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An experimental and kinetic modeling study of the auto-ignition of natural gas blends containing C_1–C_7 alkanes

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Abstract

Ignition delay time measurements for multi-component natural gas mixtures were carried out using a rapid compression machine at conditions relevant to gas turbine operation, at equivalence ratios of 0.5–2.0 in 'air' in the temperature range 650–1050 K, at pressures of 10–30 bar. Natural gas mixtures comprising C_1–C_7 *n*-alkanes with methane as the major component (volume fraction: 0.35–0.98) were considered. A design of experiments was employed to minimize the number of experiments needed to cover the wide range of pressures, temperatures and equivalence ratios. The new experimental data, together with available literature data, were used to develop and assess a comprehensive chemical kinetic model. Replacing 1.875% methane with 1.25% *n*-hexane and 0.625% *n*-heptane in a mixture containing C_1–C_5 components leads to a significant increase in a mixture's reactivity. The mixtures containing heavier hydrocarbons also tend to show a strong negative temperature coefficient and two-stage ignition behavior. Sensitivity analyses of the C_1–C_7 blends have been performed to highlight the key reactions controlling their ignition behavior.

Keywords: Natural gas; Ignition delay time; Rapid compression machine; Kinetic modeling

1. Introduction

The potential of natural gas (NG) as an alternative fuel for transportation and heavy-duty power generation applications has led to an increase in demand for conventional and non-conventional NG sources. NG is primarily composed of methane with some heavier alkanes ranging from ethane to

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heptane [1,2]. Thus, to achieve highly efficient and safe use of NG, experimental and kinetic modeling studies are needed for a wide range of NG mixtures to verify their varying combustion characteristics. One of the fundamental combustion characteristics of a fuel is auto-ignition which can be measured experimentally at relevant reaction times using both rapid compression machines (RCMs) and shock tubes (STs). Methane, being a major component of NG, has been studied extensively in the literature [3–8] and there are many available mechanisms describing its oxidation at conditions relevant to combustion devices [9–13]. Studying blends of alkanes with compositions similar to available sources of NG can provide tangible targets in predicting the combustion characteristics of these alternate NG mixtures to test their suitability for use in practical combustors.

A summary of experimental studies of methane with larger hydrocarbons was presented previously [1,7,14] and a summary is updated and added as Supplementary material (SM). Ignition delay times (IDTs) of binary NG blends of methane/ethane up to methane/*n*-heptane were studied experimentally using RCMs and STs over a wide range of combustion conditions [15–17,19–30]. The results showed an increase in negative temperature coefficient (NTC) behavior and a decrease in the onset of ignition temperature with increasing concentrations of higher order hydrocarbons in the mixtures. A recent study of CH_4/*n*-C_6H_{14} mixtures by He et al. [22] showed a significant decrease in IDTs with increasing *n*-hexane content at low temperature. A kinetic analysis showed that a strong effect stems from the decomposition of H_2O_2 which induces the production of $\dot{O}H$ radicals. Liang et al. [21] studied a different CH_4/*n*-C_7H_{16} mixtures in a ST. The results showed that the fuel composition with methane concentrations of less than 75% had IDTs close to pure *n*-heptane. Kinetic analyses showed that dominant reactions occurred between *n*-heptane and the radicals, particularly $\dot{O}H$ and $H\dot{O}_2$ and methane consumption occurred close to the ignition event. Similar behavior was also observed for CH_4/*n*-C_6H_{14} ST experiments [22].

IDT measurements of ternary blends, including $CH_4/C_2H_6/C_3H_8$ as well as higher alkanes with volume percentages of up to 50% of the entire fuel composition have also been studied [18,23,27,29,31,32]. De Vries and Petersen [29] observed that adding higher hydrocarbons up to *n*-pentane strongly reduces the activation energy at high pressures and low temperatures with an observed faster and stronger ignition behavior for all of the blends compared to pure methane. C_1–C_4 ST experiments were also studied [33] for highly dilute mixtures containing 14.29% ethane, 7.14% propane, 7.14% *n*-butane, and 71.43% methane. It was found that IDTs were shortened by up to a factor of 13 compared to pure methane. Recently, C_1–C_5 alkanes blends were studied in both an RCM and in a ST with higher hydrocarbons up to 37.5% by volume of the fuel composition [14,34,35]. Beerer and McDonell [18] used a turbulent flow reactor to measure IDTs for a lean ($\varphi = 0.6$) mixture containing C_1–C_6 species at $p = 9$ atm, in the temperature range 845–895 K. They showed that the inclusion of higher alkanes can help reduce NOx emissions by decreasing the onset of ignition temperatures for NG mixtures.

The declining concentration of $>C_2$ species on a volume/mol basis is an observed trend in samples of NG found around the world. These are supplied to Siemens by potential customers who are interested in ensuring their feasibility as fuels for engine applications and understanding the limitations in terms of pollutants, power range, or fuel supply systems. Although several studies have explored C_1–C_5 *n*-alkanes mixtures with limited work performed on C_1–C_6 alkane blends [18]. However, to our knowledge no IDT measurements are available for C_1–C_7 alkane blends. The aim of the present work is to provide useful measurements of IDTs for C_1–C_7 *n*-alkanes blends at conditions relevant to gas turbine (GT) operation and to develop an accurate chemical kinetic mechanism to understand the underlying kinetics of NG mixture combustion at the specified conditions.

2. Experiments

Experiments were conducted using the RCM at NUI Galway, which was described previously [36]. A brief description of the machine and the experimental procedure are provided as SM. Table 1 shows the C_1–C_7 *n*-alkanes blends by volume percentage, reported as NG1 to NG10.

Initially the NG1–NG3 blends were selected, where NG1 and NG2 compositions are very similar to North American and European natural gases, respectively. NG3 is an extension of the compositions along the NG mixture trends in order to capture the increasing content of $> C_2$ species. The new natural gas mixtures NG4–NG10 are intended to consider both the impact of C_6 and C_7 *n*-alkane addition and higher amounts of $> C_2$ species. The motive in the increased content of $> C_2$ is to ensure that future natural gas compositions can be included. Constant volume simulations were performed for all of the NG blends in Table 1 as shown in Fig. S1 in SM1 to help select the final experimental conditions. NG2 experiments which had been studied previously in our laboratory [14,34] helped in validating the new experiment targets and confirm the reliability of the old data. The NG3 and NG6 experiments were performed to study the effect of replacing 1.875% methane in the NG3 blend with *n*-hexane and *n*-heptane at the same conditions of pressure and dilution concentrations. Fi-

Table 1
Natural gas blends.

Species	NG1	NG2	NG3	NG4	NG5	NG6	NG7	NG8	NG9	NG10
Methane (CH_4)	98.125	81.25	62.5	98.03125	80.3125	60.625	72.635	45.27	63.107	35.601
Ethane (C_2H_6)	1	10	20	1	10	20	10	20	10	20
Propane (C_3H_8)	0.5	5	10	0.5	5	10	6.667	13.33	8.0	14.815
n-Butane(C_4H_{10})	0.25	2.5	5.0	0.25	2.5	5.0	4.44	8.89	6.40	10.974
n-Pentane (*n*-C_5H_{12})	0.125	1.25	2.5	0.125	1.25	2.5	2.965	5.93	5.12	8.129
n-Hexane (*n*-C_6H_{14})	–	–	–	0.0625	0.625	1.25	1.976	3.95	4.097	6.021
n-Heptane (*n*-C_7H_{16})	–	–	–	0.03125	0.3125	0.625	1.317	2.63	3.276	4.460

Table 2
Experimental conditions studied in the RCM.

Blend	φ	p_C / bar	T_C / K	
NG2	0.5, 1.0, 2.0	10,18, 20, 30	711–1054	[14,34], current study
NG3	1.0	20, 30	754–952	[14,34], current study
NG6	1.0	20, 30	670–1032	current study
NG7	0.5, 1.0, 1.5	10, 20, 30	688–952	current study
NG8	1.0	20, 30	679–960	current study
NG10	0.5, 1.0, 1.5	10, 20, 30	650–1052	current study

nally, NG7, NG8, and NG10 were chosen so that different levels of higher hydrocarbon in the blends with different conditions can be tested. Developing a chemical kinetic mechanism that can reproduce well the experiments in the different conditions will be useful in predicting other NG blends that have not been studied experimentally. Concerning the DOE approach, we have not applied the methodology in a strict manner implied by the terminology but rather a sensitivity analysis was performed to identify the experiments that would be the most informative to develop/validate/calibrate the mechanism within the large parameter space of pressure, equivalence, temperature, and natural gas compositions considered. Table 2 shows the experimental conditions with the NG blends which were chosen in the current study. The measured IDT is quantified from the reactive pressure-time trace as shown in Fig. S2. Each experimental point is repeated at least three times and the IDTs measurement uncertainty in the current study is estimated to be ±15%.

3. Kinetic modelling

The detailed chemical kinetic mechanism employed here, NUIGMech1.0, is built in a hierarchical way and has been derived by merging our C_0–C_5 base chemistry [37–40] with the hexane isomer mechanisms from Zhang et al. [41]. Rate constants for the *n*-heptane sub-mechanism are incorporated from a previously published model by Zhang et al. [42]. This mechanism has been validated against the experimentally measured IDTs from the present work across a wide range of temperature (T_C = 650–1500 K), equivalence ratio (φ = 0.4–2.0), and pressure (p_C = 10–100 bar) as well as a variety of natural gas mixture compositions [31,35,22,32] as shown in Figs S10–S16. A detailed description of the important reactions for the conditions studied here identified in sensitivity analyses are provided in the following sections. In addition, the performance of NUIGMech1.0 is compared with that published by Zhang et al. [42] and Mehl et al. [43].

4. Results and discussion

The results of the IDTs for the tested NG blends listed in Table 1 are provided in this section. The term "in air" in the figures refers to the oxidizer mixture containing O_2/diluent in the ratio of 1:3.76. The diluent was either 100% N_2 or 45:55 N_2: Ar. The fuel compositions, initial conditions, IDT data, and pressure/time histories for the simulations are all provided as SM.

4.1. Experimental validation

Fig. 1 and Figure S3 show that the current IDT measurements for NG2 at different compressed gas temperatures and NG3 at stoichiometric conditions are comparable with our previously published data [14,34]. Moreover, simulations of the new IDTs using three kinetic models, C5_49 which was previously used to simulate the NG2 and NG3 data [14], that from Zhang et al. [42], and NUIGMech1.0. The three models show good agreement with the experiments, with NUIGMech1.0 showing particularly good agreement, especially at low temperatures. Overall, there is good agreement among the old and new data and the difference which appears clearly in the fuel-lean and stoichiometric conditions at temperature above 900 K stems from the use of 100% Ar as the diluent gas in the old

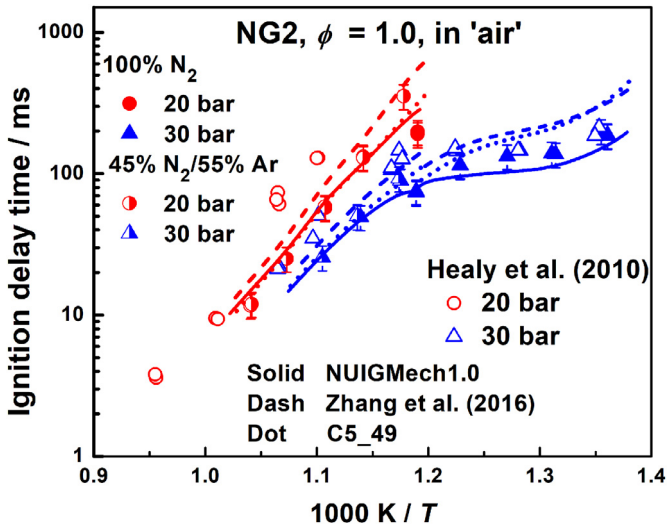

Fig. 1. Comparison of current study IDTs measurements for NG2 verse NG2 previous study [34] and the simulations, NUIGMech1.0 (solid line, Zhang et al. [42] (dash lines), and C5_49 [14] (Dotted line).

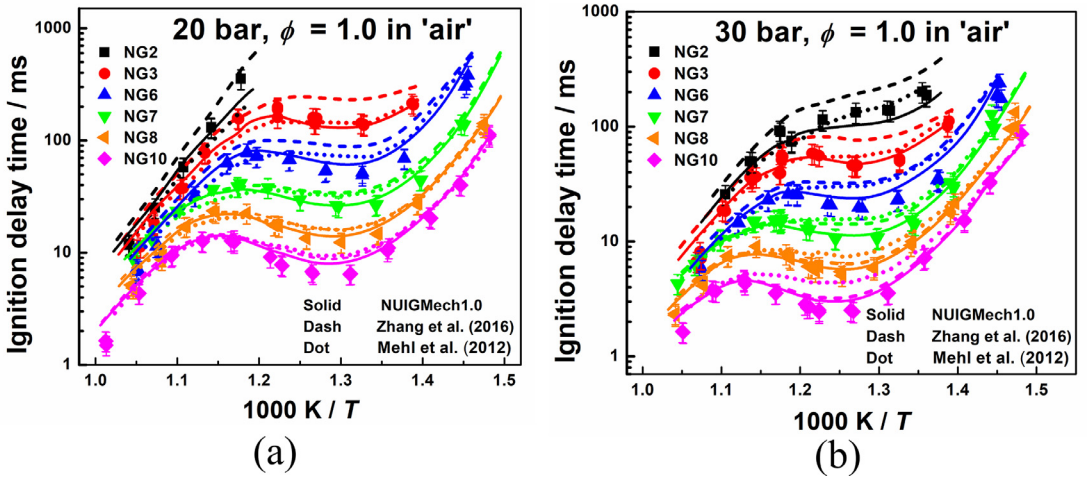

Fig. 2. Comparison of experimental (symbols) and model predicted (lines) IDTs of various NG mixtures at $\varphi = 1.0$, $p_c =$ (a) 20 bar, (b) 30 bar, measured in an RCM.

data. Using only Argon as a diluent makes the IDTs longer as reported by Würmel et al. [44] whereas in the new data 45% N_2/55% Ar is used. At fuel-rich conditions for NG2 the same diluent was used for both studies and they show very good agreement, Fig. S3(c).

4.2. *Effect of fuel composition*

Comparisons of the IDTs of the different NG mixtures, NG2, NG3, NG6, NG7, NG8, and NG10, studied here are presented in Fig. 2 for stoichiometric mixtures at 20 bar and 30 bar and 675–1000 K. It is observed that NG2 and NG3 mixtures containing highest percentage of smaller alkanes (C_1–C_3) amongst all fuels exhibit the lowest reactivity, with reactivity increasing with the increasing percentage of higher order hydrocarbons present. Mixture NG10, which has a total of almost 10% nC_6H_{14} and nC_7H_{16}, exhibits the highest reactivity. The effect of composition on the IDTs is seen to be the largest in the temperature range 700–900 K. For NG3 at 770 K, 20 bar, the IDT is ~150 ms while for NG10 the IDT is ~6 ms, showing that there is more than an order of magnitude reduction in reactivity with changing fuel compositions. Fig. 2 also shows that NUIGMech1.0 can predict the IDTs with very good agreement for the range of NG mixtures at

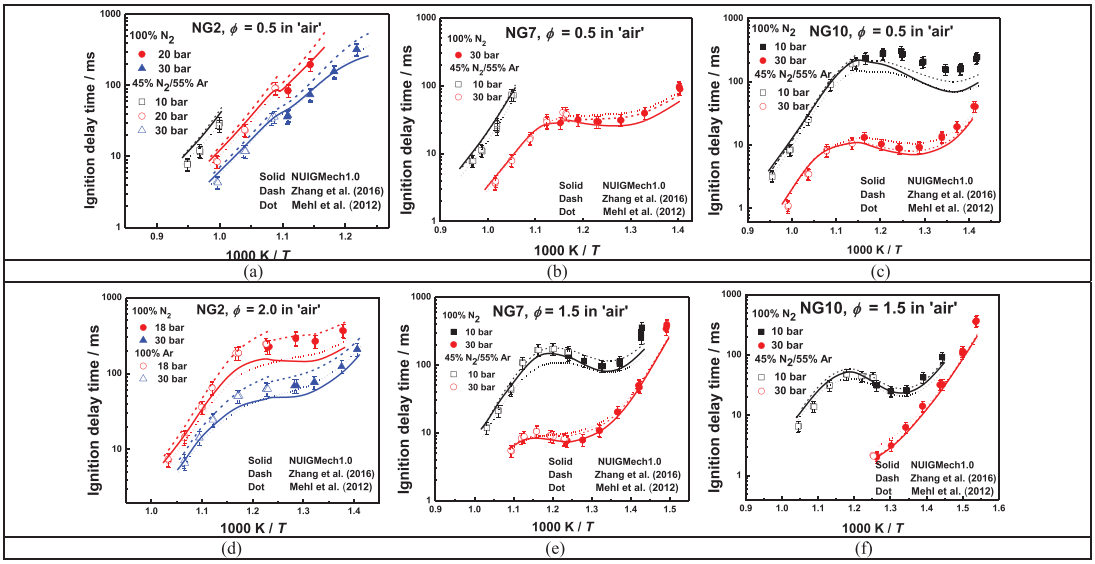

Fig. 3. Ignition delay times at different p_C (a) NG2, $\varphi = 0.5$; (b) NG7, $\varphi = 0.5$; (c) NG10, $\varphi = 0.5$; (d) NG2, $\varphi = 2.0$; (e) NG7, $\varphi = 1.5$; (f) NG10, $\varphi = 1.5$.

both 20 and 30 bar and also accurately reproduces the NTC behavior. The Zhang et al. [42] model under-estimates the reactivity of the mixtures by a factor of two for the NG3 and NG6 mixtures. The agreement becomes better for NG mixtures with higher alkanes but still over-predicts the IDT by factor of 1.5 compared to the experiments in the NTC region. Moreover, the Mehl et al. [43] model over-estimates the reactivity of NG2 and NG3 and begins to under-estimate the reactivity of the mixtures with increasing higher order hydrocarbons in NG6–NG10 and by increasing the pressure from 20 bar to 30 bar. A detailed sensitivity analysis is presented in the chemical kinetics analysis section to gain insights on the underlying kinetics at different conditions. Figure S6 shows reactive *p*/t histories for the conditions similar to Fig. 2-b for NG7, NG8, and NG10 at T_c ~770 K along with simulated *p*/t histories using the experimental non-reactive p/t trace to include the effect of heat loss. It is obvious that the mechanism can also capture the first stage and total ignition very well.

4.3. Effect of pressure and equivalence ratio

Fig. 3 shows a comparison of model predictions with IDT measurements for fuel-lean and fuel-rich NG mixtures at 10–30 bar. A similar comparison for the stoichiometric mixtures is provided in Fig. S7. The IDTs for all mixtures decrease with increasing pressure, thus showing an increase in reactivity. This is primarily due to the increasing concentration of the reactant molecules with pressure. The sensitivity of IDT with pressure shows a non-linear trend with respect to temperature. For stoichiometric NG6–NG10 mixtures, the IDT shortens by a factor of 1.5 at $T_C < 700$ K as the pressure increases from 20 to 30 bar, while it reduces by a factor of 2 at $T_C > 700$ K until the end of NTC region. The dependence on pressure again decreases with a further increase in temperature. For fuel-lean and fuel-rich mixtures, an increase in pressure from 10 bar to 30 bar leads to a reduction in IDT of almost a factor of nine in the NTC region, as shown in Fig. 3. Comparisons of model predictions with measurements (Figs. 3 and S7), show that NUIGMech1.0 is able to successfully predict the IDTs with very good agreement for a wide range of pressures (10–30 bar) and equivalence ratios ($\varphi = 0.5$–2.0).

4.4. Chemical kinetics analysis

Fig. 4 shows the brute-force sensitivity analysis for NG3, NG6 and NG10 mixture blends at $\varphi = 1.0$, $pc = 30$ bar, and $T_C = 830$ K. Modifications have been made to some of these important reactions and the choice of the updated rate constants are discussed here.

The reactivity of the NG mixtures (NG3, NG6 and NG10) is highly sensitive to $\dot{O}H$ radical reactions with propane producing *n*-propyl and *iso*-propyl radicals, via $C_3H_8 + \dot{O}H \leftrightarrow n\dot{C}_3H_7 + H_2O$ and $C_3H_8 + \dot{O}H \leftrightarrow i\dot{C}_3H_7 + H_2O$, respectively. The previous model [42] utilised the rate constant measured by Droege and Tully [45] at temperatures below 900 K. More recently, Sivaramakrishnan et al. [46] directly measured site-specific rate constants for the $C_3H_8 + \dot{O}H$ system at high temperatures (927–1146 K). Their measurements

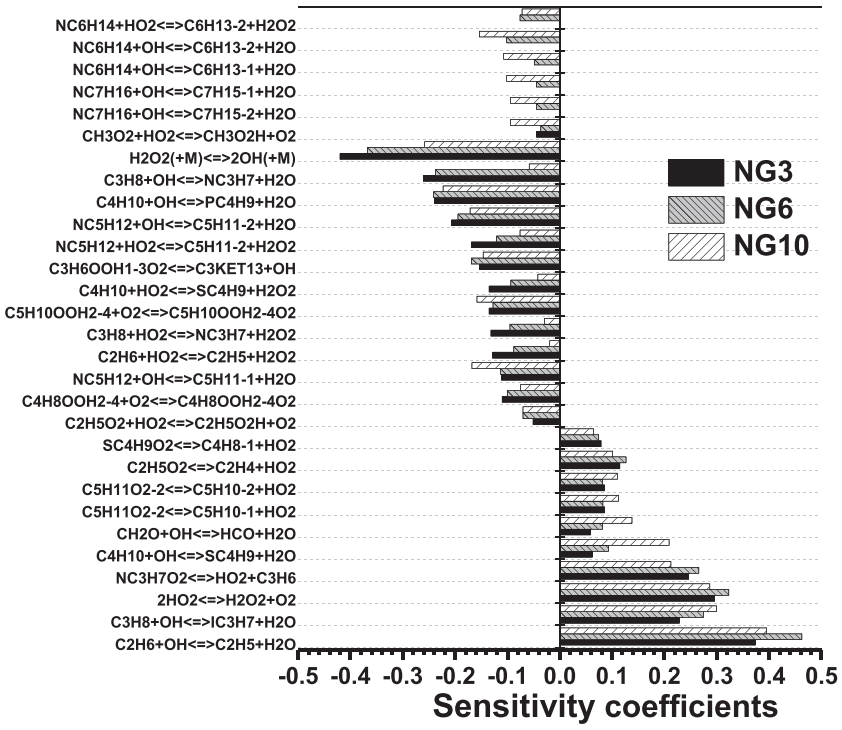

Fig. 4. Brute-force sensitivity analysis of various NG mixtures (NG3, NG6, NG10) IDTs at $\varphi = 1.0$, $p_c = 30$ bar, and $T_C = 830$ K.

showed a slightly higher branching fraction to $i\dot{C}_3H_7$ than measured by Droege and Tully [45]. The current model applies a fit which takes account of the direct measurement for $C_3H_8 + \dot{O}H \leftrightarrow i\dot{C}_3H_7 + H_2O$ by Sivaramakrishnan et al. [46]. It is evident from Fig. 4 that for all NG mixtures direct hydrogen-abstraction from C_2H_6 by $\dot{O}H$ radical has the largest inhibiting effect on the NG ignition. In the present model, the rate constant for $C_2H_6 + \dot{O}H \leftrightarrow \dot{C}_2H_5 + H_2O$ is adopted from the fit recommended by Krasnoperov and Michael [47]. A sensitivity analysis also shows that the low temperature reactions pertaining to C_3H_8 chemistry influence the overall reactivity of NG mixtures. The formation of carbonyl hydroperoxide species via the isomerization reactions of $C_3H_6OOH1\text{–}3\dot{O}_2$ promotes the overall reactivity of the NG mixtures containing higher concentration of *n*-hexane and *n*-heptane fuels (NG6 and NG10). Whereas the concerted elimination reaction, producing $C_3H_6 + H\dot{O}_2$, inhibits NG oxidation at low temperatures. For the reaction $nC_3H_7O_2 \leftrightarrow C_3H_6 + H\dot{O}_2$, the rate constant used in the previous model was based on the calculation by Villano et al. [48] while for ($C_3H_6OOH1\text{–}3O_2 \leftrightarrow C_3KET13 + \dot{O}H$), the rate parameters were taken from the study of Sharma et al. [49]. In the current model, the rate constant for these reactions are adopted from the high-level quantum chemical calculation by Goldsmith et al. [50], and these updates improved the model predictions as shown in Fig. 2.

The chain terminating reaction between $H\dot{O}_2$ radicals ($H\dot{O}_2 + H\dot{O}_2 \leftrightarrow H_2O_2 + O_2$) is an important reaction that inhibits reactivity under these conditions, while the decomposition of H_2O_2 is the most important reaction enhancing reactivity of NG mixtures for all conditions. For the reaction $H\dot{O}_2 + H\dot{O}_2 \leftrightarrow H_2O_2 + O_2$, we use the rate constant from the recent high-level ab-initio theoretical study by Klippenstein et al. [51]. Notably, this value is slightly lower than the rate constant assigned in our previous model [42], in which the rate parameters were taken from the experimental work of Hong et al. [52]. Interestingly, in NG6 and NG10 mixtures, the sensitivities of the important promoting reactions from the C_2H_6 to *n*-C_5H_{12} sub-mechanism are reduced significantly as compared to the NG3 mixture. However, the *n*-C_6H_{14} and *n*-C_7H_{16} chemistries begin to control the reactivity for NG6 and NG10. The H-atom abstraction from the *n*-C_6H_{14} and *n*-C_7H_{16} by $\dot{O}H$ radicals become more important for NG10.

Fig. 5 depicts brute-force sensitivity analyses performed for the NG10 mixture at pc = 10 and 30 bar, and at an intermediate temperature of

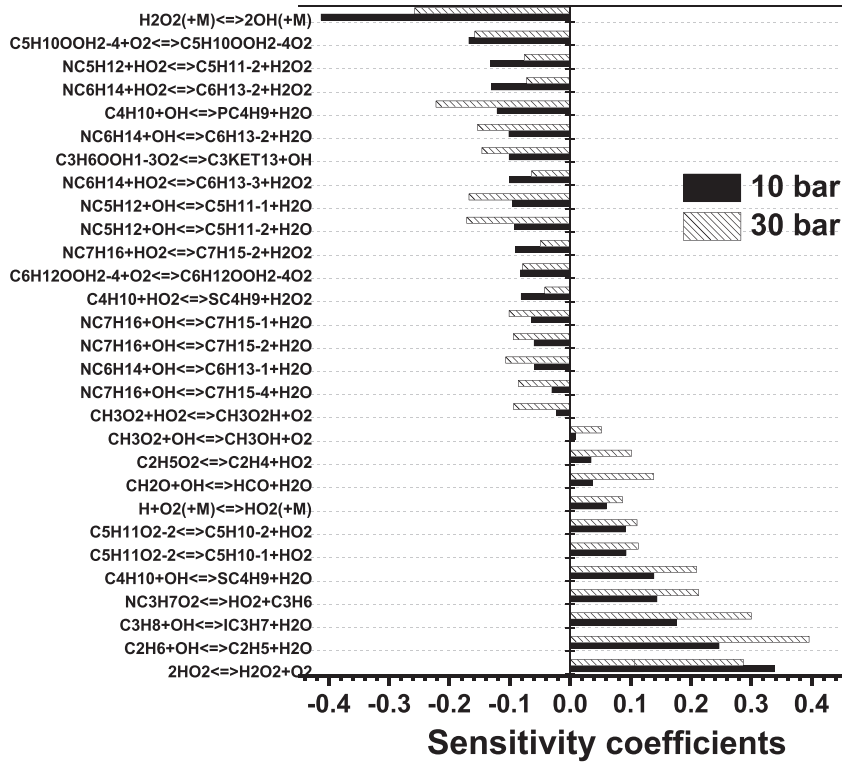

Fig. 5. Brute-force sensitivity analysis of NG10 mixtures at $\varphi = 1.0$, T_C =830 K, for both $p_C = 10$ bar and $p_C = 30$ bar.

830 K. Fig. S9 shows the sensitivity analyses comparisons for different equivalence ratios (φ = 0.5, 1.0 and 1.5) for the NG10 mixture at 30 bar pressure and at an intermediate temperature of 830 K. The most important reactions are governed by the hydrogen abstraction reactions by $\dot{O}H$ and $H\dot{O}_2$ radicals that initiate the fuel consumption. The low-temperature chemistries such as the addition of $\dot{C}_5H_{10}OOH2$–4 and $\dot{C}_6H_{12}OOH2$–4 radicals to O_2 are also sensitive reactions that promote the reactivity. The concerted elimination reactions, producing an olefin + $H\dot{O}_2$, inhibits NG ignition. Meanwhile $H\dot{O}_2 + H\dot{O}_2 \leftrightarrow H_2O_2 + O_2$ is the most inhibiting reaction. The resultant H_2O_2 generates two $\dot{O}H$ radicals through H_2O_2 (+M) $\leftrightarrow \dot{O}H + \dot{O}H$ (+M). Fig. S9 shows that, for fuel-lean conditions, the chain branching reaction H_2O_2 (+M) $\leftrightarrow \dot{O}H + \dot{O}H$ (+M) dominates the reactivity and exhibits higher sensitivity than at stoichiometric and fuel-rich conditions. A similar trend in sensitivity coefficients at 10 bar and 30 bar (Fig. 5) indicates that the chemistry is not responsible for the increase in reactivity at 30 bar, but rather the higher fuel concentration causes the observed reduction in IDTs.

5. Conclusions

In the current study, ignition delay time measurements for C_1–C_7 n-alkanes blends were performed by using NUI Galway RCM at conditions relevant to GT operating conditions. Six compositions of natural gas mixtures with methane being the major component were chosen for the study. The measurements were carried out for mixtures in 'air' in the temperature range of 650–1050 K at equivalence ratios 0.5, 1.0, 1.5 and 2.0 and pressures varying from 10 to 30 bar. The wide range of conditions provides a comprehensive overview of the reactivity of the natural gas mixtures. The experimental results showed that for the range of fuel-compositions considered in this study, the IDTs of the mixture shortened by an order of magnitude at the same pressure and temperature conditions. For NG3 mixture, the IDT measured was approximately 150 ms while for NG10 the IDT was as low as 6 ms at T_C = 770 K and p_C ~20 bar. Significantly different IDTs measured over a wide range of conditions provide a strong validation target for developing accurate and robust chemical kinetic mechanisms. The new detailed kinetic mechanism NUIGMech1.0, with update reaction rates based on recent theoretical and experimental studies together with the heptane mechanism developed

by Zhang et al. were chosen to simulate the experimental conditions in this study. The NUIGMech1.0 model showed excellent agreement with the IDT measurements for mixtures with compositions ranging from quinternary mixtures (C_1–C_5) to seven-component mixtures (C_1–C_7) represented by NG6–NG10. The Zhang et al. model showed reasonable agreement with mixtures containing *n*-heptane but overestimated the IDTs by more than 50% in the NTC region for mixtures containing large amounts lower hydrocarbons (NG2–NG6). The agreement of NUIGMech1.0 with measurements recorded in this study along existing literature data highlights its robustness.

Declaration of Competing Interest

None.

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Supplementary materials

Supplementary material associated with this article can be found, in the online version, at doi:10.1016/j.proci.2020.06.015.

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