INVESTIGATION OF A COST-EFFECTIVE METHOD OF NITROGEN INERTING OF MULTICOMPONENT HYDROCARBON GAS MIXTURES IN LARGE STORAGE TANKS

A Thesis

by

NITISH NIKHIL KELEKAR

Submitted to the Office of Graduate and Professional Studies of
Texas A&M University
in partial fulfillment of the requirements for the degree of

MASTER OF SCIENCE

Chair of Committee,	M. Sam Mannan
Co-Chair of Committee,	Mahmoud El-Halwagi
Committee Member,	Debjyoti Banerjee
Head of Department,	M. Nazmul Karim

August 2018

Major Subject: Chemical Engineering

ABSTRACT

The heavy dependence of the world on oil and gas for daily activities has made it highly vital that we do not lose them to incidents such as fires, spills, etc. In addition to economic losses, these incidents also result in damage to life and property. One of the most common forms of tank fires are those caused due to ignition of hydrocarbons in the vapor space of these tanks. And consequently, lightning has been found to be one of the major sources of ignition. The first choice of protection against such fires is complete purging of the vapor space with an inert gas such as nitrogen.

Preventing ignition of flammable gases requires that we have accurate data of their flammability characteristics. This project focuses on experimentally developing a section of the flammability diagram between the lower and upper flammability limits by spark discharge method in a vertical cylindrical vessel. The system under study is a mixture of methane, ethane and propane. The flammability data developed here helps to determine the exact amount of nitrogen gas required to partially inert the gas mixture, as an alternative to completely purging it with inert gas. The cost-effectiveness of addition of air versus addition of nitrogen over a range of mixture compositions was compared and the more feasible option was identified.

ACKNOWLEDGEMENTS

I would like to thank my committee chair, Dr. M. Sam Mannan, and my committee members, Dr. Mahmoud El-Halwagi, and Dr. Debjyoti Banerjee, for their advice, guidance and support throughout the course of this research.

I thank my colleague Ning Gan for training and aiding me with my work, and my team lead Dr. Harendra Mondal for all the help and support and that he provided throughout my time here.

I also thank my friends and colleagues at the Mary Kay O'Connor Process Safety Center, and the department faculty and staff for making my time at Texas A&M University a great experience. And, a special thanks to my parents for their encouragement, patience and love.

CONTRIBUTORS AND FUNDING SOURCES

This work was supervised by a committee consisting of Dr. M. Sam Mannan [Advisor] and Dr. Mahmoud El-Halwagi of the Department of Chemical Engineering and Dr. Debjyoti Banerjee of the Department of Mechanical Engineering. Financial support for the research carried out in this project was provided by Dr. M. Sam Mannan. All work for the thesis was completed independently by the student.

TABLE OF CONTENTS

LIST OF FIGURES

Page

LIST OF TABLES

1. INTRODUCTION

The fuels that we extract from crude are commercially stored in large tanks. Due to the volatility of hydrocarbons, light hydrocarbons (C_1 – C_4) tend to vaporize and occupy the space between the liquid surface and roof/walls. Since air is also present along with the vaporized gases, the system only requires a source of ignition to cause an incident. During situations like thunderstorms and lightning, the hydrocarbon-air mixture in the tanks could easily ignite and lead to fires (ring fires) and explosions. Figure 1 illustrates the most common tank designs used for above ground storage.

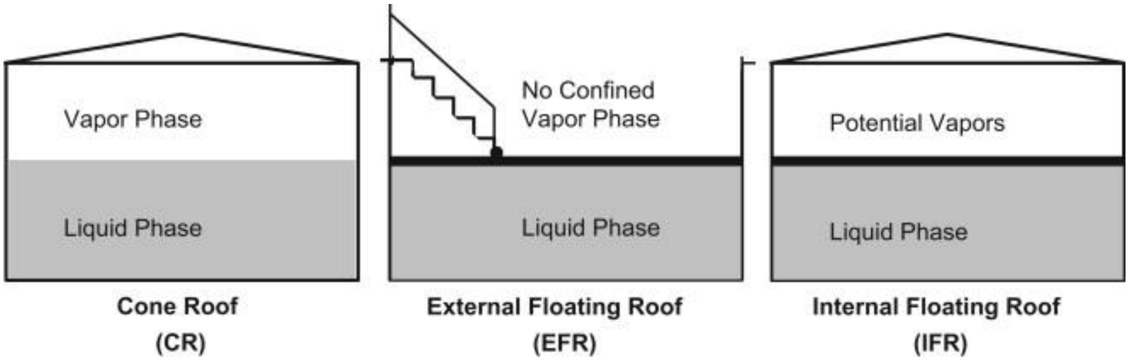


Figure 1: Frequently Used Storage Tank Designs (Reprinted from [1])

Previous studies have shown that lightning is one of the major cause of incidents [2]. Between 1960 and 2003, about 242 storage tank fire cases were reported [3]. Around 80 (about 33%) of these occurred because the tanks were struck by lightning. Similarly, between 2007 and 2011, nearly 240 tank fire incidents were reported among which about 81 were caused by lightning strikes [4]. Tables 1 and 2 emphasize the adverse effect of lighting on industry. Table 3 highlights the need to mitigate lightning related tank fires in the industry.

Table 1: Industrial activities involved in lightning-induced accidents [5]

Industry	Number of Incidents
Petrochemical	125 (65.1 %)
Oil and Gas	58 (30.1%)
Pharmaceutical and Fine Chemicals	3 (1.6%)
Metallurgic and Galvanic	3 (1.6%)
Other	3 (1.6%)

Table 2: Equipment categories involved in lightning-triggered Natech accidents [5]

Equipment	Number of Incidents
Storage Tanks	289 (59.6%)
Flare Stacks	64 (13.2%)
Electrical and Electronic Equipment	56 (11.5%)
Piping	55 (11.3%)
Compressors/Pumps	21 (4.4%)

Table 3: Accident scenarios initiated by lightning strikes – Data on 280 events involving storage tank [5]

Incident Type	Number of Incidents
Loss of Containment	1 (0.4%)
Roof Fire	10 (3.6%)
Explosion	36 (12.8%)
Fires	116 (41.4%)
Other	117 (41.8%)

To prevent such incidents and avoid losses of fuel storage, the vapor space in storage tanks is usually flushed with an inert gas (usually Nitrogen) to dilute the concentration of oxygen and hydrocarbons. For safety consideration, many plants will purge the storage tank long enough that all flammable gases in the vapor space are replaced by the inert gas. However, this process can be expensive and time consuming.

The research carried out in this project is an attempt to assist the cost reduction of inerting, while maintaining the safety of the process. The study will investigate the effectiveness of using LOC and LFL as target purging concentration, as well as the reduction of inert gas quantities and the cost.

2. LITERATURE REVIEW

2.1 Flammability Parameters

The flammability of gas mixtures in air is frequently characterized by several parameters. Three of those that will be used frequently are defined below:

- Lower Flammable Limit (LFL) in air:

  The minimum concentration of a combustible substance that is capable of propagating a flame in a homogeneous mixture of the combustible and a gaseous oxidizer under the specified conditions of test [6]. Below this concentration the mixture is too lean to burn.

- Upper Flammable Limit (UFL) in air

  The maximum concentration of a combustible substance that is capable of propagating a flame in a homogeneous mixture of the combustible and a gaseous oxidizer under the specified conditions of test [6]. Above this concentration the mixture is too rich to burn but may become flammable upon mixing with air.

- Limiting Oxygen Concentration (LOC)

  Below the limiting oxygen concentration, it is not possible to support combustion, independent of the fuel concentration. The LOC is expressed in units of volume percent of oxygen. The LOC is dependent on the pressure and temperature, and on the inert gas. [7]

The flammability limit data of some typical hydrocarbons is mentioned in Table 4.

Table 4: Flammability Limits of some Typical Hydrocarbons [7]

Compound	LFL	UFL
Methane	5.00	15.00
Ethane	2.90	13.00
Propane	2.00	9.50
Butane	1.50	9.00
Ethylene	2.70	36.00
Propylene	2.00	11.00
Acetylene	2.50	80.00

2.2 Flammability Diagram

The following triangle diagram (Figure 2) is a general way of representing the flammability of gas or vapor fuel. The axes are used to plot the concentrations of the fuel, oxygen and inert (like Nitrogen), and each apex of the triangle represents 100% concentration of either one of these. Any point (A) within or on the triangle represents a particular composition of the gas mixture. Any point that lies within the dotted region represents an ignitable mixture of fuel, oxygen and nitrogen, whereas all the compositions outside the dotted area are not. The “Air Line” shown on the diagram represents the set of all compositions that result when fuel is mixed with air (21% Oxygen and 79% Nitrogen). Any point on the “Air Line” lying in between the flammability envelope (dotted line) represents a flammable mixture of atmospheric air and fuel. The figure also shows the flammability limits that have been defined above.

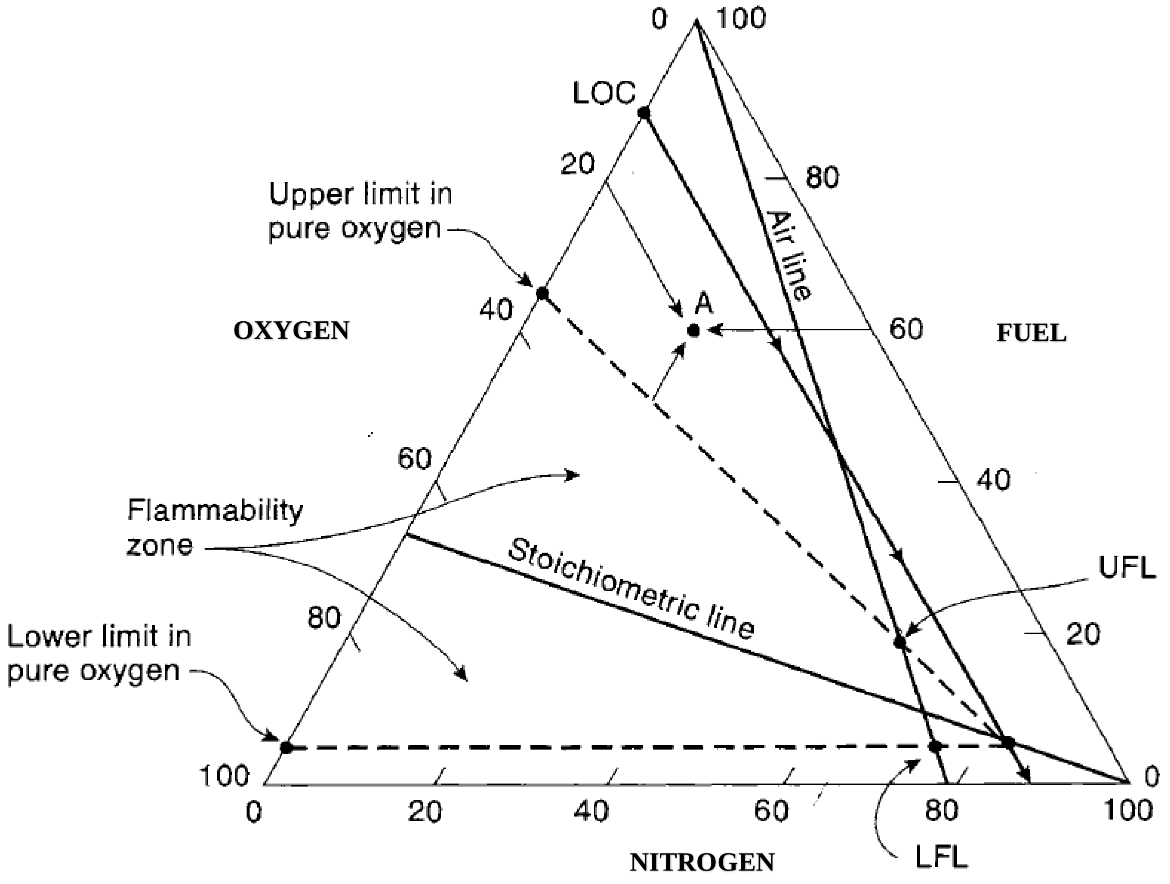


Figure 2: Flammability Diagram (Reprinted from [8])

Minimizing the risk of fires in fuel storage tanks is one of the major concerns. The usual step taken towards attempting to prevent fires is to flush inert gas into the vapor space to reduce the concentration of fuel vapors and oxygen in the region, such that the resulting composition is represented by a point that lies outside the flammability envelope in Figure 2 and hence becomes unignitable.

2.3 Flammability Research

Extensive research has been done in the area of flammable gases and their characteristics, since preventing fires and explosions requires accurate data of flammability limits.

A joint study by Occidental Permian and Trimeric Corporation reviews the data available on the flammability limits of mixtures of carbon dioxide and nitrogen with hydrocarbons and the existing methods for predicting flammability of mixtures, and the existing methods for testing flammability in order to appropriately predict the same for better safety in operations [9].

Zlochower and Green experimentally generated the Limiting Oxygen Concentration data for methane, propane, ethylene, carbon monoxide, hydrogen and their binary mixtures in the presence of air and using nitrogen as inert gas using spark discharge in spherical laboratory vessels. They also modified the Le Chatelier mixing rule to predict LOCs [10].

The flammability limits, and minimum inert gas/combustible gas ratio (ICR) have also been determined for hydrogen/carbon monoxide/nitrogen/air mixtures for varying hydrogen mole fractions in the fuel mixture at atmospheric conditions and at elevated temperatures [11].

Razus et. al investigated a means of estimating the Limiting Oxygen Concentration of methane, propylene and propane gas systems containing nitrogen, carbon dioxide and water vapor as the inert. They calculated the adiabatic flame temperature (CAFT) at the Lower Explosive Limit and LOC of these mixture and developed a correlation which could be used to estimate other LOC [12]. Similarly, research by Vidal et. al. developed an approach to evaluate the LFLs of paraffinic and unsaturated hydrocarbons with nitrogen and carbon dioxide, by an algebraic method and SuperChems^{TM} with CAFT as the basis for calculations [13].

A paper by Giurcan et. al explores a new method for estimating the flammability range of fuel-oxidizer gaseous mixtures based on measurements of explosivity properties e.g. the peak explosion pressure and maximum rate of pressure rise recorded during closed vessel laminar explosions of fuel-oxidizer mixtures far from limits. The data from their tests were used to examine the accuracy of estimated flammability limits (LFL, UFL and LOC) and the Minimum Inert Concentration (MIC) [14].

A paper from the Pittsburgh Research Laboratory reports the LFL values of methane, propane, hydrogen, and deuterium determined using electric spark method and pyrotechnic ignition sources in explosion chambers of different volumes and compares them with existing literature data. They illustrated the effect of buoyancy, turbulence, diffusion, ignitor strength and chamber size on the flammability limits [15].

A joint research program by the Health and Safety Laboratory (Buxton, UK) and the Health and Safety Executive (Merseyside, UK) used CFD modeling and experimental tests to study the effects of carbon dioxide and nitrogen on the flammability limits, and combustion stability of their mixtures with propane, and hydrogen [16].

Another model was derived for estimation of flammability envelopes of mixtures containing inert gases, and the combustion products along the flammability boundaries were analyzed by Fourier Transform Infrared Spectroscopy (FTIR) to verify the assumptions for acetone, methyl formate, methanol, and isopropanol with either steam or nitrogen as the inert gas. The LFL and UFL predicted by their model was found to be in good agreement with reported values [17].

Mendiburu et. al developed an empirical method to determine the flammability limits of a number of combustible gas mixtures in air with carbon dioxide and nitrogen as the diluent. A factor was introduced and approximated by means of correlations. The factor varies with diluent concentration, and the average value of the factor represented the variation of flammability limits with diluent concentration [18].

A paper by Zhao and Mannan analyses the effect of inert gas dilution on the LFL, UFL and minimum inert concentration (MIC) for methane, ethane, propane, ethylene, propylene and binary their mixtures in air and nitrogen. They also modified Le Chatelier's mixing rule by introducing an inert gas dilution parameter and used the equation to estimate the flammability limits and the MIC [19].

Zhao, Rogers and Mannan also experimentally measured the flammability limits of binary mixtures of methane, ethylene, propane, propylene, acetylene and butane using the same equipment described in this document and compared their results with the Le Chatelier mixing rule and its modified form developed from curve fitting for each binary mixture [20].

2.4 Storage Tank Safety Research

There have also been investigations directed towards improving protection of fuel storage tanks. A research study was carried out to investigate a method of charging nitrogen gas into a floating roof tank seal ring up to a calculated safe oxygen content, with the aim of preventing rim-seal fires caused by lightning [21]. Necci et. al focused their research on identifying event sequences and scenarios during lightning strikes on storage tanks and outlined a methodology that would allow the prediction of frequencies of final scenarios that could arise (1). On similar lines, another methodology was proposed that allowed quantitative risk assessment of large tank fires caused by lightning. It was used to calculate the probabilities of lightning strikes, damage to tank wall/roof, and failure of fire protection systems [22].

There has been extensive research into the flammability characteristics of combustible gases, as well as storage tank safety solutions. But, there haven’t been sufficient attempts to use the flammability limit data to mitigate fires and explosions in storage tanks. The following research focuses on experimentally determining the flammability envelope of a known composition of hydrocarbon gas mixtures in air, by addition of nitrogen, as inert gas, into the system to render the mixture unignitable. It is an attempt to study partial inerting as a substitute to completely purging the system with inert gas.

3. METHODOLOGY

For a hydrocarbon gas mixture in air, the flammable region between the UFL and LFL will be generated via experiments. A second objective of this project is to make a comparison between the cost effectiveness of using the LOC or the LFL, as the target purging concentration instead of complete purging with N_2 gas.

The experimental procedure involves addition of an inert gas (Nitrogen in this case) into a known composition of the fuel-air. The fuel selected can either be a single pure hydrocarbon such as methane, ethane, propane, ethylene or butane, or can be a mixture of 2 or more of these gases. In this project, a mixture containing 85% methane, 7.5% ethane and 7.5% propane serves as the fuel.

As the N_2 concentration in the fuel-air system is increased, the fuel to oxygen ratio (F : O) remains constant, and the system composition follows a path towards the 100% N_2 vertex of the triangle diagram as shown in Figure 3. For every fuel-air mixture, as we add more N_2, we will arrive at a point will where the mixture does not ignite. At this point, the system composition has reached a point that lies outside the flammable region of the triangle diagram and no further addition of N_2 is necessary.

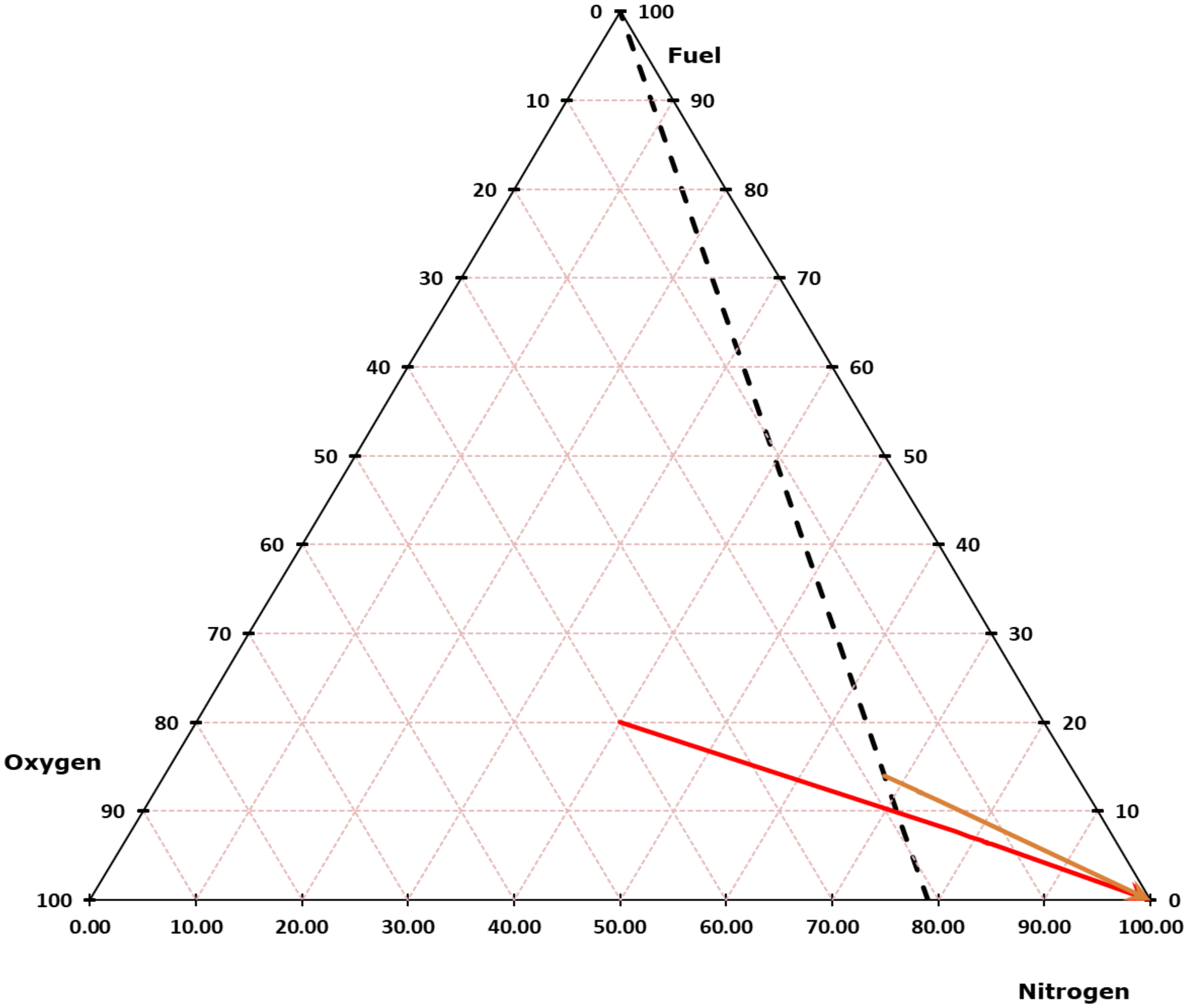


Figure 3: Path followed by System on Addition of Pure Nitrogen to a Fuel-Air Mixture

3.1 Experimental Apparatus

The apparatus is modified and upgraded based on the original design by Wong [23] and Zhao [24]. With additional parts and improved detectors, the new developed instrument is capable of measuring the flammability limits at initial temperature up to 300°C and initial pressure up to 2 atm. It consists of six parts: (1) chemical supply; (2) feeding system; (3) mixing system; (4)

reaction system; (5) ignition system; (6) data acquisition system. A detailed description of each part is provided below.

1) Chemical Supply

The chemicals currently used in this project are ultra-high purity hydrocarbon fuels (methane, ethane, propane), nitrogen, and air. All of these chemicals are stored in pressurized cylinders.

2) Feeding System

The feeding system includes a manifold which connects the chemical cylinders, to the vacuum pump, the mixing vessel and the reaction vessel (Figure 4).

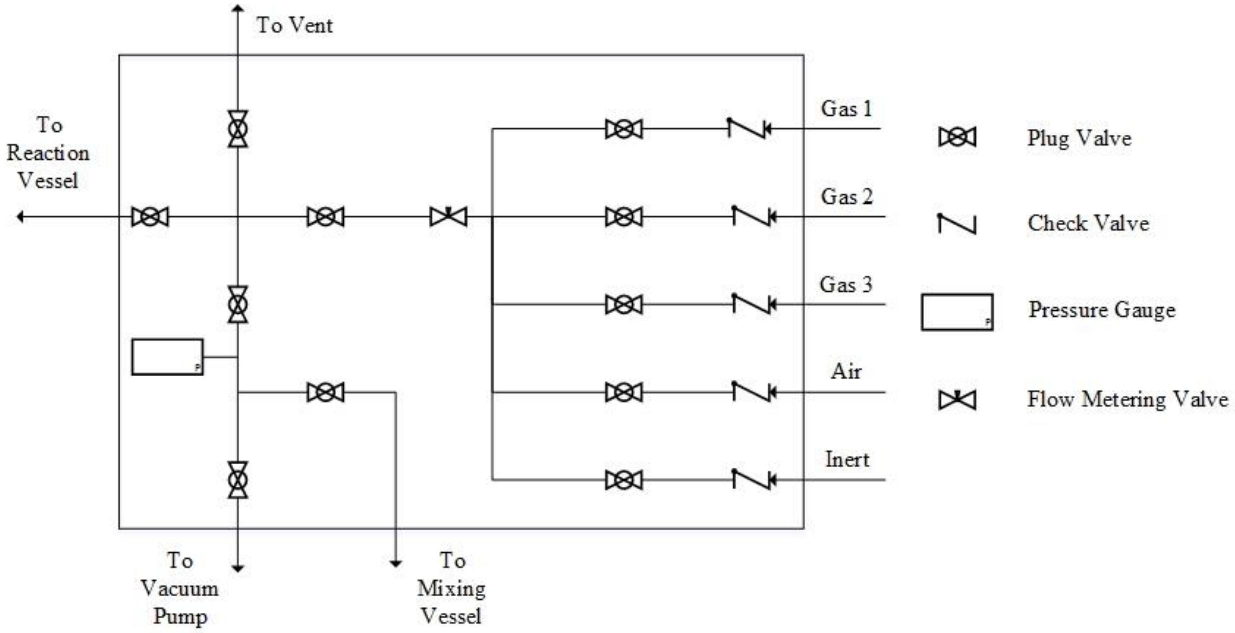


Figure 4: Gas Feeding Manifold

The lines connecting the fuel, inert, and oxidizer cylinders to the gas feeding manifold contain check valves to prevent reverse gas flow in case of valve failure or operator error. The junction area from all pressurized cylinders has a pressure transducer that provides pressure information for loading the gas to specified pressure and plug valves that allow isolation of each section from the gas line and each other. The vent line releases the manifold contents, as well the gases in the reaction vessel and the mixer during different stages of gas loading, directly into a laboratory vent to prevent the collection of flammable gases in laboratory.

3) Mixing System

The mixing vessel is a cylinder (internal diameter: 9.8 cm and a length: 75 cm) that can be rotated for mixing of gases. A cylindrical Teflon block is present within the vessel that slides along the length of the vessel. The block diameter is slightly smaller than the cylinder internal diameter, allowing smooth movement of the block. When the vessel is rotated, the block falls toward the lower end. Gases move between the block and vessel wall creating high turbulence zones in front of and behind the moving block, which facilitate fast mixing of gases. Figure 5 shows the schematic diagram of the mixing vessel. A DC motor is coupled to the shaft connected with the vessel, and this is used to rotate it. The motor is powered by a variable voltage controller which enables selection of rotation speed by voltage adjustment. The mixing vessel is connected to the feeding manifold during the loading phase, with a quick connector fitting and flexible metal hose. The hose and mixing vessel are disconnected while the vessel is rotated during mixing.

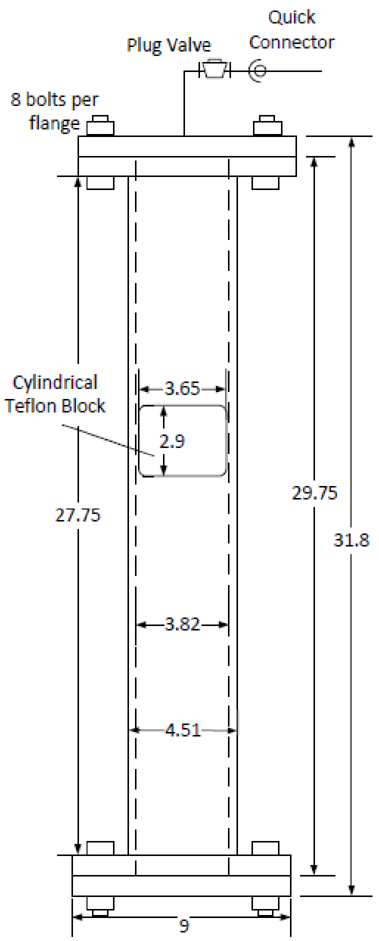


Figure 5: Mixing Vessel Schematic (in inches)

4) Reaction System

From the mixing vessel, the gases are transferred to the reaction system for combustion. The reaction system consists of two major parts, the reaction vessel and the heating unit.

The reaction vessel is made of four parts: i) the hanging plate with a hole in the middle for the plate for the gas line and thermocouple to pass through. ii) the top flange, where the gas line and thermocouple will go through to the inside of reaction vessel, also the pressure relief valve is installed on the top flange. iii) the reaction vessel body, is a 100 cm long and 4-inch nominal diameter (inner diameter = 10.2 cm, outer diameter = 11.3 cm), 316 stainless steel cylinder with welded flanges at both ends. iv) the bottom flange where the ignition fuse wire and the evacuation gas line are installed. The bottom flange and the top flange are bolted directly to the reactor body. The vessel is sealed against vacuum and pressure with O-ring. At the bottom of the reaction vessel, a ball valve is installed and connected with a flexible hose to the fume hood for the purpose of venting gas after combustion reaction is completed.

For conducting tests at elevated conditions, the reactions vessel is outfitted with a heating system. It consists of high temperature heating tape (Heavy Insulated, 1045W output) and temperature controller (accuracy = ±0.3%, Fish Spine thermocouple) box. The heating tape is connected to the temperature controller box to switch on/off the voltage input and change the temperature. Also, a thermocouple (K type) is installed outside the reaction vessel at different position to monitor the temperature and make sure the vessel is heated uniformly.

5) Ignition System

The igniter that holds the fuse wire (American Wire Gauge 40, tinned copper wire) consists of a wire holder section and a vessel seal section. The wire holder section is a pair of square copper rods with a spring-loaded wire grip section mounted on a cylindrical platform made of non-conducting polymer. The fuse wire is connected to the igniter circuit via the copper rods, which are soldered to wiring that leads outside the reaction vessel via the vessel seal section. The wire holder section is connected to the seal section with a short stainless-steel tube, which also contains the circuit wiring. The center of the gland is fitted with a stainless-steel plug and welded. The circuitry wiring is routed through a hole in the plug, which is filled with epoxy to provide a hermetic seal. The igniter port on the bottom of the ignition vessel consists of a tapped hole with the face seal male connector portion installed. The pressure seal is accomplished by inserting the igniter into the port and tightening the screw cap.

6) Data Acquisition System

In this experiment, pressure and thermal sensors are used to detect combustion in this apparatus. Figure 6 shows the sensor configuration in the reaction vessel.

The pressure generated within the reaction vessel is monitored via a dynamic pressure transducer (Honeywell STJE, 500 PSI, 0 – 5V output signal, ± 0.05 % accuracy, 3 KHz response) mounted on the top plate. It is mounted on the top plate so that it is sufficiently distant from the ignition source and heat does not affect the pressure reading. Maximum pressure is obtained by integrating the portion of the dynamic pressure vs. time curve that is above the baseline, and applying a conversion factor of 51.02 psi per V·s.

The thermal sensors are eight thermocouples (K type probes, 10ms response time, ungrounded). They are located at 20 cm (TC1), 35 cm (TC2), 50 cm (TC3), 65 cm (TC4) and 80 cm (TC5-1 & TC5-2) from the top. The flame front generated during combustion may not have a uniform shape Therefore, two thermocouples are installed at the 80 cm mark in order to confirm that the flame has propagated to the top. There are several advantages to using thermocouples instead of thermistors or resistance temperature detectors (RTD). Firstly, thermocouples can withstand higher temperatures as well as shock and vibration effects. Secondly, an ungrounded thermocouple has 0.01s response time which is quick enough to detect the flame propagation and temperature change. And finally, a thermocouple has a diameter of 0.04 inch, which makes them last longer. These advantages are significant for measurements during combustion events where response time and stability are major considerations.

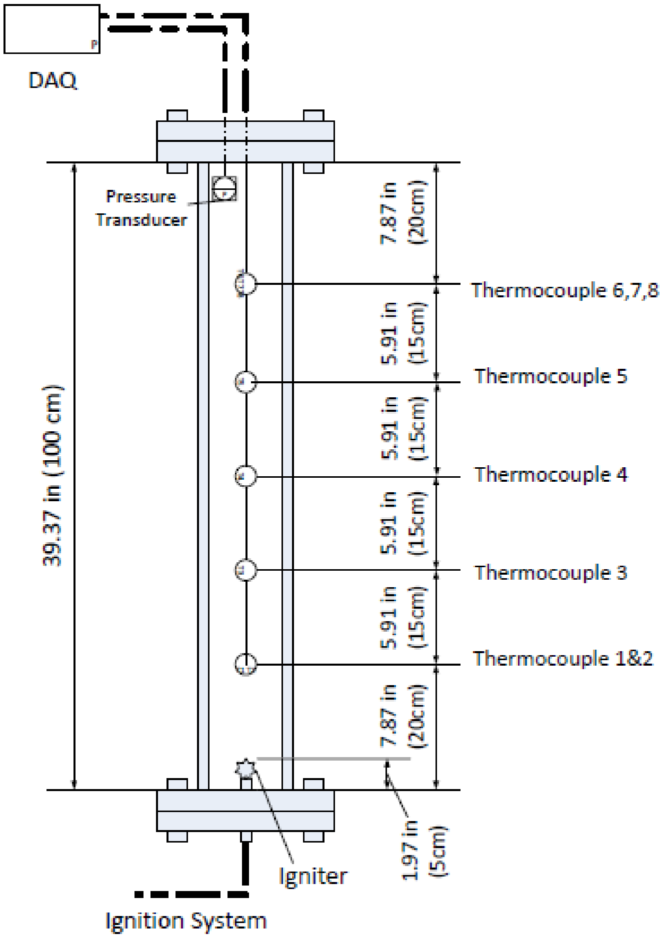


Figure 6: Reaction Vessel Internal Schematics

The thermocouples are suspended at the center axis of the reaction vessel at different lengths from the top plate and connect outside the reaction vessel by a multiconductor feedthrough.

Data is recorded with a desktop computer (USB connection, 24-bit resolution, 8 inputs, ± 0.05% accuracy) and a data acquisition card with a screw-type terminal attachment. The data acquisition card measures differential voltages, allowing it to measure both the thermocouples as well as the pressure transducer. The measurement process is controlled by a Labview® program which then automatically transfers the data to a spreadsheet with a preset name and location.

3.2 Experimental Procedure

Figure 7 shows the entire flammability set up along with valve numbers. The experiment runs will be carried out as follows:

1. Open the required gas cylinder and adjust the gas cylinder regulator to appropriate pressure. (Default setting: Fuel cylinders 15 – 35 psia, oxidizer 44.7psia, air 70 – 90 psia and inert 50.7psia)
2. Start the vacuum pump.
3. Connect the quick connector (QC-1) to mixing vessel. Open valve 7, 10, 11, 12. Make sure flow meter valve (FMV-1) stays open.
4. Vacuum the mixing vessel and manifold for 3 mins. Then close valve 7 and 10.
5. Open valve 1 to fill in fuel 1.
6. Use valve 7 to regulate flow of fuel 1 into the mixing vessel. When pressure reading on the meter approaches desired value (close to the calculation value, but do NOT overfill), close valve 7. Then close valve 1.
7. If the reading does not reach the desired value, open valve 7 slowly to add exact amount of fuel 1 and then close valve 7. Enter the final pressure in the excel sheet.
8. Close valve 11. Ensure valve 1 is closed before opening valve 7. Turn on the vacuum pump. Open valve 10 and vacuum the manifold for 3mins. Then, close valve 7 and 10.

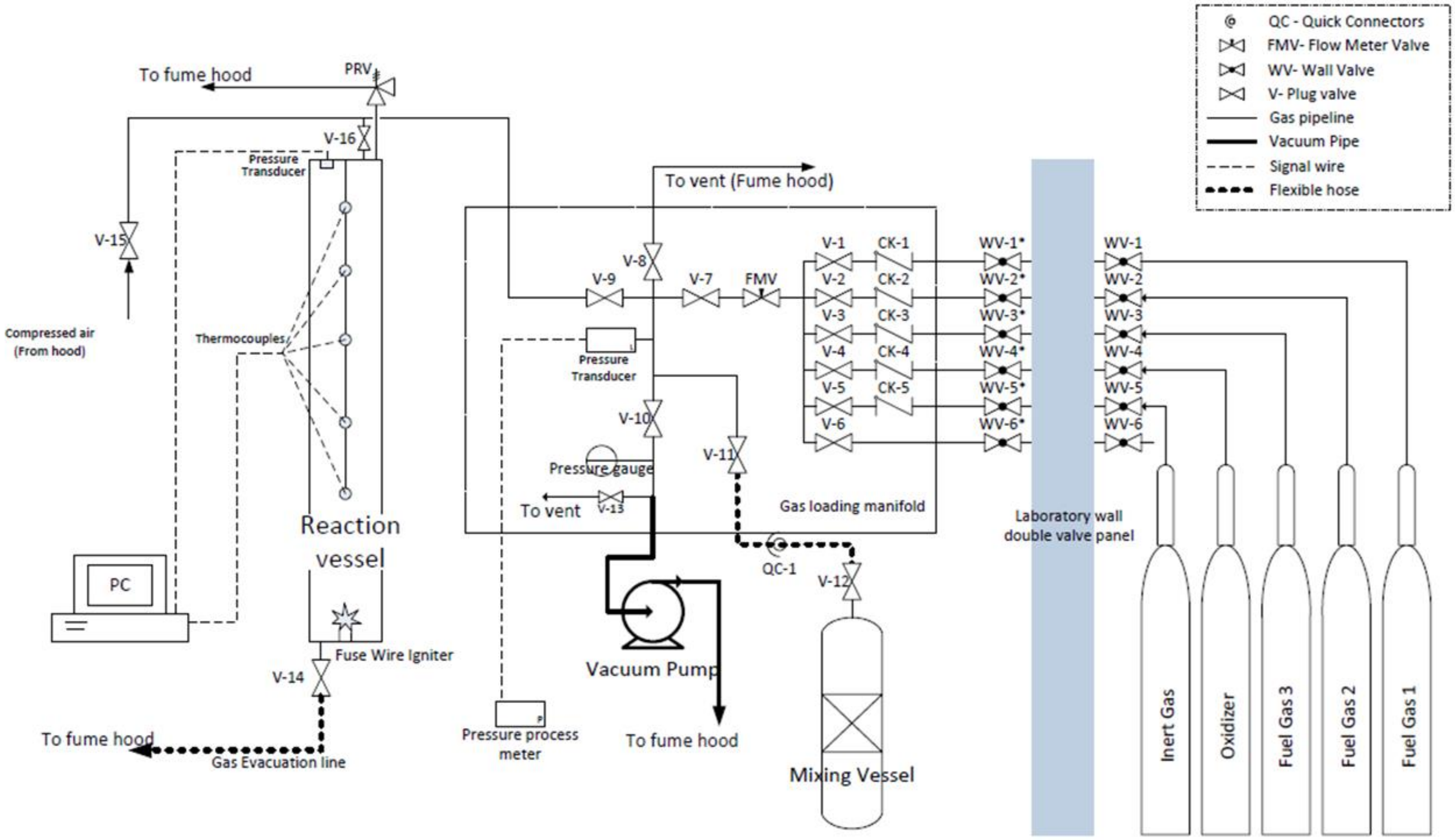


Figure 7: Schematic representation of experimental apparatus

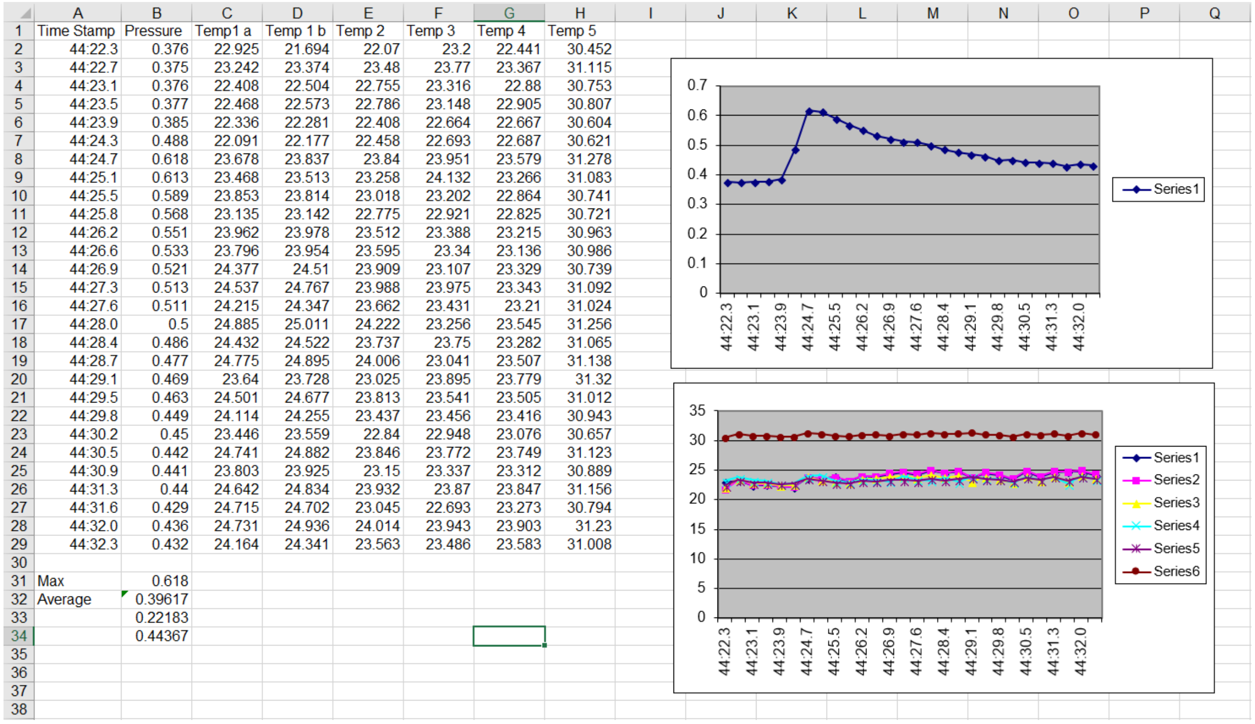
9. If a second fuel is required, repeat steps 6 – 8 while using valve 2 instead of valve 1.
10. If inert gas is required, repeat steps 6 – 8 while using valve 5 instead of valve 1.
11. For filling oxidizer, repeat steps 6 – 8 while using valve 4 instead of valve 1.
12. After loading all of the gases into the mixing vessel, make sure valve 11, 12 are closed. Disconnect the quick connector (QC-1) and start the DC motor. Set the voltage controller to 20 flips/min. Let the mixing continue for 3 mins.
13. To vacuum the reaction vessel, check the vessel has reached the desired temperature. If not, wait till the temperature is raised up. Close valve 14 and open valve 9, 10. Open valve 16 with actuator switch. Let the vacuum pump run for 3mins. Close valve 9, 16.
14. Before transferring gas from mixing vessel to reaction vessel, connect the quick connector (QC-1). Open valve 11 and vacuum for another 1min. Close valve 10, 11. Open valve 9, 12, 16. Then open valve 11 slowly to fill the reaction vessel. When pressure reading on the meter approaches desired value (DO NOT overfill), close valve 11. Then close valve 9, 16.
15. If the reading does not reach the desired value, open valve 9, 16. Then slowly open valve 11 to add exactly amount of mixed gas. Close valve 11. Then close valve 9, 16.
16. Put down the pressure inside the excel file. Let the mixed gas heat up for 5 mins.
17. Using the software on the PC, ignite the mixture in the reaction vessel and observe the pressure and temperature plots recorded by it.
18. The pressure and temperature data are automatically transferred to a spreadsheet.
19. Next, drain the reaction vessel through the fume hood by opening valve 14. Then open valve 16 using the actuator switch and keeping valve 14 open, flush air through the vessel to clean out any residual gases.

20. To save time in continuous experiments, the vent procedure can be done when the mixed gas is heated. Open valve 11, 12. Turn on the vacuum pump. Open valve 10 to vacuum the manifold and mixing vessel till the pressure reading stop dropping. Close valve 10, 11. Turn off the vacuum pump. Open valve 7. Repeat step 5 - 20 to load gas for next experiment.

3.3 Data Analysis

The pressure and temperature data recorded in the spreadsheet (For example, see Figure 8) can be used to study the combustion behavior.

The maximum pressure (in psi) recorded is identified and the average initial reaction vessel pressure (in psi) before ignition, is calculated. The difference gives the pressure rise observed when the mixture is ignited. A mixture is considered flammable if the pressure rise is more than 7% and a minimum temperature change of 5^oC is recorded on the lowest thermocouples during the explosion. For an initial pressure of 1 atm, a 7% pressure rise corresponds to 6.9 kPa (1.0 psi)—this value was used as a flammability criterion in all the runs. This means that gas composition being tested in that run is considered to be non-flammable only if the maximum pressure rise recorded by the transducer was lower than 1.0 psi.



Time Stamp	Pressure	Temp1 a	Temp 1 b	Temp 2	Temp 3	Temp 4	Temp 5
44:22.3	0.376	22.925	21.694	22.07	23.2	22.441	30.452
44:22.7	0.375	23.242	23.374	23.48	23.77	23.367	31.115
44:23.1	0.376	22.408	22.504	22.755	23.316	22.88	30.753
44:23.5	0.377	22.468	22.573	22.786	23.148	22.905	30.807
44:23.9	0.385	22.336	22.281	22.408	22.664	22.667	30.604
44:24.3	0.488	22.091	22.177	22.458	22.693	22.687	30.621
44:24.7	0.618	23.678	23.837	23.84	23.951	23.579	31.278
44:25.1	0.613	23.468	23.513	23.258	24.132	23.266	31.083
44:25.5	0.589	23.853	23.814	23.018	23.202	22.864	30.741
44:25.8	0.568	23.135	23.142	22.775	22.921	22.825	30.721
44:26.2	0.551	23.962	23.978	23.512	23.388	23.215	30.963
44:26.6	0.533	23.796	23.954	23.595	23.34	23.136	30.986
44:26.9	0.521	24.377	24.51	23.909	23.107	23.329	30.739
44:27.3	0.513	24.537	24.767	23.988	23.975	23.343	31.092
44:27.6	0.511	24.215	24.347	23.662	23.431	23.21	31.024
44:28.0	0.5	24.885	25.011	24.222	23.256	23.545	31.256
44:28.4	0.486	24.432	24.522	23.737	23.75	23.282	31.065
44:28.7	0.477	24.775	24.895	24.006	23.041	23.507	31.138
44:29.1	0.469	23.64	23.728	23.025	23.895	23.779	31.32
44:29.5	0.463	24.501	24.677	23.813	23.541	23.505	31.012
44:29.8	0.449	24.114	24.255	23.437	23.456	23.416	30.943
44:30.2	0.45	23.446	23.559	22.84	22.948	23.076	30.657
44:30.5	0.442	24.741	24.882	23.846	23.772	23.749	31.123
44:30.9	0.441	23.803	23.925	23.15	23.337	23.312	30.889
44:31.3	0.44	24.642	24.834	23.932	23.87	23.847	31.156
44:31.6	0.429	24.715	24.702	23.045	22.693	23.273	30.794
44:32.0	0.436	24.731	24.936	24.014	23.943	23.903	31.23
44:32.3	0.432	24.164	24.341	23.563	23.486	23.583	31.008
Max	0.618						
Average	0.39617						
	0.22183						
	0.44367						

Figure 8: Example of the Data Recorded by the Labview Program

Combustion behavior in the reaction vessel can be classified into five different types over a range of concentrations that span the LFL to the UFL for flammable gas mixtures [20].

1) Non-propagation

Non-propagation lacks a flame propagation after ignition, which can be due to a variety of factors, such as very low fuel or oxidizer concentrations, low ignition energy input or low ignition energy density [20, 23]. Normally, this type of behavior shows absence or negligible temperature and pressure fluctuations.

2) Flash combustion

Flash combustion is characterized by vertical flame propagation, with little or no horizontal propagation, which terminates within a short distance of the ignition source to produce a minor temperature and pressure increases [20, 23]. A reasonable explanation for this is that a combusting gas mixture will travel upward because of buoyancy force, and due to rapid heat loss, its temperature will decrease until it drops to ambient temperature of gas mixture. This project observes more flash combustion over non-propagation.

3) Discontinuous flame propagation

Discontinuous flame propagation is characterized by a flame that propagates vertically and horizontally but terminates before reaching the top of the reaction vessel [20, 23]. This differs substantially from the profiles of flash combustion. since the maximum pressure is significantly greater than the pressure rise caused by flash combustion because a greater portion of the gas in the reaction vessel participates in combustion than that in the flash combustion behavior.

4) Continuous flame propagation

Continuous flame propagation is observed when the flame propagates vertically and horizontally to the top of the reaction vessel [20, 23]. In this case, all the thermocouples detect the flame front in succession and then the temperatures slowly decrease in value as the gas around the thermocouples cools. Hence, they exhibit similar temperature profiles. Comparing this with flash and discontinuous flame propagation, we see a greater pressure rise, which indicates more gas has combusted.

5) Violent continuous flame propagation

Violent continuous flame propagation is described by a violent combustion of the gas. The flame propagates upward and dynamic pressure varies much more rapidly than the temperate continuous flame propagation [20].

4. RESULTS

4.1 Flammability Envelope

The sample fuel selected for this project was a mixture of 85% methane, 7.5% ethane and 7.5% propane. With proper mixing of the fuel and air, the fuel concentration was varied from 4% to 16%, then additional nitrogen was added increasingly for each test until the gas mixture was tested as non-flammable.

The experimental result tables for each fuel to air ratio test are presented in the Appendix. Each table shows the overall composition of fuel and air, and the additional nitrogen added to the system at each run, as well as the recalculated final concentration of each fuel species, oxygen and nitrogen. The tables also show the maximum explosion pressure generated by the flame, and the highest thermocouple level that the flame reached.

Figure 9 shows the flammability limit envelope developed from this experimental analysis. Each colored line represents a fixed number of fuel to oxygen ratio (or fuel to air). To each of these fixed ratios, nitrogen was added and the resulting mixture was tested for flammability. Each point on the lines represents a mixture created with a new different nitrogen but fixed fuel to oxygen concentration, and the quantity of nitrogen increases downward. A ‘solid circle’ represents a mixture that ignited and a ‘cross’ represents a mixture that is non-flammable. The dotted line represents the air line, and the solid black line is outlines the points at which the gas mixture just transitioned into the non-ignition zone. The LFL and UFL of the mixture are as tested and represented by the outermost points on the flammability envelope.

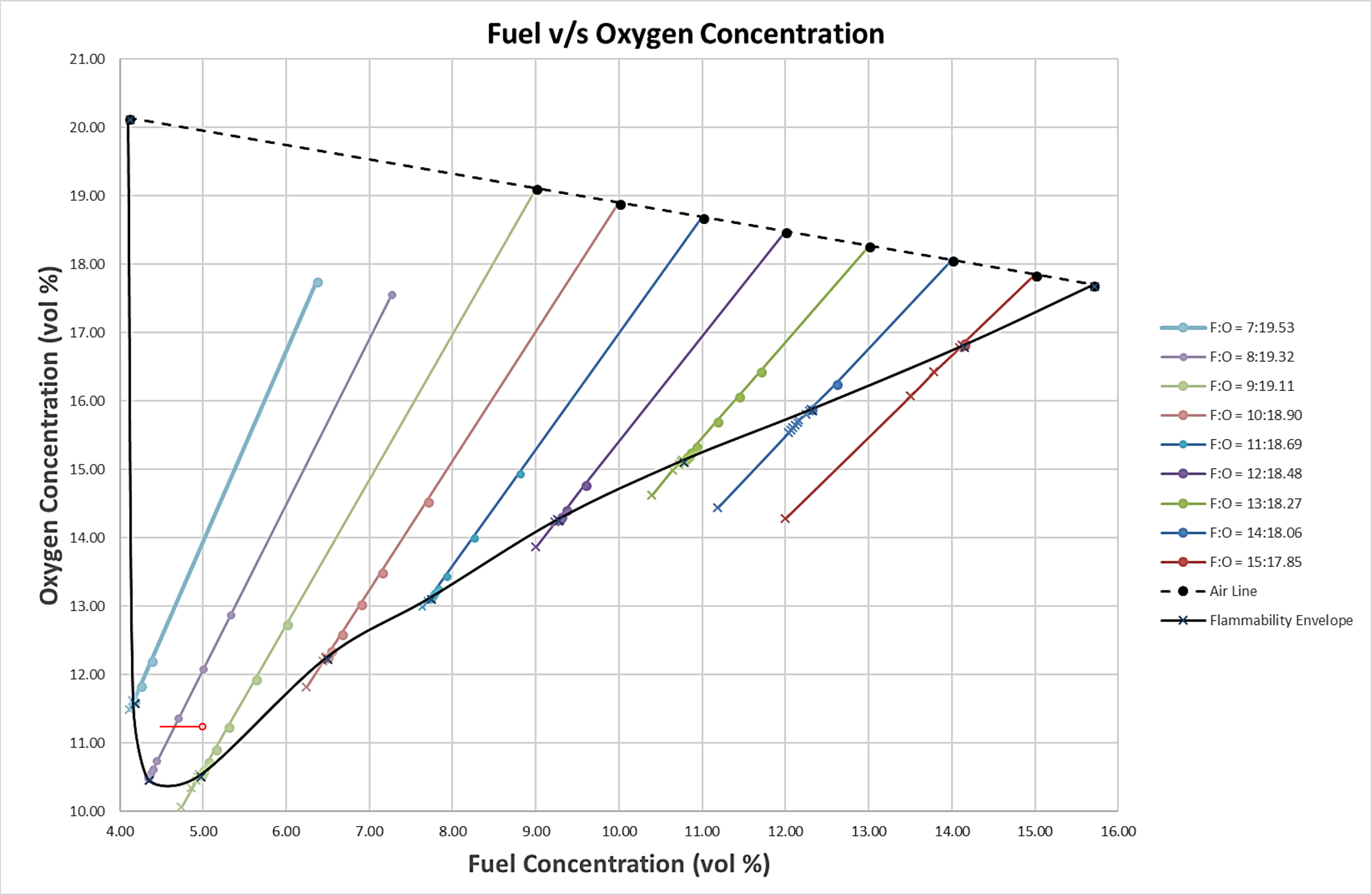


Figure 9: Flammability Limit Envelope Generated from Experiments

The experimentally developed flammability envelope is transferred to a triangle flammability diagram in Figure 10. The fuel refers to the gas mixture which is under study. The solid curve represents the flammability envelope with the points of non-ignition marked on them.

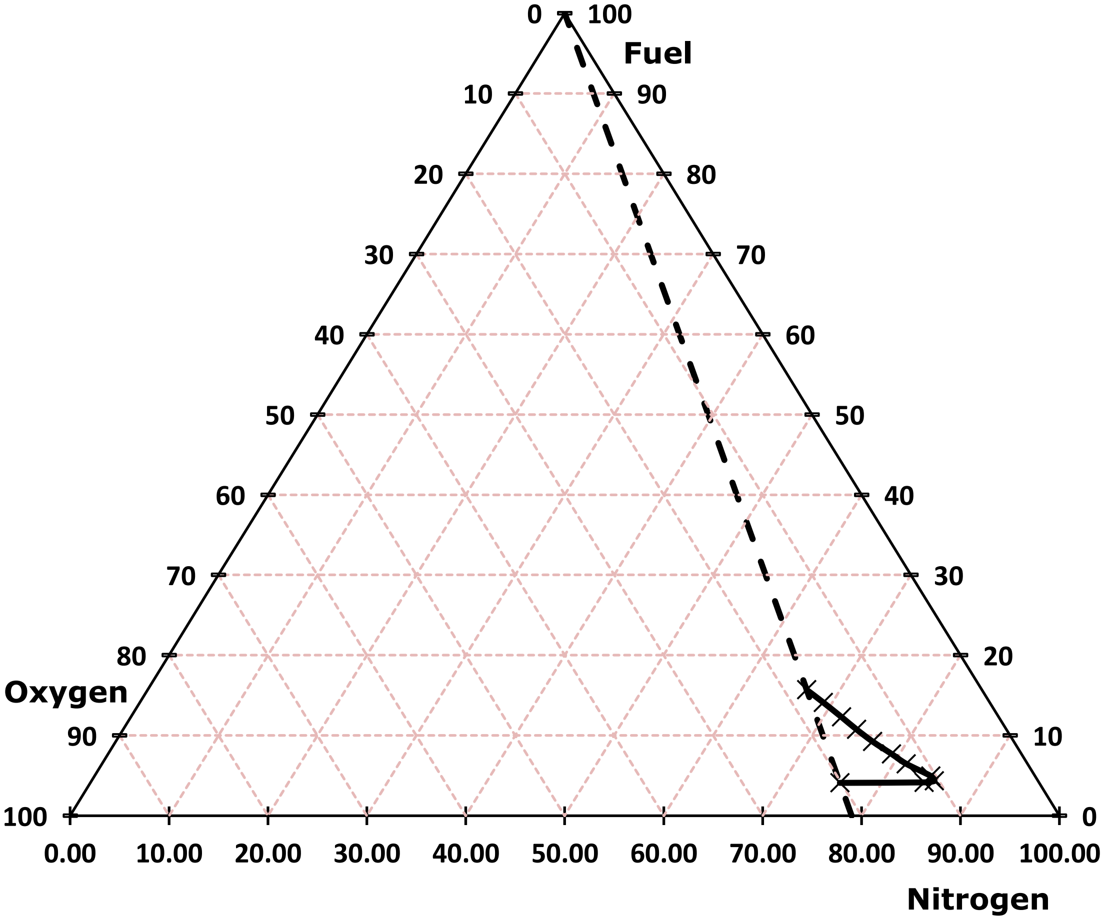


Figure 10: Experimental Results represented on a Flammability Diagram

The fuel being tested has a majority of methane, and small amounts of ethane and propane. This mixture was chosen with motive of attempting to mimic natural gas. Usually methane makes up about 85 to 95% of natural gas with the rest being small concentrations of ethane, propane, butane, ethylene. A very high concentration of methane would have made the flammability tests of the mixture behave very similarly to that of methane. Also, this experimental procedure involves manual addition of gas to mixing vessel based on pre-calculated values, and therefore very small gas concentrations would have been difficult to handle accurately. Additionally, the presence of substantial concentrations of ethane and propane help to highlight their combined effect on the LFL, UFL and LOC of methane. Table 5 provides a comparison of the three flammability limits for methane and the fuel mixture studied here.

Table 5: Comparison of Flammability Limits for Methane and Study Fuel Mixture

Fuel	**LFL (vol %)**	**UFL (vol %)**	**LOC (O_2 vol %)**
Methane	5.0 [10]	15.8 [10]	11.1 [10]
Experiment Fuel	4.1	15.7	10.38

Le Chatelier proposed an empirical mixing rule to determine the Lower Flammability Limit of flammable gas mixture using just their pure fuel LFL data and mole fractions. An equivalent form of the mixing rule was then put to use for calculating the Upper Flammability Limit as well. Equations 1 and 2 are the mixing rules [25].

$$\mathrm{LFL_{mix}} = \frac{1}{\sum_{i=1}^{N} {y_i}/{\mathrm{LFL_i}}} \qquad -(1)$$

$$\mathrm{UFL_{mix}} = \frac{1}{\sum_{i=1}^{N} {y_i}/{\mathrm{UFL_i}}} \qquad -(2)$$

where y_i is the mole fraction of the i^{th} gas species in the mixture, LFL_i and UFL_i are the lower and flammability limits of the i^{th} component (in vol%). These equations were used to calculate the theoretical values of the flammability limits of the experiment mixture and these values were compared to the experimentally obtained values in table 6. The pure component LFL and UFL values were given in table 4.

Table 6: Comparison of Theoretical and Experimental Flammability Limits

	Theoretical	**Experimental**
Lower Flammability Limit (vol%)	4.28	4.1
Upper Flammability Limit (vol%)	14.22	15.7

The comparison shows that the mixing rule for the LFL nearly agrees with the experimental value, while varies significantly in case of the UFL. The reason for this can be explained using the thermodynamic derivation conducted by Mashuga and Crowl [25]. The deviation arises mainly from the assumption that gas heat capacities remain constant. This supposition is acceptable in case of the mixing rule for LFL since the flammable gas concentrations are small and can be considered to be independent of each other, but not so in case of the UFL because of the significant concentrations of flammable gases and their complex mixture with oxygen and nitrogen. The larger gas concentrations along with the complexity of the mixture can alter the heat capacities. They also assumed that combustion kinetics of the gas species are independent of each other and that the adiabatic temperature rise is the same for all gas components. Towards the Upper

Flammability Limit, these aspects are also affected due to soot formation and other unexplained complex effects at the UFL.

4.1.1 Secondary Observations

The result of every run is affected by the location on the flammability diagram. This means that from the LFL to the UFL, the combustion behavior varies. Generally, the drops in pressure rise that would be observed from 0% nitrogen to flammability boundary can roughly be split into the following stages – (i) Greater than 80 psi; (ii) About the order of 60 psi (~50 to 80); (iii) About the order of 30 psi (~20 to 40); (iv) About the order of 10 psi (~5 to 15); (v) 1 to 5 psi; (vi) Less than 1 (not flammable). Not all stages are observed always. Closer to the LFL, the lower pressure rise stages are more prevalent than the higher ones. That is, stages (iii), (iv), (v) and (vi) were clearly observed when LFL testing was performed. On the other hand, the higher pressure-rise stages become more pronounced towards the UFL and the lower stages may get skipped. Around the UFL, observed pressure rises jumped from stage (v) to stage (ii) without exhibiting the lower stages.

When the 0% nitrogen value (air line concentration) for the lower fuel compositions of 7%, 8% and 9%, were being tested, a phenomenon was observed in which a "sound" was produced within the reaction vessel during ignition. In this region, the flame propagation speed is significantly higher than that in the vicinity of the upper flammability limit. The exact explanation for the noise is unclear, but it could be considered as an indication of flame speed change (i.e., there could be a possible transition from deflagration to detonation). This was assumed to be harmful to the equipment, and hence all mixtures up to the 9% composition have their 0% nitrogen test values reported in figure 9, but those were not tested for the 7% and 8% mixtures.

4.2 Cost Effectiveness Comparison

The gaseous fuels in the vapor space of storage tanks would be mixed with air. These mixtures can be rendered non-flammable by altering the concentration such that the system ends up at a point outside flammable region of the flammability diagram. This can be done in 2 ways – i) by adding more air into the system to dilute the fuel concentration to below its Lower Flammability Limit, or ii) by adding nitrogen to the system as was done in this project.

The flammability envelope data generated here was further used to compare the cost effectiveness of using air or nitrogen to prevent the hydrocarbon gas system from igniting. The quantity and cost of additional air required to render the system inert was calculated and compared to the additional nitrogen required to the same.

Table 7 gives the values of minimum additional air required to make the given mixture of fuel and air inert, by reducing the concentration to below its lower flammability limit. It compares it with the minimum additional nitrogen required to alter the composition of the mixture such that it lies outside the flammability envelope and is inert. A 50% safety margin has been assumed in case of the LFL, which means the LFL considered for calculation is 2% instead of the observed 4.1%. Similarly, a 2% safety margin has been assumed for nitrogen dilution of the system, implying that 2% more nitrogen is required. Cost of nitrogen gas has been assumed to be \$5 per m^3 (at standard temperature and pressure), and that of air has been assumed as \$0.50 per m^3 (at standard temperature and pressure).

Table 7: Comparison of Air and Nitrogen required for Inerting

Initial Conditions		For Inerting			
		Additional Nitrogen		Additional Air	
Fuel (vol%)	Air (vol%)	Vol %	Cost ($/m^3)*	Vol %	Cost ($/m^3)*
7.00	93.00	103.35	5.17	241.46	1.21
8.00	92.00	128.06	6.40	290.24	1.45
9.00	91.00	123.91	6.20	339.02	1.70
10.00	90.00	84.41	4.22	387.80	1.94
11.00	89.00	68.09	3.40	436.59	2.18
12.00	88.00	50.68	2.53	485.37	2.43
13.00	87.00	39.17	1.96	534.15	2.67
14.00	86.00	30.13	1.51	582.93	2.91
15.00	85.00	20.50	1.03	631.71	3.16

*The cost is in term of $ per m^3 of vapor space volume. Air and N_2 volumes have been incorporated

The values given in the table can be used to decide whether, for a given fuel-air mixture, the addition of air or the addition of nitrogen is the more cost-effective option. Though the amount of air required is significantly higher than the nitrogen required, it is clearly seen that or the lower fuel composition systems addition of air proves to be the less expensive choice. On the other hand, using nitrogen to render the system non-flammable is a better choice for the higher fuel composition mixtures. The prices for additional air and nitrogen become equal at an approximate fuel concentration of 12.12%. The reason for this switch is that nitrogen is more expensive than air due to the additional cryogenic processing required to separate it from air which makes it less economical for the lower fuel concentrations. While, for the higher fuel values, the quantity of air required becomes very high and would neither be feasible nor cost effective.

5. CONCLUSION AND FUTURE WORK

5.1 Conclusions from this Research

In this research, the flammability limit envelope was experimentally generated at standard conditions (atmospheric pressure and room temperature). The experiments employed an innovative design of equipment, in which 6 thermocouples placed at varying heights worked as the flame front temperature detection system, and a transducer recorded the pressure developed during combustion of the gas mixture studied.

A mixture of methane, ethane and propane in air was selected and nitrogen was used as the inert gas. By varying the fuel to air ratio and adding varying amounts of nitrogen the section of the flammability envelope between the upper flammability limit and lower flammability limit was generated.

The flammability envelope developed here helps to determine the exact amount of nitrogen gas required to partially inert the gas mixture, that is, the system is just sufficiently moved out of the flammable zone. This would greatly aid in reducing the nitrogen gas required if complete purging of the vapor space was carried, and consequently, it would decrease the cost of the maintaining the safety of the storage tanks. From the tests, the LFL for this system was found to be 4.1%, and the UFL was 15.7%. The LOC for the system was identified at 10.38% oxygen concentration.

The second objective of the project was to consider the cost-effectiveness of using additional air to reduce the flammable gas concentration below the lower flammability limit, versus the cost-effectiveness of adding nitrogen to render the system non-flammable. It was identified that addition of air appeared to be more cost effective than addition of nitrogen for the lower fuel concentrations, and this reversed at a fuel concentration of 12.12% above which nitrogen addition appeared to be more feasible.

5.2 Future Work

This research was focused on developing a section of the flammability envelope for just one gas mixture, at standard conditions. A lot more work can be done in the future with this study as its basis –

- The rest of the flammability envelope can be developed using pure oxygen and nitrogen.
- This can be extended to other gas mixtures, preferably for mixtures found in the real system. An important gas mixture that can be tested is Shale Gas, since it is an upcoming major source of fuel and a flammability limit studies that accommodate this mixture would play a very significant role in storage safety of these gases.
- The entire flammability envelope can be generated at elevated conditions for this as well as other gas mixtures.

REFERENCES

1. Necci, A, et al., Accident scenarios triggered by lightning strike on atmospheric storage tanks, Reliability Engineering & System Safety, 2014, Vol. 127, pp. 30-46.

2. Nivolianitou, Z, et al., A Methodology for the Hazard Assessment in Large Hydrocarbon Fuel Tanks, Chemical Engineering Transactions, 2012, pp. 171-176.

3. Chang, James I. and Lin, Cheng-Chung., A study of storage tank accidents, Journal of Loss Prevention in the Process Industries, 2006, pp. 51-59.

4. Campbell, Richard. News & Research. NFPA. [Online] August 2014. https://www.nfpa.org/-/media/Files/News-and-Research/Fire-statistics/Occupancies/osflammableorCombustibleLiquidtankStorageFacilities.ashx?la=en.

5. Renni, E., Krausmann, E. and Cozzani, V., Industrial accidents triggered by lightning, Journal of Hazardous Materials, 2010, Vol. 184, pp. 42-48.

6. Standard Test Method for Concentration Limits of Flammability of Chemicals (Vapors and Gases). ASTM International. [Online] http://www.astm.org/cgi-bin/resolver.cgi?E681-01.

7. Perry's Chemical Engineers Handbook Section 23. McGraw Hill, 2008.

8. Mashuga, C.V and Crowl, D.A., Application of the Flammability Diagram for Evaluation of Fire and Explosion Hazards of Flammable Vapors., Process Safety Progress, 1998, pp. 176-183.

9. MacCullum, R.N, Fisher, K.S and McIntush, K.E. Flammability of Mixtures of CO2 and Hydrocarbons.

10. Zlochower, I.A and Green, G.M., The Limiting Oxygen Concentration and Flammability Limits of Gases and Gas Mixtures, Journal of Loss Prevention in the Process Industries, 2009, pp. 499-505.

11. Van den Schoor, F, et al., Flammability limits, limiting oxygen concentration and minimum inert gas/combustible ratio of H2/CO/N2/air mixtures, International Journal of Hydrogen Energy, 2009, pp. 2069-2075.

12. Razus, D., et al., Estimation of LOC (limiting oxygen concentration) of fuel–air–inert mixtures at elevated temperatures by means of adiabatic flame temperatures, Chemical Engineering and Processing, 2006, pp. 193-197.

13. Vidal, M, et al., Evaluation of lower flammability limits of fuel–air–diluent mixtures using calculated adiabatic flame temperatures, Journal of Hazardous Materials, 2006, pp. 21-27.

14. Giurcan, Venera, et al., Prediction of flammability limits of fuel-air and fuel-air-inert mixtures from explosivity parameters in closed vessels, Journal of Loss Prevention in the Process Industries, 2015, pp. 65-71.

15. Cashdollar, Kenneth L, et al., Flammability of methane, propane, and hydrogen gases, Journal of Loss Prevention in the Process Industries, 2000, Vol. 13.

16. Thyer, A. M, et al. Investigations into the Effects of Carbon Dioxide and Nitrogen on the Flammabilty Limits of Gas Mixtures, Symposium Series. 2009, 155.

17. Liaw, Horng-Jang, et al., Flammability limits estimation for fuel–air–diluent mixtures tested in a constant volume vessel, Process Safety and Environmental Protection, 2016, pp. 150-162.

18. Mendiburu, A. Z, de Carvalho, J. A and Coronado, C. R., Method for determination of flammability limits of gaseous compounds diluted with N2 and CO2 in air, Fuel, 2018, Vol. 226, pp. 65-80.

19. Zhao, F and Mannan, M. S., Numerical analysis for nitrogen dilution on flammability limits of hydrocarbon mixtures, Journal of Loss Prevention in the Process Industries, 2016, pp. 600-613.

20. Zhao, F, Rogers, W. J and Mannan, M. S., Experimental measurement and numerical analysis of binary hydrocarbon mixture flammability limits, Process Safety and Environmental Protection, 2009, Vol. 87, pp. 94-104.

21. Zhang, Fei-fei, Jiang, Hui-ling and Zhang, Cheng., Study of Charging Nitrogen to External Floating Roof Tank to Prevent Rim-seal Fires from Lightning, Procedia Engineering, 2014, pp. 124-129.

22. Wu, Dongyin and Chen, Zhen, Quantitative risk assessment of fire accidents of large-scale oil tanks triggered by lightning, Engineering Failure Analysis, 2016, Vol. 63, pp. 172-181.

23. Wong, W. K:. Measurement of Flammability in a Closed Cylindrical Vessel with Thermal Criterion. Chemical Engineering, Texas A&M University, 2006. PhD Dissertation.

24. Zhao, Fuman. Experimental Measurements and Modeling Prediction of Flammability Limits of Hydrocarbon Mixtures. Chemical Engineering, Texas A&M University, 2008. Master of Science Thesis.

25. Mashuga, C.V and Crowl, D.A., Derivation of Le Chatelier's Mixing Rule for Flammable Limits, Process Safety Progress, 2000, pp. 112-117.

APPENDIX

Experimental Data

This Appendix contains the data tables generated during the experiment runs performed for this project. The experiments were conducted at standard conditions (atmospheric pressure and room temperature. Initial fuel compositions chosen were 7 vol% to 15 vol%.

Tables 8 to 16 show the initial fuel and air conditions, and the final fuel and oxygen compositions after addition of required amount of nitrogen gas. The concentrations of the individual gases methane, ethane and propane are also given to ensure that the mixture composition does not fluctuate significantly, that is, the 85:7.5:7.5 proportion is maintained throughout. The tables also contain maximum pressure recorded by the transducer during the combustion reaction, as well as the highest thermocouple level (TC1 = Top, TC2 = 4th, TC3 = 3rd, TC4 = 2nd, TC5 – 1 and TC5 – 2 = 1st) that detected a temperature rise larger than 5^oC. If the signal recorded was just slightly greater than 5^oC, it has been marked as "weak".

Tables 17 and 18 were generated while testing the Lower and Upper Flammability Limits of the mixture. Only the concentration of the fuel and air was altered and did not require any additional nitrogen for testing.

Table 8: Results of 7% Fuel to 93% Air Mixture

Desired Reaction Conditions			Concentration after N_2 Addition					Reaction Results		Flammable ?
Fuel (vol%)	Air (vol%)	N_2 (vol%)	Fuel (vol%)	Methane (vol%)	Ethane (vol%)	Propane (vol%)	O_2 (vol%)	Observed P (psi)	T (Thermocouple Level)	
7.00	93.00	71.00	4.09	84.95	7.53	7.53	11.42	~0.21	No	No
7.00	93.00	70.00	4.12	85.03	7.49	7.49	11.49	~0.28	No	No
7.00	93.00	68.30	4.16	85.19	7.41	7.41	11.60	~0.59	No	No
7.00	93.00	68.20	4.16	85.19	7.41	7.41	11.61	~1.02	1st (weak)	Yes
7.00	93.00	68.00	4.17	85.19	7.41	7.41	11.63	~1.1	1st (weak)	Yes
7.00	93.00	65.00	4.24	84.97	7.77	7.25	11.84	~6.9	Top (weak)	Yes
7.00	93.00	60.00	4.37	84.92	7.54	7.54	12.21	~14.3	Top	Yes
7.00	93.00	10.00	6.36	84.83	7.59	7.59	17.76	~104	Top	Yes

Table 9: Results of 8% Fuel to 92% Air Mixture

Desired Reaction Conditions			Concentration after N_2 Addition					Reaction Results		Flammable ?
Fuel (vol%)	Air (vol%)	N2 (vol%)	Fuel (vol%)	Methane (vol%)	Ethane (vol%)	Propane (vol%)	O_2 (vol%)	Observed P (psi)	T (Thermocouple Level)	
8.00	92.00	84.50	4.34	84.85	7.58	7.58	10.47	~0.67	No	No
8.00	92.00	84.40	4.34	84.85	7.58	7.58	10.48	~2.3	1st	Yes
8.00	92.00	84.30	4.34	84.85	7.58	7.58	10.48	~2.3	1st	Yes
8.00	92.00	84.10	4.34	84.85	7.58	7.58	10.49	~1.9	1st	Yes
8.00	92.00	84.00	4.35	84.85	7.58	7.58	10.50	~2.2	1st	Yes
8.00	92.00	83.00	4.37	84.92	7.54	7.54	10.56	~3.7	3rd (weak)	Yes
8.00	92.00	82.00	4.40	85.00	7.50	7.50	10.62	~8.1	3rd	Yes
8.00	92.00	80.00	4.44	85.15	7.43	7.43	10.73	~7.4	Top (weak)	Yes
8.00	92.00	70.00	4.71	85.05	7.48	7.48	11.36	~20	Top	Yes
8.00	92.00	60.00	5.00	85.02	7.49	7.49	12.07	~60	Top	Yes
8.00	92.00	50.00	5.33	85.12	7.44	7.44	12.88	~78	Top	Yes
8.00	92.00	10.00	7.27	84.89	7.55	7.55	17.56	~122	Top	Yes

Table 10: Results of 9% Fuel to 91% Air Mixture

Desired Reaction Conditions			Concentration after N_2 Addition					Reaction Results		Flammable ?
Fuel (vol%)	Air (vol%)	N2 (vol%)	Fuel (vol%)	Methane (vol%)	Ethane (vol%)	Propane (vol%)	O_2 (vol%)	Observed P (psi)	T (Thermocouple Level)	
9.00	91.00	90.00	4.74	85.12	7.44	7.44	10.06	~0.1	No	No
9.00	91.00	85.00	4.86	84.68	7.66	7.66	10.33	~0.68	No	No
9.00	91.00	83.00	4.92	84.82	7.59	7.59	10.44	~0.18	No	No
9.00	91.00	82.00	4.95	84.89	7.56	7.56	10.50	~0.28	No	No
9.00	91.00	81.50	4.96	84.96	7.52	7.52	10.53	~0.89	No	No
9.00	91.00	81.40	4.96	84.96	7.52	7.52	10.53	~0.31	No	No
9.00	91.00	81.30	4.96	84.96	7.52	7.52	10.54	~2.7	1st (weak)	Yes
9.00	91.00	81.00	4.97	84.96	7.52	7.52	10.56	~2.3	1st (weak)	Yes
9.00	91.00	80.50	4.99	85.02	7.49	7.49	10.59	~3	3rd (weak)	Yes
9.00	91.00	80.00	5.00	85.02	7.49	7.49	10.62	~2.3	3rd (weak)	Yes
9.00	91.00	78.00	5.06	85.15	7.42	7.42	10.74	~14	Top (weak)	Yes
9.00	91.00	75.00	5.14	84.68	7.66	7.66	10.92	~17	Top (weak)	Yes
9.00	91.00	70.00	5.29	85.06	7.47	7.47	11.24	~17	Top	Yes
9.00	91.00	60.00	5.63	85.10	7.45	7.45	11.94	~73	Top	Yes
9.00	91.00	50.00	6.00	84.67	7.66	7.66	12.74	~81	Top	Yes
9.00	91.00	0.00	9.00	84.88	7.56	7.56	19.11	~57	Top	Yes

Table 11: Results of 10% Fuel to 90% Air Mixture

Desired Reaction Conditions			Concentration after N_2 Addition					Reaction Results		Flammable ?
Fuel (vol%)	**Air (vol%)**	**N2 (vol%)**	**Fuel (vol%)**	**Methane (vol%)**	**Ethane (vol%)**	**Propane (vol%)**	**O_2 (vol%)**	**Observed P (psi)**	**T (Thermocouple Level)**	
10.00	90.00	60.00	6.25	85.16	7.42	7.42	11.81	~0.2	No	No
10.00	90.00	55.00	6.45	84.98	7.51	7.51	12.19	~0.15	No	No
10.00	90.00	54.50	6.47	85.03	7.48	7.48	12.23	~0.2	No	No
10.00	90.00	54.30	6.48	85.03	7.48	7.48	12.25	~0.27	No	No
10.00	90.00	54.20	6.48	85.08	7.46	7.46	12.26	~22	Top	Yes
10.00	90.00	54.00	6.49	85.08	7.4	7.46	12.27	~20	Top	Yes
10.00	90.00	53.00	6.54	85.14	7.43	7.43	12.35	~24	Top	Yes
10.00	90.00	50.00	6.67	84.87	7.57	7.57	12.60	~30	Top	Yes
10.00	90.00	45.00	6.90	84.76	7.62	7.62	13.03	~72	Top	Yes
10.00	90.00	40.00	7.14	85.19	7.41	7.41	13.50	~68.5	Top	Yes
10.00	90.00	30.00	7.69	85.10	7.45	7.45	14.54	~88	Top	Yes
10.00	90.00	0.00	10.00	85.02	7.49	7.49	18.90	~68	Top	Yes

Table 12: Results of 11% Fuel to 89% Air Mixture

Desired Reaction Conditions			Concentration after N_2 Addition					Reaction Results		Flammable ?
Fuel (vol%)	Air (vol%)	N2 (vol%)	Fuel (vol%)	Methane (vol%)	Ethane (vol%)	Propane (vol%)	O_2 (vol%)	Observed P (psi)	T (Thermocouple Level)	
11.00	89.00	44.00	7.64	85.01	7.49	7.49	12.98	~0.22	No	No
11.00	89.00	42.87	7.70	85.10	7.45	7.45	13.08	~0.2	No	No
11.00	89.00	42.47	7.72	85.14	7.43	7.43	13.12	~0.24	No	No
11.00	89.00	42.25	7.73	85.19	7.41	7.41	13.14	~78	Top	Yes
11.00	89.00	42.06	7.74	85.19	7.41	7.41	13.16	~82	Top	Yes
11.00	89.00	41.84	7.76	85.23	7.39	7.39	13.18	~24	Top	Yes
11.00	89.00	41.66	7.77	85.23	7.39	7.39	13.19	~68	Top	Yes
11.00	89.00	41.42	7.78	84.79	7.61	7.61	13.21	~79	Top	Yes
11.00	89.00	40.84	7.81	84.83	7.58	7.58	13.27	~34	Top	Yes
11.00	89.00	38.91	7.92	85.00	7.50	7.50	13.46	~64	Top	Yes
11.00	89.00	33.32	8.25	85.07	7.47	7.47	14.02	~70	Top	Yes
11.00	89.00	24.99	8.80	85.00	7.50	7.50	14.95	~69	Top	Yes
11.00	89.00	0.01	11.00	84.83	7.58	7.58	18.69	~112	Top	Yes

Table 13: Results of 12% Fuel to 88% Air Mixture

Desired Reaction Conditions			Concentration after N_2 Addition					Reaction Results		Flammable ?
Fuel (vol%)	Air (vol%)	N2 (vol%)	Fuel (vol%)	Methane (vol%)	Ethane (vol%)	Propane (vol%)	O_2 (vol%)	Observed P (psi)	T (Thermocouple Level)	
12.00	88.00	33.35	9.00	84.88	7.56	7.56	13.86	~0.26	No	No
12.00	88.00	29.91	9.24	85.20	7.40	7.40	14.23	~0.3	No	No
12.00	88.00	29.55	9.26	84.83	7.58	7.58	14.27	~0.4	No	No
12.00	88.00	29.36	9.28	84.87	7.57	7.57	14.29	~33	Top	Yes
12.00	88.00	29.04	9.30	84.47	7.53	8.00	14.32	~24	Top	Yes
12.00	88.00	28.20	9.36	84.98	7.51	7.51	14.42	~70.5	Top	Yes
12.00	88.00	25.11	9.59	84.90	7.55	7.55	14.79	~78	Top	Yes
12.00	88.00	0.01	12.00	85.04	7.48	7.48	18.48	~105	Top	Yes

Table 14: Results of 13% Fuel to 87% Air Mixture

Desired Reaction Conditions			Concentration after N_2 Addition					Reaction Results		
Fuel (vol%)	Air (vol%)	N2 (vol%)	Fuel (vol%)	Methane (vol%)	Ethane (vol%)	Propane (vol%)	O_2 (vol%)	Observed P (psi)	T (Thermocouple Level)	Flammable?
13.00	87.00	25.03	10.40	84.99	7.61	7.40	14.62	~0.3	No	No
13.00	87.00	22.10	10.65	85.12	7.44	7.44	14.99	~0.38	No	No
13.00	87.00	21.21	10.73	84.84	7.58	7.58	15.07	~0.44	No	No
13.00	87.00	20.92	10.75	84.73	7.54	7.74	15.11	~0.99	No	No
13.00	87.00	20.77	10.76	84.90	7.55	7.55	15.13	~0.74	No	No
13.00	87.00	20.63	10.78	84.93	7.54	7.54	15.15	~4	Top (weak)	Yes
13.00	87.00	20.49	10.79	84.93	7.54	7.54	15.16	~86	Top	Yes
13.00	87.00	20.32	10.80%	84.99	7.51	7.51	15.18	~81	Top	Yes
13.00	87.00	20.20	10.82	84.96	7.52	7.52	15.20	~70	Top	Yes
13.00	87.00	20.06	10.83	84.99	7.51	7.51	15.22	~3.6	Top	Yes
13.00	87.00	19.76	10.85	85.02	7.49	7.49	15.26	~1.66	1st (weak)	Yes
13.00	87.00	19.04	10.92	85.08	7.46	7.46	15.35	~3.2	5th (weak)	Yes
13.00	87.00	16.31	11.18	85.04	7.48	7.48	15.71	~3	4th	Yes
13.00	87.00	13.66	11.44	85.03	7.49	7.49	16.08	~80	Top	Yes
13.00	87.00	11.12	11.70	84.99	7.50	7.50	16.44	~68	Top	Yes
13.00	87.00	0.00	13.00	85.11	7.45	7.45	18.27	~94	Top	Yes

Table 15: Results of 14% Fuel to 86% Air Mixture

Desired Reaction Conditions			**Concentration after N_2 Addition**					**Reaction Results**		**Flammable ?**
Fuel (vol%)	**Air (vol%)**	**N_2 (vol%)**	**Fuel (vol%)**	**Methane (vol%)**	**Ethane (vol%)**	**Propane (vol%)**	**O_2 (vol%)**	**Observed P (psi)**	**T (Thermocouple Level)**	
14.00	86.00	25.10	11.19	84.44	7.78	7.78	14.43	~0.27	No	No
14.00	86.00	16.26	12.04	84.88	7.65	7.47	15.53	~.45	No	No
14.00	86.00	16.03	12.07	84.81	7.59	7.59	15.57	~0.44	No	No
14.00	86.00	15.77	12.09	84.63	7.59	7.78	15.60	~0.49	No	No
14.00	86.00	15.49	12.12	84.81	7.59	7.59	15.64	~0.45	No	No
14.00	86.00	15.19	12.15	84.56	7.72	7.72	15.68	~0.46	No	No
14.00	86.00	15.13	12.16	84.86	7.57	7.57	15.72	~0.46	No	No
14.00	86.00	14.28	12.25	84.97	7.51	7.51	15.80	~0.47	No	No
14.00	86.00	13.90	12.29	84.97	7.51	7.51	15.86	~0.58	No	No
14.00	86.00	13.74	12.31	84.90	7.64	7.46	15.88	~0.54	No	No
14.00	86.00	13.74	12.31	84.57	7.80	7.62	15.89	~2	1st	Yes
14.00	86.00	11.07	12.60	85.02	7.49	7.49	16.25	~4.9	Top	Yes
14.00	86.00	0.05	13.99	84.45	7.78	7.78	18.06	~83	Top	Yes

Table 16: Results of 15% Fuel to 85% Air Mixture

Desired Reaction Conditions			Concentration after N_2 Addition					Reaction Results		Flammable ?
Fuel (vol%)	Air (vol%)	N_2 (vol%)	Fuel (vol%)	Methane (vol%)	Ethane (vol%)	Propane (vol%)	O_2 (vol%)	Observed P (psi)	T (Thermocouple Level)	
15.00	85.00	24.99	12.00	85.01	7.50	7.50	14.28%	~0.2	No	No
15.00	85.00	11.10	13.50	84.76	7.62	7.62	16.06%	~0.4	No	No
15.00	85.00	8.81	13.79	84.76	7.62	7.62	16.42%	~0.5	No	No
15.00	85.00	6.40	14.10	84.65	7.75	7.60	16.78%	~0.92	No	No
15.00	85.00	6.17	14.13	85.05	7.48	7.48	16.81%	~0.71	No	No
15.00	85.00	6.07	14.14	85.07	7.47	7.47	16.83%	~1.01	1st (weak)	Yes
15.00	85.00	6.04	14.14	84.83	7.59	7.59	16.85%	~7.59	Top	Yes
15.00	85.00	0.01	15.00	85.04	7.48	7.48	17.85%	~3	4th	Yes

Table 17: LFL Results for the Gas Mixture

Desired Reaction Conditions			Concentration after N_2 Addition					Reaction Results		Flammable ?
Fuel (vol%)	Air (vol%)	N2 (vol%)	Fuel (vol%)	Methane (vol%)	Ethane (vol%)	Propane (vol%)	O_2 (vol%)	Observed P (psi)	T (Thermocouple Level)	
4.00	96.00	0.00	4.00	84.70	7.65	7.65	20.16	0.52	No	No
4.10	95.90	0.00	4.10	84.95	7.53	7.53	20.14	0.98	No	No
4.20	95.80	0.00	4.20	85.26	7.37	7.37	20.12	1.5	1st (weak)	Yes
4.30	95.70	0.00	4.30	84.69	7.65	7.65	20.10	18	Top	Yes
4.50	95.50	0.00	4.50	85.29	7.35	7.35	20.05	23.5	Top	Yes
5.00	95.00	0.00	5.00	85.02	7.49	7.49	19.95	27	Top	Yes

Table 18: UFL Results for the Gas Mixture

Desired Reaction Conditions			Concentration after N_2 Addition					Reaction Results		Flammable ?
Fuel (vol%)	Air (vol%)	N2 (vol%)	Fuel (vol%)	Methane (vol%)	Ethane (vol%)	Propane (vol%)	O_2 (vol%)	Observed P (psi)	T (Thermocouple Level)	
15.30	84.70	0.00	15.30	85.04	7.48	7.48	17.79	1.8	1st	Yes
15.50	84.50	0.00	15.50	84.96	7.52	7.52	17.74	1.5	1st (weak)	Yes
15.60	84.40	0.00	15.60	85.05	7.48	7.48	17.72	1.3	1st (weak)	Yes
15.70	84.30	0.00	15.70	84.90	7.55	7.55	17.70	1	No	No
16.00	84.00	0.00	16.00	85.12	7.44	7.44	17.64	0.66	No	No
17.00	83.00	0.00	17.00	84.99	7.50	7.50	17.43	0.27	No	No