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Effect of Storage Condition of the Refined Palm Oil on its Heat Bleachability

Joon Shick Rhee

Department of Biological Science and Engineering
The Korea Advanced Institute of Science
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탈산 팜유의 저장조건이 그의 고온 탈색도에 미치는 영향

이 준 식

한국과학원 생물공학과
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Abstract

A series of tests were conducted to find out whether continuous heat bleaching of the refined Malaysian plam oil stored in different conditions could reduce color of the finished oil in an actual plant situation. When the refined oil was stored in a stainless steel tank and was not abused by heat during 5 month storage period, heat bleaching followed by clay bleaching and deodorization resulted in a substantial reduction in color of the finished oil in comparison to conventional process (clay bleaching of the refined oil followed by deodorization) (2.6 vs 1.3 red in Lovibond color). However, when the refined oil was stored in a carbon steel tank and was highly abused by heat in the presence of iron picked up from the tank (6.53 ppm) during the same storage period, heat bleaching followed by clay bleaching and deodorization did not help reduce color of the finished oil in comparison to the conventional process (2.7 vs 2.8 red in Lovibond color). It was also shown that oxidation values were not good indices for heat bleachability. Heat bleaching caused slight increase in polymer content of the oil. However, trans isomers were not increased when the oil was heat bleached.

Introduction

World wide palm oil utilization as an edible vegetable oil is ever increasing and is anticipated to do so in future, as Malaysian palm growers increase the acerage of palm trees[1] and as favorable conditions for the economic advantage, product acceptibility and standard of quality prevail[2]. At the present time, most of the palm oil are exported as refined oil or as refined, bleached and deodorized oil (RBD) by Malaysian oil processors. In case of the oil being imported as refined oil, the oil is required to be processed by oil processors in imported countries to finished oil by clay bleaching followed by deodorization. However, color of the oil is deep red which is objectionable to the end users of the oil for manufacture of shortening and margarine. Further, it was suspected that degree of oxidation and abusement

by heat of crude oil or refined oil would affect the color of the finished oil. It was reported that α- and β-carotenes among carotenoids were believed to be most responsible for the red color and the destruction rate of the carotenoids doubled for every 20°C[3]. Objective of this study was to find out whether color of the oil stored in various storage conditions could be reduced in actual plant situation by pilot scale continuous heat bleaching process.

Materials and Methods

Material

During unloading of refined Malaysian plam oil from oil tanker to tank farm at the Long Beach Harbor, California, U.S.A., approximately 600 gallons of the oil (Sample I) were obtained and stored in an insulated 700 gallon carbon steel oil storage tank under nitrogen head space for about five months before this test. During the storage period, the oil was kept molten (38~60°C) by periodically heating once in every 2~3 days by recycling through a steam heat exchanger. On many occasions, it was imperative to heat the oil up to 93°C before long holiday week ends in order to keep the oil from being solidified. This undoubtedly abused the oil quite badly. Another batch of the same oil (Sample II) was simultaneously stored in 600 gallon stainless steel oil storage tank under nitrogen head space for five months. During the storage period, the oil was not required to be kept molten, since the tank had an agitator and hot water heating coil. Instead, the oil was heated to 65°C max. whenever sampling was required for storage tests.

Equipment

The refined oil stored for five months in the two tanks were processed by conventional process and heat bleaching process as shown in Fig. 1. Clay bleaching and deodorization were done according to the standard methods[4,5]. Fig. 2 shows a schematic diagram of the continuous heat bleaching system. The refined palm oil was transferred from the storage tanks to 55 gallon feed vessel (V-1). The oil in the nitrogen blanketed vessel was recirculated through a pump(P-1) and a heat exchanger (HX-1) to maintain temperature of the oil at 77°C. The feed oil was fed to a preheater (HX-2) continuously by a metering pump (P-2) (Minarik model W63RM) at a predetermined rate of 946-1045 grams per min. Temperature of the oil out of the preheater and Therminol heater (HX-3) (Whitlock AHT-1-A-SS, 6-W-35) were 166°C and 271°C, respectively. Heating media of preheater and Therminol heater were steam at 177°C and Monsanto's Therminol 55 at 288°C, respectively. Two water coolers (HX-4 and HX-5) were used since a larger capacity cooler was not available. Temperature of the oil out of the first and second coolers were 115~148°C and 57~65°C, respectively. The material of construction for the system including lines connecting the system(3/8 inch tubing) was 316 stainless steel.

Analysis

Samples of the refined, in-process and finished oil were analyzed for color [6a], free fatty acid[6b] peroxide value[6c], moisture [6d], phosphorous[6e], trans isomers[6f], sopas[6g], anisidine value[7], polymers[8], and iron[8].

Results and Discussion

Table I shows analytical results for the refined palm oil as received from the tanker and for Sample I and II which were stored for five months under two different conditions (see the material section). Color of Sample I was reduced to 9.0 red in Lovibond color (1 inch cell) from 19 red in five months, whereas color of Sample II remained virtually the same during the same period. Free fatty acid and iron content for Sample I were increased to 0.50% and 6.53 ppm from 0.21% and 0.49 ppm, respectively, whereas those for Sample II remained virtually the same in five months. These results showed that the refined oil stored under the unfavorable conditions underwent severe quality changes.

It appeared that oxidation values (peroxide value, anisidine value and totox value) did not reflect the degree of abusement of the oils. They were highly erratic and inconsistent seemingly due to

1. Conventional process method

Refined palm oil → [Clay Bleaching] → [Deodorization] → Finished palm oil

Clay Bleaching	Deodorization
Clay=1% Fitrol 105	Temp=235°C
Temp=80°C	Time=1 hr @ 235°C
Time=20min.	Vacuum=4~6mmHg
N_2 Atmosphere	Steam=3%

2. Heat bleaching method

Refined palm oil → [Heat Bleaching] → [Clay Bleaching] → [Deodorization] → Finished palm oil

Heat Bleaching	Clay Bleaching	Deodorization
See Fig. 2 for details	Clay=1% Fitrol 105	Temp=235°C
	Temp=80°C	Time=1hr @ 235°C
	Time=20 min	Vacuum=4~6mmHg
	N_2 Atmosphere	Steam=3%

Fig 1. Experimental design for refined palm oil heat bleaching test

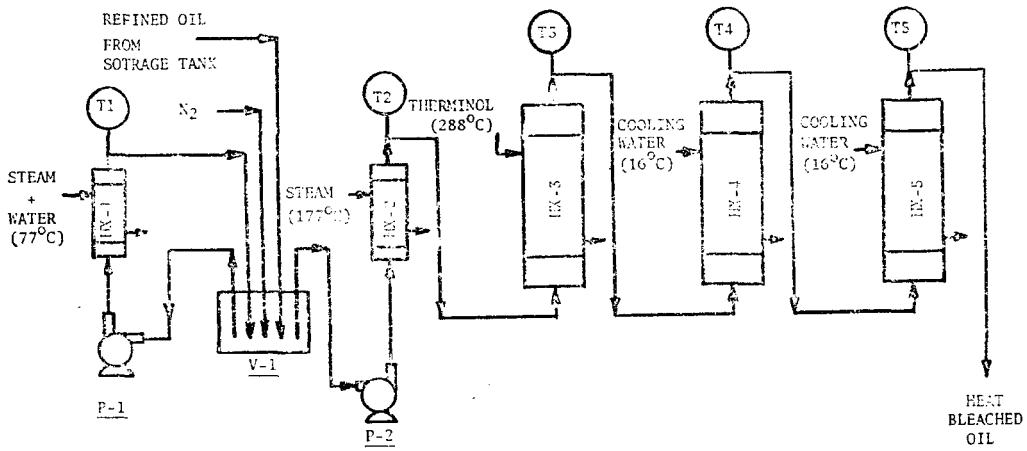

Fig. 2 Schematic diagram of continuous heat bleaching system

NOTE: V-1: Feed vessel
P-1: Recycle pump
P-2: Feed pump
HX-1: Steam+water heater
HX-2: Preheater
HX-3: Therminol heater
HX-4 and HX-5: water cooler
All lines: 3/8 inch SS tubing

their dynamic nature. Peroxide value is defined as a method of determination of hydroperoxides and other similar products of primary fat oxidation (AOCS official and tentative method Cd 8-53). Anisidine value is defined as a method of determination of the two alkynals (α- and β-unsaturated aldehydes of secondary oxidation products) (Hunt-Wesson test method HA-010). These products are highly unstable and easily oxidized further to polymerization if the conditions are unfavorable, i. e., high temperature, presence of oxygen and iron etc. Totox value is defined as the sum of two times of peroxide value plus anisidine value (Totox=2PV+AV).

Thus, it can be concluded that the oxidation values are valid, only if the sample history is less complicated (such as temperature, frequency of heating and transportation, degree of air exposure, etc.). Soap content of the refined oil was 23.3ppm and phosphorous content increased somewhat after five months which could not be explained.

Table 2 shows analysis of in-process and finished oils for Sample Ⅰ and Ⅱ. For sample Ⅰ, heat bleaching did not improve the color of the finished

Table 1. Analysis of refined palm oil as received from tanker and stored for 5 months at two different conditions (Sample I and II)

Analysis	As received	After 5 month-storage	
		Sample I	Sample II
Color (Lovibond red in 1 inch column)	19	9.0	18
Free fatty acid (%)	0.21	0.50	0.23
Moisture (%)	0.04	0.03	0.05
Peroxide value (*meq/kg*)	17.0	0.8	33.3
Anisidine value	33.8	35.6	2.0
Totox (2PV+AV)	67.8	37.2	68.6
Iron (ppm)	0.49	6.53	0.50
Copper (ppm)	0.034	0.035	0.032
Phosphrous (ppm)	0.90	1.5	1.7
Soap (ppm)	23.3	—	—
Trans isomers (%)	—	2.5	3.1
Polymers (%)	—	—	0.2

Table 2. Analysis of in-process and deodorized palm oils

Analysis	Sample I					Sample II				
	Conventional		Heat bleaching			Conventional		Heat bleaching		
	Clay bleached	Deodorized	Heat bleached	Clay bleached	Deodorized	Clay bleached	Deodorized	Heat bleached	Clay bleached	Deodorized
Color(Lovibond red in 5 1/4 inch column)	5.8	2.8	9.0	3.1	2.7	5.5	2.6	3.4	1.5	1.3
Free fatty acid (%)	—	0.06	0.72	—	0.05	—	0.04	0.21	—	0.02
Iron (ppm)	—	0.07	6.61	—	0.08	—	0.07	0.57	—	0.07
Peroxide value (*meq/kg*)	—	0	1.4	—	0	—	0	0.7	—	0
Anisidine value	—	11.5	27.8	—	8.8	—	12.3	56.9	—	19.7
Trans isomers (%)	—	2.7	3.1	—	3.0	—	2.8	2.8	—	2.8
Polymers (%)	—	1.1	3.7	—	2.8	—	1.0	2.4	—	2.2

oil (2.8vs 2.7 red in 5 1/4inch cell), even though the two finished oil samples were analytically more or less the same. However, iron content of the heat bleached oil was 6.61 ppm which was close to that for the refined oil stored for five months. This was undoubtedly responsible for the deep red color of the heat bleached oil (9.0red in 5 1/4 inch cell). Even though subsequent clay bleaching followed by deodorization removed the iron content to 0.08 ppm, color of the oil was believed to be fixed in the oil and deodorization did not help remove the color. In a separate test where the refined oil was clay bleached to remove the iron and then heat bleached followed by clay bleaching and deodorization, color of the oil was 2.1 red in 5 1/4 inch cell. In another separate test where the refined oil was clay bleached twice and then deodorized, color of the oil was 2.3 red. This indicates that the heat bleaching did not improve the color even though the iron in the oil was substantially removed by clay bleaching before heat bleaching.

For Sample II, however, heat bleaching improved color of the finished oil substantially(2.6 vs 1.3 red in 5 1/4 inch cell). The results of this experiment

showed that heat bleaching process was effective to reduce color of the finished palm oil, if the refined oil was not abused by heat and/or oxygen and if extreme care was taken to minimize iron pickup during the storage and processing.

Free fatty acid content of the finished oil for Sample Ⅱ were slightly lower than that for Sample Ⅰ. Peroxide values for both samples were zero after deodorization regardless of the processing methods (conventional vs. heat bleaching). Here again, oxidation values did not give the true picture of the degree of oxidation of Sample Ⅰ and Ⅱ. Heat bleaching did not affect trans isomers for both samples regardless of the processing methods. However, it caused a slight increase in polymer content for both samples.

요 약

식용유 정제 공장에서의 실제적인 조건 하에서 저장된 말레이시아산 탈산팜유(refined palm oil)의 연속식 고온 탈색 공정(continuous heat bleaching process)의 가능성을 알아 보기 위하여 일련의 실험을 하였다. 그 결과를 보면, 5개월간의 저장 기간 중 종종 試料 採取 時를 제하고는 계속해서 고체상으로 stainless steel 저장 탱크에 저장한 경우, 연속식으로 고온 탈색 후 산성 백토에 의한 탈색과 탈취 공정을 거친 최종 팜유는 탈색 및 탈취만을 거치는 재래식 공정에 의해서 얻은 최종 팜유 보다 붉은 색이 훨씬 감소 되었고, Lovibond color로 각각 1.3 red와 2.6 red 이었다.

한편 5개월간의 저장 기간 중, 질소 가스 존재하에 carbon steel 저장 탱크에서 38~60°C의 온도하에서 액체상으로 저장한 경우, 고온 탈색 공정을 거친 최종 팜유와 재래식 공정을 거친 최종 팜유의 붉은 색은 Lovibond color로 각각 2.7 red와 2.8 red이었으며, 고온 탈색 공정이 탈색에 별 도움이 되지 못하였다. 그 이유는 주로 저장 기간 중 저장 탱크에서 비교적 높은 온도 때문에 용해된 철분 (6.53 ppm)과 고온에 의한 열화 현상 때문인 것으로 판단되었다.

과산화 값, 아니시딘 값 등의 산화 값(oxidation value)은 고온 탈색도(heat bleachability)와 상관 관계가 없었고 트랜스 이성체 생성에 영향이 없었으나 중합물 생성에는 약간의 영향이 있었다.

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