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SONOTRODE DEVELOPMENT FOR HIGH INTENSITY ULTRASOUND AND ITS EFFECT ON THE DYNAMIC FLOW OF A LYOPHOBIC SOLUTION

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by

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ABSTRACT

High intensity ultrasound is being used in various applications in industry, such as healthcare, food science, mechanical cleaning, etc. It has proven to be a truly diverse approach that has not yet been explored for all of its uses. It is a powerful tool for mixing to create meta-stable emulsions when considering lyophobic solutions. Lyophobic colloids have no attraction between the dispersed particle and the dispersing medium. Stable lyophobic emulsions are difficult to create; they become even more difficult when the fluids are placed in a dynamic scenario in which energy is already causing motion. High intensity focused ultrasound can be proven to be an efficient method of creating a lyophobic emulsion. The ultrasound is transmitted from the piezoelectric material to the fluid through a resonant body called a sonotrode. The understanding of how to best process such emulsions in-flow is herein advanced through the use of theory, simulation, and experiments.

Two applications for the benefits of lyophobic emulsions will be discussed. The first being biodiesel production in which the colloid is used directly to create the final product. The other being the cleaning of metal chips in which the emulsion will be the byproduct. Investigations into this byproduct will be performed to help determine the effectiveness of the cleaning technology. Using ultrasonic emulsifiers has the benefit of producing lyophobic emulsions using minimal energy and time with promising trends for scaling to industrial production processes.

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TERMINOLOGY

Back-Mass: Body of material behind transducers to prevent loss of ultrasonic energy.

Biodiesel (B100): "Fuel comprised of mono-alkyl esters of long chain fatty acids derived from vegetable oils or animal fats [11]."

Cavitation: Formation and immediate collapse of micro-void within a liquid due to high pressure differentials.

High Intensity Focused Ultrasound (HIFU): Direction controlled energy caused by ultrasonic waves resulting in heat and shockwaves [2].

Immiscible: Fluids of opposite polarity that cannot be mixed to homogeneity.

Lyophobic Emulsion: A colloid of immiscible fluid that when the dispersed phase is small enough and evenly dispersed it appears homogeneous.

Piezoelectric Effect: "A dielectric material in which polarization is induced by the application of external forces [**6**]."

Resonance: "Condition of vibration at which the absolute value of the driving-point impedance is a minimum [2]."

Sonotrode: System comprising of ultrasonic transducers, electrodes, back-mass, ultrasonic horn, and binding components, also termed mechanically resonant body.

Transducer Stack: Ultrasonic transducers layered such that the poled directions oppose each other to optimize displacement.

Ultrasonic Horn: Front-mass or body of material used to transfer ultrasonic energy from ultrasonic transducer to next media; can be used to focus or transform ultrasonic wave [2].

Ultrasonic Transducer: Device which transforms an electrical current pulse into an ultrasonic wave [1].

Ultrasound: Sound waves about the detection of the human ear (17 kilohertz) [1].

Working Face: Surface of the ultrasonic horn or sonotrode surface exposed to media ultrasonic wave energy is being transmitted to (fluid).

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Chapter 1

Introduction

1.1 Historical Preface

Ultrasound, much like ultraviolet light, is radiation at a higher frequency than the human ear can perceive. The typical human ear can detect frequencies from 20 hertz (Hz) up to 17 kilohertz (kHz). Sound travels in waves similar to the waves in water. Sound, like light, is energy traveling as a conservative media in the form of a wave. In the case of sound, a wave is representative of the mechanical energy traveling conservatively in an elastic body or fluid. The Greek philosopher Chrysippus observed waves in water around 240 B.C. and speculated sound also took form in waves. This theory was later proven to be correct, but it wasn't until the end of the 16th century that Marin Mersenne and Galileo developed the first laws governing sound. In 1688, Sir Isaac Newton developed the first mathematical theory that took into account pressure pulses transmitted between particles; this is known to be the first mathematical equation involving energy transfer due to sound theory allowing for phenomena such as diffraction due to waves to be accounted for mathematically. Later this theory was used by Euler, d'Alembert, and Lagrange to develop the wave equation [**1**].

Industrial ultrasonic applications, much like many engineering theories, were rapidly developed in the early 19th and 20th centuries. Since the industrial revolution, technology has been developing at an astounding rate [**2**]. Humans have come a long way from hunter-gathering to farming. Mankind has gone from traveling by horse and mailing letters to using planes and cell phones, respectively. Technology is increasing more rapidly currently than ever before. With this demand for new technologies, it is critical to stay on the front line of the next new concept or application. As part of the new technology there is also the need for energy conservation and minimizing resource waste. One way of optimization is to take present technologies and modifying them to fit new uses. Ultrasonic devices were originally developed by the U.S. Navy for underwater communications [**2**]. From their initial involvement in Navel applications, they are now very commonly used in the medical field. Previously, viewing a baby as it was developing would mean using x-ray imaging. Now, ultrasound has developed for viewing embryo development without the hazard of x-ray exposure. When used at high frequencies, in the megahertz (MHz) and gigahertz (GHz) ranges, ultrasound provides the ability to penetrate surfaces without causing harm. This diagnostic technique has proved to not only been useful for the biomedical field but also in an industrial application in safety evaluation techniques, called non-destructive evaluation (NDE) [**3**].

1.2 Justification for Research

As the demand on the world's energy supplies increases, there is a need to develop industrial processes consuming less energy than conventionally. This trend can be seen in almost every facet of industry as more processes are being improved from an energy or material standpoint. Typically, the technology in ultrasonic devices uses less energy than traditional methods. This can be seen in the medical field with ultrasound for prenatal imaging. An x-ray could be prepared; however, there is not only cause for concern for the fetus but also for large amounts of energy. By contrast, low energy consumption can be observed with a handheld, battery powered ultrasonic imager, such as the General Electric Vscan (vscan.gehealthcare.com).

Ultrasound is not just applicable to the medical field. One of its largest applications is in non-destructive evaluation (NDE) tests for quality control monitoring of systems. The ability to prevent a problem from occurring by early warning detection is of extreme value. Waves transmitted through solids and liquids are one of the best attributes of ultrasound. Man's ability to both understand these waves and create them has allowed for the technology to progress rapidly in many fields.

It is not simply creating and understanding the waves, but rather the control of the waves, that expands the possibility of where ultrasonic technology can be employed. Through many different concepts, such as phased arrays and ultrasonic horn technology, one can develop new applications. Through array technology we can both predict the presence of a defect or anomaly, and guide a wave front using the Huygens-Fresnel principle. Likewise, through horn and sonotrode technology, waves can be focused and amplified to perform functions and the energy produced can be applied for a specific purpose [**2**].

While ultrasound is employed for analysis purposes, such as ultrasonic scans at high frequency or non-linear ultrasound for material properties, it can also be used in a *destructive* manner. Destructive ultrasound, better termed process ultrasound, involves waves meant to either produce a change in or alter the effects on media. This is typically termed high intensity focused ultrasound (HIFU) [**2**]. To properly understand HIFU, it must first be broken down into two parts, focused and high intensity ultrasound. Focused ultrasound has already been discussed where ultrasonic waves are directed in a desired manner through the understanding of the Huygens-Fresnel principle. The theory explains that through constructive and destructive interference, waves can be channeled into one direction.

High intensity ultrasound can be more deceiving in the phrasing of the terms. It means that the energy caused by the wave results in heat and shockwaves. High intensity is not to be confused with high frequency. Therefore, HIFU is a destructive form of ultrasound. Process ultrasound has many applications, from its use to heat molecules to destroy cells in the form of ablation to cleaning application by shockwave energy removing particles from the surface of a material [**2**].

HIFU has proved to be useful in medical application. With the ability to focus the ultrasound toward an object worth removing, specialists are able to direct the waves to the object, apply the necessary frequency, and cause the object to be destroyed through heating and shockwave energy. Once the object has been reduced to a finely sized mass, it can be passed naturally by the body without harming other cells [**4**], [**5**].

High-intensity ultrasound has also proven useful in non-medical fields like mixing and surface cleaning with ultrasonic baths. Energy from ultrasound shockwaves form tiny cavitation bubbles which can be used for different applications. Piezoelectric materials serve as the basis of transducers, which are devices that convert electrical energy into mechanical strains, or vice versa [**6**]. Energy transfer from piezoelectric materials can be higher than that of other conventional forms of electrical to mechanical conversion systems. However, there are still other issues to be considered when dealing with ultrasound, specifically those properties which affect mechanical resonance, namely, material properties, geometric and aspect ratios, and mechanical impedance between boundary materials. Resonance is the frequency at which the displacement amplitude of mechanical oscillation achieves a maximum for a given system. Resonant frequencies may be found in almost all mechanical objects. They represent the points at which a standing wave is achieved.

The standing wave condition occurs when the pattern of the wave does not move left or right but rather stays in one position and the locations of its maxima and minima do not change [**7**]. Finding the resonant frequency for a system ensures that the maximum amplitudes can be achieved; likewise, these points of maximum and minimum amplitudes are points of maximum and minimum energy transfer, respectively. Once the resonant frequency is reached from the system, the system can then be optimized to transfer the most energy to another system in the most efficient manner.

The optimization of the system efficiency is what separates one system from another; it allows a system to perform to its highest efficiency. It also allows for the proper functionalization of the system. With ultrasonic systems branching into so many different industries, the more optimal the ultrasound control, the better the end result.

1.3 Thesis Impact and Scope

Ultrasound has a vast impact on the progression of many industrial processes. Biomedical and NDE fields have already been discussed in some detail. While ultrasound has many different applications, there are new uses for the energy produced by the wave.

This thesis will consider the development of a mechanically resonant body for creation of a lyophobic emulsion from immiscible fluids. Ultrasonic waves were created by piezoelectric transducers purchased from Piezo Kinetics Inc. Therefore, the development of the ultrasonic transducers and their shape will not be discussed. However, the choice for the excitation frequency of the transducers is relevant to this dissertation.

The two colloids to be developed will consist first of oil and water and oil and methanol. Each colloid impacts a different industry and concept for further development, either by using that emulsion for the process itself or the solution is created as a byproduct. Both systems are considered to be novel uses of ultrasound.

The first industry considered is the production of biodiesel. While implementation of ultrasound for mixing applications is not considered a new concept, it is a novel concept in relation to biofuels. The other novel system is of the metal chips produced from machining. Although cleaning via ultrasound is not a revolutionary concept, the frequency and application are novel to the metal processing community. While the lyophobic emulsion is not the desired product, by creating the emulsion the chips are cleaned.

1.3.1 Biodiesel

Fossil fuels have been the means for power generation and transportation since the Industrial Revolution. With high energy and power densities as well as the ability to be stored relatively easily, they are a highly attractive power sources. One major downside of fossil fuels is their inability to be reused once they have been depleted. Such scares of these depletions can be seen through history. In the 1980's there was the first oil crisis. With the growth of countries such as India and China, there is concern about when current sources of fossil fuels will cease to be available. Increasing fuel prices are the first evidence in the decline of fossil fuels.

As fossil fuels are depleted there is more push to develop alternative sources of energy which can easily be replenished. Some of these sources include solar and wind power, battery technologies, and biofuels. All of these are considered "green technologies" for their environmentally friendly production and their ability to be replenished. Biodiesel is one such biofuel which is created chemically using plant oils, recycled cooking oils and animal fats; therefore it is a renewable energy source [**8**]. Biodiesel has a lower energy density than petroleum diesel, 118,296 Btu/gal vs. 129,500 Btu/gal respectively. Currently, pure biodiesel is not typically used alone, but rather is blended with petroleum diesel at a 20% to 80% blend, also known as B20 [**9**]. While biodiesel has lower energy content, it is still higher than that of gasoline. Likewise, diesel engines tend to have a higher operating efficiency, about 40%, compared to gasoline engines at 30%. Diesel engines, although heavier than spark-ignition engines, have significant torque advantages and are easily converted to run on B20, which is the competition-mandated fuel for diesel engines. However, diesel engines have greater NOx and particulate emissions which are harmful to the environment [**10**].

Biodiesel is made through the chemical process of transesterification, where glycerin is separated from the fat or vegetable oils. The product from the chemical process is methyl esters and glycerin [**11**]. To separate the glycerin, the oil or fat is combined with an alcohol, typically methanol, at a ratio of 1:3 stoichiometrically.

Figure **1-1** is a visualization of the transesterification process for biodiesel using triglycerides and methanol.

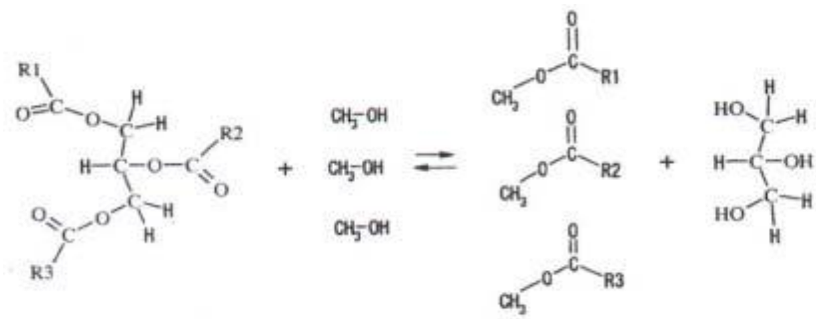

Figure **1-1**: Alkali-catalyzed transesterification [**12**]

Biodiesel is one alternative fuel which, while being more environmentally friendly, does not cost less than diesel fuel from current production and distillation processes. On paper and through stoichiometric calculations biodiesel should be cheaper to produce than diesel; however, supplying biofuel to proper specification has proven to be the demise of many companies. Without government subsidies, many companies cannot keep production costs under fuel prices. While the stoichiometric calculation of the chemistry of biodiesel shows that the ratio of alcohol to oil is about 3:1, in practice this ratio tends to be more along ratios of 6:1 or 8:1 and the process requires introduction of a catalyst to help stimulate the reaction [**13**].

While batch reactions are simple and yield a salable product, they also leave room for large losses if the reactions are not properly executed. The development of a piped system utilizing ultrasound and microwave technology has a great advantage over traditional systems. The ultrasound provides the mixing for the system while the electromagnetic radiation supplies the heat necessary to stimulate reaction.

The Kropf Multi-Energy Optimization Process stimulates reaction time through the use of ultrasound and microwaves shows that more energy efficient application can be achieved to help decrease overall production cost [**14**], [**15**].While ultrasound is not a new concept to be utilized in the production of biodiesel in an industrial application, it is typically used to supplement the mixing process in the biodiesel system [**16**]. The microwave technology is used to replace conventional heating sources. With consideration to the immiscible fluids, alcohol is polar and oil is non-polar; therefore, due to the dipolar relaxation peak of polar materials in relation to electromagnetic radiation, alcohol can be excited by microwaves. Both the oil and alcohol must be heated for the transesterification process to occur. By creating a lyophobic emulsion of the alcohol and oil using ultrasonic emulsifiers, it appears as though it is one homogeneous material if the alcohol droplets are evenly dispersed and small enough in radius. If it appears homogeneous then transesterification process can occur using electromagnetic radiation. This thesis focuses on the creation of lyophobic emulsions and the development of the emulsifiers; therefore more detail of the microwave energy process will not be discussed.

1.3.2 Metal Chip Cleaning

When parts are formed in machine shops the process typically involves the lathe reduction of a larger piece of material. The size, shape, and complexity of the part produced govern the duration of the machining operation and temperature control of the material. During machining, small chips or coils (curlicues) separate from the parent material. Figure **1-2** shows some of the different geometries of metal chips that can be created as a result of the machining process. When that material is metallic, the chips are collected, cleaned and recycled as scrap for re-melting and processing into bar stock.

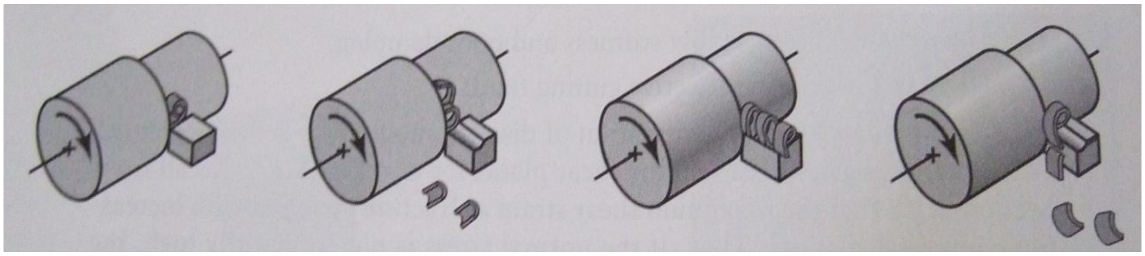

Figure **1-2**: Different geometrical shapes that can be formed from the machining process [**17**].

Prior to melting, the chips must first be cleaned to remove deposits of oil, scale and fine particulates from the machining process. Currently, commercial chip cleaning typically employs hot water, a highly alkaline detergent, and some type of kettle or rotation mechanism to ensure chip movement, similar to an industrial washing machine [**18**], [**19**]. This process has basically been the same for over 50 years when metals companies started reclaiming chip scrap. This process tends to be very crude, expensive to operate and many times the solution and detergents used are not environmentally friendly.

As technology further develops, new applications can be considered and original processes become reconsidered to decrease cost and maintain efficiency. Ultrasound has been used to clean the surfaces of precious metals in the jewelling profession for years in tank baths to remove attendant impurities. The benefit of ultrasonic cleaning is that it can be paired with other chemical cleaning processes as well as to remove debris from complex configurations [**20**]. The application of ultrasound industrially is a novel concept especially when moving from ultrasonic baths to single ultrasonic stacks.

1.3.3 Fluid Dynamics

When dynamics are added to any system there are always some further complications to be associated with it. In relation to fluids there are many new conditions and situations which must be taken into consideration depending on the type of dynamic scenario.

1.3.3.1 Stagnant

A stagnant fluid pool is the most basic scenario to anticipate the results of ultrasound treatment. It is also easy to obtain a standing wave within the fluid as well as resonance of the ultrasonic stack. Static scenarios allow for generalizations of function and restrictions. Resonance is easily achieved because there are no other vibrations to be taken into consideration.

Static simulations, theory, and experiments allow a base to be developed to ensure proper assumptions and tests. From this base, the concepts can be expanded to more complex cases.

1.3.3.2 Perpendicular Flow

When liquid flow is normal to the working face of the emulsifier, fluid energy must be taken into consideration. The situation can be simplified easily because of the nature of the motion. When considering fluid mechanics, while there are still eddy currents and dispersion energies evident, there is not much influence of boundary layers.

The energy from the fluid motion is perpendicular to the surface making it easier to characterize. At low flow speeds these results tend to look similar to static tests or simulations.

As liquid flow rate increases, the complexity of the process increases. Larger forces are involved and pressure differentials from the fluid motion must be considered along with the ultrasound. Since the fluid motion is parallel to the wave propagation the forces typically work in favor of each other.

1.3.3.3 Parallel Flow

The situation of a fluid moving parallel to the emulsifying surface becomes the most difficult scenario to conceptualize. The effective range of the ultrasound drastically changes from the no motion situation. The fluid cannot typically reach a satisfactory level of resonance to sustain a standing wave depending on the flow rate. Boundary layers and no-slip conditions become components that must be considered as flow rates increase. No-slip conditions mean that the fluid parallel to a static surface will appear as though it is not flowing. The boundary layer concept builds off the fact that as the fluid gets closer to the static surface it slows more and more due to drag forces. These components of multi component fluid regimes present complications to theory, models, and experiments [**21**].

1.4 Thesis Organization

This thesis has been organized to help the reader understand the proper back matter as well as the core concepts and test performed to reach findings pertaining to industrial scale emulsifiers in relation to developing lyophobic emulsions under various flow conditions. As stated in the beginning portions of this chapter the basic industries being considered for this technology in relation to this thesis are biodiesel production and metal chip cleaning.

Chapter 2 is organized to develop the basic understandings of ultrasonic wave propagations and how these waves differ between solid and liquid media. Piezoelectric transducers are explained in relation to their basic properties and their ability to generate ultrasonic waves. The components comprising the resonant body and the concept of how cavitation is affected by fluid dynamics are discussed in detail. Chapter 2 mentions current sonochemistry devices currently available and their limitations.

Chapter 3, Methodology, discusses the methods used to reach the conclusions, being computer simulations and the development of ultrasonic emulsions. The simulations section debates the benefits of a finite element analysis system as well as some of the necessary assumptions and settings for the program. In the ultrasonic emulsions section, the basic principles of how the ultrasonic emulsions are created for tests. Also the basic equations in relation to both the settling rates of emulsions and necessary equations to be used for transferring ultrasound and developing resonance are deliberated. The understanding of how flow affects the development of the emulsion is reviewed.

Experimentation and Testing, Chapter 4, covers the different experiments performed through simulations, resonant frequency scans, sonotrode development, biofuels, and metal chip cleaning. In the simulations section, all of the steps taken in developing the different concepts for each of the simulations are discussed, such as model types, constraints, voltages applied, etc. Resonant frequency scans are performed monitoring voltage potential drops in relation to frequency applied. Materials used, assumptions made, and limitations are discussed in relation to sonotrode development. In biofuels, the relationship between emulsifiers used and the reaction process for developing biodiesel is reviewed as well as the LabVIEW program used to drive the emulsifiers. Metal chip cleaning concludes the section in discussing foil depletion tests, optical diffraction measurements taken, emulsion settling experiments, and residual carbon content analysis of remaining debris on the metal.

Chapter 5 presents the results in a manner in which assumptions and comparisons between testing types are made. The findings of the research are discussed both quantitatively and qualitatively. Overall trends are analyzed to prove or disprove concepts.

In the conclusions the research performed is compared to previous works and the overall concepts proven are reviewed in relation to the objective. Assumptions made from the findings and future works to be tested are given. Possible new industrial applications are also presented.

Chapter 2

Ultrasound Review

When comparing ultrasound to other wave forms, such as light, interpretation opposite to intuition is required. Light travels its fastest in vacuum and slows as the medium becomes denser. Sound waves move at high velocities in solid media and slow in air. They cannot propagate into or through vacuum [**1**]. The physics involved with both sound and light makes sense when taking into account energy transfer. Sound involves movement of a molecule within space in an oscillatory pattern, with its spring constant related to the mechanical properties of the body. Therefore, the more molecules tightly packed the faster and more easily the wave energy can be transferred from one molecule to a neighbor. Light, however, consists of the transfer of electromagnetic energy, which exhibits a loss to molecules during propagation.

Wave propagation can come in many different motions. Each wave form has different benefits or advantages to an application. The two most common motion forms come from the plane wave approximation which distinguishes between two modes, transverse and longitudinal. In the transverse mode, a particle moves perpendicular to the direction of the wave propagation. This mode is also called a shear wave. Low viscous fluids such as water and air do not support shear stresses and thus do not experience shear waves. A longitudinal wave has particle displacement that moves parallel to the direction of the wave propagation. A longitudinal wave mode is also called a pressure wave because the stresses of compression and rarefaction of the particle are along the propagating direction [**1**].

2.1 Technique Overview

To create an ultrasonic wave, there has to be a transmission source. The source can be anything that causes mechanical motion. A device that transforms an electrical current pulse into an ultrasonic wave is typically referred to an ultrasonic transducer [**1**]. Transducers allow easy generation and control of ultrasonic waves. Piezoelectric materials have become the predominant material used in transducer designs due to their unique property of converting an electrical potential into a mechanical response through polar molecule alignments with crystallographic orientation.

Ultrasonic transducers vary in shapes, sizes and material. By definition, a transducer is a device actuated by power from one source of energy and transfers the power to another form of energy [**22**]. Moreover, a transducer is an energy conserving medium that translates one form of energy into another. Therefore in relation to piezoelectric materials, an ultrasonic transducer is the piezoelectric that takes the electric potential and creates mechanical energy. Figure **2-1** visually demonstrates the electric potential generated by a piezoelectric material from a mechanical force where P is the poling direction. In relation to lead-zirconium-titanate (PZT), a common transducer material, the poling direction is related to the titanium atom being shifted off center within the crystalline structure resulting in a dipole.

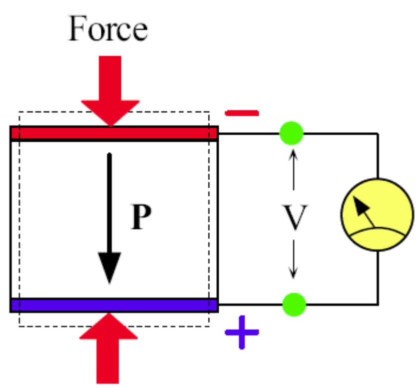

Figure **2-1**: Piezoelectric material in relation to mechanical force, voltage, and poling direction [**23**].

Some consider a transducer to be the entire casing and all other components to transfer the electrical energy to the next medium. For this thesis, the term transducer will refer to the PZT material and silver paste adhered to the poled surfaces by the manufacturer used as an electric conductor, separate from the remaining components comprising the mechanically resonant body, or sonotrode. Figure **2-2** is a three dimensional (3D) computer drawing of a sonotrode will all of the components labeled. Transducers can be layers upon each other with like charged electrodes touching to increase the overall displacement; this is typically called a transducer stack. There are other critical components necessary to optimize the amount of ultrasonic waves transferred from the electrical potential. These components include: an electrode, a back-mass, and a working face used to transfer the ultrasonic waves into the next medium which with the addition of the ultrasonic transducer, collectively make up what is called the sonotrode, or working body. The sonotrode is intended to conserve the ultrasonic energy within the system and direct it toward the working horn and working face. The electrode provides for transfer of electric potential to the transducer surface. The back-mass serves several purposes, it is to prevent ultrasonic waves from being lost or transferred to the environment and it also helps to achieve resonance of the structure. The working face, or applicator, is the interface between the piezoelectric material and the medium into which energy is being transferred. It is a critical component in the development of the system; it helps to prevent loss through reflection of ultrasonic waves due to different impedances between the transducer. It is also a way to focus the beam in a particular direction. Like the back-mass, it too affects the resonant frequency of the system by the percentage of the waves reflected within the structure and transferred into other waveforms.

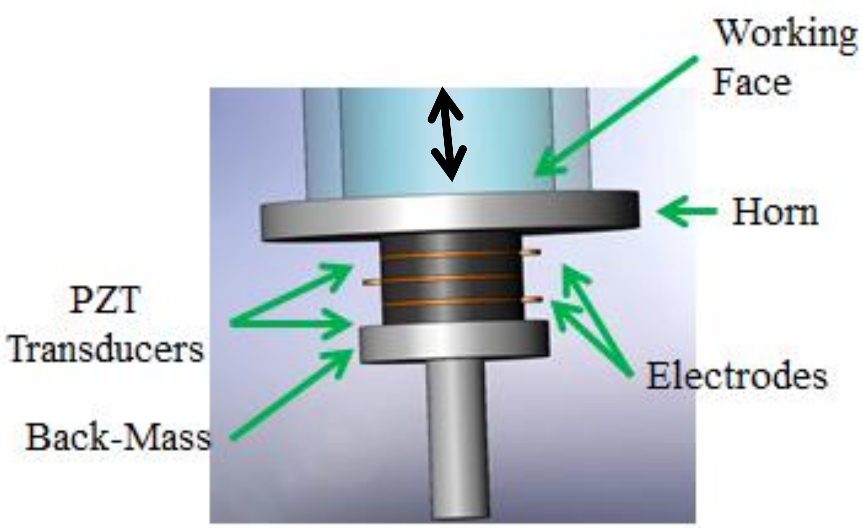

Figure **2-2**: Computer drawing of a sonotrode with all components labeled and direction of displacement given by the double arrows.

In order for the system to function properly the components must be kept in close contact. This could be many things, such as glue or adhesive, a casing, or a nut and bolt system. This casing not only holds everything together and in close contact, but for piezoelectric transducers it provides pressure to help increase the efficiency of the transducers.

Impedance is another large factor when considering energy transfer. Impedance may be calculated through Eq. **2.1**, in which ρ is the density and c the speed of sound in the material [**3**]. In ultrasound, it is important to keep the impedance between the piezoelectric material and sonotrode components as close as possible to decrease the amount of energy being reflected back into the system. However, when it comes to the fluid and working face, the greater the impedance, the larger the displacement will be. In order to perform work on a process medium using high intensity ultrasound impedance, mismatch is unavoidable. The main emphasis for impedance mismatch is within the sonotrode.

$$Z = \rho c \qquad \textbf{2.1}$$

Using Eq. **2.2** and Eq. **2.3,** the reflection and transmission, respectively, of an acoustic wave at a normal incident to the plane boundary can be determined in the form of a fraction of wave energy. The symbol *T* represents the transmitted wave, *R* the reflected wave, *Z* is the impedance of the materials and the subscript *1* and *2* represent the change in medium, either transducer to horn or horn to fluid.

$$R = (Z_2 - Z_1)/(Z_2 + Z_1) \qquad \textbf{2.2}$$

$$T = (2Z_2)/(Z_1 + Z_2) \qquad \textbf{2.3}$$

The resonance of the structure has greatest effect on the energy being transmitted. Optimizing resonance helps to offset the loss in wave energy through attenuation.

Attenuation is the loss in intensity of the wave with distance and time [**2**]. Since resonance is the maximum point of displacement it plays the largest role in designing a sonotrode and emulsion chamber. It is crucial to ensure the displacement of the sonotrode is maximized. In standing waves, there are nodal and anti-nodal regions. It is important to position the displacement surface at the anti-node since this is where the maximum peak-to-peak displacement occurs. Using the natural frequency equation, Eq. **2.4**, the anti-nodal and nodal regions can be calculated, where n is the mode number, V_l is the speed of sound and l is the length of the body [**3**].

$$f_n = \frac{nV_l}{2l} \qquad \textbf{2.4}$$

Piezoelectric materials are not perfectly efficient, therefore there is energy being dissipated. The wasted energy is released thermodynamically through heat. Likewise, there is also heat generated from the friction of the mechanical motion. Piezoelectric materials are created through heating to their Curie temperature, then allowing them to cool under an electric field to align their poles within the material. It is important to prevent overheating of the piezoelectric disks because in the same manner in which the disks are created they can be de-poled by prolonged heating. Since piezoelectric materials are stimulated by an electrical pulse, it is more difficult to cool them using conventional cooling systems, such as water or ethylene glycol. Alternative methods for cooling must be practiced such as provision for sufficient thermal mass between the applicator and back-mass components of the sonotrode.

The shape of the piezoelectric component must also be taken into consideration, not only because its shape can make it more difficult to cool, but also because it will change the shape in which the wave will propagate. Cylindrical piezoelectric materials allow for the wave to propagate in an annular shape. This shape allows the outer side of the piezoelectric stack to be cooled by convection of ambient air.

2.2 Ultrasound in Solids

As mentioned before, ultrasound travels faster and easier through a solid medium. This is due to molecules being in closer proximity to each other allowing for energy to be transferred easily. In ultrasonics, there are several different factors that allow ultrasonic energy to be transferred. One factor is the speed of sound in a medium. While this is a factor in all media, there are more forces that become prominent in other medium types, such as fluids, that are negligible in solid media for ultrasound. Both the longitudinal and shear waves can be calculated for a given isotropic material knowing the density, Poisson's ratio, and Young's modulus [**3**].

2.3 Ultrasound in Liquids

As mentioned previously, in liquids the wave speed of ultrasound is less than that of solids due to the larger spacing between molecules. This spacing means that there is a greater distance a molecule must travel to transfer its energy to the next molecule. Therefore, due to restrictive forces, such as friction, energy dissipates faster. These factors make it harder to transfer energy through liquids. Liquids also undergo other motions internal to their physical boundaries that solids do not typically experience such as translational, rotational, and vibrational motions due to the spacing between molecules and their ability to move. These motions cause more complications when trying to transfer a wave from a solid medium into a liquid. When considering the different wave forms capable of being formed in a medium, this will depend on the liquid. In water the only wave form capable of being transferred is longitudinal wave. This is because waves cannot move in shear motion [**1**].

When transferring from the sonotrode to the liquid the wave is transferred via the displacement of the sonotrode. The ultrasound causes the surface of the sonotrode to displace small amounts at a rapid rate. This displacement is what causes the movement of the molecules of the liquid. This movement is also what causes the cavitations to be formed as well as streaming. Streaming gives the same effect as shear mixing [**24**]. With the proper development of the sonotrode cavitation and streaming can be controlled and anticipated.

2.3.1 Cavitation

Cavitation is the formation and then immediate implosion of voids in a liquid. Cavitation can be achieved by rapid pressure changes within a liquid where bubbles form in the low pressure areas. With the creation of these bubbles, as shown in Figure **2-3,** and the immediate implosion of them, the result can be either highly mixed fluids or surface cleaning.

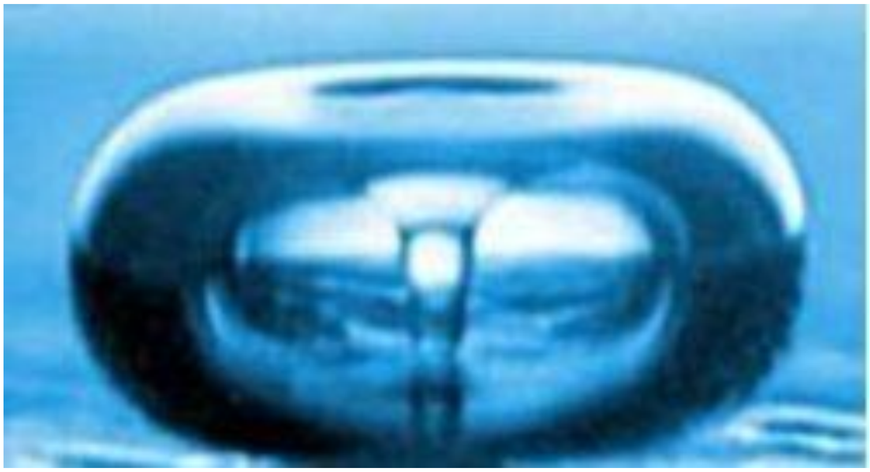

Figure **2-3**: Image of implosion of cavitation void showing micro-jetting of fluid through the center of the bubble [**25**].

There are two types of cavitation, stable and unstable. Unstable cavitation results in the most energy dissipation at a given point in time, however as the name alludes it is not a constant dissipation of energy. Since the bubbles need to form to their maximum allowable size then fully implode, there tends to be large shockwaves of energy followed by a rest period. During this implosion a micro-jet of fluid passes through the center of the bubble helping to create the mixing effect sought after. This micro-jet of fluid can be seen in the image in Figure **2-3**. Stable cavitation is when the bubbles do not fully implode; it is more of an oscillation in the volume of the bubble size resulting in a shockwave. While the energy is not nearly as much as in unstable cavitation, there is less time between intervals and results in more of a steady energy pulse at a higher constant frequency.

Prediction of cavitation is an extremely difficult process, even when local pressure conditions are known. It is far from easy to predict its occurrence because one must estimate the size and distribution of the nuclei present. Cavitation is a general fluid mechanics phenomenon that occurs whenever a liquid is used in a machine which induces pressure and velocity fluctuations in the fluid. The first mention of cavitation was in a 1754 paper at the Berlin Academy of Science and Arts by the Swiss mathematician Euler. In the paper, Euler discussed the possibility of a phenomenon, which today is called cavitation, occurs on a particular design of water wheel and the influence this design might have on its performance. Cavitation later became of particular interest to naval ships and torpedoes where it occurs on the impellers and hulls due to the stagnation point [**26**].

2.3.1.1 Cavitation with respect to fluid dynamics

In kinetics, it is easy to simplify the problem when there is one energy source; however, when there are multiple sources of energy the problem become much more complicated. Fluid flow is one such energy to be taken into consideration when developing a system. Once flow is introduced to the fluid, ultrasound intensity changes as flow rate increases. It becomes much more difficult to predict how the results will differ.

When fluid flow is introduced to a cavitation field, the cavitation bubbles are dispersed due to fluid motions. This can be the case in both circulation and stirring of a fluid. Even with multiple transducers and multiple power outputs, it may be difficult to maintain stable cavitation fields [**27**]. Using ultrasound alone makes cavitation difficult to create. The cavitation field can be strengthened if there are voids or other bubbles already present within the fluid [**28**].

2.3.1.2 Commercial Sonochemistry Devices

There is a limited market for sonochemistry devices that use the power of ultrasound for forming emulsions. One of the most common and earliest sonochemistry devices is the ultrasonic bath, which uses ultrasonic transducers, typically resonating at 40 kHz, to either mix fluids or clean surfaces. These systems use high intensity ultrasound to create emulsions. Typically, they lack a horn to transmit the wave through but rather by passing the wave energy through a thin plate. They use the concept of low or no flow over a large dispersion area to create mixing.

Another system is an ultrasonic probe concept, in which ultrasonic transducers are attached to a probe focusing the ultrasonic energy to a small working face to increase the intensity at one key location. With emulsification becoming more prominent in the biodiesel industry, industrial versions of this system are becoming more prominent. One such industrial system is produced by Hielscher (www.hielscher.com). In their system, a horn resonates at 20 kHz using 1000 W to emulsify the oil and methanol as they pass by, shown in Figure **2-4** [**29**]. While this technology works, it still limits the advantage of resonant frequencies in the emulsification chamber to achieve higher levels of emulsification. Likewise, it was not developed strictly for biodiesel emulsifying, that is just one of its various applications.

Figure **2-4**: Image of multiple Hielscher UIP100hd emulsifying probes designed for continuous flow mixing in biodiesel production [**29**].

Chapter 3

Methodology

Simulations as well as ultrasonic emulsifications are deliberated in relation to the method in which they are applicable to determine results. The benefits of using simulations as real world representations are conversed. Justifications for the chosen simulation program are given. The ultrasonic emulsification section presents some of the basic sedimentation rate equations as well as equations relevant to ultrasonic emulsifier development. Fluid dynamics and its effect on the creation of an emulsion is debated in further detail.

3.1 Simulations

Simulations allow for a theory or concept to be tested without the high cost associated with the build of a testing apparatus. Materials, design structures, component shapes, and other details can be altered easily with faster results to help develop the concept before building. This helps to keep cost low and give more of a guarantee that the system will function as anticipated once built.

It is critical that all simulations be as accurate as possible with the most details taken into account to ensure that once the concept is built it will perform as anticipated. Creating an accurate simulation tends to be difficult. There are many forces in real life applications not taken into considerations when thinking through a system, such as friction points, reflection surfaces, and boundary layers. These must be accounted for in simulations by the developer. Many times these tend to be more difficult to anticipate or account for depending on the software package being used.

There are many finite element analysis (FEA) software packages available. When considering the level of complications with ultrasonic simulations it becomes critical to pick a software company that was designed with the proper level of physics and materials built into the program. This choice is more important depending on the level of the user. Comsol Multiphysics (www.comsol.com) was chosen for resonant body simulations. Figure **3-1** is an image of a Comsol design showing the different components of the sonotrode as well as the fluid body. An added benefit to the Comsol program is that it has the ability to simulate the transfer of the displacement of a solid body into a pressure differential in a fluid medium. This allows for the simulations to help anticipate large pressure drops within the fluid. These pressure changes can help to anticipate locations of cavitation.

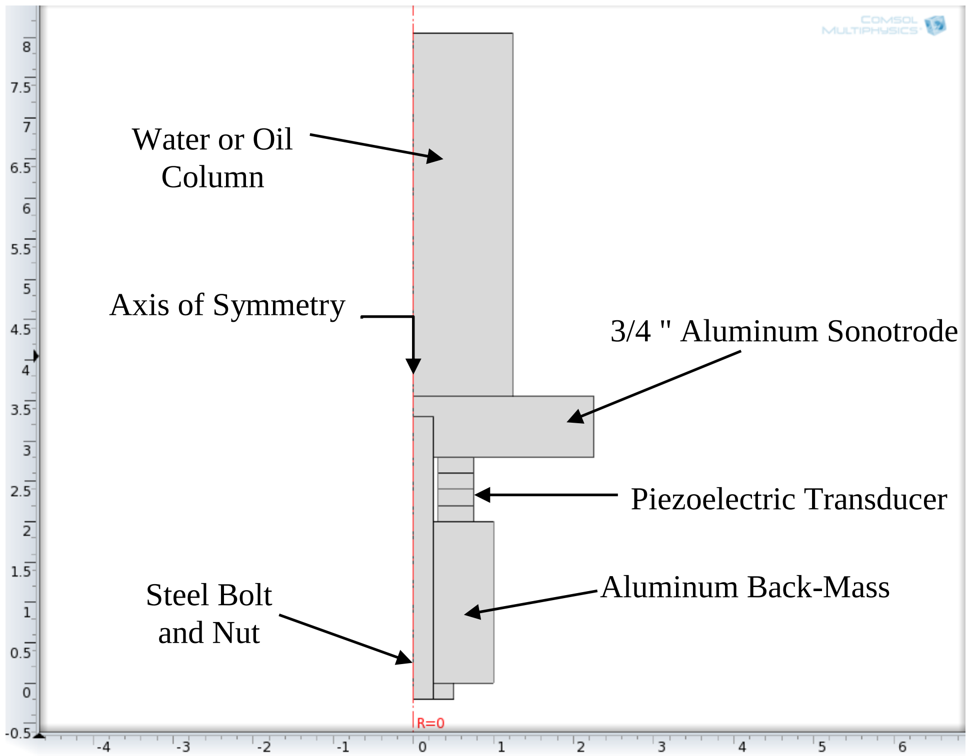

Figure **3-1**: Comsol image of an ultrasonic stack with a 3/4" aluminum applicator and water or oil column depending on test being simulated.

3.2 Ultrasonic Emulsification

Emulsions created ultrasonically are the bases for the experiments. They are used in several applications such as biodiesel production and metal chip cleaning. The properties of the emulsion help to determine how well the ultrasound is being produced. An emulsion is the suspension of a liquid within another liquid. Ultrasound energy is used through cavitations to create the emulsion. When a cavitation event implodes, it creates a micro-jet of fluid that, when the fluid slows, can form tiny micro bubbles of a fluid within the dispersing medium. These micro bubbles are what make up the emulsion [**24**].

When the fluids are immiscible, such as oil in water or alcohol in oil, the resulting emulsion is called a lyophobic emulsion since they consist of polar and non-polar molecules. The stability of the emulsion can be determined by the size of the dispersed droplets in the continuous phase as well as how quickly they separate. Ultrasound proves to be an effective method for creating emulsions. Through cavitation, the dispersed phase can be formed into micro and nano-scale droplets. The stability of an emulsion is a function of the size of the droplets of the dispersed phase. The study of destabilization can be beneficial when considering the stability of an emulsion. Eq. **3.1** is Stoke's derivation of sedimentation rate of a solid sphere through creaming, where u is sedimentation rate, g is the acceleration due to gravity, r is particle radius, ρ is the density, and η the viscosity. Stoke's equation was derived using a solid particle in settling; however, for two liquids the equation changes form to Eq. **3.2**. This equation was developed for a standard radius of particle, however in most emulsion the droplet size is not standard but rather a distribution as is the case in Eq. **3.3**, where r_i is the distribution of droplet radius [**30**].

$$u = \frac{2gr^2(\rho_1 - \rho_2)}{9\eta_2} \qquad \textbf{3.1}$$

$$u = \frac{2gr^2(d1 - d2)}{3\eta_2} * \frac{\eta_1 + \eta_2}{3\eta_1 + 2\eta_2} \qquad \textbf{3.2}$$

$$\bar{u} = \sum_i \frac{8\pi}{27\eta V} g n_i r_i^3 (\rho_1 - \rho_2) \quad \textbf{3.3}$$

The dispersion rate of an emulsion can be difficult to determine through calculations. This becomes even more difficult when considering lyophobic emulsions since there are other factors contributing like repulsion forces from the polar and non-polar molecules. One way to help stabilize a lyophobic emulsion is through the use of a catalyst or surfactant. This can help to weaken repulsion forces and even functionalize some of the outer bonds [**31**].

The movement and motion of the emulsion become substantial concepts in development. In lab tests, it can be sufficient to have no flow like in ultrasonic baths or probes, but in design for commercializing, flow must be implemented while the emulsion is being created in both simulations and experimentation.

3.2.1 No Flow

Stagnant fluid models and experiments are performed to determine if these simplified systems can provide substantial results. The results from the static experiments are expanded to develop new concepts and theories into other conditions such as fluid flow. The zero flow rate experiments create a base line for other experiments.

3.2.2 Perpendicular Flow

Fluid flow normal to the sonotrode surface is used to develop secondary understandings of how cavitations can be effected when flow is induced. Tests and models are developed using trends anticipated as a result from static systems. Theories are expanded further and generalizations made based on the results.

3.2.3 Parallel Flow

With parallel fluid flow, it becomes more difficult to achieve a steady level of cavitation since the dynamic flow does not typically allow for the cavitation bubbles to reside in the same location [**28**]. Results from the static and perpendicular flows are used to develop models and tests for fluid dynamic scenarios where the flow is parallel to the working face of the sonotrode. These test results help to develop full commercial scale systems where assumptions from small scale cannot be made since the flow rates are increased as well as size in industrial applications.

Chapter 4

Experimentation and Testing

Finite element analysis simulations, resonant frequency scans, sonotrode development, automated biodiesel production, and ultrasonic metal chip cleaning comprise the experiments and tests performed. Constraints and assumptions made are discussed in relation to model types developed for the simulations. The basic understanding of the determination of the resonant frequency scans and how they are relevant to tests is presented. With a better understanding from simulations and resonant frequency scans, new sonotrode concepts developed in relation to new materials and mounting locations. New industrial sonotrode types are built and emulsifiers are tested in the production of biodiesel using novel concepts. Automation of these emulsifiers and sonotrodes benefit this process as well as test preformed for industrial ultrasonic metal chip cleaning. Carbon content remaining on the chips as well as multiple analyses performed on the resulting emulsion byproduct can help generate trends and concepts to better understand the overall goal of lyophobic emulsions.

4.1 Simulation

Simulations in Comsol Multiphysics (Comsol) are set in two dimensional axisymmetric models. This allows for the time to compile the simulation to be greatly decreased yet still capable of yielding fairly reliable results. Since the system is axisymmetric the results can be displayed in both two dimensions (2D) and two-thirds view rotated about the center axis.

Comsol has many materials and application built within its software. As well as having standard materials such as aluminum, steels, etc., it also has several more uncommon materials such as piezoelectric materials, including several PZT. One benefit of the program is that it is able to adequately create models using piezoelectric materials to develop ultrasonic waveforms and surface displacements. When comparing the properties provided by Piezo Kinetics Inc. with the pzt-5a material in Comsol, the materials are sufficiently close to be used for the simulations.

In the program, Comsol allows for a voltage to be placed on one surface and ground to the other in relation to the poled directions of the PZT. Using standards provided by Piezo Kinetics Inc., different voltages were able to be iterated from very low, 1/2 volt, to the maximum allowable voltage, 5 volts, to determine which voltage provides the best resonant mode. The understandings of the use of linear elastic body in the models to show the propagation of the ultrasonic waves through displacement of the elastic materials, such as aluminums and steels, in the FEA program, the results are anticipated to be best in the lower voltages since the assumptions made are small displacements.

The simulations also allowed for multiple sonotrode shapes and materials to be tested in order to best optimize the ultrasonic system. With relation to the shape, different mounting locations were tested through iterations to determine which position yielded the best results in relation to maximum displacement while maintaining axial symmetry. Depending on the design of the system, different mounting options were tested to see what best represented the mounting technique. For example, if the system was held in place by a clamping force on two separate surfaces, then a roller restriction was used since the clamping force was only applied on the top and bottom surfaces but did not restrict the movement of the sides, as shown in Figure **4-1** by the arrows. This type of mounting can be considered when the sonotrode is bolted to the emulsifying chamber. The constraining forces are typically seen as surface forces rather than a rigid fixture since the tolerances of the bolt holes would allow for small lateral movement, therefore surface roller constraints over particular areas were used.

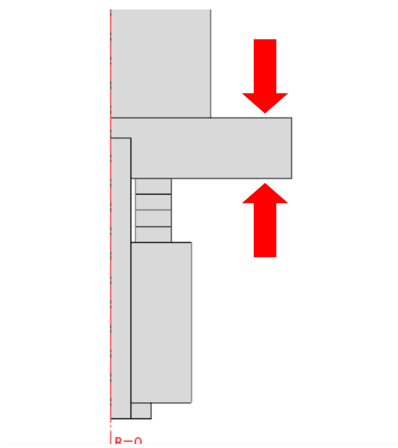

Figure **4-1**: Position of roller constraints on sonotrode restricting movement in the direction of the arrows but on restriction lateral direction.

Typically the simulations were developed to test the resonant frequency, called the Eigen frequency in Comsol. Since the models were being developed to achieve a particular resonant frequency, the simulation was set to scan for resulting frequencies within the range of 28-50 kHz. This range was chosen in relation to the ability to create an emulsion with a tight distribution and small micro bubbles [**14**], [**15**].

After a model has been developed for displacement of the working face in relation to the resonant frequency and pressure differentials determined for the fluid, the next step is to test how the pressure gradients are affected by the fluid flowing within the model. As fluid moves across the surface, the energy from both the fluid and the mechanical displacement of the working face change the pressure fields. As fluid speed is increased, the results are monitored to determine where meta-stable cavitations could occur.

Through iteration of different parameters, simulations can be used to predict results in relation to physical components. While there are many assumptions that go into creating a model, making educated choices when incorporating these assumptions can help to prove the results.

4.2 Determination of Resonant Frequency

Determining the resonant frequency is a critical step in developing a system to optimize ultrasound in creating an emulsion. Using LabVIEW software the resonance of the ultrasonic stack can be determined. The software is set up to measure the potential change from the positive and ground electrodes on the piezoelectric transducers. The change in voltage is related to the energy being converted into mechanical energy by the transducers.

Once the transducers are compressed with the sonotrode, there is a shift from the resonance of the transducer to the resonance of the system. The LabVIEW program measures the change in voltage and, likewise, the change in resonance for the entire stack system. The program uses the frequency generator card in the LabVIEW program box to change the frequency of a sine wave that controls the output voltage. The voltage is run through a range of frequencies to determine the resonant frequencies. When the voltage changes at a certain frequency, this indicates that the frequency is a resonance point for the structure. The peak-to-trough voltage change determines the efficiency of that resonant frequency. The frequency is plotted in relation to the voltage change in order to visually show the results. Figure **4-2** is a general example of an image of a frequency scan from 20 kHz to 90 kHz. As resonance modes are reached the potential drops in relation to the electrical energy being converted to mechanical. Therefore when a scan is performed large drops in the RMS voltage can be used to calculate how much electric potential is being converted at a given frequency. As Figure **4-2** shows there can be multiple resonant points within a scan. Isolating the particular frequency of interest depends on the function of the sonotrode.

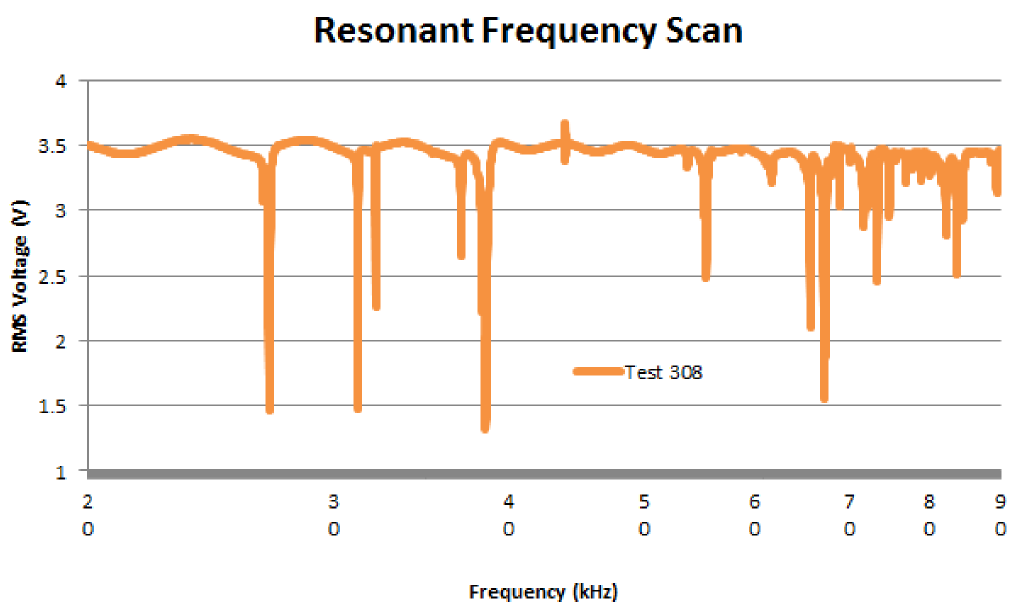

Figure **4-2**: Image of a LabVIEW resonant frequency scan from 20 kHz to 90 kHz showing multiple resonance points.

The static resonance of the system also changes as the transducers are compressed. As the stack is compressed via a bolt and nut, the conversion efficiency increases and the frequencies shift. This frequency shift can be tracked as the system is tightened. The more compression applied to the transducers the more efficient they become. As they become more efficient, the resonance frequency becomes more sharp and distinct.

4.3 Sonotrode

In ultrasound there is so much emphasis on the materials being used. The shape, material type, flaws, and surface coatings become controlling factors in the way the waves can be transmitted and received. The basic function of the horn is to transfer the wave energy from the transducers to the next medium. Depending on the material and its particular qualities govern how affective it is as performing this task.

Material choice is a larger factor for the optimization of the sonotrode. When transmitting ultrasonic waves from material to material, there are many considerations that must be taken into account for the transition to happen properly. Eq. **2.2** and Eq. **2.3** determine the reflection and transmission respectively of an acoustic wave at a normal incidence to the plane boundary. The closer the match between the impedances of the materials the more wave energy can transfer from one medium to the other.

Many of the sonotrodes developed in this thesis used aluminum 6061 for its low cost, ease of machining, and close impedance match to PZT. Titanium is another commonly used material for ultrasonic horns because of its close impedance match and high resistance to wear. Due to the cost of the material it was not used for this project. For small scale testing, aluminum proved to be sufficient, however as scale up of projects to continuous use in industrial applications is considered, oxidation layers and reactions with other chemicals, such as catalysts, become a greater concern. Therefore, other materials with low reactivity, such as food quality stainless steel, are being considered and developed.

Sonotrodes allow for many concepts to come together in one design. In Figure **4-3** the sonotrode develops such that it allows fluid to be passed across the surface. A hole drilled through the bolt in the center of the sonotrode allows fluid to pass through the system and out the cap on the top through small orifices. Since the working face is what is mechanically oscillating, it is important to have the cross flow as close to the surface as possible. This allows for maximum energy transfer while helping to decrease the effects of boundary layers from impeding the fluid movement.

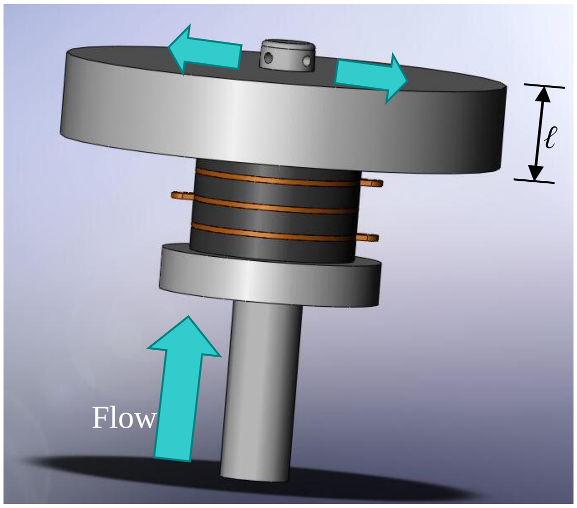

Figure **4-3**: Ultrasonic stack using a basic cylindrical horn with the ability to pass fluid through the sonotrode and across the working face, as shown by the arrows.

One of the simplest ultrasonic horn concepts is a cylinder or uniform bar. In this concept the horn is developed to use the basic understanding of ultrasonic wave propagation that the largest displacement occurs at the anti-nodal regions. Therefore if the contact point with the transducer is an anti-nodal region then, for the horn to achieve resonance, the length of the horn, ℓ, is governed by Eq. **4.1**, where λ is the wavelength, c is the speed of sound in the material, and f is the frequency [**2**]. This type of horn is also referred to as a 1/2 λ horn. Using aluminum 6061 as the horn material the length for the horn should be 0.0774m (or 3.047in).

$$\ell = \frac{\lambda}{2} = \frac{c}{2f} \quad \textbf{4.1}$$

Since the cylinder is a uniform bar, its displacement should be equal at either end. This is not necessarily the case; this assumption is made with the idea that there are no losses in the system due to damping. Eq. **4.2** is the ultrasonic horn equation with damping losses taken into account, where ω is the angular frequency, ρ is the density, c is the speed of sound, and R_m is the damping coefficient [**2**]. When damping is taken into consideration the displacement amplitude at the transducer surface is not the same at the 1/2 λ surface, or a shift in frequency could occur.

$$\frac{\partial^2 v}{\partial x^2} + \frac{1}{S}\frac{\partial S}{\partial x}\frac{\partial v}{\partial x} - j\frac{\omega R_m}{\rho c^2}\frac{\partial v}{\partial x} + \frac{\omega^2}{c^2} v = 0 \quad \textbf{4.2}$$

4.4 Biofuels

In biofuels, in particular biodiesel, ultrasound is used to create an emulsion of the initial components in order to maximize reaction surface area and create a more stable and efficient reaction [**14**], [**15**]. The pre-reacted components, methanol and vegetable oil, are flowed across the working face where the ultrasonic energy mixes them. The ultrasound is run at a continuous wave in order to establish mechanical resonance and create cavitations in the process media.

The programming for the ultrasound is run through a LabVIEW program and shown in Figure **A-1**, Figure **A-2**, Figure **A-3**, Figure **A-4**. The program outputs from the LabVIEW computer go to an amplifier, then to the ultrasonic stack. The program not only runs the frequency but it also monitors the energy output by the stack to determine if there is a resonant frequency shift.

While LabVIEW is running the stack at the optimum frequency it might not be resulting in the proper transfer of energy. The properties of the emulsion can be used to determine the efficiencies of the ultrasound of the fluids in conjunction with the LabVIEW program through checking the impedance change, Figure **A-5**. The size of the micro methanol bubble within the oil helps to determine to what degree the cavitation shockwaves are causing the methanol and oil to be mixed.

There are two types of cavitations to benefit the transesterification process, the organic chemical reaction which is necessary for biodiesel production. The first is at the liquid-liquid interface. The micro-jetting that occurs at this interface causes a thin high speed jet of fluid to the other phase. When the jet of fluid slows, a droplet is formed within the other fluid [**30**]. The other type occurs when cavitations are in a meta-stable state, in which rather than a full collapse of the bubbles, there is an oscillation in size which creates a pressure gradient and allows for mixing to occur.

The more power input into the fluids the faster the final emulsion size can be achieved. The amount of power does not affect the emulsion size, only the rate [**14**], [**15**], [**32**]. The power input (P_{fwd}) compared to the power reflected back (P_{rev}) from the stack, as displayed by the amplifier, is an indication of how efficiently the system is functioning. Through Eq. **4.3** the efficiency of the system can be determined. This method is a quick form of determining how the system is functioning.

$$[(P_{fwd} - P_{rev})/P_{fwd}] * 100 = \text{Energy Efficiency} \qquad \mathbf{4.3}$$

The LabVIEW program also monitors the starting power forward and reflected as well as the current power levels. If the levels change more than 5% then the LabVIEW program performs another scan for the optimum frequency.

Ideally the mixture should be reacted immediately through microwaves when using the Kropf Multi-Energy Optimization Process, in order to create the biodiesel and not allow for the micro-bubbles of methanol to agglomerate and form larger bubbles [**14**], [**15**]. From the reaction the percent conversion can be a direct comparison to how small the micro bubbles of methanol are within the oil or how well the heating source is functioning. If the heat source stays constant then changes can be tied to the emulsion. In relation to the microwave heating, methanol is microwave reactive, meaning it is affected by microwaves, while oil is microwave transparent. Therefore, if the emulsion is not stable enough and the methanol bubbles are not small and evenly spaced then the methanol will be "flashed off," meaning quickly heated and phase change from liquid to gas, and the reaction will not be completed. If the microwaves are absorbed sufficiently and the reaction occurs it can be tested to ensure it is properly completed by comparing total methylesters to the remaining mono-, di-, and triglycerides [**33**].

4.5 Metal Chip Cleaning

Ultrasound used for the cleaning of metal chips left as a byproduct of machining is very similar to that of the biofuels process. For the chip cleaning process, the metal chips and water with a small percentage of soap are passed across the working face. Through cavitations, the shockwaves remove oil, dirt, and other particles from the surfaces of the chips. The soap helps to keep the oil and dirt from re-depositing on the surface of the chips. The same LabVIEW program is used to control the ultrasound as the biodiesel process. Similarly, the program will test the efficiency and adjust depending on a change in the ultrasound. Also, Eq. **4.3** can be used in relation to the amplifier to determine if the energy is being transferred to the system.

There are several other methods for being able to determine the effectiveness of the ultrasound. Since the ultrasound is the only component other than slight fluid flow and low heat it can easily be determined to what level the ultrasound is effective.

In the review paper by Zhu et al., the concept of cavitations was tested in three 100 Watt ultrasonic baths at varying frequencies, 28 kHz, 45 kHz, and 100 kHz. The tests were performed with a thin foil test to determine the degree of destruction caused by cavitations. The results from the test showed that the foil in the 28 kHz bath sustained the most damage [**12**]. Similar to the Zhu et al. experiments, foil tests are performed to determine the location and degree of cavitations with the fluid.

Optical diffraction is one technique to measure the size of the oil particles suspended within the liquid byproduct of the cleaning process. Optical diffraction testing uses light to measure the refraction angle in relation to the scattering of the beam on other particles. The machine used to perform this test, the Horiba LA 920, can use this data to determine the size of the particles, in this case oil droplets suspended in water. Figure **4-4** is an image of the droplet radius dispersion of the oil in the water. From the image it can be seen that the droplets span a large size distribution.

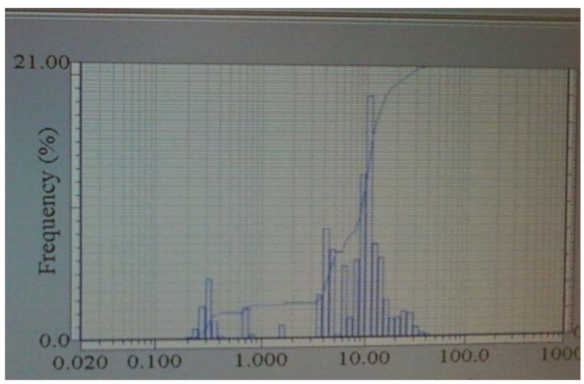

Figure **4-4**: Image of a droplet size distribution of the dispersed phase as presented from the Horiba LA 920 showing two peaks and a large dispersion size.

Another method for determination of the stability of the emulsion is to time how long it takes the oil to agglomerate and separate from the water. Since oil is non-polar and water is polar they will want to be repelled from each other. As time progresses, the oil will eventually form a layer on the top of the water, as shown in Figure **4-5**. Likewise, the water will become clearer as the oil and other particles settle out. This time can help to determine how effective the ultrasound was at creating a meta-stable emulsion.

Figure **4-5**: Micro oil bubbles agglomerate to form an oil layer.

Carbon content remaining on the surface of the chip proved to be a viable way to determine the effectiveness of the ultrasound. The metal chips were separated by their difficulty to clean based on size and shape. Once separated, they were processed in the ultrasonic emulsifier. Warm water, averaging 150^{o}F, and soap were added to create a slurry. Table **4-1** designates the chip type and the percent of soap to be added to the slurry. The chips were designated by difficulty to clean. This segregation was done through the shape of the chips. Easy to clean chips are flat and provide direct access to the cut surface. Hard to clean chips are chips where the surface is not exposed easily, they are typically curled, spiral pieces of metal with different contours and geometries. Tests were run using stagnant water, water flowing perpendicular to the working face, and water flowing with periodic mixing of chips by hand. The time of emulsification was also varied to determine the time to clean the chips to sufficient levels of carbon content.

Table **4-1**: Chip designation and percent soap added.

Chip Type	Easy	Medium	Hard or Very Difficult
Soap Added (%)	0.2	0.4	1.0

Visual monitoring also gives insight into the cleaning process. Oil and dirt can be seen being removed from the chip surfaces in Figure **4-6,** which shows an image of oil and debris plumes caused by ultrasonic emulsification. While the plumes are visually representing the oil and other items being removed, it is difficult to quantitatively represent the findings without further testing. The visual oil clouds help to strengthen the claim of cleaning via ultrasonic emulsification.

Figure **4-6**: Image of oil and debris being removed from the surface of the metal chip via ultrasonic emulsification.

Using both optical diffraction and visual oil layer measurements the degradation of the emulsion can be tracked. Multiple optical diffraction measurements on the same liquid byproduct allow for the oil particle agglomeration to be tracked. Also, by visually tracking the amount of oil separating to the surface over time allows another way of determining the settling out of the immiscible fluids, as well as determining the amount of oil removed from the metal chips.

Chapter 5

Results

There are many assumptions to be made from general knowledge of basic systems, results from testing help to validate these assumptions and prove hypothesizes. Results given both quantitatively and qualitatively show trends, verifications, and validations of concepts. Side by side comparisons strengthen findings from different tests as well as standalone tests. Predictions are made from findings in simulations, resonant frequency scans, optical diffraction tests, foil film degradations, etc. By pairing multiple results from different tests, better understandings of the capabilities of the system are made and allow for future concepts to be developed.

5.1 Determination of Resonant Frequencies

Resonant frequencies determined through resonant frequency sweeps are natural frequencies associated with the entire structure. As the piezoelectric transducers are compresses they are better able to transfer their ultrasonic energy to different mediums. As the entire system is compressed together the resonant frequency shifts from being simply the transducer stack frequency to the resonant frequency of the entire structure.

To measure how much energy is being converted from electrical energy to mechanical energy the change in RMS voltage can be tracked. This helps to determine how efficient the transducers are at a particular resonant frequency. Figure **5-1** is the resonant frequency sweep in relation to a plate emulsifier, Figure **4-3**. By using a general efficiency equation modified for voltage drop, Eq. **4.1**, the energy transfer efficiency can be monitored. Using the maximum voltage before the resonance peak, circled in red, and the minimum voltage at resonance, circled in green, the energy conversion efficiency for the frequency of 37.8 kHz is 71%.

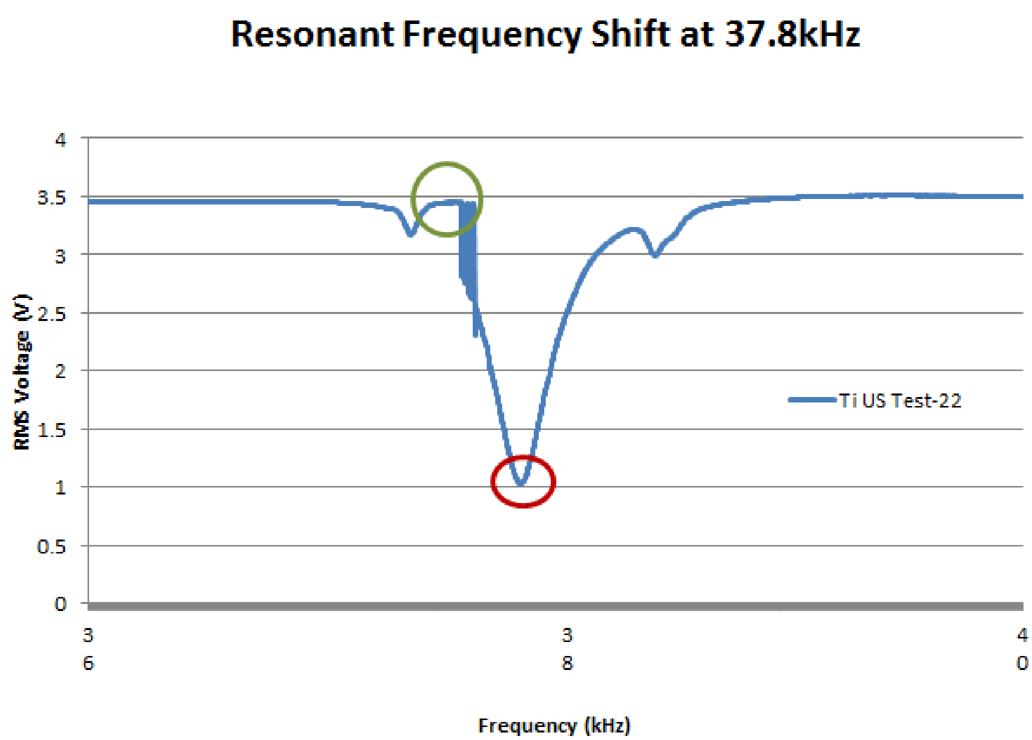

Figure **5-1**: Resonance peak for plate emulsifier at 37.8 kHz.

$$\frac{(V_{max} - V_{min})}{V_{max}} * 100 = \%\ Conversion\ Efficient \qquad \textbf{5.1}$$

In relation to developing resonance of a system it is important to consider the connections being made with other components and where material interfaces will be situated. Figure **5-2** shows the resonant frequency change and mounting components are removed. Test 361 shows the frequency with the mounting bracket connected to the system, while test 364 show the resonance of just the ultrasonic horn. The concept being viewed is energy loss. As more components are connected to the system, there are more locations for the ultrasonic wave energy to transfer to, thus the less wave energy to be transferred to the working face [**34**]. In order to decrease loss to connection points, it is critical that the design be built to allow connections at the points where the results will least effect the efficiency. This furthers the reason for proper calculations and simulations to strengthen the design.

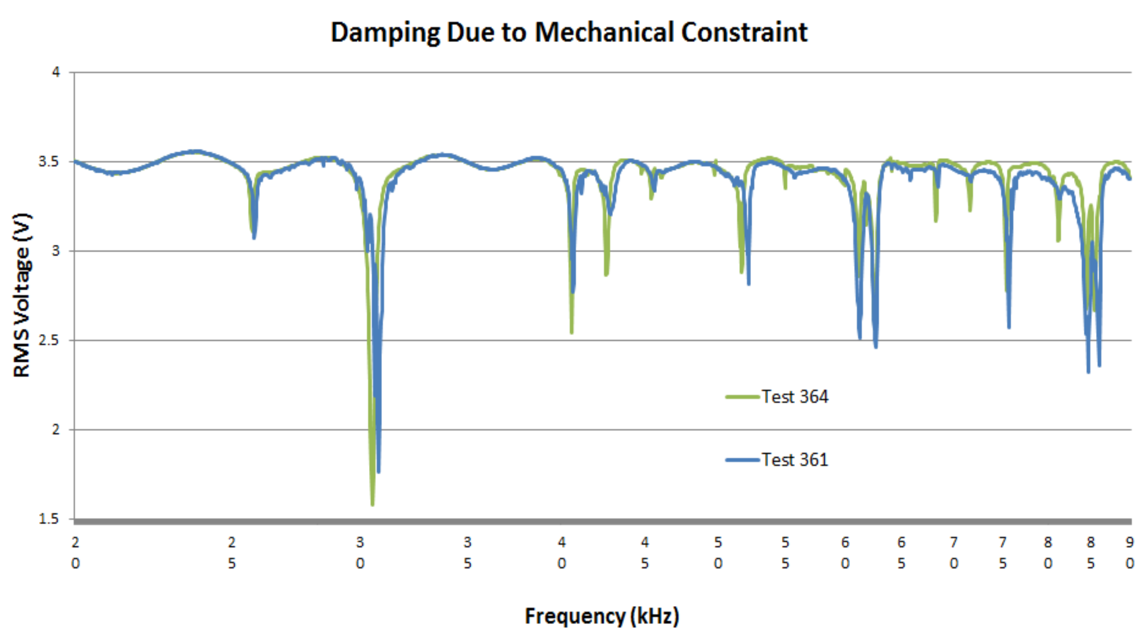

Figure **5-2**: Frequency shift with and without mounting components.

The change in the resonant frequencies can be tracked if the system is compressed slowly and monitored. Table **5-1** aligns the torque being compressed on the system to the resonant frequency and the electric potential conversion efficiency. The steel bolt securing the system and creating the compressive force begins to yield over 60 ft-lbs.

Therefore, the maximum torque being applied is 60 ft-lbs. Once all of the tests to the maximum torque were complete a final test was taken one day later to ensure the stresses were able to distribute between all of the transducers and sonotrode components since there had been previously noted that there was a small frequency shift.

Table **5-1**: Compressive Torque Applied for Test Frequency Scans.

Torque Applied (ft-lbs)	Resonant Frequency (kHz)	Efficiency (%)
0	**40.61**	62.7
5	**41.42**	10.3
10	**28.58**	12.4
15	**29.20**	31.9
20	**29.58**	35.3
25	**29.73**	38.3
30	**29.82**	41.5
35	**29.94**	45.0
40	**29.99**	47.3
45	**30.00**	48.4
50	**30.03**	52.2
55	**30.06**	53.8
60	**30.06**	54.1
60 (one day relation period)	**30.15**	54.1

As torque is applied to the stack the frequencies shift from a resonant frequency of the single stack being 40.61 kHz to the resonance of 30.15 kHz. Since there are multiple resonance points within the structure the optimal resonance point can be found by looking at the peak-to-trough change in the RMS Voltage.

To better view the shift in relation to torque the scan was performed isolating the area around 30 kHz. Figure **5-3** shows the scan isolating the peak at 30 kHz in relation to the resonant frequency that occurs there. From this scan it is apparent that the torque applied directly affect the resonant frequency. Since the piezoelectric materials function better under high compression, the results are reasonable.

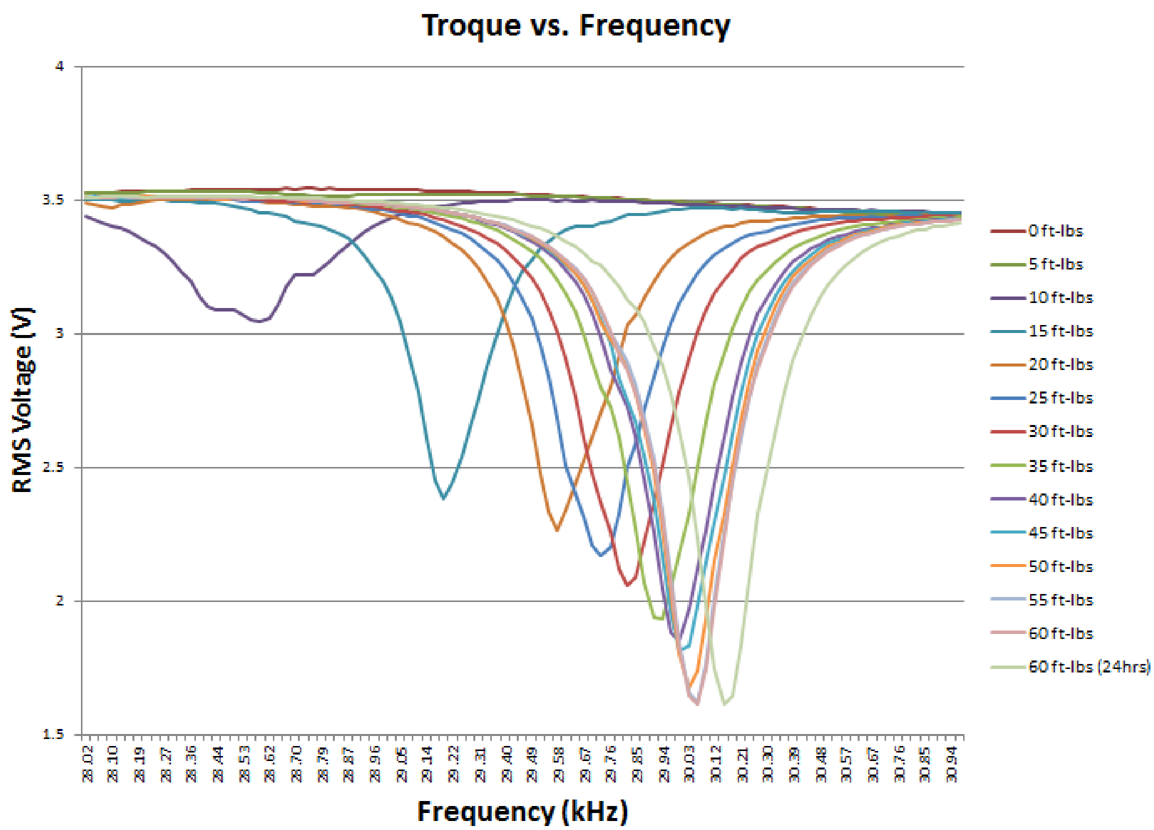

Figure **5-3**: Frequency shift isolating 30.15 kHz to show the change in frequency in relation to the torque applied, Table **5-1**.

In the understanding of mechanics of materials, when a force is applied it is not a point source but rather a distributed load. Therefore, it has different contact points in relation to different locations within the structure. Since piezoelectric materials are affected by stress applied, it is important to understand that the stress may not be the same in every location. Likewise, if a stress is applied abruptly there will most likely be a change in the distribution over time due to slow changing residual stresses within the material. PZT is known to show immediate response when a load is applied without a stress relaxation effect, therefore changes in the stack due to stress distribution may be accounted in softer materials like the copper electrodes or other sonotrode materials. Figure **5-4** shows the change in the resonant frequency once a load has been applied abruptly then allowed to distribute throughout the structure in two scenarios. The image on the left show the frequency and voltage slowly increasing while the image on the right shows the frequency increase and the voltage decrease slightly. With an increase in voltage means there is a decrease in the efficiency.

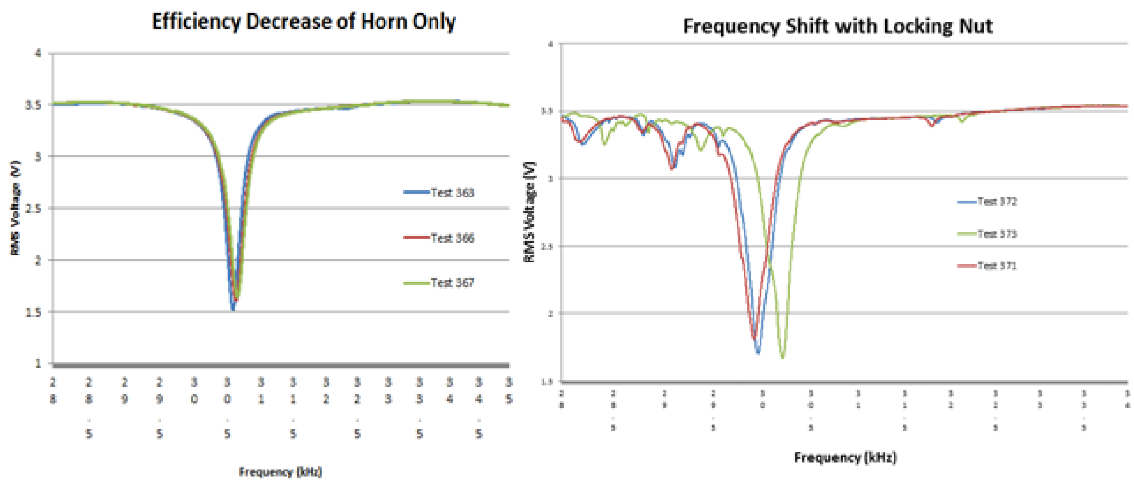

Figure **5-4**: Test comparing the resonant frequency shift of 3.2in sonotrode in relation to compression being lost (left) and a frequency shift with increased efficiency when a locking nut was used in the design (right).

In the determination of the resonance of the system there were many experiments show different progressions and concerns that must be taking into consideration. With resonance being such a key issue it was critical to ensure the pressure on the transducers was not lost due to design flaws. When comparing the resonant frequency shift overnight due to the relaxation of stress concentration points it can be evident that there is not only a frequency shift if the load was applied abruptly but also a slight decrease between test

366 and test 373 in Figure **5-4**. When the lock nut was attached to the bolt that secures and compresses the piezoelectric transducers the resonant frequency appears to be more stable and allows for the residual stress to distribute. Since there is a slight increase in the peak RMS voltage in test 367, it is believed that the nut slowly loosened as the stresses are distributed. While it was not much of a change between one day this would cause more problems if left over time and allowed for the stack to be excited. Causing ultrasonic wave to be transferred into a non-locking nut could result in the nut slowly loosening and causing a decrease and shift in the resonant frequency.

Resonant frequency allows for the most energy transfer of piezoelectric transducers. There are many components that effect resonant frequencies in ultrasonic horns and emulsifiers. As these effects are better tracked and understood properly, assumptions can be made in the simulations to more accurately represent the final design.

5.2 Simulation

Simulations give rise to different information based on what is being tested and compared. Frequencies can be isolated and sonotrode shapes can be controlled. This allows for the concepts to be testing at a steady state point as well as in time intervals. Simulations also give results in colors to allow for ease of determining differentiations.

In order to confirm concepts seen in other tests, such as resonant frequency scans, simulations are created of the designs to test for resonant frequencies, displacements and pressure changes. These simulations can validate and confirm equations and concept used to develop the sonotrode. With verification that the simulations prove real world concepts new designs can be developed with the understanding that the results will yield similar results when built.

5.2.1 Validation through Simulations

From resonant frequency scans performed, it was determined that the transducer stack resonant frequency occurs around 41 kHz. A simulation was tested to determine the resonant frequency of the stack. Figure **5-5** shows a scan of the displacement at the resonant frequency of 41.2 kHz with an electrical potential of 1V being applied (left). The model shows that the transducers are at resonance; however the rest of the sonotrode is not experiencing much displacement. A pressure acoustic model was created (center) to ensure there was no large pressure differentials within the water column. While there were small pressure changes, they were all very small and did not provide a sufficient pattern to believe there was any real resonance within the fluid. When comparing the results from the displacement model to the scan of the resonant frequency of the transducer stack (right), it is evident that the frequency of excitation for the stack confirms the findings of the displacement model. From these findings it proves that proper assumptions are being made in the model in relation to realistic findings from measurement of the resonant frequency of the transducer stack.

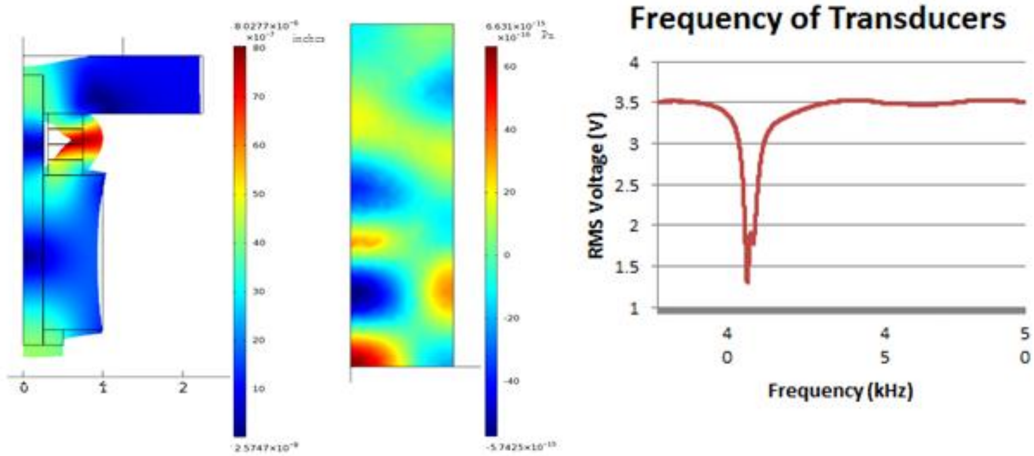

Figure **5-5**: Displacement test isolating 41.2 kHz at 1V applied to transducers (left), pressure acoustic model of water for the same simulation (center), and a resonant frequency scan of the excitation frequency of 41.4 kHz for just the transducer stack (right).

Comsol simulations provide insight into the displacements made by the working face as well as through the entire structure of the sonotrode. Figure **5-6** shows the displacement of the working face for a sonotrode designed with a flat plate front mass, similar to that of Figure **4-3**. From the simulation it can be seen that the maximum displacement is at the center of the working face. According to the scaling the maximum displacement is $x10^{-18}$ in. This correlates to the understanding of displacements of piezoelectric materials, where the displacement is not the greatest attribute of the system, but rather the entire resonance of the structure. Performing resonance scans on the sonotrode with the same design proved that the resonant frequency was 37.8 kHz. While the frequencies are not exactly the same, they are fairly close. These differences can be attributed to items like minor differences in a measurement or transducer cycle life. These findings helps to further validate assumptions made in the model and confirm calculations and understanding of resonance made.

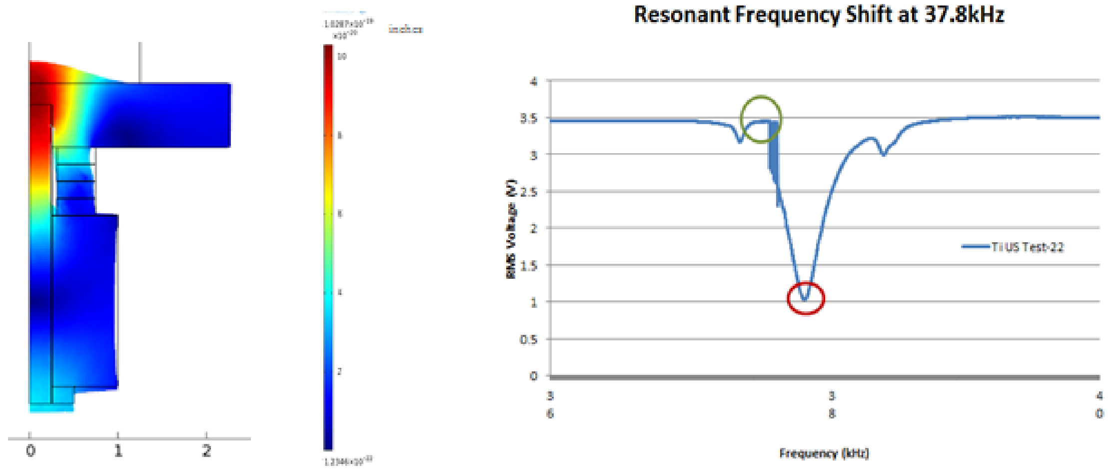

Figure **5-6**: Comsol image of the displacement at the resonant frequency of 38.4 kHz for a PZT stack with a potential of 3.5V applied and a flat plate front mass (left) as compared to the resonant frequency of the sonotrode built with same design (right).

All flat plate system was constrained using rollers in the top and bottom surface, as in Figure **4-1**, to act as though there were a bolt through the surface. When a bolt is used it is the tension from the bolt structure that drives the contact force on the top and bottom. A bolt can be used for a shear force application, however, this was not the consideration for these experiments, the bolt provided only the contact forces between the nut on the bottom and the mount it was connecting to on the top. Since the displacements are small in relation to the tolerance to the holes for the bolts there lateral force can be neglected. It is difficult in adding constraint forces from a bolt to a two dimensional (2D) simulation since in three dimensional (3D) applications there are spaced bolt hole patterns. In 2D simulation this cannot be properly simulated. However, since the major concern is in fact the inner area of the simulation a generalized roller constraint can be used since it would only cause slight variation on the outer edge of the front mass.

To complement the results for the displacement of the sonotrode in Figure **5-6**, a fluid acoustic model was developed to test the pressure gradients within the fluid. For this simulation water was used as the media being transmitted. The right image in Figure **5-7** show that there are multiple points of high pressure change within the media in which cavitations could occur. When compared to the displacement of Figure **5-6** the first pressure change occurs directly above the maximum displacement point. This logically makes sense since it would be expected to see a pressure change where large amounts of displacement occur. A foil test was performed to determine the range in which cavitation occurs, shown to the left in Figure **5-7**. Through cavitations the foil will be broken apart in the cavitation field which can be determined to be the range in which the ultrasound is most effective. The foil test performed using one ultrasonic plate with a resonant frequency of 37.8 kHz at a 25% gain using 48W of power. There are areas in which the foil has been completely removed, as well as areas where there is pitting from the cavitation. The evidence of cavitation occurring in locations with high pressure gradients as anticipated with the Comsol model was validated. The effective distance the cavitation occurred was about 3/4 of an inch from the working face. The shape of the cavitation field appears to be parabolic in nature, similar to that of the model.

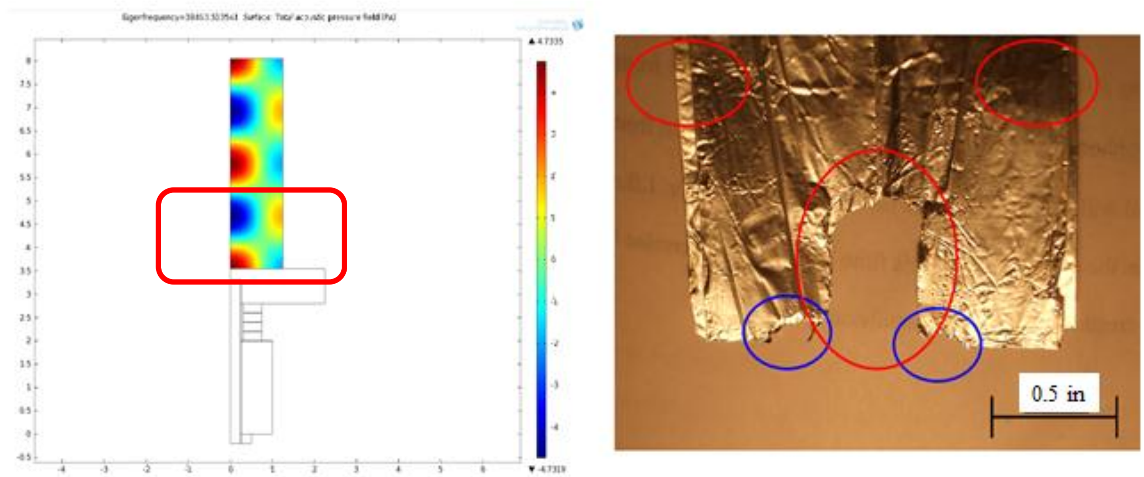

Figure **5-7**: Fluid acoustic model show pressure gradients within a water column with a rectangle highlighting the area of pressure change near the working face (left) as compared to the results of a foil test showing the regions of material removed or affected by cavitation, as circled (right).

The resonant frequency to create a pressure differential capable of creating meta-stable cavitations proved to not shift greatly between the oil or water simulations. When the water column was replaced with an oil column of the same size, shape, and constraints the model resulted in almost identical pressure differentials.

With positive results from the flat plate test, other geometrical shapes were considered. Since the transducers are annular in shape, cylindrical shape front masses allow for the shape not to restrict the overall direction of the wave front. Figure **5-8** is a simulation using a cylindrical front mass to test the concept of containing the wave form better. The simulation was iterated many times testing different mounting locations on the front mass cylinder to achieve maximum displacement of the working surface. Likewise several iterations of the voltage were tested to determine the maximum displacement in relation to the voltage used. The maximum displacement was achieved with a fixed constraint located 0.6 inches from the working face and a voltage of 3.5V.

Another iteration that showed potential for having large displacement was with an electrical potential of 5V, however the maximum displacement occurred at the outer edge of the cylinder rather than near the center. Since the model is using the concept of linear elastic body as part of the model, the best results are in small displacements in the elastic region of the material. This corresponds to seeing better results at lower voltages rather than at higher ones.

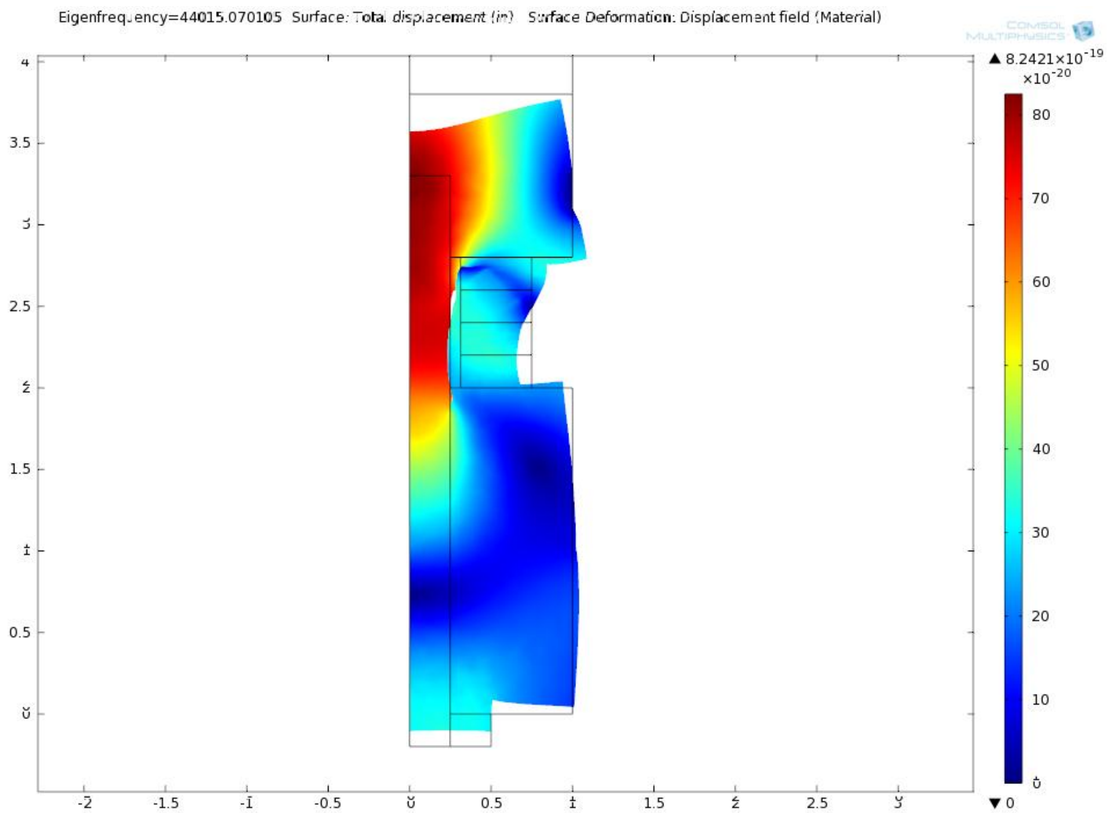

Figure **5-8**: Cylindrical horn with a resonant frequency of 44.0 kHz tested with a voltage of 3.5V and a fixed constraint located on a line placed on the cylinder's outer wall, 0.6 inches from the working face.

A resonant fluid acoustic model was also created to accompany the displacement model. Figure **5-9** is the pressure acoustic model that accompanies Figure **5-8**. It shows again that there are several locations in which there are multiple pressure differentials.

The pressure acoustic model features a 2/3 view of the results show ellipsoid pressure changes.

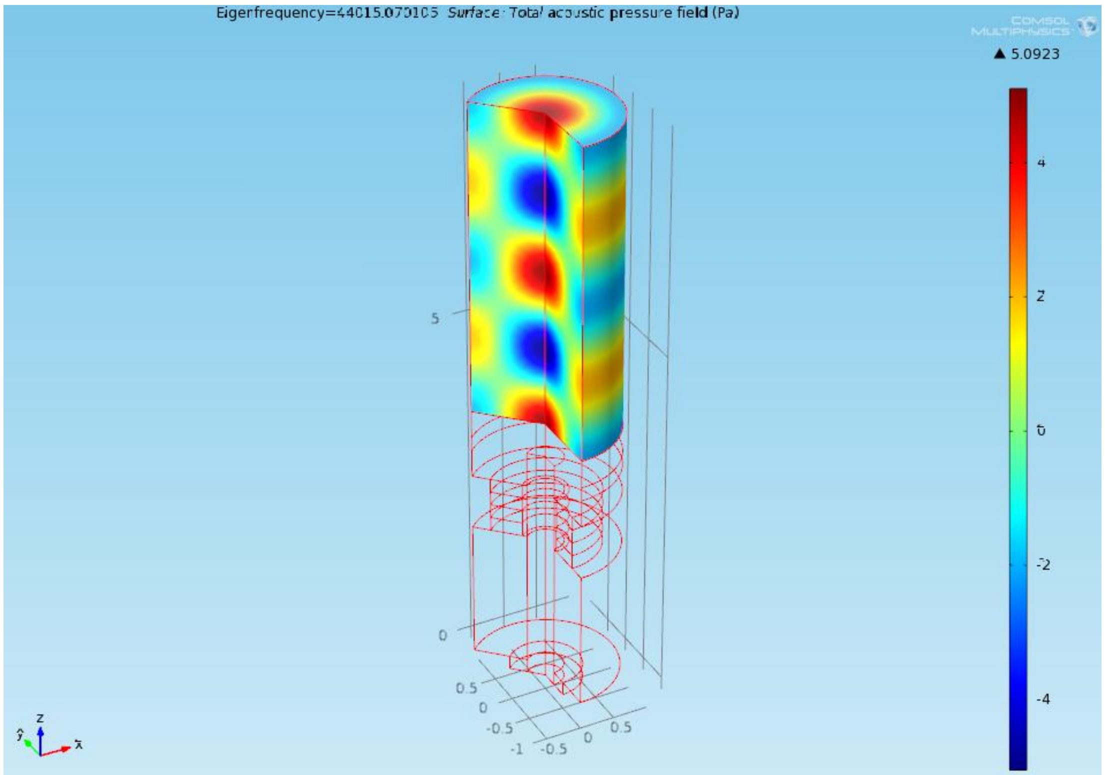

Figure **5-9**: Fluid acoustic model showing pressure gradients within a water column with a maximum pressure of 5.09Pa with an overall pressure change of 10.1Pa between positive and negative pressure fields.

A simulation was created using the length calculated for the 1/2λ ultrasonic horn. Figure **5-10** is a model developed using the length determined for the horn as well as a back mass of a length to that of the 1/4λ, since at 1/4λ there should be a nodal region in which there is the minimum displacement. For the model a fixed constraint was placed at the 1/4λ location on the horn to allow for mounting. This point proved to be a sufficient location to apply a constraint in order to not damp the maximum displacement. However, two other locations near the transducer interface and the working face proved to also yield useful mounting locations. A pressure acoustic model proved similar to others in the pressure gradient locations in relation to the other fluid models.

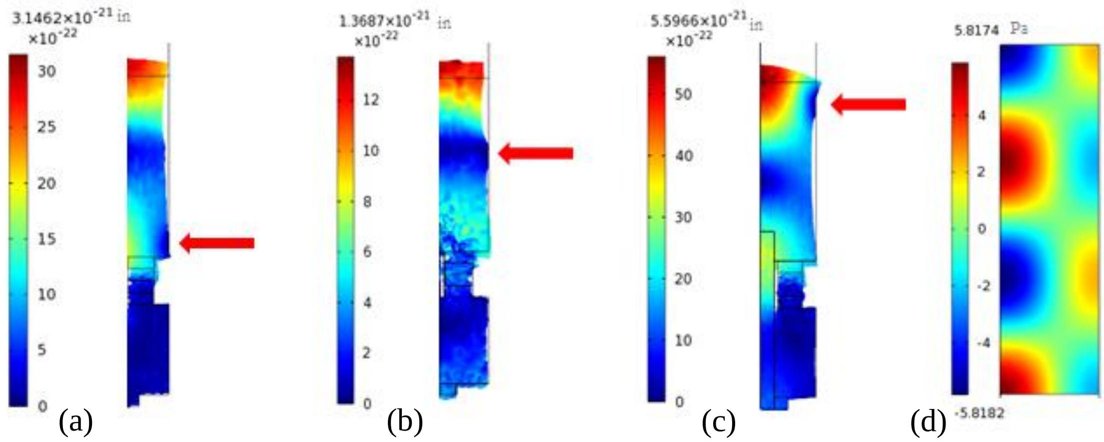

Figure **5-10**: Displacement for the 1/2λ ultrasonic horn with 3.5V applied and a resonant frequency of 40.5 kHz., (a) shows the mounting location near the transducer interface, (b) is a mounting location near the 1/4λ node, (c) utilizes the mounting location near the working face, (d) is a representative pressure acoustic model which stayed fairly consistent in locations and pressure changes between mounting locations.

With successful modeling of static conditions using different horns and configurations achieved, the next step was modeling simulations that incorporate fluid dynamics. Since fluid dynamics affects both resonance and the cavitation pattern, simulations were created to test different dynamic scenarios to determine the changes found in the sonotrode. Figure **5-11** shows the fluid flowing perpendicular to the working face of an ultrasonic emulsifying plate. The plate was developed under the same conditions as Figure **5-6**. The model shows that the resonant frequency shifted with the application of allowing internal flow through the stack. A displacement change can also be determined between increasing flow rates. In order to maintain the same displacement more power must be used as the flow rate is increases.

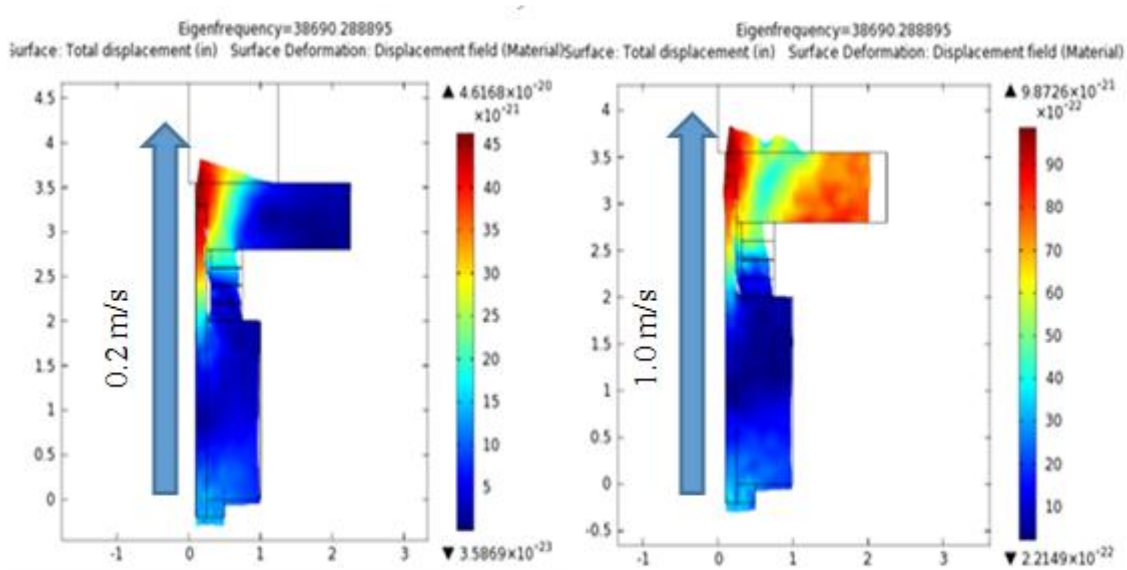

Figure **5-11**: Comparison between displacement change in low fluid flow (left) and increased fluid flow (right) at 38.6 kHz with flow normal to the working face.

When fluid is passes parallel to the working face, there are more considerations to be taken into account. A fluid model was developed to represent a fluid passing parallel to the horn surface. The same emulsifier criterion, shown in Figure **5-8**, was used for the model. Fluid was passed from the top of the fluid cavity down toward the working face and out via a side outlet. Figure **5-12** shows similar results to Figure **5-11** in relation to decreasing displacement as flow rate increases. The simulations also proved that the displacement is not affected as much as when the flow passes across the working face as opposed to through the sonotrode.

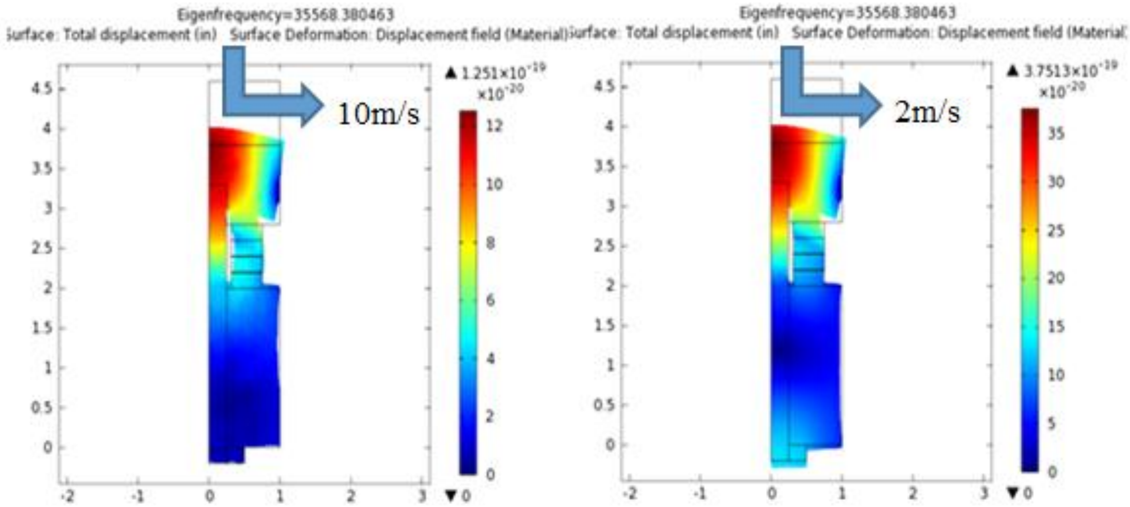

Figure **5-12**: Displacement model showing that with increasing flow rate across the displacement surface the maximum displacement decreases.

With sufficient models, cavitation fields can be estimated. Models allow for a general understanding of shapes and designs as a base for testing and experimentation. Models also strengthen concepts developed early and can visualize phenomenon occurring. While these simulations prove many concepts there are still variations between models and physical measurements. Likewise, correlations between the fluid flow and its effect on the pressure acoustic model could not be proven. Therefore further simulations must be performed in order to help develop future concepts.

5.3 Biofuels

5.3.1 Emulsions

The sizes of the micro-bubbles of methanol in the emulsion have many benefits when considering the reaction of the biodiesel. It is critical to ensure the bubbles are small and evenly distributed within the emulsion. Images of the emulsion can be taken to show the size of the micro-bubbles. It has been proven that the bubble size is directly affected as a result of the frequency used [**14**], [**15**]. From these results, emulsifiers were developed to try to isolate the frequency range between 30 kHz and 45 kHz. Using simulation results and basic calculations, horn concepts were developed and tested.

For initial testing of the Kropf Multi-Energy Optimization Process, a bench reaction system was created utilizing a multimode microwave, 1 foot glass pipe, and single plate emulsifier with the capability of passing the fluids across the working face, shown in Figure **4-3**. The system proved to be capable of creating a standing wave within the reactor. Figure **5-13** is evidence of the standing wave created within the reactor.

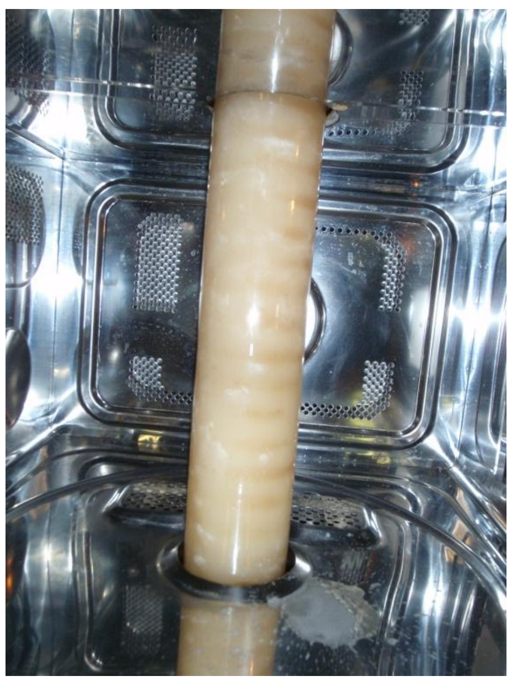

Figure **5-13**: Image of evidence of a standing wave within the reactor [**34**].

While a standing wave could be created, the power levels necessary cause extreme heating and fracturing of the PZT disks. The reactor was capable of producing fuel within ASTM specifications for free and bound glycerin, however with the high power necessary to create the standing wave; the cycle life of the transducers was greatly decreased causing a redesign of the reactor to be necessary.

With a redesign of the reactor, the opportunity for a scale up of the ultrasonic system was created. The system was upgraded to a pilot scale reactor capable of producing fuel at 10 gallons per hour. To better achieve a standing wave and accommodate for the increased flow rate, an emulsifier was developed using two ultrasonic emulsifiers and a 4 inch glass pipe. Figure **5-14** is an emulsifier capable of creating stable cavitation emulsions at a flow rate of 10 gallons per minute.

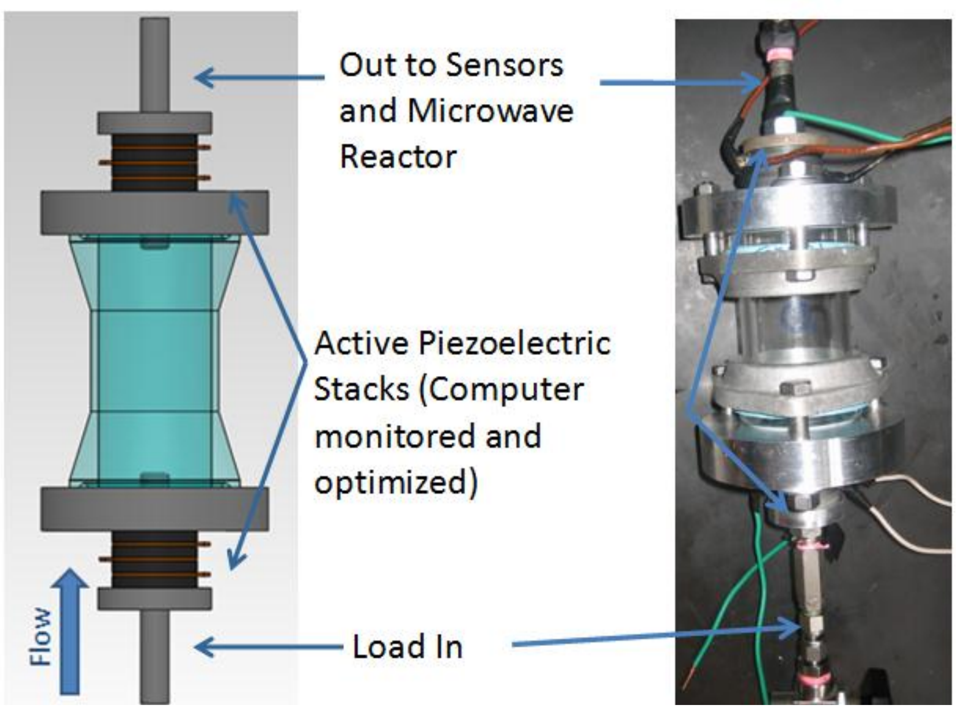

Figure **5-14**: Computer model image and photo of emulsifier capable of 10 gallons per hour with flow perpendicular to the surface.

With anticipations of scaling to higher flow rates, advances were taken to consider an emulsifier that combines static mixing with areas of cavitation. An emulsifier was developed to perform such a task. Figure **5-15** is a model and final component developed. The triangular components were developed to allow for static mixing as the fluid passes over. Similar to the concept of cavitation occurring at the stagnation point in impellers, the circles show the anticipation points of cavitation. The system featured the concept of thin plates for the transfer of the ultrasonic energy rather than a horn since the concept was to see if a thin plate would have better transmission than the losses due to damping in a horn.

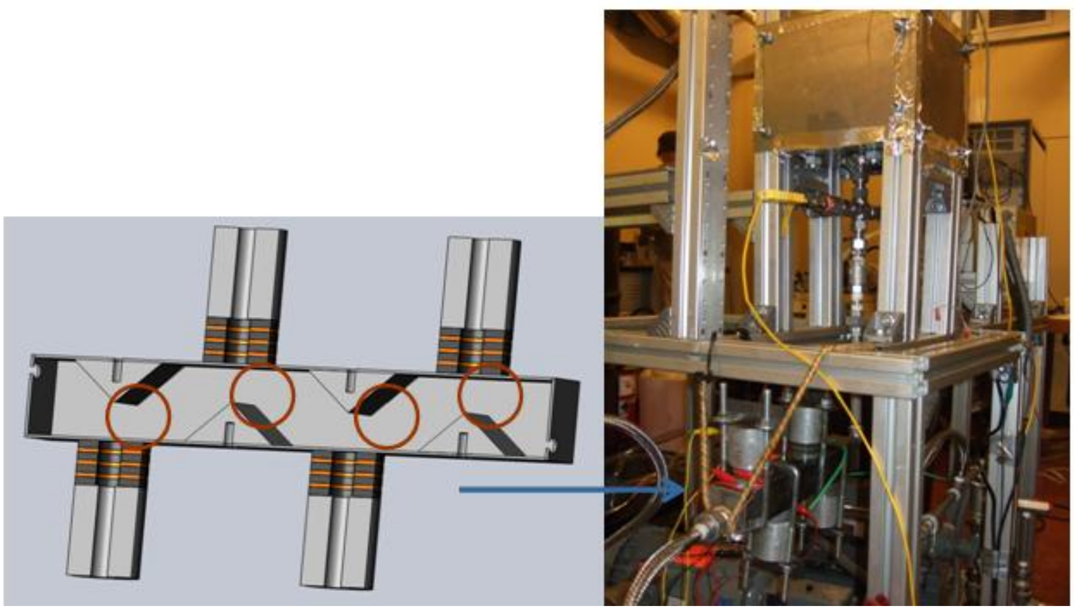

Figure **5-15**: Computer design of an emulsifier combining static mixing and areas of anticipated cavitation, circled (left) and its integration into the biodiesel pilot plant (right).

While the idea of the combined static mixer and ultrasonic emulsification unit appeared to be a feasible concept, there were complications with the design. Since the concept involved a thin plate design when the PZT transducers were compressed, the plate failed under the force. This prevented the system from functioning as designed.

Utilizing the concept of static mixing and continuing the idea of scaling up to commercial scaling a new emulsification unit was developed. The system involved separate chambers where ultrasound is applied. With varying sizes between chambers, the fluid increases and decreases speed helping to create static mixing. With increasing camber sizes the fluid slows in speed and allows for cavitation to occur. The depth of the chamber is governed by the results from the determination of the cavitation zones in which the effective range of cavitation occurs within about 1/2-3/4 inches over the center of the sonotrode. Figure **5-16** is the engineering drawing for the new static mixing, ultrasonic emulsifier.

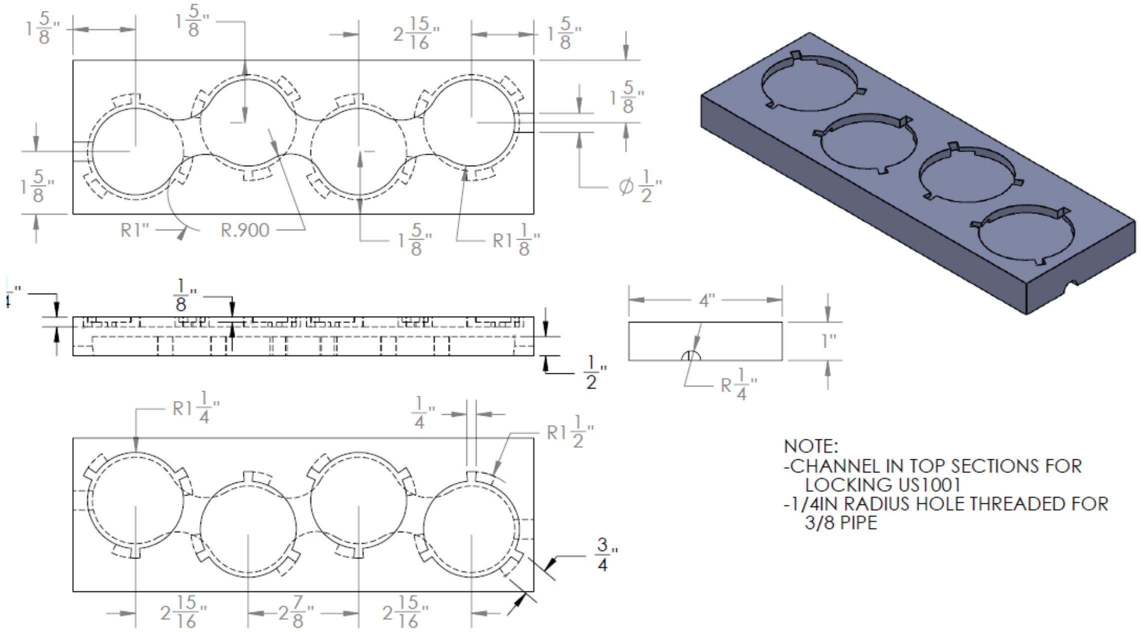

Figure **5-16**: Engineering drawing of concept for one side of the ultrasonic emulsification chamber.

The design can take high temperature and pressure as is expected in the Kropf Multi-Energy Optimization Process. To address the complication of the compression needed for the transducers, a separate sonotrode assembly was created. Figure **5-17** shows the engineering drawings for the sonotrode assemble featuring a 1/2λ horn, 1/4λ back mass, transducer stack sealed from environmental conditions, and a hexagonal head for ease of applying compressive forces. The system is threaded to allow for ease in assembly. The sonotrode connects to the emulsifying chamber via feet which insert into the chamber and are secured by set screws.

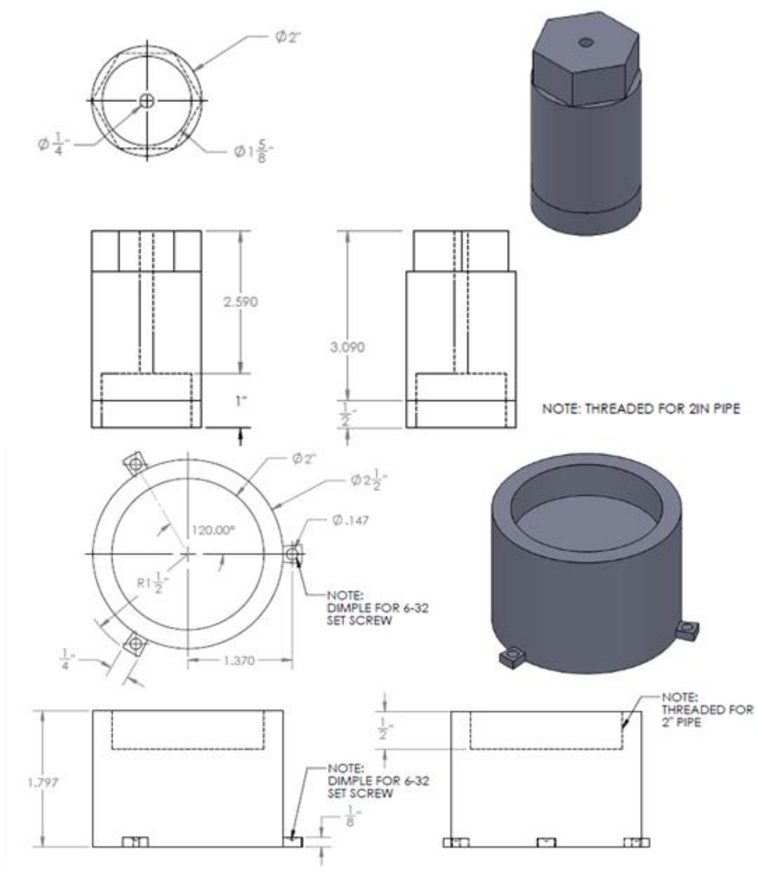

Figure **5-17**: Engineering drawings for sonotrode assembly utilizing 1/2λ horn, 1/4λ back mass, transducer stack sealed from environmental conditions, and a hexagonal head for ease of applying compressive forces.

Separate sonotrode attachments allow for the ability to increase emulsifying power if necessary as flows increase. It also allows for the ease of replacing a transducer set in the event of a malfunction. Sonotrode systems can be added or removed to accommodate various flow rates and materials. Figure **5-8** supports the development of the horn technology through displacement and Figure **5-12** validated the development of cavitation within the emulsifying chamber under a fluid flow condition.

5.3.2 Percent Reaction Completed

There are many complications that can arise to prevent the completion of the biodiesel transesterification process necessary to produce quality biodiesel. Gas chromatography analysis is one way of determining the level of free and bound glycerin in the final product. Free and bound glycerin determines the quality of the final product [**11**]. Using this understanding, the system can be evaluated for the percent of reaction completed [**32**]. Utilizing a flow rate of 10 gallons per hour in the Kropf Multi-Energy Optimization Process with a single mode microwave and emulsion chamber utilizing two ultrasonic emulsifiers, shown in Figure **5-14**, a percent reaction completed of 99.806% with less than 0.2% catalyst used. This validates the concept that the emulsion had micro bubbles small enough for the use of microwaves to stimulate the reaction.

5.4 Metal Cleaning

5.4.1 Emulsions

Scans of the liquid byproduct, a lyophobic emulsion, can be performed to determine the stability of the system. Optical diffraction tests can be made to determine the size and quantity of the particles. Many of the diffraction tests gave distributions with multiple peak points and large distributions, shown in Figure **4-4** . As time increased and the amount of soap decreased the distributions were larger and less centralized around the mean particle size. Also as the time of emulsification increased the mean particle size remained closely the same, but the distribution tightened around the mean size. This is consistent with other ultrasound test performed where emulsion time is compared with distribution size [**14**], [**15**], [**32**]. Unfortunately due to the age of the computer recording data for the Horiba the distributions could not be removed and shown. The byproduct necessary to develop a distribution is shown in Table **5-2**. The table compares the time of emulsification and percent soap used with the necessary amount of byproduct used to take a reading at both 1.5 and 24 hours. From this table it can be seen that with both the use of a surfactant and an increased emulsification time, more stable emulsions can be created.

Table **5-2**: Comparing between emulsion time and soap used to the amount of byproduct necessary to achieve a distribution result.

Test (emulsion time, soap added)	**Byproduct (mL)**	
	1.5hr	24hr
5mins, 0.2% Soap	30	150
10mins, 0.2% Soap	25	125
15mins, 0.2% Soap	25	75
5mins, 0% Soap	200	N/A
10mins, 0% Soap	150	N/A
15mins, 0% Soap	75	N/A

From the scans, the average mean particle size was recorded. Figure **5-18** is a plot of the average mean particle size in relation to the time the metal chips were emulsified. The test also compared the amount of surfactant used to assist in cleaning. It may be seen from the results that while the mean particle size varies in relation to the time of emulsification, the use of a surfactant does not greatly affect the mean average size. The amount of surfactant did alter the distribution of particle sizes. When the surfactant was used, the distribution was more centralized around the average size; however, with zero detergent the distribution had a greater range and more liquid byproduct was necessary to determine a result.

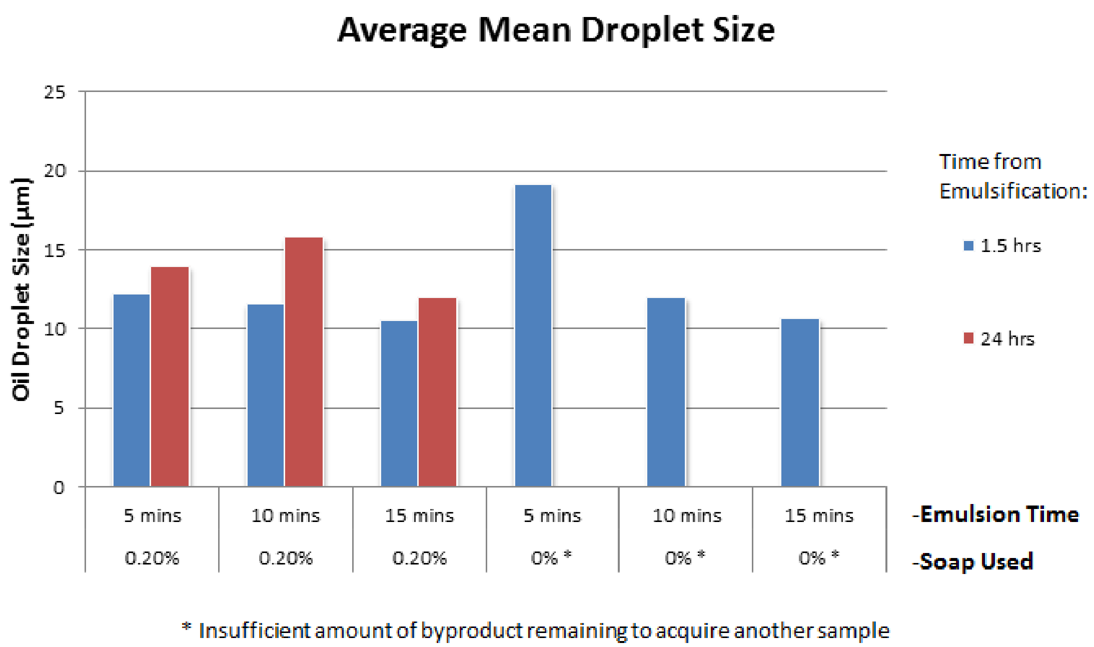

Figure **5-18**: Average mean particle size recorded compared to the time of ultrasonic emulsification.

5.4.2 Emulsion Degradation

As time progresses, the micro particles of oil begin to agglomerate and become larger. Tests were performed to measure both in time and size. Optical diffraction tests were made to measure the change in size of a micro bubble after 24hrs. In these tests, it was evident that not only did the mean average of the bubble increase in size but the distribution of size also shifted and more byproduct was necessary to measure the average size, shown in Table **5-2**.

Degradation was also assessed through longer time tests in which the oil was allowed to emerge from the water and form a separate oil film. Oil film growth was monitored over several weeks to track the increase in both size and clarity of the emulsion. As the emulsion degrades, the water clarity increases. From this test it can be noted that there is not much change in growth after 5 weeks. Likewise, the difference between the uses of a surfactant, i.e. soap, does not substantially change the amount of oil removed.

5.4.3 Carbon Deposit Results

Once the chips have been run through the ultrasonic field, their cleanliness may be determined from an analysis of their carbon contents. With the metal chips being separated by the difficulty to clean, the chips were cleaned using an ultrasonic emulsifier. The amount of soap used depended on the type of chip to be cleaned, as shown in Table **4-1**. Times of ultrasonic emulsification as well as fluid parameters were changed to determine the most effective cleaning strategy. Once the metal chips have been cleaned they can be tested for the remaining carbon content left on the surface of the chips. This information can then be used to determine if the amount of carbon remaining on the surface is within levels low enough for further recycling. Figure **5-19** shows the percent of carbon remaining on chip samples as compared with the time of emulsification. The solid line represents the maximum percent of carbon allowed for the chips to be processed to bar stock. The parameters of the tests varied from static scenarios to fluid flow with periodic mixing.

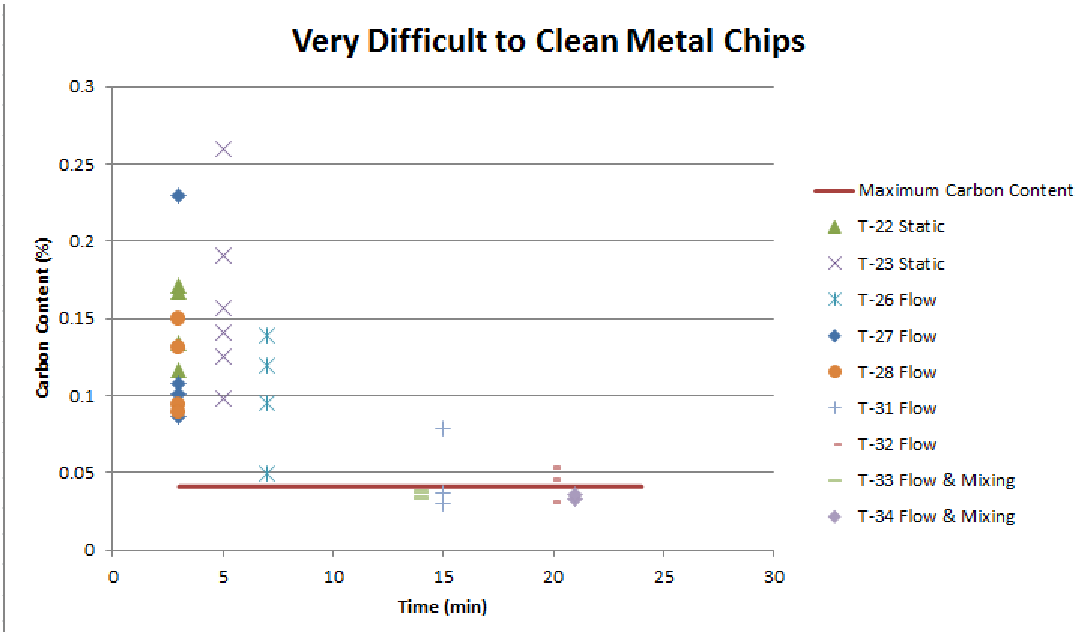

Figure **5-19**: Percent of carbon and time of ultrasonic emulsification plotted with varying testing parameters of static fluid, low fluid flow and low fluid flow with periodic mixing for hard to clean metal chips.

From Figure **5-19** it can be seen that the best cleaning results allowed for the chips to move through the cavitation field while fluid was passed over the chips to remove oil and prevent re-depositing. Test 33 and 34 confirm this concept. Since the chips are too heavy to be mixed from the fluid flow and ultrasonic energy being transferred to them, periodic mixing was employed to move the chips back within the cavitation zones. From these tests, it can be determined that the minimum amount of time to clean the chips with soap content, temperature, and fluid speed held constant is 14 minutes for hard, or very difficult, to clean chips.

Measuring the carbon content of the chips at varying conditions allowed for the maximum allowable carbon content to be met. This trend proved to be consistent for all chip types, however the time for emulsification decreased as the chips were deemed easier to clean. Using a standard set for the most difficult chips allows for sorting of chip type to be unnecessary. With the information and trends determined development of designs for an industrial have begun. Trends also determined in the biodiesel production emulsifiers for the pilot plant can be applied to concepts for the metal cleaning pilot plant to decrease time to production.

Chapter 6

Conclusions and Future Works

The findings from the results are reiterated as well as the objective. The findings will be compared to what can be proven and what is an assumption. From these findings future works and applications can be developed.

6.1 Review of Objective

The goal set to be achieved is development of ultrasonic emulsifiers to create lyophobic emulsions in flow conditions. This is a large and complex task and for it to be achieved requires the optimization of many systems variables and disciplines. The focus of this study was to provide insight into the development of several methods for achieving this goal.

6.2 Review of Findings and Contributions

The range and effectiveness of ultrasound in liquid is highly affected by many factors. Resonance of the structure, shape of the sonotrode, fluid type, and fluid flow all become factors that must be taken into consideration. Through simulation, testing, and experimentation a better understanding of how these factors work become clearer. To create a meta-stable lyophobic emulsion, it becomes very important to properly design and calibrate systems to achieve the highest efficiency of ultrasound consumption. These emulsions can be used for many applications, but for this study they were specific to metal chip cleaning and biodiesel production. While ultrasonic emulsions are not a new concept, the applications are considered fairly novel to their industrial partners.

Simulations proved to be key in understanding the displacement point in relation to proper mounting locations. It helps to determine not only resonant frequencies for the entire system but also show resonance of the transducers. They give insight into locations where cavitations could occur. This feature was later validated through experimentation. Once fluid flow is induced, it becomes more difficult to directly determine where cavitations happen, but flow can be correlated with changes in displacement in the working face.

Resonance testing proved to be substantial to both determining loss of ultrasonic energy due to mounting locations, resonance shift as torque is applied, and shift due to distribution of stress within the transducer stack and resonant body. Resonant frequency scans also ensure the emulsifier is matched with the proper system to yield positive results.

Development of high efficiency, industrial emulsifiers proved to be most beneficial from development work in production of biodiesel through the Kropf Multi-Energy Optimization Process. New concepts were designed and validated to handle high capacities with positive results. The concepts proved that cavitation could be created and controlled with increased fluid flow.

Foil tests performed in water confirmed the findings from simulations of the location and shape of cavitation fields. By moving metal chips through a cavitation field and exposing them to ultrasonic emulsification, they could be cleaned of oil and debris.

Through optical diffraction and monitoring the growth of the oil film, the stability of the emulsion can be determined and the amount of oil removed can be determined.

6.3 Future Works

Further work in this subject area will involve development of several hypotheses and theses, mainly those of Kropf and Verlinich [**14**], [**15**], [**34**]. This work will move from the progression of bench top testing to pilot scale models of systems with the ultimate goal of making it to commercialization. In the push to develop systems capable of handling industrial scale flows and use there are many developments that must first be achieved.

- Refinement of simulation assumptions to better represent physical conditions
- Advanced simulation models adding incorporating flow with changes in pressure and moving toward three dimensional analyses.
- Better understanding of cavitation occurrences with relation to varying flow test regimes.
- Further studies into the agglomeration of micro bubbles as a function of time.
- Progressive development of commercial ready industrial ultrasonic emulsification units capable of sustaining high cycle life.

6.3.1 Alternative Applications

As a better understanding emerges about how to gain the most efficiency out of materials and structures, there will be more uses for the technology. Diversifying the application of the technology expands for new challenges and better understandings of what is able to be achieved. While currently focused on the transesterification process and metal cleaning, other applications in which high levels of mixing are desirable would be suited for the technology. The chemical industry has invested much time and energy into the use of ultrasonic mixers, this technology could be useful to many of their processes when considering moving from labs to higher yields. The food industry could also benefit from the process since many emulsion books are related to food sciences.

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Appendix

LabVIEW Programs

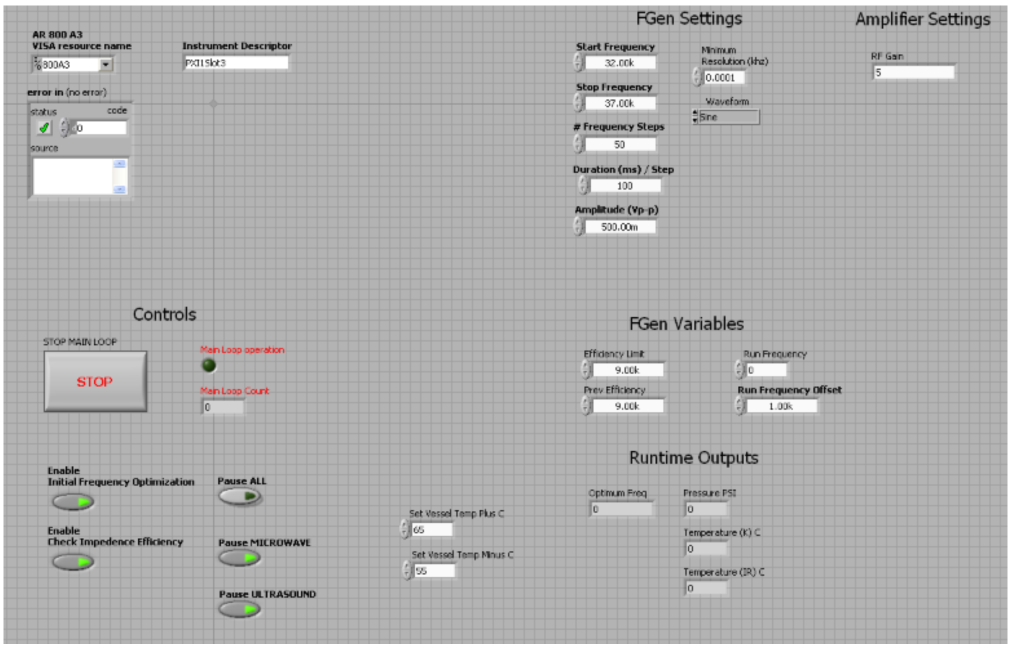

Figure **F-1**: GUI for controlling frequency optimization and monitoring temperature.

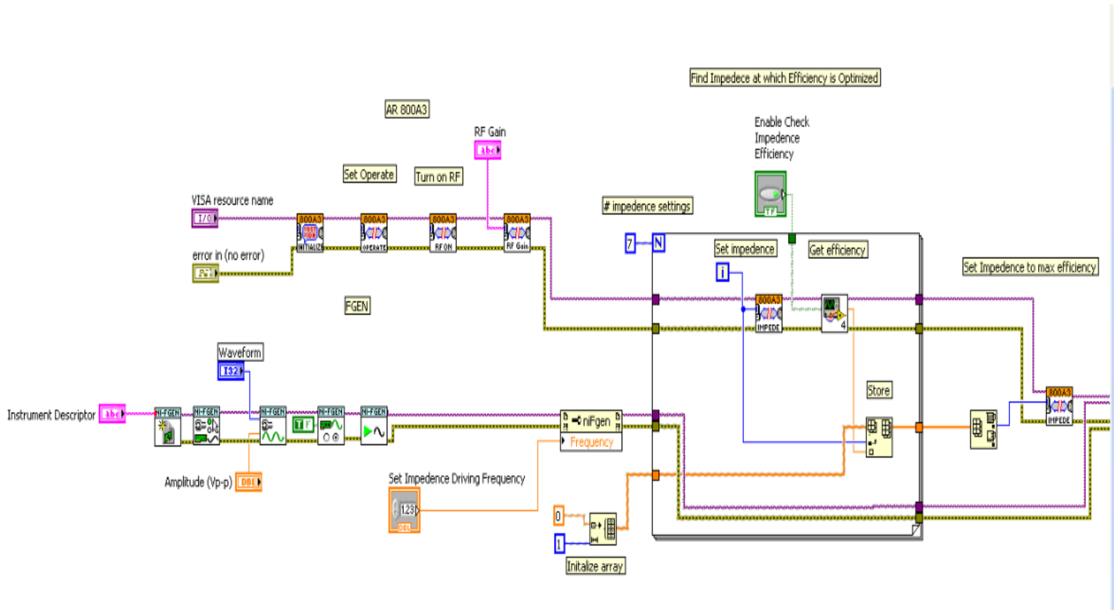

Figure **F-2**: Part 1 LabVIEW program for frequency optimization and temperature monitoring.

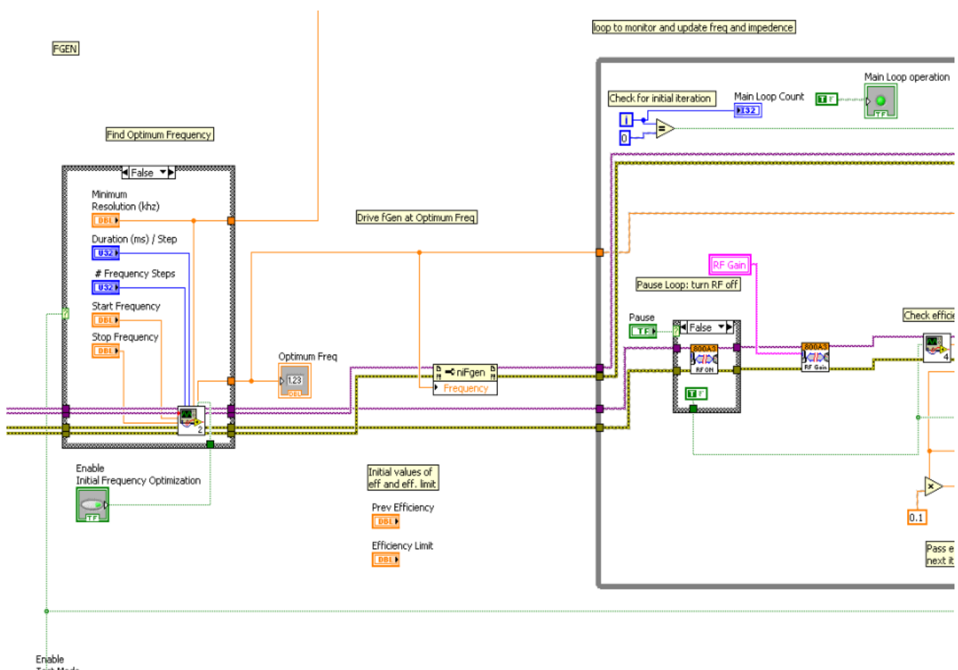

Figure **F-3**: Part 2 LabVIEW program for frequency optimization and temperature monitoring.

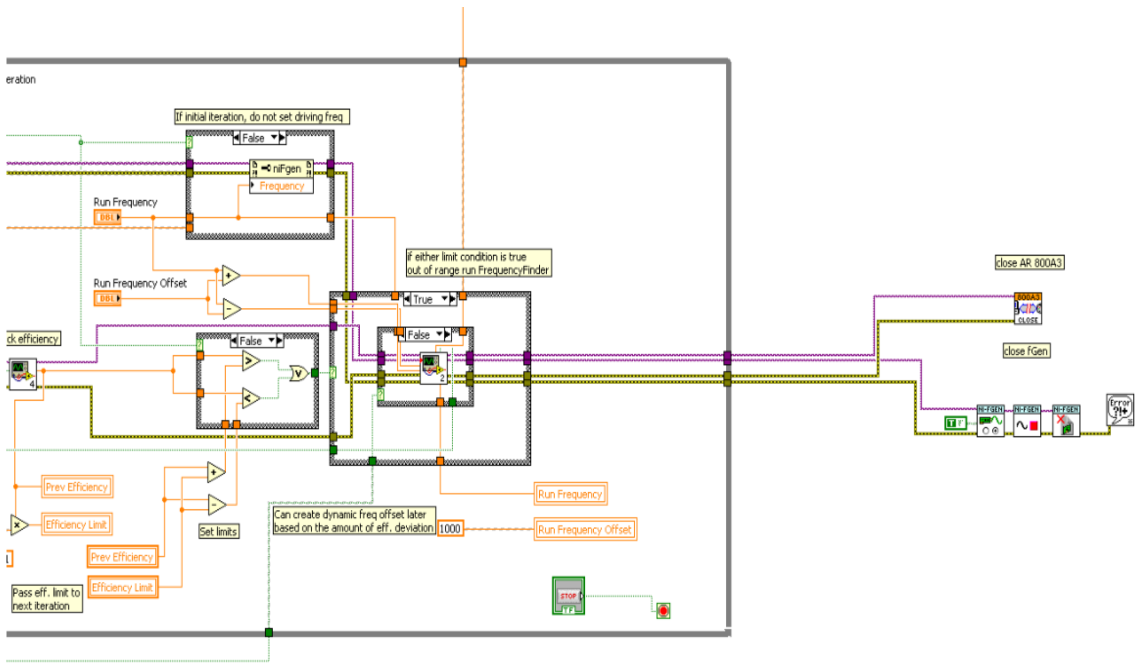

Figure **F-4** Part 3 LabVIEW program for frequency optimization and temperature monitoring.

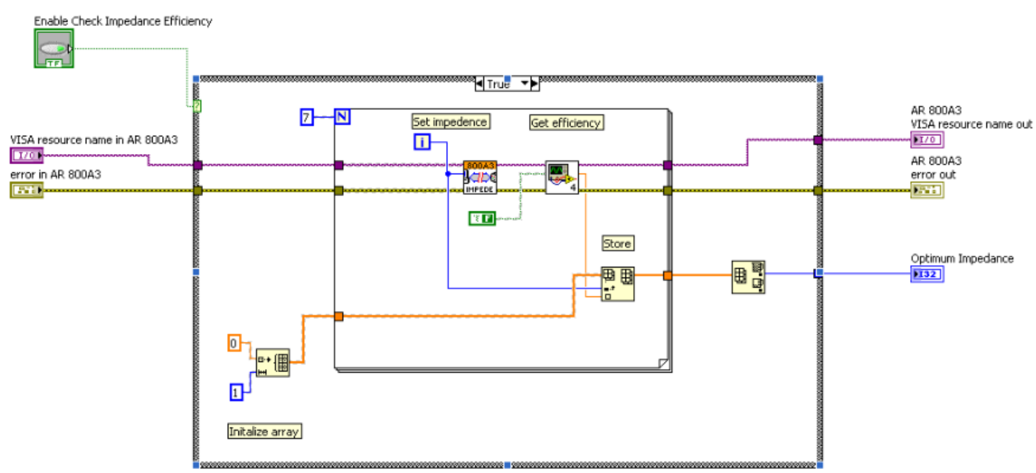

Figure **F-5**: LabVIEW model of impedance check.