IGNITION DELAY CHARACTERISTICS OF METHANE FUELS

L. J. SPADACCINI and M. B. COLKET III
United Technologies Research Center, East Hartford, CT 06108, U.S.A.

Received 22 July 1994

Abstract—A comprehensive literature search and a series of shock-tube experiments were undertaken to determine the ignition delay times for mixtures of methane with ethane, propane or butane, and for a typical natural gas fuel. Ignition delay experiments were conducted at equivalence ratios of 0.45–1.25 for temperatures 1300–2000 K and pressures 3–15 atm. The combined data were used to develop general correlations for predicting the ignition delays of binary methane–hydrocarbon mixtures and multicomponent natural gas mixtures in terms of temperature and the initial fuel and oxygen concentrations. For natural gas, the ignition delay was correlated by the empirical expression

\[ t = 1.77 \times 10^{-14} \exp \left( \frac{18693}{T} \right) [O_2]^{-0.03} [CH_4]^{0.08} [HC]^{-0.39} \]

in which concentrations are expressed in molecules per cubic cm and the [HC] factor represents the total molar concentration of all non-methane hydrocarbons. Chemical kinetic modeling was also performed to define the ignition mechanisms, and to permit extrapolation of data and prediction of the effects of using vitiated air for combustor testing.

CONTENTS

1. Introduction 431
2. Background 432
   2.1. Preignition Process 432
   2.2. Experimental Techniques 433
      2.2.1. Continuous flow devices 433
      2.2.2. Shock tubes 433
   2.3. Methane Autoignition Investigations 434
      2.3.1. Methane–air 434
      2.3.2. Methane–oxygen 435
      2.3.3. Methane–hydrocarbon mixtures and natural gas 439
3. Autoignition Experiments 441
   3.1. Test Apparatus and Procedures 441
   3.2. Methane Ignition Delay Measurements 442
   3.3. Effects of Hydrocarbon Contaminants 443
   3.4. Natural Gas Ignition Delay 445
4. Chemical Kinetic Model 451
   4.1. Reactions Controlling Ignition Delay 451
   4.2. Model Description 453
   4.3. Model Predictions 454
   4.4. Effects of Vitiation on Engine Testing 456
5. Conclusions 458
Acknowledgements 458
References 459

1. INTRODUCTION

The ready availability, low-cost and clean-burning attributes of commercial-grade methane fuel (natural gas) support its use in many ground-based gas turbine and diesel applications. In addition, its high heat of combustion (15% greater than jet fuel) and high heat-sink capacity (can be heated to 750 K without decomposition) make it an attractive fuel for supersonic and hypersonic propulsion. In order to minimize pollutant emissions from oxides of nitrogen formation, lean-premixed burner designs are preferred. However, an intrinsic problem with premixed systems is the potential for spontaneous ignition of the fuel–air mixture prior to reaching the primary combustion zone. Such an occurrence could result in flashback and flame stabilization at the injector, leading to off-design performance and, in the extreme, to physical damage to combustor hardware. While the combustor inlet air temperatures during low-power operation may preclude autoignition of pure methane, there is concern at the higher power...
conditions. Furthermore, although pure methane may be the fuel-of-choice for high-pressure-ratio gas turbine and diesel powerplants or hypersonic-speed commercial aircraft, natural gas may be a more practical substitute from economic considerations. Since natural gas is a mixture of methane with other hydrocarbon species in varying amounts (depending on the source), the small concentrations of hydrocarbon impurities normally present can greatly affect the reactivity of the fuel and promote ignition. Thus, an essential task in the design and development of premixed combustion systems is early determination of the autoignition characteristics of the fuel.

Ignition delay information for methane fuels is required to ascertain if a compromise is feasible between the mixing lengths required for fuel-air uniformity and the length limitations imposed by the spontaneous ignition delay times. Therefore, a comprehensive literature search and an experimental investigation were conducted to compile an extensive autoignition database for methane and natural gas fuels. Data reported for methane and methane-hydrocarbon mixtures were tabulated in terms of temperature, pressure, composition, stoichiometry and ignition delay time. These were entered into a computer-based databank. Ignition information from various sources was compared, and linear regression analyses of the commingled data were made to obtain correlations of ignition delay times for methane and natural gas fuels.

It was found that previous studies of methane-hydrocarbon ignition were not conducted over a sufficiently wide range of conditions to permit development of reliable correlating equations. Consequently, shock-tube experiments were performed to measure the ignition delay of methane in the presence of a variety of hydrocarbon impurities, as well as the ignition delay of one typical natural gas. Pure methane was also tested to validate the experimental techniques, since comparisons could be made readily with the large database in the literature. Measurements of ignition delay times were made behind reflected shock waves by observing the time delay to the onset of emission from excited hydroxyl radicals. By combining these data with those in the literature, correlations were developed for binary mixtures of methane with small relative concentrations of ethane, propane, or butane. In addition, correlations were developed for describing ignition delays of natural gases (multicomponent methane fuels). To support these correlating procedures and develop a tool for extrapolation beyond the test conditions, detailed chemical kinetics calculations were performed using reaction mechanisms found in the literature. In addition, the chemical kinetics model was also used to investigate the effects on autoignition of vitiated air preheater contamination typical of that generated in ground testing of ramjet combustors for hypersonic aircraft.

2. BACKGROUND

2.1. Preignition Process

Autoignition is a spontaneous process whereby a combustible mixture undergoes chemical reaction leading to the rapid liberation of energy at a rate sufficient to sustain combustion in the absence of an external energy source such as a flame or spark. It is widely recognized that ignition of a fuel-air mixture comprises a series of overlapping physical and chemical processes which have characteristic times that combine to form an overall induction or ignition delay time. During early stages, the induction period is probably dominated by physical processes and at later stages by chemical processes. Typically, the induction period is equated to the characteristic chemical time for ignition and, consequently, experiments have been designed to minimize the total time associated with the physical processes. For gaseous fuels such as methane, the physical processes involve heating, diffusion, and mixing of reactants; whereas the chemical processes involve the kinetics of pre-flame reactions. Chain branching reactions result in the oxidative decomposition of fuel hydrocarbon species and an increase in concentrations of intermediate free-radical species, so-called ignition precursors, to a level where ignition will occur. During ignition, there is a rapid depletion of the primary fuel, very high radical concentrations, and an exponential rise in temperature and pressure. The ignition delay time can be defined as that period between the creation of a combustible mixture, as by injection of fuel into an oxidizing environment, and the onset of the rapid reaction phase leading to the rise in temperature and pressure.

The ignition delay time is a readily measurable quantity that is a function of the initial temperature, pressure, and composition of the reactant mixture. For methane, it has been found that the ignition delay time can be correlated in the form:

\[ t = A \exp \left( \frac{E}{RT} \right) \left[ \text{CH}_4 \right] \left[ \text{O}_2 \right] \]

where the term \( E \) is a parameter equivalent to a global activation energy and \( A \) is an empirically determined constant. The terms \( \left[ \text{CH}_4 \right] \) and \( \left[ \text{O}_2 \right] \) are the molar concentrations (mol/cc) of methane and oxygen, respectively, in the combustible mixture. The empirical exponents \( a \) and \( b \) of these terms express the power dependencies of ignition delay time on fuel and oxidizer concentrations. The concentrations are determined by

\[ [\cdot] = x_i P/RT \]

where \( x_i \) is the mole fraction of fuel or oxygen, \( P \) is the pressure, \( T \) is the temperature of the mixture at the point of ignition and \( R \) is the universal gas constant. Correlation of experimental data for methane by means of these equations shows that ignition delay time decreases for both increasing temperature and increasing pressure.

432 L. J. SPADACCINI and M. B. COLKET III
2.2. Experimental Techniques

The spontaneous ignition temperature of a combustible fuel–air mixture is not an absolute property of that mixture. Consequently, all spontaneous ignition data need to be interpreted carefully with regard to the test apparatus and methods used for their determination. Ideal ignition experiments should be independent of the test configuration and free of surface effects. In addition, mixing of the fuel and air should be nearly instantaneous, or else the effects of mixing must be determined, which is a very difficult task. Moreover, temperature and pressure gradients and boundary layer effects should be negligible, and residence time must be determined accurately. Over the years, a wide variety of experimental techniques have been used to measure ignition delay times of fuels, including constant-volume bombs, continuous-flow test apparatus, and shock tubes. Early ignition studies employed the constant-volume bomb technique, but results from this body of work are greatly dependent upon configuration (shape, surface and volume) and surface material. Few methane ignition data were derived from this technique and, because of their limitations, they are not considered applicable to gas turbine or ramjet combustion. In contrast, methane autoignition data derived from both continuous flow devices and shock tube studies were found which have direct application and are reported herein.

2.2.1. Continuous flow devices

In a continuous flow device, fuel is injected into a flowing air stream at high temperature and the combustible mixture ignites at some distance downstream of the fuel injection location, depending upon the velocity of the flow. The normal procedure to acquire ignition delay data consists of first establishing a prescribed condition within the test duct regarding pressure, composition and flow rates of reactants. Then, the inlet air temperature (and fuel temperature if necessary) is gradually increased until autoignition of the fuel–air mixture occurs within or at the exit of the duct. The occurrence of autoignition is determined by observance of a visible flame and a rapid increase in temperature at the flame front location. Ignition delay times are calculated from the known length of the test duct, defined as the distance between the injector and flame front location, and the mean freestream flow velocity. Ideally, the reactor simulates plug flow conditions to minimize complications due to non-uniform temperature and velocity distributions.

As an integral part of the design of a continuous flow device, it is important to have a fuel injector that provides for rapid, uniform fuel–air mixing so that ignition delay measurements are not dependent upon the test apparatus configuration. In particular, blunt base regions of the injector must be eliminated so that downstream recirculation zones having unknown residence times are minimized. The overall goal is an injector that produces a homogeneous fuel–air mixture, thereby reducing the time associated with the physical process of mixing and allowing the chemical processes affecting ignition delay to be isolated and quantified experimentally.

Continuous-flow devices for ignition studies permit ample time for measuring and regulating many of the important variables of interest such as temperature, pressure, stoichiometry and flow rate (or residence time). However, because they utilize electrical resistance-type air heaters, their inherent limitation is in the maximum level of air temperature which they provide. In general, the upper temperature limit is in the order of 1000 K, which is below the range of interest for most high-speed ramjet conditions. Consequently, as will be discussed subsequently, methane autoignition data obtained by shock tube experimental techniques have more relevancy to ramjet design and operating conditions.

2.2.2. Shock tubes

A shock tube is used in ignition studies to produce a high temperature gas under well-controlled test conditions. A limitation of this technique is that the test is of short duration, but this limitation is overcome by the use of commercially available, fast-response instrumentation. A shock tube is a tube of cylindrical or rectangular cross-section in which a transverse diaphragm separates two masses of gas initially at rest. One mass is at high pressure and is considered the driver section of the tube. The other mass, in the driven section, is at low pressure and forms the ignitable mixture of interest. The diaphragm is burst by either mechanically piercing it or by exceeding its structural strength through over-pressurization of the driver section. This action sends a strong shock wave into the low pressure section increasing the static pressure and temperature of the mixture. The shock wave is reflected at the end boundary wall of the tube resulting in an additional increase in pressure and temperature. By tailoring pressure levels within the two sections of the tube, a variety of shock strengths can be produced leading to a wide range of test conditions.

Either the incident or reflected shock wave can be used to create test conditions suitable for autoignition studies. Reflected waves stagnate the gas and, through reinforcement of the shock strength, produce higher temperature conditions than incident waves. Furthermore, the reflected shock technique has been widely used in studies to elucidate the mechanisms and kinetics of methane oxidation reactions. Most of the published methane autoignition data have been derived by using reflected shocks to produce temperatures in the range of 1500–2500 K. Few methane ignition studies have been conducted using the incident shock wave technique.
There is a physical limitation to the use of incident waves. Shocks strong enough to ignite the combustible mixture can be accelerated by the strong density gradients behind the wave. This phenomenon increases the shock strength along the length of the tube and can lead to detonation. Tests conducted with reflected shock waves are usually not complicated by this problem. Another limitation in applying the incident shock technique to methane autoignition studies is that it requires long shock tube lengths because methane has long induction times at low temperatures and requires greater residence times.

The reflected shock technique has three advantages over that of the incident shock: (1) it produces higher temperatures, (2) it eliminates spurious ignition caused by diaphragm bursting, and (3) it creates an essentially quiescent gas behind the reflected wave. However, there are some inherent limitations of concern. Whereas density and temperature values immediately behind an incident shock agree quite well with values calculated from shock velocity using ideal theory, such properties behind a reflected shock do not conform as well. Because of the growth of the boundary layer along the walls of the shock tube, the shock wave attenuates with time, necessitating an empirical correction to gas properties. In addition, the reflected shock interacts with the incident gas boundary layer under certain conditions to form a complex shock configuration near the walls of the tube commonly called bifurcation. Bifurcation generates large temperature fluctuations during and after passage of the reflected shock. In turn, this causes a residual temperature gradient in the quiescent gas behind the shock leading to a non-uniform temperature distribution and to non-uniform heating rates. Therefore, the application of ideal one-dimensional theory to determine the state of the gas in the reflected shock region is limited to conditions where the bifurcation interaction is small. Fortunately, nearly ideal reflected shock heating can be obtained with monoatomic gases. Therefore, in shock tube studies, the accepted practice is to highly dilute the test gas mixture with argon or helium and use a monoatomic driver gas such as helium. For methane autoignition data obtained from the shock tube technique, the bifurcation problem is not noted as a serious one in the published literature (elated flow non-idealities have been analyzed and reviewed in depth by several investigators; however, a detailed discussion of the role of gasdynamic effects in shock tube ignition delay measurements is beyond the scope of this article).

Applied to the shock tube technique, the ignition delay is defined as the time between shock heating of the gas mixture and the onset of the rapid-reaction phase. The properties of the gas mixture prior to ignition are calculated from the ideal shock equations, assuming no chemical reaction occurs ahead of the shock wave and the gases behave ideally with complete equilibrium of internal modes. For use in the calculations, values of shock velocity are measured by means of thermal or pressure transducers separated along the tube at known distances. The onset of the rapid-reaction phase (i.e. ignition) is detected by one or more of the following types of measurements: (1) pressure change by means of rapid-response, piezoelectric-type transducers, (2) rate of chemi-ionization by means of ionization probes, and (3) emission from electronically excited species (OH, CH, C2) or vibrationally excited species (CO, CO2, H2O, CH4), or absorption by species (OH, CH2), by means of photomultiplier instrumentation. Generally, when more than one measurement technique has been used, agreement of ignition delay times has been found to be good with few discrepancies noted in comparison of the data.

2.3. Methane Autoignition Investigations

Methane autoignition investigations reported in the literature can be divided into studies of methane–air and methane–oxygen–inert mixtures. The bulk of the data exists for methane–oxygen mixtures, and was acquired in studies conducted using the shock tube technique. Both continuous flow devices and shock tubes were used in the few reported investigations of methane–air autoignition.

2.3.1. Methane–air

A summary of methane–air autoignition studies reported in the literature is presented in Table 1. The table lists the experimental technique, method of measurement used to obtain ignition delay times, and the range of test conditions. Values of the equivalence ratio (E.R.) are stated as a ratio of the actual fuel–air ratio to the stoichiometric methane–air value of 0.1046 (by volume). A cursory examination of the range of test conditions shows that, with the exception of Mullins' work,¹ the use of the continuous flow device was restricted to the lower temperature range from 860 to 990 K at generally higher pressures than used in shock tube tests. The temperature range tested in the shock tube extended from the higher limit of continuous flow tests to as high as 2200 K.

One of the first to obtain ignition delay data for methane–air using a continuous flow device was Mullins.¹ He employed the so-called N.G.T.E. flow method using test apparatus developed at the National Gas Turbine Establishment in Great Britain having a three-degree diffuser test section supplied with high-temperature vitiated air. However, ignition delay data obtained from this device have been found subsequently to have much higher times than later shock tube results, perhaps due to H2O vapor formed in the preheater. Mullins' work is of interest because, based upon extensive studies with a variety of hydrocarbon fuels, he reported ignition delay for lean mixtures to be inversely proportional to oxygen...
concentration and independent of fuel concentration, thereby influencing the development of early correlations.

More recently, methane–air autoignition studies have been carried out in continuous flow devices at Purdue University by Cowell and Lefebvre and at the United Technologies Research Center by Wagner. Both of these devices consist of a constant diameter cylindrical test section having a distributed-source fuel injector and both use electrically heated air. The fuel injector used in the Purdue apparatus is formed from a ring-shaped tube having eight evenly spaced injection orifices drilled through its downstream face. The UTRC fuel injector consists of a 19-hole concentric array of venturi-shaped air passages with independently controlled fuel injection into the converging section of each venturi. The diverging sections of the venturis are extended to the points of intersection in order to eliminate blunt base regions.

In the study by Cowell and Lefebvre, experimental data were obtained to show the effects of variations in temperature, pressure and fuel concentration on ignition delay times for methane-air mixtures. It was found that ignition delay times could be expressed in terms of these parameters by an equation of the form

\[ t = A \exp\left(\frac{E}{RT}\right)\left(\text{CH}_4\right)^{-0.0}\left(\text{O}_2\right)^{1.0} \]

where a value of 25.0 kcal/mol was determined for the global activation energy. Thus, ignition delay time is seen to be exponentially dependent on temperature, inversely proportional to pressure, and weakly dependent upon fuel concentration. Although this correlation omits any dependency of ignition delay time on oxygen content, a first order dependence is implied through the pressure.

Wagner conducted his methane-air ignition tests at significantly higher pressures. He found that varying the equivalence ratio from 0.4 to 1.2 had little effect on ignition delay. Although Wagner did not present his ignition delay results in correlation form, the activation energy obtained from his data agrees well with that reported by Cowell and Lefebvre.

Shock tube investigations of methane–air autoignition were conducted by Asaba et al., Snyder et al., and Walker et al. All three investigations used the reflected wave technique. The methane–air ignition data reported by Asaba and co-workers were part of a larger study of methane–oxygen mixtures to understand the kinetics of methane oxidation. For rich methane–air mixtures, ignition delay time was found to be correlated by

\[ t = A \exp\left(\frac{E}{RT}\right)\left(\text{CH}_4\right)^{-0.9}\left(\text{O}_2\right)^{1.0} \]

with the value of the activation energy given by 52.9 ± 4.6 kcal/mol. In this equation, as in all subsequent correlations reported herein, ignition delay time is given in seconds when \( E \) is in cal/mol, \( T \) is in degrees K, and the concentration terms are in mol/cc. Snyder et al. reported ignition delay times for methane-air mixtures in tabular form but did not present a correlation of the data. Walker et al. presented extensive tabulated shock tube results for a stoichiometric mixture of methane-air that were correlated in the form of

\[ t = 2.77 \times 10^{-12} \exp\left(\frac{20.012}{RT}\right)\left(\text{O}_2\right)^{1.0} \]

The results of Walker et al. were found to be in good agreement with those of Asaba et al. for lean methane-oxygen mixtures.

2.3.2. Methane-oxygen

The methane-oxygen reaction has been studied by a number of investigators over the past several years. From this work, a large quantity of methane-oxygen-diluent autoignition data has been acquired by the shock tube technique and reported in the literature. A summary of experimental studies of methane-oxygen ignition is presented in Table 2, which describes the shock method used (incident or reflected wave), the method of measurement used to obtain ignition delay time, diluent used in the test mixture, and range of test conditions. Values of the equivalence ratio are stated as a ratio of the actual test value of fuel-air ratio to the stoichiometric
methane–oxygen value of 0.5. It can be seen from an examination of Table 2 that methane–oxygen–diluent autoignition investigations have been conducted over a wide variety of test conditions but generally at temperatures higher than 1250 K.

Most of the methane–oxygen–diluent ignition data have been acquired by use of the reflected wave method to produce shock heating. Ignition delay times have been determined from a variety of measurement techniques including pressure response and emission and/or absorption of radiation from excited radicals (OH, CH, C₂, HCO, CH₃) as well as from reactions of chemical species (CH₄, H₂O, CO₂, CO). Shock tube studies have been conducted for lean,

<table>
<thead>
<tr>
<th>Ref.</th>
<th>Investigators</th>
<th>Shock method</th>
<th>Ignition measurement</th>
<th>Diluent</th>
<th>Equivalence ratio</th>
<th>Temperature, K</th>
<th>Pressure, atm</th>
</tr>
</thead>
<tbody>
<tr>
<td>7</td>
<td>Skinner and Ruchwein</td>
<td>Reflected wave</td>
<td>Radiation (visible)</td>
<td>Ar</td>
<td>3.0–8.0</td>
<td>1150–1740</td>
<td>3–10</td>
</tr>
<tr>
<td>8</td>
<td>Kistiakowsky and Richards</td>
<td>Reflected wave</td>
<td>Radiation (OH)</td>
<td>Ar</td>
<td>0.4–4.0</td>
<td>1800–2700</td>
<td>—</td>
</tr>
<tr>
<td>4</td>
<td>Asaba, Yoneda, Kakihara and Hikita</td>
<td>Reflected wave</td>
<td>Pressure</td>
<td>None</td>
<td>0.2–3.0</td>
<td>800–2000</td>
<td>7</td>
</tr>
<tr>
<td>9</td>
<td>Miyama and Takeyama</td>
<td>Reflected wave</td>
<td>Pressure radiation (OH)</td>
<td>Ar</td>
<td>1.6–6.0</td>
<td>1400–2200</td>
<td>10</td>
</tr>
<tr>
<td>10</td>
<td>Glass, Kistiakowsky, Michael and Niki</td>
<td>Reflected wave</td>
<td>Radiation (CH)</td>
<td>Ar</td>
<td>—</td>
<td>2000–2300</td>
<td>—</td>
</tr>
<tr>
<td>11</td>
<td>Higgin and Williams</td>
<td>Reflected wave</td>
<td>Pressure radiation (OH)</td>
<td>Ar</td>
<td>0.25–2.0</td>
<td>1800–2500</td>
<td>0.3</td>
</tr>
<tr>
<td>12</td>
<td>Bowman</td>
<td>Reflected wave</td>
<td>Radiation (CO₂, CO, H₂O)</td>
<td>Ar</td>
<td>0.25–4.0</td>
<td>1700–2500</td>
<td>2.6</td>
</tr>
<tr>
<td>13</td>
<td>Seery and Bowman</td>
<td>Reflected wave</td>
<td>Pressure radiation (OH)</td>
<td>Ar</td>
<td>0.2–5.0</td>
<td>1350–1900</td>
<td>1.5–4.0</td>
</tr>
<tr>
<td>14</td>
<td>White</td>
<td>Reflected wave and incident wave</td>
<td>Radiation (OH, CH, C₂, CO)</td>
<td>Ar, N₂</td>
<td>0.04–1.0</td>
<td>1100–2000</td>
<td>0.7–5.8</td>
</tr>
<tr>
<td>15</td>
<td>Lifshitz, Scheller, Burcat and Skinner</td>
<td>Reflected wave</td>
<td>Pressure radiation (CH₄, CO₂, OH, CH₃)</td>
<td>Ar</td>
<td>0.2, 1.0, 2.0</td>
<td>1200–2100</td>
<td>3–300</td>
</tr>
<tr>
<td>16</td>
<td>Tsuboi and Wagner</td>
<td>Reflected wave</td>
<td>Pressure radiation (OH, CH, CO, CO₂, H₂O)</td>
<td>Ar</td>
<td>0.5–1.0</td>
<td>1500–2150</td>
<td>0.5–2.0</td>
</tr>
<tr>
<td>17</td>
<td>Jachimowski</td>
<td>Incident wave</td>
<td>Radiation (O–CO reaction)</td>
<td>Ar–CO₂</td>
<td>0.8, 1.0, 1.2</td>
<td>1790–2584</td>
<td>1.2–1.7</td>
</tr>
<tr>
<td>18</td>
<td>Cooke and Williams</td>
<td>Incident wave</td>
<td>Radiation (OH, CO₂)</td>
<td>Ar</td>
<td>0.5, 1.0, 2.0</td>
<td>1648–2179</td>
<td>0.2–0.5</td>
</tr>
<tr>
<td>19</td>
<td>Seery and Bowman</td>
<td>Reflected wave</td>
<td>Pressure radiation (OH, CH, CO, C₂, H₂O)</td>
<td>Ar–N₂</td>
<td>0.5, 1.0, 2.0</td>
<td>1350–1900</td>
<td>1.7–6.0</td>
</tr>
<tr>
<td>20</td>
<td>Grillo and Slack</td>
<td>Reflected wave</td>
<td>Radiation (OH, H₂O, CO₂)</td>
<td>Ar–N₂</td>
<td>1.0, 2.0</td>
<td>1640–2150</td>
<td>1–6</td>
</tr>
<tr>
<td>21</td>
<td>Heffington, Parks, Sulzmann and Penner</td>
<td>Reflected wave</td>
<td>Radiation (OH, CH, C₂, CO, H₂O)</td>
<td>Ar–H₂O</td>
<td>0.2, 1.0, 1.0</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>22</td>
<td>Krishnan and Ravikumar</td>
<td>Reflected wave</td>
<td>Pressure radiation (visible)</td>
<td>Ar</td>
<td>0.2–4.0</td>
<td>1600–2100</td>
<td>1–6</td>
</tr>
<tr>
<td>23</td>
<td>Cheng and Oppenheim</td>
<td>Reflected wave</td>
<td>Pressure</td>
<td>Ar</td>
<td>0.5, 1.0</td>
<td>1700–2200</td>
<td>1–3</td>
</tr>
<tr>
<td>24</td>
<td>Brabbs and Robertson</td>
<td>Reflected wave</td>
<td>Pressure radiation (CO)</td>
<td>Ar–H₂</td>
<td>0.5, 1.0, 2.0</td>
<td>1500–1920</td>
<td>3</td>
</tr>
<tr>
<td>25</td>
<td>Hwang, Rabinowitz, Gardiner and Robinson</td>
<td>Reflected wave</td>
<td>Pressure radiation (CH₃)</td>
<td>Ar</td>
<td>0.2–1.0</td>
<td>1500–1900</td>
<td>4</td>
</tr>
</tbody>
</table>

Table 2. Experimental studies of methane–oxygen autoignition using shock tube technique

| Present work | Spadaccini and Colket | Reflected wave | Pressure radiation (OH) | Ar | 0.45–1.25 | 1350–2000 | 3–15 |
ignition delay characteristics of methane fuels

437

stoichiometric, and rich methane–oxygen mixtures. Most of the mixtures have been highly diluted (80–95%) using argon as the diluent. However, Asaba et al. conducted tests using undiluted methane–oxygen mixtures as well as mixtures diluted with argon. Seery and Bowman used mixtures having dilution levels as low as 50%. Some studies have been made using diluents other than argon, such as helium or nitrogen, and others with argon and a small amount of either carbon monoxide, nitrogen, water or hydrogen. Although early shock tube studies reported an influence of the type of diluent on induction time, this was not confirmed in later studies using highly diluted methane–oxygen mixtures.

Before discussing the methane–oxygen investigations, some comments are appropriate on the quality of ignition data obtained from this work. An evaluation of the reported work indicates there are some discrepancies in results among the investigators. As a general explanation, it must be noted that the reported experimental conditions vary over a wide range of mixture compositions and operating conditions. In addition, a variety of different measurement techniques were used to determine ignition delay times. Experimental technique has a large bearing on quality of the data and, in particular, the sensitivity of the measuring instrumentation can influence quantitative values of the induction time. This later factor, i.e. instrumentation sensitivity, is thought to be responsible for differences between early and more recent measurements. It has been noted by Brabb and Robertson that some scatter in the ignition data is due to inaccurate measurement of the incident shock velocity. Bowman has estimated that inaccuracies in measured shock velocities can result in ±20 and ±50 K uncertainties in temperatures behind incident and reflected waves, respectively. In other cases, an incorrect evaluation of the shock wave velocity may influence ignition results. The effects of shock wave attenuation were not carefully considered in some of the early investigations. As suggested by Tsuboi and Wagner, a temperature correction of approximately 20 K should be made to account for non-ideal behavior of the shock wave on the basis of 2% attenuation per meter. Finally, a fundamental problem over the years has been an inconsistent definition of the ignition delay time in experimental studies. Some investigators have used the time to the initial rise in pressure or radiation as detected by a sensing device for indication of ignition, whereas others have used the time to a peak value of pressure or light emission or to some arbitrary fraction of the peak.

Several, but not all, of the investigators cited in Table 2 developed correlations for expressing ignition delay time in terms of test parameters. The general form they have used is the same as previously stated with the addition of a concentration term for the diluent in the gas mixture, or

\[ t = A \exp\left(\frac{E}{RT}\right)\left[\text{CH}_4\right]^a\left[\text{O}_2\right]^b\left[\text{Ar}\right]^c \]

where, as before, \( A \) is an empirically determined constant, \( E \) is an equivalent activation energy, \( R \) is the universal gas constant and \( T \) is temperature. The brackets indicate concentrations of methane, oxygen and diluent in the mixture with their power dependencies noted by \( a, b \) and \( c \), respectively. Ignition delay time \( t \) is given in seconds when \( E \) is in cal/mol, \( T \) is in degrees Kelvin, and the concentration terms are in mol/cc.

Asaba et al. obtained ignition data that suggested two different mechanisms exist during methane oxidation, depending upon the equivalence ratio of the mixture. For lean mixtures, the branching chain mechanism at relatively low temperatures governs the reaction during the induction period. Data are correlated in terms of the oxygen concentration and an activation energy of approximately 21 kcal/mol. For rich mixtures, Asaba et al. report that the thermal chain mechanism governs the reaction at high temperatures. Data are correlated in terms of both the methane and oxygen concentrations and an activation energy of 53 kcal/mol.

For a mixture slightly leaner than stoichiometric, Miyama and Takeyama report ignition delay to be inversely proportional to the oxygen concentration with no dependency on fuel concentration. However, they found different values of the activation energy depending on whether pressure rise or radiation measurements were used to determine the delay time. It is suspected that the discrepancy was a result of local ignition caused by inadvertent hot spots in the shock tube. In a subsequent investigation, they correlated induction time as being inversely proportional to both oxygen and fuel concentrations, using a higher value of the activation energy than previously found.

Several other investigators have found ignition delay time for methane–oxygen mixtures to be inversely proportional to oxygen concentration with no apparent dependency on methane concentration. Higgin and Williams show their ignition delay data to correlate very well with those of Asaba et al. and Miyama and Takeyama over an identical temperature range using the oxygen concentration. However, Higgin and Williams also state that a correlation using both oxygen and methane concentrations was consistent with their experimental data. They do not report values of the correlating parameters to permit quantitative determination of ignition delay time. White conducted experiments with lean mixtures, including an extremely lean one of 2% methane in oxygen (\( ER = 0.04 \)). He correlated the ignition delay times in terms of the oxygen concentration using a value of 51 kcal/mol for \( E \), a significantly larger value than found by other investigators for that form of correlation. In one of the few shock tube studies of methane–oxygen ignition using the incident wave for shock heating, Cooke and Williams used lean, stoichiometric, or rich mixtures at low pressures. They found that their complete data
set for methane could be correlated without a dependency on methane concentration claiming that the influence of fuel concentration is less pronounced at lower pressures.

Bowman and Seery\textsuperscript{12,13} conducted investigations to study the oxidation of methane and reported the power dependencies of ignition delay on the composition of the gas mixture. Their results show a slight increase in induction times as the mixture equivalence ratio increases from lean to rich, in agreement with results reported by Skinner and Ruehrwein.\textsuperscript{7} Furthermore, they found measured times for both lean and rich mixtures were related to the total mixture concentration to the 1.2 power with methane and oxygen concentrations correlated by the 0.4 and -1.6 powers, respectively. They noted that this dependency is similar to that found from flow reactor and flame studies. Bowman originally reported differences in activation energy for lean or rich mixtures, although not as great as those reported by Asaba et al. In later work, Seery and Bowman\textsuperscript{13} reported a single value of $E$ regardless of equivalence ratio. Based on their experimental results, Seery and Bowman made an analytical study of the methane oxidation process and formulated a 13-step mechanism to model it. Comparison of calculated and experimental induction times showed good agreement. Cheng and Oppenheim\textsuperscript{23} conducted a limited number of shock tube studies of methane ignition as part of a larger investigation primarily directed toward studies of autoignition in methane–hydrogen mixtures. They used a non-linear regression of their data and reported nearly an inverse square dependency of ignition delay on oxygen concentration. This is a singular result found by no other investigators.

In the work cited up to this point, the power dependencies of the concentration terms were determined by trial and error testing, fitting assumed values to the experimental data or, in the case of Cheng and Oppenheim, by applying regression procedures. Lifshitz and co-workers\textsuperscript{15,27} were the first to deduce them by means of carefully designed experiments to independently measure each exponent. Their experiments confirmed that the argon diluent has no effect on the induction time. They compared data from other investigations that they thought to be most reliable and found good agreement with their correlation over a range of temperatures from 1300 to 2500 K. These values found for the power dependencies of methane and oxygen concentrations have, with some slight adjustments, been used by all following investigators. For example, Jachimowski\textsuperscript{17} used the correlation directly in studies of the methane oxidation process. Grillo and Slack\textsuperscript{20} used the exponent values derived by Lifshitz and co-workers but found a slightly larger value of the activation energy to apply. In one of the most recent investigations of methane ignition, Brabbs and Robertson\textsuperscript{24} also used this correlation with larger values for $E$. In fact, they report a slight difference in the activation energy, depending on the equivalence ratio of the mixture.

The potential influence of inert diluents, e.g. argon and nitrogen, on the ignition delay of methane has been evaluated by several investigators. Seery and Bowman\textsuperscript{19} and White\textsuperscript{14} measured ignition delays behind reflected shocks for methane–oxygen mixtures diluted by either argon or nitrogen, and did not observe any effect of the diluent on the ignition process. Snyder et al.\textsuperscript{5} investigated methane–air ignition behind reflected shock waves. Their ignition delay times agree very closely with measurements by Seery and Bowman\textsuperscript{13} on methane–oxygen–argon mixtures at comparable conditions. Furthermore, Grillo and Slack\textsuperscript{20} concluded, on the basis of their investigations, that molecular nitrogen has little or no influence on the ignition delay times of methane–oxygen mixtures.

Tsuboi and Wagner\textsuperscript{16} conducted methane shock tube studies over a wide range of conditions. They obtained data at pressures considerably higher (by more than an order of magnitude) than any other investigators. A correlation of induction time was obtained for their wide range of conditions which is similar to that derived by Lifshitz and co-workers having only slightly adjusted values for the concentration exponents. However, for very dilute mixtures, Tsuboi and Wagner found an increase in the value of $E$ and a change in the concentration dependence of the delay time. The final study of methane ignition to be discussed is that of Krishnan and Ravikumar.\textsuperscript{22} They reviewed the work of previous investigators, noted the discrepancies in results, and attempted to optimize experimental conditions in an investigation of methane ignition behind reflected shock waves. By means of a least square fit of their experimental data, Krishnan and Ravikumar found that induction time could be represented by a form of the Lifshitz and co-workers correlation with only slightly adjustment to values for the activation energy and the exponent of the oxygen concentration. They applied their modified correlation to the data of Higgin and Williams, Seery and Bowman, Lifshitz and co-workers and Tsuboi and Wagner and found very good agreement over a temperature range from 1400 to 2100 K.

In summary, a great deal of autoignition data has been obtained for pure methane. A correlation of more than 500 of the most reliable methane ignition delay measurements that have been reported by 13 different investigators using both shock tubes and continuous flow devices is presented in Fig. 1. The figure shows that the methane ignition delay expression proposed by Lifshitz and co-workers and improved upon by Krishnan and Ravikumar

\[ t = 2.21 \times 10^{-14} \exp(22659/T)\left[\text{O}_2\right]^{-1.05}\left[\text{CH}_4\right]^{0.33} \]

represents the shock tube measurements reasonably well over the temperature range 1250–2500 K, although the temperature dependence of the data is slightly higher than the correlation, leading to small
overpredictions above 2200 K and underpredictions below 1800 K. At lower temperatures (represented by the continuous flow experiments of Cowell and Lefebvre, and Wagner) there seems to be a decrease in the activation energy, thus caution should be used in extrapolating the correlation to low temperatures (this apparent lower activation energy could be due to an enhanced effect of low concentrations of impurities, such as ethane, at low temperatures).

2.3.3. Methane-hydrocarbon mixtures and natural gas

Natural gas is a mixture comprising principally methane with other hydrocarbon species; there is no fixed, or even typical, composition. The typical compositions of several natural gas fuels that can be obtained from various world-wide sources are shown in Table 3. As noted, the amount of methane in natural gas can vary over a wide range, for example, from 80 to almost 100% for Abu Dhabi and Alaska fuels, respectively. Hydrocarbon species typically found in natural gas along with methane include ethane, propane, butane and pentane. The concentration levels of ethane and propane are usually more than 1% by volume (note that Abu Dhabi fuel has over 15% ethane), whereas the levels of the other hydrocarbon species are usually less than 1%.

The presence of the minor hydrocarbon species can have a profound influence on the combustion properties and, in particular, the ignition characteristics of natural gas. Methane by itself with its primary carbon-hydrogen bonds has stronger bond energies than the other hydrocarbon species which have a variety of weaker secondary and tertiary carbon-hydrogen bonds. Furthermore, the methyl radical, the primary hydrocarbon radical formed from methane decomposition, is relatively stable and not easily oxidized. Other more reactive hydrocarbon radicals can be separated from the larger hydrocarbon molecules with weaker bonds to form precursors for initiating chemical reaction more quickly, thereby decreasing ignition delay times. This effect has been confirmed by several investigators in a variety of experimental studies. For example, Burcat et al.22 made a systematic study of ignition delay times behind reflected shock waves for the individual alkane fuels methane through pentane. For stoichiometric mixtures, methane was found to be significantly less reactive than the other fuels having ignition delay times approximately one order of magnitude longer.

Westbrook and co-workers28,29 at the Lawrence Livermore National Laboratory have studied the induction period of methane-hydrocarbon mixtures using numerical modeling techniques. Using a 75-
TABLE 4. Experimental studies of simulated natural gas autoignition using shock tube technique

<table>
<thead>
<tr>
<th>Ref.</th>
<th>Investigators</th>
<th>CH₄</th>
<th>C₂H₆</th>
<th>C₃H₈</th>
<th>n-C₄H₁₀</th>
<th>i-C₄H₁₀</th>
<th>O₂</th>
<th>Air</th>
<th>Temperature, K</th>
<th>Pressure, atm</th>
</tr>
</thead>
<tbody>
<tr>
<td>11</td>
<td>Higgin and Williams</td>
<td>1.9</td>
<td>-</td>
<td>-</td>
<td>0.02</td>
<td>-</td>
<td>-</td>
<td>8.0</td>
<td>-</td>
<td>1560-2100</td>
</tr>
<tr>
<td>15</td>
<td>Lifshitz, Scheller, Burcat and Skinner</td>
<td>3.5</td>
<td>-</td>
<td>0.073</td>
<td>-</td>
<td>-</td>
<td>7.0</td>
<td>-</td>
<td>-</td>
<td>1380-1750</td>
</tr>
<tr>
<td>33</td>
<td>Crossley, Dorko Scheller and Burcat</td>
<td>3.5</td>
<td>0.05</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>7.0</td>
<td>-</td>
<td>-</td>
<td>1370-1870</td>
</tr>
<tr>
<td>34</td>
<td>Frenklach and Bornside</td>
<td>9.5</td>
<td>-</td>
<td>0.19</td>
<td>-</td>
<td>-</td>
<td>19.0</td>
<td>-</td>
<td>-</td>
<td>1300-1530</td>
</tr>
<tr>
<td>35</td>
<td>Zellner, Niemitz, Warnatz, Gardiner, Eubank and Simmie</td>
<td>1.0</td>
<td>0.2</td>
<td>-</td>
<td>-</td>
<td>0.1</td>
<td>98.9</td>
<td>-</td>
<td>-</td>
<td>1240-1540</td>
</tr>
<tr>
<td>36</td>
<td>Eubank, Rabinowitz, Gardiner and Zellner</td>
<td>1.0</td>
<td>0.2</td>
<td>0.1</td>
<td>-</td>
<td>-</td>
<td>98.8</td>
<td>-</td>
<td>-</td>
<td>1200-1610</td>
</tr>
<tr>
<td>Present work</td>
<td>Spadaccini and Colket</td>
<td>3.4</td>
<td>0.1</td>
<td>0.3</td>
<td>0.1</td>
<td>3.5</td>
<td>0.4</td>
<td>3.5</td>
<td>0.35</td>
<td>7.0</td>
</tr>
<tr>
<td></td>
<td></td>
<td>3.3</td>
<td>0.2</td>
<td>3.4</td>
<td>0.1</td>
<td>3.3</td>
<td>0.2</td>
<td>3.3</td>
<td>0.1</td>
<td>7.0</td>
</tr>
<tr>
<td></td>
<td></td>
<td>3.5</td>
<td>0.04</td>
<td>3.4</td>
<td>0.1</td>
<td>3.3</td>
<td>0.2</td>
<td>3.3</td>
<td>0.1</td>
<td>7.0</td>
</tr>
<tr>
<td></td>
<td></td>
<td>3.4</td>
<td>0.2</td>
<td>3.4</td>
<td>0.1</td>
<td>3.3</td>
<td>0.2</td>
<td>3.3</td>
<td>0.1</td>
<td>7.0</td>
</tr>
<tr>
<td></td>
<td></td>
<td>3.3</td>
<td>0.2</td>
<td>3.3</td>
<td>0.1</td>
<td>3.3</td>
<td>0.2</td>
<td>3.3</td>
<td>0.1</td>
<td>7.0</td>
</tr>
</tbody>
</table>

step reaction scheme for methane-ethane oxidation. Westbrook and Haselman studied the effects of ethane addition on methane-air ignition, and found that the presence of small amounts of ethane (5–10%) sharply reduced the induction time of the mixture relative to that for pure methane. They conclude that this is a result of enhanced early radical generation by the more reactive minor species leading to more rapid reaction. In a subsequent study, Westbrook and Pitz reported that the ignition behavior of a methane-ethane-air mixture is most sensitive to the addition of amounts less than approximately 10% of a hydrocarbon (propane) additive; at higher concentrations, the incremental sensitivity decreases. Also, they concluded from the modeling studies that it is necessary to consider each non-methane species of a ternary fuel mixture rather than treating the additive hydrocarbons as a single species in a binary fuel mixture. The autoignition of methane-ethane and methane-butane mixtures was studied in a collaborative investigation comprising experiments at the University of Leeds and analytical modeling at Lawrence Livermore. Autoignition temperatures were measured in a closed, spherical reaction vessel at atmospheric pressure. (The problems with this technique have been discussed previously, but the device can be used to evaluate the reactivities of different fuels on a comparative basis). For either binary fuel mixture, the greatest sensitivity of the autoignition temperature to variations in composition was observed when the level of ethane or butane was less than 10% by volume of the fuel, thereby confirming analytical predictions. Westbrook and Pitz have also applied their numerical modeling techniques to the study of autoignition and the tendency to knock in diesel engines fueled by natural gas. For stoichiometric fuel-air mixtures, they computed ignition delay times in a diesel environment and found that the presence of a minor hydrocarbon species such as ethane sharply reduced delay times. Probably the most useful information pertaining to natural gas autoignition in high-pressure-ratio gas turbines and ramfans can be found from shock tube studies using simulated mixtures of natural gas. Many of these studies are extensions to better understand the kinetic sensitization of the methane oxidation process. A summary of this work is presented in Table 4 listing the simulated natural gas mixtures investigated, test conditions, and the range of reported ignition delay times. As noted, the majority of these investigations were conducted using methane-oxygen-argon mixtures, but two used methane-air to which minor hydrocarbon species were added. None of the investigators listed in the table report any attempts to correlate test results in a
form useful for quantifying ignition delay time as a function of mixture composition.

One of the first studies to report the influence of hydrocarbon additives on methane mixtures was Higgin and Williams\(^\text{11}\) who found that the addition of trace amounts of n-butane greatly reduced ignition delay times. The significantly lower times they reported were obtained at much higher temperatures than tested in the other studies listed. Higgin and Williams\(^\text{11}\) state that the addition of 1% n-butane reduced the ignition delay by a factor of three, 5% by a factor of six and 10% by a factor of ten. They attribute this result to the ease of dissociation of n-butane by carbon–carbon bond fission.

Lifshitz et al.\(^\text{15}\) at the USAF Aerospace Research Laboratories investigated the influence of varying amounts of propane (2 and 5% of the total fuel content) on methane ignition and found the addition of propane to shorten the ignition delay time. Additional investigations at the same laboratory were conducted to study in greater detail the effect of higher alkanes on the induction time of methane.\(^\text{32,33}\)

All additive tests were made using a stoichiometric methane mixture. A great deal of scatter is noted in the experimental results and it is difficult to separate temperatures and ignition delay times for each individual additive. Therefore, the values given for these parameters in Table 4 represent ranges reported for all mixtures tested. In general, it was found that all alkane additives that were tested produced appreciable reductions in ignition delay time. This effect was attributed to a chemical coupling of the oxidation reactions whereby alkyl radicals (e.g. CH\(_3\)) are formed at the beginning of the ignition process by the decomposition of the additive fuel.

Frenklach and Bornside\(^\text{34}\) measured ignition delay times behind reflected shock waves for methane–oxygen–argon mixtures to which varying amounts of propane were added, up to 20% by volume of the methane content. They reported that as the amount of propane was increased, ignition delay time was increasingly lowered compared to a methane mixture without propane. Furthermore, Frenklach and Bornside\(^\text{34}\) used a computer model composed of 140 reactions and 34 species to analyze the sensitization of the methane oxidation process by propane, and they were able to predict quite well the ignition delay time as a function of propane content.

Finally, as previously mentioned, in two of the investigations listed, ignition delay times of methane–hydrocarbon mixtures were obtained in air using reflected wave shock heating. Zellner et al.\(^\text{35}\) studied methane mixtures having 10% by volume of ethane, propane or iso-butane additive. They found that each additive markedly shortened the induction time, but by approximately the same amount regardless of the alkane type. In related work, Eubank, Rabinowitz, Gardiner and Zellner\(^\text{36}\) investigated the effect of a combination of alkanes on methane ignition. They found the effect to be additive; that is, the ignition delay time for a mixture of methane and ethane was further reduced by the addition of propane and still further reduced by the addition of n-butane. They conclude that all hydrocarbon species of a fuel mixture must be considered in characterizing the ignition behavior of a fuel.

In summary, it can be concluded from existing information that the presence of small amounts of hydrocarbon species has a significant effect on ignition characteristics of methane. Therefore, it is important to develop a quantitative database for the autoignition of methane–hydrocarbon mixtures so that ignition delay times can be satisfactorily predicted and limits of contaminant levels determined for a particular application. Although sophisticated chemical kinetics modeling is available to many researchers, what is clearly desirable as a combustor design tool is an empirical correlating expression that accounts for compositional variations of a methane–hydrocarbon mixture and offers adequate accuracy over the range of conditions encountered in practical devices. Unfortunately, the existing data base is very narrow and represents only a small variation in the independent variables. It has been shown that computer models are able to predict induction times satisfactorily for some fuel mixtures, but these models are complex and need extensive experimental validation. Therefore, additional experiments and measurements are required to permit development of generalized correlations.

3. AUTOIGNITION EXPERIMENTS

3.1. Test Apparatus and Procedures

Measurements of ignition delay were obtained behind reflected shock waves using a stainless-steel shock tube apparatus shown in Fig. 2. The shock tube had an internal diameter of 3.8 cm and the driven section was extended to 526 cm so that residence times up to 1.8 ms could be achieved at elevated temperatures and pressures. The driver section was 88 cm long. The test procedure consisted of preloading a fuel–oxygen–argon mixture at low pressure in the driven section. The pressure of helium in the driver section was then raised until a prestressed aluminum diaphragm burst, propagating a shock wave down the tube past a series of pressure transducers (rise times of 2 \(\mu\)s). The pressure transducers were located 167-, 90.8-, 14.6-, and 17.6-cm from the end wall. Signals from the transducers were monitored on a high-speed Nicolet storage oscilloscope, with a time resolution of one microsecond per point. From the arrival times of the wave at each of the transducers, shock velocities could be calculated. A small decay in velocity was accounted for by extrapolating velocities to the end wall to calculate the shock strength at the end wall and initial temperatures and pressures behind the reflected shock.
Ignition delay times were monitored in two ways at the measurement station located 1.7 cm from the end wall. After arrival of the reflected wave and an appropriate rise in pressure, ignition was accompanied by another rapid pressure rise. The time delay between the arrival of the reflected wave and the rise in pressure due to ignition was one measure of the ignition delay time. A second and usually more sensitive technique for measuring the ignition delay involved monitoring the emission from electronically excited hydroxyl radicals formed during the induction period. The OH emission was monitored using a narrow bandpass filter centered at 307 nm and a 9659QB-EMI photomultiplier (PMT) attached near the end of the shock tube as shown in Fig. 3. Slits located next to the sapphire windows and near to the entrance of the photomultiplier tube minimized signals from internal reflections. Overall response time of the optical system (slits, PMT electronics) was about 3–6 μs. Ignition delay times were determined by measuring the time from arrival of the reflected shock wave to the initial rapid rise of OH emission. Occasionally a short rise appeared preceding the OH signal, indicating either early formation of electronically excited OH or internal reflections in the shock tube. This phenomenon was ignored and may have contributed to some of the scatter in the present ignition delay data. Hydroxyl emission signals and pressure profiles near the end wall were recorded on a LeCroy digital storage oscilloscope under control from a personal computer.

Test mixtures of fuel, oxygen and argon were premixed to obtain the desired compositions using a stainless-steel mixing rack, and they were stored in stainless-steel cylinders and/or quartz bulbs prior to usage. Gases were blended, using partial-pressure mixing techniques, and allowed to thoroughly mix overnight prior to testing. All components were obtained at high purity; argon diluent was 99.999% pure, methane was 99.97% pure and oxygen was 99.99% pure. Other hydrocarbons, viz. ethane, propane, n-butane, and i-butane, were obtained with respective stated purities of 99.99, 99.97, 99.9 and 99.99%, respectively. Estimated uncertainties in the final mixture compositions using the partial-pressure mixing technique are about 3% of the stated values.

3.2. Methane Ignition Delay Measurements

Methane autoignition experiments were conducted for five mixtures (listed in Fig. 4) with equivalence
Ignition delay characteristics of methane fuels 443

10^{-5}

10^{-6}

10^{-7}

10^{-8}

10^{-9}

methane correlation

FIG. 4. Correlation of methane ignition delay experimental data

ratios of 0.45–1.25 and methane concentrations of 3.5 and 6.0% by volume. Pre-shock pressures were typically 100–400 torr (0.13–0.53 atm) and post-shock pressures ranged from about 3 to 15 atm. Ignition delay times were measured over the temperature range of 1350–2000 K. For these conditions, initial methane concentrations ranged from about $8 \times 10^{-7}$ to $5 \times 10^{-6}$ mol/cc. Methane ignition delay data are listed in Table 5.

The measured data were compared to the empirical expression obtained from the literature survey. Small deviations from the literature correlation occurred for ignition delay times that were either relatively long or relatively short. Because of the possibility of uncertainties associated with the shock front, all data having ignition delay times shorter than 30 μs were discarded. Also, to correct for a small post-shock pressure decay evident after long delay times, the ignition temperatures and pressures were assumed to be the arithmetic average between the initial post-shock conditions and those existing at the onset of ignition. Temperatures at the time of ignition were calculated assuming adiabatic, isentropic decompression. The temperature corrections were typically 5–30 K, although corrections approaching 100 K were applied to the longest ignition delay measurements. A comparison between the corrected experimental data and the literature correlation is shown in Fig. 4. Consistent with the literature data shown in Fig. 1, the test data lie slightly above the correlation line. In addition, the results suggest that for the higher methane concentration (i.e. 6%), the ignition delay times may be shortened relative to the predictions for temperatures of 1400 to 1600 K. As will be shown later, this result is in agreement with detailed chemical kinetic modeling.

3.3. Effects of Hydrocarbon Contaminants

As mentioned previously, it was desirable to perform methane–hydrocarbon autoignition tests to increase the size of the ignition delay database so that regression analyses could be performed and correlating expressions developed for binary and multicomponent mixtures. A total of 72 experiments were performed on ten nearly stoichiometric methane–oxygen–hydrocarbon mixtures listed in Table 4 to evaluate the individual effects of ethane, propane, normal-butane and iso-butane contaminants at concentration levels of the hydrocarbon in methane ranging from 1 to 10% by volume. Specific run conditions and ignition delay measurements are provided in Table 6. These data are compared to the correlation for methane ignition delay in Fig. 5a–c for the ethane, propane and butane additive tests, respectively. Essentially no difference was found between the effects of normal- and iso-butane. All the ignition delay data for binary mixtures of methane and hydrocarbon contaminant species is commingled and presented in Fig. 5d. Generally, the higher molecular weight hydrocarbons significantly reduce the ignition delay relative to that of pure methane alone, although the amount of reduction appears to be a function of the type and concentration of the contaminant. Butane addition appears to have a greater effect in reducing the ignition delay than either ethane or propane. Also, increasing the contaminant concentration shortens the ignition delay times.

In addition to the above data, a few researchers have investigated the autoignition of methane in the presence of other hydrocarbons. These experiments were discussed above, and the test conditions are listed in Table 4. Ignition delay correlating equations that account for compositional variations of binary methane–hydrocarbon mixtures were developed by
commingling the present data with the literature data and performing regression analyses. The data were correlated using the now familiar general expression, extended to include the concentration of contaminant:

\[ t = A \exp\left(\frac{E}{RT}\right) [O_2]^{a} [CH_4]^{b} [C_xH_y]^c \]

The oxygen concentration dependency was arbitrarily assigned to be the same as obtained for pure methane. Correlations for mixtures of methane with ethane, propane or butane in the above format are shown in Figs 6–8, for hydrocarbon contaminant concentrations in the range 2–20% and temperatures from 1250 to 1800 K. The empirical constants determined in these analyses are summarized in Table 7, along with the range of experimental parameters over which they are applicable (the table also includes coefficients for multicomponent natural gas mixtures, to be discussed below). As can be seen, overall activation energies are slightly lower than for pure methane. This result indicates that the differences between ignition delay times for pure methane and those for methane–hydrocarbon mixtures increase with decreasing temperature. Also note that the exponent for the hydrocarbon contaminant is negative, so that increases in concentrations of these components decrease ignition delay times; whereas increases in methane concentrations increase delay times. A comparison of the concentration exponents determined for the different hydrocarbon additives does not reveal any particular trend. Moreover, the reader should be cautioned against drawing unfounded conclusions from the relative values of the exponents in the above expressions. These empirical equations should simply be used for predictive pur-

### Table 5. Autoignition of methane

<table>
<thead>
<tr>
<th>T, K</th>
<th>P, atm</th>
<th>t, s</th>
<th>X_{CH4}</th>
<th>X_{O2}</th>
<th>[CH_4], mol/cc</th>
<th>[O_2], mol/cc</th>
<th>10000/T</th>
</tr>
</thead>
<tbody>
<tr>
<td>1705</td>
<td>6.55</td>
<td>1.15E-04</td>
<td>0.0350</td>
<td>0.0700</td>
<td>1.64E-06</td>
<td>3.28E-06</td>
<td>5.86</td>
</tr>
<tr>
<td>1672</td>
<td>6.28</td>
<td>2.36E-04</td>
<td>0.0350</td>
<td>0.0700</td>
<td>1.60E-06</td>
<td>3.20E-06</td>
<td>5.98</td>
</tr>
<tr>
<td>1918</td>
<td>7.97</td>
<td>2.20E-05</td>
<td>0.0350</td>
<td>0.0700</td>
<td>1.80E-06</td>
<td>3.60E-06</td>
<td>5.56</td>
</tr>
<tr>
<td>1516</td>
<td>5.78</td>
<td>5.93E-04</td>
<td>0.0350</td>
<td>0.0700</td>
<td>1.63E-06</td>
<td>3.26E-06</td>
<td>6.60</td>
</tr>
<tr>
<td>1525</td>
<td>5.90</td>
<td>5.93E-04</td>
<td>0.0350</td>
<td>0.0700</td>
<td>1.65E-06</td>
<td>3.30E-06</td>
<td>6.56</td>
</tr>
<tr>
<td>1820</td>
<td>8.28</td>
<td>4.30E-05</td>
<td>0.0350</td>
<td>0.0700</td>
<td>1.94E-06</td>
<td>3.88E-06</td>
<td>5.49</td>
</tr>
<tr>
<td>1759</td>
<td>4.02</td>
<td>1.46E-04</td>
<td>0.0350</td>
<td>0.0700</td>
<td>9.76E-07</td>
<td>1.95E-06</td>
<td>5.69</td>
</tr>
</tbody>
</table>

...and so on.
Fig. 5. Effect of contaminants on methane autoignition

Fig. 6. Autoignition of methane-ethane mixtures

poses, since statistical analyses to develop multi-
parameter fits may not be indicative of all the under-
lying chemical or physical phenomena.

3.4. Natural Gas Ignition Delay

An objective of this work has been to understand
the differences in autoignition characteristics among
the various natural gas fuels that are available
throughout the world. One typical natural gas, desig-
nated Matheson commercial-grade methane, was
tested in this program; it is compared to other natural
gases in Table 3. Fuel-oxygen-argon mixtures were
prepared for testing at equivalence ratios of approxi-
mately 1.0 and 0.45, and with natural gas concen-
trations of 3.5 and 6% by volume. Specific test con-
ditions and ignition delay times measured using these
mixtures are listed in Table 8. The results of these
tests are presented in Fig. 9 and indicate that the
Matheson natural gas has ignition delay times
approximately one-third those of pure methane
TABLE 6. Autoignition of methane-hydrocarbon mixtures

| T, K | P, atm | T, s | X_{CH4} | X_{O2} | X_{C2H6} | X_{C3H8} | X_{C4H10} | [CH4], mol/cc | [O2], mol/cc | [C2H6], mol/cc | [C3H8], mol/cc | [C4H10], mol/cc | 10000/T |
|------|-------|------|---------|--------|----------|----------|----------|---------------|-------------|----------------|----------------|----------------|----------------|-----------|
| 1418 | 4.33  | 8.62E-04 | 0.0340  | 0.0700 | 0.0010   | 1.26E-06 | 2.60E-06 | 3.72E-08      | 7.05         | 5.74           | 5.38          | 5.08          | 5.81      |
| 1742 | 7.43  | 5.30E-05 | 0.0340  | 0.0700 | 0.0010   | 1.77E-06 | 3.64E-06 | 5.20E-08      | 5.74         | 5.74           | 5.38          | 5.08          | 5.81      |
| 1722 | 7.52  | 3.70E-05 | 0.0340  | 0.0700 | 0.0010   | 1.81E-06 | 3.73E-06 | 5.32E-08      | 5.81         | 5.81           | 5.42          | 5.13          | 5.91      |
| 1698 | 8.05  | 4.30E-05 | 0.0340  | 0.0700 | 0.0010   | 1.96E-06 | 4.04E-06 | 5.78E-08      | 5.89         | 5.89           | 5.52          | 5.24          | 5.99      |
| 1589 | 6.80  | 1.44E-04 | 0.0329  | 0.0700 | 0.0021   | 1.72E-06 | 3.65E-06 | 1.09E-07      | 6.29         | 6.29           | 5.96          | 5.68          | 6.37      |
| 1698 | 8.06  | 4.60E-05 | 0.0329  | 0.0700 | 0.0021   | 1.90E-06 | 4.05E-06 | 1.21E-07      | 5.89         | 5.89           | 5.52          | 5.24          | 5.99      |
| 1354 | 5.37  | 1.12E-03 | 0.0329  | 0.0700 | 0.0021   | 1.59E-06 | 3.38E-06 | 1.01E-07      | 7.39         | 7.39           | 6.86          | 6.58          | 7.37      |
| 1455 | 6.23  | 4.65E-04 | 0.0329  | 0.0700 | 0.0021   | 1.72E-06 | 3.65E-06 | 1.10E-07      | 6.87         | 6.87           | 6.45          | 6.17          | 6.75      |
| 1560 | 7.21  | 1.03E-04 | 0.0329  | 0.0700 | 0.0021   | 1.85E-06 | 3.94E-06 | 1.18E-07      | 6.41         | 6.41           | 6.00          | 5.71          | 6.30      |
| 1609 | 7.86  | 8.10E-05 | 0.0329  | 0.0700 | 0.0021   | 1.96E-06 | 4.16E-06 | 1.25E-07      | 6.21         | 6.21           | 5.83          | 5.55          | 6.21      |
| 1681 | 8.66  | 3.40E-05 | 0.0329  | 0.0700 | 0.0021   | 2.07E-06 | 4.40E-06 | 1.32E-07      | 5.95         | 5.95           | 5.67          | 5.40          | 5.95      |
| 1803 | 3.92  | 2.06E-04 | 0.0329  | 0.0700 | 0.0021   | 9.81E-07 | 2.09E-06 | 6.26E-08      | 6.24         | 6.24           | 5.96          | 5.68          | 6.33      |
| 1714 | 7.66  | 4.30E-05 | 0.0350  | 0.0700 | 0.0004   | 1.91E-06 | 3.81E-06 | 1.91E-08      | 8.03         | 8.03           | 7.65          | 7.37          | 8.03      |
| 1723 | 8.31  | 4.30E-05 | 0.0350  | 0.0700 | 0.0004   | 2.06E-06 | 4.11E-06 | 2.06E-08      | 8.03         | 8.03           | 7.65          | 7.37          | 8.03      |
| 1682 | 8.18  | 1.09E-04 | 0.0350  | 0.0700 | 0.0004   | 2.07E-06 | 4.15E-06 | 2.07E-08      | 9.59         | 9.59           | 9.21          | 8.93          | 9.62      |
| 1445 | 6.07  | 4.12E-04 | 0.0350  | 0.0700 | 0.0035   | 1.79E-06 | 3.58E-06 | 1.79E-07      | 6.92         | 6.92           | 6.54          | 6.26          | 6.87      |
| 1669 | 7.45  | 3.70E-05 | 0.0350  | 0.0700 | 0.0035   | 1.90E-06 | 3.81E-06 | 1.90E-07      | 5.99         | 5.99           | 5.61          | 5.33          | 5.99      |
| 1544 | 6.65  | 1.68E-04 | 0.0350  | 0.0700 | 0.0035   | 1.84E-06 | 3.67E-06 | 1.84E-07      | 6.48         | 6.48           | 6.10          | 5.82          | 6.54      |
| 1634 | 7.50  | 3.70E-05 | 0.0350  | 0.0700 | 0.0035   | 1.96E-06 | 3.91E-06 | 1.96E-07      | 6.12         | 6.12           | 5.74          | 5.46          | 6.12      |
| 1486 | 6.44  | 2.24E-04 | 0.0350  | 0.0700 | 0.0035   | 1.85E-06 | 3.70E-06 | 1.85E-07      | 6.73         | 6.73           | 6.35          | 6.07          | 6.73      |
| 1549 | 7.13  | 1.43E-04 | 0.0350  | 0.0700 | 0.0035   | 1.96E-06 | 3.93E-06 | 1.96E-07      | 6.46         | 6.46           | 6.08          | 5.80          | 6.46      |
| 1572 | 7.26  | 1.12E-04 | 0.0350  | 0.0700 | 0.0035   | 1.97E-06 | 3.94E-06 | 1.97E-07      | 6.36         | 6.36           | 6.00          | 5.72          | 6.36      |
| 1652 | 8.00  | 5.30E-05 | 0.0350  | 0.0700 | 0.0035   | 2.07E-06 | 4.13E-06 | 2.07E-07      | 6.05         | 6.05           | 5.70          | 5.43          | 6.05      |
| 1572 | 7.39  | 1.00E-04 | 0.0350  | 0.0700 | 0.0035   | 2.00E-06 | 4.01E-06 | 2.00E-07      | 6.36         | 6.36           | 6.00          | 5.72          | 6.36      |
| T, K | P, atm | T, s | XCH₄ | XO₂ | XC₃H₈ | XC₄H₁₀ | [CH₄], mol/cc | [O₂], mol/cc | [C₃H₈], mol/cc | [C₄H₁₀], mol/cc | 10000/T |
|------|-------|-----|------|-----|-------|--------|---------------|--------------|---------------|---------------|-----------|---------|
| 1581 | 7.66  | 5.30E-05 | 0.0329 | 0.0700 | 0.0021 | 1.94E-06 | 4.13E-06 | 1.24E-07 | 6.33 |
| 1420 | 6.22  | 4.40E-04 | 0.0329 | 0.0700 | 0.0021 | 1.75E-06 | 3.73E-06 | 1.12E-07 | 7.94 |
| 1641 | 8.25  | 4.60E-05 | 0.0329 | 0.0700 | 0.0021 | 2.02E-06 | 4.29E-06 | 1.29E-07 | 6.09 |
| 1351 | 5.53  | 8.56E-04 | 0.0329 | 0.0700 | 0.0021 | 1.64E-06 | 3.49E-06 | 1.05E-07 | 7.40 |
Table 7. Empirical correlations of ignition delay times for temperatures between 1200 and 2000 K

<table>
<thead>
<tr>
<th>Description</th>
<th>A</th>
<th>E/R</th>
<th>a</th>
<th>b</th>
<th>c</th>
<th>R²</th>
</tr>
</thead>
<tbody>
<tr>
<td>Methane (Ref. 22)</td>
<td>2.21 x 10⁻¹⁴</td>
<td>22500</td>
<td>-1.05</td>
<td>0.33</td>
<td>0</td>
<td>—</td>
</tr>
<tr>
<td>Methane with ethane*</td>
<td>1.32 x 10⁻¹³</td>
<td>18772</td>
<td>-1.05</td>
<td>0.61</td>
<td>-0.24</td>
<td>0.86</td>
</tr>
<tr>
<td>Methane with propane*</td>
<td>4.04 x 10⁻¹⁴</td>
<td>21553</td>
<td>-1.05</td>
<td>0.95</td>
<td>-0.46</td>
<td>0.93</td>
</tr>
<tr>
<td>Methane with butanes*</td>
<td>1.49 x 10⁻¹⁵</td>
<td>19586</td>
<td>-1.05</td>
<td>0.88</td>
<td>-0.68</td>
<td>0.90</td>
</tr>
<tr>
<td>Natural gas and methane-hydrocarbon mixtures*</td>
<td>1.77 x 10⁻¹⁴</td>
<td>18963</td>
<td>-1.05</td>
<td>0.66</td>
<td>-0.39</td>
<td>0.88</td>
</tr>
</tbody>
</table>

*Correlations valid over ranges indicated in Tables 6 and 8.

[ ] concentrations in mol/cc; R² = correlation coefficient

FIG. 7. Autoignition of methane-propane mixtures

FIG. 8. Autoignition of methane-butane mixtures

(similar to the binary methane-hydrocarbon mixtures).

However, what is needed is a general correlating expression that can be used to predict ignition delay for any natural gas. Forms of the correlation that include the concentrations of each of the individual hydrocarbon species in natural gas will have a large number of independent variables and require a very large database to develop reasonable solutions. Therefore, the following formulation was chosen for the correlating expression:

\[ t = A \exp \left( \frac{E}{RT} \right) \left[ \left[ O_2 \right]^{a} \left[ CH_4 \right]^{b} \left[ HC \right]^{c} \right] \]

where the oxygen power was again held constant,
Table 8. Autoignition of Matheson commercial-grade methane

<table>
<thead>
<tr>
<th>$T$, K</th>
<th>$P$, atm</th>
<th>$t$, s</th>
<th>$X_{\text{CH}_4}$</th>
<th>$X_{\text{O}_2}$</th>
<th>$X_{\text{WC}}$</th>
<th>$[\text{CH}_4]$, mol/cc</th>
<th>$[\text{O}_2]$, mol/cc</th>
<th>$[\text{HC}]$, mol/cc</th>
<th>10000/$T$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1425</td>
<td>5.66</td>
<td>5.46E-04</td>
<td>0.0338</td>
<td>0.0700</td>
<td>0.0012</td>
<td>1.63E-06</td>
<td>3.39E-06</td>
<td>5.80E-08</td>
<td>7.02</td>
</tr>
<tr>
<td>1556</td>
<td>7.37</td>
<td>1.40E-04</td>
<td>0.0338</td>
<td>0.0700</td>
<td>0.0012</td>
<td>1.95E-06</td>
<td>4.04E-06</td>
<td>6.93E-08</td>
<td>6.43</td>
</tr>
<tr>
<td>1614</td>
<td>8.45</td>
<td>7.10E-05</td>
<td>0.0338</td>
<td>0.0700</td>
<td>0.0012</td>
<td>2.16E-06</td>
<td>4.47E-06</td>
<td>7.66E-08</td>
<td>6.20</td>
</tr>
<tr>
<td>1677</td>
<td>9.38</td>
<td>1.71E-04</td>
<td>0.0338</td>
<td>0.0700</td>
<td>0.0012</td>
<td>2.30E-06</td>
<td>4.77E-06</td>
<td>8.18E-08</td>
<td>5.96</td>
</tr>
<tr>
<td>1499</td>
<td>6.80</td>
<td>3.37E-04</td>
<td>0.0338</td>
<td>0.0700</td>
<td>0.0012</td>
<td>1.87E-06</td>
<td>3.87E-06</td>
<td>6.64E-08</td>
<td>6.67</td>
</tr>
<tr>
<td>1439</td>
<td>6.70</td>
<td>4.34E-04</td>
<td>0.0338</td>
<td>0.0700</td>
<td>0.0012</td>
<td>1.92E-06</td>
<td>3.97E-06</td>
<td>6.81E-08</td>
<td>6.95</td>
</tr>
<tr>
<td>1518</td>
<td>7.80</td>
<td>1.84E-04</td>
<td>0.0338</td>
<td>0.0700</td>
<td>0.0012</td>
<td>2.12E-06</td>
<td>4.39E-06</td>
<td>7.52E-08</td>
<td>6.59</td>
</tr>
<tr>
<td>1539</td>
<td>7.67</td>
<td>1.34E-04</td>
<td>0.0338</td>
<td>0.0700</td>
<td>0.0012</td>
<td>1.97E-06</td>
<td>4.07E-06</td>
<td>6.98E-08</td>
<td>6.50</td>
</tr>
<tr>
<td>1399</td>
<td>6.80</td>
<td>4.34E-04</td>
<td>0.0338</td>
<td>0.0700</td>
<td>0.0012</td>
<td>1.92E-06</td>
<td>3.96E-06</td>
<td>6.82E-08</td>
<td>6.38</td>
</tr>
<tr>
<td>1439</td>
<td>6.70</td>
<td>1.37E-04</td>
<td>0.0338</td>
<td>0.0700</td>
<td>0.0012</td>
<td>1.92E-06</td>
<td>3.98E-06</td>
<td>6.82E-08</td>
<td>6.38</td>
</tr>
<tr>
<td>1518</td>
<td>7.80</td>
<td>1.34E-04</td>
<td>0.0338</td>
<td>0.0700</td>
<td>0.0012</td>
<td>1.97E-06</td>
<td>4.07E-06</td>
<td>6.98E-08</td>
<td>6.50</td>
</tr>
<tr>
<td>1539</td>
<td>7.67</td>
<td>1.34E-04</td>
<td>0.0338</td>
<td>0.0700</td>
<td>0.0012</td>
<td>1.97E-06</td>
<td>4.07E-06</td>
<td>6.98E-08</td>
<td>6.50</td>
</tr>
</tbody>
</table>

and the $[\text{HC}]$ factor represents the total molar concentration of all non-methane hydrocarbons. Westbrook and Pitz\textsuperscript{29} recommended against treating all of the non-methane hydrocarbon components as...
a single species for modeling purposes. However, the
induction lengths computed in Ref. 29 for methane/
ethane/propane mixtures indicate that each of the
hydrocarbon impurities behaves similarly in enhanc-
ing autoignition. Furthermore, one hydrocarbon, viz.
ethane, is the principal contaminant in natural gas,
with the other alkanes present in significantly smaller
concentrations. Although the formulation chosen is
imperfect, the uncertainties associated with its use
appear to be no greater than the uncertainties in the
experimental data, and it is much simpler than other
possible expressions involving all the different hydro-
carbon impurities.

Combining the natural gas autoignition data
(Table 8) with all of the previous and present autoigni-
tion data for methane–hydrocarbon mixtures (Tables
4 and 6, respectively) yielded an ignition delay data
base of more than 330 points with sufficiently wide
variation in the independent variables to provide a
meaningful correlation. The results, shown in Fig.
10, demonstrate that the simple form of the equation
represented by:

$$ t = 1.77 \times 10^{-14} \exp\left(\frac{18693}{T}\right) \times \left[\frac{1}{O_2}\right]^{1.05} \left[CH_4\right]^{0.66} \left[HC\right]^{-0.39} $$

does a satisfactory job of correlating all the data. Furthermore, although it is difficult to visualize in
the figure, the general correlation does a very good
job of fitting the Matheson natural gas data alone.

Using the preceding empirical correlations, igni-
tion delays of the several different natural gases
specified in Table 3 were calculated. The correlating
equation for pure methane was used to represent the
Alaska and China fuels since they are composed
principally of methane, and have a negligible
concentration of other alkanes. For the remainder of
the methane fuels, the general correlating equation
for natural gas was used. Ignition delay times were
predicted for 1254 K and 6.5 atm (a typical ram-
burner condition) as a function of equivalence ratio.

The results are compared in Fig. 11. Under these
conditions, the Alaska and China fuels have pre-
dicted ignition delays ranging from about 2 to
4 msec, with the shorter times for lean mixtures. The
other methane fuels have delay times that are one-third to one-seventh of the high purity methane, with the Brunei, Indonesian and Abu Dhabi fuels having the highest concentrations of hydrocarbon contaminants and, consequently, the shortest ignition delay times. The latter of these fuels has delay times ranging from 0.4 to 0.6 ms. Since there is such a high concentration of ethane (16%) in the Abu Dhabi fuel, the ignition delay times predicted by the natural gas correlation should be close to those predicted using the methane-ethane correlation. This comparison was made and the difference between the predictions was only 25%.

4. CHEMICAL KINETIC MODEL

4.1. Reactions Controlling Ignition Delay

Reaction chemistry controlling methane ignition is discernibly different from that defining reaction in a flame front. Warnatz\textsuperscript{37} differentiates between these two processes as radical poor (ignition) and radical rich (combustion). Reactions that promote ignition are those that lead to the build up of radical concentrations sufficient to initiate and sustain rapid radical chain propagation and heat release. Inhibiting reactions are those that lead to radical termination. Reactions of secondary importance are those that convert relatively unreactive radicals, such as methyl (CH\textsubscript{3}) and hydroperoxy (HO\textsubscript{2}), into reactive species, such as H-atoms.

Many authors have modeled the kinetics of the ignition delay of methane\textsuperscript{37} \textsuperscript{43} and performed sensitivity analyses to determine the relative importance of reactions, species or concentration levels. In a recent study, Frenklach, Wang and Rabinowitz\textsuperscript{43} concluded that the induction period for stoichiometric mixtures is most sensitive to the rates of the chain branching processes

\begin{equation}
\text{CH}_3 + \text{O}_2 \leftrightarrow \text{CH}_3\text{O} + \text{O}
\end{equation}

and

\begin{equation}
\text{H} + \text{O}_2 \leftrightarrow \text{OH} + \text{O}
\end{equation}

The latter of these is, perhaps, the most critical reaction in the high temperature combustion of hydrocarbons. Sloane\textsuperscript{42} reached a similar conclusion, although the methyl oxidation step was found to be of less importance at high temperatures (\textgreater 2000 K) and fuel-rich conditions. In addition, the reactions

\begin{equation}
\text{CH}_3 + \text{CH}_3 (+M) \leftrightarrow \text{C}_2\text{H}_6 (+M)
\end{equation}

and

\begin{equation}
\text{H} + \text{CH}_4 \leftrightarrow \text{CH}_3 + \text{H}_2
\end{equation}

were also shown to play an important role by inhibiting the induction process. The first of these reactions is an important radical termination step, while the second, in the forward direction, competes with the H + O\textsubscript{2} chain branching process and converts reactive H-atoms into relatively stable methyl radicals. Sloane's analysis also suggests the importance of

\begin{equation}
\text{CH}_3 + \text{CH}_3 \leftrightarrow \text{C}_2\text{H}_5 + \text{H}
\end{equation}

which converts methyl radicals into H-atoms.

A surprising result of these sensitivity analyses is the relatively minor roles attributed to the initiation steps

\begin{equation}
\text{CH}_4 (+M) \leftrightarrow \text{CH}_3 + \text{H}(+M)
\end{equation}

and

\begin{equation}
\text{CH}_4 + \text{O}_2 \leftrightarrow \text{CH}_3 + \text{HO}_2
\end{equation}

In contrast, Warnatz\textsuperscript{37} found the rate constants for these two steps to be the most important ones. Interestingly, the bimolecular reaction with oxygen can have an overall inhibiting effect on ignition. Although the forward step plays an important role in starting the build up of radicals, the reverse step leads to radical termination. Skinner et al\textsuperscript{37} and Seery and Bowman\textsuperscript{13} have shown that this oxidation step plays a minor role relative to the pyrolytic initiation above 1750 K.

Sensitivity analyses are most useful when the reaction mechanism and associated rate constants are well established. When this information exists, they can help determine the key reactions for which the most accurate rate constants are required. Additional information about a proposed reaction mechanism can be obtained by performing a reaction pathway analysis. This approach has been successfully utilized by Warnatz to identify key reaction pathways critical to the destruction and/or formation of selected chemical species. Many important reactions which are either very fast or have few competing processes may not be identified in a more conventional sensitivity analysis; yet, the existence of such steps can be key to the overall process of interest.

To determine the reaction steps (as distinguished from the reaction sensitivity) that contribute to the build-up of radicals during the induction period leading to the ignition of methane, calculations were performed using the Frenklach et al\textsuperscript{43} mechanism with O-atoms assumed to be diradicals. The conditions correspond to experiments and modeling performed in Refs 34 and 43 that resulted in an ignition delay time of 550 ms. The rates of production of radicals are plotted in Fig. 12. Prominent in Fig. 12a are the bimolecular, chain branching reactions of O\textsubscript{2} with H-atoms and with methyl radicals. An important radical sink is the methyl radical recombination step. Also prominent is the thermal decomposition of hydrogen peroxide, principally because the unimolecular decomposition is fast at 1500 K and there are no other H\textsubscript{2}O\textsubscript{2} removal steps that can compete effectively with this reaction under these conditions. In spite of the importance of this decomposition reaction, ignition delay is not sensitive to its rate constant. The rate limiting steps in the hydrogen peroxide decomposition are the formation of hydro-
peroxy radicals and hydrogen peroxide (i.e. hydrogen peroxide attains quasi-equilibrium concentration). Consequently, ignition delay calculations are found to be more sensitive to the values of the rate constants for these HO$_2$ and H$_2$O$_2$ forming reactions.

Consistent with the results of Sloane and of Frenklach the two reactions

\[ \text{CH}_4 (+M) \rightarrow \text{CH}_3 + \text{H} (+M) \]

and

\[ \text{CH}_4 + \text{O}_2 \rightarrow \text{CH}_3 + \text{HO}_2 \]

do not appear in Fig. 12a. To elucidate the role of these reactions, radical production rates early in the induction period are plotted in Fig. 12b. From these curves, it is apparent that radical production from these two reactions initiates the ignition process. Despite the importance of these reactions to initiating radicals, the low sensitivity of ignition delay to them is due in part to the much greater contribution of reactions such as \( \text{CH}_3 + \text{O}_2 \) to the production of radicals during the ignition delay period. Other contributing factors are that these reactions are strongly endothermic (reducing temperature) and that they produce the relatively unreactive radicals CH$_3$ and HO$_2$ which play important roles in radical termination (even H-atoms, produced by the thermal decomposition of methane, can be rapidly converted to methyl radicals). Alternatively, oxidation of H-atoms and methyl radicals are much less endothermic and produce reactive radicals (O and OH) which lead to chain propagation and exothermic reactions.

The ignition sequence (near 1500 K) can be envisioned by examining Fig. 12. Radicals are initially produced by direct thermal decomposition and oxidation of the parent hydrocarbon, methane. This radi-
these rate constants may represent the greatest un-
the two more recent compilations for methyl radical
values recommended in the most recent compilations
recombination. Consequently, the uncertainty in
between the Frenklach
for the CH₃ + O₂ reaction and (2) the difference
Perhaps of greatest concern are: (1) the different
sensitivity analyses, is presented in Table 9. Overall,
reactivity or a reaction path analysis are dependent on
reaction mechanism and the rate constants used.
For example, a comparison of recommended rate
constants for Refs 37 and 43 were calculated using the Lindemann expression. Rate
constants for Refs 49 and 40 were calculated using procedures described therein.

### Table 9. Comparison of recommended rate constants at 1500 K for several reactions important to ignition delay of methane

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Ref. 43 (cc atm⁻¹ cm⁻³ s⁻¹)</th>
<th>Ref. 50 (cc atm⁻¹ cm⁻³ s⁻¹)</th>
<th>Ref. 40 (cc atm⁻¹ cm⁻³ s⁻¹)</th>
<th>Ref. 37 (cc atm⁻¹ cm⁻³ s⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH₃ + O₂ → CH₃O + O</td>
<td>1.39 x 10⁹</td>
<td>3.51 x 10⁹</td>
<td>1.13 x 10⁹</td>
<td>0.99 x 10⁹</td>
</tr>
<tr>
<td>H + O₂ → OH + O</td>
<td>6.29 x 10¹¹</td>
<td>7.07 x 10¹¹</td>
<td>6.84 x 10¹¹</td>
<td>6.06 x 10¹¹</td>
</tr>
<tr>
<td>H + CH₃ → CH₂ + H₂</td>
<td>2.92 x 10¹²</td>
<td>3.01 x 10¹²</td>
<td>4.02 x 10¹²</td>
<td>3.945 x 10¹²</td>
</tr>
<tr>
<td>CH₄(+ M) → 2CH₂H(+ M)</td>
<td>5.65 x 10³</td>
<td>0.88 x 10⁹</td>
<td>0.365 x 10³</td>
<td>2.97 x 10³</td>
</tr>
<tr>
<td>CH₄ + O₃ → CH₃ + H₂</td>
<td>0.358</td>
<td>0.109</td>
<td>0.119</td>
<td>0.194</td>
</tr>
<tr>
<td>CH₄ + HO₂ → CH₃ + H₂O</td>
<td>3.88 x 10⁴</td>
<td>2.04 x 10⁵</td>
<td>2.06 x 10⁵</td>
<td>-</td>
</tr>
<tr>
<td>CH₄ + HO₂ → CH₁ + H₂O₃</td>
<td>1.10 x 10¹⁰</td>
<td>2.30 x 10⁹</td>
<td>3.55 x 10⁸</td>
<td>-</td>
</tr>
<tr>
<td>CH₃ + CH₂ → C₂H₆ + H</td>
<td>1.06 x 10¹¹</td>
<td>3.23 x 10¹¹</td>
<td>-</td>
<td>1.09 x 10¹¹</td>
</tr>
<tr>
<td>CH₄O + O₂ → HCO + HO₂</td>
<td>1.48 x 10⁸</td>
<td>7.17 x 10⁷</td>
<td>4.33 x 10⁷</td>
<td>-</td>
</tr>
</tbody>
</table>

Units: cc, mol, s
Reactions denoted with (+ M) are in the fall-off regime; the collision partner is assumed to be Argon at 1 atm. Rate constants for Refs 37 and 43 were calculated using the Lindemann expression. Rate constants for Refs 49 and 40 were calculated using procedures described therein.

cal production is quickly countered by methyl radical recombination. The H + O₂ and CH₃ + O₂ reactions (particularly the latter) quickly add to these production rates. HO₂ concentrations grow through primary initiation but, more significantly, through H-atom abstraction reactions with molecular oxygen. Although HO₂ is lost via a variety of paths, a reaction important to ignition at temperatures below 1500 K is

\[
\text{CH}_4 + \text{HO}_2 \leftrightarrow \text{CH}_3 + \text{H}_2\text{O}_2
\]

which eventually leads to additional radical formation via rapid decomposition of the product, hydrogen peroxide. The buildup of H₂O₂ and its subsequent decomposition into hydroxyl radicals is an important feature of the ignition process. Simultaneously, formaldehyde (CH₂O) concentrations increase and radical production is supplemented by its oxidation. Although the rates of radical production are nearly (but not quite) balanced by increases in radical termination, eventually radical production overtakes, as heat released from overall reactions such as

\[
\text{CH}_4 + 3/2\text{O}_2 \leftrightarrow \text{CH}_3\text{O} + \text{H}_2\text{O}_2 + 41 \text{kcal/mol}
\]
as well as from CO and water production, leads to temperature increases and further enhancements in reaction.

Obviously, conclusions drawn from either a sensitivity or a reaction path analysis are dependent on the reaction mechanism and the rate constants used. For example, a comparison of recommended rate constants for several key reactions, as identified by sensitivity analyses, is presented in Table 9. Overall, the agreement among the reported values is good; however, there still is at least a factor of three differential for the rate constants of six of the nine reactions. Perhaps of greatest concern are: (1) the different values recommended in the most recent compilations for the CH₄ + O₂ reaction and (2) the difference between the Frenklach et al.⁴³ suggested value and the two more recent compilations for methyl radical recombination. Consequently, the uncertainty in these rate constants may represent the greatest un-
certainty in the ignition delay calculations. Also of potential importance, especially at low temperatures, is the factor of thirty difference in the recommended rate constants for the CH₄ + HO₂ reaction.

Westbrook and co-workers⁴⁰,²⁹,³¹,⁴⁴ have discussed many of the changes in ignition chemistry that occur when alkanes are added to methane. Radical production rates corresponding to the presence of 5% ethane in the methane fuel are plotted in Fig. 13. Although conditions are essentially the same as for the calculations for pure methane in Fig. 12, several fundamental differences are apparent. Firstly, the induction period is shortened. Secondly, formation of radicals via ethane decomposition is dominant early in the induction period, but the role of this reaction quickly reverses as it resumes its normal status as an important radical terminator. It is not until late in the induction period that other reactions, such as,

\[
\text{HO}_2 + \text{OH} \leftrightarrow \text{H}_2\text{O} + \text{O}_2
\]

begin to play a dominant role. Thirdly, the radical production and destruction rates are both very high and tend to counterbalance each other. Thus, rapid methyl-methyl termination and the low reactivity of methyl radicals easily counter the effects of high radical production. Undoubtedly these phenomena contribute to the non-linearities (and similarities among different hydrocarbons) that are observed experimentally when small concentrations of hydrocarbons are added to methane.

### 4.2. Model Description

Detailed chemical kinetics calculations have been performed to support the empirical correlating procedures and develop a tool for extrapolation beyond the test conditions. The methane reaction mechanism proposed by Frenklach et al.⁴³ was adopted and small alterations were made to the rate expressions in order to make them compatible with the formulation of the CHEMKIN II⁴⁵ and SENKIN⁴⁶ software.
used to calculate ignition delay times (the thermodynamics files accompanying this software were used in these calculations). Comparisons between this mechanism and the experimental data were found to be good without any changes to the mechanism. This result is not surprising, since the authors performed a multiparameter optimization using the published ignition delay data. The chemical kinetic mechanism includes kinetics of ethane formation and decomposition. In fact, any broadly useful mechanism should include such reactions, since methyl radical recombination to form ethane is an important and sometimes dominant loss mechanism for methyl radicals. Consequently, this same mechanism could be tested for its ability to predict the effect of ethane impurities on ignition delay in methane. Since several of the natural gas fuels contain significant concentrations of propane, predictions were made by adding the related propane and propene reactions, as presented by Tsang as well as several reactions involving allene. As in the previous case, some small changes were made to make the formulation consistent with the CHEMKIN input format.

4.3. Model Predictions

A comparison of the empirical correlation for auto-ignition of pure methane with predictions based on the reaction mechanism proposed by Frenklach et al. is shown in Fig. 14. As can be seen, the predictions are slightly higher than the correlation line;
Ignition delay characteristics of methane fuels

much of the deviation can be attributed to differences in the definition of the onset of ignition. The apparent lack of trend in the data with respect to the concentrations supports arguments that the empirical correlating expression provides a reasonable estimate for ignition delays over a range of conditions.

Ignition delays were also predicted for stoichiometric methane–air mixtures containing 1, 3, 6 and 10% ethane at a pressure of 8 atm. These data are compared to the methane correlation in Fig. 15. Also in this figure, for reference, are comparable data for ignition delays of pure methane. As noted above, the model predicts slightly longer delay times for pure methane than does the correlation. The predictions are also plotted in Fig. 16 against the correlation for methane–ethane mixtures. The correlation does a good job collapsing the data for temperatures above 1500 K, but is less effective at lower temperatures. This apparent deficiency may be due (1) to lack of data under these conditions which would enable a more accurate fit, (2) to inaccuracies in the ethane kinetics at low temperatures, or (3) to limitations of the proposed formulation. Similar calculations for mixtures containing low concentrations of propane (not shown) indicate that the reduction in the ignition delay is slightly greater than that predicted for added ethane. Thus the model results are generally consistent with the experimental data.

In order to support the applicability of the empirical correlations and identify any possible limitations, calculations were performed using the detailed chemical kinetic mechanism to compare ignition delay times for methane against those for the Matheson and the Abu Dhabi natural gases. Hydrocarbon species larger than C3 were assumed to be propane;
conversion was made on a mole to mole basis. The results are compared in Fig. 17. At stoichiometric conditions, the kinetic model predicts ignition delays for these three fuels which agree quite well with those predicted using the empirical correlating equations (see Fig. 11). The rapid increase in ignition delay at very lean conditions predicted by the detailed chemistry is not surprising since, as equivalence ratio goes to zero, ignition delay must go to infinity. In general, this trend should be expected because a reduced hydrocarbon concentration leads to a slower production rate of radicals which, in turn, leads to a lengthened ignition delay time. The opposing trend observed for methane is presumably due to a unique situation wherein the primary hydrocarbon produced from methane is the methyl radical which is very stable; it does not easily oxidize nor decompose to secondary radicals. Consequently, high concentrations of methane inhibit the onset of ignition, since the radical termination rate increases with the square of the methyl concentration. Only at extremely low equivalence ratios, when termination can be neglected, does this trend reverse.

The apparent failure of the empirical correlations to predict lengthening ignition delay times under very lean conditions is probably due to the absence of data for very low equivalence ratios. All of the binary and multicomponent mixtures tested in this work were for stoichiometric or slightly lean conditions. However, some of the multicomponent low-temperature, low-equivalence-ratio data obtained by Eubank et al.\textsuperscript{36} support the model prediction of increased ignition delay at very lean conditions. Thus, these results suggest that the correlations should not be extrapolated to very low equivalence ratios.

4.4. Effects of Vitiation on Engine Testing

In engine ground testing, high Mach number simulations require that vitiated air preheaters be used to simulate the high combustor inlet temperatures. In order to assess the effects of such vitiated air streams on autoignition, calculations were performed using the detailed kinetic mechanism with some assumptions about the state of the vitiated air. First, an order-of-magnitude analysis was made to determine the effects on autoignition of free radical species in the vitiated air stream (probable effects of oxides of nitrogen, NO\textsubscript{x}, on altering ignition delay were initially ignored in these calculations). The free radicals could represent equilibrium concentrations present in the flow at high temperatures, or super-equilibrium concentrations formed in the flame zone of the preheater which have not had sufficient time to recover to equilibrium levels. The simplifying assumption in this set of calculations is that the mole fractions of H atoms, O atoms, OH radicals, and CH\textsubscript{3} radicals are all equal to each other. Obviously this is chemically unrealistic, but it permits some qualitative evaluation of the effects of radicals on the induction process. In Fig. 18, the ratio of ignition delay times for vitiated air relative to clean air are plotted as a function of the assumed initial concentration of free radicals in the vitiated air stream. Calculations were performed for several typical ramburner test conditions. For temperatures above 1250 K, the effect of an initial concentration of radicals is relatively small, less than 25% reduction in ignition delay. However, at 950 K the presence of free radical species dramatically reduces the ignition delay. Ignition delay is, in a large sense, a measure of how long it takes for a given chemical system to produce a sufficient
concentration of radicals so that chain branching processes will dominate radical initiation and termination steps. At high temperatures, radicals form quickly and an initial small concentration has little effect; however, at low temperatures the build up of free radicals can take a long time, so the extra reactive species in the incoming vitiated air provide the chemical reaction with a significant 'head start'.

A second set of ignition delay calculations was performed with the free radical concentrations assumed to be in equilibrium at the incoming air stream conditions. The vitiated air composition was determined, based on precombustion of propane to increase the temperature of the air stream and replenishment of oxygen to 20.9%. The results, normalized with respect to clean air, are presented in Fig. 19 for fully vitiated air and for air preheated electrically to 700 K prior to vitiation. (Typically, preheating a portion of the air electrically only slightly mitigates the effects of full vitiation.) The total shift in calculated times relative to the ignition in pure air is relatively small (10% or less), at least for stoichiometric conditions. Clearly, the effect of vitiation at low equivalence ratios is much more dramatic, with reductions of as much as 30% predicted. For a given set of inlet air conditions, the initial radical concentrations do not vary; however, the concentrations of radicals relative to the parent hydrocarbon concentration do increase substantially as the equivalence ratio is decreased. Thus, vitiation has a more pronounced effect on ignition delays at lean conditions than at stoichiometric conditions. Also apparent in the figure is the larger effect of vitiation at high temperatures than at low temperatures. This behavior counters that depicted previously for the assumed (nonequilibrium) radical concentrations, and is simply due to the fact that equilibrium radical concentrations are a strong function of temperature. In fact, the difference between equilibrium levels of OH radicals at the high and low temperatures considered in Fig. 19 is nearly four orders of magnitude. Pressure effects appear to be negligible. Finally, the
above calculations have been performed assuming pure methane as the fuel. Based on the observations and interpretations described above, it is expected that reductions in ignition delay due to vitiation will be less when hydrocarbon contaminants are present because radicals will be normally produced at a higher rate.

All of the above calculations have ignored possible contribution of NO₂ produced during the direct heating process. It is well known that NO₂ can significantly reduce ignition delay times for methane. NO may have a similar accelerating effect, since it has been observed to enhance the reaction of hydrogen and higher-order hydrocarbons at temperatures below 1000 K. The increase in reaction rates is generally recognized to be dependent on temperature and NO concentration, and is due to

\[ \text{NO} + \text{HO}_2 \rightarrow \text{NO}_2 + \text{OH} \]

which converts a relatively inactive radical, HO₂, to an active one, OH. Methane autoignition calculations have been performed with 100 ppm NO₂ (principally as NO) added to both clean and vitiated air. The NO-related chemistry was adopted from Glarborg et al., with the exception of low-temperature reactions which were added for the formation and destruction of methylperoxy radical (CH₃O₂) and the sequence

\[ \text{CH}_3 + \text{NO}_2 \rightarrow \text{CH}_3\text{O} + \text{NO}. \]

For temperatures up to 1000 K and when significant concentrations of CH₃O₂ can be formed, the above catalytic reaction sequence significantly decreases the ignition delay times (by as much as a factor of ten). However, as temperature increases above 1200 K, the methylperoxy radical thermally decomposes into a methyl radical and molecular oxygen to shut off the above reaction sequence. As a result, the presence of NO (as an NO/NO₂ mixture at levels of 100 ppm or less) has a small (< 15%) effect on ignition delay at temperatures above 1200 K.

5. CONCLUSIONS

Ignition delays of (a) pure methane, (b) methane with low concentrations of either ethane, propane or butane, and (c) a typical multicomponent natural gas have been measured for temperatures of 1300–1900 K, pressures of 3.5–15 atm, and equivalence ratios of 0.45–1.25. Experiments were performed in a shock tube by measuring the time between shock arrival and the onset of emission from excited hydroxyl radicals. The results are in excellent agreement with reported literature values, and the experiments significantly extend the existing ignition delay data base for binary and multicomponent methane–hydrocarbon mixtures. The previously reported observation that small concentrations of hydrocarbon contaminants shorten ignition delay times relative to that of pure methane was confirmed. Butane was slightly more effective in reducing ignition delay than either ethane or propane, and virtually no difference was found between normal- and iso-butane. Empirical correlating equations (Table 7) were developed for predicting the ignition delays of the various binary methane–hydrocarbon mixtures and for multicomponent natural gases. The correlating equation for natural gas groups all the hydrocarbon contaminants into a single term for simplicity, and is justified by the fact that all the typical hydrocarbon contaminants have similar effects on ignition delay times, independent of the structure or size of the molecule. The correlating equation was used to predict the ignition delay times of several different natural gases, and should be of significant value for designing premixed combustion systems. At a typical ram-burner condition, the ignition delays varied among the different natural gases by a factor of seven. The validity of the correlating equations has not been demonstrated for temperatures below 1200 K. Extension of the correlations to lower temperatures is a worthwhile area for future research, particularly with regard to gas turbine applications.

A detailed chemical kinetic model was constructed to extend the experimental results to lower temperatures and different fuel concentrations. The kinetic mechanism included reactions representing methane, ethane and propane chemistry. Radical production rates were calculated at 1500 K and they demonstrated the importance of the build-up and decomposition of hydrogen peroxide to the autoignition process. Furthermore, the analysis showed that the low activity and rapid recombination of methyl radicals counteracts high radical formation rates and helps to explain the non-linear effect of alkane addition on the ignition delay of methane. Model predictions compared well with the experimental data for methane, methane–hydrocarbon mixtures and natural gas. The empirically determined correlating equations were found to be in good agreement with the model predictions for temperatures as low as 1000 K. However, for very lean mixtures, the kinetic model predicts lengthened ignition delays that are not predicted by the empirical correlating equations because of the paucity of experimental data at the very lean conditions. The model was also used to estimate the effects of test facility vitiated air contamination on ignition delay. Vitiation can result in a significant generation of free radicals and active species such as OH, O, H and CH₃ which will accelerate the ignition process, particularly at very lean equivalence ratios.

Acknowledgements—A portion of this paper is based on work performed for the New Energy and Industrial Technology Development Organization (NEDO), as part of the Japanese National Project on Super/Hypersonic Transport Propulsion Systems (HYPR) of the Ministry of International Trade and Industry (MITB) in Japan. The Authors
REFERENCES


