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# Autoignition of Premixed Liquefied Petroleum Gas in a Rapid Compression Machine: Experimental Results and Chemical Kinetic Mechanism Reduction

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**Abstract:** Liquefied petroleum gas (LPG) has many properties that make it an attractive alternative fuel such as lower cost than conventional fuels and an established distribution infrastructure. The development of high efficiency, spark ignited LPG engines is currently limited by engine knock and misfire. The knock and misfire limits are further complicated by the wide range of chemical reactivity in LPG, particularly in international markets. In this study, a rapid compression machine (RCM) was used to characterize the effects of variation in LPG fuel reactivity, equivalence ratio, and exhaust gas recirculation (EGR) on autoignition of LPG/oxidizer/inert/EGR blends. Experiments were conducted with 100% propane ($C_3H_8$) and blends of propane with propene, ethane, isobutane, and n-butane. EGR was simulated with mixtures of Ar, $CO_2$, CO, and NO at substitution percentages from 0 to 30 mass percent. Equivalence ratio was varied from 0.75 to 1.5. Ignition delay period under homogeneous autoignition conditions was measured at compressed pressures and temperatures of 23 to 25 bar and 701 to 921 K, respectively. Zero-dimensional simulations of the RCM experiments were performed using Chemkin with several detailed chemical kinetic mechanisms to determine their suitability at predicting ignition delay periods. Multiple reduced chemical kinetic mechanisms were created from the NUIGMech1.1 mechanism to determine the optimal balance between accuracy and computational efficiency for future three-dimensional, time-dependent spark-ignited engine computations.

**Keywords:** Ignition Delay, LPG, Rapid Compression Machine, Mechanism Reduction

## 1. Introduction

The heavy trucking and transportation industries mainly rely on compression ignition (CI) engines powered by petroleum diesel fuel. While liquefied petroleum gas (LPG) has seen modest market penetration in delivery vehicles and school buses, it is not currently in use as a fuel for heavy duty trucking. In recent years, because of increases in domestic oil and gas production, there exists an overabundance in the U.S. supply of LPG, the constituents of which are produced during the extraction of natural gas and during petroleum refining. The resulting decreased cost in LPG has provided the incentive to increase the penetration of LPG engines into the heavy-duty trucking market, provided that these engines can meet efficiency and performance standards required in that market. In addition to lower fuel costs, LPG engines also have the benefit of reduced emissions in comparison to diesel engines, which require costly aftertreatment devices to reduce particulate matter (PM) and oxides of nitrogen ($NO_x$).

Spark ignited (SI) LPG engines have the potential to provide the same thermal efficiency as diesel engines while producing less emissions and with lower capital costs than diesel powered CI engines. LPG engines would also require less overhead cost and infrastructure investment compared to other low carbon fuels such as compressed natural gas (CNG). In response to this opportunity, Cummins recently developed a purpose-built direct injected spark ignited (DISI) 6.7L LPG engine that reaches 41% brake thermal efficiency (BTE) at peak torque while also producing less $CO_2$ emissions than other medium duty LPG engines [1]. More recently, the U.S. Department of Energy has funded a partnership between Colorado State University (CSU), Cummins and Argonne National Laboratory to develop a heavy duty, 15L DISI LPG engine for on-road heavy trucking applications that achieves 44% BTE.

LPG is primarily a mixture of propane ($C_3H_8$), propene ($C_3H_6$) and butane ($C_4H_{10}$) and is produced during the extraction of natural gas or during petroleum refining. In the United States, the standard LPG mixture used as automotive fuel is HD-5. HD-5 is a more stringent standard than commercial propane, which enables it to be used for internal combustion engines. Based on the standard, HD-5 must consist of at least 90% propane by volume, with a maximum of 5% propene and 5% other gases such as butane and ethane ($C_2H_6$) [2]. Sampling from around the United States shows that the mean composition of HD-5 is 96.06% propane, 2.48% ethane, 0.96% isobutane, 0.29% propene, and 0.18% n-butane by volume but samples have exhibited levels of ethane as high as 6% and n-butane/isobutene as high as 7% [3].

To make the most efficient heavy-duty LPG engine, several strategies must be simulated, analyzed, and implemented. Optimizing these strategies requires a comprehensive understanding and model of the combustion of homogeneous LPG under engine-like conditions with varying fuel compositions, equivalence ratios, and exhaust gas recirculation (EGR) levels. Central to the current high efficiency engine development work is the use of controlled end-gas autoignition (C-EGAI), which uses sophisticated control algorithms to enable a specified fraction of combustion to occur via autoignition upstream of the propagating flame. Further efficiency gains can be provided by stratified combustion via direct injection (DI), EGR dilution, and optimized combustion chamber design. These design strategies require computational modeling with chemical kinetic mechanisms that are accurate enough to capture the combustion physics of flame propagation and end-gas autoignition, but sufficiently compact ($\approx$ 100 species) to facilitate reasonable computational times. Maximizing the efficiency of LPG engines through this combined experimental/computation approach will result in LPG engines as viable alternatives to current engine offerings, at which point the fuel cost savings will offset any initial price difference when distributed over the product life cycle.

The goal of the present study is to develop a reduced chemical kinetic mechanism that can be used to accurately model three-dimensional, time-dependent, DISI, LPG engine simulations. The mechanism must predict ignition delay and flame speed across a range of fuel composition, temperature, pressure, equivalence ratios, and EGR substitution rates. Moreover, since previous work has shown reactive species such as nitric oxide (NO) present in EGR gas can affect autoignition propensity in the end-gas [4], the reduced LPG mechanism must also include $NO_x$/ hydrocarbon chemistry. The reduced mechanism will be validated against experimental data available in the literature as well as new experiments performed in a rapid compression machine (RCM) under engine-relevant conditions. The RCM experiments will include homogenous compression ignition experiments (as described in this paper) and laser ignited experiments, which enable measurement of flame speed and end-gas autoignition fraction.

## 2. Methods / Experimental

### *2.1 Rapid Compression Machine*

The RCM at Colorado State University is an opposed-piston system and can operate in compression ignition mode or laser spark mode. Compression ignition mode is used to measure the ignition delay period of a homogeneous mixture of fuel and air. The initial chamber pressure, temperature, and inert gas composition are adjusted to produce the desired thermodynamic conditions at piston top dead center (TDC). The compression duration for the RCM is approximately 8.5 ms with a TDC volume of 30.0 $cm^3$. Creviced pistons are used to reduce the effects of turbulence on the adiabatic core of the RCM. The premixed reactant mixture reaches a pressure of 23.92 ± 0.96 bar and a temperature of 700 to 921 K. A thermally compensated, high speed pressure transducer (Kistler 601CAA) is used to measure pressure inside the combustion chamber. The pressure data are recorded using a Picoscope 4424 data acquisition system with a sample rate of 2 MHz. The homogeneous ignition delay period is defined as the time interval between the maximum compressed pressure at TDC and the maximum pressure rise rate during combustion [4]. The layout of the RCM is shown in Fig. 1.

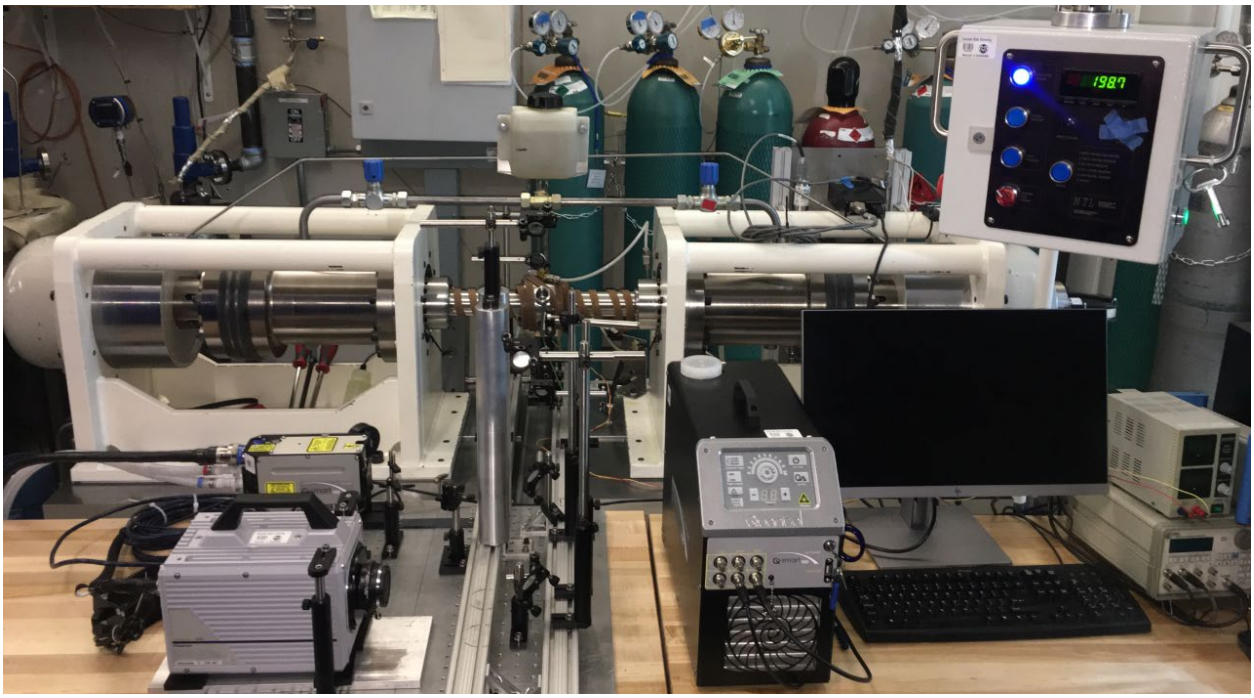

**Figure 1.** Photograph of the rapid compression machine experimental setup.

All RCM experiments described in this paper were conducted using mixtures of $C_3H_8/O_2$/inert with varying ratios of $N_2$/Ar and varying initial temperature to adjust the compressed temperature. Tests were performed by beginning at the lowest initial temperature for each reactant mixture and then increasing the temperature of the reactant mixture tank and RCM combustion chamber by 2 K increments for each subsequent test. As inert composition was varied, initial pressure was adjusted to maintain constant compressed pressure at TDC. In this paper, the results of $C_3H_8/O_2$/inert at three equivalence ratios ($\phi$ = 0.75, 1.0, and 1.5) are presented, along with comparisons against detailed and reduced chemical kinetic mechanism.

*2.2 Chemical Kinetic Modeling*

Zero-dimensional simulations of RCM experiments were performed using Ansys Chemkin-Pro. Both constant volume and transient, variable-volume simulations were performed. To perform a transient simulation that captures the non-idealities of the RCM such as pressure decrease due to constant volume heat loss after piston TDC, an effective temporal volume profile is created from the pressure and mixture composition data. Using the effective temporal volume profile with an initial temperature, pressure, and mixture, the Chemkin model simulates the compression stroke followed by constant volume heat loss in RCM experiments with 0-dimensional compression-expansion process that reproduces the experimental pressure/temperature history during the chemical kinetic induction period.

Five detailed chemical kinetic mechanisms were evaluated to determine which were the most accurate at reproducing experimental data from the literature and the RCM experiments and to select the mechanism that represents the best starting point for LPG mechanism reduction. The mechanisms that were evaluated are summarized below in Table 1.

**Table 1**. Chemical kinetic mechanisms considered for simulations.

| Detailed Mechanism | Origin | Species | Reactions |
|---|---|---|---|
| AramcoMech3.0 [5] | NUI Galway | 581 | 3.034 |
| NUIGMech1.1 [6] | NUI Galway | 2,746 | 11,279 |
| San Diego Mech [7] | UC San Diego | 58 | 268 |
| USC Mech Version II [8] | University Southern California | 111 | 784 |
| C1-C3 + NOx [9] | Polytechnic University of Milan | 159 | 2,459 |

## 3. Results and Discussion

*3.1 Ignition Delay Period Measurements*

The ignition delay period experiments were performed at lean, stoichiometric, and rich conditions ($\phi$ = 0.75, 1.0, and 1.5) for $C_3H_8/O_2$/inert mixtures over a temperature range of approximately 700 to 900 K. The compressed pressure at TDC for all experiments was 24 bar. The ignition delay period results are plotted as a function of 1000/T in Fig. 2. Under these conditions, negative temperature coefficient (NTC) behavior was observed for the rich, lean and stoichiometric mixtures. The experimental results also showed that the rich fuel mixture exhibited the shortest ignition delay periods, and the lean mixtures the longest for the majority of the temperature range. At higher temperatures, preliminary experimental results suggest that the lean mixtures had shorter ignition delay periods than the stoichiometric mixtures. As discussed further below, the chemical kinetic modeling did not capture this effect and work is ongoing to confirm the experimental results.

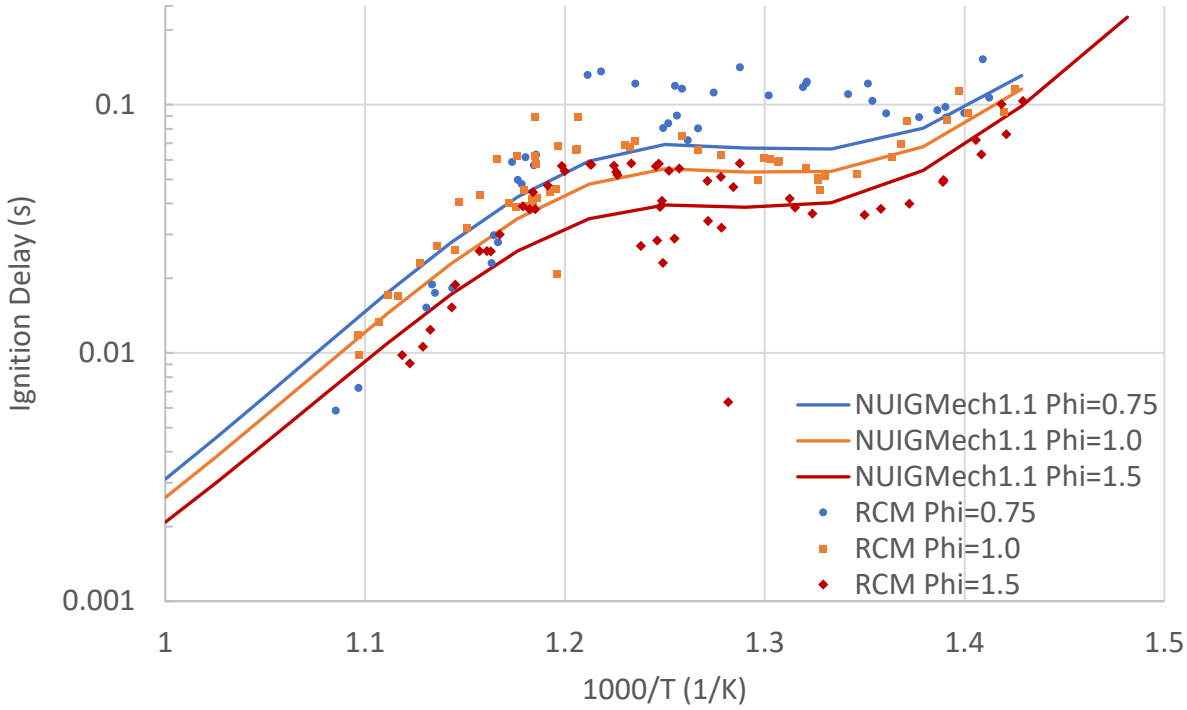


**Figure 2**. Experimental RCM ignition delay period measurements (symbols) and simulated fixed volume homogeneous autoignition delay period (lines) of $C_3H_8/O_2$/inert at 24 bar pressure using NUIGMech1.1 chemical kinetic mechanism.

*3.2 Performance of Detailed Chemical Kinetic Mechanisms*

Performance of the detailed chemical kinetic mechanisms listed in Table 1 was evaluated by comparing predicted ignition delay periods from constant volume, stoichiometric, 30 bar closed reactor simulations over a range of initial temperatures from 500-1000 K using Chemkin. The results of the simulations are shown in Fig. 3. The simulations were compared against the RCM experimental data above, as well as prior data from Ramalingam et al. [10]. All of the mechanisms showed reasonable agreement with the experimental data at temperatures above 900 K. The USC Mech Version II mechanism [8] and C1-C3 + $NO_x$ mechanism [9] did not predict any low temperature reactivity behavior at lower temperatures and were therefore immediately eliminated as candidates for mechanism reduction. The San Diego Mechanism [7] captured the NTC effect but appeared to be overly reactive at lower temperatures. NUIGMech1.1 [6] and AramcoMech 3.0 [5] behaved similarly with the former being slightly less reactive over the entire temperature range. Since the NUIGMech1.1 mechanism contains recent updates to various sub-mechanisms and also contains detailed $NO_x$ chemistry, it was decided to proceed with NUIGMech1.1 for mechanism reduction.

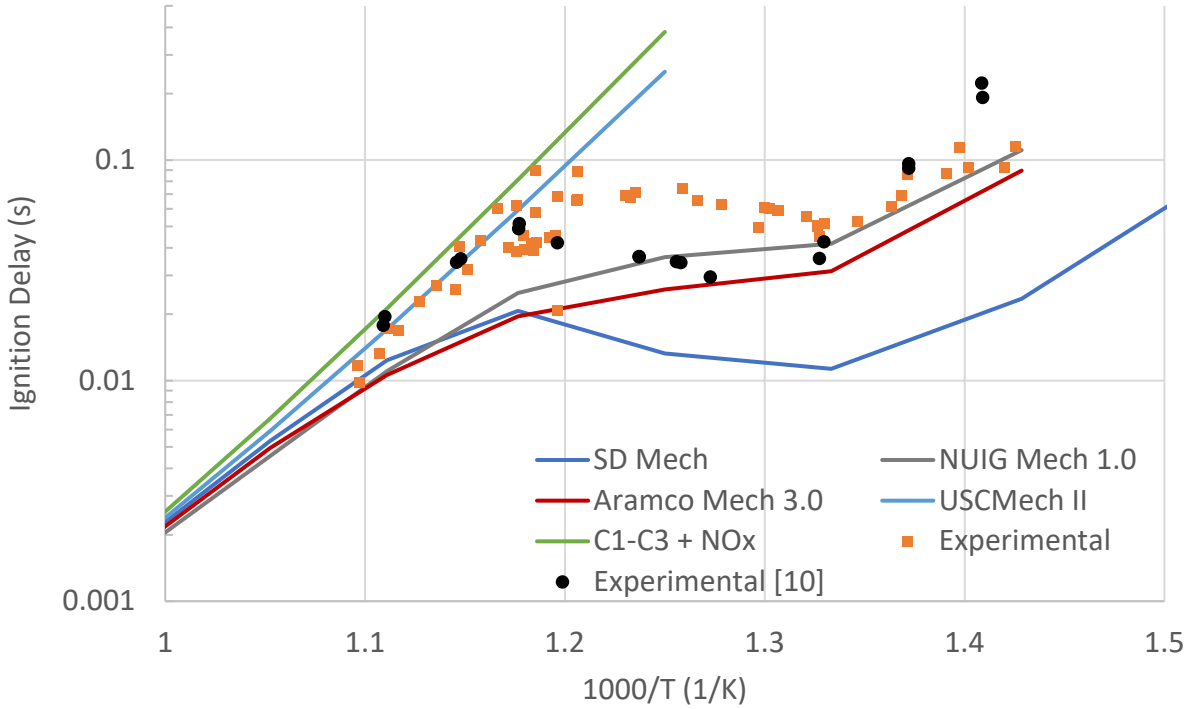


**Figure 3**. Fixed volume homogeneous autoignition of stoichiometric propane/air at 30 bar pressure as predicted by five chemical kinetic mechanisms (solid lines) in comparison with experimental RCM results from Ramalingam et al. [10] (black circles) and this work (orange squares).

*3.3 Chemical Kinetic Mechanism Reduction*

Mechanism reduction was performed in Chemkin Reaction Workbench initially using the directed relation graph with error propagation (DRGEP) method [11] with the autoignition results from stoichiometric propane combustion using NUIGMech1.1 as the target. The reduced mechanisms produced by this method became too inaccurate as the species count neared 100. In addition, both isobutane and n-butane were removed since they were not explicitly identified in the target model. Accordingly, more computationally intensive methods were used to improve the reduction results. A reduction operation sequence of DRGEP, DRG, DRG with path flux analysis (DRGPFA), followed by the same three methods with added sensitivity analysis was used to achieve much greater accuracy in the reduced mechanisms [11]. To ensure that the reduced mechanism contained all of the needed reactions to predict ignition delay for the possible species present in LPG, autoignition of a fuel blend containing 60% propane, 10% ethane, 10% propene, 10% isobutane, and 10% n-butane was used as the target model. The details of the reduced mechanisms are listed in Table 2.

**Table 2.** Mechanism reduction schemes and reduction results for NUIGMech1.1 mechanism.

| Reduction Method | Fuel | Tolerance | Species | Reactions |
|---|---|---|---|---|
| DRGEP | Propane | 5% | 192 | 1,367 |
| DRGEP | Propane | 10% | 143 | 1,036 |
| DRGEP | Propane | 15% | 114 | 810 |
| DRGEP, DRG, DRGPFA, sensitivity | Blend | 1% | 219 | 1,761 |
| DRGEP, DRG, DRGPFA, sensitivity | Blend | 5% | 128 | 965 |
| DRGEP, DRG, DRGPFA, sensitivity | Blend | 10% | 102 | 717 |

As shown in Fig. 4, for stoichiometric blend of 60% $C_3H_8$/10%$C_2H_6$/10%$C_3H_6$/10% i-$C_4H_{10}$/ 10%n-$C_4H_{10}$ with air, the 128 species reduction of NUIGMech1.1 predicts ignition delay periods to within 1 ms of the full mechanism at all but the lowest temperature point. While the 219 species mechanism has the best relative accuracy to NUIGMech1.1, it is too large to be computationally efficient in 3-D simulations. Although not shown in Fig. 4, ignition delay periods using the 128 species reduction of NUIGMech1.1 for constant volume, $C_3H_8$/air at 24 bar with varying equivalence match the values given by the full mechanism as well.

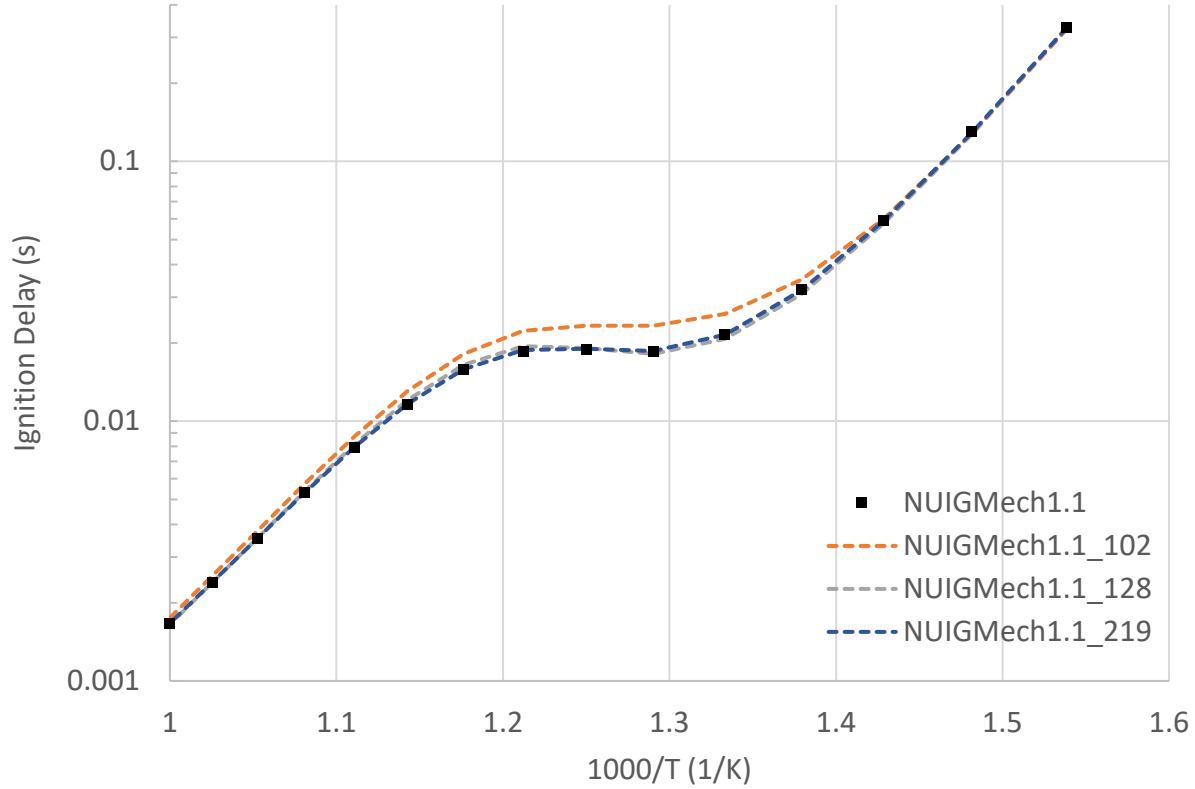


**Figure 4**. Predicted constant volume homogeneous autoignition of stoichiometric blend of 60% $C_3H_8$/10% $C_2H_6$/10%$C_3H_6$/10% i-$C_4H_{10}$/10%n-$C_4H_{10}$ with air at 30 bar pressure from full NUIGMech1.1 mechanism in comparison with 102, 128 and 219-species reduced mechanisms.

As a further test of the performance of the 128-species reduction of NIUGMech1.1, simulations were also performed with the reduced and full mechanisms to compare the predicted ignition delay periods of binary mixtures of 80% propane with 20% ethane, 20% propene, 20% isobutane, and 20% n-butane, respectively, with air at 24 bar pressure. As shown in Fig. 5, the ignition delay

results from the reduced mechanism compare very well with the full detailed mechanism for 100% propane and the propane/ethane blend, but deviate slightly for the other blends. For example, at 725 K, the reduced mechanism results for the propane/n-butane, propane/isobutane, and propane/propene differ from the detailed mechanism by 1.98 ms (5.75%), 3.24 ms (7.47%), and 9.18 ms (12.68%), respectively. The performance of the detailed and reduced mechanisms will be tested further in future RCM experiments as part of this ongoing study, and further attempts at mechanism reduction will be conducted as necessary.

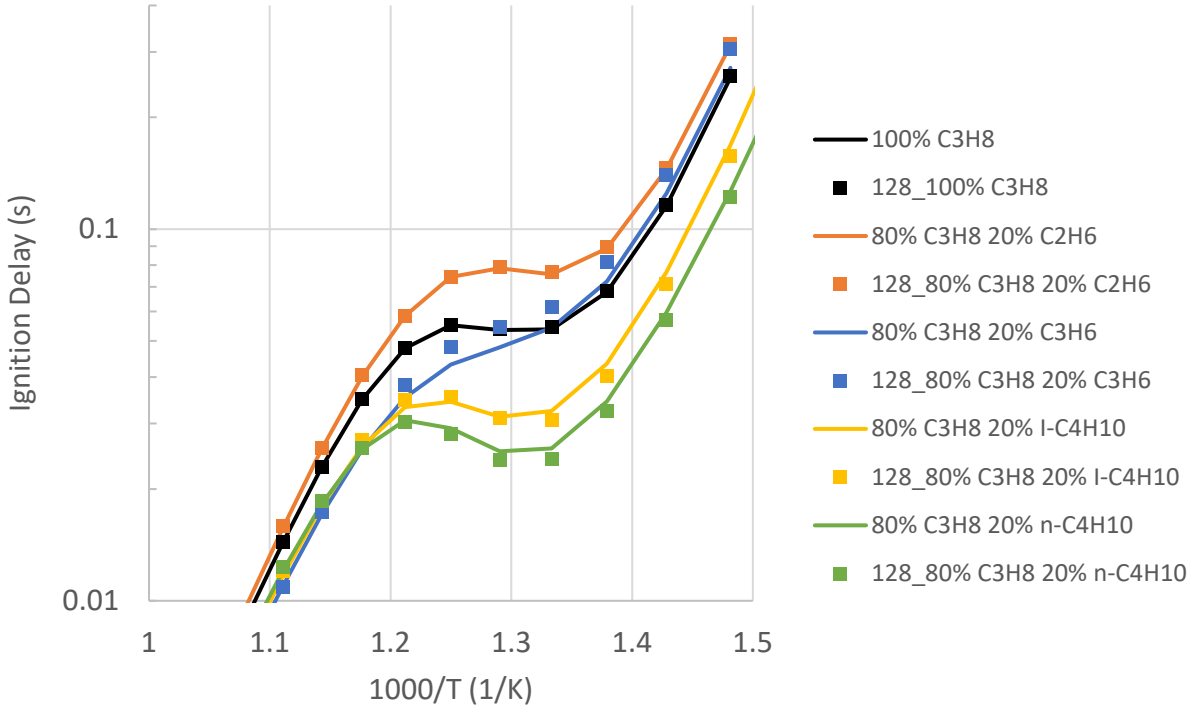


**Figure 5.** Fixed volume homogenous autoignition of stoichiometric, binary blends of 80% propane with 20% ethane, 20% propene, 20% isobutane, and 20% n-butane with air at 24 bar using the full NUIGMech1.1 mechanism (solid lines) [5] and a 128-species reduction of NUIGMech1.1 (symbols) [this work].

The effects of increasing EGR substitution rate on homogeneous ignition delay period using both a non-reactive EGR (NR-EGR) (79% $N_2$, 21% $CO_2$), and a reactive EGR (R-EGR) (78.65% $N_2$, 20.65% $CO_2$, 0.35% NO, 0.35% CO) were also analyzed using the full NUIGMech1.1 for comparison to future experiments. Figure 6 contains a plot of computed ignition delay period for stoichiometric $C_3H_8/O_2$/inert for 0% EGR, 30% R-EGR and 30% NR-EGR substitution by mass.

These EGR blend compositions were used by Mohr et al. in a similar study on the effect of natural gas composition and EGR levels on knock propensity of natural gas [4]. The EGR composition used in future RCM experiments and associated simulations will be derived from exhaust gas data from an LPG engine. As expected, the addition of the NR-EGR suppresses autoignition across the range of temperatures due to the decrease in concentration of the fuel and oxidizer. However, the presence of NO in the R-EGR results in increased ignition delay period at low temperatures but decreased ignition delay at temperatures higher than approximately 835 K. The ignition delay behavior of the EGR mixtures at high temperatures is consistent with the results of Mohr, et al. [4], in which the ignition delay of natural gas with R-EGR at 1000 K was shorter than the natural gas without any EGR, and significantly shorter than natural gas with NR-EGR.

At lower temperatures, however, the results deviate from Mohr, et al. because of the competition between the branching reaction pathways such as $C_3H_7O_2 \rightarrow C_3H_6OOH \rightarrow C_3H_6O+OH$ that enhance reactivity at low temperatures and reactions such as $NO+C_3H_7O_2 \rightarrow C_3H_7O+NO_2$ that suppress reactivity at low temperatures.

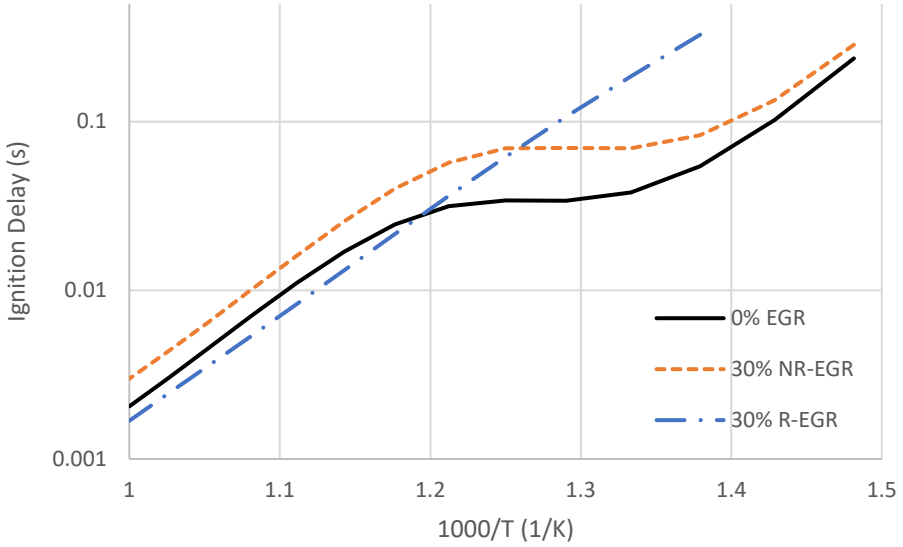


**Figure 6.** Fixed volume homogeneous autoignition of propane/$O_2$/inert at 30 bar with 0% EGR, 30% R-EGR and 30% NR-EGR substitution by mass as predicted by the NUIGMech1.1 mechanism.

## 4. Conclusions

The results of this study are just the first steps toward creating a robust, reduced chemical kinetic mechanism that can accurately model ignition delay periods and flame speed for the combustion of LPG under a variety of engine like conditions. Such a mechanism will be an important step toward accurately modeling 3-D or in-engine LPG combustion to develop higher efficiency LPG engines. NUIGMech1.1 has been shown to accurately predict propane ignition times across a range of temperatures and equivalence, with the 128 species reduced mechanism serving as a good balance between mechanism size and accuracy. Further experiments and mechanism validation include varying EGR substitution rate, testing binary fuel mixtures that are more representative of LPG composition, and conducting flame speed measurements using the laser spark ignition mode of the RCM.

## 5. Acknowledgements

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