

Use of Ultrasonics for the Quality Assessment of Frying Oil

¹Driss Izbaïm, ¹Bouaazza Faiz, ²Ali Moudden, ³Naima Taifi and ¹Adil Hamine

¹Faculty of Sciences, Ibn Zohr University, Agadir, Morocco

²Superior School of Technology, Ibn Zohr University, Agadir, Morocco

³Faculty of Sciences, El-Jadida University of Chouaib Doukkali, El-Jadida, Morocco

Abstract: The main objective of this study is to evaluate quality changes of Soybean Oil (SBO) during frying. Traditional methods are expensive and time consuming techniques, requiring technical personnel and laboratory facilities. Fatty Acids (FA) value, total Polar Component (PC) and Free Fatty Acids (FFA) of oil samples were used as chemical indicators of different quality levels of oil and then compared with ultrasonic measurements. The study demonstrated that using ultrasonic properties, we obtain reliable results to monitor and control oil quality.

Key words: Ultrasonics, frying oil, soybean oil, fatty acids, polar compounds, free fatty acids

INTRODUCTION

Frying has become the most popular food preparation technology due to its flavour and the easy preparation. Important characteristics of industrial frying oils are high oxidative stability, high smoke-point, low foaming, low melting point, bland flavour and nutritional value. However, complex physical and chemical changes occur during deep-fat frying leading to thermal and oxidative decomposition. Physical changes are mainly increased viscosity and foaming, colour changes and decreased smoke-point. Main chemical changes are increased free fatty acids and polar components as well as decreased levels of unsaturation, flavour quality and nutritive value (Warner, 2002).

Pokorny (1989) has demonstrated that increases in the polar fraction resulted in an eventual degradation in food quality. Many countries consider the polar compounds measurement to be the single most important test for the degradation state of oil and have established the value of around 25% as its regulatory limits in frying oils (Firestone, 1996), some other countries also use free fatty acids. Free fatty acids produced in the frying operation of an oil contribute to the smoke haze and therefore has a substantial effect on its smoke point, which affects oil absorption by the fried food (Orthofer *et al.*, 1996).

There are several methods for controlling and assessing degradation of oil during deep frying, but are time-consuming, costly and usually require analytical expertise. In this respect, ultrasonic techniques are fast, non-invasive and convenient. Many studies have been conducted to assess the composition of different types of

food products using ultrasound (McClements, 1997; Mulet *et al.*, 1999). Velocity is the ultrasonic parameter most used because of its reliable results.

The objective of this study is about the changes in ultrasonic measurements during thermoxidation of SBO and the relationships between ultrasonic measurements and chemical results.

MATERIALS AND METHODS

SBO was obtained from Cristal S.A. (Casablanca, Morocco). The oils was heated in a domestic fryer at 180°C for 8 h day⁻¹ over 4 days, for a total of 32 h. Samples of 150 mL were periodically removed and kept at -18°C for further analysis.

Ultrasonic measurements: The experimental setup (Fig. 1) used for the experiments consisted of ultrasonic transducer (5 MHz, 0.5 inch crystal diameter, A309S-SU model, panametrics, Olympus), attached to a cubic container (50×50×50 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 sample was cooled from 50-30°C. The transducer was linked to a pulser-receiver (Sofranel Model 5073 PR, Sofranel Instruments), which sent the electrical signal to a digital storage oscilloscope (LeCroy 9310 M, LeCroy Cor).

The ultrasonic impulse is propagated in water and crosses the oil sample contained in the vessel before reflecting on a Plexiglas surface of plate 2 (Fig. 2). Figure 3 shows, the experimental signal composed of echoes A1 to A4.

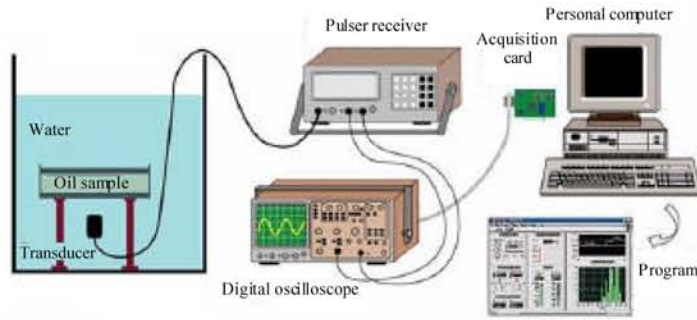


Fig. 1: Experimental set-up

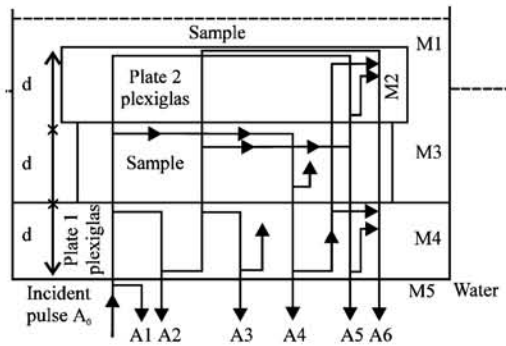


Fig. 2: Schematic of echoes reflected by the sample (A1 to A6 are observed echoes reflected from the interfaces between media Mi)

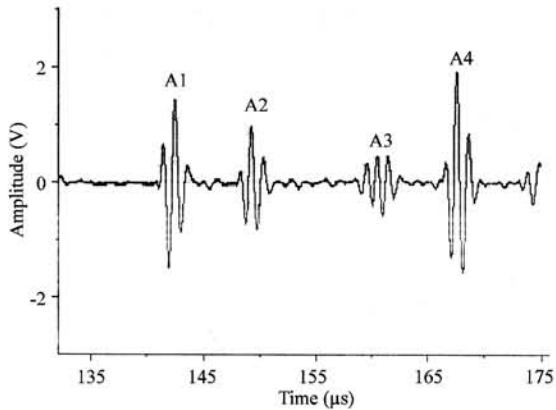


Fig. 3: Typical waveform of the reflected ultrasonic signal with the 5 MHz transducer

For ultrasonic velocity measurement, eight signal acquisitions were taken and averaged. It can be written as:

$$C_{\text{sample}} = 2\omega L / \phi_{A4} - \phi_{A2} \quad (1)$$

with $\omega = 2\pi\nu$

To obtain the phase experimentally, the FFT of signals A2 and A4 are calculated (Bakkali *et al.*, 2001).

The attenuation coefficient α was computed by fitting the experimental data to equation:

$$\ln A = \ln A_0 - \alpha d \quad (2)$$

Where:

d = The distance travelled by the wave

A_0 = The initial amplitude of the signal measured as the peak-to-peak voltage

A = The amplitude of the signal at distance (d)

Eight ultrasonic echoes were considered to compute attenuation.

Chemical analysis:

Fatty acids: The FA profile analysis was performed by derivatization to their corresponding methyl esters (Hartman and Lago, 1973) prior to the analysis by GC. Oil samples (50 mL) are diluted in the hexane to obtain a solution to be analyzed (about approximately 0.1%).

A VARIAN 3800 chromatograph on a CP Select CB (VARIAN) capillary column (50 m × 0.25 mm i.d., film thickness 0.25 μm), was used under the following temperature program: 185°C (40 min), 15-250°C/10 min. Samples injection is 1 μL (split ratio 1:100) at 250°C and the flow rate of Helium, used as carrier gas, was 1.2 mL min⁻¹. Temperature of both split injector and flame ionization detector was 250°C.

Free fatty acids: FFA content as the percentage of oleic acid was determined using AFNOR NF T 60-204 standard method. Acid value was defined as the amount (mg) of KOH required to neutralize FFA in 1 g of oil sample dissolved in a mixture of diethyl ether and ethanol in the presence of phenolphthalein.

Polar compounds: The content of total polar compounds was determined following the method proposed by the IUPAC (1992).

RESULTS AND DISCUSSION

Chemical characteristics: Table 1 shows the results for the Fatty Acids (FA) profiles of the SBO carried out on the oil samples at different heating periods. The FA profile of the frying oils changed as a result of cyclization, polymerization and hydrolytic, oxidative and other chemical reactions promoted by frying conditions (Nawar, 1996). The degradation affected unsaturated fatty acids more than saturated fatty acids. The FA composition of particular oil has marked effects on its frying performance as well as on its physical and chemical behaviour. The linoleic acid level in deep-frying oils appears to be an obviously negative factor in oil stability. Indeed, previous studies indicated that a lowered linoleic acid content in soybean oil resulted in improved oil quality during cooking and frying (Tompkins and Perkins, 2000). Changes in the FA profile during frying provide only limited information about these compositional changes, which are associated with oil degradation.

The regular limits in many countries for PC on frying fats and oils are around 25% and in some others are around 0.3% for FFA as the official regulations.

During oxidation and hydrolysis, FFA are formed, as a result of the cleavage of triglycerides (Perkins and Erickson, 1996). FFA content is the most frequently used test, but it is not recommended to use it as the only indicator of oil quality. Oils with high FFA are known to have a lower smoke point (Augustin *et al.*, 1987) and the surfactant effect of FFA contributes to the foaming, which leads to further oxidation of the oil. Previous studies of frying oils have shown that the FFA content increases during deep-frying (Kalapathy and Proctor, 2000). As expected, FFA content of the SBO increased significantly during frying and after 20 h, its content is 0.31% (Table 2).

Many researchers consider measurement of TPC to be one of the most reliable indicators of the state of the oil deterioration (Fritch, 1981; Gere, 1982). According to Billek *et al.* (1978) and Paradis and Nawar (1981), polar compounds indicate the degradation of oils and the breakdown of triglycerides. Table 2 shows that TPC in SBO increased significantly during frying. After 32 h of frying, the final TPC level is 25%. The TPC-based stability is 32 h of frying for SBO not to exceed the established limit. This would have occurred at even shorter time if the oil was used for frying foods swamp.

Ultrasonic measurements: The ultrasonic velocity and attenuation depend on the physico-chemical properties of the medium. Ultrasonic velocity decreases with the temperature in fat (McClements, 1997). Figure 4 shows the

Table 1: Soybean oil FA compounds at several frying times (%)

Frying conditions	0 h	8 h	16 h	24 h	32 h
C16:0	10.75	11.24	11.50	11.86	12.29
C18:0	3.32	4.53	5.56	6.70	7.77
C18:1	22.30	23.02	29.94	32.62	35.68
C18:2	54.21	53.61	47.62	42.97	38.78
C18:3	5.88	5.67	4.80	3.90	3.49

Table 2: Soybean oil polar compounds and free fatty acids at several frying times (%)

Contents	0 h	4 h	8 h	12 h	16 h	20 h	24 h	28 h	32 h
PC (%)	3.8000	7.75	12.50	16.6	18.12	20.00	21.90	23.75	25.0
FFA (%) (as oleic acid)	0.1155	0.14	0.16	0.2	0.24	0.31	0.37	0.44	0.5

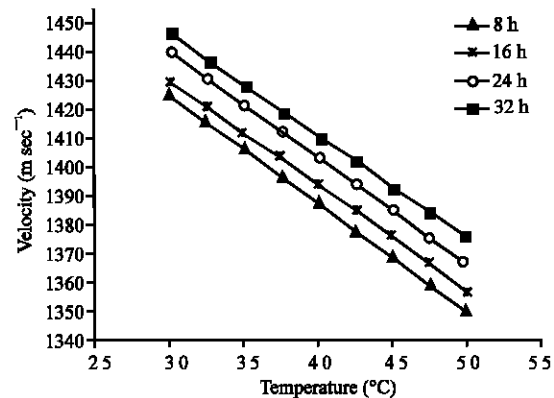


Fig. 4: Variation of velocity with temperature for different frying times

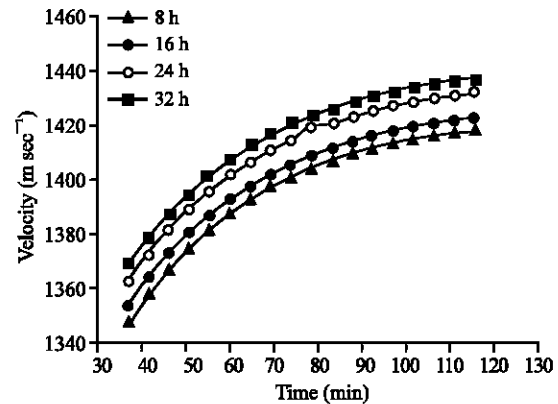


Fig. 5: Variation of velocity with time of cooling for different frying times

influence of temperature on the ultrasonic velocity measurements, for 8, 16, 24 and 32 h. As expected, the ultrasonic velocity decreases in line as the temperature increases. The average velocity temperature coefficient is -3.78 m/sec/°C. On the other hand, the ultrasonic velocity increases as the time of cooling increases (Fig. 5).

The time of cooling allows making the difference between the various frying. Every sample of the oil is

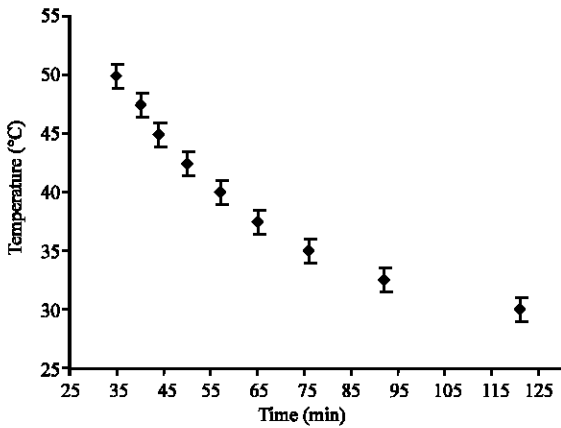


Fig. 6: Relationship between the temperature and the time of cooling for different frying times ($\pm 1^\circ\text{C}$)

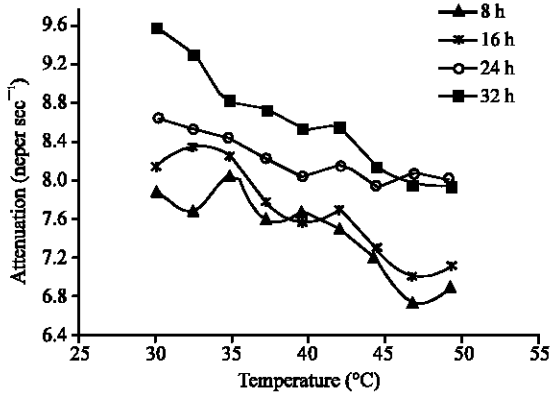


Fig. 7: Variation of attenuation with temperature for different frying times

differently cooled from others according to the duration of frying. Therefore, we can distinguish two fryings without using the temperature.

The ultrasonic velocity is related to the temperature, which in its turn is related to the time of cooling. Figure 6 shows the relationship between the temperature and the time of cooling. This curve is almost the same one for the various fryings.

The ultrasonic attenuation is also affected by temperature (Fig. 7). However, velocity is the ultrasonic parameter most used because of its reliable results (Benedito *et al.*, 2002).

It is not easy to determine the useful life of oil because, it depends on many factors, especially the composition of the oil and the type of oil used. Significant polynomial fits were found when relating the ultrasonic measurements and the chemical parameters.

Figure 8a and b show the possibility to detect the limits of the degrees of the polar components and free

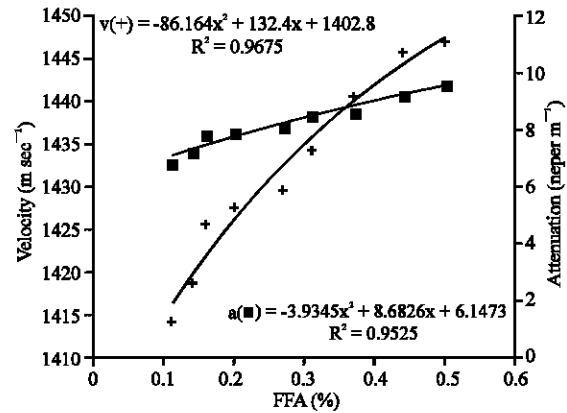


Fig. 8a: Relationship between the ultrasonic measurements and the percentage of free fatty acids at 30°C

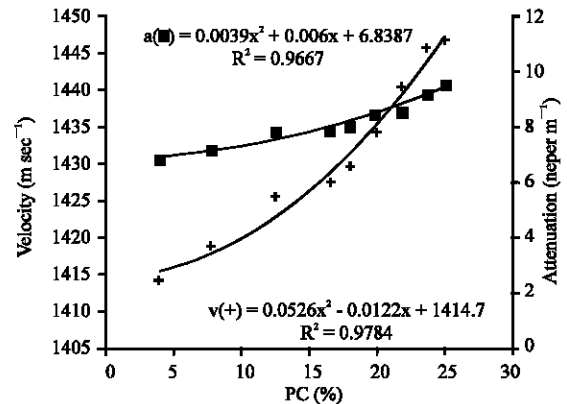


Fig. 8b: Relationship between the ultrasonic measurements and the percentage of polar compounds at 30°C

fatty acids (PC = 22%, FFA (as oleic acid) = 0.37%) using the ultrasonic measurements. The ultrasonic measurements are related to the chemical results, which show the feasibility of using an automated ultrasonic system to monitor the oil quality.

CONCLUSION

The chemical changes are linked to changes in ultrasonic parameters, which show that ultrasound can be used to assess and monitor oil quality. The velocity evolution obtained according the time of cooling appears to be also an indicator of oil degradation, in addition to the evolution of velocity according to the temperature.

The feasibility of using ultrasonic techniques to rapidly evaluate quality parameters for heated edible oils was investigated.

REFERENCES

- Augustin, M.A., T. Asap and L.K. Heng, 1987. Relationships between measurements of fat deterioration during heating and frying in RBD olein. *J. Am. Oil Chem. Soc.*, 64: 1670-1675. DOI: 10.1007/BF02542501. <http://dx.doi.org/10.1007/BF02542501>.
- Bakkali, F., A. Moudden, B. Faiz, A. Amghar, G. Maze, F. Montero de Espinosa and M. Akhnak, 2001. Ultrasonic measurement of milk coagulation time. *Meas. Sci. Technol.*, 12: 2154-2159. DOI: 10.1088/0957-0233/12/12/317. <http://dx.doi.org/10.1088/0957-0233/12/12/317>.
- Benedito, J., A. Mulet, J. Velasco and M.C. Dobargane, 2002. Ultrasonic assessment of oil quality during frying. *J. Agric. Food Chem.*, 50: 4531-4536. DOI: 10.1021/jf020230s. PMID: 12137472. <http://dx.doi.org/10.1021/jf020230s>.
- Billek, C., C. Cuhur and J. Waibel, 1978. Quality assessments of used frying fats: A comparison of four methods. *J. Am. Oil Chem. Soc.*, 55: 728-33. DOI: 10.1007/BF02665370. <http://dx.doi.org/10.1007/BF02665370>.
- Firestone, D., 1996. Regulation of Frying Fat and Oil, Chapter 19 from *Deep Frying: Chemistry, Nutrition and Practical Applications*. 1st Edn. In: Perkins, E.G. and M.D. Erickson (Eds.). AOCS Press, Champaign, IL, pp: 323-334. ISBN: 978-0935315752.
- Fritch, C.W., 1981. Measurements of frying fat deterioration: A brief review. *J. Am. Oil Chem. Soc.*, 58: 272-274. DOI: 10.1007/BF02582355. <http://dx.doi.org/10.1007/BF02582355>.
- Gere, A., 1982. Studies of the changes in edible fats during heating and frying. *Die Nahrung*, 26: 923-32.
- Hartman, L. and R.C.A. Lago, 1973. Rapid preparation of fatty acids methyl esters, laboratory practices (lab. pract), 22: 475-476.
- IUPAC (International Union of Pure and Applied Chemistry), 1992. In: IUPAC (Ed.). *Standard Methods for the Analysis of Oils, Fats and Derivatives* (1st Supplement to the 7th Edn.). Oxford, England: Pergamon Press, ISBN: 0632033371. <http://old.iupac.org/publications/books/author/dieffen.html>.
- Kalpathy, U. and A. Proctor, 2000. A new method for free fatty acid reduction in frying oil using silicate films produced from rice hull ash. *J. Am. Oil Chem. Soc.*, 77: 593-598. DOI: 10.1007/s11746-000-0095-4. <http://dx.doi.org/10.1007/s11746-000-0095-4>.
- McClements, D.J., 1997. Ultrasonic characterization of food and drinks: Principles, methods and applications. *Crit. Rev. Food Sci. Nutr.*, 37: 1-46. PMID: 9067087. <http://www.scopus.com/record/display.url?view=extended&origin=recordpage&eid=2-s2.0-0031066037&noHighlight=false>.
- Mulet, A., J. Benedito, J. Bon and N. Sanjuan, 1999. Low intensity ultrasonics in food technology. *Food Sci. Technol. Int.*, 5: 285-297. DOI: 10.1177/108201329900500401. <http://dx.doi.org/10.1177/108201329900500401>.
- Nawar, W.W. and Lipids, 1996. In *Food Chemistry*. 3rd Edn. In: Fennema O.R. (Ed.). Marcel Dekker, New York, 5: 225-319. ISBN: 978-0824796914.
- Orthofer, F.T., S. Gurkin and K. Liu, 1996. Dynamics of Frying. 1st Edn. In: Perkins E.G. and M.D. Erickson (Eds.). *Deep Frying: Chemistry, Nutrition and Practical Applications*. Champaign, IL, AOCS Press, pp: 223-244. ISBN: 978-0935315752.
- Paradis, A.J. and W.W. Nawar, 1981. A gas chromatographic method for the assessment of used frying oils: Comparison with other methods. *J. Am. Oil Chem. Soc.*, 58: 635-38. DOI: 10.1007/BF02672382. <http://dx.doi.org/10.1007/BF02672382>.
- Perkins, E.G. and M.D. Erickson, 1996. *Deep frying: Chemistry, nutrition and practical applications*, AOCS Press, Champaign, pp: 357. ISBN: 978-0935315752.
- Pokorny, J., 1989. Flavor Chemistry of Deep-fat Frying in Oils. In: Min D.B. and T.H. Smouse (Eds.). *Flavor Chemistry of Lipid Foods*. Chapter 7, AOCS Press, Champaign, IL, pp: 113-155. ISBN: 978-0935315240.
- Tompkins, C. and E.G. Perkins, 2000. Frying performance of low-linolenic acid soybean oil. *J. Am. Oil Chem. Soc.*, 77: 223-229. DOI: 10.1007/s11746-000-0036-2. <http://dx.doi.org/10.1007/s11746-000-0036-2>.
- Warner, K., 2002. *Chemistry of Frying Oils*. 3rd Edn. In: Akoh, C.C. and D.B. Min (Eds.). *Food lipids: Chemistry, nutrition and biotechnology*. New York, USA, CRC Press, pp: 205-222. ISBN: 978-0824707491. <http://www.informaworld.com/openurl?genre=article&isbn=978-0-8247-0749-1&volume=1&issue=1&spage=205>.