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Most activated carbons manufactured in China and the USA are coal-based

Activated carbon is used to remove a wide range of impurities during edible oil processing, and producers must take into account properties such as particle size, activation level and base materials when designing an activated carbon to meet refining requirements

Dr Patrick Howes

Design and use of activated carbon

Activated carbon has been utilised as an adsorbent for many years in the refining of edible oils, particularly for the removal of impurities that are not so efficiently dealt with by bleaching earths alone. Activated carbons also impart clarity and enhanced stability in fully refined oil.

The ability to remove a wide range of impurities including pigments, dioxins, pesticides, polycyclic aromatic hydrocarbons (PAHs), polychlorinated biphenyls (PCBs), chlorine, chloride and organo-chlorine molecules makes activated carbon an important processing aid in the refining of edible oils.

While activated carbons are very useful adsorbents of impurities, historically, there have been problems associated with their use. This has been mainly due to the breakdown of the activated carbon particles into fines, the high unit cost of the activated carbons, and high oil retention of the spent activated carbons. High oil retention in the spent carbon results in increased refining costs.

The activated carbons utilised in edible

oil refining are in powdered form and are either added separately or pre-blended with bleaching earths. Due to the difficulty of cleanly handling 100% activated carbon, it is more convenient for refiners to utilise activated carbons that are pre-blended with bleaching earths.

The above mentioned factors need to be considered when designing activated carbons for use in edible oil refining.

Particle size, activation level

Particle size distribution is an important factor in an activated carbon. Generally, it is a good idea to have an average particle size slightly larger than that of bleaching earths, for example, 29 microns versus about 25 microns for bleaching earths.

The proportion of fine particles below 5 microns should be lower than that for bleaching earths, thus minimising the likelihood of breakdown into sub-micron fines that are problematic with poorly designed activated carbons.

It is important to utilise a low-shear blender when mixing activated carbons



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Activated carbons are used to remove a wide range of impurities in edible oils including pigments, dioxins, pesticides, PAHs, PCBs, chlorine and chloride and organo-chlorine molecules

- ▶ with bleaching earths. Pneumatically conveying the activated carbon and its blends with bleaching earths should be carried out in pipework, with no sharp or small radius bends to reduce shearing forces. This is to minimise particle breakdown into fines.

Fines generated from the breakdown of the activated carbon particles at the bleaching stage are mainly due to inter-particle attrition from shear at pumps. The fines can break through at the filters, passing through the polishing filters into the deodoriser. They can also break through at the deodoriser polishing filters into the storage tanks, and thereafter carried forward to a certain extent in the fully refined oil.

When it comes to activation levels in activated carbon, it should be noted that higher levels result in greater porosity, resulting in more oil loss in the spent activated carbon and weaker, less durable particles. It is therefore necessary to activate the carbon only to a level where it still retains sufficient mechanical strength to withstand the forces encountered during the bleaching and filtration processes.

These activated carbons will not have the highest possible performance but can be utilised without encountering the problems of fines generation and high oil retention.

The yield of moderately activated carbons is higher than that for highly activated carbons, so the production costs are lower. For this reason, a greater

dosage of activated carbon can be more affordable.

Once the activation level has been matched to the strength/attrition resistance requirements, the next step is to consider the type of carbon-rich base material from which to produce an activated carbon.

Carbon-rich base material

Activated carbons can be manufactured from a wide range of carbon-containing materials.

There is an increasing move towards sustainable sources and particular interest in the utilisation of 'waste' materials.

The selection of the material from which activated carbon is made from is important in terms of the durability and adsorption properties of the resulting activated carbon.

Some common materials from which activated carbons are made from are coals (bituminous, lignite, anthracite); shells (including coconut, palm kernel and hazelnut shells); woods (such as pine, acacia and eucalyptus); and other materials such as peat, olive stones and bamboo. Waste materials such as sugarcane waste, used tyres, agricultural waste (seeds, shells), plastics (PET), clothes (polyacrylnitrile – PAN), and biomass rich in lignocellulosic materials (such as palm fronds and trunks) can also be utilised for the manufacture of activated carbons for certain edible and non-edible applications.

Kosher and Halal requirements must

always be adhered to when verifying the source of the carbon-rich base material as the activated carbon will be utilised in the processing of edible oils.

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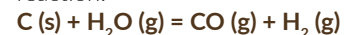
Producing activated carbon

The first step in the production of activated carbon is called pyrolysis. It involves heating the carbon-rich base material at about 450°C in the absence of air, to remove most of the volatile components, to form charcoal.

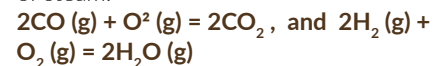
This stage may be followed by a washing step to remove components such as soluble ashes.

The charcoal is then further activated with steam and/or chemicals such as zinc chloride (ZnCl₂), sulphuric acid (H₂SO₄), phosphoric acid (H₃PO₄), potassium hydroxide (KOH) and hydrochloric acid (HCl) to enhance the porosity and modify the surface of the activated carbon.

Steam activation at about 1,100°C develops the pore structure by removing some of the carbon via the following reaction:



The carbon monoxide and hydrogen formed are burnt to provide energy for the heating of the carbon and generation of steam:



The steaming process takes about one hour and removes some of the carbon, increasing the porosity.

The removal of carbon results in reduced yield of the activated carbon, thus increasing the production costs for the activated carbon.

Chemical activation is carried out at lower temperatures, for a much shorter period, resulting in an increased production rate, lower energy costs and higher yields. These factors help to reduce the production costs.

Steam-activated carbons are preferred for many applications as their surfaces tend to adsorb impurities without otherwise modifying the oil being processed.

Chemically-activated carbons, while still predominantly adsorbents, are more likely to act as catalysts that can modify the oil being processed.

Such modifications of the oil may not be beneficial to the colour and oxidative stability of the oil.

The nutritional benefits of the oil may also be adversely affected by *cis*- to *trans*-isomerisation or a double bond shift.

However, the different nature of the

surfaces in chemically-activated carbons can be advantageous for the adsorption of certain impurities. The structure of the carbon-rich base material can be beneficially retained in some activated carbons, whereas other activated carbons may be less structured or amorphous.

Pore size

Activated carbons can have a wide range of pore sizes within a single material. These pores are classified into micro-, meso- and macro-pores (see Figure 1, right) and their ranges are shown in the following table (see Table 2, below). It should be noted that there is no pore-classification system that is universally accepted.

The various sizes of pores are beneficial as each type allows preferential adsorption of impurities of a size that fits snugly into that size of pore. The macropores and mesopores also act as pathways for the impurities to be transported to the micropores. The tenacity at which the impurities are held in the pores depends on the nature of the various sites on the adsorption surface.

Adsorption measurements in activated carbons normally utilise one or more of the following materials: nitrogen, butane, iodine, methylene blue, molasses and tannins (see Table 1, below).

While nitrogen Brunauer-Emmett-Teller (BET) measurements can measure both the surface area and pore size distribution of activated carbons, it should be noted that the surface area as measured in nitrogen BET measurements may not be available for all the impurities to be removed, as it depends on the size, shape and nature of the impurity.

That is why it is useful to consider the adsorption properties using a range of probe molecules of different sizes and shapes.

Molasses have a molecular weight of about 200. Tannins are large molecules with molecular weights from about 500 to over 3,000 and are useful for measuring the larger pores in activated carbons.

Surface of activated carbon

The nature of the surface of the activated carbon is also important with respect to the tenacity with which the various impurities are held within the activated

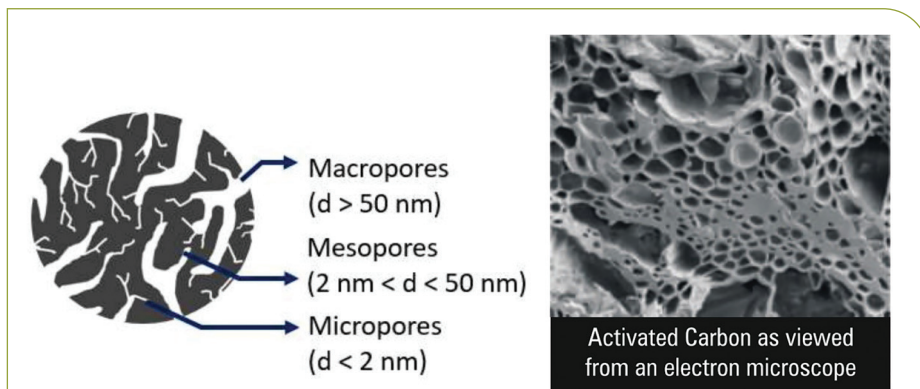


Figure 1: Classification of activated carbon pore sizes



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carbon. This is particularly important during the steaming/blowing stage for the spent adsorbent on the filters, where the impurities could be lost back into the filtered oil if not held strongly within the activated carbon containing filter-cake.

The nature of the surfaces has been designated H- and L-type activated carbons. H-type steam-activated carbons – being hydrophobic – absorb H⁺ ions from water and are alkaline.

L-types absorb hydroxide (OH⁻) from water and are acidic.

There are several types of different adsorption sites possible on activated carbon surfaces including graphitic and oxidised sites.

Conclusion

When selecting activated carbon for a specific application, factors such as the molecular size, shape and type of the particular impurity to be removed are important. This may be difficult when refining an edible oil as there can be a wide range of impurities present, all of which need to be removed. One strategy is to use more than one type of activated carbon blended with the bleaching earth, so that a wide range of impurities can be removed at the bleaching stage.

Activated carbons pre-blended with bleaching earth are now the choice of many for everyday refining, as the blended products remove the widest range of impurities, resulting in fully refined oils of good colour, enhanced stability, and crisp bright appearance.

Dr Patrick Howes is technical director of Natural Bleach Sdn Bhd, Malaysia and will be speaking on 'Designing Bleaching Earths and Activated Carbon' at OFI International 2024 in Rotterdam on 9-11 September www.ofimagazine.com/ofievents

N2	3Å (angstroms) = 0.3nm	for micropores (BET pore size distribution)
Butane	4.7Å	for micropores
Iodine	4.94Å	for micropores
Methylene blue	17.0 x 7.6 x 3.3Å	for large micropores >15Å and mesopores
Molasses	>20Å	for mesopores above 20Å
Tannins	>30Å	for larger mesopores and macropores

Table 1: Adsorption measurements in activated carbon using various materials

Type	IUPAC (1985)	McDougall 1991	OFI (TIGG)
Micropores	< 2nm (<20Å)	0.8 to 10nm (8-100Å)	<10nm (<100Å)
Mesopores	2 to 50nm (20-500Å)	10 to 50nm (100-500Å)	10-100nm (100-1,000Å)
Macropores	> 50nm (> 500Å)	50 to 2,000nm (50-20,000Å)	>100nm (>1,000Å)

Table 2: Range of pore sizes in activated carbon