A New Method for Free Fatty Acid Reduction in Frying Oil Using Silicate Films Produced from Rice Hull Ash

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ABSTRACT: Sodium silicate films were produced from rice hull ash silica, and their application in reducing free fatty acid (FFA) in frying oil was investigated. Sodium hydroxide concentration of these films was 32, 28, 24, and 20% with silica concentration of 45, 50, 55, and 60%, respectively. Moisture contents of these films were 20–23%. Adsorption performance of the films was investigated in frying oil at 80°C for 10–40 min. FFA content gradually decreased with treatment time for all films. There were no significant differences in FFA content among films for treatments up to 30 min. Treatment with 45 and 50% silica films for 40 min led to significantly larger reduction in FFA compared to treatment with 60% silica film. Differences between the FFA content of oil treated for 40 min with 55% silica and the FFA content of oils treated with other silica films were insignificant. FFA content of oil decreased from 0.8 to 0.55, 0.55, 0.57, and 0.59% after 40 min treatment with 45, 50, 55, and 60% silica film, respectively. Peroxide values (PV) of treated oils slightly increased from 48 to about 60 meq/kg for films with 45, 50, and 55% silica. Treatment with 60% silica led to a decrease in PV values to 42 meq/kg. Soap content of oil increased from 51 to over 100 ppm as a result of silicate film treatment.

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KEY WORDS: Free fatty acid, frying oil, rice hull ash, silicate films.

Frying, an important food preparation method, is widely used by the food industry. Oils used for frying are hydrophobic substances consisting predominantly of triglycerides. Although oils are stable under proper storage conditions, decomposition of oil occurs at high temperatures (300–400°F) generally used for frying (1). Hydrolysis due to the presence of moisture in the foods and thermal oxidation are major causes for frying oil decomposition. This decomposition results in poor performance of frying oil and off-flavor formation and may influence nutritional quality and food safety. Peroxides and volatile products are formed due to thermal oxidation of oils. Free fatty acids (FFA) are formed due to oil hydrolysis. As a result of this, FFA content normally increases from <0.1 to 0.5–0.8% (1). Fatty acids are more volatile than glycerides, and hence the smoke, flash, and fire points of oil decrease as the FFA content of oil increases.

The use of rice hull ash (RHA) in removing FFA from soy oil has been investigated (2,3). Adsorption on amorphous RHA silica was attributed to the FFA (4). Alkali refining which involves caustic (NaOH) addition has been used by the oil industry to remove FFA in oil (5). Alkali reacts with FFA to form soap. Most of the soap formed during this process may be removed by centrifugation followed by water washing. Silicates have been widely used in edible oil refining and frying oil treatment as an alternative to caustic addition. Since soaps formed in frying oil are not removed after FFA reduction, the treated oil usually has higher soap content compared to the untreated oil. Silicate treatment has the advantage of reduced oil losses and soap contamination. Silicates have been added in powdered form to the oil to be purified and are subsequently removed by filtration (6). The effect of active filtering medium consisting of silicates as one of the active components in reducing FFA from oils has been investigated (7). Silicate films could be used as an alternative to silicate powder and active filter medium. Silicate films can be easily removed from the oil after the treatment and hence could eliminate the filtration step required for traditional methods. Currently, silicates are produced by smelting quartz sand and alkali in a high-temperature furnace. However, the simplicity of a low-energy chemical method developed to extract amorphous silica from RHA (8,9) makes RHA, a co-product of rice industry, an economical source for silicate production. Silicate produced from RHA has the potential to be used in a variety of applications for oil purification.

The objectives of this study were to (i) demonstrate the performance of sodium silicate films produced from RHA silica in removing FFA from frying oil at an elevated temperature and (ii) determine the interaction of silicate films with frying oil components by diffuse reflectance Fourier transform infrared (FTIR) spectroscopy.

MATERIALS AND METHODS

RHA was obtained from Producers Rice Mill (Stuttgart, AR), and used frying oil was from Tyson Foods, Inc. (Springdale, AR).

Silicate film production. Silica was extracted from RHA using the method of Kalapathy *et al.* (10). A 60-mL portion of 1 N NaOH was added to 10 g of RHA and boiled in a cov-

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*To whom correspondence should be addressed at Department of Food Science, University of Arkansas, 272 Young Ave., Fayetteville, AR 72704. E-mail: ukalapat@comp.uark.edu ered 250-mL Erlenmeyer flask for 1 h with constant stirring to dissolve the silica and produce a sodium silicate solution. This solution was filtered through Whatman No. 41 ashless filter paper, and the carbon residue was washed with 100 mL of boiling water. The filtrate and washing were combined and heated to reduce the final volume to 60 mL and allowed to cool to room temperature.

The silica extract produced was used to produce silicate films by reducing the volume to obtain 16, 20, 24, and 30% silica concentration. All silicate solutions were adjusted to 3 N NaOH prior to volume reduction to prevent silica precipitation at higher silica concentrations. Isopropyl alcohol was added (1 mL/100 mL film-forming solution) as a wetting agent in all film-forming solutions. Four layers of cheesecloth were placed in a weighing boat with hexagonal base (5.0 cm each side), and 12.0 mL of silicate solution was poured into the boat and allowed to dry at room temperature (23°C) for 48 h. Films were manually removed from the weighing boat and stored in Ziplock bags until testing.

Silica, sodium, and moisture contents. Silica content was determined gravimetrically by lowering the pH of 50 mL film-forming solution from 12 to 7 to precipitate silica. Silica precipitate was washed twice with 100 mL water, dried at 110°C for 12 h, and weighed. Silica content of films was reported as amount of silica per gram of silicate film.

Sodium content of films was calculated based on the concentration (3 N) in the film-forming solution and the weight of the silicate films, and reported as the amount of NaOH per gram of silicate film.

Moisture contents of the films were determined using an air oven method. Film samples (0.5 g) were heated in aluminum moisture pans at 130°C for 1 h. The samples were cooled in a dessicator and weighed. The weight losses (%) were recorded as the moisture content of samples.

The weights of the cheesecloth were excluded in all calculations.

Silicate film treatment. Frying oil (100 g) was placed in a 1000-mL beaker, and the oil was preheated to 80°C using a stirrer/hotplate. Silica film was placed in a plastic basket which exactly fit into the beaker and was immersed in the oil. Oil was gently stirred, and the temperature was maintained at 80 ± 2°C using the lowest setting of the hotplate. Oils were treated with film for 10, 20, 30, and 40 min, and oil samples were collected for FFA, peroxide value (PV), and soap determinations. A control treatment was performed using cheesecloth instead of silicate film. All treatments were performed in triplicate.

FFA, PV, and soap determinations. FFA content, PV value, and soap concentration in treated and untreated oil samples were determined using AOCS methods (11).

Structural analyses. Diffuse reflectance FTIR spectra were obtained by adding 100 interferograms using an Impact 410 Nicolet instrument (Nicolet Analytical Instruments, Madison, WI). Films were washed with hexane three times (100 mL each) to remove free oil on the film surface. The FTIR spectra of hexane-washed film surfaces were obtained by placing circular pieces of films on the diffuse reflectance sample holder (Spectra-Tech Inc., Shelton, CT). For all FTIR spectra measurements, background spectra were obtained using respective sample holders without the samples. All FTIR spectra were automatically corrected for background spectra by the software used (Omnic 3.0; Nicolet Analytical Instruments) for data collection.

Statistical analyses. Data were analyzed by analysis of variance, and means were separated by the least significant difference when significant F ($P < 0.05$) values were observed (12).

RESULTS AND DISCUSSION

Film composition. Silica concentration was 16% in the 1 N NaOH extract obtained from RHA. Silica extract was concentrated and adjusted to 3 N NaOH to produce flexible silicate films. Adjustment of film-forming solutions with 3 N NaOH was necessary to solubilize silica at concentrations required to produce films with up to 60% silica. Concentrations of NaOH were 22, 26, 29, and 33% (w/w, based on film weight) for films with 60, 55, 50, and 45% silica (w/w, based on film weight), respectively. Moisture content of 60, 55, and 50% silica films was 20%, while that of 45% silica was 23%. Average film thickness varied between 0.84 to 1.0 mm. Although films could be formed without cheesecloth reinforcement (10), their physical structures were not maintained when they were placed in the oil at 80°C. However, when cheesecloth reinforcement was used, the films maintained their physical structure without any deformation even at temperatures higher than 80°C. Hence, cheesecloth-reinforced films were more suitable for FFA reduction in frying oil and were used for further studies.

FFA reduction. As shown in Figure 1, FFA decreased from 0.82 to about 0.7% after 10 min treatment with silica films. FFA acid contents gradually decreased with increasing treatment time. The differences in FFA content after treatment time of 10, 20, 30, and 40 min were significant ($P < 0.05$). However, there were no significant differences in FFA content among films, for treatments up to 30 min. After 40 min, oil treated with 45 and 50% silica films had significantly ($P < 0.05$) lower FFA content than film treated with 60% silica oil/film. The differences between the FFA content of oil treated for 40 min with 55% silica and other silica films were insignificant. Hence, this observation demonstrated that Na^+, not silica, was responsible for FFA reduction. Further, the difference in Na^+ content did not have a significant effect on FFA reduction for treatment time of 30 min or less. Apparently, the surface concentrations of Na^+ in all the films tested were sufficient to lower FFA content from 0.82 to about 0.6% for treatments up to 30 min. However, as the surface Na^+ concentration decreased with increasing treatment time due to the reaction of Na^+ with FFA to form soap, the remaining surface Na^+ concentration of 45 or 50% silica film was sufficient to impart significant differences in FFA reduction in comparison to 60% silica film.

PV and soap content of treated frying oil. Figure 2 shows the effect of silicate film treatment on the PV of the oil. Films

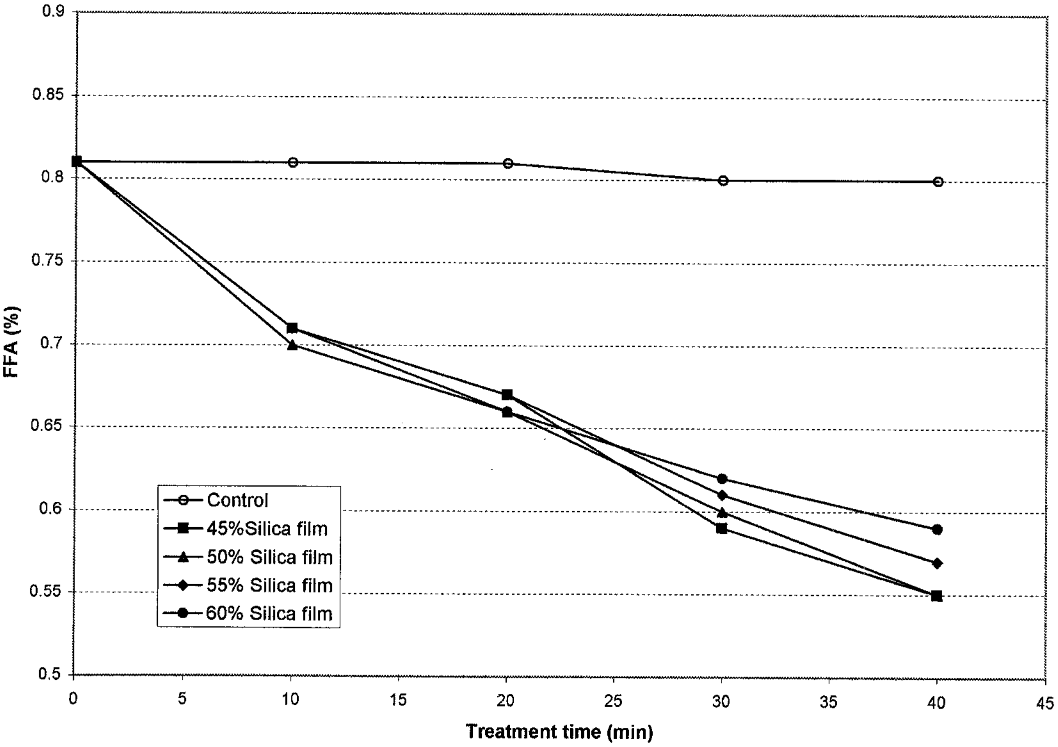

FIG. 1. The effect of silicate film treatment on free fatty acid (FFA) content of frying oil. Standard error for FFA determinations ranged from 0.006 to 0.009%.

containing 45, 50, and 55% silica resulted in a slight increase in the PV of the oil. However, no significant differences in PV were observed for film containing 45, 50, and 55% silica films. The PV were significantly higher compared to the control for treatment times of 20 min or longer. However, a slight decrease in PV was observed for treatment with 60% silicate

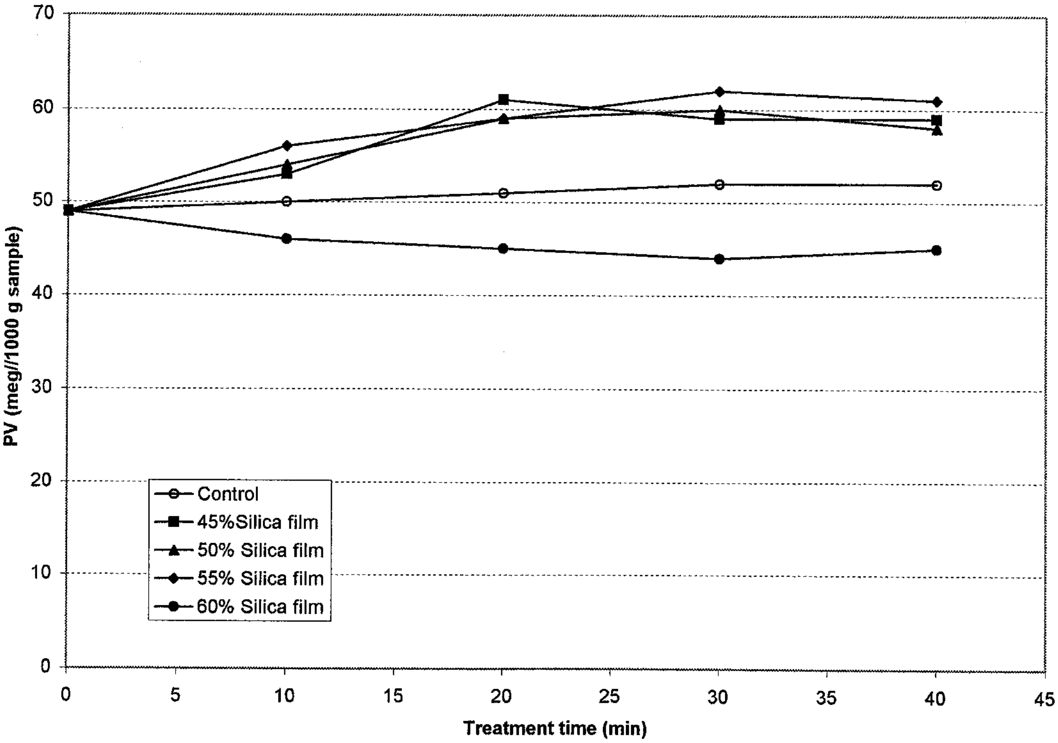

FIG. 2. Peroxide values (PV) of frying oil after treatment with silicate films. Standard error for PV determinations ranged from 1.24 to 1.84 meq/kg.

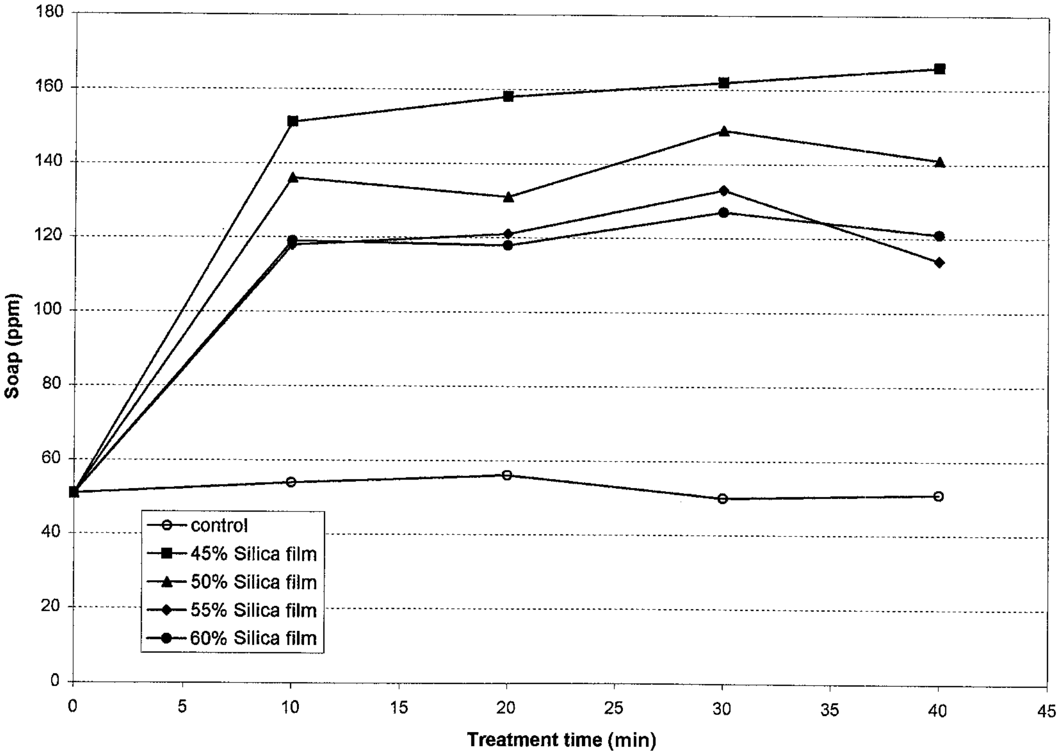

FIG. 3. Soap concentration of frying oil after treatment with silicate films. Standard error for soap determinations ranged from 2.08 to 12.43 ppm.

film with a significant decrease after 30 min or longer treatment time. The differences in PV between 45, 50, or 55 and 60% silica films may have resulted from the opposing effect of heating and adsorption of peroxides by silica. While heating can promote lipid oxidation, silica can adsorb oxidation products (2). Further, FFA also compete for adsorption sites in the silicate film. As a result of increasing adsorption sites with increasing silica concentration, the 60% silica film caused a net reduction in PV, while films with lower silica concentrations led to a net increase in PV values.

Figure 3 shows the soap content of the oil after treatment with silicate films. Treatment for 10 min resulted in a sharp increase in soap content from 51 to 151, 136, 118, and 119 ppm for 45, 50, 55, and 60% silica films, respectively. However, no significant changes in soap content were observed with increasing treatment time. As soap formed due to the reaction of FFA with sodium silicate, the majority of it was released into the oil. Further, stirring the oil also would have induced release of the soap into the oil. However, some of the soap could be bound to the film surface, and inconsistency in releasing and binding soap might be a cause for the small fluctuation observed in the soap content. For all treatment times, oils treated with 45% silica film had significantly higher soap content compared to 55 and 60% silica films. The differences in the soap content between oil treated with 50% silica films and 45, 55, or 60% silica films were insignificant for all treatment times.

Silicate film interaction. Structural features of silicate film surfaces are shown in the FTIR spectra (Fig. 4). All silicate films showed identical surface structural features regardless of sodium and silica concentration. The major absorbance peak between 1100 and 1400 cm^{-1} was due to siloxane bonding in the film (4,13,14). The bands below 900 cm^{-1} were due to skeletal network vibration in the film structure. The OH stretching and bending vibrations resulting from moisture in the film appeared as broad bands above 3000 cm^{-1} and 1750 to 2100 cm^{-1}, respectively. FTIR spectra of the surface of hexane-washed film after subtraction of silicate background are shown in Figure 5. The silicate background-subtracted spectra clearly show the physically and chemically adsorbed components on the treated film surface. The absorbance peaks of carboxylate ion and hydrogen-bonded carbonyl group appeared at 1554 and 1721 cm^{-1}, respectively. A comparatively larger peak due to carboxylate ion indicated that the adsorbed components were predominantly FFA in the form of soap. Further, this observation confirmed the hypothesis that a portion of soap formed was not released into the oil, causing inconsistency in the soap content of treated oil. However, the surface concentration of carboxylate ion in the hexane-washed films was similar, as indicated by similar carboxylate peak size. The peaks at 1464, 2854, and 2926 cm^{-1} were from CH_2 deformation, asymmetric CH stretching, and symmetric CH stretching, respectively, of CH_2 groups in the adsorbed oil and FFA.

Our results demonstrate that silicate film treatment could be used as an alternative to traditional methods that use sili-

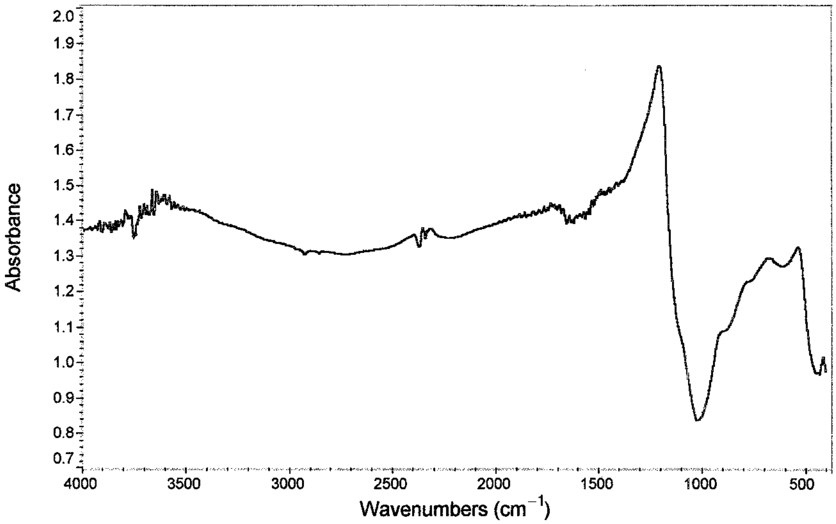

FIG. 4. Fourier transform infrared spectra of the surface of silicate film with 45% silica.

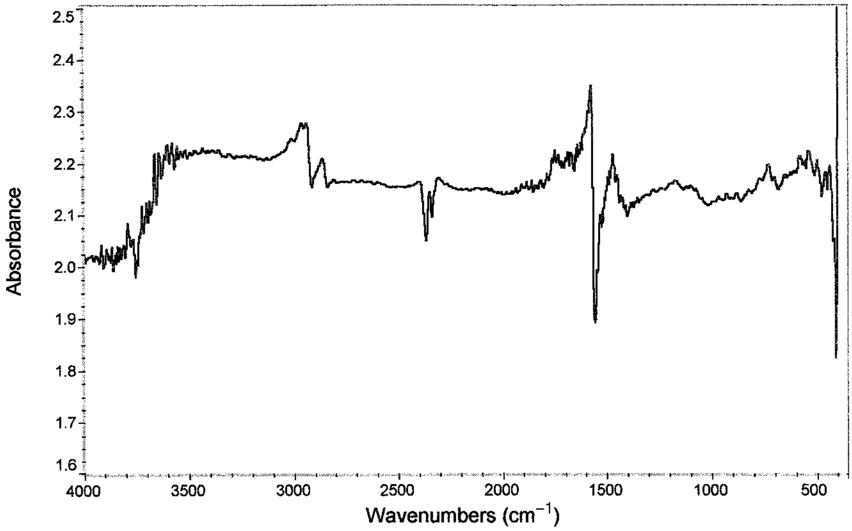

FIG. 5. Fourier transform infrared spectra of physically and chemically adsorbed oil components on 45% silica film after 40-min treatment (obtained by subtracting spectra of film surface before treatment from the spectra of film surface after treatment). The film was washed with hexane after treatment to remove unbound oil components.

cate powder as a filtering medium for FFA reduction in frying oil. It should be noted that the 25% decrease (0.8 to 0.6%) in FFA content of frying oil was due to one treatment with a single silicate film. The efficiency of the film treatment could be improved by using a cascade of films and repeated treatment. Further studies are needed to modify silicate film surface for simultaneous reduction of soap content and peroxides during the FFA reduction. Silicate film is a nonfilter adsorbent and easily can be removed from the oil medium. The advantage of using silicate film is that it eliminates the filtration step required for the traditional methods.

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