path was modeled by using oxygen and fuel as third-bodies for the lean and rich conditions, respectively. To reduce the reaction rate of the chain branching cycle in flame propagation at high pressures, the reaction from OH to H_2O_2 and its reverse reaction were included. Additionally, a reverse reaction from CO_2 to CO was included to reproduce I-CO, reaction progress parameter in a flame, for all the combustion properties in this study. Accordingly, impacts of rate constants on combustion properties were characterized as shown in Figure 2. For example, rate constant of R1 has a strong impact on ignition delay time, while it has a less impact on laminar burning velocity.

Computational results of 10-STEP and a comparison to those of NgIII are shown in Figure 3. Here, combustion properties by 10-STEP showed a good agreements with those by detailed NgIII. 10-STEP was able to reproduce all the combustion properties in this study.

Since 10-STEP includes some artificial reactions, a special attention would be necessary for its limitation

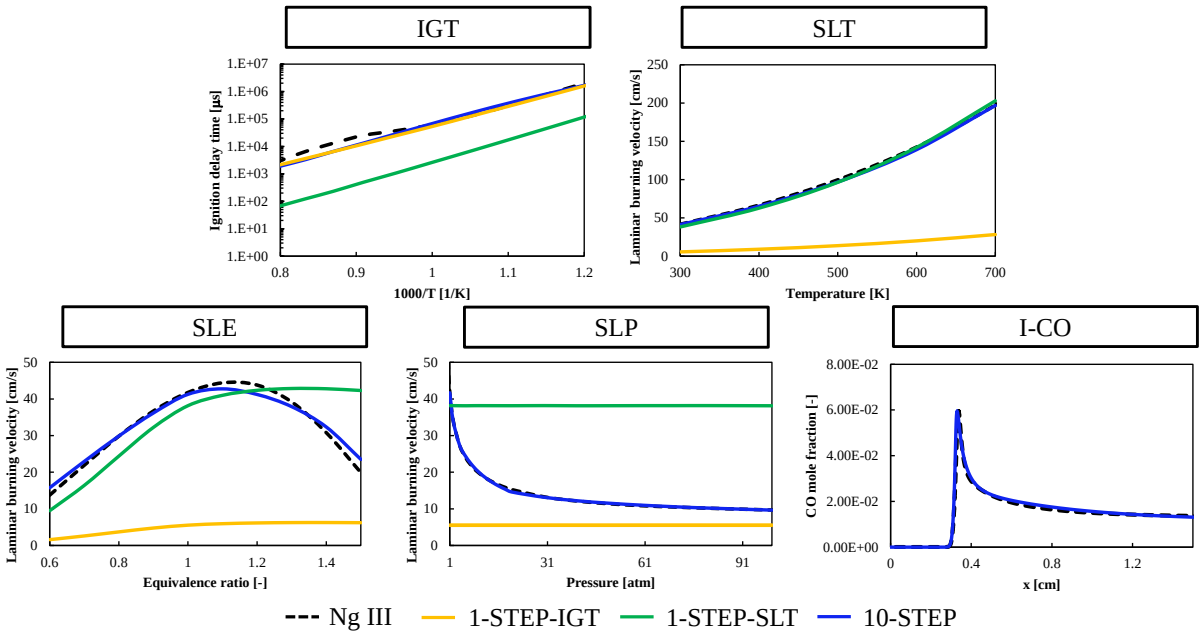

Figure 3. Computational results of 10-STEP.

and application to CFD. For instance, 10-STEP cannot be applied for problems with exhaust gas recirculation (EGR) and recirculation zone of burned gas. It is because 10-STEP employed fuel, oxygen and CO_2 as third bodies in some reactions. In such cases, reactants, i.e., fuel and oxygen flow, would be largely diluted and initial CO_2 fraction would significantly increase which may result in non-realistic outcomes in CFD. Another example is that 10-STEP could not perfectly reproduce time-histories of heat release rate profiles in ignition process and exhibited gentler temperature gradient than NgIII. This occurs in later half of ignition process due to inclusion of the reaction with small activation energy while 10-STEP well reproduced IGT, i.e., the initiation of ignition process. The reaction with small activation energy, R9, was essential for reproducing reaction zone thickness in flames (I-CO). The adiabatic flame temperature and the maximum temperature in ignition process were not included as target combustion properties at this time. To reproduce them, it is needed to increase the numbers of species and reactions or to decrease combustion properties as the indexes. In summary, capability and limitation of simple reaction mechanisms including 10-STEP need to be examined before applying it to CFD. The validity and limitation of the simple mechanisms constructed by the present methodology for CFD has been under further examination and will be reported in the near future.

5 Conclusions

Simple reaction mechanisms for propane/air mixtures were constructed based on five combustion properties, which are IGT, SLT, SLE, SLP and I-CO. The following results were obtained.

1. Identical overall one-step reaction mechanism is not capable of reproducing both flame propagation and ignition properties simultaneously. Multi-step reaction mechanisms are needed for this purpose.
2. When the dominant decomposition path was modeled by using oxygen and fuel as third bodies, it is possible to reproduce the equivalence ratio dependence of laminar burning velocities.
3. Introduction of reaction of H_2O_2 production and its reverse reaction enabled to reproduce slow reaction rate of the chain branching cycle at higher pressures.

4. Introduction of reverse reaction from CO_2 to CO enabled to reproduce I-CO, i.e., reaction progress parameter in a laminar flame represented by CO profile.
5. The capability and limitation of simple reaction mechanism including 10-STEP need to be examined before applying it to CFD.

Acknowledgements

This work was partially supported by Council for Science, Technology and Innovation(CSTI), Cross-ministerial Strategic Innovation Promotion Program (SIP), "Innovative Combustion Technology" (Funding agency: JST) and JSPS KAKENHI Grant Number 25630061. The part of the study was supported financially by the Ministry of education and science of Russian Federation (Project 14.Y26.31.0003).

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