Ultrasonic method for identifying oil types and their mixtures

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Abstract

The study focused on the efficacy of ultrasonic method for identifying vegetable oils and their mixtures in formulation of frying oil and its ability in authentication of virgin olive oil. The ultrasonic propagation properties (velocity and Time of Flight (TOF)) were used to classify oil samples and their mixtures and at 1 MHz. The results revealed ability to classify oil types in terms of its level of un-saturation, besides it is to identify oil mixtures. Each oil sample could be grouped in different clusters using ultrasonic parameters. Hence, ultrasonic could be used to discriminate the vegetable oil types and its mixtures effectively as a rapid and continuous method in industrial in-line quality control system of vegetable oils and its mixtures.

Key Words: Ultrasonic, Vegetable oils, Time of Flight (TOF), Oils Mixtures

Introduction

Ultrasound is a non-invasive technique and is thus potentially suitable for monitoring the progress of industrial processes in real time. In the literature many applications can be found regarding the use of ultrasound in different types of products, ranging from solid to liquid materials (Benedito, 2002). The multipurpose character of ultrasonic assessment can be seen from the wide range of products that have been previously examined. Composition assessment by using ultrasonic has also been widely reported in the literature. The solid fat content has also been ultrasonically assessed because it has an important implication on the texture, spread ability and consistency of many materials such as margarine or butter (Coupland & Mcclements, 1997)

Ultrasonic can also be applied to solve some problems found in the oil related industries. In this respect, ultrasonic velocity has been measured to determine the chemical structure of different oils including the chain length and

degree of un-saturation. Therefore, velocity measurements can be used to assess oil composition and adulteration (Coupland & Mcclements, 1997)

Ali and Ali, (2014) revealed that the ultrasonic velocity depends on the % of UFA and SFA contained by the various Edible oils. In terms of the frequency range studied, it can be concluded that these edible oils responded better at 1 and 2 MHz frequencies than at 3 and 5MHz. Perhaps the ultrasonic velocity at 1 and 2 MHz may be taken as the base values and can be used to detect any adulteration component if these pure oils are adulterated. Velocity has also been correlated to rheological properties of edible oils (castor, olive, groundnut, sunflower and rapeseed) Benedito et al.,(2007).

Benedito et al.,(2007) mentioned that velocity was the ultrasonic parameter used in most of the aforementioned studies. However, when low attenuative materials (mainly liquids) are examined, attenuation can also be considered. Both velocity and attenuation can be related to the Physico-chemical properties of the analyzed materials, like- for example-; composition or structure, and can be used for their analysis. The advantages of the ultrasonic techniques are that they are non-destructive, low cost and can be easily automated on-line for real time analysis.

Experiment of Pal et al.,(2004) was successful in using ultrasonic velocimetry to monitor and study the crystallization process of fats and the results confirmed by Martini et al.,(2005). Crystallization process of fats can be monitored using ultrasonic. Besides that both of the papers confirmed the specific relationships exist between the ultrasonic velocity and Solid Fat Content (SFC) that enable the measurement of SFC during crystallization; Martini et al., (2005) recommended this technology that is can be used to perform on-line measurements. In spite of that ,Pal et al., (2004) revealed that ultrasonic velocity it is also a function of polymorphism/microstructure. Thus, extreme care should be taken when using this technique to make sure that changes in solids' content are being monitored, rather than changes in polymorphism and/or microstructure.

Ultrasonic is becoming an increasingly popular tool for characterizing fatty materials. The benefits to the fats and oils industry are substantial. On-line sensors can give manufacturers better control over product composition during processing which leads to improved product quality and reduced manufacturing costs. In addition, ultrasound can be used to provide valuable information about the fundamental Physico-chemical properties of fats and oils. The application of ultrasound in this area will continue to grow.

The aim of this work was to evaluate, whether measurements of ultrasonic wave propagation characteristics as a rapid, reliable, and fully automated method can be used in-line quality control measurements for classifying oil types and formulating frying oils mixtures.

Material and Methods

Oil sample Preparation

Two main groups of oils collected from local markets of Budapest, Hungary were examined. These groups are classified according to the level of unsaturation of the oils to (Mono Unsaturated, Poly Unsaturated).Mono unsaturated group was contained Virgin Olive Oil, Pomace Olive Oil and High-Oleic Sunflower oil; on the other hands, Poly unsaturated group contained Corn oil, Soybean Oil and Sunflower Oil. All oils samples were kept in the refrigerator at around 7°C ± 1 and the samples taken at the time of the analysis. High Oleic frying oil mixtures were tested at different High Oleic Sunflower Oil and Soybean Oil ratios: 0:100, 25:75, 50:50, 75:25 and 100:0 percentages. Each sample was tested in 4 to 6 replicates to ensure the statistical reliability.

Instrumental setup

The setup of the system used to study the relationship between oil types and ultrasonic parameters is shown in Figure 1. This figure shows the two ultrasonic transducers operating in contact mode (no air between the transducers and the sample). The crystallization cell was designed with two polypropylene windows where the transducers were placed. Windows were made of polypropylene since this material has minimal effect on ultrasonic wave propagation. A good contact between the transducers and the windows was achieved by means of vacuum grease. Both transducers were aligned so that one of the transducers generated the ultrasonic wave and the other one received it (transmission mode).

Ultrasonic measurements

For measurement of the ultrasonic wave propagation properties, ULTRAN WD50-1 piezoelectric transducers were applied (broadband Dry Coupling Direct Contact sensors of 1 MHz center-frequency). A Vellemann PCSGU250 computer controlled Function Generator and Oscilloscope was used as pulser and receiver.

Due to the attenuation and dispersion of the investigated material, the simplest transmit signal (a single pulse of appropriate width) results in a noisy, low level received signal of distorted shape, so the determination of the Time-Of-Flight (TOF) is uncertain or impossible. To increase the sensitivity and accuracy of the

TOF-detection, a special wave form of more characteristic - conclusively more easy to recognize – pattern was used: a “chirp” signal of increasing frequency between 0 and 2 MHz, modulated by a half sine wave, as it is shown on the Figure 2.It has a well-determined spectrum with the maximum at 1 MHz (center frequency of the transducer) Figure 3.

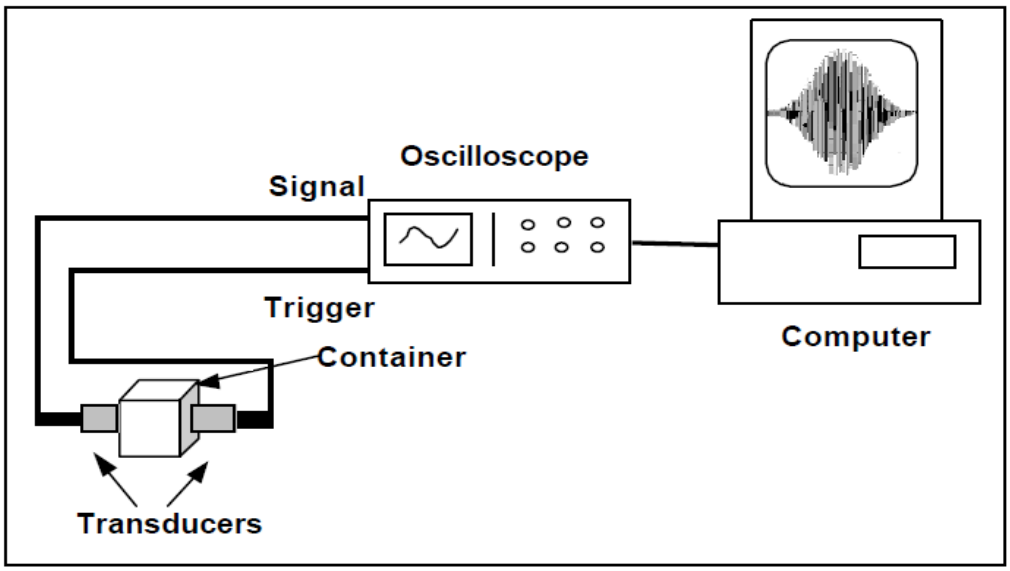

Figure 1: Ultrasonic set-up for the measurements of oil samples

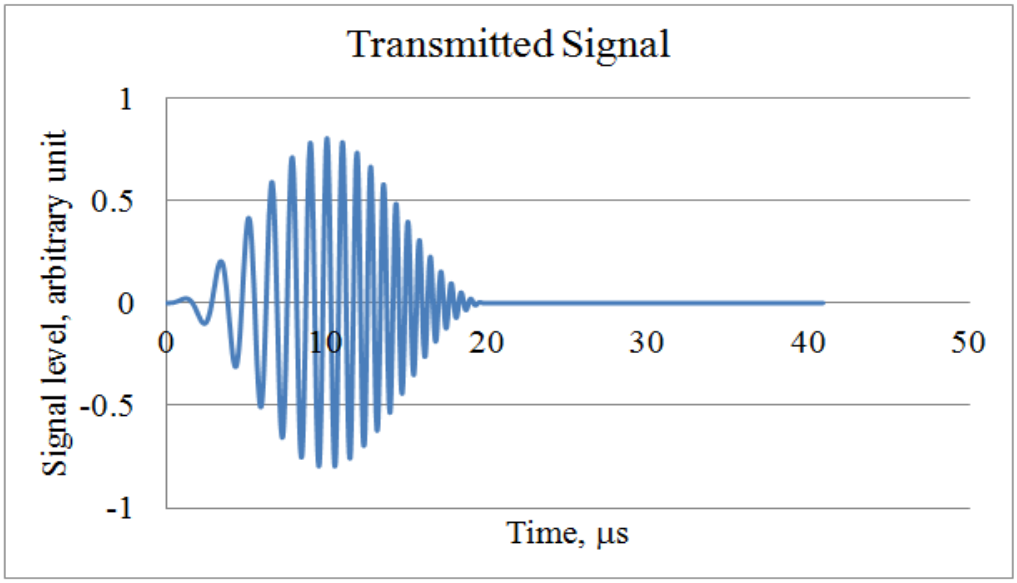

Figure 2. Chirp signal (time domain)

The time delay was calculated by the cross-correlation of the transmitted and received signals. It was determined by the following equation:

$$CrossCorr(t) = IFFT(\overline{FFT(U1)} \cdot FFT(U2))$$

Where

- U1 and U2 are the transmitted and received signals, respectively
- $\overline{FFT(U1)}$ is the complex conjugate of the Fast Fourier Transformed value of U1
- $FFT(U2)$ is the Fast Fourier Transformed value of U2
- IFFT() is the inverse Fourier transform

CrossCorr(t) is a time-domain function, and its maximum corresponds to the TOF-value (the maximal similarity between the transmitted and received signals).

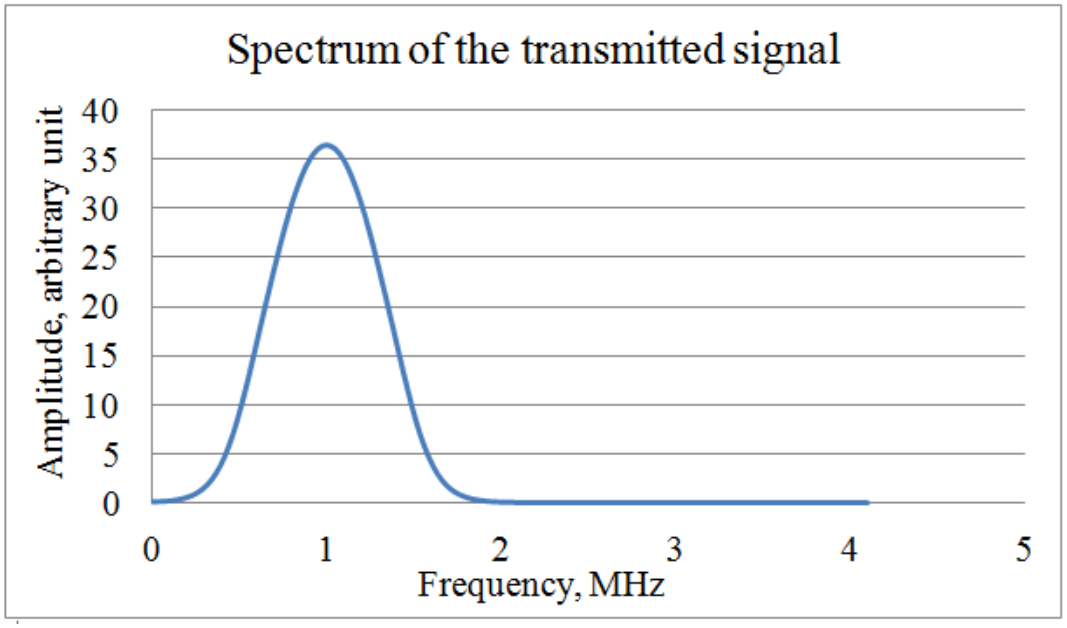

Figure 3: Typical chirp Signal (frequency domain)

Statistical analysis

Statistical analysis of data from instrumental measurements was carried out using a complete randomizes design (CRD). It was used for evaluating the effect of the level of unsaturation to the ultrasonic velocity and Time of Flight. The results are presented as means of four replicates with 95% confidence intervals for means. Coefficient of determination was determined between the percentage of mixing High Oleic Sunflower Oil and Time of Flight. The results are presented as means of six replicates with standard deviations.

Results and Discussion

A- Temperature Dependency

The results obtained revealed that TOF in oil samples is a function of temperature for all oil samples under this investigation. Figure 3 shows the temperature dependency for Sunflower Oil.

These results in the experiment are confirmed these data obtained by Wassell et al.,(2010) as sound velocity determined in rapeseed oil as function of temperature with a correlation coefficient of 0.997. The results showed the SFC values as a function of temperature for 30% palm stearin and 70% rapeseed oil fat blend. The best correlation (R^2 = 0.99) lies between the temperature range for 15 –35°C.

In the same context, Wassell et al., (2010) suggested that the in-line Doppler-based Ultrasound Velocity Profiling (UVP) technique (Takeda, 1991), with Pressure Difference (PD) measurements, commonly known as (UVP-PD) measurements provide valid results to estimate the Solid Fat Content (SFC) of a two-component fat blend over a wide range of temperatures; Moreover, solid fat content measurements made in-line under dynamic process conditions with the UVP-PD equipment showed excellent correlation (r = 0.99) with standard SFC measurements from traditional p-NMR over a wide range of temperatures. These findings confirm that time of flight is predictable for a given sample at a given temperature. Therefore, measurement of ultrasonic velocity and time of flight is suitable to use in-line measurements for continuous quality control processes for observing the changes in SFC in oil mixtures.

Further development to validate ultrasonic velocity and TOF measurements by coupling the results with rheology measurement techniques it could see the advantage of these measurements as an essential tool for both industrial in-line process control, and further academic understanding of fat blends structuring.

B- Ability of Classification

Speeds of ultrasound propagation in different types of oils at 23°C were illustrated in table 1. The results revealed that there are significant differences between oil types. The measurement of the speed of ultrasound in different oil samples revealed that this measurement is able to classify edible oils and fats according to their degree of unsaturation in two main groups Mono Unsaturated Fatty Acids (MUFA) oils and Poly Unsaturated Fatty Acids (PUFA) oils. However, the PUFA and MUFA groups are significantly different and MUFA oils can be distinguished, there are no significant differences could be detected between

the PUFA oils. Therefore, speed of ultrasound propagation could be classified one of the promising techniques for investigating vegetable oils.

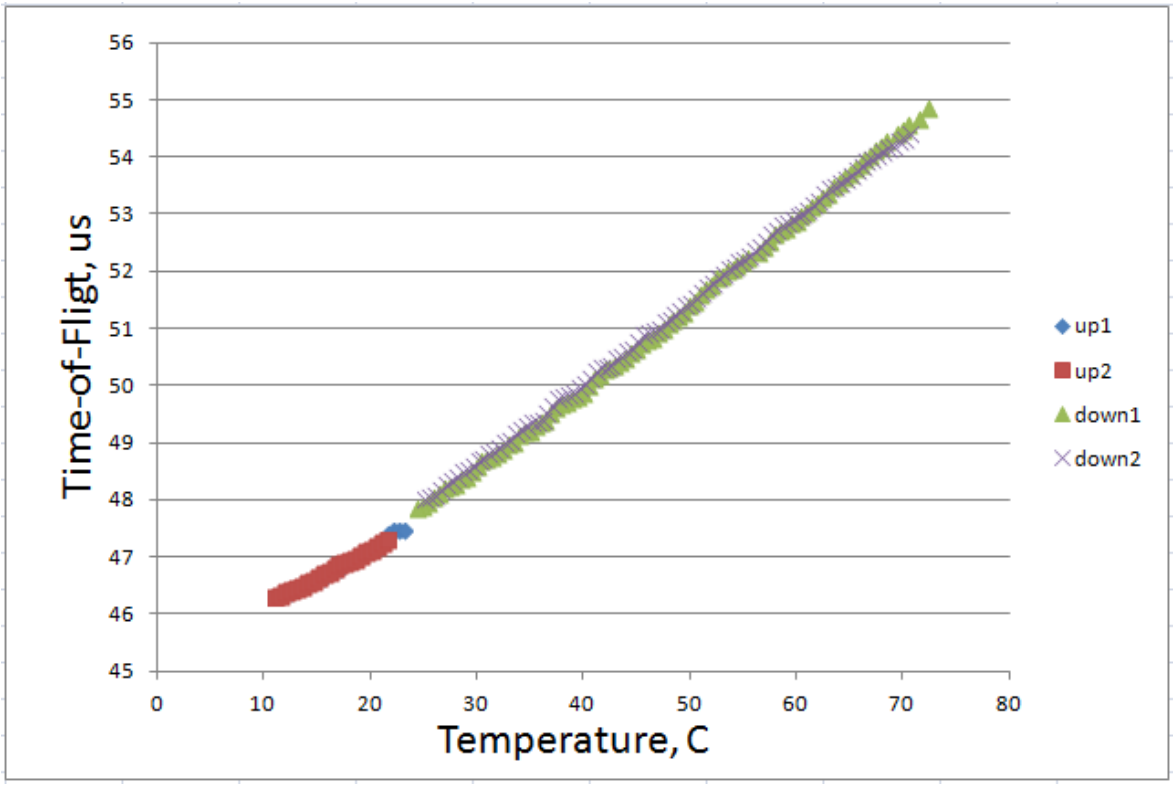

Figure 3 shows the temperature dependency for Sunflower Oil.

Oil Types	Kind of Oil	Ultrasound speed (m/s)
Mono Unsaturated	Virgin olive oil	1436,3 ± 0.3
	Pomace Olive Oil	1437,6 ± 0.3
	High Oleic Sunflower oil	1438,6 ± 0.3
Poly Unsaturated	Corn Oil	1441,8 ± 0.3
	Soybean Oil	1442,6 ± 0.3
	Sunflower Oil	1442,3 ± 0.3

Table 1. Speed of ultrasound propagation in different types of Oils at (23°C)

C- Ability of identification frying oil mixtures

Frankel, (1994) mentioned that the aims for formulating frying oil mixtures is preparing more stable vegetable oils with a wide range of desired fatty acid compositions by mixing different proportions of High Oleic Sunflower Oil with Soybean Oil. Figure 4 represents the relationship between the speed of ultrasound and the percentages of High-Oleic Sunflower Oil in frying mixtures. The results

revealed that speed of ultrasound is strongly connected with a high correlation R^2=0.9479 with the ratios of High-Oleic Sunflower Oil in frying oil mixture components.

These results confirmed Ali and Ali, (2014) findings that ultrasonic velocity depends on the % of UFA and SFA contained by the various edible oils. Moreover, the ultrasonic velocity at 1 MHz may be taken as the base values and can be used to detect any adulteration component if these pure oils are adulterated. Therefore, ultrasonic method is suitable for continuous quality inspection system in formulating frying oil mixtures.

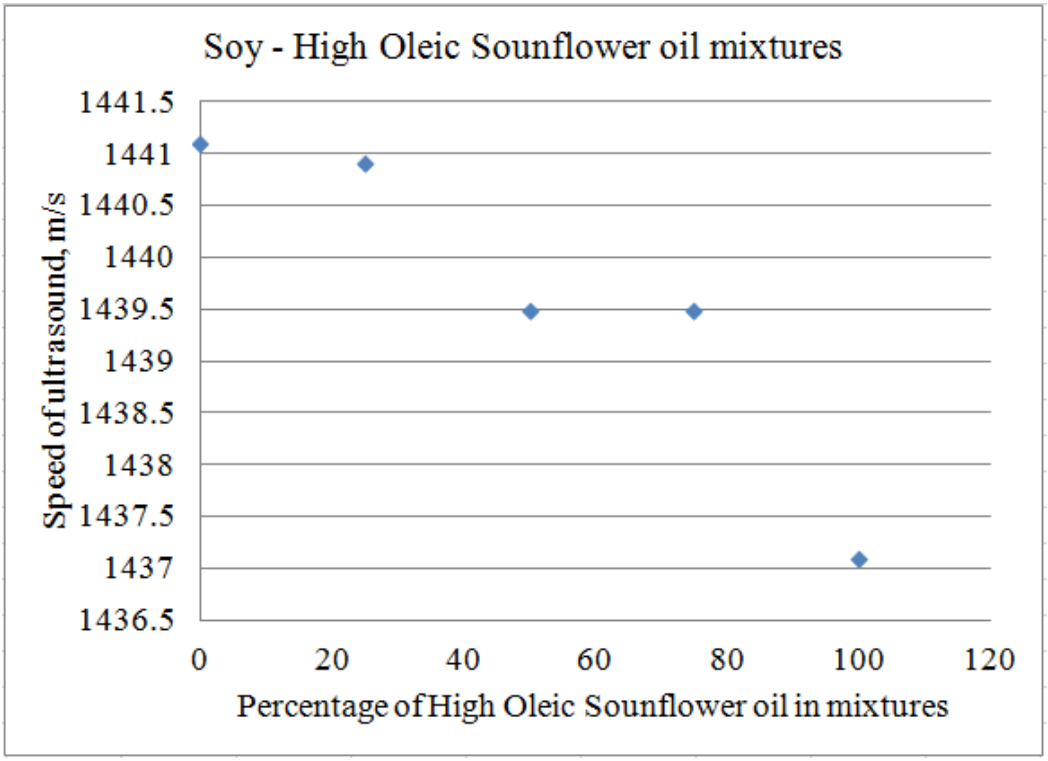

Figure 4. Representation of the relationship between the percentages of High-Oleic Sunflower Oil in frying mixtures

Conclusion

Variation of ultrasonic velocity and TOF with temperature in high viscous vegetable oils is one of the most effective physical measurements in vegetable oils industries. It is observed that ultrasonic velocity of vegetable oils decreases with the increase of temperature. Therefore, the method is giving the possibilities for predicting time of flight at a given temperature. Velocities of sound in various vegetable oils vary based on composition of fatty acid and degree of saturation of

oils. Moreover, it is a sensitive method for detection the changes in the composition significantly. Hence, speed of ultrasound propagation for vegetable oils is one of sensitive methods for investigating oil in industrial in-line process control of oil systems and their mixtures.

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