Development of Natural Gas Chemical Kinetic Mechanisms and Application in Engines: A Review

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ABSTRACT: In this paper, the brief development of chemical kinetic modeling of natural gas is discussed, with emphasis on the development of chemical kinetic mechanisms describing fuel oxidation. The addition of ethane and/or propane to natural gas not only decreases the ignition delay times but also increases flame speeds. Thus, the mixture of methane, ethane, and propane rather than bare methane obtains more accurate predictions for the combustion and emission characteristics of natural gas. This paper also evaluates different comprehensive mechanisms employed for natural gas engines and pointed out their advantages and disadvantages, giving guidance for the selection of mechanisms during the development of natural gas engines.
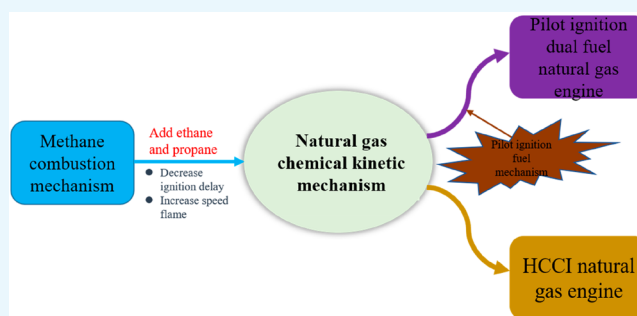
1. INTRODUCTION

With the rising demand of global energy, natural gas plays an important strategic role in energy supply. In 2019, throughout the year, the world's main sources of energy were oil, coal, and natural gas, accounting for 33.1%, 27.0%, and 24.2%, respectively.[1] Meanwhile, the total worldwide proved reserves of natural gas were 198.8 trillion cubic meters (tcm) at the end of 2019, with a growth of approximately 16.60% compared with the end of 2009 (170.5 tcm) and 49.70% compared with the end of 1999 (132.8 tcm).[1] As a kind of clean and environmentally friendly high-quality energy, natural gas produces less carbon dioxide (CO_2) than other fossil fuels, resulting in a lower Greenhouse Effect, so it can fundamentally improve the environmental quality. Natural gas, which is an alternative fuel for crude oil fuels, has been widely used as the energy source for internal combustion engines in the past decades.

The potential of natural gas as an alternative fuel for transportation and heavy-duty power generation applications has led to an increase in demand owing to its high fuel economy, lean combustion characteristics, and relatively low cost. Thus, the combustion science of natural gas has a well-defined purpose in society today, promoting the study and analysis of the problems associated with the generation of air pollutants.[2] In the study of Curran,[2] they showed a diagram of the layers of information required to fully understand the combustion of a fuel from a molecular level, leading ultimately to their use in modern combustors with reduced emissions and improved efficiency (Figure 1), and four broad levels of development that combustion researchers studied were presented (Table 1).

Natural gas is primarily composed of methane with some heavier alkanes ranging from ethane to heptane. Thus, it is necessary to first generate a detailed understanding of the oxidation and pyrolysis kinetics of methane, ethane, and propane when studying the chemical kinetics of natural gas. Methane is an exceedingly important practical fuel, which makes up about 90% of natural gas. More importantly, the oxidation of methane plays an essential role in the combustion of many large hydrocarbon molecules due to its apparent simplicity. Ethane is widely found to be the intermediate in the oxidation of many hydrocarbons, e.g., methane, ethylene, propane, propylene, and higher hydrocarbons, while the thermochemical and combustion properties of propane are similar in many ways to more complex practical hydrocarbon fuels. However, a review of the mechanisms of ethane and propane, which have become an important part of the natural gas combustion process, was not included. Therefore, it is meaningful to make a comprehensive review for methane/ethane/propane mechanism optimization employed during the development of natural gas.

In this paper, the oxidation mechanisms for natural gas are emphasized from two main aspects, i.e., the development of the mechanisms for methane and the optimization for the
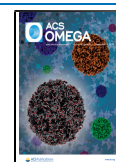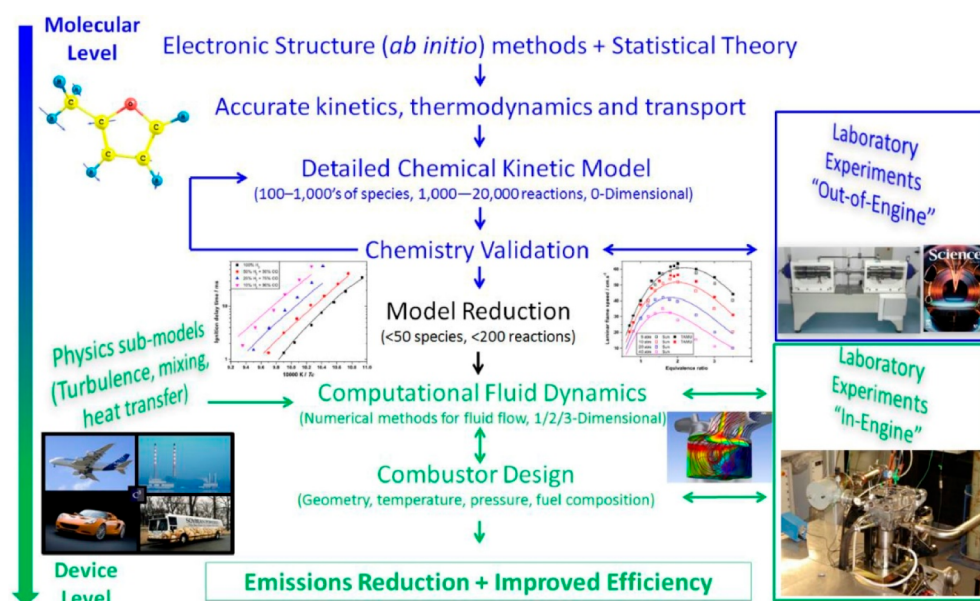
Figure 1. Schematic diagram showing the steps in the development of the understanding of combustion and application to real devices. Reprinted with permission from ref 2. Copyright 2018, Elsevier.

Table 1. Four Broad Levels of Development That Combustion Researchers Study

| levels	description of the level	application and/or validation
(i)	quantum mechanics and direct kinetic measurements of rate constants and reaction intermediates and products	electronic structure, ab initio methods, and statistical theory
(ii)	fuel structure and fundamental chemistry	detailed chemical kinetic mechanisms, validated with experimental measurements (homogeneous reactors, rapid compression machines and engines, and laminar flames)
(iii)	CFD studies with reduced chemistry	reduced chemical kinetic mechanisms retaining target features (ignition delay time, flame speed, etc.) and novel designs of cleaner, more efficient combustors
(iv)	practical applications	jet engines, diesel engines, natural gas safety, fuel inhibition, etc.

reactions with C_2 and C_3 species. The development of the mechanisms for methane is discussed in Section 2 to give guidance for the selection of models or correlations used in the development process of natural gas mechanisms. In this section, the detailed, reduced, and global mechanisms of methane chemical kinetics are evaluated to gain the adaptable range of different mechanisms. Afterward, the optimization for the reactions with C_2 and C_3 species is assessed in Section 3 to give reference to lump and reduce mechanisms. The mechanisms of natural gas associated with other fuels that were employed for natural gas engines are summarized in Section 4. Finally, the most instructive conclusions are provided in Section 5.

2. REACTION MECHANISMS FOR METHANE COMBUSTION

More modeling work has been devoted to the combustion of methane rather than all other hydrocarbon fuels. The early mechanisms are gradually being refined until the current mechanisms can involve more elementary reactions. Table 2 contains a summary of the methane reaction mechanisms (including detailed, reduced, and global reaction mechanisms) for different conditions and combustion environments.

Westbrook and Dryer[3] produced detailed and reduced mechanisms for application to combustion systems, and in 1984 they[4] developed a detailed methane mechanism validated with oxidation and pyrolysis data over a range of equivalent ratios and at elevated pressures in a hierarchical structure.

Here, the reaction and corresponding single-step mechanism from Westbrook and Dryer[3] are

$$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O \tag{1}$$
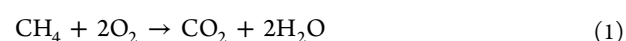
$$k_1 = 1.3 \times 10^8 \exp(-48.4/RT)[CH_4]^{-0.3}[O_2]^{1.3} \tag{2}$$

The two-step global mechanism is similar, but the intermediate species, carbon monoxide (CO), is added:

$$CH_4 + 3/2O_2 \rightarrow CO + 2H_2O \tag{3}$$

$$CO + 1/2O_2 \rightarrow CO_2 \tag{4}$$
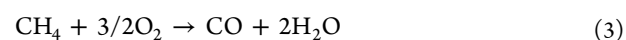
$$k_1 = 2.8 \times 10^9 \exp(-48.4/RT)[CH_4]^{-0.3}[O_2]^{1.3}$$

or

$$k_1 = 1.5 \times 10^7 \exp(-30/RT)[CH_4]^{-0.3}[O_2]^{1.3} \tag{5}$$

$$k_2 = 10^{14.6} \exp(-40/RT)[CO]^1[H_2O]^{0.5}[O_2]^{0.25} \tag{6}$$

$$k_{-2} = 5 \times 10^8 \exp(-40/RT)[CO_2]^1 \tag{7}$$

In the study of Bechtel et al.,[5] a mechanism for methane intended for local measurement of temperature and species concentrations in flames was published. The comparison between the model and the experiment showed that the flame temperature and species concentration of CH_4, O_2, H_2O, CO, CO_2, and OH were in good agreement. However, there was a systematic deviation in the distribution of H_2 concentration.

Table 2. Summary of the Reaction Mechanisms for Methane

ref	mechanism	reactions	species	validation data	pressure/atm	temperature/K	ϕ range
3	Westbrook 1981	1	4	one-step global mechanism	1	298	1
3	Westbrook 1981	2	5	two-step global mechanism	1	298	1
4	Westbrook 1984	168	36	oxidation and pyrolysis	1–15	800–2500	0.07–1.59
5	Bechtel 1981	28	13	species concentrations	1	no data	0.8–1.48
6	Jones 1988	4	6	four-step global mechanism	1	500–2000	0.8–1.48
7	Dagaut 1991	200	38	JSR, shock tube, IDTs	1–13	900–2000	0.1–2.0
8	Leung 1995	451	87	IDTs, species profiles	1	no data	no data
9	GRI Mech 1.2	175	32	species profiles, shock tube, IDTs	0.25–20	no data	0.75–1.25
10	GRI Mech 2.11	277	49	low pressure speeds	0.25–1	900–1400	0.5–1.5
11	GRI Mech 3.0	325	53	shock tube, laminar flame speeds	0.1–10	1000–2500	0.1–5.0
12	Bromly 1996	232	49	species concentrations	No Date	773–973	no data
13	Li 2000	128	31	shock tube	0.1–25	1000–2000	0.4–3.0
14	Konnov 2000	1207	127	shock tube, flame, flow reactor	no data	no data	0.6–1.6
15	Leeds Mech	351	37	IDTs, flame speed and profiles	1	500–2050	0.4–0.6
16	Petrova 2005	177	37	shock tube, laminar speeds	1–8	1000	0.2–2.0
17	Petersen 2007	663	118	shock tube, IDTs	0.05–87	298–2700	0.2–6.0
18	USC 2.0	784	111	shock tube, flow reactor, flame	0.6–15	no data	no data
19	Healy 2008	1580	289	shock tube, RCM	1–50	770–1580	0.5–2.0
20	Healy 2010	1328	230	shock tube, RCM, IDTs	10–30	660–1330	0.5–2.0
21	Slavinskaya 2008	86	19	laminar flame speed	0.1–20	1000–2500	0.7–1.4
22	Azimov 2011	29	16	species profiles, pressure	1–2.2	450	0.5–0.85
23	AramcoMech 1.3	766	124	shock tube, JSR, flames, flow	0.98–69	900–2500	0.1–4.0
24	Wang 2013	428	56	IDTs, laminar flame speed	1–20	1000–1700	0.5–2.0
25	Burke 2015	710	113	shock tube, RCM, IDTs	7–41	600–1600	0.3–2.0
26	SanDiego 2005	235	46	shock tube	1–2	no data	0.5–2.0
27	SanDiego 2012	244	50	shock tube	1–2	500–1000	0.5–2.0
28	Hu 2018	4	6	four-step global mechanism	no data	1200–1800	no data
29	CRECK Mech	1999	114	JSR, PFR, IDTs, flame speeds	0.76–3.77	373–2000	0.1–1.6

Table 3. Jones and Lindstedt Global Combustion Mechanism with Chemical Kinetic Rate Data[a]

reaction	A (cm)	b (s)	E (cal)	reaction orders (mol)
$CH_4 + H_2O \rightarrow CO + 3H_2$	7.82×10^{13}	0	30000	$[CH_4]^{0.5}[O_2]^{1.25}$
$CH_4 + 1/2O_2 \rightarrow CO + 2H_2$	3.00×10^{11}	0	30000	$[CH_4][H_2O]$
$CO_4 + H_2O \rightarrow CO + H_2$	2.75×10^{12}	0	20000	$[CO][H_2O]$
$H_2 + 1/2O \rightarrow H_2O$	1.21×10^{18}	−1	40000	$[H_2]^{0.5}[O_2]^{1.5}$

[a]A = pre-exponential factor. b = temperature exponent of the pre-exponential factor. E activation energy of a chemical reaction.

In 1988, Jones and Lindstedt[6] developed a four-step global mechanism to accurately predict strained methane counterflow diffusion flames. The four-step global mechanism was shown in Table 3, and the forward rate constants for the global reaction scheme were also included. In addition, the global reaction schemes involving only major species could combine with good agreement for flame speeds, flame thickness, and species profiles in both premixed and coflowing diffusion flames.

In 1991, Dagaut used his jet-stirred reactor (JSR) and resulting experimental methane data to validate a detailed mechanism.[7] The proposed mechanism could reproduce the experimental data obtained in the high-pressure JSR and the ignition delay times (IDTs) measured in the shock tube in the pressure range 1–13 atm. It was also able to correctly reproduce H and O atom concentrations measured in a shock tube at 2 atm at 1850−2500 K.

The following work by Leung with Lindstedt resulted in a detailed mechanism[8] validated with the experimental data about methane/air diffusion flames as well as laminar flame speeds. The study used a systematic reaction path flux to highlight the most important reaction paths in methane diffusion flames. Computational results using the mechanism showed good agreement with experimental measurements of major species in the diffusion flame at atmospheric pressure. Despite a thorough analysis, this mechanism was not suitable for use at a wide range of temperatures and equivalence ratios.

Similarly, GRI-Mech[9−11] was an optimized mechanism designed to provide sound basic kinetics, which also was one of the first mechanisms freely available on the Internet used to simulate natural gas combustion and included NOx chemistry[11] to help with emission predictions. It was validated with an extensive collection of experimental data from IDTs and species profiles to laminar flame speeds using sensitivity analysis to drive a systematic optimization striving for minimal computational time and maximum accuracy. Methane ignition delay was well predicted, but flame speeds tended to be slightly overpredicted.[11]

In the year 1996, Bromly et al.[12] proposed a detailed mechanism of methane oxidation, which was extended to include high-temperature hydrocarbon and NOx species. The reaction mechanism for the low-temperature oxidation of methane in the presence of NOx was found to be very close to the high-temperature menthane oxidation mechanism. In order to produce a good fit of the experimental data, the parameters

for CH_3NO_2 and CH_3O_2 had to be adjusted within their range of uncertainties.

In 2000, Li and Williams[13] developed a detailed C_1-C_3 mechanism (referred to as CECR-Mech) to predict methane autoignition based on most shock tube experiments, which was derived from their previous mechanism by deleting nitrogen chemistry. The results of the mechanism prediction of the temperature sensitivity were in good agreement with shock tube experiments. The CECR-Mech also could be significantly simplified when it was applied to predict the knock in dual-fuel engines for equivalence ratio between 0.5 and 1.5 and temperature from 800 to 1500 K with pressure ranging from 50 to 150 bar.

That same year, Konnov[14] published a more detailed methane/natural gas mechanism in CHEMKIN format, which was validated with data focused on H_2, CO, N_2O, and NO_2 species and also dealt with C_2 and C_3 hydrocarbons and NOx formation in flames. The mechanism matched methane flame speeds more closely but slightly overpredicted propane flame speeds. The mechanism also offered a more detailed N−H−O chemistry than other similar mechanisms.

In 2001, a comprehensive chemical mechanism (Leeds Mech) to describe the oxidation of methane was developed by Hughes et al.[15] This mechanism also accounted for the oxidation kinetics of hydrogen, CO_2, ethane, and ethene. It had been tested against a variety of experimental data and compared with three different mechanisms between 1000 and 2000 K to provide an assessment of the similarity of the rate expressions. The mechanism slightly overpredicted experimental methane/air laminar flame speeds but matched ignition delay times more closely.

In 2005, Petrova and Williams[16] reported a small but detailed mechanism whose reactions are all reversible. The mechanism combined multiple well-predicted mechanisms with another for C_3 species, the results of which were tested at temperatures above 1000 K and pressures below about 100 atm. The mechanism overpredicted ignition times at low temperature and underpredicted ignition times slightly at fuel-rich conditions.

Soon after, a comprehensive mechanism,[17] which was based on a validated hydrogen submechanism, a methane/ethane submechanism, and a propane submechanism, was developed to further understand the ignition and oxidation of methane/propane fuel blends intending to cover the data range of industrial gas turbines. To simulate experimental ignition delay times well under high-pressure and low-temperature conditions, Petersen et al.[17] re-estimated the rate constant for the reaction $CH_3O_2 + CH_3 \rightarrow CH_3O + CH_3O$ to be 1.0×10^{13} $\exp(-1000 \text{ cal mol}^{-1}/RT)\text{cm}^3/\text{mol/s}$. The mechanism was in good agreement with the experimental data at 6 and 18 atm but underpredicted the ignition delay time slightly at 29 atm.

The latest version of another detailed mechanism describing the oxidation of H_2 and CO and the high-temperature chemistry of C_1-C_4 hydrocarbons was released in 2007.[18] This mechanism, referred to as USC-Mech II, was developed on the basis of several previously successful mechanisms. The simulation results of the USC mechanism were compared with a large number of experimental data of H_2, CO, and C_1-C_4 oxidation. The methane/air flame speed data that were obtained from the mechanism displayed a satisfactory consistence with the experimental data; unfortunately, the author did not provide more data on methane oxidation.

After a year, Healy and his team[19] proposed a detailed chemical kinetic mechanism to describe methane/propane mixture oxidation at high pressure and a wide range of temperatures (740−1550 K). The mechanism was based on the hierarchical nature of hydrocarbon combustion mechanisms and contained the H_2/O_2 submechanism, together with the CO/CH_4 and lager hydrocarbon submechanisms, and some rate constants from the literature were adopted. They compared the mechanism to data presented by Petersen et al.[17] of high-pressure shock-tube measurements of CH_4/O_2 ignition at high temperatures. Overall, good agreement was observed between the model and the experiment. Subsequently, they published another mechanism[20] by updating the present mechanism[19] to study the oxidation of methane, ethane, and propane mixtures under similar conditions. The simulation results had excellent consistency with experimental data obtained in both the RCM at lower temperatures and in the shock tube at higher temperatures. In 2010, Healy and co-workers[30] established a comprehensive chemical kinetic mechanism to measure methane/n-butane ignition delay, which was combined with their previous mechanisms[19,20] with C_4 submechanism. Simulations using the model were found to be a very close approach to experimental data from RCM and shock tubes and were particularly sensitive to the concentration of n-butane in the blend. Under lean conditions and at high pressures, the methane/n-butane mixture ignition delay times were shorter across the entire temperature range compared to the pure methane simulated times.

In 2008, Slavinskaya et al.[21] published a reduced mechanism for methane combustion in gas turbines intended to predict reliability for pressures up to about 20 atm. To achieve a much better agreement with the flame speed on the basis of sensitivity and reaction rate analysis, they modified the rate coefficients of two reactions $OH + CO \rightarrow CO_2 + H$ and $HCO + M \rightarrow CO + H + M$, and these data were taken from the CEC data. In addition, all other kinetic parameters were identical to GRI-Mech 3.0.[11] The reduced mechanism only slightly underpredicted the flame speed data for stoichiometric mixtures.

In 2011, Azimov et al.[22] developed a reduction mechanism to evaluate the in-cylinder pressure during dual-fuel engine combustion, which was constructed from the nine-step reduced mechanism for CH_4 autoignition by Li et al.[13] and combined with a reduced mechanism for H_2 combustion as well as a detailed mechanism for CO/CO_2 combustion. The model predicted the engine performance well, but results began to deviate from the experimental data as the equivalence ratio increased above 0.8.

In 2013, Metcalfe and co-workers[23] published Aramco-Mech 1.3 to describe the oxidation of small hydrocarbon species. This mechanism was built on work published from NUI Galway and was validated against a large array of experimental measurements including data from shock tubes, JSRs, flow reactors, flame speeds, and flame species profiles. The authors also performed various sensitivity analyses in an attempt to initially understand and to further explain the chemical kinetic systems encountered in the mechanism. They then performed detailed comparisons on the reactions with the highest sensitivities between experimental data and other mechanisms like the Leeds mechanism[15] and GRI-Mech 3.0.[11] However, they had chosen not to include a wide range of validation comparisons due to paper spatial constraints. The other two versions of this mechanism, AramcoMech 2.0 and 3.0, were

developed by the Combustion Chemistry Center NUI Galway and were optimized to characterize the kinetic and thermochemical properties of a large number of C_1-C_4 hydrocarbons and oxygenated fuels under a wide range of experimental conditions.

Similarly, Wang[24] self-published a skeletal mechanism that could maintain the accuracy of predicted fuel combustion properties for high-temperature combustion of H_2 and C_1-C_4 hydrocarbons. The skeletal mechanism was reduced from the USC II mechanism[18] and validated against ignition delay time, species profiles, laminar flame speeds, and flame structures over typical simulation conditions. Methane laminar flame speed was well-predicted, but other fuel laminar flame speeds tended to be slightly overpredicted. The skeletal mechanism was also validated for different mixtures, and good agreement was obtained in comparison to the detailed mechanism. Moreover, the central processing unit time cost of the skeletal mechanism is about 1/3 of the detailed mechanism.

In 2005, Burke et al.[25] developed an accurate chemical kinetic mechanism to predict the combustion of methane and dimethyl and validated it with experimental ignition delay time data covering a range of conditions relevant to gas turbine environments. The mechanism consisted of the H_2/CO submechanism, the C_1-C_2 base submechanism, as well as the propene mechanism. In addition to the CH_4/DME blends, high-pressure data for pure methane were obtained. Where possible, the data were compared with existing experimental data, with good agreement.

The San Diego mechanism,[26,27] updated by the UC San Diego Combustion Research Group from 2001 to 2016, was designed to focus on conditions relevant to flames, high-temperature ignition, and detonations. The species and reactions of this mechanism were kept to the minimum needed to minimize the uncertainties in the rate parameters employed as much as possible. The philosophy of this mechanism was that the rate parameters of a relatively small number of elementary reactions are of crucial importance. Meanwhile, there were a large number of steps with contributions that seldom had more effects. In 2012, Prince and Williams[27] published a detailed mechanism based on the San Diego mechanism,[26] which was revised and augmented to produce the low-temperature ignition and negative temperature coefficient (NTC) behavior. The prediction of this mechanism was compared with the experimental data from RCM and static reactors, and good agreement was obtained.

In the year 2018, Hu et al.[28] developed a four-step global mechanism under moderate and intensive low-oxygen dilution (MILD) oxy-combustion by optimizing the Jones and Lindstedt four-step global mechanism.[6] The mechanism was compared with five other global mechanisms and validated with two detailed mechanisms under three different combustion conditions. This mechanism significantly improved the prediction of peak and equilibrium concentrations of main components under MILD, oxy-fuel, and MILD oxy-combustion conditions. However, for the reaction conditions without experiment data for validation, the global mechanism was validated with two detailed mechanisms. The comparisons showed that the global mechanism obtains trends similar to two detailed mechanisms under three different combustion conditions, but the valve of species concentration between three mechanisms is significantly different.

In 2020, in the study of Bagheri and his co-workers,[29] they updated the CRECK detailed kinetic mechanism to validate

experimental data on MILD and oxy-fuel combustion of methane. They also made use of a thorough kinetic analysis to identify aspects of the mechanism that required further version. The mechanism was based on the Aramco-Mech 2.0, together with the acetaldehyde submechanism to achieve further enhancements. Such a large number of data were analyzed by means of the mechanism, and good agreement with experimental data was obtained. In addition, they found that H_2O and CO_2 dilution in lean methane mixtures reduced the system reactivity and significantly reduced laminar flame speeds.

More recently, Baigmohammadi and his co-workers[31] developed a detailed mechanism to study the ignition delay time characteristics of the C_1-C_2 hydrocarbons over a wide range of temperature, pressure, and equivalence ratio. The comprehensive mechanism was referred to as NUIGMech1.1, consisting of 11 274 elementary and 2746 species. The performances of NUIGMech 1.1 were evaluated using all of the available and measured experimental IDT data. The results showed that the current mechanism could accurately predict the measured IDTs.

3. ETHANE/PROPANE MECHANISM

In order to achieve highly efficient and safe use of natural gas, the kinetic model needs to be used in various mixtures of natural gas to verify its changing combustion characteristics. Natural gas mixtures containing methane, ethane, and propane were the most suitable for analyzing the combustion chemistry of natural gas.

It is well-known that methane reactivity is significantly enhanced by higher alkanes, which thereby decrease the IDTs and increase the burning velocities. There are also studies that have found that when the proportion of ethane increased in natural gas the mole fraction of NO decreased. Thus, it is meaningful to study the optimization process of the combustion submechanism of ethane and propane.

3.1. Optimizing the Ethane Mechanism. Ethane is widely found to be the intermediate in the oxidation of many hydrocarbons, e.g., methane, ethylene, propane, propylene, and higher hydrocarbons,[32] and also is the second largest natural gas component after methane. Furthermore, for the recombination of methyl radicals to produce ethane, with further consumption producing ethylene and acetylene,[2] the flux diagram was shown in Figure 2.

The formation of ethane and its subsequent reactions is characterized by great complexity, so any ignition analysis of methane-oxygen-rich mixtures must involve the analysis of ethane combustion. Cooke and Williams[33] studied the ignition and combustion of ethane and slightly rich methane mixtures at high temperatures where little fuel degradation occurred and only moderate concentrations of C_2H_4 and C_2H_2 were produced during ignition. Dagaut et al.[32] developed a detailed reaction mechanism of ethane oxidation to reproduce the ethane ignition delay times at high temperature and obtained good agreement with the experiment data.

By updating the mechanism to describe ethane oxidation, Rota et al.[34] primarily relied on measurements of species concentrations to simulate and compare experimental data. The parameter sensitivity analysis and a comparison with other mechanisms indicated that the direct oxidation of the C_2H_3 radical should be included in the mechanism. The updated mechanism was able to reproduce reasonably well the main species concentrations.
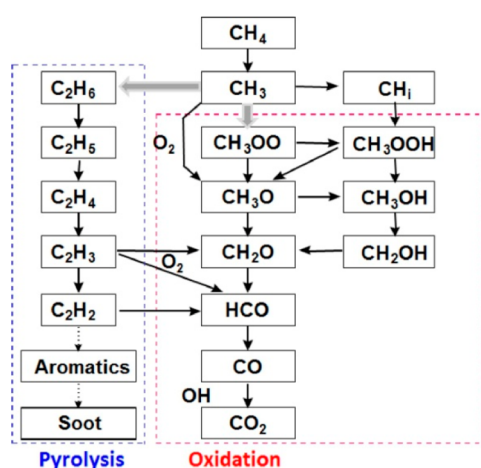
Figure 2. Flux diagram of methyl radical recombination. Adapted with permission from ref 2. Copyright 2018, Elsevier.
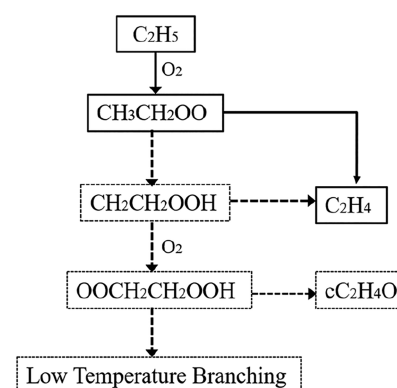

Figure 3. Simplified reaction path diagram for low-temperature, high-pressure oxidation of ethane, emphasizing the importance of NTC-type chemistry. Adapted with permission ref 40. Copyright 2017, Elsevier.

Younessi-Sinaki et al.[35] updated the mechanism for ethane oxidation by removing the reactions containing species with an oxygen atom and adjusting the rate constants, based on the determinations for the literature, for the reaction $C_2H_5 + H$, and the rate coefficient of this reaction was increased to about 22.5 times its initial value.

Prince and Williams[27] developed a mechanism to describe low-temperature ignition of ethane using rate constants from the literature and adjusted the rates of reaction $C_2H_5 + O_2$ based on ignition time measurements in rapid-compression machines under a wide range of conditions for initial temperatures above about 1000 K.

For the reaction of $C_2H_5 + O_2$ as the center in the oxidation of ethane, some scholars use different methods to study the importance of this reaction step. More relevant information is shown in Table 4.

Furthermore, Hidaka and co-workers[38] also evaluated the rate constants of the reactions $C_2H_5 + H \rightarrow C_2H_4 + H_2$ and $C_2H_5 + O_2 \rightarrow C_2H_4 + H_2O$ whose values are significantly different from accepted values, respectively. Moreover, Konnov et al.[39] studied the oxidation of ethane at low temperature, and the results indicated that the rate of reaction $C_2H_5 + O_2$ is crucial to the accuracy of the model. The rate constant of C_2H_5 decomposition has close sensitivity coefficients in lean, stoichiometric, and rich mixtures.

Recently, Hashemi et al.[40] proposed a mechanism for ethane oxidation based on high-pressure oxidation of hydrogen, syngas, and C_1-C_2 species. They adjusted the rate constants for the reactions $C_2H_5 + O_2$ and $C_2H_4 + HO_2$ and modified Arrhenius fits of calculated rate constants for $CH_3CH_2OO \rightarrow CH_2CH_2OOH$. Figure 3 showed a simplified pathway diagram for conversion of C_2H_5 of Hashemi's work.[40]

3.2. Optimizing the Propane Mechanism. Unlike hydrocarbon fuels with simpler structures such as methane or ethane, the thermochemical and combustion properties of propane are similar in many ways to more complex practical fuels. In the early years, Westbrook and Pitz[41] published a comprehensive mechanism to describe the oxidation and pyrolysis of propane and propene and emphasized that the existence of small amounts of propane in natural gas can have a significant influence on its ignition property. Many other detailed chemical kinetic mechanisms describing propane kinetics have been developed over the years including those for propane combustion chemistry from Qin et al.,[42] a low- and high-temperature mechanism of propane oxidation from Titova et al.,[43] a comprehensive mechanism involving C_1-C_5 alkane oxidation from Healy and co-workers,[44] and a suitable kinetic mechanism for modeling natural gas combustion from Gokulakrishnan et al.[45]

Some literature studies have proved that some key reactions in the propane mechanism play an incredible role under different pressures and temperatures and also can affect the ignition delay time. Recently, Hashemi et al.[49] adjusted the rate constant, based on recent determinations for the literature, for the reaction $C_3H_8 + O_2$ and their own flow reactor measurements of species profiles versus temperature. The specific relationship between propane oxidation reactions and basic state parameters (i.e., temperature and pressure) is shown in Table 5.

Figure 4 shows model-simulated laminar speed flames for propane, propanal, n-propanol, and acetone oxidation in air at 1 atm and 393 K using a mechanism by Gong et al.[50] To achieve good agreement with experimental results, the C_1-C_4 submodel was updated to the AramcoMech 1.3 mechanism

Table 4. More Relevant Information about the Reaction $C_2H_5 + O_2$

literature	computational methods	research content	discussion and analysis
Quelch (36)	ab initio theoretical methods	molecular geometries, vibrational frequencies, and energetics and implications for kinetics modeling	ethylperoxy radical
Kiracofe (37)	highly sophisticated electronic structure methods	geometric structures, vibrational frequencies, and thermodynamic and electronic considerations	ethylperoxy radical and energetics of each mechanism
Hidaka (38)	simulation using the reported GRI-MECH 1.2 mechanism	new experimental data for the pyrolysis and oxidation of ethane at high temperatures	the rate constants for pyrolysis and oxidation
Konnov (39)	kinetic mechanisms and mechanistic modifications	modeling the ethane oxidation promoted by NO	the effect of temperature variation, ethane/O_2 concentration; sensitivities of NO consumption

Table 5. Relationship between Propane Oxidation Reactions and Temperature/Pressure

| reactions	relationship	experimental validation	ref
reactions of $C_3H_8 + HO_2$(i) and $C_3H_8 + O$(ii)	the relative contribution of reaction (i) increases with pressure, while that of reaction (ii) decreases	jet-stirred flow reactor	46
hydrocarbon reactions involved in the formation of the HO_2 radical and the H_2O_2 molecule	these reactions play a dominant role at temperatures lower than 1100 K and can reduce the ignition delay times	shock tube	47
some of the key reactions involving propylperoxy radicals	these reactions are the key steps to control the rate of oxidation in the NTC region under high-pressure conditions	high-pressure flow reactor	48
reactions about H-abstraction by HO_2 from propane	the reaction of $CH_3 + HO_2$ inhibits ignition at the lower pressure of 10 bar; the reactions of $C_3H_8 + OH$ accelerate ignition at 900 K but inhibit reaction at 1100 K	laminar flow reactor, shock tube, rapid compression machine	49
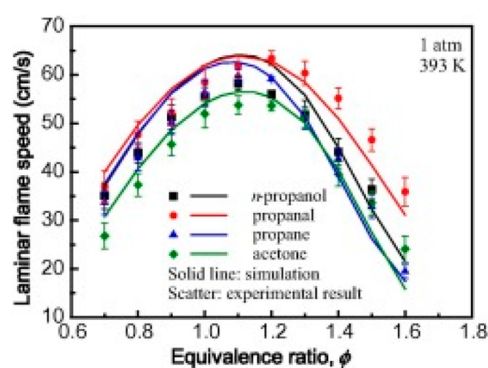
Figure 4. Model-predicted laminar speed flames for propane, propanal, n-propanol, and acetone oxidation in air at 1 atm and 393 K and compared with experimental results. Adapted the permission from ref 50. Copyright 2015, Elsevier.

and the n-propanol submechanism as well as the propanol submechanism.

More recently, Bramltte and Depcik[51] summarized a large number of available propane–air kinetic mechanisms and selected the detailed San Diego mechanism to model the combustion process of a ramjet engine design. The San Diego mechanism was in agreement with the experimental ignition delay across a wide range of equivalence and temperatures. Due to the excessively long computational times, they developed a reduced mechanism by removing all the reactions not affecting the ignition delay at the 1 ms level and compared it with the original mechanism and experimental ignition delay. The results are shown in Figure 5.

4. COMPREHENSIVE MECHANISMS EMPLOYED FOR NATURAL GAS ENGINES

Natural gas is mainly composed of methane and some heavier alkanes from ethane to heptane. It was also found that natural
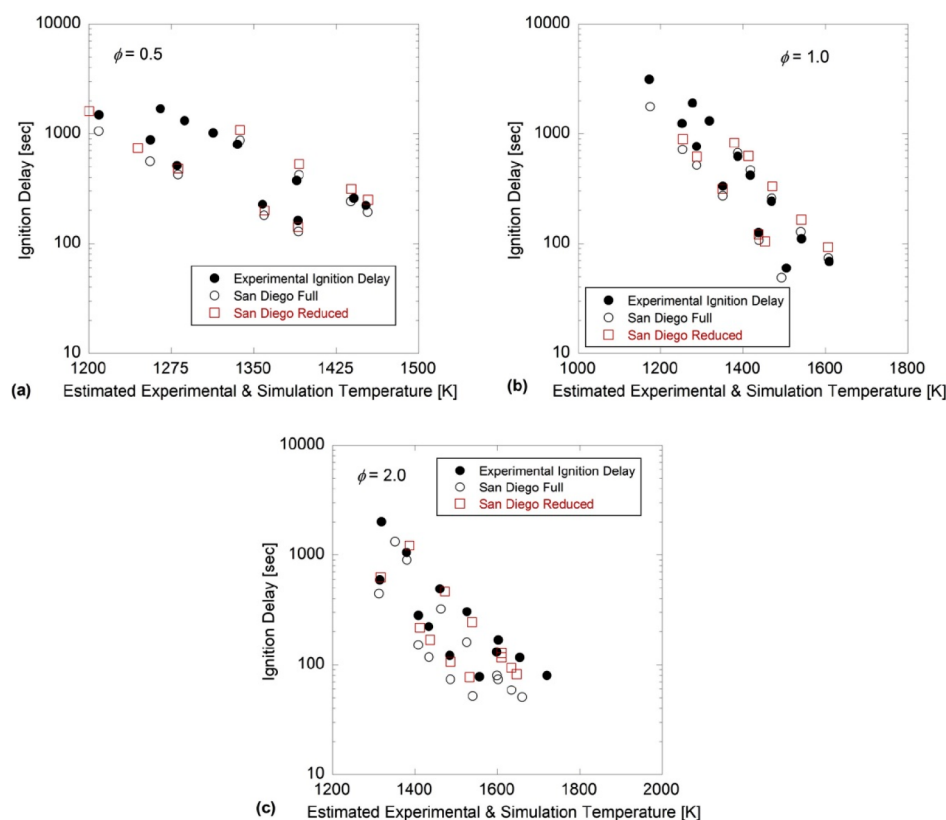

Figure 5. Comparison of the full and reduced San Diego mechanism ignition delays for 1-D shock tube simulations against experimental data for (a) ϕ = 0.5, (b) ϕ = 1.0, and (c) ϕ = 2.0. Adapted with permission from ref 51. Copyright 2020, Elsevier.

gas mixtures containing methane, ethane, and propane were the most suitable for analyzing the combustion chemistry of natural gas.

Westbrook and Dryer[3] not only discussed the kinetic mechanism of C_0-C_4 fuels in detail but also proposed the hierarchical structure of the reaction mechanisms for complex fuels. Dagaut et al.[7,46] published a natural gas mechanism and studied the numerical simulation of natural gas combustion in high-temperature conditions. To improve the prediction for the ignition delay time of natural gas, Mohamed et al.[52] adopted an optimized mechanism validated against a wide range of experimental conditions; nevertheless, the prediction of ignition delay time was not verified for the temperature above 1050 K, suggesting that ignition delay time may not be well reproduced by the mechanism. The comprehensive skeletal mechanism developed in the study of Xue et al.,[53] which is reduced using six direct relation graph (DRG) related methods for different key species could predict the important characteristics for single-component fuels reasonably. Obviously, the skeletal mechanism cannot reproduce the combustion properties of all multicomponent mixed fuels. Besides, many detailed mechanisms, such as the Leeds mechanism,[15] the GRI-Mech mechanism,[9−11] as well as CRECK Mech[29] and Aramco Mech,[23] have been developed by research institutions and validated for current experimental data together with available literature data. It also includes San Diego Mech II[27] that is only suitable for low-temperature conditions. These detailed mechanisms are involved in the combustion chemistry of natural gas and have evolved in different ways but also quite similar versions of the same mechanism involving similar reactions but with different rate constants.

Even though natural gas is considered as a clean alternative fuel, due to its low cetane number, it should be ignited by some pilot fuels with a high cetane number, so the combustion of natural gas could produce a non-negligible unwanted quantity of pollutants like NOx and soot emissions. NOx formation from natural gas combustion becomes relevant above 1200 °C, and thermal NO formation dominates when temperatures are higher than 1600 °C. Natural gas components like acetylene, propyne, and propene play a major role in the formation of soot as their decomposition leads to the production of more free radicals that promote the formation of polycyclic aromatic hydrocarbons (PAHs) and the further growth of soot particles.

To match the mechanism with the actual situation, the mechanism has been optimized to a certain extent in practical application. Bahlouli et al.[54] presented an optimized chemical kinetic mechanism for an *n*-heptane−NG blend used in a homogeneous charge compression ignition (HCCI) engine. Similarly, in order to solve the problem of HCCI engine combustion timing control, Reyhanian and Hosseini[55] published a comprehensive chemical reaction mechanism for a natural gas, *n*-heptane, and iso-octane blend. The developed model was validated for mentioned fuels at various percentages of syngas using a single-cylinder engine, and the results showed that increasing the syngas fraction in the fuel mixture advanced the combustion time of natural gas fuel, retarded the combustion of *n*-heptane, and had little effect on iso-octane combustion. Then, Pan and Wallace[56] developed a low-temperature natural gas (LTNG) combustion mechanism for compression ignition engine application, and the reliability of the mechanism was validated in a direct-injection natural gas engine. When the temperature is lower than 1300 K, the

LTNG mechanism could more accurately predict the ignition delay than the well-developed GRI 3.0 mechanism. The results also indicated that the LTNG mechanism can well predict the formation of important carbon-containing gaseous species, such as C_2H_2 and CO_2.

The diesel/NG dual-fuel mechanism constructed in the study of Zhang et al.[57] and the GXU mechanism published in the study of Huang et al.,[58] which have been validated for the ignition delay and laminar flame speed, could predict the combustion characteristics of fuel precisely. However, the mole fraction traces of the key species, which are vital for emission prediction during fuel oxidation, remains invalidated. The simulation results obtained by Zhang et al.[57] overpredicted the laminar flame speed at a temperature of 337 K but underpredicted the laminar flame speed at 443 K. As pointed out by Huang et al.,[58] the modeled laminar flame speed of methane was overpredicted at high pressure, and the comparison of experimental NOx and soot emissions with simulated results did not agree well.

In the study of Zhao et al.,[59] a skeletal dual-fuel mechanism for heavy-duty engines fueled by diesel and natural gas was developed. With the purpose of a reducing mechanism, sensitivity analysis and directed relation graph error propagation (DRGEP) were employed. In order to verify the accuracy of the skeletal mechanism, ignition delay testing against shock tube experimental results and engine validation (i.e., in-cylinder pressures, HRR, emissions) against engine testing results were performed. The prediction accuracy of the main species fraction traces, however, was not validated for this mechanism, suggesting that the prediction for the oxidation and emission formation process of natural gas may not be reliable in their numerical study. Liu et al.[60] proposed a four-component reduced mechanism with 847 reactions among 150 species to predict combustion characteristics and emissions from diesel/NG dual-fuel engines. The validation of the reduced mechanism was performed based on ignition delay and laminar flame speed; however, the accuracy is still not sufficient for the prediction under various engine conditions. In the later study of Li et al.,[61] a new comprehensive mechanism for high-precision prediction of soot precursors used in pilot-ignited direct injection natural gas engines was developed; the validation of the novel mechanism, including ignition delay, mole fraction traces of key species, and mole fraction traces of PAH species for all surrogate fuels, was provided, and the simulation results had achieved good consistency.

5. CONCLUSIONS

After summarizing plenty of the published literature on methane/ethane/propane/natural gas combustion mechanisms, the following conclusions could be drawn from different aspects:

(1) Methane is an exceedingly important practical fuel and makes up about 90% of natural gas. The mechanism of methane combustion is also constantly updated and optimized over time. Meanwhile, the addition of ethane and/or propane improves the prediction accuracy of the mechanism, decreases the IDTs, and increases flame speeds.

(2) Ethane is intermediate between the smallest alkane methane and the large alkanes such as propane and butane. The key reaction in oxidation of ethane at intermediate temperature is $C_2H_5 + O_2$. At the same

time, the optimization of the mechanism of ethane oxidation begins with changing the rate constant of this reaction.

(3) The oxidation properties of propane, a minor but sensitive component in natural gas, are similar to more complex practical fuels. Propane oxidation plays a valuable role in propane combustion and has a significant effect on ignition delay. The ignition can be accelerated at low and medium temperatures, and the ignition delay will be promoted at higher temperatures.

(4) When the natural gas mechanism is employed to describe the combustion characteristics of fuel in a dual-fuel natural gas engine, as supersonic jet simulation should be involved in the in-cylinder working process, the consumption of computation sources is higher than conventional natural gas engines. In this case, a reduced or skeletal chemical mechanism has been considered as a reliable and high-accuracy option for the combustion and emission formation prediction.

(5) In the optimization process of natural gas mechanisms, most of the mechanisms have evolved in different ways but also have quite similar versions of the same mechanism involving similar reactions but with different rate constants. Experimental measurements and high-level quantum chemical calculations of reaction rate constants in the C_0-C_4 subsystem are essential for accurate prediction of all advanced hydrocarbons and oxygen-containing hydrocarbon species.

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■ ACKNOWLEDGMENTS

■ REFERENCES

(1) British Petroleum. *Statistical Review of World Energy* (2020). https://www.bp.com/en/global/corporate/energy-economics/statistical-review-of-world-energy/natural-gas.html.

(2) Curran, H. J. Developing detailed chemical kinetic mechanisms for fuel combustion. *Proc. Combust. Inst.* **2019**, *37* (1), 57−81.

(3) Westbrook, C. K.; Dryer, F. L. Simplified Reaction Mechanisms for the Oxidation of Hydrocarbon Fuels in Flames. *Combust. Sci. Technol.* **1981**, *27* (1−2), 31−43.

(4) Westbrook, C. K.; Dryer, F. L. Chemical kinetic modeling of hydrocarbon combustion. *Prog. Energy Combust. Sci.* **1984**, *10* (1), 1−57.

(5) Bechtel, J. H.; Blint, R. J.; Dasch, C. J.; Weinberger, D. A. Atmospheric pressure premixed hydrocarbon-air flames: Theory and experiment. *Combust. Flame* **1981**, *42*, 197−213.

(6) Jones, W. P.; Lindstedt, R. P. Global reaction schemes for hydrocarbon combustion. *Combust. Flame* **1988**, *73* (3), 233−249.

(7) Dagaut, P.; Boettner, J.-C.; Cathonnet, M. Methane Oxidation: Experimental and Kinetic Modeling Study. *Combust. Sci. Technol.* **1991**, *77* (1−3), 127−148.

(8) Leung, K. M.; Lindstedt, R. P. Detailed kinetic modeling of C1-C3 alkane diffusion flames. *Combust. Flame* **1995**, *102* (1−2), 129−160.

(9) Frenklach, M.; Wang, H.; Yu, C.-L.; Goldenberg, M.; Bowman, C. T.; Hanson, R. K.; Davidson, D. F.; Chang, C. J.; Smith, G. P.; Gardiner, W. C.; Lissianski, V. 1995. http://www.me.berkeley.edu/gri_mech/.

(10) Bowman, C. T.; Hanson, R. K.; Davidson, D. F.; Gardiner, W. C.; Lissianski, V.; Smith, G. P.; Golden, D. M.; Frenklach, M.; Goldenberg, M. 1996. http://www.me.berkeley.edu/gri_mech/.

(11) Smith, G. P.; Golden, D. M.; Frenklach, M.; Moriarty, N. M.; Eiteneer, B.; Goldenberg, M.; Bowman, C. T.; Hanson, R. K.; Song,

S.; Gardiner, W. C.; Lissianski, V.; Qin, Z. 1999. http://www.me.berkeley.edu/gri_mech/.

(12) Bromly, J. H.; Barnes, F. J.; Muris, S.; You, X.; Haynes, B. S. Kinetic and Thermodynamic Sensitivity Analysis of the NO-Sensitised Oxidation of Methane. *Combust. Sci. Technol.* **1996**, *115* (4−6), 259−296.

(13) Li, S. C.; Williams, F. A.; Gebert, K. A Reduced Reaction Mechanism for Predicting Knock in Dual-Fuel Engines. *SAE Tech. Pap. Ser.* **2000**, DOI: 10.4271/2000-01-0957.

(14) Konnov, A. A. *Detailed Reaction Mechanism for Small Hydrocarbons Combustion,* Release 0.5, 2000. https://web.archive.org/web/20201107061326/http://homepages.vub.ac.be/~akonnov/science/mechanism/main.html

(15) Hughes, K. J.; Turányi, T.; Clague, A. R.; Pilling, M. J. Development and testing of a comprehensive chemical mechanism for the oxidation of methane. *Int. J. Chem. Kinet.* **2001**, *33* (9), 513−538.

(16) Petrova, M.; Williams, F. A small detailed chemical-kinetic mechanism for hydrocarbon combustion. *Combust. Flame* **2006**, *144* (3), 526−544.

(17) Petersen, E. L.; Kalitan, D. M.; Simmons, S.; Bourque, G.; Curran, H. J.; Simmie, J. M. Methane/propane oxidation at high pressures: Experimental and detailed chemical kinetic modeling. *Proc. Combust. Inst.* **2007**, *31* (1), 447−454.

(18) Wang, H.; You, X.; Joshi, A. V.; Davis, S. G.; Laskin, A.; Egolfopoulos, F.; Law, C. K. *USC Mech Version II. High-Temperature Combustion Reaction Model of H2/CO/C1-C4 Compounds.* http://ignis.usc.edu/USC_Mech_II.htm, May 2007.

(19) Healy, D.; Curran, H. J.; Dooley, S.; Simmie, J. M.; Kalitan, D. M.; Petersen, E. L.; Bourque, G. Methane/propane mixture oxidation at high pressures and at high, intermediate and low temperatures. *Combust. Flame* **2008**, *155* (3), 451−461.

(20) Healy, D.; Curran, H. J.; Simmie, J. M.; Kalitan, D. M.; Zinner, C. M.; Barrett, A. B.; Petersen, E. L.; Bourque, G. Methane/ethane/propane mixture oxidation at high pressures and at high, intermediate and low temperatures. *Combust. Flame* **2008**, *155* (3), 441−448.

(21) Slavinskaya, N.; Braun-Unkhoff, M.; Frank, P. Reduced Reaction Mechanisms for Methane and Syngas Combustion in Gas Turbines. *J. Eng. Gas Turbines Power* **2008**, *130* (2), 021504.

(22) Azimov, U.; Okuno, M.; Tsuboi, K.; Kawahara, N.; Tomita, E. Multidimensional CFD simulation of syngas combustion in a micro-pilot-ignited dual-fuel engine using a constructed chemical kinetics mechanism. *Int. J. Hydrogen Energy* **2011**, *36* (21), 13793−13807.

(23) Metcalfe, W. K.; Burke, S. M.; Ahmed, S. S.; Curran, H. J. A Hierarchical and Comparative Kinetic Modeling Study of C₁− C₂ Hydrocarbon and Oxygenated Fuels. *Int. J. Chem. Kinet.* **2013**, *45* (10), 638−675.

(24) Wang, Q. D. Skeletal Mechanism Generation for High-Temperature Combustion of H2/CO/C1−C4 Hydrocarbons. *Energy Fuels* **2013**, *27* (7), 4021−4030.

(25) Burke, U.; Somers, K. P.; O'Toole, P.; Zinner, C. M.; Marquet, N.; Bourque, G.; Petersen, E. L.; Metcalfe, W. K.; Serinyel, Z.; Curran, H. J. An ignition delay and kinetic modeling study of methane, dimethyl ether, and their mixtures at high pressures. *Combust. Flame* **2015**, *162* (2), 315−330.

(26) *Chemical-Kinetic Mechanisms for Combustion Applications, San Diego Mechanism web page, Mechanical and Aerospace Engineering (Combustion Research), University of California at San Diego* (http://combustion.ucsd.edu).

(27) Prince, J. C.; Williams, F. A. Short chemical-kinetic mechanisms for low-temperature ignition of propane and ethane. *Combust. Flame* **2012**, *159* (7), 2336−2344.

(28) Hu, F.; Li, P.; Guo, J.; Liu, Z.; Wang, L.; Mi, J.; Dally, B.; Zheng, C. Global reaction mechanisms for MILD oxy-combustion of methane. *Energy* **2018**, *147*, 839−857.

(29) Bagheri, G.; Ranzi, E.; Pelucchi, M.; Parente, A.; Frassoldati, A.; Faravelli, T. Comprehensive kinetic study of combustion technologies for low environmental impact: MILD and OXY-fuel combustion of methane. *Combust. Flame* **2020**, *212*, 142−155.

(30) Healy, D.; Kopp, M. M.; Polley, N. L.; Petersen, E. L.; Bourque, G.; Curran, H. J. Methane/n-Butane Ignition Delay Measurements at High Pressure and Detailed Chemical Kinetic Simulations. *Energy Fuels* **2010**, *24* (3), 1617−1627.

(31) Baigmohammadi, M.; Patel, V.; Martinez, S.; et al. A Comprehensive Experimental and Simulation Study of Ignition Delay Time Characteristics of Single Fuel C1−C2 Hydrocarbons Over a Wide Range of Temperature, Pressure, Equivalence ratio, and Dilution. *Energy Fuels* **2020**, *34* (3), 3755−3771.

(32) Dagaut, P.; Cathonnet, M.; Boettner, J. Kinetics of ethane oxidation. *Int. J. Chem. Kinet.* **1991**, *23* (5), 437−455.

(33) Cooke, D. F.; Williams, A. Shock-tube studies of the ignition and combustion of ethane and slightly rich methane mixtures with oxygen. *Symp. (Int.) Combust., [Proc.]* **1971**, *13* (1), 757−766.

(34) Rota, R.; Bonini, F.; Servida, A.; Morbidelli, M.; Carra, S. Validation and Updating of Detailed Kinetic Mechanisms: The Case of Ethane Oxidation. *Ind. Eng. Chem. Res.* **1994**, *33* (11), 2540−2553.

(35) Younessi-Sinaki, M.; Matida, E. A.; Hamdullahpur, F. Kinetic model of homogeneous thermal decomposition of methane and ethane. *Int. J. Hydrogen Energy* **2009**, *34* (9), 3710−3716.

(36) Quelch, G. E.; Gallo, M. M.; Schaefer, H. F., III Aspects of the reaction mechanism of ethane combustion. Conformations of the ethylperoxy radical. *J. Am. Chem. Soc.* **1992**, *114* (21), 8239−8247.

(37) Rienstra-Kiracofe, J. C.; Allen, W. D.; Schaefer, H. F. The C2H5+ O2Reaction Mechanism: High-Level ab Initio Character-izations. *J. Phys. Chem. A* **2000**, *104* (44), 9823−9840.

(38) Hidaka, Y.; Sato, K.; Hoshikawa, H.; Nishimori, T.; Takahashi, R.; Tanaka, H.; Inami, K.; Ito, N. Shock-tube and modeling study of ethane pyrolysis and oxidation. *Combust. Flame* **2000**, *120* (3), 245−264.

(39) Konnov, A. A.; Barnes, F. J.; Bromly, J. H.; Zhu, J. N.; Zhang, D. K. The pseudo-catalytic promotion of nitric oxide oxidation by ethane at low temperatures. *Combust. Flame* **2005**, *141* (3), 191−199.

(40) Hashemi, H.; Jacobsen, J. G.; Rasmussen, C. T.; Christensen, J. M.; Glarborg, P.; Gersen, S.; et al. High-pressure oxidation of ethane. *Combust. Flame* **2017**, *182*, 150−166.

(41) Westbrook, C. K.; Pitz, W. J. A Comprehensive Chemical Kinetic Reaction Mechanism for Oxidation and Pyrolysis of Propane and Propene. *Combust. Sci. Technol.* **1984**, *37* (3−4), 117−152.

(42) Qin, Z.; Lissianski, V. V.; Yang, H.; Gardiner, W. C.; Davis, S. G.; Wang, H. Combustion chemistry of propane: A case study of detailed reaction mechanism optimization. *Proc. Combust. Inst.* **2000**, *28* (2), 1663−1669.

(43) Titova, N. S.; Kuleshov, P. S.; Starik, A. M. Kinetic mechanism of propane ignition and combustion in air. *Combust., Explos. Shock Waves* **2011**, *47* (3), 249−264.

(44) Healy, D.; Kalitan, D. M.; Aul, C. J.; Petersen, E. L.; Bourque, G.; Curran, H. J. Oxidation of C1−C5 Alkane Quinternary Natural Gas Mixtures at High Pressures. *Energy Fuels* **2010**, *24* (3), 1521−1528.

(45) Gokulakrishnan, P.; Fuller, C. C.; Klassen, M. S.; Joklik, R. G.; et al. Experiments and modeling of propane combustion with vitiation. *Combust. Flame* **2014**, *161* (8), 2038−2053.

(46) Dagaut, P.; Cathonnet, M.; Boettner, J. C. Kinetic modeling of propane oxidation and pyrolysis. *Int. J. Chem. Kinet.* **1992**, *24* (9), 813−837.

(47) Jachimowski, C. J. Chemical kinetic reaction mechanism for the combustion of propane. *Combust. Flame* **1984**, *55* (2), 213−224.

(48) Koert, D. N.; Pit, W. J.; Boelli, J. W.; Cernansky, N. P. Chemical kinetic modeling of high-pressure propane oxidation and comparison to experimental results. *Symp. (Int.) Combust., [Proc.]* **1996**, *26* (1), 633−640.

(49) Hashemi, H.; Christensen, J. M.; Harding, L. B.; Klippenstein, S. J.; Glarborg, P. High-pressure oxidation of propane. *Proc. Combust. Inst.* **2019**, *37* (1), 461−468.

(50) Gong, J.; Zhang, S.; Cheng, Y.; Huang, Z.; Tang, C.; Zhang, J. A comparative study of n-propanol, propanal, acetone, and propane combustion in laminar flames. *Proc. Combust. Inst.* **2015**, *35* (1), 795−801.

(51) Bramlette, R. B.; Depcik, C. D. Review of Propane-Air Chemical Kinetic Mechanisms for a Unique Jet Propulsion Application. *J. Energy Inst.* **2020**, *93* (3), 857−877.

(52) Mohamed, A. A. E. S.; Panigrahy, S.; Sahu, A. B.; Bourque, G.; Curran, H. J. An experimental and kinetic modeling study of the auto-ignition of natural gas blends containing C1−C7 alkanes. *Proc. Combust. Inst.* **2021**, *38* (1), 365−373.

(53) Xue, J.; Xi, S.; Wang, F. An extensive study on skeletal mechanism reduction for the oxidation of C0−C4 fuels. *Combust. Flame* **2020**, *214*, 184−198.

(54) Bahlouli, K.; Atikol, U.; Saray, R. K.; Mohammadi, V. A reduced mechanism for predicting the ignition timing of a fuel blend of natural-gas and n-heptane in HCCI engine. *Energy Convers. Manage.* **2014**, *79*, 85−96.

(55) Reyhanian, M.; Hosseini, V. Various effects of reformer gas enrichment on natural-gas, iso-octane and normal-heptane HCCI combustion using artificial inert species method. *Energy Convers. Manage.* **2018**, *159*, 7−19.

(56) Pan, K.; Wallace, J. S. A low temperature natural gas reaction mechanism for compression ignition engine application. *Combust. Flame* **2019**, *202*, 334−346.

(57) Zhang, W.; Chang, S.; Wu, W.; Dong, L.; Chen, Z.; Chen, G. A diesel/natural gas dual fuel mechanism constructed to reveal combustion and emission characteristics. *Energy* **2019**, *179* (15), 59−75.

(58) Huang, H.; Lv, D.; Zhu, J.; Zhu, Z.; Chen, Y.; Pan, Y.; Pan, M. Development of a new reduced diesel/natural gas mechanism for dual-fuel engine combustion and emission prediction. *Fuel* **2019**, *236*, 30−42.

(59) Zhao, W.; Yang, W.; Fan, L.; Zhou, D.; Ma, X. Development of a skeletal mechanism for heavy-duty engines fuelled by diesel and natural gas. *Appl. Therm. Eng.* **2017**, *123*, 1060−1071.

(60) Liu, Z.; Yang, L.; Song, E.; Wang, J.; Zare, A.; Bodisco, T. A.; Brown, R. J. Development of a reduced multi-component combustion mechanism for a diesel/natural gas dual fuel engine by cross-reaction analysis. *Fuel* **2021**, *293* (1), 120388.

(61) Li, M.; Wei, Z.; Liu, X.; Wang, X.; Zhang, Q.; Li, Z. A numerical investigation on the effects of gaseous fuel composition in a pilot ignited direct injection natural gas engine. *Energy* **2021**, *217*, 119467.