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Effects of Process Conditions on Sardine Oil During Bleaching and Deodorization

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Abstract

For use of sardine oil as an ingredient of food and feed, crude sardine oil obtained by rendering was processed to RBD sardine oil. Alkali deacidification was found to be most efficient with a concentration of 2.5N NaOH and 0.5% excess level at 75°C. Treatment with activated clay alone at 105°C for 20 *min* without air admission was effective in reduction of the color intensity of the oil without any formation of the conjugated dienes and trienes of polyunsaturated fatty acids. In deodorization process, as the temperature was increased, color of the oil was to become lighter. The amount of conjugated compounds was, however, increased drastically at higher temperatures above 180°C for 1hr, and content of polyunsaturated fatty acids was significantly decreased.

Introduction

Triglyceride-based oils of marine origin differ from most vegetable oils in that they have a very complex fatty acid composition and contain acids with a wide range of chain lengths, and unsaturations[1-9]. Recently, a series of intensive studies have reported that ω-3 polyunsaturated fatty acids (ω-3 PUFA), i.e., eicosapentaenoic acid (EPA, 20:5ω3) and docosahexaenoic acid (DHA, 22:6ω3) of fish oils inhibit the synthesis of VLDLs and increase the excretion of choresterol and they also may reduce fatty acid synthesis in liver cells[4]. These apparent effects of ω-3 PUFA components of fish oil offer a promising approach for formulating dietary regimens or practices for prevention of coronary heart disease and atherosclerosis[5].

The prospect of using ω-3 PUFAs in foods offers not only a potentially large market of fish oil and PUFA concentrates for the food industry but also some technical challenges such as the stability of products.

Some quantities of sardine have been caught off Korean coast since 1980, and about 15,000 metric tons of crude fish oil mainly from sardine oil is produced as a by-product of fish meal industry in 1986. Most of the fish oils produce in Korea have been utilized as a raw material of paint because of its poor quality and unstability. A considerable amount of fish oil, however, has been imported to meet the demand of food oil industry in which the fish oil is hydrogenated to use as a cheap source of the processed oil and fat such as margerine and shortening.

We have carried out a series of studies for the efficient utilization of the crude fish oil as a source of ω-3 PUFAs and a direct ingredients of food and feed. This report deals with the neutralization, bleaching, and deodorization conditions for the crude sardine oil produced by fish meal industry.

Materials and Methods

Materials

The crude sardine oil used was commercially prepared by redering at 90°C at a local fish meal plant. All reagents were of analytical grade unless otherwise specified.

Refining Procedures

The processing techniques, employed to produce a finished RBD oil from the crude sardine oil are outlined on the flowsheet shown in Fig. 1.

Deacidification was done according to AOCS Official Method[6] with some modifications. The crude oil was placed in 2 ℓ beaker and move into a water bath of appropriate temperatures. When the temperature of the oil reached to 75°C, NaOH solution ranging from 2.0 to 3.0 N was added to the oil during rapid stirring under nitrogen gas stream and stirring was continued for 15 min. The volume of NaOH solution added to the oil was sufficient to neutralize the free fatty acid content and to provide

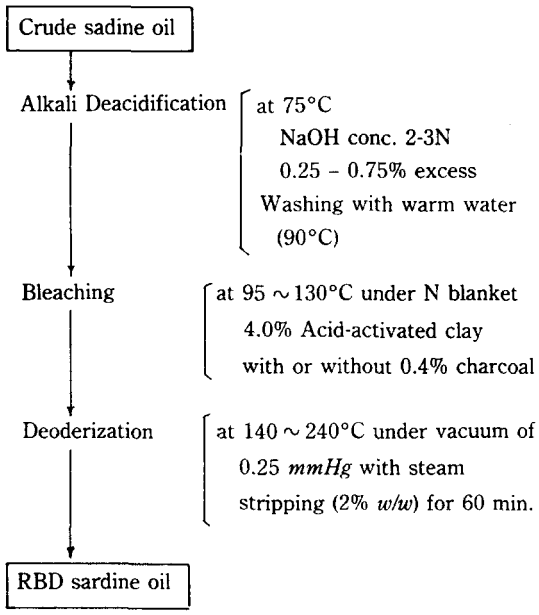

Fig. 1. Schematic diagram of refining procedure of sardine oil

excess NaOH from 0.25 to 0.75 % (*w/w* dry basis) of the oil. The beaker was transfered to a 60°C water bath and the emulsion agitated slowly for 10 min, then allowed to stand for 30 min. The soap stock was removed by centrifugation at 10°C for 20 min at 20K × G and washing three times with hot water of 90°C.

Deacidified oil was bleached using acid-activated clay (Tonsil Std. FF) alone or combined with activated charcoal at 10% level of clay. Bleaching was accomplished by heating the oil under nitrogen gas stream in an oil bath thermostat with vigorous stirring. When the oil reached the desired temperature within the range of 95-130°C, the bleaching agent were added, and stirring was continued for period of 5 to 30 min. The bleached oil was cooled rapidly to room temperature, and filter through fine sintered glass layered with 1 *cm* thick of celite 504.

Deodorization was done using the steam refining apparatus with some modifications[7]. Pressure in the system was maintained at 0.25 *mmHg* and steam was sparged to the oil at a fixed rate of 2% of the oil during deodorizing period of 1 hr. Still jar was heated using a heating mantle thermostsat and the temperature of the oil was controlled within the range of 140-240°C.

Analytical Methods

Acid value, peroxide value and iodine number were measured by the AOCS Official Methods[6]. Oil color was measured using Lovibond Tintometer (Model E) with 5.25″ cell.

UV spectra of the oil in iso-octane as solvent were recorded by means of a self-registering Beckman-Model 8 spectrophotometer. Absorbances of 1 volume percent at 232 and 268 *nm* were meausred as index of the conjugated diene and triene compounds, respectively.

Neutral, phospho and glycolipid fractions of crude sardine oil were analyzed using silisic acid column according to Cater et. al,[8]. Fatty acid compositions of oils were obtained by gas chromatography method as described in previous report[9].

Results and Discussions

Polar lipid components in the crude oil used in this study was only 3.6% (Table 1), which was much less than that in the solvent-extracted sardine oil that had been reported to cotain about 10% of the total lipids[9]. During rendering, the polar lipid components had been transfered into waste water by hydration, which made it possible to eliminate the degumming step.

The effects of NaOH concentration and excess level for deacidification are shown in Table 2. NaOH concentration for deacidification reached an optimum at about 2.5 N and an excess of 0.5% in terms of recovery yield of oil. Color intensity was reduced from that in crude oil as the alkali concentration increased, but the different excess level of alkali did not appear to have a significant effect on color or residual free fatty acid.

Table 1. Analysis of crude sardine oil obtained by rendering

Items	Values
Lipid components (%)	
Neutral lipids	96.4
Phoshpolipids	2.1
Glycolipids	1.5
Acid value (mg KOH/g oil)	8.40
Peroxide value (m eq./kg oil)	19.18
Iodine number	178.1
Lovibond color (5 1/4″ cell)	R 16.4
	Y 90.1
	B 4.8

Table 2. Effect of NaOH concentration and excess level on sardine oil

NaOH		%	Acid value	Lovibond color (5 1/4")		
Conc.(N)	Excess level(%)	Oil recovery	(*mg* KOH/*g*)	R	Y	B
0	—	—	8.40	16.4	90.1	4.8
2.0	0.25	70.1	0.49	12.4	1.0	
	0.50	67.7	0.43	12.3	58.1	0.9
	0.75	65.5	0.41	12.2	55.1	0.9
2.5	0.25	73.1	0.43	12.3	57.0	0.8
	0.50	74.4	0.31	11.5	56.8	0.8
	0.75	72.2	0.38	11.0	49.1	0.8
3.0	0.25	71.7	0.47	10.2	49.0	0.7
	0.50	68.4	0.47	10.0	48.0	0.6
	0.75	65.0	0.61	9.4	42.8	0.6

The addition of charcoal at 10% level of the clay weight did not improve decolorization when the clay was added at the amount above 2.5% of the oil as shown in Fig. 2. As bleaching clay was increased from 0.5 to 4.0%, Lovibond red unit decreased from 9.7 to 1.8, but the increase of clay over 4.0% did not show any additional reduction in color. When bleaching temperature was increased from 95 to 105°C, the time reached 2.0 Lovibon red unit was reduced from 25 to 15 min, but at the temperature above 115°C, the red value of bleached oil was increased after 15 min (Fig. 3). As bleaching temperature was increased from 95 to 130°C, the acid value was increased slightly from 0.31 to 0.39 *mgKOH/g* and the peroxide value from 2.51 to 3.01 *m eq./Kg* as presented in Table 4. This is consistent with reported optima of bleaching times and temperatures which are dependent on the kind of oil being bleached[13]. But iodine number of the oil bleached at various temperatures within the range of this experiment showed no significant differences.

Table 5 shows the effect of temperature of deodoriza-

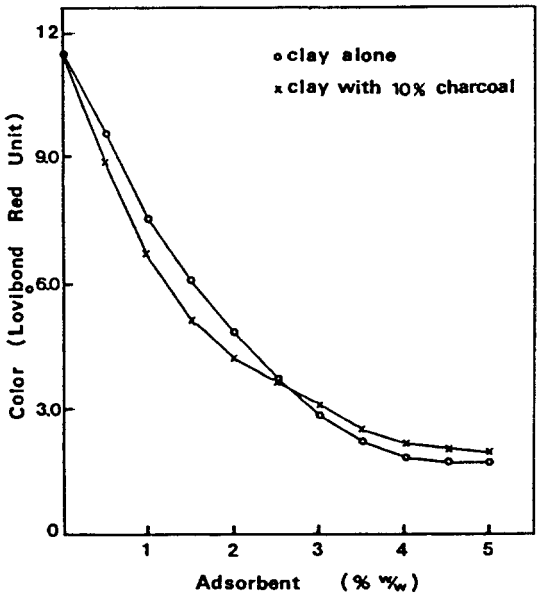

Fig. 2. Effect of addition amount of adsorbent on color of sardine oils bleached at 105°C for 20 min under nitrogen

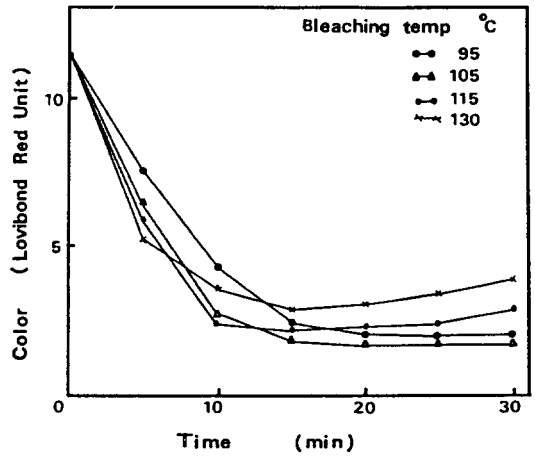

Fig. 3. Effects of bleaching temperature and time on color of sarding oils bleached with 4% acitvated clay under nitrigen

Table 3. Effect of bleaching temperature on sarding oil

Temperature (°C)	Acid value (KOH/*g*)	Peroxide value (*m eq./kg*)	Iodine number	Lovibond color R	Lovibond color Y
—	0.31	11.91	178.9	11.5	56.8
95	0.31	2.51	179.4	1.9	38.0
105	0.35	2.37	179.9	1.8	33.0
115	0.33	2.97	178.7	2.4	42.0
130	0.39	3.01	177.8	2.9	49.3

* Bleached with 4% activated clay for 20 min under nitrogen

Table 4. Effect of deodorizing temperature on sardine oil

Temperature (°C)	Acid vlaue (mg KOH/g)	Peroxide value (m eq./kg)	Iodine number	Lovibond color R	Lovibond color Y
Bleached Oil	0.35	2.37	179.9	1.8	38.0
140	0.17	1.03	179.6	1.8	38.0
160	0.15	1.20	179.7	1.4	38.0
180	0.12	0.31	177.3	1.4	38.0
200	0.08	0.40	176.9	1.2	26.0
220	0.04	0.42	174.0	1.2	20.0
240	0.08	0.41	161.0	1.0	17.4

tion at the conditions described in refining procedures. As temperature was increased, acid value and Lovibond color value were decreased since free fatty acids were distilled out and color compounds were thermally bleached at high temperature. The peroxide value, however, showed a minimum value at 180°C. Above 180°C, the iodine number was also drastically decreased as the increase of temperature. Regarding the influence of temperature on the absorption maxima of UV spectra of the oils; the higher the temperature, the more conjugated compounds formed (Table 6). Below the temperature 180°C, there is a slight formation of conjugated compounds with little difference from bleached oil. It was noted that a number of artifacts of polyen appears in the fatty acid profile of the gas chromatogram as a results of deodorization (not shown here). In general, the formation of artifacts is favoured by use of high temperature. It can be seen in Table 6 that significant falls in polyunsaturated fatty acids took place progressibly as the temperature of deodorization rises. It is thought that this fall of polyenes is a reflection of conversion of these acids into polymerized products and/or smaller molecules by degradation[11].

Table 5. UV absorpton at different maxima of sardine oils deoderized at various temperatures

Temperature (°C)	$E^{1\%}_{1cm}$ 232 nm	$E^{1\%}_{1cm}$ 268 nm
Bleached oil	7.38	0.61
140	7.25	0.68
160	7.67	0.97
180	8.87	2.05
200	10.04	5.63
220	14.91	18.18
240	20.10	21.37

* The absorption maxima were measured in 1 volume percent solutions in iso-octane.

The study reported here demonstrates the inevitability of chemical changes in the polyunsaturated fatty acids of fish oils under the deodorization at 220-240°C, even if this temperature range was normal for common vegetable oils.

Table 6. Changes of fatty acid composition in sardine oils deodorized at various temperatures for 1 hr

Fatty acid	Bleached oil	Deodorization temperature (°C)					
		140	160	180	200	220	240
14:0	7.47	7.56	7.66	7.27	7.42	7.34	7.37
16:0	17.42	17.70	17.52	17.57	17.93	17.88	17.92
18:0	3.43	3.41	3.42	3.56	3.55	3.54	3.51
24:0	1.05	1.05	1.07	1.08	1.07	1.06	1.09
Saturates	29.37	29.72	29.67	29.48	29.97	29.82	29.89
16:1	8.25	8.39	8.31	8.24	8.43	8.96	8.87
18:1	12.60	12.69	12.61	12.81	13.08	12.96	13.23
20:1	6.78	6.80	6.78	6.99	7.08	7.31	7.35
22:1	5.33	5.36	5.33	5.49	5.74	5.43	5.32
24:1	0.68	0.83	0.83	0.80	0.59	0.64	0.67
Monoenes	33.64	34.07	33.86	34.33	34.92	35.30	35.44
18:2	3.46	3.48	3.39	3.42	3.13	3.16	3.11
20:2	3.24	3.27	3.21	3.16	3.10	3.02	2.98
20:4	0.97	0.95	0.96	0.98	1.03	0.99	1.02
20:5	15.38	15.38	15.22	14.99	14.60	13.96	13.77
22:5	2.06	2.06	2.07	2.10	2.09	2.10	1.99
22:6	9.49	9.45	9.45	9.29	9.08	9.03	8.93
Polyenes	34.60	34.59	34.30	33.94	33.03	32.26	31.80

Though these changes are of small consequence so far as the quality and acceptability of oil is concerned, these are of nutritional importance for direct food usage of fish oil. It can be concluded that sardine oil has to be deodorized at an higher vacuum and below 180°C in order to avoid the fomation of artifacts of polyunsaturated fatty acids in the oil.

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정어리유에 대한 탈색 및 탈취조건의 영향

김철진 · 안병학 · 황성연* · 신현경

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Rendering에 의하여 추출된 정어리 조유를 이용하여 식품 및 사료의 원료로 직접 사용할 수 있는 정제 정어리유를 제조하기 위하여 탈산, 탈색 및 탈취등의 정제 실험을 실시하였다. 4%의 산성활성백토를 가하여 105℃에서 20분간 질소가스하에서 탈색하는 것이 conjugated 화합물의 생성없이 가장 효과적이었다. 탈취온도가 높을수록 conjugated 화합물의 생성이 촉진되었으며, 요오드가 및 고도불포화지방산의 함량이 감소되는 경향이 뚜렷하여 정어리유의 경유 180℃이하에서 탈취하는 것이 바람직한 것으로 밝혀졌다.