The Pennsylvania State University The Graduate School College of Engineering

# A COMPARISON OF SPEED OF SOUND AND ACOUSTIC NONLINEARITY PARAMETERS AS BIOFUEL CHARACTERIZATION TECHNIQUES

A Thesis in

Engineering Mechanics

by

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Submitted in PartialFulfillment of the Requirements for the Degree of

Master of Science

May 2010

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## ABSTRACT

Quality is of paramount importance in the biofuel production community. The current method for identifying the nature of a biodisel involves the sometimes expensive and time consuming technique of gas chromatography. Two possible indicators of quality are the speed of sound and acoustic nonlinear parameters. This study presents the efforts in establishing an automated setup and procedure to measure the nonlinear  $\frac{B}{A}$  parameter and the speed of sound for a variety of materials. The nonlinear parameter measures the distortion of an acoustic wave as it travels through a medium. The setup utilizes through transmission and digital signal analysis while carefully compensating for the transducers' frequency response. Finally, results will be presented to examine the reliability of the acoustic nonlinear parameter and speed of sound measurements as possible biodiesel quality indicators.

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## Acknowledgments

This work is supported by the Pennsylvania Soybean Board. I thank Penn State Biodiesel Group (Ryan Johnson, Joseph Perez) for Biodiesel Samples and Gas Chromatography Analysis. I would like to give many thanks to Ivan Kuletz for his help with the editing and formatting of this thesis. I would also like to thank labmates John Mulry, Dr. Matthew Kropf, Manton Guers, Brian Reinhardt, and David Parks for their time, advice, and support with this project.

## Dedication

To the memory of Hyeong Sick Ju. Thank you for your patient help with the world of nonlinear acoustics.

#### 1. INTRODUCTION

The need for a low-cost, real-time method for evaluating the phase and quality of a fluid in the chemical, food, and water quality industries is pressing. In particular, the biodiesel industry is faced with quality as the paramount issue to broad scale adoption. Current American Society for Testing and Materials (ASTM) specifications require producers to conduct extensive analytical tests, often requiring procedures and equipment too expensive for the small producer. For example, the current method to identify the extent of completion a biodiesel sample is processed, it is compared to Biodiesel Specification ASTM D 6751-8, D 6584 uses Gas Chromatography to determine the percent free and total glycerin. This procedure requires extensive capital investment in laboratory equipment and staff or expensive outsourcing to analytical labs. Alternative methods are of interest if they allow the producer to make quality measurements on a regular basis with less cost.

A possible indicator of the quality of biodiesel samples is an ultrasonic measurement of the nonlinear parameter,  $\frac{B}{A}$ . Another potential indicator of sample quality is the speed of sound measurement. That is what this study aims to determine.

Acoustic waves are usually approximated to travel linearly though a medium. Because the repelling forces between molecules is usually stronger than the compressing force of the wave, the high pressure areas end up traveling faster than the low pressure areas. This causes the crest of the wave to catch up to the trough and forces some of the energy initially carried at the forcing frequency to be move into the higher harmonics. Some theorists have attempted to predict the nonlinearity of a substance with mathematical models. It has been found that the  $\frac{B}{A}$  value for a gas obeying the perfect-gas law is  $\frac{B}{A} = \gamma - 1$  where  $\gamma$  is the ratio of specific heats,  $\frac{C_p}{C_v}$  for the gas.[18]

Some theorists have attempted to predict the values of  $\frac{B}{A}$  in liquids. [23] [32] [14] [36] These simulations were based on the idea that intermolecular potential energy is the dominating factor in Mie potential parameters. The majority of these studies [32] [14] [36] modeled the molecules as a group of hard spheres. Their results turned out not to agree with experimental data. Sharma recently incorporated thermoacoustic data into the models of Hartmann, Madigosky, Endo, and Sarsikov and obtained a good agreement between experimental results and his predictions.[38] Aside from these theoretical predictions, Ballou found a linear relation between  $\frac{B}{A}$  and reciprocal sound speed. Although some theoretical foundation has been mentioned by Hartmann, [23] this law remains uncertain, given the huge scattering of data. It has already been suggested [19] that a nonlinear relation seemed more appropriate between these variables and that each family of chemicals should have its own trend.

The  $\frac{B}{A}$  parameter of a liquid can be measured in several different ways. The thermodynamic method measures the change in sound speed as a function of pressure and temperature changes and was first introduced in 1965 by Coppens, et. al. [9] The isentropic phase method also monitors the change in sound speed but during a sufficiently rapid and smooth pressure change in a process that is considered thermodynamically reversible. [24] [13] [41] [37] [16] It has been shown that the precision with which  $\frac{B}{A}$  can be measured is 5% for the thermodynamic method and 4% for the isentropic phase method.

The third method is the one used in this investigation and is known as the finite amplitude method. This method involves measuring the growth of the second harmonic at a resonant frequency in a given substance. Extensive nonlinear work using the finite amplitude method has been performed by Cobb [8], Dunn [11], Germain [21] and Saito [35] who have all determined it is difficult to get the error of the finite amplitude method lower than 10%. The finite amplitude method was chosen partly due to the low cost of the required equipment and the short time needed to make a single measurement. The main reason the finite-amplitude method was chosen was for it's ability to be performed in-situ. This would be very advantageous for making measurements during the biodiesel production process.

Comparisons between the accuracy and precision of the finite amplitude method and the thermodynamic method have been made [31] [25] although it is difficult to declare one method the winner. This is because while the thermodynamic method was seen to be more accurate, the finite amplitude method can be used in vitro, thus making it more appealing as a diagnostic agent. [31]

The nonlinear community has used the above methods to measure the nonlinearity of a wide range of liquids at various temperatures. [9] [30] [41] [40] [3] The motivation for determining the nonlinear parameter for a given material is that it has the potential to be used as a tissue characterization tool, particularly for diagnostic purposes. This was first suggested when a correlation between the nonlinearity of a tissue and it's molecular and macroscopic qualities was noticed. [7] [3] In 1996 Frank [19] suggested the existence of a nonlinear relation between the nonlinear parameter and the reciprocal speed of sound and that each family of chemicals should have its own trend of nonlinearity. In 2000 Banchet [3] published data to support a theory that there is a correlation between nonlinearity and the length of the fatty acid chain of a molecule. Because the size of a fatty acid molecule is the determining factor in the quality of a biodiesel sample, one can hypothesize that there is a relation between the nonlinear parameter,  $\frac{B}{A}$ , and the grade of the fuel.

The theory, methodology, and results of the acquisition of the nonlinear parameter and the speed of sound for various liquids are detailed in this thesis. The sensitivity of this data acquisition system will be compared with gas chromatography results on biodiesel samples representing acceptable fuel quality and partially reacted, out of specification biodiesel.

### 2. THEORETICAL BACKGROUND

#### 2.1 The Nonlinear Parameter

For fluid media there is an equation of state which regulates the careful balance between pressure, density and absolute temperature. For a perfect gas that equation is:

$$p = \rho RT \tag{2.1}$$

Where p is the total pressure in Pascals,  $\rho$  is the density in kilograms per cubic meter, R is the specific gas constant and T is the absolute temperature in kelvins.

For fluids other a perfect gas the adiabat is more complicated. A solution to Eq. 2.1 is found by performing a Taylor series expansion about the equilibrium values of density and entropy:

$$p = p_0 + \left(\frac{\partial p}{\partial \rho}\right)_{0,s} \left(\rho - \rho_0\right) + \left(\frac{\partial^2 p}{\partial \rho^2}\right)_{0,s} \frac{\left(\rho - \rho_0\right)^2}{2} + \dots$$
(2.2)

Where  $p_0$  is the hydrostatic pressure, and  $\rho_0$  is the equilibrium density. For changes that induce temperature gradients small enough so that appreciable heat flow does not occur during a fraction of an acoustic period, the system is said to be adiabatic. If we also say that the system is thermodynamically reversible, the entropy can be assumed to be a constant. Such a system is said to be isentropic. By taking the derivatives at  $\rho = \rho_0$  and assume constant entropy, and limiting the equation to third order terms we obtain:

$$p(\rho) = p - p_0 = A \left[\frac{\rho - \rho_0}{\rho_0}\right] + \frac{B}{2!} \left[\frac{\rho - \rho_0}{\rho_0}\right]^2 + \frac{C}{3!} \left[\frac{\rho - \rho_0}{\rho_0}\right]^3 + \dots$$
(2.3)

Where  $\frac{(\rho-\rho_0)}{\rho_0}$  is the fractional change in density of the propagating medium. Since the first derivative in Eq. 2.2 of the infinitesimal sound velocity  $c_0^2$  and we can set  $A = \rho_0 c_0^2$ . The nonlinearity of a propagating wave can be indicated by the ratio of the coefficients of the first and second terms:

$$\frac{B}{A} = \frac{\rho}{c_0^2} \left(\frac{\partial^2 p}{\partial \rho^2}\right)_{0,s} \equiv \frac{\rho_0}{c_0^2} \left(\frac{\partial c^2}{\partial \rho}\right)_{0,s} = 2\rho_0 c_0 \left(\frac{\partial c}{\partial p}\right)_{0,s} \tag{2.4}$$

In 1959 Robert T. Beyer had solved the isentropic equation of state, by expanding derivative  $\left(\frac{\partial c}{\partial p}\right)_{0,s}$ . [4]

$$\frac{B}{A} = 2\rho_0 c_0 \left[ \left( \frac{\partial c}{\partial p} \right)_T \right]_{\rho = \rho_0} + \frac{2c_0 T \kappa_e}{\rho_0 c_p} \left[ \left( \frac{\partial c}{\partial T} \right)_p \right]_{\rho = \rho_0} \equiv \left( \frac{B}{A} \right)' + \left( \frac{B}{A} \right)'' \quad (2.5)$$

Where  $c_0$  and c represent the infinitesimal velocity of sound in the liquid and the local velocity of sound in the finite amplitude wave, T is the absolute temperature, and  $\kappa_e$  and  $c_p$  denote the volume coefficient of thermal expansion and the specific heat at constant pressure, respectively. The first term of Eq. 2.5, represented by  $\left(\frac{B}{A}\right)'$  represents the relative increase in the phase velocity due to pressure. The second term of Eq. 2.5, represented by  $\left(\frac{B}{A}\right)''$ represents the relative increase in the phase velocity due to Temperature.[34]

Substance	Value	Error	Temp $(C)$	Source
Water	4.2		0	[5]
Water	5.11	$\pm 0.20$	20	[41]
Water	5.18	$\pm 0.03$	30	[40]
Methanol	9.42		20	[9]
Methanol	9.64		30	[9]
Olive Oil	11.136	$\pm 0.042$	20	[15]
Olive Oil	11.066	$\pm 0.641$	30	[15]
Peanut Oil	10.911	$\pm 0.065$	20	[15]
Peanut Oil	10.680	$\pm 0.038$	30	[15]
Ethanol	10.42		0	[15]
Ethanol	10.52		20	[15]
Ethanol	10.60		40	[15]
n-Propanol	10.47		0	[15]
n-Propanol	10.69		20	[15]
n-Propanol	10.73		40	[15]

Tab. 2.1: Some values of B/A for common liquids

Several scientists have published found values for  $\frac{B}{A}$  as seen in Table 2.1.

Physically, this parameter,  $\frac{B}{A}$ , describes steepening of acoustic waves. Figure 2.1 is a visual description of the evolution of a propagating acoustic sinusoidal wave. As the wave moves through the medium, energy initially carried at the forcing frequency is moved into the higher harmonics as the wave steepens due to the cumulative effects of nonlinearity. Since the particle speed cannot be triple valued (as seen at the starburst), a shock wave is formed. This occurs at a given distance away from the source based on the nonlinear properties of the liquid. This distance is known as the discontinuity distance.



Fig. 2.1: The waveforms show increasing distortion as the crest of the wave catches the trough.

#### 2.1.1 Calculation of the Discontinuity Distance

To ensure that the nonlinear measurements taken in this study were performed before the formation of a shock wave, it is necessary to calculate the discontinuity distance.[20]

The discontinuity distance can be approximated by the following equation: [28]

$$D = \frac{1}{\left(1 + \frac{B}{2A}\right)Mk} \tag{2.6}$$

Where D is the discontinuity distance, M is the Mach number and k is the wavenumber. This equation can be solved by making the following assumptions:

- 1. The  $\frac{B}{A}$  value will not be more than 12.
- 2. The wavenumber, k, is  $\frac{1}{wavelength}$  and will not be more than 3857.0085  $m^{-1}$ .
- 3. The Mach number is  $< 0.46 * 10^{-3}$

This means the discontinuity distance for this investigation is greater than 25 cm. This is acceptable for this investigation because the length of the cavity used is 3.189 cm.

#### 2.1.2 Mixture Laws for the Nonlinear Parameter

Previous studies [18] have consistently indicated that if the nonlinear parameters of each of an n-component mixture of materials are known it is possible to derive the corresponding nonlinear parameters of the mixture as a whole. This would imply that the contents of liquid X could be determined based on knowing its nonlinear parameter and the nonlinear parameters of its components. [17]

$$\alpha^2 \beta = \sum_{i=1}^n X_i \alpha_i^2 \beta_i \tag{2.7}$$

Where  $X_i$  is the volume fractions of component  $i, \beta$  is the coefficient of nonlinearity, and  $\alpha$  is the adiabatic compressibility given by

$$\alpha = \sum_{i=1}^{n} X_i \alpha_i \tag{2.8}$$

where the subscripted quantities refer to the component properties.  $\beta$  is related to  $\frac{B}{A}$  by  $\beta = 1 + \frac{B}{2A}$ . This also means that if the samples in this study are contaminated with foreign particles, like water, it will affect their speed of sound and nonlinearity.

## 2.1.3 The Finite Amplitude Method

It has been found by Funbini, [20] Hargrove [22] and Keck [26] that the amplitudes of the harmonics in the distorted ultrasonic wave are given by:

$$p_n(d) = \frac{2p_1(0)}{nd} J_n(nd)$$
(2.9)

Where d = x/L is the ratio of the propagation distance to the discontinuity distance and n is the harmonic number. If we focus on the second harmonic (say n = 2) using Eq. 2.9 and expand the Bessel function in a power series and drop the higher order terms we get: [1]

$$\frac{2\rho_0 c_0^3}{x\pi f} \frac{p_2}{p_0^2} - 2 = \frac{B}{A} \tag{2.10}$$

Where f and x represent the operating frequency and distance between the transducers, respectively.

As stated in the introduction the precision with which  $\frac{B}{A}$  can be measured is about 10%. [31] Equation 2.10 suggests then, to find the nonlinear parameter for a liquid, one needs to find the amplitudes of the first and second harmonic of a signal as it propagates through the liquid.

## 2.2 Speed of Sound in Fluids

The speed of sound is regulated by the equation:

$$c^2 = \frac{\mathfrak{B}}{\rho_0} \tag{2.11}$$

Where c is the speed of sound, and  $\mathfrak{B}$  is the adiabatic bulk modulus from:

$$\mathfrak{B} = \rho_0 \frac{\partial p}{\partial \rho_{\rho_0}} \tag{2.12}$$

Like the nonlinear parameter, the speed of sound is easier to measure than predict in liquids. However, it is possible to show theoretically that  $\mathfrak{B} = \gamma \mathfrak{B}_T$  where  $\mathfrak{B}_T$  is the isothermal bulk modulus and  $\gamma$  is the ratio of specific heats. Since  $\mathfrak{B}_T$  is much easier to measure experimentally than  $\mathfrak{B}$  a convenient expression for the speed of sound in liquids is obtained from Eq. 2.13 and  $\mathfrak{B}_T$ .

$$c^2 = \gamma \frac{\mathfrak{B}_T}{\rho_0} \tag{2.13}$$

Where  $\gamma$ ,  $\mathfrak{B}_T$  and  $\rho_0$  all vary with the equilibrium temperature and pressure of the liquid. Since no simple theory is available for predicting these variations, they must be measured experimentally and the resulting speed of sound expressed as a numerical formula.[28]

#### 2.2.1 Mixture Laws for the Speed of Sound

It has been suggested that the speed of sound of a liquid is proportional to its components.[39] This law was also suggested to be true for vegetable oils. [33]

$$v = \left(\sum_{i=1}^{n} \frac{\phi_i}{v_i^2 \rho_i} \sum_{i=1}^{n} \phi_i \rho_i\right)^{-\frac{1}{2}}$$
(2.14)

Where v is the velocity,  $\rho$  is the density and  $\phi$  is the volume fraction and n is the number of components.

Substance	Velocity (m/s)	Temp $(C)$	Source
Water	1402.387	0	[6]
Water	1481	20	[28]
Water	1509.144	30	[6]
Methanol	1118.91	20	[2]
Methanol	1085.57	30	[2]
Olive Oil	1464.0	20	[10]
Olive Oil	1432.0	30	[33]
Peanut Oil	1465.9	20	[10]
Peanut Oil	1432.0	30	[33]
Soy Oil	1469.8	20	[10]
Soy Oil	1437.5	30	[33]
Canola Oil	1468.4	20	[10]
Canola Oil	1435.7	30	[33]
Ethanol	1150	20	[28]

Tab. 2.2: Some speed of sound values for common liquids at atmospheric pressure.

### 2.3 Biodiesel Production

The process of of biodiesel production involves reacting vegetable oils or animal fats catalytically with a short-chain aliphatic alcohol. The specific type of short-chain aliphatic alcohol used in the production of this biodiesel is methanol. The alcohol reacts with the fatty acids to form the mono-alkyl ester (or biodiesel) and crude glycerol. Natural fatty acid chains contain four to 28 carbons which may be saturated or unsaturated. Fatty acid chains which contain double bonds are considered unsaturated while fatty acids chains that contain only single bonds are saturated.



Fig. 2.2: Several types of fatty acids. [29]



Fig. 2.3: Model of methyl linoleate, of linoleic acid methyl ester, a common methyl ester produced from soybean or canola oil and methanol. The red represents oxygen atoms, the light grey represents hydrogen atoms and the dark grey represents carbon atoms [29]



Fig. 2.4: Transesterification Biodiesel Reaction

Figure 2.3 depicts an example of a fatty acid chain. The differences in chain length and bond structure indicate whether the molecule is from a soybean or a peanut, for example. The reaction between the biolipid and the alcohol is called transesterfication and is a reversible reaction so the alcohol must be added in excess to drive the reaction towards the right and ensure complete conversion. Figure 2.4 shows an example transesterfication reaction equation. [27]

A high-quality biodiesel has a low amount of glycerol bound to the fatty acids that make up the biodiesel. This study aims to determine if speed of sound or the nonlinear parameter are better indicators of the level of bound glycerol in a biofuel.

#### 3. METHODOLOGY

#### 3.1 System Specifics

A visualization of the experimental system setup can be seen in Figure 3.3. A pitch-catch transducer setup was used. This system is controlled using Labview. The embedded controller (NI PXI-8196) coordinates the activities of the function generator (NI PXI-5422 16-bit 200 Msamples/second Arbitrary Wave Generator), the Oscilloscope (NI PXI-5125 12 bit 200 Msamples/second Digitizer), and the Thermocouple Input (NI 9211 80mV 24-Bit). The transducers used are Harisonic 3.5 MHz Lead metaniobate submersible transducers.

#### 3.2 Nonlinear Parameter Methodology

The data acquisition program, written with Labview software, goes through the following steps: The function generator is initialized and a continuous wave is generated at the transmitting transducer. The oscilloscope is initialized and detects the incoming waves at the receiving transducer on which the computer performs a Fast Fourier Transform (FFT) to analyze the frequencies of the signal. A peak detect function is used to find the amplitudes of the first and second harmonics with results written to a data file. In general, the 1st harmonic was an average of 50 decibels lower than the input signal and the 2nd harmonic was an average of 46 decibels lower than the 1st harmonic.



Fig. 3.1: Experimental setup.



Fig. 3.2: Photo of experimental setup.



Fig. 3.3: A close-up photo of the experimental setup.

#### 3.2.1 Calibration

System parameters which have to be accounted for include: equating received voltage to applied pressure on the transducer, DC offset of received signal, and the energy loss in the transducers. Because the goal of this study was to see if the nonlinear parameter could indicate a difference in quality it is important to not multiple in a difference with the density, frequency and speed of sound. This is why I chose to compare the raw  $\frac{A_2}{A_0^2}$  values of each liquid. Where  $A_2$  and  $A_0$  are the amplitudes of the  $2^{nd}$  harmonic and fundamental frequency, respectively. This equation enables the comparison of relative nonlinear measurements. The amplitudes of the  $1^{st}$  and  $2^{nd}$  harmonic had to normalized with respect to the frequency response of the transducer. This is because these experiments were performed operating outside of the peak transducer operating frequency. Figure 3.5 indicates the frequency response curve of the transducer.

The experiments were performed in the 2.6MHz to 2.9MHz range and the frequency response curve changes amplitude with respect to each temperature and liquid. This is why it was important to find the frequency response of the transducer at our operating frequency before each nonlinear measurement was made. This was done by finding the peak amplitude of the  $123^{rd}$  harmonic and the  $246^{th}$  harmonic. This gave me a better view of the expected natural amplitude of a signal at that frequency and temperature, so that I could better judge the results. The results were plugged into Eq 3.1 before then being used to calculate  $\frac{B}{A}$ .

$$A_2 = \frac{A_2'}{A_{2N}} \quad A_0 = \frac{A_0'}{A_{0N}} \tag{3.1}$$

Where  $A'_2$  and  $A'_0$  are the unnormalized measured voltages of the  $2^{nd}$ and  $1^{st}$  harmonic of the signal through the liquid, respectively.  $A_{2N}$  and  $A_{0N}$  are the measured natural responses of the transducer at the 2nd and 1st harmonics, respectively.

#### 3.3 Speed of Sound Methodology

The speed of sound as a function of temperature was measured in each liquid. This parameter is a possible quality indicator and therefore was measured three different ways to ensure accuracy.

#### 3.3.1 Speed of Sound Method 1:Difference Between Resonant Frequencies

The first way the speed of sound was measured was by the application of a frequency sweep from 2.6 to 2.9 MHz to the transmitting transducer while the amplitude of response at the receiving element was monitored.



Fig. 3.4: Example frequency sweep indicates resonant frequencies.

An example frequency sweep is shown in Figure 3.4. Here the spikes in amplitude indicate resonant frequencies.

The following equation governs the locations of the resonant frequencies:

$$f_r = \frac{nc}{2L} \tag{3.2}$$

Where  $f_r$  is a resonant frequency, n is a whole number which represents the number of wavelengths generated in the cavity and c and L are the speed of sound in the liquid and the length of the cavity, respectively. From Eq 3.5 one can solve for the difference between two consecutive resonant frequencies:

$$\Delta f_r = \frac{n_0 c}{2L} - \frac{(n_0 - 1) c}{2L} = \frac{c}{2L}$$
(3.3)

This relationship was used to solve for the speed of sound. The difference

between the spikes was measured and averaged.

$$(average\Delta f_r)2L = c \tag{3.4}$$

The frequency sweep was performed over a short period of time (< 4 seconds) to reduce the influence of a possible change in temperature.

# 3.3.2 Speed of Sound Method 2:Temperature Dependant Resonant Frequency

The second way the speed of sound was measured was by monitoring the shift in the resonant frequency as the temperature of the liquid increased. This was done by first finding a ballpark speed of sound. Then, before a nonlinear measurement was taken, the resonant frequency of 123 wavelengths was found. Set n = 123 in Eq. 3.5 and obtain:

$$\frac{2f_rL}{123} = c \tag{3.5}$$

The reason The reason 123 wavelengths was chosen was because that number of wavelengths corresponds to around 2.8 MHz depending of the transmission fluid. That particular frequency is a good one to use because at that frequency, as you can see from Figure 3.5 the first harmonic has approximately the same transducer response as the 2nd harmonic. Figure 3.5 also indicates these transducers have a peak response at 4.2 MHz.



Fig. 3.5: The response of the transducer from 1 to 7 MHz.



Figure 3.6 shows the scan for a single resonant frequency.

Fig. 3.6: The first frequency sweep for the 123rd resonant frequency in water.

This frequency could then be plugged into Eq 3.5 and by setting n=123. This enables one to solve for the speed of sound in a way which guaranteed accuracy. The liquid was unintentionally heated slightly each time a nonlinear measurement was taken. This was because finite thermal conductivity results in a conversion of acoustic energy into random thermal energy. [28] The heating of the liquid caused the speed of sound to decrease slightly. The opposite is true for water in which case the speed of sound increases with temperature. In any case this change in speed of sound causes the resonant frequencies to shift slightly. Nonlinear effects are especially apparent at the resonant frequencies of a cavity [28]. It is for this reason the resonant frequency was found before each nonlinear measurement.



Fig. 3.7: After 2 frequency sweeps.



Fig. 3.8: After 3 frequency sweeps.

Figs 3.7 and 3.8 demonstrate the rescanning of the resonant frequency for each subsequent iteration.

#### 3.3.3 Speed of Sound Method 3: Time of Flight

The third way the speed of sound was measured was the traditional "time of flight" setup. This is a commonly known procedure in the ultrasound community. A visualization of the experimental setup can be seen in Figure 3.9. The function generator creates a pulsed electronic signal and the transducer sends an acoustic signal through the liquid and the oscilloscope measures the time it takes to bounce back.

$$\frac{4\Delta l}{\Delta t} = c \tag{3.6}$$



Fig. 3.9: The arrangement of equipment for the time of flight experiment.



Fig. 3.10: An example waveform from the time of flight experiment.

Each of the spikes in Figure 3.10 indicates an increase in energy recieved in the transducer over time. By measuring the distance between these spikes, one can find the time it took the signal to bounce off of the bottom of the container. The travel distance is then changed by a known distance  $\delta l$  and therefore the speed of sound in the liquid can be calculated.



Fig. 3.11: The time of flight setup.



Fig. 3.12: A picture of the time of flight experimental setup.

#### 4. RESULTS

One application to important to biodiesel industry, is the determination of fuel quality via reaction completion from triglyceride to methylester. Currently ASTM Method D-6584 utilizes Gas Chromatography methods to determine the amount of unreacted vegetable oils, with a limit of 0.2% bound glycerol. The feasibility of using an ultrasonic non-linear measurement and/or speed of sound to determine biodiesel quality was assessed comparing 10 samples that have been analyzed via the ASTM Gas Chromatography method.

The nonlinearity as a function of temperature is shown for various canola, olive and peanut oils in Figures 4.1 to 4.8. The quality of each oil is indicated by the amount of bound glycerol. A low amount of bound glycerol is more desirable as it indicates the transesterification process is more complete and thus the fuel is more ready for use.

### 4.1 Nonlinear Results



Fig. 4.1: The nonlinear parameter in water, methanol and various grades of processed canola oil as a function of temperature.

Published  $\frac{A}{B}$  values indicate that the nonlinearity of biodiesel, Fatty Acid Methyl Esters (FAMEs), should be higher than that of water[18]. Figure 4.1 indicates that the system detects the correct relation between water and various grades of canola oil.



Fig. 4.2: A closer look at the nonlinear parameter in various grades of processed canola oil.



*Fig. 4.3:* The nonlinear parameter in methanol and various grades of processed olive oil as a function of temperature.



Fig. 4.4: A closer look at the nonlinear parameter in various grades of processed olive oil as a function of temperature.



Fig. 4.5: The nonlinear parameter in methanol and various grades of processed soy oil as a function of temperature.



*Fig. 4.6:* A closer look at the nonlinear parameter in various grades of processed soy oil as a function of temperature.



Fig. 4.7: The nonlinear parameter in methanol and various grades of processed peanut oil as a function of temperature.



Fig. 4.8: A closer look at the nonlinear parameter in various grades of processed peanut oil as a function of temperature.

As you can see there is not a very strong correlation between the non-

linearity of the various grades of oils and the amount of bound glycerol.

## 4.2 Speed of Sound Results

The speed of sound as a function of temperature is shown for various canola, olive and peanut oils in Figures 4.9 to 4.16.



*Fig. 4.9:* The speed of sound in methanol and various grades of processed canola oil as a function of temperature.



Fig. 4.10: A closer look at the speed of sound in various grades of processed canola oil.



Fig. 4.11: The speed of sound in methanol and various grades of processed olive oil as a function of temperature.



Fig. 4.12: A closer look at the speed of sound in various grades of processed olive oil as a function of temperature.



Fig. 4.13: The speed of sound in methanol and various grades of processed soy oil as a function of temperature.



Fig. 4.14: A closer look at he speed of sound in various grades of processed soy oil as a function of temperature.



Fig. 4.15: The speed of sound in methanol and various grades of processed peanut oil as a function of temperature.



Fig. 4.16: A closer look at he speed of sound in various grades of processed peanut oil as a function of temperature.

As you can see there is a very strong correlation between the speed of sound and the amount of bound glycerol. This corresponds to the mixture laws discussed in Chapter 2:Theoretical Background. To further examine the correlation between the amount of bound glycerol and the speed of sound, the y-intercept was examined. This is because the slope of the speed of sound curves are roughly the same but the y-intercepts are different with respect to the level of bound glycerol.



Fig. 4.17: The correlation between % Bound Glycerol and the y-intercept of the speed of sound for various peanut oils.



Fig. 4.18: The correlation between % Bound Glycerol and the y-intercept of the speed of sound for various canola oils.

## 4.3 Repeatability



Fig. 4.19: A comparison of the resonance frequency method, the time of flight method, and published values for speed of sound data

Substance	$r^2$ for resonant frequency method	$r^2$ for time of flight method
Water	0.4893	0.2349
Unprocessed Soy	0.9992	0.0981

Tab. 4.1: The coefficients of determination for the various speed of sound methods.

The correlation of these measurements can be quantified by the coefficient of determination,  $r^2$ .

Substance	$r^2$ for Nonlinear parameter	$r^2$ for Speed of Sound
Water	0.8934	0.9994
Methanol	0.0321	0.9485
Canola A	0.0010	0.9974
Canola B	0.0009	0.9984
Canola C	0.1446	0.9964
Canola D	0.0228	0.9976
Olive A	0.4363	0.9992
Olive B	0.4900	0.9986
Olive C	0.1018	0.9982
Peanut A	0.0001	0.9966
Peanut B	0.0151	0.9980
Peanut C	0.0151	0.9960

Tab. 4.2: The coefficients of determination for the nonlinear parameter and the speed of sound parameter.

#### 5. CONCLUSIONS

This study examined the reliability of the speed of sound and acoustic nonlinearity parameters. The literature indicates that the nonlinear parameter has promise as a diagnostic tool. This study utilized the finite amplitude method because of its simplicity. It was found that this method is accurate enough to discern differences between liquids with large differences in molecular structure, like water and oil. There was not a strong correlation between the nonlinearity and the quality of biofuels. The literature agrees that it is difficult to get an error smaller than 10% with the finite amplitude method. [18] It may be possible to increase the precision of the nonlinear measurement in grades of biofuels by utilizing a different method. This would somewhat defeat the purpose of using the nonlinear parameter as a quality identification tool because it could not be used in-situ.

The speed of sound measurement was shown to be a much more reliable indicator of the quality of a biofuel. The speed of sound parameter was shown to discern the amount of bound glycerol within oil families. This study showed that a difference in bound glycerol levels of 0.02% is able to be detected with the speed of sound parameter. This is important because the ASTM standards required the GC test be accurate within 0.2% bound glycerol. Because the speed of sound can be found almost instantaneously, this technique serves as an alternative to the monetary expense and time consumption of gas chromatography.

## 5.1 Applications

During the biodiesel manufacturing process, often the situation arises where there are layers of fluids separated because of their density differences. If one uses a modification of the time of flight method it is possible to find the level of each liquid. This is done by bouncing the acoustic signal off of the fluid/fluid interface and the fluid/air interface. Figure 5.1 shows how the transducer is aimed upward.



Fig. 5.1: The setup of the acoustic fluid level experiment.



Fig. 5.2: Graph of various oil/water level configurations. The error bars indicate the accuracy of the acoustic fluid layer indicator method.

### 5.2 Future Work

The nonlinear parameter has potential to indicate quality in biofuels after an improvement in precision. The thermodynamic method or the isentropic phase method would probably prove to be more reliable. The precision of this system might be improved by the introduction of a tone-burst signal rather than a continuous wave. The variance of the cavity length might also prove to increase accuracy. In terms of the speed of sound, future work should aim to calibrate the speed of sound to a broader range of known biodiesel standards. APPENDIX

## A. LIST OF SYMBOLS

- $\mathfrak{B}$  adiabatic bulk modulus
- $\frac{B}{A}$  Nonlinear parameter
- c Speed of sound
- $c_p$  Specific heat at a constant pressure
- $C_p$  Heat capacity at a constant pressure
- $C_v$  Heat capacity at a constant volume
- D Discontinuity distance
- d Ratio of propagation distance to discontinuity distance
- f Frequency
- $J_n$  Bessel function of nth kind
- k Wavenumber
- *l* Length
- L Length of the cavity
- M Mach number
- n A whole integer
- p Pressure
- R Specific gas constant
- s Entropy
- T Temperature
- x Distance between transducers
- $X_i$  Volume fractions of component i

- $\alpha$  Adiabatic compressability
- $\beta$  Coefficient of nonlinearity
- $\gamma$  Ratio of specific heats
- $\kappa_e$  Volume coefficient of thermal expansion
- $\rho$  Density

## B. LABVIEW SYSTEM USER MANUAL

An updated copy of the Nonlinear Labview System User Manual is on file in Dr. Bernhard Tittmann's Lab. Please contact Dr. Bernhard Tittmann or the author for more information.

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