Title
Design and Verification of a Speed of Sound Sensor for Biogas for Future use in a Fuel Flexible Burner

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IRVINE

Design and Verification of a Speed of Sound Sensor for Biogas for Future use in a Fuel Flexible Burner

THESIS

Submitted in partial satisfaction of the requirements for the degree of

MASTER OF SCIENCE

in Mechanical & Aerospace Engineering

by

Dimas Avila

Thesis Committee:
Professor Scott Samuelsen, Chair
Professor Vincent McDonell
Professor Yun Wang

2016
DEDICATION

To my parents, Rosa and Jose,

My girlfriend Monica,

My siblings Maria, Tania, and Ulises

And to my friends and family

For their support and encouragement
Acknowledgements

I would like to thank my advisors Dr. Vince McDonell and Dr. Scott Samuelsen for all of their help and support throughout the entire thesis project. I would also like to thank Jamie Ibrahim who helped me make the first few iterations of the speed of sound sensor. Furthermore, I would like to thank Professor Wang for providing his time to review my thesis. Finally, I would like to personally acknowledge Robert Flores, who was the first to help me code in Matlab and in extension to that helped me code my attenuation model and my code for the sensor.

As a final personal acknowledgement, I would like to thank my parents Jose and Rosa Avila for all their support throughout my academic studies. I would also like to thank my girlfriend Monica Sell, who helped make this step in my life go as smoothly as it possibly could. Her support as a life partner and friend was a foundation for the success I achieved as a graduate student.
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Abstract of Thesis

Design and Verification of a Speed of Sound Sensor for Biogas for Future use in a Fuel Flexible Burner

By

Dimas Avila

Master of Science in Mechanical and Aerospace Engineering

University of California, Irvine, 2016

Professor Scott Samuelsen, Chair

Due to strict emissions regulations, combustion systems in California are required to attain and maintain ultra-low emissions while achieving high efficiencies. Further, an increasing desire to utilize fuels that are derived from renewable sources to help mitigate emission of greenhouse gases is requiring more flexibility of these systems. As a result, combustion systems are adopting an increasing array of sensors and controls to achieve the desired performance.

The subject of this thesis is the development of a speed of sound (SOS) sensor for use in fuel flexible combustion systems. The goal is to facilitate the ability of the combustion system to self-tune to selected combustion characteristics, primarily the fuel stock. The fuel of primary interest is biogas, also known as digester gas, which is promoted by California’s energy policy as a renewable and carbon neutral fuel. In order to make such a system commercially available and help offset natural gas consumption with the underutilized fuel an inexpensive speed of sound sensor was developed to detect fuel compositions. The sensor was designed using acoustic attenuation models to select a suitable transducer for detection of the speed of sound. It was found that by detecting the speed of sound of a gas mixture up to two components from a gas mixture could be found. The model used to design the sensor was later verified by measuring
the excitation of transmitting and receiving transducers in different digester gas mixtures.

Utilizing this speed of sound sensor would help reach ultra-low NO\textsubscript{X} emissions while operating at lean conditions.
1. Introduction

1.1. Outline

Exploiting underutilized fuel stocks of California like digester gas has been identified as a benefit due to its potential to offset the state’s natural gas consumption. Such fuel stocks are available from waste water, landfill, and agricultural facilities. This fuel stock is primarily composed of carbon dioxide (CO₂) and methane (CH₄) (Baukal 2013). By turning the facilities’ waste stream into this useful product natural gas consumption can be reduced along with concomitant emission of the harmful greenhouse gas (GHG) methane into the atmosphere. One problem with the fuel source is the feedstock that is needed to make digester gas. This feedstock, while consistent, can vary in quality. This variation in quality can directly affect the quality of the fuel on hourly time scales. This along with other difficulties gives rise to concerns regarding digester gas’ impact on operation of a combustion system and limited return-on-investment. Such concerns have created barriers for these facilities to implement digester gas driven combustion systems.

In order to convert the waste stream that comes in through these facilities into useful energy the use of an anaerobic digester is needed. Anaerobic digestion involves the degradation of organic materials present in waste streams under low oxygen (anaerobic) conditions by microbial organisms and results in the formation of digester gas. Digester gas is a mixture that is primarily composed of CO₂ and CH₄. The fuel is considered a carbon neutral fuel because the source material, the waste, is composed of carbon chains which is then formed into the CO₂ portion of the digester gas and during combustion that same amount of CO₂ is the same volume of CO₂ that is released. Anaerobic digestion for the production of digester gas has been commercially
implemented in European countries but has seen a slower introduction in the United States due to high capital costs necessary to get the a digestion system running (Robbins 2013). Furthermore, while the gas is primarily composed of CH₄, the gas also has a high volume fraction of CO₂ which poses as a problem due its diluent behavior in lowering the energy content of the fuel as the CO₂ percentage increases.

Furthermore combustion systems which have been designed to achieve high fuel economy, very low emissions, and high turndown are usually designed for a single fuel stock such as pipeline quality natural gas, propane, or a specific biogas mixture (Richards et al. 2001). Newer combustion systems that have been designed for low emissions premix the fuel and air which opens up the potential for instabilities such as flashback and lean blow off (LBO). The first of this occurs due to two of the three components necessary for combustion being available upstream of an ignited mixture. If the flame speed of the mixture suddenly becomes greater than that of the incoming fuel and air mixture then the flame can propagate back into the premixed fuel and air. Additionally, controlling emissions such as oxides of nitrogen (NOₓ) requires operating at very lean conditions (high amounts of air) which could lead to costly LBO of the flame. Thus a widely varying fuel could result in costly damages and wear to the combustion system. It is already well known that natural gas is a gas that can vary based on region and this slight change in gas composition is enough to change entire combustion systems (Commission 2007). Digester gas, just like natural gas, can also vary – even on an hourly basis and with its higher CO₂ content achieving low emissions near unstable points can become an issue due to instabilities such as LBO and flashback and a need for higher volume flow rates to provide the same heat content as other fuels.
To complicate matters further, different fuels require different fuel to air mixtures to achieve equivalent ultra-low emissions. So the narrow window that has already been set forth by a single fuel’s operating point at which emissions are lowest is a problem due to the need to adjust air and fuel valves to achieve low emissions on different fuels. Systems that list themselves as fuel flexible due to the ability to switch between propane and natural gas however even these cannot switch in real time.

Looking at it through an energy efficiency perspective, the metric to consider when thinking about fuel switching is maintaining a consistent heat or power output. As mentioned in the sections above, digester gas which is primarily composed of CH₄ also has large fractions of CO₂ which significantly reduce the heat content of the fuel because CO₂ contributes zero energy to the fuel. A good indicator for this metric is the Wobbe Index which estimates the compatibility of several fuel stocks. However even this has become an outdated measure since different fuels have different flame speeds, temperature, and heat release ratios. Even when the Wobbe index is matched between different fuels emissions and flame stability can still be different (Mcdonell et al. 2012). So while a service interruption could occur to change between fuels on a fuel flexible burner the real advantage occurs when a combustion system is able to switch between fuels and detect the fuel content while burning the changing gas mixture efficiently and with low emissions. A fuel sensor that can detect varying compositions of fuels and can update a combustion system real time would be extremely useful in controlling the combustion to meet emission criteria and maintain stability.

This thesis examines the development of a speed of sound sensor that was used in a control system to fine tune the performance metrics of a boiler by measuring the composition of the fuel. This speed of sound sensor was able to detect a fuel change between varying digester gas
compositions and propane gas. The speed of sound of the gas was detected by emitting and
detecting the propagation time of an ultrasonic wave and from it detecting two components of a
gas mixture. This was implemented by using an ultrasonic distance sensor that detects varying
distances in different gas mixtures. The sensor also accommodated for acoustic phenomena that
occurs in gas mixtures by modeling this physical behavior. Using a thermocouple the
temperature dependence of the wave propagation was also accounted for. Different fuel mixtures
of simulated digester gas and propane were also tested.

1.2. Goal and Objectives

The goal of this thesis is to develop a low cost speed of sound sensor that can detect the
range of fuel compositions that are typical of anaerobic digester gas produced at water resource
recovery facilities.

This was accomplished by doing the following:

- Task 1 – Research transducers capable of detecting the speed of sound of gas mixtures
  that are expected at waste water facilities by modeling their acoustic phenomena.
- Task 2 – Design a laboratory fuel control circuit to run waste water digester gas mixtures
  and test the sensor in a laboratory setting.
- Task 3 – Select a capable microcontroller for speed of sound sensor
- Task 4 – Perform real world tests at a waste water facility that produces digester gas (i.e.
  Rancho Santa Margarita – RSM).
2. Background

The following section will cover a more detailed look into the necessity of a speed of sound sensor for the control of an RSM boiler. Topics that will be covered include emissions from both legacy burners and newer Dry Low NOx burner technologies that could be equipped with the speed of sound sensor. Alternatives to the low cost speed of sound sensor that was developed in this project will also be covered. Additionally, the topic of the renewable fuel, digester gas will also be discussed and its role in helping provide the ever increasing energy demand. Finally, the attenuation of acoustic signals will be discussed to address its physical behavior on different frequency transducers and gas mixtures.

2.1. Renewable Fuels

In recent years California has seen legislation call for a decrease in emissions that until just last year was unseen by the rest of the nation. In 2006 California laid out a plan, Assembly Bill 32 (AB 32), that aimed to cut emission levels back to 1990 levels by 2020 (April and Code 2010). The nation soon followed in California’s footsteps by setting a nation-wide standard of achieving 32% below 2005 levels by 2030 (EPA Clean Power Plan 2015).

When looking at the portion of carbon emissions that are produced through the electricity sector in Figure 2-1 nearly 75% is contributed by coal power plants. California has since cut back completely on their coal power plants but has relied heavily on natural gas due to the shutdown of a major contributor, the San Onofre Nuclear Power Plant, and reduced hydroelectricity from the ongoing drought. Thus legislation has passed (Senate Bill, SB, 1078) that calls for 33% of the energy produced to come from renewable sources by 2020 (California Public Utilities Commission 2015). This section will cover some of the emissions that are
targeted by legislation as well as renewable fuels in this study that can help meet the 33% renewable portfolio standard (RPS).

Figure 2-1. Nationwide Carbon Emissions by Sector (C2ES 2015)

With the passage of assembly bill 32, also known as the California Global Warming Solutions Act, in 2006 the bar was set by California and soon the rest of the country’s transition to a sustainable low carbon future. It was the first piece of legislation that introduced a program to tackle climate change with a long term plan. The overall plan was to reduce GHG’s to 1990 levels by 2020. This was a level that was 15 percent below what would be expected if the state continued “business as usual” (Pavley and Nunez 2006). Five years later a bill that had been introduced in 2002 as Senate Bill 1078 became Senate Bill X1-2 which called for 33 percent of all electricity retailers including publicly owned utilities’ loads to come from renewable sources (Commision 2015). Digester gas can help tackle both problems as it is composed of CH₄ and CO₂ which are both potent GHG’s and it is considered to have a zero net CO₂ footprint (Lefebvre and Ballal 2010).
2.1.1. Biogas

The decomposition of organic material into useful gases like methane is done through the process of anaerobic digestion. This process is accomplished by bacteria which break down organic material such as that which may come from agricultural or municipal waste (Chen et al. 2008). A variety of factors affect the rate of digestion by the bacteria and the ensuing biogas production. The most important is temperature, which needs to be kept in a certain range otherwise bacteria activity, and thus biogas production begins to drop off. Other factors that affect the output rate of biogas include pH levels, water/solid ratios, carbon/nitrogen ratios, and the mixing of the waste feedstock (Baukal 2013).

It is an attractive practice since it achieves both pollution control and energy recovery through the making of useful gas. The reduction of pollution by use of anaerobic digestion is two-fold. The first is if the process were not implemented waste streams would not be diminished. Secondly, these waste streams can achieve anaerobic digestion and the methane and carbon dioxide that is produced would be escaping into the atmosphere.

Upon completion of anaerobic digestion, biogas can achieve several varying compositions based upon source. Some of these varying compositions can be seen in Table 2-1. As can be seen sewage waste and organic waste are primarily CH₄ and CO₂. There are other trace gases present such as hydrogen sulfide and siloxanes however they are much smaller than the values listed in Table 2-1. Although they are small they require attention since even the trace amounts that are found can be detrimental to a combustion system and certain cleanup procedures are required to remove these trace gases from the fuel stream. Throughout this paper the assumption is made that the majority contributors to digester gas come from CH₄ and CO₂.
<table>
<thead>
<tr>
<th>Source</th>
<th>CH₄</th>
<th>CO₂</th>
<th>N₂</th>
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<tr>
<td>Sewage</td>
<td>55%-65%</td>
<td>35%-45%</td>
<td>&lt;1%</td>
</tr>
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</table>

Table 2-1. Typical biogas compositions from waste water facilities (Baukal 2013)

The problem that arises when trying to operate a combustion system on a fuel such as biogas and a backup fuel such as methane or propane is the large contribution of CO₂ in the biogas mixture. CO₂ contributes zero energy into the energy content of the fuel. This is a problem when trying to flow a certain amount of fuel into a combustion system that operates at a specific firing rate with propane or methane. Since CO₂ constitutes a large proportion of the biogas mixture a larger amount of biogas has to be flowed to achieve the same heating rate as propane or methane. Another problem arises when trying to burn biogas, once again, due to the diluted heat content of the fuel from the CO₂ contribution due to a reduced flame speed (Hinton and Stone 2014). This can cause problems for equipment and thus being able to read fuel quality real time is a major benefit for this type of fuel.

One type of indexing scheme that helps identify combustion systems with useable fuels is the Wobbe index. Since most combustion systems are designed for a specific fuel the Wobbe index helps compare fuels for compatibility amongst different combustion systems. The equation that helps characterize the wobbe index is as follows:

\[ WI = \frac{HHV}{\sqrt{SG}} \]  

\textbf{Equation 2-1}

Where HHV is the higher heating value of the gas mixture and SG is the specific gravity.

SoCal gas, a southern California natural gas utility, applies a similar scheme for gases that are suitable for the natural gas pipelines. This is because most combustion systems such as heating stoves are designed for a specific wobbe index of natural gas. However, despite
its feature of being able to identify interchangeability through energy content of a fuel it lacks other physical characteristics that could prove to be disastrous for differing combustion systems. The flame speed, for one, is not captured based on energy content. Despite being able to match differing fuel mixtures on energy content, the exact composition could lead to other different physical factors which can prove to be disastrous.

Therefore, most combustion systems continue to be designed on a single type of fuel. To be able to tap into the energy resource of digester gas a combustion system would have to also be fuel flexible since the composition of Table 2-1 change on timescales of a minute! Biogas is also not always available and combustion systems must be dynamic enough to be able to switch between different types of fuel. Therefore, the applicability of a speed of sound sensor such as what is being proposed in this thesis that detects the quality of biogas can be applied to be able to burn these varying fuels effectively. It would provide waste water plants and other sources of biogas the ability to tap into a free energy source and help offset other energy needs that are traditionally met by fossil fuels.

2.1.2. Landfill Gas

Another type of alternative fuel that is attractive is landfill gases. According to information provided by the Landfill Outreach Program, an EPA program, there are over 400 candidate landfill sites that do not have equipment to extract this useful source generated at these sites (EPA 2015). Additionally, at least 50% of landfills are at capacity and no longer accept waste streams (EPA 2015). When this happens the methane produced at these sites can leak out for as long as 50-70 years after closure. It can prove to be an attractive source since the fuel stock produced by this process is much larger than what is produced by sewage waste.
As can be seen in Table 2-2 landfill gas can have an even larger contribution from \( \text{N}_2 \) which is also a diluent. Most of these waste stream source fuels usually have propane gas as a backup fuel. Referring back to the WI mentioned in section Biogas this would require a larger flow of the fuel to achieve the same power output as propane gas which would need to be accounted for fuel flexible combustion systems implemented at these waste sites. If these fuels along with biogas from waste water facilities can be monitored for quality they can help contribute to society’s energy demands.

<table>
<thead>
<tr>
<th>Source</th>
<th>( \text{CH}_4 )</th>
<th>( \text{CO}_2 )</th>
<th>( \text{N}_2 )</th>
</tr>
</thead>
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<tr>
<td>Landfills</td>
<td>45%-55%</td>
<td>30%-40%</td>
<td>5%-15%</td>
</tr>
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Table 2-2. Typical Landfill Gas Compositions (Baukal 2013)

2.2. Traditional Gas Sensing Methods

In order to satisfy this growing interest in opportunity energy sources like renewable fuels there needs to be methods to identify their compositions. As was mentioned in the Renewable Fuels section the fuel composition can vary from site to site and with time depending on the quality of the feedstock as well as processing parameters (Plaines 2012). Due to this variance being potentially damaging to engine hardware research in real time gas sensing methods has been pursued. As was also seen in order to dynamically tune to combustion systems to meet emission criteria and maintain operability some techniques have been implemented. These however are have limited abilities due to their lack of control for fuel composition changes. Therefore an investigation was performed into traditional gas sensing methods in order to deduce varying compositions of anaerobic digester gas. Some of these methods include gas chromatography, spectroscopy, and calorimetry. Each of these will be discussed in the following
sections along with the primary gas sensing method (acoustic sensor) that is the focus of this thesis.

2.2.1. Gas Chromatography

At present gas chromatography (GC) is the most widely used gas sensing method on the market. This method works by separating and analyzing compounds for purity (The Linde Group 2015). The method works by flowing a sample gas into a stream of inert gas (carrier gas). The inert gas is usually of high purity. This combined gas stream is then passed through a packed column through which gas molecules that do not interact with the packing material pass through. As the gas streams pass through the column they are quantified by a detector. While this method is capable of detecting gas mixtures down to the ppm level it is extremely costly. Additionally, carrier gases, and reference gases must be purchased which can expensive depending on what kinds of gas mixtures are being tested. Finally, while the gas chromatograph offers ultra-precise readings, it comes with the caveat of time. Usual response times for these sensors are on timescales of 10 minutes or longer reducing their appeal as a real time monitoring device.

2.2.2. Gas Spectroscopy

Spectroscopy is another type of method that is often deployed for gas sensing. One type of spectroscopy is infrared (IR) spectroscopy which measures the absorption of infrared light by a gas sample (The Linde Group 2015). Its high selectivity allows for the estimation of complex gas samples. There are different types of spectroscopy methods that can be used including Fourier transform infrared (FTIR), and non-dispersive infrared (NDIR).

FTIR uses the mathematical Fourier transform (FT) process to convert raw data measured by spectroscopy into an actual spectrum. It does so by using an interferometer which is the
combination of a fixed and moving mirror and at different positions it has different information about every infrared frequency that is emitted by the IR light source. The FT is applied to convert data from light absorption at each mirror position to light absorption at each wavelength. Again high purity gases like nitrogen are needed to zero this sensor and multiple cylinders of high accuracy are required to generate calibration curves for gas mixtures that are to be tested. Since all of these features bring in some of the complexities introduced by the GC method the pricing for these devices is also high.

The NDIR method works by passing an IR beam through a gas chamber and each gas component absorbs some particular IR frequency (The Linde Group 2015). In parallel to this is usually a reference gas like nitrogen. The NDIR sensor usually measures the amount of absorbed IR at a selected frequency to correlate it to concentration of the gas component that absorbs that frequency. The method is known as non-dispersive portion because the wavelength of light that passes through the gas chamber is not filtered. An optical filter is instead placed at the opposing end of the light beam and gas chamber. The filter eliminates all light except the wavelength of light that can be absorbed by the specific gas which correlates it back to the concentration of that gas component in the gas mixture. These sensors are usually used to measure the concentration of carbon oxides like CO₂ and CO due to their selective absorbance of IR light. Although these sensors can be purchased at a reduced price this usually comes with the inability to distinguish between gases that absorb the same wavelength of light as CO₂.

2.2.3. Gas Calorimetry

Gas Calorimeters are another type of method that can be employed to measure the fuel quality of a gas. This technology has been employed for the past several decades and is different from GC and spectroscopy since it does not measure gas constituents. Instead, the method works
by measuring the energy content of the fuel. (Plaines 2012) As was mentioned previously in the Renewable Fuels, despite knowing the energy content of the fuel, other fuel parameters such as flame speed can be detrimental to the combustion system. On top of this the calorimeter is both costly and slow to respond for a real time application (Plaines 2012).

2.3. Acoustic Methods for Gas Sensing

One novel method that has garnered a lot of attention due to its low cost are acoustic sensors. Since the cost to implement energy recovery of an opportunity fuel like biogas is so high a low cost rugged sensor could prove to be a viable option. Acoustic methods work by measuring a physical property of a fuel gas mixture, the speed of sound, and from it correlating it back to the quality of the fuel. This method was first proposed in the mid 1980’s to detect binary gas mixtures. A few years later it would be used to determine combustion properties of fuels. The evolution of this sensor is discussed in the following sections.

2.3.1. Using Acoustic Methods (Prior Work) to determine gas compositions and molecular properties

As was mentioned in the previous sections several methods have been employed for measuring general binary gas mixtures. Tinge et al first used the method for determining the speed of sound in mixture of C₃H₈ and ethane C₂H₆ (Tinge et al. 1986). They were able to accurately determine the change in composition down to 0.008% by volume. Their method employed measuring phase shifts between a transmitter and a receiver at the opposing end which correlated to certain fuel blends. Polturak et al employed their in house machined resonators to correlate the change in measured resonance frequencies to changes in He²⁻He⁴ and O₂⁻N₂ mixtures (Polturak et al. 1986). Their sensor was able to measure changes of 0.1% by volume.
Colgate et al used a similar approach by machining a spherical resonator which uses the normal mode vibrations of an elastic system (Colgate et al. 1990). The speed of sound comes into play due to the standing waves that are formed in the spherical resonator of which the dimensions are known to calculate gas mixtures. They used their tests to determine second virial coefficients of gases. While deciphering these gas mixtures had their advantage acoustic sensor priorities began to take a turn when they began to be used for detection of gas compositions in fuels.

2.3.2. Using Acoustic Methods (Prior Work) to determine combustion properties

In the early 1990s the thought arose amongst two different groups to use the speed of sound to correlate it to combustion properties of fuels. They realized that the concentration of natural gas which is used in an unprocessed state varies substantially from region to region and the literature was starting to show the problems that occurred for combustion systems that had varying fuel compositions (Liss et al. 1992). The first group to use the acoustic sensor for natural gas composition detection was Richard Lueptow and Scott Phillips from Northwestern University. Lueptow and Phillips correlated the speed of sound to specific fuel properties. They found that the speed of sound did not correlate well with natural gas mixtures with high amounts of inert gases. They did, however, find that it correlated well with molecular weight, density, and lower flammability limit. The second group led by Beck used research from the Southwest Research institute which found a good correlation between fuel properties and the H/C ratio of saturated hydrocarbon fuels (Kubesh et al. 1992). In effect Beck et al used the speed of sound to correlate it to H/C ratios of these gaseous fuels to determine fuel properties (Beck et al. 1993). They found a good correlation between the speed of sound and H/C ratio (Beck et al. 1993).
2.3.3. Acoustic Dispersion Zones

What the two groups did not take into account when implementing the acoustic methods was that by perturbing the gas with ultrasonic waves, the gas’ acoustic characteristics could also change including the speed of sound! This dispersion zone can be seen in Figure 2-2 for the two major gas components in biogas, CO$_2$ and CH$_4$ with small additives of air. This acoustic dispersion is coupled with another physical phenomena, acoustic attenuation, which diminishes the sound energy induced in gas mixtures. This absorption is divided into two types: One of which is called classical attenuation which comes about due to diffusion, conduction, and viscosity. The other is referred to as a non-classical component (relaxation) that is associated with long relaxation times of molecular vibrational modes. The latter phenomena will be covered in the Attenuation Theory section since this phenomena needs to be taken into account for ultrasonic transducers which operate in the frequency range where relaxation attenuation is greatest.

![Figure 2-2. Dispersion Curves (a) 98%/2% CO$_2$/Air (b) 98%/2% CH$_4$/Air (Zhang et al. 2013)](image-url)
2.3.4. Similar Speeds of Sound

The other thing that needed to be taken into account was the actual composition of these multi-constituent gas mixtures. The speed of sound as the only measurement really only relays the molecular weight of the gas (Petculescu and Lueptow 2012). Yet molecular weight can really become an issue when molecules of the same molecular weight are present. For natural gas it can be compromised of mainly CH$_4$ with trace amounts of other hydrocarbons and inert gases. One of those hydrocarbons is C$_3$H$_8$ and one of the inert gases is CO$_2$ which each have the same molecular weight of 44 amu. The variance in the speed of sound for different gas mixtures of these three components can be seen in Figure 2-3. As can be seen for pure mixtures of CO$_2$ or C$_3$H$_8$ (top and bottom left corners of Figure 2-3) the speed of sounds are very similar. This can be a problem since each contributes significantly different attributes in the field of combustion! Therefore in order to account for this a separate speed of sound sensor will be implemented in the fuel train upstream of the boiler. One dedicated to the biogas fuel train and one to measure the mixture of C$_3$H$_8$ with biogas.

![Ternary Plot of CO$_2$-CH$_4$-C$_3$H$_8$ Speed of Sound Values [298K]](image)

**Figure 2-3.** Ternary Plot of CO$_2$-CH$_4$-C$_3$H$_8$ Speed of Sound Values at 298K
2.4. Attenuation Theory

In order to make a design selection for the transducer to be used to monitor the biogas composition acoustic properties of the fuel need to be known. One of these properties is acoustic attenuation. It arises due to the exchange of energy between external (translational) and internal (relaxational) degrees of freedom. It will be covered in more detail in the sections that follow.

The physical phenomena of acoustic attenuation has garnered attention since the early 20th century. It was in this time period that the foundations were being laid for the physical explanation by the early work of Landau and Teller (Landau and Teller 1936). Their work which is known in the literature as LT Theory was of great importance and would continue to be fine-tuned in the ensuing years. Approximately two decades later one of these adjustments came by the way of three of scientists, Schwartz, Slawsky, and Herzfeld (SSH). While the Landau Teller was a relatively good approximation of acoustic attenuation it relied heavily on classical physics due to the constriction that the vibrational energy ($\hbar \omega$) was much smaller than Boltzmann factor ($k_B T$) (Nikitin and Troe 2008). Additionally, the LT model was restricted to collinear collisions in a 1D space. What SSH theory did was take a quantum approach and apply the solution to a 3D space (Schwartz et al. 1952). Up until the beginning of the 21st century there had been some alternatives to the SSH theory but no one had applied the SSH theory to any gas mixtures besides pure gases and binary gas mixtures. At this time two scientists from Northwestern University, Dain and Lueptow, introduced their own theory (DL Theory) to multi-constituent gas mixtures (Dain and Lueptow 2001).
2.4.1. DL Theory

DL Theory not only looks at multi-constituent gas mixtures but also involves polyatomic molecules. It seeks a solution in the form of the acoustic attenuation of an ultrasonic wave by using the Euler equations linearized around equilibrium pressure, density and temperature to describe a plane acoustic wave’s propagation in a gas mixture (Dain and Lueptow 2001).

Additionally the model relies heavily on transition probability calculations that were modeled by Tanczos (Tanczos 1956) and will be discussed in the section titled Tanczos. This model does not include classical attenuation which accounts for viscosity and heat transfer. This type of attenuation can be solved for separately. Several other assumptions are also made which include assuming there is no diffusion of acoustic gas components, that only one quantum vibrational jump (between 0 and 1) can be made by the mixture components and that the model is only considered at relatively low temperatures (i.e. room temperature). Since only low temperatures are considered only the lowest vibrational modes of the gas components can be activated. The Euler equations mentioned previously are accompanied by nonlinear semi-macroscopic population equations for any number of molecules in a given energy state and are governed by the following

\[
\frac{P}{P_0} = \frac{T}{T_0} + \frac{\rho}{\rho_0}
\]

\[
\frac{\partial \rho}{\partial t} + \rho_0 \frac{\partial u}{\partial x} = 0
\]

\[
\frac{\partial u}{\partial t} + \rho_0^{-1} \frac{\partial P}{\partial x} = 0
\]

\[
\frac{\partial \varepsilon}{\partial t} + P_0 \rho_0^{-2} \frac{\partial \rho}{\partial t} = 0
\]
\[ \epsilon = c_v T + \sum_{i}^{N} \alpha_i c_{i}^{vib} T_{i}^{vib} \]  \hspace{2cm} \text{Equation 2-6}

\[ \sum_{i}^{N} \alpha_i = 1, c_v = \sum_{i}^{N} \alpha_i c_{i}^{v} \]  \hspace{2cm} \text{Equation 2-7}

\[ c_{i}^{vib} = g_i R \left( \frac{\theta_{i}^{vib}}{T_0} \right)^2 \frac{\exp \left( \frac{\theta_{i}^{vib}}{T_0} \right)}{ \left( \exp \left( \frac{\theta_{i}^{vib}}{T_0} \right) - 1 \right)^2} \]  \hspace{2cm} \text{Equation 2-8}

Where, \( \theta_{i}^{vib} = \frac{hn_i}{k_B} \)

Where \( P, \rho, u, \epsilon, \) and \( T \) are small variations in of equilibrium pressure, density, velocity, energy, temperature. The mole fraction of the constituents is represented by \( \alpha_i \) while translational specific heat capacities of the mixture constituents are represented by \( c_{i}^{v} \).

Additionally \( T_{i}^{vib} \) are the internal vibrational temperatures of the gas constituents and \( c_{i}^{vib} \) are the vibrational specific heat capacities of gas components for each active vibrational mode of gas constituents. As mentioned previously \( \epsilon \) from Equation 2-6 represents the small fluctuations of the total energy of the gas mixtures and its equation requires the need to calculate the vibrational specific heat capacities of the gas components which is defined by the Planck-Einstein Function (Equation 2-8) (Holman 1988). This equation calls for \( R \) the universal gas constant, \( \theta_{i}^{vib} \), the characteristic temperature for vibration, and \( g_i \), the degeneracy of a vibrational mode. The characteristic temperature for vibration, \( \theta_{i}^{vib} \), can be further characterized by the second part of Equation 2-8 which uses \( h (6.626 \times 10^{-34} \text{ J s}) \) and \( k_B \left( 1.380 \times 10^{-23} \frac{\text{J}}{K} \right) \) which are Planck’s constant and Boltzmann’s constant respectively. Finally, \( n_i \), which is in the second part of
Equation 2-8 refers to the active vibrational modes of the gas constituents that can be activated around room temperature or are resonant with other active vibrational modes.

The deduction of the system of equations that make up the relaxation matrix are a function of the vibrational temperatures and vibrational modes that are participating for the gas components are modeled by the DL model as follows (Dain and Lueptow 2001):

\[
\frac{d T_j^{\text{vib}}}{dt} = \frac{T - T_j^{\text{vib}}}{\tau_j^{\text{tran}}} + \sum_{k=1}^{N} \frac{1}{\tau_{j,k}^{\text{vib}}} \left( 1 - \exp\left(-\frac{hn_j}{k_B T_0}\right) \right) \left( 1 - \exp\left(-\frac{hn_k}{k_B T_0}\right) \right) \equiv x \left[ (T - T_j^{\text{vib}}) - \frac{n_k}{n_j} (T - T_k^{\text{vib}}) \right], j = 1, ..., N
\]

Equation 2-9

Where the translational relaxation time, \( \tau_{j,k}^{\text{vib}} \), which appears in Equation 2-9 is defined by the following equation:

\[
\frac{1}{\tau_j^{\text{tran}}} = \sum_{i=1}^{N} \frac{\alpha_i}{\tau_{j,i}^{\text{tran}}}
\]

Equation 2-10

In special cases multiple vibrational modes may be activated for a single gas component if another available vibrational mode is resonant with a vibrational mode with the active vibrational mode of a different gas specie. In this case the translational relaxational times are calculated as follows:

\[
\frac{1}{\tau_j^{\text{tran}}} = \sum_{i=1}^{N-1} \frac{\alpha_i}{\tau_{j,i}^{\text{tran}}} + \frac{\alpha_{N-1}}{\tau_{N,N}^{\text{tran}}}, j = 1, ..., N - 1
\]

Equation 2-11

The translational relaxation of each collision between different gas components and each of their active vibrational modes is calculated as follows:
\[ \frac{1}{\tau_{\text{tran}}^{j,i}} = Z(j, i)P^1_0 \rightarrow 0(j, i) \left(1 - \exp\left(-\frac{hn_j}{k_B T}\right)\right) \]  \hspace{1cm} \text{Equation 2-12} \]

Where \( Z(j,i) \) is the collision rates of molecules of species \( j \) with molecules of species \( k \). This collisional rate can be expressed as follows when assuming that the gas molecules are rigid spheres.

\[ Z(j,k) = 2N_k \left(\frac{\sigma_j + \sigma_k}{2}\right)^2 \left(\frac{2\pi k_B T}{\mu}\right) \]  \hspace{1cm} \text{Equation 2-13} \]

Where \( N_k \) is the number of molecules of species \( k \) per unit volume, \( \sigma_j \) and \( \sigma_k \) are the collision diameters of two colliding gas molecules and \( \mu \) is the reduced mass of the colliding molecules.

The transition probabilities, \( P^1_0 \rightarrow 0 \), from Equation 2-12 is based on the Schrödinger equation for binary collisions of two molecules in a mixture. It is solved by assuming specific collisional conditions and based on molecular properties of the species which can be found in Table 2-4. An approximation was made by Tanczos in the 1950s and it will be described in the Tanczos section.

The vibrational relaxation times for excitation processes with two vibrational modes can be described by the following:

\[ \frac{1}{\tau_{\text{vib}}^{j,k}} = \alpha_k g_k Z(j,k)P^1_0 \rightarrow 0(j, i), j, k = 1, \ldots, 4, j \neq k \]  \hspace{1cm} \text{Equation 2-14} \]

As mentioned before the transitional probability, \( P^1_0 \rightarrow 0(j, i) \), in this case for vibrational-vibrational energy exchanges, will also be discussed in the section titled Tanczos.

The relaxation system from Equation 2-9 can be written in vector form as follows:
\[
\frac{dT_{\text{vib}}}{dt} = -AT_{\text{vib}} + qT
\]

Equation 2-15

Where the matrix A, and the vector q, are both functions of the mole fraction of the gas constituents which can be described as:

\[A_{jj} = \frac{1}{\tau_j^{\text{tran}}} + \sum_{k=1}^{N} \frac{1}{\tau_{j,k}^{\text{vib}}} \frac{1 - \exp \left( -\frac{hn_j}{k_B T_0} \right)}{1 - \exp \left( -\frac{hn_k}{k_B T_0} \right)}\]

Equation 2-16

\[A_{jk} = \frac{-1}{\tau_{j,k}^{\text{vib}}} \frac{1 - \exp \left( -\frac{hn_j}{k_B T_0} \right)}{1 - \exp \left( -\frac{hn_k}{k_B T_0} \right)} n_k\]

\[q_j = \frac{1}{\tau_j^{\text{tran}}} + \sum_{k=1}^{N} \frac{1}{\tau_{j,k}^{\text{vib}}} \frac{1 - \exp \left( -\frac{hn_j}{k_B T_0} \right)}{1 - \exp \left( -\frac{hn_k}{k_B T_0} \right)} \left[ 1 - \frac{n_k}{n_j} \right],\]

\[j, k = 1, ..., N, j \neq k\]

2.4.2. Solution for DL Model

Using Equation 2-2-Equation 2-5 which are described by the Euler equations, nonlinear population equations and Equation 2-16 which gives a system of equations the attenuation of an acoustic wave in a gas mixture can be solved for. The solution for this system of equations as mentioned before is sought in the form of a harmonic plane wave with all quantities \( P, \rho, u, \epsilon, T, \) and \( T_{j}^{\text{vib}} \) expressed in the plane wave form:

\[f = \tilde{f} \exp \left( -i(\omega t - kx) \right)\]

Equation 2-17

Here \( \tilde{f} \) is the amplitude of the quantity. Substituting in the solution given by the previous equation provides a new homogenous system of equations described as follows.
\[
\begin{align*}
\frac{\bar{P}}{P_0} - \frac{\bar{T}}{T_0} - \bar{\rho} &= 0 \\
-\omega \bar{\rho} + \rho_0 k \bar{u} &= 0 \\
\omega \bar{u} - \rho^{-1} k \bar{P} &= 0 \\
\bar{\varepsilon} - P_0 \rho^{-2} \bar{\rho} &= 0
\end{align*}
\]

Equation 2-18

The molecular relaxation system of equations can likewise be represented in vector form as follows:

\[
(i \omega I + A)\bar{T}^{\text{vib}} - q\bar{T} = 0
\]

Equation 2-19

Where the rows of matrix A correspond to the vibrational modes and the columns correspond to their matching reactions, and I is the identity matrix. Combining Equation 2-18 and Equation 2-19 gives the following equation:

\[
B y = 0, \left(\bar{\rho}, \bar{u}, \bar{P}, \bar{T}, \bar{T}^{\text{vib}}\right)
\]

Equation 2-20

\(B\) here is an 8x8 matrix that is dependent on the gas concentrations, \(\alpha_i\), the angular frequency \(\omega\), and the coefficients of the relaxation system A. Setting the determinant of matrix \(B\) equal to zero will provide a dispersion relation which when solved numerically will provide the wave number \(k\) as a function of \(\omega\).

The wave number, \(k\), when solved for numerically is complex value in the following form:

\[
k = \frac{2\pi}{\lambda} + i\alpha
\]

Equation 2-21

Where is \(i\) the imaginary number, \(\alpha\) is the attenuation coefficient, and the real part determines the actual speed of wave propagation of the gas mixture, making the speed of sound frequency dependent. This can otherwise be described as follows:
\[ c = \frac{\omega \lambda}{2\pi} \]  

Equation 2-22

These equations were all solved for, for mixtures of biogas using values each gas component that can be found in the literature. The resolved dispersion curves and attenuation curves for specific types of biogas mixtures can be found in the Results section which were solved using the Matlab script in Appendix section Matlab code for attenuation model.

2.4.3. Tanczos

The first extension of the SSH theory to polyatomic molecules was done by Franc Tanczos when he applied it to his study of relaxation times in chloromethanes (Tanczos 1956). One of the underlying assumptions from SSH theory that gets carried through by Tanczos as well as DL theory is the assumption that vibrational energy only gets transferred in collision processes. Such collisions can result in two separate transitions both of which can be physically interpreted by Ehrenfest’s Adiabatic Principle (Lambert 1977). This principle says that if a changing force (external) acts on a quantized periodic motion (internal) the process will be adiabatic if the change of force is small during the periodic motion or non-adiabatic if that change of force is large during the periodic motion. For Tanczos’ case this is looking at the non-adiabatic processes in which efficient energy transfer will take place. As mentioned before two separate transitions can occur one of which is \( P_{0}^{1} \rightarrow 0(j, i) \) from Equation 2-12 and involves only a singular change in vibrational state of one of the colliding molecules evident in the variable’s subscript 0\( \rightarrow 0 \) indicating only change in one molecule. The complex kind of transitions \( P_{0}^{1} \rightarrow 0(j, i) \) which was seen in Equation 2-14 involved a simultaneous change in both colliding molecules. For either type of change the probability that a pair of molecules that
originally have the vibrational states \(i_a\) and \(i_b\) will arrive at vibrational states \(f_a\) and \(f_b\) is given by (Tanczos 1956):

\[
P(a, b) = P_0(a)P_0(b)P_cV^2(a)V^2(b)\sqrt{\frac{\pi}{3}} \left(\frac{8\pi^3\mu\Delta E}{(\alpha^*)^2\hbar^2}\right)^2
\]

\[
* \sqrt{\xi} \exp\left[-3\xi + \frac{\Delta E}{2k_BT} + \frac{\phi_0}{k_BT}\right]
\]

Where

\[
\xi = \frac{\mu(v_0^*)^2}{2k_BT} = \frac{2\pi^4\mu^2(\Delta E)^2}{((\alpha^*)^2\hbar^2k_BT)^{1/3}}
\]

And

\[
\Delta E = \hbar n_a(i_a - f_a) + \hbar n_b(i_b - f_b)
\]

This equation can be split up into 4 different factors. These will be discussed in sections that follow.

2.4.4. Steric Factors

\(P_0(a)\) and \(P_0(b)\) of Equation 2-23 are required to account for the assumption that the molecules really are not hard rigid symmetrical spheres (Lambert 1977). They are also needed since the orientation of the molecules at the onset of the collisions may be more effective in different directions. For 2-atomic and stretching modes (symmetrical and asymmetrical) of linear polyatomic molecules this value is taken as 1/3 (Lambert 1977). For non-linear polyatomic molecules and bending modes of linear molecules the value is usually 2/3 (Lambert 1977). For methane which has 4 surface atoms the value depends on the vibrational jump (Tanczos 1956).

\[
P_0(i_a \rightarrow i_a) = 1, P_0(i_a \rightarrow i_a + 1) = \frac{2}{3}
\]
It is assumed that the orientation remains constant throughout the collision which is invalid for molecules with very low moments of inertia such as hydrogen and hydrides.

2.4.5. Collision Cross-Reference Factor

The collision cross reference factor, $P_c$ relates probabilities calculated for a cross section of $\pi r_c^2$ to the usual elastic cross section of kinetic theory, $\sigma$. Both factors will be discussed in a section Kinetic Theory. This factor is approximately

$$P_c = 1.364 \left(1 + \frac{C}{T}\right)^{-1} \left(\frac{r_c}{\sigma}\right)^2$$

Where $C$ is the Sutherland constant, $r_c$ is the distance between the centers of molecules at the point of closest approach, and $\sigma$ is the distance when the molecules have zero potential energy between each other.

2.4.6. Vibrational Factor

The vibrational factor, $V^2$, is the square of the matrix element for vibrational transition between two states of a molecule (Lambert 1977). It depends on the repulsion parameter $\alpha^*$ which will be discussed in the Kinetic Theory section as well as the frequency and amplitude, $\bar{A}^2$, of the molecule’s vibration. This factor can be represented by the following

$$\tilde{V}_{iafa}^2 = \left(i_a + \frac{1}{2} \pm \frac{1}{2}\right)\left(\frac{\alpha_{aa}^*\bar{A}^2\hbar}{2\omega_a}\right)$$

$$f_a = i_a$$

$$f_a = i_a \pm 1$$

For polyatomic molecules $\bar{A}^2$ must be obtained by performing a normal coordinate analysis of the molecules molecular vibrations (Wilson et al. 1955).
2.4.7. Translation Factor

The rest of Equation 2-23 is considered the translational factor. It gives expression to any change in kinetic energy involved in the inelastic collision. The parameters involved in this factor include the reduced mass, $\mu$, and the temperature $T$, which together determine the velocity of approach which will be discussed in the Kinetic Theory section. $\Delta E$, which is the amount of vibrational energy transferred during a collision evidenced by the vibrational modes $n_i$ involved in its calculation. The last portion of this factor is the repulsion parameter, $\alpha^*$ which was mentioned before and the exponential term with a value $\phi_0$. This value, $\phi_0$ is the attractive potential between two colliding molecules and is the point at which repulsive forces take over from attractive forces between the two molecules (Lambert 1977).

2.4.8. Kinetic Theory

At the heart of all of these other collisional attenuation theories lies the kinetic theory of collisions between inert gas molecules. There are several potential energy curves that help describe elastic collisions between molecules but the most famous and widely used is the intermolecular energy curve given by the Lennard-Jones equation (Lambert 1977). This curve can be seen in Figure 2-4 and is represented by the following equation:

$$V(r) = 4\phi_0 \left[ \frac{(\sigma/r)^{12}}{1} - \frac{(\sigma/r)^{6}}{1} \right]$$

\textbf{Equation 2-24}
Figure 2-4. Lennard Jones Potential

Where $V(r)$ represents the potential energy of two molecules at a distance $r$. The term that is raised to the $6^{th}$ power represents long range attractive forces. In the case of inert gases this is due to London dispersion forces. As the molecules begin approaching each other (moving to the left of the curve in Figure 2-4) there is a gentle decrease in $V(r)$. The first term that is raised to the $12^{th}$ power represents the short repulsive forces since at these distances there is an overlap of orbitals. At this point there is a much steeper rise in the potential energy as the distance between the molecules becomes smaller. $\phi_0$ is the “potential depth” and it is the minimum point in Figure 2-4 at which $F=0$ and thus repulsive forces become dominant over attractive forces. The zero potential point, $\sigma$ which has been seen in multiple equations including Equation 2-13 is also known as the “collision diameter”. In Figure 2-4 this is represented by the point at which the molecules have zero potential energy between each other. There are several other potential curves that give better approximations of specific collisions (non-spherical, polar molecules), however, inert gases and simple polyatomic molecules show fair approximations when
represented by the Lennard Jones potential. The potential depth and collision diameters for some molecules are listed in Table 2-3 along with their corresponding vibrational modes, degeneracy of those modes, and vibrational amplitude coefficients which are all used for the calculation of the transition probabilities (Equation 2-23).

<table>
<thead>
<tr>
<th>Gas</th>
<th>( \sigma , (\text{Å}) )</th>
<th>( \phi_0 , (\text{cal mol}^{-1}) )</th>
<th>Modes of Vibration ((\text{cm}^{-1}))</th>
<th>( g )</th>
<th>Vibrational Amplitude Coefficients ((\text{a.m.u.}^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>O(_2)</td>
<td>3.548</td>
<td>175</td>
<td>( \nu =1554 )</td>
<td>1</td>
<td>0.0625</td>
</tr>
<tr>
<td>N(_2)</td>
<td>3.546</td>
<td>159</td>
<td>( \nu =2331 )</td>
<td>1</td>
<td>0.0714</td>
</tr>
<tr>
<td>CH(_4)</td>
<td>3.759</td>
<td>286</td>
<td>( \nu_1 =2915 )</td>
<td>1</td>
<td>0.9921</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>( \nu_2 =1534 )</td>
<td>2</td>
<td>0.9921</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>( \nu_3 =3019 )</td>
<td>1</td>
<td>0.9923</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>( \nu_4 =1306 )</td>
<td>3</td>
<td>0.8368</td>
</tr>
<tr>
<td>H(_2)</td>
<td>2.761</td>
<td>75.5</td>
<td>( \nu =4160 )</td>
<td>1</td>
<td>1.0</td>
</tr>
<tr>
<td>CO(_2)</td>
<td>3.99</td>
<td>378</td>
<td>( \nu_1 =1333 )</td>
<td>1</td>
<td>0.05</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>( \nu_2 =667 )</td>
<td>2</td>
<td>0.05</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>( \nu_3 =2349 )</td>
<td>1</td>
<td>0.05</td>
</tr>
</tbody>
</table>

Table 2-3. Vibrational modes and parameters for Lennard Jones Potential (Herzberg 1966).

In Table 2-3 vibrational modes are numbered according to spectroscopic conventions. The frequencies are therefore also expressed in spectroscopic convention by listing them in terms of inverse wavelength. To get the frequencies in units of Hertz (Hz) one must multiply those values listed in Table 2-3 by the speed of light \( \left(3 \times 10^{10} \, \text{cm s}^{-1}\right)\).

2.4.9. Fitting an Exponential Potential to the Lennard Jones Potential

Some of the last terms that are necessary to solve for the transition probabilities (Equation 2-23) include \( \alpha^* \), the repulsion parameter, and \( r_c \), the classical turning point. A method was taken by Schwartz and Herzfeld (Schwartz and Herzfeld 1954) in their refinement of the
SSH theory. It requires an exponential potential be fit to the Lennard Jones Potential (Equation 2-24) since the assumption was made by LT that only the repulsive part of the LJ potential was steep enough to influence any energy transfer. They did this by using the following equation:

\[ V_{\text{exp}}(r) = (\phi_0 + E^*) \exp[\alpha^*(r_c - r)] - \phi_0 \]  

**Equation 2-25**

Where \( E^* \equiv \frac{\mu v_0^*}{2} \) and \( v_0^* \) is the transition favorable incident velocity. While all gases have a distribution of molecular speeds given by the Boltzmann equations and at different temperatures there is a speed \( v_0^* \) which gives the highest transition probability. This value can be found from Equation 2-23 in the definition of \( \xi \) and reorganizing some parameters to solve for \( v_0^* \) in terms of the repulsion parameter, \( \alpha^* \).

\[ v_0^* = \frac{2k_B T}{\mu} \left( \frac{\Delta E^2 \mu \pi^2}{2\alpha_{ab}^* \hbar k_B T} \right)^{\frac{1}{3}} \]  

**Equation 2-26**

As can be seen in Figure 2-5 the shifted exponential curve is matched at two distances \( r_c \) and \( \sigma \). At these two points \( V(\sigma) = V_{\text{exp}}(\sigma) = 0 \) and \( V(r_c) = V_{\text{exp}}(r_c) = E^* \).

Therefore this gives two equations and two unknowns, with the knowns being the classical
turning point and the repulsion parameter. The unknown values can be solved for by matching the potential functions iteratively. When considering different molecular collision pairs the potential depth $\phi_0$ and zero potential point $\sigma$ are solved for as follows.

$$\phi_{0ab} = (\phi_{0aa}\phi_{0bb}) \text{ and } \sigma_{ab} = \frac{\sigma_{aa} + \sigma_{bb}}{2} \text{ Equation 2-27}$$

Some values of $\alpha^*$ and $r_c$ are listed in Table 2-4. These were solved using the Matlab script for several different gases that can be found in section FindingRcAlpha function in the appendix.

<table>
<thead>
<tr>
<th>Pair</th>
<th>$\alpha^*(\text{Å}^{-1})$</th>
<th>$r_c (\text{Å})$</th>
</tr>
</thead>
<tbody>
<tr>
<td>N$_2$</td>
<td>5.093</td>
<td>2.941</td>
</tr>
<tr>
<td>H$_2$O</td>
<td>4.530</td>
<td>4.002</td>
</tr>
<tr>
<td>CH$_4$(v$_4$)</td>
<td>4.796</td>
<td>3.490</td>
</tr>
<tr>
<td>CH$_4$(v$_2$)</td>
<td>4.775</td>
<td>3.465</td>
</tr>
<tr>
<td>CH$_4$(v$_2$) and CH$_4$(v$_4$)</td>
<td>5.081</td>
<td>3.733</td>
</tr>
</tbody>
</table>

Table 2-4. Parameters for LJ and Exponential Potentials (Petculescu and Lueptow 2005)

2.5. Using Acoustic Dispersion theory to design ultrasonic speed of sound sensor

The literature shows the active need for a low cost speed of sound sensor that can relay fuel gas composition to a combustion system. Current technologies are either too expensive, require regular calibration, or are too slow as was discussed in section 2.2. Consequently, the acoustic sensor was investigated in order to design a sensor capable of detecting digester gas compositions that are typical of anaerobic digestion from waste water facilities. The literature suggests that acoustic methods have been used previously as was shown in Section 2.3. However, biogas mixtures have not been investigated and the attenuation theory that was introduced in Section 2.4 will be used to appropriately design an ultrasonic sensor that caters to
detecting digester gas compositions. Therefore, it was apparent that the theory needed to be modeled to take into account how this theory interacts with varying digester gas compositions.

The goal of this thesis is to investigate necessary parameters to run the model on digester gas compositions and then use the model to properly design a speed of sound sensor. To validate the overall approach and sensor performance, a field test at an actual waste water treatment plant will be conducted.
3. Approach

As was addressed in Chapter 2 a speed of sound sensor used acoustic properties to detect fuel compositions after it was decided that available technology was not up to the task due to cost barriers, slow response, and regular need for recalibration. An acoustic sensor offers a cost effective method to detect compositions of binary gas mixtures like digester gas. To accomplish the goal of constructing a speed of sound sensor that detected varying compositions of digester gas the acoustic theory was modeled to analyze how dispersion zones affected the speed of sound of digester gas mixtures and how much attenuation occurred. A fuel circuit was also constructed in order to simulate biogas compositions. A suitable microcontroller was selected in order to perform the necessary calculations to extract gas compositions from the speed of sound. Finally the speed of sound sensor was installed at the waste water host facility in Rancho Santa Margarita to verify the speed of sound sensor’s capabilities.

3.1. Task 1. Research transducers capable of detecting the speed of sound of typical digester gas mixtures by modeling their acoustic phenomena

Previous sections highlighted why it was important to consider how acoustic attenuation theory interacts with different gas compositions. In order to model the DL theory that was discussed in section DL Theory parameters necessary to model compositions of biogas were investigated. The model was implemented in MATLAB 2015 in order to be able to deduce attenuation curves and dispersion zones for multiple gas compositions. The m-file and all other necessary function scripts that were run to model the acoustic attenuation can be found in the
Appendix under section A.1. Once the model was run, it was used as a design variable in order to correctly select transducers that avoid both the acoustic dispersion zone and attenuation peaks of the modeled gas compositions.

3.2. Task 2. Design of a laboratory fuel control circuit to run waste water digester gas mixtures and test the sensor in a laboratory setting

A flow circuit was built to supply a consistent flow to the speed of sound sensor. The fuel control circuit would also allow a means to control simulated biogas mixtures. This was accomplished by installing a set of sonic orifices that were selected based on flowrates for different gas components. They were calibrated with the use of laminar flow elements (LFEs) to correlate pressures upstream of the sonic orifice to flowrates at the injection point of the speed of sound sensor. Three separate lines were installed in order to control biogas blends and allow for fuel switching detection with a propane line.

3.3. Task 3. Select a capable microcontroller for speed of sound sensor

Several sensors were needed in order to design a speed of sound sensor that was both portable and had the capability to log measurements. Some of the sensors that were needed included a temperature sensor due to the speed of sound’s dependence on temperature, the ultrasonic transducer to detect changes in speed of sound, and pressure to monitor the pressure of the sensor. One choice that provides an easy to use development board is the Arduino® which operates at low voltages and can take either analog or digital signals. Several pins would be
required to read into the Arduino and thus an Arduino Mega ® was purchased. Additionally results from the attenuation and dispersion curves were used in order to purchase a transducer that would operate best in mixtures of biogas.

To prepare the sensor for its real world implementation, digester gas was simulated using compositions ranging from 30%/70% CO₂/CH₄ to 55%/45% CO₂/CH₄ by volume. This range is based on typical digester gas compositions seen in varying digester gas producing facilities (Baukal 2013). Additionally, propane gas will be introduced into the sensor to detect a change in fuel.

3.4. Task 4. Perform real world tests at a waste water facility that produces digester gas (i.e. Rancho Santa Margarita – RSM)

Finally, in order to quantify the sensors capability the sensor was installed in a real world setting using a host waste water facility located in Rancho Santa Margarita. The sensor was installed upstream of the Capstone micro turbines installed at the facility due to the extensive fuel treatment train that the turbines have installed upstream. The speed of sound sensor was tested twice at this facility after initial results indicated a design change was required. This would also help assess the capability of the sensor for future real world installations.
4. Experimental Development and Setup

4.1. Sensor Setup

The speed of sound sensor went through several iterations based on feasibility and performance. These iterations were mainly based on real world testing results and the need to enclose more sensors. The different versions that were made will be covered in the following subsections.

4.2. Version 1.0

The first iteration of the sensor began with a 150 kHz transducer that was supplied by Migtaron (RPS 426A-80) and was constructed for PIER contract 500-10-048. The sensor was housed in an aluminum chassis with ½ inch for the inlet and outlet ports (see Figure 4-1). A type-K thermocouple was installed downstream of the sensor on the outlet side for temperature compensation. The Migatron ultrasonic transducer was position on one end of the aluminum frame. The outputs from the transducer and the temperature were read into a FieldPoint 1000 data acquisition (DAQ) board. The readings from this (DAQ) board fed directly into a computer and were deciphered by LabVIEW software.
The Migatron transducer was capable of detecting distances anywhere in the range of 4” to 40” in air. The sensor outputs a voltage corresponding to the distance it senses. Since the sensor is calibrated to detect distances in air a correction must be applied. The procedure is as follows:

1. The sensor reads the distance from the end of the chamber to the face of the transducer. This distance is then logged and recorded.
2. Knowing how far away the end of the chamber is from the face of the transducer a new gas mixture may be introduced. The sensor then outputs a new voltage since the speed of sound will vary based on the gas that is input into the chamber. The corresponding distances according to gas mixture can be seen in Figure 4-2.
3. A new distance will be measured but the sensor will continue to think it is still reading air. So knowing the temperature and the speed of sound of air at that temperature a correction can be applied in order to solve for the speed of sound of the new gas mixture. This is done by first solving for the time the wave travels by using the following equation which also uses the new measured distance.

\[ t = \frac{c_{\text{air}}}{2d_{\text{gas}}} \]  

**Equation 4-1**

4. Knowing this new time the speed of sound of the new gas can be solved for by using the distance measured in pure air and the time found from the previous equation by solving for the following:

\[ c_{\text{gas}} = \frac{2d_{\text{air}}}{t} \]  

**Equation 4-2**

The sensor was readily capable of reading simulated natural gas compositions of methane and propane. It correlated the speed of sound of gas mixtures to heating value properties as was done by Beck et. al. However, when the sensor was tested on simulated biogas mixtures the sensors output would immediately flat line in biogas mixtures with concentrations higher than 15%. Therefore, further research was conducted to help understand why this phenomena was occurring with the 150 kHz transducer sensor.

### 4.3 Version 2.0

After taking a closer look at the literature the overall consensus was that acoustic attenuation was taking place in the 150 kHz sensor as was discussed in the Attenuation Theory Section. This required finding attenuation curves for the biogas compositions as can be seen in Figure 4-3.
4.3.1 Version 2.0 Periphery Equipment

Looking at Figure 4-3 it became immediately evident that at 150 kHz, which is the center operating frequency of the Migatron sensor, the peak of biogas mixtures between 30-50% CO₂ was encountered. As the concentration of CO₂ grew the intensity of the ultrasonic wave was diminished further. Therefore an ultrasonic distance sensor needed to be purchased in order to avoid these high attenuation peaks. Additionally, the sensor needed to avoid the dispersion curve in order to avoid referencing a speed of sound which was off by a few m/s. Figure 4-4 displays a normalized value of the speed of sound of the gases as a function of frequency. The speed of sound is normalized by the ideal speed of sound if there were no dispersion occurring. As can be
seen for biogas mixtures between 30-50% CO₂ a change of 2% in the speed of sound is seen at frequencies of 1 MHz. Therefore a transducer was chosen that avoided this dispersion of the speed of sound and also avoided the attenuation peaks of biogas mixtures.

![Dispersion curves for biogas mixtures](image)

**Figure 4-4.** Dispersion curves for biogas mixtures

Taking into account this acoustic phenomena a 40 kHz PING ultrasonic distance sensor from Parallax Inc. ® was purchased (See Figure 4-5). It could also be integrated very easily with the Arduino Mega board. It only required a 5V power source and it had a bidirectional transistor to transistor logic (TTL) pin that also output a high 5V pulse based on the duration of an emitted ultrasonic wave. This means that the sensor would output a 5V pulse to the distance sensor initiating an ultrasonic pulse and when the pulse returned to the sensor a 5V pulse would be sent back to the Arduino.
A new chassis was also constructed out of PVC piping due to its easy machinability and poor acoustic properties meaning if an ultrasonic wave hit the sides of the frame it would be absorbed. Therefore a steel reflective surface was installed at the opposing end of the sensor.

An exploded view of version 2.0 can be seen in Figure 4-6. Along with the speed of sound sensor a thermistor was also installed in order to accommodate for changes in temperatures in the gas mixture. This was done by installing a 10K resistor in parallel with the resistor and using a set of interpolation laws that provide the temperature the thermistors read. A ½” electrical wiring feedthrough was also installed to feed signal wires from the PING))). sensor and the thermistor to the Arduino. A 3d printed enclosure was fabricated to slide over one of sensors plugs to secure all of the electronics in an aesthetically pleasing package.
An LCD (2.8” TFT Touch Shield V2.0) display supplied by Seeed Studio was included in order to show in real-time what the sensor was outputting. This LCD display also had an onboard SD card slot in order to actively log measurements made by the speed of sound sensor. The SD component of the LCD display communicated with the Arduino via 4 pin Serial Periphery Interface (SPI) communication. This type of communication is in sync with the Arduino’s generated clock signal in order to receive or transmit data. The Arduino’s clock which is an oscillating signal that is driven between high and low voltage clock signals indicates to the periphery components on either a falling or rising clock signal to communicate. The sensors incorporated in this design communicate on the rising edge and are equipped with MISO (Master in slave out) and MOSI (Master out slave in) pins in order to both receive information from the Arduino when the clock pin signals a high voltage. Additionally a slave select pin is also incorporated in order to choose between several different components operating on SPI communication. This pin is held low in order to activate periphery components. Along with the
SD card a RTC (real time clock) (DS324) module was also equipped which operated with SPI communication to keep track of time that had elapsed during the sensor’s operation.

With the exception of the RTC module all periphery electronics operated at 5V. A total of 1.9 watts is needed to power the Arduino when taking into account the current draw and voltage needed for each electronic component in the sensor. Since the sensor runs off a 12V source with a maximum of 500 mA available the Arduino was able to handle such a power requirement. A schematic of all of the electronics along with their power requirement is listed in Figure 4-7.

![Schematic of electronics](image)

**Figure 4-7. V2.0 Electronics**

### 4.4 Version 3.0

The results which will be discussed in Version 2.0 CWRP Results prompted a new design change. The factors that lead to a design change included mounting issues with the PING)))) ultrasonic distance sensor that resulted in erroneous readings that were coming from received
acoustic pulses at varying angles. This lead to the purchase of a new sensor with mounting features that did not allow room for much movement.

4.4.1. Version 3.0 Periphery Equipment

The ultrasonic distance sensor that was purchased to replace the PING))) sensor was a MB7380 Ultrasonic Distance Sensor from Maxbotix® Inc. The benefit here over the PING))) sensor was that the MB7380 sensor offered better precision than the PING))) sensor with the .2” (5 mm) resolution readings. The drawback was that the sensor could only read over 11.8” (30 cm), otherwise anything below that would be measured by the sensor as 11.8”. This was avoided by designing the chassis to be longer than 12 inches so that biogas mixtures that were expected to result in shorter distances read by the MB7380 would still be read. The MB7380 along with a type-K thermocouple were installed into the aluminum chassis that was originally constructed for the 150 kHz transducer. The assembly can be seen in Figure 4-8.

A new temperature sensing device was also implemented since the thermistor, while inexpensive, really was not as precise as the thermocouple that was installed for version 2.0 of
the sensor. The thermocouple’s electronics that were needed to be read into the Arduino can be seen in Figure 4-9. The thermocouple amplifier (Max 6675) needed to amplify the thermocouple signal was supplied by adafruit. It had a two pin terminal block to connect the leads of the thermocouple and a 3 pin SPI configuration. Since the Arduino does not need to provide information back to the thermocouple only three pins are necessary here as opposed to the 4 pin configurations needed for the SD card and the RTC. The amplifier could be supplied by a 5 V source.

The MB7380 can also be seen in Figure 4-9. The MB7380 only needed one I/O just like the previous PING))) ultrasonic distance sensor. It output a PWM signal proportional to the distance that it measured. This number was read into the Arduino as millimeters. Figure 4-9 also displays the power requirements for each of the electronic components of version 3.0 of the speed of sound sensor. Immediately it is evident that the power requirements for the MB7380 and the Max6675 are less than each component’s counterpart in version 2.0. The total power requirement for this version of the sensor was 1.52 Watts which is again easily met by the 12V 500 amp source provided by the Arduino.

![V3.0 Electronics](image)

**Figure 4-9. V3.0 Electronics**
4.5 Acoustic Attenuation Measurements

In an effort to validate the results from the attenuation and to potentially use it for gas composition detection the acoustic attenuation of biogas mixtures were tested. This attenuation was tested using the 40 kHz PING))) transducers (see Figure 4-5) that were used in version 2.0 of the speed of sound sensor along with 49.5 kHz electrostatic transducers that were supplied by SensComp (see Figure 4-10). This provided an array of transducers that could help map out the attenuation over a range of frequencies for different biogas mixtures. The measurements were taken by first knowing the voltage pulse that was sent by the transmitting transducer which was measured at the leads of the transducer. The reduced voltage signal was then measured at the receiving transducer either at the leads or after the op-amp that it fed into if the return voltage signals were unknown. This required measuring the gain on the op amps for each transducer.

![Figure 4-10. SensComp 49.4 kHz transducer](image)

4.5.1 SensComp Acoustic Attenuation Measurements

The electronics equipped on the SensComp smart sensor can be seen in Figure 4-11. The red box indicated as 1 is the output of the first op amp for the receiving transducer. A wire was soldered to this junction to be monitored by an oscilloscope. The red box indicated as 2 in
Figure 4-11 is the wired to the transmitting side of the transducer and was also monitored once to see the voltage output of the electrostatic transducer. Finally the last box, box 3, is the receiving lead of the transducer which could be monitored however sometimes voltages received at this lead were too small to detect so voltages monitored at box 1 were logged.

![SensComp Electronic Schematic](image)

**Figure 4-11. SensComp Electronic Schematic**

The SensComp was installed in the chassis from Version 2.0 and the transducer for this sensor was held in place by a 3-D printed mount. The sensor was installed at one end of the chassis and a single transducer was used to monitor voltage changes for different gases. The PkPk voltages were used for both the transmitting and receiving voltage signals to monitor attenuation. This voltages were used since the voltage directly translated to a certain pressure of the ultrasonic wave. The oscilloscope that was used for both attenuation measurements was a Yokogawa DL7100 oscilloscope (seen in Figure 4-12).
4.5.2 PING))) Acoustic Attenuation Measurements

The voltages that were monitored from the PING))) transducers were also monitored at the corresponding leads on the PING))) ultrasonic transducer. These leads can be found in Figure 4-13. The leads of the transducer labeled 1 and 2 for the transmitter and receiver respectively were monitored to measure the change in PkPk voltage signals. If receiving signals were too low the receiving signals coming out of the Texas Instrument Op-Amp TLC274C labeled 3 in Figure 4-13 was measured by soldering a wire to this output.
The 40 kHz transducers were each removed from the printed circuit board and fixed in 3-D printed mounts. The two transducers were then installed facing each other in the version 2 chassis as seen in Figure 4-14.
4.5.3 AirMar Attenuation Measuring Equipment

In an effort to more fully map out the attenuation over a spectrum of frequencies a 200 kHz transducer (ATK 200) from AirMar was purchased (see Figure 4-15). This particular transducer operates off of piezoelectric properties by emitting voltage signals based on deforming of the transducer. Alternatively, if a voltage signal is applied across the transducer it can deform. Therefore a transmitter has a voltage send across it in order to pulse an ultrasonic wave and a receiver receives the pulse and emits a voltage.

![AirMar ATK200 200 kHz Piezoelectric Transducer](image)

**Figure 4-15. AirMar ATK200 200 kHz Piezoelectric Transducer**

In this case a pitch and catch setup was arranged seen in Figure 4-16. This setup consisted of 1” SS tubing and the transducers were installed at the ends of 1” T’s with a Swagelok nuts and ferrules in order to provide a good seal. The Yokogawa previously mentioned in 4.5.1 was also used in this configuration. One of the transducers was equipped with a T1 module from Airmar in order to produce the ultrasonic wave. The receiving transducer’s leads were equipped straight onto the Yokogowa oscilloscope. Since the receiving voltages were extremely low an assortment of 1” SS tubes were made that were tested in order to be able to deduce a receiving voltage without auxiliary electronic equipment such as an Op-Amp. Therefore shorter SS tubes were used for gas mixtures that attenuated an ultrasonic pulse the most.
4.6 Fuel Supply

The fuel supply was designed to be a set of sonic orifices in order to supply a steady stream of fuel to the speed of sound sensor. Simulated biogas could be made based on volumetric flow of each component of gas from each sonic orifice. Very low flowrates were selected for this test in order to prevent frosting of CO₂ and CH₄ that occur at higher flowrates. Since usual biogas mixtures range anywhere between 25%/75% CO₂/CH₄ to 50%/50% CO₂/CH₄ the sonic orifices that were selected were able to provide these gas mixtures. The sonic orifice configuration can be seen in Figure 4-17. Each pressure gauge could be set up to a pressure of 100 PSI. The sonic orifices were calibrated using a laminar flow element (LFE) to find the correlation between the flowrate at the point of injection into the sensor and the pressure set on the pressure gauges seen in Figure 4-17. There were three separate circuits to supply CO₂, CH₄, and C₃H₈ and they all recombined downstream of the sonic orifices. The CO₂ was supplied by a 99% pure CO₂ pressurized tank set at 120 PSI. The CH₄ was supplied by either a natural gas line or a 99% pure CH₄ pressurized tank set to 120 PSI or delivered by the natural gas line at 120 PSI as well. When the natural gas was used it was assumed to be 100% CH₄. The C₃H₈ was supplied into the lab via a C₃H₈ fuel line that was pressurized by a manifold with C₃H₈ pressure tanks set to 180 PSI.
Each component used for each gas was the same except for the size of the piping upstream of the pressure gauges. The CO$_2$ which was supplied by a pressurized tank had a pressure gauge attached to it to set the pressure delivered to the fuel manifold. The exit of the regulator had a $\frac{1}{4}''$ to $\frac{1}{2}''$ adapter to connect to upstream of the CO$_2$ through $\frac{1}{2}''$ Teflon tubing, which connected to $\frac{1}{2}''$ stainless steel tubing and was finally connected to the entrance of the CO$_2$ regulator on the fuel manifold. The CH$_4$ was either supplied by $\frac{1}{2}''$ stainless steel tubing through a natural gas line or the same sort of configuration as the CO$_2$ tank except with a CH$_4$ tank. The C$_3$H$_8$ line entered into the lab through $\frac{1}{2}''$ steel tubing. This was then connected to a $\frac{1}{4}''$ adapter which was then lead into the entrance of the pressure gauge for C$_3$H$_8$ on the fuel manifold. The two sets of rows were connected into a junction that met with the corresponding column regulator in the manifold through a valve (see Figure 4-17). Therefore, to prevent any
one pressure gauge from causing back pressure on its corresponding column gauge, each sonic orifice was connected on a different column from each other.

4.7 System Layout

The sensor with the Arduino Mega to control all of the electronics was approximately 20’ downstream from the fuel manifold. The fuel readings were either read from the LCD screen or the serial monitor when the sensor was connected to a laptop. The system layout for this equipment can be seen in Figure 4-18.

![Figure 4-18. System Layout](image-url)
4.8 System Layout

4.8.1 Laboratory Experimental Approach

The sensor was first filled with air in order to calibrate the distance between the end of the chamber and the face of the transducer. The sensor then begins logging speeds of sound that correspond to CO₂ and CH₄ ratios. The pressures on the regulators were set according to flowrates that gave a certain mixture and the sensor was given time to both read the newly introduced gas mixture and stabilize. Once the sensor readings had stabilized to what was expected for a few readings the mixture would be changed and the process would repeat. When testing for fuel switching between biogas and propane both of the valves for the CO₂ and CH₄ were shut off and the propane manifold was opened. The sensor would also know when this occurred and take the last biogas mixture and moving forward would calculate ratios of the biogas mixture it logged right before the switch and propane.

4.8.2 CWRP Installation Experimental Approach

Once the speed of sound sensor was designed, built, and verified for stability in the lab the sensor was taken to the CWRP facility to be installed and monitor the varying biogas composition. The installation point for the speed of sound sensor on CWRP’s fuel line was strategically selected to provide accurate results and provide enough of a safety assurance for any concerns CWRP’s safety officers might have. The location of the installation was right outside of the boiler room near the gas treatment train (see Figure 4-19) that is upstream of a set of Capstone micro turbines installed at the facility. Just upstream of the sensor a pressure gauge was installed that brought down the fuel pressure line which was up around 25-30 PSI for the micro turbines down to a moderate 10-15 PSI for the speed of sound sensor. The first installation of the speed of sound sensor occurred for the period of November to early January. That installation
can be seen in Figure 4-20. The second speed of sound sensor installation occurred in mid-July and that can be seen in Figure 4-21. The results for each of these installations can be found in the Results section.

Figure 4-19. Gas Treatment Train at CWRP Facility

Figure 4-20. First Installation of speed of sound sensor at CWRP
Figure 4-21. 2nd installation of speed of sound sensor at CWRP
5. Results

Before the sensor was ever installed at the plant the sensor was first designed and tested in the lab. Once the sensor showed that it was capable of detecting biogas mixtures in the lab the sensor was installed at the CWRP plant for the first time. Preliminary tests at the waste water facility occurred from November to January and the results were mixed. Some day’s it would vary between a few percent and other days it would change drastically from day to night with a nearly 20% change in CO₂! On the days when these drastic compositions were read there were also occurrences of mixed readings that were of no value since the sensor would just jump between several values. Therefore, the sensor was brought back to the lab, modified, rebuilt, and tested in order to make sure the sensor provided reliable results. Both sets of data and all of the lab data will be discussed in the sections that follow.

5.1 Version 2.0 Results

Version 1.0 Results are not presented since the measured values for biogas mixtures did not return a signal. This was due to the large attenuation that was suffered in biogas mixtures at for a 150 kHz ultrasonic pulse. There could have been a returned signal but the onboard electronics could have been registering the returned reduced signals as noise since the sensor is designed for air it is not used to expecting such small returning signals.

5.1.1 Version 2.0 Lab Results

After discovering that the 150 kHz transducer was incapable of detecting distances in biogas mixtures the speed of sound sensor was redesigned with a whole new ultrasonic distance sensor. As was already mentioned in section Version 2.0 the attenuation of the curves and dispersion curves were taken into account in order to find an ultrasonic distance sensor that
worked well for biogas mixtures. Looking deeper (see Figure 5-1) into the attenuation from both sensor configurations one can see that the attenuation for the 42 kHz transducer was even lower than the 150 kHz transducer except for pure CO₂.

![Attenuation for Biogas as a function of %CH4](image)

**Figure 5-1. Attenuation as a function of biogas composition for different transducer frequencies**

Therefore testing of the sensor proceeded by first filling the sensor with air. The sensor would then detect the distance between the face of the transducer and the end of the chamber. This distance would be logged and the ultrasonic distance sensor would proceed to detect how long an ultrasonic wave traveled in biogas mixtures to detect biogas compositions. Some of the preliminary lab results can be found in the Figure 5-2 - Figure 5-5.
Figure 5-2. 20-25% CO2 by volume

Figure 5-3. 40-45% CO2 by volume
Figure 5-4. 20-55% CO2 by volume

Figure 5-5. 55-20% CO2 by volume
When first looking at the results produced by the speed of sound sensor it was immediately evident that some reoccurring trends occur. First of all, the sensor was more capable of detecting lower percentages of CO2. This may simply be due to the faster speed of sound at these lower gas mixtures and the PING))) sensor’s better capability at these lower “apparent” distances. This can be explained further by Figure 5-6. This figure shows good agreement with CO2 values between 25%-40% with larger deviations seen at higher concentrations of CO2 starting at 45%. Additionally the sensor was constructed with one port for easy installation at the waste water facility. Therefore readings were a little slower than a speed of sound sensor that would have an inlet and exit due to the diffusion of different mixtures needed a settling time before. The effect it has on the sensor’s response time can be seen in Figure 5-4 and Figure 5-5. Figure 5-4 shows a large change in composition took the sensor approximately 100 seconds to differentiate. Figure 5-5 which shows the reverse change in composition took nearly ten times as long to settle off at to a steady reading. However this was seen as satisfactory since the facility only logged CO2 compositions once every 3 months so a nearly 20 minute settling time for such a drastic change in composition would be sufficient. The other factors, the larger errors in for certain biogas readings would also be ignored for the time being since the range of 25-45% was within acceptable error and was the most often read composition for the waste water facility.

Analyzing the results even further from this version of the speed of sound sensor shows that measured versus actual readings correlate pretty well. These two data variables can be seen plotted against one another in Figure 5-6. The data points are plotted and a trend line is formed with an intercept set at zero to show that each data point should line up well. As mentioned before the readings that line up best with this trend line are those that are within 25-45% CO2 which is the expected biogas composition range.
5.1.2 Version 2.0 CWRP Results

Moving forward with the sensors’ progress the sensor was installed at CWRP as was mention in section CWRP Installation Experimental Approach. The first installation took place right before thanksgiving weekend and continued on until the first week of January. A handful of days were selected from the tests taken at the facility and are presented in Figure 5-7 – Figure 5-12. Some of the November readings showed results that were very intriguing including Nov. 27th (Figure 5-7) which resulted in a drop of CO₂ concentration at approximately 7 PM. This was an interesting find since operators at CWRP indicated the biogas quality to never soar far below 40% CO₂. This was also the case seen on November 29th (Figure 5-8), December 3rd (Figure 5-9), and many other days not shown in the figures listed here which showed the fuel quality hovering around 40-45% CO₂. While this information was useful and interesting to us the

Figure 5-6. Linear Trend Line of Actual and Measured SOS at different compositions
speed of sound sensor seemed to fluctuate a lot and the information taken from January 16\textsuperscript{th} proved to be the most erroneous. On this day the speed of sound sensor swung anywhere from 25\% to 50\% CO\textsubscript{2} with no real indication of a steady value. The speed of sound sensor was returned to the lab and further testing revealed that the measurements taken would rely to the positioning of the transducer relative to the opposing reflective surface. Therefore we decided to purchase a new transducer which could be mounted easier and would be parallel to the opposing surface at all times.

![Graph](image)

Figure 5-7. Nov. 27-Nov. 28 CO\textsubscript{2}\% by volume measurements
Figure 5-8. Nov. 29-Nov. 30 CO₂% by volume measurements

Figure 5-9. Dec. 3 – Dec. 4 CO₂% by volume measurements
Figure 5-10. Dec. 24 – Dec. 25 CO₂% by volume measurements

Figure 5-11. Jan. 8 – Jan. 9 CO₂% by volume measurements
Figure 5-12. Jan. 16 – Jan. 17 CO$_2$% by volume measurements

5.2 Version 3.0 Results

In order to help decipher what was making the sensor produce such inaccurate results like those seen in Figure 5-12 the speed of sound sensor was brought back into the lab and what we discovered was the sensor with a tapered cap provided inaccurate results depending on the orientation of the transducers to the opposing wall. This was due to the inability to mount the speed of sound sensor completely parallel to the opposing steel reflective surface. Therefore, a new transducer was purchased from Maxbotix range finders (MB7380) with better mounting features. The temperature sensor was also upgraded from a thermistor to a thermocouple for more accurate temperature measurements.
5.2.1 Version 3.0 Lab Results

The lab results for this newest version of the sensor can be seen in Figure 5-13. The immediate differences between what is measured in this sensor as opposed to the previous version of the speed of sound sensor is the sensor’s improved readings at higher CO₂ concentrations. While it does fluctuate a little more at these higher CO₂ concentrations it is still a large improvement over the previous iteration which would swing across a span of 10% for higher CO₂ volume concentrations. This speed of sound sensor at the expected CO₂ percentage in biogas of 45% only fluctuates approximately 3%. Moreover, this plot displays the error that is taken into account for the error in the gas concentrations and the sonic orifice calibrations. Therefore this fluctuation could in effect be a lot smaller. Figure 5-14 also shows pressure readings of the speed of sound sensor as the CO₂ volume concentration increases. This is due to the closed volume being exposed to a higher volumetric flow and thus a slight increase in pressure in the speed of sound sensor chamber. This slight increase in pressure chamber may have well have been the cause of V2.0’s fidgety response at these higher concentrations which may have been moving the PING))) transducer. Therefore, the speed of sound sensor proceeded with these promising results and the sensor was once again installed at the CWRP facility.
Figure 5-13. CO2 Percentage versus Time for Version 3.0 Speed of Sound Sensor

Figure 5-14. CO2 Readings for Version 3.0 Speed of Sound sensor with pressure readings
5.2.2 CWRP Version 3.0 Results

After verification of the upgraded sensor’s robustness and accuracy the sensor was installed at CWRP to test for sensitivity to real world tests. The sensor was reinstalled at the CWRP facility for the first two weeks of July 2015. Figure 5-15 through Figure 5-18 show some of the results produced from this second installation at the facility.

Figure 5-15. July 1 – July 2 CO₂% by volume measurements
Figure 5-16. July 3 – July 4 CO₂% by volume measurements

Figure 5-17. July 8 – July 9 CO₂% by volume measurements
These results proved that while the sensor was still a little noisy the sensitivity was an improvement from the previous iteration of the sensor. This small fluctuation of the noise could also be attributed to the low number of values that the sensor filters out. The filter implemented is a mode filter so it will take 20 readings and take the mode value as the actual reading. Filtering with a bigger sample size may help ease the noise. The sensor was updated after this one last time in order to try and accommodate an additional CO$_2$ NDIR sensor. The NDIR sensor however was never implemented after it was unable to distinguish CO$_2$ in CH$_4$. However the results showed that this new housing provided even better results than the previous version just discussed.
5.3 Version 4.0 Results

As was just mentioned the sensor was upgraded one last time and this model of the sensor was only tested in a laboratory setting. The results will be presented below.

5.3.1 Version 4.0 Lab Results

Looking at the laboratory results (Figure 5-19) for this sensor showed that the sensor was within 1% of experimental error. This was a significant improvement over previous iterations and was decided as being the final version of the sensor. Additionally the sensor was tested with a fuel switch between biogas (40% CO2/ 60% CH₄) and propane (C₃H₈) and the results are shown in Figure 5-20. It is evident that for biogas mixtures the measured results are within 1% error of calibration errors. Additionally the change of fuel between a 40% CO₂/ 60 % CH₄ mixture to full propane can immediately detect a change and begin to steady out after approximately a minute.

![CO₂% Versus Time](image)

*Figure 5-19. Laboratory results for Version 4.0*
5.3.2 Version 4.0 Cost

The overall cost of speed of sound sensor was taken into account as a way to compare it against some state of the art composition detecting sensors. The cost of the speed of sound sensor along with a bulk of its necessary auxiliary electronics are included in Table 5-1. It can be seen that at a total cost of approximately 400 dollars it decidedly is a frontrunner for fuel composition devices since state of the art composition detection devices such as gas chromatography, calorimeters, or non-dispersive infrared can cost thousands of dollars. (Docquier and Candel 2002) Therefore, the affordability and relatively good measurements results prove the speed of sound sensor can be deployed for control of combustion systems.

Figure 5-20. Ternary gas (Biogas – C3H8) mixture results
### Table 5-1. Total Cost for Version 4.0 of Speed of Sound Sensor

<table>
<thead>
<tr>
<th>Parts</th>
<th>#</th>
<th>Unit Price [$USD]</th>
<th>Total [$USD]</th>
</tr>
</thead>
<tbody>
<tr>
<td>MB 7380 42 kHz Ultrasonic Distance Sensor</td>
<td>1</td>
<td>109.95</td>
<td>109.95</td>
</tr>
<tr>
<td>Weld-On Fittings for Curved Tanks</td>
<td>2</td>
<td>9.52</td>
<td>19.04</td>
</tr>
<tr>
<td>Type K Thermocouple</td>
<td>1</td>
<td>28.00</td>
<td>28.00</td>
</tr>
<tr>
<td>16 GB SD Card</td>
<td>1</td>
<td>9.99</td>
<td>9.99</td>
</tr>
<tr>
<td>Arduino Mega</td>
<td>1</td>
<td>45.95</td>
<td>45.95</td>
</tr>
<tr>
<td>TFT Touch Shield</td>
<td>1</td>
<td>44.99</td>
<td>44.99</td>
</tr>
<tr>
<td>Steel Tank</td>
<td>1</td>
<td>150.00</td>
<td>150.00</td>
</tr>
<tr>
<td><strong>Total</strong></td>
<td></td>
<td></td>
<td><strong>407.92</strong></td>
</tr>
</tbody>
</table>

5.4 Attenuation Results

As was mentioned in the experimental approach the attenuation was also measured to test the validity of the attenuation model. These results were monitored with a Yokogawa DL 7100 oscilloscope. The transducers used in these tests are listed in Table 5-2 along with some of their operating parameters.

### Table 5-2. Different Transducers used along with operating parameters

<table>
<thead>
<tr>
<th>Transducer</th>
<th>Frequency [Hz]</th>
<th>PkPK Signal [V]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ping Parallax</td>
<td>40,000</td>
<td>8.5</td>
</tr>
<tr>
<td>SensComp</td>
<td>49,400</td>
<td>2</td>
</tr>
<tr>
<td>Airmar ATK 200</td>
<td>200,000</td>
<td>69</td>
</tr>
</tbody>
</table>
Some of the results can be seen in Figure 5-21-Figure 5-25. These measurements were then used to calculate the attenuation in these gas mixtures. As can be seen by the measurements the return echoes can sometimes be numerous. Therefore the echo that was in line with what was expected knowing the distance and speed of sound of the gas mixture is what was used for the calculation of the attenuation. It is easy to see why so much electronic signal processing is required for these sensors due to surround objects causing multiple echoes to be detected. Additionally lower voltage signals which are measurable in this case due to the availability of the oscilloscope would be ignored by the onboard electronics.

Figure 5-21. 42.5% CO₂ 57.5% CH₄ Oscilloscope measurement
Figure 5-22. 100% CH\textsubscript{4} 40 kHz Oscilloscope measurement

Figure 5-23. 100% CH\textsubscript{4} 49.4 kHz Oscilloscope measurement
Figure 5-24. 57.5% CH₄ 200 kHz Oscilloscope measurement at 16.2 cm

Figure 5-25. 100% CH₄ 200 kHz Oscilloscope measurement at 15.3 cm
In order to account for any diffraction that may occur in the ultrasonic wave a correction was applied to the Beer-Lambert Law (See. This correction is known as Pinkerton’s method. (Pinkerton 1948)

\[ V = V_0 e^{-\alpha z} \left\{ \sin \left[ \frac{1}{2} k \left( z^2 + R^2 \right)^{\frac{1}{2}} - z \right] \right\} \]  

Equation 5-1

Where \( V_0 \) is the voltage for the emitter, \( k=2\frac{\pi}{\lambda} \), the wave number, \( z \) is the distance between the emitter and the receiver, and \( R \) is the radius of the transducer (Pinkerton 1948).

Therefore the only unknown in the equation is the attenuation coefficient which can be normalized by the wavelength, \( \lambda \) of the gas. Using this correction and the measurements displayed in the Yokogawa oscilloscope provided the results seen in Figure 5-26. The tabulated results can be seen in Table 5-3.

<table>
<thead>
<tr>
<th>Gas</th>
<th>Frequency (Hz)</th>
<th>( \alpha ) measured</th>
<th>( \alpha ) predicted</th>
</tr>
</thead>
<tbody>
<tr>
<td>100% CH4</td>
<td>40,000</td>
<td>0.014355681</td>
<td>0.0102</td>
</tr>
<tr>
<td></td>
<td>49,400</td>
<td>0.013355273</td>
<td>0.0102</td>
</tr>
<tr>
<td></td>
<td>200,000</td>
<td>0.03208105</td>
<td>0.0282</td>
</tr>
<tr>
<td>100% CO2</td>
<td>40,000</td>
<td>0.08132633</td>
<td>0.1073</td>
</tr>
<tr>
<td></td>
<td>200,000</td>
<td>0.047102566</td>
<td>0.0414</td>
</tr>
<tr>
<td>57.5% CH4</td>
<td>40,000</td>
<td>0.019570084</td>
<td>0.0245</td>
</tr>
<tr>
<td></td>
<td>49,400</td>
<td>0.053777186</td>
<td>0.0526</td>
</tr>
<tr>
<td></td>
<td>200,000</td>
<td>0.05448015</td>
<td>0.0584</td>
</tr>
</tbody>
</table>

Table 5-3. Attenuation Results for different frequency transducers

As can be seen there were no results for pure CO\(_2\) when using the 49.4 kHz transducer as there was no return signal that was observed on the oscilloscope display. Another key point is some of the predicted measurements for lower frequency transducers are quite a ways off from the measured results. This was attributed to the low PkPk voltages created by the transducers which would in turn create low intensity echo pulses. The results for 200 kHz however prove to show the best measured results of the three. This was due to large PkPk voltages that could be created.
across the AirMar piezoelectric transducers and thus larger pressure pulses. The error from these measurements were all within 10% error. Despite the results being ways off from predicted measurements at lower frequencies they trend in the correct direction. As CO\textsubscript{2} concentration increases so does the attenuation measured. Therefore if low frequency transducers that are capable of inducing larger voltages are available for future tests they would be great in helping verify the model developed. If results like those measured for the 200 kHz transducers can be implemented at lower frequencies it could ultimately be used as a third equation in deducing ternary gas mixture compositions. This could be done by adjusting the pressure of the chamber since it is easier to adjust the f/P term seen in Figure 5-26 than to change the frequency of a transducer. This could be done by constructing a vessel capable of withstanding larger pressures.

![Graph showing attenuation results for different gas mixtures for 40, 49.4, & 200 kHz](image)

*Figure 5-26. Attenuation results for different gas mixtures for 40, 49.4, & 200 kHz*
5.5 Application: Speed of Sound Sensor in Boiler Setting

As was mentioned previously in section 0, the end goal of an overall project funded by the CEC will result in this sensor being used to increase the performance of a boiler operating on anaerobic digester gas (ADG) with propane as a backup fuel using a low swirl injector. The boiler to be used for demonstration of dynamic fuel switching of anaerobic digester gas and propane gas is a 3 MMBtu/hr Johnston 4 pass fire tube Boiler installed at the Rancho Santa Margarita Chiquita Water Reclamation Plant (see Figure 5-27) which operates at 2 MMBtu/hr to meet its permit’s emissions standards. Despite its slow response to change in heat demand this type of boiler, a fire tube boiler, is the most common fire tube boiler found in today’s plants due to its compactness, ease of maintenance, and low initial cost (Woodruff et al. 1998).

![Figure 5-27. Johnston 4 Pass Fire Tube Boiler](image)

The boiler currently comes equipped with devices on separate fuel trains to switch between ADG and propane. The problem that it currently has is that it runs off temperature
measurements for operability of the boiler and in order to switch between ADG and propane gas the system requires a 2 minute purging cycle that wears the system over time due to cyclic ramps between fuels. The ADG fuel line can be seen in Figure 5-28. The system currently sets a temperature measurement which it tries to reach by adjusting the fuel to air ratio set by a micro ratio valve. When it reaches that temperature it tries to stay at that point and if it momentarily jumps over the temperature setting the fuel delivery completely shuts off through its two block shutoff series valves. Since this puts stress not only on the boiler but also the motors in the shutoff valves a better suited control of the boiler would be through the use of a speed of sound sensor that updated the boiler on gas composition. This way it would be tuned by controlling fuel flow through a mass flow controller and air flow would be adjusted by a variable frequency drive (VFD) to keep temperatures low.

Figure 5-28. ADG Fuel Train at RSM CWRP
The proposed fuel train change in order to make the mentioned adjustments can be seen in Figure 5-29. Here the speed of sound sensor would be installed upstream of the flow controller. Other additions would be a mass flow controller for control of the fuel flow rate, a VFD controlled blower to maintain specific equivalence ratios, and a lambda sensor to check that set equivalence ratios are matched. This proposed fuel train adjustment also includes changes to certain equipment in order to readily match needed operating conditions to create a homogenous mixture of fuel and air into the boiler system. This type of control could easily be met by using just the lambda sensor and adjusting the VFD controlling the blower to run so that the lambda sensor reads 3% excess oxygen during operation which is typical of boilers. This type of control has been implemented previously on a gas turbine (Docquier et al. 2001) but the problem that arises in this situation is how the fuel composition changes. Therefore while the VFD could be driven to meet a certain equivalence ratio the uncertainty in fuel composition makes this an improvement over typical lambda sensors which are set for a certain fuel. Therefore updating the lambda sensor on fuel composition would give the overall system a better idea of what operating point it is at.
Figure 5-29. Proposed ADG fuel train change
6. Summary and Conclusions

6.1 Summary

The goal of this thesis was to develop and construct a speed of sound sensor capable of distinguishing varying compositions of digester gas from waste water facilities. The speed of sound sensor ended up using ultrasonic measurements due to its ability to deliver accurate results at a low cost. In comparison to available technology it is also quicker and does not require a regular calibration. Previous research using this method for gas composition detection had focused on several different gas compositions but an investigation into digester gas mixtures had not been done. Therefore this thesis. Therefore, there was an examination of ultrasonic phenomena that occurs in digester gas mixtures to properly assemble a speed of sound sensor capable of reading gas compositions.

Using this information a model was developed in Matlab that provided insight into how ultrasonic phenomena such as ultrasonic dispersion and acoustic attenuation affected digester gas mixtures over a range of frequencies. The model used several parameters that were available in the literature for the major components of digester gas, CO₂ and CH₄. This model provided two separate results that displayed how acoustic phenomena changed as the frequency of an ultrasonic pulse changed in different digester gas compositions. The first results displayed the dispersion zone for different digester gas compositions which showed a frequency range in which the speed of sound of digester gas compositions changed. This zone was avoided when designing the speed of sound sensor in order to deduce a speed of sound that matched what was calculated from an ideal equation. The second results displayed how the intensity of an ultrasonic pulse changed as a function of frequency due to molecular collisions of gas particles. This
attenuation spectrum for a gas usually has a certain peak in a frequency range which was also avoided due to the diminishing of an ultrasonic pulse’s intensity in that region.

A transducer was then selected and housed in a rugged PVC housing. This design was then tested in the laboratory were a flow panel was designed to deliver several digester gas compositions that resembled those that would be expected at a waste water facility. When testing the speed of sound sensor at the Rancho Santa Margarita waste water facility it was found that the results had a significant amount of noise and this may have been due to the high pressures in the gas turbine line that caused the transducer to move and thus read erroneous speeds of sound. It was then discovered that a transducer that could be mounted in a more stable manner would be a needed improvement. Therefore a new transducer was purchased and housed in an aluminum chassis and this provided better results.

Finally it was decided that acoustic attenuation could be detected to try and decipher digester gas compositions from this measurement and this was done by utilizing an oscilloscope. While lower frequency results didn’t exactly match the results from the attenuation model they trended in the expected manner and can be investigated in future research. The 200 kHz measurements provided the best results and could help pave a way to constructing a speed of sound sensor that could potentially deduce compositions of ternary gas mixtures since the attenuation would essentially provide a third equation for a “three unknown” set of equations.

6.2 Conclusion

This section summarizes conclusions drawn from the modeled attenuation physics which guided the design of the optimal speed of sound sensor and the takeaways from the attenuation measurements which were later used to help verify the model.
The acoustic attenuation model provided a way to optimize the speed of sound sensor design. Previously a 150 kHz transducer was used, and biogas compositions resulted in the speed of sound sensor incapable of detecting changes in composition due to the large amount of attenuation that occurs in biogas mixtures. Therefore, once the model was made it was verified that the 40 kHz transducer that was purchased avoided the attenuation that was suffered by the larger frequency transducer due to the capability of measuring the speed of sound with these lower frequency transducers. Additionally the onboard electronics on the transducer could have been in an issue disregarding the low voltage echo pulses since generally the transducers were designed for air and would not suffer such large attenuation of the ultrasonic pulses.

A transducer was selected that operated in the range of digester gas compositions expected from waste water facilities but extra caution needed to be considered in the mounting of the transducer. It was discovered that the parallel orientation of the surface of the transducer with the opposing reflective surface needed to be maintained. Once this discovery was made the speed of sound sensor was redesigned with a 42 kHz transducer that could be mounted and maintain its orientation with the opposing surface.

Early acoustic attenuation measurements show that it is a promising direction in gas detection. While the lower frequency transducer acoustic attenuation measurements presented in this thesis do not exactly line up with what is predicted by the physical model they do trend in the right direction and the fault here may lie in the fact that these transducers are not sensitive enough to changes in composition. The higher frequency measurements however, are all within 10% error and using these transducers in a suitable
housing chamber could help map out the attenuation curve. These provided better results due to the larger ultrasonic pulses emitted by the transducers.

- **A small amount of error can be distinguished between the gas composition that is being simulated by the flow panel and what is read by the speed of sound sensor.** This small amount of error can be attributed to a variety of factors which include the calibration of the sonic orifices which control the flow of separate gases into the speed of sound sensor, the purity of these gases, and the fact that the transducer itself has a certain amount of error with its readings. When taking into account all of these errors the actual measurement is actually not far off from what is being flown through the sensor and therefore is sufficient for the application it is being built for. The total error between what was measured and taking into account calibration errors was within 1% error.

- **The speed of sound sensor can respond to changes in gas composition over a few seconds which is a significant improvement with what was currently being implemented by the RSM waste water facility.** This improvement could ultimately not only be used to optimize boiler performance but also to potentially monitor overall plant performance such as the production of more digester gas.

- **The speed of sound sensor while rugged in design provides measurable composition changes at a fraction of competitive available technology.** The speed of sound sensor was produced for approximately $500 which is a large reduction in price when compared to commercially available gas composition detecting devices.

### 6.3 Recommendations

In an effort to improve upon results and cost of the speed of sound sensor the following recommendations should be considered.
• In an effort to make precise measurements of the speed of sound a transducer could be purchased and equipped with the proper signal processing electronics to deduce speeds of sound in the tested gas mixtures. Currently an ultrasonic distance sensor was used due to its ease of use but a transducer without onboard circuitry could provide better results and potentially reduce the overall cost of the speed of sound sensor as well.

• The acoustic attenuation model could also be tested with different model input parameters as was done in (Petculescu and Lueptow 2005). This could be required since there are several different model parameters listed for different gases that could affect the model results.

• Costs could also be reduced by considering producing a microcontroller out of bare essential electronics. An Arduino was selected due to the feasibility of integration into this project but one could easily be made out of an embedded microcontroller with necessary auxiliary electronics such as resistors and capacitors. Additionally if these products are bought in bulk the speed of sound sensor could be produced at a fraction of the cost was produced in this Master’s thesis.

• A closer investigation into the attenuation measurement procedure could help provide a key measurement into deducing gas compositions from ternary gas mixtures. This could be done by using either two transducers that operate at different frequencies to help produce an attenuation curve and from it predict the corresponding gas mixture. Alternatively the same could be done by producing a sensor that could withstand higher pressures and change the pressure with one transducer to produce the attenuation curve of the measured gas mixture. This inclusion of the attenuation as a measurement would
also require the speed of sound sensor to be insulated since the attenuation is also a function of temperature.

- Another viable opportunity for the speed of sound sensor could also be in the production of syngas (CO/H₂). Since syngas is also predominantly a binary gas mixture the speed of sound sensor could be used to close the loop on the production of syngas in order to fine tune any upstream steps made in the production of syngas.
7. Bibliography


Nostrand Reinhold Company.


A. Appendix

A.1 Matlab code for attenuation model

This model works by changing the composition of the gases through the alpha terms. If there are multiple vibrational modes that will be active for a gas component then there will be repeat alpha variables. For example carbon dioxide has a lowest vibrational mode of 667 cm$^{-1}$ but its vibrational mode of 1388 cm$^{-1}$ will also be activated since it is resonant with methane’s lowest vibrational mode of 1306 cm$^{-1}$. Also if pure gas mixtures’ attenuation need to be calculated the indexTau vector needs to be updated in order to take into account which relaxation times for certain collisions will be calculated. Another vector is also included indexVT which takes into account that only the lowest vibrational mode of each gas component will be used when calculating the vibrational-translational relaxation time of collisions. Additionally, properties taken from refprop must be explicitly defined in the refpropm command by defining which gas components are called and the temperature and pressure at which the attenuation model will be created. Collisional parameters must all be referenced correctly in a separate excel sheet in order to find collisional parameters like the repulsion parameter and the critical turning point correctly. External functions that are called include FindingRcAlpha, vibtranprob, vibvibprob, and C.

FindingRcAlpha is used to find the critical turning point and the repulsion parameter. This function requires global variables listed in the main script. Additionally variables passed through to this function are called out through a separate excel sheet that holds certain collision parameters. The function vibtranprob calculates the probability of vibrational translational energy exchanges occurring, and vibvibprob calculates the probability of vibrational-vibrational
energy exchanges occurring. The function C calls to a function that has Sutherland constants for
gas components interacting in collisions. These values were calculated using refprop in a certain
temperature range for each gas component.

Finally two graphs are generated when this model executes correctly. The first is the
dispersion curve for the gas mixture in question over a desired frequency range. The frequency
range can be adjusted by changing the function ezplot’s second input range. The second plot that
is produced is the attenuation curve for the gas mixture. Again the frequency range can be
adjusted by changing the second input in ezplot function for this plot. Alternatively plots could
be generated for changes in attenuation or dispersion curves by setting a certain frequency by
uncommenting the fourth line and setting a loop for concentration changes. The ezplot function
would then have to be changed to the plot function with the concentration range as the x variable
and the dispersion and attenuation as the y variable.

clc
clear all
global Na k_B h red_h T_0 P_0 tweak
%%Calculation of relaxation of CH4-CO2 Gas Mixture
%f = 40000;
tweak = .9983;
% Mixture Fractions
% 1 - CH4 - 1306
% 2 - CH4 - 1534
% 3 - CO2 - 667
% 4 - CO2 - 1333
alpha(1,1)=0.5;
alpha(2,1)=0.5;
alpha(3,1)=0.5;
alpha(4,1)=0.5;
indexVT=[1; 0; 1; 0];
indexTau=[1; 1; 1; 1];

%% Gas Properties - From RefProp
T_0=297.15; %[K]
P_0=101.325; %[kPa]
%Density and Cv and molar mass of Mixture Components at 20C and 101.325 kPa
%Density [kg/m3]
%Specific Heat [J/kg-k]
%Molar Mass [kg/kmol - g/mol]
[rho_N2,cv_N2,cp_N2,MWN2] = refpropm('DOCM','T',T_0,'P',P_0,'nitrogen');
\[
\begin{align*}
[rho_{H2O}, cv_{H2O}, cp_{H2O}, MWH2O] &= \text{refpropm('DOCM', 'T', 373.15, 'P', 101.325, 'water');} \\
[rho_{CH4}, cv_{CH4}, cp_{CH4}, MWCH4] &= \text{refpropm('DOCM', 'T', T_0, 'P', P_0, 'methane');} \\
[rho_{CO2}, cv_{CO2}, cp_{CO2}, MWCO2] &= \text{refpropm('DOCM', 'T', T_0, 'P', P_0, 'CO2');}
\end{align*}
\]

% Molecular Weight of the Mixture and density of Mixture
MWmix=MWCH4*alpha(1,1)+MWCO2*alpha(3,1);
% Mass Fraction
% mfN2=alpha(1,1)*MWN2/MWmix;
% mfH2O=alpha(2,1)*MWH2O/MWmix;
mfCH4=alpha(1,1)*MWCH4/MWmix;
mfCO2=alpha(3,1)*MWCO2/MWmix;
% Density and isochoric specific heat of gas mixture
rho2=[rho_{CH4}/MWCH4*1000;rho_{CH4}/MWCH4*1000;rho_{CO2}/MWCO2*1000;rho_{CO2}/MWCO2*1000];
rho_0=rho_{CH4}*alpha(1,1)+rho_{CO2}*alpha(3,1);
cv=(mfCH4*cv_{CH4}+mfCO2*cv_{CO2});
cp=(mfCH4*cp_{CH4}+mfCO2*cp_{CO2});

%% Constants
h=6.626*10^{-34}; % [J-s]
red_h=1.0546*10^{-34}; % [J-s]
k_B=1.3807*10^{-23}; % [J/K]
R=8.314; % [J/mol-K] [m3-Pa k-1 mol-1] [m2-kg s-2 k-1 mol-1]
u=1.6605390402*10^{-27}; % [kg/amu] [amu-g/mol-kg/kmol]
Na=6.022*10^{23}; % [atom/mol]
P_0=P_0*1000; % [Pa]

%% Vibrational Frequencies Hz
vib(1,1)=xlsread('Collisional Parameters Biogas.xlsx','Sheet1','H9');
vib(2,1)=xlsread('Collisional Parameters Biogas.xlsx','Sheet1','H7');
vib(3,1)=xlsread('Collisional Parameters Biogas.xlsx','Sheet1','H11');
vib(4,1)=xlsread('Collisional Parameters Biogas.xlsx','Sheet1','H10');

%% Degeneracy of vibrational modes
deg(1,1)=xlsread('Collisional Parameters Biogas.xlsx','Sheet1','D9');
deg(2,1)=xlsread('Collisional Parameters Biogas.xlsx','Sheet1','D7');
deg(3,1)=xlsread('Collisional Parameters Biogas.xlsx','Sheet1','D11');
deg(4,1)=xlsread('Collisional Parameters Biogas.xlsx','Sheet1','D10');

%% Zero Point Potential Values [Angstrom] % One possible change is zero point potential of H2O
sigma(1,1)=xlsread('Collisional Parameters Biogas.xlsx','Sheet1','B48')*10^{-10};
sigma(2,1)=xlsread('Collisional Parameters Biogas.xlsx','Sheet1','B49')*10^{-10};
sigma(3,1)=xlsread('Collisional Parameters Biogas.xlsx','Sheet1','B50')*10^{-10};
sigma(4,1)=xlsread('Collisional Parameters Biogas.xlsx','Sheet1','B51')*10^{-10};

%% Vibrational amplitude coefficients [a.m.u.^{-1}]
vibampcoeff1=xlsread('Collisional Parameters Biogas.xlsx','Sheet1','E9')/u;
vibampcoeff2=xlsread('Collisional Parameters Biogas.xlsx','Sheet1','E7')/u;
vibampcoeff3 = xlsread('Collisional Parameters Biogas.xlsx', 'Sheet1', 'E11')/u;
vibampcoeff4 = xlsread('Collisional Parameters Biogas.xlsx', 'Sheet1', 'E10')/u;

% Well Depth Values [Actually eps/kb [K]]
epsilon(1,1) = xlsread('Collisional Parameters Biogas.xlsx', 'Sheet1', 'C48');
epsilon(2,1) = xlsread('Collisional Parameters Biogas.xlsx', 'Sheet1', 'C49');
epsilon(3,1) = xlsread('Collisional Parameters Biogas.xlsx', 'Sheet1', 'C50');
epsilon(4,1) = xlsread('Collisional Parameters Biogas.xlsx', 'Sheet1', 'C51');

%% Steric Factors
% Need to Consider Tanczos Point for V-T Collisions P=1 For CH4
SF(1,1) = xlsread('Collisional Parameters Biogas.xlsx', 'Sheet1', 'F9');
SF(2,1) = xlsread('Collisional Parameters Biogas.xlsx', 'Sheet1', 'F7');
SF(3,1) = xlsread('Collisional Parameters Biogas.xlsx', 'Sheet1', 'F11');
SF(4,1) = xlsread('Collisional Parameters Biogas.xlsx', 'Sheet1', 'F10');

%% AMU
AMU = [MWCH4; MWCH4; MWCO2; MWCO2];

%% Well Depth Values of unlike colliding molecules
for i = 1:length(SF)
    for j = 1:length(SF)
        % Reduced Masses of Unlike Molecules
        reducedM(i,j) = AMU(i)*AMU(j)/(AMU(i)+AMU(j))*u;
        eps(i,j) = sqrt(epsilon(i)*epsilon(j));
        sigma_all(i,j) = 1/2*(sigma(i)+sigma(j));
        if i == 3 || i == 4
            eps(i,j) = sqrt(epsilon(i)*epsilon(j));
            if j == 3 || j == 4
                eps(i,j) = 1.00569256452592*sqrt(epsilon(i)*epsilon(j));
            end
        end
    end
end

%CALCULATING Energy Exchanges
% When i==j energy exchange is only between vibrational DOF of like
% molecules. Anytime else the difference between interacting energies is
% taken into account.
for i = 1:length(SF)
    for j = 1:length(SF)
        % Need this before the if statements otherwise overwrites if
        % statements
        DelE(i,j) = red_h*2*pi*(vib(i,1)-vib(j,1));
        if i == j && j == 1
            DelE(1,1) = red_h*2*pi*vib(1,1);
        end
        if i == j && j == 2
            DelE(2,2) = red_h*2*pi*vib(2,1);
        end
        if i == j && j == 3
            DelE(3,3) = red_h*2*pi*vib(3,1);
        end
        if i == j && j == 4
            DelE(4,4) = red_h*2*pi*vib(4,1);
        end
    end
end
% Classical turning point [Angstrom]
% Difference between the two is how the potential values are set equal to at
% the critical turning point either Kbt or Kbt*Factor
[r_c,astar]=FindingRcAlpha(vib,reducedM,eps,sigma_all,DelE);
% Previously found these manually until making the external matlab function
% above - now finds values based on method discussed in Lueptow Paper

%% Vibrational Factors for like collisions
V(1,1)=astar(1,1)^2*vibampcoeff1*red_h/(4*pi*vib(1,1));
V(2,1)=astar(2,2)^2*vibampcoeff2*red_h/(4*pi*vib(2,1));
V(3,1)=astar(3,3)^2*vibampcoeff3*red_h/(4*pi*vib(3,1));
V(4,1)=astar(4,4)^2*vibampcoeff4*red_h/(4*pi*vib(4,1));

%% Zeta and cross sectional factor for V-T Transitional Probabilities
for i=1:length(astar)
    for j=1:length(astar)
        if i==1
            Zeta(i,j)=((DelE(1,1)^2)*reducedM(i,j)*(pi^2)/(2*(astar(i,j)^2)*(red_h^2)*k_B*T_0))^(1/3);
        end
        if i==2
            Zeta(i,j)=((DelE(2,2)^2)*reducedM(i,j)*(pi^2)/(2*(astar(i,j)^2)*(red_h^2)*k_B*T_0))^(1/3);
        end
        if i==3
            Zeta(i,j)=((DelE(3,3)^2)*reducedM(i,j)*(pi^2)/(2*(astar(i,j)^2)*(red_h^2)*k_B*T_0))^(1/3);
        end
        if i==4
            Zeta(i,j)=((DelE(4,4)^2)*reducedM(i,j)*(pi^2)/(2*(astar(i,j)^2)*(red_h^2)*k_B*T_0))^(1/3);
        end
        P_c(i,j)=1.364*((1+C(i)/T_0)^-1)*(r_c(i,j)/sigma_all(i,j))^2;
    end
end

%% Calculation of Probability - Translational - Vibrational Collisional
% Exchange of Molecules in Gas Mixture
[PVT]=VibTranProb(SF,P_c,Zeta,V,reducedM,astar,eps,DelE, vib);

%% Finding collision rates
for i=1:length(astar)
    for j=1:length(astar)
        % Andi model gives same mol/vol for vib collisions
        Nk1(i,j)=Na*rho2(j);
        Nk2(i,1)=Na*rho2(i);
        Z1(i,j)=2*Nk1(i,j)*(sigma_all(i,j)^2)*sqrt(2*pi*k_B*T_0/reducedM(i,j));
Z2(i,j)=4*Nk1(i,j)*(sigma_all(i,i)^2)*sqrt(pi*k_B*T_0/(AMU(i)*u));

end

%% Inverse Relaxation Time for vi-tran interactions
for i=1:length(astar)
    for j=1:length(astar)
        tau_tran(i,j)=indexTau(j)*Z2(i,j)*PVT(i,j)*(1-exp(-red_h*2*pi*vib(i)/(k_B*T_0)));
    end
end

%% Zeta and cross sectional factor for v-v collisions
for i=1:length(astar)
    for j=1:length(astar)
        zeta(i,j)=((DelE(i,j)^2)*reducedM(i,j)*(pi^2)/(2*(astar(i,j)^2)*(red_h^2)*k_B*T_0))^(1/3);
    end
end

%% Calculation of Probability - of Vibrational - Vibrational Collisional Exchange of Molecules in Gas Mixture
[PVV]=VibVibProb(SF,P_c,zeta,V,reducedM,astar,eps,DelE,vib);

%% Inverse Relaxation Time for vib-vib interactions
for i=1:length(astar)
    for j=1:length(astar)
        tau_vib(i,j)=alpha(j,1)*Z1(i,j)*PVV(i,j)*(1-exp(-red_h*2*pi*vib(i)/(k_B*T_0)))*indexTau(j);
    end
end

%% Vibrational Specific heats for vibrational modes
theta_vib=zeros(length(vib),1);
c_i_vib=zeros(length(vib),1);
for i = 1:length(vib)
    theta_vib(i,1)=h*vib(i,1)/k_B;
    if i==1
        c_i_vib(i,1)=deg(i,1)*R*((theta_vib(i,1)/T_0)^2)*exp(-theta_vib(i,1)/T_0)/(1-exp(-theta_vib(i,1)/T_0))^2;
    end
    if i==2
        c_i_vib(i,1)=deg(i,1)*R*((theta_vib(i,1)/T_0)^2)*exp(-theta_vib(i,1)/T_0)/(1-exp(-theta_vib(i,1)/T_0))^2;
    end
    if i==3
        c_i_vib(i,1)=deg(i,1)*R*((theta_vib(i,1)/T_0)^2)*exp(-theta_vib(i,1)/T_0)/(1-exp(-theta_vib(i,1)/T_0))^2;
    end
    if i==4
        c_i_vib(i,1)=deg(i,1)*R*((theta_vib(i,1)/T_0)^2)*exp(-theta_vib(i,1)/T_0)/(1-exp(-theta_vib(i,1)/T_0))^2;
    end
end
%% Calculating Relaxation System Components
q=zeros(length(tau_tran),1);
A=zeros(length(tau_tran),length(tau_tran));

%% Calculating V-T and V-V relaxation times needed to solve Temperature Vector solution
for i = 1:length(vib)
    for j = 1:length(vib)
        feff(i,j) = 0;
        switch abs(sign(i-j))
            case 0
                for k=1:length(vib)
                    feff(i,j) = feff(i,j) + alpha(k)*tau_tran(i,k)*indexVT(k);
                end
            case 1
                feff(i,j) = tau_vib(i,j);
        end
    end
end

%% Relaxation matrix:
A = [];
for i = 1:length(vib)
    for j = 1:length(vib)
        A(i,j) = 0;
        switch abs(sign(i-j))
            case 0
                for k=1:length(vib)
                    A(i,j) = A(i,j) + feff(i,k)*((1-exp(-h*vib(i,1)/(k_B*T_0)))/(1-exp(-h*vib(k,1)/(k_B*T_0))));
                end
            case 1
                A(i,j) = -feff(i,j)*((1-exp(-h*vib(i,1)/(k_B*T_0)))/(1-exp(-h*vib(j,1)/(k_B*T_0))))*vib(j)/vib(i);
        end
    end
end

%% q vector of Relaxation Matrix
for i = 1:length(vib)
    q(i) = feff(i,i);
    for j = 1:length(vib)
        q(i) = q(i) + feff(i,j)*(1-vib(j)/vib(i))*((1-exp(-h*vib(i,1)/(k_B*T_0)))/(1-exp(-h*vib(j,1)/(k_B*T_0))));
    end
end

clear i % reserve "i" for imaginary.
%% Symbolic Symbols
syms f
Aomega = A+2*pi*f*eye(length(alpha))*sqrt(-1);
gammal = Aomega\q;
up = cv*MWmix/1000;
down = cp*MWmix/1000;

for i=1:length(alpha)
    up = up + alpha(i)*c_i_vib(i,1)*(gamma1(i)-1);
    down = down + alpha(i)*c_i_vib(i,1)*(gamma1(i)-1);
end

%ksquare=(2*pi*f)^2*(density/P)*up/down;    % ORIGINAL
c2mix0 = R*1000*T_0*(cp/cv)/(MWmix);    % static SOS^2
c2mix = R*1000*T_0*(down/up)/(MWmix);    % SOS of mixture
ksquare=(2*pi*f)^2./c2mix;    % Using SOS from ideal-gas equ of state of mixture --> gives right values for SOS.

re=real(ksquare);
im=imag(ksquare);
speed=(2*pi*f)*2^0.5./sqrt(re+sqrt(re.^2+im.^2));    % i.e. c=w/Re(k)
alphal=sqrt((sqrt(re.^2+im.^2)-re)/2);    % i.e. alpha=Im(k)
ALP= alphal*speed/f;    % SEE ANDI'S NOTES pg. 54

A.1.1 FindingRcAlpha function

function[r_c,astar]=FindingRcAlpha(vib,reducedM,eps,sigma_all,DelE)
global k_B red_h T_0 P_0

%Changing eps to J
eps=eps*k_B;

% Calculating Rc and Alpha
for a=1:length(vib)
    for b=1:length(vib)
        for i=1:5000;
            if i==1
                rc(i,1)=6; %Angstrom WAS 4
            end
    end
end
else
    rc(i,1)=rc(i-1)-.001;
end

%Repulsion Parameter in units of m
alpha_s(i,1)=(((DelE(a,b)^2)*reducedM(a,b)*(pi^2)/(2*(red_h^2)*k_B*T_0))^.5) *((k_B*T_0)^1.5)/((4*eps(a,b)*((sigma_all(a,b)/(rc(i,1)*(10^-10))))^12- (sigma_all(a,b)/(rc(i,1)*(10^-10))))^6))^.5));

Estar(i,1)=(((DelE(a,b)^2)*reducedM(a,b)*(pi^2)/(2*(alpha_s(i,1)^2)*(red_h^2)*k_B*T_0))^(1/3))*k_B*T_0;

Vexp(i,1)=((eps(a,b)+Estar(i,1))*exp(alpha_s(i,1)*((rc(i,1)*(10^-10))-sigma_all(a,b))))-eps(a,b);

if i>1
    if Vexp(i-1,1)<0 && Vexp(i,1)>0 && isreal(Vexp(i-1,1)) == 1
        astar(a,b)=alpha_s(i,1);
        r_c(a,b)=rc(i,1)*10^(-10);
    end
    end
end
end

A.1.2 VibTranProb Function

function [PVT]=VibTranProb(SF, P_c, Zeta, V, reducedM, astar, eps, DelE, vib)

global h red_h k_B T_0 tweak
%%V-T Probability Equations Derived from Tanczos simplification of the transition probability equations
%% Calculation of PVT for all collisions this takes into account that a PVT % Collision cannot occur between a molecule a similar molecule
for i=1:length(astar)
    for j=1:length(astar)
        if i==1
            PVT(i,j)=SF(i,1)*SF(j,1)*P_c(i,j)*V(i,1)*8*sqrt(pi/3)*((2*pi*reducedM(i,j)*DelE(i,1)/(astar(i,j)^2)*red_h^2))^(2)*sqrt(Zeta(i,j))*exp(-3*Zeta(i,j)+DelE(i,1)/(2*k_B*T_0)+eps(i,j)/T_0);
        end
        if i==2
            PVT(i,j)=SF(i,1)*SF(j,1)*P_c(i,j)*V(i,1)*8*sqrt(pi/3)*((2*pi*reducedM(i,j)*DelE(i,2)/(astar(i,j)^2)*red_h^2))^(2)*sqrt(Zeta(i,j))*exp(-3*Zeta(i,j)+DelE(i,2)/(2*k_B*T_0)+eps(i,j)/T_0);
        end
        if i==3
            PVT(i,j)=SF(i,1)*SF(j,1)*P_c(i,j)*V(i,1)*8*sqrt(pi/3)*((2*pi*reducedM(i,j)*DelE(i,3)/(astar(i,j)^2)*red_h^2))^(2)*sqrt(Zeta(i,j))*exp(-3*Zeta(i,j)+DelE(i,3)/(2*k_B*T_0)+eps(i,j)/T_0);
        end
    end
end
\[
1E(i, 3)/((astar(i, j)^2)*(red_h^2))^2)*sqrt(Zeta(i, j)) \times \exp(-3*Zeta(i, j)+DelE(i, 3)/(2*k_B*T_0)+eps(i, j)/T_0);
\]

\[
\text{if } j>= 3
\]

\[
t_1=-(tweak+0.5)/(tweak-0.5)*1/k_B./T_0*(gamma(tweak+0.5)/gamma(tweak)*sqrt(2*pi*reducedM(i, j))/astar(i, j)*abs(DelE(i, 3))*k_B.*T_0*2*pi/h).^(1/(tweak+0.5));
\]

\[
t_2=DelE(i, 3)/(2*k_B.*T_0);
\]

\[
PVT(i, j)=SF(i, 1)*SF(j, 1)*P_c(i, j)*V(i, 1)*8*sqrt(pi/3)*((2*pi*reducedM(i, j)*DelE(i, 3)/((astar(i, j)^2)*(red_h^2)))^2)*sqrt(Zeta(i, j))*exp(t1+t2);
\]

\[
\text{end}
\]

\[
\text{end}
\]

\[
\text{if } i==4
\]

\[
PVT(i, j)=SF(i, 1)*SF(j, 1)*P_c(i, j)*V(i, 1)*8*sqrt(pi/3)*((2*pi*reducedM(i, j)*DelE(i, 4)/((astar(i, j)^2)*(red_h^2)))^2)*sqrt(Zeta(i, j))*exp(-3*Zeta(i, j)+DelE(i, 4)/(2*k_B*T_0)+eps(i, j)/T_0);
\]

\[
\text{if } j>= 3
\]

\[
t_1=-(tweak+0.5)/(tweak-0.5)*1/k_B./T_0*(gamma(tweak+0.5)/gamma(tweak)*sqrt(2*pi*reducedM(i, j))/astar(i, j)*abs(DelE(i, 4))*k_B.*T_0*2*pi/h).^(1/(tweak+0.5));
\]

\[
t_2=DelE(i, 4)/(2*k_B.*T_0);
\]

\[
PVT(i, j)=SF(i, 1)*SF(j, 1)*P_c(i, j)*V(i, 1)*8*sqrt(pi/3)*((2*pi*reducedM(i, j)*DelE(i, 4)/((astar(i, j)^2)*(red_h^2)))^2)*sqrt(Zeta(i, j))*exp(t1+t2);
\]

\[
\text{end}
\]

\[
\text{end}
\]

\[
A.1.3 \text{ VibVibProb Function}
\]

\[
\text{function}\ [PVV]=\text{VibVibProb}(SF, P_c, Zeta, V, reducedM, astar, eps, DelE, vib)
\]

\[
\text{global } h \ red_h \ k_B \ T_0 \ tweak
\]

\[
\% \ V-V \ Probability
\]

\[
\text{for } i=1:length(astar)
\]

\[
\text{for } j=1:length(astar)
\]

\[
\text{if } i==j
\]

\[
PVV(i, j)=0; \% \ This \ type \ of \ vib \ probability \ does \ not \ occur
\]

\[
\text{end}
\]

\[
\text{if } i~j
\]

\[
PVV(i, j)=SF(i, 1)*SF(j, 1)*P_c(i, j)*V(i, 1)*V(j, 1)*8*sqrt(pi/3)*((2*pi*reducedM(i, j)*DelE(i, j)/((astar(i, j)^2)*(red_h^2)))^2)*sqrt(Zeta(i, j))*exp(-3*Zeta(i, j)+DelE(i, j)/(2*k_B*T_0)+eps(i, j)/T_0);
\]

\[
\text{if } abs((vib(i, 1)-vib(j, 1))/(3*10^10))<50
\]

\[
PVV(i, j)=SF(i, 1)*SF(j, 1)*V(i, 1)*V(j, 1)*64*(pi^2)*reducedM(i, j)*k_B*T_0/((astar(i, j)^2)*(h^2))*exp(eps(i, j)/T_0);
\]

\[
\text{end}
\]

\[
\text{end}
\]

\[
102
\]
if \ j \geq 3 \\
    t1=-(tweak+0.5)/(tweak-0.5)*1/k_B./T_0* \gamma(tweak+0.5)/\gamma(tweak)*(2*pi*reducedM(i,j))/astar(i,j)*abs(DelE(i,j))*k_B.*T_0*2*pi/h).^(1/(tweak+0.5)); \\
    t2=DelE(i,j)./(2*k_B.*T_0); \\
    PVV(i,j)=SF(i)*SF(j)*P_c(i,j)*V(i,1)*V(j,1)*8*sqrt(pi/3)*((2*pi*reducedM(i,j)*DelE(i,j)/((astar(i,j)^2)*(red_h^2)))^2)*sqrt(Zeta(i,j))*exp(t1+t2); 
end 
end 
end 
end

C Function

% Found sutherland constants using refprop in temperature range of 290K to 300K for each gas component 
function S=C(n1) 
switch n1 
    case 1 %CH4 (1306 cm^{-1}) 
        S=175; 
    case 2 %CH4 (1534 cm^{-1}) 
        S=175; 
    case 3 %CO2 (667 cm^{-1}) 
        S=240; 
    case 4 %CO2 (1388 cm^{-1}) 
        S=240; 
end

A.2 Arduino code for speed of sound sensor

This code is run to calculate the change in speed of sound and relate it to a corresponding gas mixture. The first block of code is a comment showing the iterations of the code with changes in electrical equipment. There are certain libraries that must be included to the computer uploading this code to an Arduino. These include the TFTv2.h, SPI.h, SD.h, and max6675.h. The TFT file header is necessary to be able to call file types which are used to display graphics on the Seeedstudio touch screen. The SPI header is required to the SPI communications that are run by the thermocouple amplifier and the SD card on the touch screen. Finally the SD and max6675
header files are required for other SD functions and to be able to successfully read values from
the max6675 thermocouple amplifier.

The code is input with an array of specific heat values over a temperature range to be able to
deduce specific heats for active gas components at certain measured temperatures. Additionally
an array of CO₂ fractions is input so that a for loop can check measured speed of sound values
with this array of fractions in order to check which fraction comes closest to the measured value.
External functions at the end of the code are used to speed up the run time of the code. These
include drawscreen(), isort(), and mode(). The drawscreen() file is called to draw updated
measured values on the TFT screen. The isort() and mode() functions are used to sort out
measured time of flight values and pick the mode out of these values. The number of values
picked for this function can be changed by changing the second input of the isort() and mode()
values to control sample size of measured time of flight values.

/*
   Gas Sensor Code v5.1
   v1.0
distance detected - co2 percentage was determined after with matlab
temperature considered constant
Used Parallax Distance Sensor

Update 1 - v1.1
speed of soundn detected - co2 percentage determined after with matlab

Update 2 - v2.0
CO2 and CH4 fractions determined by iterating through preconfigured
array of co2 percentages

Update 3 - v2.1
Temperature compensation added as well as pressure sensing

Update 4 - v3.0
Installed new Maxbotix 42 kHz ultrasonic distance sensor

Update 5 - v3.1
Maxbotix sensor a little noisy
Added mode filter
Update 6 - v4.0
CO2 and CH4 fractions determined by interpolating between two points
specific heat data pulled from REFPROP software and uploaded into
arduino

Update 7 - v4.1
CO2 now determined separately with new COZIR sensor
SOS detects remaining fractions of C3H8 and CH4

Update 8 - v4.2
CH4 % array now starts from 70% - if it starts from zero propane percent
might get picked
up instead

Update 9 - v5.0
Removed CO2 sensor - could not distinguish CO2 in biogas mixtures
Reintroduced pressure sensor to monitor changes in CO2 readings (from
SOS)

Update 10 - v5.1
Added switch to distinguish when propane is introduced into mixture
Uses Interruptible Service Request in order to process switch as well as
debounces the request

Written by: Dimas Avila (for LBNL SmartBurner)

This sketch uses 4 different sensors.
Phidget Pressure Sensor 1140
COZIR CO2 Sensor
MAX6675 K Thermocouple Temperature Sensor
Maxbotix MB7380 Distance Sensor

pin connections
TBD

/*

//libraries
#include <TFTv2.h>
#include <SPI.h>
#include<SD.h>
#include <max6675.h>

#define YP A2   // must be an analog pin, use "An" notation!
#define XM A1   // must be an analog pin, use "An" notation!
#define YM 54   // can be a digital pin, this is A0
#define XP 57   // can be a digital pin, this is A3

//for PING))) ultrasonic distance sensor
const int pingPin = 28; //Digital Pin from which arduino communicates with
PING sensor **16 is for mega 2560**

const int cs = 38; //chip select for RTC
// Pressure Pin ***Coded out for now
int PressurePin = A13;

// Humidity and Temperature
int thermoDO = 31;
int thermoCLK = 37;
int thermoCS = 35;

MAX6675 thermocouple (thermoCLK, thermoCS, thermoDO);

// Arrays for comparing to sos to calculate co2 percentage
// Specific Heats run from 280 to 315 K
// To be used to calculate at certain temperatures
int temps[8] = {280, 285, 290, 295, 300, 305, 310, 315};
double co2cp[8] = {0.8334, 0.8382, 0.8430, 0.8478, 0.8526, 0.8574, 0.8622, 0.8669};
double co2cv[8] = {0.6391, 0.6442, 0.6493, 0.6543, 0.6594, 0.6643, 0.6693, 0.6742};
double ch4cp[8] = {2.1937, 2.2035, 2.2139, 2.2246, 2.2359, 2.2476, 2.2597, 2.2722};
double ch4cv[8] = {1.6698, 1.6799, 1.6904, 1.7014, 1.7129, 1.7247, 1.7370, 1.7497};
double MWCO2 = 44.01;
double MWCH4 = 16.0;

// Array to hold CH4 percentage values
double co2percentage[116] = {7.5, 8.0, 8.5, 9.0, 9.5, 10.0, 10.5, 11.0, 11.5, 12.0, 12.5, 13.0, 13.5, 14.0, 14.5, 15.0, 15.5, 16.0, 16.5, 17.0, 17.5, 18.0, 18.5, 19.0, 19.5, 20.0, 20.5, 21.0, 21.5, 22.0, 22.5, 23.0, 23.5, 24.0, 24.5, 25.0, 25.5, 26.0, 26.5, 27.0, 27.5, 28.0, 28.5, 29.0, 29.5, 30.0, 30.5, 31.0, 31.5, 32.0, 32.5, 33.0, 33.5, 34.0, 34.5, 35.0, 35.5, 36.0, 36.5, 37.0, 37.5, 38.0, 38.5, 39.0, 39.5, 40.0, 40.5, 41.0, 41.5, 42.0, 42.5, 43.0, 43.5, 44.0, 44.5, 45.0, 45.5, 46.0, 46.5, 47.0, 47.5, 48.0, 48.5, 49.0, 49.5, 50.0, 50.5, 51.0, 51.5, 52.0, 52.5, 53.0, 53.5, 54.0, 54.5, 55.0, 55.5, 56.0, 56.5, 57.0, 57.5, 58.0, 58.5, 59.0, 59.5, 60.0, 60.5, 61.0, 61.5, 62.0, 62.5, 63.0, 63.5, 64.0, 64.5, 65.0};

double check[116] = {};

// Declaring log file to write to in SD card
File logfile;

// State for input pin signaling input of propane

void setup()
{
  // Declaring I/Os
  pinMode(4, OUTPUT);  // digital pin 4
  pinMode(10, OUTPUT);  // chip select pin for SD card
pinMode(11, INPUT);
pinMode(12, INPUT);
pinMode(13, INPUT);
Serial.begin(9600);

Serial.print("Initializing SD card...");

//initializing SD card and touch screen
SPI.begin();
Tft.TFTinit();
DDRB |= 0x04;
if (!SD.begin(4)) //SPI_QUARTER_SPEED,
{ //53 is used as chip select pin
    Serial.println("SD reading failed!");
    while (1);
}

Serial.println("SD OK!");

//draws primary display screen
drawScreen(); //Draw info that does not change once drawTxtButton();

    //Write Log File Header
    File logFile = SD.open("DataLog.csv", FILE_WRITE);
    if (logFile)
        {
            logFile.println(", , , ,"); //Just a leading blank line, incase there
             String header = "Speed of Sound, Temperature, CO2%, C3H8%"; //PRessure
            logFile.println(header);
            logFile.close();
            Serial.println(header);
        }
    else
        {
            Serial.println("Couldn't open log file");
        }

    } // end of void setup

void loop()
{

double ch4cpnow, ch4cvnow, co2cpnow, co2cvnow;
double MolecularWeight, cp, cv, heatRatio, Speed;
double co2percent, c3h8percent=0.0, CO2, yCh4, yCo2, yC3H8, yBIOGAS;
double duration, cm, sec, sos;
long pulse;
double distance, cAir, time, time_new;
double myArray[15];
int i = 0, j = 0;
char sosChar[20];
String str;
String str2;
String str3;
char tempChar[4];
char c3h8Char[20];
char co2Char[20];
char ch4Char[20];
double BIOGAScp, BIOGAScv, MWBIOGAS;

//Temperature Readings
float temperature = thermocouple.readCelsius()+273.15; //K
double Tc = thermocouple.readCelsius();
temperature = (int)(temperature);

//speed of sound calculations
for (int i = 0; i < 16; i++){

delay(20);
pinMode(pingPin, INPUT);
pulse=pulseIn(pingPin, HIGH);
distance=double(pulse)/1000; //distance in m

time = distance/((20.05*sqrt(Tc+273.15))/2.0); //time adjusted to air
sos
delay(150);
//sos calculations
myArray[i] = time;    //cm to be calibrated to fixed distance in sensor

if (i == 15){
    isort(myArray,16);
    time_new = mode(myArray,16);
    sos = 2.0*.388/time_new;
} //if statement for mode of sos values taken from SOS for loop
} //end of SOS for loop

//first for loop calculates specific heats as function of temperatures
for (i = 0; i < 8; i = i + 1){
    if (temperature == temps[i]){ 
        ch4cpnow = ch4cp[i];
        ch4cvnow = ch4cv[i];
        co2cpnow = co2cp[i];
        co2cvnow = co2cv[i];

    } //end of if statement
    //interpolation
    else if ((temperature)>temps[i-1] & temperature<temps[i]){
ch4cvnow = ((temperature-temps[i-1])*ch4cp[i]+(temps[i]-temperature)*ch4cp[i-1])/(temps[i]-temps[i-1]);
ch4cvnow = ((temperature-temps[i-1])*ch4cv[i]+(temps[i]-temperature)*ch4cv[i-1])/(temps[i]-temps[i-1]);
co2cvnow = ((temperature-temps[i-1])*co2cv[i]+(temps[i]-temperature)*co2cv[i-1])/(temps[i]-temps[i-1]);
co2cvnow = ((temperature-temps[i-1])*co2cv[i]+(temps[i]-temperature)*co2cv[i-1])/(temps[i]-temps[i-1]);
}

}}

for (j = 0; j < 116; j = j + 1){
MolecularWeight = co2percentage[j]*MWCO2/100.0 + (100.0-co2percentage[j])*MWCH4/100.0;
yCo2=co2percentage[j]/100.0*MWCH4/MolecularWeight;
yCh4=(100.0-co2percentage[j])/100.0*MWCO2/MolecularWeight;
cp = yCo2*co2cpnow/100.0 + yCh4*ch4cpnow/100.0;
cv = yCo2*co2cvnow/100.0 + yCh4*ch4cvnow/100.0;
heatRatio = cp/cv;
Speed = sqrt(heatRatio*8314.0*(double)temperature/MolecularWeight);
}

check[j] = abs(sos - Speed); //array to hold difference between measured speed of sound and calculated speed
if (j == 0){
co2percent = co2percentage[j];
}
if (j >= 1){
if (check[j]<=check[j-1]){ 
co2percent = co2percentage[j]; //if the difference between the current calc sos is less than the previous calculation
}
}
for (j = 0; j < 116; j = j + 1){
delayMicroseconds(3000);
//strings made from float variables
dtostrf(sos, 1, 2, sosChar); //converts sos floating data to string to print on LCD
str = String(temperature); //converting temperature int data to string
str.toCharArray(tempChar, 4); //converting temperature string to a char array to print on LCD
dtostrf(co2percent, 1, 2, co2Char);
dtostrf(c3h8percent, 1, 2, c3h8Char);

//printing sensor value to LCD screen
Tft.fillRectangle(120, 40, 120, 15, BLACK); //clear old text
Tft.drawString(sosChar, 120, 40, 2, CYAN); //printing sos data on LCD screen
Tft.fillRectangle(120, 70, 120, 15, BLACK); // Clear old text
Tft.drawString(tempChar, 120, 70, 2, WHITE); // Printing temp data on LCD screen
Tft.fillRectangle(120, 100, 120, 15, BLACK); // Clear old text
Tft.drawString(co2Char, 120, 100, 2, CYAN); // Print co2%
Tft.fillRectangle(120, 130, 120, 15, BLACK); // Clear old text
Tft.drawString(c3h8Char, 120, 130, 2, CYAN); // Print RTC

String dataString = String(sos) + "," + String(temperature) + "," + String(co2percent) + "," + String(c3h8percent);
//open a file to write data to
//only one file can be open at a time!!! ********
File myFile = SD.open("DataLog.csv", FILE_WRITE); //opening DATALOG file and writing

// if the file opened okay, write to it:
if (myFile) {
    Serial.print("Writing to test.txt...");
    myFile.println(dataString);
    // close the file:
    myFile.close();
    Serial.print('t');
    Serial.println(dataString);
    //Serial.println(sos);
}
else {
    // if the file didn't open, print an error:
    Serial.println("error opening test.txt");
}

delay(2000);

}// end of void loop

//TFT functions

void drawScreen()
{
    Tft.drawRectangle(0, 3, 238, 30, BLUE); //Header Title
    Tft.drawString("DISPLAY DATA", 20, 15, 2, WHITE); //Header name
Tft.drawString("SOS:", 2, 40, 2, CYAN);            //drawn in same place
everytime for sos
Tft.drawString("Temp:", 2, 70, 2, WHITE);   //drawn in same pace
everytime for temp
Tft.drawString("CO2%:", 2, 100, 2, CYAN);
Tft.drawString("C3H8%:", 2, 130, 2, WHITE);

} 

void isort(double *a, int n){
  // *a is an array pointer function  
  for (int i = 1; i < n; ++i) 
  {
    double j = a[i];
    int k;
    for (k = i - 1; (k >= 0) && (j < a[k]); k--)
    {
      a[k + 1] = a[k];
    }
    a[k + 1] = j;
  }
}

//Mode function, returning the mode or median.  
double mode(double *x, int n){
  int i = 0;
  int count = 0;
  int maxCount = 0;
  double mode = 0;
  int bimodal;
  int prevCount = 0;
  while(i<(n-1)){
    prevCount=count;
    count=0;
    while(x[i]==x[i+1]){
      count++;
      i++;
    }
  if(count>prevCount&count>maxCount){
    mode=x[i];
    maxCount=count;
    bimodal=0;
  }
  if(count==0){
    i++;
  }
  if(count==maxCount){//If the dataset has 2 or more modes.
    bimodal=1;
  }
  if(mode==0||bimodal==1){//Return the median if there is no mode.
    mode=x[(n/2)];
  }
  return mode;}
A.3 Emissions

In order to effectively use the speed of sound sensor knowing how emissions change as the dynamics of the burner change is essential. This section covers some of the emission reduction for certain gases that are prioritized in the field of combustion.

A.3.1 Oxides of Nitrogen

While carbon emissions play a huge role in GHG emissions another type of molecule that is harmful for the environment is oxides of nitrogen. This is a grouping of three types of molecules, nitric oxide (NO), nitrogen dioxide (NO₂), and nitrous oxide (N₂O). The first two gas molecules are commonly grouped together and are usually referred to as NOₓ. The main portion of NOₓ (~95%) produced from combustion comes in the form of NO while the rest is contributed by NO₂ (Turns 2000). There are different kinetic mechanisms that can lead to the formation of NOₓ and when released into the environment can react in many different and harmful ways. Because of this NOₓ reduction is often prioritized.

A.3.1.1 Creation of NOₓ

The chemical mechanisms that produce and destroy NO and NO₂ during the combustion pathways are classified into three different categories (Bowman 1992). These include the extended Zeldovich (thermal) mechanism, mechanisms that produce NO more rapidly than what is predicted by the Zeldovich mechanism, and the fuel bound nitrogen mechanism.

A.3.1.2 Zeldovich Mechanism

During the process of combustion there are highly reactive intermediate species known as radicals that are formed. What typically happens during the process is that the species are formed
slowly but just as soon as they are formed they are destroyed by another reaction. This can be summarized by the Zeldovich Mechanism which forms NO and the reactive intermediate species is the N atom:

\[
\begin{align*}
O + N_2 & \rightarrow NO + N \\
N + O_2 & \rightarrow NO + O
\end{align*}
\]

The first reaction is the rate limiting step since it is slow and the second reaction is much faster. It is a rate limiting step since it has a high activation energy and thus is slow at low temperatures (Ragland and Bryden 2011). This mechanism is triggered at a certain temperature limit and is thus often called the thermal mechanism. This temperature limit usually occurs around 1900K (Zel’dovich 1946). Its peak in combustion usually occurs at slightly less than stoichiometric points due to the increased availability of O atoms from air. Thus one way to reduce formation of NO is to avoid stoichiometric points either by reducing temperature or avoiding near stoichiometric points. This will be covered in the NOx Mitigation Strategies.

A.3.1.3 Prompt NO

The prompt mechanism is also commonly known as the Fenimore mechanism and is particularly important in rich combustion. This mechanism is intimately linked to the combustion chemistry of hydrocarbons. This mechanism was discovered by Fenimore when he was studying laminar premixed flames when he found that NO was rapidly being produced in the flame zone, long before there would be time for the Zeldovich mechanism to form NO (Fenimore 1971). This mechanism is brought upon by hydrocarbon radicals reacting with molecular nitrogen to form amines (HCN, CN). These amines are then converted to intermediate compounds that help form NO in high temperature regions where O and N can be present in excess of equilibrium concentrations (Ragland and Bryden 2011).
The Fenimore mechanism can be visualized by the complex interconnected reactions seen in Error! Reference source not found. The N\textsubscript{2}O intermediate mechanism becomes important in fuel lean, low temperature conditions and its importance will be covered in NOx Mitigation Strategies. Additionally NO formed by the prompt mechanism is usually smaller compared to NO formed by the Zeldovich Mechanism, but as thermal NO is reduced, prompt NO becomes important.

![Figure A-1. Fenimore Mechanism (Bowman 1992)](image)

A.3.1.4 Fuel Bound Nitrogen (FBN) NO Formation

NO can also be produced from organic nitrogen compounds in the fuel. Some fuels that have organic nitrogen include oil which contains 0.1-0.2% nitrogen and coal which contains 1.2%-1.6% nitrogen (Ragland and Bryden 2011). Low BTU (British thermal unit) fuels like digester gas can have trace amounts of nitrogen as well. As these nitrogen containing fuels are burned an intermediate in the form of hydrogen cyanide (HCN) is made, which then reacts with O, OH, and H to form NO in the post-flame zone. Nitrogen conversion to NO from FBN can represent a substantial portion of the total NO depending on the degree of conversion. (Merryman and Levy 1975).
A.3.1.5 NOx Mitigation Strategies

When attempting to reduce NOx the primary concern is avoiding high reaction temperatures. Included with this primary concern is avoiding hot spots or temperature variations in the burned gas mixture as well as reducing the time available for the formation of NOx. All of these can be accomplished by either including more air in the primary combustion zone to lower temperatures, promote mixing of fuel and air upstream of the combustor, and reducing combustor residence time. However there is an indirect coupling with carbon monoxide (CO) and unburned hydrocarbons (UHC) and NOx that with the reduction of one leads to problems with the other. Some of the strategies that will be covered include reducing peak temperatures, decreasing activation energy, and removing emissions from the exhaust stream.

Reducing peak temperatures can considerably reduce NOx emissions. This is due to the high temperature requirements necessary to get the mechanism discussed in the previous sections to start. One example of doing this is mixing flue or exhaust gases with the fresh air or fuel. This is known as exhaust gas recirculation, often denoted as EGR or FGR (flue gas recirculation). The effect EGR has is that it increases the heat capacity of the burned gases for a certain amount of
heat release which helps lower the temperature (Ragland and Bryden 2011). In some cases the NO\textsubscript{X} emissions in the exhaust stream can be re-burned when they are recirculated. Its effect can be visualized by Figure A-2 which shows the correlation of NO reduction with an increase in diluent heat capacity.

Another method that is often taken is similar to EGR in the sense that diluent heat capacity is introduced. This is called lean premixed combustion (LPM) and it is done by introducing an excess amount of air upstream of the combustor to premix with the fuel. This eliminates hot spots that can arise without any premixing but has the caveat of potentially inducing flashback into the fuel and air mixture. This occurs when the flame begins to propagate back into the fuel and air mixture potentially causing damage to upstream instruments. As can be seen in Figure A-3, by evading near stoichiometric points NO production can be reduced. Despite lean burn’s effect of reducing temperatures and thus NO production it can also introduce another instability known as lean blow off (LBO). This can be costly and also cause unwanted wear on the combustion system. For aero engines this can also prove to be a safety hazard.

Another name for this method is also known as the dry low NO\textsubscript{X} (DLN) method. It gained this name after replacing legacy low NO\textsubscript{X} systems which would inject steam into the combustion chamber to reduce temperatures. The method of injecting water can either be directly injected into the combustion zone or injected into air that subsequently flows into the combustion zone (Lefebvre and Ballal 2010). While it could be advantageous to the DLN method due to DLN raising the primary zone’s velocity which adversely affects stability, water injection can be costly and increase potential for corrosion of hot section products (Lefebvre and Ballal 2010). Additionally water injection can also increase CO and UHC emissions.
A new method was introduced in the 1980s that took advantage of the low NO production at both the fuel rich and lean combustion areas and is known as RQL combustion. The strategy can be visualized by Figure A-4 which initially operates at fuel rich conditions and thus results in low NO production rates due to lower temperatures and can be seen in Figure A-3. It then transitions into a point where air is quickly brought in to avoid the peak in NO rates (high temperatures) that were also seen in Figure A-3 and finally bringing in dilution jet air to burn the rest of the fuel in lean conditions. This is a much more stable condition than LPM since a rich flame is more stable than a lean flame which can be useful in aero engines. RQL is also heavily exploited to handle fuels of great complexity and varying composition like digester gas.

In an alternative approach catalytic combustion can be employed to initiate and promote chemical reactions at leaner conditions than is physically possible with gas-phase combustion. This drop in equivalence ratios allows temperatures to decrease dramatically and thus also
reduces NOx emissions. The principle of catalytic combustion can be seen in Figure A-5 where fuel and air are premixed upstream of the catalytic reactor which can have many stages. The benefit of the catalyst is that it promotes chemical reactions to proceed and can get the combustion started at temperatures of around 700 K without being consumed or changed in the process (Lefebvre and Ballal 2010). The last portions are the thermal reactor which raise the gas temperature to burn out the CO and UHCs. This is a great strategy that avoids temperatures to reduce NOx, however, it can introduce complexities since the catalyst must undergo extreme temperature gradients which can lead to thermal shock. The burning out of CO and UHC also introduces complexities such as rerouting a part of the fuel to combust these pollutants. Despite these problems the potential for ultra-low NOx emissions can be enough of incentive to overcome the challenges that are presented by the technology.

![Figure A-5. Schematic representation of catalytic combustor. (Lefebvre and Ballal 2010)](image)

The get out of jail free card can be implemented by post combustion clean up. This is executed by implementing another type of catalyst to promote the conversion of the NOx to N2 and H2O by injecting ammonia into the exhaust stream. The principle reactions in this selective catalytic reduction (SCR) are:

\[
6NO + 4NH_3 \rightarrow 5N_2 + 6H_2O \\
6NO_2 + 8NH_3 \rightarrow 7N_2 + 12H_2O
\]
The problem with this approach is that large catalyst beds are required along with “slip free” systems which do not allow the ammonia to leak out of the system (Glassman and Yetter 2008). There is also an alternative of injecting urea as opposed to ammonia however its chemistry is temperature sensitive and some reactions may lead to the formation of $N_2O$ which is more potent than other greenhouse gases (GHGs).

A.3.1.6 Effects of NO$_X$

The reason all these strategies are implemented are due to the environmental and safety hazards NO$_X$ poses. The release of NO$_X$ into the atmosphere can lead to the destruction of stratospheric ozone (O$_3$) by the following mechanism (Turns 2000):

$$\begin{align*}
NO + O_3 & \rightarrow NO_2 + O_2 \\
NO_2 + O & \rightarrow NO + O_2
\end{align*}$$

As is evident by the mechanism O$_3$ is destroyed in the first reaction by NO, meanwhile NO is regenerated in the second reaction only to reenter the first reaction. This is harmful for us since the removal of O$_3$ in the atmosphere leads to more harmful ultraviolet solar radiation to penetrate to Earth’s surface.

While NO$_X$ itself does not pose a major health concern the production of O$_3$ from NO$_2$ through the net reaction (Glassman and Yetter 2008):

$$Light + NO_2 + O_2 \leftrightarrow NO + O_3$$

Can lead to the formation of O$_2$ to O$_3$. Regions like the Los Angeles basin are prone to keeping high levels of these emissions intact due to temperature inversions the basin provides at night and the high levels of NO$_X$ production from the basin. This production of O$_3$ can be lethal to
humans who have respiratory problems like asthma and also induce eye irritation (Haagen-Smit 1952).

A.3.2 Carbon Monoxide Emissions

While CO does not play a primary role in environmental effects it can pose significant health risks. It is one of the six so-called criteria pollutants listed by the National Ambient Air Quality Standards (Act 1990). This calls for CO emissions to be below 9 ppm over an 8 hour averaging time and less than 35 ppm over an 1 hour averaging time (Act 1990).

A.3.2.1 Formation of CO

The formation of CO can be made at both the rich and lean side of combustion. On the rich side there is insufficient oxidation of the excess fuel that does not carry the oxidation of CO into CO$_2$. Meanwhile, on the lean side of combustion the excess amount of air dramatically reduces the burning rate of the fuel again leaving CO without sufficient oxidation.

As can be seen by Figure A-6 there is a temperature range where both CO and NO$_x$ emissions meet. At a certain temperature limit NO$_x$ emissions may continue to drop, however the excess amount of air will lead to insufficient burning rates to transform CO to CO$_2$. Other potential methods for CO production include quenching of CO due to cold surfaces. This stops the oxidation of CO to CO$_2$ (Newhall 1969).
A.3.2.2 CO Mitigation Strategies

In order to achieve low CO emissions a compromise must be made on NO\textsubscript{X} emissions as was just discussed in the last section. There is a tight window where a further reduction in NO\textsubscript{X} will only lead to a steep rise in CO and UHC emissions due to insufficient burning rates. Another method that is implemented is to increase the residence time so that CO reaches equilibrium and useful energy can be extracted from the combustion products. However this also has its source of caveats as NO\textsubscript{X} can linearly increase with residence times as seen in Figure A-7. Thus a compromise must be made between air/fuel operating conditions and residence time of the exhaust gases.
A.3.3.3 CO Health Hazards

As mentioned previously CO can have severed health concerns and the extent of these concerns are highlighted in Figure A-8. It shows the percent of carboxyhemoglobin along the y axis which is a stable molecule that forms in red blood cells upon contact with carbon monoxide. Depending on CO ppm levels and exposure time this molecule can increase to lethal levels in the body. The figure shows that when exposed to CO volume fraction levels of 100 ppm headache and reduced mental acuity can begin to occur after exposure times of more than 1.5 hours. At CO levels of 600 ppm after the same amount of exposure death can occur. Therefore, enough incentive is provided by the potential health effects of that CO poses to bring CO emissions levels down.
Figure A-8. Effects of CO exposure on humans. (Turns 2000)