RELATIONSHIP BETWEEN PHYSICO-CHEMICAL AND ULTRASONIC MEASUREMENTS IN FRYING OLIVE OIL

PACS REFERENCE: 43.35.Zc

Benedito, Jose; Clemente, Gabriela; García-Pascual, Pablo and Mulet, Antonio.
Department of Food Technology. Polytechnic University of Valencia.
Cno. de Vera s/n, 46071
Valencia
Spain
Tel: +34-963877368
Fax: +34-963879366
E-mail: amulet@tal.upv.es

ABSTRACT

The quality of the frying oil changes during frying due to chemical reactions. The assessment of the discarding point is of great importance for the food processing and service industries. The aim of this work was to relate the changes of frying olive oil quality, to ultrasonic measurements. Velocity and attenuation were found to be related to viscosity measurements through a classical equation for viscous liquids. The ultrasonic measurements were also related to the percentage of polar compounds. The results obtained show the feasibility of using ultrasonic parameters to assess the frying oil quality.

INTRODUCTION

The use of low intensity ultrasonics (LIU) in food related applications has been extended to, among others, meat, fish, dairy products, vegetables, fruits and fats and oils (McClements, 1997; Mulet et al., 1999). LIU have been used not only for well known process control applications but also for product quality control. Within this second type of applications, meat composition assessment is extensively covered in the existing literature (Cros and Belk, 1994; Benedito et al., 2001). The sugar content of melons (Mizrach et al., 1991) and the fat percentage of milk (Wagner and Winder, 1975) are also examples of ultrasonic composition assessment. The textural properties of fruits, vegetables, fatty tissue and cheese have also been assessed by means of ultrasonic measurements, mainly velocity and attenuation (Miles et al., 1985; Mizrach et al., 1996; Benedito et al., 2000).
Although several studies have used ultrasonic parameters derived from the frequency spectrum and also attenuation, velocity is the most popular measurement, probably due to the fact that it is the simplest and more reliable ultrasonic measurement.
The ultrasonic velocity has been used to estimate the chemical structure of different oils (Javanaud and Rahalkah, 1988) with the aim of adulteration assessment. The rheological properties of edible (castor, olive, sunflower and rapeseed) oils have been related to ultrasonic measurements (Gladwell et al., 1985).
During oil frying, several reactions take place, resulting in hydrolysis, oxidation and polymerization of the oil. Regulations have been established in many countries to control the oil quality in order to guarantee the quality and safety of the fried foods. The percentage of polar compounds is considered as the limiting factor for discarding the oil in most of the official

regulations, although viscosity is also considered. Official methods are in general expensive, time-consuming and require technical personnel and laboratory facilities.
The aim of this work was to relate the ultrasonic measurements to the commonly used frying oil quality indicators and to show the feasibility of using fast and reliable ultrasonic measurements for determining the oil discard point.

MATERIALS AND METHODS

Virgin olive oil was heated in a laboratory fryer at 200ºC for 16h. Periodically samples of 150 ml were removed and analyzed periodically.

Ultrasonic Measurements

The ultrasonic set-up (Figure 1) consisted of two narrow band ultrasonic transducers (1MHz, 0.75'' crystal diameter, A314S-SU Model, Panametrics, Waltham, MA), attached to a cubic container (49 x 49 x 49 mm) where the oil samples were placed. The container was introduced into a temperature controlled bath to maintain the sample temperature and the oil was moderately stirred to avoid formation of bubbles. The ultrasonic measurements were carried out while the oil was cooled from 35 to 25 ºC. The transducers were linked to a pulser-receiver (Toneburst Computer Controled, Model PR5000-HP, Matec Instruments, Northborough, MA) which sent the electrical signal to a digital storage oscilloscope (Tektronix TM TDS 420, Tektronix, Inc. Wilsonville, OR). For each ultrasonic measurement, five signal acquisitions were taken and averaged. Velocity and attenuation were computed.

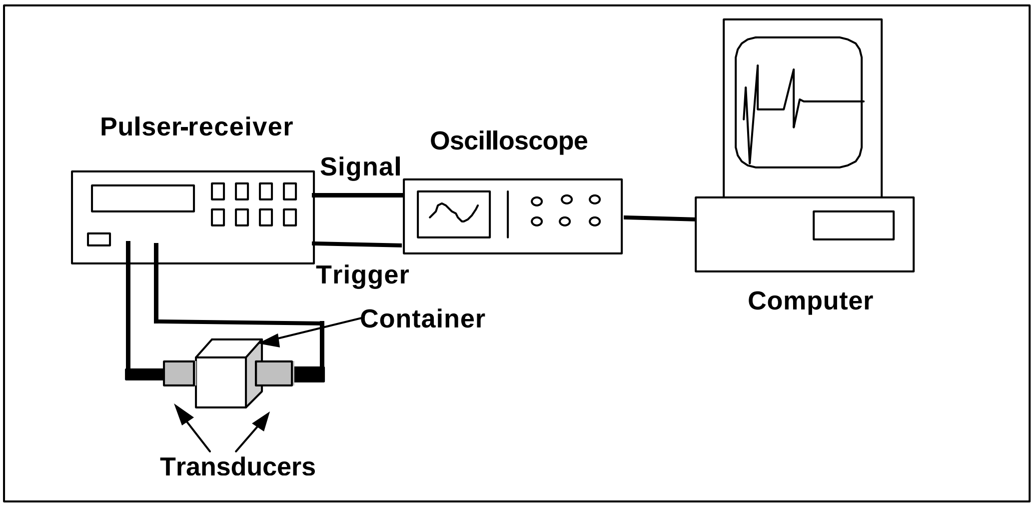

Figure 1. Ultrasonic set-up for the measurements of oil quality.

Viscosity and Density

The viscosity of the samples was measured using a falling ball viscometer (Haake falling ball viscometer C, Karlsruhe, Germany) for transparent liquids. The experiments were carried out by triplicate and the average was considered. The density of the samples was measured with a specific gravity hydrometer (Proton, Mod. 72082, Barcelona, Spain) at 20ºC.

Chemical Analyses

Polar compounds were quantified by adsorption chromatography following the IUPAC Standard Methods 2.507.

RESULTS AND DISCUSSION

The physico-chemical characteristics of the olive oil changed during frying. Viscosity at 30 ºC increased with time (t) following the equation: $\mu= 0,1477\ t^2+0,4059\ t+ 53,9231$ ($R^2= 0,991$) and changing from 50,3 mPa s (0 h) to 100,4 mPa s (16 h). On the other hand, the percentage of polar compounds (PC) varied according the following relationship: $PC= -0,0668\ t^2+3,4039\ t +6,6113$ ($R^2= 0,985$), increasing from 6,2 % (0 h) to 45,7 % (16 h). The increase of viscosity and the PC has been found by other authors (Larusso and Zelinotti, 1985; Dobarganes and Márquez-Ruiz, 1998) and can be considered a good indicator of the quality evolution of the fried oil. The oil in Belgium is discarded when viscosity exceeds 25 mPa s (at 50 ºC) and in several established regulations such as the Spanish a limit, of around 25 % of PC is considered. Polar compound levels in samples heated for less than 6 hours were compatible with the established regulations on frying fats and oils (around 25%) although it is not strange to find used frying oils and fats with polar compound percentages as high as those found for olive oil heated for 16 hours (46 %) (Dobarganes and Márquez-Ruiz, 1998).

Ultrasonic Measurements

The physico-chemical properties of the medium, and consequently the ultrasonic velocity and attenuation, are highly dependent on the sample temperature. The ultrasonic velocity decreases with increasing temperature in fats and oils (McClements, 1997). The influence of temperature on attenuation is scarcely reported in the literature. Figure 2 shows the variation of velocity and attenuation with the temperature for oil fried 2, 10 and 16 h. The ultrasonic velocity decreases linearly with temperature as reported by other authors (McClements, 1997; Benedito et al., 2001). The average slope of the linear relationships was $-3,4\ m\ s^{-1}\ ºC^{-1}$, very close to that reported by McClements (1997) for liquid oils ($-3,3\ m\ s^{-1}\ ºC^{-1}$). The decrease of the attenuation with the temperature is probably due to the decrease of viscosity.

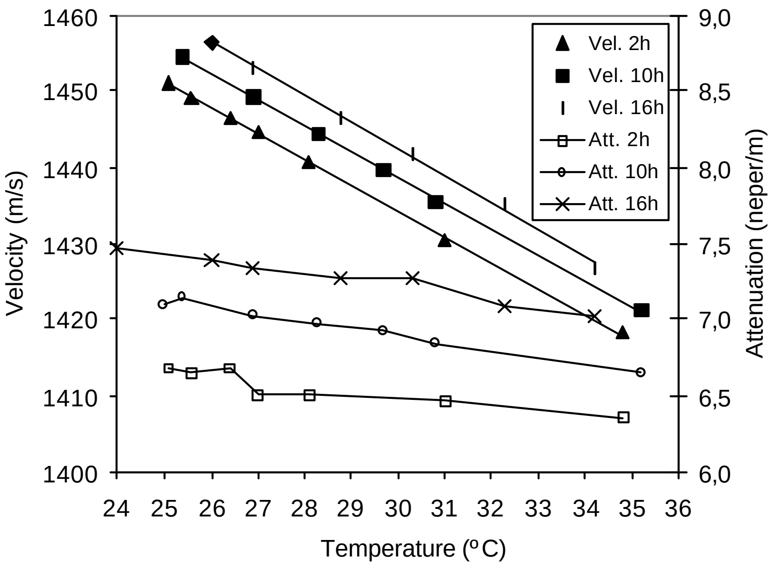

Figure 2.Ultrasonic velocity and attenuation dependence on temperature.

As shown in figure 2, velocity and attenuation increase during frying due to the changes in the oil properties. A similar increase of velocity, measured at 30 ºC during frying of corn oil at 170 ºC, was also reported by Lacey and Payne (1994). These authors found an increase of 8 m/s very similar to the increase found in this study (9 m/s, from 1433 to 1442 m/s at 30 ºC). The attenuation increased from 6,4 to 7,2 neper/m.

Figure 3 shows the relationship between velocity (v) and the % PC and viscosity. A close and significant (p< 0001) fit was found when relating velocity to the % PC and viscosity using a polynomial model of second order.

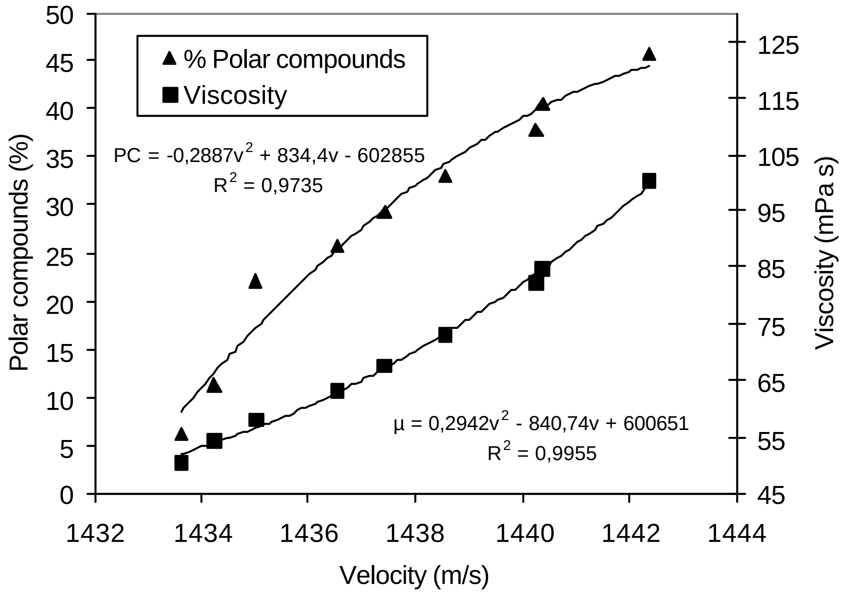

Figure 3. Relationship between velocity and the olive oil quality indicators.

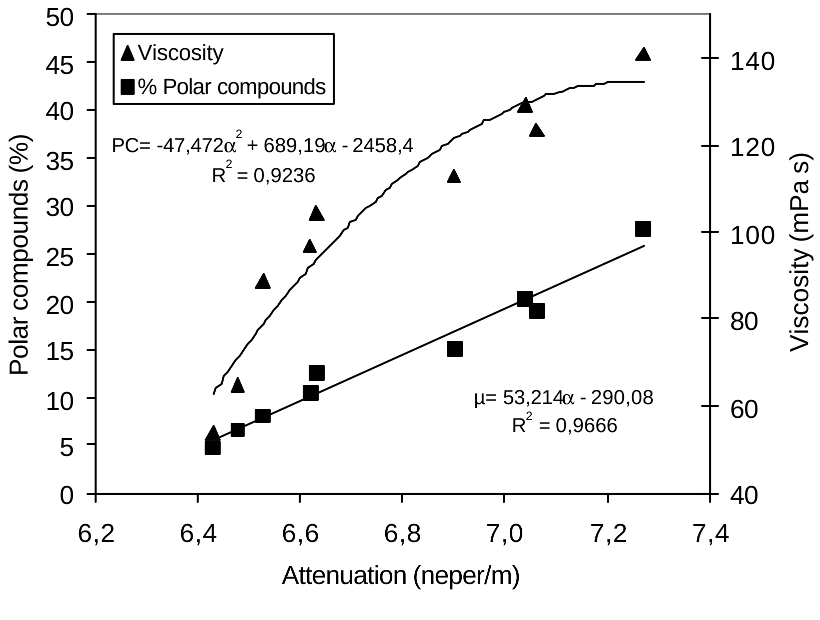

Figure 4. Relationship between attenuation and the olive oil quality indicators.

The % PC was related to attenuation (α) using also a second order polynomial while viscosity was linearly related to attenuation (figure 4).
Viscosity was also related to attenuation and velocity using equation 1, derived from the classical equation of attenuation in viscous fluids (McClements, 1997).

$$m = \frac{\alpha v^3}{c} - d \qquad (1)$$

Where c and d are two constants.
Viscosity was calculated from equation 1. For that purpose the constants c and d were computed using the tool Solver from Excel^{TM}, minimizing the square differences between the experimental viscosity and viscosity calculated using equation 1. The regression coefficients were c= 0,0647 (Neper/m) (cm^3/s^3) / (mPa s) and d=240, 32 (mPa s).

The percentage of explained variance was 97%, poorer than that found considering only velocity, which is probably due to the higher variability found for the attenuation measurements (figure 2).
The results found in this study show that ultrasonic non-invasive measurements can be carried out to monitor the alteration of frying olive oil and therefore to determine the discard point. This technology could replace traditional methods in order to reduce the time for carrying out the analysis and the need of qualified personnel.

CONCLUSIONS

Velocity and attenuation are related to the changes of the physico-chemical parameters that determine the quality of fried olive oil. Therefore and automatic ultrasonic system based on the measurement of these parameters could be used to assess oil quality, replacing traditional analytical methods. The feasibility of using this technology for other oils, as well as the influence of different fried products should be studied.

ACKNOWLEDGEMENTS

The authors would like to acknowledge the financial support from the Instituto Nacional de Investigación y Tecnología Agraria y Aimentaria (CAL01-077-C3-1). Ministerio de Ciencia y Tecnología, Spain.

REFERENCES

Benedito, J., Carcel, J., Clemente, G. and Mulet, A. 2000. Cheese maturity assessment using ultrasonics. J. Dairy Sci., 83, 248-254.

Benedito, J., Carcel, J.A., Rossello, C. and Mulet, A. 2001.Composition assessment of raw meat mixtures using ultrasonics. Meat Science, 57, 365-370.

Cross, H. R. and Belk, K. E. 1994 Objective measurements of carcass and meat quality. Meat Science. 1994, 36, 191-202.

Dobarganes, M.C. and Márquez-Ruíz, G. 1998. Regulation of Used Frying Fats and Validity of Quick Tests for Discarding the Fats. Grasas y Aceites, 49, 331-335.

Gladwell, N., Javanaud, C., Peers, K.E. and Rahalkar, R.R. 1985. Ultrasonic behavior of edible oils: correlation with rheology. Journal of the American Oil Chemists' Society, 62, 1231-1236.

IUPAC. Standard Methods for the Analysis of Oils, Fats and Derivatives, 1st Supplement to the 7th Edition, 1992. International Union of Pure and Applied Chemistry, IUPAC (Ed), Pergamon Press, Oxford, England.

Javanaud, C. and Rahalkah, R.R. 1988. Velocity of ultrasound in vegetable oils. Fat Sci. Technol, 90, 73-75.

Lacey, R. E. and Payne, F. A. 1994. Ultrasonic velocity in used corn oil as a measure of oil quality. Transactions of the ASAE, 37, 1583-1589.

Lorusso, S. and Zelinotti, T. 1985. Analytical data for evaluation of deterioration of heated fats. Revista della Societa Italiana di Scienza dell'Alimentazione, 14, 209-214.

McClements, D.J. 1997. Ultrasonic Characterization of food and drinks: Principles, methods and applications. Critical Reviews in Food Science and Nutrition, 37, 1-46.

Miles, C.A., Fursey, G.A.J. and Jones, R.C.D. 1985. Ultrasonic estimation of solid/liquid ratios in fats, oils and adipose tissue. J. Sci. Food Agric., 36, 215-228.

Mizrach, A., Galili, N., Rosenhouse, G. and Teitel, D.C. 1991. Acoustical mechanical and quality parameters of winter grown melon tissue. Trans. ASAE, 34, 2135-2138.

Mizrach, A., Galili, N., Gan-mor, S., Flitsanov, U. and Prigozin, I. 1996. Models of ultrasonic parameters to asses avocado properties and shelf life. Journal of Agricultural Engineering Research, 65, 261-267.

Mulet, A., Benedito, J., Bon, J. and Sanjuan, N. 1999. Low intensity ultrasonics in food technology. Food Sci and Technology International, 5, 285-297.

Wagner, R. J. and Winder, W. C. 1975. Automatic fat standarization of raw milk with the Darison Composition Controller. J. Dairy Sci., 58 (5), 800-801.