Cottonseed Oil Soap Stock

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CRUDE cottenseed oil on account of its strong characteristic odour, and a dark reddish brown colour, is not suitable for edible purposes and for many technical applications. It is therefore, refined with caustic soda solution which causes reduction in free fatty acid content and colour. Neutralizing the free fatty acids with caustic soda produces soap which is not soluble in oil and which coagulates along with other impurities into a flocculant mass that can be separated out. This residue from the alkali refining is called the *soap stock.*

Generally the soap stocks from oils like groundnut, coconut and sesame oils are not deep in colour and therefore there is no great problem in their utilization. The cottonseed oil soap stock is however, dark red in colour[1], although the locality of oil and strength of lye used in refining cause variation from light dirty yellow to dark green. The consistency of the soap stock may vary from a soft pasty mass to a hard putty like mass depending upon the amount of alkali and the strength of alkali solutions, as well as the skill of the refiner. Soap stock with high percentage of water ferments in hot weather and white fungus grows on it. It can be best preserved at low temperatures.

Indian cottonseed oil generally yields a much larger quantity of soap stock on alkali refining[2], about 16-20%, as compared to 6-7% from the American cottonseed oil. This is largely due to careless storage and processing of seeds and other factors such as higher proportion of free fatty acids, colouring matter and albuminous matter in the crude oil.

Composition :

The value of soap stock is determined by its total fatty acids content which varies considerably according to the method of refining. In the following table are given analytical values of a few typical samples.

Sample No.	Moisture %	Fatty acids %	Na_2O %	Organic Matter %	Glycerine %	Inorganic salts %
1	36·0	50·0	3·2	8·2	3·98[1]	—
2	20·6	66·2	3·3	3·5	3·7	2·45[3]
3	45·6	24·0 (as soap)	3·3	8	—	— 18% (neutral oil)
*4	—	45—58	1·6–3·3 (oxidized acids)			0·9–1·7[5] (Insoluble impurities)
**5	—	25—35	2·0–4·7 (oxidized acids)			0·6–2·3[5] (Insoluble impurities)

* from caustic refined oil.

** from soda ash refined.

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Utilization of soap stock :

Even though the soap stock is a cheap waste product, the economic success of a refinery depends to some extent on how it is disposed off. It constitutes a valuable source of fatty acids for the soap maker, fatty acid distiller and other industries wherein the fatty acids are used. In the U.S.A., the soap stock is sold on 50% total fatty acid basis or in a concentrated form known as "acidulated" soap stock or "Acid Oil," wherein the total fatty acid content should be of the order of 95%[6]. The acid oil is prepared by boiling the soap stock with sulphuric acid. The liberated fatty acids, along with the neutral oil present in the original soap stock, float over the aqueous layer and are skimmed off.

The problem of the disposal and utilization of the soap stock is generally attacked in one of the two following ways: The impurities present in the soap stock may be removed by some means to get a better coloured soap, or the fatty acids may be first obtained from the soap stock and then processed so as to give a mixture of pure fatty acids.

Refining of the soap stock by means of alkali :

Most of the impurities present in the soap stock are soluble in caustic lye. The soap stock is first of all treated with a slight excess of caustic lye (on the basis of the neutral oil content of the soap stock) to insure complete saponification. The soap so formed is repeatedly grained out with caustic soda solutions. The colouring matter is also soluble in dilute salt solutions ; strong brine, however, renders it insoluble. The lye from the saponification charge carries the bulk of organic and colouring matters. Proper washing of cottonseed soap stock requires considerable care and experience.

Keith *et al.*[5] found that gums are soluble in 6-10% caustic solution. They centrifuged the mixture of the grained soap phase (45-60% total fatty matter) and the aqueous alkaline phase obtained by using the above-mentioned dilute alkali and found that the ratio of oxidized acids and insoluble impurities to the centrifuged soap was much lower than in the raw soap stock. Yakubov *et al.*[7] heated a mixture of the soap stock and a concentrated solution of NaOH (45-50% concentration, 20% excess of the amount required to saponify the neutral fat) to 170-250°C. Palmitic and acetic acids were formed from the oleic acid as in Varentrap's reaction, and the resulting soap was hard and light coloured. The alkali grained soap is used as the basis of various textile soaps. Mixed with soaps from harder fats and rosin, it forms the basis of many cheap laundry soaps. It is by far the cheapest soap making material.

Recovery of neutral oil from the soap stock :

Various attempts have been made to recover the neutral oil which gets entrapped with the soap during the process of refining of oil. Karl Jurke[8] has patented a process of recovering the neutral oil in a continuous way, by directing a spray of soap stock at right angles to a spray of steam. It is stated by Zinovev *et al.*[9] that 90-92% neutral oil is separated if the soap stock is dissolved in 3 volumes of water at 90-95°, followed by the addition of 2% NaCl (on the weight of the soap stock). $AlK(SO_4)_2$-$12H_2O$ with 0.02% H_2SO_4 causes separation of 87% of oil.

The undiluted soap stock (from the soda ash refined oil) may be passed continuously through a high speed centrifugal separator. An example is that of "Aktiebolaget Separator".[10]

Bleaching of the soap stock or the acid oil :

Resaponified soap stock fatty acids were treated with several successive portions of H_2O_2 or NaOCl at 40-50° by Bispyatov[11]. C. Paquot and M. Paquot[12] using $SnCl_2$ as the activator for $NaClO_2$ as the bleaching agent found that the soap stock could be successfully bleached.

Pack and Goldblatt[13] of Southern Regional Research Laboratories have conducted some experiments with a view to find some outlet for the soap stock. (1) The dried cottonseed oil soap stock (dried by azeotropic distillation) was refluxed with benzyl chloride for 2-4 hours and the resulting mixture was filtered while warm, and the filtrate was distilled. Crude benzyl, methyl benzyl and dimethyl benzyl esters were thus prepared. These were, however, found to be unsuitable as primary plasticizers. (2) Acidulated soap stock added in small quantities (0.5 to 2.0%) to dry meals (for cattle feed), keeps the dust down and aids pelleting operations. It is, however, necessary that the gossypol be destroyed from the cottonseed oil soap stock. This was achieved by heating the dilute soap stock with ferrous or ferric salts at 100°C. Alternately, the gossypol content could be reduced by heating the soap stock out of contact with air. Alkaline soap stock is far easier to free from gossypol than acidulated soap stock.

Phosphatides from the soap stock :

The cottonseed oil soap stock has been treated[14] with selective solvents, such as petroleum ether, ethyl ether, benzene, ethylene dichloride, trichloroethylene, carbontetrachloride, for dissolving one or the other of the associated materials to effect their separation from each other.

Urea adducts of fatty acids :

Formations of crystalline adducts of fatty acids with urea, in the presence of ethanol, has been the basis of a patented process[15], for recovery of light coloured fatty acids, from the soap stock acids. The advantage claimed in the process is that two distinct fractions, one with low I.V (57-87) and the other with a high I.V (122-151) are obtained. The process essentially consists in refluxing a mixture of the crude fatty acids and urea with 95% ethanol, cooling overnight, filtering and washing the precipitates by alcohol till free of colour. After recovering alcohol from the filtrate, boiling of the precipitate and the filtrate with water, yields the two required fractions of fatty acids.

Esterification followed by hydrogenetion :

Another patented process by J. H. Kirby[16], involves esterification of acid oil by gradual heating under regulated pressure and elevated temperature. Diglycerides and sterols are esterified by part of the acid present. The esterified product is found to be more fluid than the acid oil. Moreover there is no foaming or emulsification, as is found when attempting to remove the water vapour, which if not removed interferes with the hydrogenation. A single apparatus can be used wherein first by gradually heating, the material is esterified, after which Ni catalyst is added to the hot esterified black mass. Hydrogenetion is then carried out in the usual manner.

Dry distillation of the cottonseed oil soap stock :

This was carried out by Chang Mang Tu and Fu Yan Pan[17]. The product consisted of about 11% (by weight) light oil, 17% middle oil and 10% heavy oil. Insertion of a vapour phase cracking unit, increased slightly the amounts of light and middle oils at the expense of the heavy oil ; moreover many gaseous products were produced. Yung Seng Chao[18] dry distilled the dried and powdered soap stock, which yielded a gasoline fraction among other products.

This gasoline after refining, was essentially the same as the commercial gasoline, except for its odour and high I.V. Very satisfactory results were claimed on actual road test. From 400 lb. of original wet soap stock, 5 gallons of refined gassoline, 7.3 gallons of crude kerosene, 77.8 lb. of coke, 31.5 lb. of Na_2CO_3, 13.2 lb. of ammonia liquor and 4.89 cu. ft. of combustible gas were obtained.

Distillation of fatty acids :

All the above mentioned methods of utilizing the soap stock, except that of alkali graining, have been more or less on a laboratory scale. Distillation of the fatty acids obtained from the soap stock, is on the other hand, a commercial process. Generally, the soap stock is sent to distillers in form of acid oil. If it contains higher percentage of neutral oil, the first step is that of hydrolysing it. Bhushan *et al.*[3] subjected 10 samples of artificially prepared foots, to hydrolysis at 100-110 p.s.i. in an autoclave of 6 liters capacity for 6-12 hours. A check on the acid value of the sulphuric acid-treated and washed product at different intervals, revealed that for complete hydrolysis, the soap stock (already containing 20.6% H_2O) should be further diluted with their own weight of water and heated for 6-7 hours at a pressure of 100-110 p.s.i. The dark viscous mass obtained by heating the hydrolysed product with dilute sulphuric acid, washing and drying, was distilled twice with superheated steam (240-260°) at 400-420 mm. pressure, to give practically colourless fatty acids. (A.V. 198 ; yield 70.8% on total fatty acid basis).

Processors who refine and distill fatty acids, prefer to saponify the neutral oil of the soap stock and then split it, to avoid the step of hydrolysing it. However, direct vacuum distillation of the crude fatty acid from the saponified soap stock does not yield pure white fatty acids. A number of patents and experiments describe the methods of treating the acids or the soap stock prior to distillation, to improve the colour or colour stability. A patent by Bamag Ltd.[19] recommends the addition of 1-2% fuller's earth as bleaching agent during distillation. An alternate method is to distill the acids, bleach them with fuller's earth and then redistill. For the redistillation, earth need not be removed. McClain[20] claims that cottonseed oil soap stock boiled with an excess of caustic, grained out, acidulated and then distilled, will yield lighter fatty acids, if boiling is conducted in presence of 0.05—0.5% potassium persulphate. Keith *et al.*[21] have conducted a series of experiments on pilot plant scale, consisting of continuous purification by caustic alkali, centrifuging, again graining by salt, followed by centrifuging and finally acidulating. Acidulation of purified soap stock, by dilute sulphuric acid (4%), at 175-195°F, in presence of dispersing agents, yields clear brown fatty acids. These had an acid value of about 188, unsap 3% and oxidized fatty acids 3-5%. This product on vacuum distillation gave better coloured fatty acids.

The stearin pitch obtained in the distillation vessel as a residue during steam distillation of fatty acids is used in the manufacture of inks, paints, and varnishes ; as insulation materials for wires and cables and in brake lining[22].

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