EFFECTS OF PROpane OR ETHANE ADDITIVES ON LAMINAR BURNING VELOCITY
OF METHANE-AIR MIXTURES

by

JOCELYN HUNG

A THESIS SUBMITTED IN PARTIAL FULFILLMENT OF
THE REQUIREMENTS FOR THE DEGREE OF
MASTER OF APPLIED SCIENCE

in

THE FACULTY OF GRADUATE STUDIES
Department of Mechanical Engineering

We accept this thesis as conforming
to the required standard

THE UNIVERSITY OF BRITISH COLUMBIA
April, 1986

© JOCELYN HUNG, 1986
In presenting this thesis in partial fulfillment of the requirements for an advanced degree at the University of British Columbia, I agree that the Library shall make it freely available for reference and study. I further agree that permission for extensive copying of this thesis for scholarly purposes may be granted by the Head of my Department or by his or her representatives. It is understood that copying or publication of this thesis for financial gain shall not be allowed without my written permission.

Department of Mechanical Engineering

The University of British Columbia
1956 Main Mall
Vancouver, Canada
V6T 1Y3

Date June, 1986
ABSTRACT

Laminar burning velocities of stoichiometric methane-air, ethane-air, propane-air as well as methane with propane and ethane additives have been determined from pressure-time records during combustion in a constant-volume spherical combustion bomb with central ignition. Additives up to 20 volume percent were used. Initial pressure ranged from 1 to 8 atm. Results show that these additives increase the burning velocity of methane-air by an amount depending on the concentration and initial pressure. Ethane appeared to be more effective than propane for the same volume percent.

Two analytical methods were used to deduce the laminar burning velocity: Metghalchi and Keck (M and K) model and linear model. The M and K model is a procedure to satisfy the conservation of mass and energy for a mixture consisting of two homogeneous regions, burnt and unburnt, separated by a flame of negligible thickness. The linear model, from the assumption that the fractional pressure rise is linearly proportional to the fractional mass burnt, calculates the burning velocity based on the mass conservation equation. Results from these two methods agree to within 5%. Dissociation reactions, when neglected, were found to give values of burning velocities that are 10% too low.

Ionization probes were used to detect flame arrival times at specific radial locations. Experimental and calculated results agree to within 2%.
# TABLE OF CONTENTS

<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>Abstract</td>
<td>ii</td>
</tr>
<tr>
<td>List of Tables</td>
<td>v</td>
</tr>
<tr>
<td>List of Figures</td>
<td>vi</td>
</tr>
<tr>
<td>Nomenclature</td>
<td>ix</td>
</tr>
<tr>
<td>Acknowledgements</td>
<td>x</td>
</tr>
<tr>
<td>1. Introduction</td>
<td>1</td>
</tr>
<tr>
<td>2. Literature Review</td>
<td>3</td>
</tr>
<tr>
<td>2.1 Introduction</td>
<td>3</td>
</tr>
<tr>
<td>2.2 Techniques for Measuring Burning Velocities</td>
<td>4</td>
</tr>
<tr>
<td>2.3 Determination of Burning Velocity with Constant-Volume Spherical Bomb Method</td>
<td>5</td>
</tr>
<tr>
<td>2.3.1 Determination of Burning Velocity from Expansion Ratio</td>
<td>5</td>
</tr>
<tr>
<td>2.3.2 Determination of Burning Velocity from Direct Measurement of Unburnt Gas Velocity</td>
<td>9</td>
</tr>
<tr>
<td>2.3.3 Determination of Burning Velocity from Pressure-Time Records</td>
<td>10</td>
</tr>
<tr>
<td>2.4 Prediction of $S_u$ From Theoretical Models</td>
<td>13</td>
</tr>
<tr>
<td>2.5 Summary</td>
<td>13</td>
</tr>
<tr>
<td>3. Experimental Design</td>
<td>15</td>
</tr>
<tr>
<td>3.1 Apparatus</td>
<td>15</td>
</tr>
<tr>
<td>3.2 Procedures</td>
<td>16</td>
</tr>
<tr>
<td>3.3 Test Conditions</td>
<td>17</td>
</tr>
<tr>
<td>4. Data Reduction Model</td>
<td>18</td>
</tr>
<tr>
<td>4.1 Metghalchi and Keck Method</td>
<td>18</td>
</tr>
<tr>
<td>4.2 Linear Method</td>
<td>22</td>
</tr>
<tr>
<td>5. Discussion</td>
<td>24</td>
</tr>
<tr>
<td>5.1 Experimental Results</td>
<td>24</td>
</tr>
<tr>
<td>5.2 Comparisons of Methods of Analysis</td>
<td>29</td>
</tr>
</tbody>
</table>
TABLE OF CONTENTS (Continued)

<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>5.3 Ionization Probe Results</td>
<td>30</td>
</tr>
<tr>
<td>5.4 Error Analysis</td>
<td>31</td>
</tr>
<tr>
<td>5.4.1 Uncertainties in Measurements</td>
<td>31</td>
</tr>
<tr>
<td>5.4.2 Uncertainties in Pressure Data</td>
<td>32</td>
</tr>
<tr>
<td>6. Conclusions</td>
<td>34</td>
</tr>
<tr>
<td>7. Recommendations</td>
<td>35</td>
</tr>
<tr>
<td>Tables</td>
<td>36</td>
</tr>
<tr>
<td>Figures</td>
<td>45</td>
</tr>
<tr>
<td>References</td>
<td>89</td>
</tr>
<tr>
<td>Appendices</td>
<td></td>
</tr>
<tr>
<td>I. Gas Chromatography Calibrations</td>
<td>94</td>
</tr>
<tr>
<td>II. Initial Temperature Calibration</td>
<td>99</td>
</tr>
<tr>
<td>III. Calculation of Stoichiometric Coefficients</td>
<td>100</td>
</tr>
<tr>
<td>IV. Program Verification</td>
<td>107</td>
</tr>
<tr>
<td>V. Burnt Gas Properties</td>
<td>113</td>
</tr>
<tr>
<td>VI. Linear Model Equation Derivation</td>
<td>115</td>
</tr>
<tr>
<td>VII. Calculation of Error in Equivalence Ratio</td>
<td>119</td>
</tr>
<tr>
<td>Table</td>
<td>Page</td>
</tr>
<tr>
<td>-------</td>
<td>------</td>
</tr>
<tr>
<td>1 Composition (mol %) of natural gases from different regions</td>
<td>36</td>
</tr>
<tr>
<td>2 Comparisons of results obtained by previous and present investigators on the burning velocity of methane-air mixture</td>
<td>37</td>
</tr>
<tr>
<td>3 Comparisons of results obtained by previous and present investigators on the burning velocity of propane-air mixture</td>
<td>38</td>
</tr>
<tr>
<td>4 Test mixtures matrix</td>
<td>39</td>
</tr>
<tr>
<td>5 Initial conditions for text mixtures</td>
<td>40</td>
</tr>
<tr>
<td>6 Table of coefficients of $S_{u_0}$ and $\beta$ for single and split correlation</td>
<td>41</td>
</tr>
<tr>
<td>7 Comparisons of coefficients of $S_{u_0}$, $\alpha$ and $\beta$ with previous work</td>
<td>42</td>
</tr>
<tr>
<td>8 Ionization probe test results</td>
<td>43</td>
</tr>
<tr>
<td>9 Circuit independence test results</td>
<td>44</td>
</tr>
</tbody>
</table>
LIST OF FIGURES

Figure

1  The dependence of laminar burning velocity on initial pressure for mixtures of air and methane, ethane, propane (present work) and octane [55].

2  Laminar burning velocity of methane-air mixtures published during 1916 to 1972, as compiled by Andrew and Bradley [8].

3  Comparisons of burning velocity of stoichiometric propane-air mixtures obtained by Metghalchi and Keck, Kuehl and present work. This figure is adapted from Ref. 23.

4  Comparisons of predicted and experimental temperature dependence of stoichiometric methane-air mixtures at atmospheric pressure. This figure is adapted from Ref. 8.

5  Comparisons of predicted and experimental pressure dependence of stoichiometric methane-air mixtures at 298 K. This figure is adapted from Ref. 8.

6  Schematic of the experimental apparatus.

7  View of the experimental apparatus.

8  Gas chromatograph calibration apparatus.

9  Ionization probe construction.

10  A typical ionization probe signal.

11  Schematic of combustion bomb showing positions of spark plug, ionization probes, and pressure transducer.

12  Photograph of the spherical combustion bomb.

13  A typical pressure-time record during combustion.

14  Laminar burning velocities for stoichiometric methane-air mixtures at initial pressures of 1, 2, 4, 6, and 8 atm.

15  Laminar burning velocities for stoichiometric ethane-air mixtures at initial pressures of 1, 2, 4, 6, and 8 atm.

16  Laminar burning velocities for stoichiometric propane-air mixtures at initial pressures of 1, 2, 4, 6, and 7 atm.

17  Comparisons of laminar burning velocities for stoichiometric mixtures of methane-air, ethane-air and propane-air at initial pressure of 2 atm.
LIST OF FIGURES (Continued)

18 Comparisons of laminar burning velocities for stoichiometric mixtures of methane-air, ethane-air and propane-air at initial pressure of 4 atm.

19 Comparisons of laminar burning velocities for stoichiometric mixtures of methane-air, ethane-air and propane-air at initial pressure of 6 atm.

20 Effects of ethane at various relative percent ($\%$C$_2$H$_6$/CH$_4$) on the laminar burning velocities of methane-air mixtures at an initial pressure of 2 atm. All mixtures are of stoichiometric proportions.

21 Effects of ethane at various relative percent ($\%$C$_2$H$_6$/CH$_4$) on the laminar burning velocities of methane-air mixtures at an initial pressure of 4 atm. All mixtures are of stoichiometric proportions.

22 Effects of ethane at various relative percent ($\%$C$_2$H$_6$/CH$_4$) on the laminar burning velocities of methane-air mixtures at an initial pressure of 6 atm. All mixtures are of stoichiometric proportions.

23 Effects of ethane at various relative percent ($\%$C$_2$H$_6$/CH$_4$) on the laminar burning velocities of methane-air mixtures at an initial pressure of 8 atm. All mixtures are of stoichiometric proportions.

24 Effects of propane at various relative percent ($\%$C$_2$H$_6$/CH$_4$) on the laminar burning velocities of methane-air mixtures at an initial pressure of 2 atm. All mixtures are of stoichiometric proportions.

25 Effects of propane at various relative percent ($\%$C$_2$H$_6$/CH$_4$) on the laminar burning velocities of methane-air mixtures at an initial pressure of 4 atm. All mixtures are of stoichiometric proportions.

26 Effects of propane at various relative percent ($\%$C$_2$H$_6$/CH$_4$) on the laminar burning velocities of methane-air mixtures at an initial pressure of 6 atm. All mixtures are of stoichiometric proportions.

27 Effects of propane at various relative percent ($\%$C$_2$H$_6$/CH$_4$) on the laminar burning velocities of methane-air mixtures at an initial pressure of 8 atm. All mixtures are of stoichiometric proportions.

28 Percent change in the burning velocity of stoichiometric methane-air mixture due to various relative percent of ethane.

29 Percent change in the burning velocity of stoichiometric methane-air mixture due to various relative percent of propane.

30 Comparisons of laminar burning velocities obtained from M and K model, M and K model without dissociation, and linear model for stoichiometric methane-air mixtures.
LIST OF FIGURES (Continued)

31 Comparisons of laminar burning velocities obtained from M and K model, M and K model without dissociation, and linear model for stoichiometric ethane-air mixtures.

32 Comparisons of laminar burning velocities obtained from M and K model, M and K model without dissociation, and linear model for stoichiometric propane-air mixtures.

33 Comparisons of ionization probe results with that of the radius-time curves calculated from M and K and linear model. The ionization probes are located at the same radius. (Mixture composition: CH$_4$+0.22 C$_3$H$_8$.)

34 Comparisons of ionization probe results with that of the radius-time curves calculated from M and K and linear model. The ionization probes are located at different radii. (Mixture composition: CH$_4$+0.22 C$_3$H$_8$.)

35 Sensitivity of the laminar burning velocities calculated from M and K model to initial temperature and stoichiometry. Actual condition was: $P_1 = 1$ atm, $\phi = 1.00$, $T_1 = 298$ K.

36 Sensitivity of the laminar burning velocities calculated from M and K model to initial temperature and stoichiometry. Actual condition was: $P_1 = 8$ atm, $\phi = 1.00$, $T_1 = 292$ K.

37 Repeatability tests of pressure-time records for stoichiometric methane-air mixtures taken from the same mixing tank (1 tank).

38 Repeatability tests of pressure-time records for stoichiometric methane-air mixtures taken from the two separately prepared mixing tanks (2 tanks).

39 Laminar burning velocities corresponding to the pressure-time records in Figure 37.

40 Laminar burning velocities corresponding to the pressure-time records in Figure 38.

41 Typical digital signal in micro-scale.

42 Comparison of raw and smoothed pressure data and their slopes.

43 Laminar burning velocity plotted against unburnt gas temperature at various $N$, number of points for smoothing.

44 Maximum error introduced from the smoothing technique on the laminar burning velocities of stoichiometric methane-air mixtures at initial pressures of 1 and 8 atm.
A  Area [m²]
E  Energy content of mixture [kg/kmol]
E_l  Expansion ratio
M  Mass of mixture [kg]
P  Pressure [kPa]
R  Radius of bomb [cm]
S_u  Burning velocity [cm/s]
S_f  Flame speed [cm/s]
T  Temperature [K]
V  Bomb volume [m³]
W  Molecular Weight
e  Specific energy [kJ/kg]
m  mass [kg]
n  fraction burnt
r  radius [cm]
t  time [msec]
x  mass fraction

α  temperature dependence coefficient
β  pressure dependence coefficient
γ  ratios of specific heats
ρ  density
ϕ  equivalence ratio

Subscript
b  burnt
e  end
f  flame
i  initial
u  unburnt
ACKNOWLEDGEMENTS

I would like to thank Professor P.G. Hill for his supervision of the thesis and also Professors R.L. Evans, E.G. Hauptmann and Ahlborn for the guidance given during my graduate studies. I wish to thank the Environmental Engineering Laboratory of the Civil Engineering Department for allowing me to use the Gas Chromotograph, and in particular, Ms. Paula Parkinson for her assistance in the operation of the instrument. I wish to thank Dr. Teo for advice on the techniques of calibration and sampling.

This work was supported through a contract from Energy Mines and Resources Canada.

- x -
As a fuel for internal combustion engines natural gas (consisting primarily of methane) offers the following advantages. It is readily available in North America and relatively inexpensive. Methane has a higher octane number (130) than gasoline (92); this makes it possible for a methane-fuelled engine to operate at relatively high compression ratio.

However, methane has the disadvantage of low critical temperature. Even with high storage pressures, energy density is low and this tends to limit vehicle range. A more significant disadvantage is the slow burning velocity of methane at engine pressures. The pressure dependence of stoichiometric methane-air, ethane-air, propane-air and octane-air mixtures is shown in Figure 1. Although the burning velocity in engines is typically very dependent on turbulence, the laminar burning velocity is thought to affect the randomness of ignition delay and the combustion duration.

It must be recognized that "natural gas" is not solely methane and that the other constituents may have substantial effects on combustion properties and storage density. Knock, for example, can be strongly dependent on propane content. The main constituents of natural gas are methane, ethane, and propane. The natural gas found in British Columbia, Canada, consists of 94% (by volume) methane, 3.3% ethane, 1.0% propane, 0.41% other hydrocarbons, and 1.3% other gases. However, the composition varies significantly over geographic locations, as shown in Table 1, and the effects of such variation on the combustion properties of natural gas as an engine fuel have not been fully documented. It is common practice to
extract propane and ethane from natural gas before distribution. The question then might be asked; what constitutes the optimum composition for engine use? Little data is available for study of combustion properties of relevant mixtures.

The laminar burning velocity of methane-air mixtures has been determined by many previous investigators using various techniques. However, as shown by Figure 2, the results scatter over a wide range (± 20%) even for standard temperature and pressure. The laminar burning velocity corresponding to engine pressures and temperatures is still more uncertain. In recent years several measurements have been made of the laminar burning velocity of propane-air mixtures but no data have been found for ethane-air or for methane with propane or ethane additives. The effect of pressure and temperature on burning velocity of methane and propane have been correlated by various kinds of relationships including power law, but the data was limited to the low pressure range (-0.5 < P_i < 4 atm).

The objective of the present work was to obtain data on laminar burning velocity of methane-air mixtures with propane or ethane additives over a wide range of pressures and temperatures. Measurements were made in a high pressure spherical combustion chamber with central ignition. The burning velocities were determined by analysis of the rate of pressure rise in the chamber during combustion; ionization probes were used to confirm the validity of the method of analysis.

The experimental mixtures were approximately stoichiometric combinations with air of methane plus up to 20 percent of either propane or ethane additive. Laminar burning velocities were measured for initial pressures of 1 to 8 atm and room temperature. In the case of constant-volume combustion the unburned gas pressures range from 1 to 80 atm, and the temperatures range from 300 to 500K.
2. LITERATURE REVIEW

2.1 Introduction

The laminar burning velocity is a property of a premixed gaseous combustible mixture. It is defined as the rate at which a plane flame front propagates, normal to its surface, into the unburnt gas. A flame is the result of the release of energy associated with a chemical reaction and is usually made visible by the luminosity of the burning gases. A flame front is the surface separating the luminous zone and the unburnt gases. As the burnt gas expands, velocity is induced in the unburnt gas. The burning velocity $S_u$ is defined as the difference between the observed flame speed $S_f$ and the unburnt gas velocity $S_g$ given by

$$S_u = S_f - S_g.$$  \hspace{1cm} (2-1)

The burning velocity can also be expressed, based on the mass continuity across a flame front of negligible thickness, as

$$S_u = -\frac{1}{A_f \rho_u} \frac{dm_u}{dt} = \frac{1}{A_f \rho_u} \frac{dm_b}{dt}. \hspace{1cm} (2-2)$$

The principal parameters for the determination of burning velocity are mixture composition, mixture strength, pressure, and unburnt gas temperature.

This review is primarily concerned with the determination of burning velocities of methane-air and propane-air mixtures from pressure-time records following central ignition of these mixtures in a spherical bomb.
However, other methods and their typical results are also reviewed. No published data on mixtures of ethane-air, or methane-air with propane and ethane additives were found.

2.2 Techniques for Measuring Burning Velocities

Methods of measurement fall basically into two categories: those involving stationary flames and those involving propagating flames. In the stationary flame method the velocity of the premixed gas entering a flat stationary flame is the burning velocity. Some examples are various types of burners such as circular tube, rectangular slot-type, nozzle and orifice. Most of the earlier burning velocity data available have been obtained by these methods. The methods of measurement and their difficulties are discussed in detail by Andrews and Bradley [1], Garforth and Rallis [2], and Gaydon and Wolfhard [3].

In the propagating flame method, the flame travels through an initially quiescent mixture. One of the earliest methods involving propagating flames is the tube method. Other methods are the soap bubble or constant-pressure method, which is possibly the simplest, and the constant-volume spherical bomb method. The latter is the technique employed in the present work and will be discussed in greater detail in the following sections.

Andrews and Bradley [1] and Garforth and Rallis [2] evaluated various techniques used by previous investigators. They concluded that the constant-volume spherical bomb method is the most versatile and accurate. A comparison by Andrews and Bradley [1] of the maximum burning velocity data of methane-air mixtures (reported since 1916) revealed a wide scatter of data ($28 < S_u < 50$ cm/sec, see Figure 2). Measurements of burning velocity of stoichiometric mixtures of methane and air at standard
temperature and pressure, made using the bomb method, range from 31 to 49 cm/s.

Of particular interest to this work are data obtained at conditions comparable to those of engine operation. Halstead et al [4] obtained, from a rapid compression machine, a burning velocity for stoichiometric methane-air mixture at 19.4 atm and 710 K of 66 ± 10 cm/sec. Kuehl [5] measured the burning velocity of propane-air mixtures over a range of temperatures and equivalent ratios from a modified slot burner. At stoichiometry, 1 atm and 311 K, he reported a burning velocity of 48 cm/sec.

2.3 Determination of Laminar Burning Velocity From Constant-Volume Spherical Bomb

The constant-volume spherical bomb method has the advantage of providing burning velocities over a fairly wide range of pressure and temperature in a single experiment. In this method, the mixture in a spherical chamber is ignited centrally. From the rate of pressure rise during explosion, the burning velocity can be deduced. Three approaches have been used to measure this property:

1. Determination of density ratio or expansion ratio during the pre-pressure period,
2. Direct measurement of unburnt gas velocities and flame speeds,
3. Evaluation of burning velocity from pressure-time records.

Each method is now discussed in turn.

2.3.1 Determination of Burning Velocity from Expansion Ratio

The first method is based on the essentially isobaric combustion process during the early stages of flame propagation. The assumptions made are:
1. The combustion process is adiabatic and at constant pressure,
2. Both burnt and unburnt gases behave as perfect gases,
3. The burnt gas is at chemical equilibrium,
4. The flame front is spherical,
5. The pressure is uniform throughout the combustion bomb.

The burning velocity $S_u$ can be determined from the relations

$$S_u = \frac{\rho_b}{\rho_o} S_f$$

and

$$S_u = \frac{S_f}{E_i}$$

in which $\rho_b$, $\rho_u$ are the densities of the burnt and unburnt gases,
$\rho_o$ is the mixture density before combustion,
$S_f$ is the flame speed,
$E_i$ is the expansion ratio calculated from the relation

$$E_i = \frac{W_u T_b}{W_b T_u}, \quad (2.3)$$

where $W_{b,u}$, $T_{b,u}$ are the molecular weights and temperatures of the burnt and unburnt gases. The derivation is shown in Appendix V.

Typically, the only experimental data is the flame position versus time curve which is recorded by a high speed camera or schlieren. The density of the unburnt gas is assumed to be equal to the mixture density before combustion, since negligible pressure rise (and therefore temperature rise) has occurred. The temperature of the burnt gas is assumed to be the adiabatic flame temperature and is calculated from thermodynamic rela-
tions. However, the effect of flame front thickness and curvature on burning velocities were shown to be important in the prepressure period [2,6]. Babkin et al [6] showed that these effects were significant for a flame radius less than 3 mm in stoichiometric methane-air mixtures. Consequently, some investigators corrected for this effect by computing an average burnt gas temperature based on an assumed temperature profile across the flame front.

Agnew and Graiff [7] determined the burning velocities of methane-air, propane-air and other mixtures at pressures of 0.5 to 20 atm. They measured flame speed with ionization probes. The presence of these probes did not appear to have disturbed the flame. They varied the ignition energy and concluded that it did not affect the flame speed. No correlation of the pressure dependence of the burning velocities of propane-air mixtures was given, but for stoichiometric methane-air mixture they reported that their data were represented by the relationship

\[ S_u = -6.78 \ln P_1 + 32.9 \text{ cm/sec} \]

Andrews and Bradley [8] measured the flame speed with three optical methods - vertical knife edge schlieren, reflection plate schlieren interferometry and Gayhart-Prescott fine-wire schlieren interferometry. All three methods were found to give the same value of flame speed. They determined the burning velocities of methane-air mixtures over a wide range of equivalence ratios. They measured the flame thickness with a Gayhart-Prescott schlieren interferometry and showed that the neglect of flame thickness in the pre-pressure period would lead to values of burning velocity that are too low. They expressed the density ratio in the form:
\[ \frac{\rho_b}{\rho_o} = \frac{nT_u I}{T_b}, \]

where \( n \) is the number of moles of burnt gas at adiabatic temperature per mole of unburnt gas and is assumed to be constant across the flame, \( I \) is the correction factor, \( T_b \) is the adiabatic flame temperature and \( \rho_b \) is the average burnt gas density calculated based on temperature profiles previously measured. They showed a correction factor of 1.22 at the flame radius of 25 mm with \( P = 1 \) atmosphere, \( T_u = 300 \) K and a flame thickness of 1.1 mm and 0.75 mm, measured by Dixon-Lewis and Wilson [9] and Janisch [10], respectively. They also found that \( I \) was a function of \( \phi \). They correlated the pressure and temperature dependence separately by the relationship

\[ S_u = 43 P^{-0.5} \]

\[ S_u = 10 + 0.000371 T_u^2 \text{ cm/sec} \]

in which \( P \) is in atm. and \( T \) is in K.

Agrawal [11] photographed flame growth with a rotating drum camera. By assuming that the heat released for one mole of fuel-air mixture burnt at constant pressure is equal to that burnt at constant volume, he expressed the expansion coefficient as a function of the pressure ratio, \( P_e/P_1 \), where \( P_e \) is the end pressure. He plotted \( E_1 \) with the experimental pressure ratio and found that there existed a linear relationship between \( E_1 \) and \( P_e/P_1 \) represented by the approximation
\[
E_1 = 0.848 \frac{P_e}{P_1}.
\]

This approximation enabled him to obtain $S_u$ solely from experimental radius-time records and pressure ratio. He compared the approximate expansion ratios with those computed using Eq. (2-3) and reported a maximum deviation of 1.8%. His results differed by a maximum of 4.5% from those of Agnew et al and 4.15% from those of Babkin et al [6].

Gülder used the density ratio method to obtain $S_u$ data for a number of fuel-air mixtures including methane and propane-air. He did not present the method of measurement or analysis but compared and evaluated correlations adopted by previous investigators [12]. He proposed the following empirical expression to correlate the burning velocity data given by

\[
S_u = S_{uo} \left( \frac{T_u}{T_0} \right)^{\alpha} \left( \frac{P}{P_0} \right)^{\beta},
\]

where

\[
S_{uo} = W \eta \exp[-\xi(\phi - 1.075)^2].
\]

The values of $W$, $\eta$, $\xi$, $\alpha$ and $\beta$ are constants for a given fuel. The constants for methane-air and propane-air mixtures are given in Tables 2 and 3 respectively.

2.3.2 Determination of Burning Velocity From Direct Measurement of Unburnt Gas Velocity

In the second approach, the unburnt gas velocity is measured with a hot-wire anemometer and the flame growth by optical means such as Schlieren or high-speed camera. The burning velocity is obtained from the definition (Eq. 2-1)
Bradley and Hundy [13] used a hot-wire anemometer to measure the unburnt gas velocity in a cylindrical vessel, 12" in diameter and 12" in length, with central ignition. Values of $S_u$ were obtained for stoichiometric methane-air mixture at pressures of 0.25 to 1.5 atm and equivalent ratios of 0.7 to 1.2. Their results were higher than those of previous investigators (see Figure 2). They used a reflection-plate interferometer for flame visualization and showed "undistorted spherical flame development" in methane-air mixtures.

The assumption of spherical flame propagation has been investigated by numerous researchers. Ellis [14], in 1934, obtained photographs showing spherical propagation from a central ignition point in a spherical glass vessel. For slow-burning mixtures such as carbon monoxide, convective rise was observed. Flame front irregularities have been observed at high velocities and pressures in constant pressure experiments [15,16].

Andrews and Bradley [8] used a hot-wire anemometer to measure the unburnt gas velocity in a spherical bomb. They recorded the flame front position with three different optical methods as discussed in 2.3.1. Burning velocities calculated from density ratio method using an average burnt gas temperature (see 2.3.1) and those measured directly compared to within 5%.

2.3.3 Determination of Burning Velocity From Pressure-Time Records

In the third approach, the pressure history, together with the flame growth records are used to determine burning velocities from derived equations. These equations are discussed by Lewis and Von Elbe [17], Fiock
et al [18], Rallis and Tremeer [19], Rallis and Garforth [8], and Metghalchi and Keck [12]. The basic assumptions made were

1. The flame front is smooth, thin, and spherical,
2. The pressure is uniform throughout the bomb,
3. The unburnt gas is compressed isentropically,
4. The burnt gas is at chemical equilibrium.

Garforth [20] used a modified Michelson interferometer system to measure density in the unburnt gas. He showed the error introduced by assuming adiabatic compression of the unburnt gas was on the average 1.5%, and did not exceed 3%.

Garforth and Rallis [21] determined the burning velocity for stoichiometric methane-air mixtures for pressures of 0.59 to 2.26 atm and temperatures of 29 to 525 K. The effect of flame thickness was taken into account by using the thick flame equation and they concluded that corrections were important at pressures near the region of the initial pressure. For an initial pressure of 1 atm, they showed that corrections to burning velocities were significant only for pressures of less than 0.15 MPa. They used the temperature distribution through the flame from burner tests given by Dixon-Lewis and Wilson's [9,10] plane flame data to calculate an average burnt gas density. They showed that the neglect of both the temperature and density distribution results in error as large as 12% in burning velocity. No correlations for the pressure and temperature dependence were given.

Sharma et al [22] used a rotating drum to measure flame growth during combustion. They obtained laminar burning velocity of methane-air for pressures of 0.5 to 8 atm, temperatures of 300 to 600 K and equivalence ratios of 0.8 to 1.2. They calculated the burning velocities with six
different equations derived by previous investigators (refer to Ref. 21 for
details). They correlated the pressure, temperature and mixture strength
dependence into relations given by

\[ S_u = C_4 \left( \frac{T_u}{300} \right)^{1.68/\sqrt{\phi}} \quad \text{for } \phi < 1.0 \]

and

\[ S_u = C_4 \left( \frac{T_u}{300} \right)^{1.68/\phi} \quad \text{for } \phi > 1.0, \]

where \( C_4 \) is a function of \( \phi \) (see Table 2). Values obtained by this
equation compare with results of other investigators to within 4.5 to 34%.
However, the natural gas they used contained 94.52% methane, 4.765% ethane,
0.596% propane, and 0.119% other gases but they computed the burning
velocity assuming the gas to be methane.

Metghalchi and Keck [23] determined, from the pressure-time record
alone, the burning velocity of propane-air for pressures of 0.4 to 40 atm,
temperatures 298 to 750 K, and equivalence ratios of 0.8 to 1.5. Their
analysis is based on the conservation of energy and volume. This method of
analysis is used in the present work and will be discussed in greater
detail in Chapter 5. A curve fit over the experimental data gave the
following pressure and temperature dependence

\[ S_u = 31.9 \left( \frac{T_u}{T_0} \right)^{2.27} \left( \frac{P}{P_0} \right)^{-0.17} \]

where \( T_0 = 298 \) K, \( P_0 = 1 \) atm. Three ion probes placed at the perimeter of
the combustion bomb measured the flame arrival time and they concluded that
the flame is symmetrical. Comparison of the results with those measured by
Kuehl and present work is shown in Figure 3.
2.4 Prediction of Burning Velocity From Theoretical Models

In theoretical studies of laminar flame propagation, a set of differential equations are obtained from a prescribed reaction mechanism. The governing equations are conservation of mass and energy, and species continuity. These equations are discussed by Spalding [24] and Tsatsaronis [25]. The basic assumptions are negligible heat loss and ideal gas behaviour. However, solution to these equations requires a knowledge of the mechanisms involved and data on chemical kinetic constants such as reaction rates and transport coefficients. In practice it is often too expensive to solve the system of relevant equations. Spalding et al [24] have successfully applied a computational procedure originally developed for the solution of steady two-dimensional boundary layers equation to solve equations of one-dimensional unsteady flame propagation model. Details of the procedure are given in Ref. 33.

Bradley and Hundy [13] attempted to obtain a theoretical value of $S_u$ for methane-air flames from Spalding's expression. Their results suggested that rate-determining reaction is in the breakdown of the hydrocarbon molecule. Smoot et al [26] and Tsatsaronis [25] used Spalding's computation procedure to determine the laminar burning velocity of methane-air mixtures. They predicted the pressure and temperature dependence and found good agreement with experimental data. However, Tsatsaronis modified the kinetic data to obtain better agreement. The predicted and experimental results are compared in Figures 4 and 5.

2.5 Summary

Experimental results and empirical correlations obtained by various methods and investigators are compared in Tables 2 and 3. The values of $S_u$
at 1 atm and 298 K falls in the range 32 to 46 cm/sec for stoichiometric methane-air mixtures. The predicted and experimental pressure and temperature dependence of laminar burning velocity for methane-air is shown in Figures 4 and 5. Only limited data is available for propane-air mixtures. No data on methane with propane and ethane additives were found.
3. EXPERIMENTAL DESIGN

3.1 Apparatus

A schematic of the experimental set-up and details of the spherical bomb are shown in Figures 6 and 11. The apparatus consists of a constant-volume spherical bomb, fuel system, ignition system, ionization probes, and the data acquisition system. Figure 7 shows a view of the set up.

The combustion bomb consisted of two flanged hemispherical sections which when bolted together, form a spherical chamber of 15.24 cm (6.0 in.) internal diameter. These sections were cast from a heat-resistant stainless steel (ACI type HK), then machined to the desired dimensions. The design pressure is 50 atm, with a safety factor of 4. The design stress of the material is calculated from supplier's specification.

A capacitance absolute pressure transducer (MKS type 222BHS) with an accuracy of ±0.3% of reading was used to measure pressures greater than 1 atm. For pressures less than 1 atm, a bourdon gauge accurate to ±0.5 mmHg was used. The mixture strength was determined from the gas chromatograph located in the Environmental Engineering Laboratory. Mixtures of methane-air, ethane-air and propane-air with known compositions over the range of equivalence ratios, $0.0 < \phi < 1.05$, were obtained to calibrate the instrument. Each calibration mixture was prepared by injecting the predetermined volume of fuel with a gas-tight syringe into a flask of known volume filled with test air initially at atmospheric pressure. The apparatus is shown in Figure 8. Details of the gas chromatograph calibration are given in Appendix I.

A standard capacitive discharge ignition system similar to those used in automobiles was employed. The spark plug, modified from an Auburn
ignitor (type I63), together with a stainless steel ground electrode, form a spark gap of 0.013 cm (0.05 in) at the center of the bomb. The tips of the electrodes were tapered to a point to ensure central ignition. The electrode of the spark plug was covered with a ceramic sheath to prevent sparks from forming across to the bomb wall.

The ionization probes employed a rod-within-a-tube construction as shown in Figure 9. The brass electrodes were insulated from each other and a potential of 75 volts was applied across them during operation. The signals were amplified and recorded on the oscilloscope. The flame arrival time was assumed to be the time at which a sharp rise in voltage occurred. A typical ionization probe signal is given in Figure 10. The locations of the probes relative to the center of the bomb were measured with a depth gauge placed on fixed supports as illustrated in Figures 11 and 12.

The pressure-time record was measured by an air-cooled AVL piezoelectric pressure transducer, calibrated to give a reading of 0.05 V/psi. The pressure transducer was located at approximately one diameter from the inside bomb wall. The pressure signal was transmitted by a low noise cable to an AVL charge amplifier (model 3059) and then displayed on a Nicolet digital storage oscilloscope. The test data were then transferred to an IBM PC and stored on floppy diskettes, which were later transferred to the host computer (VAX/VMS) for processing. A typical pressure trace is shown in Figure 13.

3.2 Procedures

The mixing tank and the fuel system were first evacuated with a vacuum pump and then flushed a few times with the air used in the tests. The fuel and air were mixed initially by partial pressures calculated from the
ideal gas law. The components, starting with the smallest quantity, were admitted to the mixing tank until the desired pressures were reached. At least 24 hours were allowed for thorough mixing to take place before a sample was drawn for composition analysis. From the stoichiometry measured by the gas chromatograph, appropriate corrections were applied to the mixture. Another sample was taken for analysis after 24 hours. Corrections continued until stoichiometry was attained.

When the mixture was ready, the combustion bomb was evacuated and flushed a few times with the test mixture. It was then filled to the desired initial pressure. A waiting time of 10 minutes was allowed for the mixture to become quiescent. To check that this is sufficient, tests involving waiting times of 5 to 60 minutes were conducted. No effect was observed and ten minutes was considered a reasonable interval. A thermocouple placed on the outside bomb wall was used to infer the initial temperature of the gas inside. A temperature rise as high as 6°C was registered after an explosion at high initial pressure. To determine the gas temperature, a correlation with the outside wall temperature was established as a function of time immediately after explosion. It was found that after 10 minutes, the gas temperature came within 1°C of the outside wall temperature which was uniform over the entire surface (see Appendix II). Therefore, a minimum of 15 minutes was allowed between tests.

3.3 Test Conditions

Stoichiometric mixtures of methane-air, ethane-air, propane-air, and selected mole fractions of ethane or propane in methane were tested at initial pressures of 1, 2, 4, 6, 8 atm. Table 4 lists the mixture matrix and Table 5 lists the test conditions for each run.
4. **DATA REDUCTION**

4.1 **Metghalchi and Keck (M and K) Method**

The principal method of analysis is based on that presented by Metghalchi and Keck [12]. The analysis assumes:

i) The flame propagates spherically.

ii) The flame front is smooth and thin.

iii) Pressure is uniform throughout the bomb.

iv) Both burnt and unburnt gases behave as ideal gases.

v) The unburnt gas is isentropically compressed as the burnt gas is expanded.

vi) The burnt gas is at thermodynamic equilibrium.

vii) There is no heat transfer until the end of combustion which is indicated by peak pressure.

viii) Combustion is complete.

At any instant during combustion, the mixture is considered to consist of two homogeneous regions - a burnt region at $P, \bar{T}_b$, and an unburnt region at $P, \bar{T}_u$. The equations to satisfy are conservation of energy and volume:

\[
\frac{E}{M} = \int_0^x e_b \, dx + \frac{1}{x} \int e_b \, dx
\]

\[
\frac{V}{M} = \int_0^x v_b \, dx + \frac{1}{x} \int v_b \, dx
\]

where $M =$ mass of mixture in bomb

$E =$ energy of mixture in bomb
\[ e_b, e_u = \text{specific energy of the burnt, unburnt gas} \]
\[ v_b, v_u = \text{specific volume of the burnt, unburnt gas} \]
\[ x = \text{mass fraction of burnt gas} \]

For the unburnt gas:
\[
\begin{align*}
v_u &= v_u(P, T_u) \\
e_u &= e_u(P, T_u)
\end{align*}
\]

where the pressure \( P \) is obtained experimentally and the unburnt gas temperature \( T_u \) is calculated from relations on isentropic compression (assumption \( v \)),
\[
\frac{T_{u2}}{T_{u1}} = \frac{P_2}{P_1} \left( \gamma_u - 1 \right)
\]

For the burnt gas:
\[
\begin{align*}
v_b &= v_b(P, T_b) \\
e_b &= e_b(P, T_b)
\end{align*}
\]

However, the burnt gas is not all at the same state because the gases burnt at different times are compressed along different isentropes. The burnt gas specific energy and specific volume can be expressed as:

\[
\begin{align*}
e_b &= e_b(P, \bar{T}_b) + \left( \frac{\partial e_b}{\partial T} \right)_{P} \int_{T_b}^{T_{\text{avg}}} (T - T_b) \, dT + \frac{1}{2} \left( \frac{\partial^2 e_b}{\partial T^2} \right)_{P} \left( T - T_{\text{avg}} \right)^2 + \ldots \\
v_b &= v_b(P, \bar{T}_b) + \left( \frac{\partial v_b}{\partial T} \right)_{P} \int_{T_b}^{T_{\text{avg}}} (T - T_b) \, dT + \frac{1}{2} \left( \frac{\partial^2 v_b}{\partial T^2} \right)_{P} \left( T - T_{\text{avg}} \right)^2 + \ldots
\end{align*}
\]

where \( \bar{T}_b \) is the mass average temperature of the burnt gas:
Neglecting terms of order \((T - \bar{T}_b)\) and higher, the conservation equations become:

\[
\bar{T}_b = \frac{1}{x} \int_0^x T_b \, dx
\]

\[
\frac{E}{M} = x e_b(P, \bar{T}_b) + (1-x) e_u(P) \quad (4-1)
\]

\[
\frac{V}{M} = x v_b(P, \bar{T}_b) + (1-x) v_u(P) \quad (4-2)
\]

Metghalchi and Keck estimated the error in \(x\) for a temperature spread of 500 K is less than 0.002 which is negligible.

The two unknowns, \(x\) and \(\bar{T}_b\), are solved by an iterative procedure. Properties of the burnt gas are first computed from an assumed average burnt gas temperature, \(\bar{T}_b\). The mass fraction burnt, \(x\), is then determined from Eq. (4-1). The volume computed from Eq. (4-2) based on this \(x\) was then compared to the actual bomb volume, \(V\). A proportional chopping technique is then used to reduce the difference between the calculated and actual volume, to 0.1%. When evaluating \(\bar{T}_b\), six dissociations reactions are considered:

A. \(CO = CO + 1/2 O_2\)
B. \(H_2O = 1/2 H_2 + OH\)
C. \(H_2O = H_2 + 1/2 O_2\)
D. \(1/2 N_2 + 1/2 O_2 = NO\)
E. \(H_2 = 2 H\)
F. \(O_2 = 2 O\)
The burning velocity, $S_u$, is obtained from mass continuity, (Eq. 2-2),

$$S_u = \frac{Mx(t)}{\rho_u A_f},$$

and the flame speed, $S_f$, from the definition,

$$S_f = \frac{dR_f}{dt}$$

From assumption 1, the flame area, $A_f$, and the flame radius, $R_f$, can be expressed as:

$$A_f = 4\pi R_f^2$$
$$R_f = \left(\frac{3}{4} Mx v_b\right)^{1/3}.$$ 

The advantage of this analysis is that the pressure-time record and the initial condition are the only experimental data required.

A computer program was developed to calculate the laminar burning velocity from the pressure history. A progressive burning procedure was used to model the combustion process. The smoothed pressure history was divided into equal time intervals except for the first 8 ms interval which has insignificant pressure rise. Procedure for smoothing and its errors are discussed in Chapter 5.4.2. The state of the mixture prior to ignition was the initial conditions used to obtain the properties of the first time step. The properties of each subsequent time step were calculated based on properties of the previous time step. This process continued until the end of combustion which was assumed to occur at peak pressure. Details of the calculation procedure is given in Appendix III.
The program is verified by comparing calculated with known adiabatic temperatures and dissociated species concentrations (see Appendix IV). A listing of the program is given in Appendix VIII. To determine the importance of dissociation, the dissociation reactions were neglected in the calculation of burnt gas temperature and results were compared.

4.2 Linear Method

The M and K method involves an elaborate computer model to evaluate the properties of the burnt gas. To obtain an approximate check value of \( S_u \), the linear model is introduced. In this model, an expression for the burning velocity is derived from the mass continuity for the unburnt gas (Eq. 2-2),

\[
\frac{dm_u}{dt} = -S_u A_f / \rho_u
\]

to be dependent on pressures only:

\[
S_u = \frac{\frac{R}{3} \left( \frac{1}{P-e-P_o} \right) \frac{dP}{dt}}{\left( \frac{P}{P_o} \right)^{1/\gamma_u} \left[ 1 - \left( \frac{P}{P_o} \right) \left( \frac{e-P}{P-o} \right) \right]^{1/\gamma_u} 2/3}
\]

The derivation is shown in Appendix VI. The major assumption is that the mass fraction burnt is calculated from the approximation derived by Lewis and Von Elbe [16] (see Appendix VI for derivation):

\[
x = \left( \frac{P-P_o}{e-P_o} \right)
\]
where $P_e$ is the pressure at the end of combustion, and $P_0$ is the initial pressure. This approximation greatly simplifies the determination of $S_u$, since it is independent of the burnt gas properties.
5. RESULTS AND DISCUSSION

This chapter presents the results of calculations of the burning velocity of methane, ethane, propane, and methane with ethane or propane additives. In the calculations the M and K method of analysis was used except where otherwise noted. Comparisons with previous results as well as the uncertainty of the present results are discussed.

The burning velocity data are plotted as functions of unburnt gas temperature $T_u$; the initial value of $T_u$ is approximately 300 K in each case; the test conditions are listed in Table 5. Each curve is the result of one ignition and the value of $T_u$ was determined (as shown in Section 4.1) from the instantaneous pressure using the isentropic relationships.

5.1 Experimental Results

The burning velocities of stoichiometric methane, ethane and propane-air mixtures of various initial pressures are shown in Figures 14, 15 and 16. For any particular run, the burning velocities were found to increase with increase in unburnt gas temperature $T_u$ except possibly near the end of the run. Comparing different runs of the same mixture at a given $T_u$ it may be seen that the burning velocity decreases as pressure increases. The relative decrease in burning velocity pressure was greatest for methane, least for ethane.

For an initial pressure of 2 atm it was observed (Figures 14-16, 17-20 and 24) that the form of the $S_u-T_u$ curve is characteristically different from those at other initial pressures. This characteristic was observed for all mixtures tested. One possible explanation could be that at a certain combination of pressure and temperature some chain-branching radicals become active and therefore alter the rate of combustion.
At the initial stage of combustion when the burnt volume was small, the pressure rise was insignificant. Therefore, the determination of the pressure-time derivative (and thus the calculated value of $S_u$) during that period was uncertain. Consequently, the values of $S_u$ shown were not expected to be very accurate for $T_u < 350$ K.

Figures 17 to 19 show comparisons of burning velocities of methane, ethane and propane at various initial pressures. For methane-air combustion (Figure 14) it was observed that for $T_u > 450$ K the calculated values of $S_u$ began to decline well before the maximum $T_u$ (i.e. maximum pressure) was reached. This tendency was not observed for propane or ethane (Figures 15 and 16). Since the burning velocity of methane was found to be the slowest (ethane the fastest), this effect may be due to buoyancy which could be expected to influence the flame geometry. Above an unburnt gas temperature of approximately 470 K, for methane and methane with propane or ethane additive mixtures (Figures 14, 20 to 27), the burning velocity was found to decrease. The flame front of a spherically propagating flame would have reached a radius equal to approximately 93% of the bomb radius at 470 K. Therefore, even if buoyancy effects were small, the upper part of the flame could have entered the thermal diffusion layer near the chamber wall and became partially extinguished. The effect of buoyancy could explain why the calculated values of $S_u$ (which were dependent on the rate of pressure rise) decline rapidly near the end of the combustion period. Consequently, for methane-air mixtures, the values of $S_u$ at high $T_u$ (> 450 K) were not considered reliable and the best results may be found in the range $350 < T_u < 450$ K.

Figures 20 to 23 show the effects of various ethane concentrations on the burning velocities of methane-air mixtures for initial pressures of
2,4,6 and 8 atm. Figures 24 to 27 show the effects of various propane concentrations on the burning velocities of methane-air mixtures for initial pressures of 2, 4, 6 and 8 atm. For both ethane and propane, the effects of trace quantities (< 1% by volume) and quantities up to 20% are presented. Except for \( P^\_1 = 4 \) atm (Figures 21, 25) trace quantities of ethane or propane appeared to have no significant effect. Even for \( P^\_1 = 4 \) atm, the differences in \( S_u \) due to either additive were found to be within experimental uncertainty (section 5.4) for the range \( 350 < T_u < 450 \) K. In general, there was a smooth progression in burning velocity as the fuel was varied from 100% methane to 100% ethane or 100% propane. The mixtures were approximately stoichiometric in all cases.

A few burning velocity curves (Figures 14, 22, 26) were particularly ragged in appearance. This occurrence was found to be independent of initial conditions or mixture type. Excess noise in the digital signal was believed to be the cause. The author was uncertain of the source of the noise.

Figures 28 and 29 show the relative effectiveness of ethane and propane in increasing the burning velocity of stoichiometric mixtures. These curves were approximate fits to the experimental data of Figures 20-27 at an unburnt gas temperature of 400 K. It was observed that:

1) The percent change in \( S_u \) increases as the additive concentration was increased.
2) Substantial increases in additive concentrations were required to induce substantial increases in \( S_u \).
3) The percent changes in \( S_u \) increases as the initial pressures was increased.
4) For the same volume percent, ethane appeared to be more effective than propane in raising burning velocity.

A plot, using logarithmic coordinates, of the burning velocity $S_u$ against the instantaneous pressure $P$, at constant $T_u$ provides a straight line with slope $-\beta$ so that

$$S_u \propto P^{-\beta}$$

Similarly, a logarithmic plot of $S_u$ versus $T_u$ at constant $P$ resulted in a straight line with slope $\alpha$ so that

$$S_u \propto T_u^\alpha$$

The entire set of experimentally derived $S_u$ values for each fuel-air mixture were fitted to the formula

$$S_u = S_{uo} \left( \frac{T_u}{T_o} \right)^\alpha \left( \frac{P}{P_o} \right)^\beta$$

where $P_o = 101.3$ kPa and $T_o = 298$ K. The resulting values of $S_{uo}$, $\alpha$ and $\beta$ are given in Table 6. The standard deviations of the fit for all mixtures were 7% at most. Splitting the data set into two pressure ranges, $1 < P < 4$ atm and $4 < P < 7$ atm, gave somewhat different values of $S_{uo}$, $\alpha$ and $\beta$ as shown in Table 6. Taking experimental uncertainty into account, however, the differences appeared to be insignificant. The standard deviations for the split-range fits were less than 5%.

Comparisons of the present work and previously reported results for the pressure and temperature dependence of $S_u$ for stoichiometric methane-air mixtures are given in Figures 4 and 5.

In previous work, various experimental techniques and methods of data analysis were used to determine $S_u$. The pressure and temperature
dependence obtained here were calculated using the power law with $\alpha = 1.8$ and $\beta = -0.3$ (Table 6).

In both figures, even at 1 atm and 298 K, there was at least 20% spread in the values of $S_u$ as determined by various investigators. In view of this, it was not unexpected that there was a large scatter in the high pressure data. The differences are associated with differences in experimental techniques and methods of data analysis. For the bomb technique, Gülter [12] and Andrew and Bradley [8] all reported a pressure coefficient of $-0.5$ as compared to $-0.3$ from the present work. Although the pressure coefficients were quite different, the values of $S_u$ for the range $1 < P < 10$ atm were found to agree to within experimental uncertainty. It should be noted that these investigators calculated the burning velocities using the density ratio method. As discussed in 2.3, this method was based on the essentially constant-pressure combustion process during the initial stages of flame propagation. Flame thickness and curvature may have been sources of error in their calculations of $S_u$, though the work of Andrews and Bradley [8] may be taken as an indication that this is not so.

Comparisons of present results for propane-air mixtures with those obtained by Metghalchi and Keck [23], who used basically the same technique and method of analysis, are shown in Figure 3. It may be seen that the present data agree quite closely with the correlation of Metghalchi and Keck for stoichiometric propane-air mixtures. These authors have analyzed possible errors due to heat transfer to the outer wall from the unburnt gases, radiation from the burnt gases to the unburnt, heat loss to the electrodes, temperature gradients in the burnt gases, and flame thickness. They found that the possible error in $S_u$ due to each of these effects would be of the order of 1%. Therefore, it appears that the present method of
analysis is quite accurate. The ionization probe data (to be discussed later) further supports this conclusion.

Ryan and Letz [56] have also determined the burning velocities of propane and methane-air mixtures. Their results, however, were considered questionable because the method of analysis they adopted appeared to be incorrect. Metghalchi and Keck [23] have concluded that the assumption made by Ryan and Letz of constant volume combustion for each time step "leads to an incorrect value of the entropy for the burnt gas which could in turn affect the calculated flame speeds".

5.2 Comparisons of Method of Analysis

Comparisons of the burning velocities computed from the M and K and linear models, discussed in Chapter 4.1 are shown in Figures 30 to 32. The absence of dissociation reactions for the M and K model led to a higher computed burnt gas temperature and therefore higher burned gas specific volume at a given pressure. Thus, the mass burned fraction required to account for a given pressure rise would be lower. This in turn would result in a lower value of $S_u$ (which is proportional to mass burning rate). The effect due to dissociation was found to be quite important. Its neglect was found to produce a 10% difference in $S_u$, depending on the fuel and the pressure.

Figures 30 to 32 show that the simple linear model in which the assumption

\[ x = \frac{P-P_0}{P_e-P_0} \]
was made. The value for $P_e$ used in the calculation was the experimental maximum pressure which was less than the adiabatic pressure due to wall heat transfer. Agreement between the linear model and the M and K model was found to be the best at higher pressures because this was the region in which $dP/dt$ was most accurately estimated. At lower pressures, the agreement between these two models was worse because this was the region in which the estimation of $dP/dt$ was most uncertain.

5.3 Ionization Probes Results

The ionization probes were used to check the flame symmetry. More importantly, they provided a direct measurement of the flame arrival times against which the computed values can be compared. Therefore, they are a means to assess the accuracy of the method of analysis.

By placing two ionization probes at the same radius, one can compare the flame arrival times - which would be equal if the flame is spherical. Two different radii were tested and the results are shown in Figure 33. The signals differ by approximately 1.2 ms in both cases. One possible explanation for this error is that there exists a difference in response characteristic of the probes.

To evaluate the accuracies of the models, experimental flame arrival times at known radii are compared with those computed using the linear and M and K models. There is generally good agreement between the measured and calculated values of either model. The results, shown in Figure 34, appeared to favour the M and K model. However, within experimental error, no conclusion can be drawn as to which model is better. Since the linear model is much simpler to use, it appeared to provide a good approximation in the determination of burning velocity.
5.4 Error Analysis

The maximum error from all sources on the burning velocity is estimated to be 10%. The contributing factors are discussed in the following sections.

5.4.1 Uncertainties in Measurements

The potential sources of uncertainties are in the measurement of equivalence ratios, pressures - time derivative and initial temperature.

The maximum error in equivalent ratios is estimated to be 1.2%, with 0.9% due to impurities of the gases and 0.3% to errors in the calibration of the gas chromatograph. Details of the calculations is given in Appendix VII. For small quantities of additive, the error in the mole fraction can be as large as 2%. However, this has insignificant effect on the value of the equivalence ratio. The initial pressures are accurate to 0.3% according to manufacturer specification. The sensitivity of calculated values of $S_u$ to equivalence ratio is shown in Figure 35. A 1% change in equivalence ratio has virtually no effect on the burning velocity.

Because the initial temperature was measured by a thermocouple placed on the combustion chamber wall, and because the chamber wall temperature rose somewhat with repeated firings the thermocouple may not have accurately indicated the temperature of the fresh charge entering the chamber. The estimated uncertainty in the initial temperature, allowing for this difference plus inaccuracy of calibration is estimated to be 2 K. Figure 36 shows the sensitivity of the calculated burning velocity to large changes in the initial temperature. Changes in initial temperature shift the entire curve to one side or the other depending on the sign of the error. The maximum error due to a 2 K deviation from the input initial temperature is 1-2%.
The repeatability of the pressure history for the same prepared mixture (1 tank) and separately prepared mixtures (2 tanks) of the same composition is shown in Figures 37 and 38. The corresponding effects on burning velocities are shown in Figures 39 and 40. The variations in pressure-time records introduced a maximum uncertainty of 3% on the values of $S_u$, except at the extremes where the values are most uncertain. The values at the start of combustion are subject to errors due to flame thickness and curvature effects and those at the end, wall effects. Therefore, values at the extreme are not presented and were excluded from the determination of pressure and temperature dependence.

5.4.2 **Uncertainties in Pressure - Time Derivative**

Smoothing was used to filter out fluctuations in the digital signals. The pressure signal in micro-scale is shown in Figure 41. Smoothing was applied to the voltage before conversion to pressure took place. The pressure trace was recorded as 4000 points over the selected time span on the oscilloscope. It was found that no significant pressure rise occurred during the first 8 ms. Therefore, a straight line was fitted over the first N points corresponding to 8 ms. Subsequent data were also fitted with straight lines, but over every 25 points. Linear regression was performed over each of these intervals. Pressures were computed at the mid-points of each of these regression lines. The smoothed curve was then constructed from these smoothed pressures and the corresponding times. The slopes were computed using the smoothed curve. Comparisons between the raw data and that smoothed by straight line and their corresponding slopes are shown in Figure 42. Every 25 points was chosen because it gave a reasonable mean of the observed fluctuations not only in the pressure signals,
but also in the resulting burning velocities. For a large value of \( N \), the burning velocity was found to deviate significantly from the mean values. The effect of \( N \) was illustrated in Figure 43.

The errors due to the smoothing technique are shown in Figure 44. They were computed based on a pressure rise to the observed values rather than the smoothed values. They were found to differ by a maximum of 5%.
6. CONCLUSIONS

Laminar burning velocities of stoichiometric mixtures of methane-air, ethane-air, propane-air and methane with ethane or propane additives were measured in a constant volume chamber, for pressures of 1 to 80 atm and with unburnt gas temperatures in the range 300 to 500 K, with an experimental uncertainty of about 10 percent. The pressure and temperature dependence of the burning velocities were correlated for the whole range of experimental conditions for each fuel-air mixture by the relationship

$$S_u = S_{uo} \left(\frac{T}{T_o}\right)^\alpha \left(\frac{P}{P_o}\right)^\beta$$

with a standard deviation of not more than 7 percent.

The validity of the method of calculation of burning velocities from pressure-time data was confirmed by ion-probe measurements of flame arrival time, by agreement with an independent method of analysis (the linear model) and by comparison with the determinations of other workers of the burning velocity of methane and propane.

At a given pressure and temperature and with stoichiometric mixtures, propane and methane additives increased the burning velocity of methane-air mixtures substantially. The greatest relative increase in burning velocity was at highest pressure, for a given temperature. Trace amounts of propane or ethane do not appear to have significant effects on the burning velocity.

For the same volume fraction of additives, ethane raises the burning velocity of methane-air mixtures more than propane does.
7. **RECOMMENDATIONS**

This work was primarily concerned with pressure effects in a fairly low temperature range. It would be desirable to extend the experiments to higher temperatures.

Because of interest in the combustion of lean mixtures in engines, the effects of additives should be investigated over a range of equivalence ratios.

The possible effect of buoyancy was not investigated in the present work. It is recommended that this be studied, especially with slow burning mixtures, with the aid of additional ion probe measurements.

Since error in initial temperature contributed to a significant uncertainty in the burning velocity, direct measurement of the initial mixture temperature should be made.

The accuracy of pressure derivative determination could be improved by using other smoothing techniques such as spline fits.
Table 1 Composition (mol %) of natural gases from different regions

<table>
<thead>
<tr>
<th>Region</th>
<th>B.C. Canada</th>
<th>N.Zealand Kapuni</th>
<th>California</th>
<th>Netherlands Groningen</th>
<th>North Sea</th>
<th>Brunei</th>
<th>Libya</th>
<th>Algeria</th>
<th>Nigeria</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH₄</td>
<td>94.0</td>
<td>82.80</td>
<td>87.0</td>
<td>81.3</td>
<td>94.8</td>
<td>88.0</td>
<td>71.4</td>
<td>86.5</td>
<td>88.1</td>
</tr>
<tr>
<td>C₂H₆</td>
<td>3.3</td>
<td>9.23</td>
<td>8.0</td>
<td>2.85</td>
<td>3.0</td>
<td>5.1</td>
<td>16.0</td>
<td>9.4</td>
<td>6.3</td>
</tr>
<tr>
<td>C₃H₈ -n</td>
<td>1.0</td>
<td>4.16</td>
<td>1.6</td>
<td>0.39</td>
<td>0.6</td>
<td>4.8</td>
<td>7.9</td>
<td>2.6</td>
<td>2.1</td>
</tr>
<tr>
<td>C₄H₁₀ -i</td>
<td>0.2</td>
<td>0.93</td>
<td>0.1</td>
<td>0.13</td>
<td>0.2</td>
<td>1.8</td>
<td>3.4</td>
<td>1.1</td>
<td>0.3</td>
</tr>
<tr>
<td>C₅H₁₂ -n</td>
<td>0.02</td>
<td>0.13</td>
<td>0.1</td>
<td>0.03</td>
<td>0.2</td>
<td>0.2</td>
<td>1.3</td>
<td>0.1</td>
<td>1.1</td>
</tr>
<tr>
<td>C₆H₁₄ -i</td>
<td>0.01</td>
<td>0.01</td>
<td>0.01</td>
<td>0.01</td>
<td>0.01</td>
<td>0.01</td>
<td>2.1</td>
<td></td>
<td></td>
</tr>
<tr>
<td>CO₂</td>
<td>0.3</td>
<td>2.07</td>
<td>0.6</td>
<td>0.9</td>
<td>1.2</td>
<td>0.1</td>
<td></td>
<td>0.3</td>
<td></td>
</tr>
<tr>
<td>N₂</td>
<td>1.0</td>
<td>0.68</td>
<td>2.5</td>
<td>14.3</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>O₂</td>
<td>---</td>
<td>0.1</td>
<td>1.2</td>
<td>0.1</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Table 2 Comparisons of results obtained by previous and present investigators on the burning velocity of methane-air mixtures

<table>
<thead>
<tr>
<th>Author</th>
<th>Ref</th>
<th>Approach*</th>
<th>Experiment</th>
<th>Range</th>
<th>*</th>
<th>Equation</th>
<th>$S_u$ in cm/sec</th>
<th>$S_u$ ($\phi=1$, 1 atm, 298K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Agnew &amp; Graff</td>
<td>3</td>
<td>1</td>
<td>$r_b-t$ by ion probe</td>
<td>$\phi$</td>
<td>1</td>
<td>$P [\text{atm}]$</td>
<td>$T_u[k]$</td>
<td>$S_u$</td>
</tr>
<tr>
<td>Andrew &amp; Badley</td>
<td>8</td>
<td>1 &amp; 2</td>
<td>$r_b-t$ by optical means</td>
<td>$P$</td>
<td>0.5-20</td>
<td>$S_u=S_f/E_f$</td>
<td>$S_u=32.9$</td>
<td>$32.9$ cm/s</td>
</tr>
<tr>
<td>Garforth &amp; Rallis</td>
<td>2</td>
<td>1</td>
<td>$r_b-t$ by photographs P-t records</td>
<td>$P$</td>
<td>0.6-1.6</td>
<td>$S_u=S_f/\rho_g S_f$</td>
<td>$S_u=43 P^{-0.5}$</td>
<td>$P &gt; 5$ atm</td>
</tr>
<tr>
<td>Agrawal</td>
<td>11</td>
<td>1</td>
<td>$r_b-t$ by photographs</td>
<td>$P$</td>
<td>0.8-1.2</td>
<td>$S_u=S_f/0.848 P_e-x_e$</td>
<td>$S_u=33.6$</td>
<td></td>
</tr>
<tr>
<td>Bradley &amp; Hundy</td>
<td>13</td>
<td>5</td>
<td>$r_b-t$ by optical means</td>
<td>$P$</td>
<td>0.7-1.2</td>
<td>$S_u=S_f/0.848 P_e-x_e$</td>
<td>$S_u=46$</td>
<td></td>
</tr>
<tr>
<td>Sharma et al</td>
<td>21</td>
<td>3</td>
<td>$S_f$ by photographs P-t records</td>
<td>$P$</td>
<td>0.8-1.2</td>
<td>$S_u=C_u(T_u/300)^{1.68}/P \ \ (\phi&lt;1.0)$</td>
<td>$S_u=33.3$</td>
<td></td>
</tr>
<tr>
<td>Childer</td>
<td>12</td>
<td>1</td>
<td>$S_f$ by ion probes</td>
<td>$P$</td>
<td>1-80</td>
<td>$S_u=\rho_b/\rho_g S_f$</td>
<td>$S_u=41(P)^{0.5} (T_u/298)^{2.0}$</td>
<td>$41$</td>
</tr>
<tr>
<td>Present Work</td>
<td>3</td>
<td>3</td>
<td>$P-t$ records</td>
<td>$P$</td>
<td>1</td>
<td>$1-80$</td>
<td>$S_u=33(P)^{0.3} (T_u/298)^{1.68}$</td>
<td>$33$</td>
</tr>
</tbody>
</table>

*1 Density ratio or expansion ratio method
2 Direct measurement
3 From P-t records
Table 3 Comparisons of results obtained by previous and present investigators on the burning velocity of propane-air mixtures

<table>
<thead>
<tr>
<th>Author</th>
<th>Ref</th>
<th>Approach*</th>
<th>Experiment</th>
<th>$\phi$</th>
<th>$P$ atm</th>
<th>$T_u$ K</th>
<th>Equation</th>
<th>Correlation</th>
<th>$S_u(\phi=1, 1$ atm, 298K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Metghalchi &amp; Keck</td>
<td>23</td>
<td>3</td>
<td>P-t records</td>
<td>0.8-1.5</td>
<td>0.4-40</td>
<td>298-750</td>
<td>$E/M=x_e V_e+(1-x)E_u V_u$</td>
<td>$S_{uo}(P)^{\beta}(T_u/298)^{\alpha}$</td>
<td>32</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>$V/M=x_v V_v+(1-x)E_u V_u$</td>
<td>$\phi=1, S_u=31.9(P)^{-0.17}(T_u/298)^{2.13}$</td>
<td></td>
</tr>
<tr>
<td>Kuehl</td>
<td>5</td>
<td></td>
<td>$r_b-t$ photographs</td>
<td>0.7-1.7</td>
<td>0.25-1.0</td>
<td>311-870</td>
<td>Standard angle method</td>
<td>$S_u=6.036-4.93810g[10^{[4/T_u+900/T_1}]P^{-0.82}$</td>
<td>48</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>$P$ in inHg</td>
<td>$P$ in inHig</td>
<td></td>
</tr>
<tr>
<td>Guider</td>
<td>12</td>
<td>1</td>
<td>$S_f$ by ion probes</td>
<td>Not Available</td>
<td></td>
<td></td>
<td>$S_u=T_u/\rho_u S_f$</td>
<td>$S_u=S_{uo}(P)^{\beta}(T_u/298)^{\alpha}$</td>
<td>43</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>$S_{uo}=0.446\phi^{0.12}\exp[-4.95(\phi-1.075)^2]$</td>
<td>$\phi=1: S_u=43(P)^{-0.2}(T_u/298)^{1.77}$</td>
<td></td>
</tr>
<tr>
<td>Present Work</td>
<td>3</td>
<td></td>
<td>P-t records</td>
<td>1</td>
<td>1-80</td>
<td>300-500</td>
<td>$E/M=x_e V_e+(1-x)E_u V_u$</td>
<td>$S_u=35(P)^{-0.13}(T_u/298)^{1.66}$</td>
<td>35</td>
</tr>
</tbody>
</table>

*1 Density ratio or expansion ratio method
3 From P-t records
Table 4 Test mixtures matrix

<table>
<thead>
<tr>
<th>CH$_4$</th>
<th>C$_2$H$_6$</th>
<th>C$_3$H$_8$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>0</td>
<td>1</td>
<td>0</td>
</tr>
<tr>
<td>0</td>
<td>0</td>
<td>1</td>
</tr>
<tr>
<td>1</td>
<td>0.0070</td>
<td>0</td>
</tr>
<tr>
<td>1</td>
<td>0.110</td>
<td>0</td>
</tr>
<tr>
<td>1</td>
<td>0.215</td>
<td>0</td>
</tr>
<tr>
<td>1</td>
<td>0</td>
<td>0.0076</td>
</tr>
<tr>
<td>1</td>
<td>0</td>
<td>0.0090</td>
</tr>
<tr>
<td>1</td>
<td>0</td>
<td>0.110</td>
</tr>
<tr>
<td>1</td>
<td>0</td>
<td>0.220</td>
</tr>
<tr>
<td>Mixture</td>
<td>( P_0 ) kPa</td>
<td>( T_0 ) °C</td>
</tr>
<tr>
<td>--------------</td>
<td>---------------</td>
<td>--------------</td>
</tr>
<tr>
<td>( CH_4 )</td>
<td>102.45</td>
<td>25</td>
</tr>
<tr>
<td></td>
<td>202.7</td>
<td>23</td>
</tr>
<tr>
<td></td>
<td>405.6</td>
<td>25</td>
</tr>
<tr>
<td></td>
<td>608.3</td>
<td>22</td>
</tr>
<tr>
<td></td>
<td>811.2</td>
<td>22</td>
</tr>
<tr>
<td>( C_2H_6 )</td>
<td>118.8</td>
<td>26</td>
</tr>
<tr>
<td></td>
<td>202.5</td>
<td>22</td>
</tr>
<tr>
<td></td>
<td>405.3</td>
<td>27</td>
</tr>
<tr>
<td></td>
<td>607.7</td>
<td>25</td>
</tr>
<tr>
<td></td>
<td>810.4</td>
<td>21</td>
</tr>
<tr>
<td>( C_3H_8 )</td>
<td>101.6</td>
<td>18</td>
</tr>
<tr>
<td></td>
<td>202.7</td>
<td>26</td>
</tr>
<tr>
<td></td>
<td>404.9</td>
<td>26</td>
</tr>
<tr>
<td></td>
<td>608.2</td>
<td>21</td>
</tr>
<tr>
<td></td>
<td>696.6</td>
<td>20</td>
</tr>
<tr>
<td>( CH_4 + 0.007 \ C_2H_6 )</td>
<td>108.7</td>
<td>25</td>
</tr>
<tr>
<td></td>
<td>202.5</td>
<td>25</td>
</tr>
<tr>
<td></td>
<td>404.8</td>
<td>25</td>
</tr>
<tr>
<td></td>
<td>607.7</td>
<td>24</td>
</tr>
<tr>
<td></td>
<td>810.2</td>
<td>20</td>
</tr>
<tr>
<td>( CH_4 + 0.11 \ C_2H_6 )</td>
<td>104.3</td>
<td>21</td>
</tr>
<tr>
<td></td>
<td>202.5</td>
<td>18</td>
</tr>
<tr>
<td></td>
<td>405.2</td>
<td>22</td>
</tr>
<tr>
<td></td>
<td>607.7</td>
<td>22</td>
</tr>
<tr>
<td></td>
<td>810.0</td>
<td>19</td>
</tr>
<tr>
<td>( CH_4 + 0.215 \ C_2H_6 )</td>
<td>104.7</td>
<td>24</td>
</tr>
<tr>
<td></td>
<td>202.9</td>
<td>23</td>
</tr>
<tr>
<td></td>
<td>405.6</td>
<td>24</td>
</tr>
<tr>
<td></td>
<td>607.7</td>
<td>26</td>
</tr>
<tr>
<td></td>
<td>809.6</td>
<td>22</td>
</tr>
<tr>
<td>( CH_4 + 0.0076 \ C_3H_8 )</td>
<td>169.2</td>
<td>23</td>
</tr>
<tr>
<td></td>
<td>203.1</td>
<td>25</td>
</tr>
<tr>
<td></td>
<td>405.1</td>
<td>22</td>
</tr>
<tr>
<td></td>
<td>607.7</td>
<td>25</td>
</tr>
<tr>
<td></td>
<td>810.2</td>
<td>21</td>
</tr>
<tr>
<td>( CH_4 + 0.0090 \ C_3H_8 )</td>
<td>109.8</td>
<td>24</td>
</tr>
<tr>
<td></td>
<td>202.8</td>
<td>21</td>
</tr>
<tr>
<td></td>
<td>405.2</td>
<td>27</td>
</tr>
<tr>
<td></td>
<td>607.7</td>
<td>26</td>
</tr>
<tr>
<td></td>
<td>810.1</td>
<td>25</td>
</tr>
<tr>
<td>( CH_4 + 0.11 \ C_3H_8 )</td>
<td>104.9</td>
<td>23</td>
</tr>
<tr>
<td></td>
<td>202.9</td>
<td>24</td>
</tr>
<tr>
<td></td>
<td>405.1</td>
<td>22</td>
</tr>
<tr>
<td></td>
<td>607.7</td>
<td>25</td>
</tr>
<tr>
<td></td>
<td>810.5</td>
<td>21</td>
</tr>
<tr>
<td>( CH_4 + 0.22 \ C_3H_8 )</td>
<td>102.5</td>
<td>24</td>
</tr>
<tr>
<td></td>
<td>202.5</td>
<td>23</td>
</tr>
<tr>
<td></td>
<td>405.2</td>
<td>24</td>
</tr>
<tr>
<td></td>
<td>607.6</td>
<td>20</td>
</tr>
<tr>
<td></td>
<td>810.9</td>
<td>18</td>
</tr>
</tbody>
</table>
Table 6 Table of coefficients $S_{uo}$, $\alpha$ and $\beta$ for single and split correlation

$$S_u = S_{uo} \left(\frac{T}{T_0}\right)^\alpha \left(\frac{P}{P_0}\right)^\beta$$

<table>
<thead>
<tr>
<th>Stoichiometric Coefficient</th>
<th>$1 &lt; P_1 &lt; 8 \text{ atm}$</th>
<th>$1 &lt; P_1 &lt; 4 \text{ atm}$</th>
<th>$4 &lt; P_1 &lt; 8 \text{ atm}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{CH}_4$</td>
<td>$\text{C}_2\text{H}_6$</td>
<td>$\text{C}_3\text{H}_8$</td>
<td>$S_{uo}$</td>
</tr>
<tr>
<td>1</td>
<td>0</td>
<td>0</td>
<td>32.9</td>
</tr>
<tr>
<td>0</td>
<td>1</td>
<td>0</td>
<td>34.6</td>
</tr>
<tr>
<td>0</td>
<td>0</td>
<td>1</td>
<td>34.2</td>
</tr>
<tr>
<td>1</td>
<td>0.0070</td>
<td>0</td>
<td>32.0</td>
</tr>
<tr>
<td>1</td>
<td>0.110</td>
<td>0</td>
<td>33.2</td>
</tr>
<tr>
<td>1</td>
<td>0.215</td>
<td>0</td>
<td>33.5</td>
</tr>
<tr>
<td>1</td>
<td>0</td>
<td>0.0076</td>
<td>32.3</td>
</tr>
<tr>
<td>1</td>
<td>0</td>
<td>0.0090</td>
<td>33.3</td>
</tr>
<tr>
<td>1</td>
<td>0</td>
<td>0.110</td>
<td>33.0</td>
</tr>
<tr>
<td>1</td>
<td>0</td>
<td>0.220</td>
<td>33.1</td>
</tr>
</tbody>
</table>
Table 7 Comparisons of coefficients of $S_{uo}$, $\alpha$ and $\beta$ with previous work

<table>
<thead>
<tr>
<th>Mixture</th>
<th>Investigator</th>
<th>$S_{uo}$</th>
<th>$\alpha$</th>
<th>$\beta$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{CH}_4$-$\text{Air}$</td>
<td>Andrew &amp; Bradley [8]</td>
<td>43</td>
<td>-</td>
<td>-0.5</td>
</tr>
<tr>
<td></td>
<td>Gulder [12]</td>
<td>41</td>
<td>2.0</td>
<td>-0.5</td>
</tr>
<tr>
<td></td>
<td>Present Work (1 &lt; $P_1$ &lt; 4 atm)</td>
<td>33</td>
<td>1.69</td>
<td>-0.27</td>
</tr>
<tr>
<td>$\text{C}_3\text{H}_8$-$\text{Air}$</td>
<td>Metghalchi &amp; Keck [23]</td>
<td>31</td>
<td>2.13</td>
<td>-0.17</td>
</tr>
<tr>
<td></td>
<td>Gulder</td>
<td>43</td>
<td>1.77</td>
<td>-0.2</td>
</tr>
<tr>
<td></td>
<td>Present Work (1 &lt; $P_1$ &lt; 4 atm)</td>
<td>35</td>
<td>1.56</td>
<td>-0.12</td>
</tr>
</tbody>
</table>
### Table 8 Ionization probe test results

<table>
<thead>
<tr>
<th>Mixture</th>
<th>$R_1$</th>
<th>$R_2$</th>
<th>RUN#</th>
<th>$t_1$</th>
<th>$t_2$</th>
<th>$\Delta t$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{CH}_4 + 0.22\text{C}_3\text{H}_8$</td>
<td>5.06</td>
<td>5.02</td>
<td>1</td>
<td>23.00</td>
<td>24.08</td>
<td>1.08</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>2</td>
<td>20.68</td>
<td>22.14</td>
<td>1.46</td>
</tr>
<tr>
<td>$\text{CH}_4 + 0.11\text{C}_3\text{H}_8$</td>
<td>2.87</td>
<td>5.09</td>
<td>1</td>
<td>12.4</td>
<td>22.6</td>
<td>10.2</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>2</td>
<td>11.9</td>
<td>22.4</td>
<td>10.5</td>
</tr>
<tr>
<td>$\text{CH}_4 + 0.11\text{C}_2\text{H}_6$</td>
<td>2.87</td>
<td>5.09</td>
<td>1</td>
<td>13.22</td>
<td>26.16</td>
<td>12.94</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>2</td>
<td>11.58</td>
<td>24.20</td>
<td>12.62</td>
</tr>
</tbody>
</table>
Table 9 Circuit independence test results

<table>
<thead>
<tr>
<th>Probe #</th>
<th>Circuit #</th>
<th>$t_{[ms]}$</th>
<th>$\Delta t$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1</td>
<td>30.4</td>
<td>2.0</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>28.4</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>1</td>
<td>32.4</td>
<td>2.1</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>30.3</td>
<td></td>
</tr>
</tbody>
</table>
Figure 1. The dependence of laminar burning velocity on initial pressure for mixtures of air and methane, ethane, propane (present work) and octane [55].
Figure 2. Laminar burning velocity of methane-air mixtures published during 1916 to 1972, as compiled by Andrew and Bradley [2].
Figure 3. Comparisons of burning velocity of stoichiometric propane-air mixtures obtained by Metghalchi and Keck, Kuehl and present work.
Figure 4. Comparisons of predicted and experimental temperature dependence of stoichiometric methane-air mixtures at atmospheric pressure. This figure is adapted from Ref. 8.
Figure 5. Comparisons of predicted and experimental pressure dependence of stoichiometric methane-air mixtures at 298 K. This figure is adapted from Ref. 8.
Figure 6. Schematic of the experimental set-up.
Figure 7. General overview of the experimental set-up.
Figure 8. Gas chromatograph calibration apparatus.
Figure 9. Ionization probe construction.
Figure 10. A typical ionization probe signal.
Figure 11. Schematic of combustion bomb showing positions of spark plug, ionization probes, and pressure transducer.
Figure 12. Photograph showing details of the spherical combustion bomb.
Figure 13. A typical pressure-time record during combustion.
Figure 14. Laminar burning velocities for stoichiometric methane-air mixtures at initial pressures of 1, 2, 4, 6 and 8 atm.
Figure 15. Laminar burning velocities for stoichiometric ethane-air mixtures at initial pressures of 1, 2, 4, 6 and 8 atm.
Figure 16. Laminar burning velocities for stoichiometric propane-air mixtures at initial pressures of 1, 2, 4, 6 and 8 atm.
Figure 17. Comparisons of laminar burning velocities for stoichiometric mixtures of methane-air, ethane-air and propane-air at initial pressure of 2 atm.
Figure 18. Comparisons of laminar burning velocities for stoichiometric mixtures of methane-air, ethane-air and propane-air at initial pressure of 4 atm.
Figure 19. Comparisons of laminar burning velocities for stoichiometric mixtures of methane-air, ethane-air and propane-air at initial pressure of 6 atm.
Figure 20. Effects of ethane at various relative percent ($\%C_2H_6/CH_4$) on the laminar burning velocities of methane-air mixtures at an initial pressure of 2 atm. All mixtures are of stoichiometric proportions.
Figure 21. Effects of ethane at various relative percent ($\%{\text{C}_2\text{H}_6}/\text{CH}_4$) on the laminar burning velocities of methane-air mixtures at an initial pressure of 4 atm. All mixtures are of stoichiometric proportions.
Figure 22. Effects of ethane at various relative percent ($\% C_2H_6/CH_4$) on the laminar burning velocities of methane-air mixtures at an initial pressure of 6 atm. All mixtures are of stoichiometric proportions.
Figure 23. Effects of ethane at various relative percent (%C$_2$H$_6$/CH$_4$) on the laminar burning velocities of methane-air mixtures at an initial pressure of 8 atm. All mixtures are of stoichiometric proportions.
Figure 24. Effects of propane at various relative percent (%C$_2$H$_6$/CH$_4$) on the initial laminar burning velocities of methane-air mixtures at an initial pressure of 2 atm. All mixtures are of stoichiometric proportions.
Figure 25. Effects of propane at various relative percent (\%C_2H_6/CH_4) on the laminar burning velocities of methane-air mixtures at an initial pressure of 4 atm. All mixtures are of stoichiometric proportions.
Figure 26. Effects of propane at various relative percent ($%\text{C}_2\text{H}_6/\text{CH}_4$) on the laminar burning velocities of methane-air mixtures at an initial pressure of 6 atm. All mixtures are of stoichiometric proportions.
Figure 27. Effect of propane at various relative percent ($\% C_6H_8/CH_4$) on the laminar burning velocities of methane-air mixtures at an initial pressure of 8 atm. All mixtures are of stoichiometric proportions.
Figure 28. Percent change in the burning velocity of stoichiometric methane-air mixture due to various relative percent of ethane.
Figure 29. Percent change in the burning velocity of stoichiometric methane-air mixture due to various relative percent of propane.
Figure 30. Comparisons of laminar burning velocities obtained from M and K model, M and K model without dissociation, and linear model for stoichiometric methane-air mixtures.
Figure 31. Comparisons of laminar burning velocities obtained from M and K model, M and K model without dissociation, and linear model for stoichiometric ethane-air mixtures.
Figure 32. Comparisons of laminar burning velocities obtained from M and K model, M and K model without dissociation, and linear model for stoichiometric propane-air mixtures.
Figure 33. Comparisons of ionization probe results with that of the radius-time curves calculated from M and K and linear model. The ionization probes are located at the same radius. (Mixture composition: CH$_4$+0.22 C$_3$H$_8$.)
Figure 34. Comparisons of ionization probe results with that of the radius-time curves calculated from M and K and linear model. The ionization probes are located at different radii. (Mixture composition: CH$_4$+0.22 C$_3$H$_8$.)
Figure 35. Sensitivity of the laminar burning velocities calculated from M and K model to initial temperature and stoichiometry. Actual condition was: $P_i = 1$ atm, $P_o = 1.00$, $T_i = 298$ K.
Figure 36. Sensitivity of the laminar burning velocities calculated from M and K model to initial temperature and stoichiometry. Actual condition was: $P_i = 8$ atm, $\phi = 1.00$, $T_i = 292$ K.
Figure 37. Repeatability tests of pressure-time records for stoichiometric methane-air mixtures taken from the same mixing tank (1 tank).
Figure 38. Repeatability tests of pressure-time records for stoichiometric methane-air mixtures taken from the two separately prepared mixing tanks (2 tanks).
Figure 39. Laminar burning velocities corresponding to the pressure-time records in Figure 37.
Figure 40. Laminar burning velocities corresponding to the pressure-time records in Figure 38.
Figure 41. Typical digital signal in micro-scale.
Figure 42. Comparison of raw and smoothed pressure data and their slopes.
Figure 43. Laminar burning velocity plotted against unburnt gas temperature at various $N$, number of points for smoothing.
Figure 44. Maximum error introduced from the smoothing technique on the laminar burning velocities of stoichiometric methane-air mixtures at initial pressures of 1 and 8 atm.
REFERENCES


APPENDIX:

I  Gas Chromatograph Calibration
II Initial Temperature Calibration
III Computer Program Calculation Procedures
IV Program Verification
V Expansion Coefficient Derivation
VI Linear Model Equation Derivation
VII Calculation of Errors in Equivalence Ratio
The gas chromatograph used a single Parapak Q column to separate the hydrocarbons and air. Each component is identified by the retention time, time for the component to go through the column, which is a function of column temperature. The component then goes through a wheat-stone bridge detector. The change in resistance due to the presence of the component produces a peak on the recorder. The area under this peak is proportional to the volume injected. Thus, the volume percent can be determined from the area percent. Three chromatograms of the same mixture is shown in Appendix IA. The repeatability in the area percents was found to be within 0.3%. The calibration curves are shown in Appendix IB, IC and ID.
APPENDIX IA  Typical Output from Gas Chromatograph

<table>
<thead>
<tr>
<th>RT</th>
<th>AREA</th>
<th>AREA %</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.27</td>
<td>0.00</td>
<td>0.00%</td>
</tr>
<tr>
<td>3.26</td>
<td>0.00</td>
<td>0.00%</td>
</tr>
</tbody>
</table>

INJ 1

1.27
3.26
STOP

AREA %
1.27 326128 94.31
3.26 19667 5.687

HP 3388A
DLY OFF
MV/M .30
REJECT OFF

INJ 2

1.28
3.29
STOP

AREA %
1.28 326705 94.32
3.29 19683 5.681

HP 3388A
DLY OFF
MV/M .30
REJECT OFF

INJ 3

1.28
3.30
STOP

AREA %
1.28 327992 94.32
3.30 19750 5.679

HP 3388A
DLY OFF
STOP 15
REJECT OFF
APPENDIX IB Calibration Curve for Methane-Air

\[ \frac{\text{Volume of Methane}}{\text{Volume of Air}} \times 100\% \]

\[ \frac{\text{Area of Methane}}{\text{Area of Air}} \times 100\% \]

Equation: \[ V = 0.0445 + 1.2159A \]
APPENDIX IC Calibration Curve for Ethane-Air

\[ \frac{\text{Volume of Ethane}}{\text{Volume of Air}} \times 100\% \]

\[ \frac{\text{Area of Ethane}}{\text{Area of Air}} \times 100\% \]

\[ EGH: V=0.0128 + 0.8318A \]
APPENDIX ID  Calibration Curve for Propane-Air

\[
\frac{\text{Volume of Propane}}{\text{Volume of Air}} \times 100\% = 0.0115 + 0.6677P
\]
## APPENDIX II - INITIAL TEMPERATURE CALIBRATION

<table>
<thead>
<tr>
<th>TRAIL</th>
<th>TIME (min)</th>
<th>TEMPERATURE °C</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>BOMB</td>
<td>GAS</td>
</tr>
<tr>
<td>1</td>
<td>0</td>
<td>24</td>
</tr>
<tr>
<td></td>
<td>5</td>
<td>22</td>
</tr>
<tr>
<td></td>
<td>7</td>
<td>22</td>
</tr>
<tr>
<td></td>
<td>10</td>
<td>21</td>
</tr>
<tr>
<td></td>
<td>13</td>
<td>21</td>
</tr>
<tr>
<td>2</td>
<td>0</td>
<td>33</td>
</tr>
<tr>
<td></td>
<td>5</td>
<td>30</td>
</tr>
<tr>
<td></td>
<td>10</td>
<td>30</td>
</tr>
<tr>
<td></td>
<td>15</td>
<td>29</td>
</tr>
<tr>
<td>3</td>
<td>0</td>
<td>30</td>
</tr>
<tr>
<td></td>
<td>5</td>
<td>29</td>
</tr>
<tr>
<td></td>
<td>11</td>
<td>27</td>
</tr>
<tr>
<td></td>
<td>23</td>
<td>26</td>
</tr>
</tbody>
</table>
1. Calculation of Stoichiometric Coefficients

For complete combustion of \(NCH\) kmol of hydrocarbon fuel, \(C_{CNH}^{HM}\), with \(AC\) kmol of additive, \(C_{CH}^{H}\) at a relative air to fuel ratio, the combustion equation is:

\[
(NCH)C_{CNH}^{HM} + (AC)C_{CH}^{H} + (O2)_{2} + (N2)N_{2} + (C)2CO_{2} + (H2O)CO_{2} + (N2)N_{2} (E02)O_{2}
\]

where () are stoichiometric coefficients for complete combustion. In program,

Program Symbol

- \(O2\) = number of kmols of \(O_{2}\) if \(\phi = 1\)
- \(O2T1\) = total number of kmols of \(O_{2} = O_{2}\)
- \(N2\) = number of kmols of \(N_{2}\) if \(\phi = 1\)
- \(N2T1\) = total number of kmols of \(N_{2} = N_{2}\)
- \(E02\) = number of kmols of unburnt \(O_{2} = 0\) for \(\phi > 1\)

Mass balance for each element gives:

- \(CO_{2} = CN + C*AC\)
- \(H2O = (HM + H*AC)/2\)
- \(O2 = (2*CO_{2} + H2O)/2\)
- \(N2 = 3.76*O2\)
- \(E02 = (2*LAM*O2 - 2*CO_{2} - H2O)/2\)

The total number of kmols of reactants, \(SUMNS\), is:

\[
SUMNS = NCH + AC + O2T1 + N2T1
\]
2. **Calculation of Burning Velocity**

Pressure data are divided into equal time intervals. For each input pressure subroutine COMB is called to calculate properties of the burnt and unburnt gas. Properties at the end of a time interval become properties at the beginning of the next time interval. Changes in mass fraction burnt, and hence the mass fraction burnt rate (DXPR) can be calculated.

The burning velocity, \( S_u \), and the flame speed, \( S_f \), can be obtained from:

\[
S_u = \frac{M\dot{x}(t)}{\rho_u A_f}
\]

\[
S_f = \frac{dR_f}{df}
\]

where

- \( M \) = total mass of mixture in Kg,
- \( \dot{x} \) = mass fraction burnt rate in sec\(^{-1}\),
- \( \rho_u \) = density of the unburnt gas in Kg/m\(^3\),
- \( A_f \) = flame front area in m\(^2\),
- \( R_f \) = flame front radius in m.

From the spherical flame front assumption, the flame radius can be expressed as:

\[
R_f = \left[\frac{3}{4\pi}V_b\right]^{1/3}
\]

where

- \( V_b \) = volume of the burnt gas
  
  \[= M\dot{x}V_b [m^3]\]
The flame area is:

\[ A_f = 4\pi R_f^2 \, . \]

The burning velocity can be rewritten as:

\[ S_u(t) = \left[ M \dot{x}(t) \rho_u \right]/\left[ 4\pi \left( 3 M \dot{x} \rho_b / 4\pi \right)^{1/3} \right] \]

The unknowns, specific volumes, \( v_u \), \( v_b \), and mass fraction burnt as a function of time, \( x(t) \), are calculated in subroutines COMB, ENRCT, and ENERGY.

3. \textbf{Calculation of Properties}

Subroutine ENRCT and ENERGY calculate the specific energy, specific volume, mole fraction of each component, gamma and specific heats of the unburnt and burnt gases at a given temperature and pressure.

\textbf{Assumptions}

A mixture of gases is considered to be comprised of ideal gases which obey the following:

i) The gas mixture as a whole obeys the equation of state, \( PV = N_{mix} RT \), where \( N_{mix} \) is the total number of kmols of components.

ii) The total pressure of the mixture equals the sum of the pressures each component would exert if it alone occupied the whole volume at the same temperature.

iii) The internal energy and enthalpy of the mixture equals the sum of the internal energy and enthalpies each component would have if it alone occupied the whole volume at the same temperature.
3.1 Calculation of Mixture Energy

From assumptions (ii) and (iii), the energy equation is:

\[
\text{Energy of Mixture} = \sum \text{Energy of component} = \sum n_i (\tilde{h}_{i,T,P} - RT) [KJ]
\]

where

- \(n_i\) = number of kmols of the \(i^{th}\) component
- \(\tilde{h}_{i,T,P}\) = enthalpy at temperature and pressure \(T, P\)
- \(\bar{R}\) = universal gas constant = 8.314 [KJ/KMOL K]

The specific energy of the unburnt gas (SEU) and the burnt gas (SEB) are calculated as:

\[
e_u = \sum \left[ n_i \left(\tilde{h}_{i,T,P} - RT\right) / M\right]_{\text{Reactants}} [KJ/KG]
\]

\[
\text{SEU} = \frac{EU}{MRCT} \text{ in program}
\]

\[
e_b = \sum \left[ n_i \left(\tilde{h}_{i,T,P} - RT\right) / M\right]_{\text{Products}} [KJ/KG]
\]

\[
\text{SEB} = \frac{EB}{MPROD} \text{ in program}
\]

where

- \(MRCT\) = mass of the reactants
- \(MPROD\) = mass of the products

The enthalpies \(\tilde{h}_{i,T,P}\) are given by

\[
\tilde{h}_{i,T,P} = \tilde{h}_f^o + \Delta h
\]
where

\[ \overline{h}_f^0 \] = enthalpy of formation at 0.1 MPa, 298K

\[ \Delta \overline{h} \] = difference of enthalpy from the reference state of 0.1 MPa, 298K

The delta h values of each of the reactants (DHR) and products (DH) are found using equations given in Ref. 50, 51 and values from expressions given in Ref. 52.

The components of the unburnt gas are the reactants, \( C_{CN}H_{HM}, C_{CH}H, O_2 \) and \( N_2 \). The components of the burnt gas are the dissociated products, \( CO_2, H_2O, N_2, O_2, CO, O, H_2, OH, H, NO \).

3.2 Dissociation Calculations

The dissociation reactions considered are:

a) \( CO_2 \leftrightarrow CO + 1/2 O_2 \)

\[-A \quad A \quad 1/2 A \]

b) \( H_2O \leftrightarrow 1/2 H_2 + OH \)

\[-B \quad 1/2 B \quad B \]

c) \( H_2O \leftrightarrow H_2 + 1/2 O_2 \)

\[-C \quad C \quad 1/2 C \]

d) \( 1/2 N_2 + 1/2 O_2 \leftrightarrow NO \)

\[-1/2 D \quad -1/2 D \quad D \]

e) \( H_2 \leftrightarrow 2H \)

\[-E \quad 2E \]

f) \( O_2 \leftrightarrow 2O \)

\[-F \quad 2F \]
where A,B,C,D,E,F, are the change in kmols of each component due to dissociation.

For a dissociation reaction

\[ v_a A + v_b B \longleftrightarrow v_c C + v_d D \]

a dissociation equation can be written in the form

\[ \frac{y_C^{v_c} \cdot y_D^{v_d}}{y_A^{v_a} \cdot y_B^{v_b}} = \frac{K}{P^{v_c + v_d - v_a - v_b}} \]

where \( P^o \) is the standard pressure 0.1 MPa, \( K \) is the equilibrium constant found by fitting curves of the form \( \ln K = A + B \ln T \) to the data given in Ref. 52 and \( y_i \) is the mole fraction of the \( i \)th component given by:

\[ y_i = \frac{x_i}{\sum x_i} \]

If \( K,L,M,N \) represents the number of kmols of \( \text{CO}_2, \text{H}_2\text{O}, \) unburnt \( \text{O}_2 \), and \( \text{N}_2 \), respectively, before dissociation, the number of kmols of each component after dissociation are given by:

Program
Symbols

\[
\begin{align*}
X(1) &= \text{CO}_2 = K - A \\
X(2) &= \text{CO}^0 = A \\
X(3) &= \text{H}_2\text{O} = L - B - C \\
X(4) &= \text{H}_2 = C + B/2 - E \\
X(5) &= \text{O}_2 = M - F + (A + C - D)/2 \\
X(6) &= \text{N}_2 = N - D/2 \\
X(7) &= \text{NO} = D \\
X(8) &= \text{H} = 2E \\
X(9) &= O = 2F \\
X(10) &= \text{OH} = B \\
S = \sum X(1) &= K + L + M + N + (A + B + C)/2 + E + F
\end{align*}
\]
Therefore the six dissociation equations are:

<table>
<thead>
<tr>
<th>Program</th>
<th>Symbol</th>
<th>Equation</th>
</tr>
</thead>
<tbody>
<tr>
<td>a) CO₂</td>
<td>( \frac{A}{S} \cdot \frac{(M-F+\frac{(A+C-D)}{2})^{1/2}}{S} \cdot \frac{(K-A)^{1/2}}{S} )</td>
<td>( \frac{K_{CO₂}}{P^{1/2}} )</td>
</tr>
<tr>
<td>b) H₂O(OH)</td>
<td>( \frac{B+C-E}{S} \cdot \frac{(2)^{1/2}}{S} \cdot \frac{(B)^{1/2}}{S} )</td>
<td>( \frac{K_{H₂O(OH)}}{P^{1/2}} )</td>
</tr>
<tr>
<td>c) H₂O (O₂)</td>
<td>( \frac{B+C-E}{S} \cdot \frac{\frac{M-F+\frac{(A+C-D)}{2}}{S}}{S} \cdot \frac{(L-B-C)^{1/2}}{S} )</td>
<td>( \frac{K_{H₂O(O₂)}}{P^{1/2}} )</td>
</tr>
<tr>
<td>d) N₂</td>
<td>( \frac{D}{S} \cdot \frac{1}{S} )</td>
<td>( \frac{K_{N₂}}{S} )</td>
</tr>
<tr>
<td>e) H₂</td>
<td>( \frac{(2x)^{2}}{S} \cdot \frac{C+B/2-E}{S} )</td>
<td>( \frac{K_{H₂}}{S} )</td>
</tr>
<tr>
<td>f) O₂</td>
<td>( \frac{(2x)^{2}}{S} \cdot \frac{M-F+\frac{(A+C-D)}{2}}{S} )</td>
<td>( \frac{K_{O₂}}{P^{1/2}} )</td>
</tr>
</tbody>
</table>
Given:

Fuel = 1 kmol of CH\textsubscript{4}

\( \phi = 1.0 \)

initial pressure = 101.3 KPa

initial temperature = 298 K

1. **Stoichiometry**

Given a reaction: \( \text{CH}_4 + a\text{O}_2 + b\text{N}_2 + c\text{CO}_2 + d\text{H}_2\text{O} + e\text{N}_2 + f\text{O}_2 \), the stoichiometric coefficients \( a, b, c, d, e, \) and \( f \) can be determined from mass balance for each element:

Since \( f = 0.0 \) for complete combustion

C balance: \( c = 1 \)

H balance: \( 4 = 2d \) or \( d = 2 \)

O balance: \( 2a = 2c + d \) or \( a = 2 \)

N balance: \( b = 3.76a = d \) or \( b = d = 7.52 \)

Reaction is:

\[ \text{CH}_4 + 2\text{O}_2 + 7.52\text{N}_2 + \text{CO}_2 + 2\text{H}_2\text{O} + 7.52\text{N}_2 \]

2. **Calculations of Initial Properties**

Number of kmols of mixture initially, \( N_{\text{mix}} \), is:

\[ N_{\text{mix}} = 1 + 2 + 7.52 = 10.52 \]

Mole fractions, \( n_i 's \):
\begin{align*}
n_{\text{CH}_4} &= \frac{1}{10.52} = 0.0951 \\
n_{\text{O}_2} &= \frac{2}{10.52} = 0.1901 \\
n_{\text{N}_2} &= \frac{7.52}{10.52} = 0.7148
\end{align*}

2.1 **Mixture Molecular Weight (MWMIX)**

\[
\text{MWMIX} = \frac{\text{Total Mass of Mixture}}{\text{Total Number of Moles of Mixture}}
\]

\[
= \frac{16.04(1) + 31.999(2) + 28.013(7.52)}{10.52}
\]

\[
= 27.6327 \text{ kg/kmol}
\]

2.2 **Mixture Specific Volume (v_{mix})**

Assume mixture behaves as ideal gas:

\[
PV = nRT
\]

or

\[
V = \frac{nRT}{P} = \frac{(10.52)(8.3143)(298) \text{ KJ}}{101.3 \text{ KN/m}^2}
\]

\[
= 257.3055 \text{ m}^3/\text{kmol of CH}_4
\]

\[
v_{mix} = \frac{V}{\text{MW}_{mix}N_{mix}} = \frac{257.3055 \text{ m}^3}{(27.6327)(10.52) \text{ kg}}
\]

\[
= 0.885 \text{ m}^3/\text{kg per kg of reactant mixture}
\]
2.3 **Gamma (γ)**

\[
\begin{align*}
\gamma & = \frac{C_p}{C_v} \\
C_v & = C_p - \bar{R} \\
C_p & = \sum (nC_p)_i
\end{align*}
\]

On a per kmol basis:

\[
\begin{align*}
C_p(CH_4) & = (2.2537 \text{ KJ/kg K})(16.04 \text{ kg/kmol}) = 36.15 \text{ KJ/kmol K} \\
C_p(O_2) & = (0.9216)(31.999) \text{ KJ/kg K} = 29.49 \text{ KJ/kmol K} \\
C_p(N_2) & = (1.0416)(28.013) \text{ KJ/kg K} = 29.18 \text{ KJ/kmol K} \\
C_p_{mix} & = (0.0951)(36.15) + (0.1901)(29.49) + (0.7148)(29.18) \\
& = 29.9018 \text{ KJ/kmol K} \\
C_v & = 29.9018 - 8.31434 = 21.5874 \text{ KJ/kmol K} \\
\gamma & = \frac{29.9018}{21.5874} = 1.3851 (1.3853)
\end{align*}
\]

2.4 **Specific Energy**

\[
E_{total} = \sum n_i (\bar{h}^o_f + \Delta \bar{h} - \bar{R}T)_i
\]

But, at standard pressure and temperature, \( \Delta \bar{h} = 0.0 \), also, \( \bar{h}^o_f = 0.0 \) for \( O_2 \) and \( N_2 \), therefore,

\[
E_{total} = [n\bar{h}^o_f]_{CH_4} - n\bar{R}T \\
= 0.0951(-74873) + 10.52(8.31434)(298) \\
= -9594.7773 \text{ KJ/Kmol/CH}_4
\]

\[
e = \frac{E}{M} \\
= -9594.7773 \text{ KJ} \\
= \frac{27.6327 \text{ kg}}{27.6327 \text{ kg}} \\
= -347.23 \text{ KJ/kg} (-347.28)
\]
3. Flame Temperature

3.1 With no Dissociations

Reaction is:

\[ \text{CH}_4 + 2\text{O}_2 + 7.52\text{N}_2 + \text{CO}_2 + 2\text{H}_2 \to 7.5\text{N}_2 \]

\[ H_R = -74873 \text{ KJ} \]

\[ H_P = [-393522 + \bar{h}_{\text{CO}_2}] + 2[-241827 + \bar{h}_{\text{H}_2\text{O}}] + 7.52[\bar{h}_{\text{N}_2}] \]

<table>
<thead>
<tr>
<th>TEMP</th>
<th>( \Delta \bar{h}_{\text{CO}_2} )</th>
<th>( \Delta \bar{h}_{\text{H}_2\text{O}} )</th>
<th>( \Delta \bar{h}_{\text{N}_2} )</th>
<th>( H_P )</th>
</tr>
</thead>
<tbody>
<tr>
<td>[K]</td>
<td>[KJ/kmol]</td>
<td>[KJ/kmol]</td>
<td>[KJ/kmol]</td>
<td>[KJ]</td>
</tr>
<tr>
<td>2200</td>
<td>103575</td>
<td>83036</td>
<td>63371</td>
<td>-130979</td>
</tr>
<tr>
<td>2300</td>
<td>109671</td>
<td>88295</td>
<td>67007</td>
<td>-87022</td>
</tr>
<tr>
<td>2400</td>
<td>115788</td>
<td>93604</td>
<td>70651</td>
<td>-42884</td>
</tr>
</tbody>
</table>

By interpolation, the adiabatic flame temperature is found to be 2328 K (program value: 2323 K).

3.2 With Dissociations

Reaction is (from program):

\[ \text{CH}_4 + 2\text{O}_2 + 7.52\text{N}_2 + 0.9047\text{CO}_2 + 0.0953\text{C}0 + 1.9492\text{H}_2\text{O} + 0.0498\text{O}_2 \]
\[ + 0.0375\text{H}_2 + 0.0258\text{OH} + 0.0202\text{NO} + 0.0022\text{H} + 0.0042\text{H} + 7.5\text{N}_2 \]

\[ H_R = -74873 \text{ KJ} \]

\[ H_P = 0.9047[-393522 + \Delta \bar{h}_{\text{CO}_2}] + 0.0953[-110529 + \Delta \bar{h}_{\text{C}0}] \]
\[ + 1.9492[-241827 + \Delta \bar{h}_{\text{H}_2\text{O}}] + 0.0498[\Delta \bar{h}_{\text{O}_2}] + 0.0375[\Delta \bar{h}_{\text{H}_2}] \]
\[ + 0.0258[39463 + \Delta \bar{h}_{\text{OH}}] + 0.0202[-90592 + \Delta \bar{h}_{\text{NO}}] \]
\[ + 0.0022[249195 + \Delta \bar{h}_{\text{H}}] + 0.0042[217986 + \Delta \bar{h}_{\text{H}}] + 7.5099[\Delta \bar{h}_{\text{N}_2}] \]
By interpolation, the flame temperature is found to be 2223 K (program value: 2222 K).

4. Equilibrium Constants

For a dissociation reaction

\[ \nu_a A + \nu_b B \leftrightarrow \nu_c C + \nu_d D \]

a dissociation equation can be written in the form

\[ \frac{y_c^{\nu_c} \cdot y_d^{\nu_d}}{y_A^{\nu_a} \cdot y_B^{\nu_b}} = \frac{K}{P^{\nu_c + \nu_d - \nu_a - \nu_b}} \]

Given: \[ P^o = 101.3 \text{ KPa} \]
\[ P = 523 \text{ KPa} \]

From program: \[ T_b = 2505.2 \text{ K} \]

Mole Fractions:

- \[ \text{CO}_2 = 0.07829 \]
- \[ \text{CO} = 0.01553 \]
- \[ \text{H}_2\text{O} = 0.1786 \]
- \[ \text{H}_2 = 0.005787 \]
- \[ \text{O}_2 = 0.007102 \]
\[ \begin{align*}
N_2 &= 0.7034 \\
NO &= 0.007102 \\
OH &= 0.005613 \\
o &= 0.0005551 \\
H &= 0.0008697 \\
\end{align*} \]

**Dissociation reaction: \( K_{\text{table}} \) \( K_{\text{calculated}} \)**

\[ \begin{align*}
\text{a) } CO_2 & \leftrightarrow CO + \frac{1}{2}O_2 & 0.037 & 0.038 &= \frac{(0.01553)(0.007102)^{1/2}}{0.07829} \left( \frac{523.0}{101.3} \right)^{1/2} \\
\text{b) } H_2O & \leftrightarrow \frac{1}{2}H_2 + OH & 0.053 & 0.054 &= \frac{(0.005787)^{1/2}(0.005613)}{0.1786} \left( \frac{523.0}{101.3} \right)^{1/2} \\
\text{c) } H_2O & \leftrightarrow H_2 + \frac{1}{2}O_2 & 0.0061 & 0.0062 &= \frac{(0.005787)^{1/2}(0.005613)}{0.01786} \left( \frac{523.0}{101.3} \right)^{1/2} \\
\text{d) } \frac{1}{2}N_2 + \frac{1}{2}O_2 & \leftrightarrow NO & 0.059 & 0.059 &= \frac{0.04189}{(0.7034)^{1/2}(0.007102)^{1/2}} \left( \frac{523.0}{101.3} \right)^0 \\
\text{e) } H_2 & \leftrightarrow 2H & 0.00064 & 0.00067 &= \frac{(0.0008697)^2}{0.005787} \left( \frac{523.0}{101.3} \right) \\
\text{f) } O_2 & \leftrightarrow 2O & 0.00022 & 0.00022 &= \frac{(0.0005551)^2}{0.007102} \left( \frac{523.0}{101.3} \right) \\
\end{align*} \]
APPENDIX V - EXPANSION COEFFICIENT DERIVATION

1. Derivation of a General Burning Velocity Equation

Assumptions:

1) Spherical flame propagation
2) Isentropic compression of the unburnt gas
3) Ideal gas behaviour for both burnt and unburnt gases
4) Thin flame.

Mass continuity across a flame of negligible thickness:

\[ \dot{m}_b = \frac{1}{\rho_b} \frac{dm_b}{dt} \]

\[ m_b = \frac{4}{3} \pi r_b^3 \rho_b \]

\[ \therefore \frac{dm_b}{dt} = \frac{4}{3} \pi r_b^3 \frac{d\rho_b}{dt} + 4\pi \rho_b r_b^2 \frac{dr_b}{dt} \]

Assumption (2):

\[ \frac{P}{\gamma_b \rho_b} = \text{constant} = c \]

\[ \rho_b = \left( \frac{1}{c} P \right)^{1/\gamma_b} \]

\[ \frac{d\rho_b}{dt} = \frac{1}{\gamma_b \rho_b} \frac{dP}{dt} \]

\[ \frac{dm_b}{dt} = \frac{4}{3} \pi r_b^3 \frac{1}{\gamma_b} \rho_b \frac{dP}{dt} + 4\pi \rho_b r_b^2 \frac{dr_b}{dt} \]
2. **Equation for Constant-Pressure Combustion**

For constant pressure combustion:

\[
\frac{dP}{dt} = 0 \quad \rho_u = \rho_o
\]

\[
\frac{dm_b}{dt} = 4\pi r_b^2 \rho_b \frac{dr}{dt} = A_f \rho_b S_f
\]

\[
\therefore \quad S_u = \frac{\rho_b}{\rho_o} S_f
\]

**Assumption (3):**

From equation of state: \( \frac{P}{\rho} = \frac{RT}{W} \)

where \( \bar{R} \) = universal gas constant

\( W \) = molecular weight

\[
\rho = \frac{P W}{\bar{R} T}
\]

\[
\frac{\rho_b}{\rho_o} = \frac{W_b T_o}{W_o T_b}
\]

Let \( E_f = \frac{W_o T_b}{W_b T_o} \)

\[
\therefore \quad S_u = \frac{S_f}{E_f}
\]
1. **Burning Velocity Equation**

Mass continuity across the flame gives:

\[
\frac{dm_u}{dt} = -S_A \rho_u
\]

But, \( m_u = M(1-x) \)

\[
-x = \frac{m_u}{M} - 1
\]

\[
\frac{-dx}{dt} = \frac{1}{M} \frac{dm_u}{dt} = \frac{-S_A \rho_u}{M}
\]

\[
\therefore S_u = \frac{M}{A_f \rho_u} \frac{dx}{dt} \frac{dP}{dt}
\]

For spherical flame propagation: \( A_f = 4\pi r_f^2 \)

For spherical with radius \( R \):

\[
M = \rho_o \frac{4}{3} \pi R^3
\]

\[
\therefore S_u = \frac{\rho_o}{\rho_u} \left( \frac{R}{r_f} \right)^2 R \frac{dx}{dt} \frac{dP}{dt}
\]

\[
V = V_b + V_u
\]

\[
= V_b + (1-x) \frac{\rho V}{\rho_u} \Rightarrow V_b = V(1-(1-x) \frac{\rho_o}{\rho_u})
\]

\[
\left( \frac{R}{r_f} \right)^2 = \left( \frac{V}{V_b} \right)^{2/3} = (1-(1-x) \frac{\rho_o}{\rho_u})^{-2/3}
\]

But \( \frac{\rho_u}{\rho_o} = \left( \frac{P}{P_o} \right)^{1/\gamma_u} \)

\[
\therefore S_u = \frac{1}{3} \left( \frac{P}{P_o} \right)^{1/\gamma_u} \frac{R}{\frac{dx}{dP}} \frac{dP}{dt}
\]

\[
= \left( 1-(1-x) \frac{\rho_o}{\rho_u} \right)^{2/3}
\]
Using Lewis and Von Elbe's approximation:

\[ x = \frac{P - P_0}{P_e - P_0} \]

\[ \frac{dx}{dP} = \frac{1}{P_e - P_0} \]

\[ \therefore S_u \text{ can be expressed as } f(P) \text{ only:} \]

\[ S_u = \frac{R}{3} \frac{1}{P_e - P_0} \frac{dP}{dt} \left[ \frac{P}{P_0} \right]^{1/\gamma_u} \left[ 1 - \frac{P_e - P}{(P_e - P_0)} \right]^{1/\gamma_u} \]

\[ r_f = R \left[ 1 - \frac{P_e - P}{P_e - P_0} \left( \frac{P}{P_0} \right) \right]^{1/3} \]

where \( P_e \) = experimental peak pressure, \( P_f \)

2. **Mass Fraction Approximation**

Adiabatic compression gives:

\[ F = \frac{P^{1/\gamma}}{v_{\text{mole}}} = \frac{P(1-\gamma)/\gamma}{RT} \]

for volume \( v_{\text{mole}} \) occupied by 1 mole of gas.

Before combustion of mass: fraction \( dn \)

\[ F_u = P \frac{(1-\gamma_u)\gamma_u}{RT_u} = P_1 \frac{(1-\gamma_u)\gamma_u}{RT_1} \] (1)
where subscripts \( u, i \) denotes unburnt gas and initial state of mixture, respectively.

This assumes that over the temperature range \( T_i \) to \( T_u \), the specific heats, and therefore \( \gamma_u \), remain constant.

After combustion of mass fraction \( dn \), its temperature rise from \( T_b \) to some temperature \( T_{bp} \), corresponds to the subsequent pressure:

\[
F_b = \frac{RT_b}{P} \frac{(1-\gamma_b)/\gamma_b}{m_e} = \frac{m_e}{m_i} \frac{RT_b}{P} \frac{(1-\gamma_b)/\gamma_b}{m_i}
\]

where \( m_e \) = moles in the vessel after complete combustion

\( m_i \) = moles in the vessel before combustion.

This assumes \( \gamma_b \) is constant over the temperature range \( T_b \) to \( T_{bp} \).

Since total volume of the vessel is constant and equal to \( m_i RT_i/P_i \),

\[
\frac{m_i RT_i}{P_i} = \frac{R}{P} (m_e \int_o^n T_{bp} \, dn + m_i T_u (1-n))
\]

Combine equations (1), (2) and (3),

\[
\int_o^n F_b \, dn = \frac{RT_i}{P_i} \frac{1/\gamma_b}{P} - F_u (1-n) \frac{P}{P_i} \frac{1/\gamma_b - 1/\gamma_u}{P}
\]

Differentiating:

\[
F_b = F_u \frac{1}{\gamma_b - 1/\gamma_u} + \frac{RT_i}{P_i} \left( \frac{(1-\gamma_b)/\gamma_b}{P} - F_u (1-n) \frac{1/\gamma_b - 1/\gamma_u}{P} \right) \frac{dP}{dn}
\]
Assume $C_v(b)$ and $C_v(u)$ are constant, energy equation becomes:

$$m_e C_v(b) (T_b - T_p) = m_i C_v(u) (T_u - T_i)$$  \hspace{1cm} (5)

Combine (1), (2) and (5):

$$\frac{1}{\gamma_b - 1} p F_b - \frac{1}{\gamma_u - 1} p F_u = K$$  \hspace{1cm} (6)

where $K$ is a constant.

Solve $F_b$ from Eq. (6), substitute in Eq. (4), integrate between limits of $n$, and apply the boundary condition $P=P_e$ when $n=1$;

one obtains:

$$1 - n = \frac{RT_1}{P_e - P_i} \frac{P_e - P_i}{P_i}$$  \hspace{1cm} (7)

But:

$$\frac{RT_1 (\gamma_b - \gamma_u)}{(\gamma_u - 1)} \ll (\gamma_b - 1)K$$

and

$$P = P_i, \; T_u = T_i \quad \text{when} \; n = 0$$

An approximate equation for $n$ is:

$$n = \frac{P - P_i}{P_e - P_i}$$
APPENDIX VII - CALCULATION OF ERROR IN EQUIVALENCE RATIO

Gas Composition

<table>
<thead>
<tr>
<th>Gas</th>
<th>Minimum Purity</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH₄</td>
<td>99%</td>
</tr>
<tr>
<td>C₂H₆</td>
<td>99%</td>
</tr>
<tr>
<td>C₃H₈</td>
<td>99.5%</td>
</tr>
<tr>
<td>Air</td>
<td>99.96%</td>
</tr>
</tbody>
</table>

Calculation of error in stoichiometry:

Stoichiometric CH₄-air combustion:

\[
\text{CH}_4 + 2\text{O}_2 + 2(3.76)\text{N}_2 \rightarrow \text{CO}_2 + 2\text{H}_2\text{O} + 7.52\text{N}_2
\]

Theoretical fuel to air ratio: \( \frac{1}{2+7.52} = 0.1050 \)

Error due to impurities:

\[
0.99\text{CH}_4 + 0.9996(2\text{O}_2 + 2(3.76)\text{N}_2) + 0.99\text{CO}_2 + 1.98\text{H}_2\text{O} + 7.52\text{N}_2 + 0.04\text{O}_2
\]

Fuel/Air = \( \frac{0.99}{0.9996(2+7.52)} = 0.0140 \)

Error = \( \frac{0.1050 - 0.1040}{0.105} \)

\( \Delta \text{Fuel/Air} = 0.009 \)

Similarly: for C₂H₆, \( \Delta \text{Fuel/Air} = 0.0005 \)

C₃H₈, \( \Delta \text{Fuel/Air} = 0.0008 \)

Actual \( \phi = \frac{0.105}{0.104} = 1.01 \)

\( \Delta \phi = 0.01 \)