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Oil and Oilseed Processing III

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Crude Oil Refining and Preparation for Biodiesel Production

Crude oil obtained by both solvent extraction and mechanical pressing contains desirable and undesirable compounds. Desirable compounds include triacylglycerides (TAGs) (neutral lipids) and health beneficial compounds such as tocopherols and phytosterols. Free fatty acids (FFAs), phospholipids (PLs), also referred to as gums, and lipid oxidation products are the major impurities removed during oil refining. There are several unit operations in a crude oil refining operation. Degumming, deacidification/refining, bleaching, deodorization and winterization are commonly used for edible oil production. Vegetable oils to be used for biodiesel production must be at least degummed and deacidified.

Degumming

PLs are natural components of oils and oilseeds. They are not desirable because they settle out of the oil during shipping and storage. PLs have adverse effects on the color and flavor of oil. They are surface-active compounds that reduce interfacial tension between immiscible liquids, i.e. water/oil. The presence of PLs creates problems during oil processing and some food applications, i.e. frying. PLs are removed from oil during the degumming process.

There are two types of PLs: hydratable and nonhydratable. In general, crude vegetable oils contain a small amount of nonhydratable PLs. However, the amount may vary significantly depending on quality of the seed, type of seed and conditions during the oil milling operation. Oil degumming is usually carried out at the crushing or

extraction plant. Hydratable PLs can be removed from the oil by water-degumming. Hot water (at 160-176°F) or steam is injected into the warm oil. The amount of water/steam added depends on the amount of hydratable PLs present in the oil. As a rule of thumb about 2 percent water is added to oil and mixed for one hour during a batch operation. Continuous degumming processes utilize an on-line mixer for mixing oil and water (2 percent based on oil amount) and the residence time is usually 10-15 minutes. During this process, PLs absorb water and lose their lipophilic (affinity to lipids) characteristics, become oil insoluble and agglomerate into a gum phase. Gums are separated by centrifugation and added back to meal. Gums can be further processed to produce lecithin, which is used as an emulsifier in food and feed applications. The residual phosphorous level in degummed oil is about 100 parts per million after water degumming. PL content of the oil can be further decreased to about 30-50 parts per million by adding 1500-2500 parts per million organic acid into the oil at 104-131°F, a process called super-degumming. The oil from the degumming centrifuge is cooled to 90-100°F before entering a feed tank for the refining operation.

There are also enzymatic degumming processes, which are already competing with traditional processes. Enzymatic degumming increases oil yields by converting hydratable PLs to diacylglycerols that remain in neutral oil and are not lost during the centrifugation process.

Deacidification/Refining

Good quality oil contains more than 95 percent neutral lipids (TAGs). Commercial crude oils usually contain

about 1-3 percent FFAs. High quality oils contain 0.5 percent or less FFA. However, palm, olive, fish and some specialty oils such as wheat germ and rice bran oils may contain 20 percent or more FFAs. As an industry rule, the FFA content of refined oils should be less than 0.1 percent. Although most of the long-chain FFAs do not significantly impair the taste of the oil, the short-chain FFAs may have a soapy and rancid flavor. Furthermore, FFAs accelerate oxidation reactions, consequently, reducing the oxidative stability of the oils. Crude oils are traditionally deacidified or refined by chemical methods. During chemical refining, a heavy soapstock (sodium or potassium salts of fatty acids) is formed. Soapstock is separated from refined oil by gravity settling, filtration or centrifugation. Sodium hydroxide, also referred to as caustic or lye, is widely used for chemical oil refining. The proper strength and amount of lye is critical for achieving high FFA removal with minimal neutral oil loss and degradation, and needs to be determined by trials for different oil types and quality. Not only the FFA content, but also the presence of color and surface-active compounds in oil make reaction of FFAs with lye highly variable. The amount of lye needed for refining soybean oil can be calculated from the following equation:

$$[(\% \text{FFA} \times 0.142 + \% \text{ excess}) \times 100] / (\% \text{NaOH in caustic})$$

(E.G. Latondress, *Journal of the American Oil Chemists Society*, vol. 61, no. 8, pp: 1380-1382, August 1984).

In oil refineries lye strength is measured by its specific gravity and expressed in degrees Baumé. The percentage of excess lye for degummed soybean oil is usually 0.10-0.12 percent and the lye used for refining oil is 14-18°Bé (9.5-12.7 percent NaOH in water). Details for the calculation of lye requirement for refining can be found in Bailey's *Industrial Oil and Fat Products (3rd edition, editor, D. Swern, John Wiley & Sons, Inc., N.Y., 1964, pp.735-740)*. The degummed oil at 90-100°F is mixed with the required amount of lye and pumped through a high shear mixer. The mixing time is 5-10 minutes. Then, oil is heated to 165°F and centrifuged to remove soapstock (sodium salts of FFAs). Soda ash or sodium carbonate also can be used to remove FFAs from crude oil. However, carbon dioxide released during refining causes foaming. In addition, entrainment of gas in the soapstock prevents proper settling.

In cottonseed, gossypol, a complex polyphenolic compound, contributes to oil toxicity and dark color and is regarded as an undesirable component. However, recent studies have shown that gossypol possesses an-

titumor and contraceptive activities in males. Today, gossypol is considered a value-added natural product from cottonseed with health beneficial properties. Nevertheless, during cottonseed processing, gossypol must be removed to produce edible oil and animal feed. Gossypol in crude cottonseed oil is typically removed in the miscella (mixture of oil + hexane) before hexane removal from the oil at the hexane extraction plants. In this process, the crude oil-hexane mixture (45-65 percent oil:35-55 percent hexane) is filtered to remove any meal, scale or insoluble impurities that may be carried from the extraction process. Next, the crude miscella is pumped to a reaction vessel, where lye is added and mixed thoroughly until the impurities in the crude oil precipitate in the soap phase. Then, the light-colored refined miscella is separated from the dark, gummy, fluid soapstock by using a specially designed centrifuge. The light yellow miscella is pumped to a stripper to recover hexane. Leaving the stripper at 220°F, the refined oil passes to a pressure leaf-type filter to remove the last traces of soap and any impurities before cooling and entering the storage tank. During miscella refining, FFAs and PLs also are removed along with gossypol from hexane miscella.

Although it is not widely used, selective solvent extraction is practiced by small operations to neutralize oils with very high FFA content, e.g. cocoa butter from rinds and olive oil from the oil cake. Isopropanol is the choice of solvent for selective extraction of FFAs. Water soluble silicates such as sodium silicate also are effective in neutralizing FFAs. This process allows soapstock removal by filtration or decanting. Silicate concentrations between 10-50 percent in aqueous solutions have been used to neutralize FFAs. At high silicate concentrations, the soapstock tends to agglomerate into a firm solid phase. Refined oil, with less than 0.02 percent FFAs, can be obtained with minimal oil loss. The soluble silicate refining increases oil yield, eliminates centrifugation for separating soapstock and water washing of the oil.

Physical refining, also known as deacidification by steam distillation, is a process where FFAs and other volatile compounds are distilled off the oil. Physical refining, a viable alternative for the caustic/chemical refining process, is based on the higher volatility of FFAs than TAGs at high temperatures and low pressures. During the process, volatile compounds, including FFAs, are volatilized and neutral oil droplets are entrained within the stripping steam. The final FFA content in the refined oil can be reduced to 0.005 percent when physical refining is used.

Adsorption processes also have been examined to remove FFAs from oils. A process, which utilizes magnesium oxide as adsorbent to remove FFAs from oils, has been patented. Aluminum hydroxide gel also is effective for removing FFAs.

Bleaching

Oils are usually bleached after deacidification/refining and before deodorization. Originally bleaching was used to remove color compounds such as carotenoids and chlorophyll. Today, bleaching is designed to remove undesirable oil components including peroxides, aldehydes, ketones, phosphatides, oxidative trace metals, soaps and other contaminants such as pesticides and polycyclic aromatic hydrocarbons.

Clays used for bleaching are commonly called "Bentonites." Activated carbon, alumina, silicic acid, aluminium- and magnesium-silicate, silica gel and synthetic silicates also are used to adsorb impurities from refined oil. The bleaching is normally carried out under vacuum (20-30 mm Hg) to minimize oxidation reactions and control moisture levels. Preheated oil (194°F) is pumped into a slurry tank and adsorbent is added to the tank simultaneously. After mixing, the clay/oil system is fed into a vacuum bleacher. The bleaching process takes 15-30 minutes in a temperature range of 176-248°F. Although high temperature increases the adsorption efficiency, bleaching at very high temperatures is not recommended because it promotes undesirable reactions. The temperature should be high enough to maintain a low oil viscosity, which improves diffusion and mass transfer rates. Wet bleaching is practiced when processing oils containing PLs, because water will act as a carrier for the PLs into the bleaching clay particle. The optimal amount of water used for wet bleaching is about 50-100 percent of the adsorbent used for the process. Initially oil (about 0.5 percent moisture) is treated with water and adsorbent (8-15 percent moisture) at 158-194°F for 20 minutes under atmospheric conditions. Then, bleaching is carried out under a vacuum for 15-30 minutes. The amount of adsorbent required for bleaching depends on the types of adsorbent and the oil and its pre-treatment. The adsorbent dosage range is quite wide, usually 0.1-2.0 percent (of oil processed), but in some cases it can be as high as 5 percent. Physically refined oils require a higher amount of adsorbent than chemically refined oils. After bleaching, oil is filtered and separated from the adsorbent.

Deodorization

Deodorization is a steam-distillation process in which volatile and odoriferous compounds are stripped off with steam. The objective is to produce a bland and stable product. Deodorization removes FFAs, aldehydes, ketones and peroxides from bleached oil. Temperature plays a critical role during deodorization. If the temperature is increased from 350°F to 400°F, the rate at which odor compounds are removed is expected to triple. If the temperature is further raised to 450°F, that rate can be expected to triple again. This means higher deodorization temperature reduces processing time. However, high temperatures cause development of undesirable polymers. Hence, optimization of time and temperature is necessary for a given process. High vacuum is desirable for deodorization because it inhibits oil hydrolysis. The volume of stripping steam needed in the deodorizer also is affected by vacuum. For example a deodorizer operating at 12 mm Hg pressure would require twice the stripping steam of a unit operated at 6 mm Hg. Currently, 6 mm Hg vacuum is commonly used for vegetable oil deodorizers. Batch, continuous and semi-batch deodorizers are available for vegetable oil processing (<http://www.desmetgroup.com/refining.html#Anchor-Deodorising-3800>, <http://www.crowniron.com/userimages/DeoMaxN3.pdf>).

Winterization

Winterization is a separation process by which higher melting point acylglycerides and waxes that are responsible for the turbidity of some edible oils in the winter or after refrigeration are crystallized and removed. Composition of the oil, rate of cooling, temperature of crystallization and mobility of TAG molecules in the oil are critical factors affecting efficiency of winterization. These factors play a significant role both in separating the solid phase and then separation of the solids from the liquid portion. The edible oil industry utilizes the liquid fraction to make high-quality salad oils, whereas the solid fraction is used in shortening or margarine formulations. During the winterization process, the oil is cooled from room temperature to a predetermined temperature of crystallization. The cooled oil is kept at this temperature for a certain period of time prior to the separation of solid phase from the liquid oil by filtration of the oil-solid fat slurry. In a winterization process, cooling rate and temperature of crystallization are extremely important. Too low a temperature and high cooling rates will result in high viscosity and reduce crystal growth rate. A mild

agitation is recommended to provide a gentle motion to the crystals to enhance their growth rate and keep the temperature and composition uniform in the bulk oil. The agitator design should be such that no shear to break the crystals is generated. In commercial winterization operations crystal modifiers or an appropriate solvent are used to facilitate filtration of solid phase from the liquid oil. In certain applications, scrape surface heat exchangers are preferred.

Tips for Preparing Crude Oil for Biodiesel Production

In general, crude oil preparation for biodiesel production includes at least degumming, neutralization and drying. Oil to be converted to biodiesel should have the following specifications:

Phosphorous content: 2-10 ppm

Water content: 500-1000 ppm

Acid value: 0.05-0.25 percent FFA, max

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