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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 idelectric spectroscopy could be a useful tool to evaluate frying oil.

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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 frving 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 deepfrying 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:

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

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 ω 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 abovementioned 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 frequencydependent 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.

2. Experimental

2.1. Material (oil sample and paste sample)

Soybean oil (Food Sales & Distribution Co. Ltd, Beijing, China) and wheat flour (Guchuan Co. Ltd, Beijing, China) were purchased from a local market. The ingredient list on the Soybean oil packages writes that the total fatty acid is 80%, in which polyunsaturated fat acid is 60%, monounsaturated fat acid is 25% and saturated fat acid is 15%. The water content should be very low (according to the national standard of the People's Republic of China, it is lower than 0.2%).

2.2. Dough preparation

The compositions of dough samples used for frying and their preparing method of the samples with different compositions (different moisture contents) are listed in Table 1: (a) control group, oil was heated without dough; (b)~(e) flour-water, dough samples with moisture content of 0, 20%,40%, 60%, separately. Sample (b) ~(d) were prepared by mixing 40 g the wheat flour with specific amount of water in ziploc bags. Each sample was divided into six portions for one-hour frying test, and each portion of (b)~(d) was flattened into a sheet with a diameter of 4-5 cm and a hight of 0.5 cm (sample (e) was paste, which was taken out by spoon each time).

2.3. Oil samples preparation

Oil samples were numbered in the same way as dough sample (Table 1). For oil sample (a), 350 ml soybean oil was kept at the temperature range of 180–190 °C in a stainless steel container; oil was heated for 6 h per day, and the total frying time was 30 h (this is based on the consideration that in some restaurants the edible oil for cooking is used repeatedly, at least in China). 3~4 ml oil was taken at the end of each day. More specifically, 5 oil samples correspond to heating after 6 h, 12 h, 18 h, 24 h, and 30 h were obtained. Each sample was kept in a sealed vial at low temperature (4 °C). For oil samples (b)-(e), each dough sheet (or paste for sample (e)) prepared in 2.2 was fried one time, in 350 ml soybean oil and in a 500 ml fryer. The frying temperature was 180–190 °C. Each dough was fried for 7 min, and then was discarded. In order to allow temperature of the oil coming back to the correct range, the next dough was added after 3 min. The oil samples were collected and stored similarly as that for oil sample (a). All the samples were tested together for dielectric analysis.

2.4. Dielectric measurements

Table 1

The complex dielectric permittivity of oil samples were measured by using a 4294A precision impedance analyzer (Agilent Technologies over the frequency range from 40 Hz to 101 MHz at room temperature (18 °C). The amplitude of the applied alternating field was 500 mV, which is a very small value and can't damage the chemical composition of the oil. The measuring cell was a cylinder

composed with two resin discs, and each disc has an electrode about 1 cm in diameter. The distance between the two electrodes was about 2 mm, and the volume of this cell was about 1 ml. To eliminate the errors from the residual inductance (L_r) and stray capacitance (C_r) (the values of L_r , C_r and cell constant C_l have been determined by using three standard substances (air, ethanol and pure water) and KCl solution of varying concentrations are 1.46 E-8 (in farads per square siemens), 2.25 pF and 4.71 pF, respectively) according to the literature (Schwan, 1963), the raw experimental data, capacitance C_x and conductance G_x were corrected according to Schwan's method from the following equations (Asami et al., 1973):

$$C_{S} = \frac{C_{X}(1 + \omega^{2}L_{r}C_{X}) + L_{r}G_{X}^{2}}{(1 + \omega^{2}L_{r}C_{X})^{2} + (\omega L_{r}G_{X})^{2}} - C_{r},$$
(2)

$$G_{\rm S} = \frac{G_{\rm X}}{\left(1 + \omega^2 L_r C_{\rm X}\right)^2 + \left(\omega L_r G_{\rm X}\right)^2},\tag{3}$$

$$\varepsilon = \frac{C_s}{C_l},\tag{4}$$

$$\varepsilon^{''} = \frac{\kappa}{\omega\varepsilon_0},\tag{5}$$

$$\kappa = \frac{G_{s}\varepsilon_{0}}{C_{l}},\tag{6}$$

$$\kappa'' = \omega \varepsilon_0 \varepsilon, \tag{7}$$

Where ω ($\omega = 2\pi f$, f is measurement frequency) is angular frequency. The corrected capacitance C_s and conductance G_s are converted to the corresponding permittivity ε and conductivity κ through the equations $\varepsilon = C_s/C_l$ and $\kappa = G_s \varepsilon_0/C_l$ ($\varepsilon_0 = 8.8541 \times 10^{-12}$ F/m is the vacuum permittivity as defined before).

2.5. Density measurements

The density of oil was measured by pycnometer (CNS, GB 5526-85) every day after frying for 6 h. The formula used for the determination of density was as follow:

$$\rho = \frac{\mathbf{d}_{\mathbf{x}} - \mathbf{d}_{\mathbf{0}}}{(\mathbf{d}_{\mathbf{w}} - \mathbf{d}_{\mathbf{0}})\mathbf{V}} \tag{8}$$

Where d_0 is the weight of pycnometer, d_w is the weight of water, d_x is the weight of sample, and V = 25 ml. All the parameters were measured at 20 °C.

The preparing method and the compositions of dough samples used for frying.

Sampling	Moisture content by weight (%)	Dough preparation
(a)	_	-
(b)	0	Mix and knead 40 g flour with proper portion of water. Divide the dough into six portions. Flat each portion to a sheet.
(c)	20	
(d)	40	
(e)	60	Mix 40 g flour with 60 g water to paste.

3. Results and discussion

3.1. Dielectric properties of heated soybean oil without frying dough

3.1.1. Dielectric properties as a function heating time

Fig. 1 shows the dielectric spectra of sovbean oil samples being heated for 0 (fresh oil without heating), 6, 12, 18, 24 and 30 h. As is shown in Fig. 1(a), it is obvious that remarkable relaxation can be observed around at 10^7 Hz. It is worth noting that the scattered data points at low frequency $(<10^3 \text{ Hz})$ is from the polarization of oil and electrode interface, a experimental error, not from the oil system itself, and the noise had no influence on the getting of the dielectric parameters, τ and $\Delta \varepsilon$, because it is located long away from the relaxation time at about 10⁷ Hz. The dielectric constant (dielectric permittivity or permittivity, similarly hereinafter) ε increased when the heating time increased while the characteristic relaxation frequency f_0 virtually remains unchanged, which was in agreement with the present reports (Chu and Luo, 1994; Fritsch et al., 1979; Wegmüller, 1994). The mechanism of the relaxation can be considered to be caused by the dipole orientation polarization of triglyceride which is main component of soybean oil under the applied electric field. The fact that both the permittivity ε and the dielectric loss ε'' increased with the heating time shows the increment of polar components formed during the heating process, the polar components may include free fatty acids, diglycerides, hydroperoxides (Chang et al., 1978; Stevenson et al., 1984).

3.1.2. Dielectric parameters depended on heating time

The dielectric parameters of different heating time were obtained by fitting *the dielectric data to* the Cole–Cole equation (equation (9) to the dielectric data, where i = 1) and are listed in Table 2 along with the densities of these oil samples.

$$\varepsilon^* = \varepsilon_h + \sum_i \frac{\Delta \varepsilon_i}{1 + (j\omega\tau_i)^{\beta_i}} + A\omega^{-m}$$
(9)

Where $\Delta \varepsilon$ is the dielectric increment defined as $\Delta \varepsilon = \varepsilon_{\rm l} - \varepsilon_{\rm h} (\varepsilon_{\rm l})$ and $\varepsilon_{\rm h}$ are limit value of permittivity at low and high frequency respectively). $\tau_{\rm i} (= 1/2\pi f_{oi}, f_{oi}$ is the characteristic relaxation frequency) is the relaxation time, and $\beta_{\rm i}$ is the distribution parameter of the relaxation time of the relaxation numbered *i*. A ω^{-m} is the electrode polarization item obtained by fitting the dielectric spectra (Cole and Cole, 1941).

For clarity, the values of permittivity ε and the dielectric loss ε'' together with the density ρ of oil were plotted as a function of heating time in Fig. 2. As can be seen that both ε and ε'' increase linearly with the heating time, which is in agreement with the

 Table 2

 Dielectric parameters of soybean oil with different heating time.

Time/h	ϵ_l	$\Delta \epsilon$	ε″	$\kappa_{l}/s \ m^{-1}$	f_0/Hz	τ/s	$ ho/g\ cm^{-3}$
0	4.028	0.2422	0.1123	8.718E-8	1.678E7	9.486E-09	0.9581
6	4.122	0.2891	0.1285	7.769E-8	1.678E7	9.486E-09	0.9616
12	4.213	0.3521	0.1498	7.570E-8	1.678E7	9.486E-09	0.9662
18	4.327	0.4310	0.1728	7.931E-8	1.461E7	1.090E-08	0.9709
24	4.388	0.4979	0.1906	8.85E-8	1.461E7	1.090E-08	0.9766
30	4.507	0.5652	0.2089	1.023E-7	1.107E7	1.438E-08	0.9798



Fig. 2. Dielectric increment $\Delta\epsilon$, dielectric loss factor ϵ'' and density ρ of soybean oil heated for 0, 6, 12, 18, 24 and 30 h.

change of density o. The increase of oil density with heating time is due to the accumulation of polymers (mainly dipolymers) during heating (Topallar et al., 1995). Fig. 3 shows both of the dielectric increment $\Delta \varepsilon$ and the dielectric loss ε'' depend linearly the density of the oil samples. This means that the density of oil is in direct proportion to the deterioration of the oil. In the same way, the dielectric increment $\Delta \varepsilon$ and the dielectric loss ε'' increased with heating time because of the accumulation of polar components (Hein et al., 1998; Wegmüller, 1994), and polymers were included. In addition, because ε'' and $\Delta \varepsilon$ are all sensitive to hydroperoxides which are noxious for human health, as reported by El-Shami (El-Shami et al., 1992), we can evaluate oil deterioration degree from the value of these dielectric parameters, because the amount of polar components in frying oil is proportional to the dielectric increase $\Delta \varepsilon$ dielectric loss ε'' . Besides, we know that the accumulation of hydroperoxides (which are dipolar and noxious for human health) by linear relation between dielectric parameters ($\Delta \varepsilon$ or dielectric loss ε'') and frying time as shown in Fig. 6, therefore, we can provide rough information on oil deterioration.



Fig. 1. Frequency dependence of ε (a) and dielectric loss (b) of soybean oil heated for 0, 6, 12, 18, 24, 30 h.



Fig. 3. Density dependence of dielectric increment $\Delta \epsilon$ (a) and dielectric loss factor ϵ'' (b).

The values of low-frequency conductivity κ_l for the soybean oil at different heating times were direct read at about kHz range where the conductivity is basically a constant and are plotted in Fig. 4(a), and the relaxation time τ of different heating times are plotted in Fig. 4(b). While the oil was being continuously heated, its low frequency conductivity k₁ decrease and reaches a minimum value near 12 h, and then increase with heating time from 12 h to 30 h. This may be explained as a possibility that the conductivity of oil was deeply influenced by the impurities. Besides, water evaporation is also an important factor: although the soybean oil sold as commercial contains only very small amount of water, the water molecules still contributes a lot to the conductivity. During the early stage of heating (0-12 h), water evaporated as well as some watersoluble impurities, which led to a decrease in conductivity. With the heating time, new decomposition products, such as aldehydes, ketones and alcohols, formed from the decomposition of hydroperoxides (Chang et al., 1978; Dobarganes et al., 2000; Gertz, 2000), which mainly contributed to the conductivity of oil. As a result, the conductivity increase when heating time exceeded certain value, 12 h in this work.

The relaxation time τ basically maintains constant with heating time (Fig. 4(b)), which might be considered that the species and size of the polar components remained largely unchanged during the present heating time scale. This is because the components that cause dielectric relaxation are the fatty acid part, the size of which did not change either in triglycerides or their decomposition products after heating or frying, as well as the dipole moment. If the polar components changed-fracture for example, which reduces the size of the dipole moment, the relaxation time would decrease and the relaxation would move towards the high frequency, but this is not observed in our experiments.

Summing up the above, the permittivity ε , the dielectric increment $\Delta \varepsilon$ and the dielectric loss ε'' all increase linearly with the increase in heating time, this suggest a possibility that the polar components are accrued gradually with the heating because in

addition to polar dipole orientation polarization there are no reasons that cause the dielectric relaxation. Therefore, the change of these dielectric parameters can directly reflect the deterioration of the oil, and evaluate the quality of oil by measuring. Although commercial technique (FOS) that measure the permittivity is considered as a useful tool to evaluate oil quality, the result obtained by FOS can be adversely affected by the impurities, especially water (Stier, 2004). This is because the following two reasons: The presence of impurities may cause interface polarization which will give additional dielectric increase that can not be distinguished from the oil. Another is that water is very sensitive to permittivity of measuring system at microwave range, this limit the use range of FOS. While in the measurement of dielectric spectroscopy that can show us relaxation, $\Delta \varepsilon$ caused by the dipole orientation polarization obtained from the analysis of the relaxation is connected only to the deterioration products. Even we measure microwave dielectric spectroscopy, the contribution of water molecular to permittivity can also be distinguished from the whole dielectric spectroscopy data. Therefore, the influence of impurities can be eliminated by using dielectric increment $\Delta \varepsilon$ while monitoring the quality of frying oil. Meanwhile, dielectric parameters are sensitive to hydroperoxides, which makes dielectric spectroscopy a good tool to reflect specific noxious components, as well as the total polar components.

3.2. Dielectric properties of fried soybean oil

3.2.1. Dielectric spectra of fried soybean oil

Fig. 5 shows the dielectric spectra of soybean oil during frying dough of different moisture contents (0(a), 20(b), 40(c) and 60%(d)). Apparently, the dielectric behaviors of these fried oil were similar to that of heating oil shown in Fig. 1. A dielectric relaxation around at 10^7 Hz is also observed, and it is clear from the insets of these figures that the dielectric increment increased with frying time. By using the same way as mentioned in Section 3.1.2, the dielectric parameters of every oil samples were also obtained.



Fig. 4. Dependence of low-frequency conductivity κ_l (a) and relaxation time τ (b) of the oil on heating time.



Fig. 5. Dielectric spectroscopy of soybean oil during frying of dough with different moisture contents: 0 (a), 20 (b), 40 (c) and 60% (d).

Frying time dependence of these dielectric parameters was shown in Fig. 6(a) and (b), respectively.

3.2.2. Frying time dependence of soybean oil

The changes in the dielectric increment $\Delta \varepsilon(a)$, the dielectric loss factor $\varepsilon''(b)$ and density $\rho(c)$ of soybean oil during frying of dough of different moisture contents (0, 20, 40 and 60%) are presented in Fig. 6. From the Fig. 6 it can be seen that $\Delta \varepsilon$, ε'' and ρ of all these groups increased with frying time because of the accumulation of deterioration products, which was in agreement with the control group (heated oil). However, the value of $\Delta \varepsilon$, ε'' and ρ of these oil samples during frying were lower than that during heating, which were different from present report (Fritsch et al., 1979). This may be interpreted that oil deterioration is connected to the frying or heating temperature (Dobarganes et al., 2000). In our frying experiment, because just 350 ml oil was used temperature of the whole system was significantly influenced by the doughs when they are added into the oil. As a result, average temperature of the oil during frying was lower than that of heating in our experiments. As the case to the reported works, they usually use 4-5 L oil, so the dough has relatively little influence on the temperature in their system. This might account for the differences between our result and the previous literature. However, it is clear from the Fig. 6 that the changes of dielectric parameters of these soybean oil during frying were in agreement to the changes of oil density, therefore, this adequately support the conclusions in 3.1.2 that dielectric increment $\Delta \varepsilon$ and dielectric loss ε'' are the important parameters to evaluate the quality of frying oil.

It can also be found from Fig. 6 that the values of $\Delta \varepsilon$, ε'' and ρ of oils with the same frying time slightly grew as the moisture content

of the dough increased. This might be interpreted as following: on one hand, as the water in the dough vaporized under high temperature, the contact with oil and the oxygen molecular in the air was promoted. As a result of this process, the oxidation reactions was intensified, resulting in more decomposition products. On the other hand, because usually food moisture promoted hydrolytic reactions (Dobarganes et al., 2000) with products like diglycerides, free fatty acids formed, these products cause the increase of dielectric parameters. To conclude, the deterioration of frying oil can be intensified by the increase of food moisture content, while the effect of food moisture content is smaller than that of heating or frying time.

Fig. 7 shows the time dependence of low frequency conductivity κ_l for the oil systems after frying the dough of different moisture (including heating soybean oil). At the beginning of frying or heating, the values of the conductivity κ_1 for each group decreased with the increase in frying or heating time, this is because the vaporization of the volatile impurities, especially water. Also, it is also obvious from Fig.7that the conductivity of all the frying oil were lower than that of the heating oil at any time; this could be explained with the same reason showing as in the Section 3.2.2. Similarly, as analyzed in Fig. 4, during heating the conductivity of oil increased with the increase of time after 12 h due to the accumulation of decomposition products. However, it is clear that the conductivity of oil during frying of dough changed little after 6 h with the time, which was different from that of the heated oil. In addition, because the volatile decomposition products spilled out during frying, we can assume that the volatile decomposition products mainly attribute to the change of the conductivity of frying oil.



Fig. 6. Dielectric increment Δε (a), dielectric loss factor ε" (b) and density ρ (c) of soybean oil during frying of dough with different moisture contents (0, 20, 40 and 60%).



Fig. 7. Low frequency conductivity κ_1 of soybean during frying of dough with different moisture contents (0, 20, 40 and 60%) and heated oil.

To conclude, water in food could accelerate the hydrolysis and oxidation reactions, namely, the higher food moisture content, the faster deterioration of the frying oil, which has been reflected in our experiments.

4. Conclusions

The dielectric properties of soybean oil after frying the dough of different moisture or heating the oil were investigated at temperature of 18 °C from 40 Hz to 110 MHz. A remarkable dielectric relaxation phenomenon caused by the dipole orientation polarization around at 10⁷ Hz was observed Dielectric parameters (permittivity ε , dielectric increase $\Delta\varepsilon$, dielectric loss factor ε'' , relaxation time τ , and low frequency conductivity κ_l) were obtained by fitting Cole–Cole equation to the dielectric data. ε , $\Delta\varepsilon$ and ε'' all increased linearly with the frying or heating time, which was in agreement to the change of the density of oil that was measured separately in this work. This suggests a relevance between the increment of dielectric parameters and the amount of polar components formed during the heating process. The relaxation time τ remained unchanged with the increase in heating time, this is interpreted that the size of the polar components hadn't changed. The difference of κ_l between heating oil and frying oil indicates that the volatile decomposition products mainly attribute to the change of the conductivity of frying oil. In addition, the water in food showed adverse effect on oil, namely, the water in food could accelerate the deterioration of oil. Therefore, one can evaluate the quality of frying oil by measuring the dielectric properties through dielectric spectroscopy. With the advantages of non-invasive, simple and rapid, dielectric spectroscopy can replace the conventional methods to evaluate the quality of frying oil.

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