Burning Speeds, Flame Kernel Formation and Flame Structure of Bio-jet and JP8 Fuels at High Temperatures and Pressures

by

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Those who went in pursuit of knowledge
Soared up so high, stretched the edge
Were still encaged by the same dark hedge
Brought us some tales ere life to silence pledge.

Omar Khayyam (1048—1131 AD)
To my parents:

*Shamsi and Hassan Eisazadeh-Far*

*Who always have inspired me with their love*

AND

To the memory of Professor James C Keck (1924-2010)

*Who taught me the art of simple assumptions achieved from deep understanding*
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Abstract

Fundamental concepts of laminar flames have been studied both experimentally and theoretically. Topics such as, thermodynamic properties of gases at high temperatures, plasma formation in argon and air, flame kernel development, flame structure, burning speed of jet fuels such as ethanol, JP-8 and biomass based fuel have been studied.

The formation and propagation process of flame were studied in detail by a new model. Three important parameters affecting the formation and propagation of flame are: electrical discharged energy, chemical energy and energy transfer to the gas and electrodes. The roles of these parameters were studied and fundamental properties of laminar flames like laminar burning speed were measured at constant temperatures and pressures. As a part of this study the thermodynamic properties of inert gases including oxygen, nitrogen, air, argon and helium were measured at extremely high temperatures. These properties were necessary for the model developed for plasma and flame kernel growth.

Laminar burning speeds of jet fuels (JP-8) and their biomass based alternatives which were R-8 (POSF 5469) and ethanol are measured at high temperatures (500-650 K) and pressures (1-7 atm). The experiments were carried out in two constant volume spherical and cylindrical vessels. The laminar burning speeds of these fuels were compared with each other and also with results of other researchers.

Flame structure of premixed spherical flames was studied in shadowgraph optical system and an advanced Planar Laser Induced Fluorescence (PLIF) system. Flame structure study includes cell instability analyses, cell formation, and profile of OH molecule within the flame. The effect of different diluents like argon and helium were investigated at several temperatures and pressures. One of the main goals was to achieve laminar flames at higher pressures. The important parameters which were investigated were pressure, temperature, equivalence ratio, flame thickness, diluent type and stretch factor.

Introduction of a new experimental set up which is an advanced Planar Laser Induced Fluorescence (PLIF) system: Installation, design, and operation of this system are one of important objectives of this thesis. This system is used for combustion diagnostics and flame behavior study. The details of PLIF system will be described in chapter 1 (introduction).
1. Introduction
1. Introduction

1.1. Introduction

1.1.1. Importance of Flame Formation, Laminar Burning Speed, Flame Structure

Among the important thermo-physical properties of every fuel, is its laminar burning speed. Burning speed is used in turbulent combustion modeling as well as validating chemical kinetic models. There are various methods to measure laminar burning speed [1-16]. The important point is to use a method by which laminar burning speed can be measured in a wide range of pressures and temperatures with a high accuracy. In this thesis laminar burning speeds are measured by two different techniques: 1- a new model (constant pressure model) which measures burning speeds at constant pressure and temperature, and 2-pressure rise method by performing experiments in constant volume vessel to measure the burning speed at high temperatures and pressures.

Constant pressure model investigates the formation and propagation of premixed flames. Flame kernel formation and development are important phenomena in premixed flames. It involves the evolution of flame from plasma to a self-sustained region when diffusion and transport phenomena take over the propagation of flame. In this thesis some fundamental properties of flame including laminar burning speeds are measured using a new model which includes the properties of the hot gas in plasma region. The results of this model demonstrate the role of three different major terms which are: electrical energy added to mixture by spark electrodes, energy released due to chemical reactions in flame front and energy transfer from burned gas to the spark electrodes. The new model works just in constant pressure conditions.

The second approach is use of pressure rise in the vessel: in this method the burning speeds are measured in variant temperatures and pressures by conducting experiments in a constant volume combustion chamber. Higher temperatures and pressures will be obtained by changing the diluent from nitrogen to helium. Another feature of this research is addition of Extra Diluent gases (ED) which is (N₂+CO₂) to the mixture to investigate their effect on laminar burning speed and flame structure. ED gases can simulate exhaust gas recirculated diluent (EGR) gases which exist in internal combustion engines. ED gases increase the heat capacity of the mixture,
decrease the adiabatic flame temperature and decrease the laminar burning speed. A shadowgraph optical system has been used to observe the shape of the flames and ensure that they were laminar. The effect of mentioned parameters (temperature, pressure, equivalence ratio, ED gases, and other diluents) on instability and turbulence initiation in spherical flames has been investigated by conducting and analyzing the relevant experiments.

1.1.2. Fuels

Different fuels have been used in this research for measurement of laminar burning speeds and flame structure study. These fuels include fossil-based Jet Propellant (JP-8) and its bio-based alternative fuels. These are ethanol and R-8 fuel.

1.1.2.1. JP-8

Currently, JP-8 which is a fossil-based fuel is widely used in aircrafts and diesel engines. This fuel not only is applied as the main source of energy in combustors but also as coolant and lubricant. JP-8 and Jet A-1 have similar chemical structures because JP-8 is formed from Jet A-1 using some special additives to improve thermal stability characteristics [17]. JP-8 can be used as an alternative for diesel fuel because of their similar thermal and chemical properties. Due to its acceptable thermal stability parameters, its low freezing point of <-60 °C, and its dual application as both a coolant and an energy source, JP-8 is widely applied to aircraft engines and gas-turbines [18].

JP-8 is a complex chemical component composed of aromatics, n-paraffins, and cycloparaffins [19-20]. It also includes other chemical components which are difficult to detect. However, the main constituent of this fuel are paraffins and aromatics. The concentrations of chemical components are different for several versions of JP-8 produced in refineries. But gas chromatography studies prove that the main components which are paraffins and aromatics have identical concentrations. Figure 1 shows the gas chromatograph of JP-8 (4658+additives) fuel. This figure demonstrates that n-paraffins in the range of C9-C15 have the highest concentrations in the fuel.
1.1.2.2. Biofuels

Bio-jet fuels are important alternative energy resources for aviation purposes. These fuels can be obtained from several resources like corn, sugar, algae, biomass, etc. due to water and food resources limitation in the world it is preferred to use non-edible resources to produce bio-jet fuels. One of the reliable resources for obtaining bio-jet fuels is biomass. Biomass is abundant in nature and it does not waste edible resources. Biomass is a renewable resource of energy. The produced CO₂ from the combustion of biomass fuels can be a part of biomass creation cycle loop in the nature. Therefore the net emitted CO₂ of bio-fuel production and combustion is low and it makes it a renewable and fairly clean fuel.

There are various classes of aviation biofuels. The most common ones are alcohol fuels. They can be produced both from edible resources like corn and non-edible resources like biomass. Among alcoholic fuels ethanol is the most popular one; it is widely used in land based engines but not so popular in aviation engines. The ideal fuel for aviation fuel is the one which can be used both as energy source and coolant. Currently, JP-8 fossil fuel is widely used in aviation and satisfies the mentioned requirements. The attempt is focused on finding the best bio-jet fuel which is similar to JP-8. The class that is most advanced is "hydrotreated renewable jet"
(HRJ), which is hydrotreated fats/oils. This fuel is very similar to Fischer-Tropsch synthetic paraffinic kerosene. The fuel called R-8 (POSF 5469) is a fuel produced by hydrotreating fats/oils (triglycerides) and contains n-paraffins and iso-paraffins. HRJ fuels are predominantly n-paraffins and iso-paraffins. The other fuel is produced from biomass by a different process, and contains aromatics. The applied bio-jet fuels in this research will be ethanol and R-8 (POSF 5469). Table 1 presents the properties of conventional fossil-based and bio-based fuels which are JP-10, JP-8, ethanol and R-8.

Table 1: properties of fossil-based and bio-based fuels

<table>
<thead>
<tr>
<th></th>
<th>JP-10</th>
<th>JP-8</th>
<th>Ethanol</th>
<th>R-8</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chemical formula</td>
<td>C_{10}H_{16}</td>
<td>C_{12}H_{23}</td>
<td>C_{2}H_{5}OH</td>
<td>C_{10.9}H_{23.9}</td>
</tr>
<tr>
<td>Heat of combustion: (MJ/kg)</td>
<td>42.01</td>
<td>42.8</td>
<td>29.7</td>
<td>44.1</td>
</tr>
<tr>
<td>Flash point (K)</td>
<td>327.4</td>
<td>311</td>
<td>285.15</td>
<td>321</td>
</tr>
<tr>
<td>Volatility Density (kg/L)</td>
<td>0.94</td>
<td>0.81</td>
<td>0.79</td>
<td>0.75</td>
</tr>
<tr>
<td>Distillation Initial boiling point (K)</td>
<td>460.2 ± 0.2</td>
<td>320</td>
<td>351.5 ± 0.2</td>
<td>342</td>
</tr>
<tr>
<td></td>
<td>460.2 ± 0.2</td>
<td>426</td>
<td>351.5 ± 0.2</td>
<td>398</td>
</tr>
<tr>
<td></td>
<td>460.2 ± 0.2</td>
<td>435</td>
<td>351.5 ± 0.2</td>
<td>424</td>
</tr>
<tr>
<td></td>
<td>460.2 ± 0.2</td>
<td>450</td>
<td>351.5 ± 0.2</td>
<td>469</td>
</tr>
<tr>
<td></td>
<td>460.2 ± 0.2</td>
<td>481</td>
<td>351.5 ± 0.2</td>
<td>509</td>
</tr>
<tr>
<td></td>
<td>460.2 ± 0.2</td>
<td>498</td>
<td>351.5 ± 0.2</td>
<td>560</td>
</tr>
<tr>
<td>Fluidity Viscosity (mm²/s @253 K)</td>
<td>1.3</td>
<td>2.12</td>
<td>2.9</td>
<td>5.5</td>
</tr>
<tr>
<td></td>
<td>-79</td>
<td>-47</td>
<td>-114</td>
<td>-49</td>
</tr>
</tbody>
</table>

Figure 2 shows the chromatograph of R-8 fuel. It can be seen that this fuel is composed of several elements and the major ones are n-paraffins.

1.2. Burning Speed Measurement

Among the important thermo-physical properties of each fuel, are its burning speed and flame structure. Burning speed is used in turbulent modeling of internal combustion engines as well as validating chemical kinetic models. These combustion characteristics need to be measured both for different JP-8 fuels and its surrogates in a wide range of pressure and temperature. This information will be also used in validating chemical kinetics models. These combustion
characteristics will be measured in the Combustion Laboratory of Northeastern University.

![Figure 2: Chromatogram of R-8 fuel](image)

1.2.1. Experimental Facilities

1.2.1.1. Spherical Vessel

Burning speed measurements will be made in the existing spherical and cylindrical combustion chambers. The spherical chamber consists of two hemispheric heads bolted together to make a 15.24 cm inner diameter sphere. The chamber was designed to withstand pressures up to 425 atm and is fitted with ports for spark electrodes, diagnostic probes, and ports for filling and evacuating it. A thermocouple inserted in one of the chamber ports will be used to check the initial temperature of the gas inside the chamber. A Kistler 603B1 piezo-electric pressure transducer with a Kistler 5010B charge amplifier will be used to obtain dynamic pressure vs. time records from which the burning speed will be determined. Ionization probes mounted flush with the wall located at the top and bottom of the chambers will be used to measure the arrival time of the flame at the wall and to check for spherical symmetry and buoyant rise.

The spherical chamber is housed in an oven which can be heated up to 500 K. Liquid fuel is stored in a 115 cc heated pressure chamber and is transferred through a heated line (500 K) to
the spherical chamber in the oven. Several thermocouples are located on the line from the fuel reservoir to the chamber to monitor temperature of the fuel passageway. A heated strain gauge (Kulite XTE-190) in the oven is used to measure partial pressure of fuel in the chamber.

1.2.1.2. Cylindrical Vessel

The companion cylindrical chamber is made of SAE4140 steel with an inner diameter and length of 133.35 mm. The two end windows are 34.93 mm thick Fused-silica with a high durability against pressure and temperature shocks as well as having very good optical properties. This chamber was designed to operate over the same pressure and temperature range as the spherical chamber and is equipped with similar access ports. This chamber is used to measure pressure rise due to combustion process and to permit optical observation of the flame.
shape and structure under conditions as close as possible to those in the spherical chamber and to insure the initial development of the flame and pressure rise are identical in both chambers. Two band heaters and a rope heater wrapped around the cylindrical chamber are used to heat up the chamber to 500 K. This chamber is equipped with a heated liquid fuel line system, a pressure strain gauge and thermocouples similar to the spherical chamber. A Z-type Schlieren/Shadowgraph ensemble has been set up to visualize the flame propagation. The light source for the optical system is a 10-Watt Halogen lamp with a condensing lens and a small pinhole of 0.3 mm in diameter, which provides a sharp and intense illumination throughout the whole system. Two aluminized spherical mirrors with 1/8 wavelength surface accuracy, over-coated with silicon monoxide and mounted in metal-stands with a diameter of 152.4 mm and focal length of 1524 mm, are placed on two sides of the chamber. A high speed CMOS camera (1108-0014, Redlake Inc.) with a capture rate of up to 40,000 frames per second is placed very close to the focal point of the second mirror. The capture rate and shutter speed of the camera are optimized depending on the burning speed of the mixture and the brightness of the flame. Figure 4 shows the configuration of the shadowgraph system.
1.3. Structure of Thesis

The structure of this thesis is based on the manuscripts published and submitted to journals during PhD years. Each chapter is represented by a paper. Chapter 2 discusses about a recently designed and developed Planar Laser Induced Fluorescence (PLIF) system. Chapters 3-5 discuss about the thermodynamic properties of inert gases at temperature range of 300-100,000 K, plasma kernel formation of argon and air, and formation and propagation of premixed flames. Chapter 6 describes details of the thermodynamic model which measures the laminar burning speeds of spherical flames by pressure rise method. Chapter 7 and 8 present the laminar
burning speeds of JP-8/oxidizer/diluent mixtures at high temperatures and pressures along with a detailed study on flame structure of JP-8/oxidizer/diluent flames at various temperatures, pressures, equivalence ratios, and diluent types. Chapter 9 is laminar burning speeds of biofuels. Chapter 9 studies ethanol/air/diluent mixtures. Chapter 10 investigates the molecular structure of R-8 fuel along with laminar burning speed data.

References


2. Planar Laser Induced Fluorescence (PLIF) System
2. Planar Laser Induced Fluorescence (PLIF) System

2.1. Planar Laser Induced Fluorescence (PLIF) System

PLIF device is an advanced system for combustion diagnostics. It is composed of a Nd-Yag laser, a Dye laser, a power supply, a CCD camera and optical devices like mirrors, lenses and scopes. A cylindrical chamber has been designed and installed in PLIF system. Its geometry and structure is like the shadowgraph system chamber, but it has two more optical windows at its sides to allow the laser beam to come inside and excite the molecules. The ignition and data acquisition system are synchronized by the DaVis software (laser professional software). There are different filters and Dye materials which enable the system to operate at different wavelengths to measure the concentrations of other molecules like CH and NO. The camera is a Lavision advanced camera coupled with the computer to analyze the fluoresced data from the chamber. A flat flame burner is installed with this system to calibrate the OH concentration measurement. After calibration process, the OH concentrations will be measured at high temperatures and pressures. In following sections the devices are described in more detail.

2.1.1. Pump Laser

A Spectra-Physics Quanta-Ray Lab-190 Laser is used to produce the initial pump laser beam. A generalized diagram is shown in Figure 1.
The Lab-190 uses a flash lamp to optically stimulate neodymium-doped yttrium aluminum garnet (Nd:YAG) in the crystal’s red and near infrared absorption bands. This absorption causes a population inversion, depicted in Figure 1. Atoms in the crystal are excited from energy level $E_1$ to $E_4$ by the flash lamp; however the atoms are unstable in this elevated level.

Since there is a greater transition probability to $E_3$ than back to $E_1$ the atoms quickly decay to $E_3$. This third level is metastable, so the atoms remain at this level for a relatively long amount of time.
time, roughly 230 μs. From E₃, there are several other energy levels (not pictured) that the atoms could decay to, the most probable being E₂. The transition from E₃ to E₂ is called the lasing transition because this is where the fundamental wavelength of 1064 nm is generated. The E₂ state is also unstable, so once atoms decay from E₃, they quickly transition down from E₂ back to E₁. This behavior causes the population of atoms in the third energy level to grow larger than that of the second level, hence the population inversion. This inversion is what allows light passing through the crystal to be amplified, with a larger inversion producing a larger amplification [2].

The pump laser also uses a Q-switch to produce short bursts of high intensity beams. Without it, the length of the laser pulse would be similar to the length of the flash lamp and have a low maximum power. The Q-switch allows the Nd:YAG crystal to reach the maximum population inversion at which point the switch quickly opens causing a quick release of energy, forming a beam that is less than 10 ns long and a peak optical power of tens of megawatts. This high powered beam is then sent through several non-linear conversion processes. Two such processes, frequency doubling and frequency mixing, occur in the Nd:YAG’s Harmonic Generator (HG) which houses potassium dideuterium phosphate (KD*P) crystals. Depending on the configuration of these crystals, the HG can be used to either polarize the fundamental wavelength (1064 nm) or generate the second harmonic (532 nm), third harmonic (355 nm) or fourth harmonic (266 nm). The second and third harmonics are often used with dye laser systems because they have high dye conversion efficiency. Finally, just before the beam exits the Nd:YAG, it is reflected by two Dichroic mirrors which are designed to reflect only specific wavelengths of light and allow everything else to pass through it [2].

2.1.2. Dye Laser

The dye laser is a Sirah Precision Scan SL Dye Laser. A simplified diagram of the dye laser is shown in Figure 3.
The dye laser works on similar principles as the pump laser except that the dye laser cannot generate its own beam and thus is dependant on an external source. However, dye lasers are very important in fluorescence studies because of their ability to selectively emit a specific wavelength. This output wavelength needs to be tunable in order to excite certain quantum transitions of the intermediate species under study, causing them to fluoresce. Dye lasers use liquids as a lasing medium because they generate a much broader range of wavelengths when compared to solid mediums like an Nd:YAG [1].

When the pump beam exits the Nd:YAG it is reflected 180° upward by two mirror boxes and into the dye laser. The pump beam passes through the first beam splitter, M1, where a small portion of the beam’s power is diverted toward the 20 mm dye quartz cell. This portion of the beam stimulates the dye and causes it to fluoresce. Take for example Coumarin 153, shown in Figure 4. When this dye solution is stimulated by a pump beam at 355 nm, it fluoresces within the range and efficiencies shown.
A fundamental wavelength can be selected out of this broad spectrum by the use of the prism expander (PE) and the mirror/gratings G₁ and G₂, see Figure . The section of the dye laser (the 20 mm dye quartz cell, PE, G₁ and G₂) makes up the Resonator. Once the beam is generated in the Resonator, it passes through a series of polarizing plates called Brewster Plates, a turning prism and then reflected back into the same 20 mm dye quartz cell. As this happens, the remainder of the beam passes through M₁, is reflected by 2 turning prisms and passes through a second beam splitter, M₄. Another small portion of the beam is reflected onto the 20 mm dye quartz cell as the large majority of the original pump beam passes through M₄. The secondary split beam intersects the beam from the Resonator (that was reflected back into the dye quartz cell) causing stimulated emission. This action amplifies the beam by a small amount and is called the Preamplifier [3].

The preamplified beam that is emitted from the 20 mm dye quartz cell is expanded through a telescope and enters the 40 mm dye quartz cell where the beam is intersected yet again. However, the remaining 75% of the pump beam’s original power is incident on the 40 mm dye quartz cell and results in the final amplification of the dye laser beam. This dye quartz cell is the Main Amplifier. The final beam passes through three more devices before finally exiting the laser housing. The first device is the Frequency Conversion Unit (FCU), which doubles the
frequency and halves the wavelength of the fundamental beam. The compensator steers the beam back to its original path after it has passed through the FCU. Lastly, a wavelength separation unit, comprised of four Pellin-Broca prisms, diverts the residual fundamental beam onto a beam dump to ensure that only the second harmonic passes through and exits the dye laser [3].

2.1.3. Camera

The camera used in this research is specially designed to image photons emitted from fluoresced species. The LaVision NanoStar camera is an intensified charge-coupled device (ICCD) camera of which the basic operation is explained in [1]. The lens currently installed on the camera does not have any direct magnification capability and can only be focused between roughly 2.5 and 15 feet. To “zoom,” the whole camera must be physically moved. The lens’ focus range therefore limits the distance between the camera and the combustion event, which directly affects the camera’s zoom and thus the size of the imaged object.

2.1.4. Combustion Facilities of PLIF System

The experimental apparatus used to generate combustion events are described. The combustion system includes the combustion vessel, where combustion occurs, the gas manifold system which is used to fill the combustion vessel with the appropriate fuel-oxidizer mixture, and the ignition system, which initiates combustion.

The combustion events occurred in a four window constant volume cylindrical vessel diagramed in Figure 9. The four window cylindrical vessel is based on a two window cylindrical vessel used for imaging flame structure in a shadowgraph system. It is constructed of 316 SS and measures 13.5 cm in diameter and 13 cm long. Two large Pyrex windows provide a line of sight through the vessel and allow the combustion event to be imaged by the Nanostar camera. Two smaller windows allow the experimental laser sheet to pass into the vessel, through the flame, and out of the vessel to terminate in the beam dump. The vessel is fitted with spark electrodes which are used to create center point ignition. It is filled through an evacuated 3 mm tube which connects the bottom of the vessel to a gas manifold system.
2.1.4.1. Facilities

A general experimental system diagram is given in Figure 10. An experimental recording of a species concentration is acquired by triggering a charge-coupled device (CCD) camera to take a picture at the same time that a laser beam pulse is passing through a transient flame in the constant volume cylindrical vessel. The experimental laser pulse is emitted from a dye laser, which is pumped by a Nd:YAG laser. The pump beam leaves the Nd:YAG laser, passes through an open shutter box and is reflected by two mirrors into the dye laser. The dye laser generates the experimental pulse. This pulse passes through an energy monitor, which is used to monitor pulse to pulse energy fluctuations. The experimental pulse is next turned into a sheet with set of sheet optics. The size of the sheet is controlled by truncating the beam with an iris diaphragm. The beam enters the cylindrical vessel, passes through the combustion event, and terminates in the beam dump. The CCD camera is triggered by using the Q-switch signal from the control computer and a set of timing electronics.
2.1.4.2. Control and Data Acquisition Computer
The computer, which runs the LaVision software package, DaVis 7.1.1 is used for all aspects of the experiment including adjusting the system, acquiring data, and post-processing results. The LaVision built central processing unit includes a programmable timing unit (PTU). Data communication lines from the lasers, energy monitor, and camera are input to the computer. A unique USB dongle is also plugged into the back of the computer and prevents the use of software on more than one machine at a time. See LaVision software manuals for more information about this software package [4, 5].

2.1.5. Calibration and Synchronization of the System

in order to measure the concentrations of OH molecule, it is required to calibrate the laser system. We have calibrated our PLIF system using a flat flame burner with my colleague, Mr Colin Fredette in Northeastern University combustion lab and more details can be found in his master thesis [6]. After calibration DaVis, which is a professional software developed in LaVision company, for laser diagnostics, measures the concentrations of OH radical in different conditions. Figure 11 shows the results of OH molecule florescence of stoichiometric methane-air flame. These images are taken on atmospheric pressure and the temperature of the unburned ...
gas is 300 K. This figure demonstrates that the concentration of OH is the highest in flame front and then after reaching equilibrium condition in the burned gas region its concentration decreases.

![Figure 7: OH radical fluorescence in methane/air flames, T = 300K, P = 1 atm, $\phi = 1$](image)

References


3. Thermodynamic Properties of Ionized Gases at High Temperatures

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3. Thermodynamic Properties of Ionized Gases at High Temperatures

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Abstract

Thermodynamic properties of ionized gases at high temperatures have been calculated by a new model based on local equilibrium conditions. Calculations have been done for nitrogen, oxygen, air, argon and helium. The temperature range is 300-100,000 K. Thermodynamic properties include specific heat capacity, density, mole fraction of particles, and enthalpy. The model has been developed using statistical thermodynamics methods. Results have been compared with other researchers and the agreement is good.

Keywords: thermodynamic properties, ionized gases, high temperature, plasma

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3.1. Introduction

The purpose of this paper is to provide the thermodynamic properties of nitrogen, oxygen, air, argon, and helium at high temperatures. These properties are needed for the study of spark discharges where the electrical energy is deposited in a small kernel and converted to thermal energy in the gas. This is a high temperature process leading to the formation of plasmas with very high degrees of ionization. The initial processes and the mechanisms of plasma kernel formation are beyond the scope of this paper and more details can be found in other references\textsuperscript{1-5}. However, as the electrical energy is converted to the thermal energy, the temperature of the plasma increases rapidly and the kernel grows. It is to calculate this growth process that the thermodynamic properties of the plasma, in particular the specific heat capacity at constant pressure, are needed.

Prior calculations of the thermodynamic properties of high temperature plasmas have been carried out by several investigators using a variety of models. Capitielli et al\textsuperscript{6} have calculated the thermodynamic properties of air at high using empirical correlations. They calculated the specific heat capacity, density, molecular weight, thermal conductivity, viscosity, entropy, enthalpy, and mole fraction of species over the temperature range 50,000 to 100,000K. Giordano et al\textsuperscript{7} have calculated the thermodynamic properties using statistical mechanical methods. Yos\textsuperscript{8} calculated the transport properties of air and its constituents in the temperature range 300-30,000 K. Sher et al\textsuperscript{9} studied the birth of spark channels. For this purpose they calculated the specific heat capacity and mole fractions of the air at high temperatures using a simplified thermodynamic model but their results are not very accurate. Other studies performed in last few decades include: Behringer et al\textsuperscript{10}, Jordan and Swift\textsuperscript{11}, Kopainsky\textsuperscript{12}, Pateyron et al\textsuperscript{13}. Most of these calculations cover the properties up to 50,000 K. However, for plasmas other than air, such as the inert gases helium and argon, the available data in temperature range up to 100,000 K is limited.

In this paper, we present a new model based on statistical mechanics which is both simple and accurate. Calculations have been made for nitrogen, oxygen, air, argon, and helium. The temperature range is 300-100,000 K at constant atmospheric pressure. The calculated properties include specific heat capacity, density, enthalpy, and the number of particles. Results have been compared with existing prior data and where the conditions overlap the agreement is generally good.
3.2. General Model

The general model is based on statistical thermodynamic methods and it is assumed that the species are in thermodynamic equilibrium. The physical constants of the ions and species are taken from Fay\textsuperscript{14} and Moore\textsuperscript{15}. For nitrogen, oxygen, and air the considered species are N\textsubscript{2}, N, N\textsuperscript{+}, N\textsuperscript{2+}, N\textsuperscript{3+}, N\textsuperscript{4+}, N\textsuperscript{5+}, N\textsuperscript{6+}, O\textsubscript{2}, O, O\textsuperscript{+}, O\textsuperscript{2+}, O\textsuperscript{3+}, O\textsuperscript{4+}, O\textsuperscript{5+}, O\textsuperscript{6+}, O\textsuperscript{7+}, and e (electron). In addition to nitrogen, oxygen, and air plasma the properties of two inert gases, argon and helium, have been studied as well. The assumed species for argon are Ar, Ar\textsuperscript{+}, Ar\textsuperscript{2+}, Ar\textsuperscript{3+}, Ar\textsuperscript{4+}, Ar\textsuperscript{5+}, and Ar\textsuperscript{6+} and for helium are He, He\textsuperscript{+}, and He\textsuperscript{2+}.

We assume a diatomic gas at low temperatures. The number of elemental atom number is then given by

\[ EA = 2A_2 + \sum_{\varepsilon=0}^{z} A^\varepsilon \quad \varepsilon = 0, 1, 2, 3 ... z \]  

where \( \varepsilon \) is the charge number of the ions.

Total number of moles is given by

\[ M_A = A_2 + e + \sum_{\varepsilon=0}^{z} A^\varepsilon \]  

Assuming charge neutrality, the mole number of free electrons is given by

\[ e = \sum_{\varepsilon=0}^{z} \varepsilon A^\varepsilon \]  

The equation of state is:

\[ pV = M_A RT \]  

where \( p \) is the pressure, \( V \) is the volume, \( R \) is the universal gas constant, and \( T \) is the temperature.

3.2.1. Dissociation

For a dissociation reaction
\[ A_2 \rightarrow 2A + \Delta H_d \]  

(5)

\( \Delta H_d \) is the dissociation enthalpy. The equilibrium constant based on concentration is defined by

\[ K_{cd} = \frac{A^2}{A_2 V} \]  

(6)

Using eq 4 to eliminate \( V \) in eq 6 we obtain

\[ \frac{A^2}{A_2 M} = \frac{K_{cd} RT}{p} = \frac{K_{pd}}{p} \]  

(7)

At low temperature there are no ions (e \( \approx \) 0) and eqs 1 and 2 reduce to

\[ A_2 = \frac{(EA - A)}{2} \]  

(8)

\[ M_A = \frac{(EA + A)}{2} \]  

(9)

Substituting eqs 8 and 9 in eq 7 we will have:

\[ 4B_dy^2 = 1 - y^2 \]  

(10)

where

\[ y = \frac{A}{EA} \]  

(10.1)

\[ B_d = \frac{p}{K_{pd}} \]  

(10.2)

and \( K_{pd} \) is the equilibrium constant based on pressure.

Solving eq 10 we obtain

\[ y_0 = \left(1 + 4B_d\right)^{-\frac{1}{2}} \]  

(11)

Where
From eqs 8 and 9

$$y_2 = \frac{A_2}{EA} = \frac{1 - y_0}{2}$$

Figure 1 shows the variation of $y_0$, $y_2$, and $M_A/EA$ for nitrogen dissociation. The normalized number of moles $M_A/EA$, increases due to dissociation of the molecule to atoms. The concentration of $y$ must decrease at higher temperatures due to ionization. In next section, ionization process will be described to complete the predictions.

3.2.2. Ionization Process

The governing equations for ionization will now be described.

For a typical ionization reaction

$$A^{\varepsilon-1} \rightarrow A^\varepsilon + e + \Delta H_\varepsilon \quad \varepsilon = 0, 1, 2, 3 ... z$$

$\Delta H_\varepsilon$ is the ionization enthalpy. The equilibrium constant based on concentration is given by

$$K_{ei} = \frac{A^\varepsilon}{A^{\varepsilon-1}V}$$

Using eq 4 to eliminate $V$ in eq 15 we obtain

$$\frac{A^\varepsilon}{A^{\varepsilon-1}M} = K_{ei}RT \frac{K_{pi}}{p}$$

The number of elemental atoms involved in reaction (14) is:

$$EA = A^{\varepsilon-1} + A^\varepsilon$$

The total mole numbers is:

$$M_A = EA + e$$
The number of moles of electrons is:

\[ e = (\varepsilon - 1)A^{\varepsilon-1} + \varepsilon A^\varepsilon \]  
(19)

Combining eqs 17-19 we obtain

\[ A^{\varepsilon-1} = EA - A^\varepsilon \]  
(20)

\[ M_A = \varepsilon EA + A^\varepsilon \]  
(21)

\[ e = (\varepsilon - 1)EA + A^\varepsilon \]  
(22)

Substituting eqs 20-22 in eq 16 then gives

\[ (y^\varepsilon)^2 + (\varepsilon - 1)y^\varepsilon - \frac{\varepsilon}{1 + B_\varepsilon} = 0 \]  
(23)

Solving this second-order equation, we find

\[ y^\varepsilon_0 = \frac{1}{2} \left\{ \frac{(\varepsilon - 1)^2 + \frac{4\varepsilon}{1 + B_\varepsilon}}{1 + B_\varepsilon} \right\} - (\varepsilon - 1) \]  
(24)

\[ y^\varepsilon_0 = y^\varepsilon + y^{\varepsilon+1} + ... + y^z \]  
(25)

\[ y^\varepsilon = y^\varepsilon_0 - y^\varepsilon_0^{\varepsilon+1} \]  
(26)

It can be seen in eq 25 that \( y^\varepsilon_0 \) involves the potential concentration of other ions in upper levels; so it increases and eventually reaches unity. The actual concentration of \( y^\varepsilon \) is achieved by correcting \( y^\varepsilon_0 \) in eq 26 by taking into account the effect of next ionization. Figure 2 shows the variations of \( y^\varepsilon, y^\varepsilon_0 \) and \( y^\varepsilon_0^{\varepsilon+1} \) versus temperature during the ionization process. The physical basis of this model is that ionization is an endothermic process and the progress of each reaction requires additional energy. Therefore it can be assumed that ionization is a step by step process and the level of ionization increases with temperature. Figure 3 shows the sketch of this model. The calculations are performed in parallel and the individual packages are in mutual equilibrium. The starting point is the bottom package (\( A_2 \leftrightarrow 2A \)). The normalized mole fraction of \( A \) versus elemental number of nitrogen atoms is entered to the next package and the
calculations proceed; in the next package the output will be $A^+$ and the same pattern flows to the next ones. In each package, thermodynamic equilibrium calculations are performed and the concentration of each species is computed. The mole fractions of species are normalized by the elemental number of atoms to ensure the conservation of mass. Given the temperature, pressure and composition all the thermodynamic properties of the plasma can be calculated.

The enthalpy is defined as:

$$ H_A = h_{A_2}(T)A_2 + \sum_{\varepsilon=0}^{z} h^\varepsilon(T)A^\varepsilon $$

where $h_{A_2}(T)$ is the enthalpy of molecule $A_2$, and $h^\varepsilon(T)$ is the enthalpy for specie $A^\varepsilon$.

Normalized enthalpy will be:

$$ \frac{H_A}{EA} = h_{A_2}(T)y_2 + \sum_{\varepsilon=0}^{z} h^\varepsilon(T)y^\varepsilon $$

Heat capacity of the mixture is defined by:

$$ \frac{c_{p,A}}{EA} = \left( \frac{\partial H_A}{\partial T} \right)_p = \frac{\partial h_A}{\partial T}y_2 + \sum_{\varepsilon=0}^{z} \frac{\partial h^\varepsilon}{\partial T}y^\varepsilon + \sum_{\varepsilon=0}^{z} \left( \frac{\partial y^\varepsilon}{\partial T} + \frac{\partial h^\varepsilon}{\partial T}y^\varepsilon \right) $$

$c_p$ is the combination of translational, rotational, vibrational, and electronics energy modes. It is defined by:

$$ c_p = (c_p)_{translational} + (c_p)_{rotational} + (c_p)_{vibration} + (c_p)_{electronics} $$

An important feature of this model is that the properties of the individual ion packages are first calculated and then coupled to form the system of packages. This flexibility permits a wide range of conditions to be covered by just one generic set of equations. For example, the model can treat the system of oxygen plasma, nitrogen plasma, and air plasma simultaneously.

### 3.3. Results and Discussion

Figure 4 and 5 show the mole fractions of oxygen and nitrogen plasma up to 100,000 K. The mole fractions in these two figures are defined by:
\[ x_e = \left( \frac{A_e}{E_A} \right) \left( \frac{M_{f_e}}{E_A} \right) \] for monatomic species and \[ x_{e_m} = \left( \frac{A_{e_m}}{E_A} \right) \left( \frac{M_{f_{e_m}}}{E_A} \right) \] for molecule

(31)

It can be seen that for both atoms, one dissociation and five ionizations (N\(^{5+}\) and O\(^{5+}\)) occur. The onset of ionization occurs around 6000 K and as the ionization proceeds, the mole fraction of species decrease. This is due to the increasing mole fraction of electrons. Figure 6 and 7 show the mole fractions of argon and helium.

Figure 8 shows the mole fractions of air plasma. The peaks of this figure correspond to those in figures 4 and 5.

Figure 9 shows normalized particle numbers of oxygen, nitrogen, air, argon, and helium versus temperature. The particle numbers have been normalized by the elemental number of atoms. It can be seen that under constant pressure condition, the number of particles increase dramatically. It shows the effect of ionization and increasing number of electrons. It is seen that the level of ionization determines the number of particles. Since in helium there are just two electrons, the number of particles does not increase as much as for other species.

Figure 10 shows specific heat capacities of oxygen, nitrogen, air, argon, and helium versus temperature. The several peaks at this figure represent the reactions and production of atoms and ions, which increase the heat capacity of the system. For oxygen and nitrogen molecules the role of rotational and vibrational energy modes on heat capacity is important at lower temperatures. However, after dissociation, the only energy mode of each species is translational and electronic and the increase in the heat capacity is just due to the ionization and the change of species concentration as can be seen in eq 29.

A comparison between figures 4-8 and figure 10 shows that the peak values of heat capacities correspond to the stage where the rate of dissociation and ionization is maximum. For example for air, first two peaks represent the equilibrium reaction of oxygen and nitrogen molecules and atoms and the rest of peaks correspond to the ionization reactions. Since there are just two ionization reactions in helium, consequently, only two peaks are observed in the figure. The behavior of this figure can be understood by the terms appeared in eq 29.

Figure 11 shows enthalpies of oxygen, nitrogen, air, argon, and helium versus temperature. At higher temperatures the enthalpy of helium exceeds the enthalpy of air. This is due to the higher heat capacity of helium at higher temperatures.
3.4. Comparison with Other Calculations

Figure 12 shows values of specific heat and the comparison with the results of Capitelli and coworkers\textsuperscript{6}, Sher et al\textsuperscript{9} and STANJAN equilibrium code\textsuperscript{16} in temperature range of 300-5000 K. Except for Sher et al, the agreement is good. In this range of temperature the concentration of ions is almost zero and the increase in heat capacity is due to the excitement of the vibrational energy modes and dissociation of oxygen atom.

Figure 13 compares the heat capacities of air calculated in this study with those of Capitelli and Sher over the temperature range 300-100,000 K. This figure shows good agreement with the results of Capitelli up to 70,000 K. Beyond 70,000 K, Capitelli et al underestimate the heat capacity due to the neglect the N\textsuperscript{5+} and O\textsuperscript{5+} ions in their study. Sher’s results are limited to low temperatures are in poor agreement with the others.

References


Figure 1: the variation of $y_0$, $y_2$, and $M_A/EA$ versus temperature during the dissociation process.
Figure 2: variation of $y_0^\varepsilon$, $y_0^{\varepsilon+1}$ and $y^\varepsilon$ versus temperature during the ionization process
Figure 3: the sketch of equilibrium packages

\[
A^5+ \leftrightarrow A^6+ + e \\
A^4+ \leftrightarrow A^5+ + e \\
A^4+ \leftrightarrow A^5+ + e \\
A^3+ \leftrightarrow A^4+ + e \\
A^3+ \leftrightarrow A^4+ + e \\
A^2+ \leftrightarrow A^3+ + e \\
A^2+ \leftrightarrow A^3+ + e \\
A^+ \leftrightarrow A^2+ + e \\
A^+ \leftrightarrow A^2+ + e \\
A \leftrightarrow A^+ + e \\
A_2 \leftrightarrow 2A
\]
Figure 4: mole fractions of oxygen species versus temperature
Figure 5: mole fractions of nitrogen species versus temperature
Figure 6: mole fractions of argon plasma versus temperature
Figure 7: mole fractions of helium plasma versus
Figure 8: mole fractions of air species versus temperature
Figure 9: Plasma particle numbers normalized by elemental atom numbers
Figure 10: Heat capacities of oxygen, nitrogen, argon, and helium versus temperature

a: helium and argon, b: air, oxygen, and nitrogen
Figure 11: enthalpies of different species versus temperature

a: argon and helium, b: air, oxygen, nitrogen
Figure 12: heat capacity of air versus temperature and comparison with other researchers (300-5000 K) — , ref 6; — , ref 9; — — , ref 16; — — , present study
Figure 13: heat capacity of air versus temperature and comparison with other researchers

(300-100,000 K), ---, ref 6; ----, ref 9; ----, present study
4. A Thermodynamic Model for Argon Plasma Kernel Formation

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4. A Thermodynamic Model for Argon Plasma Kernel Formation

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Abstract

Plasma kernel formation of argon is studied experimentally and theoretically. The experiments have been performed in a constant volume cylindrical vessel located in a shadowgraph system. The experiments have been done in constant pressure. The energy of plasma is supplied by an ignition system through two electrodes located in the vessel. The experiments have been done with two different spark energies to study the effect of input energy on kernel growth and its properties. A thermodynamic model employing mass and energy balance was developed to predict the experimental data. The agreement between experiments and model prediction is very good. The effect of various parameters such as initial temperature, initial radius of the kernel, and the radiation energy loss have been investigated and it has been concluded that initial condition is very important on formation and expansion of the kernel.

Keywords: Argon plasma, kernel formation, thermodynamic model, ionization

4.1. Introduction

Since plasma kernel is the beginning of flame propagation process in many systems, understanding of this process is very important. In plasma kernel formation of a non-combustible gas by an external energy source like spark, there are two important processes involved in the
phenomena: The first part of plasma formation which is very short (microseconds) is formation of spark channel between two electrodes, and the second part which is longer (milliseconds) is absorbing most of electrical energy and beginning the ionization and plasma kernel expansion. In the case of existence of a combustible gas, the third stage will be evolution of plasma kernel to a self sustained flame.

There have been some theoretical and experimental researchers who investigated first and third stages (Maly (1981), Ziegler et al (1985), Lee et al (2000), Pischinger and Heywood (1991), Mantel (1992), Kravchik and Sher (1994), Sher et al (1992), Sher and Keck (1986), Bradley et al (2004), Yossefi et al (1993)). Maly and Vogel (1979) in a theoretical and experimental study determined that the most important component of spark discharge is the breakdown process. They mentioned that the other processes including arc and glow discharge are less important because their electrical energy is dissipated into the electrodes. Sher et al (1992) did a fundamental study on spark formation in air and proposed a model to calculate the spark kernel temperature after breakdown. They concluded that the initial spark kernel is a very high temperature region, but the temperature drops rapidly due to energy dissipation. They determined that beyond a specific limit, the energy of the spark affects only the initial flame kernel radius, and not the temperature. They concluded that the spark kernel is grown in two steps. The first, shorter stage consists of a pressure wave emission. This is followed by a longer period, in which diffusion occurs. Chen and Ju (2007) studied the evolution of the ignition kernel to a flame ball and they concluded that radiation plays a very important role in transition of initial flame kernel to the actual self-sustained flame.

Most of the cited research focus on first and third stage of ignition and a semi quantitative understanding of them has been achieved. In this paper we will focus on second part of ignition which is formation and expansion of the plasma kernel by adding electrical energy. We will study plasma kernel of an inert gas, argon, to avoid the complexities of reacting gas mixture and existence of multiple species.

4.2. Experimental System

The experimental system includes a cylindrical vessel. It is fitted with two extended spark plug electrodes which provide a central point ignition source for the chamber. The thickness of electrode (de) is 0.381 mm. A shadowgraph system is used with cylindrical system to take
images from kernel growth. A CMOS camera with the capability of taking pictures up to 40,000 frames per second has been used in these experiments. A computer driven system has been used to prepare the initial condition. Figure 1 shows the sketch of the experimental system. Additional information about the experimental facility can be found in previous publications (Rahim et al (2008), Eisazadeh-Far et al (2010), Eisazadeh-Far et al (2010), Parsinejad et al (2006) and Parsinejad et al (2007)).

Ignition system: An important detail of the ignition system is the 5 select-switch, which allows the energy stored in the capacitors to be varied. The capacitors storing this energy discharge to a transformer and therefore to spark plugs. Voltage and current across the spark plug gap during the electrical discharge have been measured to calculate the discharge energy. This has been achieved by setting up a detection circuit employing two resistors. The resistors are placed in parallel to the spark plugs to allow only a very small but measurable portion of the current to flow through the detection circuit. These small portions were then sampled by an oscilloscope. In this system the voltage difference across one of the resistors in the detection circuit is 1/201 of the voltage across the spark plugs. Another similar method was used to calculate the current across the spark plug, which in this case is exactly equal to amperage flowing through the parallel circuit.

4.3. Experimental Results

4.3.1. Discharge Energy

Using a voltage divider circuit, the voltage and current across the gap were measured. Figure 2 shows the experimentally determined voltages and currents across the spark plug gap for each voltage setting on the ignition system in argon. The spike, approximately at 5-10 microsecond in duration, shows the breakdown stage which is the beginning of spark discharge. In this stage the gap is bridged by the avalanche of electrons flowing from cathode to anode.

Figure 3 shows the discharged power calculated by product of measured values of current and voltage for two different stored energies in the ignition system. Discharged energy, DE, can be calculated having by \( DE = \int VI \, dt \). It should be noted that discharged energy is different from the electrical energy converted to the thermal energy in the gas. A portion of the discharged energy is dissipated by conduction into the electrodes.
4.3.2. Image Capturing

Figures 4 shows the snapshot of argon plasma kernel. It can be seen that the boundary layer surrounding the plasma kernel is very thin. Figure 5 shows the radii of kernel at two different spark energies. It can be seen that spark energy has a remarkable effect on the size of the kernel.

4.4. Thermodynamic Model

In this section the thermodynamic model for the predicting the growth of argon plasma kernel will be described. Figure 6 shows the schematic diagram of the control mass and energy transformation across the boundary.

The major assumptions are as following:

1- It is assumed that the plasma kernel is spherical.

2- All calculations start after breakdown stage. It is assumed that the shock wave is emitted and pressure is constant.

3- Since the relaxation time scale of different energy modes (translational, rotational, vibrational, electronic) are too small \((O\sim 10^{-9} \text{ s})\), all species are in local thermodynamic equilibrium (Maly (1981), Sher et al (1992), Sher and Keck (1986), and Maly and Vogel (1979)).

4- There are no mass transport processes involved in the model. It is assumed that the plasma kernel is a constant-mass system and expands in a constant pressure process.

5- Energy losses are due to radiation, cathode-anode fall dissipations, and conduction through thermal boundary layer to the electrodes.

The governing equations are, equation of state, and mass conservation, and energy balance.

The equation of state is given as

\[ pV = nRT \]  

(1)

where \( p \) is the pressure, \( V \) is the volume of kernel, \( n \) is number of moles, \( R \) is the universal gas constant, and \( T \) is the temperature. Total number of moles is determined by:

\[ n = \sum_{i=1}^{z} n_i \]  

(2)

where \( z \) is the number of species.
The number of elemental atom number is then given by

\[ EA_r = \sum_{\varepsilon=0}^{z} Ar^\varepsilon \]

\[ \varepsilon = 0, 1, 2, 3, \ldots z \]  

(3)

In this equation, \( \varepsilon \) is the charge of ions.

The equation for energy balance is given by:

\[ n c_v (T - T_0) = DE - p(V - V_0) - Q_{rad} - Q_{cond} \]  

(4)

Equation (4) can be rewritten as:

\[ \frac{c_p}{R} p(V - V_0) = DE - Q_{rad} - Q_{cond} \]  

(5)

where \( T \) is the temperature, \( c_v \) and \( c_p \) are the heat capacities, \( V_0 \) is the initial volume of the kernel, \( Q_{rad} \) is the radiation energy loss, and \( Q_{cond} \) is the conduction energy loss to the electrodes by thermal boundary layer.

In equation (5):

\[ DE = \int_{0}^{b} IVdt + \int_{b}^{t} (IV_{fall}) dt + \int_{0}^{b} (IV_{col}) dt = \int_{0}^{b} IVdt + Q_{ca} + SE \]  

(6)

In this equation, \( Q_{ca} \) is the cathode-anode fall dissipation by conduction into the electrodes, and \( SE \) is the net spark energy converted to thermal energy in the plasma.

Conduction to electrodes in the thermal boundary layer is:

\[ Q_{cond} = -\int - k_r A_{e} \left( \frac{dT}{dr} \right) dt \]  

(7)

where

\[ \delta = \sqrt{\alpha t} \]  

(8)

as the thermal boundary layer thickness. Equation (7) can be rewritten as:

\[ Q_{cond} = -\int k_r A_{e} (T - T_0) \frac{dt}{\sqrt{\alpha t}} \]  

(9)

In this equations (7-9), \( k_r \) is the thermal conductivity of the gas; \( A_{e} \) is the contact area of
electrodes with the gas, $T_o$ is the temperature of the electrode, and $\alpha$ is the thermal diffusivity of argon. Experimental data of Wilbers et al (2002), which have been collected at high temperatures under optically thin conditions, have been used to model radiation losses.

4.4.1. Thermodynamic Properties

the thermodynamic properties of argon have been calculated by statistical thermodynamic methods. These parameters include $c_p$ and the enthalpy of the mixture. For argon the species are $\text{Ar}$, $\text{Ar}^+$, $\text{Ar}^{2+}$, $\text{Ar}^{3+}$, $\text{Ar}^{4+}$, $\text{Ar}^{5+}$, $\text{Ar}^{6+}$ and e (electron). Additional information can be found in (Eisazadeh-Far et al (2010)). In the theoretical model, values of specific heat in needed in very high temperatures of 300 – 100,000 K. Figure 7 shows the heat capacity of argon in this temperature range. Figure 8 shows the normalized number of species of argon. The results of equation (2) have been normalized by the sum of the elemental atom numbers defined in equation (3). It can be seen that number of particles increase as the temperature of the gas increases.

4.5. Results and Discussion

Equations 1 through 9 have been used to determine the radii and temperature of plasma kernel for different initial temperature and volume of the kernel and input electrical energy. The values of initial radius and initial temperature depend on discharged energy, pressure, gas type and energy losses during the breakdown. The effect of initial parameters on the size and temperature of the kernel is investigated in following section.

4.5.1. Initial Radius

Figures 9 and 10 demonstrate the effect of initial radius of the plasma kernel on growth and temperature of the plasma kernel. It can be seen that the size of plasma kernel is not dependent on initial radius but the temperature of the kernel is very sensitive to the initial radius.

4.5.2. Initial Temperature

Figures 11 and 12 show the effect of initial temperature on plasma kernel growth and its temperature. It is shown that initial temperature does not have a major effect on the size of the kernel but it can change the temperature of the hot plasma strikingly. Initial temperature depends on breakdown energy and its duration. The range of initial temperature for plasma is 5,000-7,000 K.
4.5.3. Result of Calculations

Table 1 shows the values of the initial condition. Figure 13 shows the results of the calculations and the comparison with the experiment. There are two curves in each figure which are the calculations with and without radiation. As it can be seen radiation is a major source of energy losses. The radiation becomes important especially when temperature is high. It can also be concluded that the decrease of argon plasma radius is due to radiation energy losses. In higher discharged energies not only the temperature of the kernel but also the area of kernel increases and it causes higher radiation energy losses.

Table 1: initial conditions for calculations

<table>
<thead>
<tr>
<th></th>
<th>Argon (DE = 26 mJ)</th>
<th>Argon (DE = 46 mJ)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Initial radius (mm)</td>
<td>0.25</td>
<td>0.34</td>
</tr>
<tr>
<td>Initial temperature (K)</td>
<td>5000</td>
<td>7000</td>
</tr>
<tr>
<td>$DE$ (mJ)</td>
<td>26</td>
<td>46</td>
</tr>
<tr>
<td>$SE$ (mJ)</td>
<td>2.2</td>
<td>14.7</td>
</tr>
</tbody>
</table>

Figure 14 shows the fraction of energy terms in argon plasma. It can be seen that a large part of energy is dissipated by cathode-anode fall conduction dissipations. Clearly, the amount of radiation loss depends on the value of discharged energy. This percentage is strongly a function of current and the temperature of the arc (Hermann and Schade (1970)). Another important source of energy loss is the radiation from hot gas. Figure 14 shows that in higher discharged energies, the amount of radiation energy losses are higher, which is due to larger surface area of the kernel and higher temperature of the plasma kernel. Figure 14 shows that just about 3-5 % of discharged energy is converted to thermal energy. This result is in good agreement with experimental measurements of Teets and Sell (1988).
Table 1: Summary of fractional energy terms

<table>
<thead>
<tr>
<th></th>
<th>Argon (DE = 26 mJ)</th>
<th>Argon (DE = 46 mJ)</th>
</tr>
</thead>
<tbody>
<tr>
<td>cathode-anode fall losses</td>
<td>88.80%</td>
<td>68.20%</td>
</tr>
<tr>
<td>thermal boundary layer conduction</td>
<td>0.20%</td>
<td>0.30%</td>
</tr>
<tr>
<td>radiation losses</td>
<td>6%</td>
<td>27%</td>
</tr>
<tr>
<td>converted to thermal energy (present study)</td>
<td>5%</td>
<td>3.50%</td>
</tr>
<tr>
<td>converted to thermal energy (Teets and Sell (1988))</td>
<td>7%</td>
<td></td>
</tr>
</tbody>
</table>

Acknowledgment

This work has been partially supported by Office of Naval Research (ONR), grant number N00010-09-1-0479, under technical monitoring of Dr. Gabriel Roy.

References


Figure 1: the experimental set up of the system
Figure 2: Voltage and current versus time for high and low energy: Argon
Figure 3: Spark discharge power of argon at low and high energies

Figure 4: Argon plasma kernel, $P = 1$ atm, $DE = 46$ mJ
Figure 5: argon radii at two different spark energies ($DE = 26$ and $46$ mJ)

Figure 6: the sketch of the model
Figure 7: Specific heat capacity of argon at high temperatures

Figure 8: particle numbers of argon normalized by elemental atom numbers
Figure 9: The effect of initial radius on kernel size of argon,

\[ \text{Ti} = 7000 \text{ K}, \ DE = 46 \text{ mJ}, \ Q_{\text{rad}} = 0 \]

Figure 10: The effect of initial radius on kernel temperature of argon,

\[ \text{Ti} = 7000 \text{ K}, \ DE = 46 \text{ mJ}, \ Q_{\text{rad}} = 0 \]
Figure 11: the effect of initial temperature on argon kernel growth,

Ti = 7000 K, ri = 0.34 mm, DE = 46 mJ, Q_{rad} = 0

Figure 12: the effect of initial temperature on argon kernel temperature,

Ti = 7000 K, ri = 0.34 mm, DE = 46 mJ, Q_{rad} = 0
Figure 13: argon plasma radii and the comparison with experiments in
a: $DE = 26$ mJ and b: $DE = 46$ mJ
Figure 14: fraction of energy terms for argon plasma kernel,

a: $DE = 26$ mJ, b: $DE = 46$ mJ
5. On Flame Kernel Formation and Propagation in Premixed Gases

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5. On Flame Kernel Formation and Propagation in Premixed Gases

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Abstract

Flame kernel formation and propagation in premixed gases have been studied experimentally and theoretically. The experiments have been carried out at constant pressure and temperature in a constant volume vessel located in a high speed shadowgraph system. The formation and propagation of the hot plasma kernel has been simulated for inert gas mixtures using a thermodynamic model. The effects of various parameters including the discharge energy, radiation losses, initial temperature and initial volume of the plasma have been studied in detail. The experiments have been extended to flame kernel formation and propagation of methane/air mixtures. The effect of energy terms including spark energy, chemical energy and energy losses on flame kernel formation and propagation have been investigated. The inputs for this model are the initial conditions of the mixture and experimental data for flame radii. It is concluded that these are the most important parameters effecting plasma kernel growth. The results of laminar burning speeds have been compared with previously published results and are in good agreement.

Keyword: flame kernel, plasma, laminar burning speed, spark ignition

5.1. Introduction

An understanding of the spark ignition process is important for the improving the fuel efficiency and reducing the emissions of IC engines and burners. Prior research carried out over the past several decades by a large number of investigators [1-21] has shown that the ignition process involves three distinct stages. The first stage, which occurs on a time scale of microseconds, involves the formation of a narrow spark channel followed by the formation of an equilibrium plasma kernel with a radius of approximately 0.5 mm and a temperature of 7000 K. The second stage, which occurs on a time scale of milliseconds, involves the subsequent growth of a constant mass plasma kernel of atomic ions and electrons due to the input of additional electrical energy from the ignition system. The third and final stage involves the ignition of the combustible gas mixture surrounding the hot plasma kernel to produce a propagating flame. The first and third stages of this ignition process have been extensively investigated in prior work and a semi quantitative understanding of them has been achieved. Maly and Vogel [1] in a theoretical and experimental study determined that the most important component of spark discharge is the breakdown process. They mentioned that the other processes including arc and glow discharge
are less important because their electrical energy is dissipated into the electrodes. Maly [2] and Ziegler et al [3] studied the formation of lean methane-air flames based on the theories proposed in [1]. They concluded that the best ignition system is the one with highest level of energy and shortest time interval. Sher et al [4] did a fundamental study on spark formation in air and proposed a model to calculate the spark kernel temperature after breakdown. They concluded that the initial spark kernel is a very high temperature region, but the temperature drops rapidly due to heat dissipation. They determined that beyond a specific limit, the energy of the spark affects only the initial flame kernel radius, and not the temperature. Sher et al [5-8] applied the proposed model in [4] to study the formation of actual methane-air flames and the effect of variables on the initial flame kernel. They concluded that the spark kernel is grown in two steps. The first, shorter stage consists of a pressure wave emission. This is followed by a longer period, in which diffusion occurs. Initial flame kernel is formed during the second stage in a constant pressure process. They could estimate the burning speed of methane-air flames in early stages [8]. However, the estimation of initial conditions in early stages and other parameters such as initial temperature of the kernel, radiation from hot gas, heat conductivity, and transport properties is challenging. Ko et al [9, 10] theoretically and experimentally studied the spark ignition of propane-air mixtures. They indicated the existence of a critical radius which depends strongly on equivalence ratio. They also showed the importance of spark electrode gap, spark modes (breakdown, arc, and glow), and cathode-anode falls on ignition process. Chen and Ju [11] studied the evolution of the ignition kernel to a flame ball and they concluded that radiation plays a very important role in transition of initial flame kernel to the actual self-sustained flame.

There are also numerous works which deal with the effect of geometry and type of spark electrodes on kernel characteristics and flame propagation [12-21]. Most of these papers illustrate the importance of energy losses in early stages, minimum initial radius, ignition energy modes and their effects on flame formation.

The purpose of the present paper is to present a quantitative model for the intervening second and third stages of process which study the electrical energy input to plasma, flame kernel formation, and measuring the laminar burning speed.

5.2. Experimental System

Figure 1a shows the overall experimental system. Experiments were conducted in a cylindrical combustion chamber with an inner diameter and length of 133.35 mm. Figure 1b
shows the cylindrical vessel. The combustible mixture was spark-ignited at the center of the chamber using two spark plugs with extended electrodes. Two different sets of electrodes were used to study the effect of electrode geometry on heat loss. They had diameters of 2.54 mm and 0.381 mm. Both of electrodes were of stainless steel. Both sets had a free length of 40 mm and the spark gap was 1.0 mm. Two extended spark electrodes, shown in Figure 1b, initiate the combustion process from the center.

**Ignition system:** An electronic ignition system consists of high voltage capacitor discharge controlled by the data acquisition program which provides a spark with the necessary energy. Ignition system has been designed with variable voltages and capacitors to produce ignition with different energies. Voltage and current across the spark plug gap during the electrical discharge have been measured by a voltage divider.

**Optical system:** a Z-type Shadowgraph ensemble has been set up to visualize the flame propagation. A high speed CMOS camera (HG-LE, Redlake Inc.) with a capture rate of up to 40,000 frames per second is placed at the focal point of the second mirror. The capture rate and shutter speed of the camera were optimized depending on the burning speed of the mixture and the brightness of the flame. The light source for the optical system is a 10-Watt Halogen lamp with a condensing lens and a pinhole of 0.3 mm in diameter, which provides a sharp and intense illumination throughout the whole system. Additional information about the optical set up can be found in previous works [22-24].

5.3. Experimental Results

5.3.1. Discharge Energy Measurements

Figure 2 shows the measured voltages and currents as a function of time for a spark plug in air for maximum and minimum discharge energies \((DE)\). The spike which is seen approximately at 5-10 \(\mu\)s shows the breakdown stage preceding the spark discharge. In this stage the gap is bridged by the avalanche of electrons flowing from cathode to anode. Breakdown energy depends on the spike magnitude and duration of the spark. In our experiments the breakdown energy is about 0.3-0.6 mJ. The oscillations seen starting around 1 ms are feedback through the electrical system. Figure 2 also shows the current flow through the spark plug gap and it can be seen that increasing the discharge energy \((DE)\) increases the current flowing across the gap. When the current passes a threshold (~0.3 A) a transition occurs from glow to arc which decreases the voltage abruptly. This transition is caused by thermionic effects causing electron
emission from the high temperature cathode. In lower discharge energies, because of relatively low current, there is no arc mode. The glow discharge voltage (normal voltage $V_n$) is independent of the current. It is a function of wire material and the gas. For air with steel as the electrode material, the value of $V_n$ is 270 volts [2, 25 and 26]. Our experimental observations are very close to these values, as shown in Figure 2.

Once current and voltage are known as a function of time one can easily calculate the instantaneous discharge power ($DP$) from $DP=VI$. Consequently the discharge energy from the spark jump is $DE=\int VI dt$. Figure 3 shows the instantaneous power across the spark plug gap. For higher energies, there is a sudden drop and rise in the power which is due to the voltage drop in arc-glow transition. It should be noted that discharge energy is larger than the electrical energy converted to thermal energy in the gas because a portion of the discharge energy is dissipated by conduction into the electrodes. It is very difficult to measure the amount of energy dissipated in the plasma but, as will be shown in subsequent sections, a good estimation can be made based the anode and cathode voltage drops measured by others.

5.3.2. Shadowgraphs of the Kernel

Figures 4 and 5 show high speed shadowgraphs of plasma kernels for pure-air and methane/air. As can be seen in Figure 4, the kernel radii for pure-air and methane/air flames are almost identical at early times. In this stage (0-2 ms), the amount of heat released by chemical reactions is negligible [8]. Therefore, the volume and temperature of the kernel depends only on the electrical energy dissipated in the plasma kernel.

Figure 5 also shows that about 4 ms after spark, the air kernel becomes stable but the methane/air continues to grow into a self-sustained propagating flame. In this stage chemical energy and transport processes are the drivers of flame.

5.3.3. Kernel Growth for Air

Figure 6 shows the measured air radii as a function of time for two different spark energies. It can be seen that the kernel radii increase significantly with time independent of discharge energy ($DE$) but the final values increase only slightly with increasing discharge energy ($DE$).

5.4. Thermodynamic Model

A thermodynamic model has been developed to describe the growth of the plasma kernel.
subsequent to the breakdown phase. Figure 7 shows the sketch of the model.

The major assumptions are as following:

6- All calculations start after breakdown stage and it is assumed that the pressure is constant.
7- Since the relaxation time scale of different energy modes (translational, rotational, vibrational, electronic) compared to plasma expansion time are small ($O \sim 10^{-9}$ s), all species are in local thermodynamic equilibrium at a single temperature [1, 4, and 5].
8- Since the thermal boundary layer is thin, it is assumed that the kernel is a constant-mass system.
9- It is assumed that the kernel is approximately spherical.
10- Assumed energy losses are (i) radiation from the plasma to the surroundings, (ii) heat loss associated with anode and cathode voltage drops, and (iii) conduction losses to the thermal boundary layers around the electrodes.

The governing equations are energy balance, equation of state, and mass conservation. The equation for energy balance is given by:

$$\frac{\partial E}{\partial t} = \frac{dDE}{dt} - \dot{Q}_{\text{cond}} - \dot{Q}_{\text{rad}} - \frac{c_p}{R} p \dot{V}$$  \hspace{1cm} (1)$$

where $E$ is the energy of the plasma kernel, $dDE/dt$ is the electrical energy dissipation rate, $\dot{Q}_{\text{cond}}$ is the conduction energy loss to the thermal boundary layer, $\dot{Q}_{\text{rad}}$ is the radiation energy loss, $c_p$ is the heat capacity, $R$ is the gas constant, $p$ is the pressure, and $\dot{V}$ is the volume of kernel.

The equation of state is

$$p \dot{V} = nRT$$  \hspace{1cm} (2)$$

where $n$ is number of moles and $T$ is the temperature. The total number of moles is determined by:

$$n = \sum_{i=1}^{z} n_i$$  \hspace{1cm} (3)$$

where $z$ is the number of species.

The mass conservation equation is
\[ EB = 2B_2 + \sum_{\varepsilon=0}^{z} B^\varepsilon \quad \varepsilon = 0, 1, 2, 3, \ldots, z \]

(4)

In this equation, \( EB \) is the elemental atom number of atom \( B \), and \( \varepsilon \) is the charge of ions.

### 5.4.1. Thermodynamic Properties

The thermodynamic properties of air have been calculated by statistical thermodynamic methods. These parameters, including \( c_p \) and the enthalpy of the mixture, have been calculated in temperature range of 300-100,000 K. More details about calculations can be found in [27]. For air the considered species are \( N_2, N, N^+, N^2+, N^3+, N^4+, N^5+, N^6+, O_2, O, O^+, O^2+, O^3+, O^4+, O^5+, O^6+, O^7+, \) and \( e \) (electron). Figure 8 shows the number of species for an air plasma normalized by the number of the elemental atoms in the system. It can be seen that the number of species increases rapidly with temperature due to the large increase in the number of electrons at high temperature. Figure 9 shows the heat capacity of air at high temperatures. The peaks in this curve are associated with the energy required to dissociate and ionize the components of air and are responsible for most of its heat capacity.

### 5.4.2. Electrical Energy

The calculations start after breakdown phase. A negligible portion of discharge energy is consumed in breakdown phase. Equation (5) is the discharge energy balance:

\[
DE = \int_0^b IVdt + \int_0^t (IV_{fall})dt + \int_0^b (IV_{col})dt = \int_0^b IVdt + Q_{ca} + SE
\]

(5)

The first term is the energy associated with breakdown, second term is anode and cathode fall energy \( (Q_{ca}) \) which is dissipated into the electrodes, and the last term is the electrical energy dissipated within the plasma kernel \( (SE) \).

As previously discussed, the experimental data show that breakdown is a very short process \( (O\sim 10^{-6} \text{ s}) \) and its net energy is a small fraction of total energy. After the breakdown phase, arc or glow modes are established (based on the amount of current). In this stage a part of energy is dissipated into the electrodes by conduction. We will show in subsequent sections that in addition to conduction, radiation is an important source of energy losses.
5.4.3. Conduction to Electrodes by Thermal Boundary Layer

Conduction to electrodes was calculated using an unsteady conduction process in the boundary layer. It can be shown that

\[ Q_{\text{cond}} = 2 \int k_T A_e (T - T_0) \, dt \tag{6} \]

In this equation \( k_T \) is the thermal conductivity of the gas; \( A_e \) is the contact area of electrodes with the gas, \( T_0 \) is the temperature of the electrode, and \( \alpha \) is the thermal diffusivity.

5.4.4. Effect of Initial Temperature

Initial temperature of the kernel is important to the ionization process of the kernel. As mentioned before, the calculations start after the emission of the shock wave. The initial temperature of the kernel mainly depends on the breakdown energy and the initial volume of the kernel. Figures 10 and 11 show the effect of initial temperature on kernel growth and temperature. Figure 10 shows that lower initial temperatures result in larger kernel radii, because for a constant volume initial kernel the number of particles is higher for lower initial temperatures. Figure 11 demonstrates that initial temperature affects the temperature profile dramatically. The appropriate range of initial temperature proposed by other researchers is about 6000-7000 K [1, 2, 4-6].

5.4.5. Effect of Initial Radius

Figures 12 and 13 show the effects of initial radius on flame kernel growth and temperature. Initial radius does not have a big influence on the growth rate of the kernel but it has a remarkable effect on the temperature of the kernel. Increasing the initial radii just by 0.05 mm increases the final temperature by about 10,000 K.

5.4.6. Best Fit to the Model

The inputs of the model are initial radius, initial temperature, and the spark energy. The initial radius is measured in the experiments by a high resolution camera. The initial temperature of the plasma for air depends on breakdown energy. However, the agreed range among researchers for a wide range of breakdown energies is 6000-7000 K. Table 1 shows the values of initial conditions.
Figure 14 shows the comparison between the model and experiment for air. This figure also shows the effect of radiation on predictions of the model. The correlations of air radiation are taken from Schreiber et al [28] who collected data for transport properties of air at high temperatures in optically thin conditions. Experimental data presented in Figure 14 show a decline in the radii of kernel after a peak which depends on spark power and duration. Figure 14 shows that in zero radiation condition the radius remains constant after the peak. But the addition of the radiation term in equations predicts a decline in radii which is observed in experiments as well. The importance of radiation strongly depends on the temperature. Figure 14b demonstrates that at higher discharge energy, the effect of radiation becomes more important which is due to larger area of the kernel and higher temperature of the plasma. By including radiation term, the predictions show good agreement with experiment. Major terms which control the growth of the kernel are heat capacity, cathode falls and radiation losses.

5.4.8. Fraction of Total Energy Losses

Figure 15 shows different energy terms in air kernels. It can be seen that in air plasma, radiation can dissipate 20-60% of discharge energy ($DE$) depending on spark duration and temperature. This percentage strongly depends on the current and the temperature of the arc [29]. 25-30% of the discharge energy is dissipated by the cathode fall conduction and thermal boundary layer dissipations. A small portion of the discharge energy is dissipated by thermal boundary layer around the electrodes. By this token, just about 10-25% of discharge energy is converted to the thermal energy. Although Teets and Sell [30] state that the major part of energy dissipation is due to conduction losses to the electrodes the results are in agreement with net results of Teets and Sell [30] and Maly et al [1-2]. Table 2 shows the summary of energy dissipations in air.

5.5. Methane/Air Mixture

5.5.1. Flame Radius

In this section the growth of methane/air flames will be discussed. The experiments have been done with various equivalence ratios from 0.7-1.4. The discharge energies were 24 and 81 mJ and two electrodes were used whose specifications were explained in previous sections. Figure 16 shows the flame radii of the mixtures at stoichiometric condition, low and high variant spark energies, and two different spark electrodes. It is shown that spark electrode geometry does not affect the flame speed. Figures 16b show the effect of spark energy on flame propagation. These
figures demonstrate that energy of spark affects the location of flame, but asymptotic flame growth rate is independent.

5.5.2. Model Equations

Figure 17 is the sketch of the model. It is assumed that the flame is spherical and propagates in a constant pressure process. The mass is added to the burned gas region by burning the unburned gas. The mass conservation equation on the flame front is:

\[
\frac{\partial m}{\partial t} = \dot{m}_b = \rho_u A S_u [1 - \exp(-t / \tau_c)]
\]  

(7)

where \( m \) is the mass of the burned gas zone, \( \dot{m}_b \) is the mass burning rate, \( \rho_u \) is the density of unburned gas, \( A \) is the flame area, \( S_u \) is the laminar burning speed, and \( \tau_c \) is a characteristic time scale. As it will be shown in experimental data the flame speed tends to an asymptotic value after a specific time scale which depends on chemical and thermodynamic properties of the mixture. The exponential term and the corresponding time scale \( \tau_c \) in equation (7) represent this behavior.

The energy balance is given by:

\[
\frac{\partial E}{\partial t} = \dot{m}_b (c_{pu} T_u + h_u) + \frac{dSE}{dt} - \dot{Q}_{\text{cond}} - \dot{Q}_{\text{rad}} - \rho \dot{V}
\]  

(8)

\[ E = m(c_{vb} T_b + h_b) \]  

(9)

where, \( E \) is the energy of the burned gas region, \( h \) is the enthalpy and \( c_{vb} \) is the heat capacity at constant volume. \( \frac{dSE}{dt} \) is the rate of spark energy variations inside the plasma.

The equation of state is:

\[ p = \rho_b R_b T_b = \rho_u R_u T_u \]  

(10)

where \( \rho \) is the density.

Equation (8) can be written as
\[
\frac{\hat{\nabla}}{\hat{\theta}} \left( \frac{c_{pb}}{R_b} \rho \nabla \right) = \frac{c_{pb}}{R_b} pA \hat{r} = \hat{m}_b c_{pb} T_b + \frac{dSE}{dt} - \hat{Q}_{\text{cond}} - \hat{Q}_{\text{rad}}
\]  (11)

Let:

\[
\hat{r}_c = \frac{\hat{m}_b R_b T_b}{pA} = \frac{\hat{m}_b R_b T_b}{\rho_u R_u T_u A} = \frac{\rho_u S_u (1 - \exp(-t/\tau_c))}{\rho_b}
\]  (12)

\[
\hat{r}_{\text{elec}} = \frac{R}{c_p} \frac{dSE}{dt} \frac{1}{pA}
\]  (13)

\[
\hat{r}_{\text{cond}} = \frac{R}{c_p} \frac{\hat{Q}_{\text{cond}}}{pA}
\]  (14)

\[
\hat{r}_{\text{rad}} = \frac{R}{c_p} \frac{\hat{Q}_{\text{rad}}}{pA}
\]  (15)

In equations 11-15, \( A \) is the area of the flame and \( r \) is the radius of the flame. By dividing Equation (11) by \( \frac{c_{pb}}{R_b} pA \), we will have:

\[
\hat{r} = \hat{r}_c + \hat{r}_{\text{elec}} - \hat{r}_{\text{cond}} - \hat{r}_{\text{rad}}
\]  (16)

In this equation the role of each energy term on flame speed has been involved. In equation (16), \( \hat{r}_c \) is the flame speed term corresponding to chemical energy, \( \hat{r}_{\text{elec}} \) is the flame speed term corresponding to electrical energy, and \( \hat{r}_{\text{cond}} \) and \( \hat{r}_{\text{rad}} \) are the effects of conduction and radiation energy losses on flame speed. Having experimental data on the radius of flame and electrical energy, the experimental data were fitted by equation (16). The achieved parameters after fitting are \( S_u \) and \( \tau_c \). Figure 18 shows the flame speed values measured by experiments and fitted by the model. The symbols represent the experimental data. The fluctuations in early stages are associated with the oscillations of heat capacity in early stages which affects the dynamics of the kernel. Later on, the oscillations are due to acoustic waves. In Figure 18 the effect of other terms presented in equation (16) is also shown. High flame speed values in the beginning are due to very high temperature plasma gas. In almost all cases radiation plays an important role in early stages due to the emission of high temperature gas. Figure 18 indicates that chemical energy term has an exponential behavior and it takes time to become asymptotic. Experimental data from
Dreizler et al [31] show that deposition of chemical energy in the kernel begins in the early stages of flame formation but in the first 2 ms the energy supply is dominated by electrical energy. The amount of energy supplied by electrical energy is almost three orders of magnitude higher than the chemical energy. After 2 ms the electrical energy is eliminated and the chemical energy becomes the driver of the flame. Based on conditions, laminar flame becomes asymptotic ultimately. In early stages of ignition the flame speed is more dominated by expansion of the plasma kernel which is a constant pressure and mass process. The experimental data verify this theory as well. Figure 5 shows that in early stages the radii of air and methane/air mixture do not differ dramatically. The transition process from constant mass expansion to the actual self-sustained flame is a complicated process and it depends on the properties of the mixture, energy loss processes, mass and heat diffusion and the rate of chemical reactions. However, the chemical energy time scale $\tau_c$ can quantitatively show the transition duration. Table 3 shows the values of $S_u$ and $\tau_c$ at two different spark energies and spark electrodes. It is shown that the laminar burning speed is almost independent of spark energy and electrode geometry. The slight difference in results can be attributed to experimental errors.

**5.6. Errors and Uncertainties**

The sources of experimental uncertainty can be errors in preparation and filling the vessel by methane/air mixture, different discharge energies, and software errors in measuring the radii. Our analyses in previous publications prove that errors due to mixture stoichiometry are $\sim 1\%$ [22-24]. The data have been collected with high resolution and high frame per second to minimize the errors of radii measurement which is $\sim 0.5\%$. Each experiment was performed at least three times at each operational condition. According to statistical methods, three identical runs are sufficient in order to ensure that the confidence level of the experiment is above 95% [32]. By this procedure and considering the human errors, the experimental uncertainties are minimized to less that 5%. The errors in calculations can be due to laminar burning speed fittings and taking derivative of radii data vs time. However, these errors never exceed 1%.

**5.7. Comparison with Other Experimental Data**

The laminar burning speeds of methane/air flames have been measured by several researchers. The experimental and theoretical data shown in Figure 19 have been obtained by different experimental methods. Figure 19 shows the comparison of present results with other
experimental and theoretical data. Our measurements are in good agreement with other data. However, the discrepancy among the data can be associated with experimental errors and different techniques used for measurements. These discrepancies increase in the vicinity of ignition limits at lean and rich conditions (0.7 and 1.3).

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References

55-77.


Figure 1: (a): the experimental set up of the system, (b): cylindrical vessel
Figure 2: Voltage and current versus time for high and low energy: Air

(Arc to glow transition is seen in high energy case)
Figure 3: Spark discharge power of air at low and high energies
Figure 4: snapshots of air and methane/air kernels, P=1 atm, T=300 K, discharge energy \((DE) = 24 \text{ mJ}\). (different contrast values of images cause the electrodes appear in different thicknesses)
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discharge energy = 24 mJ, $r_i = 0.5$ mm
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discharge energy = 24 mJ, r_i = 0.5 mm
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\[ T_i = 7000 \text{ K}, \text{ discharge energy} = 24 \text{ mJ} \]
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\[ T_i = 7000 \text{ K}, \text{ discharge energy} = 24 \text{ mJ} \]
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\[ P = 1 \text{ atm}, \ T = 300 \text{ K}, \ \phi = 1 \]
Figure 19: laminar burning speeds vs equivalence ratio and comparison with other experimental data, $P = 1$ atm, $T = 300$ K.
Table 1: initial conditions for calculations

<table>
<thead>
<tr>
<th></th>
<th>Air ($DE = 24$ mJ)</th>
<th>Air ($DE = 81$ mJ)</th>
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<tbody>
<tr>
<td>Initial radius (mm)</td>
<td>0.5</td>
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<tr>
<td>Initial temperature (K)</td>
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<td>7000</td>
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<tr>
<td>$DE$ (mJ)</td>
<td>24</td>
<td>81</td>
</tr>
<tr>
<td>$SE$ (mJ)</td>
<td>18</td>
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Table 2: Summary of fractional energy terms

<table>
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<tr>
<td>cathode-anode fall losses</td>
<td>26.60%</td>
<td>26%</td>
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<tr>
<td>thermal boundary layer conduction</td>
<td>0.40%</td>
<td>1%</td>
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<tr>
<td>radiation losses</td>
<td>48%</td>
<td>62%</td>
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<tr>
<td>converted to thermal energy (present study)</td>
<td>25%</td>
<td>11%</td>
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<tr>
<td>converted to thermal energy (Teets and Sell [30])</td>
<td>24%</td>
<td>14%</td>
</tr>
<tr>
<td>converted to thermal energy (Maly and Vogel [1])</td>
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<td></td>
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Table 3: summary of results

<table>
<thead>
<tr>
<th></th>
<th>$DE = 24$ mJ</th>
<th>$DE = 81$ mJ</th>
<th>$DE = 24$ mJ</th>
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<tr>
<td></td>
<td>$\phi = 0.8$</td>
<td>$\phi = 0.8$</td>
<td>$\phi = 1$</td>
<td>$\phi = 1$</td>
<td>$\phi = 1.2$</td>
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<tr>
<td>$S_u$ (cm/s)</td>
<td></td>
<td></td>
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<tr>
<td>$0.4$ mm</td>
<td>22</td>
<td>23</td>
<td>35.7</td>
<td>36</td>
<td>33.1</td>
<td>32.8</td>
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<tr>
<td>$2.5$ mm</td>
<td>24.2</td>
<td>23.5</td>
<td>35.6</td>
<td>34.8</td>
<td>32.8</td>
<td>32.2</td>
</tr>
<tr>
<td>$\tau_c$ (ms)</td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>$de = 0.38$ mm</td>
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<td>1.4</td>
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<td>$de = 2.54$ mm</td>
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<td>1.4</td>
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6. *A Thermodynamic Model to Calculate Burning Speed of Methane-Air-Diluent Mixtures*

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6. A Thermodynamic Model to Calculate Burning Speed of Methane-Air- Diluent Mixtures

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Abstract

The burning speeds and flame structure of methane-air-diluent mixtures over a wide range of pressures and temperatures have been studied using both a constant volume spherical chamber and a cylindrical chamber with end windows. The effect of automotive exhaust gas on the burning speeds was measured using a mixture of 86 % N₂ and 14 % CO₂ as the diluent. A thermodynamic model was developed to calculate the mass fraction burned and the burning speeds from the measured dynamic pressure rise in the chamber. The model assumes a central burned gas core of variable temperature surrounded by an unburned gas shell of uniform temperature. Heat losses due to radiation from the burned gas and conduction to the wall and electrodes are included. The effect of the temperature rise in the preheat zone at the flame front is also included. Photographic observations were made through the end windows in the cylindrical chamber using a high-speed charged coupled device (CCD) camera with variable speed of up to 8000 frames/second. Smooth, cracked and cellular flame were all observed and the regions where they occurred have been roughly determined. The measured values of burning speeds have been compared with laminar burning speeds calculated using the PREMIX flame speed code and the GRI-Mech 3.0 mechanism. This model is valid for high temperatures and low pressures and agrees well with the measurement under these conditions when the flames are smooth or cracked and lean or stoichiometric. For cellular flames at high pressures and low diluent fraction, the measured burning speeds are higher than the PREMIX values. For rich mixtures, all the flames observed were smooth but the measured burning speeds were lower than the PREMIX values. Possible reasons for this are discussed.
NOMENCLATURE

A = area
E = energy
c_p = constant pressure specific heat
c_v = constant volume specific heat
e = specific energy
h_f = specific enthalpy of formation
m = mass
p = pressure
Q = heat loss
r = radius
R = specific gas constant
S_b = mass burning speed
S_f = flame speed
t = time
T = temperature
u_g = gas speed
V = volume
V_c = combustion chamber volume
v = specific volume
x = mass fraction
y = dimensionless time
y_b = burned gas volume fraction
z = dimensionless pressure

Greek

\( \alpha \) = thermal diffusivity
\( \alpha_p \) = Planck mean absorption coefficient
\( \delta \) = boundary displacement thickness
\( \gamma \) = ratio of constant pressure and constant volume specific heats
\( \eta \) = radial distance from electrode
\( \rho \) = density
\[ \sigma \text{ = Stefan-Boltzman constant} \]
\[ \tau \text{ = characteristic burning time} \]

**Subscripts**
- \( b \) = burned gas
- \( e \) = electrode
- \( i \) = initial conditions
- \( r \) = radiation
- \( u \) = unburned gas
- \( w \) = wall
- \( eb \) = electrode boundary layer
- \( wb \) = wall boundary layer
- \( ph \) = preheat zone
- \( bs \) = isentropically compressed burned gas
- \( us \) = isentropically compressed unburned gas

**6.1. Introduction**

The purpose of this paper is to provide experimental data on the mass burning rates, burning speed, and flame structure that are important both for developing and testing fluid dynamic and chemical kinetic models of hydrocarbon oxidation and for a wide range of direct practical applications in the fields of engines, burners, explosions, and chemical processors.

Over the past several decades, a great deal of experimental [1, 2] and theoretical [3, 4] work has been done on the measurement and kinetic modeling of laminar burning speeds. This has led to the development of fairly complete and reliable flame speed codes and chemical kinetic models for predicting the laminar burning speeds of simple hydrocarbon mixtures at high temperatures and low pressures. However, relatively little effort has been devoted to measuring or developing models of laminar burning speeds at low temperatures and high pressures. Experimental and theoretical studies of ignition delays in constant volume chambers [5] and rapid compression machines [6] clearly demonstrate the importance of alkyl peroxides under these conditions. Since these have been omitted from most current models, users are explicitly advised that they are invalid at low temperatures and high pressures [7]. This is especially unfortunate because of the large number of practical applications involving low temperature/high pressure flames.
The methods used to measure burning rates and flames speeds can be characterized as either constant pressure [8-25] or constant volume [26-42]. Constant pressure methods, such as those employing flat flame burners, are limited to a relatively narrow range of temperatures and are most useful for obtaining data at atmospheric pressure. The principal disadvantages of the constant pressure methods are that they require significant corrections for flame geometry and conductive heat loss to the burner. Recently an effort has been made to measure the heat loss to the burner [43] and calculate the adiabatic burning speed, but this could only be done at atmospheric pressure and room temperature.

Constant volume methods, such as those employing spherical combustion chambers, cover a much wider range of temperatures and pressures and provide a range of data along an isentrope in a single experimental run. In addition, corrections for flame geometry or heat loss are generally quite small. Spherical chambers have been used by a number of investigators [36-38, 44] to measure burning speeds for a wide range of fuels, equivalence ratios, diluent concentrations, pressures and temperatures. Flame instabilities such as cracking, wrinkling and buoyant rise have been observed by many researchers [44-48] and have subtle effects [44].

In the current study, burning rates and flame speeds have been measured for methane-air-diluent (86 % N₂ and 14 % CO₂ ) mixtures for equivalence ratios of 0.8, 1.0 and1.2 over the pressure range 1-50 atm and unburned gas temperature range 298-500 K. The pressure rise due to combustion in a constant volume spherical chamber was recorded and a thermodynamic analysis of the pressure time record was used to calculate the burning rates and flame speeds. The flame structure was investigated using a cylindrical chamber with end windows. Buoyancy and instabilities in the flame structure were observed in this vessel. The measured values of the burning speeds have been compared to calculations made using the PREMIX flame speed code [49] with GRI-Mech 3.0 mechanism [7]. As expected, the agreement is good for high-temperature, low-pressure conditions. However for low temperature, high pressure conditions, the calculated burning speeds are significantly higher than the measured values.

6.2. Experimental Facilities

The burning speed measurements were made in both a spherical and a cylindrical combustion chamber [50-53]. The spherical chamber consists of two hemispheric heads bolted together to make a 15.4 cm inner diameter sphere. The chamber was designed to withstand pressures up to 425 atm and is fitted with ports for spark electrodes, diagnostic probes, and for filling and evacuating it. A thermocouple inserted through one of the chamber ports was used to
check the initial temperature of the gas inside the chamber. A Kistler 603B1 piezo-electric pressure transducer with a Kistler 5010B charge amplifier was used to obtain dynamic pressure vs. time records from which the burning rate was determined. Ionization probes mounted flush with the wall at the top and bottom of the chambers were used to measure the arrival time of the flame at the wall and check for spherical symmetry and buoyant rise.

The companion cylindrical chamber has a diameter and length equal to 13.3 cm, which makes its volume equal to that of the spherical chamber. This chamber was designed to operate over the same pressure and temperature range as the spherical chamber and is equipped with similar access ports. The primary purpose of this facility is to permit optical observation of the flame shape and structure under conditions as close as possible to those in the spherical chamber and the initial pressure rise and flame development are identical in both chambers. A high speed CCD digital video camera is used to obtain shadowgraphs of the flame at speeds up to 8000 frames/second.

The gas handling system consists of a vacuum pump for evacuating the system and a valve manifold connected to gas cylinders for preparation of the fuel/air/diluent mixtures. Partial pressures of the fuel mixtures were measured using Kulite strain gauge pressure transducers in the 0-15 atm range. Two spark plugs with extended 2 mm diameter electrodes were used to ignite the mixture at the center of the chambers. An electronic ignition system controlled by the data acquisition program provides the spark.

The data acquisition system consists of a Data Translations 16 bit data acquisition card, which records the pressure change during combustion at a rate of 250 kHz. The analog to digital converter card receives the pressure signal from the charge amplifier and the signals from the ionization probes. All signals are recorded by a personal computer and an output data file is automatically generated. The output data file contains information about the partial pressures and initial temperature of all the gases used: fuel, oxygen and diluent. An oscilloscope is used to monitor the ignition signal and the outputs of the ionization probes and the pressure transducer in real time to insure that the various sensors are working and that the system has fired properly.

After the chamber is filled with the proper mixture, several minutes are allowed before the mixture is ignited. This is sufficient to permit any turbulence inside the vessel to decay. At least three runs at each initial condition were made to provide a good statistical sample. Based on a statistical analysis, it was found that three runs are enough to achieve a 95% confidence level.
6.3. Theoretical Model

The theoretical model used to calculate the burning speed from the pressure rise is based on one previously developed by Metghalchi and Keck [36-38] modified to include the effects of temperature gradients in the burned gas and flame preheat zone. It is assumed that gases in the combustion chamber can be divided into burned and unburned regions separated by a reaction layer of zero thickness as shown schematically in Figure 1. It is further assumed that: the burned and unburned gases are ideal, the burned gas is in chemical equilibrium, the unburned gas composition is frozen, the pressure throughout the chamber is uniform, compression of both burned and unburned gases is isentropic, and the heat flux due to the temperature gradient in the burned gas is negligible. For the conditions of interest in the present work, all these assumptions have been validated by numerous experiments in constant volume chambers and internal combustion engines carried out over the past several decades.

6.3.1. Burned Gas Mass Fraction and Temperature

For spherical flames, the temperature distribution of the gases in the combustion chamber and the burned gas mass fraction can be determined from the measured pressure using the equations for conservation of volume and energy together with the ideal gas equation of state

\[ pv = RT \]  \hspace{1cm} (1)

where \( p \) is the pressure, \( v \) is the specific volume, \( R \) is the specific gas constant and \( T \) is the temperature.

The mass conservation equation is

\[ m = m_b + m_u = p_i(V_c - V_e)RT_i \]  \hspace{1cm} (2)

where \( m \) is the mass of gas in the combustion chamber, \( m_b \) is the burned gas mass, \( m_u \) is the unburned gas mass, \( V_c \) is the volume of the combustion chamber, \( V_e \) is the electrode volume, and the subscript \( i \) denotes initial conditions.

The total volume of the gas in the combustion chamber is

\[ V_c - V_e = V_b + V_u \]  \hspace{1cm} (3)

where

\[ V_b = \int_0^{m_b} v dm = \int_0^{m_b} v_b dm - V_{eb} \]  \hspace{1cm} (4)
\( V_b \) is the volume of the burned gas, \( v_{bs} \) is the specific volume of isentropically compressed burned gas,

\[
V_{eb} = \int_0^{m_b} (v_{bs} - v)dm
\]  

(5)

\( V_{eb} \) is the displacement volume of the electrode boundary layers,

\[
V_u = \int_{m_u}^{m_b} vdm = m(1 - x_b)v_{us} - V_{wb} - V_{ph}
\]  

(6)

\( V_u \) is the volume of the unburned gas, \( x_b = m_b/m \) is the burned gas mass fraction, \( v_{ub} \) is the specific volume of isentropically compressed unburned gas,

\[
V_{wb} = \int_{wb}^{m_b} (v_{us} - v)dm
\]  

(7)

\( V_{wb} \) is the displacement volume of the wall boundary layer,

\[
V_{ph} = \int_{ph}^{m_b} (v_{us} - v)dm
\]  

(8)

\( V_{ph} \) is the displacement volume of the preheat zone ahead of the reaction layer.

The energy conservation equation is

\[
E - Q_w - Q_e - Q_r = E_b + E_u
\]  

(9)

where \( E \) is the initial energy of the unburned gas, \( Q_w \) is the conduction heat loss to the wall, \( Q_e \) is the conduction heat loss to the electrodes, \( Q_r \) is the heat loss due to radiation from the burned gas,

\[
E_b = \int_0^{m_b} edm = \int_0^{m_b} e_{bs} dm - E_{eb}
\]  

(10)

\( E_b \) is the energy of the burned gas, \( e_{bs} \) is the specific energy of isentropically compressed burned gas,

\[
E_{eb} = \int_0^{m_b} (e_{bs} - e)dm
\]  

(11)
$E_{eb}$ is the energy defect of the electrode boundary layer,

$$E_e = \int_{m_s}^m e \, dm = m(1 - x_h)e_{us} - E_{wb} - E_{ph}$$  \hspace{1cm} (12)$$

$E_u$ is the energy of the unburned gas, $e_{us}$ is the specific energy of isentropically compressed unburned gas,

$$E_{wb} = \int_{wb} (e_{us} - e) \, dm$$  \hspace{1cm} (13)$$

$E_{wb}$ is the energy defect of the wall boundary,

$$E_{ph} = \int_{ph} (e_{us} - e) \, dm$$  \hspace{1cm} (14)$$

$E_{ph}$ is the energy defect of the preheat layer.

Using the perfect gas relation

$$e - h_f = pv/(\gamma - 1)$$  \hspace{1cm} (15)$$

where $h_f$ is the specific enthalpy of formation of the gas at zero degrees Kelvin and $\gamma = c_p/c_v$ is the ratio of the constant pressure and constant volume specific heats, and assuming constant specific heats for the gases in the boundary layers and the preheat zone, the integrals in Eqs. 11, 13 and 14 may be evaluated approximately to give

$$E_{eb} = p \int_{eb} (v_{us} - v) \, dm / (\gamma_b - 1) = pV_{eb} / (\gamma_b - 1)$$  \hspace{1cm} (16)$$

$$E_{wb} = p \int_{wb} (v_{us} - v) \, dm / (\gamma_u - 1) = pV_{wb} / (\gamma_u - 1)$$  \hspace{1cm} (17)$$

$$E_{ph} = p \int_{ph} (v_{us} - v) \, dm / (\gamma_u - 1) = pV_{ph} / (\gamma_u - 1)$$  \hspace{1cm} (18)$$

A relationship between the wall heat transfer and the displacement volume for a gas subject to a time dependent pressure has been derived by Keck [54]. In the case of rapidly increasing pressure such as that occurring during constant volume combustion, the terms representing compression work on the boundary layer may be neglected and resulting equations are
\[ Q_e = pV_{eb}/(\gamma_b - 1) = E_{eb} \]  
\[ Q_w = pV_{wb}/(\gamma_u - 1) = E_{wb} \]

in which we have used Eqs. 16 and 17. Note that, to this approximation, the heat loss to the wall exactly equals the energy defect in the boundary layer. Substituting the relation \( dm = \rho dV \) into Eqs.5, 7 and 8 we obtain

\[ V_{eb} = 2\pi r_e r_b \delta_{eb} \] (21)  
\[ V_{wb} = 4\pi c^2 \delta_{wb} \] (22)  
\[ V_{ph} = 4\pi b^2 \delta_{ph} \] (23)

where \( r_e \) is the radius of the electrodes, \( r_b \) is the radius of the burned gas, \( r_c \) is the radius of the combustion chamber,

\[ \delta_{eb} = \int_0^b \int_0^\infty (\rho(r, \eta)/\rho_{bs} - 1) d\eta dr / r_b \] (24)

\( \delta_{eb} \) is the displacement thickness of the electrode boundary layer in which \( \eta \) is the radial distance from the electrode,

\[ \delta_{wb} = \int_{wb} (\rho(r)/\rho_{us} - 1)dr \] (25)

\( \delta_{wb} \) is the displacement thickness of the wall boundary layer, and

\[ \delta_{ph} = \int_{ph} (\rho(r)/\rho_{us} - 1)dr \] (26)

\( \delta_{ph} \) is the displacement thickness of the preheat zone. Using the approximation

\[ \int_{eb} (\rho(\eta, r)/\rho_{bs} - 1)d\eta = (\alpha_b (r_b - r)/\dot{r}_b)^{1/2} (T_b / T_w - 1) \] (27)

Eq. 24 can be integrated over \( r \) to give

\[ \delta_{eb} = (2/3)(\alpha_b r_b / \dot{r}_b)^{1/2} (T_b / T_w - 1) \] (28)

where \( \alpha_b \) is the thermal diffusivity of the burned gas, \( T_w \) is the wall temperature, and \( T_b \) is the burned gas temperature.

The wall boundary layer displacement thickness can be calculated using the expression
derived by Keck [54]

\[ \delta_{wb} = (\frac{\alpha_u \tau}{\pi})^{1/2} z^{-1/2} \int_0^z (z' - z'^{1/2}) \left( \int_{z'}^z z'' dz'' \right)^{-1/2} dz' \]  

(29)

where \( \alpha_u \) is the thermal diffusivity of the unburned gas, \( \tau \) is a characteristic burning time, \( y = t/\tau \) is the dimensionless time, and \( z = p/p_i \) is the dimensionless pressure. For combustion in closed chambers, the dimensionless pressure can be approximated by

\[ z = 1 + y^3 \]  

(30)

Substituting this expression in Eq. 29 we obtain

\[ \delta_{wb} \approx \left( \frac{\alpha_u \tau}{\pi} \right)^{1/2} \left( \frac{p_i}{p} \right)^{1/2} \left( \frac{p}{p_i} \right)^{(1-1/\gamma)} - 1 \]  

(31)

The displacement thickness of the preheat zone has been evaluated assuming an exponential temperature profile

\[ T / T_u \approx 1 + \frac{T_b}{T_u - 1} \exp(-\alpha_u (r - r_b) / \dot{r}_b) = \rho_{wb} / \rho(r) \]  

(32)

Substituting Eq. 32 into Eq. 26 we obtain

\[ \delta_{ph} = - \int_{p_h}^{p_b} \left( \frac{T_b}{T_u - 1} \right)^{-1} \exp(r - r_b) \dot{r}_b / \alpha_u + 1)^{-1} (r / r_b)^2 \]  

(33)

\[ r >> \alpha_u / \dot{r}_b, \]  

Eq. 33 can be integrated approximately to give

\[ \delta_{ph} \approx - (\alpha_u / \dot{r}_b) (T_b / T_u - 1) \ln(T_b / T_u) \]  

(34)

Note that the displacement thickness of the preheat zone is negative while those of the thermal boundary layers are positive.

The radiation heat loss from the burned gas was calculated using

\[ Q_r = \int_{0}^{t} \dot{Q}_r dt \]  

(35)

where

\[ \dot{Q}_r = \alpha_p V_b \sigma T_b^4 \]  

(36)

is the radiation rate, \( \alpha_p \) is the Planck mean absorption coefficient and \( \sigma \) is the Stefan-Boltzmann
Finally combining Eqs. 3, 4 and 6 gives
\[ \int_{0}^{x} (v_{bs} - v_{us}) dx = v_i - v_{us} + (V_{eb} + V_{wb} + V_{ph}) / m \]  
\hspace{2em} (37)

and combining Eqs. 9, 10, 12 and 18-20 gives
\[ \int_{0}^{x} (e_{bs} - e_{us}) dx = e_i - e_{us} + (pV_{ph} / (\gamma_u - 1) - Q_r) / m \]  
\hspace{2em} (38)

where \( v_i = (V_e - V_c) / m \) and \( e_i = E_i / m \) are the initial specific volume and energy of the unburned gas in the chamber.

Equations 37 and 38 contain the three unknowns \( p, x_b(p), \) and \( T_b(x_b) \). Given pressure, \( p(t) \), as a function of time, they can be solved numerically using the method of shells to obtain the burned mass fraction, \( x_b(t) \), as a function of time and the radial temperature distribution \( T(r,t) \). The mass burning rate, \( \dot{m}_b = \dot{m}_b \), can be obtained by numerical differentiation of \( x_b(t) \). The thermodynamic properties of the burned and unburned used in the calculations were obtained from the JANAF Tables [56].

If the specific heats of the burned and unburned gases are assumed constant, Eq. 15 can be used to evaluate the integral in Eq. 38 and we obtain
\[ p(v_{bs}/(\gamma_b - 1) - v_{us}/(\gamma_u - 1)) = h_{ub} + p(v_i - v_{us})/(\gamma_u - 1) + (pV_{ph}/(\gamma_u - 1) - Q_r) / m \]  
\hspace{2em} (39)

where \( h_{ub} = h_{fb} - h_{jfb} \) is the difference between the enthalpies of formation of the unburned and burned gas at zero degrees Kelvin. Equations 37 and 39 are identical to those previously derived by Metgalchi and Keck [37, 38] with correction for radiation heat loss, conduction heat loss to the electrodes, and the displacement thickness of the preheat zone added. Given the pressure, they can be solved analytically to obtain an excellent approximation for \( x_b \) and \( (RT)_{bs} = pV_{bs} \). However, they do not give the temperature distribution in the burned gas. It is of interest to note that if the small correction terms for the preheat zone and the heat loss to the electrode are neglected, \( x_b \) and \( (RT)_{bs} = pV_{bs} \) depend only on the pressure and are independent of the flame shape.
6.3.2. Burning Speed, Flame Speed and Gas Speed

For closed flames, the burning speed may be defined

$$ S_b = \frac{\dot{m}_b}{\rho_u A_b} \tag{40} $$

where $A_b$ is the area of a sphere having a volume equal to that of the burned gas. This expression is valid for smooth, cracked, or wrinkled flames of any shape. For smooth spherical flames

$$ \dot{m}_b = \rho_b \dot{V}_b + \rho_b A_b \dot{r}_b \tag{41} $$

where $\rho_b$ is the average value of the burned gas density.

Differentiating the mass balance equation

$$ m_b = m - \rho_u V_u = (\rho_u / \rho_b) \rho_b (V_c - V_e - V_b) \tag{42} $$

with respect to time and neglecting the small contribution from the derivative of $\rho_u / \rho_b$, we obtain

$$ \dot{m}_b = (\rho_u / \rho_b)((V_c - V_e - V_b) \dot{\rho}_b - \rho_b A_b \dot{r}_b) \tag{43} $$

where

$$ A_b = 4 \pi r_b^2 - 2 \pi r_e^2 \tag{44} $$

is area of the reaction zone, $r_e$ is the electrode radius and $r_b$ is given by the equation

$$ V_b = (\frac{4}{3}) \pi r_b^3 - 2 \pi r_e^2 r_b \tag{45} $$

Using Eq. 41 to eliminate $\dot{\rho}_b$ in Eq. 43, gives

$$ S_f = \dot{r}_b = S_b(\rho_u / \rho_b - y_b (\rho_u / \rho_b - 1)) \tag{46} $$

where $S_f$ is the flame speed and $y_b = V_b / (V_c - V_e)$ is the burned gas volume fraction. Note that for $y_b = 0$, $S_f = (\rho_u / \rho_b) S_b$ and for $y_b = 1$, $S_f = S_b$.

The gas speed is defined by

$$ u_g = S_f - S_b \tag{47} $$

Substituting Eq. 46 into Eq. 47 we obtain

$$ u_g = S_b (\rho_u / \rho_b - 1)(1 - y_b) \tag{48} $$

This completes the equations for the burning model.
6.4. Comparison of Experimental Data with Model Predictions

For comparison with experimental results, the burning speeds of steady laminar adiabatic one-dimensional pre-mixed methane/oxygen/diluent flames have been computed using the SANDIA PREMIX code [49], marketed by Reaction Design. A reaction mechanism involving 53 species and 325 elementary reactions was taken from GRI-Mech 3.0 [7]. This mechanism is optimized for burned gas temperatures from approximately 1000 to 2500 K, pressures from 10 Torr to 10 atm, and equivalence ratio from 0.1 to 5 [7]. It was chosen for the calculations because it has been widely used for laminar flame speed calculations.

The comparisons were made for a wide range of conditions spanning both the high and low temperature regimes. The conditions, under which significant cracking or wrinkling occurred, were observed and are reported. A mixture of 86 % N₂ and 14 % CO₂ is used for the extra diluent to simulate the molar mass and specific heat of the exhaust gas in internal combustion engines. Observations of the flame structure were carried out in the cylindrical chamber. Although this vessel is not spherical, the flame propagates spherically over 90 percent of the distance to the wall. Shadowgraph photographs of flame fronts for stoichiometric methane-air-diluent mixtures with initial pressure and temperature of 1.0 atm and 298 K are shown in Figure 2 for 0-15% diluent. In these photographs, the final pressure is approximately 5 times the initial pressure. It can be seen that at all conditions, the flame front is smooth and spherical except for a single crack near the top, extending between the electrodes. This suggests that cracking may be caused at least in part an interaction between the flame front and the electrodes.

The corresponding burning speeds along isentropes computed from the pressure rise in the spherical chamber are shown by the solid points in Figure 3. All the measured values are for smooth flames with large radii and therefore represent laminar adiabatic burning speeds. The solid lines show values calculated using PREMIX with GRI-Mech 3.0 kinetics. It can be seen that adding diluent decreases both the burning speed and the final pressure achieved in the vessel. The dependence of the flame speed on percentage of diluent is reproduced reasonable well by the PREMIX calculations but the absolute values are roughly the 10-15% higher than the measurements for all conditions. This is within the uncertainty of the rate constants used in the GRI kinetics and could probably be corrected by minor adjustments.

Shadowgraph photographs of flame fronts for stoichiometric methane-air-diluent
mixtures with initial pressure and temperature of 5 atm and 298 K are shown in Figure 4 for 0-15% diluent. For the mixtures with zero diluent shown in part a, cracking can be seen for p/p_i=1.03 while for p/p_i=1.4, the flame is cellular. Parts b-d show that adding diluent results in flames that are cracked but not cellular. As the percentage of diluent increases the degree of cracking decreases indicating a more stable flame front. For 15% diluent, buoyant rise of the very slow flame can be observed.

Figure 5 shows the measured burning speeds corresponding to Fig 4. Solid symbols refer to cracked flames and open symbols to cellular flames. The results of PREMIX calculations are shown by the solid lines. Again as the percentage of diluent increases the burning speed decreases. It can be seen that the agreement between measured values and PREMIX calculations is reasonably good for cracked flames with 0-15% diluent. However for cellular flames with zero diluent, the measured burning speeds are substantially higher than PREMIX calculations. This may be due to an increased effective burning area for cellular flames.

Shadowgraphs of lean methane-air-diluent flames with equivalence ratio \( \varphi = 0.8 \) and initial pressure and temperature of 5 atm. and 298 K are shown in Fig. 6 for 0-15% diluent. All the flames in this figure show some cracks. Parts a-b show that for 0-5% diluent, cells appear on the flame surface at the highest pressure ratios. Parts c-d show buoyant rise and distortion of the slow flames with 10-15% diluent. Ionization probes mounted flush with the wall at the top and bottom of the chamber were used to check the degree of distortion and buoyant rise rate. Within the estimated experimental error of 5%, the burning areas for distorted flames determined from the shadowgraphs were equal to those calculated from the pressure data for spherical flame of the same volume. This shows that distortion of the flame front can be quite large before the expected increase in flame area becomes observable.

Figure 7 shows a comparison of the measured burning speeds with PREMIX calculations for the lean flames shown in Fig. 6. Cracked flames are shown by solid symbols and cellular flames by hollow symbols. PREMIX calculations are shown by solid lines. As previously seen in Fig 5, the measured burning speed for the cellular flames observed for 0% and 5% diluent are higher and have larger temperature coefficients than those calculated using PREMIX. For cracked flames at 0-5% diluent, the measured burning speeds agree fairly well in magnitude with PREMIX calculations but have a larger temperature coefficient. As the diluent is increased to 10-15%, the measured burning speeds drop below the PREMIX values.
Shadowgraphs of flame propagation for rich methane-air-diluent mixtures with equivalence ratio $\phi = 1.2$ and initial pressure and temperature of 5 atm and 298 K are shown in Figure 8 for 0-10% diluent. For all diluent fractions, the flames are smooth with very few cracks but some distortion and buoyant rise apparent for slow flames.

The measured burning speeds of these flames are compared with PREMIX calculations in Figure 9. It can be seen that the measured burning speeds are significantly lower than the PREMIX values for all diluent fractions. Since these flames are smooth, this indicates a failure of the GRI-Mech 3.0 kinetics as anticipated for high pressure rich flames. Other investigators [57, 58] have also observed similar discrepancies between measured burning speeds and calculations using GRI-Mech 3.0 kinetics at high pressures. The most probable reason for the discrepancy is the omission of reactions involving alkyl peroxides from GRI-Mech 3.0 kinetics.

Corrections for radiation heat loss from the burned gas and conduction heat losses to the electrodes and combustion chamber wall have all been included in the model used to calculate the burning speeds from the pressure records and were less than 2% for all cases considered. The corrections curvature and stretch associated with the preheat zone displacement volume were less than 1% for flames with radii greater than 1 cm.

Acknowledgements

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Figure 1. Schematic of the combustion chamber showing the flame geometry and the assumed radial temperature profile.
Figure 2. Shadowgraphs showing flame propagation in the cylindrical chamber for stoichiometric methane-air-diluent mixtures at several diluent fractions and $\varphi=1.0$, $p_i=1.0$ atm, and $T_i=298$ K.
Figure 3. Comparison of measured burning speeds along isentropes with PREMIX calculations for the same conditions as Fig. 2.
Figure 4. Shadowgraphs showing flame propagation in the cylindrical chamber for stoichiometric methane-air-diluent mixtures at several diluent fractions and $\varphi=1.0$, $p_i=5.0$ atm, and $T_i=298$ K.
Figure 5. Comparison of measured burning speeds along isentropes with PREMIX calculations for the same conditions as Fig. 4.
<table>
<thead>
<tr>
<th>Dilution (%)</th>
<th>Time (msec)</th>
<th>Pressure Ratio ($p/p_i$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0%</td>
<td>20</td>
<td>1.0</td>
</tr>
<tr>
<td></td>
<td>30</td>
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<td></td>
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</table>

Figure 6. Shadowgraphs showing flame propagation in the cylindrical chamber for lean methane-air-diluent mixtures at several diluent fractions and $\varphi=0.8$, $p_i=5.0$ atm, and $T_i=298$ K.
Figure 7. Comparison of measured burning speeds along isentropes with PREMIX calculations for the same conditions as Fig. 6.
Figure 8. Shadowgraphs showing flame propagation in the cylindrical chamber for rich methane-air-diluent mixtures at several diluent fractions and $\varphi=1.2$, $p_i=5.0$ atm, and $T_i=298$ K.
Figure 9. Comparison of measured burning speeds along isentropes with PREMIX calculations for the same conditions as Fig. 8.

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Abstract

Jet propellant 8 (JP-8)/air laminar burning speed was experimentally measured and its flame structure was studied at high temperatures and pressures using a high-speed camera. The experimental facilities included a spherical vessel, used for the measurement of burning speed, and a cylindrical vessel, used in a shadowgraph system to study flame shape and structure, and to measure burning speed. A thermodynamic model was developed to calculate burning speeds using dynamic pressure rise in the vessel due to combustion process. The model considers a central burned gas core of variable temperature surrounded by reaction sheet, unburned gas shell with uniform temperature and thermal boundary layers at the wall and electrodes. Radiation from burned gases to the walls was also included in the model. Burning speeds of laminar flames of JP-8/air were calculated for a wide range of conditions. Power law correlation was developed at temperatures ranging from 500-700 K, pressures of 1-6 atm and equivalence ratios of 0.8-1. Flame structure and cell formations were observed using an optical system. Experimental results showed that pressure and fuel air equivalence ratio have great influence on flame structure.

Keywords: JP-8, Laminar burning speed, flame structure, aviation fuels

7.1. Introduction

The United States Army and Air Force use JP-8 and Jet A-1 fuels as the main sources of energy for military land vehicles and aircraft [1, 2]. The North Atlantic Treaty Organization (NATO) has decided to use the same fuels in all battlefields under the ‘Single Fuel Concept’ [2, 3]. JP-8 and Jet A-1 have similar chemical structures because JP-8 is formed from Jet A-1 using some special additives to improve thermal stability characteristics [4]. JP-8 can be used as an alternative for diesel fuel because of their similar thermal and chemical properties. Due to its acceptable thermal stability parameters, its low freezing point of < -60 °C, and its dual application as both a coolant and an energy source, JP-8 is widely applied to aircraft engines and gas-turbines [1].

JP-8 is a complex chemical component composed of aromatics, n-paraffins, and cycloparaffins [2, 5-6]. This complex component makes it difficult to develop any chemical kinetics mechanism for this fuel. Some researchers try to identify surrogates for JP-8 with similar thermo-physical and thermo-chemical properties [5-7]. Validation of the developed chemical kinetics mechanism requires some reliable experimental data. Laminar burning speed is
one of the fundamental properties of every fuel which can be used to validate theoretical models. It can also be used to correlate turbulent burning speeds. Laminar burning speed is strongly affected by mixture characteristics such as equivalence ratio and diluent type, and operational conditions such as temperature and pressure. Depending on the experimental facilities and design, there are various methods for measurement of laminar burning speed [8-15]. The flexibility of system to measure the laminar burning speeds at high temperatures and pressures is very important.

Ji and co-workers [16] have measured the laminar burning speed of JP-8/air mixture at atmospheric pressure, temperature of 403 K, and various equivalence ratios using an atmospheric counter flow flame. They have also measured the laminar burning speeds of some other heavy hydrocarbons and have compared those with JP-8 laminar burning speeds. However, there are no published data about burning speed of JP-8 under conditions of combined high temperatures, high pressures, and varying equivalence ratios. In this study the laminar burning speed of JP-8 has been measured at high temperatures and pressures. A thermodynamic model, , described in section 4, using the I the pressure rise method has been employed [17-19]. A shadowgraph optical system was used to observe the shape of the flames and ensure that they were laminar. Finally, a correlation was developed for laminar burning speeds of JP-8/air as a function of temperature, pressure, and equivalence ratio.

7.2. Experimental Facility

The experimental system includes a spherical chamber and a cylindrical vessel. Both the spherical and cylindrical vessels were used to measure pressure rise caused by the combustion process. The cylindrical vessel withstands a maximum pressure of 50 atmospheres, due to having two end large windows, while the spherical vessel was used for maximum pressure of 425 atmospheres. The cylindrical vessel was used in a shadowgraph system which took pictures of flame propagation. Both vessels were filled using a control system composed of valves, pipes connected to the air, and a vacuum pump. Liquid fuel was stored in a liquid fuel reservoir which was attached to a liquid fuel manifold. The liquid fuel manifold was equipped with two Cartridge heaters to evaporate the liquid fuel. The liquid fuel was heated to evaporate completely before entering the combustion chamber. The initial temperature of the liquid fuel manifold was equal to the initial temperature of the combustion chamber. Ionization probes, screwed into the inner walls, were used to determine flame arrival time to vessel walls. A data acquisition system was
used to capture the pressure-time data as well as the signals from the ionization probes. A computer driven system has been used to make the mixture with required fuel and oxidizer and to initiate the combustion process. Figure 1 shows a schematic of the experimental system.

**Spherical Vessel:** The spherical vessel was constructed from two hemispheres, bolted together to form a sphere with a diameter of 15.24 cm. The hemispheres were constructed from 4140 steel with a thickness of 2.54 cm to withstand internal pressures up to 425 atm. The vessel was filled and evacuated through a 6 mm tube on its bottom. The vessel was fitted with two extended spark plug electrodes which provided a central point ignition source for the chamber. The ignition energy was fixed on 15 mJ. The chamber was also fitted with a piezoelectric pressure transducer, two thermocouples for measuring internal temperature and outer wall temperature, and three ionization probes which detected when the flame had reached the wall. The entire vessel was contained in a large oven capable of elevating the vessel temperature to ~500K.

**Cylindrical Vessel:** The cylindrical vessel was constructed from 316 SS and measures 13.5 cm in diameter and is 13 cm long. The vessel is fitted with 3.5 cm thick Fused silica windows at both ends which are sealed to the chamber with o-rings. The windows allow the vessel to operate to a pressure of 50 atm. The purpose of the windows is to provide a clear line of sight through the vessel for a shadowgraph setup that allows real time recording of the combustion event. The vessel is also fitted with band heaters which allow the vessel to be heated to a temperature of 500K. The vessel is fitted with spark plugs that allow for central point ignition, similar to the sphere’s, and thermocouples that measure the internal temperature of the chamber and the temperature of the vessel walls.

**Shadowgraph system:** Figure 2 presents the layout of the shadowgraph system. The shadowgraph system is setup with the cylindrical vessel to take optical recording of the combustion event. A CMOS camera with the capability of taking pictures up to 40,000 frames per second has been used for these experiments. The shadowgraph setup consists of 5 components which are shown in Figure 2. Starting from the light source, a pinpoint source of light is captured by a spherical mirror 152.4 cm away which reflects the light in a 15.24 cm circular beam which travels through the combustion vessel to the opposite spherical mirror. Once the circular pattern hits this second mirror it is again focused into a pin point 152.4 cm away onto the CMOS camera. The image that the camera receives with the shadowgraph system is very sensitive to density variation in places and allows us too see the changes in density of the
mixture as the combustion takes place.

The goal of these experiments was to study the structure of JP-8 premixed flames and to find the affective parameters of the burning speed of the JP-8/air mixtures. Each experiment was performed at least three times at each operational condition. According to statistical methods, three identical runs are sufficient in order to ensure that the confidence level of the experiment is above 95% [20]. Experiments at each operational condition were performed using both vessels. First, the experiments were performed using the cylindrical vessel to observe the shape and structure of the flame. Next, by qualitative understanding of flame treatment, the same experiments were done in the spherical chamber to measure the burning speed. Two goals were pursued by doing this procedure: 1- study of the effect of different parameters which create turbulization and cellularity of the laminar flames, 2- measurement of burning speed based on laminar cases. It must be noted that the pressure and temperature of the mixture is independent from the shape of the vessel. Figure 3 shows the comparison between the pressure data of cylindrical and spherical vessel. It can be seen that as long as the flame has not reached the cylinder vessel, pressure data are identical. In this figure it can be seen that the pressure of the mixture in the cylindrical vessel decreases faster than the spherical one after reaching the wall. This is due to energy transfer effects after touching the wall.

JP-8 is a blend of several components. The percentage and distribution of these components depend on the refining process and other technical operational conditions which are beyond the scope of this paper. More information about the manufacturing processes and types of this fuel can be found in literature [21]. JP-8 fuel used in this research was JP-8-4658, which is a mixture of Jet fuel and JP-8 additives: it was made in the Air Force Research laboratory. Table 1 shows the general properties of this fuel.

One of the important and challenging issues in the combustion of JP-8 is the initial temperature of experiments. The initial temperature must be close enough to the boiling point of the fuel to ensure that at least 90% of the fuel has been evaporated. It must be noted that JP-8 is a blend and improper evaporation will make serious errors in equivalence ratio of the mixture. Based on the information provided in Table 1, the initial temperatures of combustion chamber and liquid fuel manifold were constant at about 500 K. According to the distillation curves of JP-8, at this temperature at least 90% of the fuel was vaporized and the desired mixture was obtained.
7.3. Flame Structure

Experiments were made in the cylindrical vessel to study flame structure for a wide range of conditions. In these experiments, the variable parameters were equivalence ratio and initial pressure of the mixture. The equivalence ratio was varied from 0.8 to 1 and initial pressures were in the range of 1-3 atm. Figures 4 shows a series of snapshots of JP-8/air flames for fuel-air equivalence ratio of 0.8 and initial pressures of 1, 2 and 3 atmospheres. It can be seen that flame becomes cellular as pressure increases. Figures 5 and 6 present the same type of information for fuel-air equivalence ratio of 0.9 and 1. Two major results are observed in the pictures: 1- instability, and ultimately turbulence, originates from cells in the flame which form with increasing pressure; 2- cell formation develops earlier as the mixture becomes richer. There are some disturbances from the electrodes causing cracks which grow by propagating the flame. The cracks impose a slight deformation on flame but the instability associated with small cells on the flame appears suddenly in a certain pressure and radius. The cells appear simultaneously and cover whole surface of the flame. The reason for cell formation and instability are due to hydrodynamic and thermo-diffusive effects which are beyond the scope of this paper. Table 2 summarizes the cell formation pressures and temperatures of JP-8/air mixtures at various initial pressures and equivalence ratios. These parameters quantify the conditions at which cells are appeared on all parts of the flame. It is seen in Table 2 that cell formation strongly depends on the pressure and equivalence ratio. The cellularity pressure of the mixtures is in the same order for different initial pressures. For \( \phi = 0.8 \) cellularity pressure is about 6.1 atm, for \( \phi = 0.9 \) it is in the range of 4.8-5 atm, and for \( \phi = 1 \) it is in the range of 4-4.2 atm. Figure 7 shows the results of Table 2. These results demonstrate the importance of pressure in cell formation of premixed flames. Initial pressure does not affect critical pressure (\( P_{cr} \)) at which the flame becomes cellular. The reasons for these behaviors are the subjects of instability analyses in spherical premixed flames which are beyond the scope of this paper, however more details can be found in other works [22-25].

Since it is assumed that the unburned gas is compressed isentropically, the cell formation temperature can be calculated by the following expression:

\[
T_{cr} = T_i \left( \frac{P_{cr}}{P_i} \right)^{\frac{y-1}{y}}
\]  

(1)
Where $T_{cr}$ and $P_{cr}$ are the critical temperature and pressures of which cell formation begins, $T_i$ and $P_i$ are the initial temperature and pressure and $\gamma$ is the ratio of the specific heat at constant pressure to the specific heat at constant volume. Both of the specific heat terms are a function of temperature. While initial pressure is not significant, a critical pressure of cell formation exists for each equivalence ratio. Another conclusion is that the cell formation pressure increases as the mixture becomes leaner.

7.4. Burning Model

The theoretical model used to calculate the burning speed from the pressure rise is based on one previously developed by Metghalchi and co-workers [9]. The model has been modified to include corrections for energy losses due to the electrodes, radiation from the burned gas to the wall, and the temperature gradient in the preheat zone. It is assumed that the gases in the combustion chamber can be divided into burned and unburned gas regions separated by a reaction layer of negligible thickness. The burned gas in the center of chamber is divided into $n$ number of shells, where the number of shells is proportional to the combustion duration. The burned gas temperature of each shell is different but all burned gases are in chemical equilibrium with each other. The burned gases are surrounded by a preheat zone ($\delta_{ph}$) having variable temperature, which is itself surrounded by unburned gases. A thermal boundary layer ($\delta_{bl}$) separates the unburned gas from the wall. The effect of energy transfer from burned gas to the spark electrodes is considered by a thermal boundary layer ($\delta_{bl}$). Figure 8 shows a schematic of the model used in this work.

7.4.1. Governing Equations

The distribution of temperature in burned and unburned gas region can be achieved by equation of state

$$pv = RT$$  \hspace{1cm} (2)

In this equation $p$ is the pressure which is measured within the chamber, $v$ is the specific volume, $R$ is the specific gas constant and $T$ is the temperature.

The mass conservation equation for the burned and unburned gas region is:

$$m = m_b + m_u = \bar{\rho}_b V_b + \bar{\rho}_u V_u = \frac{p_i (V_c - V_e)}{RT_i}$$  \hspace{1cm} (3)
where $m$ is the total mass of the chamber, $m_b$ is the mass of the burned gas zone; $m_u$ is the mass of the unburned gas zone. $V_c$ is the volume of the chamber and $V_e$ is the volume of the spark electrodes. In this equation, $i$ denotes the initial conditions, and $u$ and $b$ denote the unburned and burned gas conditions, respectively. $\bar{\rho}$ is the average density and $V$ is the volume of the gas.

The total volume of the gas in the combustion chamber is

$$V_i = V_c - V_e = V_b + V_u$$

where

$$V_b = \int_0^{m_b} v'(T', p) \, dm' = \int_0^{m_b} v_{bs}'(T', p) \, dm' - V_{eb}$$

is the volume of the burned gas, $v_{bs}$ is the specific volume of the isentropically compressed burned gas,

$$V_{eb} = \int_{eb} (v_{bs}' - v') \, dm'$$

is the displacement volume of the electrode boundary layers,

$$V_u = \int_{m_u}^{m} v'(T', p) \, dm' = m(1 - x_b)v_{us} - V_{wb} - V_{ph}$$

is the volume of the unburned gas, $x_b = m_b/m$ is the burned gas mass fraction, $v_{us}$ is the specific volume of the isentropically compressed unburned gas,

$$V_{wb} = \int_{wb} (v_{us}' - v') \, dm'$$

is the displacement volume of the wall boundary layer,

$$V_{ph} = \int_{ph} (v_{us}' - v') \, dm'$$

is the displacement volume of the preheat zone ahead of the reaction layer.

The energy conservation equation is

$$E_i - Q_e - Q_w - Q_r = E_b + E_u$$

where $E_i$ is the initial energy of the gas, $Q_e$ is the conductive energy loss to the electrodes, $Q_w$ is the energy loss to the wall, $Q_r$ is the radiation energy loss,
\[ E_b = \int_0^{mb} e'(T', p) \, dm' = \int_0^{mb} e_{bs}'(T', p) \, dm' - E_{eb} \]  \hspace{1cm} (11)

is the energy of the burned gas, \( e_{bs} \) is the specific energy of isentropically compressed burned gas,

\[ E_{eb} = \int_{eb} (e_{bs}' - e') \, dm' \]  \hspace{1cm} (12)

is the energy defect of the electrode boundary layer,

\[ E_u = \int_{mb}^{m} e'(T', p) \, dm' = m(l - x_b)e_{us} - (E_{wb} + E_{ph}) \]  \hspace{1cm} (13)

is the energy of the unburned gas, \( e_{us} \) is the specific energy of the isentropically compressed unburned gas,

\[ E_{wb} = \int_{wb} (e_{us}' - e') \, dm' \]  \hspace{1cm} (14)

is the energy defect of the wall boundary,

\[ E_{ph} = \int_{ph} (e_{us}' - e') \, dm' \]  \hspace{1cm} (15)

is the energy defect of the preheat layer.

Using ideal gas assumptions

\[ e - h_f = pv/(\gamma - 1) \]  \hspace{1cm} (16)

where \( h_f \) is the enthalpy of formation of the gas at zero degrees Kelvin and \( \gamma = c_p/c_v \) is the specific heat ratio. By this relation equations 12, 14, and 15 can be written as

\[ E_{eb} = p \int_{eb} (v_{bs}' - v') \, dm' / (\gamma_b - 1) = pV_{eb} / (\gamma_b - 1) \]  \hspace{1cm} (17)

\[ E_{wb} = p \int_{wb} (v_{us}' - v') \, dm' / (\gamma_u - 1) = pV_{wb} / (\gamma_u - 1) \]  \hspace{1cm} (18)

\[ E_{ph} = p \int_{ph} (v_{us}' - v') \, dm' / (\gamma_u - 1) = pV_{ph} / (\gamma_u - 1) \]  \hspace{1cm} (19)

It was shown in [18] that in the case of rapid compression such as constant volume combustion, the compression work terms on the boundary layer may be neglected and the resulting equations
The radiation energy loss from the burned gas was calculated using

\[ Q_r = \int_0^t \dot{Q}_r(t') \, dt' = 4\alpha_p V_b \sigma T_b^4 \]

where \( \alpha_p \) is the Planck mean absorption coefficient and \( \sigma \) is the Stefan-Boltzman constant.

Finally, combining equations 4, 5, and 7 gives

\[ \int_0^v (v_x(T', p) - v_{xs}) \, dx' = v_i - v_{xs} + (V_e + V_w + V_{ph}) / m \]  

and combining equations 10, 11, and 13 gives

\[ \int_0^v (e_m(T', p) - e_{xs}) \, dx' = e_i - e_{xs} + (pV_e / (\gamma - 1) - Q) / m \]  

The above equations have been solved for two unknowns: burned mass fraction, \( x_b(t) \) and the burned gas temperature of the last layer, \( T_b(r, t) \). Given pressure, \( p(t) \) as a function of time, they can be solved numerically using the method of shells to obtain the burned mass fraction, as a function of time and temperature distribution.

Ultimately, the burning speed may be defined as

\[ S_b = \dot{m}_b / \rho_u A_b = \dot{m} \dot{x}_b / \rho_u A_b \]

where \( A_b \) is the area of a sphere having a volume equal to that of the burned gas. More details about the model can be found in [17-19, and 26].

7.5. Laminar Burning Speeds

All reported data are in regions where \( r/R > 0.4 \) (\( r \) and \( R \) are the radii of flame and chamber respectively). In these regions the effects of stretch and spark discharge are very low. Spark discharge creates a shock wave followed by an extremely high temperature region. It affects the initial flame kernel propagation speed strikingly but as soon as the temperature of the hot core
drops and flame is large enough \((r/R > 0.25)\) these effects are vanished [27 and 28]. Figures 9 and 10 show the laminar burning speed at three different equivalence ratios, initial temperature of 500 K and initial pressures of 1 and 2 atm, respectively. As expected, by increasing the equivalence ratio, laminar burning speed increases. Burning speed curves are plotted versus unburned gas temperature on isentropic lines and it is seen that at higher temperatures, laminar burning speed is increased. The oscillations observed in these figures are due to the acoustic oscillations inside the chamber.

The measured laminar burning speed data have been fitted to the following power law correlation

\[
S_u = S_{uo} \left(1 + a_1(1 - \phi) + a_2(1 - \phi)^2 \right) \left(\frac{T_u}{T_{uo}}\right)^\alpha \left(\frac{P}{P_o}\right)^\beta
\]

(26)

where \(S_{uo}\) is the burning speed at reference point \((P_o = 1\ atm, T_{uo} = 500\ K\ and \phi = 1)\). \(\phi\) is the mixture equivalence ratio, \(T_u\) is the unburned gas temperature in K, \(T_{uo}\) is the reference temperature and equal to 500 K, \(P\) is the mixture pressure in atm and \(P_o\) is the reference pressure and equal to 1 atm. \(a_1, a_2, \alpha\) and \(\beta\) are constant. Using a nonlinear least square method the values are \(S_{uo} = 93.6 \ cm/s, a_1 = -0.22, a_2 = -4.4, \alpha = 2.13\) and \(\beta = -0.18\). The negative pressure exponent -0.18 results in an overall order of reaction of less than two for the combustion process, which is consistent with general understanding.

This correlation is only for laminar burning speed of JP-8-air flames. It is valid in the pressure range of \(1 < P < P_{cr}\), temperature range of \(500 < T_u < T_{cr}\) and equivalence ratio range of \(0.8 < \phi < 1.0\). \(P_{cr}\) can be found from Table 2 and \(T_{cr}\) can be calculated from equation 1. Figure 11 shows the burned mass fraction rate \((\dot{x_b}(t))\) of JP-8/air mixtures at initial pressure of 5 atm and initial temperature of 500 K in three different equivalence ratios. According to Table 2, all of the presented data in this figure belongs to cellular flames. The data demonstrates that in early stages the slope is linear but as pressure increases the slope becomes non-linear. This trend is more obvious at equivalence ratio of 1. At higher pressures, more cells are formed. These cells increase the surface the flame, which increases mass burning rate.

Acknowledgement

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References


Mixtures. Combustion Science and Technology 2006; 178:975-1000(26)


Table 1: Cell formation analysis of JP-8/air mixtures

<table>
<thead>
<tr>
<th>Property</th>
<th>Results</th>
</tr>
</thead>
<tbody>
<tr>
<td>Distillation</td>
<td>320</td>
</tr>
<tr>
<td>Initial boiling point (K)</td>
<td>426</td>
</tr>
<tr>
<td>10% recovered (K)</td>
<td>435</td>
</tr>
<tr>
<td>20% recovered (K)</td>
<td>450</td>
</tr>
<tr>
<td>50% recovered (K)</td>
<td>481</td>
</tr>
<tr>
<td>90% recovered (K)</td>
<td>498</td>
</tr>
<tr>
<td>Final boiling point (K)</td>
<td></td>
</tr>
<tr>
<td>Flash point (K)</td>
<td>311</td>
</tr>
<tr>
<td>Density (kg/L)</td>
<td>0.81</td>
</tr>
<tr>
<td>Viscosity (mm²/s @253 K)</td>
<td>2.12</td>
</tr>
<tr>
<td>Heat Value, heat of combustion: (MJ/kg)</td>
<td>42.79</td>
</tr>
</tbody>
</table>
Table 2: Cell formation analysis of JP-8/air mixtures

<table>
<thead>
<tr>
<th>$\phi$</th>
<th>$P_1 = 1$ atm</th>
<th>$P_1 = 2$ atm</th>
<th>$P_1 = 3$ atm</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.8</td>
<td>Non-cellular</td>
<td>Non-cellular</td>
<td>$P_{cr} \sim 6.1$ atm</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>$T_{cr} \sim 587$ K</td>
</tr>
<tr>
<td>0.9</td>
<td>$P_{cr} \sim 4.7$ atm</td>
<td>$P_{cr} \sim 5.1$ atm</td>
<td>$P_{cr} \sim 4.8$ atm</td>
</tr>
<tr>
<td></td>
<td>$T_{cr} \sim 705$ K</td>
<td>$T_{cr} \sim 614$ K</td>
<td>$T_{cr} \sim 554$ K</td>
</tr>
<tr>
<td>1</td>
<td>$P_{cr} \sim 4.2$ atm</td>
<td>$P_{cr} \sim 4.05$ atm</td>
<td>$P_{cr} \sim 4.1$ atm</td>
</tr>
<tr>
<td></td>
<td>$T_{cr} \sim 690$ K</td>
<td>$T_{cr} \sim 583$ K</td>
<td>$T_{cr} \sim 534$ K</td>
</tr>
</tbody>
</table>
Figure 1: Schematic Diagram of Experimental Facilities
Figure 2: Sketch of the Shadowgraph System
Figure 3: Comparison between the pressure data of JP-8/air mixture in cylindrical and spherical vessels, $\phi = 0.8$, $T_i = 500$ K, $P_i = 5$ atm
Figure 4: JP-8/air mixture $\phi = 0.8$, $T_i = 500$ K,
Figure 5: JP-8/air mixture $\phi = 0.9$, $T_i=500$ K,
Figure 6: JP-8/air mixture $\phi = 1$, $T_i=500$ K,
Figure 7: Cell formation pressures of JP-8/air mixtures at various initial pressures and equivalence ratios, $T_i = 500$ K,
Figure 8: Schematic of different zones and their corresponding temperatures in the thermodynamics model
Figure 9: Laminar burning speeds of JP-8/air mixture at $T_i = 500$ K, $P_i = 1$ atm, and equivalence ratios of 0.8, 0.9 and 1
Figure 10: Laminar burning speeds of JP-8/air mixture at $T_i = 500$ K, $P_i = 2$ atm, and equivalence ratios of 0.8, 0.9 and 1.
Figure 11: Burned mass burning rate of JP-8/air mixture at $T_i = 500$ K, $P_i = 5$ atm, and equivalence ratios of 0.8, 0.9 and 1

Submitted to Fuel

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Abstract

Experimental studies have been performed to investigate the flame structure and laminar burning speed of JP-8/oxidizer/diluent premixed flames at high temperatures and pressures. Three different diluents including argon, helium, and a mixture of 14\% CO\textsubscript{2} and 86\% N\textsubscript{2}, were used. The experiments were carried out in two constant volume spherical and cylindrical vessels. Laminar burning speeds were measured using a thermodynamics model based on the pressure rise method. Temperatures from 493-680 K and pressures from 1-10 atm were investigated. Extra diluent gases (EDG) decrease the laminar burning speeds but do not greatly impact the stability of the flame compared with JP-8/air. Replacing nitrogen in the air with argon and helium increases the range of temperature and pressure in the experiments. Helium as a diluent also increases the temperature and pressure range of stable flame as well as the laminar burning speed. Power law correlations have been developed for laminar burning speeds of JP-8/air/EDG and JP-8/oxygen/helium mixtures at a temperature range of 493-680 K and a pressure range of 1-10 atm for lean mixtures.

Keywords: JP-8, laminar burning speed, combustion instability, diluent

8.1. Introduction

Jet Propellant-8 (JP-8) is a fuel currently used in land based engines and aviation combustors. It
would be beneficial to extend the application of this fuel under the framework of the “Single Fuel Concept” [1]. There are several theoretical studies underway to develop the chemical kinetics mechanism of this complex fuel. Validation of these mechanisms requires reliable, highly accurate experimental data. These experimental data should be available in a wide range of temperatures, pressures and equivalence ratios. Laminar burning speed, which is a fundamental property of each fuel, can be used to provide experimental data for chemical kinetics mechanisms. It is also used for the correlation of turbulent flame propagation in internal combustion engines. Currently some experimental and theoretical data exists in the literature about the laminar burning speeds of JP-8 fuel at atmospheric pressures and high temperatures [2-4]. Ji et al [2] measured the laminar burning speed at a temperature of 403 K and atmospheric pressure. They used a counter-flow flame experimental facility to estimate the laminar burning speeds after stretch corrections. Kumar et al [3] measured the laminar burning speeds of Jet-A fuels and other heavy hydrocarbons at a temperature of 470 K and atmospheric pressure by a counterflow flame similar to Ji et al. These data are reported in a limited range of temperatures and pressures. In most combustors, such as internal combustion engines, fuel is burned at high temperatures and pressures, therefore the measurement of laminar burning speeds under those conditions is essential.

Eisazadeh-Far et al [5] measured the laminar burning speeds of JP-8/air mixtures at a temperature range of 500-700 K, pressures of 1-6 atm and equivalence ratios of 0.8-1. They concluded that JP-8/air flames are sensitive to instability at high temperatures and richer mixtures. Burning speeds for smooth flames were measured by the pressure rise method and a power law fit correlation for laminar burning speed calculation was developed.

This paper investigates the effect of diluent type on the stability and laminar burning speeds of JP-8/air/EDG and JP-8/oxygen/(argon, helium) flames. The effect of EDG addition to JP-8/air/EDG on flame structure will be studied in a wide range of temperatures, pressures and equivalence ratios. Following the flame structure study, laminar burning speeds of JP-8/air/EDG and JP-8/oxygen/helium will be reported at temperatures of (493-680 K) and higher pressures (1-10 atm) compared to previously published results for JP-8/air flames [5].

8.2. Experimental Facility

Experiments have been performed using two constant volume cylindrical and spherical vessels.
Figure 1 shows the general configuration of the experimental set up. The cylindrical vessel is located in a shadowgraph system to take snapshots of flame propagation. It is equipped with two end windows, which can withstand pressures and initial temperatures up to 50 atm and 500 K respectively. The images are taken using a CMOS camera capable of taking pictures up to 40,000 frames per second. Figure 2 shows the configuration of the shadowgraph system. The spherical vessel is made of stainless steel which can withstand pressures up to 400 atm. It is located in an oven which can heat up the vessel to 500 K. Both vessels are used for laminar burning speed measurements. More information about the experimental facilities and procedure of the tests can be found in previous publications [5-7].

8.2.1. Vapor pressures and Temperatures

JP-8 is a blend of several chemical components. Setting up the proper initial temperature close to the boiling temperature is essential. A VARIAN CP-3800 Gas-Chromatography system was used to detect several analytes in JP-8 fuel. A chromatograph of gaseous JP-8 fuel is shown in Figure 3. It can be seen that C_{10}, C_{11}, and C_{12} are the dominant components of the mixture, which is in agreement with the observation of other researchers [8, 9]. The boiling temperature of JP-8 fuel should be close to that of the C_{10} and C_{11} hydrocarbons. The distillation, boiling point and other properties of the applied JP-8 fuel are presented in Table 1. The fuel used in this study has been provided by Air Force Research Laboratory (AFRL). The initial temperatures for all experiments have been fixed at a constant temperature of 493 K at which the liquid fuel is vaporized completely.

8.2.2. Fuel Cracking at High Temperatures

In both the cylindrical and spherical vessels the temperature of the unburned gases increases due to the propagating flame acting as a piston. In our experiments the temperature range is approximately 500-700 K. Thermal cracking of the fuel can cause serious errors in the burning speed results, thus it is necessary to determine if there is any thermal cracking of the fuel in this range. Edwards [10] has done several studies on the cracking and deposition of hydrocarbon aviation fuels. An important part of his research concerns the endothermicity of the thermal cracking process of hydrocarbons. He has concluded that for most of these endothermic hydrocarbons, including JP-8, the thermal cracking temperature roughly begins at 750-810 K. The thermal cracking process also depends on pressure which is intensified in higher pressures.
The important factor in the thermal cracking process is the residence time, which defines the degree of equilibrium composition of the mixture. The fuel residence times in this study are defined by the combustion process and it are short enough to ensure that cracking will not occur [5, 12-13]. Also, the range of temperatures and pressures in this paper never exceed the critical cracking temperatures and pressures expressed in literature [10, 14-15].

8.3. Experimental Results and Discussion

8.3.1. Experiments with Air and EDG

Experiments with EDG have been performed with volumetric percentages of 5% and 10%. Initial conditions were fixed at an initial temperature of 493 K, initial pressures of 1, 2, and 3 atm and equivalence ratios of 0.8, 0.9 and 1. Table 2 shows the initial conditions of the experiments. The first set of experiments was carried out in the cylindrical vessel to investigate flame structure. All pictures were taken by CMOS camera at 10,000 frames per second with a high resolution. Figure 4 shows the snapshots of stoichiometric JP-8/air mixtures without EDG with three different initial pressures. The first observation is that for lean JP-8/air mixtures increasing the equivalence ratio and pressure enhances the instability. There are some cracks on the flame around the electrodes which are due to the disturbances from the spark electrodes and which develop as the flame grows. However, smaller cells appear afterwards simultaneously all over the flame surface at critical radii.

Flame instability originates from the disturbances imposed into the flame by various sources such as spark, interactions with electrodes, density gradient, stoichiometry gradient in the mixture, etc.. These disturbances are unstable if their growth rate is higher than the flame growth rate. The mechanisms which cause and amplify the disturbances define the type of instability. For example, heat diffusivity which is lower than mass diffusivity amplifies the growth rate of perturbations and leads to thermo-diffusive instability [17-20]. Another type is hydrodynamics or Rayleigh-Taylor instabilities in which flame becomes unstable due to disturbances associated with thermal expansion [17-20]. The parameter which distinguishes the thermo-diffusive instability from the hydrodynamic instability is the Lewis number ($Le = \alpha / D_m$) which is a non-dimensional parameter. It is the ratio of thermal diffusivity, $\alpha$, to mass diffusivity, $D_m$, of deficient reactant in the flame. When $Le<1$, the observed instability of the flame is thermo-diffusive. Since the corresponding $Le$ number of lean hydrocarbon-air mixtures with more than three carbons is larger than unity [21-24], the instabilities observed in our experiments can not be
thermo-diffusive. The other evidence is that thermo-diffusive instabilities usually develop right after ignition, but for hydrodynamic instabilities there is a critical radius after which instability grows; the later case is observed in our experiments [17, 18, and 20].

Figure 4 shows the images of JP-8/air flames at various initial pressures. This figure demonstrates that flame is more sensitive to instability at higher pressures. At higher pressure flame thickness decreases which reduces its resistance to perturbations and instabilities. Table 3 shows the cell formation temperatures, pressures and expansion ratios \( \sigma = \rho_u / \rho_b \) corresponding to Fig 4. Cell formation has been observed in other experimental investigations as well [17, 18, 25, and 26]. In addition to the effect of pressure on flame thickness, Oran and Gardner [27] state that larger pressure pulses increase the amplitude of perturbations in premixed flames. They show that the vorticity generation (baroclinic vorticity growth) is stimulated by large pressure pulses along with an abrupt density gradient across the flame which consequently causes cell formation and hydrodynamic instabilities [26, 28]. As such, thinner flames result in larger density gradients \( \nabla (1/\rho) \) which boosts vorticity generation. The role of pressure is important both in thermo-diffusive and hydrodynamic instabilities. Yuan et al [29] have shown in a theoretical investigation that for several \( Le \) numbers, increasing pressure extends the unstable range in premixed flames. This theory is in agreement with experimental observations obtained in this study.

It was also observed that flame instability occurs as the equivalence ratio increases. For a heavy hydrocarbon mixture such as JP-8/air, enriching the mixture by fuel causes the deficiency of the light reactant; it lowers the \( Le \) numbers and it causes earlier instability development [30]. Bechtold and Matalon [20] have shown that the critical radius \( R_{cr} \) from which instability begins can be given by the relation, \( R_{cr} \sim \delta E_a (Le - Le^*) / \sigma^2 \), where \( \delta \) is the flame thickness, \( E_a \) is the activation energy, \( Le^* < 1 \) is the critical \( Le \) number and \( \sigma \) is the expansion ratio. This relation shows that smaller \( Le \) numbers result in smaller critical radii.

Figure 5 shows the effect of EDG on flame structure in flames with an initial pressure of 3 atm, initial temperature of 493 K and three different volumetric percentage of diluents which are 0%, 5% and 10% respectively. In these snapshots it is seen that addition of EDG does not have a remarkable effect on the stability of the flame. Tables 4 and 5 show the cell formation temperatures, pressures and expansion ratios at various experimental conditions.
An important issue in these experiments is that cells are formed at large radii; for all of reported cases $r_c/R > 0.5$. Bechtold and Matalon [20] state that for $Le > Le^*$ the onset of flame instability is delayed until a critical radius is reached. In outwardly propagating spherical flames the stretch factor $= (2/r)(dr/dt)$ decreases by growing the flame. In lean mixtures of heavy hydrocarbons it can be a decelerating factor since the $Le$ number is larger than unity. In these cases, stretch and curvature is a suppressing factor against instabilities [26, 31-32]. Liu et al [31] have shown numerically that when flame is accelerating the disturbances from burned gas are unstable, but if the flame decelerates the disturbances are stable. They have concluded that in outwardly propagating spherical flames, stretch can slow the growth of instabilities. Bradley et al [32] and Jomass et al [18] have shown experimentally that at constant temperatures and pressures, spherical flames of heavy and partially heavy hydrocarbons become cellular at larger radii where stretch is not strongly dominant. To understand the role of flame location on instability an attempt was made to normalize the critical radius. The non-dimensional number is the Peclet number ($Pe$) which is the ratio of flame thickness to flame radius ($Pe = r/\delta$). The critical Peclet number ($Pe_c$) characterizes the normalized flame radius at which there is a transition to cellularity. To estimate the $Pe_c$ the thickness of flame must be determined. There are several techniques for calculation of $\delta$ [18, 23, and 33]. In this study it has been assumed that $\delta = \lambda / \rho c_p S_u$. In this equation, $\lambda$ is the heat conductivity, $\rho$ is density, $c_p$ is the heat capacity, and $S_u$ is the burning speed. Figure 6 shows the variation of critical Peclet numbers with equivalence ratios for JP-8/air/EDG mixtures. Figure 6 shows that for lean JP-8/air mixtures, $Pe_c$ decreases by increasing the equivalence ratio. This figure indicates that in richer mixtures flame becomes cellular at smaller radii. Thus by decreasing the $Le$ number, the premixed flame becomes more sensitive to hydrodynamic instabilities. Jomass et al [18] reached the same conclusion by investigating critical $Pe_c$ for near-equidiffusive and non-equidiffusive flames. They have concluded that for non-equidiffusive mixtures, $Pe_c$ numbers associated with hydrodynamic instabilities decrease almost linearly by increasing the equivalence ratios. This indicates that heat and mass diffusion have a striking influence on flame structure.

8.3.2. Experiments with Helium and Argon

One of the goals of this research is to extend the range of laminar flames to higher temperatures and pressures. To this end nitrogen was replaced by helium and argon to investigate the effect on flame structure. Helium and argon have equal heat capacities which are smaller than air.
Adiabatic flame temperatures of the mixtures with helium and argon are greater than mixtures with air due to the difference in heat capacity. In addition, higher values of $\gamma = c_p / c_v$ result in higher temperatures of the unburned gas during the isentropic compression. Figure 7 shows the adiabatic flame temperature of stoichiometric JP-8 mixtures with air and O$_2$+He versus temperature.

Figure 8 shows the snapshots of JP-8/oxygen/(nitrogen, argon, helium) mixtures at initial temperatures of 493 K and initial pressure of 2.5 atm. It can be seen that argon as diluent is the worst option for flame stabilization. Critical pressures of JP-8/oxygen/argon flames are lower than critical pressures of JP-8/oxygen/nitrogen and JP-8/oxygen/helium flames. This can be due to the lower heat conductivity of argon and consequently lower thermal diffusivity which can enhance the instability. Helium as diluent is the best option for producing stable flames at higher temperatures and pressures. Compared to argon and nitrogen, helium has the highest heat conductivity and can smooth out and consequently stabilize the flame [19, 30]. Figure 9 shows JP-8/oxygen/helium flames at initial temperature of 493 K, initial pressure of 4 atm, and at different equivalence ratios. It can be seen that helium increases the stability range of JP-8/oxygen/helium flames compared with JP-8/air/EDG. Again, increasing the equivalence ratio causes flame instability. The higher thermal diffusion of JP-8/oxygen/helium flames compared with JP-8/air overshadows the hydrodynamic effects on instability. Figure 10 shows the critical expansion ratios for JP-8/oxygen/helium and JP-8/air flames versus the normalized pressure. This figure indicates that compared with JP-8/air flames, resistance of the JP-8/oxygen/helium flame against the disturbances associated with thermal expansion increases. Sivashinsky [19] states that thermo-diffusive processes play the first role in flame instability. Table 6 shows the cell formation pressures, temperatures and critical expansion ratios of JP-8/oxygen/helium mixtures at different initial pressures and equivalence ratios. Once again it is demonstrated that the cellularity is strongly dependent on equivalence ratio and pressure. In the case of JP-8/oxygen/helium flames cell formation occurs at higher temperatures and pressures compared to air.

8.4. Burning Speed Measurements

8.4.1. Burning Model

There are several methods used to measure the laminar burning speed [33-39]. The theoretical
model used in this work to calculate the burning speed from the pressure rise is based on one previously developed by Metghalchi and Keck [40]. The model has been modified to include corrections for energy losses due to electrodes and radiation from the burned gas to the wall, as well as the temperature gradient in the preheat zone. It is assumed that gases in the combustion chamber can be divided into burned and unburned gas regions separated by a reaction layer of negligible thickness. The burned gas in the center of chamber is divided into \( n \) number of shells where the number of shells is proportional to the combustion duration. Burned gas temperature in each shell is different but all burned gases are in chemical equilibrium with each other. The burned gases are surrounded by a preheat zone (\( \delta_{ph} \)) having variable temperature, which is itself surrounded by unburned gases. A thermal boundary layer (\( \delta_{bl} \)) separates the unburned gas from the wall. The effect of energy transfer from burned gas to the spark electrodes is considered by a thermal boundary layer (\( \delta_{bl} \)). Additional information about the model can be found in previous publications [5 and 6].

As demonstrated in Rahim et al [6], volume and energy equations are solved simultaneously:

\[
\int_0^{v_b} (v_{bs}(T', p) - v_{us}) \, dv' = v_i - v_{us} + (V_{eb} + V_{wb} + V_{pb}) \, / \, m
\]

(1)

\[
\int_0^{v_b} (e_{bs}(T', p) - e_{us}) \, dv' = e_i - e_{us} + (pV_{pb}/(\gamma_u - 1) - Q_r) \, / \, m
\]

(2)

where \( v_i = (V_c - V_u) / m \) and \( e_i = E_i / m \) are the initial specific volume and energy of the unburned gas in the chamber, \( v_{bs} \) is the specific volume of isentropically compressed burned gas, \( v_{us} \) is the specific volume of isentropically compressed unburned gas. \( V_{wb} \), \( V_{ph} \) and \( V_{eb} \) are displacement volume of wall boundary layer, displacement volume of preheat zone ahead of the reaction layer and displacement volume of electrode boundary layer respectively. \( e_{bs} \), \( e_{us} \), \( \gamma_u \) and \( Q_r \), are the specific energy of isentropically compressed burned gas, specific energy of isentropically compressed unburned gas, specific heat ratio of unburned gas and radiation energy loss from the burned gas zone, respectively. The above equations have been solved for two unknowns: burned mass fraction and the burned gas temperature of the last layer. Given pressure as a function of time, \( p(t) \), they can be solved numerically using the method of shells to obtain the burned mass fraction, \( x_b(t) \), as a function of time and temperature distribution \( T(r, t) \).
Ultimately, the burning speed may be defined as:

\[ S_u = \frac{\dot{m}_b}{\rho_u A_b} = \frac{m\dot{x}}{\rho_u A_b} \]  
(3)

where \( A_b \) is the flame area.

All measurements are performed for laminar flames at radii \((r>4 \text{ cm})\) to minimize the effects of stretch. The reported laminar burning speeds in this study are the ones whose corresponding flame stretch rates are lower than 70 \(1/\text{s}\). In this range measured laminar burning speeds are accurate enough that the effects of initial conditions such as spark fire can be neglected [5, 41-42].

### 8.4.2. Laminar Burning Speeds

Burning speeds for laminar flames have been measured at high temperatures and pressures. Given the measured values, power law fits have been developed by the least square method to calculate the burning speeds of JP-8/air/EDG and JP-8/oxygen/helium mixtures. For JP-8/air/EDG mixtures, the form of correlation is:

\[
S_u = S_{u0} (1 + a_1 (1 - \phi) + a_2 (1 - \phi)^2) \left[ \frac{T_u}{T_{u0}} \right]^\alpha \left[ \frac{P}{P_0} \right]^\beta (1 - \text{EDG})^\theta
\]

(4)

where \( S_{u0} \) is the burning speed at reference point \((P_0 = 1 \text{ atm}, T_{u0} = 500 \text{ K} \text{ and } \phi = 1)\) in cm/s, \( \phi \) is the mixture fuel-air equivalence ratio, \( T_u \) is the unburned gas temperature in K, \( P \) is the mixture pressure in atm, and \( \text{EDG} \) is the diluent mole fraction. This correlation (4) is only valid for smooth (laminar) flames, and the range of pressure and temperature depends on smoothness of the flame which is a function of equivalence ratio and diluent type. Figure 11 shows the range of pressures in which JP-8/oxidizer/diluent flames become cellular. The corresponding temperature to each pressure can be found by following equation:

\[
T = T_i (P / P_i)^{(\gamma - 1) / \gamma}
\]

(5)

Table 7 shows the values of the constants in equation (4).
Table 7: Power law fit function coefficients of JP-8/air/EDG mixture

<table>
<thead>
<tr>
<th>$S_{uo}$ (cm/s)</th>
<th>a</th>
<th>b</th>
<th>α</th>
<th>β</th>
<th>θ</th>
</tr>
</thead>
<tbody>
<tr>
<td>93.63</td>
<td>-0.22</td>
<td>-4.4</td>
<td>2.13</td>
<td>-0.185</td>
<td>3.52</td>
</tr>
</tbody>
</table>

Figure 12 shows the laminar burning speeds at three different EDG percentages. This figure shows the measured and fitted values by equation (4). It is seen that laminar burning speed decreases as EDG percentage increases. It is likely that the flame temperature decreases due to increasing the heat capacity of the mixture. Regarding the effect of equivalence ratio, there is a consistent behavior in burning speed values. In lean mixtures, laminar burning speed increases by elevating the equivalence ratio. It can be estimated by Figure 12 that by increasing the EDG fraction by 5%, the laminar burning speed decreases by about 15%. This highlights the importance of EDG in JP-8/air/EDG flames. Addition of EDG to the mixture in internal combustion engines usually decreases the power obtained. The reason can be attributed to slower burning of the mixture which decreases the work production rate.

Same procedure of measuring and fitting was done for JP-8/oxygen/helium flames. The power law fit correlation is

$$S_u = S_{uo} (1 + a_1 (1 - \phi) + a_2 (1 - \phi)^2) \left[ \frac{T_u}{T_{uo}} \right]^{a} \left[ \frac{P}{P_0} \right]^\beta$$ \hspace{1cm} (6)

where $S_{uo}$ is the burning speed at reference point ($P_0 = 4$ atm, $T_{uo} = 500$ K and $\phi = 1$). Table 8 shows the values of constants in equation 14.

Table 8: Power law fit function coefficients for the JP-8/oxygen/helium mixture

<table>
<thead>
<tr>
<th>$S_{uo}$ (cm/s)</th>
<th>a</th>
<th>b</th>
<th>α</th>
<th>β</th>
</tr>
</thead>
<tbody>
<tr>
<td>287.11</td>
<td>1.38</td>
<td>1.54</td>
<td>2.47</td>
<td>0.26</td>
</tr>
</tbody>
</table>

Correlation (6) is only valid for smooth (laminar) flames. Figure 11b shows the range of pressures in which the flame is smooth. The corresponding temperatures can be calculated using equation (4).

Figure 13 shows the measured and fitted laminar burning speeds of JP-8/oxygen/helium mixtures at initial pressures of 4.5 and 5 atm, initial temperature of 493 K and equivalence ratios of 0.8, 0.9, and 1. The percentage of helium is fixed at volumetric fraction of 79%. It is observed
that laminar burning speeds are tremendously higher than in JP-8/air mixtures. This can be attributed to the higher flame temperature of JP-8/oxygen/helium mixtures due to the lower heat capacity of helium. In addition, the heat conductivity of helium is greater which causes a higher heat transfer rate to preheat zone from flame front which increases the rate of chemical reactions and burning rate in the flame front.

Acknowledgment

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References


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Figure 1: The sketch of the experimental system

Figure 2: Shadowgraph system
Figure 3: Chromatograph of JP-8 (4658+additives)
Figure 4: Snapshots of JP-8/air flames at various initial pressures, 
\[ \phi = 1, T_i = 493 \, \text{K} \]
Figure 5: Snapshots of JP-8/air/EDG flames at several EDG percentages, 

\[ \phi = 1, T_i = 493 \text{ K, } P_i = 3 \text{ atm} \]
Figure 6: Critical Peclet numbers ($P_{ec}$) versus equivalence ratio (experimental condition of each number can be found at Table 2)

Figure 7: Adiabatic flame temperature of stoichiometric JP-8/oxygen/diluent mixtures versus unburned gas temperature
Figure 8: Snapshots of JP-8/oxygen/diluent flames with different diluents (nitrogen, argon, and helium), $\phi = 1$, $T = 493$ K, $P_i = 2.5$ atm.
Figure 9: Snapshots of JP-8/oxygen/helium flames at different equivalence ratios, 
\[ T_i = 493 \text{ K}, \ P_i = 4 \text{ atm} \]
Figure 10: Critical expansion ratios versus normalized critical pressures for mixtures with different diluents and equivalence ratios
Figure 11: Cell formation pressure versus equivalence ratio, a: JP-8/air/EDG, b: JP-8/oxygen/helium
Figure 12: JP-8/air/EDG laminar burning speeds at various EDG percentages and equivalence ratios, $T_i = 493$ K, $P_i = 2$ atm
Figure 13: JP-8/oxygen/helium mixture laminar burning speed at several initial pressures and equivalence ratios, $T_i = 493$ K
Table 1: JP-8 fuel properties

<table>
<thead>
<tr>
<th>Fuel type</th>
<th>JP-8: 4658+additives</th>
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<tr>
<td>Distillation</td>
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<tr>
<td>Initial boiling point (K)</td>
<td>320</td>
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<tr>
<td>10% recovered (K)</td>
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<tr>
<td>50% recovered (K)</td>
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<tr>
<td>Final boiling point (K)</td>
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<tr>
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<tr>
<td>Density (kg/L)</td>
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<tr>
<td>Viscosity (mm²/s @253 K)</td>
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<td>Heat Value, heat of combustion: (MJ/kg)</td>
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Table 2 summary of experimental conditions for JP-8/air/EDG mixtures

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Table 3: Cell formation analysis of JP-8/air mixtures

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<tr>
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<td>smooth</td>
<td>smooth</td>
<td>$P_{cr} \sim 6.1$ atm</td>
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<td></td>
<td>$T_{cr} \sim 587$ K</td>
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<td></td>
<td>$T_{cr} \sim 705$ K</td>
<td>$T_{cr} \sim 614$ K</td>
<td>$T_{cr} \sim 554$ K</td>
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<td>$\sigma_{cr} = 4.41$</td>
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<td>$P_{cr} \sim 4.2$ atm</td>
<td>$P_{cr} \sim 4.05$ atm</td>
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Table 4: Cell formation analysis of JP-8/air/EDG mixtures (EDG=5 %)

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<td>$P_{cr} = 3.83$ atm, $T_{cr} = 576$ K, $\sigma_{cr} = 4.39$; $P_{cr} = 4.06$ atm, $T_{cr} = 515$ K, $\sigma_{cr} = 4.83$</td>
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Table 5: Cell formation analysis of JP-8/air/EDG mixtures (EDG=10 %)

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### Table 6: Cell formation analysis of JP-8/oxygen/helium mixtures

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<th>$P_i = 2$ atm</th>
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<td>$T_{cr} = 658$ K</td>
<td>$T_{cr} = 606$ K</td>
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<td>$\sigma_{cr} = 4.54$</td>
<td>$\sigma_{cr} = 4.88$</td>
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<td>$T_{cr} = 620$ K</td>
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<tr>
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<td>$\sigma_{cr} = 4.39$</td>
<td>$\sigma_{cr} = 4.93$</td>
<td>$\sigma_{cr} = 5.16$</td>
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</tbody>
</table>
9. Laminar Burning Speeds of Ethanol/Air/Diluent Mixtures

Accepted for publication in Proceedings of Combustion Institute (33rd Symposium (International) on Combustion)
9. Laminar Burning Speeds of Ethanol/Air/Diluent Mixtures

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Abstract

Laminar Burning speed of ethanol/air/diluent mixtures have been measured over a wide range of temperature, pressure, fuel air equivalence ratio and diluent. Experimental facilities include a cylindrical vessel with two large end windows and a spherical vessel with capability to withstand pressures up to 425 atmospheres. Both of these vessels are heated for having initial temperatures of unburned gas up to 500 K. A shadowgraph system with a CMOS camera capable of taking pictures up to 40,000 frames per second is used to observe structure of propagating flames. Pressure rise due to combustion in both vessels is used to calculate laminar burning speed of the mixture. A thermodynamic model is used to calculate burning speed from combustion pressure. Laminar burning speeds of ethanol/air premixed mixtures have been measured at high temperatures and pressures. A mixture of 86% nitrogen and 14% carbon dioxide, which simulate heat capacity of residual gases in internal combustion engines, is used to determine the effect of diluent on burning speed. A correlation for laminar burning speed as a function of temperature, pressure, equivalence ratio and extra diluent gas (EDG) has been developed. The range of temperature and pressure are 300-650 K and 1-5 atm, fuel air equivalence ratio 0.8-1.1 and extra diluent gases of 5 and 10%. The measured values compare very well with available data and extend the range many folds.

*Keywords: Ethanol, biofuels, laminar burning speed, cell formation*
Nomenclature

\[A\] Area

\[c_p\] Constant pressure specific heat

\[c_v\] Constant volume specific heat

\[e\] Energy

\[EDG\] Extra diluent gases

\[m\] Mass

\[P\] Pressure

\[Q\] Energy loss

\[r\] Flame radius

\[S\] Burning speed

\[t\] Time

\[T\] Temperature

\[v\] Specific volume

\[x\] Burned mass fraction

Greek letters

\[\alpha\] Temperature exponent

\[\beta\] Pressure exponent

\[\gamma\] Ratio of specific heats

\[\delta\] Thickness

\[\theta\] Diluent exponent

\[\kappa\] Stretch rate

\[\phi\] Equivalence ratio

Subscripts

\[b\] burned gas

\[bl\] thermal boundary layer

\[bs\] isentropically compressed burned gas

\[c\] chamber

\[e\] electrodes

\[eb\] electrode boundary layer

\[i\] initial condition
9.1. Introduction

Ethanol has been widely used in engines, land-based gas turbines for power production and aircrafts [1-3]. It is important to learn more about the fundamental combustion properties of this fuel. Laminar burning speed is a thermo-physical property which is used to analyze turbulent flame propagation and it is also used to validate chemical kinetics models. Laminar burning speeds of ethanol-air mixtures have been measured by some researchers recently. Bradley et al. [4] have measured the laminar burning speeds of ethanol-air mixtures at pressures between 0.1 and 1.4 MPa, temperatures 300-393 K and equivalence ratios of 0.7-1.5. They have used a constant pressure spherical vessel with optical access to do their experiments and then by using a linear extrapolation for stretch effects; they have measured the laminar burning speeds. Gülder [5] has measured the burning speeds at pressures and temperatures up to 0.8 MPa and 500 K respectively over a wide range of equivalence ratios. Egolfopoulos et al [6] have measured the laminar burning speeds of ethanol-air mixtures at atmospheric pressure using a counter-flow flame in a temperature range of 363 and 453 K. Liao et al [7] have measured the laminar burning speeds of ethanol-air mixtures at a temperature range of 300-480 K and pressure range of 1-10 atm. They have carried out their experiments in a wide range of equivalence ratios 0.7-1.4. There are other experimental data in literature about burning speed and burning rate of ethanol but they are in a limited range of temperatures and pressures [8, 9]. The effects of extra diluent gases (EDG) on laminar burning speed and flame structure have not been investigated in any of existing literature.

In this paper, laminar burning speeds of ethanol/air/diluent premixed mixtures have been measured at higher temperatures (300-650 K) and pressures (1-5 atm), wide range of fuel air equivalence ratios, and extra diluent gases (EDG). EDG is composed of 86% nitrogen and 14% carbon dioxide to simulate residual gases in internal combustion engine. This mixture has the same heat capacity of the burned gases in engines.
9.2. Experimental Facilities

The experimental system includes a spherical chamber and a cylindrical vessel. Both the spherical and cylindrical vessels were used to measure pressure rise caused by the combustion process. The vessels have been designed such that the ratio of volume to surface is equal. The cylindrical vessel with two large end windows withstands a maximum pressure of 50 atmospheres while the spherical vessel withstands pressure of 425 atmospheres. Both vessels were fitted with two extended spark plug electrodes which provide a central point ignition source for the chamber. The vessels were equipped with heaters capable of elevating the vessel temperature to 500 K. A shadowgraph system is used with cylindrical system to take images from flame propagating flame. A CMOS camera with the capability of taking pictures up to 40,000 frames per second has been used in these experiments. A high speed data acquisition system was used to record the pressure-time data. A computer driven system has been used to make the mixture with required fuel and oxidizer and to initiate the combustion process. Method of partial pressures has been used to set the initial fuel air equivalence ratio and verified using gas chromatograph. A heated inlet manifold (500 K) has been used to have ethanol vapor. More details about the experimental facility can be found in previous publications [10, 11].

9.3. Burning Model

The theoretical model used to calculate the burning speed from the pressure rise is based on one previously developed by Metghalchi and co-workers [12-15] and has been modified to include corrections for energy losses to electrodes and radiation from the burned gas to the wall as well as inclusion of temperature gradient in the preheat zone. It is assumed that gases in the combustion chamber can be divided into burned and unburned regions separated by a reaction layer of negligible thickness. The burned gas in the center of chamber is divided into \( n \) number of shells where the number of shells is proportional to the combustion duration. The burned gases in each shell are assumed to be in chemical equilibrium with 28 species and have different temperatures. The gases that burn early have higher temperature due to compression after combustion. The burned gases are surrounded by a preheat zone \( (\delta_{ph}) \) having variable temperature, which is itself surrounded by unburned gases. A thermal boundary layer \( (\delta_{bl}) \) separates the unburned gas from the wall. The effect of energy transfer from burned gas to the spark electrodes is considered by a thermal boundary layer \( (\delta_{bl}) \). Volume and energy equations
described below are solved simultaneously:

\[
\int_0^{v_b} (v_b(T',p) - v_{us}) \, dx' = v_i - v_{us} + (V_{eb} + V_{wb} + V_{pb})/m \tag{1}
\]

\[
\int_0^{v_b} (e_b(T',p) - e_{us}) \, dx' = E_i - E_{us} + (pV_{ph}/(v_u - 1)) - Q_{rad})/m \tag{2}
\]

where \( v_i = (V_c - V_s)/m \) and \( e_i = E_i/m \) are the initial specific volume and energy of the unburned gas in the chamber, \( v_{bs} \) is the specific volume of isentropically compressed burned gas, \( v_{us} \) is the specific volume of isentropically compressed unburned gas. \( V_{wb}, V_{ph} \) and \( V_{eb} \) are displacement volume of wall boundary layer, displacement volume of preheat zone ahead of the reaction layer and displacement volume of electrode boundary layer respectively. \( e_{bs}, e_{us}, \gamma_u \) and \( Q_{rad} \), are the specific energy of isentropically compressed burned gas, specific energy of isentropically compressed unburned gas, specific heat ratio of unburned gas and radiation energy loss from the burned gas zone, respectively. The above equations have been solved for two unknowns; burned mass fraction and the burned gas temperature of the last layer. Given pressure, \( p(t) \) as a function of time, equations (1) and (2) can be solved numerically using the method of shells to obtain the burned mass fraction, \( x_b(t) \), as a function of time and temperature distribution \( T(r,t) \).

Ultimately, the burning speed may be defined

\[
S_u = \dot{m}_b / \rho_u A_b = m\dot{x} / \rho_u A_b \tag{3}
\]

Where, \( A_b \) is the flame front area. In these experiments a 10% pressure rise is needed for calculation which happens when flame radii become larger than 4 cm.

9.4. Results

Experiments were carried out in cylindrical and spherical vessels to observe flame structure and to measure laminar burning speeds. The geometry of the vessel does not have a significant effect on pressure data as shown in Fig. 1. It is clear that as long as flame has not touched the wall in cylindrical vessel, the pressures in both vessels are very close to each other. In cylindrical vessel the final pressure is lower than spherical vessel due to energy losses to the wall after the hot gases are in contact with the wall.
Fig. 2 shows the snapshots of ethanol-air premixed flames at initial temperature of 450 K, initial pressure of 1 atmosphere and three different equivalence ratios which are 0.8, 0.9, 1, and 1.1. As it can be seen the flames are fairly smooth. These snapshots demonstrate that as pressure and flame radii increase, flames become more sensitive to cellularity. In this condition due to the instability and consequent turbulence the area of flame increases abnormally and the measurement of burning speed becomes extremely difficult. Cell formation is strongly a function of pressure, flame radius, equivalence ratio and fuel type. In these experiments as well as other researchers’ results, it has been observed that increase of pressure causes cell formation and instability [16-19]. Another important parameter is the equivalence ratio. In this research, enriching the mixture decreases the resistance of the flame against instabilities. It has been shown that for heavy fuels, rich mixtures become unstable at lower pressures and temperatures [16-19]. However, the analyses and the sources of flame instabilities are beyond the scope of this paper and laminar burning speeds are reported for only stable and smooth flames.

**Stretch effects**: flame stretch is a phenomenon caused by the variation of flame area versus time. In spherical flames the stretch rate is as following relation:

\[ \kappa = \frac{1}{A} \frac{dA}{dt} = \frac{2}{r} \frac{dr}{dt} \tag{4} \]

where \( \kappa \) is the stretch rate, \( A \) is the area of flame, \( t \) is the time, and \( r \) is the radius of the flame. Depending on the conditions, stretch can affect the laminar burning speed values. It is seen in equation (4) that as the radius of flame increases the stretch rate decreases. In our measurements, flame radii are larger than 4 cm, and stretch effects are negligible. In order to check the effect of stretch in our experiments, laminar burning speeds of ethanol-air mixtures were measured at the same temperatures, pressures, and equivalence ratios but with varying flame radii and stretch rate. This is done by changing the initial temperature and pressure of the mixture along the isentropic line. Fig. 3 shows temperature and pressure of unburned gas mixture for three different experiments. Line AA’ is the locus of pressure and temperature for a stoichiometric mixture having initial temperature of 300 K and 1 atmosphere pressure. As unburned gas ahead of flame front compresses, both temperature and pressure of the mixture increases. Point A is the starting condition and point A’ is the final condition of the unburned gas ahead of flame front. All points on BB’ are conditions of another experiment having an initial condition of 2.5 atmospheres and 377 K temperature. Points on line CC’ show states of unburned gas mixture on another
experiment. Point M (T = 430 K, P = 4.5 atm) lies on all of these three isentropes while having three different radii and different stretch rates. Laminar burning speed of flames at conditions like point M having the same unburned gas properties but different radii (r > 4 cm) and different stretch rates have been determined and are shown in Fig. 4 as a function of stretch rate. As it can be seen for two conditions shown with flame radii of larger than 4 cm and stretch rates of less than 70 1/s, burning speeds do not change. Numerous studies have shown that stretch rates higher than 100 1/s can affect the laminar burning speeds [4-9]. Therefore, all reported laminar burning speed data in this paper are for stretch rates lower than 70 1/s.

**Laminar burning speeds:** Fig. 5 shows laminar burning speeds of ethanol-air mixtures at various initial conditions at four different equivalence ratios. It can be seen that for \( \phi < 1.1 \), increasing the equivalence ratio increases the burning speed. Fig. 5 shows laminar burning speeds along the isentropic line versus temperature. The corresponding pressure to each temperature can be found by following equation

\[
T = T_i (P / P_i)^{(\gamma-1)/\gamma}
\]  

(5)

In this equation \( \gamma = {c_p}/c_v \) where \( c_p \) is the specific heat at constant pressure and \( c_v \) is the specific heat at constant volume. Fig. 6 shows the effect of EDG on laminar burning speeds. This figure indicates that addition of extra diluent gases decreases the laminar burning speed. This is due to decreasing the adiabatic flame temperature by increasing heat capacity of the mixture.

In these figures the symbols are the measured laminar burning speed data by the model. The solid line is a power law correlation developed for the burning speed data. The correlation is a function of temperature, pressure, fuel air equivalence ratio and percentage of EDG in the mixture as shown in equation (6):

\[
S_u = S_{u0}[1 + a_1(1-\phi) + a_2(1-\phi)^2] \left( \frac{T}{T_0} \right)^{\alpha} \left( \frac{P}{P_0} \right)^{\beta} (1-EDG)^{\theta}
\]  

(6)

Where \( \phi \) is the equivalence ratio, \( T \) is the temperature in K, \( P \) is the pressure in atm, and EDG is the volumetric fraction of extra diluent gases. \( T_0 \) and \( P_0 \) are the reference temperatures and pressures, 300 K and 1 atm respectively. \( S_{u0} = 36.5 \) cm/s, is the laminar burning speed of the stoichiometric mixture at reference temperature and pressure of 300 K and 1 atm respectively. \( a_1 \)
and $a_2$ are constants with values of -1.01 and -1.91 respectively. $\theta$ is a exponential constant equal to 2.16. $\alpha$ and $\beta$ are two exponents which represent the dependence of laminar burning speed on temperature and pressure. It has been investigated that for most of hydrocarbons these exponents vary by equivalence ratio [4, 5, and 7]. The proposed functions for the dependency of $\alpha$ and $\beta$ on equivalence ratio are:

$$\alpha = \alpha_1 \phi + a_2 \ (0.8 \leq \phi \leq 1.1)$$  \hspace{1cm} (7)

$$\beta = \beta_1 \phi^2 \ (0.8 \leq \phi \leq 1.1)$$  \hspace{1cm} (8)

The constant values in equations (6) and (7) are: $(\alpha_1 = -0.36, \alpha_2 = 2.2)$ and $(\beta_1 = -0.21, \beta_2 = -0.22)$. The temperature range for equation (6) is $300 < T < 650$ K. The range of pressure for equation (6) is limited to smooth (non-cellular) flames. In all experiments, it was observed that flame instability is very sensitive to pressure. This sensitivity varies by equivalence ratio of the mixture. Fig. 7 shows cell formation pressure of all cases versus equivalence ratio. Experimental observations have shown that for each equivalence ratio, there is a specific range of pressure at which flame becomes cellular. The range of pressure for equation (6) is in non-cellular region of Fig. 7.

Fig. 8 shows the comparison of $\alpha$ and $\beta$ exponents with the results of other researchers. Values of $\alpha$ in this research are very close to the results of other researchers [4, 5, and 7]. Values of $\beta$ are presented in Fig. 8 and this figure demonstrates that the results of this work is in the middle of different researchers results.

9.5. Comparison with Other Measurements

The results of these experiments have been compared to those of others in the same range. As it was noted before, the significance of this research is measuring the laminar burning speeds at higher temperatures and pressures. In addition, the effect of EDG has been investigated in a wide range of temperatures and pressures. Fig. 9 shows comparison with other researchers at pressures of 1 and 2 atm. At 1 atm pressure, the agreement with other researchers is good in all temperatures and equivalence ratios. It is seen that results of Egolfopoulos et al [6] are higher, especially when mixture becomes richer. The theoretical results of Rohl and Peters [20] are
larger than experimental measurements in lean conditions. Also shown, are laminar burning speeds at temperature of 600 K for the first time. At pressure of 2 atm, the agreement is good with other researchers. It can be seen that the results of Bradley et al [4] are low because of their lower pressure exponent values. The theoretical data of Rohl and Peters [20] is again higher than experimental data in lean conditions.

Acknowledgments

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Reference:


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Figure 1: comparison between the pressure of spherical and cylindrical vessels
Figure 2: Pictures of ethanol-air mixture, $P_i = 2$ atm, $T_i = 450$ K
Figure 3: Unburned gas conditions of ethanol-air mixtures

Figure 4: Laminar burning speed versus stretch rates
Figure 5: Laminar burning speeds of ethanol-air mixtures at different temperatures, pressures and equivalence ratios.
Figure 6: Dependence of laminar burning speeds of ethanol-air mixture on EDG gases
Figure 7: Cell formation pressure versus equivalence ratio
Figure 8: values of $\alpha$ and $\beta$ exponents versus $\phi$
Figure 9: laminar burning speeds of ethanol-air mixtures and comparison with other researchers
10. Laminar burning speeds of advanced bio-jet fuels
10. Laminar burning speeds of advanced bio-jet fuels


Bio-jet fuels are important alternative energy resources for aviation purposes. These fuels can be obtained from several resources like corn, sugar, algae, biomass, etc. due to water and food resources limitation in the world it is preferred to use non-edible resources to produce bio-jet fuels. One of the reliable resources for obtaining bio-jet fuels is biomass. Biomass is abundant in nature and it does not waste edible resources. Biomass is a renewable resource of energy. The produced CO₂ from the combustion of biomass fuels can be a part of biomass creation cycle loop in the nature. Therefore the net emitted CO₂ of ethanol production and combustion is low and it makes it a renewable and fairly clean fuel.

There are various classes of aviation biofuels. The most common ones are alcohol fuels. They can be produced both from edible resources like corn and non-edible resources like biomass. Among alcoholic fuels ethanol is the most popular one; it is widely used in land based engines but not so popular in aviation engines. The ideal fuel for aviation fuel is the one which can be used both as energy source and coolant. Currently, JP-8 fossil fuel is widely used in aviation and satisfies the mentioned requirements. The attempt is focused on finding the best bio-jet fuel which is similar to JP-8. The class that is most advanced is "hydrotreated renewable jet" (HRJ), which is hydrotreated fats/oils.

This fuel is very similar to Fischer-Tropsch synthetic paraffinic kerosene. The fuel called R-8 (POSF 5469) is a fuel produced by hydrotreating fats/oils (triglycerides) and contains n-paraffins and iso-paraffins. HRJ fuels are predominantly n-paraffins and iso-paraffins. The other fuel is produced from biomass by a different process, and contains aromatics. The applied bio-jet fuels in this research will be ethanol, R-8 (POSF 5469), and POSF 5700. The laminar burning speeds of these bio-jet fuels will be measured and the results will be compared with those of JP-8.

One of our major goals is to measure the laminar burning speeds of R-8 bio-jet fuel. Before
measuring the laminar burning speed it is essential to evaluate the thermo-physical properties of this fuel. In this respect, we have used a Gas chromatography facility to analyze this fuel and measure its heat capacity, enthalpy and entropy to develop polynomial functions in NASA format. We have used a VARIAN CP-30 GC machine. Figure 1 shows the chromatograph of this fuel. It can be seen that this fuel is composed of several elements and the major ones are n-paraffins. After getting the components we have applied a statistical thermodynamic method to calculate the thermo-physical properties. The details of this model can be found in [18].

Figure 2 shows the ratio of heat capacity to gas constant versus temperature. It is shown that in initial stages the heat capacities are different but by increasing the temperature they converge.

Figure 1: Chromatograph of R-8
10.2. Laminar Burning Speeds

After calculating the thermodynamic properties of R-8 bio-jet fuel, laminar burning speeds of this fuel was measured by the same method discussed before. Figure 3 shows the results of laminar burning speeds of bio-jet fuels and ethanol. The results have been compared with the data of conventional jet fuels (JP-8 and JP-10) and ethanol. It can be seen that among these fuels JP-8 has the highest laminar burning speed. After that ethanol, JP-10 and R-8 has the lowest laminar burning speed. However, more information and study is needed to measure the laminar burning speeds of R-8.
Figure 3: Laminar burning speeds of JP-8, R-8, JP-10, and Ethanol fuels at several pressures and temperatures, $\phi = 1$
11. *Summary and Conclusions*
11. Summary and Conclusions

The summary of this thesis is described in following section. Each chapter (paper) has the individual conclusions which will be described here.

11.1. Thermodynamic Properties of Ionized Gases at High Temperatures

Thermodynamic properties of air, argon, and helium have been calculated at high temperatures using a novel cascade thermodynamic model. It was assumed that all species are in local thermodynamic equilibrium. The model is based on statistical thermodynamics methods.

The calculated properties are: specific heat capacity, enthalpy of the mixture, mole fraction of species, particle numbers, and density. It is shown that all these properties are very temperature sensitive. It is also shown that number of ions and ionization level play an important role in determining specific heat capacities and particle numbers in the mixture. Results are compared with those of other researchers and good agreement is obtained in regions where the results overlap.

11.2. A Thermodynamic Model for Argon Plasma Kernel Formation

Formation of argon plasma kernel has been studied experimentally and theoretically. The experiments were performed at constant pressure in a shadowgraph system. They have been performed with two different discharged energies to investigate the effect of spark energy. Radii of argon plasma kernel were measured optically. A thermodynamic model was developed to predict the measured radii under initial conditions of experiments. The major conclusions are:

1- It can be assumed that the plasma kernel expands in a constant pressure and constant mass condition.

2- Total number of moles increases as the temperature of the gas increases and it is the main source of kernel expansion at constant pressure and constant mass condition.

3- Increase of heat capacity of the plasma gases at high temperatures has a very important
role in temperature and growth mechanism of the kernel.

4- Initial volume and initial temperature of the kernel have a great effect on temperature of the kernel. However, they do not have a major effect on the size of the kernel.

5- Cathode-anode falls are the major source of energy losses. Radiation is another source of energy losses which becomes more important at higher discharge energies due to higher kernel temperature. A small portion of discharged energy is converted to the thermal energy depending on discharged energy amount. This portion is less than 10%.

This model can be extended to combustible mixtures as well to investigate the spark ignition and flame formation mechanism of engines and other combustors to improve combustion process.

11.3. On Flame Kernel Formation and Propagation in Premixed Gases

An experimental and theoretical study was done on flame kernel formation and propagation of premixed gases. The formation of hot plasma during the spark discharge was studied experimentally and a thermodynamic model was developed for air plasma. The effect of various parameters on plasma kernel formation and propagation were studied. The major conclusions are as follows:

1- A major part of discharge energy is dissipated by cathode fall energy losses. The amount of dissipated cathode fall energies depends on the amount and duration of discharge energy. Radiation is the important source of energy losses in plasma. The amount of radiation energy loss strongly depends on the temperature of the hot plasma. However, when self-sustained flame establishes radiation is not an important source of energy loss. Only about 10-25% of the, electrical energy is converted to thermal energy.

2- It was concluded that the plasma expands in a constant mass and pressure process with increasing number of moles due to ionization.

3- Increase in heat capacity at high temperatures is an important factor in dynamics and temperature rise in the kernel.

4- Initial temperature and initial volume of the kernel are important parameters in growth and temperature of the plasma kernel.

5- The amount of electrical energy input is important to the size and temperature of the kernel.
In second part of this study, the propagation of premixed methane/air flames was studied experimentally and theoretically. The experiments were performed on methane/air flames at atmospheric pressure and temperature, with two different spark electrodes, and two different spark energies. The conclusions are as follows:

6- The amount of input electrical energy is important in the location of flame but it does not affect the asymptotic flame speed.

7- The geometry of the spark electrode does not affect the flame speed and location of flame.

8- The laminar burning speed was measured by this model and it was in good agreement with experimental results of other researchers.

9- Laminar flame needs a certain amount of time to become self-sustained. This time scale depends on the composition of the mixture and input electrical energy. This time scale increases when the mixture becomes richer.

11.4. A Thermodynamic Model to Calculate Burning Speed of Methane-Air- Diluent Mixtures

Burning speeds for methane-air-diluent flames over a wide range of pressures, temperatures, stoichiometries, and diluent fractions have been determined from pressure measurements made in a spherical combustion chamber. The burning speed were calculated from the pressure records using a thermodynamic model which includes the effects of radiation and conduction heat losses to the wall and electrodes and the temperature rise in the preheat zone. Shadowgraphs were taken through end windows in a cylindrical chamber of the same volume as the spherical chamber to determine the shape and structure of the flames for which burning speeds were measured. Both spherical and distorted flames having smooth, cracked and cellular fronts were observed. For very slow flames, buoyant rise was also observed. For comparison with the measurements, flame speeds were calculated using the PREMIX code with GRI-Mech 3.0 kinetics. The following conclusions were drawn:

1. The measured burning speeds of stoichiometric methane-air-diluent mixtures at initial pressures and temperatures of 1.0 atm and 298 K and 0-15% diluent are in reasonable agreement with values calculated from the PREMIX code using GRI-Mech 3.0 kinetics. Under these conditions all the flames observed were smooth and spherical.
2. For initial pressures and temperatures of 5.0 atm and 298 K and 0-15% diluent, stoichiometric and lean methane-air-diluent flames were cracked at low pressures and high diluent fractions and cellular at high pressures and low diluent fractions. The measured burning speeds for cracked flames agree reasonably well with PREMIX values but are higher than PREMIX values for cellular flames suggesting that cellularity may increase the burning speed.

3. For rich methane-air-diluent mixtures at initial pressures and temperatures of 5.0 atm and 298 K, and 0-10% diluent, all the flames observed were smooth but the measured burning speeds were significantly lower than PREMIX calculations. The most probable reason for this is the omission of reactions involving alkyl peroxides form the GRI-Mech 3.0 kinetics.

4. Further work is needed to determine more precisely the conditions under which cracking and cellularity occur and whether the observed discrepancies between the measured burning speeds and PREMIX calculations are due to cellularity or a failure of the GRI-Mech 3.0 kinetics.

11.5. Flame Structure and Laminar Burning Speeds of JP-8/air Premixed Mixtures at High Temperatures and Pressures

1. The shape and structure of JP-8/air flames were studied at various temperatures, pressures and equivalence ratios. The effects of equivalence ratio and pressure on the structure of the flame were striking. Initial pressure did not play any significant role in the turbulization of the flames and there was a specific range of pressure for the cell formation of any flame in a particular equivalence ratio.

2. Laminar burning speeds were calculated for JP-8/air mixtures. The calculations were done in temperature and pressure ranges in which flames were laminar. It was observed that laminar burning speed increases as temperature increases and decreases as pressure increases.

3. Burned mass fraction rate of cellular flames were measured for various temperatures and pressures. It is concluded that the slope of burned mass fraction rate versus temperature increases as temperature and pressure increase. This is due to the increase of flame surface in a cellular flame.

4. A power law correlation was developed for the laminar speed of JP-8/air mixtures by nonlinear least square fit method. This fitted equation is valid in laminar flame cases.

The effect of diluents on flame structure and laminar burning speeds has been studied.

The addition of EDG did not have a remarkable effect on the stability of JP-8/air/EDG flames compared with JP-8/air flames, but it decreased the laminar burning speeds due to decreasing the adiabatic flame temperature. It was observed that for a heavy hydrocarbon premixed flame such as for JP-8, increasing pressure causes flame instability. For lean JP-8/air and JP-8/air/EDG flames hydrodynamic instabilities are observed. Increasing pressure decreases the flame thickness and reduces the resistance of flame against perturbations associated with expansion ratio. This leads to hydrodynamic instabilities. The other factor which causes flame instability is enriching the mixture in JP-8/air and JP-8/air/EDG mixtures. This is due reducing reduction of the $Le$ number of the flame associated with deficient reactant. Pe numbers of unstable flames were calculated and it was observed that the critical Pe number is strongly dependent on the equivalence ratio and it decreases by increasing the equivalence ratio. Clearly, it can be concluded that rich mixtures are more vulnerable to perturbations.

A set of experiments were performed with helium and argon as diluents. It was observed that argon causes more instabilities than air. This is because of the lower heat diffusivity of argon compared to air and helium. JP-8/oxygen/helium mixtures have the most stable flames. This is due to their high thermal diffusivities. It was observed in experiments that the JP-8/oxygen/helium flames are stable at higher temperatures and pressures in which JP-8/air and JP-8/oxygen/argon flame were unstable. The laminar burning speeds of JP-8/oxygen/helium flames were measured and it was indicated that helium increases the laminar burning speeds dramatically because of higher adiabatic flame temperatures.

11.7. Laminar Burning Speeds of Ethanol/Air/Diluent Mixtures

Laminar burning speeds of ethanol-air mixtures were measured at high temperatures, pressures, various equivalence ratios and with extra diluent gases to represent residual gases in engines. It was concluded that in rich ethanol-air mixtures, instability occurs at lower pressures and temperatures. It was also resulted that pressure intensifies the onset of instability in ethanol-air flames. Measured and fitted results showed that the exponents of normalized pressure and temperature vary with equivalence ratio. Laminar burning speeds were measured in temperature range of $300<T<650$ K and pressure range of $1<P<5$ atm. Extra diluent gases have an important
effect on laminar burning speed values. Addition of these gases to the mixture decreases the laminar burning speed significantly due to flame temperature reduction. The measured laminar burning speeds were fitted to a power law function and the results were in good agreement with other researchers’.