

Effects of oil and water contamination on natural gas engine combustion processes

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Abstract

Abundant availability and potential for lower emissions are drivers for increased utilization of natural gas in automotive engines for transportation applications. A novel bimodal engine has been developed that allows on-board refueling of natural gas by utilizing the engine as a compressor. Engine compression however, results in altering the initial state of the natural gas. Increase in temperature and addition of oil are two key effects attributed to the onboard refueling process. A secondary effect is the presence of water in the natural gas supply line. This study investigates the effect of upstream conditions of natural gas on three parameters - autoignition temperature, ignition delay, and laminar flame speed. These parameters play key roles in the engine combustion process. Parametric studies are conducted by varying the initial mixture temperature, water, and oil content in the fuel. The studies utilize numerical simulations conducted with detailed chemistry for natural gas with *n*-heptane used as a surrogate for oil. Water addition to natural gas at 1–5% by volume did not result in any major changes in the combustion processes, other than a slight reduction in laminar flame speeds. Oil addition of 1–5% by volume reduced autoignition temperature by 5–10% and ignition delay by 27–95% depending on the initial temperature. Sensitivity analysis showed that this was likely due to decrease in the sensitivity of two recombination reactions with oil addition. Evolution profiles of key radical species also showed increasing mole fraction of the hydroperoxy radical at lower temperature that likely aids in reducing the ignition delay. Oil addition resulted in a relatively small increase in the laminar flame speed of 1.7% along with an increase in the adiabatic flame temperature. These results help inform the combustion process and performance to be expected from the bimodal engine.

1. Introduction

There is growing motivation to incorporate natural gas as a fuel for ground transport applications in the United States. Some of the major factors behind this trend include cheap and plentiful availability, widespread supply of natural gas to homes and businesses, high octane content, and environmental benefits from reduced emissions [1]. The higher octane content of natural gas allows engines to operate with higher compression ratios, increasing thermal efficiencies to match or exceed those of gasoline engines [2]. Natural gas has a higher hydrogen-to-carbon ratio than conventional gasoline fuels and this allows for reduced CO₂ emissions. However, advanced strategies are required to keep the NO_x and unburned hydrocarbon emissions within acceptable limits [2-3].

A key barrier to adoption of natural gas as a transportation fuel is the lack of a refueling infrastructure. Fast-fill stations that store compressed natural gas (CNG) and allow for refueling times on the order of five minutes comprise less than 1% of gasoline stations [1]. While liquefaction into liquid natural gas (LNG) is an option, this process is more expensive and complex compared with producing CNG. To overcome the infrastructure barriers, a novel bimodal engine was developed that allows onboard refueling of natural

gas where available [4-5]. Further development of the engine and its implementation and packaging are the focus of current efforts [6]. This multi-cylinder engine utilizes some cylinders to compress natural gas to tank pressures on the order of 248 bar (3600 psi). The non-firing cylinders that compress the gas are powered by the firing cylinders on the engine. The system is self-contained within the vehicle and allows the operator to refuel the CNG tank using a low-pressure source of natural gas.

However, onboard refueling of natural gas in this manner results in some changes to the condition and composition of natural gas stored in the fuel tank. First, piston compression heats the natural gas considerably (greater than 200°C). Despite using heat exchangers for inter-cooling, the final tank temperature could be elevated above the initial temperature, resulting in high-temperature natural gas entering the engine cylinder. Second, as the natural gas moves through the engine cylinders, there is a high likelihood of it entraining lubrication oil. Third, pipeline natural gas can contain water [7] that would be carried through the system during the refueling process. The high gas temperatures will vaporize the water and possibly the oil as well. This would prevent easy separation of water and oil using filters planned to be incorporated into the refueling system. Therefore, there will likely be some residual content of both present in the fuel tank that can make its way into the engine cylinders with natural gas during normal engine operation. In this context, it is important to understand the downstream effects of the refueling system on the in-cylinder combustion processes.

High natural gas temperature could potentially lead to autoignition events in the engine that are detrimental to engine life due to the high rates of pressure rise associated with such events. The likelihood of this is increased in natural-gas-fueled engines that utilize higher compression ratios due to the higher octane number of natural gas. Several research studies have associated pre-ignition events with presence of oil in the engine cylinder [8-10]. This limits engine compression ratio due to the destructive nature of pre-ignition events—also known as super-knock. Finally, water content in the fuel can affect engine combustion through thermal and chemical kinetic mechanisms. Water content can reduce combustion temperatures and also play a key role in suppressing NO_x, as has been discussed in previous works [11-12].

This work presents a parametric study looking at the effects of natural gas temperature, water, and oil content on autoignition processes and key chemical kinetic parameters such as ignition delay, and laminar flame speed. The choice of parameters to be investigated relates directly to key combustion processes occurring in the natural gas-fueled engine. Autoignition refers to spontaneous end-gas autoignition relevant to a spark-ignition (SI) type cycle. It is also referred to as engine knock and is undesirable. Ignition delay pertains to the chemical delay time prior to the ignition of the mixture and is particularly relevant to a compression-ignition (CI) engine. Finally, laminar flame speed refers to the burning velocity of the fuel-air mixture and is relevant to the flame propagation and heat release in an SI engine.

These studies are performed via numerical simulations incorporating detailed chemistry for the fuel-air mixture. The paper is laid out as follows. First, the onboard refueling system and the engine under consideration are described in brief. Next, the numerical simulation tools used to investigate the different kinetic effects are described along with the chemical reaction mechanisms considered. Following this, simulation

results are presented and discussed for each phenomenon investigated in this work. Finally, conclusions are presented and discussed.

2. Engine and onboard refueling system

The engine used in this work is an 8-cylinder Ford 6.2 L Boss engine. The stock cylinder head has an overhead valve arrangement with two valves per cylinder as well as two spark plugs per cylinder. Table 1 presents the important specifications of the stock engine.

Table 1: Engine specifications and operating parameters.

Parameter	Value	Units
Displacement	6210	cm ³
	379	in ³
Bore	102	mm
Stroke	95	mm
Compression ratio	9.8	
Peak power	287	kW
	385	hp
Peak torque	550	N-m
	405	ft-lb
Speed range	1000-5500	RPM

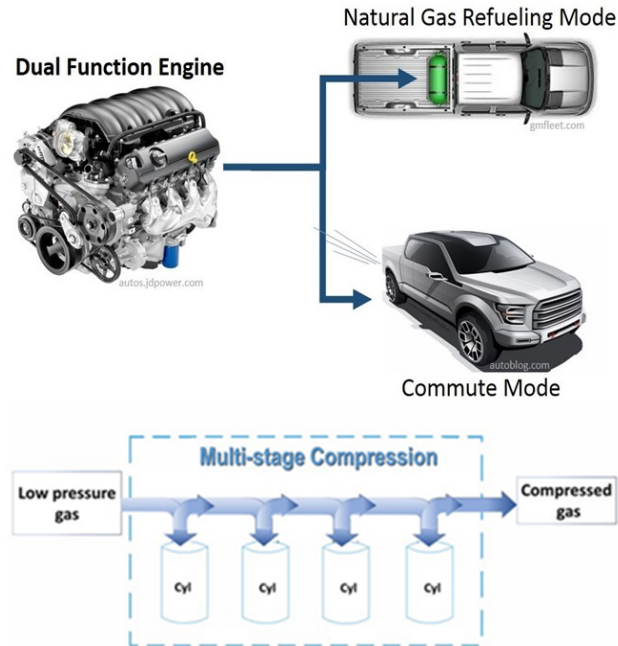


Figure 1: Schematic showing the dual-function mode of the engine as well as the compression process used to generate high pressure natural gas for tank storage (*image courtesy Onboard Dynamics*).

Figure 1 shows a simple schematic illustrating the bimodal engine functionality [4, 13]. During normal operation all eight cylinders produce power, while in the refueling mode some of the engine cylinders compress natural gas and the remaining cylinders provide

power required to perform this work. The engine is slated to run in an idling mode at about 1200 RPM during the refueling operation. The compression is performed in stages with inter-cooling provided by heat exchangers. The final temperature of the gas stored in the tank depends on the compression process and can potentially be as high as 200°C. The high-pressure gas is expanded through a pressure-reducing valve before being introduced into the intake port similar to gasoline in the stock engine.

3. **Simulation tools**

Chemical kinetic simulations were performed using Reaction Design's Chemkin Pro v.15131 [14]. Different tools were used to investigate engine autoignition, ignition delay, and laminar flame speeds. These tools and the reaction mechanism used in this work are described briefly in the following sections.

3.1 *Autoignition*

Autoignition in an engine is modeled using the homogenous charged compression ignition (HCCI) model of Chemkin. Inputs for key engine parameters are used with piston-crank relationships to describe cylinder volume as a function of time during engine operation. The simulations are carried from 180 degrees BTDC (before top dead center) to 180 degrees ATDC (after top dead center). The cylinder is treated as a single homogeneous volume and calculations are adiabatic with no heat transfer to the cylinder walls. Conservation equations are solved for mass, energy, and species. The cylinder is treated as a closed volume with initial conditions set by the equivalence ratio (ϕ), pressure, and temperature specified at the beginning of the simulation at 180 degrees BTDC. Engine speed is specified as well. The fuel composition is varied by the addition of varying amounts of oil and water. Autoignition is detected by the appearance of a sharp spike in the pressure trace accompanied by rapid consumption of the fuel-air mixture. Autoignition temperature is defined as the temperature of the unburned gases at the Intake Valve Opening [IVO] at 180 degrees BTDC required to produce autoignition during the course of the cycle.

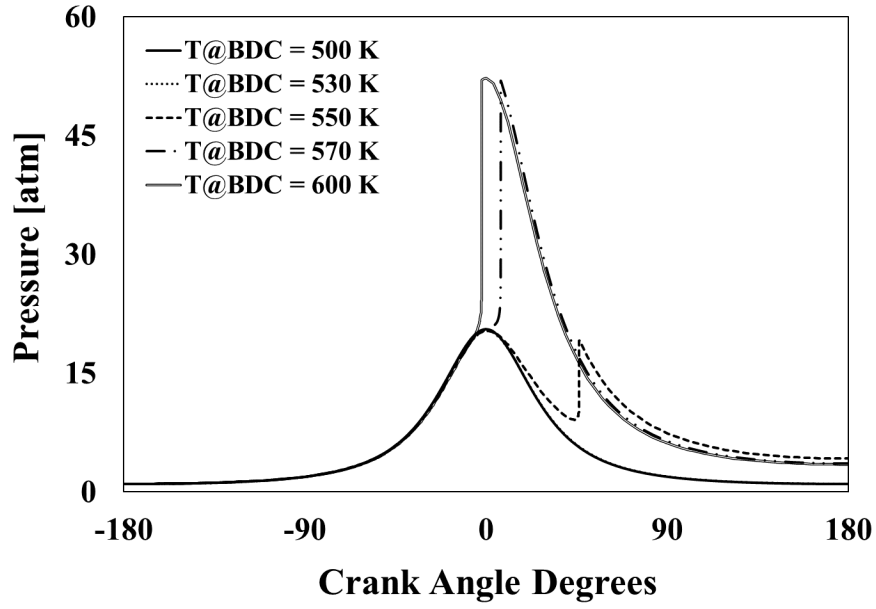


Figure 2: Cylinder pressure as a function of crank angle for different intake temperatures. Calculations are performed for an engine speed of 1200 RPM and $\phi=1.0$.

Figure 2 shows cylinder pressure traces as a function of crank angle degrees for different initial gas temperatures during the course of a single cycle. The simulations are performed for natural gas with $\phi=1$ at 1200 RPM. As seen from the figure, no autoignition is observed for initial gas temperatures below 550 K. Furthermore, increasing initial gas temperatures advance the onset of autoignition.

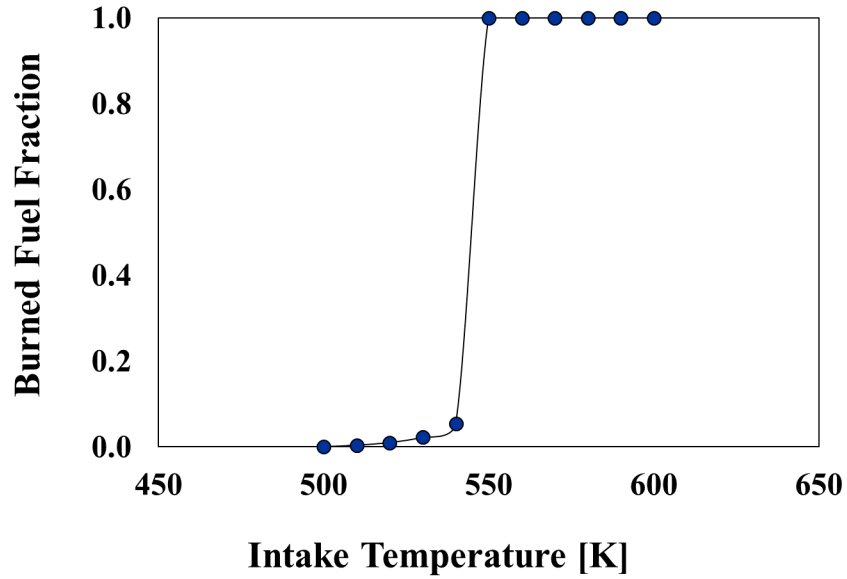


Figure 3: Burned fraction of fuel, at the end of the cycle as a function of intake temperature. Calculations are performed for an engine speed of 1200 RPM and $\phi=1.0$.

Figure 3 shows the burned mass fraction at the end of the cycle as a function of the initial gas temperature. The burned mass fraction is computed using the fuel mass fraction output by the Chemkin simulation. As expected at higher inlet air temperatures, autoignition occurs followed by complete consumption of the fuel. For an engine speed of 1200 rpm, and $\phi=1.0$ for 100% natural gas, this happens at 542 K (269°C).

3.2 Ignition delay

Ignition delay is estimated using the perfectly stirred reactor (PSR) model of Chemkin. Key input parameters are combustion chamber volume, reactor pressure, unburned gas temperature, and ϕ . The reactor pressure was kept at 30 atm, which is close to the in-cylinder pressure at TDC. The unburned gas temperature is varied from 800 to 1500 K. The gas temperature at TDC is 1090 K for an unburnt inlet gas temperature of 530 K. Simulations were run for a maximum time of 1 s. Ignition delay values were calculated for natural gas, and mixtures with varying percentages of water and oil. Ignition delay reported in this study is defined as the time needed to reach the maximum rate of rise of temperature [14].

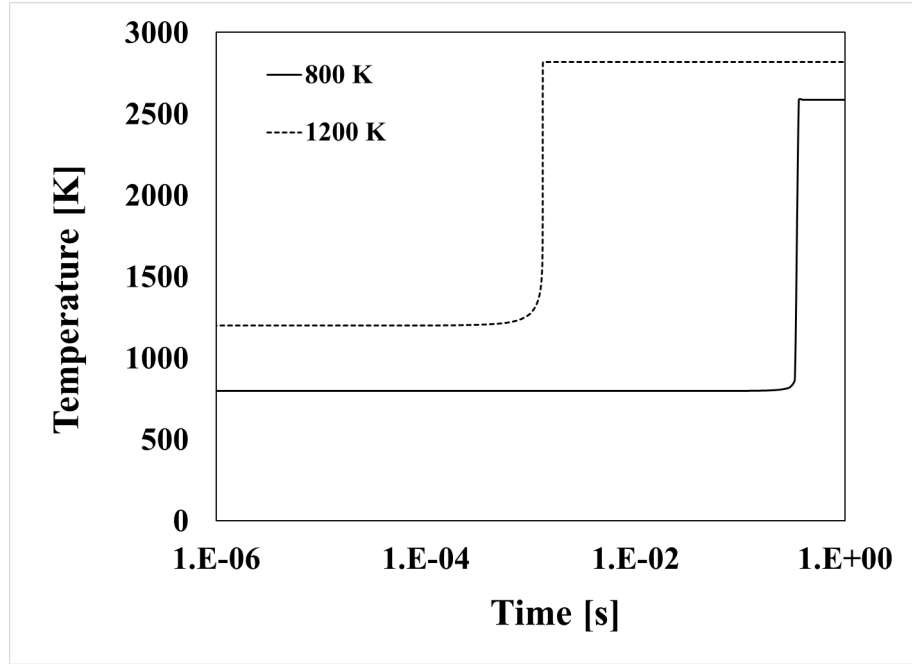


Figure 4: Temperature profiles for ignition delay simulations performed with two different unburned gas temperatures for 100% natural gas.

Figure 4 shows a plot of temperature traces for ignition delay simulations plotted as a function of time for two unburned gas temperatures of 800 K and 1200 K. These results are obtained for 100% natural gas. Once ignition occurs, a spike in temperature is observed with time. Another feature to be noted is the ignition temperature spike moves closer to the left, indicating a reduction in ignition times with increasing unburned gas temperature.

3.3 Laminar flame speed

Laminar flame speeds were calculated using the premixed laminar flame speed model in Chemkin. The model involves a freely-propagating flame, which is used to determine the characteristic flame speed of the gas mixture at specified pressures and temperatures. The input parameters to the model are ϕ , initial pressure, and unburned gas temperature.

The calculations were performed for natural gas and natural gas mixtures with water and oil in varying proportions.

3.4 Test matrix

The key motivation for this study is to identify the effects of changing water and oil content in CNG during refueling on combustion processes. Other parameters of interest in this study are pressure, unburned gas temperature, and ϕ . Test matrices were prepared to identify the range of variation of different parameters and are discussed in this section.

As per Stokes [15], gas purchase contracts limit water content in CNG to 3.18 kg per $2.83 \times 10^5 \text{ m}^3$. But, since compliance is not rigorously monitored, water content as high as 9.07–13.61 kg per $2.83 \times 10^5 \text{ m}^3$ have been measured at CNG stations [15]. This represents a water content of less than 1% by mass or by volume. In order to study the effects of water contamination, the percentage of water in fuel is varied from 0–5% to cover extreme scenarios of water composition in the supply gas.

Lubricated oil-compressors introduce oil up to 185 ppm [15] in CNG during compression, which is less than 1% of fuel. This value will highly likely increase in the current setup due to addition of oil into the gas due to blow-by of oil past the piston rings. In order to study the effects of oil contamination, the percentage of oil in fuel is varied from 0–5%.

Table 2 shows the range of parametric values investigated in the autoignition studies. In each case, the initial temperature at BDC was varied to find the minimum value required to obtain autoignition while keeping all other parameters constant. The temperature and pressure at BDC correspond to the temperature and pressure at the start of the simulation. Table 3 shows the range of parametric values investigated in the ignition delay calculations. Table 4 shows the range of parametric values investigated for laminar flame speed calculations.

Table 2: Range of parametric values for autoignition simulations.

Engine speed	T_{BDC}	P_{BDC}	Equivalence ratio (ϕ)	Water	Oil
RPM	K	atm		%	%
1200	400-600	1.01	0.7, 1.0, 1.2	0–5	0–5

Table 3: Range of parametric values for ignition delay simulations.

Initial gas temperature	Initial pressure	Equivalence ratio (ϕ)	Water	Oil
K	atm		%	%
800–1500	30	0.5–1.5	0–5	0–5

Table 4: Range of parametric values for laminar flame speed simulations.

Initial gas temperature	Initial pressure	Equivalence ratio (ϕ)	Water	Oil
K	atm		%	%
300	1.01	0.7–1.3	0–5	0–5

4. Reaction mechanism

The computational studies carried out in this work required a chemical reaction mechanism that incorporates chemical kinetics of natural gas mixtures with air. In addition, we desire to study the effects of adding of water and oil into the fuel-air mixture. The first step in considering a reaction mechanism is to fully define all the chemical species that are required to be simulated.

4.1 Natural gas composition

Natural gas is found in varying compositions. The composition studied in this work was adapted from Westbrook et al. [16]. Methane number provides an indication of knocking tendency of natural gas in spark-ignited engines, similar to octane number for liquid fuels. Methane numbers are determined from correlations given by Callahan et al. [17]. The composition chosen has a methane number of 91. Table 5 shows the percentage composition of each constituent in the natural gas mixture.

Table 5: Natural gas composition used in this work as adapted from Westbrook et al. [16].

Mixture constituent	Mean (% vol)
CH ₄	93.12
C ₂ H ₆	3.20
C ₃ H ₈	0.70
C ₄ H ₁₀	0.40
CO ₂	1.21
N ₂	1.37
Molecular Wt.	17.36 (g/mol)
Methane #	91

4.2 Oil composition

Oil contamination of the fuel primarily arises from engine oil entering the natural gas stream during refueling by blowing past the piston rings. The first step in having oil molecules entering into the firing cylinder participate in the gas-phase chemistry is for them to vaporize. Once vaporized, the next step is to describe the gas-phase chemistry of oil molecules. Due to the complicated molecular structure of these species with volatile and non-volatile components, there do not appear to be any accurate descriptions of the gas-phase chemistry of oil molecules [18]. As an alternative, an approach similar to that pursued by Maas et al. [19] has been pursued in this work. Maas et al. modeled the oil molecule as *n*-hexadecane whose physical properties are similar to that of lubricant oil. This allows for a better description of the vaporization of the oil molecule. In the gas-phase, reaction chemistry of the oil molecule is taken to be similar to that of *n*-heptane. This is justified by the fact that ignition delay times of linear *n*-alkanes from *n*-heptane to *n*-hexadecane are similar [20]. A similar approach was followed by Kuti et al. [21] who used *n*-C₁₆H₃₄, *n*-C₁₇H₃₆, and *n*-C₁₈H₃₈ as surrogates of lubricant base oil constituents for testing in an ignition quality tester.

In this work, it is assumed that the oil molecules are vaporized given the relatively high temperature of the fuel and, similar to Maas et al., the gas-phase chemistry of oil is prescribed to be the same as that of *n*-heptane.

4.3 Reaction mechanism

The reaction mechanism selected for performing parametric studies in this work is the Lawrence Livermore National Laboratory *n*-heptane detailed mechanism Version 3.1 [22].

The detailed reaction model consists of 556 species and 2540 reversible elementary reactions. This reaction mechanism has been experimentally validated for a pressure range of 3–50 atm, temperatures of 650–1200 K, and ϕ from 0.3–1.0. The mechanism performs well at both low and high temperatures over a broad pressure range important for IC engines. The mechanism has the capability to model natural gas with the composition described in Table 5 and *n*-heptane, which is used as a surrogate for engine oil in this work.

4.4 Validation studies

Validation studies were carried out to determine the performance of the *n*-heptane reaction mechanism in predicting ignition delays and flame speeds of natural gas with the composition given in Table 5. This was done by comparing the predictions of the *n*-heptane mechanism with those of the well-known GRI-Mech 3.0 [23] mechanism as well as available experimental data. The GRI-Mech 3.0 scheme consists of 53 species and 325 elementary reactions, and has been optimized for C_1 – C_3 hydrocarbons at temperatures between 800–2500 K, pressures between 10 torr to 10 atm, and ϕ of 0.1–5.0 for premixed systems.

Figure 5 shows results for ignition delays of natural gas-air mixtures for an initial pressure of 30 atm with $\phi=1$ and varying initial gas temperatures. Results obtained using the *n*-heptane detailed mechanism and GRI-Mech are compared with available experimental data. Ignition delay for natural gas predicted by the *n*-heptane detailed mechanism compares reasonably well with those from GRI-Mech as well as with available experimental data from literature, although some discrepancies arise at lower temperatures.

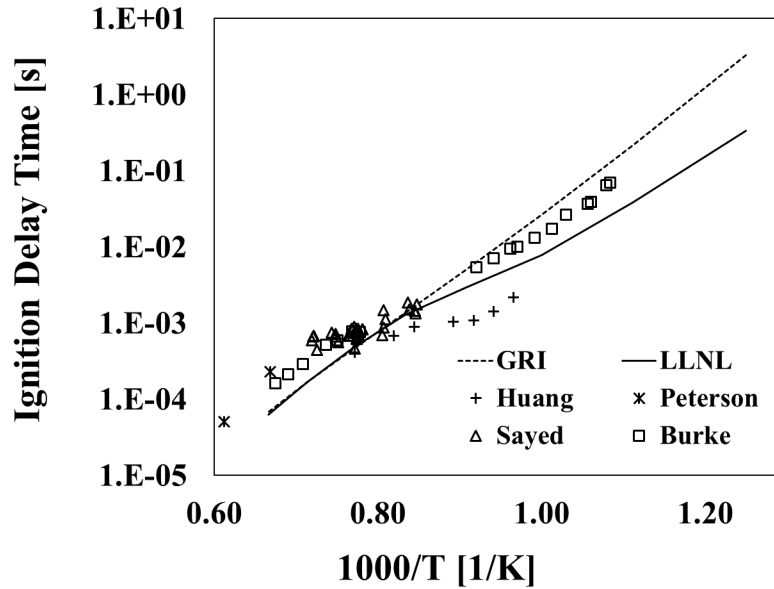


Figure 5: Comparison of ignition-delays for natural gas-air mixtures for $\phi = 1$. Experimental data taken from Huang et al. [14], Petersen et al. [25], Sayed et al. [26], and Burke et al. [27].

Figure 6 shows predictions of laminar flame speeds of a natural gas-air mixture with $\phi=1$, pressure of 1.01 atm and temperature of 300 K. Again, predictions from the two mechanisms compare reasonably well with each other and most experimental data, particularly that of Egolfopoulos et al. [28] and Bradley et al. [29]. Given the results of the

validation studies, the LLNL *n*-heptane detailed mechanism was utilized as the reaction mechanism for the autoignition, ignition delay, and laminar flame speed calculations.

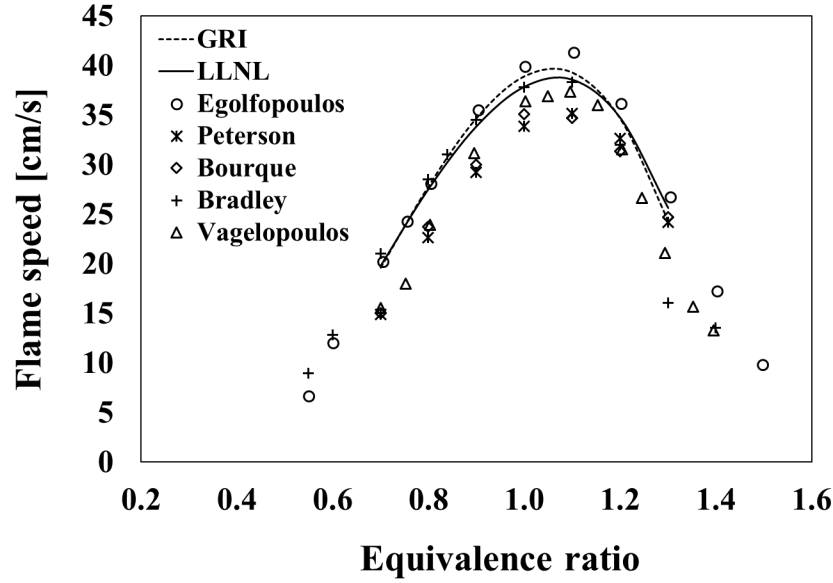


Figure 6: Comparison of laminar flame-speeds for natural gas/ air mixtures for $\phi = 1$. Experimental data taken from Egolfopoulos et al. [28], Lowry et al. [29], Bourque et al. [30], Bradley et al. [31], and Vagelopoulos et al. [32].

5. Results

The goal of this work is to study the effects of onboard refueling strategy implemented in the modified engine on the downstream combustion occurring in the engine cylinder. To accomplish this, parametric studies of autoignition, ignition delay, and flame speed were performed using the simulation tools described in Section 3 and the reaction mechanism described in Section 4. The results of these studies are described in the following sub-sections.

5.1 Autoignition

As mentioned previously, autoignition temperature is defined as the temperature of the unburned gases at IVO resulting in autoignition during the cycle. Calculations were carried out at an engine speed of 1200 RPM and intake pressure of 1.01 atm. A parametric study of the autoignition temperature was performed as per the conditions listed in Table 2.

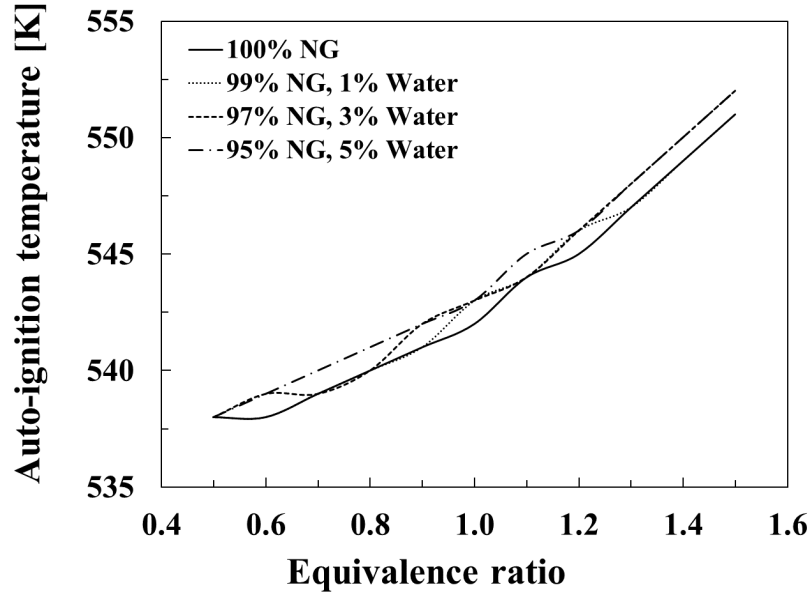


Figure 7: Effect of water addition on autoignition temperature.

Figure 7 shows the effect of adding water from 1–5% on the autoignition temperature of natural gas/air mixtures with different values of ϕ . As can be seen, the effect is negligible—in some cases, the autoignition temperature increased up to 2 K due to water addition. These results suggest that water addition to natural gas/air mixtures does not produce any significant effect on the autoignition temperature.

Figure 8 shows the effect of adding oil from 1–5% on the autoignition temperature of natural gas/air mixtures. The results show that autoignition temperature is strongly affected by the addition of oil and decreases with increasing oil content at all values of ϕ . At $\phi=1$, an increase in oil concentration from 1–5% in the fuel mixture lowers the autoignition temperature by 5–10%. The key effect related to the reduction in autoignition temperature is the decrease in ignition delay of the fuel mixture with addition of oil. This results in a decrease in the autoignition gas temperature. The specific effects of oil in reducing ignition delay of the fuel mixture will be covered in more detail in the next section.

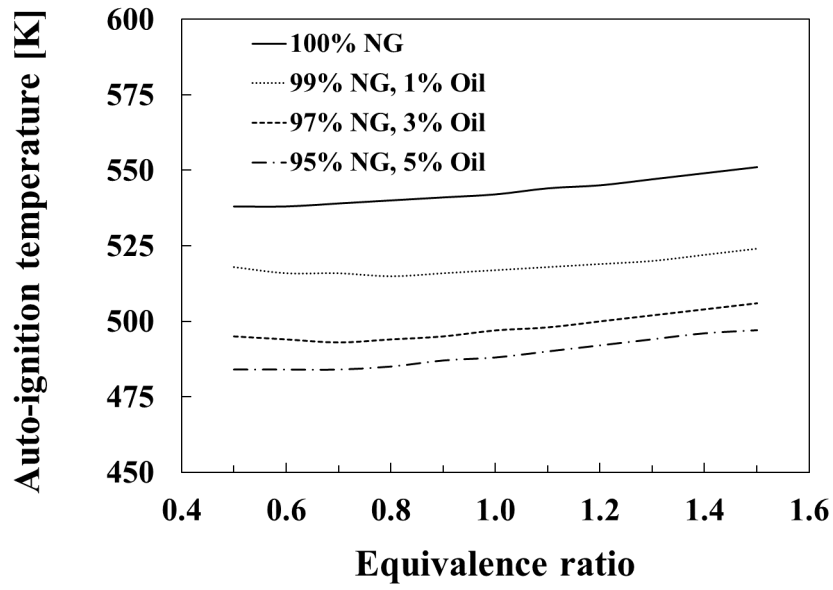


Figure 8: Autoignition temperature as a function of ϕ for natural gas/air mixtures with oil addition from 1–5%.

5.2 Ignition delay

As described previously, the perfectly stirred reactor model was used to calculate ignition delay near TDC conditions at the conditions listed in Table 3. Figure 9 shows ignition delay as a function of inverse of temperature for natural gas/air mixtures with $\phi=1$ and varying amounts of water. The results indicate that water addition from 1–5% has almost no impact on ignition delay of the fuel/air mixture.

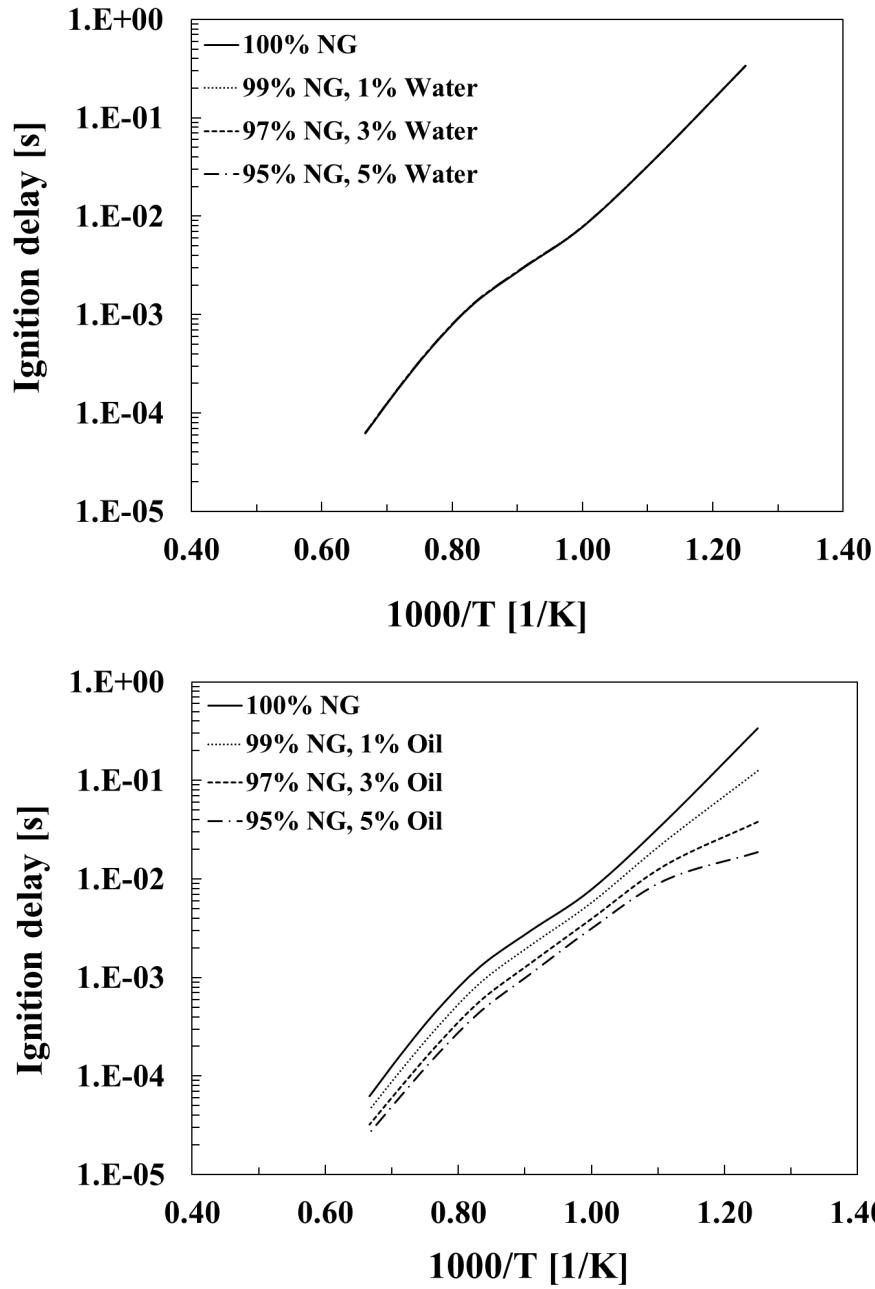


Figure 9: Ignition-delay for as a function of inverse of temperature for natural gas/air mixtures with varying water and oil content from 1–5%.

Figure 9 also shows the effect of adding oil from 1–5% on the ignition delay of natural gas/air mixtures at $\phi=1$. At the lowest initial temperature studied in this work (800 K), the ignition delay is reduced by 63–95% by the addition of oil from 1–5%. At an initial temperature of 1500 K, the ignition delay is reduced by 27–58% by the addition of oil from 1–5%.

Figure 10 shows the normalized sensitivity coefficients of ignition delay to key chemical reactions at $\phi=1$ for four cases with increasing oil concentration from 0–5%. The

sensitivity analysis is conducted by varying the reaction rate of key reactions and computing a normalized sensitivity given by the following equation [33],

$$S = \frac{\tau(2k_i) - \tau(0.5k_i)}{1.5\tau(k_i)}$$

where τ is the ignition delay of the mixture and k_i are the individual reaction rates. A negative value for the sensitivity coefficient indicates a reduction in ignition delay through a promotion of the total reaction rate while a positive value indicates an increase in the ignition delay via inhibition of the total reaction rate. The results of Fig. 10 show the highest sensitivities of ignition delay to be on the chain branching reaction $\text{CH}_3 + \text{HO}_2 \rightarrow \text{CH}_3\text{O} + \text{OH}$ that reduces ignition delay and the recombination reactions $\text{CH}_3 + \text{HO}_2 \rightarrow \text{CH}_4 + \text{O}_2$ and $2\text{CH}_3(+\text{M}) \rightarrow \text{C}_2\text{H}_6(+\text{M})$ that increase ignition delay. The sensitivity of the chain branching reaction $\text{H} + \text{O}_2 \rightarrow \text{O} + \text{OH}$ seems to be considerably lower. Upon addition of increasing amounts of oil (modeled as $n\text{-C}_7\text{H}_{16}$), the sensitivity of the branching reaction $\text{CH}_3 + \text{HO}_2 \rightarrow \text{CH}_3\text{O} + \text{OH}$ remains relatively unchanged while the sensitivity of both recombination reactions $\text{CH}_3 + \text{HO}_2 \rightarrow \text{CH}_4 + \text{O}_2$ and $2\text{CH}_3(+\text{M}) \rightarrow \text{C}_2\text{H}_6(+\text{M})$ that have the highest positive sensitivity decreases thus reducing ignition delay.

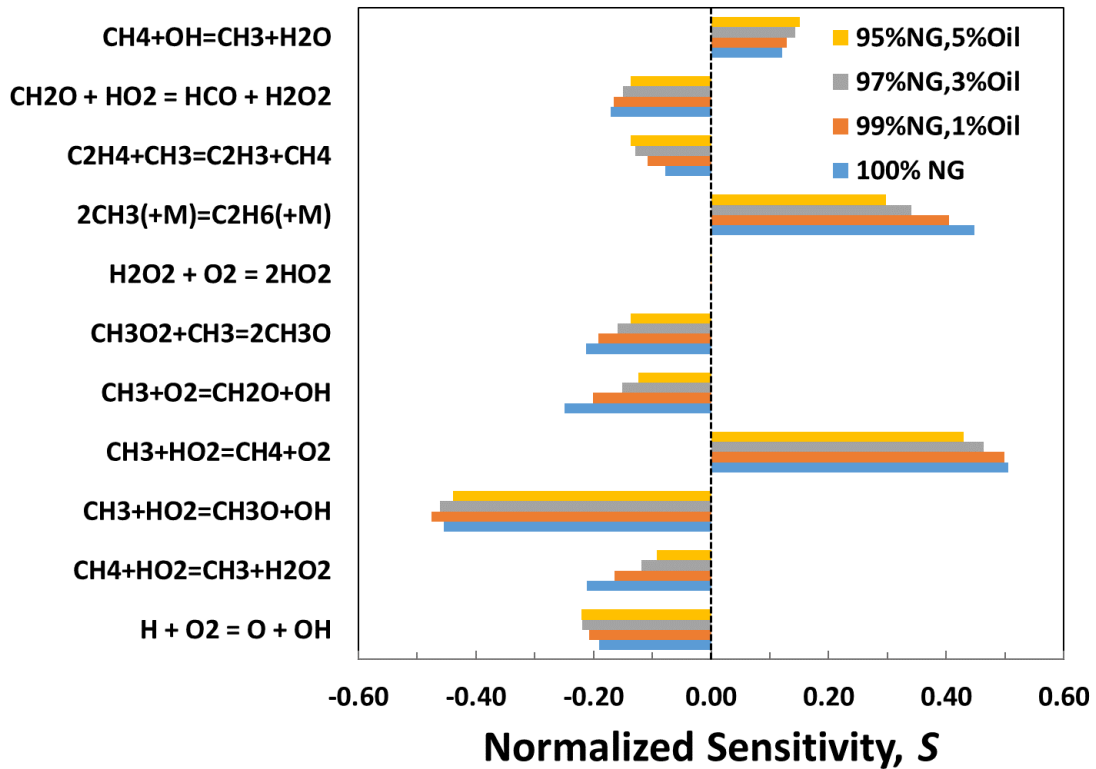
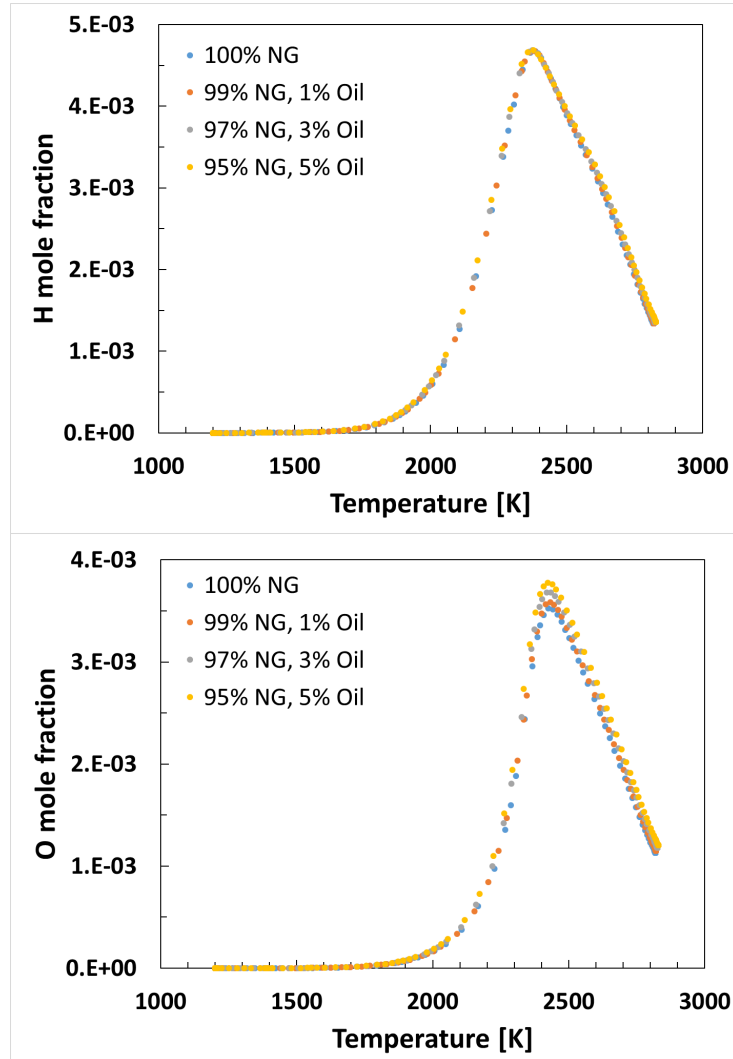


Figure 10: Sensitivity of ignition delay for natural gas-air mixtures with varying oil content from 0–5%. Initial conditions are pressure of 30 atm, temperature of 1200 K, and $\phi=1$.

Further analysis of the chemical kinetics related to ignition delay is conducted by considering the mole fraction of small radicals involved in the ignition process [34]. These free radicals (H , O , OH , HO_2 , and CH_3) act as important chain carriers and their evolution strongly affects the ignition process. Figure 11 shows the evolution profiles of the free

radicals for a case with initial pressure of 30 atm, temperature of 1200 K, and $\phi=1$ for increasing oil addition from 0–5%. The mole fractions of H, O, and OH radicals show no significant changes with temperature. More variation is seen with the HO₂ and CH₃ mole fractions. HO₂ mole fraction appears to increase with increasing oil addition and appear at lower temperatures. On the other hand, CH₃ mole fractions appear to decrease with increasing oil addition.



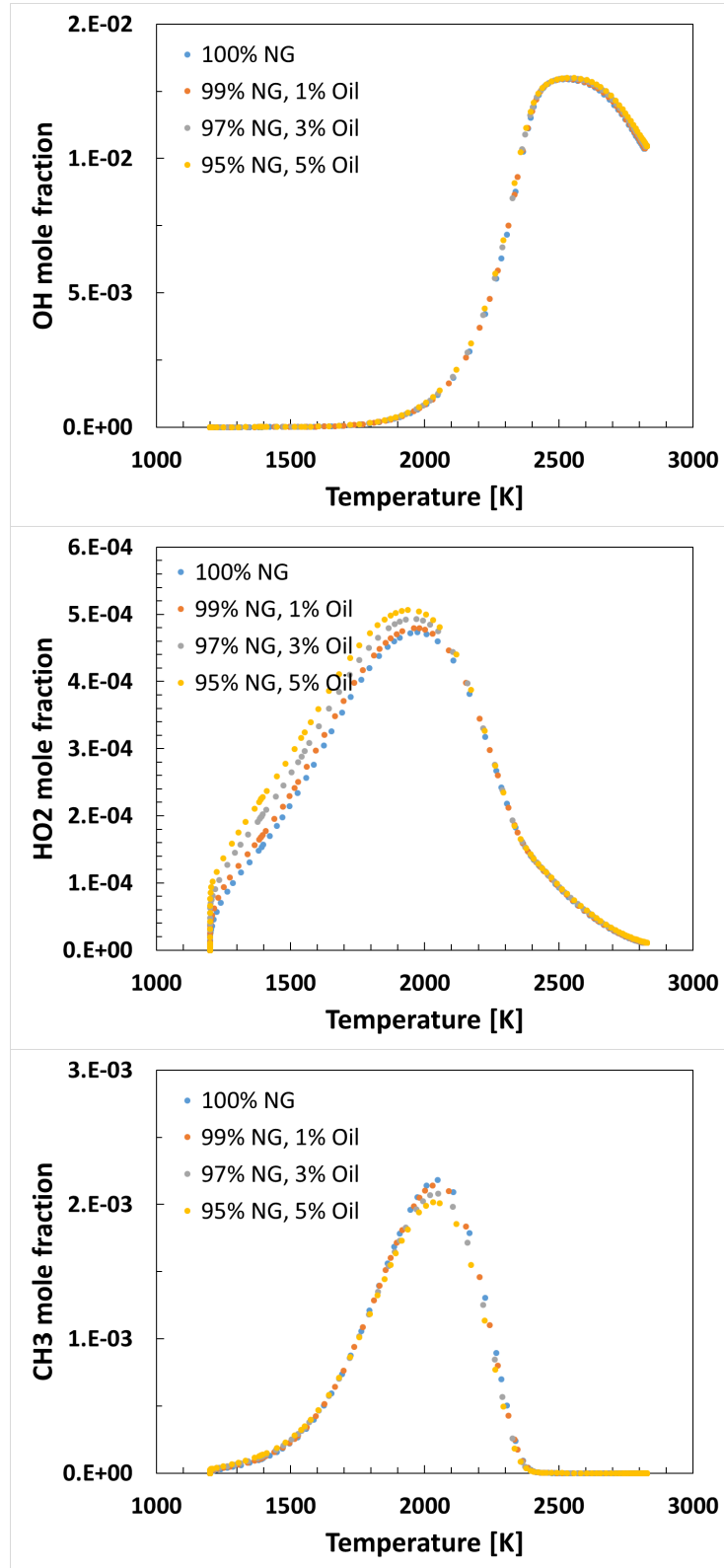


Figure 11: Evolution profiles of mole fractions of key radical species as a function of temperature for natural gas/air mixtures for varying oil concentration from 0–5%.

5.3 Laminar flame speed

Laminar flame speeds of natural gas/air mixtures were calculated for the range of parametric input values specified in Table 4. Figure 12 shows the flame speed plotted as a function of equivalence ratio for natural gas/air mixture with water addition from 1–5% for ϕ varying from 0.7 to 1.3. At stoichiometry, the flame speed decreases by about 2.0% by the addition of 5% of water. Similarly, at $\phi=0.7$, the flame speed decreases by 1.8% while at $\phi=1.3$, the flame speed decreases by 3.7%. Figure 14 also shows the effect of addition of oil on laminar flame speeds of natural gas/air mixtures for ϕ varying from 0.7 to 1.3. At stoichiometry, the flame speed increases by about 1.7% by the addition of 5% of oil. Similarly, at $\phi=0.7$, the flame speed increases by 5.3% while at $\phi=1.3$, the flame speed increases by 9.4%. For both water and oil addition, the effect on burning speed is stronger at rich mixture conditions as compared with lean or stoichiometric conditions.

The effects of water/steam addition on the flame speed of methane/air flames has been investigated previously by Fiorina et al. [35] and Poinso et al. [36]. Steam addition was found to reduce laminar flame speed linearly in both studies with a decrease of 13.6% when the relative humidity of air was increased from 0 to 100%. Water addition is found to have thermal and chemical effects on flame speed. The current simulation results were analyzed to estimate the change in sensitivities of key chemical reactions upon addition of water. However, the changes were very minor as seen in Fig. 13. The adiabatic flame temperature decreased by about 7 K when water content was varied from 0–5% for the stoichiometric case. The mole fraction of key radical species in the flame zone decreased slightly as shown in Fig. 14 for 0–5% water addition for the stoichiometric mixture. For the addition of up to 5% of water, it appears that the decrease in flame speed is primarily due to thermal effects, since no major change in sensitivity of key chemical reactions was observed.

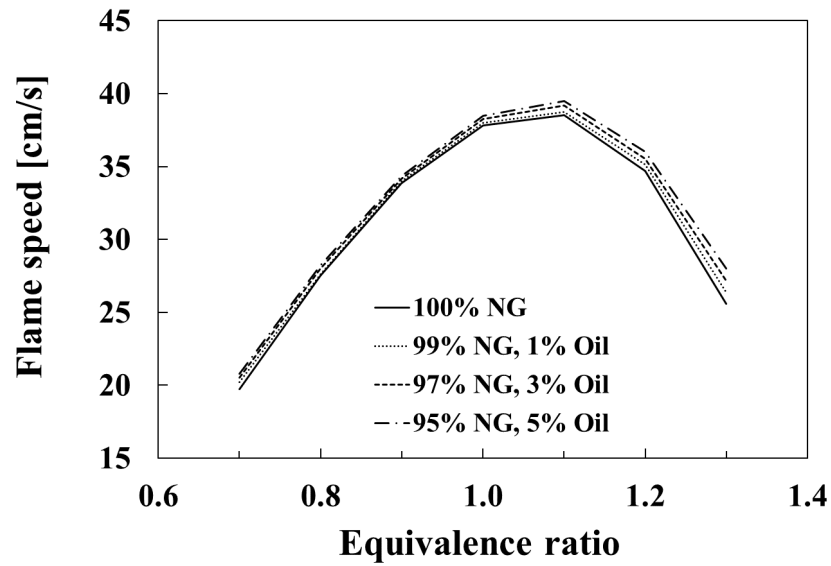
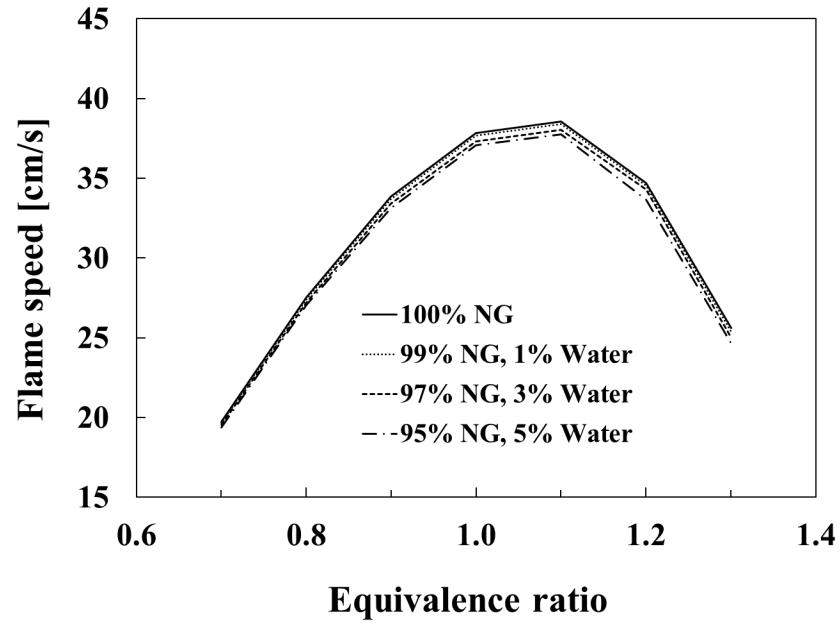
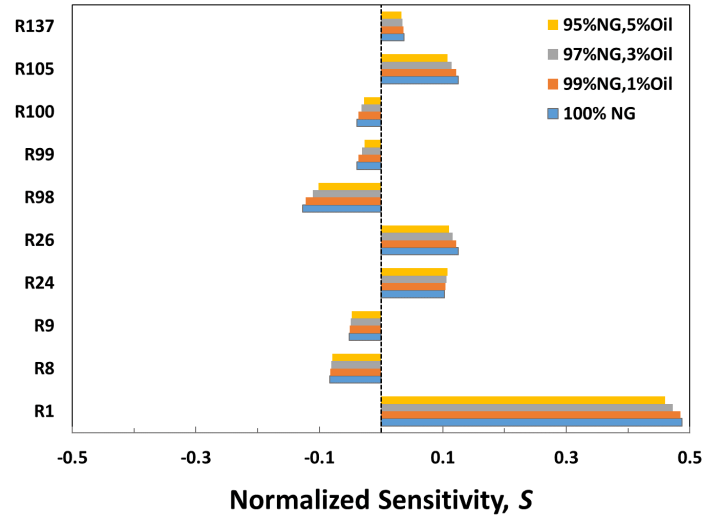
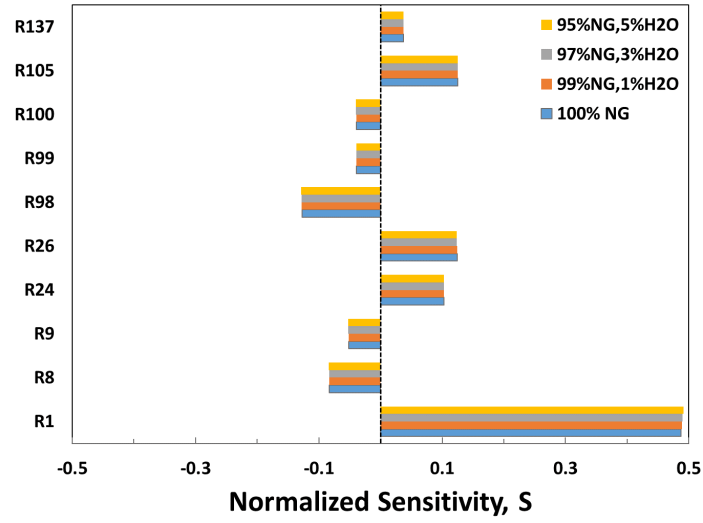


Figure 12: Flame speed as a function of equivalence ratio for natural gas/air mixtures with oil and water addition, each going from 0–5%.



R 1	$\text{H} + \text{O}_2 \rightleftharpoons \text{O} + \text{OH}$
R 8	$\text{H}_2\text{O} + \text{M} \rightleftharpoons \text{H} + \text{OH} + \text{M}$
R 9	$\text{H} + \text{O}_2(+\text{M}) \rightleftharpoons \text{HO}_2(+\text{M})$
R 24	$\text{CO} + \text{OH} \rightleftharpoons \text{CO}_2 + \text{H}$
R 26	$\text{HCO} + \text{M} \rightleftharpoons \text{H} + \text{CO} + \text{M}$
R 98	$\text{CH}_3 + \text{H}(+\text{M}) \rightleftharpoons \text{CH}_4(+\text{M})$
R 99	$\text{CH}_4 + \text{H} \rightleftharpoons \text{CH}_3 + \text{H}_2$
R 100	$\text{CH}_4 + \text{OH} \rightleftharpoons \text{CH}_3 + \text{H}_2\text{O}$
R 105	$\text{CH}_3 + \text{OH} \rightleftharpoons \text{CH}_2(\text{S}) + \text{H}_2\text{O}$
R 137	$\text{CH}_2 + \text{O}_2 \rightleftharpoons \text{CO}_2 + \text{H} + \text{H}$

Figure 13: Sensitivity analysis of burning velocity for natural gas/air mixtures with water and oil addition.

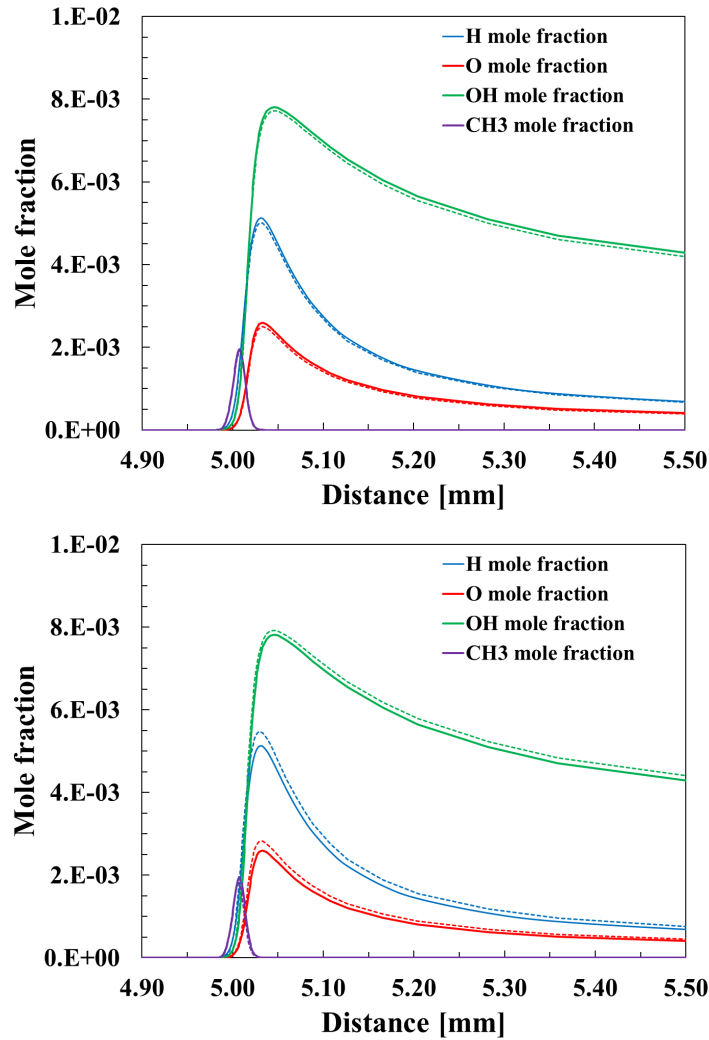


Figure 14: Mole fraction of key radical species in the flame zone for $\phi = 1$. Solid lines correspond to 0% water addition and dashed lines correspond to 5% water addition.

Thermal and chemical effects also play key roles in the changes in flame speed brought about by addition of oil. The adiabatic flame temperature increases by about 13 K for 0–5% oil addition for the stoichiometric mixture. The sensitivities of all key reactions decreased except for reaction R 24 as shown in Fig. 13. The mole fractions of key radicals including H, O, OH, and CH₃ increased in the flame zone for the stoichiometric case as shown in Fig. 14. Thus addition of oil appears to increase flame speed due to thermal and chemical effects. However, based on the relatively small increase in radical concentration, the major effect on flame speed is primarily thermal in nature.

6. Conclusions

A parametric study was undertaken to investigate the effects of natural gas conditions produced in a novel bimodal engine on the chemical kinetic phenomena taking place during normal engine combustion operation. Water addition of 1–5% by volume had no significant effect on the temperature required for autoignition or on the ignition delay at engine conditions. Water addition of 1–5% by volume had a retarding effect on laminar flame

speed primarily due to thermal factors resulting in a reduction in the adiabatic flame temperature. At stoichiometric conditions, addition of 5% of water results in a 2% decrease in laminar flame speed. In summary, water addition to natural gas at 1–5% by volume does not result in any major changes in the combustion processes, other than a slight reduction in laminar flame speeds.

Effects of engine oil contamination on combustion were modeled assuming a chemical composition of oil similar to *n*-heptane in gas phase. Oil content has a strong influence on autoignition temperature, ignition delay and the laminar flame speed. Autoignition temperatures for the fuel-air mixtures are lowered by 5–10% with addition of oil from 1–5% by volume. This is primarily driven by a decrease in ignition delay. Depending on the initial temperature of the fuel-air mixture, an addition of oil from 1–5% can reduce the ignition delay by as much as 27–95%. A sensitivity analysis shows that at the conditions studied, the chain branching reaction $\text{CH}_3 + \text{HO}_2 \rightarrow \text{CH}_3\text{O} + \text{OH}$ that promotes ignition has one of the highest sensitivities. With addition of increasing amounts of oil, the sensitivity of this reaction remains almost unchanged while that of two recombination reactions $\text{CH}_3 + \text{HO}_2 \rightarrow \text{CH}_4 + \text{O}_2$ and $2\text{CH}_3(+\text{M}) \rightarrow \text{C}_2\text{H}_6(+\text{M})$ (which delay ignition) drop considerably resulting in lowering of ignition delay. Considering the evolution of free radical species involved in ignition it is seen that the HO_2 mole fraction increasingly appears at lower temperatures with addition of oil, and could be key to the reduction in ignition delay. Oil addition also promotes the laminar flame speed. At stoichiometry, addition of oil by 5% increases laminar flame speed by 1.7%. Sensitivity analysis of flame speed does not show any significant change in key reaction steps upon addition of up to 5% oil content. A slight increase in key radical mole fractions is observed. Adiabatic flame temperature increases by about 13 K by addition of 5% of oil at stoichiometry. It is concluded that the change in laminar flame speed by oil addition is possibly due to chemical and thermal factors.

Nomenclature

<i>SI</i>	Spark Ignited
<i>CNG</i>	Compressed Natural Gas
<i>NGV</i>	Natural Gas Vehicle
<i>GGE</i>	Gasoline Gallon Equivalent
<i>EV</i>	Electric Vehicles
<i>IC</i>	Internal Combustion
<i>HCCI</i>	Homogeneous Charge Compression Engine
<i>PSR</i>	Perfectly Stirred Reactor
<i>LFS</i>	Laminar Flame Speed
<i>TDC</i>	Top Dead Center
<i>BDC</i>	Bottom Dead Center
<i>BTDC</i>	Before TDC
<i>ATDC</i>	After TDC
<i>IVO</i>	Inlet Valve Opening
<i>CA</i>	Crank Angle

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