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Quality evaluation of frying oil deterioration by dielectric spectroscopy

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ABSTRACT

Dielectric measurements were carried out on the soybean oil that already used for frying dough of different moisture or heating the oil without dough (blank oil) over a frequency range of 40 Hz–100 MHz to evaluate the deterioration of the oil with frying time. A distinct dielectric relaxation caused by the dipole orientation polarization was observed at about 10 MHz. Dielectric parameters characterizing the relaxation feature were obtained by fitting Cole–Cole equation to the dielectric data. The relaxation time stayed around at 10^{-8} s with frying time, indicating that the size of the polar components have no change during the frying. Dielectric increment and dielectric loss increased linearly with frying time and the moisture contents of the dough, which was in agreement with the density of oil (measured in a separate experiment) that is in proportion to the deterioration. The time dependence of conductivity was different for the blank oil and that of oil used to fry dough, leading to the conclusion that the conductivity was mainly affected by the volatile decomposition products. The results show that dielectric spectroscopy could be a useful tool to evaluate frying oil.

1. Introduction

Deep-frying with vegetable oil is one of the most common procedures for preparing food. Continuous heating treatment towards the oil at a high temperature leads to changes in oil composition, this could directly affect human health (Chang et al., 1978). In particular, to maximize the profits in commercial practice, the frying oil is excessively used in some restaurants, which will affect the quality of the foods fried repeatedly on the table as the concern reported by various studies (Debnath et al., 2012; Sebastian et al., 2014). Therefore, the evaluation of frying oil has always been a hot topic both in fundamental and applied research of food science (Stier, 2004; Venkatesh and Raghavan, 2004). The deterioration of deep-frying oil is due to a series of physical and chemical changes, including aeration, vaporization, thermal oxidation, thermal polymerization and hydrolysis, when the oil is continuously or repeatedly used at elevated temperature in the presence of air (Chang et al., 1978; Dobarganes et al., 2000; Stevenson et al., 1984). In order to monitor food safety, the acid value, carbonyl value, polymer content, hydroperoxides (the oxidation products of the unsaturated fat acid by air in the oil) and polar component are used to evaluate the quality of frying oil (Billek et al., 1977; Gertz, 2000; Innawong et al., 2004; Stevenson et al., 1984; Stier, 2004; Wu and Nawar, 1986). Because most of decomposition products (e.g., free fatty acids, polymer components, aldehydes and ketones) generated during the process of deep-frying are polar (Urbančič et al., 2014; Wegmüller, 1994), the sum of these components excluding the triglyceride (the main component of edible oil) is named as "polar component (PC) value" (Hagura et al., 2006) The PC value can be used as a standard to evaluate the whole deterioration products. Actually, since free fatty acid and carbonyl compounds are just parts of all the deterioration products, the acid value or the carbonyl value separately determined cannot be regarded as the quantity index to reflect the deterioration degree of frying oil completely (Li et al., 2015; Tyagi and Vasishtha, 1996). Therefore, the measurement of PC value becomes significant.

Polar components in vegetable oil will change the dielectric constant of the oil, so the quality of frying oil can be monitored and evaluated by measuring the change of dielectric constant (Chang et al., 1978). Food Oil Sensor (FOS), as an instrument detecting the change of dielectric constant has been evaluated by many researchers. Wegmüller (1994) reported that FOS data corresponded linearly with polar components of frying fats, and PC value can be determined accurately with the FOS technique. Fritsch et al. (1979). have compared FOS response to other

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analytical values obtained on three types of frying oil samples; Chu and Luo (1994) have characterized the degree of frying oil deterioration by using a food system containing various levels of water, sugar and salt. Just in recent years, many efforts have been focused on the improvement of FOS, including the evaluation for the quality changes of the oil in cooking process by FOS (Khaled et al., 2014). Alternatively, so called "capacitive sensor" which can monitor the quality change of edible oil during repeated cooking process by the changes of oil permittivity with low-cost and fast detection, has also been reported (Paiter et al., 2015; Stevan et al., 2015). These studies have showed that the change in permittivity is practically potential to evaluate the oil quality to various extent. In short, the studies on evaluating oil quality based on the changes in permittivity are continuously developed are still developing.

Although these works identified the advantage of FOS in detecting oil deterioration, the intrinsic defects of the FOS (e.g., calibration problem of FOS) had been pointed out (Stier, 2004). Furthermore, the solid substance and water suspending in oil would affect the reading in the measurements using FOS.

Frequency domain dielectric spectroscopy (FDDS) provides information about dielectric response of materials to the electromagnetic fields. The fundamental electrical response can be reflected by the complex dielectric permittivity of the material ε^*. It is mathematically expressed as:

$$\varepsilon^* = \varepsilon - j\varepsilon'' = \varepsilon - j\frac{\kappa}{\omega\pi\varepsilon_0} \qquad (1)$$

where ε and ε'' are permittivity (dielectric constant) and dielectric loss, respectively, κ is the conductivity; ε_0 is permittivity of vacuum equal to 8.854 pFm^{-1}; the angular frequency $_\omega$ is determined by $\omega = 2\pi f$ (where f is measuring frequency).

As mentioned below, generally, the voltage used in dielectric measurements is very low, and the energy will not destroy the chemical structure of the studying material, this is desirable for monitoring food preparing processes from perspective of nutriology. Therefore, the dielectric spectroscopy (DS) as a non-invasive method (Venkatesh and Raghavan, 2005), is widely being used in research of food science to evaluate various agricultural products and processed foods, such as egg, cereal, vegetables, fruits, and dairy products (Jansson et al., 2005; Laogun, 1986; Venkatesh and Raghavan, 2004; Yagihara et al., 2007; Zheng et al., 2009). Moreover, due to its advantages of quick measurement, less requirements for sample (especially optic requirement) inexpensive and small equipment in size (Venkatesh and Raghavan, 2004), the dielectric spectroscopy method has potential use in production process of food as on-the-spot detection means (Khaled et al., 2015b).

On the other hand, oil, as a kind of typical non-conductor, is especially suitable as a studying objects for the DS method. A prominent relaxation phenomenon (El-Shami et al., 1992; Inoue et al., 2002; Lizhi et al., 2007, 2008; Stier, 2004) could be observed and the dielectric properties obtained from the relaxation could be used to evaluate the quality of oil. Some researches on vegetable oil have been reported (El-Shami et al., 1992; Inoue et al., 2002; Lizhi et al., 2007, 2008; Stier, 2004). For example, the comparison between dielectric properties and other conventional analytical methods (e.g., viscosity, refractive index, and iodine value, peroxide value and free fatty acids) for evaluating the quality of frying vegetable oil, and the results show that the change of dielectric properties can predict the deterioration degree of oil during heating of the oil (El-Shami et al., 1992); continuous evaluation of oil quality under deep-frying was introduced into dielectric measurement by Inoue et al. (2002). Differences in dielectric properties between different kinds of vegetable oil have also been studied through dielectric spectroscopy (Lizhi et al., 2007, 2008). In recent years, the research on dielectric properties of edible oils in radio and microwave frequency is still remained active (Corach et al., 2014; Gjorgjevich et al., 2012; Salema et al., 2013). However, the research that focused on the influence of deep-fried foods, especially cooked wheaten food on the quality and dielectric property of oil, as well as oil quality evaluation is still seldom. This may be because that many factors could influence the dielectric properties of oil during the cooking processes.

In fact, the measurements of dielectric properties (i.e. dielectric spectroscopy DS) of oil is essentially the same as the above-mentioned FOS, at least the same with the dielectric measurements in this study, that is, both of DS and FOS evaluate the degradation of frying oil quality by detecting total polar compound (TPC) in oil with capacitance or permittivity as mentioned in some reports (Gjorgjevich et al., 2012; Khaled et al., 2015a). Therefore, both methods have the advantage of fast measurements and no requirement in property of sample, especially in optical property, particularly, no chemical reagents (many are toxic compared with food) are required. Compared with dielectric spectroscopy method, the commercial FOS instrument is more practical because of its convenience in carrying. Otherwise, it is difficult for DS method to achieve the effect of FOS without other auxiliary experiments such as viscosity or density measurements. However, FDDS still have an irreplaceable advantages to FOS because the frequency dependence of oil permittivity can provide more information on the polarization process and relaxation mechanism, from which we can speculate the extent and possibility of oxidation and hydrolysis process. Besides, DS can also detect the changes in physical (geometric) shape of the component such as large impurities and aggregates inside the oil (Asami, 2002; Fan and Zhao, 2014).

In present work, soybean oil is used to fry the dough of different moisture contents to study oil deterioration as functions of frying time and water content of the dough, being a simulated experiments of actual frying pasta food. We have also measured the densities of these oil samples separately. By analyzing the dielectric spectra of these oil samples after frying, their dielectric properties at different frying time were obtained and the relaxation mechanism was interpreted. The relation between the changes of dielectric properties and that of the components of oil was discussed, and then the qualities of the soybean oil before and after the frying were evaluated by comparing the data of oil density. Meanwhile, the effects of food moisture on the deterioration of frying oil were also discussed.

The objective of this work is to evaluate the impact of frying time and food moisture on soybean oil quality according to the change in dielectric parameters. To this end, as a simulated experiments of actual frying pasta food, we measured the frequency-dependent dielectric spectroscopy of soybean oil that had been used to fry the dough of different moisture contents, and the densities of these oil samples separately. By analyzing the dielectric spectra of these oil samples after frying, we obtained the dielectric parameters, permittivity (or dielectric increment) and relaxation time, from which the relaxation mechanism was interpreted. This provide a helpful insight into the understand of origin of the oil deterioration. The relation between the changes of dielectric parameters and that of the components of oil was discussed based on the dependence of these parameters on the frying time and food moisture, and then the qualities of the soybean oil before and after the frying were evaluated by comparing the data of oil density. Meanwhile, the effects of food moisture on the deterioration of frying oil were also discussed.