Construction of a reduced mechanism for diesel-natural gas -hydrogen using HCCI model with Direct Relation Graph and Sensitivity Analysis

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Based on the theory of direct relation graph (DRG) and sensitivity analysis (SA), a reduced mechanism for diesel-CH_4-H_2 tri-fuel is constructed. The detailed mechanism of Lawrence Livermore National Laboratory, which has 654 elements and 2827 elementary reactions, is used for mechanism reduction with DRG. Some small thresholds are used in the process of simplifying the detailed mechanism via DRG, and a skeletal mechanism of 266 elements is obtained. Based on the framework of the skeletal mechanism, the time-consuming approach of sensitivity analysis is used for further simplification, and the skeletal mechanism is reduced to 262 elements. Validation of the reduced mechanism is done via a comparison of ignition delay time and laminar flame speed from the calculation using the reduced mechanism and the detailed mechanism or experiment. The reduced mechanism shows good agreement with the detailed mechanism and with related experimental data.

Keywords: diesel, natural gas, hydrogen, reduced mechanism, DRG, SA.

INTRODUCTION

As the energy crisis and environmental problems become more serious, environmental protection awareness from all walks of life at home and abroad continues to increase. "Clean, Low-carbon, Safe, and Efficient" energy reforms have become a general trend. The exploration of lower-emission engines has become a topic of concern. This is because although the diesel-natural gas dual-fuel engine has been applied in many fields, it is not perfect in terms of power and environmental protection. Hydrogen is a pollution-free fuel and has a very good burning rate. Therefore, adding hydrogen to the engine to form a diesel-natural gas-hydrogen tri-fuel engine has become a research hotspot to obtain better power and environmental protection. Especially for large engines, such as ships and heavy trucks, the research in this direction is more significant.

In a tri-fuel engine, hydrogen is used as a mixed gas (hydrogen and natural gas), which is injected into the air inlet of the engine and mixed with air before it is injected into the cylinder. Combustion in the cylinder of the engine with the mixed gas (hydrogen and natural gas) involved is shown in Figure 1.

The characteristics of hydrogen (H_2) include a fast burning rate, less ignition energy, and no carbon, and it is recognized as a clean fuel. Therefore, for gasoline and diesel engines, the blending in a certain amount of hydrogen can effectively improve the combustion performance in the cylinder[1, 2]. In particular, using natural gas as a fuel has a more obvious improvement effect on engines. In addition, the intake amount of air decreases because of the added mixed gas, and mixed gas releases heat during combustion; this increases the in-cylinder temperature of the engine that has the added mixed gas. Because the formation of nitrogen oxides is closely related to the in-cylinder temperature, higher in-cylinder temperature leads to more emissions of nitrogen oxides, and the addition of mixed gas increases the emissions of nitrogen oxides from the engine according to a higher temperature[3]. Therefore, it is useful for the engine if a certain amount of hydrogen is added when the air is
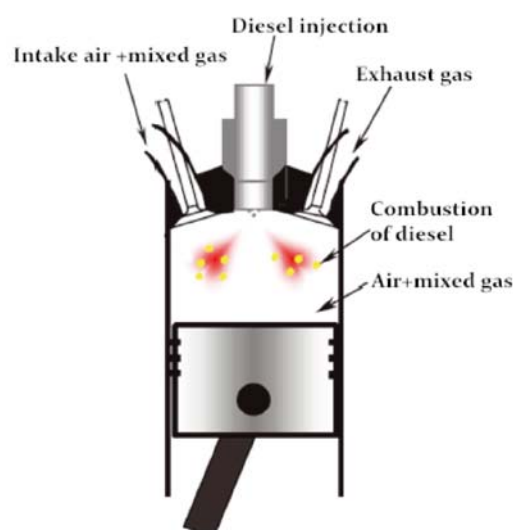

Figure 1. Schematic diagram of combustion in the cylinder

not fully consumed or when the engine works at part load. In some studies, the upper limit of the hydrogen energy fraction of the mixed gas added to the internal combustion engine can achieve to 19%[4].

Because of the addition of hydrogenated natural gas in the intake air, the injection of liquid fuel greatly improves the performance of combustion in the cylinder and increases the efficiency of tri-fuel combustion. These factors then shorten the duration of combustion in the cylinder and cause the fuel to be consumed more fully; moreover, they decrease the possibility of misfire in the cylinder. All of these factors significantly improve combustion efficiency and reduce the emissions of the engine[5, 6].

Hydrogen can easily ignite spontaneously. At the stoichiometric ratio, the ignition energy for hydrogen in air is only 0.02 mJ, whereas it is 0.29 mJ for natural gas and 0.24 mJ for gasoline[7]. The quenching distance of hydrogen is much lower than that of natural gas and gasoline, and the relevant data for hydrogen, natural gas, and gasoline are 0.064 cm, 0.203 cm, and 0.2 cm respectively[8]. Therefore, using hydrogen in engines has some problems. For example, a small high-temperature

spot can ignite hydrogen; moreover, a high-temperature spot in the residual gas in the cylinder can sometimes ignite the hydrogen-air mixture. This results in backfiring and the consumption of air in the inlet pipe, and then the engine misfires. Although hydrogen has a very high calorific value per unit weight, its calorific value per unit volume is much lower than those of natural gas and gasoline, and its calorific value is only one-third that of natural gas and one-twentieth that of gasoline. This decreases the efficiency per unit volume of the engine. In addition, the price of hydrogen is relatively high. In applications, mixing hydrogen and natural gas as a mixed gas fuel is a good solution to these problems.

To simulate a diesel-natural gas-hydrogen tri-fuel engine, a suitable reaction mechanism is needed. Although there are already many reduced reaction mechanisms for n-heptane, these mechanisms are basically based on n-heptane itself, and there are very few reduced mechanisms that take into account the effect of added hydrogenated natural gas[9]. Based on this, we developed a reduced mechanism using the detailed mechanism of Lawrence Livermore National Laboratory (LLNL), which consists of 654 species and 2827-step elementary reactions. The size of this detailed mechanism is too big for a three-dimensional simulation.

CONSTRUCTION OF THE REDUCED MECHANISM FOR DIESEL-CH$_4$-H$_2$ TRI-FUEL

There are many methods for reducing the reaction mechanism. These methods have mainly been developed with the following characteristics: sensitivity, matrix analysis, reaction rate analysis, reaction path analysis, error, and changes in entropy production. The specific algorithms include the direct relation graph (DRG), path flux analysis (PFA), quasi-steady-state approximation (QSSA), computational singular perturbation (CSP), isomer lumping, sensitivity analysis, and recently developed procedures that are based on algorithmic optimization, such as artificial neural networks.

The CSP algorithm for mechanism reduction is a purely mathematical theory. This algorithm was first raised by Lam and Goussis[10]. They extracted time information through analyzing and processing the Jacobian matrix and solved the problem of the system's rigidity by using relevant theories. It can be used to analyze the unimportant materials and reactions in a mechanism. Lu and Law et al.[11] found that CSP can be used to determine the quasi-steady-state elements in a rapid equilibrium reaction and also the non-quasi-steady-state elements that have little effect on the target. Goussis et al.[12] developed a reduced mechanism for the formation of NOx in a premixed methane air flame. There are many other researchers, such as Trevino, Solorio, Mendez, and Garcia[13, 14], who have developed reduced mechanisms based on the ignition process using the CSP method.

DRG was first proposed by Lu and Law et al.[15, 16]. The basic idea of this method is to propose some target elements that researchers are interested in and to determine how these elements are related to other elements in the mechanism. Then, the reduced mechanism can be obtained by gradually deleting the elements step-by-step according to the relationship.

The relationship between element i and j can be calculated using the following formula:

$$R_{i \to j} = \frac{\sum a \in C(i,j) |v_{ia} r_a|}{\sum a \in R(i) |v_{ia} r_a|} \tag{1}$$

In equation (1), $C(i,j)$ represents the reaction that contains both substances i and j. V_{ia} represents the coefficient of element i in reaction a, r_a represents the reaction rate, and $R(i)$ represents all of the reactions involved in element i.

Many scholars have reduced the mechanism using the DRG algorithm. For example, Luo et al.[17] developed a reduced mechanism for methane/ethane dual-fuel. Sankaran et al.[18] studied the flame structure of methane using a Bunsen burner and developed a reduced mechanism of methane. Luo et al.[19] developed a reduced mechanism for n-dodecane, and Luo et al.[20] developed a reduced mechanism for biodiesel using the DRG algorithm.

The DRG algorithm is very fast, about tens to hundreds of times that of SA. Therefore, it can be used for large mechanisms for the first step of reducing the mechanism by quickly removing unimportant elements. Tosatto et al.[21] compared various DRG-based algorithms.

The DRG algorithm[16, 22] can be used to reduce the n-heptane detailed mechanism of Lawrence Livermore National Laboratory. The HCCI engine model in the Chemkin software was adopted for the simulation. Because of the effect of adding hydrogenated natural gas, the content of natural gas, hydrogen, and diesel was set according to the operation conditions of a diesel engine. The molar ratio of mixed gas to diesel is 1:9; the equivalence ratio is 0.3; the speed of the engine is 1500 rpm; and n-C$_7$H$_{16}$, CH$_4$, H$_2$, CO, CO$_2$, O$_2$, N$_2$, and the H radical are used as the initial-searching elements of the DRG algorithm. Studies found that the reduced mechanism that is obtained via repeated reductions with some smaller threshold value is more accurate than the one that is obtained via only one reduction with a large threshold value. The threshold value is generally set according to the experience of the author. To maintain the accuracy of the reduced mechanism, the in-cylinder pressure with the detailed mechanism of the HCCI engine can be used as the criterion for the developed reduced mechanism. Also, if the deviation of the pressure is set to be no more than a certain value, then mechanisms of different sizes can be obtained.

The definition of deviation is as follows:

$$\frac{|value\ from\ master\ mech - value\ from\ skeletal\ mech|}{(R \times |value\ from\ master\ mech| + A)} \tag{2}$$
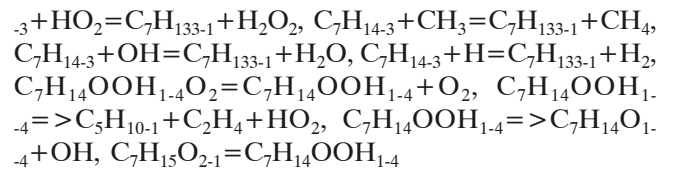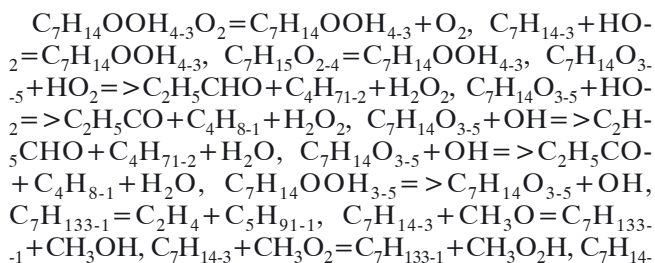
In equation (2), R is the set relative error and A is the set absolute error. If the value calculated using equation (2) is less than 1, then it is considered that the set error is satisfied.

The procedure for reducing the mechanism is described below, using the relative error of the in-cylinder pressure, which is no more than 30%, as an example. (There are 290 sample points, each of which satisfies the requirement of the pre-set deviation.) The detailed mechanism used for reduction is the detailed mechanism of the Lawrence Livermore National Laboratory, containing 654 elements and 2827 elementary reactions. With a threshold value of 0.1, a reduced mechanism with 328 elements and 1614 reactions is obtained. Then, if the requirements of the

threshold value can be satisfied after verification, the reduction procedure should continue. Next, a threshold value of 0.1 is used, and a reduced mechanism with 326 elements and 1598 reactions is obtained. Then, if the pressure requirements are satisfied, the reduction should continue. Then, a threshold value 0.15 is used, and a reduced mechanism with 240 elements and 1171 reactions is obtained. Then, the pressure requirements cannot be satisfied after verification, a smaller threshold value of 0.125 should be used to continuously reduce the mechanism with 326 species. From this, a reduced mechanism with 266 elements and 1278 reactions is obtained. Then, if the requirements of the threshold value are satisfied after verification, then the reduction should continue using a much smaller threshold value of 0.125; a reduced mechanism with 264 elements and 1251 reactions is obtained. Following these, the pressure requirements cannot be satisfied after verification, the number of elements of the two reduced mechanisms that are obtained in the end are very close (266 and 264 elements); thus, the DRG algorithm stops.

Because of the strong connection between some elements, these elements are deleted or retained at the same time while using the DRG algorithm to reduce the mechanism. However, for a given simulation target, only some of the retained elements affect the simulation target, and the other elements can be deleted. In such a case, the reaction mechanism can be continuously reduced using sensitivity analysis after it is reduced using the DRG algorithm. Sensitivity analysis reduces the mechanism by removing elements one by one. Then, the impact of the removed element on the simulation target is observed, and the elements are ranked according to the significance of their impacts. Much larger substances should be deleted second followed by the smaller ones until the deviation of the simulation target exceeds a given value. Sensitivity analysis can further reduce the reaction mechanism. However, sensitivity analysis is time-consuming, and thus, it should be performed after the DRG algorithm. Using sensitivity analysis to further reduce the reduced mechanism, a reduced mechanism with 262 elements and 1259 reactions is obtained. This reduction can still maintain the accuracy of the in-cylinder pressure with the given precision.

The four elements that were deleted using sensitivity analysis are as follows: $C_7H_{14}OOH_{4-3}$ (the error associated with this element is 28.37%), $C_7H_{14}O_{3-5}$ (the error associated with this element is 40.91%), C_7H_{133-1} (the error associated with this element is 69.37%), and $C_7H_{14}O-OH_{1-4}$ (the associated with this element is 69.63%). By comparing the two values, it is found that the sensitivity error caused by the remaining substances is greater than that of the above four substances, and the cumulative error exceeds the given relative error while continuing to delete. The deleted related reactions are as follows:

$C_7H_{14}OOH_{4-3}O_2 = C_7H_{14}OOH_{4-3} + O_2$, $C_7H_{14-3} + HO_2 = C_7H_{14}OOH_{4-3}$, $C_7H_{15}O_{2-4} = C_7H_{14}OOH_{4-3}$, $C_7H_{14}O_{3-5} + HO_2 = > C_2H_5CHO + C_4H_{71-2} + H_2O_2$, $C_7H_{14}O_{3-5} + HO_2 = > C_2H_5CO + C_4H_{8-1} + H_2O_2$, $C_7H_{14}O_{3-5} + OH = > C_2H_5CHO + C_4H_{71-2} + H_2O$, $C_7H_{14}O_{3-5} + OH = > C_2H_5CO + C_4H_{8-1} + H_2O$, $C_7H_{14}OOH_{3-5} = > C_7H_{14}O_{3-5} + OH$, $C_7H_{133-1} = C_2H_4 + C_5H_{91-1}$, $C_7H_{14-3} + CH_3O = C_7H_{133-1} + CH_3OH$, $C_7H_{14-3} + CH_3O_2 = C_7H_{133-1} + CH_3O_2H$, $C_7H_{14-3} + HO_2 = C_7H_{133-1} + H_2O_2$, $C_7H_{14-3} + CH_3 = C_7H_{133-1} + CH_4$, $C_7H_{14-3} + OH = C_7H_{133-1} + H_2O$, $C_7H_{14-3} + H = C_7H_{133-1} + H_2$, $C_7H_{14}OOH_{1-4}O_2 = C_7H_{14}OOH_{1-4} + O_2$, $C_7H_{14}OOH_{1-4} = > C_5H_{10-1} + C_2H_4 + HO_2$, $C_7H_{14}OOH_{1-4} = > C_7H_{14}O_{1-4} + OH$, $C_7H_{15}O_{2-1} = C_7H_{14}OOH_{1-4}$

In this way, the resulting mechanism contains 262 elements and their related reactions. Different given error values lead to different sizes of reduced mechanisms. In the reduction process, if mixed gas is not the initial searching element of the DRG algorithm, the obtained reduced mechanisms are different. A comparison of the number of elements of different reduced mechanisms is shown in Figure 2.
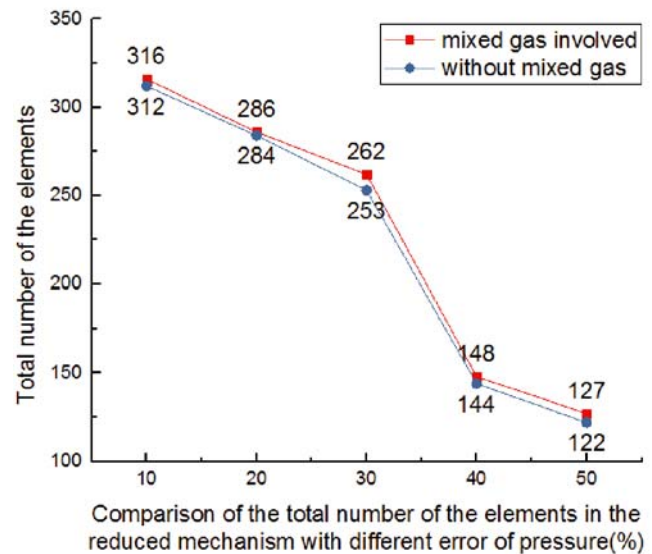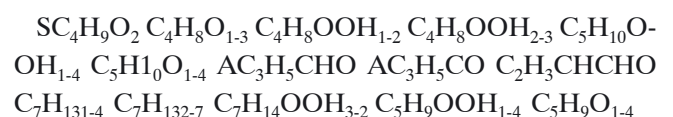

Figure 2. Size of the reduced mechanism under different conditions

For example, with a pressure error of 30%, the following elements are specifically possessed by the reduced mechanism with 262 elements:

$SC_4H_9O_2$ $C_4H_8O_{1-3}$ $C_4H_8OOH_{1-2}$ $C_4H_8OOH_{2-3}$ $C_5H_{10}O-OH_{1-4}$ $C_5H_{10}O_{1-4}$ AC_3H_5CHO AC_3H_5CO C_2H_3CHCHO C_7H_{131-4} C_7H_{132-7} $C_7H_{14}OOH_{3-2}$ $C_5H_9OOH_{1-4}$ $C_5H_9O_{1-4}$

Also, the following elements are specifically possessed by the reduced mechanism with 253 elements:

$C_3H_6OOH_{1-3}$ $C_3H_6OOH_{1-3}O_2$ $C_6H_{13}O_{2-1}$ $C_7H_{14}OOH_{1-4}$ $C_7H_{14}OOH_{4-3}$
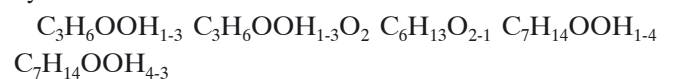
As seen, the presence of mixed gas has a certain effect on the DRG process. Several reduced mechanisms that include mixed gas are named as reduced mechanism 1 (relative pressure error of 10%), reduced mechanism 2 (relative pressure error of 20%), reduced mechanism 3 (relative pressure error of 30%), reduced mechanism 4 (relative pressure error of 40%), and reduced mechanism 5 (relative pressure error of 50%). Considering the time cost of the calculations and the accuracy of the reduced mechanism, reduced mechanisms 3, 4, and 5 are suitable for three-dimensional simulation. The pressure predictions of the above five reduced mechanisms and the detailed mechanism on the HCCI model in Chemkin software are shown in Figure 3.
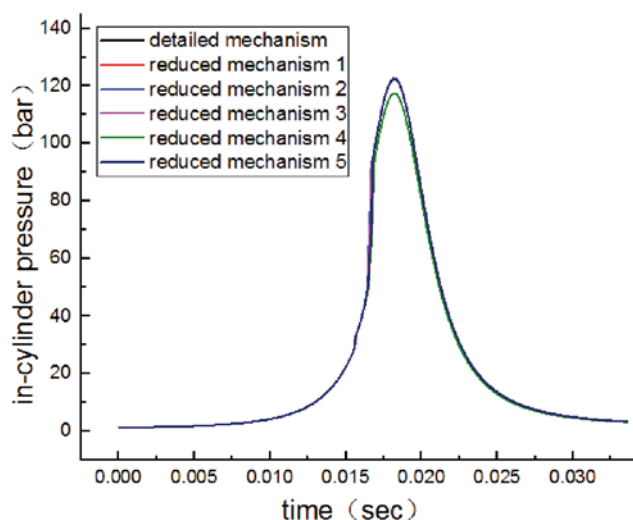
Figure 3. Comparison of different mechanisms with different in-cylinder pressure

VALIDATION OF THE REDUCED MECHANISM

Validation Based on the Ignition Delay Time .

The error on the ignition delay time of the reduced mechanism can be verified using the perfected-stired--reaction (PSR) model in Chemkin software. This model is similar to the constant-volume bomb experiment. In the constant-volume bomb experiment, the ignition time can be distinguished by observing the burning of gases. However, in the Chemkin simulation calculation, there is no sign when the ignition occurs, and hence, the Chemkin software can distinguish the ignition time according to the following three characteristics: (1) the concentration of a certain of substance, (2) the rate at which temperature increases reaches a pre-specified value, and (3) the gradient of temperature change reaches a pre-specified value. After calculating the simulation, we found that the ignition delay time did not change much under these three standards. We verified the effects of the reduced mechanism on the ignition delay time: operation condition 1: pure diesel; operation condition 2: 50% diesel and 50% mixed gas; operation condition 3: pure methane and hydrogen. The range of verified temperature is 700 K–1400 K. A comparison of the results is shown in Figures 4, 5 and 6.
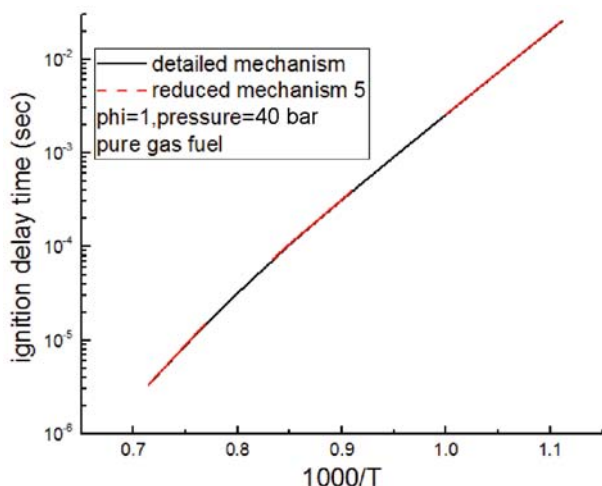

Figure 4. Comparison of the ignition delay time of pure mixed gas with detailed and reduced mechanisms

As shown in Figure 4, the ignition delay time is in good agreement in the case of pure mixed gas, and no ignition occurs in the low-temperature zone.
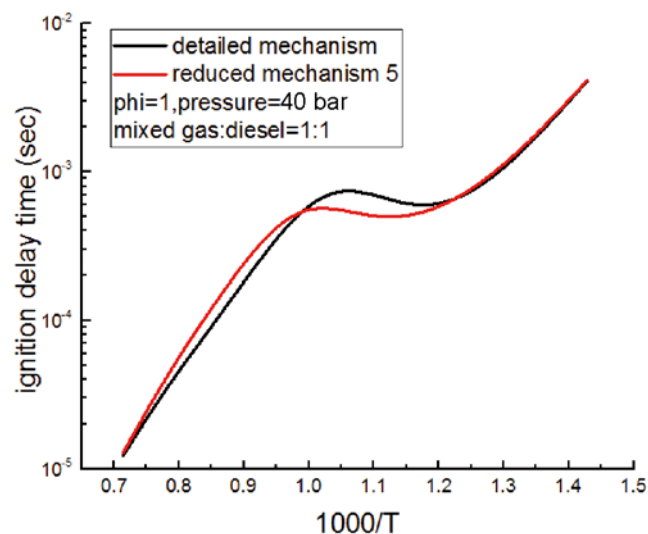

Figure 5. Comparison of ignition delay time (50:50 mol.%) with detailed and reduced mechanisms

As shown in Figure 5, in the negative temperature coefficient region, the predicted time of the reduced mechanism is a little less; in the high-temperature re-action zone, it is a little more. In general, the reduced mechanism shows good agreement with the detailed mechanism.
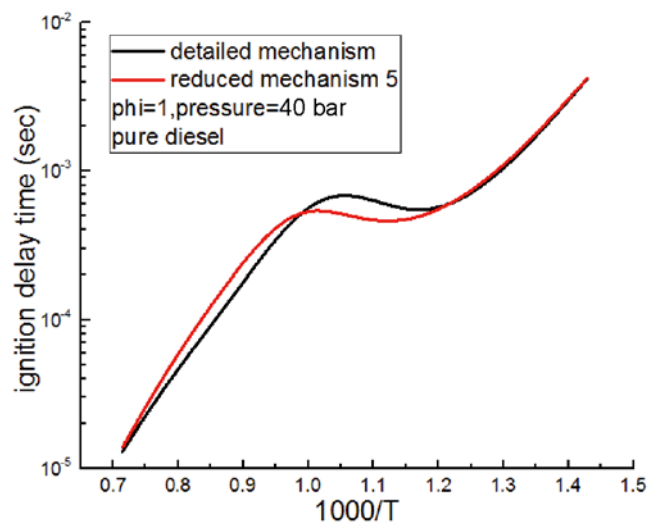

Figure 6. Comparison of the ignition delay time of pure diesel with detailed and reduced mechanisms

Figure 6 shows a comparison of the ignition delay time of pure diesel with detailed and reduced mechanisms. Since the effect of adding mixed gas is small, although the calculation process is different, for predicting the ignition delay time of pure diesel, the prediction error of reduced mechanism 5 is very similar to that of the case using diesel: mixed gas in a ratio of 1:1. Basically, the prediction for the ignition delay time of pure diesel is in good agreement with that of the detailed mechanism.

Verification Based on Flame Speed.

The ignition delay time of pure diesel was predicted using the reduced mechanism, and the results were

compared with the results measured by Ciezki et al.[23] The simulated pressure was 40 bar, and the values of the equivalence ratio were 2, 1, and 0.5. A comparison of the results is shown in Figure 7, and from this, it can be seen that the reduced mechanism is in good agreement with the experimental data.
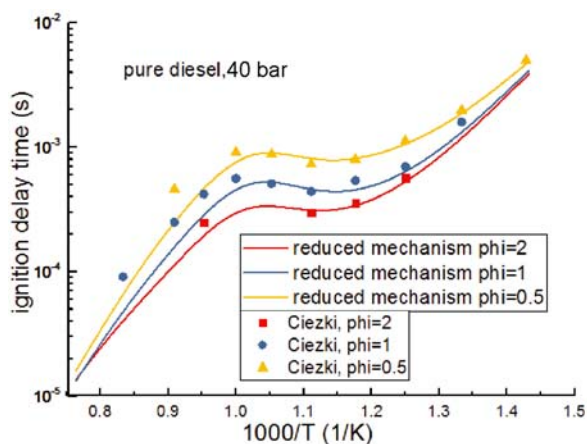

Figure 7. Comparison of the ignition delay time of pure diesel with the reduced mechanism and experiment

A related calculation was performed using the model for the calculation of laminar flame speed in Chemkin software. The given temperature was 400 K, the pressure was 1bar, and phi = 0.7–1.4. The reduced mechanism and detailed mechanism were used to calculate the laminar flame speed, and the results were compared with the experimental data of Kumar[24, 25]. A comparison of the results is shown in Figures 8 and 9.
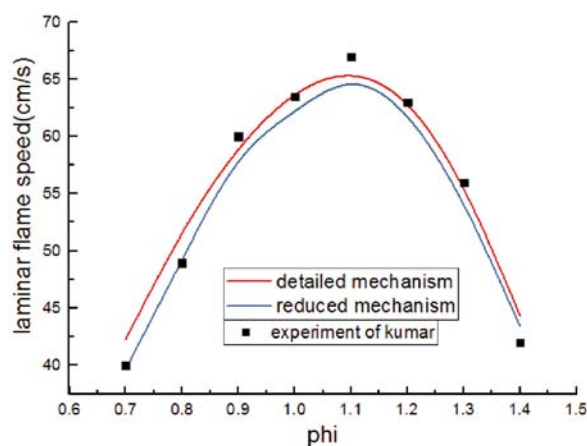

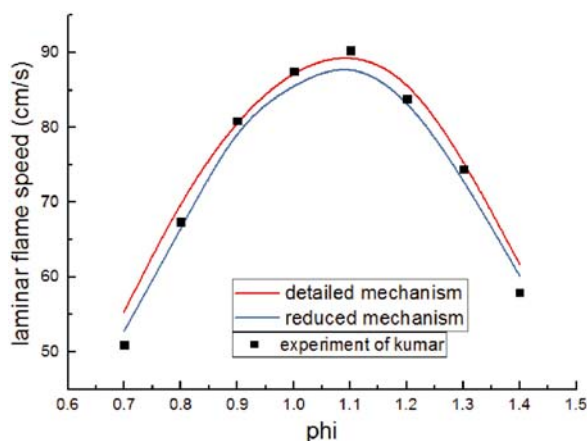**Figure 8.** Laminar flame speed of N-heptane at 400 K and 1 bar

Figure 9. Laminar flame speed of N-heptane at 470 K and 1 bar

Figure 9 shows a comparison of results obtained at 470 K, 1 bar, and phi = 0.7–1.4.

CONCLUSIONS

In this paper, a reduced mechanism for diesel-CH_4-H_2 tri-fuel is constructed. From the analysis of the direct relation graph, it is found that the presence of hydrogen in the initial searching elements has a great effect on the resulting mechanisms. Therefore, hydrogen and methane should be contained in the initial searching elements of the direct relation graph when a reduced mechanism for diesel-CH_4-H_2 is developed. The detailed mechanism is reduced by two methods. The first reduction was performed using the direct relation graph, using diesel, methane, hydrogen, and air as the initial groups. To overcome the weakness of the direct relation graph, sensitivity analysis is used for further reduction. To verify the accuracy of the reduced mechanism, we performed verification of the ignition delay time using the reduced mechanism with three conditions: mixed gas, mixed gas: diesel=1:1, and pure diesel. Also, we found that the agreement of the detailed mechanism is better. The calculation of laminar flame speed using Chemkin software with the reduced mechanism also shows good agreement with the detailed mechanism.

DATA AVAILABILITY

The data used to support the findings of this study have been deposited in the "figshare" repository (DOI: 10.6084/m9.figshare.11985189).

COMPETING INTERESTS

The authors declare that there are no competing interests in this paper.

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LITERATURE CITED

1. Shudo, T. & Takahashi, T. (2004). Influence of Reformed Gas Composition on HCCI Combustion Engine System fueled with DME and H2-CO-CO2 which are Onboard-reformed from Methanol Utilizing Engine Exhaust Heat. JSME *Internat. J.* 70(698), 2663–2669. DOI: 10.1299/kikaib.70.2663.

2. Shudo, T. (2006). An HCCI combustion engine system using on-board reformed gases of methanol with waste heat recovery: ignition control by hydrogen. *Int. J. Vehicle Des.* 41(1–4), 206–226. DOI: 10.1504/IJVD.2006.009669.

3. Li, H.L. & Karim, G.A. (2005). Exhaust emissions from an SI engine operating on gaseous fuel mixtures containing hydrogen. *Int. J. Hydrogen. Energ.* 30(13–14), 1491–1499. DOI: 10.1016/j.ijhydene.2005.05.007.

4. Tutak, W., Jamrozik, A. & Grab-Rogalinski, K. (2020). Effect of natural gas enrichment with hydrogen on combustion process and emission characteristic of a dual fuel diesel engine. *Int. J. Hydrogen. Energ.* 1(119), 901–910. DOI: 10.1016/j.ijhydene.2020.01.080.

5. D'Andrea, T., Henshaw, P., Ting, D.S.K. (2004). The addition of hydrogen to a gasoline-fuelled SI engine. *Int. J. Hydrogen Energ*. 29(14), 1541–1552. DOI: 10.1016/j.ijhydene.2004.02.002.

6. Sobiesiak, A., Uykur, C., Ting, S.K. & Henshaw, P.F. (2002). Hydrogen/Oxygen Additives Influence on Premixed Iso-Octane/Air Flame. SAE Technical Papers, 2002. DOI: 10.4271/2002-01-1710.

7. Norbeck, J.M., Heffel, J.W., Durbin, T.D., Tabbara, B., Bowden, J.M. & Montano, M.C. (1996). Hydrogen fuel for surface transportation. Society of Automotive Engineers.

8. Das, L.M. (1996). Hydrogen-oxygen reaction mechanism and its implication to hydrogen engine combustion. *Int. J. Hydrogen. Energ*. 21(8), 703–715. DOI: 10.1016/0360-3199(95)00138-7.

9. Feng, S.Q. (2017). Numerical Study of the Performance and Emission of a Diesel-Syngas Dual Fuel Engine. *Math. Probl. Eng*. (21), 1–12. DOI: 10.1155/2017/6825079.

10. Lam, S.H. & Goussis, D.A. (1994). The CSP method for simplifying kinetics. *Int. J. Chem. Kinet*. 26(4), 461–486. DOI: 10.1002/kin.550260408.

11. Lu, T.F. & Law, C.K., (2008). A criterion based on computational singular perturbation for the identification of quasi steady state species: A reduced mechanism for methane oxidation with NO chemistry. *Combust. Flame* 154(4), 761–774. DOI: 10.1016/j.combustflame.2008.04.025.

12. Goussis, D.A. & Skevis, G. (2005). Nitrogen chemistry controlling steps in methane-air premixed flames. 3rd M.I.T. Conference on Computational Fluid and Solid Mechanics. 2005, 650–653.

13. Wu, Z.Z., Qiao, X.Q. & Huang, Z.(2013). A criterion based on computational singular perturbation for the construction of reduced mechanism for dimethyl ether oxidation. *J. Serb. Chem. Soc*. 78(8), 1177–1188. DOI: 10.2298/JSC121122023W.

14. Treviño, C. & Méndez, F. (1991). Asymptotic analysis of the ignition of hydrogen by a hot plate in a boundary layer flow. *Combust. Sci. Technol*. 78(4–6), 197–216. DOI: 10.1080/00102209108951749.

15. Lu, T.F. & Law, C.K. (2006). Linear time reduction of large kinetic mechanisms with directed relation graph: n-Heptane and iso-octane. *Combust. Flame* 144(1–2), 24–36. DOI: 10.1016/ j.combustflame.2005.02.015.

16. Lu, T.F. & Law, C.K. (2005). A directed relation graph method for mechanism reduction. P Combust. Inst. 30(1), 1333–1341. DOI: 10.1016/j.proci.2004.08.145.

17. Luo, Z.Y., Lu, T.F. & Liu, J.W. (2011). A reduced mechanism for ethylene/methane mixtures with excessive NO enrichment. *Combust. Flame* 158(7), 1245–1254. DOI: 10.1016/j.combustflame.2010.12.009.

18. Sankaran, R., Hawk, S.E.R., Chen, J.H., Lu, T.F. & Law, C.K. (2007). Structure of a spatially developing turbulent lean methane-air Bunsen flame. *Proc. Combust. Inst*. 31(1), 1291–1298. DOI: 10.1016/j.proci.2006.08.025.

19. Luo, Z.Y., Som, S., Sarathy, S.M., Plomer, M., Pitz, W.J., Longman, D.E. & Lu, T.F. (2014). Development and validation of an n-dodecane skeletal mechanism for spray combustion applications. *Combust. Theory Model*. 18(2), 187–203. DOI: 10.1080/13647830.2013.872807.

20. Luo, Z.Y., Plomer, M., Lu, T.F., Som, S. & Longman, D.E. (2012). A reduced mechanism for biodiesel surrogates with low temperature chemistry for compression ignition engine applications. *Combust. Theory Model*. 99(2), 143–153. DOI: 10.1080/13647830.2011.631034.

21. Tosatto, L., Bennett, B.A.V. & Smooke, M.D. (2013). Comparison of different DRG-based methods for the skeletal reduction of JP-8 surrogate mechanisms. *Combust. Flame* 160(9), 1572–1582. DOI: 10.1016/j.combustflame.2013.03.024.

22. Lu, T.F. & Law, C.K. (2006). On the applicability of directed relation graphs to the reduction of reaction mechanisms. *Combust. Flame* 146(3), 472–483. DOI: 10.1016/ j.combustflame.2006.04.017.

23. Ciezki, H.K. & Adomeit, G. (1993). Shock-tube investigation of self-ignition of n-heptane-air mixtures under engine relevant conditions. *Combust. Flame* 93(4), 421–433. DOI: 10.1016/0010-2180(93)90142-P.

24. Kumar, K., Freeh, J.E., Sung, C.J. & Huang, Y. (2007). Laminar Flame Speeds of Preheated iso-Octane/O2/N2 and n-Heptane/O2/N2 Mixtures. *J. Propul. Power* 23(2), 428–436. DOI: 10.2514/1.24391.

25. Kumar, R., Singhal, A., Katoch, A. & Kumar, S. (2020). Experimental Investigations on Laminar Burning Velocities of n-Heptane+ Air Mixtures at Higher Mixture Temperatures Using Externally Heated Diverging Channel Method. *Energy Fuels* 34(2), 2405–2416. DOI: 10.1021/acs.energyfuels.9b04249.