Methane/ethane/propane mixture oxidation at high pressures and at high, intermediate and low temperatures

D. Healy a, H.J. Curran a,*, J.M. Simmie a, D.M. Kalitan b, C.M. Zinner b, A.B. Barrett c, E.L. Petersen c, G. Bourque d

a Combustion Chemistry Centre, National University of Ireland, Galway, Ireland
b Mechanical, Materials and Aerospace Engineering, University of Central Florida, Orlando, FL 32816, USA
c Department of Mechanical Engineering, Texas A&M University, College Station, TX 77843, USA
d Rolls-Royce Canada, Montreal, Canada

Received 21 April 2008; received in revised form 11 July 2008; accepted 14 July 2008

Abstract

The oxidation of methane/ethane/propane mixtures, for blends containing 90/6.6/3.3, 70/15/15 and 70/20/10 percent by volume of each fuel respectively in ‘air,’ has been studied over the temperature range 770–1580 K, at compressed gas pressures of approximately 1, 10, 20, 30, 40 and 50 atm, and at equivalence ratios of 0.5, 1.0 and 2.0 using both a high-pressure shock tube and a rapid compression machine. The present work represents the most comprehensive set of methane/ethane/propane ignition delay time measurements available in a single study which extends the composition envelope over an industrially relevant pressure range. It is also the first such study to present ignition delay times at significantly overlapping conditions from both a rapid compression machine and a shock tube. The data were simulated using a detailed chemical kinetic model comprised of 289 species and 1580 reactions. It was found that qualitatively, the model reproduces correctly the effect of change in equivalence ratio and pressure, predicting that fuel-rich, high-pressure mixtures ignite fastest while fuel-lean, low-pressure mixtures ignite slowest. Moreover, the reactivity as a function of temperature is well captured with the model predicting negative temperature coefficient behavior similar to the experiments. Quantitatively the model is in general excellent agreement with the experimental results but is faster than experiment for the fuel-rich (φ = 2.0) mixture containing the highest quantity of propane (70/15/15 mixture) at the lowest temperatures (770–900 K).

© 2008 The Combustion Institute. Published by Elsevier Inc. All rights reserved.

Keywords: Natural gas; Oxidation; RCM; Shock-tube; Experiments; Modeling

1. Introduction

The overwhelming economic importance of natural gas as an abundant and relatively clean fossil fuel has been responsible for numerous studies of its combustion properties. The primary fuel for industrial gas turbines is natural gas [1], which is the source of about one quarter of the world’s primary energy today and is expected to be so until 2030. Natural gas has a low greenhouse gas signature, is energy efficient and is easy to use, in that the infrastructure needed is already in place. However, because it is a mixture

* Corresponding author.

E-mail address: henry.curran@nuigalway.ie

(H.J. Curran).
of variable composition which can impact the performance of dry low emission (DLE) industrial gas turbine engines through variations in the autoignition delay time, flame dynamics, and flame speed [2–4], many fundamental studies have tried to simplify the problem by considering simple mixtures of methane, ethane and propane in the expectation that the essential characteristics of the combustion chemistry [5] can be faithfully captured in this manner [6–10].

Thus, for example, Dagaut [11] has clearly shown from jet-stirred reactor experiments conducted at approximately 1200 K that methane/ethane/propane most closely mimics natural gas under these conditions. Khalil and Karim [12] have attempted to simulate the ignition and combustion processes of natural gas in engines by a synthetic methane/ethane/propane mixture which has a more manageable detailed chemical kinetic mechanism. Turbiez et al. [13] in studies of laminar stoichiometric premixed flames have shown that higher alkanes play only a minor role in the oxidation of natural gas and therefore that a methane/ethane/propane mix can appropriately represent natural gas combustion.

Other studies have focused primarily on the development of detailed chemical kinetic models for these mixtures. Petrova and Williams [14] developed a small detailed chemical kinetic mechanism for hydrocarbon combustion including data at temperatures well above 1000 K. El Bakali et al. [15] used experimental results obtained for the oxidation of a stoichiometric premixed synthetic natural gas flame at low pressure (10.6 kPa) together with experimental results obtained in a jet-stirred reactor at atmospheric pressure and variable equivalence ratios for the oxidation of methane–ethane mixtures representative of natural gas to develop and validate a detailed reaction mechanism by comparison of computed and measured species mole fraction profiles. The ignition delays of methane/oxygen/argon and methane/ethane/oxygen at temperatures above 1300 K and at approximately 1 atm were also successfully simulated.

It could of course be argued that a surrogate mixture can never represent reality in a totally satisfactory manner, but the inherent complexity of real fuels has to be simplified in order to permit three-dimensional computational fluid dynamic simulations—as, for example, in trying to optimize natural gas burners for minimal NOx emissions [16].

The question to be answered here is: are the findings that a synthetic blend of methane/ethane/propane can mimic natural gas relevant to the more extreme conditions of higher pressures and lower temperatures such as are encountered in the combustor of a gas turbine? The driving force behind this study is the tendency of increasing diversification of sources of fuel supply which is leading to the accelerated development of flexible-fuel power plants. Although present-day sources yield natural gas compositions of 70–90% methane, 5–15% ethane and <5% higher hydrocarbons we have extended this composition envelope in this study for two reasons: (i) to cover future eventualities and (ii) to render the experiments more distinctive and therefore more useful for validation of the mechanism.

In a recent study Petersen et al. [17] considered one methane/propane blend with an 80/20 volume ratio at a pressure of 12 atm and a fuel-to-air equivalence ratio (φ) of 0.5. Subsequently, Petersen et al. [18] presented an experimental shock-tube and chemical kinetic modeling study of methane/propane/air ignition delay times over a considerably wider range of propane compositions (10–40%), equivalence ratios (0.5–3.0), temperatures (1042–1615 K), and pressures (6–28 atm) than previously covered. This work was also extended to include data recorded in a rapid compression machine at lower temperatures (740–1136 K) and to pressures in the range 10–40 atm [19]. A detailed chemical kinetic model was used to simulate the data with reasonably good agreement observed on comparison with experiment.

This current work builds upon our earlier studies by including ethane in the mixture composition. We include data recorded in both a high-pressure shock tube and in a rapid compression machine for three blends containing 90/6.6/3.3, 70/15/15 and 70/20/10 percent by volume of methane/ethane/propane in the temperature range 770–1580 K, at compressed gas pressures of approximately 1, 10, 20, 30, 40 and 50 atm, and at equivalence ratios of 0.5, 1.0 and 2.0. We use the detailed chemical kinetic model to simulate the data with overall excellent agreement observed.

2. Experimental

2.1. Rapid compression machine

Details of both the rapid compression machine [20–22] and the shock tube [18,23] have been provided previously, with a summary given in [19]. Gases used were supplied by BOC Ireland; nitrogen (CP Grade) 99.95%, argon (Research Grade) 99.9995%, oxygen (Medical Grade) 99.5% and were used without further purification. Methane, ethane and propane gases were obtained from Aldrich at 99% purity and were used without further purification. Test mixtures (Table 1) were prepared manometrically in a stainless steel container and allowed to mix thoroughly before use.

Experimental compressions times are relatively short at approximately 16 ms. Experimental pres-
Table 1
CH₄/C₂H₆/C₃H₈ mixtures tested

<table>
<thead>
<tr>
<th>Mix</th>
<th>% CH₄</th>
<th>% C₂H₆</th>
<th>% C₃H₈</th>
<th>O₂</th>
<th>Diluent</th>
<th>φ</th>
</tr>
</thead>
<tbody>
<tr>
<td>90/6.6/3.3</td>
<td>0.0410</td>
<td>0.0031</td>
<td>0.0015</td>
<td>0.2004</td>
<td>0.7540</td>
<td>0.5</td>
</tr>
<tr>
<td>70/15/15</td>
<td>0.0264</td>
<td>0.0057</td>
<td>0.0057</td>
<td>0.2021</td>
<td>0.7602</td>
<td>0.5</td>
</tr>
<tr>
<td>70/20/10</td>
<td>0.0272</td>
<td>0.0078</td>
<td>0.0039</td>
<td>0.2018</td>
<td>0.7593</td>
<td>0.5</td>
</tr>
<tr>
<td>90/6.6/3.3</td>
<td>0.0784</td>
<td>0.0058</td>
<td>0.0029</td>
<td>0.1917</td>
<td>0.7211</td>
<td>1.0</td>
</tr>
<tr>
<td>70/15/15</td>
<td>0.0510</td>
<td>0.0109</td>
<td>0.0109</td>
<td>0.1947</td>
<td>0.7325</td>
<td>1.0</td>
</tr>
<tr>
<td>70/20/10</td>
<td>0.0523</td>
<td>0.0149</td>
<td>0.0075</td>
<td>0.1943</td>
<td>0.7310</td>
<td>1.0</td>
</tr>
<tr>
<td>90/6.6/3.3</td>
<td>0.1443</td>
<td>0.0107</td>
<td>0.0053</td>
<td>0.1763</td>
<td>0.6633</td>
<td>2.0</td>
</tr>
<tr>
<td>70/15/15</td>
<td>0.0950</td>
<td>0.0204</td>
<td>0.0204</td>
<td>0.1815</td>
<td>0.6828</td>
<td>2.0</td>
</tr>
<tr>
<td>70/20/10</td>
<td>0.0974</td>
<td>0.0278</td>
<td>0.0139</td>
<td>0.1808</td>
<td>0.6801</td>
<td>2.0</td>
</tr>
</tbody>
</table>

sure profiles are measured using a pressure transducer (Kistler 603B) with the signal passing through a charge amplifier and recorded on an oscilloscope. The ignition delay time, \( \tau \), was defined as the time from the end of compression to the maximum rate of pressure rise; these were reproducible to within 10% at each \( T_C \). The composition of each mixture together with the experimental results and the initial conditions of charge composition, temperature and pressure are documented in Tables 1–27 of the supplemental material.

The compressed gas temperature, \( T_C \), was calculated from the initial temperature, \( T_I \), pressure, \( P_I \), and reactant composition, and the experimentally measured compressed gas pressure, \( P_C \), defined as the maximum pressure immediately after compression, and employing the adiabatic compression/expansion routine in Gaseq [24] which uses the temperature dependence of the ratio of specific heats, \( \gamma \), according to

\[
\ln \left( \frac{P_C}{P_I} \right) = \int_{T_I}^{T_C} \frac{\gamma}{\gamma - 1} \frac{dT}{T}
\]

while assuming frozen chemistry during compression. Even though ignition delays were observed up to 320 ms following compression (Table 27 of the supplemental material) repeat experiments which had ignition delay times greater than 100 ms showed larger percentage variations compared to those with \( \tau < 100 \) ms.

2.2. Shock tube

Each of the mixtures presented in Table 1 was studied behind reflected shock waves using the shock-tube described by Petersen et al. [23] for the higher-pressure experiments. For most of the 1-atm experiments, a second shock tube was employed. This tube (6.1 m overall length) is also made of stainless steel, has a square driven section with a 1.8 m driver section with an internal dimension of 15.24 cm and is fully described in Rotavera et al. [25]. Both shock tubes utilized helium exclusively as the driver gas. Aluminum diaphragms were used to obtain the test conditions greater than about 5 atm, and polycarbonate diaphragms were used to obtain the 1 atm conditions. Overlapping experiments were performed in both tubes at a pressure near 1 atm for four of the test mixtures (1, 5, 7 and 9). The agreement in the measured ignition delay times between the two facilities was excellent.

The test mixtures were made in a stainless steel mixing vessel using partial pressures to determine the volumetric percentage of each constituent to within 1% of their value. The three fuel blends were custom mixtures provided by Matheson using research grade (99.95%) methane, ethane, and propane. The N₂ and O₂ were both of ultra high purity grade (99.9995%).

Ignition delay times (Tables 28–36 of the supplemental material) were measured from the sharp increase in the endwall pressure trace at the time of ignition, although the CH* signal produced ignition delay times within 1% of the pressure since the ignition from these real fuel/air mixtures produced significant energy release [17,26]. Reaction progress was monitored using both pressure and CH* chemiluminescence emission near 430 nm from endwall locations. The pressure was monitored using a piezoelectric pressure transducer, and the light emission was recorded through a fused silica window mounted in the endwall, then through a narrow-band filter at 430 nm, and onto a Hamamatsu 1P21 photomultiplier tube in a homemade housing. The pressure and emission traces for the entire set of experiments showed no significant pressure increase prior to the main ignition event.

3. Computational modeling

The chemical kinetic mechanism was developed and simulations performed using the HCT (hydrodynamics, chemistry and transport) program [27].
detailed chemical kinetic model is based on the hierarchical nature of hydrocarbon combustion mechanisms containing the H₂/O₂ sub-mechanism [28], together with the CO/CH₄ and larger hydrocarbon sub-mechanisms and is published in our previous work on methane/propane mixtures [19]. A complete listing of the detailed kinetic mechanism (C5_44) consisting of 289 species and 1580 reactions is available at http://c3.nuigalway.ie/naturalgas2.html together with associated thermochemical and transport parameters.

3.1. Simulations

In our previous work on methane/propane mixtures [18], we compared our detailed chemical kinetic mechanism to data presented by Petersen et al. [29] of shock-tube measurements of CH₄/O₂ ignition at extreme pressures (40–260 bar), high-dilution (fuel plus oxidizer ≤30%), at intermediate temperatures (1040–1500 K), and at equivalence ratios as high as 6. Overall, good agreement was observed between model and experiment. Moreover, in this previous work we presented comparisons of shock-tube ignition delay measurements versus model predictions for CH₄/C₂H₆ splits of 90/10, 80/20, 70/30 and 60/40% by volume in ‘air’ at equivalence ratios from lean (φ = 0.5) through stoichiometric to rich (φ = 3.0) at test pressures from 5.8 to 27.5 atm, and in the temperature range 1042–1550 K. Overall, good agreement was observed between the model and the experiment.

Furthermore, this CH₄/C₃H₈ study was extended to lower temperatures using data obtained in a rapid compression machine [19]. These data were compared with the shock-tube data recorded at relatively higher temperatures but at similar pressure and presented in [18]. It was shown that there was very good agreement between the shock-tube and rapid compression machine data at temperatures of overlap. In addition, the detailed chemical kinetic mechanism developed in the original study [18] was also used to simulate both the shock-tube and rapid compression machine data with overall good agreement observed between the model and the experimental results.

Below we present our most recent results for methane/ethane/propane mixtures obtained in both the RCM at lower temperatures, and in the shock tube at higher temperatures. The RCM experiments by their nature involve heat losses and it is necessary to account for these in performing model simulations. Therefore, a series of experiments was undertaken whereby oxygen was replaced by nitrogen and pressure profiles recorded for ‘unreactive’ mixtures. The simulations for reactive mixtures used the data gathered for the unreactive mixtures to provide a good account of heat losses. The complete methodology employed is described in detail in our previous work on propane [22] and methane/propane mixtures [19].

4. Results

All ignition delay times measured in both the RCM and in the shock tube are provided in the supplemental material. Figs. 1–9 present the results of the experiments in comparison to the predictions of the detailed mechanism.

4.1. Effect of pressure on ignition

For all mixtures and conditions, at constant temperature increasing pressures produced greater reactivity and led to a decrease in ignition times. Figs. 1–3 depict the effect of pressure on ignition times including both experimental results and model predictions. In all, we have recorded data depicting the effect of pressure for lean (φ = 0.5), stoichiometric and rich (φ = 2.0) conditions for mixtures composing methane/ethane/propane in the ratios of 90/6.6/3.3, 70/15/15 and 70/20/10 for a total of nine different figures. We have included only three of these in this paper, but the other six are included for completeness in the supplemental material.

Fig. 1 shows the effect of pressure for 70% CH₄/15% C₂H₆/15% C₃H₈ mixtures at φ = 0.5 in ‘air’ at pressures of 1, 6.5, 10, 20 and 30 atm. It is clear that increasing pressure reduces ignition times. The RCM data show that reactivity starts at 910 K in the case of the 30 atm data but starts at 975 K at the lower pressure of 10 atm. Moreover, there is a marked change in ‘activation energy’ as a function of temperature in the region of transition from intermediate-
to high-temperature chemistry (900–975 K at 20 atm and 975–1100 K at 10 atm). At 20 atm, both RCM and shock-tube data were recorded, there is excellent agreement between the two sets of data in the temperature window of overlap, 1025–1110 K. To the authors’ knowledge, this is the first study to not only cover such a wide range of experimental conditions using both shock tubes and RCM’s, but is also the first study with significantly overlapping temperatures and pressures such as seen in Fig. 1. The model correctly reproduces this behavior and is also in excellent agreement with all the experimental results, except for the 10 atm RCM results for which the simulations are slower than experiment from 970 to 1040 K, but are in good agreement thereafter. However, at 10 atm the model does again capture the change in the activation energy for ignition as the system transitions from low- and intermediate-temperature kinetics to high-temperature reactions.

Similar comparisons depicting the effect of pressure are shown in Fig. 2 which includes data for 90% CH₄/6.6% C₂H₆/3.3% C₃H₈ mixtures at ϕ = 1.0 in ‘air’ at pressures of approximately 1.2, 10, 20, 30, 40 and 50 atm. Again, ignition delay times are faster at higher pressures. The RCM data were recorded in the temperature range 920–1060 K, while those recorded in the shock-tube ranged from 1150 to 1520 K. A direct comparison of shock-tube and RCM experimental results is available at 30 atm only but it is clear that both the RCM and shock-tube data are consistent, as the mechanism is able to reproduce both sets of data. Indeed, the mechanism is also in excellent agreement with experiment at all conditions, accurately reproducing experimental ignition times.

A similar comparison is shown in Fig. 3 for a fuel-rich equivalence ratio of 2.0 for 70% CH₄/20% C₂H₆/10% C₃H₈ mixtures at ϕ = 2.0 in ‘air’ at pressures of approximately 1.1, 10, 20 and 30 atm. Here again, ignition times are faster at higher pressure. Model simulations are in good agreement with the experimental results at 1.1 and approximately 20 atm, and also shows that the RCM and shock-tube data complement one another very well, with the RCM data recorded in the temperature range 880–1000 K, while the shock-tube data were recorded at temperatures in the range 1050–1400 K. However, we do observe that at the higher pressure of 31.5 atm, the model is becoming slightly faster in comparison to experiment at the lowest temperatures.

4.2. Effect of equivalence ratio on ignition

Figs. 4 and 5 illustrate the effect of equivalence ratio on ignition delay times. Fig. 4 shows data recorded for 90% CH₄/6.6% C₂H₆/3.3% C₃H₈ mixtures in ‘air’ at a pressure of approximately 30 atm. It is evident that fuel-lean mixtures react most slowly but are only slightly slower than stoichiometric mixtures from about 920 to 1470 K. However, fuel-rich mixtures are faster to ignite at lower temperatures but are predicted to become relatively slower to ignite at higher temperatures. This is due to the fact that under these conditions, low- and intermediate-temperature kinetics are controlling the oxidation process, where chain branching depends on fuel concentration. At higher temperatures ignition delay times for all equivalence ratios converge at approximately 1450 K. This is the point at which high-temperature kinetics start to take over where the reaction H + O₂ → O + OH becomes the most important chain branching reaction.
the system reactivity no longer depends on the fuel concentration but depends instead on oxygen concentration.

Fig. 4 also shows that there is excellent agreement between the model and experiment at $\phi = 0.5$ and 1.0, but for fuel-rich mixtures ($\phi \geq 2.0$) at temperatures below 920 K, the model tends to underpredict ignition delay times and thus predicts a greater reactivity than that measured experimentally. However, overall there is very good agreement between the model and the experimental data.

Fig. 5 shows data recorded for 70% CH$_4$/20% C$_2$H$_6$/10% C$_3$H$_8$ mixtures in ‘air’ at a pressure of 20 atm. Again it is observed that fuel-lean mixtures are slower to ignite compared to stoichiometric ones with fuel-rich mixtures fastest to ignite in the temperature range 880–1200 K. There is overall good agreement between the mechanism and the data with the relative effect of fuel addition reproduced very well by the chemical kinetic simulations. However, for these mixtures containing relatively larger concentrations of the higher order hydrocarbons, the temperature at which the crossover from low- and intermediate-temperature to high-temperature kinetics occurs is lower at 1300 K, compared to approximately 1450 K for the 90/6.6/3.3 mixtures.

Finally, Fig. 6 shows data recorded for 70% CH$_4$/15% C$_2$H$_6$/15% C$_3$H$_8$ mixtures in ‘air’ at a pressure of 20 atm. Again it is observed that fuel-lean mixtures are slower to ignite compared to stoichiometric ones with fuel-rich mixtures fastest to ignite in the temperature range 880–1200 K, with the model accurately reproducing the experimental results. However, again the temperature at which the crossover from low- and intermediate-temperature to high-temperature kinetics occurs is lower at 1200 K, compared to approximately 1300 K for the 70/20/10 mixtures and 1450 K for the 90/6.6/3.3 mixtures.

4.3. Effect of fuel composition on ignition

Figs. 7–9 illustrate the effect of composition on ignition delay time. Fig. 7 illustrates the effect for lean ($\phi = 0.5$) CH$_4$/C$_2$H$_6$/C$_3$H$_8$ mixtures in ‘air’ at 20 atm. The RCM data illustrate the effect very well for all three mixture compositions; the 70/15/15 mixture is fastest to ignite, with the 90/6.6/3.3 mixture slowest to ignite at lower temperatures. This is reasonable as the 70/15/15 mixture contains relatively more propane than the other two. As propane is known to
Fig. 7. Effect of fuel composition on ignition delay times for CH$_4$/C$_2$H$_6$/C$_3$H$_8$ oxidation, $\phi = 0.5$ ‘air,’ $p = 20$ atm. (□) RCM 90/6.6/3.3, (○) RCM 70/20/10, (●) shock tube 70/20/10, (△) RCM 70/15/15, (▲) shock tube 70/15/15. Lines are model predictions at different dilutions.

Fig. 8. Effect of fuel composition on ignition delay times for CH$_4$/C$_2$H$_6$/C$_3$H$_8$ oxidation, $\phi = 1.0$ ‘air,’ $p = 30$ atm. (□) RCM 90/6.6/3.3, (■) shock tube 90/6.6/3.3, (○) RCM 70/20/10, (△) RCM 70/15/15, (▲) shock tube 70/15/15. Lines are model predictions at different dilutions.

Fig. 9. Effect of fuel composition on ignition delay times for CH$_4$/C$_2$H$_6$/C$_3$H$_8$ oxidation, $\phi = 2.0$ ‘air,’ $p = 20$ atm. (□) RCM 90/6.6/3.3, (○) RCM 70/20/10, (●) shock tube 70/20/10, (△) RCM 70/15/15, (▲) shock tube 70/15/15. Lines are model predictions at different dilutions.

5. Conclusions

This paper presents an extensive range of experimental data for methane/ethane/propane mixtures in the temperature range 770–1580 K, at compressed...
gas pressures of approximately 1, 10, 20, 30, 40 and 50 atm, and at equivalence ratios of 0.5, 1.0 and 2.0 using both a high-pressure shock tube and a rapid compression machine. This range of conditions and fuel blends produced the most comprehensive data set on methane/ethane/propane fuel blends in ‘air’ at practical conditions. The present study also presents for the first time significantly overlapping temperatures and pressures using both a shock tube and an RCM. A detailed chemical kinetic model which has been published previously [18] has been modified and used to simulate the data herein. Overall, the mechanism performs excellently in qualitatively capturing the major features of relative reactivities of various fuel mixtures. Moreover, in most cases there is excellent quantitative agreement between model and experiment.

Acknowledgments

This work was supported primarily by Rolls-Royce Canada Ltd. Partial support for the experiments came from The Aerospace Corporation and The National Science Foundation under grant CTS-0547159. The authors gratefully acknowledge the assistance of Viktorion Antonovski, Shatra Reehal, and Christopher Aul in performing some of the shock-tube experiments.

Supplementary material

The online version of this article contains additional supplementary material.

Please visit DOI: 10.1016/j.combustflame.2008.07.003.

References