Degumming, Dewaxing and Refining

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ABSTRACT

Degumming, dewaxing and refining are aimed at removing certain fat-soluble impurities. The different operations can be done separately or in various combinations depending on, e.g., the type of feedstock and the desired refining result. State-of-the-art of water degumming and chemical (alkali) refining are discussed with special emphasis on quality and yield of products and byproducts. Dewaxing, which is of special interest for some oils such as sunflower oil, maize oil and ricebran oil, can be performed either by a filtration process or by centrifugal separation in connection with water degumming or alkali refining.

Fatty oils, when extracted from vegetable and animal tissues, contain a number of impurities which have to be removed from the oil to make this suitable for human consumption. Removal of all kinds of impurities is done in a series of processes, which together are called refining. The first step is, in many cases, water degumming followed by chemical refining or alkali refining, and then bleaching and deodorization. An alternative refining sequence is so-called superdegumming and physical refining. Dewaxing is a special process, which is of interest only for certain types of oils and this process can be carried out at different points in the refining chain.

The type of impurities to be removed more or less completely in degumming, alkali refining and dewaxing are free fatty acids (FFA), phosphatides, metal ions, waxes, oxidation products, color bodies, moisture, volatiles and solid impurities. Most of the impurities are dissolved or are in a colloidal state in the crude oil and have therefore to be removed by some kind of chemical treatment. Different types of oils require different treatments due to their different compositions. In Table I, we can see what treatments are of interest for different kinds of oils.

TABLE I

Refining Steps for Fatty Oils

	Degumming	Alkali ref.	Dewaxing
Many seed oils[1]	(Yes)	Yes	No
Sun flower, maize	(Yes)	Yes	Yes
Soya	Yes	Yes	No
Palm oils, animal fats	No	(Yes)[2]	No
Fish oil	No	Yes	No
Rice bran oil	Yes	Yes	Yes

[1] E.g. groundnut, rapeseed, sesam.
[2] Good crude qualities can be physically refined.

Water degumming is especially applicable to crude oils with high content of phosphatides like soy and maize. Dewaxing is of interest mainly for sunflower, maize and ricebran oils.

Alkali refining is the most versatile refining method available and is extensively used for all kinds of fatty oils.

DEGUMMING

The purpose of water degumming is twofold. On the one hand, it is necessary to remove almost completely phosphatides or gums from the oil in order to produce a fully refined oil, and, on the other hand, gums may be valuable byproducts. The detailed chemical nature of the phosphatide complex is now fairly well known, especially for those from soybean oils (1,2). Typical amounts of phosphatides in some vegetable oils are shown in Figure 1. Soybean oil is by far the most important source for production of commerical lecithin products but such products are produced also from sunflower oil and rapeseed oil.

When water is added to a crude oil, most of the phosphatides in the oil are hydrated and made insoluble in the oil.

This forms the principle for the water degumming process (Fig. 2). The crude oil may come directly from an extraction plant and has a temperature close to the degumming temperature of 50-70 C. At higher temperatures, degumming is less complete due to the increased solubility of the phosphatides in the oil and at lower temperature the increased viscosity of the oil makes separation of the phosphatides more difficult. Water, or in some cases live steam, is added to the oil at level of about the same quantity as the gum content of the oil, and mixed for 20-30 min in order to allow hydration of the phosphatides and agglomeration of the particles. Due to the higher specific gravity of the hydrated gums, they can be separated from the oil by cen-

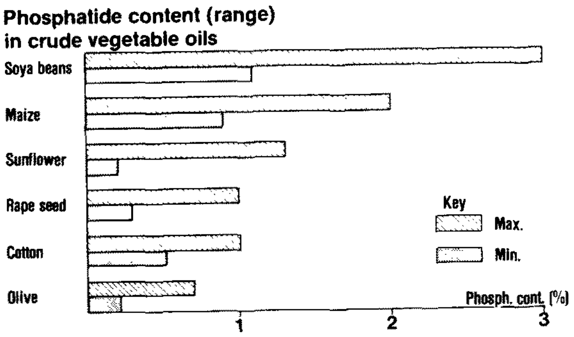

FIG. 1. Phosphatide content in crude vegetable oils.

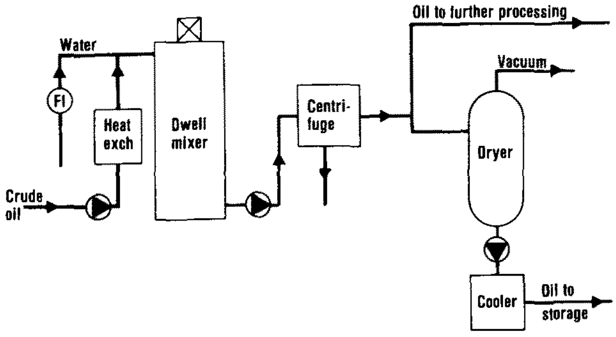

FIG. 2. Water degumming plant.

trifugation. The mixture of oil, gums and water can easily emulsify, due to the presence of several surface-active agents, among them monoglycerides and the phosphatides themselves. In order to get an efficient separation, emulsification has to be avoided and the mixture has therefore to be treated very gently, without high shear stress in the feed pump and at the inlet into the centrifuge.

The degummed oil can either go directly to subsequent process steps or it can be vacuum dried and cooled for storage. The wet gums can either be returned to the extraction plant and there be mixed with the extraction cake or can be dried in a thin film evaporator for further processing to different commercial lecithin products. Capacities of commercial water degumming plants are in the range of 50-500 tons/day, with the centrifuge very often being the limiting factor. An efficient water degumming should give a degummed oil with a low phosphatide content and gums with a low oil content to minimize the oil losses.

When oil seeds of high quality are extracted under optimal conditions, the phosphatides can be removed by water degumming to a low residual content, say, down to below 0.1% according to the Alcon process (3,4). However, due to enzymatic reactions during the extraction process, according to actual practice, a part of the phosphatides is transformed to a nonhydratable form, which means that these cannot be removed by water degumming (5,6). It is normal that most seed oils contain 0.2-0.8% of nonhydratable phosphatides. It is possible to improve water degumming by adding various chemical agents, of which a large number have been suggested and used for many years. These procedures represent an intermediate form between the classical water degumming and the newer superdegumming.

With good hydration and separation conditions, it is possible to obtain wet gums with a water content of 40-50% and a content of 65-70% of phosphatides on a dry basis. In some cases, when the phosphatides are to be further refined to special qualities, they can be bleached to some degree by adding hydrogen peroxide and benzoyl peroxide during hydration. Water degumming as described has been a well known process for decades and it seems to have reached a certain degree of maturity without any significant possibility for further development.

REFINING

The word refining is used here in the sense of caustic refining, chemical refining or alkali refining. This process has been used for more than a century for refining fatty oils and has during this time been improved in many respects to the more or less automatic continuous process we know today.

Batch Refining

Batch refining has not changed very much over the last 50 years and as the performance of such a plant is well documented in older textbooks such as Andersen (7), no further technical detials will be given.

Batch refining is still in use and has some advantages, such as: low investment costs; the equipment can often be locally manufactured; suitable for low capacities; and the fact that it can, from certain crude oil, produce a refined oil of good quality.

However, batch refining has also some serious drawbacks, such as: often high refining losses; high operation costs, due to high consumption of energy (steam) and water; gives large volumes of polluting acid water from splitting of soapstock and washwater; and some oils (e.g., those with high FFA) cannot be batch refined.

Batch refining is, therefore, nowadays only installed under special conditions and where the refining capacity is low, e.g., ca. 10 tons/day or less.

Semicontinuous Refining: the Zenith process

A new process for refining of edible oils was presented about 20 years ago, and is known as the Zenith process (8-10).

The first step is treatment of the oils with phosphoric acid, in order to remove some of the nonfatty substances, which have a great influence on forming emulsions. Oils such as rapeseed oil form appreciable amounts of phosphatidic sludge, which is removed in a centrifuge.

The second step is neutralization, which is done by feeding the crude oil in the form of droplets into the bottom of the neutralizing vessel. This contains a weak alkaline solution, through which the small droplets rise by difference in gravity and are collected in the upper part of the vessel as refined oil with low acidity and low soap content. The aqueous solution becomes gradually weaker in alkalinity with a corresponding increase of the soap content and, when the solution cannot longer be used for neutralizing, it is split with sulphuric acid to recover the acid oil.

The Zenith process can, with a selected crude stock, give refined oils of high quality with low refining losses.

Continuous Refining

Efficient separation of soapstock from neutralized oil is a crucial point in alkali refining and the idea of doing this with centrifugal separators was already conceived in the last century (11). Modern refining practice varies between countries and plants and with different kinds of oils to be refined (12,13).

Two basic systems are in use. The essential difference between them are the time and temperature of mixing with caustic. The system used in the United States allows for a relatively long mixing time (typically 5-15 min) at ambient temperature followed by heating to 70-80 C to coagulate the soap (formation of break) before centrifuging. This system is shown in Figure 3 and is known as long-mix (12).

The alternative system used in Europe and other parts of the world consists of first raising the oil temperature to 80-90 C, then mixing with caustic for a very short time (typically 1-15 sec) before centrifuging as shown in Figure 4. A second alkali refining (so-called rerefining) may also be used in this system (13).

Addition of phosphoric acid in order to assist removal of phosphatides can be introduced into either system and it is the refiner's job to decide which combination of processing systems is most suitable for the oil he has to refine. Table II

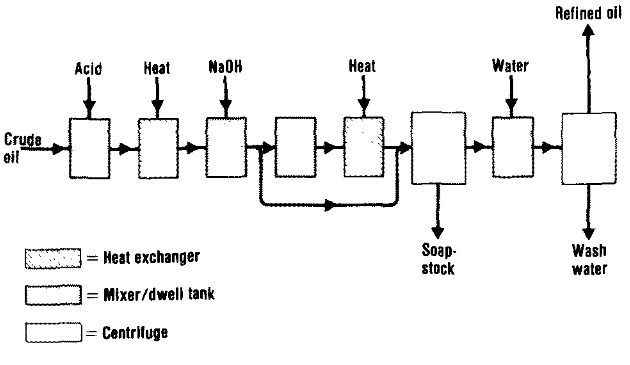

FIG. 3. Long-mix refining plant.

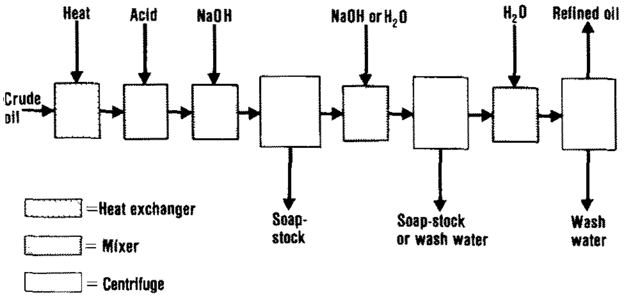

FIG. 4. Alkali refining plant, "European type".

TABLE III

Refining of Low Quality Cottonseed Oil[1]

Trial	Neutralization			Rerefining[2]	Refining loss %	Colour after washing 2" cell LB Y x R
	Mixing		Lye excess %			
	Time	Intens.				
A	4 min	Low	75	No	3.5	70 x 60
B	15 sec	High	75	No	7.1	70 x 32
C	5 sec	Low	25	Yes	4.9	35 x 3.8

[1] Crude oil: FFA = 1.4%, phosphatides = 1.6%, dark color.
[2] Rerefining with 1% (by vol.) NaOH of 7 N strength intense mixing for 15 sec.

TABLE II

Oil Quality as Function of Refining Conditions
Crude soybean oil: 0,4% FFA; 0.5% nonhydratable phosphatides

Trl.	Pretreat. with 0.1% H_3PO_4	Neutralization[1] mix time and temperature	Rerefining	Washing[2]	Refined oil			
					P ppm	Ca ppm	Soap, ppm	
							WolFF	AOCS
A	No	5 sec., 90°C	No	1x10	72	84	750	290
B	No	4 min. mix cold + + Heat bef. sep.	No	1x10	4	2	60	50
C	Yes	5 sec., 90°C	No	1x10	6	6	90	70
D	Yes	5 sec., 90°C	Yes	2x4	1	<1	30	10

[1] Lye conc. 4 N Lye excess 25%.
[2] Figures indicate numbers of washing, and amount water.

shows a series of tests on a relatively typical European soy oil with 0.4% FFA and 0.5% nonhydratable phosphatides. The first two tests are the basic short-mix and long-mix systems and it can be seen that the long-mix gives in this case better results. However, introduction of phosphoric acid into the short-mix system produces results almost equal to the long-mix and finally the combination of phosphoric/short-mix refining and double water washing gives the best results. Although this may seem to be overtreating the oil, it is in the refiner's interest to make his alkali refining as efficient as possible because of its effect on the subsequent processing stages. For example, it will lead to a reduction in bleaching earth consumption because of low soap content, better oil quality due to low phosphatide content, etc.

In the case of cottonseed oil, the refining conditions are often chosen more for their ability to improve the oil color caused by the presence of the pigment gossypol. This pigment is sensitive to heat and oxidation, forming colored compounds which are difficult to remove from the oil other than by reaction with caustic. Table III shows a series of tests on a low quality cotton oil where it can be seen that the best results are obtained (as far as color removal combined with acceptable loss) by the combination of very short contact neutralization followed by rerefining with strong lye (trial C).

Another technique used with advantage on cottonseed oil is to refine the oil as 65:35 oil hexane miscella immediately after extraction (14). This allows removal of the gossypol compounds before they have been damaged by heart, producing an oil with very low color at refining losses lower than conventional refining.

Certain crudes like olive oil, ricebran oil, fish oil, etc., with a high FFA content (10-30%) are preferably refined by neutralization with a strong lye and with an extremely short contact time (less than 1 sec) between oil and lye, in order to preclude any excessive saponification of neutral oil. Oils of this kind easily form emulsions when mixed with water or lye or other aqueous solutions, due to the presence of mono- and diglycerides. The mixture has, therefore, to be treated as gently as possible when it is fed into the centrifuge.

RECENT IMPROVEMENTS IN ALKALI REFINING

Since continuous alkali refining has been producing refined oils of high quality for many years, the developments which have taken place over the last 10 years have been concentrated on aspects of the process not concerned with quality but with the process efficiency with respect to energy, operating costs and reduced pollution.

Countercurrent Water Washing

An efficient removal of remaining impurities by water washing of the oil from the soapstock centrifuge is essential for the oil quality and for the subsequent bleaching. Washing is principally a liquid-liquid extraction. It is, therefore, more efficient if done in several stages in countercurrent. Thus, a liquid-liquid extractor would be an ideal device for this operation. Unfortunately, a solid phase is sometimes also formed during washing which would clog the extractor. Two extraction stages give satisfactory results and, therefore, two separation stages in series working in countercurrent according to Figure 5 is a good solution. As was shown in the example for soybean oil refining, it is possible to get an efficient washing with as low as 4% water used in two-stage countercurrent, which gives the advantage of saving of water and energy. Water is becoming a scant resource and the price is increasing. The energy cost for

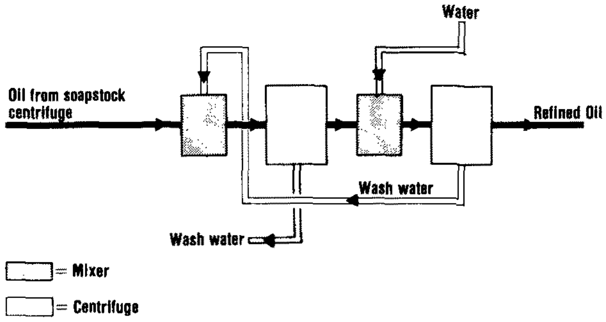

FIG. 5. Washing in countercurrent.

heating wash water is not negligible either. One of the disadvantages with caustic refining is the polluting acid water formed during splitting of the soapstock. Soapstock splitting is nowadays not a big problem and a concentrated soapstock can be split without dilution with fresh water. It is thus possible to reduce the volume of acid water to such an extent that it can be completely disposed of at acceptable costs, which would lead to a fully pollution-free caustic refining process.

Energy Savings

Energy is consumed in a caustic refining plant mainly in form of heat normally supplied as steam. A simple way to recover heat energy from hot oil is to install regenerative heat exchangers as shown in Figure 6.

The incoming oil at ambient temperature is first preheated by hot oil leaving the process and is then further heated to the processing temperature with steam, water or electricity.

If the oil will be immediately processed at high temperature, there is no point in cooling the oil. In that case, it is more practical to make an integrated heat recovery in the whole refinery as shown in Figure 7. In this case, it is assumed that deodorized oil, cooled by internal heat recovery in the deodorizer to about 120 C, is further cooled to about 40 C by cooling water, which is heated up to, say, 110 C. This water is in turn used to heat the oil in the first processing step, which normally is degumming and caustic refining.

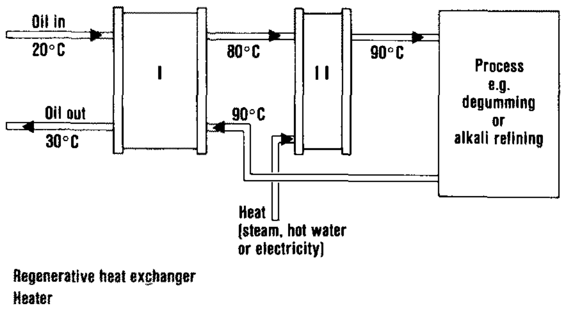

FIG. 6. Heat recovery in an oil processing plant.

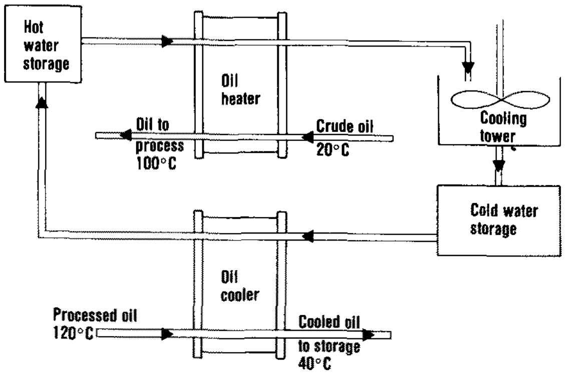

FIG. 7. Integrated heat recovery.

Electricity can mainly be saved by replacing centrifugal or ring pumps by positive displacement pumps with a speed variator for regulation of the liquid flow. A further way to save energy is to design refining plants with larger capacity, which gives a somewhat lower overall energy consumption per unit processed oil. Centrifugal separators which are the bottleneck regarding capacity in a refining plant are now available up to a daily capacity of ca. 500 tonnes. In such large units, savings in manpower also can be considerable by a tailor-made instrumentation and automation of the plant.

Improving Oil Yield

The continuous caustic refining with centrifuges got a break-through about 30 years ago, due to the considerably better yields which could be obtained compared to the then-predominating batch refining.

Today, conventional continuous refining cannot be much further improved regarding oil yield except for finding systems to monitor the process parameter to maximal yield. Considerable efforts have been done to construct such loss monitoring systems and they are mainly based on measuring the mass or volume with temperature compensation of the incoming crude oil and outgoing refined oil and comparing these values to give a difference or quotient. This is an important tool for improving the control of refining losses, but there is still place for further improvements.

Improved Working Conditions

When designing new refining plants, it is an aim to improve the working conditions for the staff, and in many countries this is also supported by legislation. Examples of such improvements are: safe handling of chemicals, less manual work for cleaning of equipment, etc., lower noise emission, and lower heat emission.

It is obvious that a large number of actions can be taken to achieve the above, and that these actions have to be adjusted to the local conditions in the individual plant.

A plant can be more or less automatized and supervised from a control room separated from the plant, with a low noise level and air conditioning.

An important improvement is the possibility today of cleaning in place (CIP) of equipment, especially of centrifugal separators. Besides the better working conditions for the staff it also opens the possibility of running a plant uninterrupted for weeks or even for months with better performance regarding oil quality, refining losses and costs.

FURTHER POSSIBLE IMPROVEMENTS IN CAUSTIC REFINING

The outcome of the present competition between the classical caustic refining and the more recently introduced physical refining will depend on many factors, such as solving the pollution problems for both systems and reducing the overall processing costs.

Reduction of Refining Losses

The refining losses for low acidity oils like soy and sunflower cannot be much further reduced by streamlining the caustic refining. However, for some high acidity oils, which are unsuited for physical refining, there is a possibility of reducing losses during alkali refining by using a hydrotrope dissolved in the lye. An example of hydrotropic agent is isopropyl alcohol.

For oils like fish oil, ricebran oil, etc., with high acidities, it is possible to reduce the total losses of fatty matter to ca. 10-20% above the FFA content.

Ammonia as Neutralizing Agent

Ammonia was suggested as a neutralizing agent more than 100 years ago but did not come into practical use. Pardun (15) has again shown interest in ammonia as a neutralizing agent from the pollution point of view. Laboratory experience has shown that this could be an interesting process. The advantage with ammonia for neutralization is that the soapstock can be split simply by distilling the soapstock, which evaporates the ammonia for reuse in the process leaving an acid oil as the distillate residue.

Flexible Refining Plant

Some processes for wet superdegumming of oils use similar equipment like reactors, centrifuges, heat exchangers, pumps, etc., as are used in alkali refining plants. It is therefore possible to design a plant which can be used either for this type of superdegumming if this can give a satisfactory refined oil quality or be used as a conventional alkali refining plant. This gives good flexibility in the refinery and is of special interest to those processors who cannot count on a steady supply of high-quality crude oils.

Further Automation

To reduce operating costs and to ensure steady production of high quality oil with a high oil yield, it is possible to improve supervision by automatization, microprocessor-based and computerized control (16). It is thus easier to supervise parameters like liquidflows, pressures and temperatures and to install certain alarms to assist the operator. However, so far their exist no good instruments for monitoring important properties in the oil like acidity, content of soap, phosphorus, trace metals and water and the oxidation status and this is mainly due to the lack of suitable sensors.

DEWAXING

Waxes are high-melting esters of fatty alcohols and fatty acids with low solubility in oils. Vegetable oils including sunflower, corn and linseed oils contain some wax from the seed shell, which makes the oils cloudy at lower temperatures. The quantity of wax in the crude oils varies from a few hundred ppm to over 2,000 ppm. To get an oil with sufficient cold stability, the wax content has to be reduced to a level of about 10 ppm and this is done by dewaxing, which procedure has been considerably improved during the last few years.

The present methods of determining whether an oil is well dewaxed or not by its appearance (so-called cold test) are not adequate, and new methods combining accuracy, simplicity and speed need to be developed.

Classic Dewaxing

The classical dewaxing process, which is normally done either after bleaching or after deodorization, consists of a careful cooling of the oil followed by crystallization of the wax, which then is removed by filtration. In order to get wax crystals of good filterability, the cooling has to be done slowly and under controlled conditions. A good summary of today's practice of dewaxing and sunflower oil describes several dewaxing plants utilizing different types of filters (17,18).

A modern dewaxing plant is described in Figure 8. The incoming oil is continuously cooled regeneratively by dewaxed oil and further with cooling liquid in a heat exchanger and a crystallizer to 6-8 C. Some filter aid is also also normally added to the crystallizer. the quantity depending on the wax content of the oil, in order to facilitate crystallization and filtration. The crystallization time is a minimum of 4 hr and the maturation time is a minimum of 6 hr. The oil is then carefully heated to 18 C and filtered in a horizontal tank filter with a rate of 40-50 kg/m^2 per hour.

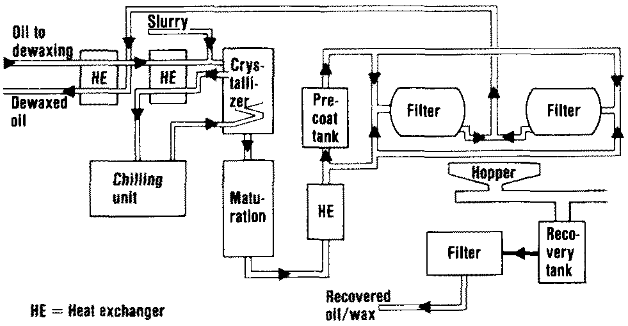

FIG. 8. Dewaxing plant for sunflower oil.

This dewaxing process works quite well with oils with low wax content, say up to ca. 500 ppm, and gives a well dewaxed oil. There is now, however, a trend to higher wax content in sunflower oil from new hybrid seeds and the wax content of 1500 ppm or higher is not unusual today. At this high wax content, the classical dewaxing process is more difficult and expensive due to lower filtration rates and higher losses of oil and costs for filter aid.

Simultaneous Dewaxing and Degumming

To overcome these difficulties, it is possible to make a predewaxing of the crude oil. The crude oil after extraction is cooled to ca. 25 C and kept at this temperature for ca. 24 hr. Then it is simply water degummed at the same temperature, e.g., some water is mixed into the oil during 30 min and the mixture is then separated continuously in a centrifuge. This predewaxing decreases the wax content in the oil to ca. 200-400 ppm.

Dewaxing in Combination with Physical Refining

If the crude oil is of high quality, a physical refining may be considered and, of course, a classical dewaxing by filtration method is applicable. However, with the increasing levels of waxes in the crude oil, filtration becomes more and more difficult and the wet dewaxing process can be used (19). The phosphatides are first removed from the oil by water degumming or superdegumming. The oil is then cooled to 8 C, 5% water containing small amount of sodium lauryl sulfate is added and the mixture is agitated for ca. 4 hr to complete crystallization. During this holding time, the wax crystals are dispersed into the water phase, the principle being the same as used for wet fractionation of oils. The oil water mixture is then separated in a centrifuge with the dewaxed oil going to the physical refining.

Simultaneous Dewaxing and Alkali Refining

Recently, a new dewaxing method has been developed. It is characterized by simultaneous alkali refining and dewaxing and by separation of the waxes from the oil in an aqueous suspension by centrifuges as shown in Figure 9. The equipment on the upper line is a conventional three-stage refining plant, and below is additional equipment needed for dewaxing.

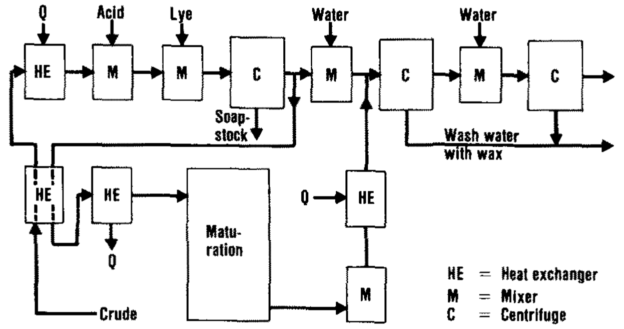

FIG. 9. Simultaneous dewaxing and alkali refining.

The crude oil at ambient temperature is heated regeneratively by hot neutralized oil to 80 C, then further heated to refining temperature and treated with phosphoric acid, neutralized with lye and separated. After regenerative cooling to 30 C and further cooling to 8 C, the oil is retained for ca. 4-5 hr under gentle stirring. The oil is then mixed with 4-6% of water and heated to 18 C by lukewarm water. During this mixing, a soapy water phase is formed, which wets and extracts the small wax crystals, thus forming a heavy suspension of wax in the soapy water. The heavy phase is centrifuged from the oil, which once again is mixed with some water and centrifuged to ensure a complete removal of wax from the oil.

This method has the advantage of lower operating costs due to no costs for filter aid, lower oil losses and lower manpower requirements. The waxy soap water is normally mixed with the soapstock before splitting, but it is also possible to treat this phase separately to recover the wax and oil for further upgrading.

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