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Improvement in the Quality of Deteriorated Blended Oil by Calcium Silicate Treatment

Fumihiko OGATA,[a] Haruka AMI,[a] Eri NAGAHASHI,[a] Takehiro NAKAMURA,[a] and Naohito KAWASAKI[*,a,b]

[a]Faculty of Pharmacy, Kindai University; 3–4–1 Kowakae, Higashi-Osaka, Osaka 577–8502, Japan; [b]Antiaging Center, Kindai University; 3–4–1 Kowakae, Higashi-Osaka, Osaka 577–8502, Japan

We prepared blended oil using soybean oil (SR10) and rapeseed oil (SR01), and evaluated the quality of deteriorated pure and blended oils (with weight/volume ratio of soybean oil to rapeseed oil of 2:1, 1:1, and 1:2) by heat treatment and aeration. The ratio of the acid value following deterioration (AV) to its initial value (AV_0) i.e., the value of AV/AV_0 was in the order SR10 (3.29) << SR01 (7.50). On the other hand, the ratio of the carbonyl value after deterioration (CV) to its initial value (CV_0) i.e., the value of CV/CV_0 decreased with increase in the proportion of rapeseed oil in the blended oil (SR01 (3.12) << SR10 (4.15)). We thus establish that the fatty acid component of the blended oil is a very important factor in the deterioration of edible oil by heat treatment and aeration. Next, we evaluated the improvement in the quality of deteriorated oil by calcium silicate adsorbent (Ca:Si = 1:3, CAS30) treatment i.e., adsorption. It is established that CAS30 exhibited the ability to remove AV and CV from deteriorated oil (treatment temperature: 80 °C < 100 °C). Moreover, we investigated the removal mechanism of AV and CV, and determined good positively or negatively linear relationship between AV or CV removal by CAS30 and the proportion of unsaturated fatty acid in deteriorated pure and blended oils. In summary, the results obtained from treatment with CAS30 provided useful information on improvement in the quality of deteriorated blended oil.

Key words   calcium silicate, soybean oil, rapeseed oil, blend oil, adsorption, deterioration

INTRODUCTION

Oil blending is often used to modify oils and fatty acids to improve their quality and thereby optimize their application in food products or to ensure high thermal oxidation stability. Therefore, there are a number of reports in the literature on the enhancement of the oxidative stability of oils by blending.[1–6] This enhancement has been attributed to the fatty acid composition of oils, which are characterized by high ratios of mono-unsaturated fatty acid content to poly-unsaturated fatty acid content and the presence of minor compounds with powerful antioxidant activity, especially polyphenols.[7,8] In addition, based on the recommendations of the World Health Organization (WHO), any oil can be characterized based on three parameters: proportions of its saturated, and mono- and poly-unsaturated fatty acid contents, proportions of essential fatty acids, and presence of antioxidants. The WHO recommends dietary ratios of 1:1.5:1 for saturated: mono-unsaturated: poly-unsaturated fatty acid contents and 5–10:1 for linoleic acid: alpha linoleic acid.[9] Therefore, the composition of fatty acids in pure or blended oil is very important for the retention of oil quality.

On the other hand, improvement in the quality of deteriorated blended oil has not been reported. However, improvement in or regeneration of the quality of deteriorated oil (pure or blended) is very important to ensure stability during oxidation (or heating) or to maintain low costs and minimize impact on human health. Until now, several methods to improve the quality of deteriorated pure (i.e., not blended) oil have been reported.[10,11] Among these, adsorption is widely employed because of its low cost and ease of practical use. Therefore, we focused on the process of adsorption to improve the quality of deteriorated oil. Researchers have reported improvements in the quality of deteriorated pure (i.e., not blended) oil achieved by adsorption onto activated carbon, activated clay, aluminum compounds, magnesium oxide, calcium oxide, and calcium silicate, etc.[12–14] Moreover, we have elucidated that calcium silicate is an useful adsorbent for improving the quality of deteriorated pure oil.[15,16] Previous study reported the removal of AV or CV using calcium silicate at different molar rations.[16] Pore volume of calcium silicate (CAS30, the molar ratio of Ca:Si=1:3) was greater than that of calcium silicate at different molar rations. Additionally, the stability of CAS30 is higher compared to other adsorbents. Therefore, we determined that the optimal molar ratio of Ca:Si in calcium silicate is 1:3. However, a demonstration using blended oil has not been reported previously.

Therefore, if the utility of calcium silicate as an adsorbent were to be explored, its value and applicability would drastically increase. Specifically, soybean oil and rapeseed oil are the most widely consumed oils in Japan, and we have focused on the pure and blended forms of these oils in this study.

The aim of this study is to blend soybean oil with rapeseed oil in different ratios to change the fatty acid composition,

analyze the characteristics of the blended oils, and examine the effects of treatment with the adsorbent i.e., calcium silicate on the removal of AV and CV from the deteriorated pure and blended oils.

MATERIALS AND METHODS

Materials Edible shirashime soybean oil (SR10) and edible rapeseed oil (SR01) were purchased from Showa Sangyo Co. Ltd., Japan, and J-Oil Mills, Inc., Japan, respectively. Blends of soybean and rapeseed oils under different conditions were prepared in this study; the weight/volume ratios of soybean oil to rapeseed oil are 2:1, 1:1, and 1:2, and these samples are denoted as SR21, SR11, and SR12, respectively. Calcium silicate adsorbent (Ca: Si = 1:3, CAS30) was obtained from Tomita Pharmaceutical Co., Ltd., Japan. The characteristics of CAS30 were previously reported in detail by Ogata *et al*.[15,16]

Deterioration of the oils prepared was performed as follows. Each oil prepared (300 mL) was heated at 180 °C with stirring at 250 rpm for 7 h per day for a total of 4 d. The oxygen flow for aeration was maintained at 300 mL/min. The deterioration of the oil prepared was evaluated by its acid value (AV), carbonyl value (CV), concentration of free fatty acid (FFA), and amount of tocopherol.

Acid Value (AV) and Carbonyl Value (CV) Estimations The samples (2.0 g) were dissolved in 100 mL of a mixture of ethanol and ether in the ratio 1:1, and the solution was titrated with 0.1 mol/L potassium hydroxide, with phenolphthalein as the indicator. The AV was calculated according to Equation (1).

$$AV = 5.611aF/M \tag{1}$$

where a (mL) is the amount of 0.1 mol/L potassium hydroxide required for the titration, F is a factor of 0.1 mol/L potassium hydroxide, and M (g) is the mass of the edible oil sample.[17]

The samples (0.25 g) were dissolved in 25 mL of 1-butanol. Subsequently, 1 mL of the sample solution and 1 mL of 2,4-dinitrophenyl hydrazine were mixed for 20 min at 42 °C. A total of 8% potassium hydroxide (8 mL) was added to the mixtures, and the samples were centrifuged at 3000×g for 5 min in a KUBOTA 3100 centrifuge (Kubota Co., Ltd., Japan). The supernatants were analyzed using a UV-1200 spectrophotometer (Shimadzu Corp., Japan). The absorbance was measured at 420 nm. All reagents were purchased from Wako Pure Chemical Industries, Ltd., Japan.[18]

Analysis of Free Fatty Acid (FFA) and Tocopherol Contents The FFA content was measured by the following method. Benzene (0.5 mL) and 14% (w/w) boron trifluoride-methanol (1 mL) were mixed with each sample (10 mg), and the suspension was heated for 2 h at 80 °C. Subsequently, 5 mL of *n*-hexane and 15 mL of distilled water were added, and the sample in the *n*-hexane layer was analyzed using a gas chromatograph equipped with a flame ionization detector (GC-2014; Shimadzu Corp., Japan). The measurement conditions were as follows: capillary column, FAMEWAX (30 m × 0.25 mm ID; Shimadzu GLC Ltd., Japan); carrier gas, He; column temperature, 200 °C; flow rate, 0.6 mL/min; and injection volume, 1 μL.

The tocopherol concentration was estimated by diluting the samples in a mobile phase (hexane: ethyl acetate, 7:3) followed by analysis using high-performance liquid chromatography (HPLC, SPD-10A*VP*, Shimadzu Corp., Japan). The measurement conditions were as follows: column, Inertsil NH$_2$ (250 mm × 4.6 mm, GL Sciences); column temperature, 30 °C; flow rate, 1.0 mL/min; wavelength of detection, 290 nm, and injection volume, 10 μL.

Adsorption The edible oil samples were obtained by the method described in "Materials". The adsorbent CAS30 (0.15 g) was added to the oil samples (15 g). The suspensions were stirred at 250 rpm for 15 min at 80 °C or 100 °C, and then filtered through a 0.45 μm membrane filter. The filtered oils were then investigated to determine their AVs, CVs, FFA concentrations, and tocopherol concentrations.

Statistical analysis The *p*-value of 0.05 ($p < 0.05$) was chosen as the significance level. Student's *t*-test was used for two group comparisons, and multiple groups were evaluated by one–way ANOVA. The data are expressed as the mean±standard deviation (S.D.) of the mean (n=3). Additionally, relationship between the removal of AV or CV and the proportion of free fatty acid was evaluated by the single regression analysis.

RESULTS AND DISCUSSION

Properties of CAS30 The characteristics of CAS30 have been previously reported.[15,16] The adsorbent CAS30 has been approved for use as a food additive in Japan. It was prepared by mixing CaO-SiO$_2$-H$_2$O and Ca$_{1.5}$-SiO$_{3.5}$-xH$_2$O. The SEM images of CAS30 show that it is spherical in shape, and its specific surface area, pore volume, and mean pore diameter are 182.61 m^2/g, 0.855 mL/g, and 176.07 Å, respectively. In addition, elemental analysis of the surface of CAS30 was carried out, and calcium (Ca) and silica (Si) were detected on the adsorbent surface. We have previously reported the removal of AV, CV, and FFA from waste edible oil and the prevention of deterioration of soybean oil by CAS30.[15,16]

Changes in AV and CV with Deterioration Ichikawa has determined the deterioration of waste edible oil using AV, CV, and peroxide values, because these values can be used to simultaneously evaluate the amounts of FFA, peroxide, aldehyde, and carboxylic acid produced by the deterioration of edible oil.[19,20] The oils used in this study (SR10, SR21, SR11, SR12, and SR01) had different components, which means that the progression of oxidative degradation and the products of the deterioration of these edible oils were also different. Therefore, it is necessary to evaluate the overall deterioration.

Firstly, changes in AV with deterioration treatment are shown in Fig. 1. The initial values i.e., AV$_0$ of SR10, SR21, SR11, SR12, and SR01 were in the range 0.12–0.24 mg/g. The value of AV/AV$_0$ is in the order SR10 (3.29) << SR01 (7.50). The difference was not statistically significant in this experimental condition. These results showed trends similar to those obtained in a previous study,[21] and indicated an increase in the stability of blended oil with its proportion of mono-unsaturated/poly-unsaturated fatty acids. (The data are described in "Treatment with Adsorbent".) In addition, changes in CV with deterioration were determined (Fig. 2). The initial values i.e., CV$_0$ of SR10, SR21, SR11, SR12, and SR01 were in the range 10.35–14.13 μmol/g. The value of CV/CV$_0$ decreased with increase in the proportion of rapeseed oil in the blended oil (SR01 (3.12) << SR10 (4.15)). There was no significant different between oils. Results previously obtained show that SR10
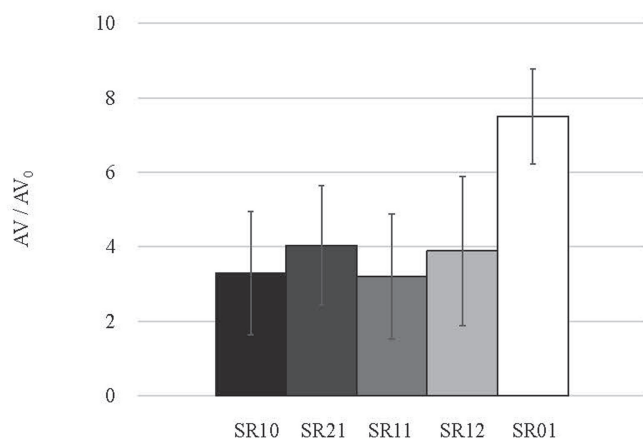
Fig. 1.   Changes in AV with Deterioration

SR01, SR21, SR11, SR12, and SR01 show that the weight/volume rations of soybean oil to rapeseed oil are 0:1, 2:1, 1:1, 1:2, and 1:0, respectively. Deterioration condition; total oil volume: 300 mL, temperature: 180 °C, agitation speed: 250 rpm, heating time: 7 h per day for a total of 4 days, oxygen flow for aeration: 300 mL/min, the data are expressed as the mean±S.D. of the mean (*n*=3)
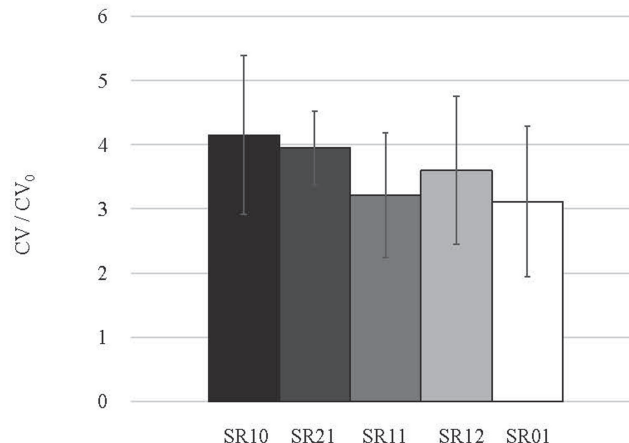

Fig. 2.   Changes in CV with Deterioration

SR01, SR21, SR11, SR12, and SR01 show that the weight/volume rations of soybean oil to rapeseed oil are 0:1, 2:1, 1:1, 1:2, and 1:0, respectively. Deterioration condition; total oil volume: 300 mL, temperature: 180 °C, agitation speed: 250 rpm, heating time: 7 h per day for a total of 4 days, oxygen flow for aeration: 300 mL/min, the data are expressed as the mean±S.D. of the mean (*n*=3)

is in a stable condition for deterioration. On the other hand, SR01 is in an unstable condition for deterioration, suggesting that the carbonyl compounds were easily decomposed to lower FFA content. Moreover, Kajimoto *et al.* reported that the deterioration (CV) of waste edible oil depended on the amount of poly-unsaturated fatty acids (linoleic acid and linolenic acid) in the oil. (The data are described in "Treatment with Adsorbent".) The results obtained in this study show trends similar to those from a previous study.[22]

Changes in Tocopherol and FFA Contents with Deterioration   The compositions of tocopherol in pure and blended oils are shown in Table 1. The main component of each oil was γ-tocopherol. Aladedunye & Przybylski reported that the relative stability of α- and γ-tocopherol was dependent on temperature, with a higher loss of α-tocopherol than γ-tocopherol.[23] Moreover, previous studies have reported that α-tocopherol degraded most rapidly during the deterioration of the oil, and subsequently γ- and δ-tocopherol were resistant to heat treatment. The hydroperoxyl radical-scavenging activity was in the order α- > β- > γ- > δ-tocopherol.[24,25] In this study, we could not detect tocopherol in all the oils after deterioration, which suggests that the tocopherol content was reduced by heat treatment and aeration. Similar trends have been previously reported.[26–28]

Figure 3 shows the changes in FFA content with deterioration. The SR10 and SR01 samples had mainly linoleic acid and oleic acid, respectively. In addition, the components of the blended oils were reflected in the characteristics of the oils. The stability of edible oils depends on their FFA compositions as well as the contents and compositions of minor components, especially tocopherols and polyphenols.[29,30] In this study, the concentrations of saturated fatty acids (palmitic and stearic acids) did not change significantly ($p < 0.05$, only stearic acid in SR12), but those of unsaturated fatty acids (oleic, linoleic, and linolenic acids) decreased with deterioration. Min and Bradley reported the relative auto-oxidation rates of oleic, linoleic, and linolenic acids as varying from 1:40 to 50:100 on the basis of oxygen uptake.[31] The relative reaction rate of linolenic acid with oxygen is much higher than those of lin-

Table 1.   The Composition of Tocopherols in Pure and Blended Oil

Samples	Composition of tocopherol (mg/100g oil)			
	α-Toc	β-Toc	γ-Toc	δ-Toc
SR10	31.1 ± 5.0	3.9 ± 1.3	234.0 ± 22.8	88.9 ± 36.7
SR21	40.1 ± 3.6	3.8 ± 0.5	223.9 ± 40.1	60.0 ± 25.5
SR11	64.0 ± 14.0	3.3 ± 1.7	213.0 ± 43.4	34.6 ± 13.4
SR12	96.3 ± 17.2	3.1 ± 1.0	206.6 ± 33.6	22.0 ± 2.4
SR01	184.9 ± 4.5	2.9 ± 1.5	199.7 ± 43.7	6.1 ± 2.6

oleic and oleic acids. Therefore, the highest reduction in linolenic acid and lowest reduction in oleic acid are expected.[32] In this study, the concentrations of linolenic acid in SR10, SR21, SR11, SR12, and SR01 after deterioration decreased by approximately 33%, 33%, 42%, 49%, and 45%, respectively, compared to the corresponding values before deterioration, indicating the abovementioned concept. Therefore, oleic acid/FFA or linoleic acid and linolenic acid/FFA contents are very important factors for the deterioration of blended oil or improvement in quality.

Treatment with Adsorbent   The removal percentages of AV and CV using CAS30 at different temperatures are shown in Figs. 4 and 5. The removal percentage of AV increased with the proportion of rapeseed oil. The removal percentages of AV are in the ranges 12.1–19.9% at 80 °C and 22.3–32.2% at 100 °C. (The initial values of AV before adsorption of SR10, SR21, SR11, SR12, and SR01 were in the range 0.69–1.00 mg/g). On the other hand, the removal percentage of CV increased with the proportion of soybean oil. The removal percentages of CV are in the ranges 7.2–15.3% at 80 °C and 15.8–27.9% at 100 °C. (The initial values of CV before adsorption of SR10, SR21, SR11, SR12, and SR01 were in the range 38.8–46.8 μmol/g). These results suggest that CAS30 is useful for the removal of AV from deteriorated blended oil. In addition, relationship between removal percentage of AV or CV and the oil at different components are statistically analyzed by one–way ANOVA. Removal percentage of CV was related to the oil components ($p < 0.05$).

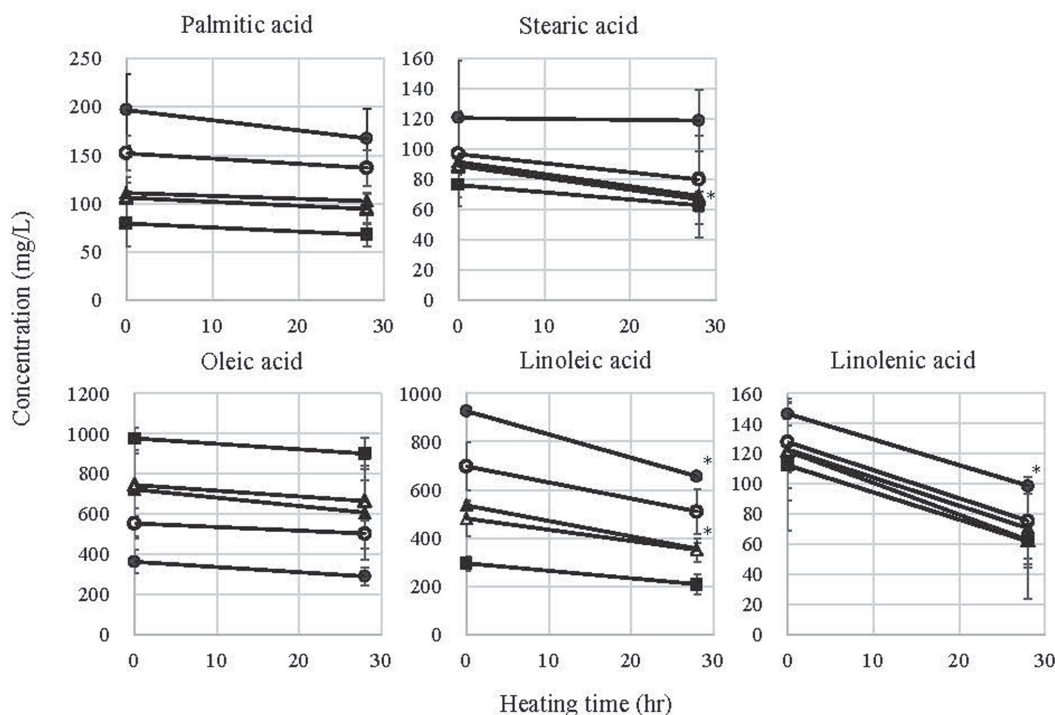As mentioned in "Changes in Tocopherol and FFA Contents

Fig. 3. Changes in Free Fatty Acids with Deterioration

SR01 (●), SR21 (○), SR11 (▲), SR12 (Δ), and SR01 (■) show that the weight/volume rations of soybean oil to rapeseed oil are 0:1, 2:1, 1:1, 1:2, and 1:0, respectively. Deterioration condition; total oil volume: 300 mL, temperature: 180 °C, agitation speed: 250 rpm, heating time: 7 h per day for a total of 4 days, oxygen flow for aeration: 300 mL/min, *p < 0.05 *vs* before deterioration, the data are expressed as the mean±S.D. of the mean (*n*=3)
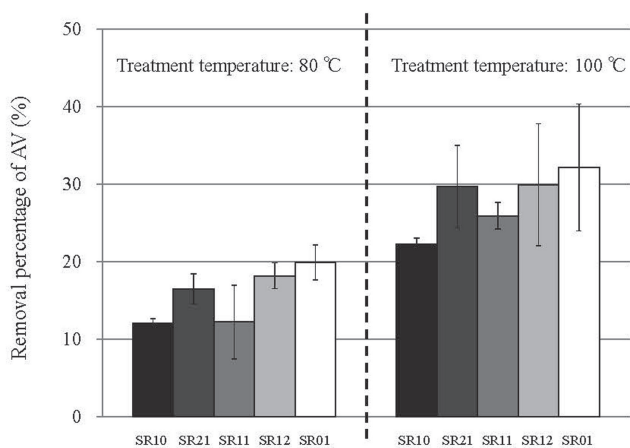

Fig. 4. Removal Percentage of AV Using CAS30 at Different Temperatures

SR01, SR21, SR11, SR12, and SR01 show that the weight/volume rations of soybean oil to rapeseed oil are 0:1, 2:1, 1:1, 1:2, and 1:0, respectively. Adsorption condition; oil sample: 15 g, amount adsorbent: 0.15 g, agitation speed: 250 rpm, temperature: 80 and 100 °C, *p < 0.05, the data are expressed as the mean±S.D. of the mean (*n*=3)
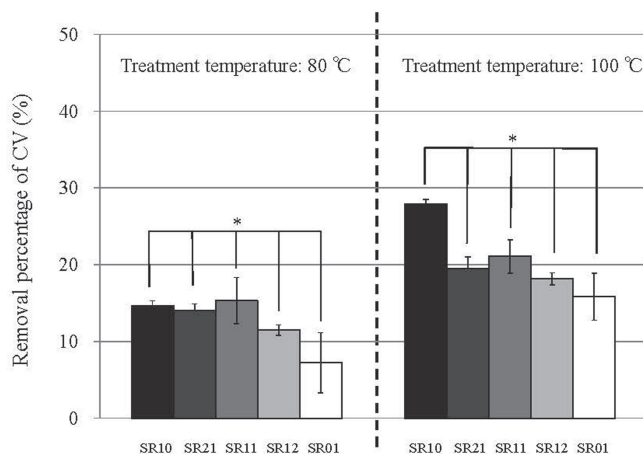

Fig. 5. Removal Percentage of CV Using CAS30 at Different Temperatures

SR01, SR21, SR11, SR12, and SR01 show that the weight/volume rations of soybean oil to rapeseed oil are 0:1, 2:1, 1:1, 1:2, and 1:0, respectively. Adsorption condition; oil sample: 15 g, amount adsorbent: 0.15 g, agitation speed: 250 rpm, temperature: 80 and 100 °C, *p < 0.05, the data are expressed as the mean±S.D. of the mean (*n*=3)

with Deterioration", the components of FFAs are very important factors for improvement in the quality of pure and blended oils. Therefore, we evaluated the relationships between AV or CV removal and the proportion of unsaturated fatty acid content by the single regression analysis (Figs. 6 and 7). The relationship between the removal percentage of AV and oleic acid/fatty acid showed a good positive linearity (*p* < 0.05, correlation coefficients of 0.818 and 0.743 at 80 °C and 100 °C, respectively), and the relationship between the removal percentage of CV and oleic acid/fatty acid showed good

negative linearity (*p* < 0.05, correlation coefficients of 0.842 and 0.831 at 80 °C and 100 °C, respectively). These results indicate that oleic acid is more resistant to oxidation (deterioration) than poly-unsaturated fatty acids, and hence leads to lower production of carbonyl compounds (i.e., lower CV) by deterioration. Therefore, the removal percentage of AV relatively increased with the proportion of oleic acid/fatty acid in oil. In addition, the behaviors seen in Fig. 7 (the proportions of linoleic acid and linolenic acid/fatty acid in oil) are opposite to those seen in Fig. 6 (the proportion of oleic acid/fatty acid in
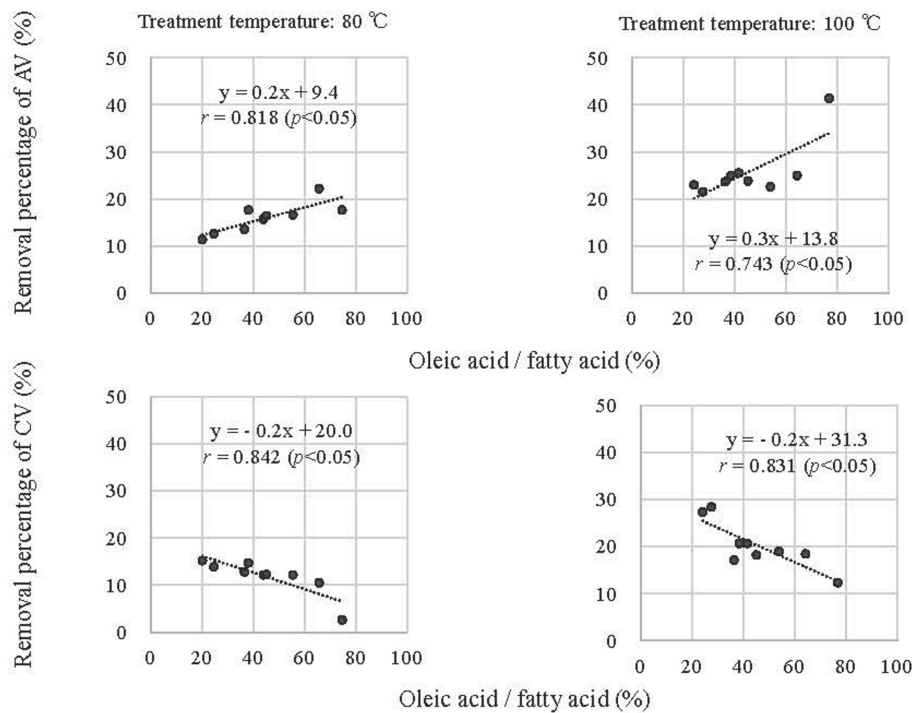
Fig. 6. Relationship Between the Removal of AV or CV and the Proportion of Oleic Acid/Fatty Acid

Oil samples are obtained after adsorption using CAS30, statistical analysis was evaluated by the single regression analysis
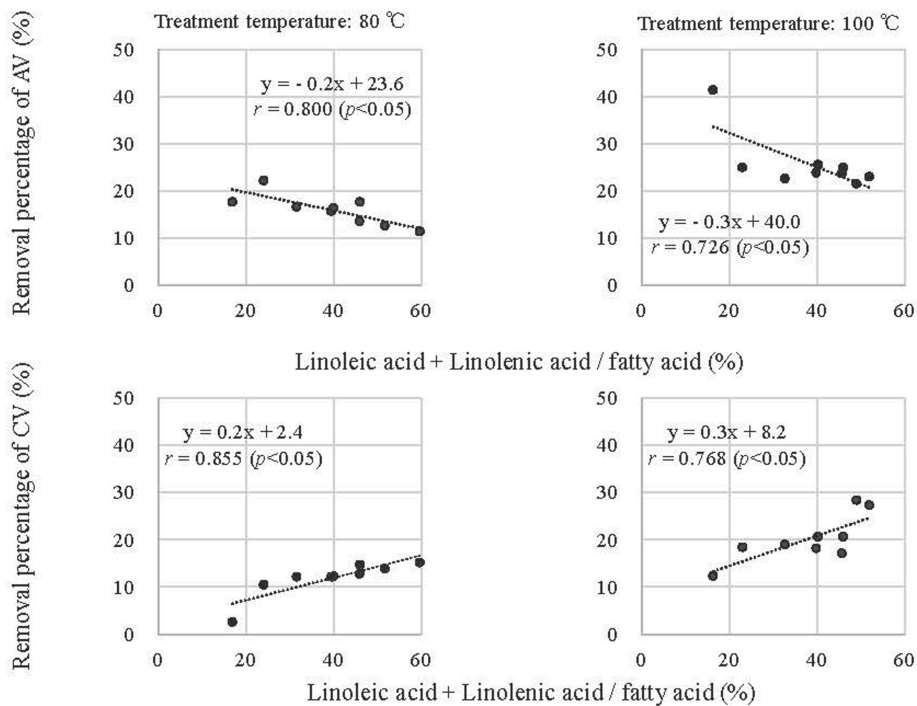

Fig. 7. Relationship Between the Removal of AV or CV and the Proportion of Linoleic Acid + Linolenic Acid/Fatty Acid

Oil samples are obtained after adsorption using CAS30, statistical analysis was evaluated by the single regression analysis

oil). The results obtained in this study indicate that CAS30 is useful for improving the quality of pure and blended oils, but adsorption using CAS30 is easily affected by the components of FFA in the oil. Therefore, we must evaluate in detail the relationship between AV or CV removal and the composition of fatty acid in deteriorated oil.

Moreover, we have previously reported the adsorption mechanism of AV and CV by CAS30. The polar compounds generated during the deterioration of edible oil were removed by adsorbents using van der Waals forces.[33] Therefore, the surface hydroxyl groups of CAS30 are very polar, and the hydroxyl groups can form hydrogen bounds with the polar

compounds generated during the deterioration of edible oil and interact with them via van der Waals forces and dipole-dipole attractions.[34] Similar trends were observed in this study.

In this study, we evaluated the quality of deteriorated blended oil (soybean oil and rapeseed oil), and demonstrated improvement in the quality of deteriorated oil using CAS30 adsorbent. The value of AV/AV_0 increased with the proportion of rapeseed oil in blended oil. On the other hand, the value of CV/CV_0 increased with the proportion of soybean oil in blended oil. These results indicate that the FFA component in blended oil is a very important factor for the deterioration of edible oil by heat treatment and aeration.

In addition, AV or CV could be easily removed from deteriorated oil by CAS30. The removal percentages of AV or CV at 100 °C were greater than those at 80 °C, indicating that CAS30 is useful for improving the quality of deteriorated oil. Moreover, the removal mechanism of AV or CV using CAS30 was related to the components of FFA (oleic acid, linoleic acid, and linolenic acid). We could establish good positively or negatively linear relationships between AV or CV removal by CAS30 and the proportion of unsaturated fatty acid in deteriorated pure and blended oils.

Collectively, treatment with CAS30 was useful in improving the quality of deteriorated oil and could prolong the oil life cycle under these experimental conditions.

Conflict of interest   The authors declare no conflict of interest.

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