

Development of a Chemical Kinetic Model for LPG Combustion Under Engine-like Conditions



WALTER SCOTT, JR.
COLLEGE OF ENGINEERING
COLORADO STATE UNIVERSITY

Colin Slunecka

Engines and Energy Conversion Lab
Colorado State University, Fort Collins, CO

Faculty Advisor: Dr. Anthony Marchese



U.S. DEPARTMENT OF
ENERGY | Energy Efficiency &
Renewable Energy

Abstract

The goal of the Advanced Liquid Propane Injection Engine (ALPINE) project is to increase the peak torque efficiency of a 15 liter liquefied petroleum gas (LPG) engine to 44%. LPG has many properties that make it an attractive alternative fuel such as lower cost than conventional fuel and an established distribution infrastructure. The development of high efficiency, spark ignited LPG engines is currently limited by engine knock and misfire. 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. Several detailed chemical kinetic mechanisms were evaluated to determine their suitability at predicting ignition delay periods. Multiple reduced mechanisms were created from the NUIGMech1.1 mechanism to determine the optimal balance between accuracy and computation efficiency for future three-dimensional combustion simulations.

Liquefied Petroleum Gas

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. To meet the HD-5 standard the LPG 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). 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/isobutane as high as 7%.

ASTM D1835-20, Standard Specification for Liquefied Petroleum (LP) Gases, ASTM International, West Conshohocken, PA, 2020, www.astm.org
Gomez, J.E., Walker, B., 2019, "National Propane Survey 2017-2018", Docket No. 21257, Southwest Research Institute, San Antonio, TX

Cummins X15 Diesel Engine

The Cummins heavy duty engine platform achieves a brake thermal efficiency (BTE) of 44% at peak torque. The X15 at CSU has been modified to operate on a single cylinder for experimentation purposes. Cummins has recently developed a 6.7 L LPG engine with a 41% BTE and 12% lower CO₂ emissions compared to a diesel engine of the same displacement.

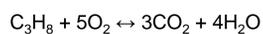


X15 Specifications

6 inline cylinders
2.5 L per cylinder
Bore: 137 mm
Stroke: 169 mm

Chemical Kinetic Mechanism

A chemical kinetic mechanism consists of chemical species, elementary reactions with rate constants, thermodynamic properties, and mass transport properties used to simulate a global chemical reaction such as:



While this reaction appears simple, it involves dozens of intermediate species and hundreds of elementary reactions. A differential equation solver such as Chemkin-Pro uses the mechanism and initial conditions that a user provides to model the reaction over time. The reaction coefficients contained in a chemical kinetic mechanism are displayed in a format like:

```
C3H8+O=>NC3H7+OH +3.71000000E+006 +2.40000000E+000 +5.50500000E+003
C3H8+OH=>NC3H7+H2O +6.86508000E+006 +2.00000000E+000 +6.77308690E+002
C3H8+OH=>C3H7+H2O +3.73838198E+005 +2.30514000E+000 -5.61322330E+002
C3H8+HO2=>NC3H7+H2O2 +2.08000000E+001 +3.59000000E+000 +1.56000000E+004
C3H8+HO2=>C3H7+H2O2 +6.32000000E+001 +3.37000000E+000 +1.37200000E+004
C3H8+CH3=>C3H7+CH4 +1.51000000E+000 +3.46000000E+000 +5.48000000E+003
C3H8+CH3=>NC3H7+CH4 +3.45000000E+001 +3.44000000E+000 +1.04000000E+004
C3H8+C2H3=>NC3H7+C2H4 +8.40000000E+002 +3.05000000E+000 +6.00000000E+003
C3H8+C2H5=>NC3H7+C2H6 +3.13200000E-001 +3.76000000E+000 +9.58580000E+003
```

where the first column contains the pre-exponential factor A, the second column is the temperature factor b, and the third is the activation energy Ea. These values are used to solve the temperature dependent reaction rate constant k using the Arrhenius form:

$$k(T) = AT^b \exp(-E_a/RT)$$

The reaction rate determines how quickly and in which direction a reaction will proceed. As a general rule the more species and reactions present in a mechanism means that it can more accurately model a combustion event. However, this greatly increases computation time if the mechanism is used in three-dimensional engine simulations. To increase computational efficiency, a reduced mechanism which contains only the most important species and reactions is used.

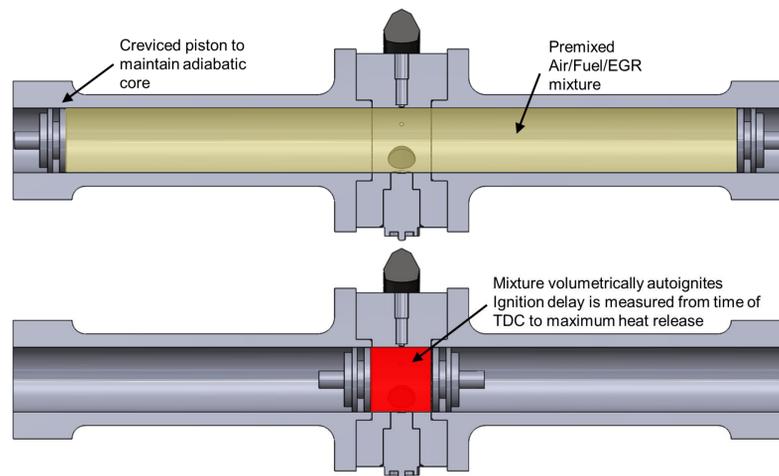
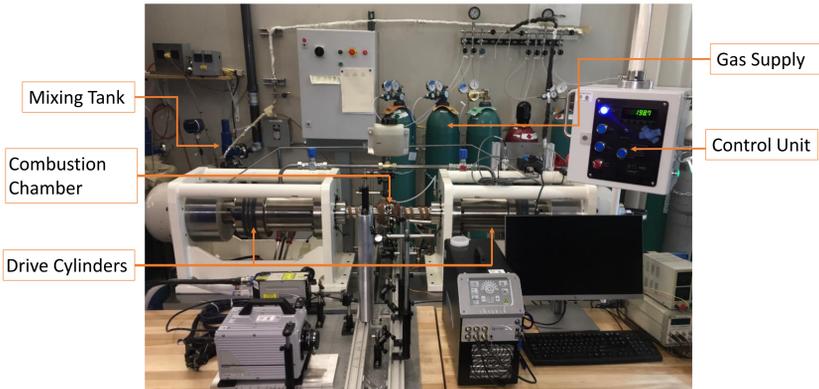
Detailed Mechanisms

The following chemical kinetic mechanisms were used in Chemkin simulations to determine which could most accurately predict the ignition delay for propane.

Mechanism	Species	Reactions
AramcoMech3.0	581	3,034
NUIGMech1.1	2,746	11,279
San Diego Mech	58	268
USC Mech Version II	111	784
C1-C3 + NOx	159	2,459

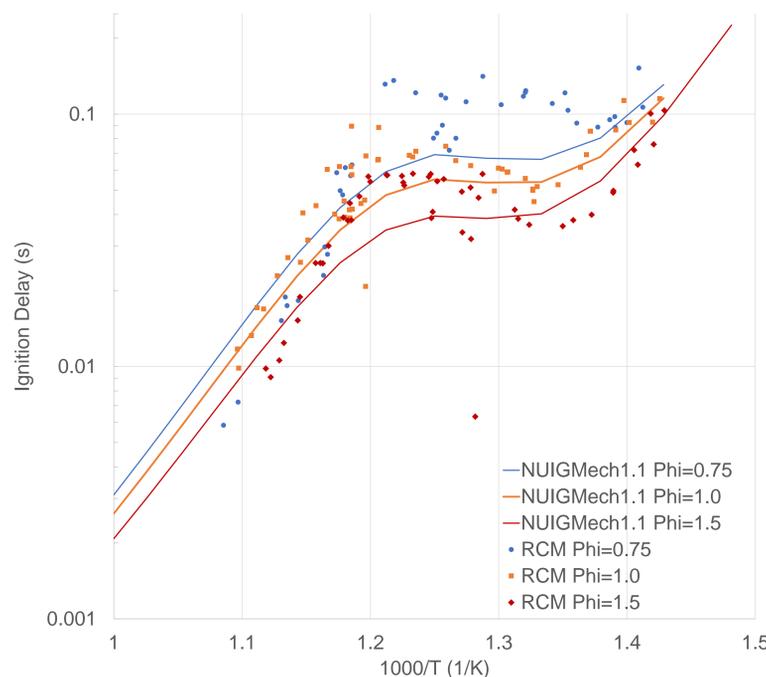
Rapid Compression Machine

The RCM at CSU 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 is approximately 8.5 ms with a TDC volume of 30.0 cm³. A high-speed pressure transducer records combustion chamber pressure from the start of compression until after ignition and the ignition delay period is the time between the maximum compressed pressure at TDC and the maximum pressure rise rate during combustion.



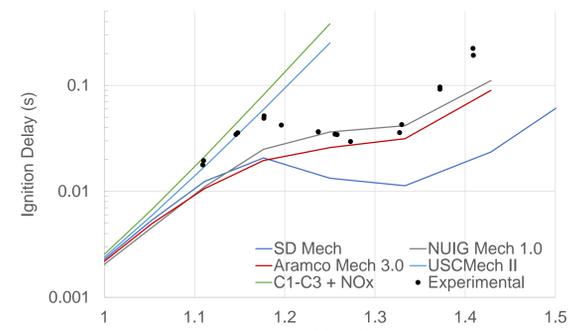
Experimental Results

The ignition delay period experiments were performed at lean, stoichiometric, and rich conditions ($\Phi = 0.75, 1.0, \text{ and } 1.5$) for C_3H_8/O_2 /inert mixtures over a temperature range of 700 to 921 K. The compressed pressure at TDC for all experiments was 23.92 ± 0.96 bar. Ignition delay results are typically plotted as a function of $1000/T$. The experimental results are compared to the zero-dimensional fixed volume combustion of C_3H_8 in air using the full NUIGMech1.1 chemical kinetic mechanism. Negative temperature coefficient (NTC) behavior was observed for all mixtures. The lean mixtures generally had the longest ignition delay while the rich mixtures had the shortest ignition delay. The difference between the constant volume simulations and experimental results is due to the simulation using ideal conditions such as fixed initial pressure, no heat loss, and an equal distribution of temperature throughout the mixture. Improved simulations that use transient volume to replicate the facility effects of the RCM should better match the experimental data.

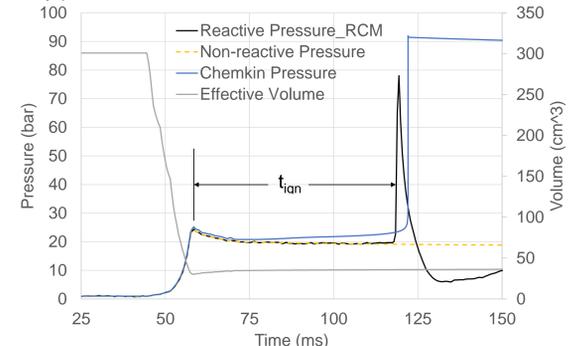


Computational Results

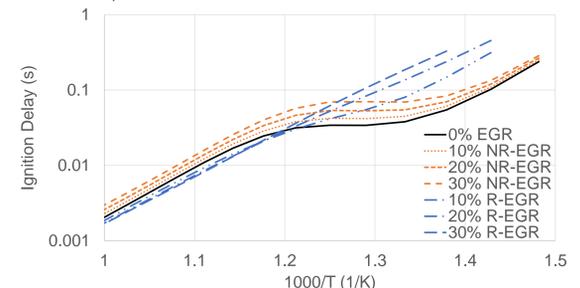
The detailed chemical kinetic mechanisms were modeled in Chemkin using a fixed volume of 30.0 cm³, initial pressure of 30 bar, and varying temperature from 500-1000 K and compared to published stoichiometric propane combustion data to determine which mechanism matched the ignition delay behavior the best. NUIGMech1.1 was the most accurate to experimental results. Ramalingam, A., Fenard, Y., Heufer, A., 2020, "Ignition Delay Time and Species Measurement in a Rapid Compression Machine: A Case Study on High-Pressure Oxidation of Propane", Combustion and Flame, Volume 211, Pages 392-405.



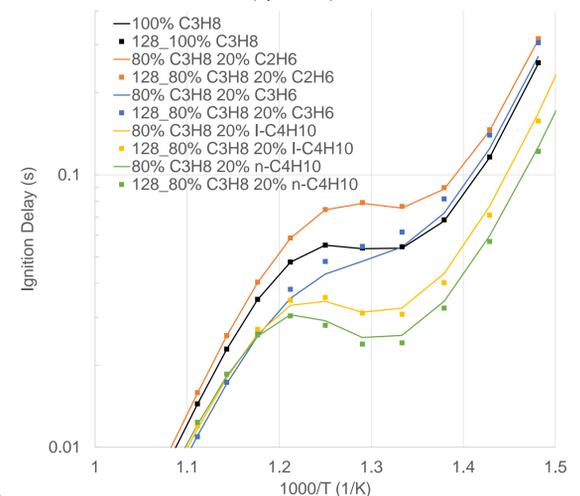
An effective volume profile was used to perform transient ignition delay simulations in Chemkin using NUIGMech1.1. By expanding the volume after piston TDC the heat and pressure loss could be replicated and provide a more accurate ignition delay period.



Ignition delay periods of stoichiometric propane/air at 30 bar pressure using varying mass substitution rates of non-reactive EGR (79% N₂, 21% CO₂) or reactive EGR (additional 3500 ppm NO and CO).

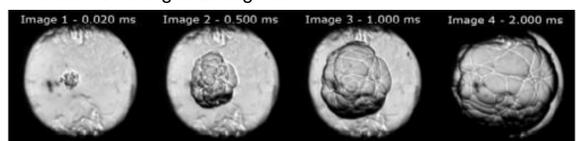


Fixed volume homogeneous autoignition of stoichiometric, binary blends of 80% propane with 20% ethane, 20% propene, 20% isobutane, and 20% n-butane with air at 24 bar using the full NUIGMech1.1 mechanism (solid lines) and a 128-species reduction of NUIGMech1.1 (symbols).



Future Work

- Perform compression ignition RCM experiments using propane with varying EGR levels and binary fuel mixtures of 80% propane/20% ethane, propene, n-butane, or isobutane.
- Further transient volume Chemkin simulations to better represent RCM conditions.
- Refine mechanism reduction if current mechanisms do not predict ignition delay or flame speed of future experiments.
- Laser spark ignited RCM experiments using similar conditions from ignition delay experiments to measure flame speed and fraction of end gas autoignition



This project was supported by a grant from the U.S. Department of Energy (DE-EE0009198). The author acknowledges the support of CSU professors Daniel Olsen (PI) and Bret Windom (co-PI), support from Andrew Zdanowicz, Siddhesh Bhoite, and Sam Vaughan on the RCM experiments, and discussions with collaborators at Cummins and Argonne National Lab.