Achieving Optimal Bleaching Performance

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Introduction

The greatest advances in the development and industrialization of vegetable oil processes have taken place within the last 100 years. Product diversity between edible and inedible vegetable oil based products places a tremendous level of pressure on every refinery to run at peak efficiency. If you have been in this industry long enough you understand one main fact about vegetable oil refining—reaching peak efficiency is not easy.

Although the overall chemical processes have been honed throughout the years, every plant is unique and demands its own optimal processing conditions. Vegetable oil processing includes four basic unit operations—degumming, refining, bleaching, and deodorization. Every unit operation in the refining process has its own complexity, and unique importance in achieving finished product quality. This article focuses on the bleaching stage of the process.

The bleaching process is the critical unit operation within the refining process responsible for the removal of the remaining soaps, phosphorus (P), trace metals and pigments (chlorophyll, carotenoids), and most of the high molecular weight oxidative products. In order to achieve this there are many variables to consider if you want to have the most economical process:

- Type and quality of your degummed and refined oil
- Characteristics of the sorbent employed
- Processing conditions
- Type of and layout of the process equipment employed

The objective of this article is to give you information on the interaction of most of these variables in the bleaching process, and how they affect the quality of the oil positively and negatively, so you can find the optimal set of conditions that give you your desired quality in the most economical way.

The Basics of Bleaching

"Bleaching is the physical and chemical interaction of a sorbent with an oil or fat to improve its quality."
— *David Brooks, Chief Research Scientist, Oil-Dri Corporation of America*

Bleaching is an intermediate step in the overall refining process. To understand its impact on oil quality we need to see what happens in the processes before and after bleaching (see figure 1). We also need to define what quality is and how the interactions of the different processing variables affect the quality parameters.

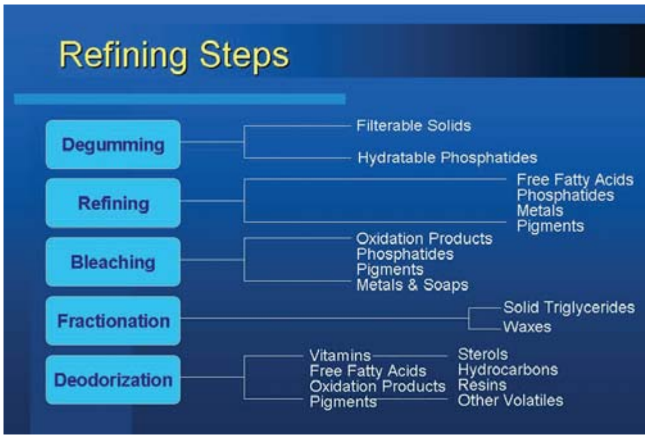

Figure 1

Bleaching Mechanisms

During the bleaching process adsorption is occurring via many different mechanisms through various physical and chemical interactions, most of them improving the quality of the oil, but some of them deteriorating it. These mechanisms include

Absorption: mechanism by which the sorbent locks onto a contaminant. This can occur three different ways:

- Physically through surface attraction involving Van Der Waals forces
- Chemically by chemical or ionic bonds to the surface of the clay
- By molecular sieves which trap contaminants under pressure inside the pores of the clay during filtration

Absorption: mechanism by which the intra-granular pores are filled with some fluid—mainly oil—and in turn what ever contaminants came along with it. Oil retention has a negative impact on the cost of running the process. As dosage increases more oil is lost when disposing the spent clay.

Filtration: mechanism of trapping or physically removing suspended contaminants. Minor contaminants adsorbed to the clay particles are subsequently removed.

Catalysis: mechanism by which contaminants are degraded by interaction with the surface of the clay. For example, peroxides are catalytically polymerized and/or decomposed into aldehydes and ketones. With excessive heat and oxidation, pigments can form color compounds that are difficult to remove or said to be "fixed." In the event of color fixation, red color is more difficult to remove by bleaching clays alone and more resistant to thermal degradation leading to higher red color after deodorization.

Quality

One definition of quality is "to reach a level of excellence." However, with respect to oil specifications, it is quite variable depending on the product and market we are dealing with. For example, P is very important to be as low as possible for deep frying oils, <0.5ppm is desired, but for salad oil, you may have a spec of <2ppm.

Various processing conditions can affect one or more of the oil characteristics that define quality specs. By balancing these conditions one against the other, you will be one step closer to a more efficient bleaching process.

To have an efficient bleaching process you must first be sure that you are getting the appropriate contaminants removed in the refining process (See figure 1). Good refined oil must be

- Low in P (good if <15ppm, very good if <10ppm and excellent if < 5ppm)
- Low in free fatty acids (FFA < 0.1% unless semi-physical refining)
- Low in soaps (< 50ppm unless silica is used).

Once you have this under control you can begin the bleaching stage where:

- Soaps are completely removed
- P is reduced to a level below 2ppm
- Iron is reduced to a level below 0.2ppm
- Chlorophyll is reduced to a level below 0.05ppm
- Peroxide is reduced to a level below 0.5

All values cited here serve as industry guidelines to meet product specs. Each refinery is unique, with its own production lines and product specifications. The bleaching stage however *is* the last opportunity in the refining process to reduce many of these contaminants.

Controlling the Process

Clay dosing in bleaching operations is typically controlled by monitoring color or chlorophyll; they are two of the easiest parameters to measure.

Monitoring chlorophyll is currently more acceptable than monitoring color. Monitoring color is not a good parameter to measure how effective your process is, except where your process and feedstock is completely stable (constant). There is enough evidence proving that, when starting with the same raw material, higher bleached colors may lead to lower deodorized colors, depending on the processing conditions used (see figure 2).

Additionally, bleached color does not correlate with chlorophyll content, especially if you have different chlorophyll content in the crude oil. In the case of soybean oil, chlorophyll levels can range from 0.3 ppm to 14.0 ppm. Bleaching oil from each end of this spectrum to the same red color value will result in different quality oil given the chlorophyll content and oxidative stability of the bleached oil.

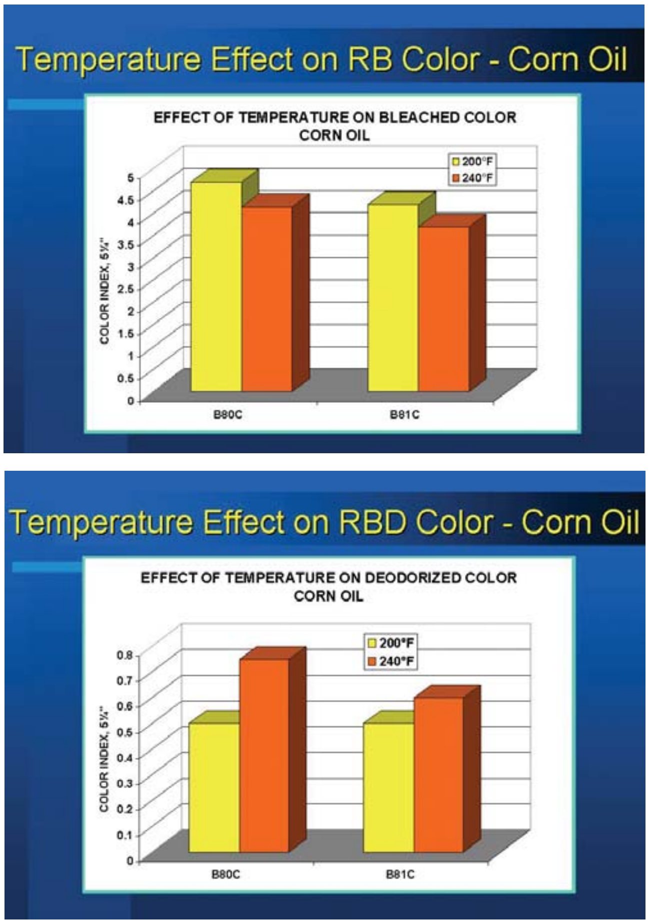

Figure 2

Understanding Interaction

There are numerous interactions between the process variables that influence the removal of oil contaminants and control the efficiency of the bleaching process. One change in a given operational condition can affect many changes in the oil properties at the same time—some good and some bad. The following sections will show the effect of the most common processing variables in the most common quality variables.

Type and Nature of Sorbent Mineral

The adsorptive capacity of sorbent minerals is dependent on its mineralogical structure and adsorptive properties including surface area, particle size distribution, porosity, and surface acidity. There are mainly two minerals in which bleaching clays are based on. One is calcium montmorillonite (commonly referred to as bentonite) and the other is a natural occurring blend of attapulgite and montmorillonite (commonly referred to palygorskite).

Bentonite minerals have limited sorptive properties in the natural state and require chemical treatment by acids to create the surface area and porosity needed for bleaching vegetable oils. Bleaching clays of this nature are commonly referred to as "acid" or "acid activated" clays.

Palygorskite minerals have a natural high affinity to adsorb oil contaminants, with exception to chlorophylls, without any acid treatment. The natural clay can be combined with mineral acids as well as chelating acids such as citric or phosphoric acids to improve chlorophyll activity.

Activation level of the bleaching clay

There are several degrees of acid activation from completely natural, as explained above, to highly acid treated clays. In general, chlorophyll, bleached color, and anisidine value, removal improves as the acidity of the clay increases (pH lowers). However, the interactive effect of using high acid clays can result in increased levels of free fatty acids, and in extreme cases increased color through the deodorizer.

Organic oils, due to the fact that they do not involve any chemical agent in their manufacturing, demand natural clays with high adsorptive capacities. As mentioned, palygorskite is naturally active and can be activated by natural acids such as citric acid.

Filtration

The filterability of a sorptive mineral, including clay minerals and diatomaceous earths, is dependent on the natural (or created) porosity, the particle size distribution (PSD) of the product, and the type of filtering media and equipment employed.

In general, flowability of oil through a given sorbent can be improved by increasing the particle size and decreasing the range of the PSD and is dependent upon the interaction between the particles in the system with respect to the PSD of the bleaching sorbent and the filter aid (if employed) and the mesh size of the filter media.

There is a trade off, however, between flowability and activity due to the fact that activity for a sorbent at a given acid level correlates with PSD such that activity increases as particle size decreases; and vice versa. For this reason, bleaching sorbents are offered with various PSD and activity to allow the operator to achieve the best match with the equipment employed for optimum balance between filterability and activity.

Temperature

Bleached oil temperatures typically range from 90–125°C (190–255°F). Temperature effects oil viscosity and adsorption kinetics. Oil viscosity decreases with increasing temperature resulting in better dispersion of particles, improved clay oil interactions, and flowability. The ability to maintain a particle in slurry suspension however is inversely related to the viscosity of the oil, implying that clays with higher PSDs will take more agitation to stay in suspension. A higher temperature may give you benefits on chlorophyll removal, bleached color, and filtration rates, but may deteriorate deodorized color, and certainly will increase the speed of oxidation reactions (see figure 3).

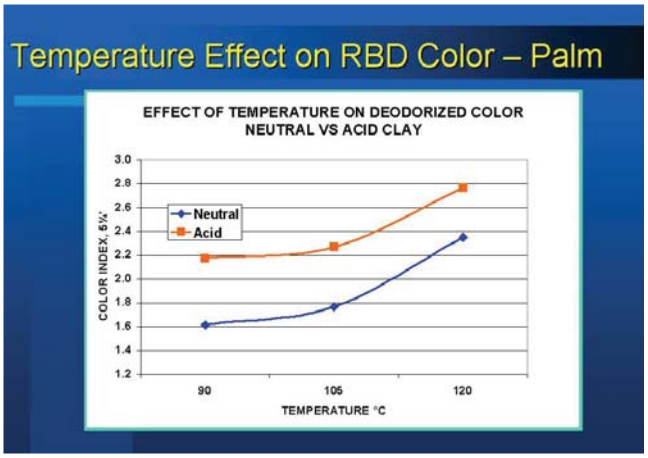

Figure 3

Contact time

Contact time refers to the total time that the bleaching clay is in contact with the oil, from slurry tank through the filter presses. In batch systems you may need to take into account the filtration time in the overall calculation for contact time. Times typically range from 15 to 45 minutes, with 20 to 30 minutes being most common. The positive effect of increased contact time is that it may improve bleached color and chlorophyll removal. Adsorption generally occurs exponentially having a diminishing point of return around 30 minutes. Excessive times may lead to increased oxidization in the bleached oil, resulting in darker red colors through the deodorizer (see figure 4).

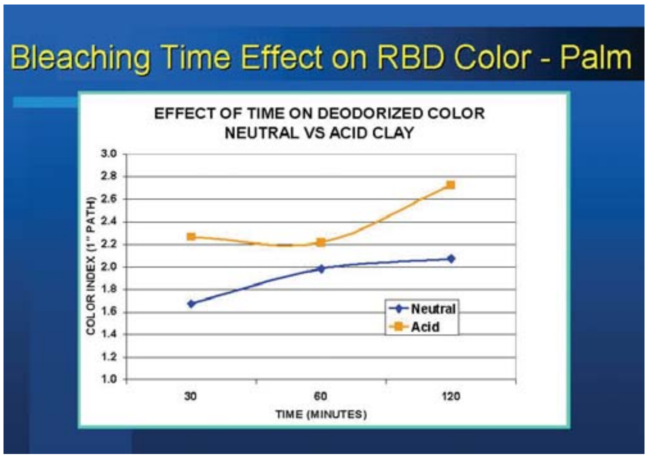

Figure 4

Oil moisture

Oil moisture typically ranges from 0.05% in vacuum dried oil to 0.35% in oil coming directly from a centrifuge into bleaching. Depending on the vacuum, the type of bleaching

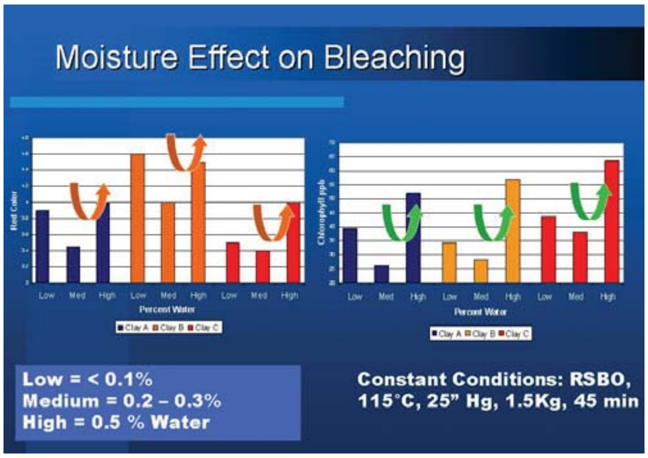

Figure 5

clay and the bleaching temperature, optimizing moisture will improve your chlorophyll and P removal (see figure 5).

The optimum moisture level going into the bleacher is typically less than 0.3%; above this range, bleaching efficiency decreases. Moisture levels, however, need to be reduced to levels below 0.05% before filtering to prevent decreased flowability through the filter presses.

Vacuum

Bleaching efficiency improves when operating pressure in the bleacher is run between 50 to 100 mmHg. Reduced pressure allows for a smooth water evaporation rate resulting in increased efficiency for phospholipids, chlorophyll, and some red pigments removal. Reduced pressure also minimizes interaction of oil and air resulting in lower peroxide values, anisidine values, and bleached oil colors.

Summary

The bleaching process is a simple operation that works to improve oil quality through the interaction of oil and a sorbent. The complexity of this interaction however, is far from simple and represents a multitude of reactions—most of which work towards improving oil quality. The bleaching process requires an effort to maximize the interactions that promote quality with minimal detriment to the oil.

As bleaching clay suppliers, we have developed several options for bleaching clays and processing conditions to help meet these demands. The key to success is to have a good working knowledge of the basic operation in order to select the right clay and the right operational conditions that maximize your efficiency in your equipment.

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