ABSTRACT

Title of Thesis: DEVELOPMENT OF THE ASTM E681 STANDARD

Peter Quillen Lomax, Master of Science, 2016

Dissertation directed by: Peter Sunderland, Associate Professor
Department of Fire Protection Engineering

ASHRAE 34, based on ASTM E681, was improved by identifying and rectifying deficiencies in ASTM E681. An ASTM E681 apparatus and procedure was developed with gaseous refrigerant testing in mind. The plumbing was improved by ensuring that the pressure readings could be constantly monitored while decreasing leakage potential. An original electrical system was designed and constructed for the ignition system. Additionally, a control panel was constructed to isolate hazardous electrical elements, and facilitate the testing, while simultaneously organizing the critical plumbing and ignition components. 3D printing efficiently produced heat-resistant, nonreactive, and structurally stable lower electrode spacers, propellers, and propeller bars. The heating system was designed to ensure even temperature throughout the apparatus. The humidity system was designed to accurately condition the air. Recommendations to improve ASTM E681 are provided. The research can be built on to improve the accuracy and reproducibility of ASTM E681.

DEVELOPMENT OF THE ASTM E681 STANDARD

by

Peter Quillen Lomax

Thesis submitted to the Faculty of the Graduate School of the
University of Maryland, College Park in partial fulfillment
of the requirements for the degree of
Master of Science
2016

Advisory Committee:

Peter Sunderland, Associate Professor, Chair
Stanislav Stoliarov, Associate Professor
James Quintiere, Professor Emeritus

Dedicated to my parents, Joe and Suzanne,
and my sister, Ellie.

Acknowledgments

I would like to thank ASHRAE for sponsoring this research. Without their contributions, this work would not be possible.

I would also like to thank my teammates along the way, including Vivien Lecoustre, Niko Thomas, Angela Hermann, Dennis Kim, Gauthier Pipard, Flavien LeHenanff, and especially Conor McCoy. I could not have done any of this without their hard work, friendship and encouragement. I also need to thank my advisor, Peter Sunderland for his guidance and support.

Finally, I would like to thank Professors Stanislav Stoliarov and James Quintiere for agreeing to be on the Advisory Committee.

Contents

1 Introduction 1

1.1 Context 1

1.2 Literature Review 2

1.3 Objectives 6

2 Description of ASTM E681 and Apparatus 7

2.1 Introduction 7

2.2 Procedure 7

2.3 Apparatus 7

2.4 Deficiencies of ASTM E681 11

3 Plumbing System 13

3.1 Introduction 13

3.1.1 Purpose 13

3.1.2 Overview of Plumbing System 14

3.2 Plumbing System: Pressure Gauge Line 15

3.3 Plumbing System: Vacuum Line 17

3.4 Plumbing System: Refrigerant Line 20

3.5 Plumbing System: Air Line 21

4 Ignition System 24

4.1 Introduction 24

4.1.1 Deficiencies 26

4.2 Ignition System: Electrodes 27

4.2.1 Introduction 27

4.2.2 Design and Construction 27

4.3 Ignition System: Circuit and Power 30

4.3.1 Introduction 30
4.3.2 Circuit and Power 31
4.3.3 Transformer 32
4.4 Ignition System: Control Panel 33
4.4.1 Introduction 33
4.4.2 Control Panel: Top Level 34
4.4.3 Control Panel: Bottom Level 35

5 Stirring System 37
5.1 Introduction 37
5.1.1 Deficiencies 38
5.2 Propeller System 38
5.2.1 Introduction 38
5.2.2 Propeller 39
5.2.3 Propeller Bar 40
5.2.4 3D Printing Issues 41
5.2.5 Other Issues 42
5.3 Propeller Bar Length Calculation 43
5.4 Gravitational Settling 45

6 Heating System 47
6.1 Introduction 47
6.2 Design of the Heating System 47

7 Humidity System 50
7.1 Design of the Humidity System 50

8 Standard Operating Procedure 53
8.1 Introduction 53
8.2 Standard Operating Procedure 53
8.3 Water Volume, Refrigerant Pressure and Air Pressure Calculations 57

9 Recommended Changes 59

9.1 Recommendations 59

9.2 Example of Flame Angle Analysis 62

10 Conclusions 66

List of Figures

1.1 ASTM E681 Apparatus developed by Chen et al. Reproduced from Chen et al. [8]. 3

1.2 ASTM E681 Apparatus developed by Kondo et al. Reproduced from Kondo et al. [10]. 4

1.3 Flammability testing apparatus developed by Liu et al. Reproduced from Liu et al. [11]. 5

1.4 NMERI Sphere. Reproduced from Heinonen et al. [9]. 5

2.1 ASTM E681 Apparatus. Reproduced from ASTM E681 [1]. . . . 8

2.2 Stopper. 9

2.3 Constructed Apparatus. 9

2.4 Constructed Apparatus Schematic. 10

3.1 Plumbing System. 13

3.2 Plumbing System: Pressure Gauge Line. 16

3.3 Plumbing System: Vacuum Line. 17

3.4 Vacuum Pump. 19

3.5 Plumbing System: Refrigerant Line. 20

3.6 Plumbing System: Air Line. 21

3.7 Desiccator. 22

4.1 Electrodes. Reproduced from ASTM E681. [1]. 24

4.2 Drawing of Lower Spacer. 28

4.3 Electrodes and Stirring System. 29

4.4 Electrical System. 30

4.5 Image of circuit up to but not including Transformer. 31

4.6 Neon Short Stop. 33

4.7 Front of the Control Panel. 34

4.8 Drawing of Relay Mesh. 36

5.1 Stirring System. Reproduced from ASTM E681. [1] 37

5.2 Stirring System. 38

5.3 Drawing of the Propeller. 40
5.4 Drawing of Propeller Bar. 41
5.5 Diagram of Stirring System in Flask 44
5.6 Diagram of Stirring System in Flask 44
6.1 Heating System: Heat Gun. 48
6.2 Heating System: Fans. 49
7.1 Humidity System. Reproduced from ASTM E681 [1]. 50
7.2 Humidity Septum Injection. 51
9.1 Test before lights are tuned off 63
9.2 Spark before flame 63
9.3 Spark before flame 63
9.4 Flame propagation 64
9.5 Flame propagation cont'd 64
9.6 Flame propagation cont'd 65

List of Tables

1 Parts List: Plumbing System 14
2 Parts List: Ignition System 25
3 Parts List: Ignition System cont'd 26
4 Parts List: Stirring System 39
5 Lengths for Calculating L_{bar}, in mm 45
6 Parts List: Heating System 48
7 Parts List: Humidity System 51

1 Introduction

1.1 Context

An ongoing push toward sustainability of refrigeration systems will require the adoption of low global warming potential (GWP) refrigerants. Owing to concerns about fire safety, the first to be adopted will be A2L, or A1 but very close to the border with A2L. The A2L designation requires a lower flammability limit (LFL) above 3.5%, a heat of combustion below 19 kJ/g, and a laminar flame speed of less than 10 cm/s. Blends of A2L and A1 refrigerants may result in A1 classification and low GWP. The ASTM E681 test is essential in determining whether a refrigerant is mildly flammable (A2L) or not flammable (A1). It is inherently difficult to accurately measure the behavior of weak flames, especially for A2L and A1 refrigerants. These limits are the subject of ASTM E681.

ASTM E681 determines the flammablity of vapors and gases. Similarly, ASHRAE 34 determines the flammability of refrigerants. In fact, ASHRAE 34 is based on ASTM E681. To better determine the difference between A2L and A1 refrigerants, a study on the deficiencies of the ASHRAE 34 standard is conducted through the ASTM E681 standard.

One such deficiency is the ASTM E681 flammabilty criteria, which defines flammable conditions as those for which the flame spreads “upward and outward to the walls of the flask [and] are continuous along an arc that is greater than that subtended by an angle equal to 90°, as measured from the point of ignition” [1]. This is a subjective visual determination, and is open to various interpretations.

This research seeks to improve ASTM E681 by seeking deficiencies in the Standard’s apparatus and procedure in an effort to more consistently determine the lower flammability limits of refrigerants.

To conduct this research, an ASTM E681 apparatus has been designed and built according to ASTM E681 [1] and Appendix B of ANSI/ASHRAE Standard 34 [2]. This paper describes the process by which the plumbing, ignition, stirring, heating, and humidity systems were designed and built. The parts used in the construction of the system are described in Tables 1 to 7.

1.2 Literature Review

A literature review was conducted to learn more about ASTM E681, how others have constructed the apparatus, and other similar methods.

ASTM E681 defines flammable mixture as flame that “spreads upward and outward to the walls of the flask [and] are continuous along an arc that is greater than that subtended by an angle equal to 90°” [1]. This flammability limit attempts to replicate when ‘true’ flame propagation occurs. A study by Richard used a large vessel (200 L cylinder) to determine when ‘true’ flame propagation occurs [3]. Richard found that ‘true’ flame propagation did in fact occur at the same concentration as the 90°criteria is met for halogenated materials, such as R-12 (Freon) [4] and R-32 [5], in a 12 L flask.

A round robin of the ASHRAE 34 testing procedure was done at various labs, with data collected by Iracki [6]. This round robin was done to test if the ASHRAE 34 had reproducable results across different labs. The test were conducted using a 40%/60% blend of R32/R134a [7]. Testing was done at consistent conditions. The results found that the ASHRAE 34 procedure was “safe [...], easy to implement [...], reliable [... and], reproducible in inter and intra lab testing”.

Chen et al. developed an ASTM E681 apparatus for the purposes of studying the flammability of dimethyl ether mixtures [8]. A drawing of their system can be seen in Figure 1.1. Chen et al. had some differences in how their apparatus was structured and how the ASTM E681 apparatus was structured. For example, Chen et al. makes use of one gas inlet and outlet line, whereas ASTM E681 does not. This method was taken into consideration when designing the plumbing system, described in Chapter 3.

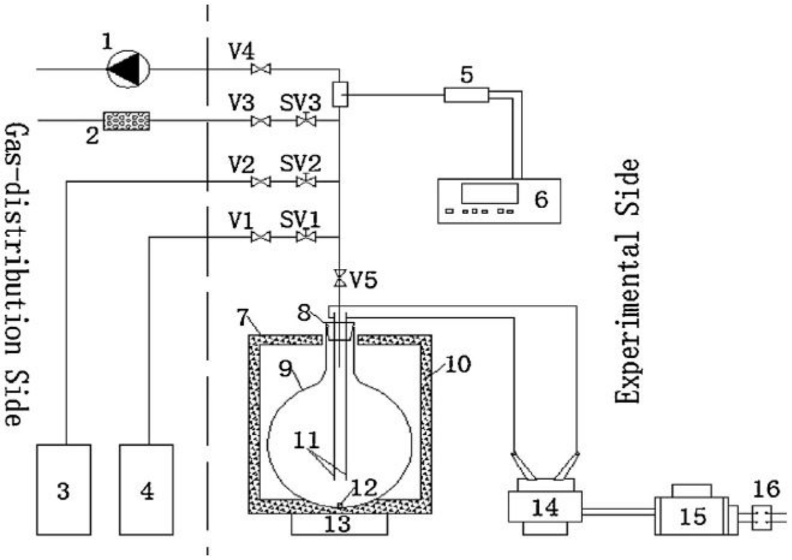


Figure 1.1: ASTM E681 Apparatus developed by Chen et al. Reproduced from Chen et al. [8].

Heinonen et al. developed an ASTM E681 apparatus for the purposes of studying the measurements and classifications of flammability [9]. Heinonen et al. had some differences in how their apparatus was structured and how the ASTM E681 apparatus was structured. For example, Heinonen uses a laboratory oven to house the flask, and to use as a heating system, in place of a metal box with a heated air source attached. A laboratory oven was considered for use in the development of this paper's apparatus. However, a laboratory oven was seen as too bulky, heavy and costly for use in research. Instead, an original heating system was developed, and is discussed in more detail in Chapter 6.

Kondo et al. developed an ASTM E681 apparatus for the purposes of studying the effects of humidity on flammability limits [10]. A drawing of their system can be seen in Figure 1.2. Kondo et al. had some differences in how their apparatus was structured and how the ASTM E681 apparatus was structured. For example, Kondo made use of a water injection system for controlling humidity, in place of an air conditioning system, shown in Figure 7.1. This method was taken into consideration when designing the humidity system, described in Chapter 7.

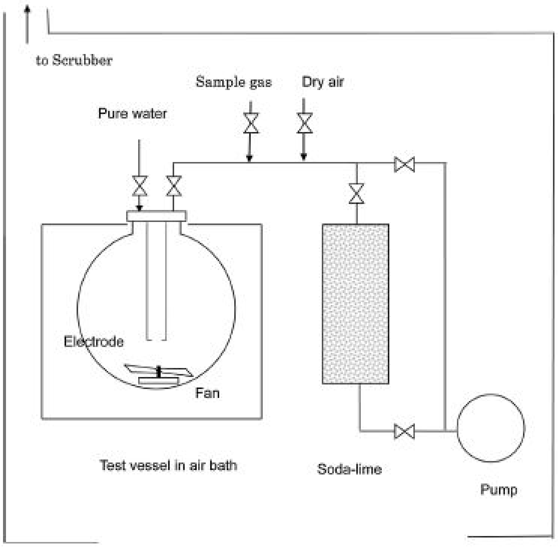


Figure 1.2: ASTM E681 Apparatus developed by Kondo et al. Reproduced from Kondo et al. [10].

In reviewing similar apparatus to ASTM E681, one such apparatus is the one developed by Liu et al. [11]. Liu et al. were studying the influence of pressure and temperature on flammability limits of hydrogen. A drawing of their system can be seen in Figure 1.3. Liu et al. designed a cylindrical explosion vessel in a water bath. Instead of a 90° criteria, Liu made use of measuring pressure. The idea of using a pressure criteria for flammability will be pursued in future research. The water bath is a possibility for heating the flask. However, this would involve a water tight apparatus. Additionally, it is not known if the visual criteria would be visible with water in place of air. For these reasons, the water bath was not pursued.

Another similar methods is the NMERI (New Mexico Engineering Research Institute) sphere, discussed in a paper by Heinonen et al [9], picuted in Figure 1.4. The NMERI sphere is an explosion vessel “orignially constructed to investigate the ability of hydrocarbons to inert propane and methane” [9]. The NMERI explosion sphere makes use of a spark gap powered by a transformer, similar to ASTM E681. The NMERI explosion sphere defines an explosion as an overpressure of 6.9 kPa. This method of using pressure to determine if there

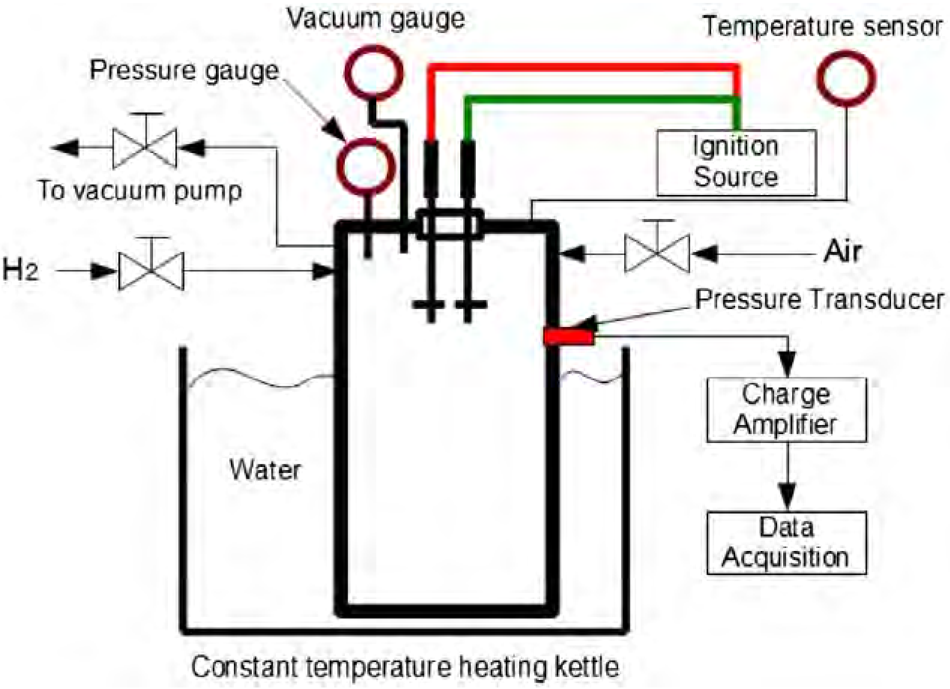


Figure 1.3: Flammability testing apparatus developed by Liu et al. Reproduced from Liu et al. [11].

is an explosion is similar to Liu's pressure criteria. The idea of using a pressure criteria for flammability will be pursued in future research.

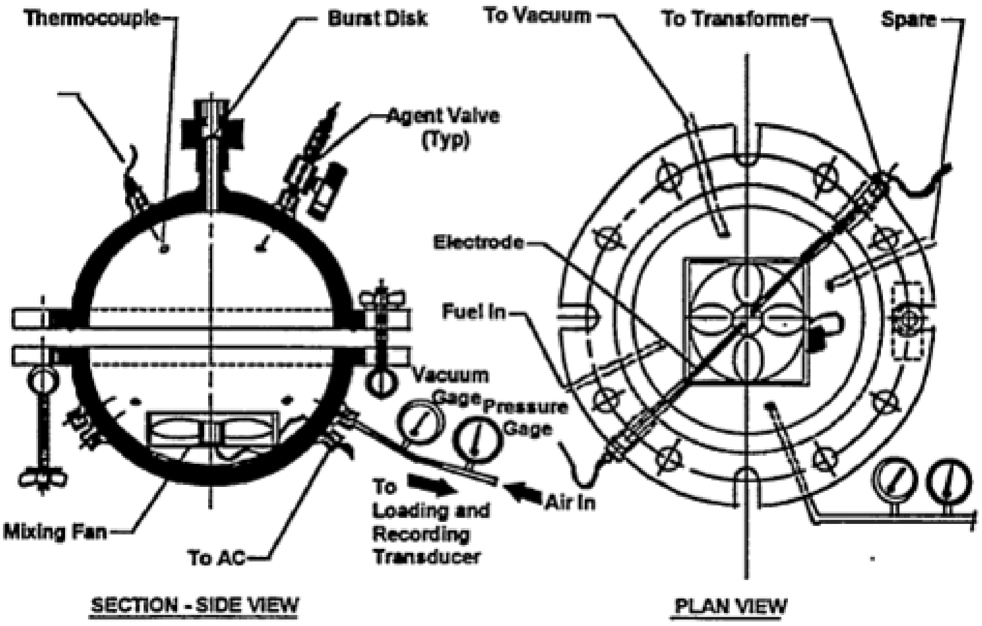


Figure 1.4: NMERI Sphere. Reproduced from Heinonen et al. [9].

1.3 Objectives

The objectives of this research are: design and build a ASTM E681 apparatus, develop a procedure, and recommend improvements. The design and construction of the apparatus are discussed in Chapters 3 to 7. The procedure is discussed in Chapter 8. By designing and constructing an apparatus and procedure, a deeper understanding of ASTM E681 is gained, and an insight into the deficiencies of the Standard are developed. From these deficiencies, recommendations to the standard can be given, and are discussed in Chapter 9.

2 Description of ASTM E681 and Apparatus

2.1 Introduction

This Chapter discusses how ASTM E681 conducts testing, and how ASTM E681 constructs the testing apparatus. From this information, the deficiencies of ASTM E681 can be identified. Once the deficiencies are identified, changes to ASTM E681 can be made in order to improve ASTM E681, and by extension ASHRAE 34.

2.2 Procedure

The ASTM E681 follows a basic procedure. The air inside the flask is evacuated using the gas outlet. Then, the flask is filled with the refrigerant. The amount of gas added is calculated by a method of partial pressures, discussed in Section 8.3. The flask is then filled with the appropriate amount of refrigerant. The flask is filled to atmospheric with air. Some refrigerants are sensitive to humidity, and if the gas is sensitive, the air must have 50 % relative humidity. The air and gas are mixed for five minutes. After mixing, the electrode is sparked. The ignition is observed, and if the 90° arc is achieved, the mixture is considered flammable. Tests are repeated until the minimum concentration is found (i.e. the lower flammability limit). The test can also be repeated to find the maximum concentration that is considered flammable to find the upper flammability limit. The procedure for conducting the experiment is discussed in Chapter 8.

2.3 Apparatus

The apparatus is shown in Figure 2.1 [1]. A 5 or 12 L flask is contained inside a metal box. The box has a door in the front to allow users to adjust the inside of the apparatus as necessary. The door is latched shut during operation. The door also contains a safety window, so as to view the combustion reaction (or lack thereof) inside the flask. The box also contains an air exit with a damper. The exit is a redundancy to ensure that the byproducts of combustion would have a exit path, should the flask break during operation. The box also contains an inlet for the heating system.

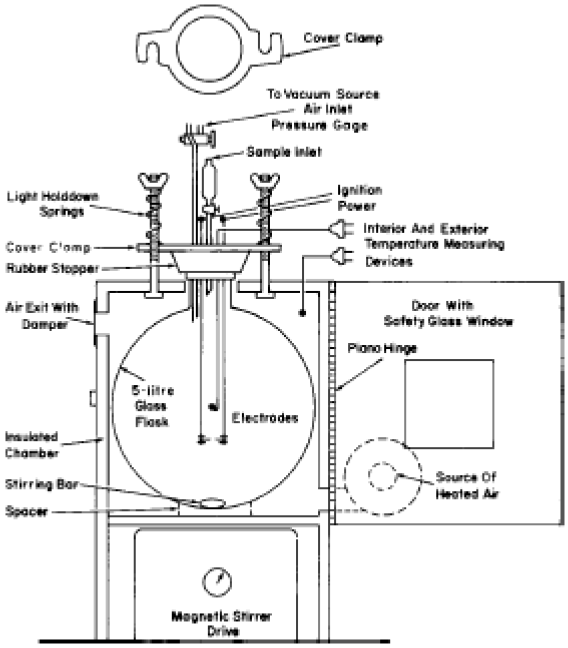


Figure 2.1: ASTM E681 Apparatus. Reproduced from ASTM E681 [1].

The flask is the part of the apparatus where the reaction takes place. On top of the flask is a rubber stopper. The stopper acts as a cover for the flask, and to house the pressure gauge line, the gas outlet and inlet and the electrodes, shown in Figure 2.2. The stopper ensures that the gases do not leak during operation. A cover clamp may also be used to secure the stopper onto the flask. The pressure gauge line connects the environment inside the flask to a pressure gauge to measure the pressure inside the flask. The gas outlet, commonly referred to as the vacuum line, evacuates the air in the flask before testing and flushes the flask after testing. The gas inlet lines inject the refrigerant and air for testing. Together, the gas outlet and inlet comprise the plumbing system, which is described in more detail in Chapter 3. The electrodes are used to ignite the mixture and are part of the ignition system. The ignition system is elaborated on in Chapter 4.

Figure 2.2: Stopper.

The flask also contains a stirring bar used for mixing. The mixing ensures a uniform concentration of refrigerant in air. The stirring system will be discussed more in Chapter 5.

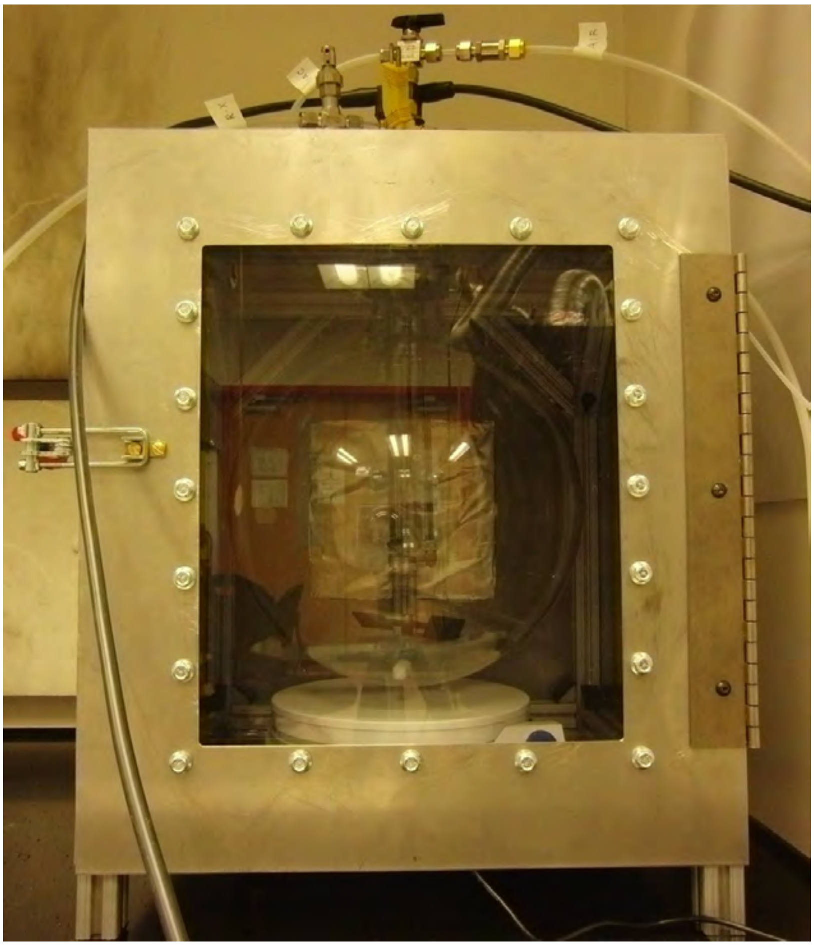


Figure 2.3: Constructed Apparatus.

Some tests are conducted at elevated temperatures. ASHRAE typically has the testing done at 60°C [2]. To use the elevated temperature, the flask needs to be heated up. This is done using the heating system, which is discussed in

Chapter 6.

The flammability of certain refrigerants is sensitive to humidity. When testing refrigerants that are sensitive to humidity, it is important to control the humidity in the air. ASTM E681 and ASHRAE typically use 50% relative humidity (RH) for testing [1] [2]. This humidity is controlled using the humidity system, which is discussed in Chapter 7. A final version of the apparatus can be seen in Figure 2.3. A schematic of the final apparatus is shown in Figure 2.4.

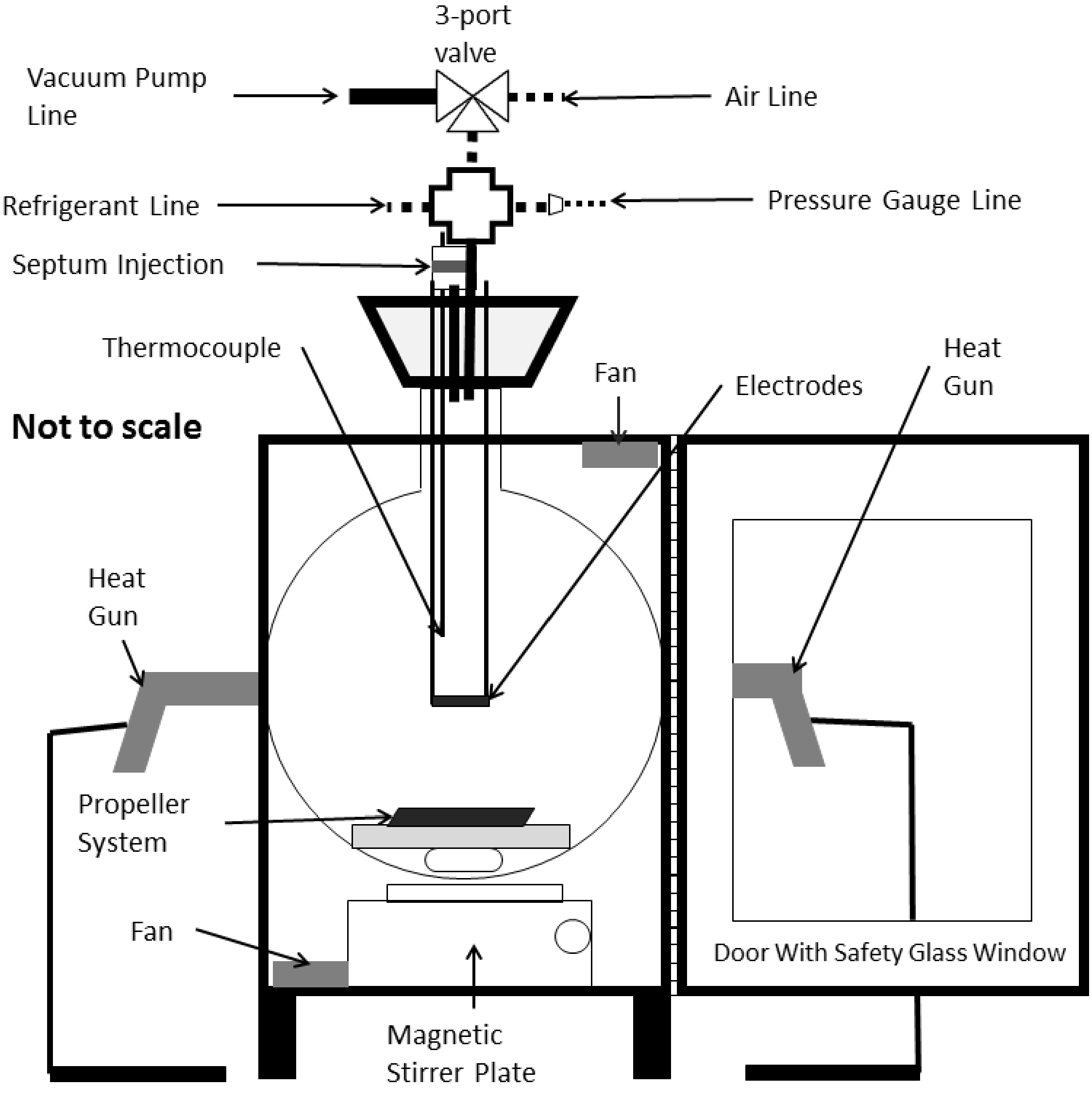


Figure 2.4: Constructed Apparatus Schematic.

2.4 Deficiencies of ASTM E681

The plumbing system contains some deficiencies. To start, ASTM E681 makes use of two plumbing penetrations. The use of two plumbing penetrations creates leakage paths through the stopper. Additionally, having the two penetrations can affect the center of mass of the stopper. If the center of mass of the stopper and the spatial center of the stopper are not aligned, the stopper can tilt, creating leakage paths between the stopper and the flask. It is critical that the use of two plumbing penetrations be fixed. Additionally, ASTM E681 makes use of a combination air/pressure gauge/ vacuum line. The use of a combination line means that the pressure inside the flask cannot be measured while air is added or a vacuum is drawn. This can make testing very difficult, as it cannot be known when a vacuum is reached, or when the air added reaches atmospheric. The use of a air/pressure gauge/vacuum line needs to be fixed.

The ignition system contains some deficiencies. To start, ASTM E681 has the glass tubes that insulate the threaded rods for the electrodes go through the stopper. This opens leakage paths through the stopper, and need to be rectified. An additional deficiency is that the threaded rods are not secured when designed according to ASTM E681. Furthermore, the tungsten wires are not properly secured in the solderless connectors. Measures should be taken to ensure that the threaded rods and tungsten wires are properly secure. Additionally, the lower spacer is constructed out of Teflon. Creating a lower spacer out of Teflon is very work intensive, and considering alternatives would be prudent.

The stirring system contains some deficiencies. The most central deficiency is that the recommended stirrer bar and propeller for the propeller version of the stirring system are no longer in production. That is, it is not possible to purchase the recommended stirrer bar and propeller, which makes constructing the stirring system problematic. This deficiency needs to be fixed. In addition, the propeller bar length recommended is too short for the propeller system to function properly, which requires fixing. In the procedure, it is recommended that the mixture be ignited within 30 to 60 seconds [2]. The rationale behind this criteria is not explicitly explained in ASHRAE 34, but longtime users of the Standard suggest the criteria is used to mitigate settling of refrigerants in air. It should be determined if there is backing to this rationale.

The central deficiency to the heating system is the heating system criteria. ASTM E681 states that the heated blower be capable of delivering "approximately 0.38 $\frac{m^3}{min}$ [...] through a variable electridc heater of approximately 2400 W" [1]. This criteria is quite obscure, and does not relate well to what the heating system is required to do. That is, maintain ± 3°C "temporally and spatially" with a capability of reaching 150°C [1]. This criteria needs to be fixed.

The main deficiency in the humidity system is the recommended humidity system. The recommended system is not inherently a deficiency, but if the recommended system cannot be developed, ASTM E681 does not provide any alternatives. The standard presents a very narrow path to the humidity system development, and needs to be widened.

ASTM E 681 has other deficiencies that do not fall into are not part of a particular system. For instance, the cover clamp that assists the apparatus in gaining a vacuum is a deficiency. If the system cannot gain a vacuum on it's own, then the problem with the apparatus should be addressed directly, rather than make use of a cover clamp. Additionally, if the cover clamp is left on during testing, an unsafe pressure buildup can generate inside the flask. The cover clamp needs to be fixed. An additional, and probably the most critical deficiency is the flammability criteria. The 90° angle is subjective, and open to different interpretations. The deficiency of the flammability criteria will be elaborated on in Section 9.2. For ASTM E681 to have more accurate and reproducible results, the flammability criteria needs to be fixed.

3 Plumbing System

3.1 Introduction

3.1.1 Purpose

The plumbing system serves multiple purposes. Evacuating the flask, adding refrigerant and air, and tracking pressure are all done through the plumbing system. The plumbing design for the ASTM E681 can be seen at the top of the apparatus in Figure 2.1 in Chapter 2. The apparatus developed here deviates from this design to overcome the deficiencies of the ASTM E681 plumbing system. A schematic of the plumbing system is show in Figure 3.1 below.

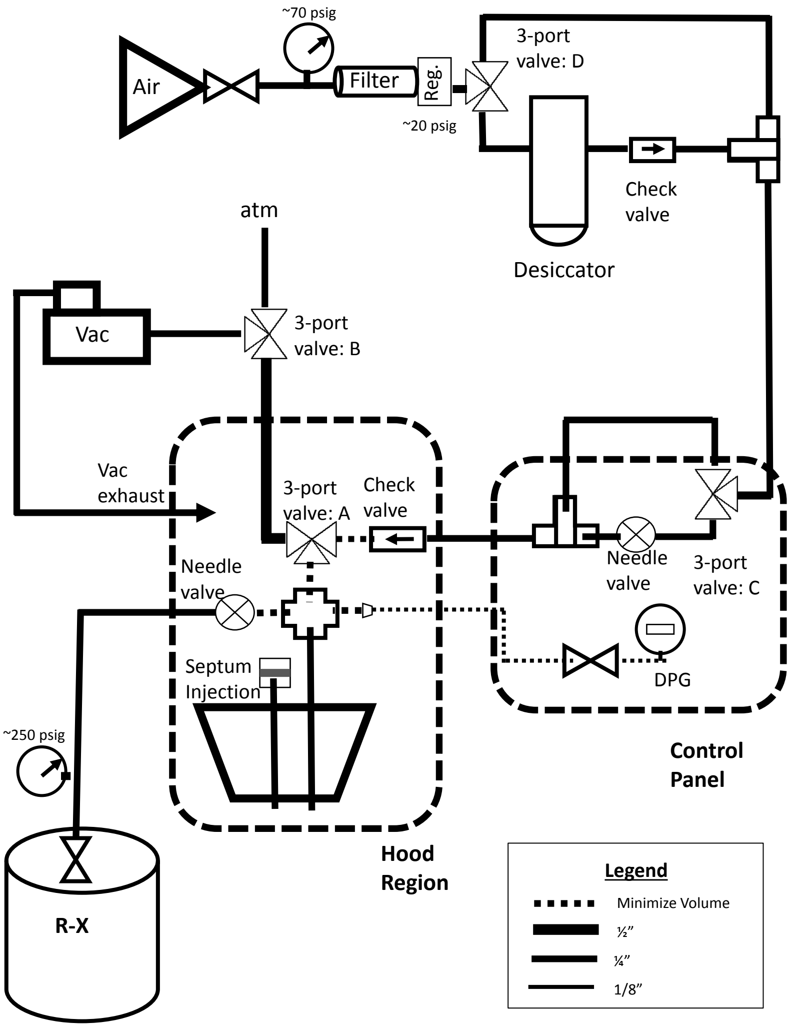


Figure 3.1: Plumbing System.

Table 1: Parts List: Plumbing System

Part/Description	Supplier	Model Number	Price
Vacuum Pressure Gauge, Measures Pressure in Flask	Cole Palmer	EW-68334-01	$311.00
No. 14 Rubber Stopper, Flask Cover	Plasticoid	Q14-M290	$22.81
Oil-Remover Air Filter/Regulator for air line	McMaster-Carr	4989K201	$107.03
Desiccator, Desiccant Air Dryer, Removes Air Humidity	McMaster-Carr	5163K18	$215.09
3-Way Ball Valve in Air Line (x2), Vacuum Line, and Union of Air and Vacuum Lines	Swagelok	SS-42GXS4	$87.00
1/8 ” (3.175 mm) Ball Valve, on Pressure Gauge Line	Swagelok	SS-41GS2	$75.50
1/4” (6.35 mm) Check Valve, 1/3 psig, Prevents Back-flow to from Vessel to Air Line and Air line to Desiccator	Swagelok	SS-4C-1/3	$47.50
1/4” (6.35 mm) Union Cross, Union of all lines	Swagelok	SS-400-4	$41.10
1/4” (6.35 mm) Flow metering Valve, for Refrigerant/Air Lines	Swagelok	SS-4MG	$100.30

3.1.2 Overview of Plumbing System

ASTM E681 makes use of two plumbing lines: a sample inlet line, and a combination vacuum/air/pressure gauge line. ASTM E681 provides little more information about the plumbing system, aside from vacuum pressure and pressure gauge criteria. The vacuum must be able to reach an absolute pressure of 0.067 kPa or less. Additionally, the apparatus must not leak under vacuum more than 0.1 kPa/min. The pressure gauge must be able to resolve the partial pressures of the gases introduced.

The plumbing system designed here deviates slightly from the Standard's design to overcome ASTM E681's deficiencies. There are 4 separate lines: the vacuum, air, refrigerant, and pressure gauge line. The vacuum and air line meet at 3-port valve A. 3-port valve A then connects to a cross. The refrigerant and pressure gauge line also meet at this cross, which connects directly to the stopper. This difference in design does not affect the apparatus' ability to run the ASTM E681 test, but resolves some of the deficiencies. This allows for one plumbing penetration through the stopper, which reduces the leakage paths through the stopper, while aligning the center of mass of the stopper with the spatial center of the stopper. Additionally, with the pressure gauge line separate from the air, vacuum, and refrigerant lines, the pressure in the flask can be monitored at all times, including when air is added or a vacuum is drawn. This overcomes the inherent deficiency created by the combination air/pressure gauge/vacuum line. A more detailed discussion of the development of the plumbing system is to follow. The parts for the Plumbing system are listed in Table 1.

When designing the plumbing system, unswept volume of the system was a central concern. Unswept volume is the portion of the plumbing system that is open during filling of refrigerant or air. When the refrigerant is filling, the unswept volume contains only refrigerant. When the air is filling, the refrigerant in the unswept volume does not mix well with the air. For this reason, the unswept volume is minimized to limit the amount of unmixed refrigerant. In Figure 3.1, the unswept volume is denoted by dashed lines.

3.2 Plumbing System: Pressure Gauge Line

The pressure gauge line is the line attached to the pressure gauge, or shown as 'DPG' (Differential Pressure Gauge) in Figure 3.1. A more detailed look of the plumbing system is shown in Figure 3.2. This line measures the pressure inside the flask. Knowing the pressure in the flask is critical in determining if the flask has a full vacuum, or how much refrigerant or air has been added.

The standard makes use of a combination pressure gauge/air/vacuum line. This has the distinct disadvantage that pressure can not be measured while filling with air or drawing a vacuum. With a separate pressure gauge line, this drawback is removed. However, a separate line does have the complication of adding more line, which can create additional leak paths. This disadvantage can be mitigated by ensuring that the fittings are properly tightened.

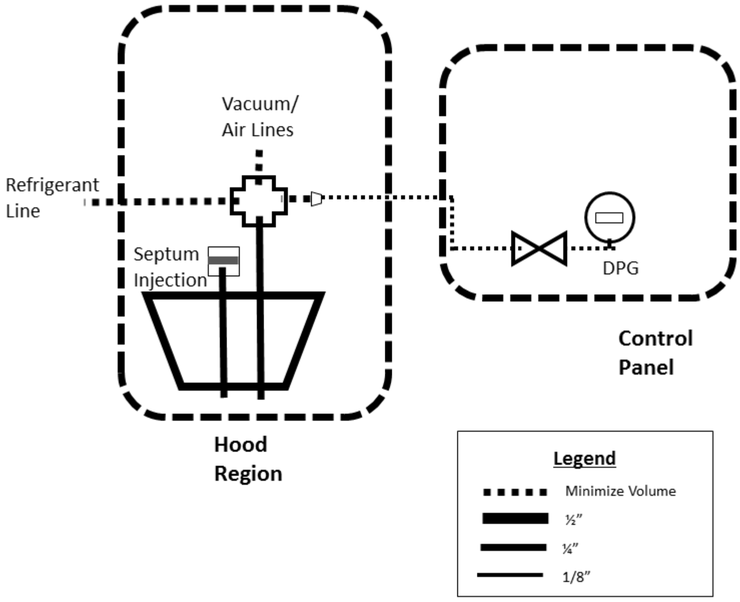


Figure 3.2: Plumbing System: Pressure Gauge Line.

According to ASTM E681, the pressure gauge should have the "accuracy, precisison and repeatability" to resolve changes in partial pressure [1]. Originally, a gauge capable of reading 0.1 kPa was selected, to resolve the 0.1 kPa/min leakage criteria. However, it was promptly realized that this was insufficient, as it could not resolve the partial pressures properly. Instead, a pressure gauge with a capability of reading up to 0.01 kPa was selected [12].

The pressure gauge line is a straight shot from the pressure gauge to the cross. There are no splits. There is a valve between the pressure gauge and the cross, to prevent combustion products from reaching the gauge. The line is $\frac{1}{8}$" (3.175 mm) up until just before the cross, which converts the line to $\frac{1}{4}$" (6.35 mm). This is done to minimize the unswept volume.

The pressure gauge line is part of the unswept volume mentioned in Subsection 3.1.2. In order to minimize the unswept volume in the pressure gauge line, the tubing used is $\frac{1}{8}$” (3.175 mm), as opposed to the standard $\frac{1}{4}$” (6.35 mm). In addition, the pressure line is kept as short as practical to minimize the volume.

3.3 Plumbing System: Vacuum Line

The vacuum line is the line attached to the vacuum pump, shown as ‘vac’ in Figure 3.1. A more detailed look of the vacuum line is shown in Figure 3.3. This line evacuates the flask before testing. This allows the refrigerant and air to be added accurately using partial pressures.

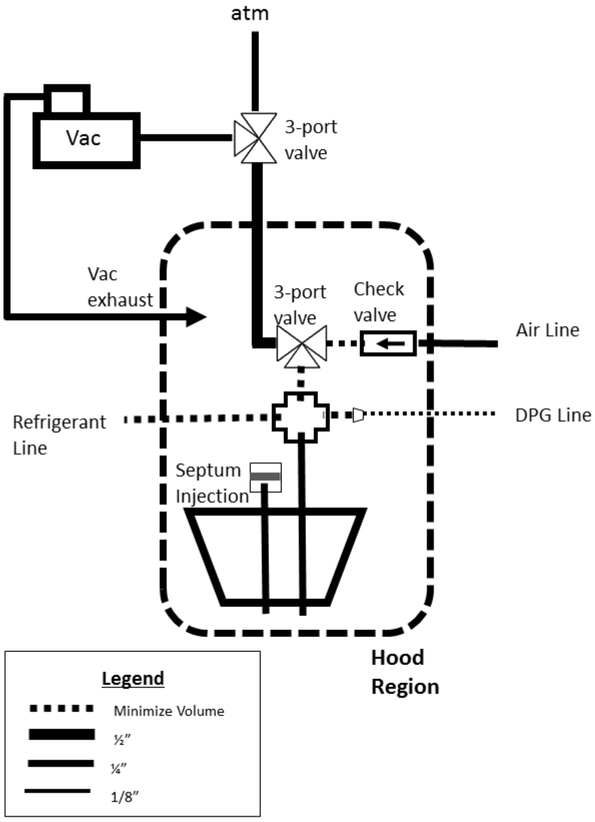


Figure 3.3: Plumbing System: Vacuum Line.

The standard makes use of a combination pressure gauge/air/vacuum line. This has the distinct complication that while a vacuum is being drawn, the pressure inside the flask cannot be measured. With a separate vacuum line, this disadvantage is removed. However, a separate line does have the drawback of adding more line, which can create additional leak paths. This disadvantage can be mitigated by ensuring that the fittings are properly tightened.

According to ASTM E681, the vacuum must be “capable of maintaining a vacuum of 0.067 kPa or less” [1]. This involves having an air tight system, as well as a vacuum capable of reaching such low pressures. The vacuum selected has the capability of reaching such low pressures [13].

The vacuum line starts at the vacuum. There are two lines that come off the vacuum: the vacuum line proper, and the vacuum exhaust. The vacuum line draws in the gases through the vacuum line proper, and expels the gas (along with some vacuum oil) out the vacuum exhaust. The exhaust is placed under the vacuum hood to prevent the foul gas from mixing with the breathing air. The vacuum line proper continues to 3-port valve B. 3-port valve B can be set to one of three positions: to the atmosphere, to 3-port valve A, or closed. The atmosphere is an option for when the vacuum is done evacuating the flask. If the line were simply closed, a vacuum would still be present in the line between the vacuum and 3-port valve B. This vacuum has the potential to draw vacuum oil from the vacuum, fouling the line. This can be prevented by opening up the line to atmospheric conditions. 3-port valve B can be opened to 3-port valve A down the line. 3-port valve A can be set to one of three positions: vacuum line, air line, or closed. When 3-port valve B is opened to 3-port valve A, and 3-port valve A is open to the vacuum line, the vacuum can evacuate the flask.

The vacuum line is not part of the unswept volume. As such, it is not necessary to minimize the volume. The line, in fact, has a large volume, due to the $\frac{1}{2}$” (12.7 mm) line. Originally, the line had a diameter of $\frac{1}{4}$” (6.35 mm). However, the vacuum inside the line would cause the $\frac{1}{4}$” (6.35 mm) line to collapse under the pressure difference. The $\frac{1}{2}$” (12.7 mm) tubing has thicker walls, allowing it to better withstand the pressure difference. In addition, a larger diameter decreases the pressure losses due to friction. This can be seen by using the Darcy-Weisbach equation:

$$\frac{\Delta P}{L} = f_D \frac{\rho}{2} \frac{V^2}{D} \tag{1}$$

where $\frac{\Delta P}{L}$ is the pressure loss per distance(Pa/m), ρ is the fluid density ($\frac{kg}{m^3}$), D is the diameter of the pipe (m), V is the mean flow velocity ($\frac{m}{S}$), and f_D is the Darcy Friction Factor [14]. V can be found using the following equation:

$$Q = \pi \frac{D^2}{4} V \tag{2}$$

where Q is the volumetric flow rate ($\frac{m^3}{s}$). This means the pressure loss is inversely proportional to the diameter to the 5th power. The switch from $\frac{1}{4}$” (6.35 mm) piping to $\frac{1}{2}$” (12.7 mm) piping doubles the diameter. This reduces the the pressure loss per length by a factor of 32. Minimizing the pressure loss is critical. If there is pressure loss, then a complete vacuum becomes more difficult, if not impossible, to achieve. For these reasons, the $\frac{1}{2}$” (12.7 mm) diameter tubing was chosen over the $\frac{1}{4}$” (6.35 mm) tubing.

Figure 3.4: Vacuum Pump.

3.4 Plumbing System: Refrigerant Line

The refrigerant line is the line attached to the refrigerant tank, shown as 'R-X' in Figure 3.1. A more detailed look of the refrigerant is shown in Figure 3.5. This line delivers refrigerant gas to the flask. The amount of refrigerant added is closely monitored to ensure that the appropriate amount is added.

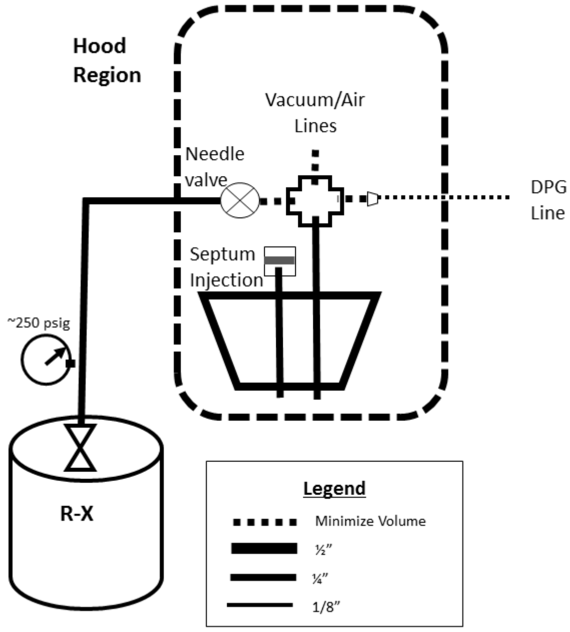


Figure 3.5: Plumbing System: Refrigerant Line.

ASTM E681 uses a single 'Sample Inlet' line to introduce the test sample. ASTM E681 allows solid, liquid and gaseous fuel for testing. For the purpose of this research, only gaseous fuel is of concern. As such, the Refrigerant line is designed with adding gas in mind.

According to ASTM E681, the LFL needs repeatability of 0.2 % [1]. A needle valve is included on the refrigerant line to ensure the refrigerant is added finely enough such that 0.2 % repeatability is reached.

The refrigerant line is a straight shot from the refrigerant tank to the cross. There are no splits. There are two valves on the line: the refrigerant tank valve and a needle valve. The refrigerant tank valve is attached directly to the refrigerant tank, which opens and closes the tank. The needle valve is used for fine adjustments of how much refrigerant is being added.

Part of the refrigerant line is contained in the unswept volume mentioned in Subsection 3.1.2. Between the needle valve and the cross is part of the unswept volume. As such, the length of this section is minimized to reduce unswept volume.

3.5 Plumbing System: Air Line

The air line is attached to the air inlet, shown as ‘Air’ in Figure 3.1. A more detailed look of the air line is shown in Figure 3.6. This line delivers air to the flask for testing and venting after testing.

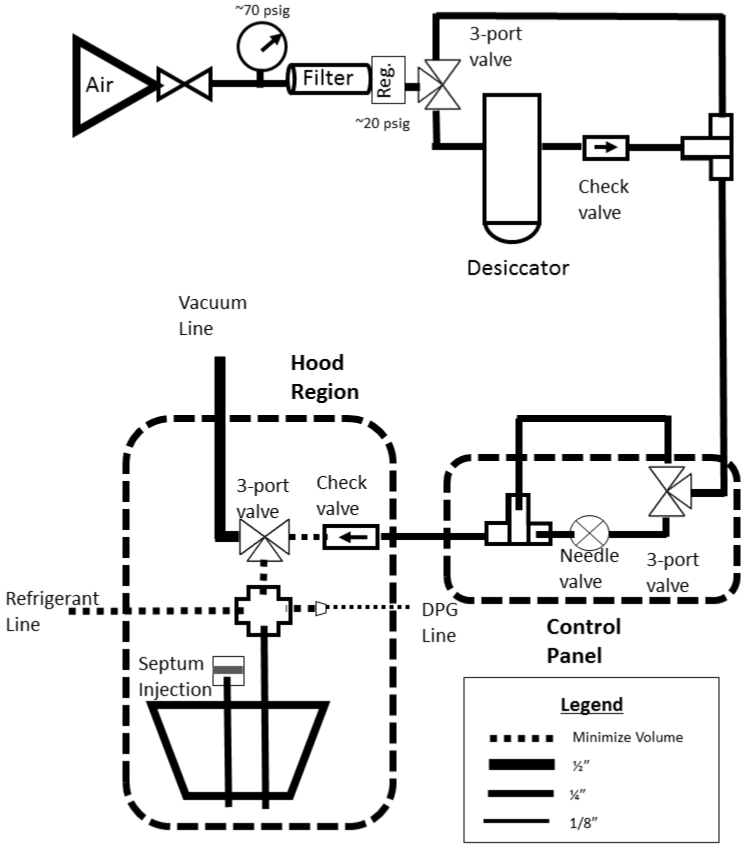


Figure 3.6: Plumbing System: Air Line.

The standard makes use of a combination pressure gauge/air/vacuum line. This has the distinct drawback that while air is being added, the pressure inside the flask cannot be measured. With a separate air line, this complication is removed. However, a separate line does have the disadvantage of adding more line, which can create additional leak paths. This drawback can be mitigated by ensuring that the fittings are properly tightened.

According to ASTM E681, the added air needs to take the pressure inside the vessel to atmospheric. A needle valve is included on the air line to ensure the air is added finely enough such that the pressure does not exceed atmospheric. Some testing was conducted just below atmospheric (-2kPa) to prevent leakage paths from being created. This is discussed more in Chapter 8.

Figure 3.7: Desiccator.

The air line is one of the more complicated lines. The air line first meets the air valve. This valve opens and close the air line. Once open, the air travels to an air filter. Shop air is used, as it is readily available and cheap. However, the air is not clean, so a filter is placed to get rid of any oils and particles down to 0.01 microns [15]. The filter also doubles as a pressure regulator. The pressure is reduced to about 20 psig. The line then goes to 3-port valve D. 3-port valve D can be set to one of three positions: Desiccator, bypass, or closed. The desiccator dries the air [16], shown in Figure 3.7. This is necessary if the refrigerant is sensitive to humidity (discussed further in Chapter 7). A check valve is placed after the desiccator to prevent backflow. The desiccator only works in one direction, so while backflow would likely not damage the desiccator, it certainly would not dry the air as intended. Therefore, the check valve is placed just to be safe. The bypass is used either if the refrigerant is not sensitive to humidity, or if the vessel is being flushed. The desiccator and bypass lines meet at a tee, which is open. From the tee, the air line travels to 3-port valve C. 3-port valve C can be set to one of three positions: Needle valve, bypass, or closed. The needle valve is used when fine filling the flask with air to atmospheric for testing. The bypass is used when flushing the flask after testing. The needle and bypass lines meet at a tee. From the tee, the air line travels to a check valve. The check valve is in place so that refrigerant or combustion byproducts are not inadvertently added to the air line. From the check valve, the air line travels to 3-port valve A. 3-port valve A can be set to one of three positions: vacuum line, air line, and closed. If the 3-port valve is set to air line, then the air can be added to the flask.

Part of the air line is contained in the unswept volume mentioned in Subsection 3.1.2. The area between the check valve and the cross is part of the unswept volume. As such, the length of this section is minimized to reduce unswept volume.

4 Ignition System

4.1 Introduction

The ignition system is used to create a spark to ignite the gas/air mixture. ASTM E681 give two methods for ignition: fuse wire and spark gap. The fuse wire method consists of $\frac{3}{4}$" (19.05 mm) 40 gauge copper wire. The copper wire is threaded around electrode rods, arranged in a loop. The wire is considered a good contact if the wire evaporates when powered. The spark gap method consists of platinum or tungsten wires $\frac{1}{4}$" (6.35 mm) apart. The wires are then sparked for an ignition source. The design presented in this paper uses the spark gap method. The fuse wire method requires the replacement of wires after each use, whereas the spark gap method does not. In addition to this, ASHRAE 34 requires the spark gap method [2].This is primarily why the spark gap method was chosen.

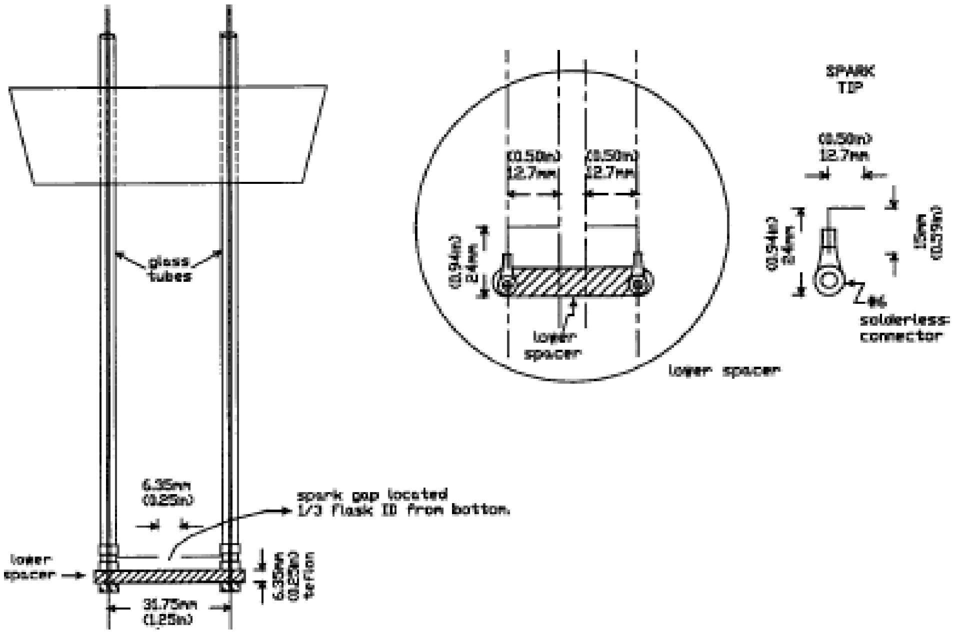


Figure 4.1: Electrodes. Reproduced from ASTM E681. [1].

The spark gap electrode design for the ASTM E681 can be seen in the center of the apparatus in Figure 2.1 in Chapter 2. A more detailed diagram of the electrodes can be seen in Figure 4.1 [1]. ASTM E681 gives little guidance on how to develop the electrical system for the spark gap method. ASTM E681 provides a power criteria of 30 mA at 15 kV. In addition, the spark duration needs to be between 0.2 and 0.4 seconds. Aside from these criteria and Figure 4.1, not much information is provided on how to construct the electrical system. The parts for the Ignition system are listed in Table 2.

Table 2: Parts List: Ignition System

Part/Description	Supplier	Model Number	Price
Lower Spacer used to separate the electrodes	3D Printed	N/A	\$0.30
Tungsten Wire, 1 mm diameter, 27.7 mm long, L-shape Electrodes	Alfa Aesar	10411-G1	\$53.38
Programmable Timer Delay Relay, Limits Spark Duration	Amico	S-99H	\$12.09
Threaded Spark Plug, Universal 8 mm Spark Plug Connectors, Wires Connected to the threaded rod	Big-Autoparts	P-IGW1053	\$31.66
Neon Transformer, Converts power from wall outlet to 30 mA at 15 kV	France [17]	P5G-2UE	\$140.31
Threaded Rods, 3.175 mm to 4.76 mm diameter stainless steel, Electrode Rods	Grainger	s6.00803202.pl.dar	\$14.80
Emergency Stop Switch, Cut-off, Dead Man's Switch, SPST-NC	McMaster-Carr	6741K41	\$32.76
High-Amp Terminal Block, Used to connect the circuit	McMaster-Carr	9130K25	\$13.22

Table 3: Parts List: Ignition System cont'd

Part/Description	Supplier	Model Number	Price
Load-Center Circuit Breakers, to turn on electrical system	McMaster-Carr	5259T4	\$7.11
Plastic Cover for Switches with Screw Terminals	McMaster-Carr	7090K55	\$1.59
Relay Socket, 8 Pin Circular, Used with Delay Relay	McMaster-Carr	7122K11	\$4.46
Snap-Acting Switch, One Circuit with Screw Terminals, ensures hood is closed	McMaster-Carr	7090K39	\$11.13
Toggle Switch, SPST, Off-On, 6 Amps, Ignition Switch	McMaster-Carr	7343K184	\$6.53
Ring Tongue Terminal for 18 - 22 AWG wire, Holds Electrodes	Molex	019203-0016	Free Sample
Neon GTO Wires, 20 feet (6.1 m), Rated 15 kV, Cable from transformer to electrodes	Neon Factory LLC	N/A	\$25.00
Neon Short Stop, For Electrical Insulation	Neon Factory LLC	N/A	\$2.00
Glass Tubes, 8 mm outer diameter, Threaded Rod Insulation	The Science Company	NC-10891	\$7.25

4.1.1 Deficiencies

The ignition system designed here deviates slightly from the Standard's design to overcome ASTM E681's deficiencies. The glass rods are partially filled with epoxy to eliminate leakage paths. Additionally, the threaded rods are secured using nuts, and the tungsten wires secured using solder. The lower spacer is created using 3D printing, which is quick and inexpensive alternative to Teflon. A more detailed discussion of the development of the ignition system is to follow.

4.2 Ignition System: Electrodes

4.2.1 Introduction

The electrodes are the component of the ignition system that does the actual igniting. For the electrodes developed in this paper, the spark gap method is used. Power is delivered to the top of the electrodes. At the bottom of the electrodes, wires $\frac{1}{4}$" (6.35 mm) apart create a spark for ignition. How the power is delivered to the top of the electrodes is discussed in Section 4.3.

4.2.2 Design and Construction

ASTM E681 gives recommendations for the design of the spark gap method of the electrodes. ASTM E681's electrodes require several components, including a rubber stopper, glass tubes, threaded rods, solderless connectors, tungsten wires, nuts, and the lower spacer. The rubber stopper holds the electrode rods in place, and is also used for the plumbing system (discussed in Chapter 3). The glass tubes insulate the threaded rod from the combustion reaction and prevent premature arcing. The threaded rods carry the electrical current to the solderless connectors. The solderless connectors carry the electrical current to the tungsten wires. The tungsten wires are bent at 90° angles, and spaced $\frac{1}{4}$" (6.35 mm) apart, and create the spark for ignition. The nuts hold the solderless connectors onto the rods. The lower spacer, made of Teflon, holds the rods steady at 1 $\frac{1}{4}$" (31.75 mm) apart.

Some changes were made to the ASTM E681 design for the spark gap method for electrodes. The initial design was for a 5 liter flask. This initial electrode design did not have the glass tubes penetrate the stopper all the way through. This has the explicit advantage of reducing leakage paths. If the glass tubes did go through the stopper, the ends of the glass tubes would be open to the atmosphere, creating a sizable leakage path. However, this method has the distinct drawback that the glass tubes are not very secure, and are prone to movement. When the 12 liter electrode design was developed, the glass tubes penetrated the stopper all the way through. To mitigate the leakage problem, the glass tubes were filled with an epoxy just above the bottoms of the tubes, and just below the tops of the tubes.

Another change to the ASTM E681 design was the addition of nuts to the top of the electrodes. ASTM E681 does not make use of nuts on the top of the threaded rods, so that the nuts would not interfere with the wire connections. This was not an issue for the development of this apparatus. The nuts have the benefit of securing the threaded rods to the glass tubes. The main disadvantage of the nuts at the top is that if the nuts are over-tightened, the glass tubes can break. This can be mitigated by not over-tightening. The added security provided by the nuts securing the threaded rods to the glass rods is why the nuts are used for the design.

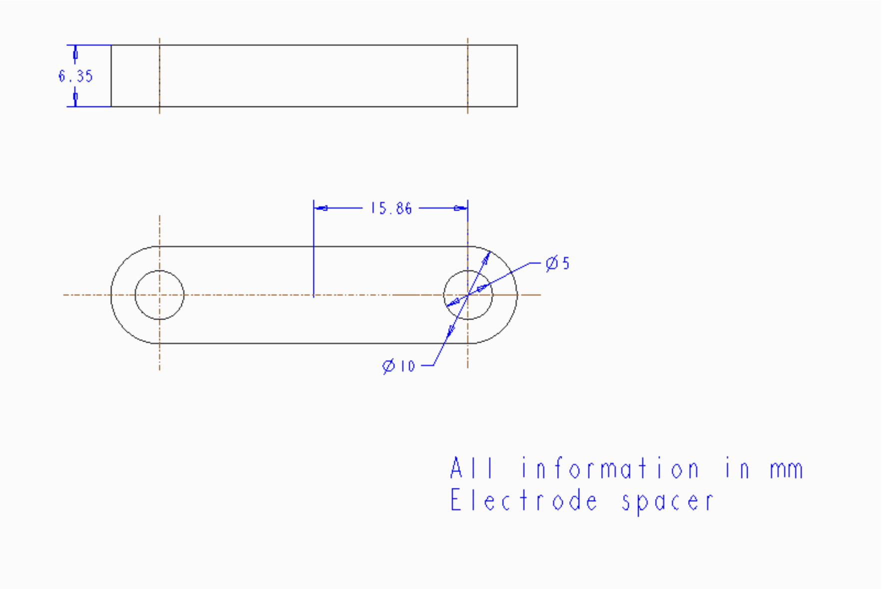


Figure 4.2: Drawing of Lower Spacer.

An additional change to the ASTM E681 design was the use of solder for the connectors. ASTM E681 makes use of solderless connectors. One possible rationale for this is that this would make construction less work intensive. However, soldering makes excellent electrical contact, also securing the tungsten wires firmly in place. For these reasons, soldering the connectors to the tungsten wires was chosen over the solderless connectors.

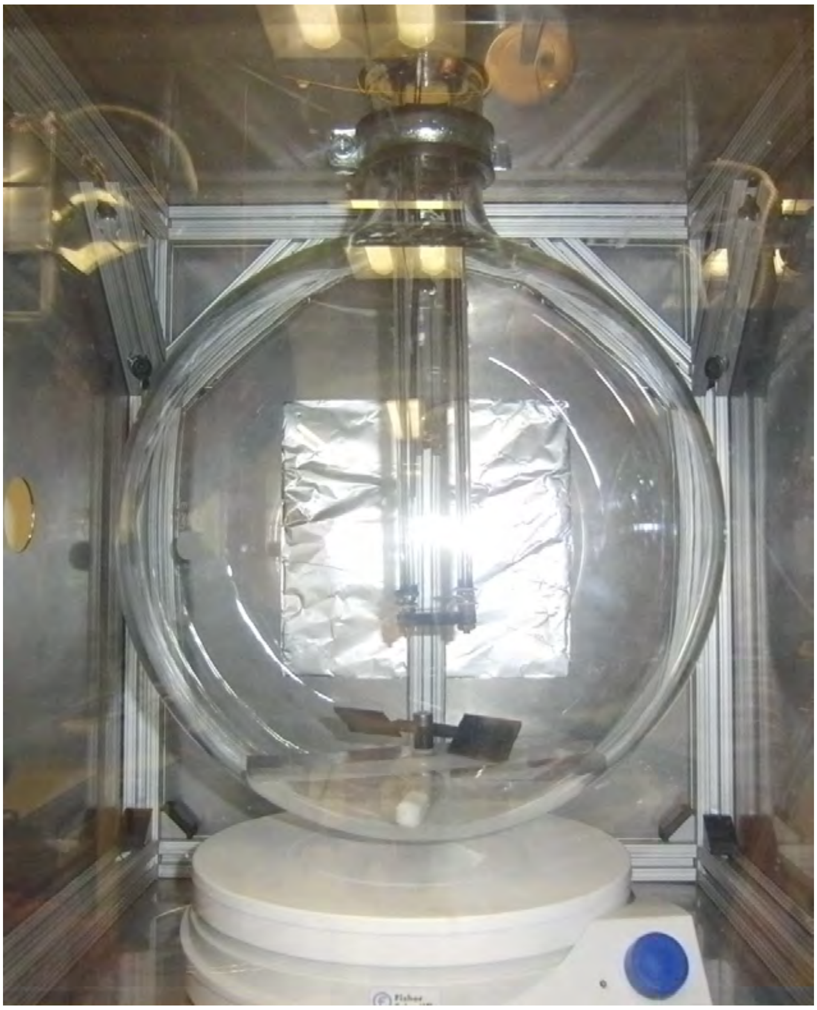


Figure 4.3: Electrodes and Stirring System.

The final change from the ASTM E681 design is the use of a 3D printed lower spacer. ASTM E681 makes use of a Teflon lower spacer. Teflon is thermally and electrically insulating, non-reactive, and widely available. The 3D printing of the lower spacer involves creating a digital 3D representation of the lower spacer (i.e. an stl file), shown in Figure 4.2. Then, the stl file is sent to a 3D printer for printing. The printing normally takes a few hours. Once printed, the spacer is ready for use. The plastic used to print this design is polylactic acid (PLA). PLA is typically very cheap (about $0.30 USD for this print). PLA is also thermally and electrically insulating, and non-reactive. When the PLA lower spacer was subjected to 60 °C, (for testing the apparatus' heating system), the lower spacer preformed perfectly. The lower spacer has not shown any signs of deterioration during standard testing. In addition, once the stl file is made, it can be reused. This is especially useful when developing multiple electrodes, or to just have a back-up. The main disadvantage of 3D printing is that printing is not always immediately available or cheap. This is not of concern for this apparatus, as 3D printing was both immediately available and inexpensive. The final product of the electrodes can be seen in Figure 4.3.

4.3 Ignition System: Circuit and Power

4.3.1 Introduction

The circuit system is the portion of the electrical system before the electrodes. ASTM E681 requires that the circuit system deliver 30 mA at 15 kV for between 0.2 and 0.4 seconds to the electrodes. The circuit system here is designed such that if the circuit is completely closed, this power will be delivered.

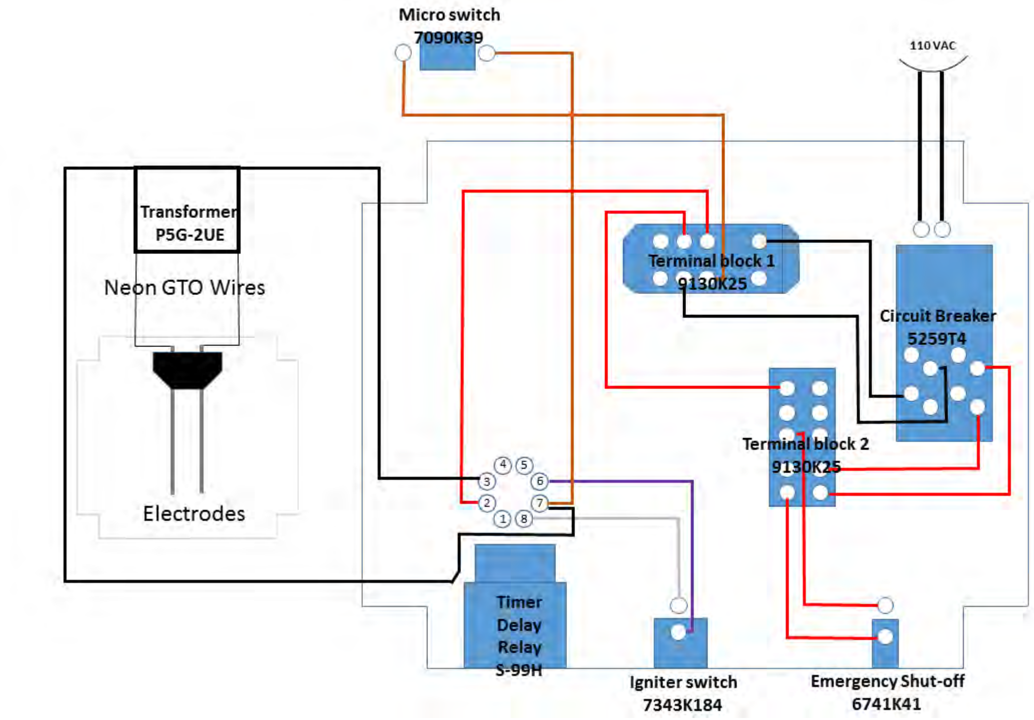


Figure 4.4: Electrical System.

4.3.2 Circuit and Power

The circuit system starts at a wall outlet (shown as 110 VAC in Figure 4.4). The outlet cable is not plugged into the wall until just before ignition for safety reasons. The power then reaches the Circuit Breaker. The Circuit Breaker features an on/off switch, so the system is not necessarily live once the outlet cable is plugged in. Once the Circuit Breaker is turned on, the power branches in two directions: to Terminal block 2 and Terminal block 1. Terminal block 2 branches in two directions: to the Emergency Shut-off and to Terminal block 1. The Emergency Shut-off acts as a 'Dead Man's switch'. That is, if someone makes contact with the 30 mA at 15 kV, the Emergency Shut-off can open the circuit, stopping the flow of the power. For common use, the Emergency Shut-off switch is closed, which closes the circuit up to Terminal block 1.

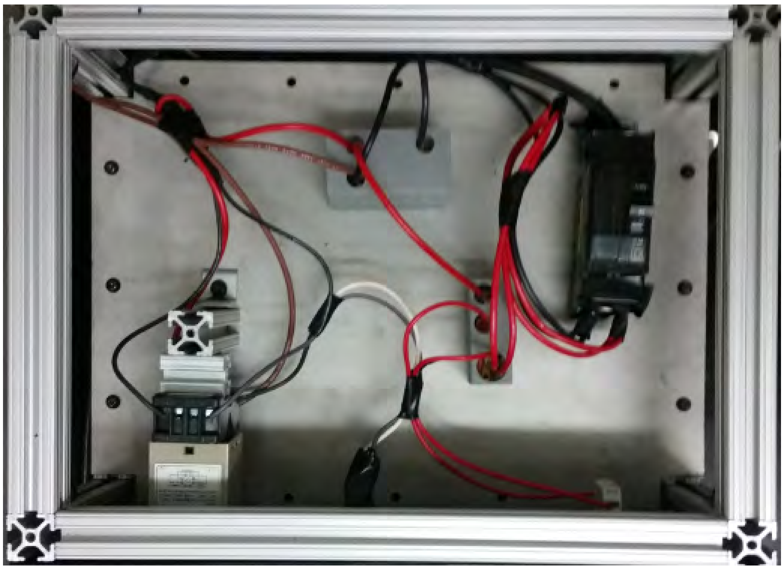


Figure 4.5: Image of circuit up to but not including Transformer.

Terminal block 1 branches in two directions: the micro switch and the relay socket. The micro switch is a safety switch, similar to the Emergency Shut-off. The Micro switch must be held down in order to complete the circuit. This is accomplished by placing the switch below the window of the vacuum hood that the apparatus is placed under. This way, ignition cannot occur unless the vacuum hood is closed. The Micro switch then delivers electricity to the relay socket. The relay socket is a complete circuit, save for the wire connections at 6 and 8. These connections lead to the Igniter switch. The Igniter switch is the final step in activating the ignition system. Flipping the Igniter switch completes the circuit up to the relay socket.

Plugged into the relay socket is the Timer Delay Relay. The Timer Delay Relay allows the user to adjust how long the power is delivered, in this case, between 0.2 and 0.4 seconds. 0.4 seconds is the time used by default. However, according to ASHRAE 34, if it is observed that the spark is still active after ignition, the time is reduced to 0.2 seconds [2]. A picture of the circuit up to this point can be seen in Figure 4.5. With the Timer Delay Relay set to the appropriate time, the power is sent to the Transformer.

4.3.3 Transformer

An electrical transformer converts primary voltage (input) into a secondary voltage (output). The input current induces an “alternating magnetic in a ‘core’ that easily conducts this flux” [18]. This flux is then ‘linked’ to a secondary coil, which yields the desired secondary voltage.

The transformer used in this design converts the power at the wall to 15 kV at 30 mA. The transformer used in this design is a neon transformer. A neon transformer differs from a standard power transformer in voltage regulation. A power transformer has considerably better voltage regulation than a neon transformer. This poor regulation limits the current delivered to the neon tubing [18].

According to ASTM E681, the power delivered by the transformer exceeds the “can’t let go” threshold and may be fatal [1] [19]. As such, it is imperative that direct contact not be made with the transformer while powered, and minimize direct contact while not powered. Several safety measures have been put into place. The terminals on each end of the transformer are covered in electrical insulating tape to prevent contact. In addition, the spades connecting to the transformer are insulated by neon short stops, pictured in Figure 4.6 [20]. The short stop is then wrapped in additional electrical insulating tape to further prevent contact. Finally, the transformer is placed behind a safety panel to ensure that contact is not made. The design of the safety panel is discussed further in Section 4.4.

Figure 4.6: Neon Short Stop.

The terminals of the transformer are connected to electrical spades. The electrical spades are connected to Neon GTO wires. The ends of the Neon GTO wires are connected to threaded spark plugs. These threaded plugs connect to the electrodes, completing the electrical system.

The ignition system starts at the wall. The power travels through the circuit, ensuring that the power delivered meets the timing criteria. The power is then sent from the circuit to the transformer. The transformer delivers the 15 kV at 30 mA [17] to the electrodes. Finally, the electrodes spark, igniting the test mixture.

4.4 Ignition System: Control Panel

4.4.1 Introduction

To facilitate operation and keep the electrical system safely arranged, a control panel was constructed. It is made of 80/20 frame, stainless steel shelves, and a plastic front cover. The front of the control panel is featured in Figure 4.7. The control panel was originally designed to solely house the electrical system, but also includes portions of the plumbing system. The control panel consists of two levels: a top level and a bottom level.

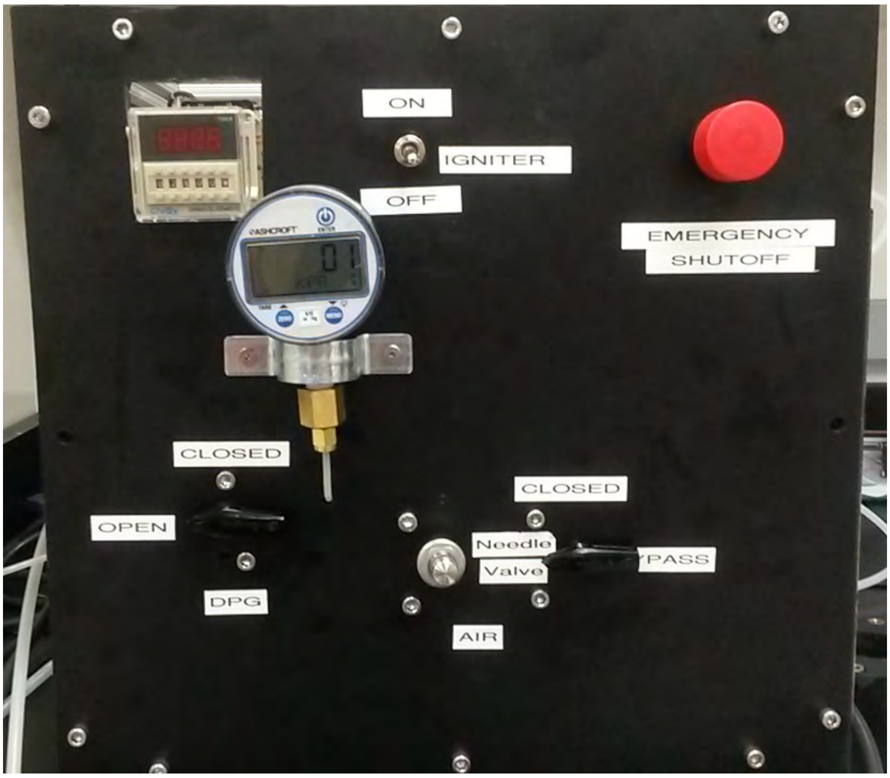


Figure 4.7: Front of the Control Panel.

4.4.2 Control Panel: Top Level

The top level of the control panel houses the circuit system. A top-view of the top level is featured in Figure 4.5. Three components of the circuit system penetrate the front of the control panel: the timer delay relay, the Igniter switch, and the Emergency Shut-off. When the timer delay relay is powered, it displays the amount of time that the circuit will be complete (i.e. 0.2 or 0.4 seconds). This display facilitates the ignition process, as knowing the duration of the spark is critical for testing. The Igniter switch, when turned on, ignites the mixture. Having this switch penetrate the front facilitates sparking, a central component of testing. The emergency shut-off switch cuts power to the electrical system, in case one makes physical contact with the electrical system. Quick and immediate access to this switch is imperative for safety to avoid delivering a potentially fatal amount of current, and the switch is therefore placed on the front of the control panel.

An additional safety measure utilized on the top level of the control panel is relay meshes. Terminal blocks 1 and 2 are exposed, which can lead to shocks if contact is made. To mitigate this, relay meshes are used. The relay mesh is created using 3D printing. A digital 3D representation of the desired mesh is created (i.e. an stl file), shown in Figure 4.8. Then, the stl file is sent to a 3D printer for printing. The printing normally takes a few hours. Once printed, the meshes are placed onto the relays, shown in Figure 4.5. The meshes are quite effective at isolating the relays.

The only components of the circuit system not included on the top level are the micro switch, the wall outlet, and the transformer. The micro switch is not placed on the top level because it is by the vacuum hood. The micro switch needs to be pressed to complete the circuit, and this is done by placing the switch under the vacuum hood door. This ensures that the vacuum hood is closed during testing. The wall outlet is not placed on the top level because it is attached to the wall. The transformer is not placed on the top level because there is insufficient room for both the transformer and the circuit system. As a result, the transformer is placed on the bottom level.

4.4.3 Control Panel: Bottom Level

The bottom level of the control panel houses the transformer and components of the plumbing system. The transformer is placed on the bottom level to isolate it from direct contact. The bottom level is difficult to reach. This is not an issue for the transformer, as it requires little maintenance.

Components of the plumbing system are also placed on the control panel through the bottom level. These components include: the vacuum pressure gauge, the vacuum ball valve, the primary air bypass three-way valve, and the air needle valve. The vacuum pressure gauge is displayed on the front of the control panel. This facilitates evacuating and filling of the flask, as the display is easy to see from the vacuum, air, and refrigerant lines. The vacuum ball valve is also included here. The vacuum pressure gauge is isolated by the valve.

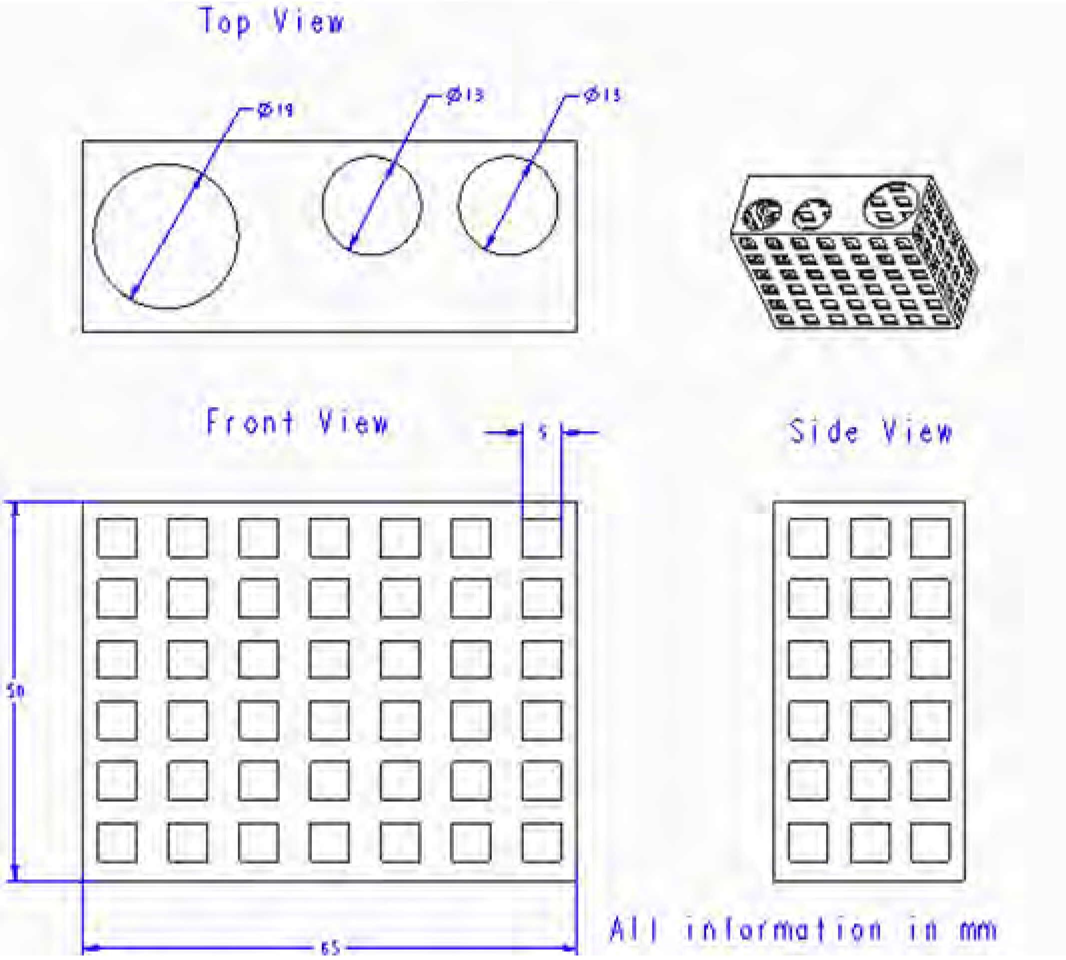


Figure 4.8: Drawing of Relay Mesh.

Isolation of the pressure gauge is typically only done during ignition, to prevent backflow of combustion products. Easy access to the vacuum valve facilitates ignition, as the mixture can be promptly ignited after closing the vacuum valve. The primary air bypass three-way valve is used immediately after ignition to flush the flask of combustion byproducts. For this reason, the three-way valve is placed near the Igniter switch to facilitate flushing. The air needle valve is on the control panel to secure it, making accurate adding of air easier. In addition, it is not really possible to place the primary air bypass three-way valve without also placing the needle valve with it. As mentioned previously, the bottom level is difficult to reach. The plumbing components do occasionally require tightening. However, the benefit of their presence on the control panel outweighs the nuisance of occasional maintenance.

5 Stirring System

5.1 Introduction

The stirring system ensure a well mixed gas when testing. A discussion of the negligibility of gravatational settling of a well mixed gas is described in Section 5.4. ASTM E681 proposes two different methods for mixing: An egg shaped stirring bar, and a propeller system. The egg shaped stirring bar is a magnet covered in plastic. The egg shaped stirrer bar is spun by a laboratory magnetic stirrer. The propeller system is similar, pictured in Figure 5.1 [1]. A magnetic stirring bar (not egg shaped) is attached to a propeller. This propeller is held up by a propeller bar, so the magnetic stirring bar does not touch the bottom of the flask. The propeller system is mandatory for ignition of "materials with large quenching distances, which may be difficult to ignite" [1]. The propeller system is used for this design. The final product of this design can be seen in Figure 5.2.

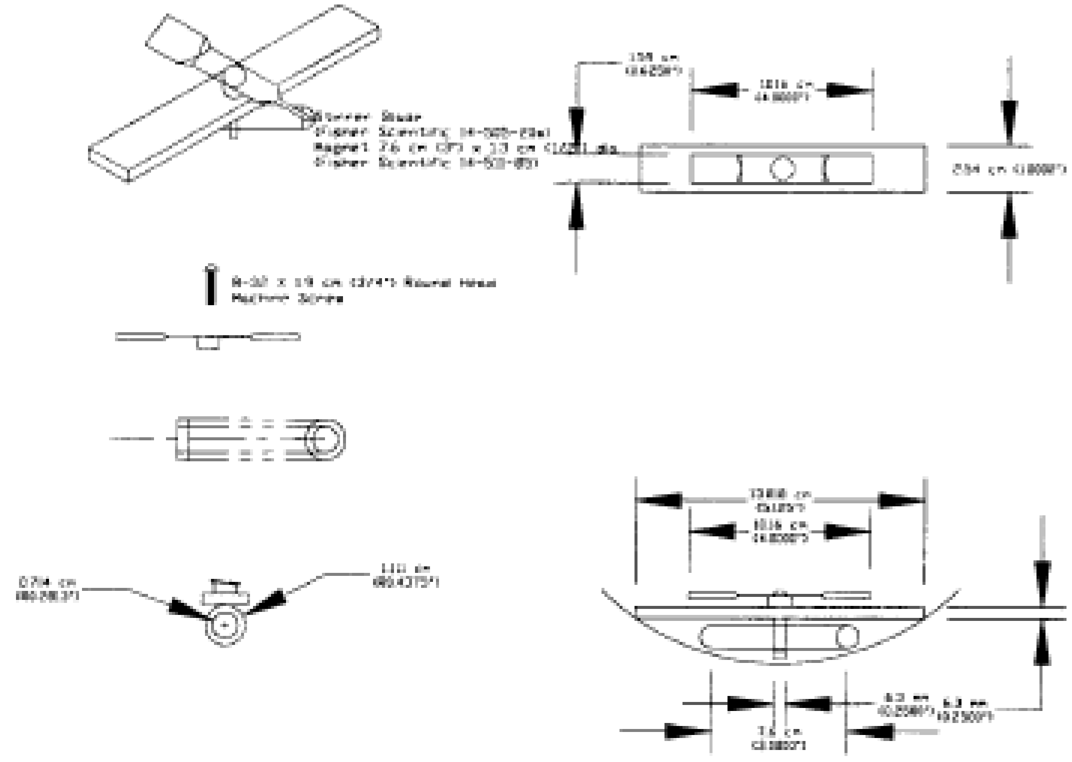


Figure 5.1: Stirring System. Reproduced from ASTM E681. [1]

Figure 5.2: Stirring System.

5.1.1 Deficiencies

The stirring system designed here deviates slightly from the Standard's design to overcome ASTM E681's deficiencies. An equivalent stirring bar was found and used, and a 3D printed propeller and propeller bar was used in place of the recommended components that are out of production. A new propeller bar length was calculated for the updated propeller system. Igniting within 30 to 60 seconds was found to be superfluous by determining that the gravitational settling that would occur is negligible. A more detailed discussion of the development of the stirring system is to follow.

5.2 Propeller System

5.2.1 Introduction

The propeller system is one of the proposed methods of stirring in ASTM E681. The propeller system consists of several components, including: the propeller, the propeller bar, the stirrer bar, the magnetic stirrer plate, and the screw. The propeller is what does the actual mixing. ASTM E681 states that the stirrer (i.e the propeller) must spin at a minimum of 400 rpm [1]. The propeller bar holds up the propeller. The stirrer bar is a magnet that turns the propeller. The stirrer bar is spun using a laboratory magnetic stirrer plate. The screw is what attaches the propeller and stirrer bar together. The stirrer bar is drilled through, allowing it to be attached to the propeller by the screw.

Table 4: Parts List: Stirring System

Part/Description	Supplier	Model Number	Price
Plastic Propeller for stirring	3D Printed	N/A	~\$0.30
Propeller Bar, to hold stirrer	3D Printed	N/A	~\$0.30
RT Basic Magnetic Stirrer, Stirring Plate	Fisher Scientific	11-676-267	\$286.00
Magnetic Stir Bar, for stirring	Fisher Scientific	1451368	\$25.00

Some changes were made to ASTM E681's design. To start, the stirrer bar could not be drilled all the way through. Instead, a nut was attached to the stirrer bar, so the magnetic stirrer bar could be attached to the screw. In addition, the recommended magnetic stirrer and propeller could not be used, as they were discontinued. A comparable magnetic stirrer is used. Moreover, no guidance is given about the propeller bar, aside from dimensions. The design of the propeller and propeller bar are discussed in Subsections 5.2.2 and 5.2.3, respectively. The parts for the Stirring system are listed in Table 4.

5.2.2 Propeller

The propeller recommended by ASTM E681 is discontinued. As a result, a propeller needed to be developed. The propeller is created using 3D printing. A digital 3D representation of the propeller is created (i.e. an stl file), shown in Figure 5.3. ASTM E681 describes the length of the propeller, but gives no other information. In creating the stl file, some assumptions needed to be made, such as the deflection angle of the blade, and how thin to make the propeller. Once finalized, the stl file is sent to a 3D printer for printing. The printing normally takes a few hours. Once printed, the propeller is ready for use. The plastic initially used to print for this design is polylactic acid (PLA). PLA is typically very inexpensive. Generally, PLA is also thermally resistant, reasonably durable and non-reactive. However, some issues arose when the propeller system was subjected to elevated temperatures (i.e. 60 °C) for extended periods. These issues are addressed in subsection 5.2.4. The propeller has not shown any signs of deterioration during standard testing (room temperature). In addition, once the stl file is made, it can be reused. This is especially useful when developing multiple propeller systems, or just to have a back-up.

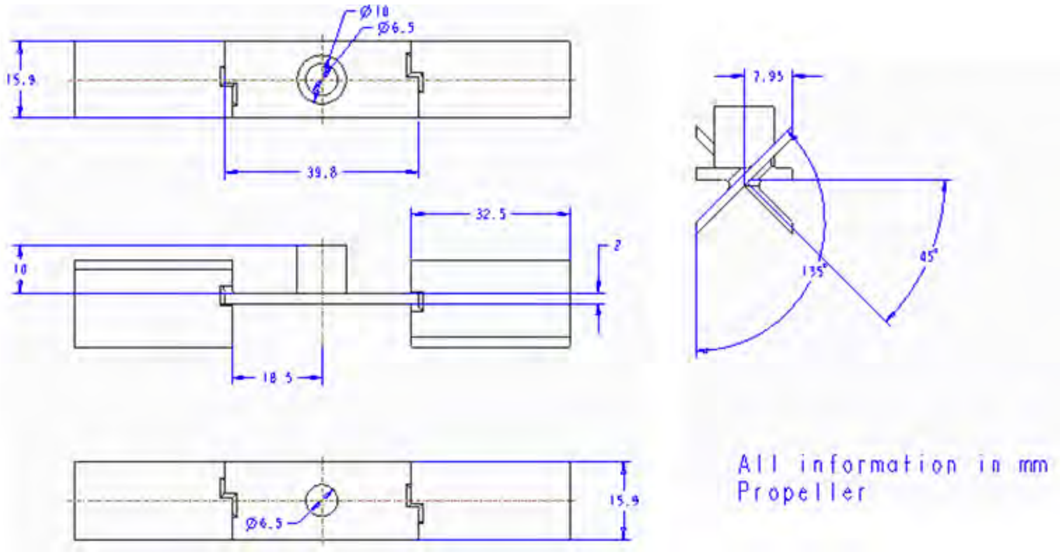


Figure 5.3: Drawing of the Propeller.

5.2.3 Propeller Bar

The propeller bar followed a similar development process as the propeller. The propeller bar is created using 3D printing. A digital 3D representation of the propeller bar is created (i.e. an stl file), shown in Figure 5.4. ASTM E681 describes how long, wide and thick the propeller bar is to be. Once finalized, the stl file is sent to a 3D printer for printing. The printing normally takes a few hours. Once printed, the propeller bar is ready for use. The plastic initially used to print for this design is polylactic acid (PLA). PLA is typically very inexpensive. In general, PLA is also thermally resistant, reasonably durable and non-reactive. Nevertheless, some issues arose when the propeller system was subjected to elevated temperatures (i.e. 60 °C) for extended periods. These issues are addressed in subsection 5.2.4. However, the propeller bar has not shown any signs of deterioration during standard testing. In addition, once the stl file is made, it can be reused. This is especially useful when developing multiple propeller systems, or to create a spare. Some issues additional issues were encountered with the propeller bar design. These are addressed in subsection 5.2.5.

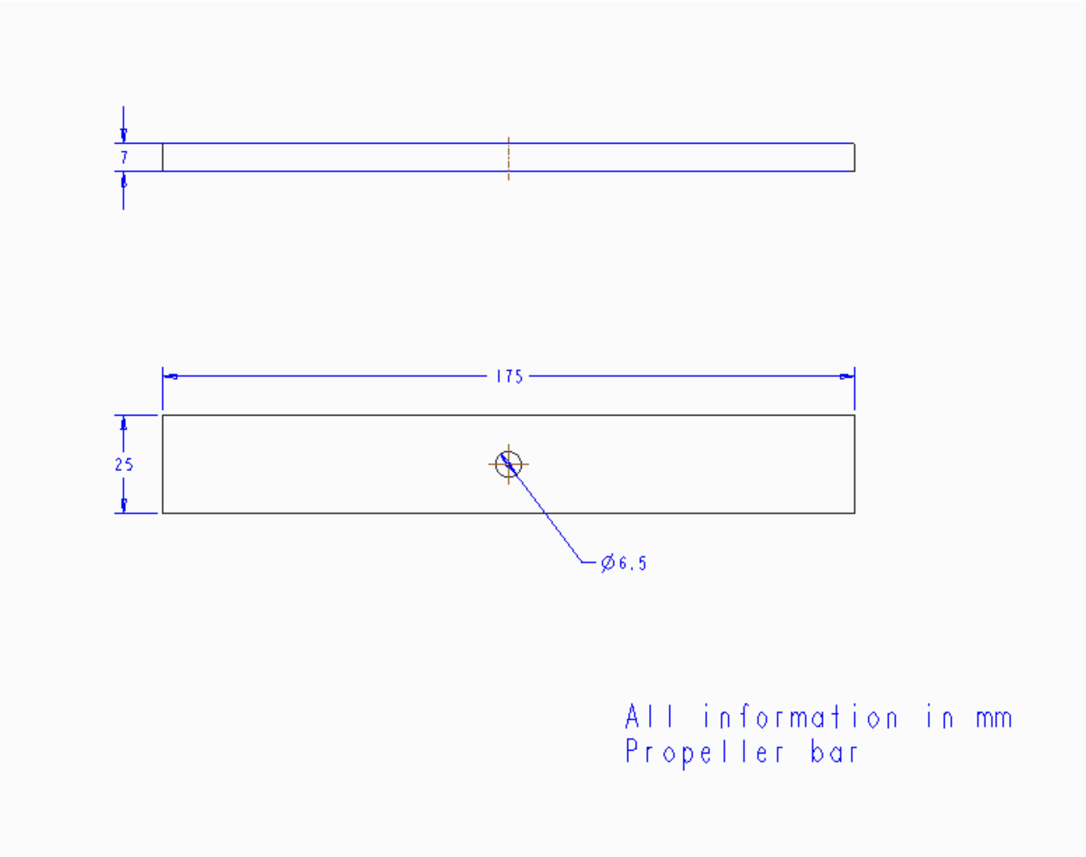


Figure 5.4: Drawing of Propeller Bar.

5.2.4 3D Printing Issues

One major issue encountered in the development of the stirring system is heat deformation. During standard testing, the stirring system shows no signs of heat deformation. However, when testing the heating system the propeller and propeller bar deformed under the heat. The lower electrode spacer, also made of PLA as mentioned in Section 4.2, did not deform when subjected to heat. It is believed that this is because the lower spacer is not subjected to a weight, and is supported by the electrodes. However, the propeller bar has the weight of the stirrer bar, which may have caused it to sag. The propeller also lacked support, which may have caused it to sag.

To mitigate the issue of heat deformation, alternative 3D printing materials are used. PLA has a heat deflection temperature of 60 °C, which is not suitable for elevated temperature testing [21]. Acrylonitrile-Butadiene-Styrene (ABS) has a heat deflection temperature of 100 °C [22]. For the purposes of this design, this is sufficient.

Some issues arose when printing the propeller in ABS. The printer would attempt to print the propeller with the 45 °deflection, but the propeller would frequently print flat and not be usable. ABS has difficulty printing thin objects, and objects that have physically unsupported features (like the propeller). After printing in various different orientations, the propeller successfully printed when oriented upside-down. Printing upside-down gave the propeller sufficient physical support. If 3D printing is used for creating propellers in the future, it is recommended that other materials are pursued before ABS. If no other heat resistant material is available or practical, ABS may be used.

An additional disadvantage of 3D printing for some users is that printing is not always immediately available or cheap. This is not of concern for this apparatus, as 3D printing is readily available and inexpensive.

5.2.5 Other Issues

There are some additional issue that arose in the development of the propeller system. For example, the flask would occasionally vibrate when stirring. To mitigate this, the stirrer plate speed was decreased until rattling ceased, then increased until 400 rpm is reached. Another issue is that the procedure to get the stirring system out of the flask proved difficult. To do so, the flask needed to be removed from the box, and turned upside down. This method only works if the stirrer bar, propeller, and propeller bar are aligned. If the three parts are not aligned, the parts would need to be adjusted until they were aligned. No easier method of removal has been developed as of the writing of this thesis.

One final issue of the stirrer system is that the length dimension of propeller bar given by ASTM E681 needs to be adjusted. The length dimension assumes that the discontinued stirrer bar is used. This results in the propeller bar being too short to properly hold up the stirrer bar. As a result, the stirrer bar makes contact with the bottom of the flask, and cannot stir. A new length of the propeller bar is calculated in Section 5.3.

5.3 Propeller Bar Length Calculation

In section 5.2.5, it is stated that the length of the propeller bar is insufficient for holding up the stirrer bar. The changes to the design caused the stirrer bar to hit the bottom of the flask, causing the stirring system to not work properly. To determine what length would be necessary, the length is calculated. For 5 liters, the bar is 126 mm long. For 12 liters, the bar is 141 mm long.

Figure 5.5 shows the stirring system in the flask. In the left figure, r, L_{bar}, L_{stir}, Δx_{bar}, and Δx_{sitr} are the radius of the flask, length of the propeller bar, length of the stirrer bar, thickness of the propeller bar, and thickness of the stirrer bar, respectively. L_{bar} is what is being solved for.

L_{bar} can be solved for using trigonometry. It is assumed that the stirrer bar is just touching the flask, as to yield Figure 5.6. Figure 5.6a shows a right triangle, with $\frac{Lbar}{2}$ as the bottom leg. Using the Pythagorean theorem [23] and isolating L_{bar}, this yields:

$$L_{bar} = 2(\sqrt[2]{2r\Delta x_t - \Delta x_t^2}) \tag{3}$$

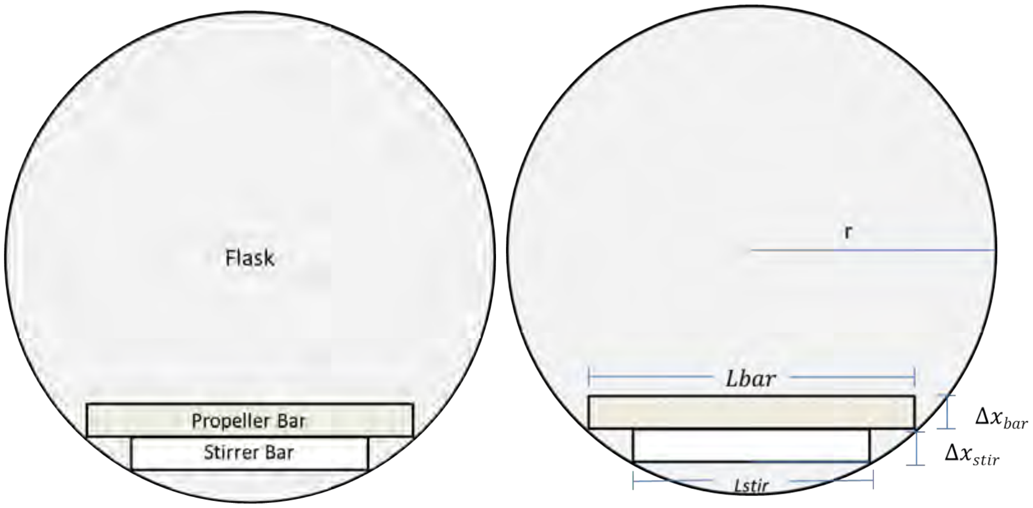
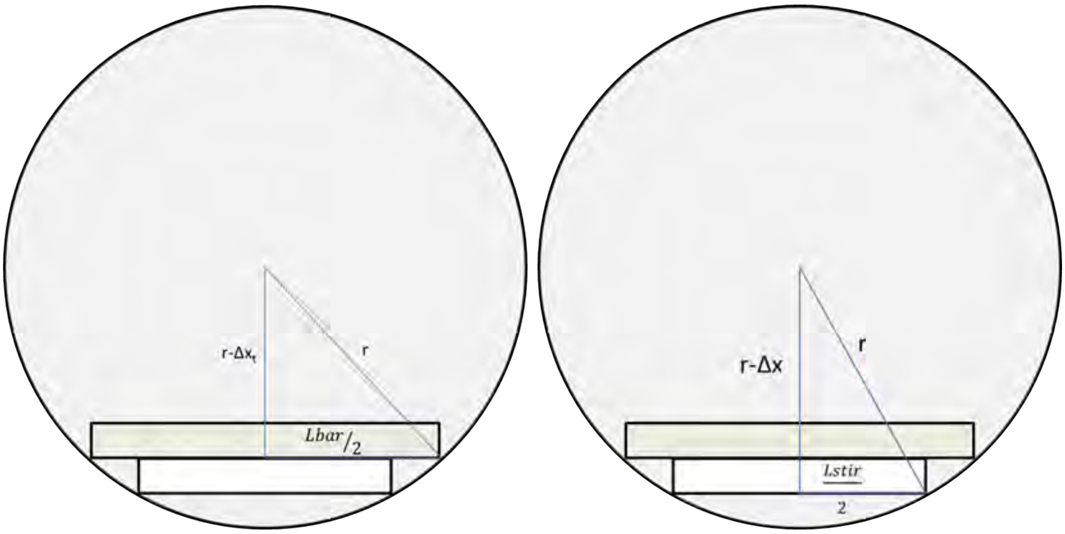


Figure 5.5: Diagram of Stirring System in Flask

where Δx_t is the total distance from the bottom of the propeller bar to the bottom of the flask. Δx_t can be written as:

$$\Delta x_t = \Delta x + \Delta x_{stir} \tag{4}$$

where Δx is the distance between the bottom of the stirrer bar and the flask.



(a) Solving for Lbar

(b) Solving for Δx

Figure 5.6: Diagram of Stirring System in Flask

Figure 5.6b shows a right triangle that can be used to solve for Δx. Using the Pythagorean theorem [23] and isolating Δx, this yields:

$$\Delta x = r - \sqrt[2]{r^2 - \frac{1}{4}L_{stir}^2} \tag{5}$$

Based on these equations and the values from Table 5, L_{bar} for 5 liters is 126 mm and 141 mm for 12 liters.

Table 5: Lengths for Calculating L_{bar}, in mm

r (5 liters)	r (12 liters)	L_{stir}	Δx_{stir}
110.5	147.5	76.2	12.7

Values from [24], [25], [26] and [26] respectively.

5.4 Gravitational Settling

Gravitational settling is of interest because it has been used to justify ignition within 60 s after stopping the stirring system. However, it is shown here that gravitational settling of a fully mixed gas in an ASTM E681 facility is negligible.

The diffusion of mixtures of air and R-32 at 14.4% in a 12 L spherical vessel at 23 °C is described here. The multi-component diffusion equation from the complete kinetic theory was obtained from Williams ([27], [28]) and Lam [29], which states concentration gradients can be dominated by diffusion velocities, pressure gradients, or differences in the body force per unit mass on molecules of different species. When the body force per unit mass is same and thermal diffusion is neglected, the diffusion of the gas in our system can be expressed as:

$$\nabla X_{R32} = (Y_{R32} - X_{R32})\nabla p/p \tag{6}$$

where Y_{R32}, X_{R32}, ∇X_{R32}, ∇p, and p are the mass fraction, mole fraction, mole fraction gradient of the component R-32, pressure gradient, and pressure in the vessel, respectively. Assuming X_{R32} varies linearly with z direction due to gravity, ∇p is found from:

$$\nabla p = -\rho g \hat{k} \tag{7}$$

where ρ, g, and $\hat{k}$ are the density of R-32, gravity, and the unit vector in the upward direction. p can be calculated from ideal gas law equation:

$$p = \frac{\rho RT}{MW_{mix}} \tag{8}$$

where MW_{mix}, R, and T are the molar masses of the gas mixture, ideal gas constant (8.314 J/mol-K), and temperature in the vessel (298 K). Quantity MW_{mix} is given by:

$$MW_{mix} = X_{air} MW_{air} + X_{R32} MW_{R32} \tag{9}$$

With the combination of Equations 6 and 7, we can write:

$$\nabla X_{R32} = -(Y_{R32} - X_{R32}) \frac{g\hat{k} MW_{mix}}{RT} \tag{10}$$

The refrigerant mass fraction is:

$$Y_{R32} = \frac{X_{R32} MW_{R32}}{MW_{mix}} \tag{11}$$

Based upon this, the values of X_{air} and X_{R32} are 0.856 and 0.144, respectively, for this case. The MW_{mix} is 137.28 g/mole. Quantity $Y_{R32} = 0.058$.

The result is $\nabla X_{R32} = 0.615 \text{ x } 10^{-5}\hat{k}$. The radius of the 12 L vessel is approximately 0.14 m. Thus, the mole fractions difference of R-32 between the flask bottom and top is 1.23 x 10^{-5}, where the average $X_{R32} = 0.144$ in the vessel.

In summary, the gas will not settle after it is well mixed by the fan. Gravitational settling can be neglected and does not need to be considered in ASTM E681.

6 Heating System

6.1 Introduction

The heating system raises the temperature of the apparatus. ASTM E681 states that the “test should be performed at the temperature(s) of interest” [1]. In addition, the heating system has to “maintain the temperature within ± 3 °C both temporally and spatially” [1]. ASTM E681 has the suggestion that the heating system be rated at 13.5 CFM through a heater of 2400 W. In the ASHRAE 34 standard, the tests are commonly conducted at 60 °C [2]. As such, the heating system was designed around the ASTM E681 and ASHRAE 34 criteria.

The heating system designed here deviates slightly from the Standard’s design to overcome ASTM E681’s deficiencies. The flow and wattage criteria was considered, but ultimately the ± 3°C “temporally and spatially” with a capability of reaching 150°C is the central criteria for the heating system. This criteria is more relevant to what the heating system does. A more detailed discussion of the development of the heating system is to follow.

6.2 Design of the Heating System

Space heaters were originally considered for the heating system. However, it was very difficult finding something that meet both the 13.5 CFM and 2400 W criteria. Most space heaters will either have the appropriate watttage, but too much air flow, or appropriate air flow, but not enough wattage. It was then decided to see if there are heat guns that meet the criteria. A heat gun was found that could deliver 8.8 to 17.7 CFM at 120 to 1200 °C at 1500 W [30]. With two of these heat guns, the flow is 17.2 to 35.4 CFM at 3000 W. This exceeds the criteria, but not by much. The parts for the Heating system are listed in Table 6.

Two heat guns are used to heat the apparatus. This is done by cutting a

Table 6: Parts List: Heating System

Part/Description	Supplier	Model Number	Price
3 pronged clamp, Holds Heat Guns	EISCO	CH0688	\$14.20
Heat Guns, 8.8 to 17.7 CFM (15 to 30 m^3/h), 120 to 1200 °F (50 to 650 °C, used to heat box	Hitachi	RH650V	\$89.99
Fans, 24 V, 0.16 A, 54.7 CFM (93 m^3/h), used to circulate heated air inside box	NMB	360KL-05W-B50-G00	\$11.64

hole on the left and right sides for the front of the heat gun to fit. The heat guns are held by 3 pronged clamps, as shown in Figure 6.1. Inside the apparatus, heat resistant fans are placed, as shown in Figure 6.2. These fans circulate the air for more even heating. In addition, the fans ensure that the condition of ± 3 °C is met spatially.

Figure 6.1: Heating System: Heat Gun.

The heating system design has a few issues. If the heating is conducted at the minimum flow and at 60 °C, the heating can take a few hours. To resolve this, the flow and temperature of the heat guns can be increased. Another issue is that the stirring system sagged when heated. The method chosen for resolving this issue is discussed in Subsection 5.2.4.

Flammability of refrigerants can depend on temperature. According to ASTM E681, "Higher temperuatrers lead to lower LFL" [1]. A study preformed by Kondo et al demonstrated that the flammability of ammonia, R-32, and R-143A are linearly related to temperature [31]. When testing refrigerants, it is important to record the temperature at which the refrigerant is being tested.

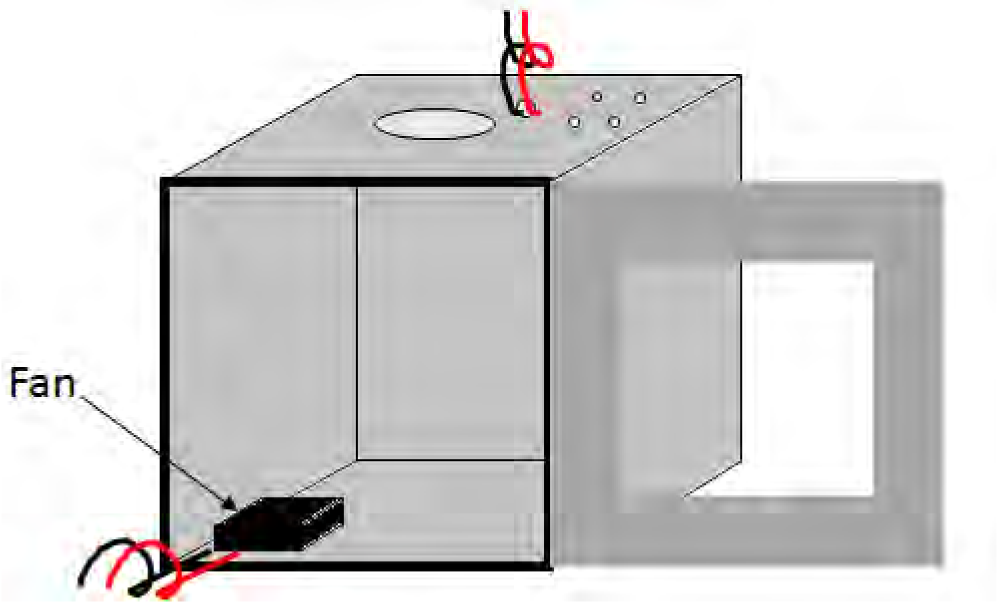


Figure 6.2: Heating System: Fans.

7 Humidity System

The humidity system controls the relative humidity of the air. In ASHRAE 34, the humidity is defined as 0.0088 grams of water per gram of dry air, or 50% RH at 23 °C and 101.3 kPA [2]. For humidity, ASTM E681 references ASTM E171 for it's humidity specification. ASTM E171 specifies that air be conditioned to 23 °C with 50 % RH, conditioned for 24 hours [32]. To condition the air, ASTM E681 recommends the use of a double bucket method, shown in Figure 7.1 [1].

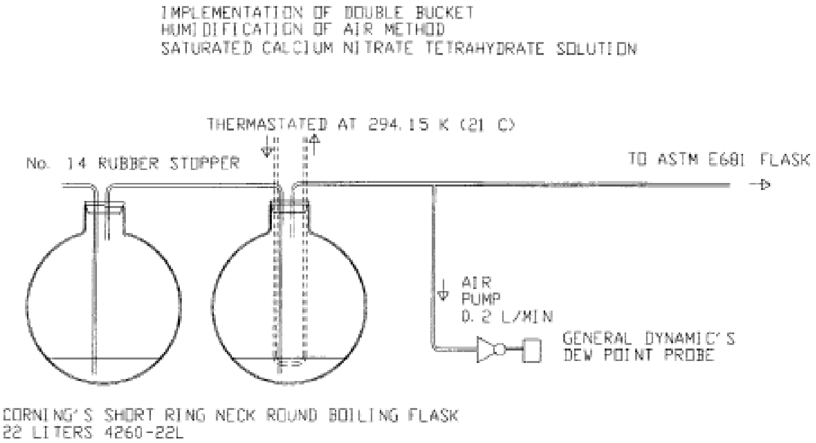


Figure 7.1: Humidity System. Reproduced from ASTM E681 [1].

The humidity system designed here deviates slightly from the Standard's design to overcome ASTM E681's deficiencies. The injection humidity system is given as an alternative to the double bucket method provided by ASTM E681. A more detailed discussion of the development of the humidity system is to follow.

7.1 Design of the Humidity System

An injection system is used in this design. A vacuum is drawn in the flask. Then, water is injected, and vaporized. The refrigerant is added, then dry air. The amount of water added is such that the relative humidity of water in air is 50% at 23 °C. This is a similar method to what Kondo et al. used for humidity [10]. The method for calculating the amount of water necessary is described in Section 8.3.

The construction of the humidity injection started with drilling a hole through the stopper. A copper pipe is then forced into the hole. A $\frac{1}{4}$" (6.35 mm) pipe union is attached to the copper pipe. A rubber septa is placed in the pipe union, securing the septa. A 0.1 mL syringe is filled with the appropriate amount of water, and injected through the septa. For adding fine amounts of water, a 100 micro liter syringe is filled with the appropriate amount of water, and injected through the septa. A representation of the humidity septum injection system is shown in Figure 7.2. The parts for the Humidity system are listed in Table 7.

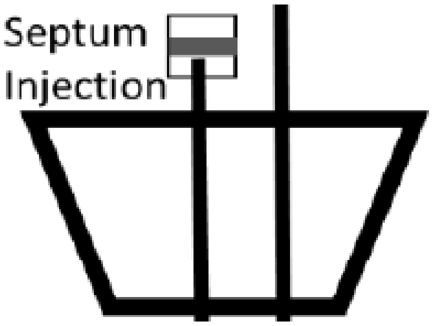


Figure 7.2: Humidity Septum Injection.

Table 7: Parts List: Humidity System

Part/Description	Supplier	Model Number	Price
100 microliter Syringe, stainless steel tip, Used to inject water	Sigma-Aldrich	Hamilton, 80630	\$56.10
1 mL Syringe, Used to inject water	Sigma-Aldrich	Hamilton, 81330	\$70.30
Rubber Septa, 9 mm diameter, operating temperature up to 200 ˚C, Acts as a membrane for syringe	Sigma-Aldrich	Hamilton, 76003	\$14.30 per pack of 12
1/4" (6.35 mm) Brass Tube Fitting Union, Holds Rubber Septa	Swagelok	B400-6	\$3.80

Flammability of refrigerants can depend on humidity. According to ASTM E681, humidity can “suppress or enhance the chemical reaction of combustion” [1]. A study preformed by Kondo et al showed that the flammability of ammonia, R-32, and R-143a is not dependent on humidity, whereas R-1234yf and R-1234ze do exhibit a dependence [31]. When testing certain refrigerants, it is important to determine if there is a humidity sensitivity. If the sensitivity is unknown, the default should be 50 % RH.

8 Standard Operating Procedure

8.1 Introduction

After the apparatus has been constructed, testing can be conducted. To ensure consistency of testing, a standard operating procedure (SOP) was developed. The SOP was based on the procedure proposed by ASTM E681 and ASHRAE 34, but needed to be adjusted for differences in apparatus [1] [2].

8.2 Standard Operating Procedure

A number of safety precautions are included in the SOP. For example, safety goggles must be worn during testing. In addition, gloves are to be worn whenever interacting with components in the vacuum hood, in case residual byproducts are present. The vacuum hood must be closed whenever it is not being used. Contact with the electrical system while active should be avoided. Additionally, contact with the box should be avoided when heated.
The Standard Operating Procedure is as follows:

1. Turn on and zero the pressure gauge
2. Place stopper on top of apparatus
3. Draw a vacuum
    (a) Turn 3-port valve A towards vacuum line (Figure 3.1)
    (b) Open refrigerant needle valve, but not the refrigerant tank valve
        i. This allows refrigerant line to be evacuated of air, ensuring that only refrigerant will be present in the flask when refrigerant is added
    (c) Set pressure gauge valve to open
    (d) Open 3-port valve B to 3-port valve A, opening the line from the vacuum pump to the flask

    (e) Turn on vacuum pump
        i. Leave on unitl the pressure reads 1.33 kPa absolute or less
    (f) Once vacuum is reached, close the refrigerant needle valve
    (g) Set 3-port valve A to closed
    (h) Set 3-port valve B to atmospheric
    (i) Turn off vacuum pump

4. Calculate water, refrigerant, and air needed according to Section 8.3
5. Heat apparatus if testing is done at an elevated temperature
    (a) Put heat guns into place
    (b) Turn heat guns onto the appropriate setting
        i. Caution: the box can get very hot during heating
6. Water is added, if refrigerant is sensitive to humidity
    (a) Fill syringes with water
    (b) Inject water
    (c) Let water evaporate
7. Add refrigerant
    (a) Open refrigerant needle valve very slightly
    (b) Open refrigerant tank valve
    (c) Monitor pressure gauge for refrigerant pressure value
    (d) Close refrigerant needle valve when pressure is reached
    (e) Close refrigerant tank valve
8. Add air
    (a) Adjust air filter to appropriate pressure, as necessary

   (b) Turn 3-port valve D to desiccator, if refrigerant is sensitive to humidity
   (c) Turn 3-port valve C to air needle valve, where air needle valve is currently closed
   (d) Turn 3-port vavle A to air line
      i. Place micro switch under vacuum hood window
   (e) Open air needle valve slightly
   (f) Open air valve
   (g) Monitor pressure gauge for air pressure value
   (h) Close air needle valve
   (i) Close air valve

9. Activate stirring system
   (a) Plug in stirrer plate
      i. Let stir for 5 minutes
   (b) Unplug stirrer plate

10. Prepare air system for flushing after flame
   (a) Turn 3-port valve D to bypass
   (b) Adjust filter pressure regulator to a higher pressure
      i. Flushing is done to remove combustion byproducts as quickly as possible, such as Hydrofluoric acid (HF) [31]. HF, aside from being hazardous [33], can etch the glass of the vessel [34].

11. Place high speed camera in front of apparatus
   (a) The testing is recorded at high speed to determine if the test meets the 90° criteria for flammability

12. Prepare ignition system
    (a) Turn on Circuit Breaker
    (b) Check if Timer Delay Relay is set to appropriate spark time
    (c) Turn off lights to visualize the ignition
13. Ignite the mixutre
    (a) Turn Igniter switch on
    (b) If mixture does not ignite, wait 5 minutes, and attempt ignition again. This is repeated up to 3 times
    (c) If mixture does ignite, flush the flask
        i. Turn on air valve
        ii. Turn 3-port valve C to bypass
        iii. Flush for 5 minutes
        iv. After 5 minutes, draw a vacuum
            A. Caution: Any vapor drops may have HF. Use plastic gloves.
        v. The process of flushing and drawing a vacuum is done at least 3 times
14. Repeat test to have 3 tests at concentration of interest
15. Analyze videos for 90° criteria
    (a) If 2 out of three pass, then the mixture is considered flammable
    (b) If at least 2 out of 3 fail, then the mixture is not considered flammable
16. For LFL
    (a) If the concentration is flammable, a lower concentration is tested next, if not already done
    (b) If the concentration is not flammable, a higher concentration is tested next, if not already done

17. For UFL
    (a) If the concentration is flammable, a higher concentration is tested next, if not already done
    (b) If the concentration is not flammable, a lower concentration is tested next, if not already done

8.3 Water Volume, Refrigerant Pressure and Air Pressure Calculations

When conducting testing, the volume of water to add (mL)and, the amount of refrigerant and air added (kPa) need to be calculated.

The volume of liquid water (mL) to add can be found using the following equation:

$$V_{water} = \frac{P_{sat} V_{flask} (x_{air}) * 10^{-6}}{R T_{amb}} \frac{MW_{water}}{\rho_{water}} \frac{RH}{100} \tag{12}$$

where $P_{sat}, V_{flask}, x_{air}, R, T_{amb}, MW_{water}, \rho_{water}, RH$ are the saturation vapor pressure (kPa), volume of the flask (cm^3), mole fraction of the air, the ideal gas constant ($\frac{J}{gK}$), temperature of air (K), molecular weight of water ($\frac{g}{mol}$), the density of water ($\frac{g}{cm^3}$), and relative humidity (%), respectively. Saturation pressure (kPa) is found using the following equation:

$$P_{sat} = P_c/100 * exp(\frac{T_c}{T_{amb}}(-7.9\nu + 1.8\nu^{1.5} - 11.8\nu^3 + 22.7\nu^3.5 - 16\nu^4 + 1.8\nu^{7.5})) \tag{13}$$

$$\nu = 1 - \frac{T_{amb}}{T_c} \tag{14}$$

where P_c is the critical pressure (Pa) and T_c is a critical temperature (K) [35]. P_c is given as 220,640 Pa, and T_c is given as 647.096 K.

V_{flask} depends on the type of flask used ($\sim$ 5254 cm^3 for 5 L flask or $\sim$ 12,716 cm^3 for 12 L).

$$x_{air} = 1 - x_{ref} \tag{15}$$

where x_{ref} is the mole fraction of refrigerant added. The mole fraction of refrigerant depends on the concentration of refrigerant is being tested (ex 14.4% is equivalent to $x_{ref} = 0.144$). The ideal gas constant does not change (8.314 $\frac{J}{gK}$). The temperature of the air is assumed to be ambient conditions, which can be determined by a lab thermocouple. The MW_{water} is constant (18 $\frac{g}{mol}$). ρ_{water} is found by looking it up in a table [36]. From here, V_{water} can be calculated with all these inputs.

The pressure of the refrigerant is solved next using the method of partial pressures [37]. The pressure of the refrigerant is the pressure at which to stop adding refrigerant. The pressure of refrigerant to add is determined by the following equation:

$$P_{ref} = P_{vac} - x_{ref}(P_{vac} - P_{test}) - (P_{vac} - P_{test}) \tag{16}$$

where P_{vac} is the gauge pressure reached by the vacuum (kPa) P_{test} is the gauge pressure at which the test is conducted (kPa). P_{test} is atmospheric by ASTM E681 and ASHRAE 34, but in practice, -2 kPa is typically used [1] [2]. This is done to prevent potential leak paths that could open at atmospheric. The pressure at which to stop adding air is the same as P_{test}.

9 Recommended Changes

9.1 Recommendations

The ASTM E681 standard has some shortcomings. Some recommendations are given to overcome these shortcomings. These changes are listed below in order of significance.

1. One critical recommendation is either a clarification of or change to the flammability criteria. ASTM E681 states that a mixture is considered flammable if the flame spreads "upward and outward to the walls of the flask [and] are continuous along an arc that is greater than that subtended by an angle equal to 90°, as measured from the point of ignition" [1]. It is not clear how this criteria should be judged. It can be interpreted as 'measure the angle that the flame makes once it hits the walls of the flask, then see if it is larger or smaller than 90 °'. It can also be interpreted as 'measure the largest angle, and see if it is larger or smaller than 90°'. This will be elaborated more on in Section 9.2. Additionally, future research will study the pressure and rate of pressure rise during the flame to determine if an alternative flammability criteria could be determined using pressure or pressure rise.

2. It would be recommended that the pressure gauge be on a separate line than the air/vacuum line. As discussed in Chapter 3, ASTM E681 makes use of a combination vacuum/air/pressure gauge line. This prevents the use of the pressure gauge while drawing a vacuum, or adding air. In the improved design, a separate pressure gauge line was utilized. This is a significant improvement, as it can be known when a full vacuum is reached, or when the pressure reaches atmospheric. For this reason, it is recommended that there be a separate pressure gauge line.

3. Additionally, it is recommended that the propeller system components are

updated. ASTM E681 recommends components of the propeller system that are no longer in production. This is a significant drawback to anyone designing the propeller system. The magnet bar does list dimensions in order to find a comparable replacement. However, the only dimension given for the propeller is the length and width. There is no thickness, or any indication of the exact shape of the propeller. Additionally, as shown in Section 5.3, the propeller bar length recommended by ASTM E681 is insufficient. To mitigate these issues, it is recommended that the dated part numbers are not included in the standard. Additionally, it is recommended that a more detailed drawing of the propeller is provided, along with a corrected propeller bar length.

4. It is recommended that the cover clamp not be used for testing. As mentioned in Section 2.3, a cover clamp may be used to secure the stopper onto the flask. The cover clamp is used to assist in achieving a vacuum, and to secure the stopper in place. A properly designed apparatus will not need the cover clamp to achieve a vacuum or secure the stopper in place. A properly designed apparatus makes the cover clamp unnecessary. Additionally, if the cover clamp is still on during ignition, it is possible that a pressure buildup inside the flask can occur. The cover clamp presents a potential danger. For these reasons, it is recommended that the cover clamp not be used.

5. It is recommended that the criteria for the heating system is revised. The current criteria stands at 0.38 m^3/min with a variable electric heater at 2400 W. This criteria seems to be completely unrelated to what is really needed of the heater, that is, heating with an accuracy of ± 3 °C. It is recommended that the heating system criteria be changed from 0.38 m^3/min with a variable electric heater at 2400 W to heating with an accuracy of ± 3 °C.

6. An additional recommendation to the plumbing system is to make use of only one penetration for the plumbing system through the stopper instead of two. Additional penetrations can create additional leakage paths, which can make achieving a vacuum more difficult, and can let refrigerant or air leak during testing. Furthermore, additional penetrations can cause the center of mass of the stopper to not be the spatial center of the flask, causing the system to tilt. This tilting can create additional leakage paths. A single penetration in the center for the plumbing eliminates these disadvantages, which is why a single penetration is recommended.

7. One recommendation for the ignition system is to seal the leakage path created by the glass tubes. This leakage path can make drawing a vacuum difficult, and can allow air and refrigerant to leak out during testing. Sealing the leakage path created by the glass tubes can be done in a number of ways, including epoxy. This will prevent a leakage path forming within the glass tubes. For this reason, sealing the glass tubes is recommended.

8. An additional recommendation for the ignition system is to make use of nuts at the top of the threaded rods to secure the electrodes. The ASTM E681 electrode design does not have any way of holding up the threaded rods. To overcome this, nuts are added to the top of the threaded rods to hold them in place. This prevents the threaded rods from falling or moving around during testing. For these reasons, nuts at the top of the threaded are recommended.

9. Another recommendation to the ignition system is the use of 3D printing as an alternative to Teflon for a lower spacer. The Teflon lower spacer is perfectly functional. However, 3D printing could be offered as an alternative method of developing a lower spacer. This will allow people to quickly and cheaply produce lower spacers. For this reason, it is recommended that the 3D printer lower spacer be offered as an alternative to

Teflon.

10. An additional recommendation for the ignition system is the use of solder connectors over solderless connectors. Soldering makes excellent electrical contact, also securing the tungsten wires firmly in place. For these reasons, soldering the connectors to the tungsten wires is recommended.

11. It is recommended that an additional suggested humidity system be introduced into the standard. The current humidity system presented by the standard, shown in Figure 7.1. This system is perfectly capable of conditioning the air. However, the system developed by Kondo et al. [10] and designed and constructed through this paper's research is a simpler alternative. It is recommended that the injection humidity system method be included in addition to the current ASTM E681 method.

9.2 Example of Flame Angle Analysis

The 90° criteria proposed by ASTM E681 has some ambiguity, as discussed in Section 9.1. To better demonstrate this ambiguity, an example is given. These images are taken from a test of 14.4% R-32 in air. The air is ambient temperature and 11% RH.

The SOP is followed, and the camera starts recording before the lights are turned off, shown in Figure 9.1. It is necessary to determine where the end of the electrodes are, in order to measure the 90° from them. It is not obvious from here where the end of the electrodes are.

In order to see exactly where the electrodes end, one uses the image of exactly when the sparking starts, shown in Figure 9.2.

From this image, a 90° can be overlaid onto the image to use for determining flammability, as shown in Figure 9.3.

From this point in time, the flame starts to burn, as shown in Figures 9.4 to 9.6.

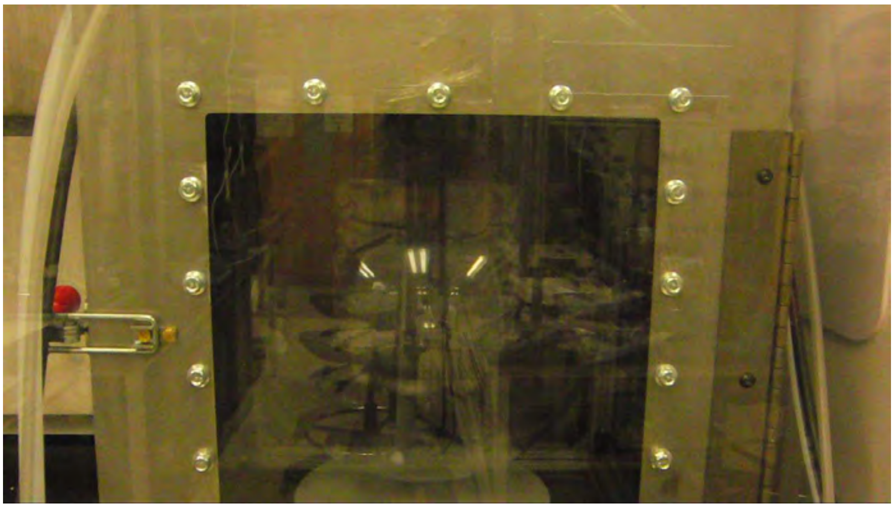


Figure 9.1: Test before lights are tuned off

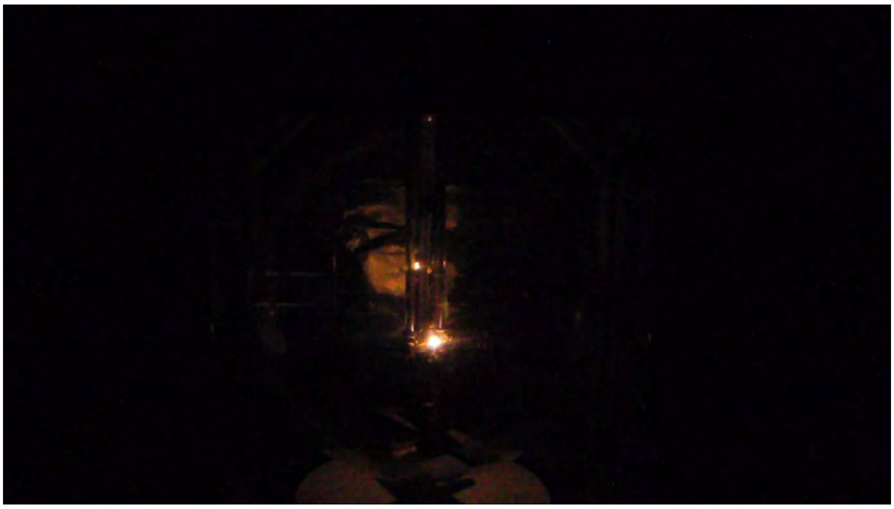


Figure 9.2: Spark before flame

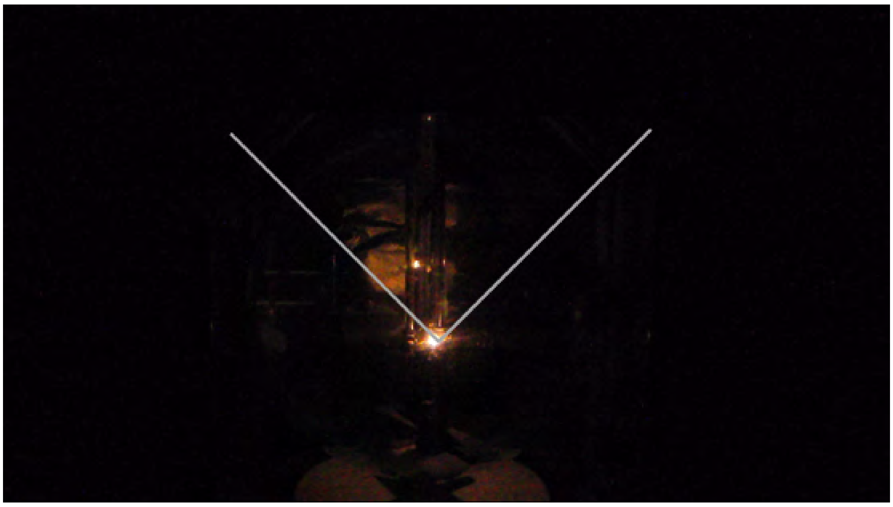


Figure 9.3: Spark before flame

Figure 9.4 shows the flame propagating upward. At this point, the flame does not meet or cross the 90° criteria.

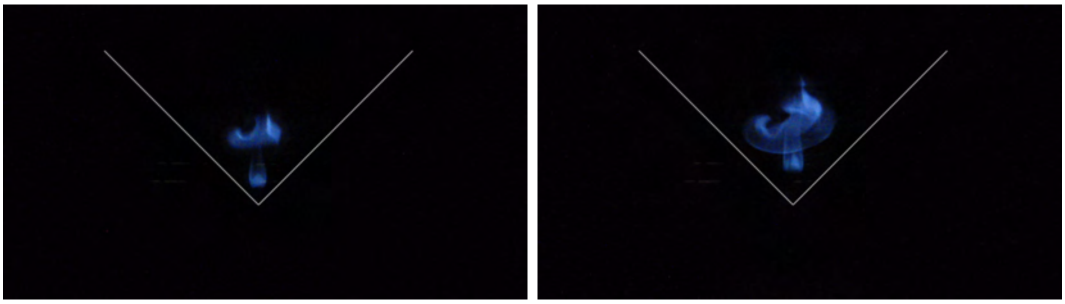


Figure 9.4: Flame propagation

The left of Figure 9.5 shows the flame propagating just before contact with the walls of the flask. The right of Figure 9.5 shows the flame as it hits the wall of the flasks. This flame crosses the 90° on the left side, but not the right. If the 90° criteria is used when the flame makes contact with the walls, then this concentration would not be considered flammable.

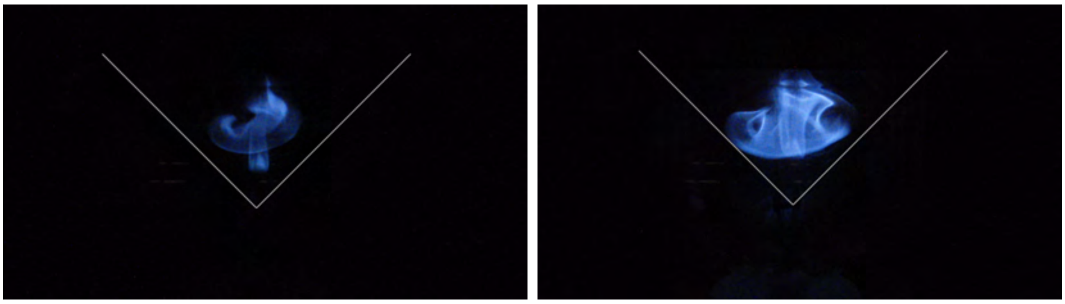


Figure 9.5: Flame propagation cont'd

The left Figure 9.6 shows a flame that may or may not be considered flammable. The flame crosses the 90° on the left side, and may cross on the right side. The right Figure 9.6 is considered flammable, as the flame is continuous and meets the 90° criteria. If the maximum flame angle criteria is used, then this mixture would be considered flammable.

In one interpretation, the flame is considered non-flammable (angle when contact is made with flask walls). Using another interpretation, the flame is considered flammable, (maximum continuous flame angle). This discrepancy can cause certain labs to consider a given concentration to be non-flammable,

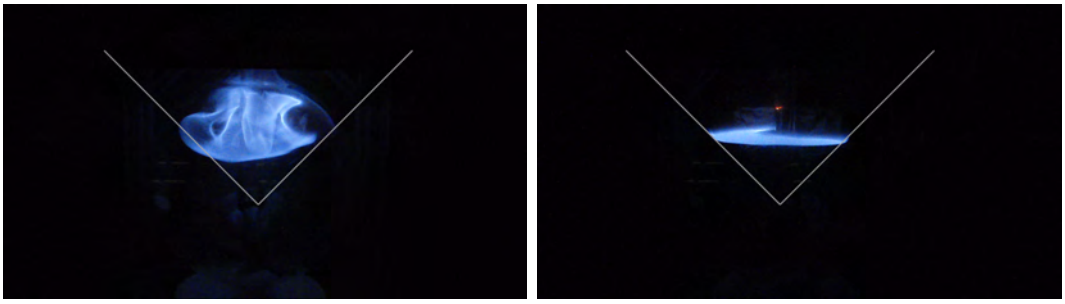


Figure 9.6: Flame propagation cont'd

while other labs would consider it flammable. For this reason, it is recommended that the wording of the flammable criteria to be clarified.

An alternative recommendation to the clarification to the flammability criteria is to change the criteria altogether. Future research will study the pressure and rate of pressure rise during the flame to determine if an alternative criteria could be determined using pressure or pressure rise.

It is recommended that this criteria be clarified to avoid confusion, such as the mixture is considered flammable if the flame spreads to the walls of the flask and are continuous along an arc that is greater than that subtended by an angle equal to 90°, as measured from the point of ignition once the flame makes contact with the walls of the flask.

10 Conclusions

The deficiencies of the ASTM E681 standard were identified. To remedy these deficiencies, an improved testing apparatus based on ASTM E681 and Appendix B of ANSI/ASHRAE 34 was designed and built. The entire system was designed with refrigerant testing in mind. The plumbing was improved by ensuring that the pressure readings could be constantly monitored, as shown in Chapter 3. An original electrical system was designed and constructed for the ignition system, as shown in Section 4.3. Additionally, a control panel was constructed to isolate hazardous electrical elements, and facilitate the testing, while simultaneously organizing the critical testing components, as shown in Section 4.4. 3D printing quickly produced heat-resistant, nonreactive, and structurally stable lower electrode spacers, propellers, and propeller bars, as shown in Section 4.2 and Chapter 5. The heating system was designed to ensure even temperature throughout the system, as shown in Chapter 6. The humidity system was designed to accurately condition the air, as shown in Chapter 7. A procedure for testing was created, as shown in Chapter 8. Recommendations to improve ASTM E681 were provided in Chapter 9. The research on improving the accuracy and reproducibility of ASTM E681 is still ongoing.

Some of the most significant recommendations are a change to the flammability criteria, using a single pressure gauge line, and changes to the propeller and heating system. These changes that require the most immediate attention.

References

[1] ASTM E-681. Standard Test Method for Concentration Limits of Flammability of Chemicals (Vapors and Gases). *American Society for Testing and Materials*, 09(Reapproved):1–12, 2015.

[2] David P. Wilson, Debra H Kennoy, A Bruce Badger, William J Brock, Warren Clough, Sean Cunningham, and Paul H Dugard. Designation and Safety Classification of Refrigerants, ANSI/ASHRAE Standard 34-2013. 2013.

[3] Robert G. Richard. Refrigerant Flammability Testing in Large Volume Vessels. *Buffalo Research Laboratories*, pages 1–11, 1998.

[4] Robert G. Richard. Refrigerant Flammability Testing in Large Volume Vessels. *Buffalo Research Laboratories*, pages 1–11, 1998.

[5] Airgass. Safety Data Sheet: Difluoromethane. pages 1–12, 2015.

[6] Edwin S. Iracki. ASTM round robin testing for E681-98. *ASHRAE 1997 Winter Meeting*, pages 1–18, 1997.

[7] AFROX. Material Safety Data Sheet: R134a. pages 1–2, 2011.

[8] Qi Chen, JiWei Yan, Guangming Chen, Yang Zhao, Yuqi Shi, Zhaoyun Zeng, and Qinglei Pan. Experimental studies on the flammability of mixtures of dimethyl ether. *Journal of Fluorine Chemistry*, 176:40–43, 2015.

[9] Everett W. Heinonen, Robert E. Tapscott, and Fred R. Crawford. Methods development of measuring and classifying flammaibity/combustibility of refrigerants. *The Air-Conditioning and Refrigerantion Technology Insititute*, pages 1–94, 1994.

[10] Shigeo Kondo, Kenji Takizawa, and Kazuaki Tokuhashi. Effect of high humidity on flammability property of a few non-flammable refrigerants. *Journal of Fluorine Chemistry*, 2014.

[11] Xueling Liu and Qi Zhang. Influence of initial pressure and temperature on flammability limits of hydrogen–air. *International Journal of Hydrogen Energy*, 39(12):6774–6782, 2014.

[12] Cole-Palmer. Ashcroft dg25, digital vacuum gauge w/ backlight, 0-30"hg. `http://www.coleparmer.com/Product/Ashcroft_DG25_Digital_Vacuum_Gauge_w_Backlight_0_30_Hg/EW-68334-01`. Accessed: 19 July 2016.

[13] ULVAC. Gld-40. `http://www.ulvac.eu/en/products/vacuum-products/oil-rotary-pumps/gld-series-direct-driven/gld-040/`. Accessed: 19 July 2016.

[14] Society of Fire Protection Engineers. *The SFPE Handbook of Fire Protection Engineering*. 1988.

[15] McMaster-Carr. Space-saver oil-removal air filter / regulator, 1/4" pipe. `http://www.mcmaster.com/#4989K201`. Accessed: 19 July 2016.

[16] McMaster-Carr. Desiccant air dryer polycarbonate bowl with steel guard, 1/4 pipe, 10 scfm. `http://www.mcmaster.com/#5163K18`. Accessed: 19 July 2016.

[17] France. P5g-2ue service master transformer. `https://a89b8e4143ca50438f09-7c1706ba3fabeeda794725d88e4f5e57.ssl.cf2.rackcdn.com/spec_sheets/files/000/002/778/original/france-15030p5g2ue-specs.pdf?1440172535`. Accessed: 19 July 2016.

[18] TiME Luminaries. Frequently asked questions - neon transformer. `http://neon-lighting.com/file/FAQ%20Neon%20Transformers.pdf`. Accessed: 19 July 2016.

[19] Leslie A. Geddes and Rebeca A. Roeder. *Handbook of Electrical Hazards and Accidents*. Lawyers and Judges Publishing Company Inc., 2005.

[20] Neon Sign Factory. Your source for neon signs and supplies. `http://www.neonsignfactory.com/Pages/NeonAccesories.aspx`. Accessed: 19 July 2016.

[21] Plastic Ingenuity. In focus: Bio-resins. `http://leadwise.mediadroit.com/files/8675PLA%20Material.pdf`. Accessed: 19 July 2016.

[22] Plastics International. ABS (acrylonitrile-butadiene-styrene). `https://www.plasticsintl.com/datasheets/ABS_FR.pdf`. Accessed: 19 July 2016.

[23] David C. Lay, Lay Steven R., and Judi J. McDonald. *Linear Algebra and Its Applications*. Pearson Eduction, 2016.

[24] Fisher Scientific. Pyrex flasks with short ring necks. `https://www.fishersci.com/shop/products/pyrex-flasks-short-ring-necks-5000ml/10065f`. Accessed: 19 July 2016.

[25] Corning. Pyrex 12L short ring neck boiling flask, round bottom (product 4260-12l). `http://catalog2.corning.com/LifeSciences/en-US/Shopping/ProductDetails.aspx?pid=4260-12L%28Lifesciences%29&cid=&productid=4260-12L%28Lifesciences%29`. Accessed: 19 July 2016.

[26] Fisher Scientific. Fisherbrand octagonal magnetic stir bars. `https://www.fishersci.com/shop/products/`

`fisherbrand-octagonal-magnetic-stir-bars-12/1451368`. Accessed: 19 July 2016.

[27] Forman A. Williams. Elementary derivation of the multicomponent diffusion equation. *American Journal of Physics*, 26(7):467–469, 1958.

[28] Forman A. Williams. *Combustion Theorey: The Fundamental Theory of Chemically Reacting Flow Systems*. The Benjamin/Cumings Publishing Company, Inc., 1985.

[29] SH Lam. Multicomponent diffusion revisited. *Physics of Fluids (1994-present)*, 18(7):073101, 2006.

[30] Hitachi. Model RH 650V Heat Gun: Instruction manual and safety instructions. `http://hitachipowertools.com/docs/default-source/default-document-library/rh650v_om.pdf?sfvrsn=0`.

[31] Shigeo Kondo, Kenji Takizawa, and Kazuaki Tokuhashi. Effect of temperature and humidity on flammability limits of several 2l refrigerants. *Journal of Fluorine Chemistry*, 2012.

[32] ASTM E-171. Standard Practice for Condidtioning and Tesiting Flexible Barrier Packaging. *American Society for Testing and Materials*, 11(Reapproved):1–2, 2015.

[33] Wisconsin Center for Applied Microelectronics. Matrial safety data sheet: Hydrofluoric acid. `http://wcam.engr.wisc.edu/Public/Safety/MSDS/Hydrofluoric%20acid,%2049%25.pdf`. Accessed: 19 July 2016.

[34] G.A.C.M. Spierings. Wet chemical etching of silicate glasses in hydrofluoric acid based solutions. *Journal of Materials Science*, 28:6261–6273, 1993.

[35] Wolfgang Wagner and Andreas Pruß. The IAPWS formulation 1995 for the thermodynamic properties of ordinary water substance for general

and scientific use. *Journal of Physical and Chemical Reference Data*, 31(2):387–535, 2002.

[36] Frostburg University. Water density. `http://antoine.frostburg.edu/chem/senese/javascript/water-density.html`. Accessed: 19 July 2016.

[37] S. Mostafa Ghiaasiaan. *Convective Heat and Mass Transfer*. Cambridge University Press, 2014.