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Practical optimisation

Bleaching is the last stage in the edible oil refining process to remove traces of impurities and contaminants in the finished product. A variety of practical steps can be taken to optimise the process

Jorge Bello

The aim of edible oil refining is to produce an oil at a competitive cost which has a good odour and taste, with nutritional value and a stable shelf life, while meeting all food safety standards.

From a crude vegetable oil, the refining process starts with degumming to remove lecithin, non-hydratable phospholipids (NHP) and metals (*see Figure 1, below*).

Neutralisation in the chemical refining process then removes soaps, NHPs, free fatty acids (FFAs) and metals.

The bleaching step is carried out to remove many different impurities such as chlorophyll, carotenes, metals, soaps, pro-oxidants, some aflatoxins, some heavy polycyclic aromatic hydrocarbons (PAHs), and some pesticides and herbicides. However, if not controlled, bleaching clays can also contribute to increased dioxins, and increase the tendency to form 3-monochloropropane diol (3-MCPD), FFAs and glycidyl esters (GEs).

The deodorisation step removes FFAs, carotenes, light PAH, pesticides and herbicides.

Bleaching process

The bleaching process can be described as the use of bleaching earths or clays to enhance the quality of the oil. Oil is placed in contact with the clay, contact between the two is promoted so that impurities are adsorbed on the clay's surface and clay with contaminants is removed by filters.

Effective adsorption is impacted by temperature, contact time, the concentration of the bleaching clay, the clay's activity, the speed with which the clay surface is saturated, the selectivity of the clay surface and the effectivity of the agitation.

Bleaching earth surface area plays a key role in adsorption and this can be developed to reach up to 400m^2/g.

The surface activity can be manipulated to increase adsorption effectiveness from hydrophilic-hydrophobic characteristics.

The pore volume can be increased while particle size distribution (PSD) can be adjusted to provide good permeability in the filter and facilitate its separation from the oil. The possibilities of adsorptive bleaching now go far beyond what could be achieved in the past, when bleaching was measured only by the colour of the refined/bleached (RB) oil.

Today, parameters such as peroxide value (less than 0.5ppm but preferably 0), soaps and phosphatides (up to 1ppm in some applications), chlorophyll (in ppb ranges) can be measured, among many other contaminants.

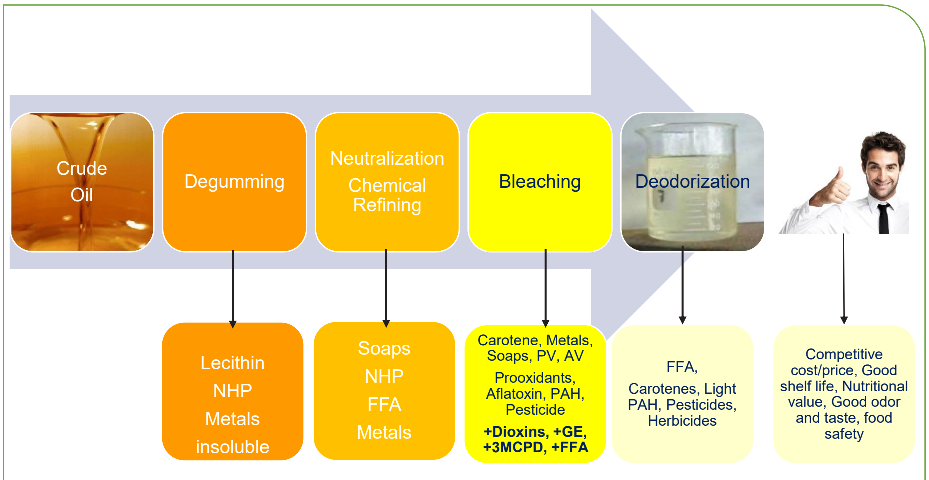

Figure 1: Processing steps in edible oil refining

Source: EP Engineered Clays Corporation

Total bleaching cost

The price of bleaching clay itself does not make up the total cost of bleaching.

The more bleaching clay is used in processing, the more oil is lost into the clay. Bleaching clay – once used – must also be disposed of and this cost must be

	CC 115 FF	Option B
DLV Price per Ton (USD/MT)	700	510
Dosage (kg Clay /MT Oil)	8.75	12.5
Material cost (USD/year)	1,120,816	1,152,783
Oil Losses (USD/year)	215,600	339,345
Disposal (USD/year)	37,370	52,356
Annual cost (USD/year)	1,373,786	1,544,485

Material Cost Component ($/MT) + Oil lost Component $/MT Oil + Disposal Cost component $/MT Oil = TCO for BC $/MT Oil

Figure 2: Total cost of bleaching

Source: EP Engineered Clays Corporation

	BE Dosage	BE Oil Retention	Disposal Cost	Contact Time	Bleaching Temperature	Moisture in system	BE Smoldering tendency
Impact	+++	++	+	++	+	++	+++
	Permeability in Filter	Vacuum in Bleacher	Soaps in unbleached Oil	P load in unbleached oil	Me++ load in unbleached oil	Chlorophyll/ carotene/ gossypol	Decrease oxidants in the load
Impact	+++	++	+	++	+	++	+

+++ Heavy Impact
++ Medium Impact
+ Low Impact

Figure 3: Impact weight of different factors on total bleaching earth cost

Source: EP Engineered Clays Corporation

accounted for. Although disposal cost is the smallest factor in the three main cost components of bleaching, it can be very expensive in some countries.

The total cost of bleaching is therefore the sum of the bleaching earth's cost, oil loss and disposal cost (*see Figure 2, above*).

For this reason, the first step a processor should take is to select the right bleaching clay according to quality needs.

The quality of the refined oil and the robustness of the adsorbent should also be considered, and the clay should be headache-free, easy to remove and one which does not require constant adjustment.

Clays have a variety of characteristics, with a range of prices and performance. They have different acidity levels, surface area, silicate content and permeability on filter, among other factors. Some of these factors will heavily affect the total cost of bleaching (*see Figure 3, above*).

Bleaching earth dosage is critical for cost, along with oil retention, as explained earlier. The contact time between the clay and oil is another important factor, the optimal requirement being between 20 and 35 minutes, depending on the oil type.

The tendency for bleaching earth to smoulder is also a safety concern.

The load of phosphorous, metals, oxidants, chlorophyll and carotene are other factors, as these are all impurities which must be removed.

Optimising bleaching

There are three steps that should be taken to optimise the bleaching process.

The first step is to measure the current status and obtain feedback from stakeholders on how satisfied they are, in order to obtain a baseline.

The second step is to implement any necessary changes.

And the third step is to monitor and track the changes, and then restart the cycle for future improvements.

Colour/chlorophyll management

Colour is a major factor in consumer opinion and choice of edible oils, and processors should aim for a light colour and clear appearance.

The colour of an oil or fat depends on the quality of the source material, with hues ranging from orange (palm oil) to browns (rendered fats). Monitoring the chlorophyll content after bleaching is a more common practice for optimising the bleaching process than monitoring the red colour. This is because chlorophyll is thermostable, unlike carotene.

If the chlorophyll level is high, a review of bleaching clay dosage is needed and the clay feeder should be checked.

A more active and robust bleaching clay should be considered if variability in the crude oil is high.

If there is enough oil in the buffer tank, a potential solution is to recirculate oil back to the filters.

If a green colour is detected, look for chlorophyll B traces and if this is present, additional bleaching clay can remove it.

Temperature plays a key role in optimising the bleaching process. A higher temperature can be beneficial in chlorophyll, colour removal, and filtration rates. However, it may worsen the colour of the deodorised oil and its oxidative stability.

The optimum bleaching contact time is 30 minutes. Shorter times may lead to low efficacy in the bleaching earth, while longer times increase energy costs. Chlorophyll out of bleaching should be controlled to less than 50ppb, at a temperature between 90-110^{0}C.

There should be effective agitation to increase collisions, no more than 30 minutes of contact, and a thick cake in the filter of one inch to improve chlorophyll removal through the filter press effect.

A led-lag configuration – which is basically the use of spent packed bed filter to pre-filter the oil – will reduce bleaching earth use. If citric acid is used, it should not exceed tne right dosage based on the chelation of calcium, magnesium and iron.

Phosphatide management

Phosphatides or gums are impurities which need to be removed from edible oils due to their emulsifying and oxidative properties.

In order to control phosphatide, its content should be less than 5ppm going into the bleacher. A good way to achieve this is by adding citric acid or phosphoric acid. Wet bleaching helps to hydrate the phosphatides while bleaching earths bond the NHPs to their surface.

In many cases, a low temperature of 90-100^{0}C facilitates better hydration of phosphatides to the bleaching earth and its removal in the filter.

If phosphoric acid is used in combination with bleaching earth, it should not exceed 50ppm per 0.5% of bleaching earth.

It is critical to have the right acid dosage for pre-treatment. More acid should be used when the contact time is shorter

Sample	ICP-OES Elements (ppm)				
	P	Ca	Cu	Fe	Mg
OxG	26.0	22.0	<0.05	10.0	4.0

Acid Treatment OxG	
P content (ppm)	26.0
Ca content (ppm)	22.0
Mg content (ppm)	4.0
Fe content (ppm)	10.0
Throughput (lb/hr)	50,000.0
Acid Concentration (%)	85.0
Acid Exess (%)	Factor
Acid treatment	
(lb/hr) H_3PO_4	12.9
(lb/hr) Citric Acid	8.4
Water Addition	
Water (lb/hr)	14.3

Sample	ICP-OES Elements (ppm)				
	P	Ca	Cu	Fe	Mg
OxG bleached	0.55	<0.05	<0.05	0.07	0.05

Lessons learned:

- Adjust the treatment formula according to contact time limitations: more acid when contact is shorter
- Adjust type of acid by a oxidation factor:
  F_{high} → 100% phosphoric acid
  F_{med} → 50% phos+50% Citric
  F_{low} → 100% Citric acid
- Watch for the amount of water in the bleacher as water is needed to hydrate gums.
- Use a robust clay able to adsorb excess of acid and traces of metals

Source: EP Engineered Clays Corporation

Figure 4: Proper acid treatment to reduce non-hydratable phospholipids (NHPs)

(*see Figure 4, above*). Monitor the amount of water in the bleacher as water is needed to hydrate gums, while a robust bleaching clay is needed to adsorb excess acid and traces of metals.

Free fatty acid (FFA) management

Oils with high levels of FFAs are more susceptible to oxidative aging and become rancid more quickly, resulting in higher refining losses.

A high level of unsaturation in edible oils will increase the tendency to hydrolysis and FFA generation.

Bleaching efficiency is highly dependent on the interaction between vacuum, moisture and temperature.

In order to avoid the formation of FFAs, oil moisture needs to be controlled as a high (0.6%) moisture content tends to convert oil into FFAs. Hydrolysis is highly dependent on factors such as bleaching temperature and contact time, bleaching earth concentration and vacuum applied during bleaching.

In order to reduce the negative effect of moisture, the moisture of water-washed oil prior to bleaching should be below 0.6%.

A high bleaching temperature will increase the generation of FFAs and bleaching temperature should therefore be adjusted to minimise FFA generation.

Contact time at the bleacher should be kept to less than 30 minutes – a long contact time increases FFA generation.

Bleaching efficiency also improves with reduced pressure, as this allows for a smooth water evaporation rate, resulting in increased efficiency in removal of phospholipids, chlorophyll and some red pigments.

Reduced pressure also minimises the interaction of oil and air, resulting in lower peroxide values (PV), anisidine values (AV) and bleached oil colour.

Smouldering management

During the handling of spent bleaching earth, there is a risk of starting a fire either at the facilities or in the landfill where spent clay is deposited. Spent clays themselves have a tendency to start to self-burn, a property called pyrophoricity.

The main factors that impact the tendency of spent clays to smoulder are: the amount of oil retained in the spent cake, the unsaturated fatty acid composition of the oil, the pyrophoric characteristics of the clay and handling during and after the blowdown step.

A long blowdown time of more than 30 minutes causes a higher tendency to smouldering, along with high pressure steam, the use of air for drying, improper tapping with water and air exposure in the dumpster.

Key safety steps to take include:

- Avoiding oxygen entering the spent cake by adding a 5-10 minute blowdown with nitrogen at the end of the blowdown cycle. This will help to replace oxygen in the spent cake.
- Wetting the spent cake with a lime solution (5%w/w) or with water from the first centrifuge where the pH is alkaline.
- Using a cooling system before stockpiling the spent clay.
- Avoiding an excess of residual oil in the spent cake by using a filter aid to drain off and cool down the spent cake, therefore reducing the blowdown time.
- Reducing heat added to the system by selecting the right clay with low pyrophoricity, reducing the bleaching temperature and using cooling systems for the spent clay, such as double shaft mixers to cool down the clay.

Filter press management

Filtration is typically the bottleneck in the process between bleaching and deodorisation and is an intensive operation in terms of manual activity and constant surveillance by operators.

The cycle length is critical but variable according to the oil and clay type, bleaching temperature, amount of soaps and gums, and moisture in the oil.

The proper pre-coat impacts the filter life and selecting the right filter aid extends cycles of chemical cleaning in the filter screens.

The flow rate during the pre-coating of the filter is recommended at a rate of two times the flow of the regular run. Clean oil is also recommended for the pre-coat, preferably RB oil to avoid gum and soap deposits.

Frequent citric acid addition in the bleacher leads to salt deposition on the screen cloth while too wet bleaching combined with low bleaching temperatures tend to leach soap and phosphorous across the filter.

Metallic compounds management

Metallic compounds are another impurity that needs to be removed. Using acidic clays, where possible, will help to minimise metals.

Using a finer PSD has proved beneficial for removal of metals, along with a pack-bed effect in a led-lag configuration and the addition of citric/phosphoric acid to neutral oil. Adding chelating agents may potentially help to capture metals and form lipophobic salts, which are easy to remove. This will reduce the load on the bleaching clay.

Contaminants and 3-MCPD

Undesirable components that need to be removed or reduced from oils include PAHs, polychlorinated biphenyls (PCBs), dioxins, pesticides, herbicides, 3-MCPD and GEs.

3-MCPD is considered a substance of concern to public health and mitigation strategies include:

- Reducing diacylglycerol (DAG) levels in crude oil by changing harvesting practices or using enzymatic treatment.
- Washing raw oils to remove chloride precursors.
- Using chemical rather than physical refining, if possible. There are several studies and practices which show that partial caustic neutralisation helps to prevent the increase of 3-MCPD.
- Using sulphuric acid-activated bleaching earth to minimise chloride ions.
- Removing 3-MCPD esters from refined oil with adsorbents, post bleaching with acid-activated clays followed by mild deodorisation.

- Minimising deodorisation temperatures or using a two-step deodorisation process.

Total oxidation value (TOTOX)

Oil oxidation is an undesirable series of chemical reactions involving oxygen that degrades the quality of an oil, eventually resulting in rancidity and accompanying off-flavours and odours.

Measuring oxidation involves testing for the primary and secondary breakdown products. The most common test is peroxide value (PV). However, very rancid oils can have a reduced PV. Therefore, the anisidine value (AV) and a total oxidation value (TOTOX) are also used.

In order to control the TOTOX of oils, it is recommended to control the AV in RBD oil to less than 3 for frying oils. Long storage times should be avoided, as well as unnecessary heating of the oil. Finished RBD oils should be blended to control the final TOTOX but refined blends should be avoided.

If the TOTOX in RBD oil is greater than 7, storage and handling conditions should be reviewed. Using citric acid with bleaching earth will break down peroxides, while increasing the bleaching temperature and vacuum will remove volatiles.It is important to review the bleaching clay dosage as more clay reduces TOTOX. Clay contact times should also be considered as long times can lead to an increase in TOTOX.

Conclusion

Although the bleaching process appears, at first glance, to be a simple mixing of adsorbent and oil, the chemical and physical reactions which occur are complex and rely on factors such as moisture levels, temperature, contact time and vacuum, and the amount and type of bleaching earth used.

A good part of bleaching optimisation is carried out across the refining process but bleaching can be considered the last step in refining to remove impurities before deodorisation.

Choosing the right bleaching earth product for the specific application leads to cost competitiveness and a high quality oil.

Bleaching cost is influenced by oil losses, disposal costs and dosage.

Maximising cake thickness to one inch and a led-lag configuration can lead to cost savings in bleaching. ●

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Minersa opens new plant in Mexico

Spain's Minersa Group has opened a new production plant in Querétaro, Mexico, for the supply of Sepigel bleaching earths, doubling its current production capacity.

The company said the new facility built on the success of its existing plants in Europe and was part of the company's commitment to innovation. The facility's strategic location in Querétaro would allow it to have an important platform in the Americas, guaranteeing efficient service and supply. It would also act as a reference R&D centre.

Minersa said it had more than 30 years of experience in developing mineral solutions for the purification, refining and bleaching of oils and fats, with sales on five continents and a presence in companies and refineries operating worldwide.

The Sepigel brand comprised a complete range of bleaching earths, from naturally active bleaching earths to highly activated clays.