Treatments of free fatty acids to prevent or decrease colour fixation in cottonseed oil

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RESUMEN

Tratamientos de ácidos grasos libres para prevenir o disminuir la fijación del color en el aceite de semilla de algodón

Se han investigado algunos tratamientos para prevenir o eliminar la fijación del color de aceite de semilla de algodón que contienen alto nivel de ácidos grasos libres, sin utilizar un exceso de hidróxido sódico en la etapa de refinación.

Los tratamientos incluyeron el uso de carbonato sódico y etanolamina antes y después, sometiendo un aceite crudo de semilla de algodón que contiene exceso de ácidos grasos libres a tratamiento de fijación del color.

Los resultados mostraron que el tratamiento carbonato/etanolamina mejoró el color del aceite por disminución de los ácidos grasos libres y gosipol en el aceite, sin utilizar un exceso de hidróxido sódico.

Llevar a cabo el tratamiento con carbonato/etanolamina sobre aceite de semilla de algodón con niveles altos de ácidos grasos libres antes que tenga lugar la fijación del color es más recomendable que llevar a cabo el mismo tratamiento sobre el mismo aceite después de que se haya fijado.

PALABRAS-CLAVE: Aceite de semilla de algodón — Ácido graso libre (tratamiento) — Carbonato sódico — Etanolamina — Fijación de color.

SUMMARY

Treatments of free tatty acids to prevent or decrease colour fixation in cottonseed oil

Some treatments have been investigated to prevent or remove colour fixation of cottonseed oil containing high level of free fatty acids without using excess of sodium hydroxide in the refining step. The treatments included use of sodium carbonate and ethanolamine before and after subjecting a crude cottonseed oil containing excess of free fatty acid to a colour fixation treatment.

The results revealed that the carbonate/ethanolamine treatment improved the oil colour by decreasing the free fatty acids and gossypol in the oil, without using any excess of sodium hydroxide.

Carrying out the carbonate/ethanolamine treatment on cottonseed oil with high levels of free fatty acid before colour fixation takes place is more recommended than carrying out the same treatment on the same oil after it has been fixed.

KEY-WORDS: Colour fixation — Cottonseed oil — Ethanolamine — Free fatty acid (treatment) — Sodium carbonate.

1. INTRODUCTION

Darkening of crude cottonseed oil accompanied with difficulties in removing the fixed pigments from the off-coloured oils by current methods of alkali refining and bleaching has been generally known as "Colour Fixation". (El-Nockrashy et al (1976), Osman et al (1976), Atteia et al (1981), Helmy et al (1987) and Zaher et al (1992)).

The work of several investigators led to the hypothesis that the problem pigments causing colour fixation could be fatty esters of gossypol. Ester reactions between gossypol and free fatty acids can possibly and similarly lead to the formation of gossypol-fatty acid complexes which in turn lead to the production of alkali-fast pigments (Berardi and Frampton (1957 and 1961)).

A description of the continuous refining of edible oils with caustic soda and soda ash was given by Tyler (1948), to increase the yields of oil.

The efficiency of four additives including ethanolamine in removal of gossypol from cottonseed oil was studied by Atteia et al (1981).

Since free fatty acids can develop in the seeds under bad storage conditions, or as a result of the attack of insects and microorganisms, and enzymatic hydrolysis of the oil, it became worthwhile to investigate treatments that prevent or remove colour fixation of cottonseed oil containing high level of free fatty acids without using excess of sodium hydroxide in the refining step. Increasing the amount of sodium hydroxide increases the refining loss and transfers some of the oil to soap.

2. MATERIALS AND METHODS

Cottonseed oil

Cottonseed Giza 75 (Gossypum barbadense) used in the present study was kindly supplied by The Cotton Research Institute of The Ministry of Agriculture.

Oil was extracted from cottonseed after crushing and milling with commercial hexane in a Soxhlet apparatus.

Oleic acid

Oleic acid used as an additive in this study was a pure grade of Merck production. It was added at 2.5% of the oil which contain 5.2% free fatty acids.

Treatment of oil + oleic acid

A) Treatment with sodium carbonate

3.1 ml of 20% sodium carbonate solution was added to 50 g oil-oleic mixture or colour fixed oil-oleic mixture, stirred for 15 minutes; centrifugated at (3000 x g), then the oil was decanted.

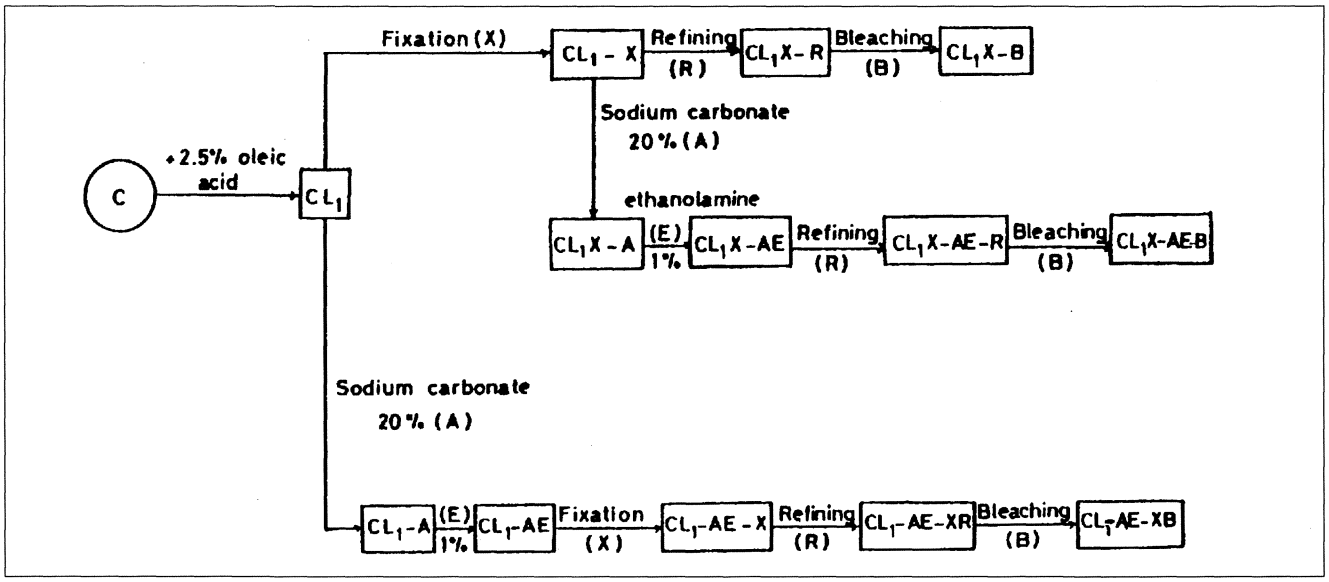

Figure 1
Schematic representation for the treatments carried out on crude cottonseed oil+2.5% oleic acid to prevent or improve their effect on colour fixation.
C: Crude oil, CL_1: Mixture oil+oleic acid, CL_1-X: Mixture oil+oleic acid after fixation.

B) Treatment with ethanolamine

50 gram oil samples treated with ethanolamine were weighed in 100 ml beakers. Ethanolamine additive was added at 1% of oil (i.e. 0.5 g) and samples were heated at 75°C for 2 hours, while stirring. Samples were cooled at room temperature and then kept in the refrigerator for 30 minutes. The precipitated residue was separated by centrifugation at (6000 x g) for 30 minutes, and the supernatant oil sample was then decanted.

Colour fixation

Crude oil samples were subjected to the accelerated colour fixation treatment, where the samples were placed in beakers and heated in an oven at 60°C for 15 days.

Figure 1 is a schematic representation of the treatments carried out on crude cottonseed oil + 2.5% oleic acids.

Refining of oil

Cottonseed oil samples were refined according to the A.O.C.S. "Official Method of Analysis" (1980). Sodium hydroxide solution was added at 75% of the calculated amount.

Bleaching of refined oil

The technique for bleaching the refined oil was essentially that described in the A.O.C.S. "Official Method" for cottonseed oil (1980).

Spectrophotometric analysis of crude, refined and bleached oils

Absorption spectra of cottonseed oil samples were determined using Shimadzu UV-Visible Recording Spectrophotometer, model UV 240 Graphtcord. A wavelength range from 300 nm to 700 nm was used.

Oil colour

Determination of the colour index implied spectrophotometric measurements. An optical density range from 400 to 550 nm has been used following the recommendations of Pons et al (1960). A total of 16 readings were taken with 10 nm difference within the above range. Carbon tetrachloride was used as a blank. The sum of the sixteen O.D. readings multiplied by 10 gives an approximation for the area under absorption curve, and the product was designated as the "colour index". The colour index indicates the concentration of the colouring matter in the oil.

Refinability, bleachability and the overall effect of additives or treatment on oil colour:

- The refinability was calculated as:

$$\frac{\text{Crude oil colour} - \text{Refined oil colour}}{\text{Crude oil colour}} \times 100$$

- The bleachability was calculated as:

$$\frac{\text{Refined oil colour} - \text{Bleached oil colour}}{\text{Refined oil colour}} \times 100$$

- The overall effect was calculated as:

$$\frac{\text{Crude oil colour} - \text{Bleached oil colour}}{\text{Crude oil colour}} \times 100$$

The colour index method was used to measure the oil colour.

Gossypol content

Gossypol content in oil samples was determined according to Pons et al (1956) procedure.

3. RESULTS AND DISCUSSION

Two successive step treatments were carried out on the crude cottonseed oil containing additional 2.5% oleic acid, before or after fixation. The first step comprises treatment of the oil with a solution of 20% sodium carbonate to neutralize most of the free fatty acids in the oil. The second step included treatment of the oil with 1% ethanolamine to remove most of the remaining gossypol.

A) Treatment with carbonate then ethanolamine before fixation

The absorption spectra of crude cottonseed oil + 2.5% oleic acid CL_1 (control), crude oil + 2.5% oleic acid treated with sodium carbonate then ethanolamine CL_1–A, crude oil + 2.5% oleic acid treated with sodium carbonate CL_1–AE, all before fixation, are represented in Figure 2. The figure also includes crude oil + oleic acid treated with carbonate then ethanolamine then subjected to colour fixation CL_1–AE–X, for comparison. Colour indices of these samples are given in Tables I and II.

It is clear that treatment of CL_1 with 20% sodium carbonate before fixation decreases its absorption spectra and colour index (CL_1–A). When this sample was treated with 1% ethanolamine to give [CL_1–AE], the absorption spectra and colour index was further decreased. The humps seen in the absorption spectra at 375, 400, 425 nm are due to the reaction of ethanolamine with gossypol. Colour fixation of this sample yields [CL_1–AE–X] with further decrease in the absorption spectra and colour index. Humps of ethanolamine gossypol complexes are still present.

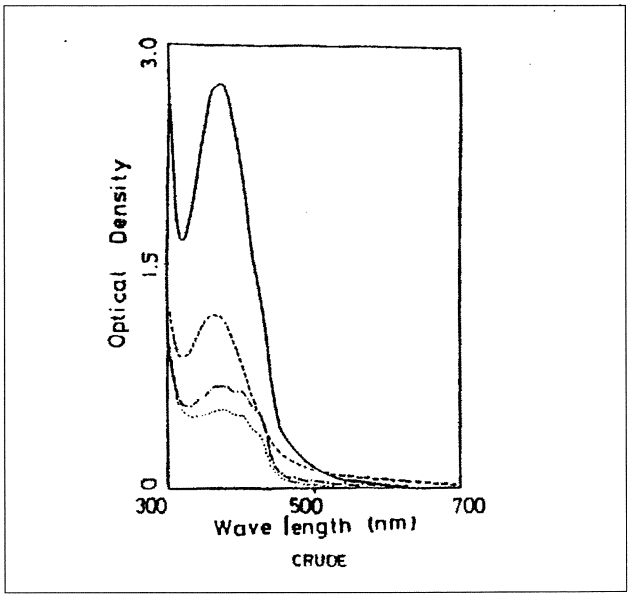

Figure 2
Absorption spectra.
(———) Crude cottonseed oil+2.5% oleic acid
(– – –) Treated with sodium carbonate
(–·–·–) then Ethanolamine then
(·····) Subjected to colour fixation

Table I. **Effect of carbonate/ethanolamine treatment on colour indices of cottonseed oil + 2.5% oleic acid**

Treatments	Colour index
CL_1 (control)	90.39
20% Sodium carbonate	
CL_1-A	40.20
CL_1X-A	66.45
20% Carbonate+1% ethanolamine	
CL_1-AE	27.66
CL_1 AEX	19.88

C = crude oil, L_1 = oleic acid, X = fixed, A = sodium carbonate, and E = ethanolamine.

Figure 3 (A–C) give the absorption spectra of oil samples after fixation CL_1–X (control) and CL_1–AE–X (treated); after refining CL_1X–R and CL_1–AE–XR; and after bleaching CL_1X–B and CL_1–AE–XB.

Colour index is represented in Table II. The absorption spectra of the refined and bleached samples show a considerable decrease when compared to the control CL_1X–R, CL_1X–B. Although the fixed gossypol did not disappear from the refined oil, yet it almost disappeared from the bleached oil. Colour index for the refined control was decreased than the refined treated fixed oil, also the

Table II. **Effect of carbonate/ethanolamine treatment on colour characteristics of cottonseed oil + 2.5% oleic acid**

Treatments	% Gossypol			Colour index			% Reduction in colour		
	C	R	B	C	R	B	Ry	By	Overall effect
20% Sodium carbonate+ 1% ethanolamine									
CL_1X (control)	0.14	0.05	0.03	71.55	82.50	56.55	88.47	31.39	92.09
CL_1-AE-X	0.06	0.02	0.00	19.83	40.95	12.15	79.32	70.24	93.85
CL_1X-AE	0.08	0.04	0.00	52.02	57.48	45.15	88.95	21.39	91.31

*C = crude oil, R = refined, B = bleached, X = fixed, Ry = refinability, By = bleachability, L = oleic acid, A = sodium carbonate and E = ethanolamine.

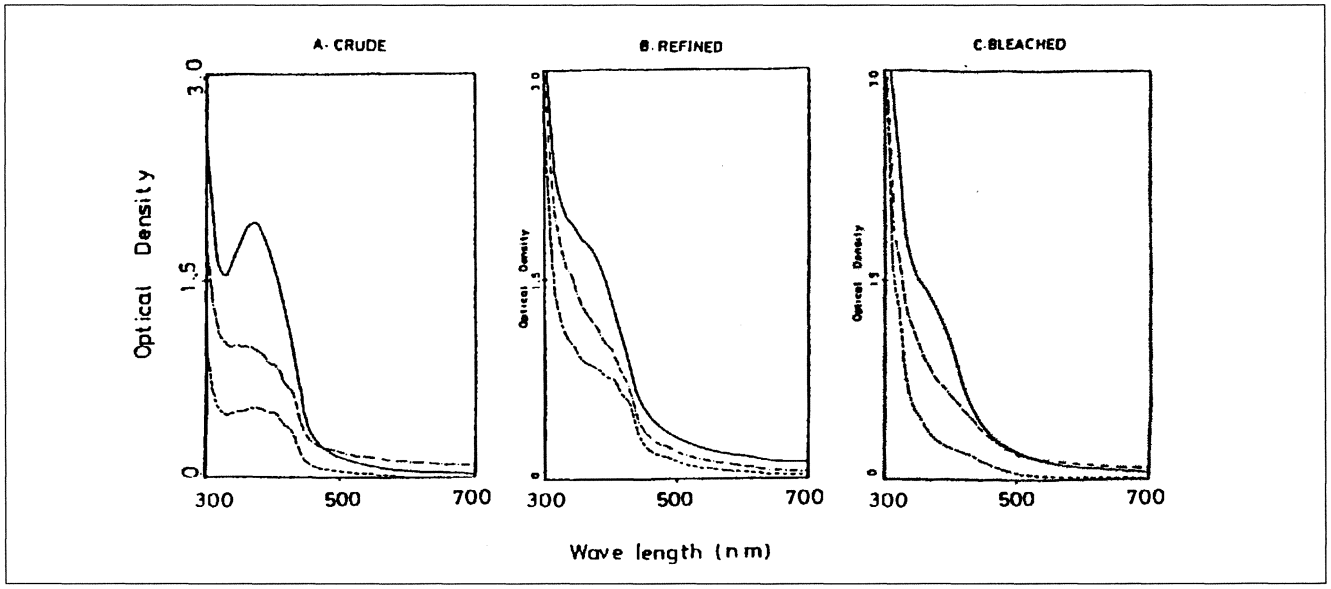

Figure 3
Absorption spectra of "fixed cottonseed oil+2.5% oleic acid" treated with sodium carbonate then ethanolamine.
(———) Cottonseed oil+2.5% oleic acid subjected to colour fixation
(– – –) Cottonseed oil+2.5% oleic acid treated with sodium carbonate+ethanolamine then subjected to colour fixation
(–·–·–) Cottonseed oil+2.5% oleic acid fixed then treated with sodium carbonate+ethanolamine

bleached control decreased than the bleached treated fixed sample.

Percentage refinability, percentage bleachability and percentage of overall effect shown in Table II give good idea about the efficiency of refining and bleaching processes, and accordingly about the treatments used. Increase in these values mean increase in the efficiency.

B) Treatment with carbonate and ethanolamine after fixation

Figure 4 gives the absorption spectra of crude cottonseed oil + 2.5% oleic acid subjected to fixation CL_1–X (control), oil + oleic acid subjected to colour fixation then treated with sodium carbonate CL_1X–A, oil + oleic acid fixed then treated with carbonate and ethanolamine CL_1X–AE, and oil + oleic acid treated with carbonate + ethanolamine then subjected to colour fixation CL_1–AE–X, for comparison. Colour indices of the samples are given in Tables I and II.

Treatment of the fixed oil + oleic acid with carbonate slightly decreases its absorption spectra. Carrying out the carbonate treatment with ethanolamine treatment further reduces the absorption spectra but humps appear indicating the reaction between gossypol and ethanolamine at wavelength 375, 400, 425 nm. Comparing the treatment of the oil before and after fixation shows that the treatments carried out on the oil before fixation yield an oil with lower absorption spectra and colour index.

The decrease in the absorption spectra is accompanied by a decrease in the colour index for CL_1–X, CL_1X–A, CL_1X–AE and CL_1–AE–X.

Figures 3 (A–C) show that the absorption spectra of the fixed treated refined sample CL_1X–AE–R and fixed treated bleached sample CL_1X–AE–B are lower than the refined fixed control CL_1X–R and bleached fixed control CL_1X–B, but still higher than treated fixed refined sample CL_1–AE–XR and treated fixed bleached sample CL_1–AE–XB. Colour indices, refinability and bleachability for CL_1X–R, CL_1X–AE–R, CL_1X–B, CL_1X–AE–B are illustrated in Table II.

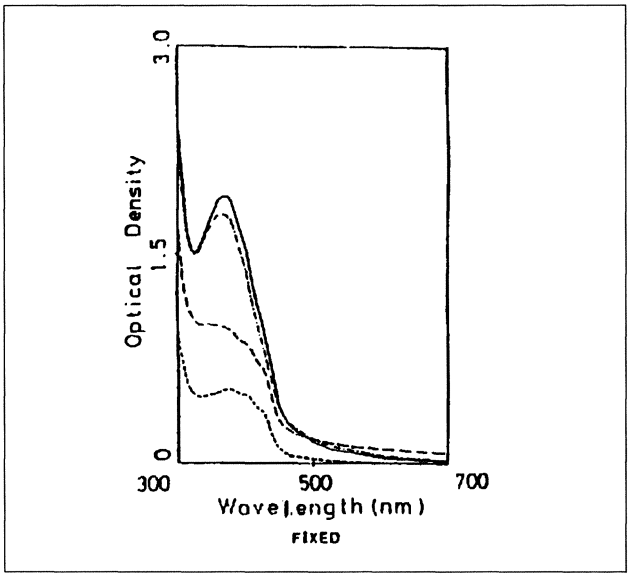

Figure 4
Absorption spectra.
(———) Crude cottonseed oil+2.5% oleic acid subjected to colour fixation
(–·–·–) then treated with sodium carbonate
(– – –) then Ethanolamine, and
(.....) Cottonseed oil+2.5% oleic acid treated with sodium carbonate then ethanolamine then subjected to colour fixation

The overall results of this experiment recommends the use of carbonate/ethanolamine treatment to decrease the effect of high levels of free fatty acids in cottonseed oil on colour fixation.

Sodium carbonate neutralizes the excess of free fatty acids, and also removes some of the gossypol which is acidic in nature. Further treatment with ethanolamine results in more reduction in the level of free gossypol.

Carrying out the carbonate/ethanolamine treatment on cottonseed oil with high levels of free fatty acid before colour fixation takes place is more recommended than carrying out the same treatment on the same oil after it has been fixed.

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