

Solvent Refining of Oils and Fats

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THE main impurities in various raw oils and fats are fatty acids, phosphatides, colouring and odoriferous matters, pigments etc. The present methods for removing these impurities are neutralization, bleaching, deodorization and solvent refining.

The most common method of refining which involves the use of alkalies to react with free fatty acids in the oil is ordinarily referred to as "neutralization". Alkali refining effects an almost complete removal of free fatty acids, which are converted into oil-insoluble soaps. The technology of alkali refining is concerned with the proper choice of alkalies, amounts of alkalies, and refining techniques, to produce the desired purification without excessive conversion of neutral oil into soap, and with methods for the efficient separation of refined oil and soapstock.

The method of bleaching is by adsorption or treatment of the oil with bleaching earth or carbon. In chemical bleaching the pigments present in oils or fats are oxidized to colourless or lightly coloured materials.

Steam deodorization is essentially a process of steam distillation, wherein relatively volatile odoriferous and flavoured substances are stripped from the relatively non-volatile oil.

Recently, liquid-liquid extraction has come into prominence as a refining method, particularly for low grade fats containing pigments that are difficult to remove by other methods. Extraction of the fat with a suitable solvent not

only separates most of the pigments and other non-fatty impurities, but if properly applied may also effectively deacidify the oil. This method of removing the impurities is also known as "solvent refining".

When a solvent e.g. alcohol and an oil containing free fatty acids as impurity are mixed together and the mixture so obtained is allowed to separate, two layers are formed viz., the upper alcohol layer and the lower oil layer. The free fatty acids are completely soluble both in alcohol and oil and therefore they get distributed in the resultant alcohol layer as well as in the oil layer. The free fatty acids being preferentially soluble in alcohol, their distribution in the two layers will be uneven and a larger amount will go in alcohol layer. The oil layer can be separated and treated with fresh alcohol to reduce the free fatty acids to a still lesser extent. Besides the free fatty acids, the alcohol layer always contains some amount of oil because oil is slightly soluble in alcohol. The quantity of neutral oil going in the alcohol layer constitutes the loss of oil in refining.

The selection of a solvent for refining a particular oil or a fat depends on many factors. It should be available in large quantities. It should be cheap. It must have a greater affinity for impurities than for glycerides. It should dissolve the impurities preferentially than oil does.

Mostly ethyl alcohol is chosen as a solvent because of its easy availability and preferential solubility for free fatty

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acids. The solubilities of fats and fatty acids in ethyl alcohol depend on their molecular weight and degree of unsaturation, water content of alcohol, temperature and the non-glyceride components in the fats. The solubility of most fatty oils (excluding castor oil) in absolute alcohol at 15°C does not exceed 2% and goes on decreasing with increasing dilution of alcohol with water; but it is considerably increased with varying amounts of free fatty acids in oil and as a rule oils containing more than 50% free fatty acids are completely soluble in alcohol. Many other solvents have been tried and amongst these may be mentioned methyl alcohol, furfural, liquid propane, butyl alcohol, etc.

Alcohol, neutral oil and mixed fatty acids when mixed together form a multicomponent system. In order to simplify this multicomponent system alcohol with water can be taken as one component, the neutral oil as the second component and the mixed fatty acids as the third component so that the system becomes a ternary system. In this system there are two pairs of miscible liquids, viz. (i) neutral oil and mixed fatty acids and (ii) alcohol and fatty acids, while the third pair of neutral oil and alcohol is partially miscible. When the above mixture is allowed to separate, two ternary solutions or phases in equilibrium are obtained. The compositions of the two phases can be found out and represented graphically using triangular co-ordinates. The equilibrium compositions for a particular mixture thus fall at the two extremities of a tie line and several such points can be found out. These points lie on a continuous curve called mutual solubility curve. The purpose of plotting such curves at definite temperatures and concentrations of a solvent is to study the suitability of the solvent for deacidification of oils.

According to Lewkowitsch¹ attempts were made on a large scale to remove

the free fatty acids and at the same time odorous substances of coconut oil by treatment with alcohol; but on account of costliness and impracticability, this process was abandoned. Fachini and Somazzi² studied the solubility of acidic and neutral olive oils in ethyl alcohol at different temperatures. They found out that in order to extract the acids from olive oil, the concentration of acids in alcohol must be less than 10% and temperature below 50°C. Otto Krebs³ has described a system for washing fatty acids from oils with alcohol. The alcohol removes the acids and is recovered in a rectifying column. Schlenker's⁴ attempt to separate free fatty acids from neutral fat was a failure. This was because of the equilibrium distribution of fatty acids in neutral fat and of neutral fat in alcohol. Margaillan and Giscard d'Estaing⁵ have given curves for the solubility of the mixed fatty acids of copra, groundnut oil and castor oil at various temperatures as a function of the alcohol strength of the solvent. They have also described the technique used. The general trends of the curves for the respective oils are quite different.

The exhaustive work of Rius and Moreno⁶ deserves much credit in the history of solvent refining of oils and fats. They worked systematically on the deacidification of olive oil and represented the ternary systems of oleic acid and olive oil with methyl and ethyl alcohols of various strengths in triangular co-ordinates. They also showed selectivity and distribution curves, as well as the effect of addition of a fourth component. For cottonseed oil⁷ they used liquid propane as solvent to reduce the acidity from 30 to 3% calculated as oleic acid. Moreno⁸ has described a plant for the refining of olive oil by alcohol. His results are as follows:—

	Analysis of starting phase	Analysis of end oil phase	Analysis of end alcohol phase
Free fatty acids	22%	2.75%	11.65%
Neutral oil	53%	89.0%	2.55%
Alcohol	25%	8.25%	85.8%

The strength of the alcohol used was 96%. For continuous deacidification of olive oil⁹ he used a tower packed with Raschig rings or pieces of solid glass. The latter was the more effective. On passing the mixture of olive oil and alcohol through the tower, it separates into an oil phase and alcohol phase, the latter containing 75-90.5% oleic acid.

Rius and Crespi¹⁰ studied the solubility and phase equilibrium data in the following ternary systems: grapeseed, walnut and linseed oils—total fatty acids—methyl alcohol at 25°C to establish a calculation basis for industrial deacidification of these oils. The known tie line correlations which permit the acquirement of equilibrium data throughout the entire range of concentrations were tried and the obtained values for the equations are given. The treatment with methyl alcohol reduces the hydroxyl number of the oils.

The work done by Seiichi Ueno *et al*¹¹ on the refining of rice-bran oil also deserves mention. They studied the extraction of rice-bran oil on an industrial scale and found out that for an industrially feasible extraction process—yield should be above 90%, loss of neutral oil 5% and lowering of acid number above 40%. Use of 75-80% ethyl alcohol about four times the volume of oil was recommended. This method is not applicable to bran oil with acid number less than 10. Bran oil with acid number 80 can be extracted to oil with acid number 10 after four successive extractions with alcohol. Loss of neutral oil was 10%.

Cama *et al*¹² in their study of suitability of ethyl alcohol for deacidification of some vegetable oils, determined a mutual solubility curve for the systems of neutral groundnut and mowrah oils—fatty acids—ethyl alcohol by agitation and turbidity methods. The solubility curves by the two methods did not agree and the deviation was greater on the side of oil; the curves indicated that 90% by weight of ethyl alcohol is nonselective at room temperature and at atmospheric pressure; as far as the mixed fatty acids and glycerides of the two oils are concerned. With the use of more dilute alcohol the region of heterogeneity is increased with a maximum at 80% ethyl alcohol; this indicates sudden decrease in the solubility of oil and its fatty acids in ethyl alcohol.

Mitra¹³ found out that solvent extraction of the bitter constituents of neem oil, leaves the oil in a purified state for industrial purposes, e.g. manufacture of soaps, medicinal cosmetics, disinfectants, emulsifying compositions for insecticidal sprays etc. He also carried out cold extraction of karanja oil¹⁴ with methyl and ethyl alcohols which ensured the isolation of the active constituents of the oil and its simultaneous purification. Kane¹⁵ studied liquid-liquid extraction of mowrah oil using ethyl alcohol of different concentrations and applied for the removal of free fatty acids. The acid value of the oil was reduced from 21 to 1.5 using 90% alcohol at room temperature in the ratio of alcohol to oil 4:1 with three successive treatments. Bhat *et al*¹⁶ found out that when karanja, neem, malkanguni and undi oils

are refluxed with 90% ethyl alcohol in the ratio 1:4 on a water bath and when the alcohol is removed from the settled oil layers, in all the samples there was reduction in colour and odour; but in the case of undi and neem oils the effect was remarkable. The colour of undi oil was reduced from dirty green to yellow and that of neem oil from dark brown to yellow. Several workers¹⁷⁻²⁰ have investigated the solvent refining of karanja oil using ethyl alcohol. Similarly extraction of undi oil²¹⁻²³ has been reported using 70% ethyl alcohol²¹ and 95% ethyl alcohol²² to separate the dark green resin present in the oil.

Recently, Venkataraman and Laddha²⁴ worked on deacidification of groundnut oil and found that ethyl alcohol selectively extracts oleic acid from the oil. Both 90 and 95% alcohols have a greater range of applicability than absolute alcohol; increasing the concentration of water in alcohol increases the immiscible area of the ternary system and decreases the solubility of oleic acid in alcohol.

Takeo Odagiri²⁵ has described a method for obtaining oil from crude rice wax using butyl alcohol. Crude rice wax (1 kg.) with saponification value 158, iodine value 85 and unsaponifiable matter 12% and 1% water are stirred with 1 kg. of butyl alcohol for 30 minutes, the solid and liquid are separated by centrifuging, the solid is washed with 1 kg. of butyl alcohol in 4 portions, and the butyl alcohol is removed to give 800 gm. oil with saponification value 178 and unsaponifiable matter 2% and 180 gm. wax, with melting point 80°C, saponification value 75 and unsaponifiable matter 42%.

Ayers²⁶ patented a method for refining of glycerides in a hydrocarbon solvent with alcoholic alkali. A single treatment of a hydrocarbon solution of crude soybean oil with alcoholic alkali in simple equipment gave a refined oil with a good colour and a lower content of free fatty acids and the constituents which

cause "break" or sludge formation. Soybean oil 25.6 gm., neo-hexane 100 gm., 99% methyl alcohol 100 gm. and sodium hydroxide 0.04 gm. are mixed, shaken well and allowed to separate. After removing the solvent by distillation, 25.4 gm of refined oil containing 0.085% free fatty acid is obtained. Scott²⁷ patented a method for continuous refining of glyceride oils. Glyceride oils are refined in a continuous flow system in which the oil solvent mixture flows up through a chamber containing a downward thrust screw which scrapes the walls and prevents plugging by soapstock. An 80% aqueous caustic solution flows countercurrent to the oil-solvent mixture which contains 1 part of oil to 1-6 parts hydrocarbon solvent, e.g. hexane.

A process (patent of Sherwin-Williams Co.) is described by Weber²⁸ for the continuous refining of oils dissolved in a solvent. The oil is in a form of a miscella containing a hydrocarbon solvent, e.g. hexane or heptane or chlorinated aqueous solution of a monohydric aliphatic alcohol, e.g. ethyl or iso-propyl alcohol. The proportions depending on the kind of oil and solvent are such that the entire miscella is a single phase solution, e.g. 20% soybean oil and 80% solvent comprising 80% hexane and 20% of 88% isopropanol. The process also includes the treatment of the miscella with an acidified, aqueous alcohol refining agent, separating the treated miscella from the refining agent, washing the treated miscella with aqueous alcohol, separating the wash alcohol from the miscella and separating the treated oil from the miscella.

Hokuriku Fats and Oils Co.²⁹ patented a method for refining highly acidic oils. In this method wax-free rice oil (20 kg.) with acid value 92 in 52.2 litres 65% ethyl alcohol containing 2.6 gm. of caustic soda per 100 ml. is allowed to stand for 2 hours at room temperature and the oily layer is washed with 51.65% ethyl alcohol and dried to obtain 10.2 kg.

neutral glyceride oil. The alcohol layer and alcohol washings are combined, neutralized with 50% sulphuric acid and the alcohol is distilled off to obtain 9.2 kg. of fatty acids with acid value 187.

Another method which can be classified under the heading of solvent refining is by Metallgesellschaft.³⁰ Oils and fats which may have previously been partly freed from impurities, are treated with alkali carbonates or mixtures with caustic alkali under vacuum, during which most of the water evaporates; the dry soaps formed from fatty acids originally present are dissolved in aqueous alcohol and salt solutions, and separated from the neutral oil by treatment with concentrated salt solutions.

De Sa *et al*³¹ treated karanja oil in three stages with 0.3, 0.1 and 0.1% concentrations of caustic soda in alcohol respectively and found out that there was considerable bleaching and deodorization effect.

From the above brief review of the work done so far on solvent refining by various workers, it can be seen that solvent refining if properly applied can effectively deacidify the oil, remove the colour and odoriferous matters and other non-fatty impurities without excessive loss of neutral oil.

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