Soybean Oil Processing: Quality Criteria and Flavor Reversion

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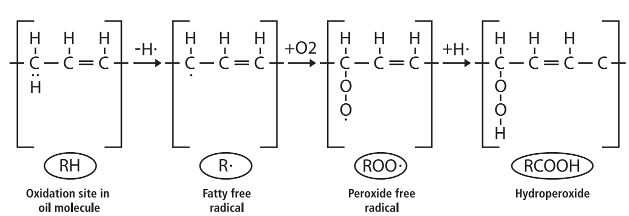
Soybean oil (SBO) has a triglyceride composition rich in monounsaturated (23% oleic acid) and polyunsaturated fatty acids (FA) (57% linoleic acid; 7% linolenic acid). This makes the oil extremely sensitive to oxidative damage and quality deterioration. This process eventually leads to color and flavor reversion, accompanied by the development of beany off-flavors, which in an advanced phase could change into a fishy and painty smell.

Many hypotheses have been formulated to explain this flavor-reversion process. Linolenic acid has been seen as the major culprit for oxidative degradation. Linolenic acid contains three unsaturated bonds, which easily can be oxidized. SBO with low-linolenic acid content also seems to be less vulnerable to flavor reversion. An intermediate oxidation of iso-linolenic acid has been suggested, even though brush hydrogenation with a considerable reduction of linolenic acid content is no absolute tool against the reversion. Ethyl linolenic polymers also can be formed. These could decompose under nitrogen, yielding flavors identical to those found in reverted SBO. Protecting the oil with nitrogen blanketing can reduce the effect but is no absolute guarantee.

The flavor effect also could be linked to residual phosphatide moieties. Nitrogen-containing intermediates have been identified: trimethylamine oxide, a hydrolysis product of lecithin, could react with linolenic acid and hydroperoxides, giving formaldehyde and dimethylamine, which has a typical fishy odor. Drastic steam deodorization, or extra use of absorbents, can reduce the residual content of unsaponifiables, which slows down the reversion effect.

Even though all these mechanisms may be simultaneously active, oxidation is the primary mechanism involved. When it comes to oxidation, linolenic acid is about ten times more vulnerable than linoleic acid and about one hundred times more than oleic acid. The oxidation of double bonds is a radical-driven process (Fig. 1). Radical reactions typically have three steps: (1) the initiation reaction, where an energy source (heat; light) generates a radical on the FA; (2) a propagation step with oxygen, giving rise to peroxides, which react with more unsaturated FA, creating new radicals; and (3) a termination reaction, where two radicals interact forming a new single bond.



Initiation $RH \xrightarrow{\text{Energy Catalyst}} R^\bullet + {}^\bullet H$

Propagation $R^\bullet + O_2 \longrightarrow ROO^\bullet$

$ROO^\bullet + RH \longrightarrow ROOH + R^\bullet$

Termination $R^\bullet + R^\bullet \longrightarrow RR$

$RH + {}^\bullet OH \longrightarrow R^\bullet + H_2O$

$ROO^\bullet + {}^\bullet R \longrightarrow ROOR$

$ROO^\bullet + R_1OO^\bullet \longrightarrow ROOR_1 + O_2$

Figure 1. Radical reaction mechanism in oxidation of unsaturated fatty acids

Oxidation not only yields volatile degradation products, but also gives rise to the formation of conjugated double bonds (due to intramolecular rearrangement reactions). This directly can be followed when measuring UV spectral characteristics of the oil: absorbance at 230 nm, 270 nm, and 318 nm, typical for these secondary oxidation products, goes up during refining and deodorization.

In order of decreasing importance, several factors can be identified, promoting SBO oxidation: oxygen, heat, pro-oxidants, light, and time. Process efficiency factors such as crude-oil quality and process specifications, however, are of equal importance.

The solubility of oxygen in vegetable oil is high with 3.2 mL per 100 mL. But oxidation can be initiated at much lower oxygen concentrations! Therefore, it is of utmost importance to avoid exposure to air during processing: avoid spraying in the air during filling and emptying of storage or holding tanks; use proper agitation systems in holding and storage tanks; avoid leakage at joints, fittings, or faulty pump seals; maintain a good vacuum where possible; avoid or eliminate the blowing of lines with air (use nitrogen where needed); protect the oil with nitrogen blanketing or sparging; use antioxidant addition.

The effect of heat is much easier to control. As with all chemical reactions, the speed of oxidation grows exponentially with the temperature of the reagents. Consequently, oil should never be kept at a higher temperature than needed; local overheating by agitating must be avoided at any step where the oil needs to be heated. The combination of air and heat can be extremely negative for the oil quality. Open-air contact of SBO should therefore never happen above 60°C.

Pro-oxidants enhance radical reactions such as oxidation. Copper and iron ions are the most potent prooxidants. They must be kept at the lowest concentration possible: less than 5 ppb copper and less than 150 ppb iron are acceptable levels. Other metal ions such as cobalt, chromium, or manganese also might be involved in oxidation. The process equipment should be absolutely free of bronze alloys (rich in copper!). Extra addition of a chelating agent to the refined, bleached and deodorized oil, such as citric acid, will block the remaining traces of metal ions and will inhibit oil oxidation.

Light is also a typical initiator for radical formation. Radical quenchers can reduce the effect of light. SBO is rich in natural radical quenchers such as tocopherols and carotenoids. Keeping these at a reasonably high level should be the objective of an optimized deodorization process.

Oil quality and processing characteristics are possibly of equal importance. Crude SBO quality is highly dependent on the quality of soybeans used in the crushing process. Crushing and refining, bleaching, and deodorization should be done according to the best available technology of the day, according to agreed-upon process standards.

Table 1 gives the major soybean quality and crushing specifications. Freshly harvested soybeans must be immediately protected. Proper handling can minimize quality degradation, although transportation and processing will never make things better.

Inappropriate harvesting cannot always be avoided. However, harvesting immature beans or sprouted beans is inexcusable. Frost damage and microbial spoilage during storage are easier to avoid. If needed, soybeans after harvest can be dried to below 14% to avoid microbiological damage and to improve storage stability. Drying must be done slowly without any overheating, which could induce hydrolysis and oxidation of oil bodies in the soybean cells. The optimal range for effective dehulling and crushing is at 9.5 to 10.5% moisture. This may require additional drying.

Damaged soybeans yield poor-quality crude SBO. During extraction, problems could arise in the hexane extractor. Partial oil and phospholipid hydrolysis will result in more nonhydratable phospholipids, which will require acid degumming to get below 200 ppm phosphorus in the crude SBO, giving low-quality soy lecithin and poor-quality crude SBO.

Lower quality directly translates into bigger losses during refining, bleaching, and deodorization: too high green color; higher levels of free fatty acids; losses in the refining process; more impurities to remove in the bleaching step; changes in the flavor and odor of the final product; a shorter shelf life. This long list of negative outcomes illustrates the importance of buying raw materials with the right quality specifications, if needed at a small premium. This will be paid back largely by reduced losses in the processing and by extra quality and shelf life of the final product.

However, in-process oil standards also are needed to guarantee this final outcome and a positive bottom-line. Process standards are at the heart of quality management. Process and quality personnel need to know these and be able to follow up all process standards. Standards start at the raw-material level and end with the bottles or containers of oil leaving the warehouse. Standards are set on the basis of each type of oil and the specific process applied. The major objective is obtaining the best quality and maximal shelf life for the oil product. A good-quality management system doesn't cost money; rather, it generates money through more intelligent purchasing, reduced losses, and maximized quality.

For crude SBO, additional specifications (Table 2) may be added for moisture (below 0.15%) and secondary oxidation products (peroxide value below 5; anisidine value below 2). Crude oil also should be essentially free of polyaromatic compounds and derivatives, a possible by-product of inappropriate drying, even though these can be removed mostly by adding active carbon in the bleaching process.

Oil should be stored in flat-bottom tanks with bottom-filling and slow mechanical agitation to avoid precipitation of gums and other impurities. A homogeneous feedstock will make it easy to set optimal steady processing conditions in the refining plant. The plant equipment is preferably made with stainless steel (Stainless Steel type 304 for high temperature units; type 316 for the bleaching and deodorization units). Remember: no open-air contact beyond 60°C; no contact points in pumps and special heat seals above 100°C.

After neutralization, the phosphorus content should be below 5 ppm, and the residual soap level below 50 ppm. Before deodorization, all soap and bleaching earth particles should be completely out. The phosphorus must be below 3 ppm; iron below 150 ppb. The vacuum in the deodorizer should be at 3–4 mm mercury, with no leaks in the system (with an absolute maximum of 2 kg air leakage per min!). Before going to storage, the SBO must be cooled to below 60°C, sparged with nitrogen, and composed of a concentrated citric acid solution (bringing the citric acid level into the ppm range). The final product is stored in cone-bottom stainless-steel tanks with nitrogen blanketing or sparging. Tanks should be used first-in-first-out and cleaned at least twice a year.

Good-quality SBO shall be clear and brilliant in appearance at 21–29°C and free of settlings or foreign matter. The oil shall be bland and free from rancid, painty, musty, soapy, fishy, metallic, beany, and other foreign or undesirable odors and flavors. The oxidation stability in the AOCS OSI Method (Cd 12b-92) should be 7 hours or more at 110°C. The refined oil can be stored for a while at 30 to 35°C, before packaging. From an oxidation point of view, cans and TetraPak are preferred before glass bottles, which are again superior to PET and PVC, and to PE.

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Table 1
Soybean and Crushing Specifications Affecting Crude Soybean Oil Quality[a]

Field-damaged Beans	a, b, c, e
Weed seed	d, f
Immature beans	f
Splits (loading/transport/unloading)	a, b, c
Bean drying & storage (t/T/humidity)	a, b, c, d
Conditioning beans for extraction	a, b, d, e
Solvent stripping oil (overheating)	b, d
Oil from stripper (overheating)	b
Crude oil storage (time/temp)	c, d

[a](a) total gums/phosphatides, (b) nonhydratable phosphatides, (c) free fatty acids, (d) oxidation products, (e) iron/metal content, and (f) pigments.

Table 2
Average Composition of Crude and Refined Soybean Oil

	Crude oil	Refined oil
Triglycerides (%)	95–97	99
Phosphatides (%)	1.5–2.5	0.003–0.045
Unsaponifiable matter (%)	1.6	0.3
Plant sterols (%)	0.33	0.13
Tocopherols (%)	0.15–0.21	0.11–0.18
Hydrocarbons (squalene) (%)	0.014	0.01
Free fatty acids (%)	0.3–0.7	<0.05
Trace metals		
Iron (ppm)	1–3	0.1–0.3
Copper (ppm)	0.03–0.05	0.02–0.06