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Effect of Metal Ions on the Oxidation of Soybean Oil and Its Fried Noodle

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各種 金屬 이온이 大豆油및 그 튀김 麵의 酸敗에 미치는 영향에 對하여

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Summary

In the present study, the proxidant effect of ferrous and cupric chlorides which added to soybean oil and its fried noodle in the same concentration of the city water and the physically refined underground water were determined. As the inhibitor of metal proxidation, BHA and citric acid which are used widely in oil industry as antioxidants were compared.

In both cases of soybean oil and its fried noodle, the addition of cupric chloride and ferrous chloride showed prominent proxidant effect. Especially, cupric chloride marked more proxidant effect than ferrous chloride by 3 to 6 times with the elapse of time.

In the inhibition activity of metal proxidation, citric acid was more effective than BHA. The 1ppm of Cu +0.01% of citric acid treated soybean oil showed less proxidant effect than the control at the later stage. The inhibition activity of citric acid on Fe^{++} in soybean oil was more effective than Cu^{++} in soybean oil.

I. Introduction

The effect of various metal ions on the oxidation processes of lipids and their relative products has been studied by many investigators. As a result of those studies, it has been known that metal ions, particularly those possessing two or more valency states with a suitable oxidation-reduction potential between them, rapidly increase the rate of oxidative deterioration of lipids.

According to Waters and others,[1-4] the mechanism of metal catalyzed autoxidation was illustrated as follows:

$$ROOH+M^{+n}\cdots\cdots\rightarrow RO^{\cdot}+OH^{-}+M^{+(n+1)}$$
$$ROOH+M^{+(n+1)}\cdots\cdots\rightarrow ROO^{\cdot}+H^{+}+M^{+n}$$

(The free radicals $RO^{\cdot}$ and $ROO^{\cdot}$ then initiate new chain reactions involving the unoxidized substrate).

Studies of the catalytic property of metals have shown that copper,[5-8] iron,[8,9] lead, manganeses,

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cobalt[5] and other metals [nickel, tin][10] considerably accelerate the oxidation of lipids. Zeils and Schumidt[5] showed that the metallic contamination during deodorization process, such as Al, Sn, Fe, Cu and Mn, greatly reduced the stability of the cottonseed oil.

Evans et al.[8] indicated that copper and iron added to soybean oil in concentration of 0.3 ppm were very detrimental to the oxidative and flavor stability, especially copper to be at least ten times more detrimental than iron.

Husaini and Saletore[11] also reported that all metals and alloys affected the storage stability of peanut oil and the order of decreasing stability that follows: Al, Fe, Zn, Sn and Cu.

Taufel and Romminger[12] studied the catalytic effect of the same amount of Cu^{++}, Fe^{++}, Mn^{++} and Ni^{++} on methyl oleate oxidation, and reported that the different intensity of pro-oxidant effect of those metals was $Cu^{++}>Mn^{++}>Fe^{++}>Ni^{++}$.

Marcuse and Fredriksson[13] prepared the emulsion of fatty acids and esters, emulsified by ultrasonic treatment after addition of 0.17% of Tween 20, and added Cu^{++}, Fe^{++}, Fe^{+++} and Co^{++} to the emulsion respectively. They reported that Cu^{++} and Fe^{+++} showed more prominent catalytic effect than Fe^{++} and Co^{++}. Mertens et al.[14] also reported that trace of copper, iron and other metals acted as powerful catalysts for oxidation of margarine.

Emanuel and Lyaskovskaya[15] stated that the contact of the lipid with metal was largely responsible for the reduced oxidation resistance of the samples taken during fat rendering under the industrial conditions.

According to the above papers and others, catalytic activity sequences of some metals are given below:

Cu>Fe>Ni>Sn[10];
Cu>Mn>Fe>Ni[12];
Cu>Li>Fe>Co[16];
Cu>Mn>Fe>Cr>Ni>Zn>Al[17].

Of those metals, Cu and Fe have been introduced by many authors[8,13,14,18] as the major catalysts on oil and the major contaminating factor in industrial point.

There has been increasing interest in preventing these metals contamination or in rendering these trace metals ineffective.

Precautions have been taken in plant practice and construction to decrease those metal contaminations by keeping the pumping lines as short as possible, by eliminating copper or iron-bearing metals in pumps and fittings, and by attempting to keep rust or corrosion of tanks and pipe lines to a minimum.

However, it seems that the water used in various processes of oil and its fried food production attracted little attention as a major factor of metal contamination.

In the case of Korean standard of city water quality, less 1ppm of Cu and less 0.3 ppm of Fe are allowed. Furthermore, the physically refined underground water, which is still being used in many industrial plants producing oil and its fried products, may be considered to contain more metal ions than the city water.

The objective of the present investigation was firstly to determine the proxidant effect of Cu^{++} and Fe^{++}, added in the same level of city water or physically refined underground water, on soybean oil and its fried noodle. Secondly, experiments were conducted in an attempt to investigate the inhibition effect of BHA and citricacid, which are now used in many industries as antioxidants, on the soybean oil and its fried noodle containing the Cu^{++} and Fe^{++} chlorides.

Ⅱ. Materials and Methods

1) Decision of Metal Concentration Added to Soybean Oil and its Fried Noodle.

In this experiment, the decision of metal concentration of city water was based on the Korean standard of city water quality; less 0.3 ppm of Fe and less 1 ppm of Cu are allowed. The metal concentration of physically refined underground water was determined by the average concentration of several underground waters collected in various regions. The metal concentrations of sample water were analysed by atomic absorption spectroscopy (Hitachi Model-207, Japan). The average concentrations of Fe and Cu were 1.05 ppm and 2.85 ppm respectively; however, the Fe and Cu concentrations of physically refined underground water used in this experiment were 1 ppm and 3 ppm respectively.

In the case of fried noodle, metal salts were added to the twice-distilled deionized watei which used in the noodle preparation at the same concentration of city water or physically refined underground water.

In the case of soybean oil, however, a somewhat arbitrary decision was made as to what concentrations of metal should be used. It was decided to use the same concentrations of the case of fried noodle because these concentrations were appropriate to observe the prominent proxidant effects of these metals on soybean oil and to compare with the case of fried noodle,

2) Chemical Analysis of Soybean Oil.

The oil used in this experiment was a refined, bleached but undeodorized soybean oil (Dong Bang Oil and Flour Mills Co., Ltd., Korea). Chemical analysis of the oil was carried out before adding the metal to subtsrate oil and befor frying the noodle. The results are shown in Table 1 and 2, The peroxide value of the oil was determined by A.O.C.S. official method (Cd. 8—53).[19] The free fatty acid value was determined by the method described by Tribold and Aurand[20] and calculated as percent free fatty acid expressed as oleic acid. The iodine value and saponification value were deter!mned by the A.O.A.C. method.[21]

3) Addition of Metal Salts and Antioxidants to Substrate Oil and Fried Noodle.

In the case of adding to the soybean oil, the metal salts and antioxidants were dissolved in 0.5ml of absolute ethyl alcohol (Merck Co., West Germany), and added directly to the soybean oil at the beginning of this experiment. The solvent was removed by heating and agitating the mixture in the water bath at 80°C for 3 min. This procedure was used because the metallic chlorides and the antioxidants could not be dissolved directly into the oil. The concentrations of metal salts are expressed by part per million with respect to the weight of the substrate oil. Antioxidants were added to the substrate in concentration of 0.01% weight of soybean oil.

In the case of adding to the fired noodle, the metal salts were dissolved directly on the water used in noodle preparation. The concentration of metal salts are expressed by part per million with respect to the weight of water used in preparation of noodle. Antioxidants were also added to the water in concentration of 0.01% weight of prepared noodle.

Table 1. Chemical analysis of the soybean oil used as substrate

Peroxide value	3.8±0.4meq/kg
Free fatty acid value	0.66±0.03%
Saponification value	193.5±2.0
Iodine value	118.7±0.8

Table 2. Chemical analysis of the soybean oil used in noodle frying

Peroxide value	1.1±0.3meq/kg
Free fatty acid value	0.68±0.01%
Saponification value	187.2±0.6
Iodine value	124.2±0.2

4) Preparations of Each Samples Used in This Experiment.

In the case of oil, each sample was prepared as follow:

A) Effect of ferrous chloride on soybean oil.

i) Soybean oil (250g)+0.5ml absolute ethyl alcohol

ii) Soybean oil (250g)+0.3ppm Fe^{++}

iii) Soybean oil (250g)+1ppm Fe^{++}

iv) Soybean oil (250g)+0.3ppm Fe^{++}+0.01% BHA

v) Soybean oil (250g)+0.3ppm Fe^{++}+0.01% citric acid

vi) Soybean oil (250g)+0.3ppm Fe^{++}+0.01% BHA +0.01% citric acid.

B) Effect of cupric chloride on soybean oil.

i) Soybean oil (250g)+1 ppm Cu^{++}

ii) Soybean oil (250g)+3 ppm Cu^{++}

iii) Soybean oil (250g)+1ppm Cu^{++}+0.01% BHA

iv) Soybean oil (250g)+1ppm Cu^{++}+0.01% citric acid

v) Soybean oil (250g)+1ppm Cu^{++}+0.01% BHA +0.01% citric acid.

C) Effect of ferrous and cupric chloride on soybean oil.

i) Soybeanoil (250g)+0.3ppm Fe^{++}+1ppm Cu^{++}

ii) Soybeanoil (250g)+1ppm Fe^{++}+3ppm Cu^{++}

iii) Soybean oil (250g)+0.3ppm Fe^{++}+1ppm Cu^{++} +0.01% BHA

iv) Soybean oil (250g)+0.3ppm Fe^{++}+1ppm Cu^{++} +0.01% citric acid

v) Soybean oil (250g)+0.3ppm Fe^{++}+1ppm Cu^{++} +0.01% BHA+0.01% citric acid.

Each test sample was divided evenly into three petri dishes and incubated at 35±0.7°C for a test period.

In the case of fried noodle, each test samples were prepared as follow:

i) Wheat flour (1200g)+400g of twice-distilled deionized water

ii) Wheat flour (1200g)+0.3ppm Fe^{++}+1ppm Cu^{++} .+400g of twice-distilled deionized water

iii) Wheat flour (1200g)+0.3ppm Fe^{++}+1ppm Cu^{++}+0.01% citric acid+400g of twice-distilled deionized water

iv) Wheat flour (1200g)+0.3ppm Fe^{++}+1 ppm Cu^{++}+0.01% citric acid+400g of twice-distilled deionized water

Each test sample was put into shallow dish and incubated at 35±0.7°C for a test period.

5) Preparation of Fried Noodle.

The preparation processes of fried noodle are shown in Table 3.

The noodle wasfried at 140°C for 90 sec. and cooled immediately to 35°C.

The composition of the major ingredients of fried noodle is shown in Table 4.

The chemical compositions of fried noodle are shown in Table 5.

Table 3. Preparation process of the fried noodle used in this experiment

1. Mixing the raw materials
2. Pressing with roller
3. Passing through the forming roller
4. Cutting
5. Frying
6. Cooling

6) Measurement of the Proxidant Activity of Metal Added in the Oil and Fried Noodle.

The proxidant effects of metals were compared on the basis of peroxide value development of oil or its fried noodle. The peroxide values were determined every three days by A.O.C.S. official method and expressed as milliequivalents of peroxides per kg. of oil.

In the case of fried noodle, the oil extraction processes were; weighing the fried noodle→adding the 5g of sodium sulfate anhydrous as a dehydrator→adding the diethyl ether with 2 times weight of noodle→shaking with the reciprocal shaker for 2 hrs. (90 strokes

Table 4. Composition of the major ingredients of the fried noodle used in this experiment

Ingredient \ Sample		Control	Control+ 0.3ppm Fe 1ppm Cu	Control+ 1ppm Fe 3ppm Cu	Control+ 0.3ppm Fe 1ppm Cu 0.01% citric acid
Wheat flour	(g)	1,200	1,200	1,200	1,200
Water	(cc)	400	400	400	400
$FeCl_2 \cdot 5H_2O$	(mg)	0	0.4280	1.4267	0.4280
$CuCl_2 \cdot 2H_2O$	(mg)	0	1.0731	3.2193	1.0731
Citric acid	(mg)	0	0	0	160

Table 5. Percent proximate composition of the noodle used in this experiment

	Control	Control+ 0.3ppm Fe 1ppm Cu	Control+ 1ppm Fe 3ppm Cu	Control+ 0.3ppm Fe 1ppm Cu 0.01% citric acid
Moisture	8.6	9.1	8.7	8.9
Crude fat	18.9	18.4	18.8	18.8
Crude protein	10.2	10.4	10.2	10.3
Total ash	0.9	1.1	1.4	1.2

All figures are mean values.

per minute)→filtering with No. 5B filter paper→seperating the diethyl ether with soxhlet in the water bath at 75°C for 30 min.→weighing the oil.

III. Results and Discussion

1) Effects of Ferrous Chloride and Cupric Chloride Independently or Simulteneously on Soybean Oil.

Each sample was coded in numerical order; No. 1, 2, 3, 4. and 5 are respectively the case of control+0.3 ppm $Fe^{\#}$+1 ppm $Cu^{\#}$, 1ppm $Fe^{\#}$+3ppm $Cu^{\#}$, 0.3ppm $Fe^{\#}$+1ppm $Cu^{\#}$+0.1% BHA, 0.3ppm $Fe^{\#}$+1ppm $Cu^{\#}$+0.01% BHA+0.01% citric acid, and 0.3ppm $Fe^{\#}$+1ppm $Cu^{\#}$+0.01% citric acid.

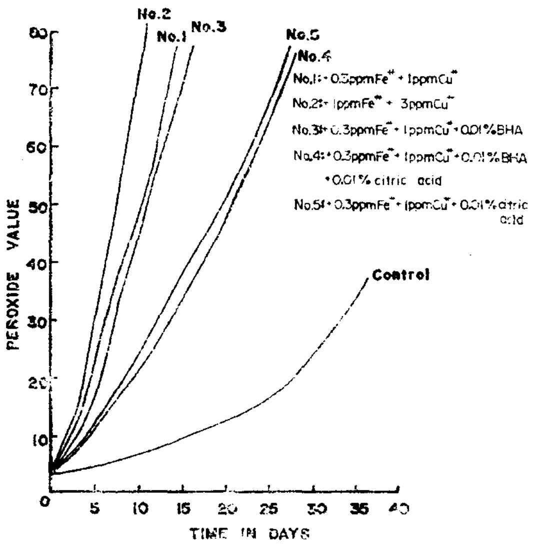

Fig. 1. Variations of peroxide values of soybean oils with the various amount of metals and antioxidants with time in days.

Table 6 summarizes the results of the peroxide determination. The peroxide developments of the each case are shown in **Fig. 1**.

All the substrates containing the metal salts alone or antioxidants with them were significantly more unstable to the rancidity development than the control. The relative rancidity developments of the various samples were, in increasing order, sample No. 2, No. 1, No. 3, No. 5and No. 4.

Of those samples, the $Fe^{\#}$+$Cu^{\#}$+BHA treated soybean oil and $Fe^{\#}$+$Cu^{\#}$ treated soybean oil were close each other in peroxide value developments. The result appears to suggest that the effectiveness of the BHA was markedly lessened by the metal. Morris et al.[10] suggested that since the catalyzed reaction of metal took place at the faster rate, the apparent efficiency of the phenolic antioxidants would be less.

On the other hand, the metal+citric acid+BHA treated soybean oil showed lower peroxide value development than the BHA only tretaed soybean oil.

The proxidant effect of ferrous chloride on same substrate oil, as shown in **Fig. 2**, had lower peroxide value development than that of curpric chloride as a whole. Significantly, the $Fe^{\#}$+citric acid treated soybean oil was more stable to the rancidity development than the control at the later stage. However, the case of cupric chloride treated soybean oils, shown in **Fig. 3**, presented the similar tendency with the cases

Table 6. Variations of peroxide values of soybean oils with various amount of metals and antioxidants with time in days

Sample No. \ Time in days	0	3	6	9	12	15	18	21
Control	3.8±0.4	4.2±0.2	5.7±06	7.4±0.3	8.7[3]	10.7±0.6	12.4±0.7	14.9±0.9
No. 1	3.8±0.4	15.2±0.9	32.0±2.1	48.1±1.9	60.5±1.9	76.5±4.6	90.1±3.7	112.4±7.7
No. 2	3.8±0.4	18.8±0.3	40.5±1.4	65.5±4.8	77.4±2.6	109.9±2.7	121.7±6.5	141.7±5.4
No. 3	3.8±0.4	14.0±1.2	30.5±0.8	45.2±2.1	58.3±2.9	73.7±2.3	89.0±3.7	107.9±6.1
No. 4	3.8±0.4	9.7±0.9	17.5±1.4	27.8±1.2	38.1±2.4	47.2±1.7	56.5±2.	69.4±5.4
No. 5	3.8±0.4	10.4±1.3	19.4±0.9	29.0±0.8	38.9±1.4	48.7±4.9	58.6±2.7	70.5±3.6

1) Peroxide values are expressed as milliequivalents of per kg. of oil.
2) Each sample was placed in an incubate kept at 35±0.7°C.
3) Figure without SD is mean value.

of ferrous and cupric chlorides simultaneously treated soybean oil.

As shown in those results, ferrous chloride and cupric chloride which added independently or simultaneously on soybean oil had prominent proxidant effect; especially, the cases of cupric chloride showed more detrimental effect than that of ferrous chloride on soybean oil oxidation. Evans[8] and others[14,18] showed the similar results to this in their investigations.

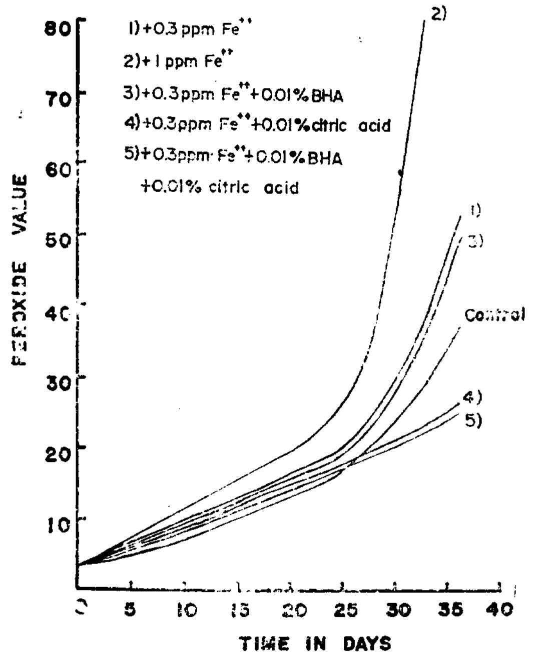

Fig. 2. Variations of peroxide values of soybean oils with the various amount of ferrous chloride and antioxidants with time in days.

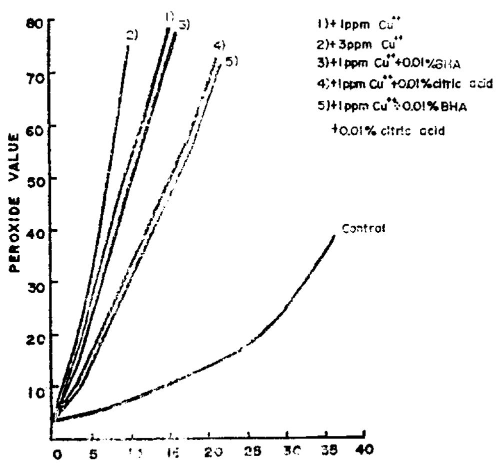

Fig. 3. Variations of peroxide values of soybean oils with the various amount of cupric chloride and antioxidants with time in days.

Effect of BHA and citric acid independently or simultaneouly was inffective to the oxidation by metal ions, exclutive of the case of ferrous chloride. As elucidated by Morris et al.,[10] this result suggested that since the catalyzed reaction of metal ion took place at the faster rate, the efficiency of the antioxidant would be less.

However, citric acid was a very good ferrous ion deactivator as shown in Fig. 2. According to Morris[10] and others,[23~25] citric acid can act as a good inactivating agent for metal and as a synergist at the same time. Owing to the capacity of citric acid for forming complexes, it probably can bind with the metal ion and removes it from the reaction zone, as indicated by Emanuel and Lyaskovskaya.[15]

2) Effects of Ferrous Chloride and Cupric Chloride on Fried Noole.

Each sample was coded in numerical order. Sample No. 1, No. 2 and No. 3 are respectively the case of control+0.3ppm Fe^{++}+1ppm Cu^{++}+0.01% citric acid, 0.3ppm Fe^{++}+1ppm Cu^{++} and 1ppm Fe^{++}+3ppm Cu^{++}.

Table 7 summerizes the results of the peroxide determination in various cases. The peroxide value developments of the each case are shown in **Fig. 4**.

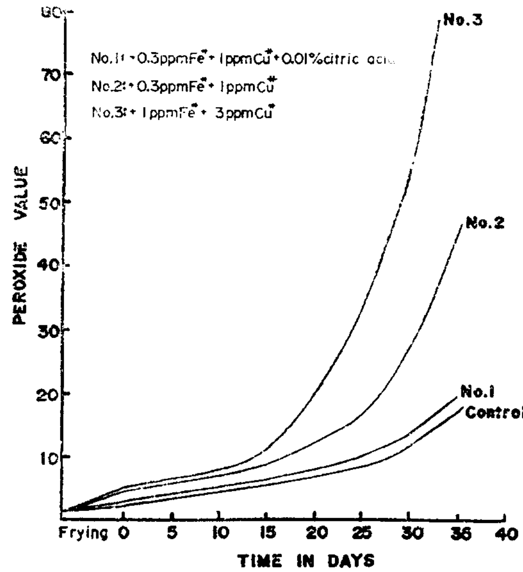

Fig. 4. Variations of peroxide values of the various noodle samples with time in days.

Table 7. Variations of peroxide vlues[1] of the various noodle sample[2] with time in days.

Time in days / Smple No.	0	3	6	9	12	15	18
Control	3.3±0.4	3.6±0.2	4.3±0.1	4.7±0.1	5.1±0.2	5.6±0.2	6.2±0.1
No. 1	3.6±0.2	3.7±0.1	4.4±0.7	4.9±0.4	5.6±0.1	6.3±0.1	7.2±0.5
No. 2	4.8±0.6	5.1±0.1	5.7±0.2	6.7±0.1	7.9±0.3	8.9±0.7	10.7±0.2
No. 3	5.0±0.3	5.2±0.1	6.0±0.2	7.0±0.5	8.5±0.4	10.9±0.4	14.3±0.4

Time in days / Sample No.	21	24	27	30	33	36
Control	7.7±0.3	8.7±0.7	9.9±1.2	11.7±0.4	13.9±0.1	17.3±0.4
No. 1	8.9±0.2	10.5±0.1	11.9±0.6	13.0±0.1	15.9±0.3	19.2±0.7
No. 2	13.0±0.6	16.5±0.4	21.0±0.8	27.0±1.2	35.9±2.2	46.9±1.8
No. 3	20.3±0.1	27.6±2.1	38.1±1.2	50.8±2.3	67.3±2.4	86.4±3.6

1) Peroxide values are expressed as milliequivalents of peroxides per kg. oil.
2) Each noodle sample was placed in an incubator kept at 35±0.7°C.

The peroxide values of each case were different after frying treament.

In the control group, the peroxide values of soybean oil which was extracted from the fried noodle were increased slightly during the first 27 days, and then increased rapidly.

The relative rancidity developments of various noodles were, in increasing order, noodle No. No.3, No.2 andNo.1. However, the peroxide value developments of all the noodle samples showed less slow increasing trend than that of oil samples.

The $Fe^{+}+Cu^{+}$ treated fried noodles, however, marked higher peroxide value significantly than the control marked; whereas, the peroxide value developments of $Fe^{+}+Cu^{++}$+citric acid treated fried noodle were very close to that of control. It is evident from this result that citric acid had a good inhibition effect on metals added to the fried noodle.

Since those metal contamination is probably detrimental to the stability and quality of soybean oil and its fried noodle, as shown in those results, it is very desirable thing to use the water treated by the metal removing process in the producing of oil and its fried products.

Ⅳ. 要 約

本 實驗은 大豆油와 그 튀김麵에, 韓國 上水道 基準 또는 物理的으로 精製한 地下水에 含有可能한量과 同一한 量의 鐵 ion과 銅 ion을 各各에 添加하여 그들에 의한 酸敗促進程度를 測定하고, 아울러 一般的으로 널리 쓰이고 있는 油脂의 抗酸化劑로서 BHA (butylated hydroxyanisole) 또는 citric acid가 이들 金屬에 依한 酸敗促進程度를 어느 정도 減少시키는 가를 比較 檢討하였다.

本 實驗의 結果, 大豆油와 그 튀김麵의 경우 모두, 鐵 ion 또는 銅 ion의 添加는 이들 ion이 添加되지 않은 경우와 比較할때 뚜렷한 酸敗促進效果를 보였다. 특히, 銅 ion이 添加된 경우에 있어서는 時間이 經過함에 따라 鐵ion이 添加된 경우보다 3倍 내지 6倍의 强한 酸敗促進效果를 보였다.

抗酸化劑인 BHA와 citric acid의 이들 金屬에 依한 酸敗促進에 對한 沮害作用度는 citric acid가 添加된 경우가 BHA添加 경우보다 컸으며, BHA가 添加된 경우 그 效果는 極히 微弱하였다.

또한 이들 抗酸化劑의 沮害作用度는 銅 ion의 경우보다 鐵 ion의 경우에 더 效果的인 것으로 보여진다.

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