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SHOCK-TUBE INVESTIGATION OF IGNITION DELAY TIMES OF BLENDS OF
METHANE AND ETHANE WITH OXYGEN

by

BRIAN CHRISTOPHER WALKER
B.S. University of Tennessee, 2000

A thesis submitted in partial fulfillment of the requirements
for the degree of Master of Science in Aerospace Engineering
in the Department of Mechanical, Materials, and Aerospace Engineering
in the College of Engineering and Computer Science
at the University of Central Florida
Orlando, Florida

Fall Term
2007

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ABSTRACT

The combustion behavior of methane and ethane is important to the study of natural gas and other alternative fuels that are comprised primarily of these two basic hydrocarbons.

Understanding the transition from methane-dominated ignition kinetics to ethane-dominated kinetics for increasing levels of ethane is also of fundamental interest toward the understanding of hydrocarbon chemical kinetics. Much research has been conducted on the two fuels individually, but experimental data of the combustion of blends of methane and ethane is limited to ratios that recreate typical natural gas compositions (up to ~20% ethane molar concentration). The goal of this study was to provide a comprehensive data set of ignition delay times of the combustion of blends of methane and ethane at near atmospheric pressure.

A group of ten diluted $\text{CH}_4/\text{C}_2\text{H}_6/\text{O}_2/\text{Ar}$ mixtures of varying concentrations, fuel blend ratios, and equivalence ratios (0.5 and 1.0) were studied over the temperature range 1223 to 2248 K and over the pressure range 0.65 to 1.42 atm using a new shock tube at the University of Central Florida Gas Dynamics Laboratory. Mixtures were diluted with either 75 or 98% argon by volume. The fuel blend ratio was varied between 100% CH_4 and 100% C_2H_6 . Reaction progress was monitored by observing chemiluminescence emission from CH^* at 431 nm and the pressure. Experimental data were compared against three detailed chemical kinetics mechanisms. Model predictions of CH^* emission profiles and derived ignition delay times were plotted against the experimental data. The models agree well with the experimental data for mixtures with low levels of ethane, up to 25% molar concentration, but show increasing error as the relative ethane

fuel concentration increases. The predictions of the separate models also diverge from each other with increasing relative ethane fuel concentration. Therefore, the data set obtained from the present work provides valuable information for the future improvement of chemical kinetics models for ethane combustion.

ACKNOWLEDGMENTS

The author wishes to thank Dr. Eric L. Petersen for advising him on this project and fellow shock tube researchers Chris Zinner, Brandon Rotavera, and Christopher (C.J.) Aul for their assistance in completing the shock-tube experiments. This thesis would not have been completed on time without their contributions.

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CHAPTER 1: INTRODUCTION

The chemical reaction kinetics of methane and ethane combustion are of high interest to many fields, including power generation gas turbine engines, high-speed propulsion, transportation, and materials synthesis. Although both fuels have been studied extensively on their own, there is limited experimental data and knowledge on the behavior of the two fuels in blended mixtures at percentages greater than what normally occurs in natural gas (<10% C₂H₆). Of particular interest is the effect of ethane on the ignition chemistry of methane and how it is affected with increasing relative amounts of ethane.

It is well known that the addition of higher hydrocarbons to methane drastically reduces ignition delay time and may affect autoignition, combustion chemistry, emissions, and flame stability. All of these issues affect engine performance and efficiency and thus are of concern to engine designers and operators. For example, there is an inherent design compromise between mixing length and ignition delay time. It is desirable to have sufficient mixing length to allow the fuel and oxidizer to thoroughly mix before entering the combustor in gas turbines employing lean, pre-mixed combustion. However, if the fuel has a short ignition delay time, it could autoignite prior to entering the combustor, which could lead to over-pressurization and structural damage to the engine components. Strict emission standards are stricter which require proper engine design for sufficient mixing to keep pollutant levels low.

Understanding the combustion and ignition characteristics of methane and ethane blends is especially important, as they are the two main components of natural gas, which is in widespread use by many industries. The components of natural gas vary widely, based on geography and production season, but typically consist of 82-96% methane and 1-16% ethane and can include small amounts of higher hydrocarbons (C_2 to C_5), carbon monoxide, and hydrogen. Natural gas is a desirable fuel as it is readily available, has a low cost, and burns cleanly with low emission levels. It is attractive to high-speed propulsion applications due to a high heat of combustion and a high heat-sink capacity. (Spadaccini and Colket; de Vries and Petersen; Lamoureux and Paillard; and Petersen et al. (2007)).

Fuel availability has tightened so a wider variety of fuel blends are being considered in both automotive (internal combustion) and gas turbine engines. Most of these alternative fuels are methane/ethane based while some, such as biomass and raw natural gas, have low methane concentrations (20-30% by volume).

Due to the increasing use of methane/ethane-based fuel blends, it is important to know the autoignition characteristics of these fuels and to develop a capability to adequately describe the chemical kinetics of their combustion. Many experimental studies have been carried out on natural gas and simulated natural gas blends, which has led to a basic level of understanding of their chemical kinetics (Petersen et al. (2007); Lamoureux and Paillard; de Vries and Petersen; Spadaccini and Colket; Goy et al.; Zellner et al.; Crossley et al.; Huang and Bushe; and El Bakali et al.). However, most of these experiments have studied blends containing low amounts of

ethane, in line with the amount found in natural gas. Knowledge is limited on the combustion of blends with high amounts of ethane. It is known that the ignition delay time of methane/ethane blends will decrease with increasing amounts of ethane, but trends show that the effect is reduced with increasing amounts of ethane – i.e. the effect is most significant with low levels of ethane. With increasing concentration of ethane, the ignition delay time of the fuel blend should approach that of pure ethane but how quickly it approaches that limit is unclear. Only with further testing will the overall ignition trends be revealed.

Insight into the combustion of methane and ethane is also beneficial because the combustion of higher hydrocarbons leads to C_2 and C species. More-detailed knowledge of the combustion of methane and ethane blends will lead to further refinement of chemical kinetic models for the combustion of higher alkanes. A comprehensive study of methane/ethane fuel blends with ignition times and species concentration time histories will clarify combustion kinetics and provide benchmark data for kinetics mechanisms to incorporate. Of most importance to verifying current chemical kinetic mechanisms and their ability to simulate combustion of methane and ethane is performing ignition tests of experimental mixtures. This provides valuable information in the form of ignition delay times and species concentration time histories that are directly comparable to model calculated predictions. This, therefore, is the primary focus of this study.

The present study concentrates on the high-temperature combustion of several mixtures of methane and ethane diluted in argon. A background section reviews literature on the pyrolysis

and oxidation of methane, ethane, and natural gas. Experimental results from a series of shock tube experiments on blends of methane and ethane taken as part of the present study are described, including ignition delay times and species concentration time histories, along with a summary of the experimental facilities and techniques. An ignition delay time correlation for mixtures of methane and ethane is presented, and the experimental results are compared to analytical predictions from two chemical kinetic models. The best kinetics model is then used to elucidate trends for mixtures and conditions not specifically tested.

CHAPTER 2: LITERATURE REVIEW

2.1 Methane Experimental Studies

A wealth of information is available on methane oxidation and ignition as it is the most exhaustively researched hydrocarbon and is probably the most studied fuel after hydrogen. Methane combustion has been studied extensively using several experimental techniques, including laminar and premixed flames, flow reactors, perfectly stirred reactors, plug flow reactors, piston-cylinder compression, and constant-volume pressure vessels. Shock-tube studies of methane are numerous and have covered a wide range of test conditions, including pressures ranging from sub-atmospheric to several hundred atmospheres.

A comprehensive review of all shock-tube studies of methane pyrolysis and combustion is beyond the scope of this review but can be found elsewhere (Petersen, 1998 and Spadaccini and Colket, 1994). A thorough literature review of the subject is offered below.

Skinner and Ruehrwein (1957) studied methane oxidation and pyrolysis behind reflected shock waves over the temperature range 1200 - 1800 K and pressure range 3-10 atm. Oxidation mixtures were fuel rich and at various levels of dilution in argon (including one non-dilute mixture). Gas samples were taken after shock passage for measurement of concentration levels of CH₄, H₂, C₂H₆, C₂H₄, C₂H₂, CO, and CO₂. Pyrolysis experiments were conducted with 12%

and 1% methane in argon at 5 atm. Concentrations of C₂H₆, C₂H₄, C₂H₂, and H₂ were measured at several temperatures, and the pyrolysis rate constant was measured versus temperature.

Induction times for various mixtures were determined in the form $\log t = A + B/T$.

Seery and Bowman (1970) studied methane oxidation behind reflected shock waves over the temperature range 1350 – 1900 K and pressure range 1.5 – 4.0 atm. Mixtures consisted of methane-oxygen diluted in argon (53 – 78%). Time resolved measurements were made of emission by OH, CH, C₂ and CO and absorption by OH. They developed an empirical correlation for the ignition delay time:

$$t_{\text{ign}} * [\text{O}_2]^{1.6} [\text{CH}_4]^{-0.4} = 7.65 \times 10^{-18} \exp(E/RT), E=51.4 \text{ kcal/mol}$$

The correlation is valid over the temperature range 1150 to 1880 K, the pressure range 1.5 to 10 atm, and ϕ from 0.2 to 8.0.

They also performed an analytical study of methane oxidation using a 13-step chemical kinetic mechanism. Ignition delay times obtained experimentally were compared with predictions of the empirical correlation and the model. Model predictions improved considerably with addition of a reaction step for combustion of formaldehyde/acetaldehyde from McKellar and Norrish (1960).

Lifshitz et al. (1971) studied argon-diluted methane-oxygen mixtures behind reflected shock waves over the temperature range 1500 - 2150 K and pressure range 2 - 10 atm. Mixture equivalence ratio varied from 0.5 to 2.0. The effect of hydrogen and propane additives (2 – 15% of total fuel content) on ignition delay time was also studied. This was among the first attempts

to specifically determine composition dependencies of ignition delay times experimentally.

Most mixtures were stoichiometric. Oddly, the authors claim their findings show that additives have no effect on methane combustion chemistry and that acceleration effects are purely thermal in nature. The following ignition delay time correlation was proposed:

$$t_{\text{ign}} = 3.62 \times 10^{-14} \exp(46.5 \times 10^3 / RT) [\text{Ar}]^0 [\text{CH}_4]^{0.33} [\text{O}_2]^{-1.03} \text{ sec}$$

The correlation is valid over the temperature range 1587 – 2025 K, the pressure range 2.55 – 13.01 atm, and ϕ range 0.5 – 2.0.

In a follow-on study, Skinner et al. (1972) compared the ignition delay correlation and experimental data from Lifshitz et al. (1971) with results from Skinner and Ruehrwein (1959), Higgin and Williams (1969), Seery and Bowman (1970), and Bowman (1970). Mixtures of methane-oxygen-argon (3.5% CH₄, 7% O₂) and methane-hydrogen-oxygen-argon (3.5% CH₄, 7% O₂, 0.5% H₂) were studied behind shock waves. Product distributions were determined by analysis of post-shock heated gas samples that were quenched after ~700 microseconds. Skinner et al. (1972) also presented a 23-step reaction mechanism for methane oxidation. Calculated data for ignition delay times and product distributions were compared with the experimental data of Lifshitz et al. (1971) and Skinner & Ruehrwein (1959).

Olson and Gardiner (1978) studied methane ignition behind reflected shock waves over the temperature range 1800 - 2700 K. Mixtures were a 9/1/90 ratio of methane/oxygen/argon. Methane concentrations were measured by laser absorption. What is essentially oxygen-initiated pyrolysis of methane was modeled by a 63-step reaction mechanism developed previously by the

authors (Olson and Gardiner, 1977), slightly revised in this paper for CH₂ and C₂H₂ chemistry. Model predictions were compared with experimental results of this study.

Oxidation behind reflected shock waves of methane-oxygen mixtures diluted in argon was studied over the temperature range 1600 - 2100 K and pressure range 1-6 atm by Krishnan and Ravikumar (1981). Equivalence ratios ranged from 0.2 to 5.0. Ignition delay times were determined from pressure and visible light emission. They proposed the following ignition delay correlation:

$$t_{\text{ign}} = 2.21 \times 10^{-14} \exp(45000/RT) [\text{CH}_4]^{0.33} [\text{O}_2]^{-1.05} [\text{Ar}]^{0.0}$$

The correlation is valid over the temperature range 1600 – 2100 K, pressure range 1 – 6 atm, and ϕ range 0.2 – 5.0.

Calculated results were compared with experimental data from Seery and Bowman (1970), Burcat et al. (1971), Lifshitz et al. (1971), and Tsuboi and Wagner (1974).

Hidaka et al. (1999) studied methane pyrolysis and oxidation behind reflected shock waves over the temperature range 1350-2400 K and pressure range 1.6-4.4 atm. Product and reactant distributions were measured from quenched samples at various temperatures. Reaction progress was monitored by recording time-histories of IR laser absorption (CH₄) and emission (CO₂).

The authors also developed an enhanced 157-reaction, 48-species methane pyrolysis and oxidation mechanism based on previous work by the authors, which was updated with revised rate constants and new reaction steps for pyrolysis and oxidation of formaldehyde, ketene,

acetylene, ethylene, and ethane. Model predictions were compared against predictions of the GRI-Mech 1.2 mechanism, current and previous experimental results by the authors, and previous data from a number of authors, including Tsuboi and Wagner (1974), Roth and Just (1975 and 1984), Seery and Bowman (1970), Spadaccini and Colket (1994), Frank and Braun-Unkloff (1987), Bowman (1974), and Lifshitz et al. (1971).

More recently, the ignition delay of non-diluted methane-air mixtures behind reflected shock waves at high pressures was studied by Zhukov et al. (2003). Experiments covered the temperature range 1200-1700 K and pressure range 3 – 450 bar. Ignition delay times were determined from OH emission and CH₄ absorption. Experimental results were compared with predictions of the GRI-Mech 3.0 mechanism. A shift in activation energy of methane was seen with higher pressures – from 22,000 to 12,000 between pressures of 3-4 to 400-500 atm. GRI-Mech 3.0 predicts a decrease in activation energy from 21,000 to 17,000 when going from low pressure to high pressure. The change in activation energy is reasoned to be due to a shift in the primary formation channels for OH radicals through methane and hydrogen peroxides.

2.2 Ethane Experiment Studies

Ethane has been studied for nearly as long as methane, and like methane, research on ethane oxidation and ignition has been performed using numerous experimental methods. Shock-tube research on ethane is plentiful but not nearly as comprehensive as for methane. A

comprehensive review of shock-tube studies of ethane oxidation is given below. Additional research on ethane pyrolysis exists in the literature (Bradley and Frend (1971), Lee and Yeh (1979), Olson et al. (1979), and Hidaka et al. (1985)) but that research is not the focus of this study and thus is not covered thoroughly in this review.

Bowman (1970) performed an experimental and analytical investigation of methane and ethane oxidation behind incident and reflected shock waves. Mixtures included methane-oxygen, ethane-oxygen, and methane-ethane-oxygen (diluted in argon). The temperature range for methane experiments was 1750-2500 K, and pressures were 1.3 and 2.6 atm. The temperature range for ethane experiments was 1300-2000 K, and pressures were 2.0 and 4.4 atm. Reaction progress was monitored by recording infrared emission from CO₂, CO, and H₂O. Experimental data were expressed as reaction times correlated with initial fuel and oxygen concentrations and temperature. Two reaction mechanisms were developed, one each for methane and ethane. The models were adjusted by comparing experimental data with an analytical study of the combustion process. The 11-step methane model was based on a 13-step reaction model by Seery and Bowman (1970). The ethane model was new and only dealt with ethane decomposition – it was assumed that the ethane combustion process would follow the methane model afterwards. Reaction times were defined as the time to reach 90% of the equilibrium emission intensity.

Burcat et al. (1971) studied ignition delay times of methane through pentane with oxygen behind reflected shock waves. Mixtures were stoichiometric and diluted in argon (~80%). The

temperature and pressure range for methane experiments was 1476-1900 K and 11.22-15.13 atm. The temperature and pressure range for ethane experiments was 1204-1700 K and 8.44-12.4 atm. Plots of ignition delay time versus temperature show, curiously, that ethane had faster ignition times over the entire temperature range than all other fuels studied. Measured ignition delay times of the other fuels varied inversely, as expected, with the number of carbon atoms.

Cooke and Williams (1971) studied the ignition of ethane-oxygen and methane-oxygen mixtures (diluted in argon) behind incident shock waves. As above, shock arrival was detected by density change using the laser-schlieren method. Ignition onset was determined from OH emission and absorption. CO₂ emission was also measured. A chemical reaction model was used to compute species concentration profiles for lean and rich methane and stoichiometric ethane mixtures. Methane experimental conditions ranged from temperatures of 1700 to 2400 K, pressures of 200 to 300 torr, and equivalence ratios of 0.5 to 2. Ethane experiments were conducted over the temperature range 1400-1800 K, pressure range 200-300 torr, and equivalence ratio 0.5 to 2.

The different ignition characteristics of methane and ethane ignition are briefly discussed in their paper. They note that only ~10% of the initial ethane fuel remains at the point of ignition, whereas very little of the methane fuel has decomposed at the point of ignition. The sequence of events seems to be that ethane is converted to ethylene, via the ethyl radical, before ignition. After ignition begins, ethylene is converted, via the vinyl radical, to acetylene. Then acetylene decays which allows for hydroxyl concentration to reach its maximum value. So combustion is a two-stage process: decomposition of ethane to ethylene, which keeps the hydroxyl concentration

below the ignition threshold value, which is followed by ignition of ethylene and ethane?, the end product being carbon dioxide.

Burcat et al. (1972) studied ethane ignition behind reflected shock waves over the temperature range 1235-1660 K, pressure range 2-8 atm, and equivalence ratios of 0.5-2. Mixtures were diluted in ~95% argon. Ignition delay times were determined from pressure time histories. Concentration levels of CH₄, C₂H₂, C₂H₄, C₂H₆, and CO were measured from gas samples over a wide range of temperatures. The authors proposed the following experimentally derived ignition delay correlation:

$$t_{\text{ign}} = 2.35 \times 10^{-14} [\text{Ar}]^0 [\text{C}_2\text{H}_6]^{0.46} [\text{O}_2]^{-1.26} \exp(34200/\text{RT})$$

The correlation is valid over the temperature range 1235 – 1660 K, pressure range 2 – 8 atm, and ϕ range 0.5 – 2.0.

Species concentration measurements show that significant decomposition of ethane occurs before ignition and that CO produced before ignition is not consumed during combustion (as opposed to propane combustion).

Ignition of argon-diluted mixtures of methane-oxygen and ethane-oxygen were studied behind incident shock waves by Cooke and Williams (1975) over the temperature range 1400-2200 K, pressure range 150-350 torr, and equivalence range 0.5-2. Shock arrival was detected by the laser-schlieren method. Ultraviolet and infrared emission were used to measure concentrations of OH radicals, CO₂, and C-H bond containing species. Correlations for induction time of major

species were developed, as well as ignition delay time correlations for methane and ethane. The activation energy of methane was found to be 31-36 kcal/mol. They proposed that the true onset of ignition is marked by a sudden increase in CO₂ emission, a change in gradient of C-H emission, a density change, and the second rise in hydroxyl emission. The characteristics of the first rise in hydroxyl emission depend on the particular fuel.

Tsuboi (1978) studied methane oxidation and pyrolysis and ethane pyrolysis behind incident and reflected shock waves over the temperature range 1400 – 2400 K, primarily in an effort to determine the extinction rate of methyl radicals. The thermal decomposition of ethane was studied over the temperature range 1700 – 2000 K and density range 2x10⁻⁶ to 1.2x10⁻⁴ mol/cm³. Reaction progress was monitored by UV absorption.

Hidaka et al. (1981) studied the oxidation of ethane, ethylene, and acetylene behind reflected shock waves. Ethane was studied over the temperature range 1380 – 1900 K, the pressure range 250 – 440 torr, and at equivalence ratios 0.78, 1.0 and 2.0. The following ignition delay time correlation was developed:

$$\tau_{\text{ign}} = 1.15 \times 10^{-10} [\text{C}_2\text{H}_6] [\text{O}_2]^{-1} \exp[30,000/RT]$$

The correlation is valid over the experimental conditions given above.

Hidaka et al. (1982) performed an experimental and analytical study of the ignition of lean and near-stoichiometric hydrocarbon-oxygen mixtures behind incident shock waves. Test conditions ranged from temperatures of 1340 to 2320 K and pressures of 0.2 to 0.35 atm. Fuels studied

included methane, ethane, ethylene, and acetylene. Reaction progress was monitored using the laser-schlieren technique. Ignition delay time was defined as the time to onset of maximum negative deflection. A previously developed 95-step chemical reaction model was compared against experimental data of ignition delay time versus temperature. The model was also used to predict reaction rates at 1700 K, midway through the induction period. The model accuracy was shown to be rather poor.

Hidaka et al. (2000) studied ethane pyrolysis and oxidation behind reflected shock waves over the temperature range 950-1900 K and pressure range 1.2-4.0 atm. Mixtures were highly diluted with Argon (92-99%). Species time histories were measured by IR absorption (C_2H_6) and emission (CO_2). Product and reactant concentrations were measured from gas samples using the single-pulse method. Three reaction mechanisms were used to calculate species time histories: the GRI-Mech 1.2 mechanism, a mechanism by Dagaut et al. (1991a), and a new C_2H_6 pyrolysis and oxidation mechanism developed by the authors that incorporated new reaction steps and rate constants for pyrolysis and oxidation of formaldehyde, detene, methane, ethylene, and acetylene. Model predictions were compared with experimental data from this study and recent studies by other authors. Hydrogen radical profiles and concentrations were compared with data from Roth and Just (1979) and Chiang and Skinner (1981). Ignition delay times were compared with data from Hidaka et al. (1982), Takahashi et al. (1989), and Spadaccini and Colket (1994). Hydrogen and oxygen profiles were compared with those reported by Bhaskaran et al. (1980).

Ignition delay times for argon-diluted mixtures of methane, ethane, and propane with oxygen behind reflected shock waves were studied by Lamoureux et al. (2002). Ignition delay time was determined from measurements of OH radical emission and was defined as the time between reflected shock passage and when the emission signal reached 10% and 50% of its maximum value. A summary of previous ignition delay time correlations for oxidation of each fuel was presented. For methane-oxygen mixtures, the correlations included those of Lifshitz et al. (1971), Tsuboi and Wagner (1974), Hidaka et al. (1978), Eubank et al. (1981), Borisov et al. (1983), Cheng and Oppenheim (1984), and Krishnan and Ravikumar (1981). Previous correlations for ethane-oxygen ignition delay times included Burcat et al. (1972) and Hidaka et al. (1981).

The authors present their own correlations for ignition delay times for methane-oxygen and ethane-oxygen mixtures:

Methane mixtures:

$$t_{\text{ign}} = 2.73 \times 10^{-15} \exp(27250/T) [\text{CH}_4]^{0.36} [\text{O}_2]^{-1.04}$$

which is valid over the temperature range 1520 – 2000 K, pressure range 365 – 1820 kPa, and ϕ range 0.5 – 2.0.

Ethane mixtures:

$$t_{\text{ign}} = 2.46 \times 10^{-15} \exp(27800/T) [\text{C}_2\text{H}_6]^{0.64} [\text{O}_2]^{-1.05}$$

which is valid over the temperature range 1270 – 1520 K, pressure range 290 – 1420 kPa, and ϕ range 0.5 – 2.0.

The correlation and experimental results for stoichiometric methane-oxygen ignition delay times were compared with correlations from Tsuboi and Wagner (1974), Eubank et al. (1981), Borisov et al. (1983), and Krishnan and Ravikumar (1981). Comparisons were also with the experimental and calculated ignition delay times from Burcat et al. (1972).

Predicted ignition delay times from two kinetic mechanisms were compared against experimental data and the authors correlations. The mechanisms used were those by Tan et al. (1994): a 78-species, 450-reaction model validated against experimental data from a well-stirred reactor, burner flames, shock-tube data from Burcat et al. (1971a, 1972) and Lifshitz (1971), and the GRI-Mech 3.0 mechanism by Smith et al. (1999). Comparisons were made for lean, stoichiometric, and rich mixtures of methane, ethane, and propane with oxygen.

Ethane pyrolysis and oxidation at very high pressures (340 and 613 bar) and temperatures (1050-1450 K) was studied by Trantor et al. (2002) using a single-pulse shock-tube. Species concentrations were determined from gas samples taken before and after shock passage. Ignition delay times were not the focus of these experiments. Data of species concentrations were compared with predictions from three chemical reaction models: GRI-Mech 3.0, a large mechanism developed by Marinov et al. (1998) for modeling aromatic hydrocarbon formation in hydrocarbon flames, and a mechanism developed by Pope and Miller (2000) to model the formation of benzene in low-pressure premixed flames of aliphatic fuels.

In a follow-on to their previous research, Trantor et al. (2002a) studied high-pressure oxidation of ethane using a single-pulse shock-tube at a pressure of 40 bar over the temperature range 1000-1400 K. Again, ignition delay times were not determined. The GRI-Mech 3.0 and Pope and Miller mechanisms were compared with the experimental data. Modifications were made to some of the reaction rates of the Pope and Miller model to improve predictions for the highly fuel rich case.

Diluted mixtures of ethane-oxygen were studied behind reflected shock waves by de Vries et al. (2007) over the temperature range 1218-1860 K and pressure range 0.57-3.0 atm. Reaction progress was monitored by OH and CH emission. The authors documented quantitative OH time histories for the first time in an ethane shock-tube study by using emission from a H₂-O₂ mixture as a reference. Ignition delay time was defined as the intersection of a line corresponding to maximum slope and initial OH or CH radical concentration. They proposed the following correlation for ignition delay time:

$$t_{\text{ign}} = 2.42 \times 10^{-7} [\text{C}_2\text{H}_6]^{0.76} [\text{O}_2]^{-0.67} [\text{Ar}]^{-0.82} \exp(38.9/RT)$$

which is valid over the temperature range 1218 – 1860 K, pressure range 0.57 – 3.0, and ϕ range 0.5 – 2.0.

Ignition delay experimental data were compared against calculations from the correlation derived in this study and previous correlations of Burcat et al. (1972), Cooke and Williams (1975), Shim et al. (1999), and Lamoureux et al. (2002). Experimental data of ignition delay time and OH radical concentrations were compared against predictions of chemical kinetics models of Wang

and Laskin (1999), Petrova and Williams (2006), and an updated version of a former San Diego mechanism by Li and Williams (1999).

2.3 Natural Gas, Methane/Ethane Blend Experiments

A limited number of shock-tube studies have been conducted on blends of methane and ethane. Most of these have focused on the combustion of simulated natural gas mixtures that include very small relative amounts of ethane, typically less than 10% of the total fuel. The largest percentage of ethane studied experimentally was a 70/30 ratio of methane/ethane by Petersen et al. (2007). Some natural gas-focused studies have also included mixtures of methane/ethane with small amounts of propane, again in attempts to recreate actual natural gas compositions. A comprehensive review of shock-tube studies of the ignition of blends of methane and ethane follows.

Skinner and Ball (1960) studied ethane pyrolysis behind shock waves over the temperature range 1057-1418 K at a pressure of 5 atm. Mixtures studied included ethane with methane, ethylene, and hydrogen diluted in argon. Molar ratio of methane/ethane mixtures ranged from 22.4/1 to 1/1.

Burcat et al. (1971) studied ignition delay times of methane through pentane with oxygen behind reflected shock waves. Mixtures were stoichiometric and diluted in argon. Methane

experiments were conducted at temperatures of 1476 to 1900 K and pressures of 11.22 to 15.13 atm. Ethane experiments were conducted at temperatures of 1204 to 1700 K. Plots of ignition delay time versus temperature show that ethane had faster ignition times over the entire temperature range than all other fuels studied. Measured ignition delay times of the other fuels varied inversely with the number of carbon atoms, as expected.

Crossley et. al (1972) conducted a shock-tube study of the effects of higher alkanes on methane ignition behind reflected shock waves. Low concentrations of ethane, propane, butane, and pentane were added to stoichiometric methane-oxygen-argon mixtures. The amount of ethane added was 1.4 to 9.5 percent of the total fuel by volume. From analysis of post-combustion gas samples and kinetic modeling results (using a 23-reaction kinetic model developed previously by the authors for methane ignition), the authors conclude that the effect of additives on methane combustion is actually based on enhancement of the chemical kinetics and not on thermal effects as had been proposed earlier by Lifshitz et al. (even though data seemed to support the thermal theory).

Eubank et al. conducted an early shock-tube study of natural gas simulated mixtures in air (1981). Fuel ratios studied included 1% CH₄ with 0.2% C₂H₆, 0.2% C₂H₆ + 0.1% C₃H₈, and 0.2% C₂H₆ + 0.1% C₃H₈ + 0.1% n-C₄H₁₀ (remaining mixture was air). Ignition delay times were measured behind reflected shock waves by laser absorption at 3.39 μm over the temperature range 1200 – 1850 K, near pressures of 4 atm. Experimental results of the study were compared

with previous experimental ignition delay times from Tsuboi and Wagner (1974) and Lifshitz et al. (1971).

Zellner et al. (1983) studied ignition delay times of lean methane, methane/ethane, $\text{CH}_4/\text{C}_3\text{H}_8$, and $\text{CH}_4/i\text{-C}_4\text{H}_{10}$ in air behind reflected shock waves. Test conditions were ~ 1600 K, 3.3 atm, and an equivalence ratio of 0.2-5.0. Mixtures included methane/oxygen/argon and 1% methane/0.1% ethane in air. A reaction mechanism developed by Warnatz (1982) was used to calculate species history and ignition delay, earlier versions of which were based on studies of flame velocity and concentration profiles of laminar flames. Experimental ignition delay time was obtained from CH_4 absorption and was defined as the point when 10% of methane is consumed.

In an oft-cited, landmark study, Spadacinni and Colket (1994) present a comprehensive literature review of methane ignition and conduct shock-tube experiments of methane-based fuel blends. Ignition delay times were measured for methane; binary mixtures of methane with ethane, propane, or butane; and a natural gas fuel.

The authors summarize previous research on methane ignition, including both methane-air and methane-oxygen mixtures, performed with flow reactors and shock-tubes and simulated natural gas ignition using shock-tubes. Ignition delay times from several previous studies are compared against the correlation originally presented by Lifshitz and coworkers (Lifshitz et al. (1971) and Skinner et al. (1972)) that was improved upon by Krishnan and Ravikumar (1981).

Ignition delay times were measured using time histories of pressure and OH radical emission. Ignition of methane and methane-based binary mixtures was studied over the temperature range 1300-2000 K, the pressure range 3-15 atm, and equivalence ratios of 0.45-1.25. Ignition delay times were measured for nearly stoichiometric binary mixtures of methane with various amounts (1-10% by volume) of ethane, propane, and butane (iso- and normal-). The amount of ethane added to methane was 1, 3, 6, and 10% by volume.

The previous ignition delay time experimental data of Eubank et al. (1981), Zellner et al. (1981), and Crossley et al. (1972) were compared against the following ignition delay correlation:

$$t_{\text{ign}} = 1.32 \times 10^{-13} \exp(18772/T) [\text{O}_2]^{1.05} [\text{CH}_4]^{.61} [\text{C}_2\text{H}_6]^{-.24}$$

which is valid over the temperature range 1200 – 2000 K. Pressure range data was not available (reference paper was missing page that included raw data for methane-ethane experiments).

Ignition delay correlations were also developed for methane-propane and methane-butane mixtures.

Ignition delay times of a natural gas blend, designated Matheson commercial-grade methane, were studied over the temperature range 1200-1750 K, the pressure range 3.3-12.9 atm, and at equivalence ratios of 0.45 and 1.0. The natural gas experimental data were compared against the methane ignition delay empirical correlation from Krishnan and Ravikumr.

An all-encompassing ignition delay time correlation was developed for mixtures of methane and higher alkanes, which includes a single generic term for all non-methane hydrocarbon components, developed from the authors experimental data:

$$t_{\text{ign}} = 1.77 \times 10^{-14} \exp(18693/T) [\text{O}_2]^{1.05} [\text{CH}_4]^{.66} [\text{HC}]^{-.39}$$

which is valid over the temperature range 1207 – 1742 K and pressure range 3.29 – 12.85 atm.

Experimental data from the authors' study and the ignition delay time correlations for methane and ethane were compared against predictions of the reaction mechanism of Frenklach et al. (1992), with added reactions for propane and propene from Tsang (1988 and 1991).

Ignition delay times of various hydrocarbon-oxygen mixtures were studied behind reflected shock waves by Lamoureux and Paillard (2003) over the temperature range 1485 – 1900 K and pressure range 0.3 – 1.3 MPa. Mixtures studied included CH₄-C₂H₆, CH₄-C₂H₆-C₃H₈, and an Algerian natural gas mixture in O₂-Ar. Maximum ethane concentration was 0.2 mole %. Ultraviolet emission from OH radicals was measured to determine ignition delay time, which was defined as time to 10% of the maximum value. The infrared emission of C-H bonds at 3.3 μm was measured for the natural gas mixture.

Two mixtures of methane-ethane-propane in oxygen-argon were studied. One was formulated to reproduce the Algerian natural gas composition; the other was equivalent to an Abu Dhabi natural gas. The Algerian natural gas included 10% higher hydrocarbons. A summary of previous ignition delay time correlations was presented, including correlations from Spadaccini

and Colket (1994) and Lamoureux et al. (2002). The ignition delay times for multi-hydrocarbon fuel mixtures were also calculated using two mathematically formulated mixture laws.

The measured ignition delay times for the methane-ethane mixtures were compared against predictions from the correlations of Spadaccini and Colket and the two mixture laws. Ignition delay times for the various mixtures are compared against each other and show that the natural gas mixtures can be simulated using an equivalent methane-ethane-propane mixture and were reasonably captured by a blend of only methane-ethane.

Two kinetic reaction models, a model developed by Tan et al. (1994a) and GRI 3.0, were used to compare calculated ignition delay times against experimental results. Both models had good agreement with each other and the experimental data at lean and stoichiometric conditions. The mathematical mixture law was also compared against the models and experimental data, with both models generally performing better.

Huang and Bushe (2006) conducted a study of ignition delay of methane-air mixtures with ethane-propane additives behind reflected shock waves at elevated pressures (16-40 bar) and intermediate temperatures (900-1400 K). Mixtures included methane-ethane, methane-propane, and methane-ethane-propane in O_2/N_2 . The highest concentration of ethane added was 0.89% (mole basis). A modified kinetic reaction model based on the GRI mechanism was used to calculate species time histories and ignition delay times. The modifications to the base model included C_2 reactions from Hunter et al. (1996), a C_3 submechanism from Frenklach and

Bornside (1984), and reactions between iso/normal propylperoxy and major alkane species from Curran et al. (2002). The final mechanism includes 278 reactions and 55 species. Experimental results showed that ignition delay time reduction due to ethane addition has a minimum around 1100 K.

The authors developed an analytical model for the ignition of methane-ethane and methane-propane mixtures by applying quasi-steady-state assumptions to the primary reaction path, resulting in a 9-step model. Analytical model predictions were compared against experimental data and the detailed kinetic model for ignition delay time and species time histories for CH_2O , CH_3 , C_2H_6 , $\text{CH}_3\text{O}_2\text{H}$, and OH .

Through analysis of the methane reaction mechanism, it was shown that the ignition pathway for methane with small amounts of ethane is dependant on temperature and explains the increased effectiveness of ethane on reducing the ignition delay time at lower temperatures. It was also shown that small amounts of higher hydrocarbon addition does not change the primary reaction path for methane and that combustion of methane is dominated by a small number of key elementary reactions. The pre-ignition reaction of methane was broken down into five steps with an additional four steps that summarize ethane reaction. It was further shown that "the kinetic effect of ethane addition comes from its contribution to the initiation phase of the induction period." Added amounts of ethane (in small concentrations) do not change the primary reaction path for methane but it does change the rate of progress of the induction period. With increasing amounts of ethane, its ability to further reduce the ignition delay time is limited due to the

negative effect of its concentration. The further exploration of the limits of ethane concentration and its effect on the ignition kinetics was a major driver for the present study.

De Vries and Petersen (2007) performed an experimental study of lean, undiluted natural-gas-based mixtures of CH_4 combined with C_2H_6 , C_3H_8 , C_4H_{10} , C_5H_{12} and H_2 behind reflected shock waves. Ignition delay time was determined from pressure and CH emission histories. A statistical design of experiments approach was used to develop a 21-mixture matrix of binary and ternary fuel blends. Experimental results were compared with predictions from the chemical kinetics models of Curran et al. (2002) and GRI-Mech 3.0 (even though the GRI mechanism is not tailored to the conditions of their study). Experimental results for 100% methane from their study were combined with data from an earlier study by the authors (Petersen et al., 2005) and compared with data from Goy et al. (2001) and calculated results from Williams et al. (2005), Konnov et al. (2000), and EXGAS (Buda et al. 2005). $\text{CH}_4/\text{C}_2\text{H}_6$ experimental results were compared with earlier data from Petersen et al. (2005) and the Spadaccini and Colket correlation.

Petersen et al. (2007) conducted shock-tube experiments and chemical kinetics modeling of ignition and oxidation of lean methane-based fuel blends at gas turbine pressures (0.54 – 25.3 atm) and elevated temperatures (1090 - 2001 K). Ignition delay times were measured behind reflected shocks for blends of CH_4 , CH_4/H_2 , $\text{CH}_4/\text{C}_2\text{H}_6$, and $\text{CH}_4/\text{C}_3\text{H}_8$. Ignition delay times obtained from CH radical emission time histories. The authors developed a chemical kinetics model based on GRI-Mech 3.0 to reproduce methane/air oxidation. Reactions involving CH_3O and CH_3O_2 were added to improve agreement with experimental data. The methane/ethane

mixtures studied were 90/10 and 70/30 blends. Ignition delay experimental data were compared with previous data from Petersen et al. (1996). A distinct drop in activation energy was seen around 1300 K for lower reaction temperatures.

2.4 Chemical Kinetic Mechanisms

Numerous chemical kinetic mechanisms have been developed over the past few decades for both methane and ethane combustion. They vary in complexity and capability from as little as 5-reaction models that model only methane to enormous models with hundreds of steps and dozens of species. The trade-off, of course, is increased computing time and resources with increased complexity, reactions, and species. Most of the earlier models are obsolete and are no longer used. As knowledge of the chemistry of hydrocarbon ignition has improved from further experimental testing, models have developed concurrently and have been integral to pinpointing critical reaction pathways and refining reaction rates. Sensitivity analyses of individual reactions are particularly useful for determining aggregate trends and chemical behavior of the overall reaction.

Olson and Gardiner (1977) conducted a survey of seven methane combustion mechanisms from previous studies of other authors and developed a new 49-reaction and 20-species chemical kinetic model from their own survey of literature on reactions concerning the combustion of H₂, CO, CH₄, C₂H₆, and C₂H₄. The new model was compared against selective parameters from

experimental studies by the seven previously developed mechanisms evaluated in this study, which included those of 1) Skinner, Lifshitz, Scheller, and Burcat (1972), 2) Cooke and Williams (1971), 3) Jachimowski (1974), 4) Bowman (1975), 5) Brabbs and Brokaw (1975), 6) Engleman (1976), and 7) Tsuboi (1976). Experimental shock-tube data used in this paper came from studies by 1) Dean and Kistiakowsky (1971), 2) Jacobs and Gutman (1971), 3) Cooke and Williams, 4) Jachimowski, 5) Brabbs and Brokaw, 6) Tsuboi (1975) and Tsuboi and Wagner (1975), and previous studies by the cited authors.

Westbrook et al. (1977) developed a 56-reaction mechanism for the oxidation of methane over the temperature range 1000-1350 K. Calculated results from the model were compared against turbulent flow reactor test data of Dryer (1972) and Dryer and Glassman (1973). The base model is a CO oxidation mechanism to which the authors added reactions from methane mechanisms proposed by Bowman (1975) and Koshi et al. (1975) and ethane oxidation reactions.

Westbrook (1979) developed a 25-species, 75-reaction kinetics model specifically for the ignition of mixtures of methane and ethane. The base model was from previous work by Westbrook et al. (1977) and was modified with an improved methane mechanism. Model predictions for ignition delay time were compared with experimental data from Burcat et al. (1971). Plots were made of model predictions of ignition delay time versus methane percentage at various temperatures and overall activation energy versus methane percentage. Interestingly, there is a predicted minimum value of 38.4 kcal/mole for the overall activation energy at a

mixture ratio of 60/40 methane/ethane. The variation in overall activation energy suggests that the transition of chemical kinetics involved from pure methane to pure ethane is smooth yet non-linear because they are so intricately connected. Plots were also made of the ignition delay time versus equivalence ratio, showing that a fuel-lean mixture has a shorter ignition delay over the entire temperature range studied than a stoichiometric mixture.

Notzold and Algermissen (1981) developed a 69-reaction, 24-species chemical kinetic model for ethane oxidation based on an established ethane pyrolysis model by Lin and Back (1966 and 1966a). Model predictions were compared against experimental shock tube data from Cooke and Williams (1971) over the temperature range 1400 – 1800 K and pressure range 0.267 – 0.375 bar and high-pressure data from Burcat et al. (1971). Model agreement with experimental results was good at low pressure but was not as accurate at higher pressures (10 bar).

Dagaut et al. (1991) developed a detailed reaction mechanism for the oxidation of methane in conjunction with an experimental study using a jet-stirred reactor. Mixtures consisted of methane and oxygen highly diluted in nitrogen. Species profiles were obtained for H₂, CO, CO₂, CH₄, C₂H₂, C₂H₄, and C₂H₆. Their mechanism is an extension of their previously developed mechanism for ethylene, propyne, and allene oxidation. Model predictions were compared against species concentration data from the JSR experimental study, ignition delay times from previous shock-tube studies of methane oxidation by Burcat et al. (1971), Lifshitz et al. (1971), Tsuboi and Wagner (1975), and Tsuboi (1976), and with H and O radical concentrations from the shock-tube study of Roth and Just (1984).

Hunter et al. (1994) developed a 207-step, 40-species chemical kinetics model for methane oxidation based on flow reactor experiments. No appreciable change in pathway reaction was observed over test conditions. The base reaction model was the mechanism of Frenklach et al. (1992), which was optimized for the prediction of shock-tube ignition delay, preignition methyl radical profiles, and laminar flame speed. Some of the reactions of the original Frenklach model were updated or modified based on previous work by other authors. Fifty-eight additional reactions were added to improve the chemistry models for methanol, methyl-hydroperoxyl, ethyl-hydroperoxyl, formaldehyde and C₂ species. The model was further fine tuned by sensitivity and flux analysis to arrive at the final model.

Rota et al. (1994) investigated ethane oxidation (highly diluted in nitrogen) in a perfectly stirred reactor. Species concentrations were measured from gas samples and compared with predictions of three detailed kinetics mechanisms. Experimental conditions of Dagaut et al. (1991a) were rerun. The three models used in the study were a mechanism by Miller and Bowman (1989), a mechanism by Dagaut et al. (1991a), and a mechanism by Kilpinen et al. (1992). The mechanism by Dagaut et al. was developed from methane and ethane oxidation using a PSR and was validated against shock-tube ignition of ethane behind reflected shock waves (1430-1755 K, 2 atm). Both the Miller and Bowman and Kilpinen et al. models are updated versions of a kinetic model developed by Glarborg et al. (1986), which itself was originally based on work by Miller and coworkers. Both models have been validated against methane ignition experiments. The authors modified the Kilipen model to better correlate acetylene concentration profiles by

adding a reaction step for the direct oxidation of C_2H_3 and a rate constant change for another reaction.

A kinetics model for the ignition of natural gas blends was developed by Tan et al. (1994). Model development was supported by an experimental study of the oxidation of hydrocarbon blends in a jet-stirred reactor. Test mixtures included methane/ethane, methane/propane, and methane/ethane/propane. Measurements of species concentrations were used to validate the kinetics model, originally presented by Dagaut et al. (1991 and 1992). Model predictions were compared against experimental species profile data of the current study and shock-tube ignition delay data for methane-propane-oxygen mixtures by Frenklach and Bornside (1984). The details of the final model are presented elsewhere by Tan et al. (1994b).

Hunter et al. (1996) studied ethane oxidation using a flow reactor under lean conditions at intermediate temperatures. Species profiles were measured of H_2 , CO , CO_2 , CH_2O , CH_4 , C_2H_4 , C_2H_6 , C_2H_4O and CH_3CHO . A new chemical kinetics model was developed by the cited authors by modifying the GRI-Mech 1.1 mechanism. The final model consists of 277 reactions and 47 species. The main source of the added reactions came from two works, the C_4 mechanism of Pitz, Westbrook, and coworkers (1991) and the mechanism of Hunter et al. (1994). Further adjustment of two rate constants improved the expanded model. Experiments showed that pressure has a significant effect on ethane decomposition. The model was also tested against the shock-tube ignition data of two teams: diluted ethane oxidation of Hikaka et al. (1982) and the stoichiometric methane oxidation of Seery and Bowman (1970).

Petersen et al. (1999) performed an analytical study of methane/oxygen ignition at elevated pressures, intermediate temperatures, and low-dilution levels. As part of the study, they developed a 38-species, 190-reaction kinetics model, RAMEC, based on the GRI-Mech 1.2 mechanism. Additional reactions were added (most from the lower temperature methane oxidation study of Hunter et al. (1994)) that are important in methane oxidation at lower temperatures, which greatly improved model predictions at high pressures and lower temperatures. Additional C₂H_y chemistry (important in fuel rich conditions) was not added to the mechanism because it was shown to not affect ignition delay times. The model was able to match experimental observations of accelerated ignition at lower temperatures (lower activation energy). Ignition delay times were determined from pressure, infrared emission, and visible emission measurements. Two correlations were used for ignition delay times that were previously presented by the authors (Petersen et al. 1999a); one for high-temperature and low-pressure conditions (rich and lean mixtures) and another for low-temperature, high-pressure conditions (fuel rich):

$$t_{\text{ign, high T}} = 1.26 \times 10^{-14} [\text{CH}_4]^{-0.02} [\text{O}_2]^{-1.20} \exp(32.7/RT \text{ kcal/mol})$$

$$t_{\text{ign, low T}} = 4.99 \times 10^{-14} [\text{CH}_4]^{-0.38} [\text{O}_2]^{-1.31} \exp(19.0/RT \text{ kcal/mol})$$

A third correlation, from Petersen et al. (1996) was also used that covers a wider range of data from previous shock-tube studies of dilute mixtures:

$$t_{\text{ign}} = 4.05 \times 10^{-15} [\text{CH}_4]^{0.33} [\text{O}_2]^{-1.05} \exp(51.8/RT \text{ kcal/mol})$$

Experimental data were compared with these correlations and a correlation from Seery and Bowman.

Hughes et al. (2001) developed a comprehensive chemical kinetics model for the oxidation of methane that includes 351 reactions and 37 species, which includes reactions for the oxidation of hydrogen, carbon monoxide, ethane and ethene. The model is tested against experimental results of laminar flame velocities, laminar flame species profiles, and ignition delay times.

Specifically, the model results were compared to the ignition delay times for methane/O₂/Ar mixtures by Tsuboi and Wagner (1974) and Seery and Bowman (1970), and the data from C₂H₆/O₂/Ar mixtures by Takahashi et al. (1989) and Burcat et al. (1972). The mechanism was based off of the mechanisms of Miller and Bowman (1989) and Glarborg et al. (1986). The most sensitive reactions steps of the model were compared against those of the GRI 3.0 mechanism and the mechanisms of Konnov (2000) and Chevalier (1993).

Li and Williams (2002) developed several models of methane combustion, including a detailed mechanism, known as the San Diego Mechanism, a 24-step short mechanism, a 9-step short mechanism, and a reduced mechanism. The full 127-step mechanism was derived from a previous 177-step reaction mechanism by Li and Williams. The nitrogen chemistry was deleted, and 2 steps were added that are important in the initiation stage of methane ignition. The 24-step mechanism is a simplified form of the full mechanism for mixtures with an equivalence ratio less than 1.5. The 9-step mechanism was further simplified from the 24-step mechanism for the temperature range 1000 – 1300 K, again for equivalence ratios less than 1.5. Further reduced five- and four-step mechanisms were developed through steady-state analysis and reduction. Two ignition delay time correlations were developed, one each for low and high temperatures.

Mechanism predictions were compared with shock-tube ignition delay data from Petersen et al. (1999) and Spadaccini and Colket (1994).

Bakali et al. (2004) studied oxidation of stoichiometric premixed synthetic natural gas flames and methane-ethane-air oxidation in a jet-stirred reactor. As a part of the study, they developed a new detailed kinetics reaction mechanism based on previous work by Dagaut and Cathonnet (1998) that focused on a comprehensive model for the reduction of NO by natural gas blends under simulated reburning conditions using a natural gas blend. Submechanisms for n-butane, isobutane, n-pentane, isopentane, and n-hexane were added to the base model. The final model contains 671 reactions and 99 species. Model predictions were compared against burning velocities and species profiles of methane-air, ethane-air, and propane-air flames obtained from the current experiment. Model predictions were also compared against jet-stirred reactor experimental data from this study and against predictions of the GRI 3.0 mechanism and a mechanism by Glarborg et al. (1998). The model was also used to calculate ignition delay times for methane-oxygen-argon and methane-ethane-oxygen-argon mixtures from previous shock-tube studies of Lifshitz et al. (1971), Burcat et al. (1971), and Crossley et al. (1972).

Turbiez et al. (2004) conducted an experimental study of combustion of low-pressure stoichiometric premixed methane, methane/ethane, methane/ethane/propane, and synthetic natural gas flames (diluted in argon). The authors show that mixtures of methane/ethane/propane can be used to accurately model natural gas mixtures that include several higher order

components in low pressure, stoichiometric conditions due to the minor role of the higher alkanes in the oxidation of primary components.

A 177-step mechanism for the reaction of C_1 - C_3 alkanes was developed by Petrova and Williams (2006) as an extension to the San Diego Mechanism. The model is limited to pressures below 100 atm, temperatures above 1000 K, and equivalence ratios less than approximately 3. The previous development of the mechanism began with a base reaction set for combustion of hydrogen and C_1 and C_2 based fuels. A reaction set for carbon monoxide combustion was added later, and additional reaction sets were added for combustion of methane and methanol, and then ethane, ethylene, and acetylene. In the study, reactions for the combustion of C_3 -based fuels were added and validated against existing experimental data, specifically for propane, propene, allene and propyne.

Despite extensive experimental testing and the availability of several highly developed reaction models, there is still no community-wide accepted baseline reaction model for methane or ethane oxidation and ignition that covers the full range of pressures, mixtures, and temperatures needed for practical applications. The current models accurately recreate NTC behavior at low temperatures, the low-pressure detonation limit, and other well-known trends but there is still uncertainty about the fundamental kinetics of methane and ethane combustion.

Chemical reaction models for hydrocarbon combustion are hierarchical in nature in that each set of reactions for a specific species is independent of and build upon each other to form a complete

model. Chemical reactions for the higher alkanes are added to those for the lower ones. Therefore, a full model for octane combustion, for example, must include sub-mechanisms for methane, ethane, propane, butane, pentane, hexane, and heptane, in addition to all C₁-C₈ species.

2.5 Impetus for Present Study

Methane and ethane combustion react by way of two separate, competing pathways. Nearly the entire amount of methane available must break down before runaway radical production can occur that initiates the ignition process. Meanwhile, ethane ignition begins before the parent fuel is completely exhausted. Interestingly, methane decomposition will lead to the production of some ethane through the recombination of methyl radicals.

Of particular interest, then, is at what point does the combustion reaction pathway transition from methane to ethane. As the amount of ethane is increased, the ethane reaction pathway will become more dominant. At some saturation point, radical consumption will be equal between the methane and ethane pathways. A sensitivity analysis of the primary reactions should reveal when this occurs. Of utmost concern, however, is obtaining a collection of experiments that will allow for verification of the trends predicted by the reaction models.

The review of available literature on the subject has shown that previous research has not produced a broad data set capable of addressing the issue. The goal of this thesis was therefore to

perform a limited set of experiments that will determine the ethane concentration level that results in the ethane reaction pathway becoming dominant over the methane reaction pathway.

CHAPTER 3: EXPERIMENTAL SETUP AND TECHNIQUE

3.1 Hardware

All experiments were performed at the University of Central Florida Gas Dynamics Laboratory, utilizing a high-pressure shock-tube (HPST) and a low-pressure shock-tube (LPST). The LPST, seen in Figure 3-1, has been described elsewhere (Rotavera and Petersen). The configuration of the shock tube and instrumentation is slightly different for this study, and a detailed description is provided herein. The stainless steel shock-tube has a circular driver section of 7.6 cm internal diameter and 2.0 m in length. The driven section is 10.8 cm square and 4.3 m in length.

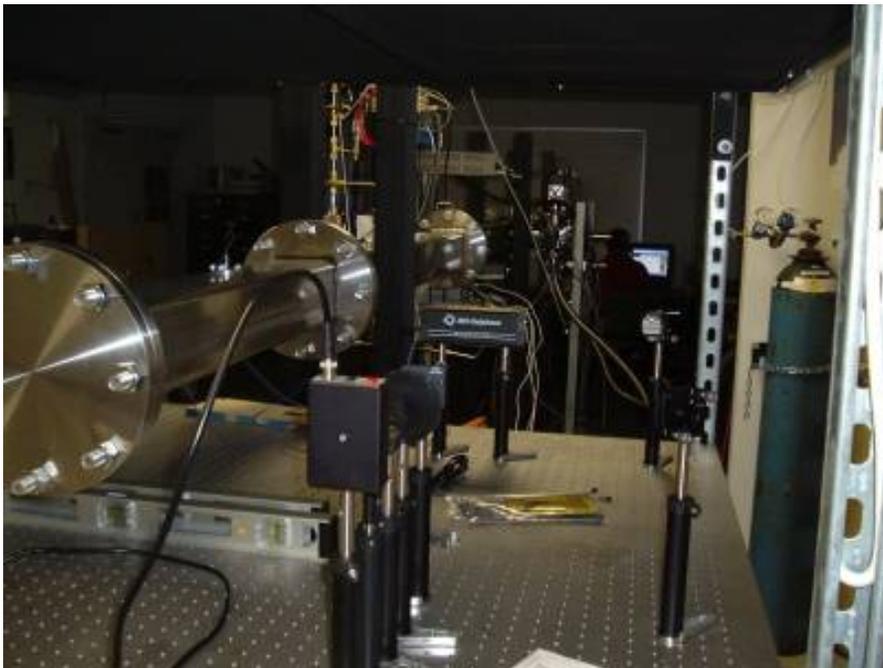


Figure 3-1: Low-pressure shock-tube at UCF Gas Dynamics Laboratory

The incident shock front velocity at the endwall is calculated by extrapolating linearly from interim measurements of four high-frequency, piezoelectric pressure transducers, located at 163.1, 117.4, 70.6, and 23.9 cm from the endwall, in conjunction with 120-MHz counter/timers (Phillips P6666). This technique has been shown by Petersen et al. to be capable of determining post-shock test temperatures with uncertainty below 10 K (2005a).

The thermodynamic state of the gas in the reflected-shock region is calculated using FROSH, MS-DOS-based software, based on the Rankine-Hugoniot ideal gas shock relations and thermodynamic properties from the Sandia thermodynamic database. Inputs used by the software are the incident shock speed and the initial pressure of the test gas in the driven section (P_1).

Reaction progress is monitored by use of pressure transducers and optical sensors in the endwall and sidewall. Pressure is monitored at the endwall by a PCB 113 A pressure transducer. Pressure at the sidewall, located 1.04 cm from the endwall, is monitored by a 500-kHz quartz Kistler 603B1 pressure transducer. CH radical ultraviolet emission is measured at the sidewall with a Hamamatsu Type 1P21 photomultiplier tube and a 430 nm bandpass filter, the signal from which is processed by a low-noise preamplifier (Stanford Research Systems SR560). The sidewall emission passes through a narrow slit to ensure adequate resolution and is reflected by a focusing mirror before arriving at the detector. Endwall emission is captured by a photodetector (New Focus, INC. model 2032). Both the pressure and emission time histories are recorded at 1

mega-samples per second on four discrete channels with two 16-bit, 10-Mhz Gage Applied Sciences data acquisition boards installed on a Microsoft Windows-based PC.

The HPST, originally described by Aul et al. (2007), is made of 304 stainless steel. A diagram of the HPST is shown in Figure 3-2. The driver section has an ID of 7.62 cm and is 2.46 m in length. The driven section has an ID of 15.24 cm, is 4.72 m long, and has a finely polished surface finish of 1 μm RMS or better. Five equally spaced PCB P113A piezoelectric pressure transducers mounted along the tube are used to measure shock wave speeds. The incident shock velocity at the endwall is linearly extrapolated from these measurements using the same technique as for the LPST. Three PCB 134A piezoelectric pressure transducers are used to monitor test pressures, one at the endwall and two in the sidewall, located 1.6 cm from the endwall. CH radical emission is measured at the sidewall using the same technique as for the LPST.



Figure 3-2: High-pressure shock-tube at UCF Gas Dynamics Laboratory

3.2 Procedure

The gases used were provided by Air Liquide and included ultra-high-purity (UHP) argon, standard purity helium, UHP oxygen, research grade methane, and research grade ethane.

To obtain sufficient experimental test data for a shock-tube oxidation and ignition study that fully addresses all variables of interest would be extremely time consuming. A Design of Experiments (DoE) approach was used to obtain data in an efficient manner and to reduce the

total number of tests required to fully capture the ignition behavior of the binary fuel blends. An L16 array, developed by Petersen and de Vries (2005) for binary blends, was used for the test matrix. It includes four factors with multiple levels each for a total of 10 degrees of freedom. The factors are the primary test variables of interest, specifically equivalence ratio, dilution percentage, pressure, and fuel blend ratio. Three levels are used for both the equivalence ratio (0.5, 1.0, and 2.0) and pressure (1, 10, and 25 atm). Four levels are used for the dilution mole fraction (75, 85, 95, and 98%) and methane/ethane blend ratio (100/0, 75/25, 50/50, and 25/75). Two additional cases were tested in addition to the 8 that make up the matrix; two mixtures of 100% ethane at 75% dilution and equivalence ratios of 1.0 and 0.5.

The full matrix consists of 16 mixtures, and the details for each are shown in Table 1. Only the experiments at 1 atm (mixtures 1-4 and 13-16) were conducted for this study. The remaining mixtures at elevated pressures will be part of a follow-on study. The component molar fractions for the mixtures studied are shown in Table 2.

Table 1: Experimental test conditions of fuel-oxidizer-argon mixtures.

Parameters shown indicate the methane/ethane blend ratio, argon molar dilution percentage, equivalence ratio, and pressure behind the reflected shock wave (P5) of the test mixtures studied

Mixture	Blend (CH ₄ /C ₂ H ₆)	Dilution (%)	equivalence	P (atm)
1	75/25	98	0.5	1
2	50/50	98	0.5	1
3	25/75	98	1	1
4	100/0	98	1	1
13	75/25	75	1	1
14	50/50	75	1	1
15	25/75	75	0.5	1
16	100/0	75	0.5	1
17	0/100	75	1	1
18	0/100	75	0.5	1

Table 2: Mole fraction of fuel, oxidizer, and diluent components of experimental mixtures

Mixture	CH ₄	C ₂ H ₆	O ₂	Ar
1	0.00261	0.00087	0.0165	0.98
2	0.00154	0.00154	0.0169	0.98
3	0.00121	0.00364	0.0152	0.98
4	0.00667	0	0.0133	0.98
13	0.0556	0.0185	0.1759	0.75
14	0.0333	0.0333	0.1833	0.75
15	0.0086	0.0259	0.2155	0.75
16	0.05	0	0.20	0.75
17	0	0.038462	0.21154	0.75
18	0	0.020833	0.22917	0.75

For each mixture, the goal was to obtain ignition delay times over a range of temperatures so that the ignition delay times spanned between approximately 50 and 1000 microseconds. For dilute mixtures, the ignition delay time was calculated by taking the difference between the arrival of

the reflected shock (from sidewall pressure measurements) and the rise in OH radical emission (measured at the same sidewall plane as the sidewall pressure transducer), determined by the intersection of the maximum slope and the pre-ignition steady-state value. Due to the high dilution levels, it was not possible to determine ignition delay times for these mixtures from the pressure traces, as there was no rise in pressure during the reaction. Figure 3-3 demonstrates this definition of ignition delay time.

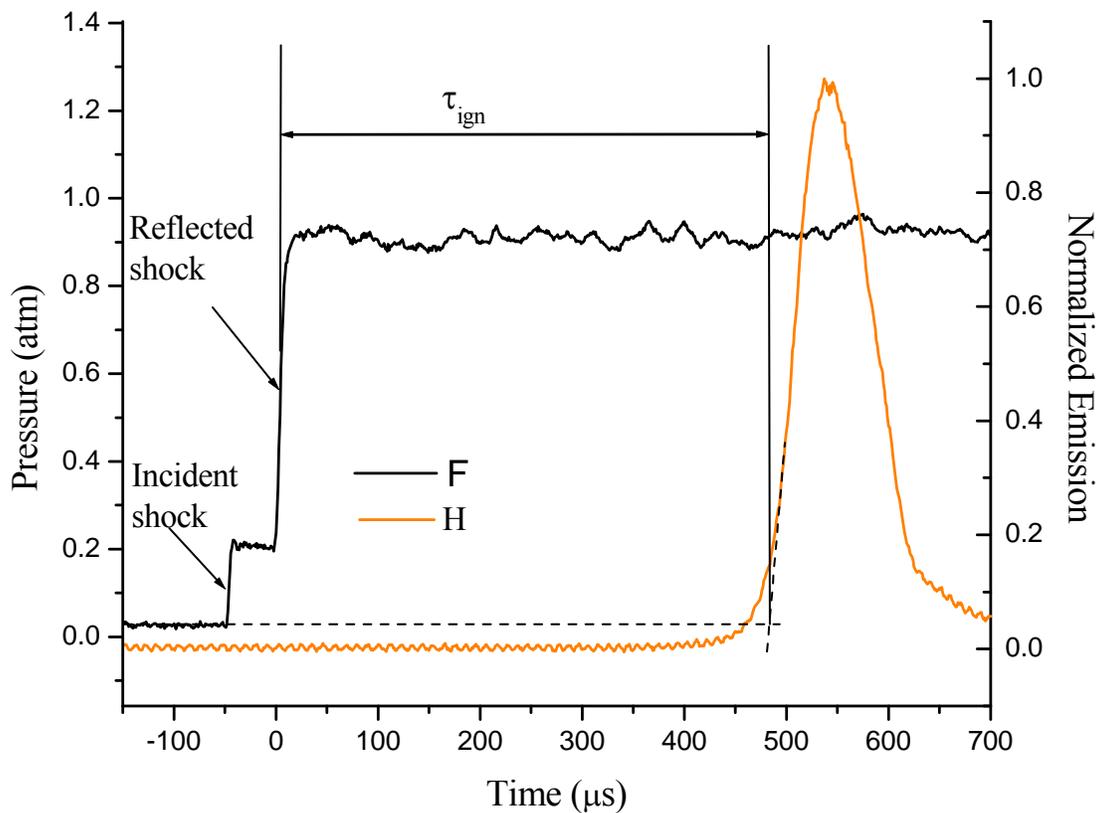


Figure 3-3: Plot of typical sidewall pressure and emission traces for a dilute mixture

Ignition delay time for the high concentration mixtures were obtained by measuring the time difference between the arrival of the shock at the endwall and the sharp pressure rise due to the onset of ignition. For these undiluted, highly exothermic mixtures, the abrupt pressure rise at ignition is clearly defined in the pressure trace. It has been shown in recent studies that the endwall pressure trace gives the true ignition delay time (Rickard et al. (2005), Kalitan et al. (2005), Frenklach and Bornside (1984), Petersen et al. (1999a), Horning et al. (2002)). When this method is indeterminate, such as for high-temperature, fast-igniting reactions where the incipient pressure rise due to ignition cannot be discerned from the initial background noise behind the reflected shock; the endwall emission trace was used to determine the onset of ignition. It was demonstrated that this method gives equivalent ignition delay times as the pressure trace for high-concentration mixtures (Petersen, 2007a). However, the post-ignition emission trace is of no value in determining ignition delay times, as the signal is an integration of subsequent ignition down the length of the tube from the endwall. Figure 3-4 shows both the endwall pressure and emission traces from a representative high-concentration mixture.

CH radical emission was not measured at the endwall for experiments conducted with the high-pressure shock tube. For those experiments, emission measured at the sidewall was used as a diagnostic guide to aid in interpreting when ignition occurred. Sidewall emission was not used to directly measure ignition delay times because ignition can be accelerated in regions away from the endwall due to the potential development of a detonation wave in high-concentration mixtures.

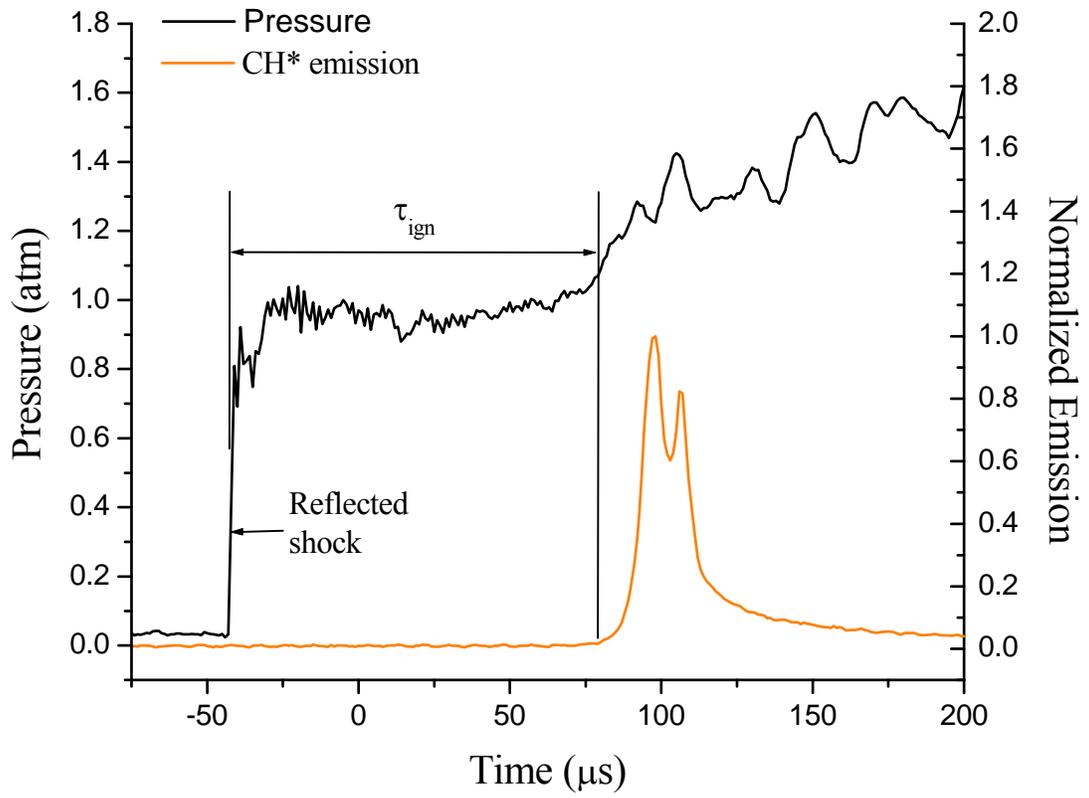


Figure 3-4: Plot of endwall pressure and emission traces for a high-concentration mixture

CHAPTER 4: EXPERIMENTAL AND MODELING RESULTS

Experimental results for ignition delay time and CH* time histories are presented for each mixture and are also compared with predictions from three chemical kinetics models. The models used in this study are GRI-Mech 3.0 (Smith et al., 1999), RAMEC, a model developed by Petersen et al. (1999), and a recent model for the oxidation and ignition of methane and higher-order hydrocarbons by Curran et al. obtained through personal communication (2007). The RAMEC model was only compared to the 100% methane mixtures as it was not optimized or baselined to for ethane combustion.

4.1 Experimental Results

Experimental ignition delay times for all mixtures studied are shown in Table 3. Specific molar percentages of each component are shown for each mixture. The temperature and pressure behind the reflected shock wave are provided for each ignition delay time data point.

Ignition delay times versus inverse temperature for mixture 16 are shown in Figure 4-1. The fuel-lean mixture (equivalence of 0.5) is composed of methane and oxygen diluted 75% with argon (all values stated are based on molar percentage). Measured ignition delay times span 86.5 – 875 microseconds over the temperature range 1575 – 1873 K and pressure range 1.031 – 1.207 atm.

Table 3: Experimental ignition delay times for mixtures 1-4 and 13-18

T (K)	P (atm)	τ (μ s)	T (K)	P (atm)	τ (μ s)
Mixture 1 ($\phi = 0.5$)			Mixture 4 ($\phi = 1.0$)		
0.26% CH ₄ + 0.09% C ₂ H ₆ + 1.65% O ₂ + 98.00% Ar			0.67% CH ₄ + 1.33% O ₂ + 98.00% Ar		
1663	1.25	42	2248	1.13	70
1630	1.33	92	2097	1.14	138
1550	1.3	155	1994	1.21	229
1478	1.32	236	1988	1.19	211
1426	1.33	295	1897	1.21	476
1359	1.32	572	1801	1.27	831
1296	1.37	988	1790	1.2	911
			1726	1.25	1447
Mixture 2 ($\phi = 0.5$)			Mixture 13 ($\phi = 1.0$)		
0.15% CH ₄ + 0.15% C ₂ H ₆ + 1.69% O ₂ + 98.00% Ar			5.56% CH ₄ + 1.85% C ₂ H ₆ + 17.59% O ₂ + 98.00% Ar		
1782	1.26	20	1593	1.039	128
1720	1.31	34	1572	1.116	127.7
1571	1.28	78	1499	1.132	204.2
1536	1.3	124	1443	1.161	405
1441	1.34	222	1353	1.192	811
1398	1.34	365	1317	1.227	1202.9
1335	1.39	540	1593	1.039	128
1328	1.3	568	1572	1.116	127.7
1302	1.39	678			
1268	1.42	1002			
Mixture 3 ($\phi = 1.0$)			Mixture 14 ($\phi = 1.0$)		
0.12% CH ₄ + 0.36% C ₂ H ₆ + 1.52% O ₂ + 98.00% Ar			3.33% CH ₄ + 3.33% C ₂ H ₆ + 18.33% O ₂ + 75.00% Ar		
1700	1.28	55	1660	1.15	74
1564	1.28	155	1479	1.224	144
1519	1.35	191	1406	1.276	264
1457	1.39	363	1368	1.32	388
1452	1.31	353	1303	1.314	689
1395	1.36	578			
1368	1.36	740			
1324	1.39	1032			

T (K)	P (atm)	τ (μ s)	T (K)	P (atm)	τ (μ s)
Mixture 15 ($\phi = 0.5$) 0.86% CH ₄ + 2.59% C ₂ H ₆ + 21.55% O ₂ + 75.00% Ar			Mixture 17 ($\phi = 1.0$) 3.85% C ₂ H ₆ + 21.15% O ₂ + 75.00% Ar		
1512	1.186	40.1	1475	1.19	76
1379	1.261	104.5	1450	1.24	46
1337	1.313	141	1401	1.25	163
1317	1.37	197.6	1350	1.32	165
1242	1.301	458.9	1319	1.31	166
1164	1.293	1338.1	1274	1.28	553
Mixture 16 ($\phi = 0.5$) 5.00% CH ₄ + 20.00% O ₂ + 75.00% Ar			1269	1.31	474
1873	1.032	86.5	1260	1.31	301
1813	1.031	134	1228	1.32	1183
1747	1.099	204.9	Mixture 18 ($\phi = 0.5$) 2.08% C ₂ H ₆ + 22.92% O ₂ + 75.00% Ar		
1727	1.092	180.9	1399	1.23	68
1666	1.062	306.5	1368	1.28	83
1643	1.102	442	1333	1.26	112
1575	1.207	875	1303	1.27	133
1873	1.032	86.5	1268	1.28	256
			1246	1.36	425
			1225	1.24	609
			1180	1.3	1487

Agreement is very good between the experimental results for mixture 16 and all chemical kinetics model predictions. RAMEC, based on an older version of the GRI mechanism (GRI 1.2), is the most accurate at high temperatures, while below approximately 1640 K the Curran mechanism is the most accurate, slightly better than RAMEC. The average error for the RAMEC, GRI, and Curran mechanisms is 22, 26, and 31 percent, respectively. The predicted

ignition delay times of the three models, RAMEC, Curran, and GRI, span 80 – 439, 72 – 466, and 71 – 401 microseconds, respectively, over the tested conditions.

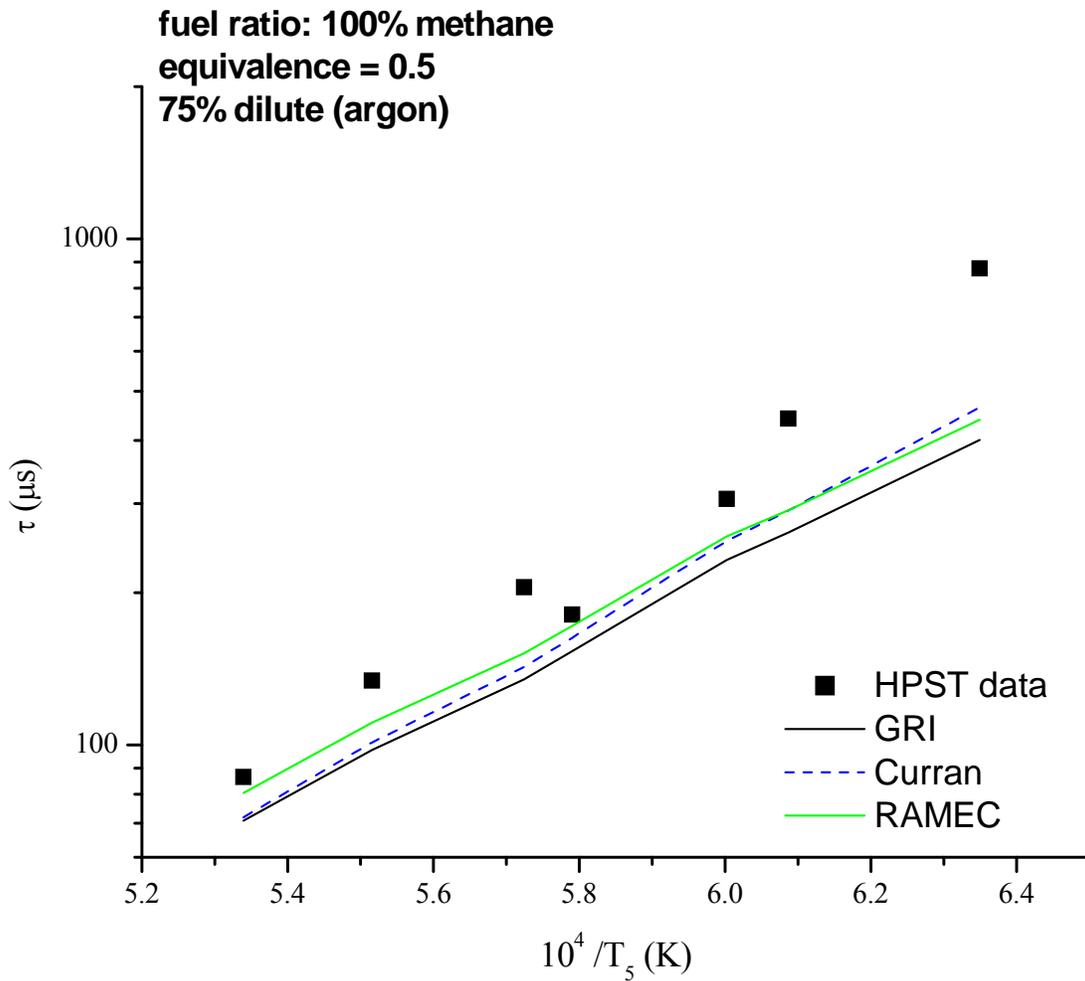


Figure 4-1: Experimental and computed ignition delay times for mix 16

Ignition delay times versus inverse temperature for mixture 13 are shown in Figure 4-2. The mixture is a stoichiometric blend of 75% methane and 25% ethane with oxygen diluted 75% with

argon. Measured ignition delay times spanned 128 – 1203 microseconds over the temperature range 1317 – 1593 K and pressure range 1.04 – 1.23 atm.

Calculated ignition delay times, based on test conditions, are 101 – 1150 and 68 – 514 microseconds for the Curran and GRI models, respectively. Predictions by the Curran model are in very good agreement with the experimental data for mixture 13, the error ranging from 3 to 21%, with an average of 11%. The GRI model is significantly poorer, the error ranging from 43 to 57%, with an average of 50%. All ignition delay times predicted by GRI are faster than the measured ignition delay times over the entire temperature range. The slope of the GRI model trend line is shallower; as a result the model predictions approach the experimental results at higher temperatures.

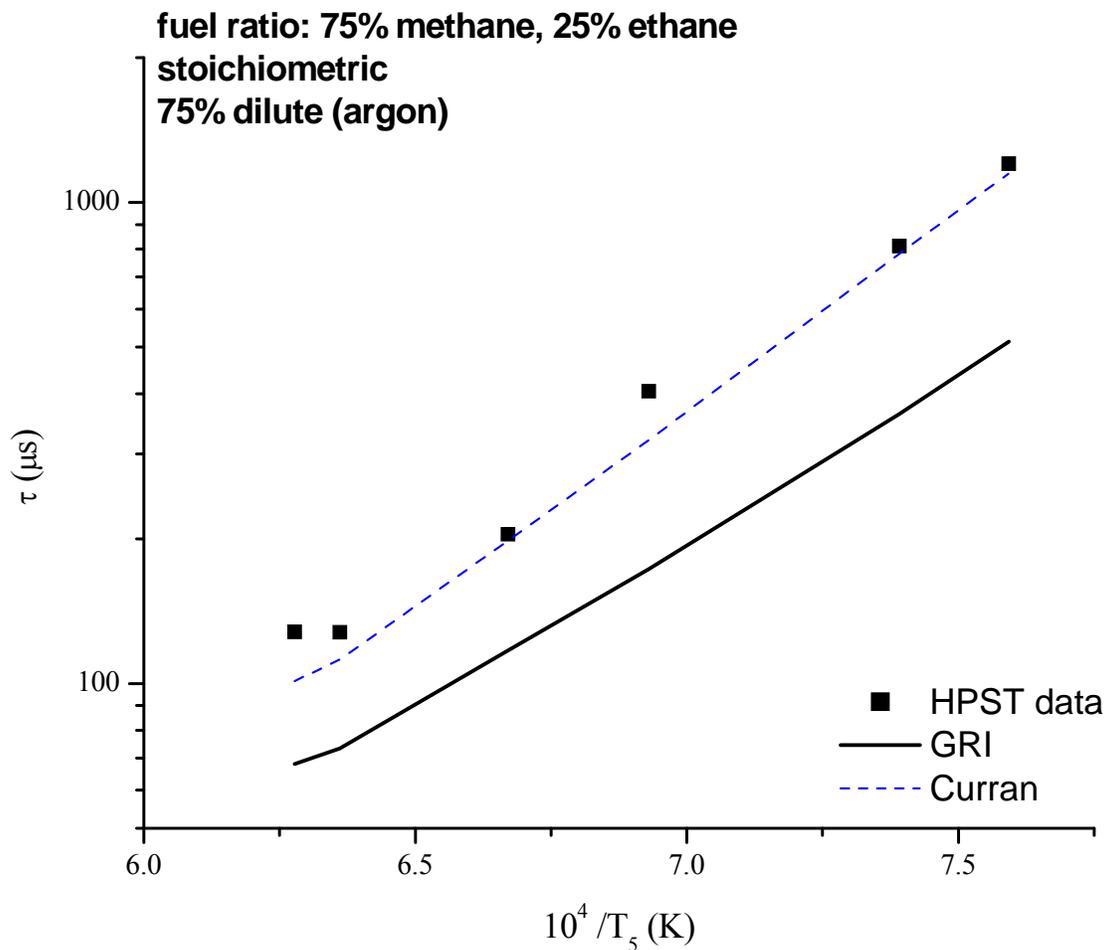


Figure 4-2: Experimental and computed ignition delay times for mix 13

Ignition delay times versus inverse temperature for mixture 14 are shown in Figure 4-3. The mixture is a stoichiometric blend of 50% methane and 50% ethane with oxygen diluted 75% with argon. Measured ignition delay times ranged from 74 – 689 microseconds over the temperature range 1303 – 1660 K and pressure range 1.15 – 1.32 atm.

The calculated ignition delay times, based on test conditions, are 30 – 549 and 44 – 739 microseconds for the GRI and Curran models, respectively. The Curran model is more accurate than the GRI model for mixture 14. Ignition delay times predicted by the Curran model are very close to the experimental results over the entire temperature range studied, save for the hottest data point. It can be seen that there is an increase in the GRI prediction trend line slope at approximately 1370 K. At temperatures higher than 1370 K, the trend line slope is similar to the experimental data suggesting there is a change in the underlying chemistry around that temperature that is not physically representative of the actual reaction chemistry. The average error for the GRI model over the temperature range studied varies from 20 to 60%, with an average of 41%. The Curran model has an average error of 7% over the same temperature range, with a much smaller deviation, ranging from 2 to 41%.

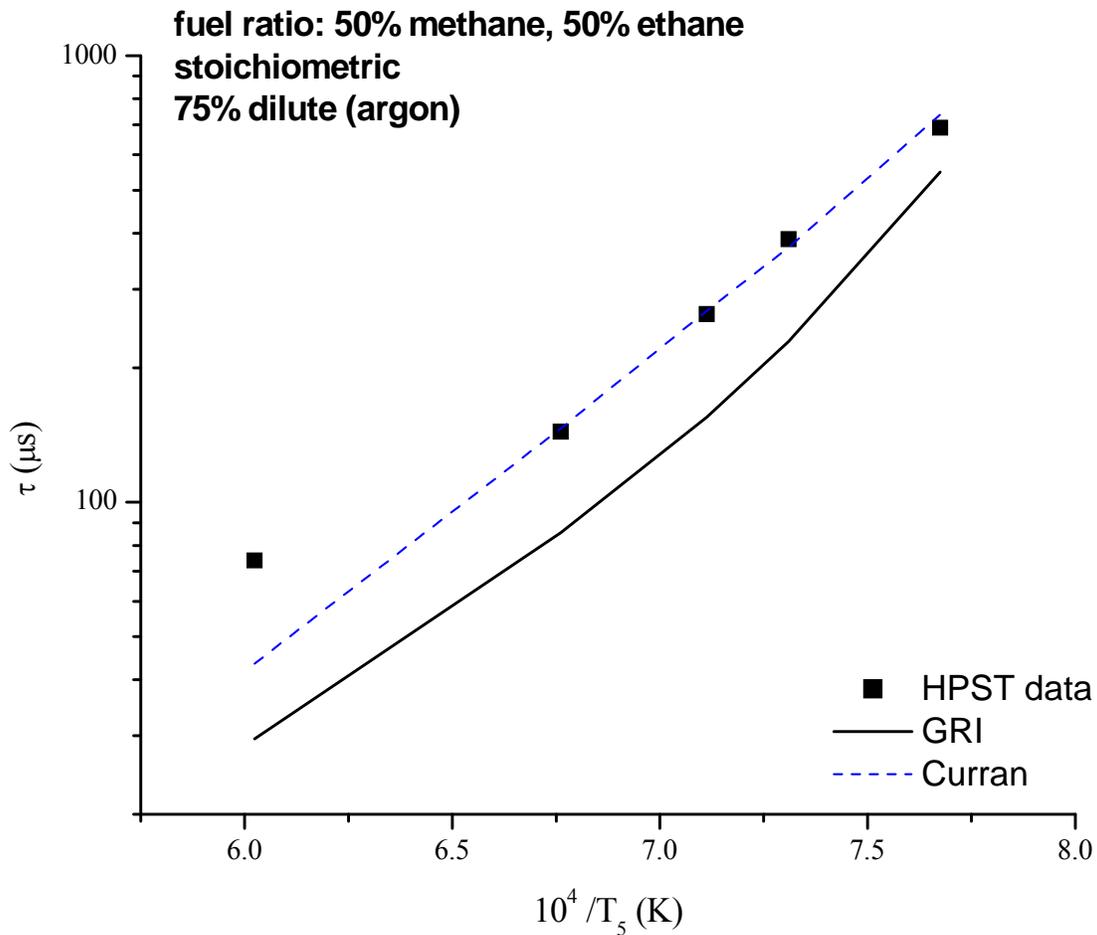


Figure 4-3: Experimental and computed ignition delay times for mix 14

Ignition delay times versus inverse temperature for mixture 15 are shown in Figure 4-4. The mixture is a fuel-lean (equivalence of 0.5) blend of 25% methane and 75% ethane with oxygen diluted 75% with argon. Measured ignition delay times ranged from 40 - 1338 microseconds over the temperature range 1164 – 1512 K and pressure range 1.19 – 1.37 atm.

Ignition delay times predicted by the Curran and GRI models are 69 – 4201 and 57 – 9055 microseconds, respectively. Neither model agrees well with the experimental data for mixture 15. Again, the Curran model trend line has a similar slope to the experimental data (and appears to have the same slope at lower temperatures) but over predicts ignition delay times by approximately a factor of two over the entire temperature range. The GRI model predicts similar ignition delay times to that of the Curran model. The slope of the GRI trend line is slightly steeper than the Curran trend line and like the mixture 14 results, there is a noticeable increase in the trend line slope around 1375 K that is not seen in the experimental data, this is also approximately where the Curran and GRI trend lines intersect. Interestingly, there is also a slight increase in slope of the Curran trend line at this point that is much less dramatic than that seen for the GRI predictions. The average error for the Curran and GRI models is 128% and 223%, respectively. The error of the Curran model ranges from 73 to 214% and the error of the GRI model ranges from 43 to 577%.

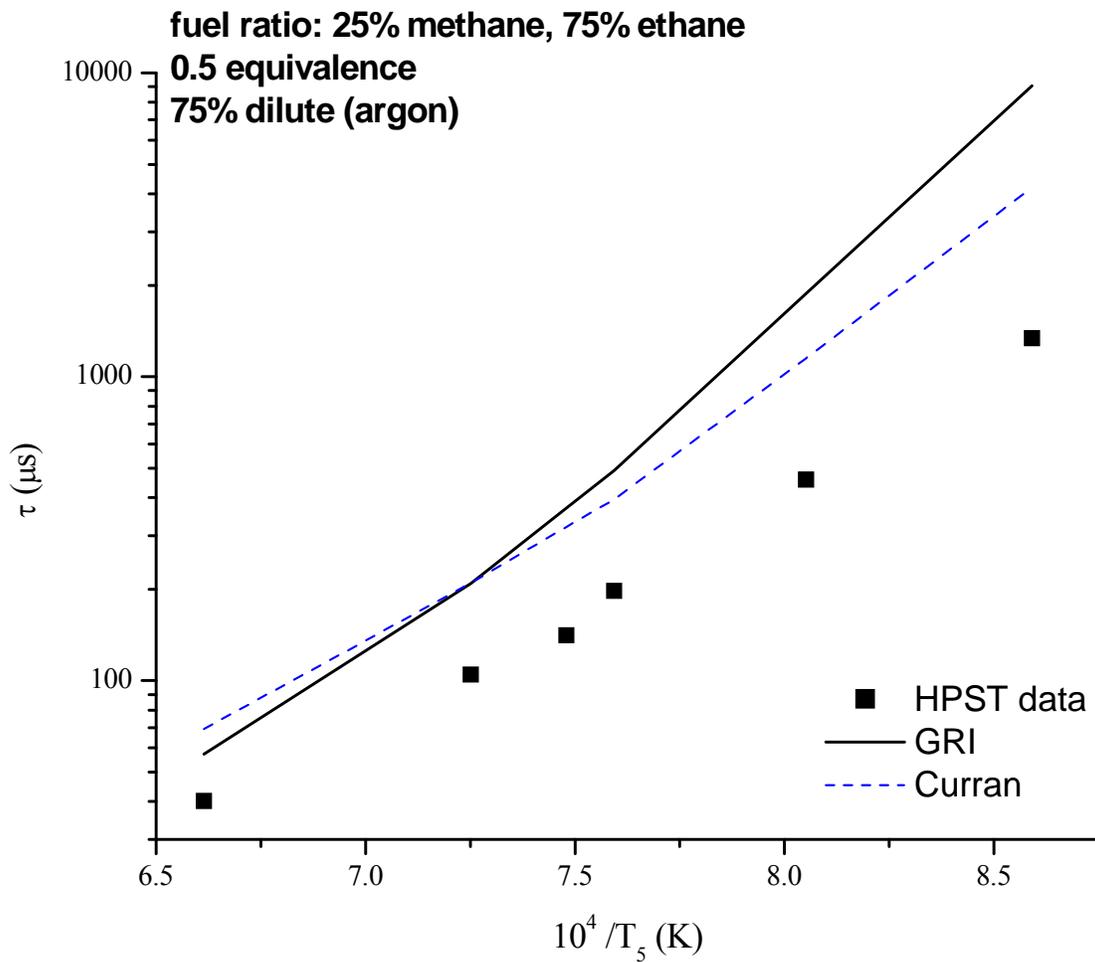


Figure 4-4: Experimental and computed ignition delay times for mix 15

Ignition delay times for mix 17 are shown in Figure 4-5. The mixture is a high-concentration (75% argon), stoichiometric mixture of 100% ethane with oxygen. Experimental ignition delay times measured 46 – 1400 microseconds over the temperature range 1450 – 1185 K and pressure

range 1.19 – 1.35 atm. There is more scatter among the data than seen in the tests with less ethane, but there is a discernable linear trend line.

The Curran model predictions form an upper bound of the experimental data, with ignition delay times of 92 – 1273 microseconds over the experimental test range. The slope of the Curran model trend line follows the general trend of the experimental data. The GRI model predicts ignition delay times of 75 – 2800 microseconds, in poor agreement with experimental results. The slope of the GRI trend line is considerably steeper than Curran. GRI predicts slightly faster ignition times than Curran at high temperatures, above 1400 K, and is slower than Curran at lower temperatures. The GRI model error increases steadily with decreasing temperature, ranging from 2 to 224%. It is difficult to draw any solid conclusions from error calculations due to the considerable experimental scatter, but for comparison purposes, the Curran model has an average error of 54%, much lower than the GRI model average error of 107%.

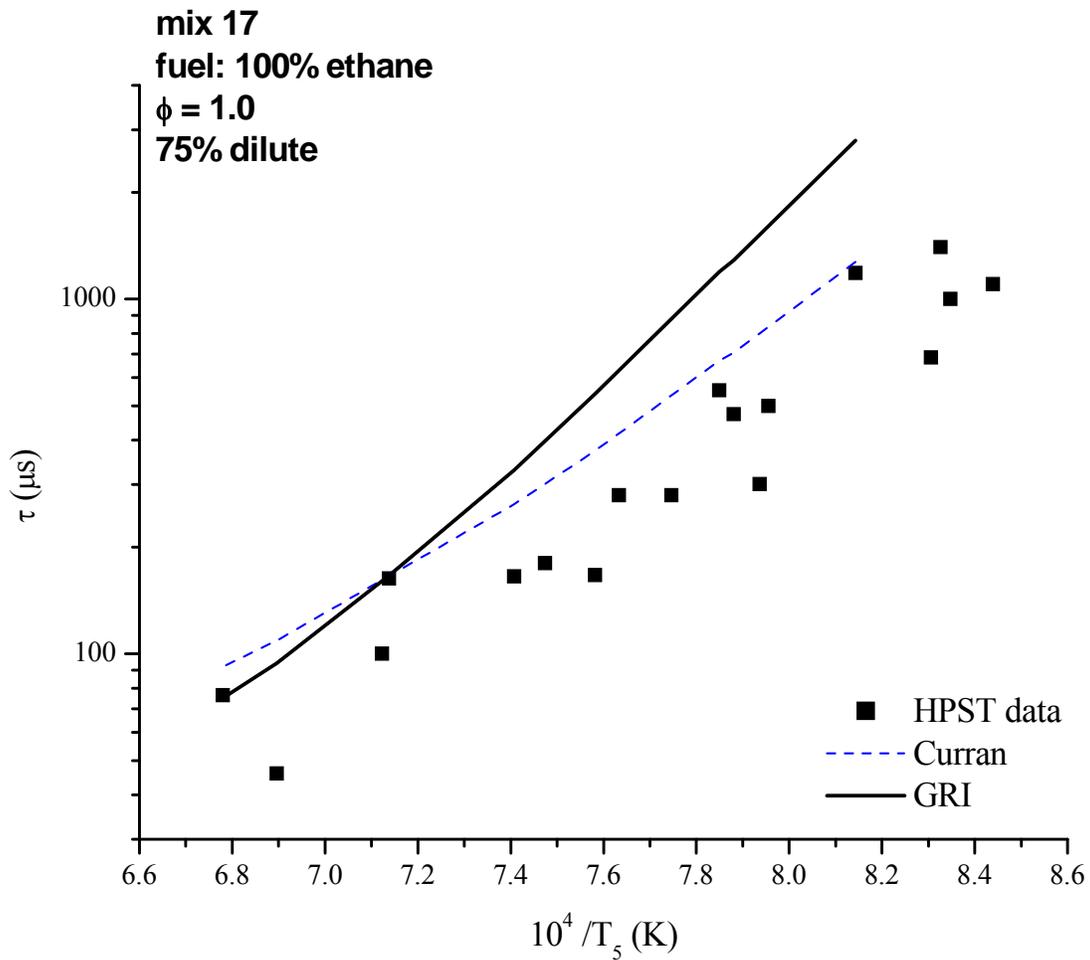


Figure 4-5: Experimental and computed ignition delay times for mix 17

Ignition delay times for mixture 18 are shown in Figure 4-6. The mixture is a high-concentration (75% argon), fuel-lean (equivalence of 0.5) mixture of 100% ethane with oxygen. Experimental ignition delay times measured 68 – 1487 microseconds over the temperature range 1399 – 1180 K and pressure range 1.23 – 1.36 atm. Note the change in slope for the three hottest data points compared to the rest of the data. This behavior is not present in model predictions by either GRI

or Curran but there is a slight shift in slope of the Curran trend line at 1250 K. Both models perform poorly over the range of experimental conditions. In fact, the GRI model is particularly bad, over predicting ignition delay times by a factor of 1.5 to 4.5. The Curran model predicts ignition delay times of 137 - 3170 microseconds, with an average error of 140%. The GRI model predicts ignition delay times of 173 – 8062 microseconds, with an average error of 349%.

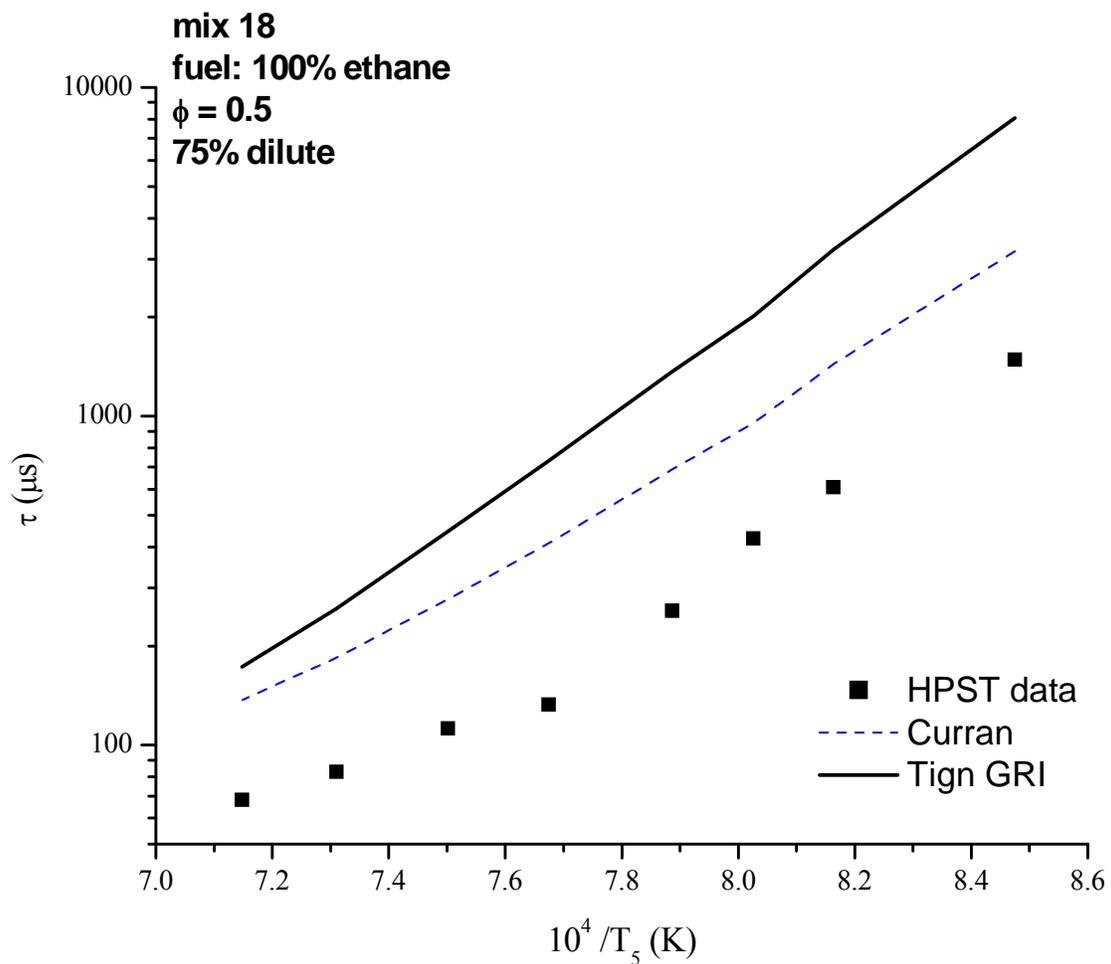


Figure 4-6: Experimental ignition delay times for mix 18

Ignition delay times for mixture 4 are shown in Figure 4-7. Measured ignition delay times vary from 70 microseconds at 2248 K and 1.1 atm to 1447 microseconds at 1726 K and 1.2 atm. This mixture, being a highly dilute (98% argon), stoichiometric mixture of methane and oxygen, has very good agreement with the models although all predicted ignition delay times are accelerated versus the experimental data. The RAMEC model has the best agreement with the experimental data with an average error of 12%. Predicted ignition delay times by RAMEC vary between 54 and 1260 microseconds for the same thermodynamic conditions given above. The GRI model predictions have slightly more than double the error of the RAMEC model, with an average error of 27%. Predicted ignition delay times by GRI vary between 46 and 1074 microseconds. The Curran model is somewhat worse than GRI, having an average error of 33%. The predicted ignition delay times by the Curran model vary between 37 and 1027 microseconds. Both the RAMEC and GRI trend lines appear to have the same slope as the experimental data while the slope of the Curran model prediction line is slightly steeper. This is evidenced by the Curran predictions being slightly worse at higher temperature and approaching the GRI trend line at lower temperatures.

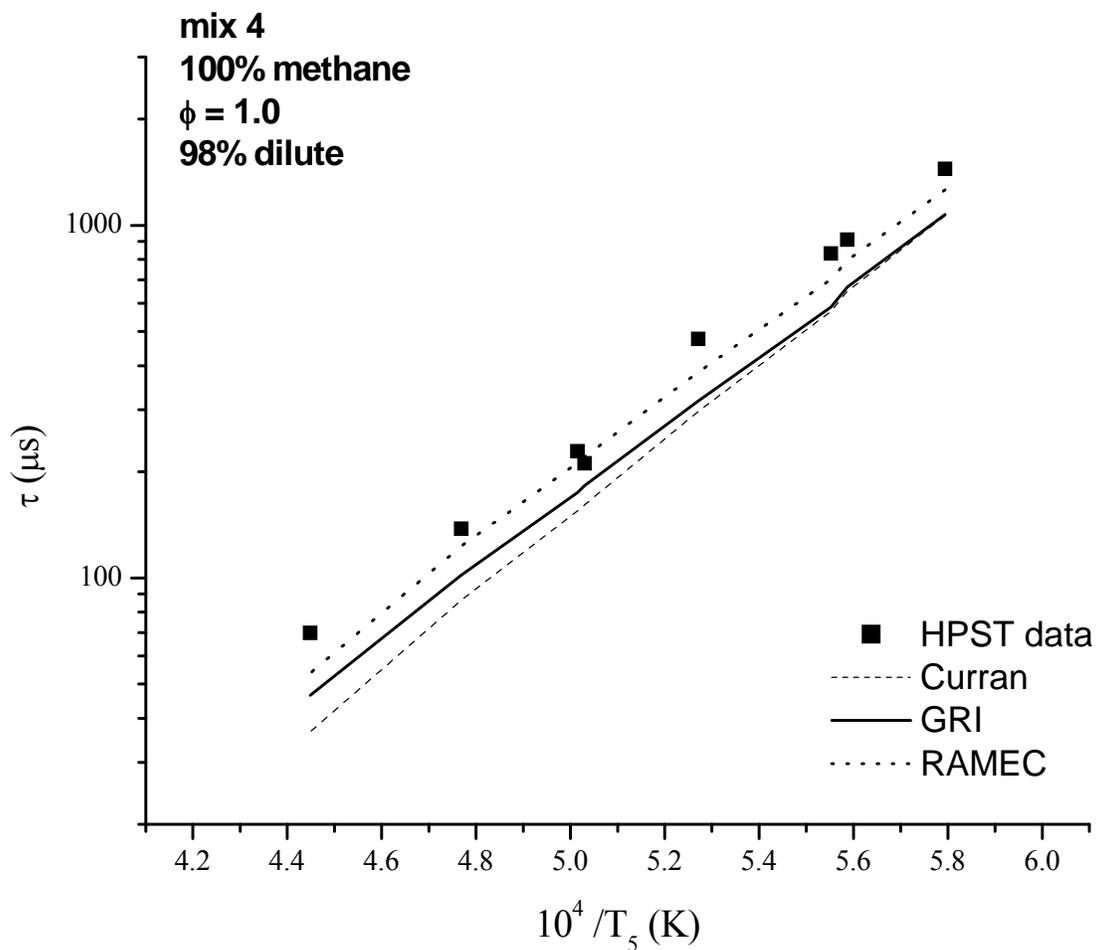


Figure 4-7: Experimental and computed ignition delay times for mix 4

Ignition delay times for mixture 1 are shown in Figure 4-8. The mixture is a highly dilute, fuel-lean (equivalence of 0.5) blend of 75/25 methane/ethane with oxygen. Measured ignition delay times for this mixture varied between 92 microseconds at 1630 K and 1.3 atm and 988 microseconds at 1296 K and 1.4 atm. Both the GRI and Curran models were very poor and

predicted much longer ignition delay times for all test conditions. The calculated ignition delay times vary between 122 and 3111 microseconds for Curran and between 132 and 2246 microseconds for GRI for the tested conditions. The GRI model has a slightly better average error of 89% versus 106% for Curran. The Curran model is better at higher temperatures, above approximately 1450 K, while the GRI model is better below that temperature. The average error for the Curran model above 1450 K is 50%. The average error for the GRI model below 1450 K is 119%. The slope of the Curran model trend line suggests that the relative error of the predicted ignition delay times will become increasingly large with decreasing temperatures below 1300 K.

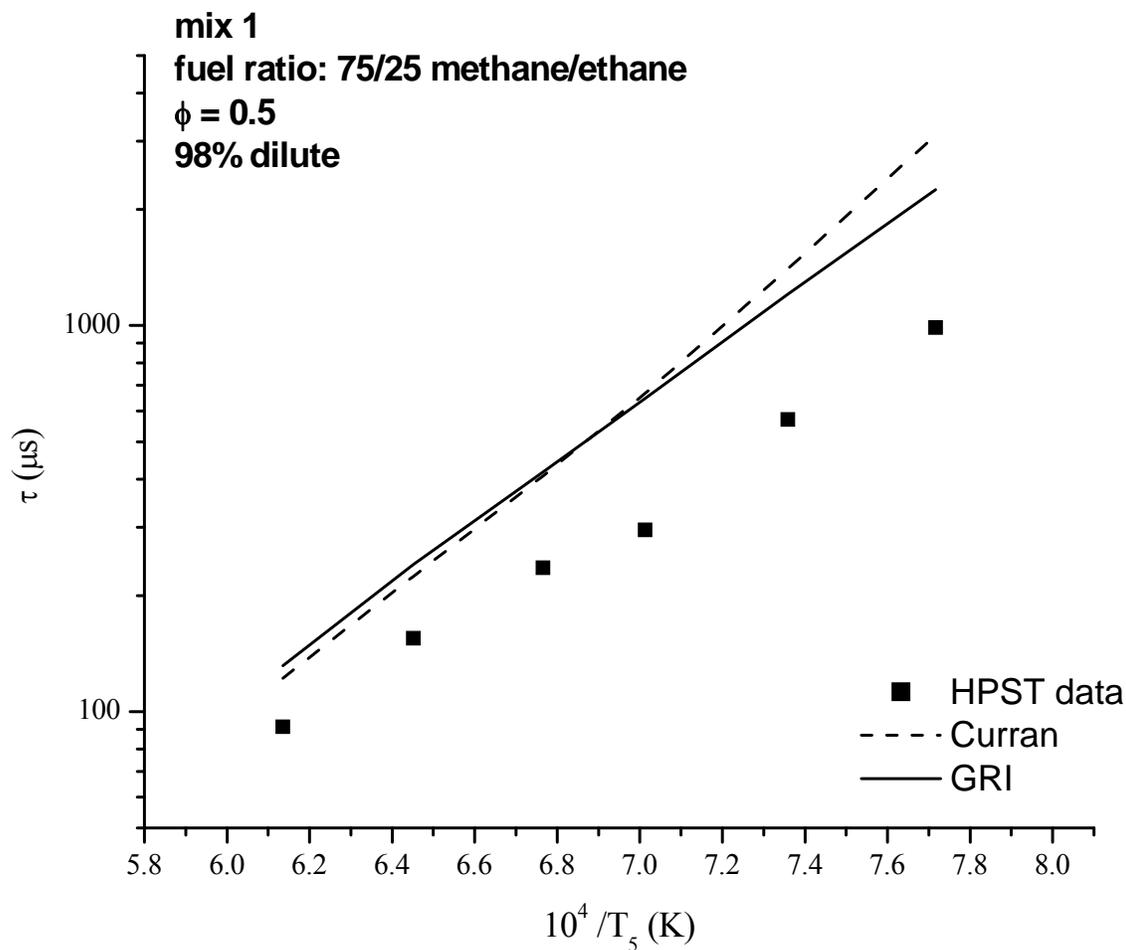


Figure 4-8: Experimental and computed ignition delay times for mix 1

Experimental and computed ignition delay times for mixture 2 are shown in Figure 4-9. The mixture is a highly diluted (98% argon), fuel-lean (equivalence of 0.5) blend of 50/50 methane/ethane with oxygen. Experimental ignition delay times measured between 77.9 microseconds at 1571 K and 1.3 atm and 1002 microseconds at 1268 K and 1.4 atm. The GRI model is noticeably better than the Curran model over most of the tested conditions, save for

temperatures above approximately 1500 K where the Curran model is more accurate than GRI. Curran predicts ignition delay times of 112.5 to 2341 microseconds, and GRI predicts ignition delay times of 123 to 1562 microseconds over the range of tested conditions. The error of the GRI model varies from 23 to 60% over the range of test conditions, with an average error of 45%. The Curran model error varies from 21 to 134%, with an average of 75%. The GRI trend line has a similar slope to the experimental data and the Curran trend line is slightly steeper, again with increasingly larger relative error with decreasing temperature.

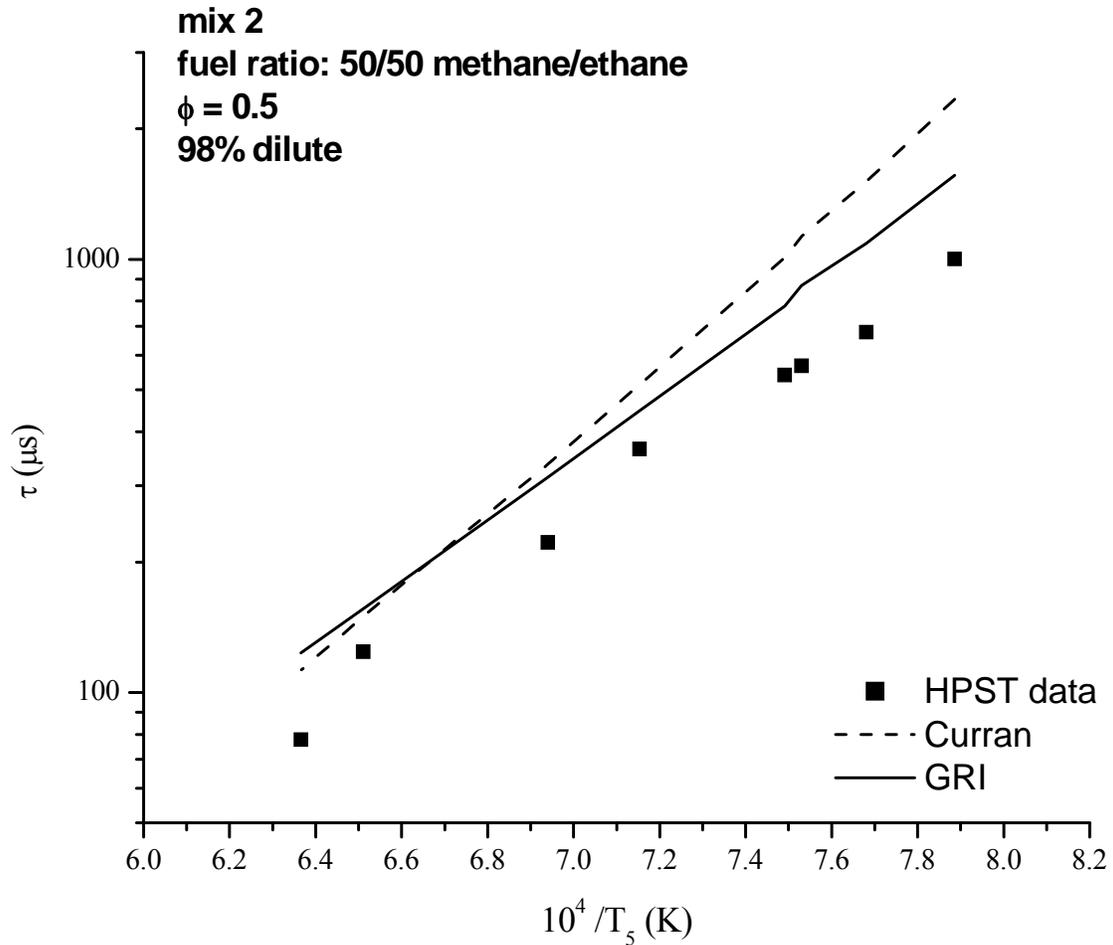


Figure 4-9: Experimental and computed ignition delay times for mix 2.

Ignition delay times for mixture 3 are shown in Figure 4-10. The mixture is a highly dilute (98% argon), stoichiometric blend of 25/75 methane/ethane with oxygen. Experimental ignition delay times measured from 55 microseconds at 1700 K and 1.3 atm to 1032 microseconds at 1324 K and 1.4 atm. The GRI model has excellent agreement with the experimental data over the tested temperature range, predicting 60 to 1138 microseconds, with an average error of 6.0% (ranging

from 2 to 12%). The Curran model predicts ignition delay times of 55 to 2021 microseconds. Like for the other highly diluted mixtures, the Curran model trend line is steeper than the experimental data and over predicts ignition delay times over the entire temperature range, except for temperatures above approximately 1640 K, and increasingly deviates from the experimental data with decreasing temperature. The error of the Curran model predictions increases linearly with decreasing temperature from 1 to 96%, with an average error of 42%.

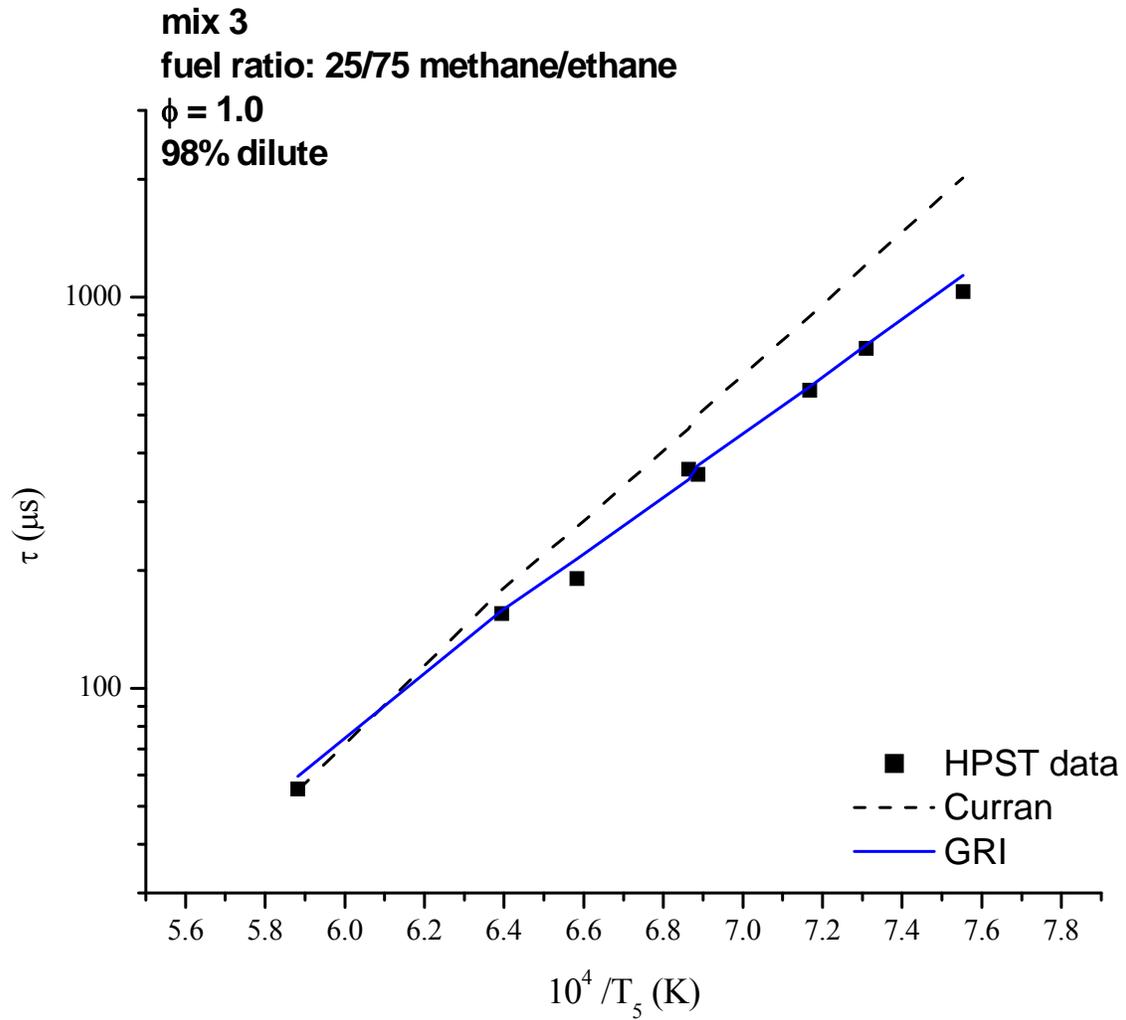


Figure 4-10: Experimental and computed ignition delay times for mix 3.

4.2 Modeling Results

Although some improvements to the kinetics models can be made, the Curran model was used to calculate ignition delay times for mixtures of interest that were not tested experimentally. This

was done to evaluate the individual effect of the fuel blend ratio, equivalence ratio, and dilution amount on ignition delay times.

Plots of model-calculated ignition delay times for several mixtures with varying blends of methane and ethane are shown in Figures 4-11 through 4-14. All mixtures in each individual plot have the same dilution and equivalence ratio. Each plot contains ignition delay time trends for five mixtures with different molar fuel ratios: 100% methane, 100% ethane, and blends of 75/25, 50/50, and 25/75 methane/ethane. Values for the activation energy divided by the ideal gas constant (E/R) were calculated from the slope of each trend line and are presented in Table 4.

Some general trends are apparent in each case. It can be seen that 100% methane is the slowest reacting mixture, and increasing the relative amount of ethane decreases the ignition delay time. The most significant reduction is achieved by the initial addition of ethane. Each successive increase in ethane further decreases the ignition delay time of the mixture, but the incremental effect decreases. The activation energies are generally slightly higher for stoichiometric mixtures versus fuel-lean mixtures and are also generally higher for highly diluted mixtures (98% argon) versus high-concentration mixtures (75% argon).

Calculated ignition delay times for stoichiometric, highly dilute mixtures of methane and ethane with oxygen are shown in Figure 4-11. E/R values range from 25.0 kcal/mol for 100% methane to 20.7 kcal/mol for 100% ethane. The activation energy generally decreases with increasing amounts of ethane, the largest change in activation energy attributed to the initial addition of

ethane. The activation energy for the 50/50 mixture is slightly higher than that for the 75% methane mixture but is probably within the margin of error for the model. There is very little change in the activation energy for mixtures with more than 25% ethane.

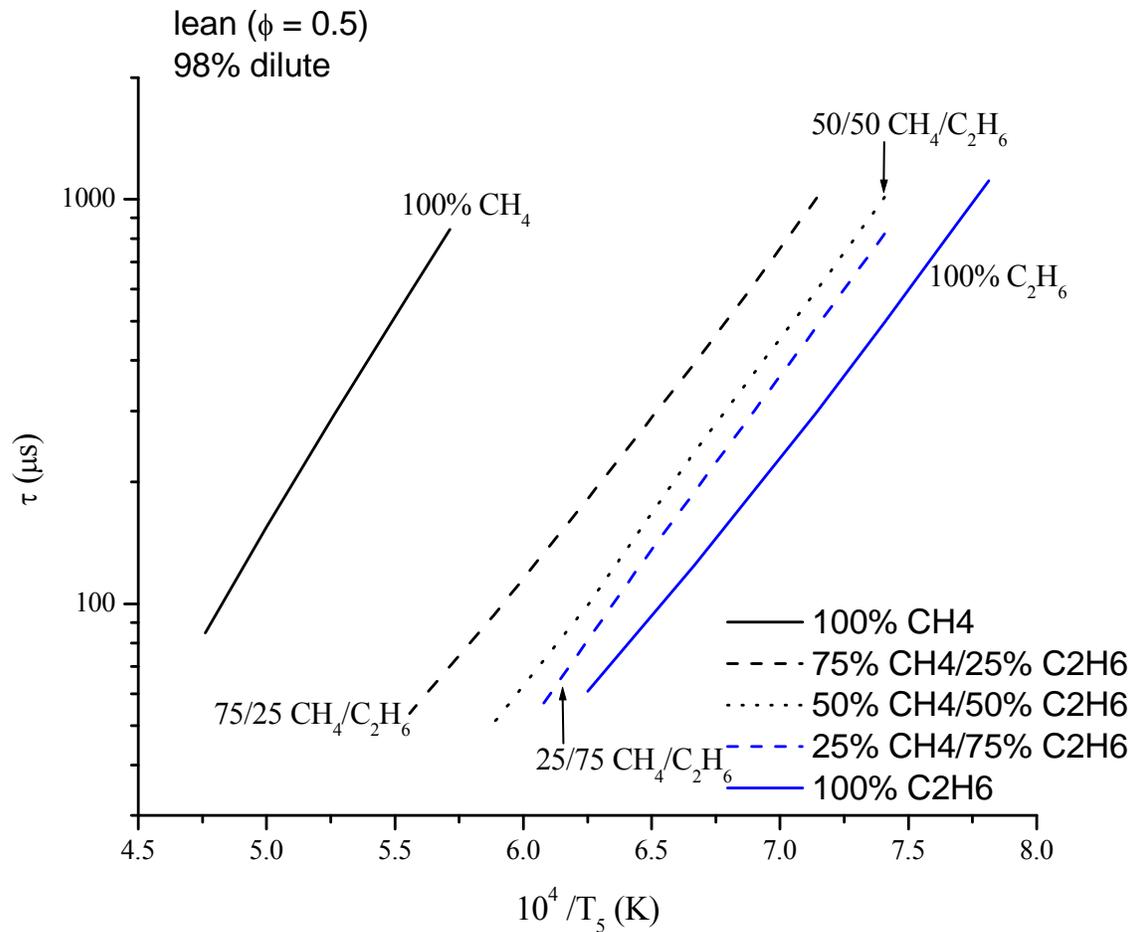


Figure 4-11: Ignition delay times for several stoichiometric, highly dilute blends of methane and ethane with oxygen, calculated by Curran.

Calculated ignition delay times for fuel-lean, highly-dilute mixtures of methane and ethane with oxygen are shown in Figure 4-12. Activation energies range from 24.1 kcal/mol for 100% methane to 18.7 kcal/mol for 100% ethane. Again, the activation energy generally decreases with increasing ethane, although it does increase from 18.5 kcal/mol for 25% ethane to 20.1 kcal/mol for 75% ethane. These changes are small compared to the drop in activation energy of pure methane with the addition of 25% ethane.

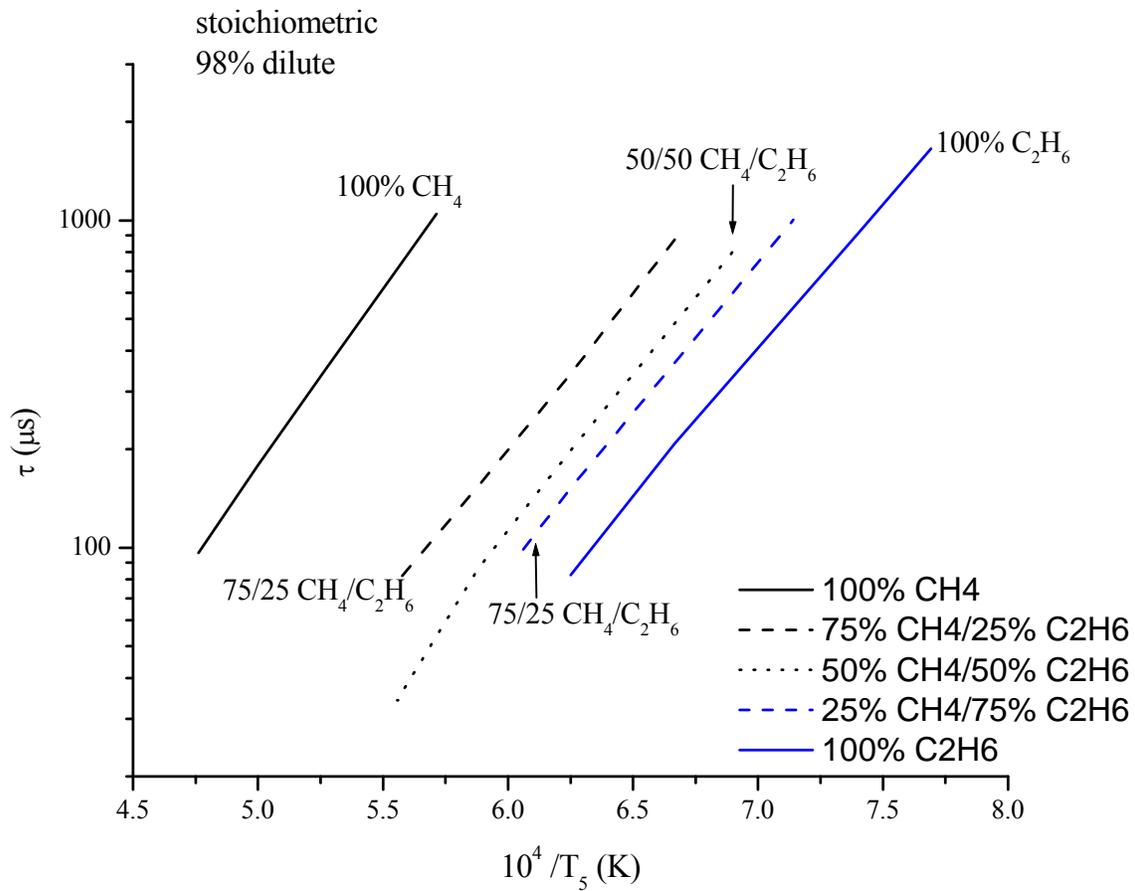


Figure 4-12: Ignition delay times for several fuel-lean, highly dilute blends of methane and ethane with oxygen, calculated by Curran

Calculated ignition delay times for stoichiometric, high-concentration mixtures of methane and ethane with oxygen are shown in Figure 4-13. Activation energies range from 21.0 kcal/mol for 100% methane to 19.1 kcal/mol for 100% ethane. Again, the activation energy decreases with

increasing amounts of ethane but does increase from 17.7 to 19.1 kcal/mol with an increase in ethane from 75 to 100%.

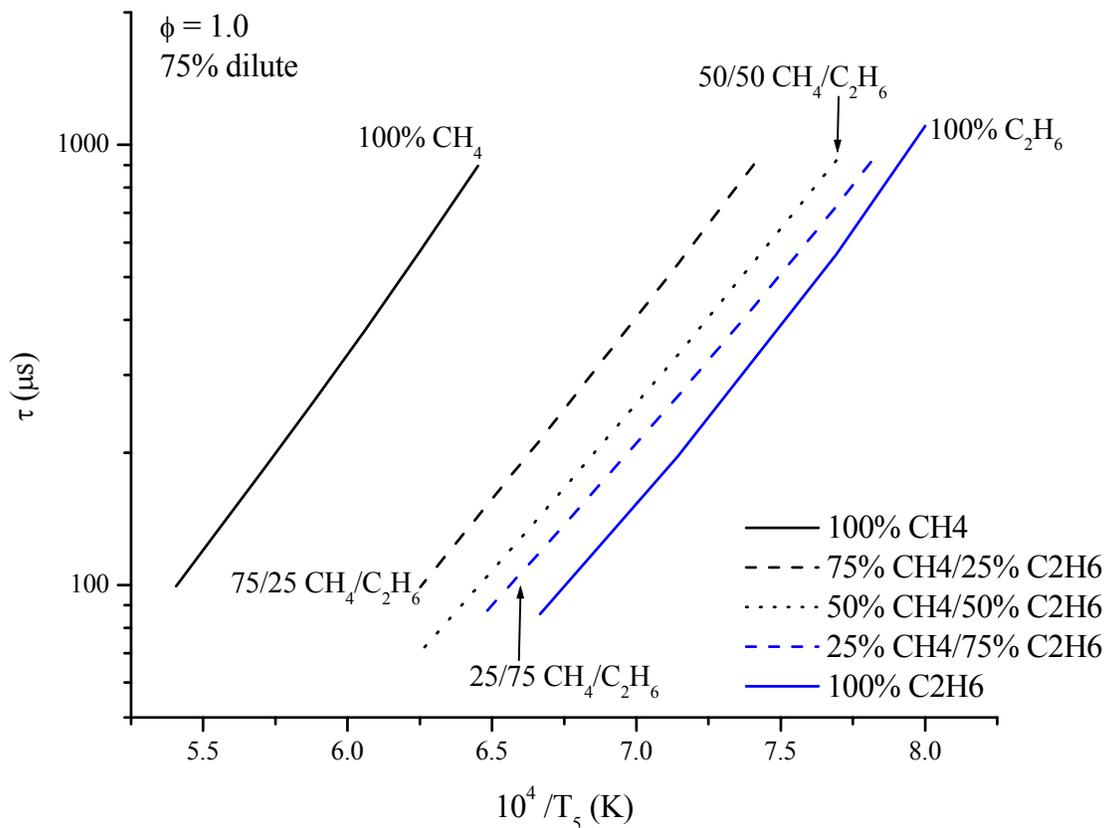


Figure 4-13: Ignition delay times for several stoichiometric, high-concentration blends of methane and ethane with oxygen, calculated by Curran.

Calculated ignition delay times for fuel-lean, high-concentration mixtures of methane and ethane with oxygen are shown in Figure 4-14. Activation energy for pure methane and ethane mixtures is 20.0 and 20.7 kcal/mol, respectively. This is counter to the trend for all other cases but it

should be noted that the overall range of activation energies for these mixtures is fairly small, 19.5 – 20.7 kcal/mol, which is similar to the other high-concentration mixtures plotted in Figure 4-13 but smaller than the high-dilution mixtures in Figures 4-11 and 4-12. The activation energy for these mixtures increases with increasing ethane percentage, from 19.5 kcal/mol for 25% ethane to 20.7 kcal/mol for 100% ethane. It is doubtful any solid conclusions could be made from this trend as it is probably within the margin of error of the model.

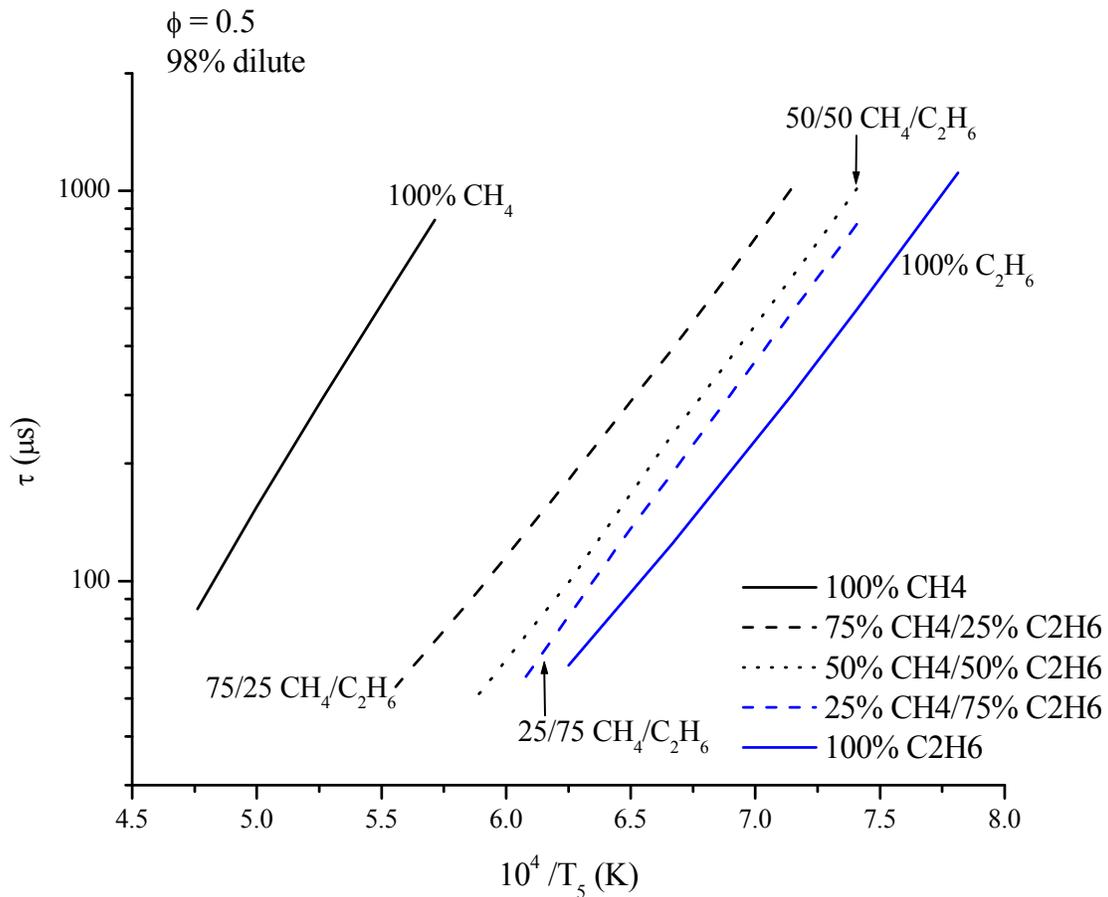


Figure 4-14: Ignition delay times for several fuel-lean, high-concentration blends of methane and ethane with oxygen, calculated by Curran.

Table 4: Activation energies (E/R) of simulated mixtures.

CH ₄ /C ₂ H ₆	Lean, high- concentration	Stoich., high- concentration	Lean, dilute	Stoich., dilute
0/100	20694	19084	18649	20704
25/75	19745	17616	20058	21367
50/50	19601	17854	19750	21813
75/25	19472	19119	18492	21721
100/0	20027	20978	24080	25003

Ignition delay times, calculated using Curran, versus the percentage of ethane in the fuel blend are shown in Figure 4-15. Three trend lines are shown, each for a single temperature (1400, 1500, and 1600 K). Each trend line resembles a decaying exponential and do not appear to vary from each other in behavior. Ignition is clearly accelerated by the addition of ethane and is continuously accelerated as the ethane percentage increases. The effect is most dramatic at low percentages with the majority of the overall reduction (from 100% methane to 100% ethane) seen over the range 0-10%.

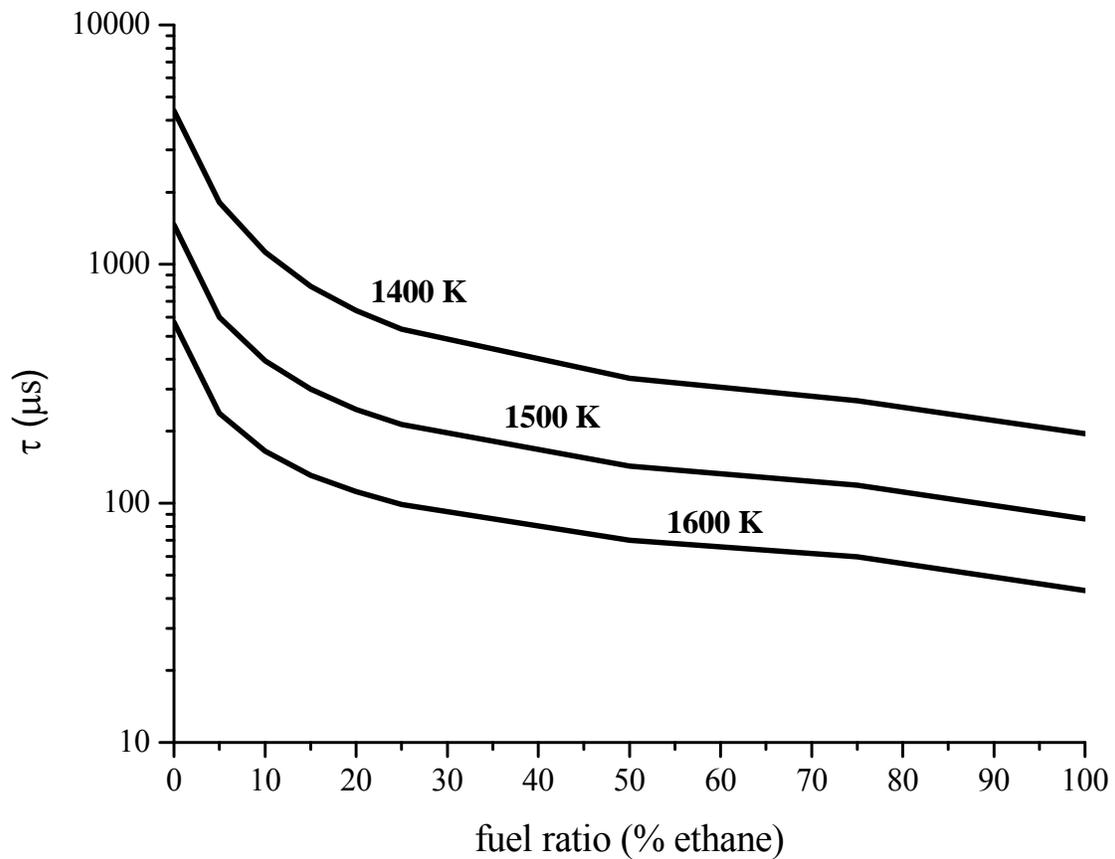


Figure 4-15: Ignition delay times as a function of ethane fuel percentage at three temperatures

Plots of model calculated ignition delay times that demonstrate the effect of equivalence ratio are shown in Figures 4-16 through 4-24. All mixtures shown in each individual plot have the same fuel blend ratio and level of dilution. Again, all model simulations were conducted at 1 atm. Some general trends are evident. For all cases, the fuel-lean mixture reacts more quickly than the equivalent stoichiometric mixture over the entire temperature range. For highly dilute

mixtures, the activation energy is higher for the lean mixture by 9.5% on average, except for the 100% methane mixtures, where the activation energy of the stoichiometric mixture is 4.7% higher than the lean mixture. In contrast, for high-concentration mixtures, the activation energy of the stoichiometric mixture is higher by 5.2% on average.

Plots of model-calculated ignition delay times that demonstrate the effect of dilution are shown in Figures 4-25 through 4-34. Again, all mixtures shown in each individual plot have the same fuel blend ratio and equivalence ratio. All model simulations were conducted at 1 atm. For all cases, the high-concentration mixture (75% argon) reacts quicker than the equivalent highly dilute mixture (98% argon). This makes sense because the high-concentration mixtures have a higher density of reactive components which should accelerate the ignition process. For stoichiometric mixtures, the activation energy of the dilute mixture is 16.9% higher, on average, than the equivalent high-concentration mixture. There does not seem to be any similar effect with lean mixtures as neither dilute or high-concentration mixtures have consistently higher activation energies. On average, the activation energy of lean, dilute mixtures is 1.5% higher. The most dramatic difference in activation energy exists between the dilute and high-concentration mixtures of 100% methane. The activation energy of the dilute mixtures is 20.2% and 19.2% higher for both lean and stoichiometric mixtures, respectively.

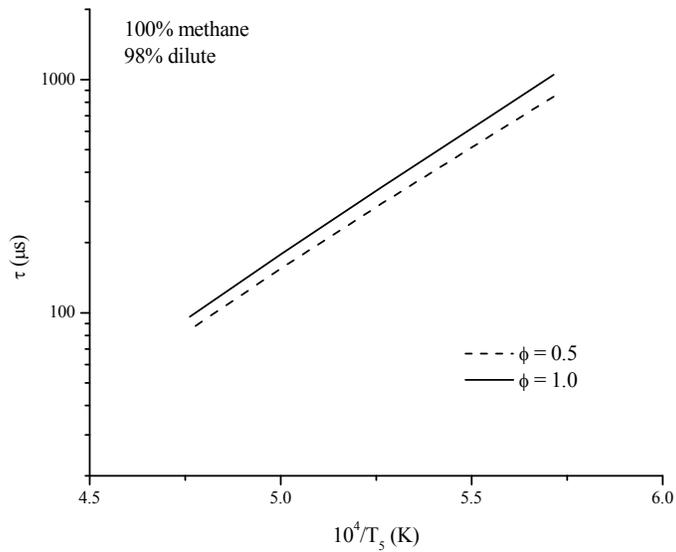


Figure 4-16: Ignition delay times for highly dilute mixtures of methane with oxygen at different equivalence ratios, calculated using Curran.

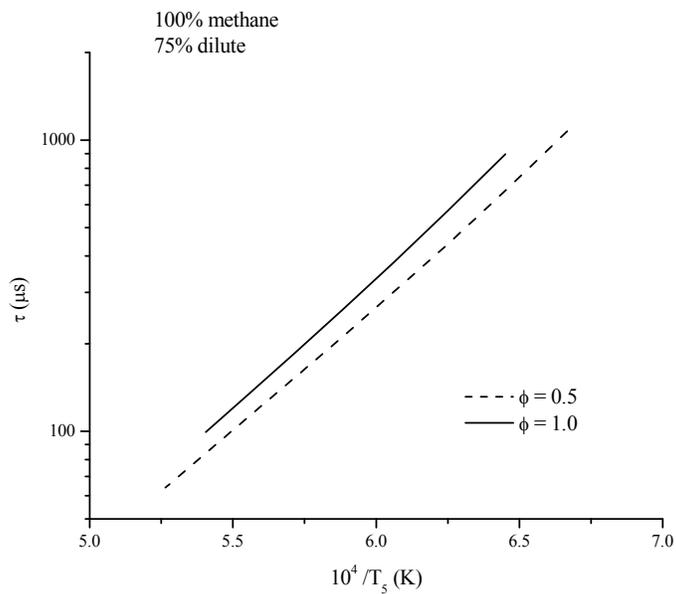


Figure 4-17: Ignition delay times for high concentration mixtures of methane with oxygen at different equivalence ratios, calculated using Curran.

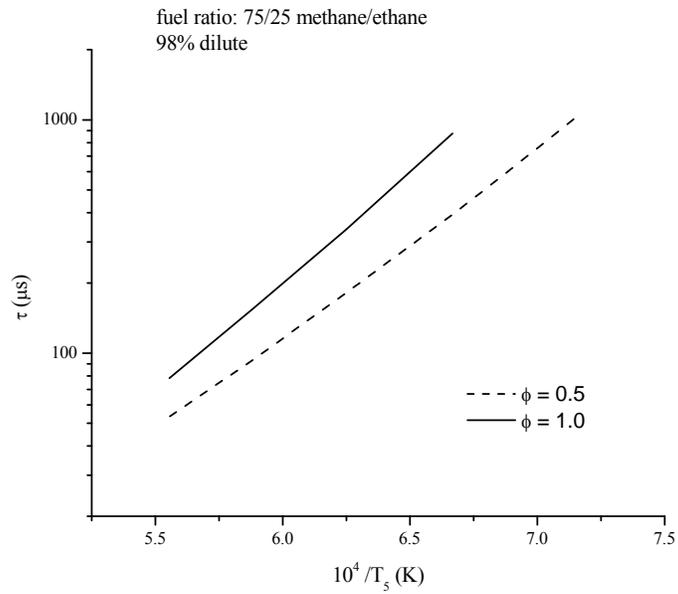


Figure 4-18: Ignition delay times for high dilution mixtures of 75/25 methane/ethane blends with oxygen at different equivalence ratios, calculated using Curran.

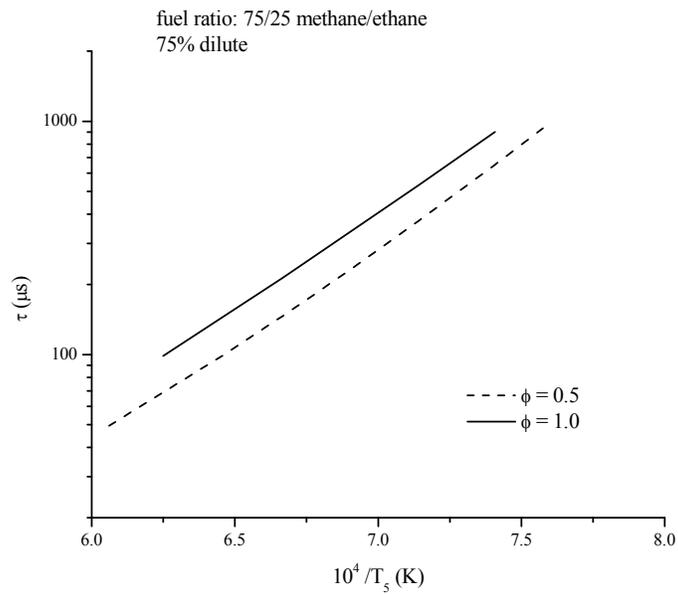


Figure 4-19: Ignition delay times for high concentration mixtures of 75/25 methane/ethane blends with oxygen at different equivalence ratios, calculated using Curran.

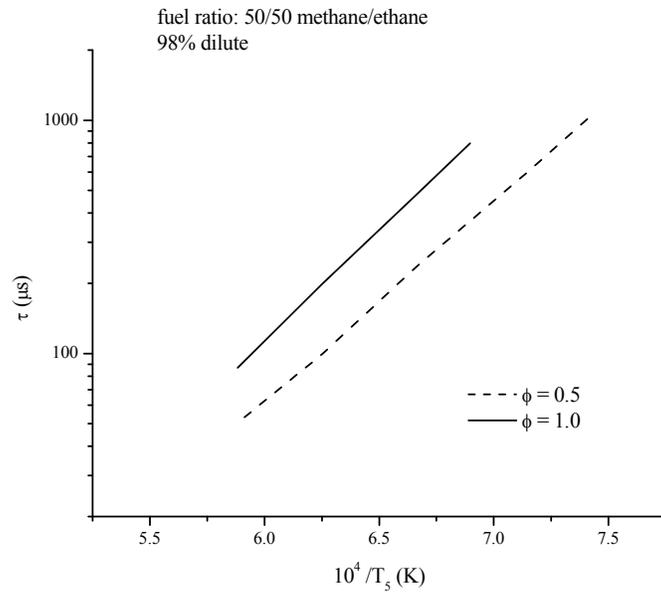


Figure 4-20: Ignition delay times for high dilution mixtures of 50/50 methane/ethane blends with oxygen at different equivalence ratios, calculated using Curran.

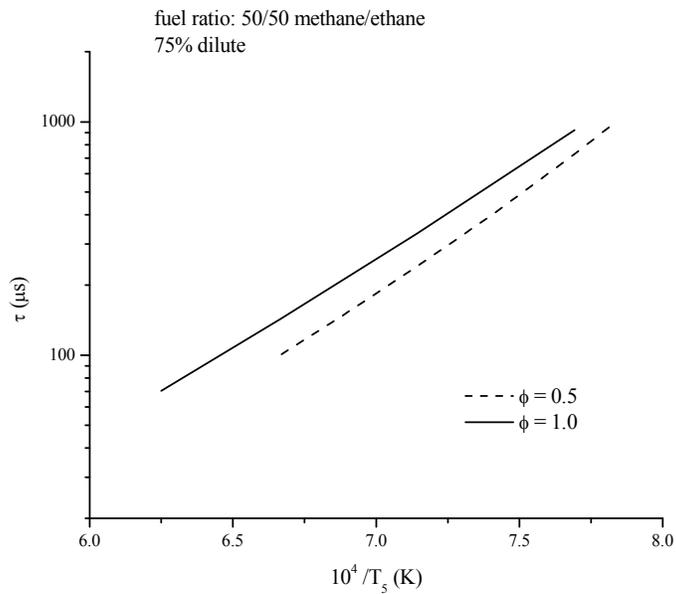


Figure 4-21: Ignition delay times for high concentration mixtures of 50/50 methane/ethane blends with oxygen at different equivalence ratios, calculated using Curran.

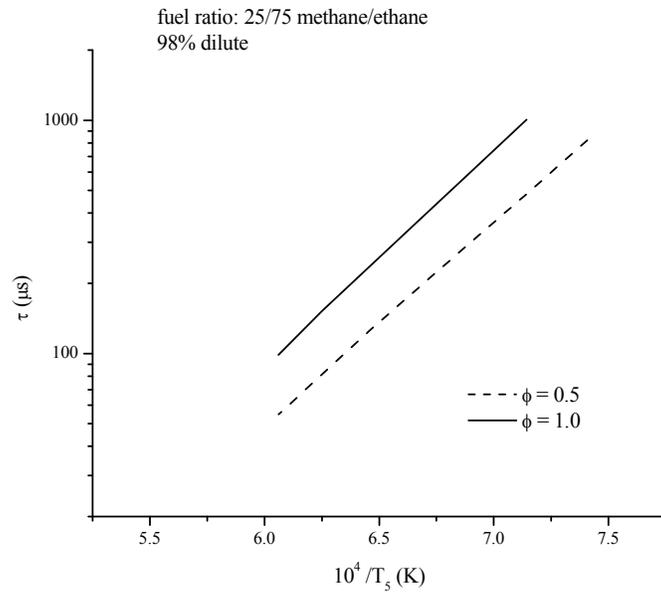


Figure 4-22: Ignition delay times for high dilution mixtures of 25/75 methane/ethane blends with oxygen at different equivalence ratios, calculated using Curran.

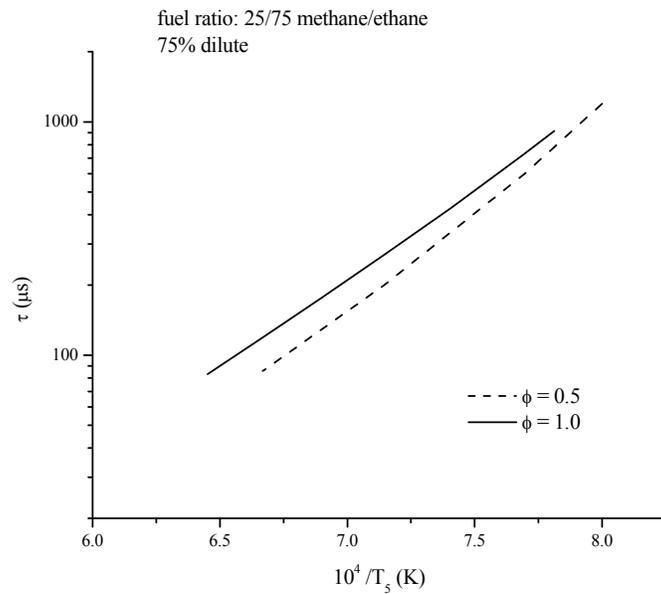


Figure 4-23: Ignition delay times for high concentration mixtures of 25/75 methane/ethane blends with oxygen at different equivalence ratios, calculated using Curran.

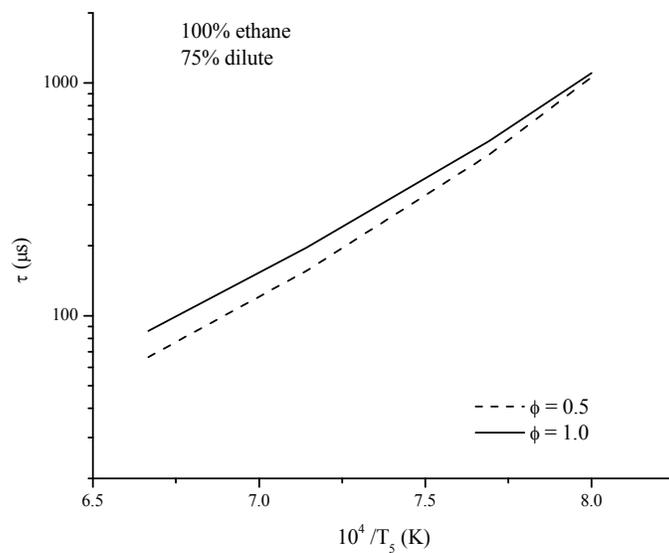


Figure 4-24: Ignition delay times for high concentration mixtures of ethane with oxygen at different equivalence ratios, calculated using Curran.

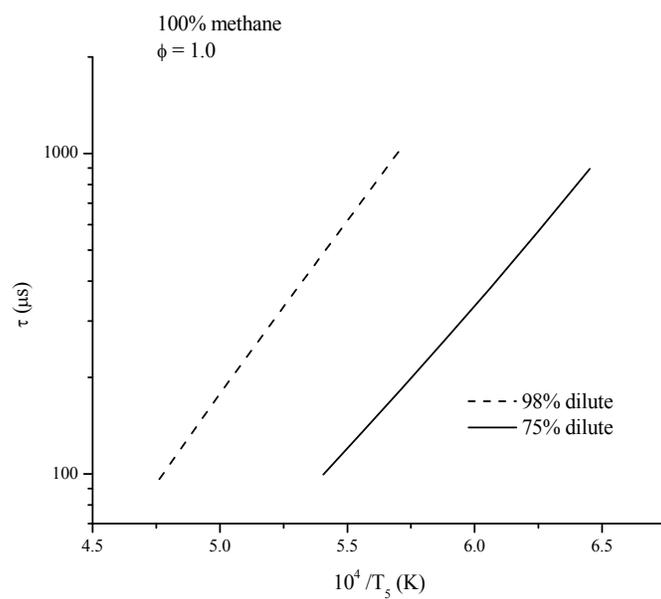


Figure 4-25: Ignition delay times for stoichiometric mixtures of methane with oxygen at different dilution levels, calculated using Curran.

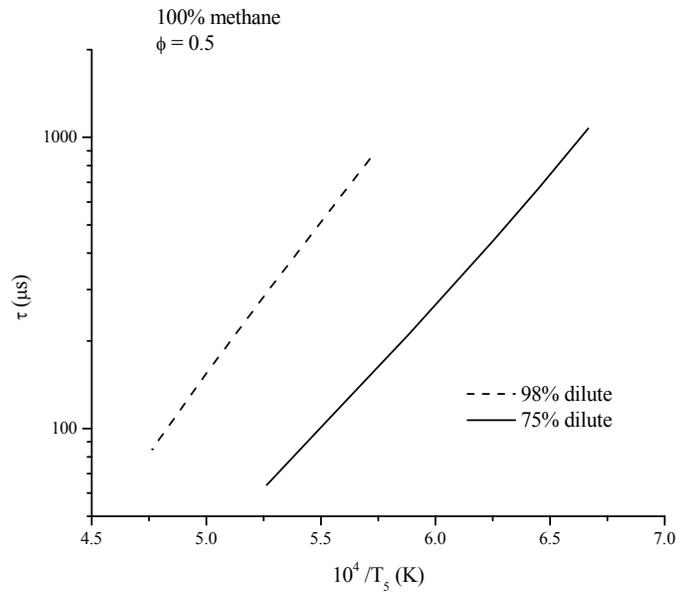


Figure 4-26: Ignition delay times for fuel-lean mixtures of methane with oxygen at different dilution levels, calculated using Curran.

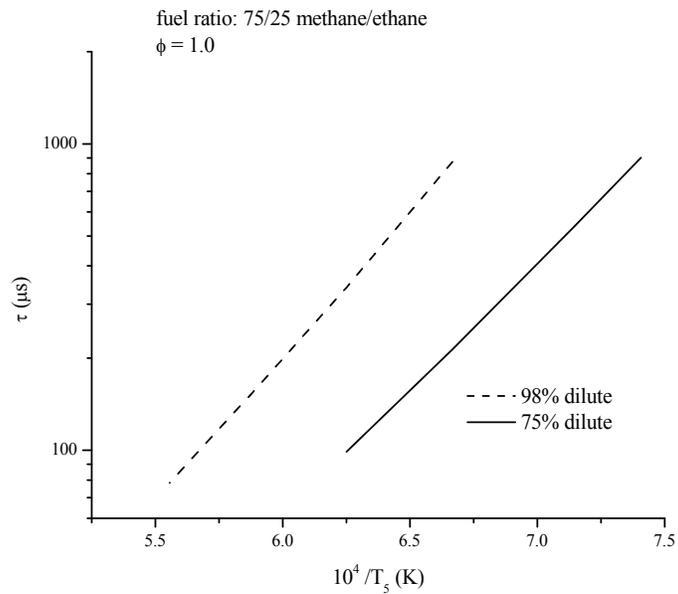


Figure 4-27: Ignition delay times for stoichiometric mixtures of 75/25 methane/ethane blends with oxygen at different dilution levels, calculated using Curran.

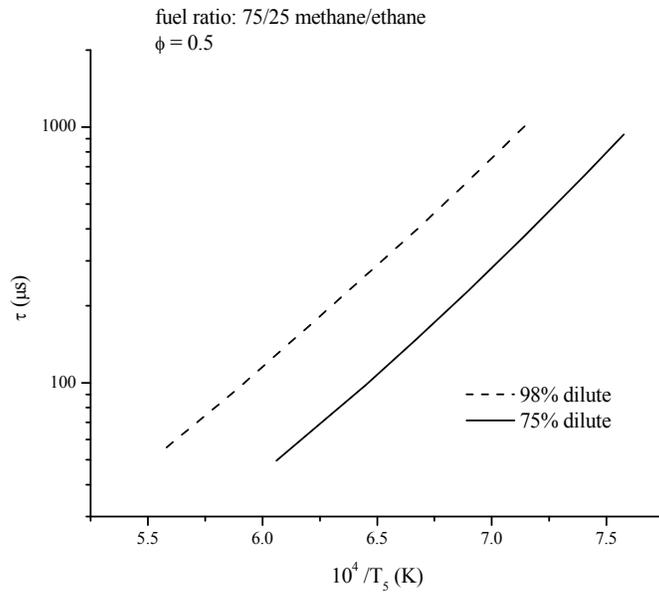


Figure 4-28: Ignition delay times for fuel-lean mixtures of 75/25 methane/ethane blends with oxygen at different dilution levels, calculated using Curran.

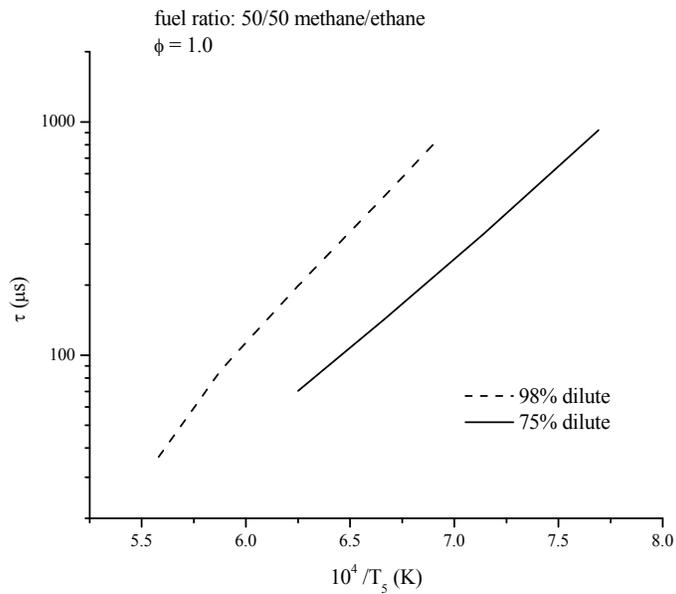


Figure 4-29: Ignition delay times for stoichiometric mixtures of 50/50 methane/ethane blends with oxygen at different dilution levels, calculated using Curran.

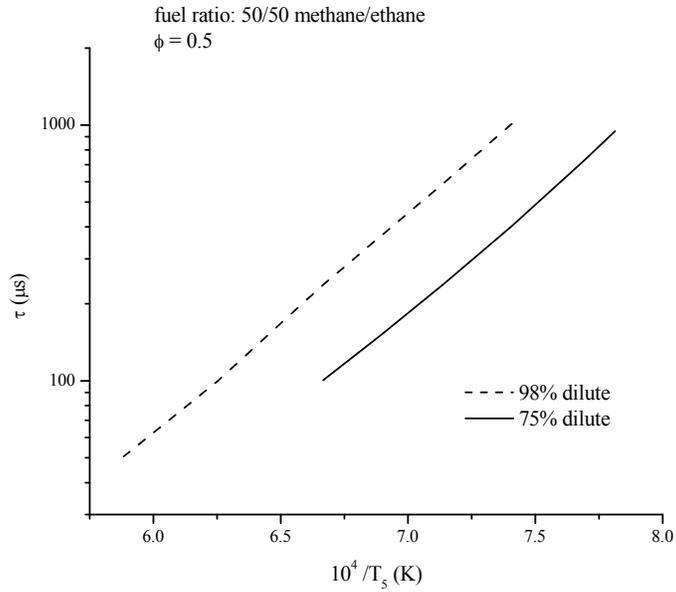


Figure 4-30: Ignition delay times for fuel-lean mixtures of 50/50 methane/ethane blends with oxygen at different dilution levels, calculated using Curran.

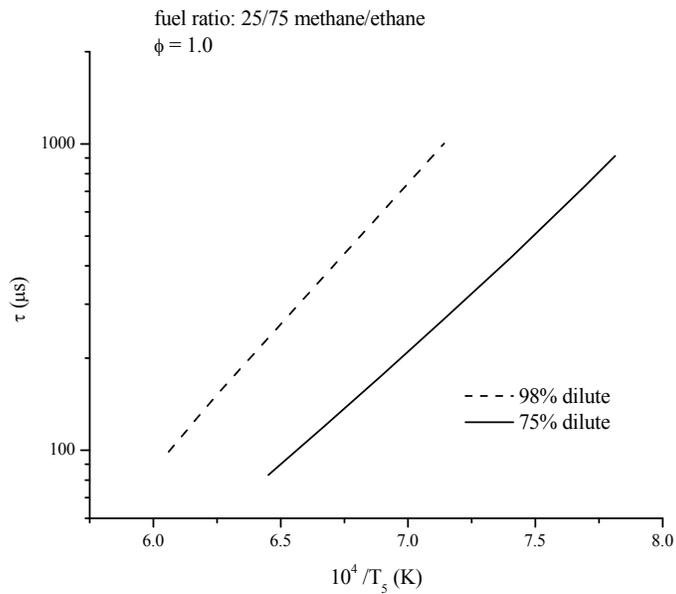


Figure 4-31: Ignition delay times for stoichiometric mixtures of 25/75 methane/ethane blends with oxygen at different dilution levels, calculated using Curran.

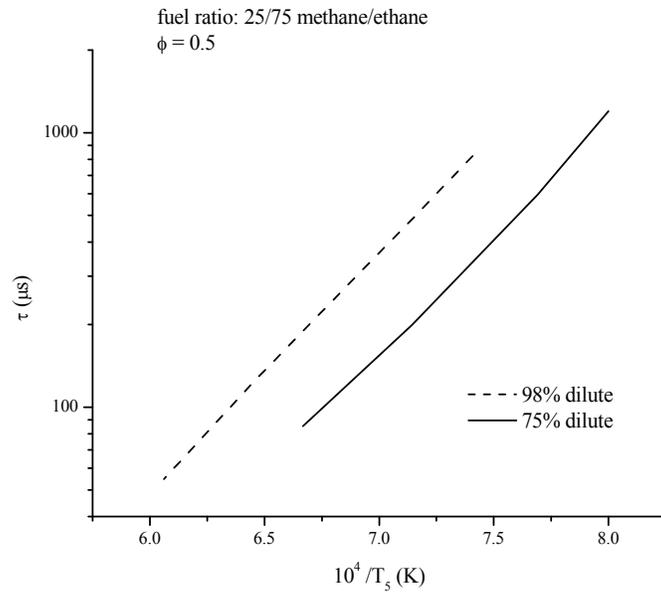


Figure 4-32: Ignition delay times for fuel-lean mixtures of 25/75 methane/ethane blends with oxygen at different dilution levels, calculated using Curran.

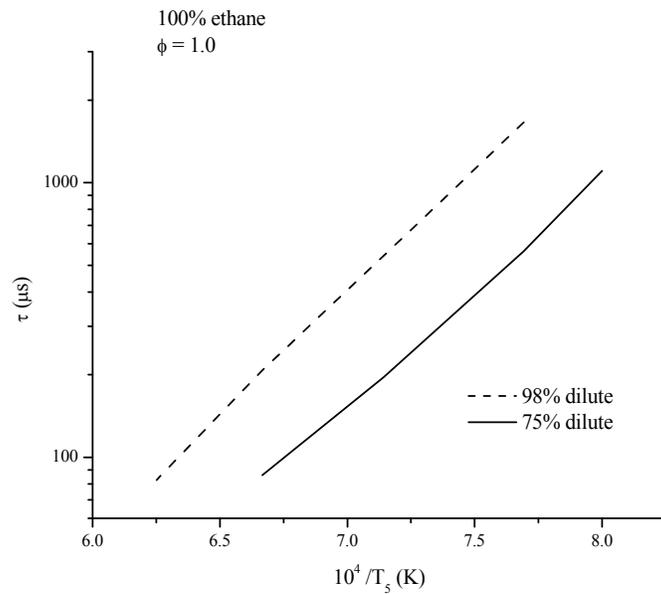


Figure 4-33: Ignition delay times for stoichiometric mixtures of ethane with oxygen at different dilution levels, calculated using Curran.

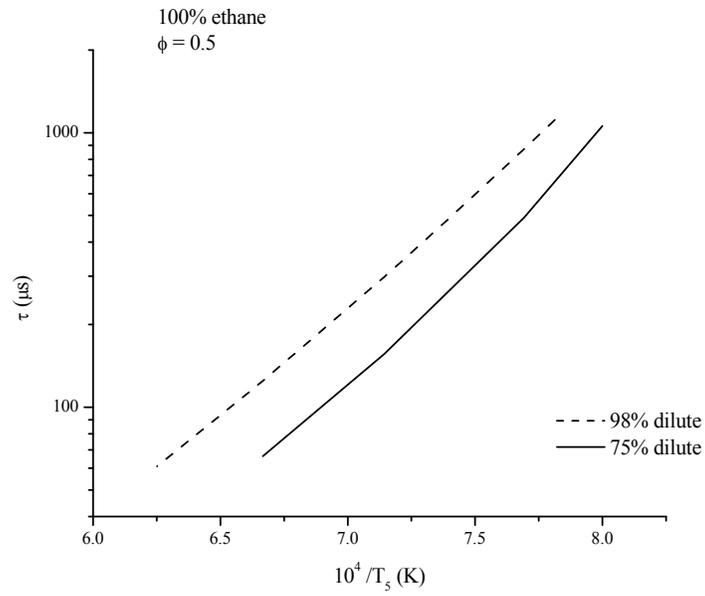


Figure 4-34: Ignition delay times for fuel-lean mixtures of ethane with oxygen at different dilution levels, calculated using Curran.

CHAPTER 5: SUMMARY

A series of shock-tube experiments has been performed on a group of ten mixtures of CH₄/C₂H₆ blends with oxygen diluted in argon. Data was collected over a wide range of varying concentrations, fuel blend ratios, and equivalence ratios (0.5 and 1.0). Post-reflected shock conditions were studied over the temperature range 1180 to 2248 K and pressure range 0.763 to 1.417 atm using a new shock tube at the University of Central Florida Gas Dynamics Laboratory. Mixtures were diluted with either 75 or 98% argon by volume. The fuel blend ratio was varied between 100% CH₄ and 100% C₂H₆. Reaction progress was monitored by observing chemiluminescence emission from CH* at 431 nm and the pressure. Ignition delay times and CH* time histories were measured and compared to predictions from three detailed chemical kinetics mechanisms.

Ignition delay time data was internally consistent for each mixture and fell close to a linear trend line when plotted as the natural log of ignition delay time versus inverse temperature. A direct comparison with previous studies is not possible since these specific blend ratios of methane and ethane have not been tested before.

The models agree well with the experimental data for mixtures of 100% methane but model accuracy varies wildly for all the other tested mixtures. The GRI model is very accurate for the stoichiometric 25/75 methane/ethane blend at 98% dilution, which is surprising given that the

model was optimized to 100% methane. The Curran model also does well at predicting ignition delay times for the stoichiometric 25/75 methane/ethane blend at 98% dilution (although not as well as the GRI model at low temperatures) and has excellent agreement with the high-concentration (75% dilution) stoichiometric 75/25 methane/ethane blend and fuel-lean 50/50 blend. Overall, the agreement of the models with the data is mixed but this is not unexpected, as they were optimized to experimental data that do not encompass the mixtures tested in this study. As mentioned above, the GRI model was baselined to 100% methane. Conversely, the Curran model was specifically designed for the combustion of methane and ethane, with reactions for heavier fuels added to the base mechanism

Some general trends of the models are directly observable. For the high-dilution mixtures, both GRI and Curran become more accurate as the ethane percentage increases. The Curran model is more consistent for these mixtures, predicting longer ignition times for all mixtures except the 100% methane mixture. Predictions by both models become slower relative to the experimental data as the ethane percentage increases for high-concentration mixtures. Again, the Curran model is more consistent across the range of blends while the GRI model predictions shift drastically, ranging from extremely accelerated ignition for the 25/75 methane/ethane mixture to doubling the ignition times for the 75/25 blend mixture.

As the Curran model was more consistent for all mixtures, it was used to conduct trend analyses. This was done by simulating untested mixtures in order to perform direct comparisons of mixtures to eliminate combined effects of multi-variables (dilution percentage, equivalence ratio,

and blend ratio). It was demonstrated that both lower dilution and fuel-lean conditions contribute in reducing the ignition delay time for all mixtures studied. It was also demonstrated that increasing the fuel ratio of ethane significantly reduces the ignition delay time under all conditions studied.

Trends with the activation energy of the mixtures are unclear. It was expected that the activation energy would reduce as the fuel ratio of ethane increased and gradually approach the activation energy of pure ethane, which is somewhat lower than methane. Preliminary data suggests that this is the case but not much beyond this conclusion can be stated with high confidence based on the analyses conducted thus far. More simulations need to be run to provide more resolution for plotting activation energies versus the fuel blend ratio.

One of the goals of this study was to determine with some confidence when ethane oxidation becomes dominant over methane oxidation. Unfortunately, this cannot be answered based on the data set collected thus far. There is no clear transition point or minimum in the activation energies that would suggest when this takes place. More resolution is needed through testing and/or simulating more methane/ethane blend ratios. The transition point may be dependent on the equivalence ratio and dilution percentage.

A broad set of ignition delay time data and CH^* time histories has been provided by this study that should provide valuable information for the future improvement of chemical kinetics models for the oxidation and ignition of blends of methane and ethane. The disagreement between the

experimental data and model predictions at the test conditions has demonstrated the need for refinement of the models. The base chemical reactions seem to be correct but temperature dependencies clearly need to be refined.

It is recommended that further work to expand upon this study should involve obtaining ignition delay times for more mixtures of methane/ethane blends, especially in the range of 10 – 50% ethane. Measuring quantitative OH* time histories would benefit chemical kinetic models by providing baseline data to test to. The most benefit would come from identifying key chemical reactions of the ignition of methane/ethane blends and conducting a sensitivity analysis on those reactions.

REFERENCES

- Aul, C. J., de Vries, J., and Petersen, E. L. (2007) "New Shock-Tube Facility for Studies in Chemical Kinetics at Engine Conditions", paper presented at the Eastern States Fall Technical Meeting of Chemical and Physical Processes in Combustion, University of Virginia
- Bakali, A. E., Dagaut, P., Pillier, L., Desgroux, P., Pauwels, J.-F., Rida, A., and Meunier, P. (2004) "Experimental and Modeling Study of the Oxidation of Natural Gas in a Premixed Flame, Shock Tube, and Jet-stirred Reactor", *Combustion and Flame* 137:109-128
- Bhaskaran, Frank, and Just (1980) Twelfth Symposium (Intl.) on Shock Tube Waves, Jerusalem, pp. 503-513
- Borisov, Dragalova, Lisyanskii, Skachkov, and Zamanskii (1983) "Kinetics and Mechanism of Methane Oxidation at High Temperature", *Oxid. Commun* 4:45
- Bowman, C. T. (1970) "An Experimental and Analytical Investigation of the High-Temperature Oxidation Mechanisms of Hydrocarbon Fuels", *Combustion Science and Technology* 2:161-172
- Bowman, C. T. (1975) *Proceedings of the Combustion Institute* 15:869-882
- Brabbs, T. A., and Brokaw, R. S. (1975) "Shock Tube Measurements of Specific Reaction Rates in the Branched Chain CH₄-CO-O₂ System", *Proceedings of the Combustion Institute* 15:893-901
- Bradley, J. N., and Frend, M. A. (1971) "Single-Pulse Shock Tube Studies of Hydrocarbon Analysis. II. The Pyrolysis of Ethane", *Journal of Physical Chemistry* 75:1492-1501
- Buda, F., Bounaceur, R., Warth, V., Glaude, P. A., Fournet, R., and Battin-Leclerc, F. (2005) "Progress toward a unified detailed kinetic model for the autoignition of alkanes from C₄ to C₁₀ between 600 and 1200 K", *Combustion and Flame* 142:170-186
- Burcat, A., Scheller, K., and Lifshitz, A. (1971) "Shock-Tube Investigation of Comparative Ignition Delay Times for C1-C5 Alkanes", *Combustion and Flame* 16:29-33
- Burcat, Lifshitz, Scheller, and Skinner (1971a) "Shock-Tube Investigation of Ignition in Propane-Oxygen-Argon Mixtures", *Proceedings of the Combustion Institute* 13:745
- Burcat, A., Crossley, R. W., Scheller, K., and Skinner, G. B. (1972) "Shock tube investigation of ignition in ethane-oxygen-argon mixtures", *Combustion and Flame* 18:115-123
- Cheng, R. K., and Oppenheim, A. K. (1984) "Autoignition In Methane-Hydrogen Mixtures", *Combustion and Flame* 58:125-139

Chevalier, C. (1993) Dissertation, Universitat Stuttgart

Chiang, C.-C., and Skinner, G. B. (1981) "Resonance Absorption Measurements of Atom Concentrations in Reacting Gas Mixtures: Pyrolysis of C_2H_6 and C_2D_6 Behind Shock Waves", *Journal of Physical Chemistry* 85:3126-3129

Cooke, D. F., and Williams, A. (1971) "Shock-Tube Studies of the Ignition and Combustion of Ethane and Slightly Rich Methane Mixtures with Oxygen", *Proceedings of the Combustion Institute* 13:757-766

Cooke, D. F., and Williams, A. (1975) "Shock Tube Studies of Methane and Ethane Oxidation", *Combustion and Flame* 24:245-256

Crossley, R. W., Dorko, E. A., Scheller, K., and Burcat, A. (1972) "The Effect of Higher Alkanes on the Ignition of Methane-Oxygen-Argon Mixtures in Shock Waves", *Combustion and Flame* 19:373-378

Curran, H. J., Gaffuri, P., Pitz, W. J., and Westbrook, C. K. (2002) "A Comprehensive Modeling Study of iso-Octane Oxidation", *Combustion and Flame* 129:253-280

Dagaut, P., Boettner, J., and Cathonnet, M. (1991) "Methane Oxidation: Experimental and Kinetic Modeling Study", *Combustion Science and Technology* 77:127-148

Dagaut, P., Cathonnet, M., and Boettner, J.-C. (1991a) "Kinetics of Ethane Oxidation", *International Journal of Chemical Kinetics* 23:437-455

Dagaut, P., Cathonnet, M., and Boettner, J.-C. (1992) J.C., "Kinetic modeling of propane oxidation and pyrolysis", *International Journal of Chemical Kinetics* 24:813-837

Dagaut, P., and Cathonnet, M. (1998) "A Comparative Study of the Kinetics of Benzene Formation from Unsaturated C_2 to C_4 Hydrocarbons", *Combustion and Flame* 113:620-623

de Vries, J., Hall, J. M., Simmons, S. L., Rickard, M. J. A., Kalitan, D. M., and Petersen, E. L. (2007) "Ethane Ignition and oxidation behind reflected shock waves", *Combustion and Flame* 150:137-150

de Vries, J., and Petersen, E. L. (2007) "Autoignition of methane-based fuel blends under gas turbine conditions", *Proceedings of the Combustion Institute* 31:3163-3171

Dean, A. M., and Kistiakowsky, G. B. (1971) "Oxidation of Carbon Monoxide/Methane Mixtures in Shock Waves", *Journal of Chemical Physics* 54:1718-1725

Dryer, F. L. (1972) Ph.D. Thesis, Princeton University, Department of Aerospace and Mechanical Sciences

- Dryer, F. L. and Glassman, I. (1973) "High-Temperature Oxidation of CO and CH₄", *Proceedings of the Combustion Institute* 14:987-1003
- Engleman, V. S. (1976) EPA Technical Report, EPA-600/2-76-003
- Eubank, C. S., Rabinowitz, M. J., Gardiner, W. C., and Zellner, R. E. (1981) "Shock-initiated Ignition of Natural Gas-Air Mixtures", *Proceedings of the Combustion Institute* 18:1767-1774
- Frank and Braun-Unkhoff (1987) Proc. Sixteenth Symposium (Intl.) on Shock Tube Waves, Aachen, 379-385
- Frenklach, M., Wang, H., and Rabinowitz, M. (1992), "Optimization and analysis of large chemical kinetic mechanisms using the solution mapping method—combustion of methane", *Progress in Energy and Combustion Science* 18:47-73
- Frenklach, M. and Bornside, D. E. (1984) "Shock-initiated ignition in methane-propane mixtures", *Combustion and Flame* 56:1-27
- Glarborg, P., Miller, J. A., and Kee, R. J. (1986) "Kinetic Modeling and Sensitivity Analysis of Nitrogen Oxide Formation in Well-Stirred Reactors", *Combustion and Flame* 65:177-202
- Glarborg, P., Alzueta, M. U., Dam-Johansen, K., and Miller, J. A. (1998) "Kinetic Modeling of Hydrocarbon/Nitric Oxide Interactions in a Flow Reactor", *Combustion and Flame* 115:1-27
- Goy, C. J., Moran, A. J., and Thomas, G. O. (2001) "Autoignition Characteristics of Gaseous Fuels at Representative Gas Turbine Conditions", 46th ASME International Gas Turbine & Aeroengine Technical Congress – ASME Paper 2001-GT-0051
- Hidaka, Y., Gardiner, W. C., and Eubank, C. S. (1982) "Shock Tube and Modeling Study of the Ignition Chemistry of Small Hydrocarbons", *Communications in Journal of Molecular Science* 2:141-153
- Hidaka, Y., Nagayama, M., and Suga, M. (1978) "The Application of a Quadrupole Mass Spectrometer to a Study of Methane Oxidation in Shock Waves", *Bulletin of the Chemical Society of Japan* 51:1659-1644
- Hidaka, Y., Sato, K., Henmi, Y., Tanaka, H., and Inami, K. (1999) "Shock-Tube and Modeling Study of Methane Pyrolysis and Oxidation", *Combustion and Flame* 118:340-358
- Hidaki, Y., Sato, K., Hoshikawa, H., Nishimori, T., Takahashi, R., Tanaka, H., Inami, K., and Ito, N. (2000) "Shock-tube and modeling study of ethane pyrolysis and oxidation", *Combustion and Flame* 120:245-264

- Hidaka, Y., Shiba, S., Takuma, H., and Suga, M. (1985) "Thermal Decomposition of Ethane in Shock Waves", *International Journal of Chemical Kinetics* 17:441-453
- Hidaka, Y., Tanaka, Y., Kawano, H., and Suga, M. (1981) "Mass Spectrometric Study of C2-Hydrocarbons – Oxidation in Shock Waves", *Mass Spectroscopy* 29:191-198
- Higgin, R. M. R., and Williams, A. (1969) "A Shock-Tube Investigation of the Ignition of Lean Methane and n-Butane Mixtures With Oxygen", *Proceedings of the Combustion Institute* 12:579-590
- Horning, D. C., Davidson, D. F., and Hanson, R. K. (2002) "Study of the High-Temperature Autoignition of n-Alkane/O/Ar Mixtures" *Journal of Propulsion and Power* 18:363-371
- Huang, J., and Bushe, W. K. (2006) "Experimental and Kinetic Study of Autoignition in methane/ethane/air and methane/propane/air mixtures under engine-relevant conditions", *Combustion and Flame* 144:74-88
- Hughes, K. J., Turanyi, T., Clague, A. R., and Pilling, M. J. (2001) "Development and Testing of a Comprehensive Chemical Mechanism for the Oxidation of Methane", *International Journal of Chemical Kinetics* 33:513-538
- Hunter, T. B., Wang, H., and Litzinger, T. A. (1994) "The oxidation of methane at elevated pressures: experiments and modeling", *Combustion and Flame* 94:201-224
- Hunter, T. B., Litzinger, T. A., Wang, H., and Frenklach, M. (1996) "Ethane oxidation at elevated pressures in the intermediate temperature regime: experiments and modeling", *Combustion and Flame* 104:505-523
- Jachimowski, C. J. (1974) "Kinetics of oxygen atom formation during the oxidation of methane behind shock waves", *Combustion and Flame* 23:233-248
- Jacobs, N. F., and Gutman, D. (1971) paper presented at the 161st National Meeting of the American Chemical Society, Los Angeles, CA
- Kalitan, D. M., Hall, J. M., and Petersen, E. L. (2005) "Ignition and Oxidation of Ethylene-Oxygen-Diluent Mixtures with and Without Silane" *Journal of Propulsion and Power* 21:1045-1056
- Kilpinen, P., Glarborg, P., and Hupa, M. (1992) "Reburning Chemistry: A Kinetic Modeling Study", *Industrial & Engineering Chemical Research* 31:1477-1490
- Koshi, M., Ando, H., Oya, M., and Asaba, T. (1975) "Shock Tube Study of Decomposition of Nitric Oxide at High Temperatures" *Proceedings of the Combustion Institute* 15:809-822

- Konnov, A. (2000) Available at <http://homepages.vub.ac.be/~akonnov/science/mechanism/main.html#software>
- Krishnan, K. S., and Ravikumar, R. (1981) "Ignition Delay of Methane in Reflected Shock Waves", *Combustion Science and Technology* 24:239-245
- Lamoureux, N., Paillard, C.-E., and Vaslier, V. (2002) "Low hydrocarbon mixtures ignition delay times investigation behind reflected shock waves", *Shock Waves* 11:309-322
- Lamoureux, N., and Paillard, C.-E. (2003) "Natural gas ignition delay times behind reflected shock waves: Application to modelling and safety", *Shock Waves* 13:57-68
- Lee, W.-M., and Yeh, C.-T. (1979) "Computer Simulation Studies of Ethane Pyrolysis in Shock Tubes at 1206 K", *Journal of Physical Chemistry* 83:771-774
- Li, S. C., and Williams, F. A. (1999) "NO_x formation in two-stage methane-air flames", *Combustion and Flame* 118:399-414
- Li, S.C. and Williams, F.A. (2002) "Reaction Mechanisms for Methane Ignition", *Journal of Engineering for Gas Turbines and Power* 124:471-480
- Lifshitz, A., Scheller, K., Burcat, A., and Skinner, G.B. (1971) "Shock-Tube Investigation of Ignition in Methane-Oxygen-Argon Mixtures", *Combustion and Flame* 16:311-321
- Lin (1966) "The Thermal Decomposition of Ethane: Part I. Initiation and Termination Steps", *Canadian Journal of Chemistry* 44:505
- Lin (1966a) "The Thermal Decomposition of Ethane: Part II. The Unimolecular Decomposition of the Ethane Molecule and the Ethyl Radical", *Canadian Journal of Chemistry* 44:2357
- Marinov, N. M., Pitz, W. J., Westbrook, C. K., Vincitore, A. M., Castaldi, M. J., Senkan, S. M., and Melius, C. F. (1998) "Aromatic and Polycyclic Aromatic Hydrocarbon Formation in a Laminar Premixed n-Butane Flame", *Combustion and Flame* 114:192-213
- McKellar, J. F., and Norrish, R. G. W. (1960) *Proceedings of the Royal Society (London)*, Ser. A, 254:147
- Miller, J.A., and Bowman, C.T. (1989) "Mechanism and Modeling of Nitrogen Chemistry in Combustion", *Progress in Energy and Combustion Science* 15:287-338
- Notzold, D., and Algermissen, J. (1981) "Chemical Kinetics of the Ethane-Oxygen Reaction Part I: High Temperature Oxidation at Ignition Temperatures Between 1400° K and 1800° K", *Combustion and Flame* 40:293-313

- Olson, D. B., and Gardiner, W. C. (1977) "An Evaluation of Methane Combustion Mechanisms", *Journal of Physical Chemistry* 81:2514-2519
- Olson, D. B., and Gardiner, W. C. (1978) "Combustion of Methane in Fuel-rich Mixtures", *Combustion and Flame* 32:151-161
- Olson, D. B., Tanzawa, T., and Gardiner, W. C. (1979) "Thermal Decomposition of Ethane", *International Journal of Chemical Kinetics* 11:23-44
- Petersen, E. L. (1998) "A Shock-Tube and Diagnostics for Chemistry Measurements at Elevated Pressures with Application to Methane Ignition," PhD Thesis, Mechanical Engineering, Stanford University
- Petersen, E. L. (2007a) "On the use of endwall emission as a shock-tube ignition diagnostic"; paper # G08, 5th US Combustion Meeting, Western States Section of the Combustion Institute, University of California at San Diego
- Petersen, E. L., Davidson, D. F., and Hanson, R. K. (1999) "Kinetics modeling of shock-induced ignition in low-dilution CH₄/O₂ mixtures at high pressures and intermediate temperatures", *Combustion and Flame* 117:272-290
- Petersen, E. L., Davidson, D. F., and Hanson, R. K. (1999a) "Ignition Delay Times of Ram Accelerator CH/O/Diluent Mixtures" *Journal of Propulsion and Power* 15:82-91
- Petersen, E. L. and de Vries, J. (2005) "Measuring the Ignition of Fuel Blends Using a Design of Experiments Approach", AIAA paper 2005-1165
- Petersen, E. L., Hall, J. M., Smith, S. D., de Vries, J., Amadio, A., and Crofton, M. W. (2007) "Ignition of Lean Methane-Based Fuel Blends at Gas Turbine Pressures", *ASME Journal of Engineering for Gas Turbines and Power*, Vol. 129
- Petersen, E. L., Rickard M. J. A., Crofton M. W., Abbey E. D., Traum M. J., Kalitan D.M. (2005a) "A Facility for Gas- and Condensed-Phase Measurements Behind Shock Waves", *Measurement Science and Technology* 16:1716-1729
- Petersen, E. L., Rohrig, M., Davidson, D. F., Hanson, R. K., and Bowman, C. T. (1996) "High-Pressure Methane Oxidation Behind Reflected Shock Waves", *Proceedings of the Combustion Institute* 26:799-806
- Petrova, M., and Williams, F. (2006) "A small detailed chemical-kinetic mechanism for hydrocarbon combustion", *Combustion and Flame* 144:526-544
- Pitz, W. J., Westbrook, C. K., and Leppard, W. R. (1991) SAE Trans. paper No. 912315

- Pope, C. J., and Miller, J. A. (2000) "Exploring Old and New Benzene Formation Pathways in Low-Pressure Premixed Flames of Aliphatic Fuels" *Proceedings of the Combustion Institute* 28:1519-1527
- Rickard, M. J. A., Hall, J. M., and Petersen, E. L. (2005) "Effect of silane addition on acetylene ignition behind reflected shock waves" *Proceedings of the Combustion Institute* 30:1915-1923
- Rota, R., Bonini, F., Servida, A., Massimo, M., and Carra, S. (1994) "Validation and Updating of Detailed Kinetic Mechanisms: The Case of Ethane Oxidation", *Industrial and Engineering Chemical Research* 33:2540-2553
- Rotavera, B., and Petersen, E. L. (2007) "Shock-Tube Combustion Studies of Atomized Fuels in the Reflected-Shock Region", AIAA (to be published)
- Roth and Just (1975) *Ber. Bunsenges Phys. Chem.* 79:682-686
- Roth and Just (1979) *Ber. Bunsenges Phys. Chem.* 83:577-583
- Roth, P., and Just, TH. (1984) "Kinetics of the High Temperature, Low Concentration CH₄ Oxidation Verified By H and O Atom Measurements" *Proceedings of the Combustion Institute* 20:807-818
- Seery, D.J. and Bowman, C.T. (1970) "An experimental study and analytical study of methane oxidation behind shock waves", *Combustion and Flame* 14:37-48
- Shim, S., Jeong, H. S., and Shin, S. (1999) "Shock Tube Study of Ignition in Ethane-Oxygen-Argon Mixtures", *Journal of the Korean Chemical Society* 42:575-578
- Skinner, G. B., and Ruehrwein, R. A. (1959) "Shock Tube Studies on the Pyrolysis and Oxidation of Methane", *Journal of Physical Chemistry* 63:1736-1742
- Skinner, G. B., and Ball, W. E. (1960) "Shock Tube Experiments on the Pyrolysis of Ethane", *Journal of Physical Chemistry* 64:1025-1028
- Skinner, G. B., Lifshitz, A., Scheller, K., and Burcat, A. (1972) "Kinetics of Methane Oxidation", *Journal of Chemical Physics* 56:3853-3861
- Smith, G. P., Golden, D. M., Frenklach, M., Moriarty, N. W., Goldenberg, M., Bowman, C. T., Hanson, R. K., Song, S., Gardiner, W. C., Lissianski, V. V., and Qin, Z. (1999) http://www.me.berkeley.edu/gri_mech/
- Spadaccini, L.J., and Colket, M.B. (1994) "Ignition Delay Characteristics of Methane Fuels", *Progress in Energy and Combustion Science* 20:431-460

- Takahashi, K., Inomata, T., Moriwaki, T., and Okazaki, S. (1989) "The addition effects of methyl halides on ethane ignition behind reflected shock waves", *Bulletin of the Chemical Society of Japan* 62:2138-2145
- Tan, Y., Dagaut, P., Cathonnet, M., Boettner, J. C., Bachman, J. S., and Carlier, P. (1994) "Natural Gas and Blends Oxidation and Ignition: Experiments and Modeling", *Proceedings of the Combustion Institute* 25:1563-1569
- Tan, Y., Dagaut, P., Cathonnet, M., and Boettner, J.-C. (1994a) "Oxidation and Ignition of Methane-Propane and Methane-Ethane-Propane Mixtures: Experiments and Modeling", *Combustion Science and Technology*, 103:133-151
- Tan, Y., Dagaut, P., Cathonnet, M., and Boettner, J.-C. (1994b) "Acetylene Oxidation in a JSR From 1 to 10 Atm and Comprehensive Kinetic Modeling", *Combustion Science and Technology* 102:21-55
- Tranter, R.S., Ramamoorthy, H., Raman, A., Brezinsky, K., and Allendorf, M.D. (2002a) "High-pressure single-pulse shock tube investigation of rich and stoichiometric ethane oxidation", *Proceedings of the Combustion Institute* 29:1267-1275
- Tranter, R.S., Sivaramakrishnan, R., Brezinsky, K., and Allendorf, M.D. (2002) "High pressure, high temperature shock tube studies of ethane pyrolysis and oxidation", *Physical Chemistry Chemical Physics* 4:2001-2010
- Tsang, W. (1988) "Chemical Kinetic Data Base for Combustion Chemistry. Part 3. Propane", *J. Phys. Chem. Ref. Data* 17(2):887-951
- Tsang, W. (1991) "Chemical Kinetic Data Base for Combustion Chemistry. Part V. Propene", *J. Phys. Chem. Ref. Data* 20(2):221-273
- Tsuboi, T. (1975) "Optische Untersuchung der Methanoxydation hinter reflektierten Stosswellen", *Japan Journal of Applied Physics* 14:1371
- Tsuboi, T. (1976) "Mechanism for the Homogeneous Thermal Oxidation of Methane in the Gas Phase", *Japan Journal of Applied Physics* 15:159
- Tsuboi, T. (1978) "UV Absorption Study on the Reaction of Methyl Radicals behind Shock Waves", *Japanese Journal of Applied Physics* 17:709-716
- Tsuboi, T., and Wagner, H. Gg. (1975) "Homogeneous Thermal Oxidation of Methane in Reflected Shock Waves", *Proceedings of the Combustion Institute* 15:883-890

Turbiez, A., El Bakali, A., Pauwels, J.F., Rida, A., and Meunier, P. (2004) "Experimental Study of a Low Pressure Stoichiometric Premixed Methane, Methane/Ethane, Methane/Ethane/Propane and Synthetic Natural Gas Flames" *Fuel* 83:933-941

Wang, H., and Laskin, A. (1999) "On initiation reactions of acetylene oxidation in shock tubes A quantum mechanical and kinetic modeling study", *Chemical Physics Letters* 303:43-49

Warnatz, J. (1982) Survey of Elementary Reaction Rate Constants in the C/H/O System, Chemistry of Combustion Reactions, edited by W.C. Gardiner, Springer-Verlag, New York

Westbrook, C. K., Creighton, J., Lund, C., and Dryer, F. L. (1977) "A Numerical Model of Chemical Kinetics of Combustion in a Turbulent Flow Reactor", *Journal of Physical Chemistry* 81:2542-2554

Westbrook, C.K. (1979) "An Analytical Study of the Shock Tube Ignition of Mixtures of Methane and Ethane", *Combustion Science & Technology* 20:5-17

Williams (2005) Available at <http://maeweb.ucsd.edu/~combustion/cermech>

Zellner, R., Niemitz, K. J., Warnatz, J., Gardiner, W. C., Eubank, C. S., and Simmie, J. M. (1981) "Hydrocarbon induced acceleration of methane-air ignition, Intl. Colloquium on gasdynamics of explosions and reactive systems", *Progress in Aeronautics and Astronautics* 88:252-272

Zhukov, V.P., Sechenov, V.A., and Starikovskii, A.Y. (2003) "Spontaneous ignition of methane-air mixtures in a wide range of pressures", *Combustion, Explosion, and Shock Waves* 39:487-495