# Moving towards natural clays

**Natural bleaching earths pre-blended with steam activated carbons have been shown to be a beneficial alternative to acid-activated bleaching earths in removing undesirable components during edible oil refining**

*Pat Howes*

Acid-activated bleaching earths have historically been the materials of choice for the bleaching of edible oils.

'Bleaching' earth is actually not a good name for the material, as bleaching earths are multi-functional absorbent/adsorbent, catalysts and ion-exchange media. The removal of both primary – and secondary – oxidation products, gums, soaps and trace metals are some of the additional beneficial features of bleaching earths.

In recent years, poly-aromatic hydrocarbons (PAHs), dioxins, 3-monochloropropane diols (3-MCPDs) and glycidyl esters (GEs) have been added to the list of undesirable components that need to be removed or reduced. Bleaching earths and related absorbents play an important role in removing these impurities.

The catalytic properties of acid-activated bleaching earths help them to decompose the hydro-peroxides, and to crack and protonate pigments that may not otherwise be absorbed within the bleaching earths.

The downside of the catalytic properties includes the promotion of double-bond shift, and conjugation of double bonds, which reduces the oxidative stability of oils that contain polyunsaturated fats, such as soyabean and canola oils. For instance, the conjugation of three double bonds may increase the oil's oxidation rate by 25 times.

Acid-catalytic cis- to *trans*-isomerisation at double bonds also occurs, resulting in unhealthy *trans*-isomers. *Trans* isomers adversely affect the cloud point of the oil. In relation to palm oil, they reduce the olein yield by about 0.1% to 0.2%.

Catalytic polymerisation of the unsaturated components in the oil leads to an increase in the oil's viscosity, which is also undesirable.

Another undesirable acid-catalytic property is the enhancement of the formation of unwanted components such as 3-MCPDs.

The desire to limit non-specific catalytic reactions in the oil is one of the drivers in the trend away from acid-activated bleaching earths and acidic surface-modified bleaching earths, towards natural non-acidic bleaching earths.

There are a range of non-acidic natural clays that are utilised as bleaching earths, including attapulgite, sepiolite, and bentonite, and other clays and their related intergrowth materials.

Attapulgites, although good at removing many impurities, are often not the most cost-effective option, due to their high oil retention. Sepiolites like attapulgites can be good natural clays, but also have high oil retention and low bulk density.

Attaplugites crystals are needle-shaped, ▶


Activated carbons are used to absorb impurities during bleaching of edible oils and are commonly made from coconut shell, coal and wood

▶ Sepiolites are fibrous, whereas bentonites are flat flakey platelets. If you taste some sepiolite-based bleaching earth, your tongue will feel like it has been in contact with fibreglass.

It should be noted that the irritant properties of those attapulgites and sepiolites do not adversely affect the quality of the oil, they are used to refine.

Bentonite and its related intergrowth materials do not generally contain fibrous silicas or other harmful silicas. The bulk density of bentonites is higher than that for attapulgites and sepiolite, and the oil retention for bentonites is lower than that for attapulgite, sepiolite and acid-activated bentonites. For these reasons, many refiners prefer bentonite-based natural bleaching earths.

The benefit of the natural clays is that they do not act as solid acid catalysts. Instead their main action is by absorption/adsorption of the pigments, primary and secondary oxidation products, residual gums, trace metals etc.

There are differences in absorption properties between natural and acid-activated bleaching earths. Natural clays have a lower pore volume than acid-activated bleaching earths. The average pore size of natural bentonite type clays is larger than that of acid-activated bentonite, due to the different cationic composition of the two materials.

Natural clays can absorb larger molecules than acid-activated bleaching earths, which is beneficial for the removal of larger components from some poor quality oils.

In addition to bleaching earths, there are other natural or non-acidic materials that are used for absorptive bleaching. Activated carbons are one such absorbent.

## Activated carbons

Activated carbons have been available for some time, and have been utilised for the absorptive bleaching of edible oils. Acid-activated carbons tend to give the lowest freshly refined oil colours, but give poorer refined oil stability. Steam-activated carbons are slightly more expensive, and generally give a fully-refined oil of crisper appearance and better stability.

Historically, the main problems with activated carbons have been their price, high oil retention, and their friability, leading to fines that are difficult to filter from the oil.

Part of the problem is that the most appropriate activated carbons have not been selected. Normally, refiners would seek activated carbons of high methylene blue (MB), high iodine value (IV), or high carbon tetrachloride (CTC) value, as these have the highest absorption capacity.

However, activated carbons of the highest absorptive capacity have the weakest structures, and more easily break down in pumps and other equipment when utilised at the refinery, leading to problems with fines.

To overcome this problem, it is best to select activated carbons that have the desired mechanical strength. These tend not to be the activated carbons with the highest MB, IV, or CTC.

Not only would the lower MB, IV and CTC material have greater mechanical strength, but they could also exhibit a greater bond strength, for the removal of the undesirable impurity, as compared with activated carbons with the highest MB, IV and CTC. Lower MB, IV and CTC activated carbons have a lower oil retention, which approaches that of attapulgites.

Activated carbons are made from a wide range of substrates; commonly used materials are coconut shell, coal and wood. Each activated carbon has its own pore size distributions, covering micro-, meso- and macro-pores.

Ideally, the refiner needs to match the porosity of the absorbent with the sizes of the impurities they wish to remove.

The formulation of bleaching earths with activated carbons provides a range of pore sizes. Optimisation is not an easy task for the refiner, especially when the composition of the oil being refined changes with time/batch.

Some bleaching earths producers utilise a number of activated carbons in their blends with natural bleaching earths. In this way, the impurity removal properties of the pre-blended bleaching earth with activated carbons will have the ability to absorb the widest range of impurities.

Pre-blended natural bentonite type bleaching earth, with the mechanically stronger activated carbons, can have a similar oil retention to acid-activated bleaching earths, while maintaining particle integrity and optimising absorptive performance.

## Increased challenges

In recent years, the challenges for refiners have increased. In addition to the removal of pigments, oxidation products, gums and trace metals, refiners now need to remove PAHs and dioxins, and mitigate 3-MCPDs and GEs. Activated carbons are good at removing PAHs, dioxins and chlorine and chlorine- containing compounds.

The formation of 3-MCPDs has been attributed to acid-catalytic reaction of chlorine/chloride with the partial glycerides present in the oil. Activated carbons blended with natural bleaching earths have been shown to reduce the formation of 3-MCPDs. This action has, in part, been attributed to the lack of acid-catalytic behavior in the natural bleaching earth and steam-activated carbon blend, and to the removal of chlorine/chloride by the activated carbon.

Natural bleaching earths pre-blended with steam activated carbons have been shown to be a beneficial alternative to acid-activated bleaching earths for refining edible oils, while minimising the formation of undesirable components such as PAHs, dioxins and 3-MCPDs. ●

*This article was written by Dr Pat Howes, technical director at Malaysia's Natural Bleach Sdn Bhd*