Antioxidant Effects of pH-Regulating Agents on the Thermal Deterioration of Vegetable Oils

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Abstract: pH-Regulating agents, such as sodium tartrate, disodium succinate, and trisodium citrate, were investigated for their antioxidant activities during the thermal deterioration of vegetable oils. Refined rapeseed and rice bran oils, supplemented with pH-regulating agents and α -tocopherol (0.1%) were heated at 180°C. After heating, acid values (AVs), carbonyl values (CVs), polar material contents, and color (absorbance at 420 nm) of each sample were measured. All pH-regulating agents gave rise to reduced AVs, CVs, and polar material contents of vegetable oils during heating relative to samples not containing a pH-regulating agent. Rapeseed and rice bran oils supplemented with sodium tartrate showed the lowest AVs, CVs, polar material contents and absorbances at 420 nm after heating. Sodium tartrate not only retarded the hydrolysis, thermal oxidation, polymerization, and coloration of both oils while heating at high temperatures, but it also showed antioxidant activity at the supplementation level of 0.01%. The antioxidant activity of sodium tartrate was higher than that of α -tocopherol during the deterioration of vegetable oils. Sodium tartrate was particularly effective retarding hydrolysis while heating at high temperatures, resulting in increase of AVs of vegetable oils. Sodium tartrate is therefore expected to be an effective antioxidant for the thermal deterioration of fats and oils during deep-fat frying.

Key words: acid value, antioxidant, carbonyl value, color, pH-regulating agent, polar materials, thermal deterioration, vegetable oil

1 Introduction

Deep-fat frying of foods with edible fats and oils is one of the oldest and most popular cooking techniques, because it imparts desirable flavor to foods that conveys its unique sensory characteristics. However, extensive heating causes deterioration of fats and oils, which not only reduces the sensory quality of fried foods, but also may diminish their nutritional value. Thermal deterioration of fats and oils during deep-fat frying involves complex and different processes¹⁻⁴. While heating, water released from the food and the surrounding moist air enables hydrolysis of triacylglycerols in the oil to produce free fatty acids. Among constituent fatty acids, unsaturated fatty acids are rapidly oxidized during deep-fat frying. Although the high-temperature oxidation of unsaturated fatty acids can produce hydroperoxides, these primary oxidation products do not accumulate during the frying process because of their instability. Hydroperoxides spontaneously decomposed to form other volatile compounds as well as polymers. The volatile compounds also contribute to both desirable and undesirable flavor. Some of these low molecular compounds and poly-

mers are toxic to humans, thereby presenting safety hazards⁵⁻¹³. Moreover, free fatty acids resulting from hydrolysis of triacylglycerols are more rapidly oxidized and catalyze thermal oxidation of the latter.

Thus, it is very important to control thermal deterioration of fats and oils during deep-fat frying, and some methods have been established to this end¹⁻⁴. Reducing the temperature can delay the thermal deterioration. The desirable temperature ranges for deep-fat frying is 160 to 190°C, and exceedingly high temperatures must be avoided. The turnover rate is also an important factor to control while frying. Fats and oils are absorbed by foods during deep-fat frying. Addition of fresh fats and oils to used ones can maintain their good condition. Filtering of frying oils to remove accumulated food particles and charred batter is also important, because it effectively removes free fatty acids and colored compounds. The performance and type of the fryer affects thermal deterioration of fats and oils. The reduced oxygen concentration and surface area of vegetable oils inside a fryer low their thermal oxidation and polymerization^{14, 15}. Polymerization

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inhibitors and antioxidants effectively slow the thermal oxidation of fats and oils^{1-4, 16}). Silicones, such as methyl silicone, are often used as polymerization inhibitors while frying fats, although their mechanism remains unknown. Synthetic antioxidants, such as BHT and BHA, are also effective for slowing the thermal oxidation of fats and oils, although they vaporize and decompose at high temperatures involved with deep-fat frying. Nevertheless, these antioxidants are partially retained and stabilize the fats and oils during deep-fat frying. However, most consumers do not prefer the use of these synthetic additives within processed foods. Natural antioxidants, such as tocopherols, can also be used to slow the oxidation of fats and oils, and oil foods. However, the effect of natural antioxidants on frying fats is controversial, because they are quickly lost during deep-fat frying. Naturally occurring tocopherols are particularly susceptible to decomposition at high temperatures and may even exhibit prooxidant activity¹⁷). To date, there are no effective natural antioxidants used for deep-fat frying.

Moreover, it is difficult to control triacylglycerol hydrolysis during deep-fat frying, because most foods are rich in moisture. Compounds that effectively slow the hydrolysis have not yet been found.

In this study, we noticed that pH-regulating agents slowed the thermal deterioration of fats and oils. These agents can change the pH of the foods that they are added to. Using alkali pH-regulating agents, we tried to neutralize the free fatty acids that catalyzed hydrolysis and oxidation of fats and oils, thereby resulting in slower thermal deterioration of fats and oils during deep-fat frying.

2 Materials and Methods

2.1 Materials and chemicals

Refined rapeseed and rice bran oils were supplied by The Nisshin Oillio Group (Yokohama, Japan) and Tsuno Food Industrial Co. Ltd. (Wakayama, Japan), respectively.

Rapeseed oil is composed of palmitic acid (16:0, 4.1%), stearic acid (18:0, 1.9%), oleic acid (18:1, 65.2%), linoleic acid (18:2, 19.5%), and linolenic acid (18:3, 7.7%). Rice bran oil is composed of 16:0 (16.5%), 18:0 (1.9%), 18:1 (44.9%), 18:2 (34.7%), and 18:3 (1.0%). Rapeseed and rice bran oils contain 695 and 998 µg/g of total tocopherols, respectively. Peroxide and acid values of both vegetable oils were lower than 0.1.

Sodium tartrate, disodium succinate, and trisodium citrate (as pH-regulating agents) were purchased from Wako Pure Chemical Industries, Ltd. (Osaka, Japan).

α-Tocopherol (>98%) and other chemicals were purchased from Wako Pure Chemical Industries, Ltd. (Osaka, Japan).

2.2 Heat testing of vegetable oils

Ten grams of vegetable oils containing pH-regulating agents or α-tocopherol (0.01~0.1%) were put in a 14 mL-glass tube and heated in an aluminum block bath at 180°C for 8 h/d, for 4 d.

2.3 Analysis

Acid values (AVs) and carbonyl values (CVs) were measured by JOCS Standard Methods for the Analysis of Fats, Oils and Related Materials (2013)¹⁸). Polar materials were measured by the TLC-FID method¹⁹). The color of vegetable oils was monitored at 420 nm in *n*-hexane solution.

Experiments were performed in triplicate. All reported data represented average values with a relative standard deviation of <10%.

3 Results and Discussion

3.1 Antioxidant activity of pH-regulating agents

Figure 1 shows the changes in AVs of rapeseed and rice bran oils supplemented with pH-regulating agents at the level of 0.1% during heating at 180°C. The AVs of rapeseed and rice bran oils increased with heating time. The supplementation of pH-regulating agents lowered the increase of AV of rapeseed oil. Sodium tartrate resulted in the lowest AV of rapeseed oil among the three pH-regulating agents used in this study. Moreover, AVs of rapeseed oil supplemented with sodium tartrate and disodium succinate were lower than AVs of oil supplemented with α-tocopherol during heating. The supplementation of pH-regulating agents also lowered the increase of the AV of rice bran oil. However, as shown in Fig. 1, there were remarkable AV differences between rice bran oil samples supplemented with pH-regulating agents and α-tocopherol during heating at 180°C. Generally, pH-regulating agents were found to slow the hydrolysis of rapeseed and rice bran oils during heating.

Figure 2 shows the changes in CVs of rapeseed and rice bran oils supplemented with pH-regulating agents during heating at 180°C. The CVs of rapeseed and rice bran oils also increased with heating time. The supplementation of pH-regulating agents lowered the increase of CVs of rapeseed and rice bran oils. However, there are no remarkable differences between CVs of vegetable oils supplemented with pH-regulating agents and α-tocopherol after heating for 32 h at 180°C. These observations show that pH-regulating agents can slow the production of carbonyl compounds by inhibiting the oxidation of vegetable oils.

Figure 3 shows the changes in the contents of polar materials in rapeseed and rice bran oils supplemented with pH-regulating agents as a function of time while heating at 180°C. Although the polar material contents for rapeseed and rice bran oil samples increased with heating time, the

Fig. 1 Acid value (AV) of rapeseed and rice bran oils supplemented with 0.1% pH-regulating agents during heating at 180°C. ● control, ■ trisodium citrate, ▲ disodium succinate, ◆ sodium tartrate, ○ α -tocopherol.

Fig. 2 Carbonyl value (CV) of rapeseed and rice bran oils supplemented with 0.1% pH-regulating agents (0.1%) during heating at 180°C. ● control, ■ trisodium citrate, ▲ disodium succinate, ◆ sodium tartrate, ○ α -tocopherol.

Fig. 3 Polar materials of rapeseed and rice bran oils supplemented with 0.1% pH-regulating agents during heating at 180°C. ● control, ■ trisodium citrate, ▲ disodium succinate, ◆ sodium tartrate, ○ α -tocopherol.

Fig. 4 The absorbance at 420 nm of rapeseed and rice bran oils supplemented with 0.1% pH-regulating agents during heating at 180°C. ● control, ■ trisodium citrate, ▲ disodium succinate, ◆ sodium tartrate, ○ α -tocopherol.

supplementation of pH-regulating agents resulted in slower production of polar materials. Notably, the contents of polar materials in rapeseed and rice bran oils supplemented with sodium tartrate and α -tocopherol were the lowest among oils tested. The main components of polar materials produced by thermal degradation of vegetable oils could be polymers, although these polar materials, which included free fatty acids and carbonyl compounds, were only present in low concentration (1–2%). Thus, these observations suggest that pH-regulating agents can also slow the polymerization of vegetable oils while heating at high temperatures.

Figure 4 shows the changes in 420 nm absorbances of rapeseed and rice bran oil samples supplemented with pH-regulating agents while heating at 180°C. Both rapeseed and rice bran oils acquired a brownish color while heating, and the 420 nm absorbances also increased. Before heating, the absorbance of rapeseed oil was higher than that of rice bran oil, because rapeseed oil contained considerable amounts of chlorophyll and carotenoid pigments. Compared to that of rice bran oil, the absorbance of rapeseed oil increased remarkably while heating. The coloration of fats and oils is derived from oxidized and polymerized polyunsaturated fatty acids, especially linolenic acid²⁰. The low absorbance of rice bran oil compared with rapeseed oil may result from the low concentration of linolenic acid in the former. The supplementation of pH-regulating agents lowered the increase of the 420 nm absorbance of rapeseed oil while heating, except in the case of disodium succinate. Disodium succinate enhanced the brownish color of rapeseed and rice bran oils during heating. On the other hand, sodium tartrate lowered the increase in the 420 nm absorbance of rice bran oils, but not other pH-regulating agents and α -tocopherol. From these results, it is suggested that sodium tartrate could be also effective at inhibiting the coloration of vegetable oils at high temperatures.

As shown in Figs. 1–4, it was demonstrated that sodium tartrate had an antioxidant activity against thermal deterioration of vegetable oils, and that this activity did not depend on the variety of vegetable oil. Moreover, the antioxidant activity of sodium tartrate was higher than that of α -tocopherol. Notably, sodium tartrate lowered the increase in the AVs of vegetable oils substantially while heating at high temperatures. It is suggested that sodium tartrate may effectively slow the triacylglycerol hydrolysis during deep-fat frying.

3.2 Effect of sodium tartrate supplementation level

Next, the effect of the supplementation level of sodium tartrate on the thermal deterioration of rapeseed oil was investigated. Rapeseed oil samples supplemented with different levels of sodium tartrate (0.01%, 0.05%, and 0.1%) were heated at 180°C. Figures 5, 6 and 7 show the changes in AVs, CVs, and the content of polar materials while heating rapeseed oil supplemented with different levels of sodium tartrate at 180°C, respectively. The AVs of rapeseed oil were lowered with increased supplementation level of sodium tartrate, as shown in Fig. 5. At sodium tartrate supplementation levels of 0.01%, 0.05%, and 0.1%, the AVs of rapeseed oil after heating at 180°C for 32 h were reduced to 89%, 79%, and 66% of those of the control, respectively. Sodium tartrate supplementation could slow the increase in the AVs of rapeseed oil while heating at 180°C at 0.01%. The CVs of rapeseed oil were reduced by supplementation with sodium tartrate, but as shown in Fig. 6, there was no significant difference in CVs of rapeseed oils supplemented with different levels of sodium tartrate. Sodium tartrate could inhibit the thermal oxidation of rapeseed oil at 0.01%. The content of polar materials in rapeseed oil also lowered with the increased supplementation with sodium tartrate, as shown in Fig. 7. At sodium tartrate supplementation levels of 0.01%, 0.05%, and

Fig. 5 Acid value (AV) of rapeseed oil supplemented with sodium tartrate during heating at 180°C. ● control, ■ 0.01%, ▲ 0.05%, ◆ 0.1% sodium tartrate.

Fig. 7 Polar materials of rapeseed oil supplemented with sodium tartrate during heating at 180°C. ● control, ■ 0.01%, ▲ 0.05%, ◆ 0.1% sodium tartrate.

Fig. 6 Carbonyl value (CV) of rapeseed oil supplemented with sodium tartrate during heating at 180°C. ● control, ■ 0.01%, ▲ 0.05%, ◆ 0.1% sodium tartrate.

0.1%, the contents of polar materials in rapeseed oil after heating at 180°C for 24 h were reduced to 88%, 75%, and 63% of those of the control, respectively. Sodium tartrate supplementation at a level of 0.01% could slow the production of polar materials from rapeseed oil while heating.

There are many factors affecting the deterioration of fats and oils, such as the presence of metals, natural antioxidants, pigments, and others. Miyashita and Takagi reported that free fatty acids had strong prooxidant activities²¹⁾, which may be ascribed to the carboxylic group contained therein. Yuki reported that free fatty acids catalyze the hydrolysis of fats and oils during deep-fat frying²²⁾. He also suggested that the removing free fatty acids from fats and oils effectively improve the shelf-life of frying oil. It was

assumed that the neutralization of free fatty acids produced in frying oil with pH-regulating agents could effectively slow the deterioration of frying oil. We investigated the antioxidant activity of pH-regulating agents on the thermal deterioration of vegetable oils. All pH-regulating agents that were tested slowed the thermal deterioration of vegetable oils. Interestingly, when compared to α -tocopherol, pH-regulating agents remarkably lowered the increase of the AVs of vegetable oil while heating at a high temperature. pH-Regulating agents may have no ability to inhibit free radical-induced oxidation. Furthermore, the antioxidant effects of pH-regulating agents are not ascribable to a synergistic effect as in the case of ascorbic acid, because they cannot regenerate natural tocopherols present in vegetable oils. It was reported that organic acids, such as citric acid and tartaric acid, could promote the thermal deterioration of vegetable oils²²⁾. However, pH-regulating agents effectively retarded the hydrolysis of vegetable oils (the increase of AVs) while heating at high temperatures. It was suggested that these agents could neutralize free fatty acids produced from triacylglycerols while heating at high temperatures. As a result, both the catalytic effect against the hydrolysis and the prooxidant effect of free fatty acids were decreased. Lowering the production of free fatty acids from vegetable oils during heating at high temperatures could slow their thermal oxidation. Among the three pH-regulating agents, it was demonstrated that sodium tartrate could be an effective antioxidant at high temperatures, such as that employed during deep-fat frying condition. The high antioxidant activity of sodium tartrate may arise from its high dispersivity in vegetable oils and its thermal stability. Although sodium tartrate is not dissolved in vegetable oils, its melting point of 150°C renders it a liquid under the condition of deep-fat

frying. Sodium tartrate does not quite decompose below 200°C, although other pH-regulating agents may decompose at high temperatures used during deep-fat frying.

From these results, sodium tartrate is expected to be an effective antioxidant that inhibits the thermal deterioration of fats and oils during deep-fat frying.

4 Conclusions

pH-Regulating agents such as sodium tartrate, disodium succinate, and trisodium citrate, could slow the thermal deterioration of vegetable oils. Among these agents, sodium tartrate was particularly effective against the thermal deterioration of vegetable oils, since it could slow the hydrolysis, thermal oxidation, and polymerization of vegetable oils while heating at high temperatures.

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