Effects of Filtration Through Bleaching Media on Thiobarbituric Acid and Carbonyl Values of Autoxidized Soybean Oil

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Effects of filtration bleaching on thiobarbituric acid values (TAV) and carbonyl values (CV) of autoxidized soybean oil were investigated by using sixteen kinds of bleaching media in order to improve oil quality. The standard activated clay was the most effective in reducing the amounts of aldehydes and ketones in autoxidized soybean oil. From the decreases in TAV and CV and physical and chemical properties of media, it was concluded that decreases of TAV and CV are mainly dominated by the acidity over the highest range, + 1.5 ~ - 5.6, rather than the acidity over the lower acid strength ranges, total acidity or specific surface area of media. From the results of chemical composition and acidity over the highest range (+ 1.5 ~ - 5.6) of the clays and TAV or CV reduction by using the heat-treated clays, it was suggested that the acidity over the highest range originated from the water contained between layers and bound water in the clay.

Soybean oil contains a high percentage of unsaturated fatty acids such as oleic, linoleic or linolenic. Free radicals formed on the unsaturated fatty acids form peroxides or hydroperoxides by reaction with dissovled oxygen. The hydroperoxides split into smaller and odorous organic compounds such as aldehydes, ketones, alcohols and acids with toxicities that are considerably stronger to animals (1). The standard activated clay effectively reduces the peroxide value of autoxidized soybean oil (2). Khoo *et al.* (3) indicated that processes involving chemical adsorption and subsequent chemical reaction proceed on the surface of activated clays. Ney (4) found that hydroperoxides of linoleic acid are decomposed into ketone or linolenic acid by activated clay. Therefore, it is necessary to investigate the amounts of aldehydes or ketones in soybean oil after filtration through bleaching media. The amounts of aldehydes and ketones are measured by thiobarbituric acid value (TAV) and carbonyl value (CV), respectively. The object of this study is to clarify a relationship between the decreases of TAV and CV and the physical or chemical properties of the media.

MATERIALS AND METHODS

Materials. Soybean oil, autoxidized soybean oil and bleaching media were the same materials as those shown in the previous paper (2).

Methods. Filtration through bleaching media was carried out by the method described previously (2). TAV was determined by the *Standard Methods of Analysis for Hygienic Chemists* (5) to measure the amount of malonaldehyde (6) in autoxidized soybean oil. CV was determined by JOCS methods 2·4·22-73 (7) to measure the amount of ketones in autoxidized soybean oil.

Acid strength and acidity of media were measured by Benesi's butylamine titration method (8), and data have been reported in our previous paper (2). Specific surface areas of media were measured by the method described previously (2), and these data also have been reported in the previous paper (2).

SiO_2, $H_2O(-)$ and $H_2O(+)$ were determined by the gravimetric method (9). Al_2O_3, Fe_2O_3, MgO, CaO, Na_2O and K_2O were determined by the atomic absorption method (9). Autoxidized soybean oil and treated soybean oil were stored in a brown desiccator over silica gel at 30°C. Samples were withdrawn periodically for measurements of TAV and CV.

RESULTS AND DISCUSSION

Effect of filtration through bleaching media. The decreases in TAV and CV of autoxidized soybean oil by filtering it through various media are shown in Table 1. The decreases of TAV and CV were measured by treating 10 g of autoxidized soybean oil (PV, 42.1 meq/kg; TAV, 2.1; CV, 10.8) with 1 g of media. The standard activated clay (medium 1) was the most effective in reducing TAV (88%) and CV (63%), and other media reduced TAV 2~66% and CV -26~27%.

Effects of concentration of media 1-3 on decreases of TAV and CV of autoxidized soybean oil are shown in Table

TABLE 1

Effects of Filtration Through Various Media on Decreases of Thiobarbituric Acid and Carbonyl Values of Autoxidized Soybean Oil

No.	Media	Decrease (%)	
		TAV	CV
1	Standard activated clay	88	63
2	Activated clay	66	18
3	Japanese acid clay	29	27
4	Synthetic zeolite	39	0
5	Bentonite	26	4
6	Kaolin	47	-26
7	Diatomaceous earth	41	-11
8	Talc	31	-15
9	Florisil	23	11
10	Celite	14	11
11	Silica gel for column chromatography	34	3
12	Sea sand	18	-8
13	Magnesium oxide	54	10
14	Titanium dioxide	50	17
15	Aluminum oxide for column chromatography	2	21
16	Basic aluminum oxide for column chromatography	12	21

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TABLE 2

Effects of Concentration of Media on Decreases of TAV and CV of Autoxidized Soybean Oil

Medium concentration[a] (%)	Amount of oil (g)	TAV decrease (%) by media[b] No. 1	No. 2	No. 3	CV decrease (%) by media[b] No. 1	No. 2	No. 3
1.64	60	70	36	9	-8	-3	7
2.44	40	74	36	19	-8	-3	7
4.76	20	79	44	35	-8	-2	21
9.10	10	88	66	29	63	18	27
16.67	5	88	80	26	47	19	30

[a]One gram of medium.

[b]See Table 1 for medium identification.

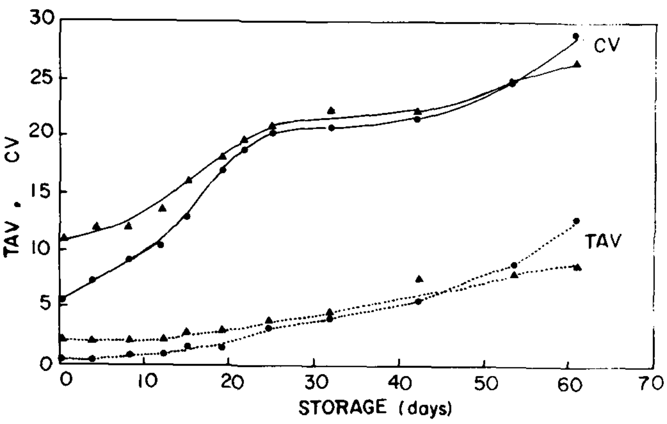

FIG. 1. TAV and CV curves of autoxidized soybean oil and treated soybean oil stored at 30°C: ▲, autoxidized oil; and ●, treated oil.

2. Decreases of TAV and CV by using the media 1-3 increased progressively with increase of media concentration up to 16.67%. At the lowest concentration of media, a decrease of TAV by using the medium 1 was 70%. At media concentrations of 4.76% or less, increases of CV using the media 1 and 2 were found.

To determine whether the stability of oil treated with medium 1 increased, autoxidized soybean oil and treated soybean oil were stored in a brown desiccator at 30°C. The results of TAV and CV measurements are shown in Figure 1. The results of storage of autoxidzed soybean oil by filtering it through medium 1 indicated that the quality of the treated soybean oil is slightly better (up to ca. 25 days). However, our assumption that removing aldehydes and ketones will renovate the autoxidized soybean oil was not borne out, and TAV and CV of the treated soybean oil were higher after it was stored for approximately 45 and 53 days, respectively.

Effects of physical and chemical properties of media on decreases of TAV and CV. The results in Tables 1 and 2 indicate that the effect on decreases of TAV and CV of autoxidized soybean oil differed with media and that the standard activated clay was the most effective for reducing TAV and CV. It is possible that differences in physical and chemical properties of media cause differences in activity for reducing TAV and CV.

Table 3 shows the correlation coefficients calculated by using the data of acidity over each acid strength range

TABLE 3

Coefficient of Determination Value Obtained by Linear Regression Between Decrease of TAV or CV and Acidity over Each Acid Strength Range or Specific Surface Area

Property	Correlation coefficient[a] TAV	CV
Acid strength, H_o		
+ 1.5 ~ - 5.6	0.686[b]	0.735[b]
+ 3.3 ~ + 1.5	0.243	-0.302
+ 6.8 ~ + 3.3	0.143	0.256
+ 6.8 ~ - 5.6[c]	0.175	0.227
Specific surface area	0.232	0.316

[a]Correlation coefficients were calculated by using the data of acidity over each acid strength range and specific surface areas reported in the previous paper (2), and decreases of TAV and CV shown in Table 1.

[b]There is significant difference at 1%.

[c]Total amounts of acid sites.

and specific surface area reported in the previous paper (2) as well as decreases of TAV and CV (Table 1). No correlations were found between decreases of TAV or CV and acidities over acid strength ranges + 3.3 ~ + 1.5, + 6.8 ~ +3.3, + 6.8 ~ - 5.6 or specific surface area of media. The relationships between decreases of TAV or CV and acidity over the highest acid strength range (+ 1.5 ~ - 5.6) were highly significant with coefficients of 0.686 and 0.735, respectively. It was concluded that decreases of TAV and CV are dominated by the amounts of acid sites of the highest acid strength range rather than the amounts of acid sites of lower acid strength range, total amounts of acid sites or specific surface areas. The conclusion on decreases of TAV and CV was in agreement with that on the decrease of PV (2).

Origin of the strongest acid site. In order to elucidate an origin of the strongest acid sites having activity for TAV or CV reduction, the chemical compositions (wt%) of the clays were determined and the data are shown in Table 4. The mole ratio of SiO_2/Al_2O_3, total acidity and acidity over the highest acid strength range are also shown in Table 4. Although it is well known that the mole ratio of SiO_2/Al_2O_3 has a correlation with acidity (10), the present value corresponded to the total acidity rather than to the acidity over the highest acid strength range, + 1.5 ~ - 5.6.

TABLE 4

Chemical Composition and Acidity of Clays

Composition	Content (wt%) Standard activated clay	Activated clay	Japanese acid clay
SiO_2	75.00	69.13	70.14
Al_2O_3	7.47	7.08	11.10
Fe_2O_3	5.65	4.22	2.56
MgO	2.24	2.58	3.72
CaO	1.59	2.75	1.18
Na_2O	0.84	0.92	0.38
K_2O	0.66	0.78	0.76
H_2O (-)[a]	1.18	0.93	1.01
H_2O (+)[b]	4.30	3.73	4.05
Total	98.93	92.14	94.80
SiO_2/Al_2O_3 (mole ratio)	17.10	16.68	10.72
Acidity over range of + 1.5 ~ - 5.6[c] (m mol/g)	2.569	0.659	0.487
Total acidity[c] (m mol/g)	28.970	22.560	5.267

[a]Weight decrease of clay due to treatment at 110°C for 4 hr.

[b]Ignition loss of clay treated at 110°C for 4 hr.

[c]Correlation coefficients of the relationship between the mole ratio of SiO_2/Al_2O_3 and acidity over the highest acid strength range + 1.5 ~ - 5.6 or total acidity were 0.611 and 0.979, respectively.

TABLE 5

Acidity of Clays Treated at Various Temperatures

Temperature (°C)	Acidity over the acid strength range + 1.5 ~ - 5.6 (m mol/g) Standard activated clay	Activated clay
110	2.569	0.659
300	0.991	0.782
500	0.806	0.690
700	0.550	0.521
900	0.073	0.000

The results indicated that the strongest acid sites did not originate from the mole ratio of SiO_2/Al_2O_3.

If the water contained between layers and bound water in a clay is an origin of the strongest acid sites, both acidity over the highest acid strength range and TAV or CV reduction would decrease with an increase in temperature of heat-treatment of the clay. Table 5 shows the acidity over the highest acid strength range (+ 1.5 ~ - 5.6) of the clays treated at various temperatures. The acidity of the heat-treated clays decreased with the rise of the treatment temperature by steps, as was expected. Figure 2 shows the decreases in TAV and CV of autoxidized soybean oil by using the clays treated at various temperatures. TAV and CV reduction of the clays decreased with an increase in temperature. The correlations between acidity over the highest acid strength range (+ 1.5 ~ - 5.6) and TAV or CV reduction by using the heat-treated clays were highly significant, with coefficients of 0.786 and 0.933, respectively. From the results of chemical composition, acidity and TAV or CV reduction, it is concluded that the acidity over the highest acid strength range (+ 1.5 ~ - 5.6) originates from the water contained between layers and bound water in the clay.

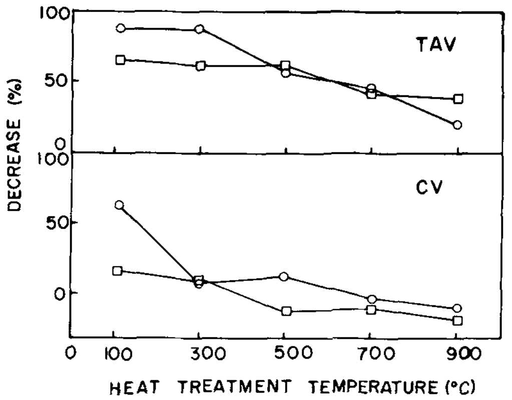

FIG. 2. Decreases of TAV and CV of autoxidized soybean oil by using the clays treated at various temperatures: ○, standard activated clay; and □, activated clay.

REFERENCES

1. Buck, D.F., *J. Am. Oil Chem. Soc. 58*:275 (1981).
2. Boki, K., S. Shinoda and S. Ohno, *J. Food Sci., 54*:1601 (1989).
3. Khoo, L.E., F. Morsingh and K.Y. Liew, *J. Am. Oil Chem. Soc. 56*:672 (1979).
4. Ney, K.H., *Fette Seifen Anstrichm. 66*:512 (1964).
5. *Standard Methods for Analysis of Hygienic Chemists*, 7th edn., Pharmaceutical Society of Japan, Nanzando, 1980.
6. Dahle, L.K., E.G. Hill and R.T. Holman, *Arch. Biochem. Biophys. 98*:253 (1962).
7. *Kijun Yushi Bunseki Shikenho*, 2·4·22-73, The Japan Oil Chemists' Society, 1986.
8. Benesi, H.A., *J. Phys. Chem. 61*:970 (1957).
9. Minato, H., in *Handbook of Clays*, 2nd edn., edited by The Japan Clay Society, Gihodo Publishing Co., 1987, pp. 360-366.
10. Kato, C., *Ibid.*, 2nd edn., edited by The Japan Clay Society, Gihodo Publishing Co., 1987, p. 271.

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