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The growing focus on renewable energy and fuel is leading to greater production of biofuels from waste feedstocks

The different processes to produce biodiesel and HVO have their own requirements for feedstock quality, requiring different pre-treatment processes and bleaching earths

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Role in biodiesel/ HVO production

There has been increasing interest in biofuels due to finite supplies of fossil fuels, the desire to reduce the carbon intensity of fuels in order to cut greenhouse gas contribution to global warming, and the general desire for a more sustainable future.

The first generation of biofuels included bioethanol and biodiesel. Bioethanol is utilised in blends with petroleum for spark ignition engines (petrol internal combustion engines), whereas biodiesel is used in compression combustion engines (diesel engines).

Bioethanol can be manufactured via the fermentation of sugars or other carbohydrates sources such as corn, maize, sugar beet and waste straw. Bioethanol is usually blended at a rate of 15% in petrol, although up to 85% bioethanol can be handled by some engines. Bioethanol is biodegradable and, due to being distilled, is clear and colourless.

Biodiesel can be manufactured from edible oils (triglyceride oils) or fatty acids, yielding fatty acid methyl esters (FAMEs). FAME biodiesel is typically blended with mineral diesel at levels of up to 30%, although 100% FAME biodiesel can be utilised in some engines.

The use of edible feedstocks to produce fuel has raised 'food vs fuel' concerns and is considered undesirable.

FAME biodiesel can also be manufactured from used cooking oils (UCO) or waste oils provided that the oils have been appropriately pre-treated before esterification and/or trans-esterification processes.

Sources of materials for the sustainable manufacturing of biodiesel are plentiful. The current global production of edible oils is more than 200M tonnes/year and continually increasing. From this, more than 40M tonnes/year of UCO is produced. There are also animal- and vegetable-based waste oils such as palm oil mill effluent (POME) and palm press fibre oil (PPFO) that can be utilised as feedstocks for biofuels once properly pre-treated. Other renewable feedstocks are continually being developed to achieve the vision of a sustainable future.

Most UCO and waste oils are collected from restaurants or industrial food processing factories, with a lesser amount from domestic users due to difficulties in logistics.

The variability in quality of the various feedstocks sometimes requires blending before feeding to the treatment plant, to keep the levels of the impurities within the capabilities of the processing plant.

The main issues with FAME biodiesel are that it easily oxidises, absorbs water from the atmosphere, has a low cloud point and, in cold weather, leads to clogging of fuel filters. At high blend ratios, FAME biodiesel can damage engine seals.

HVO

To overcome the issues related to FAME biodiesel, the next generation of biofuels are paraffinic hydrogenated vegetable oil or hydrotreated vegetable oil (HVO) fuels.

Paraffinic fuels are usually made from UCO, sludge oils or other waste oils. Paraffinic oils can be utilised at 100% as a replacement for mineral diesel, or in blends with mineral diesel. HVO paraffinic oils are cleaner than mineral diesel and are more environmentally friendly as they do not contain any aromatic hydrocarbons.

Paraffinic biofuel is typically manufactured by the hydrogenation of used or waste triglyceride oils or fatty acid distillates. After thorough pre-treatment of the feedstock, the hydrogenation process removes all the remaining oxygen, nitrogen, chlorine and sulphur. This produces a very clean, low-carbon oil with good oxidative and cold stability, with low sulphur and aromatics content and no tendency to absorb water, which has a higher hydrogen content and calorific value compared with esterified or trans-esterified biodiesels.

The composition of HVO paraffinic fuels are close to mineral diesels. One of the most promising uses of HVO is as a sustainable aviation fuel (SAF). Singapore has already mandated that from 2026, all aircraft departing from Singapore must use fuel containing SAF, with increasing proportions of SAF being phased in over successive years.

Pre-treatment

The three processes for producing biodiesel – esterification, trans-esterification and hydrogenation – each have their own requirements for the quality of the feedstock. Thus, the pre-treatment of feedstocks must be designed to meet the individual needs.

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Used cooking oil can contain a wide spectrum of impurities including burnt food fragments, spices and salts from seasonings, proteins from foodstuffs, oxidiesed and polymerised oils and fats, and dark brown melanoidin pigments formed from the Maillard reaction

When starting from virgin edible oils the pre-treatment process can be the same as that normally utilised in edible oil refineries. When the feedstock is used or waste oil, the pre-treatment processes need to be more thorough.

For the manufacture of FAME when the pre-treated oil has high free fatty acid (FFA) levels, methanol solvent with homogenous acid-catalysed esterification is used, for example, with sulphuric acid or para-toluene sulphonic acid (PTSA). This is followed by alkali trans-esterification, with methanol and a homogeneous alkaline catalyst such as sodium methoxide. For esterification and trans-esterification, the catalysts are homogeneous. For HVO, the catalyst is heterogeneous.

The composition of UCOs and waste oils can be very variable. UCO can contain a wide spectrum of impurities that need to be removed. These impurities include:

- Solids such as burnt food fragments
- Spices and salts from seasonings including sodium chloride and MSG
- Phosphorous and nitrogen compounds
- Proteins from foodstuffs
- Metals such as sodium, calcium, magnesium, iron, copper and other trace metals from the foodstuff or implements that have been in contact with the oil.
- Oxidised and polymerised oils and fats including those from the foodstuffs that have been cooked in the oil.
- Plastics that have inadvertently entered the oil such as from packaging materials or ear tags from animals in the rendering process, or deliberately added to the oil in the form of straws or plastic bags to increase the crispness of products deep-fried in the oil.
- Dark brown melanoidin pigments formed from the Maillard reaction between amino acids and reducing sugars at the high temperatures of deep fat frying

All these impurities need to be reduced or removed during pre-treatment of the oil, otherwise downstream processing will be adversely affected and the desired product specification will not be met.

Filtration

An important first step in the treatment of UCO and waste oils is to filter the oil to remove any solid impurities such as sand, food solids and plastic solids.

Water washing the filtered oil is beneficial for reducing or removing water-soluble impurities such as soaps, salts and some other polar organometallics.

Wet or dry degumming with phosphoric or citric acid, other degumming agents or enzymatic degumming is required to remove or condition the phosphorous gums and metals salts as far as possible before the bleaching stage.

Chelative degumming with citric acid enhances the removal of phosphorous and metals.

Wet degumming is preferred for UCO and waste oils even if the phosphorous level is below 50ppm, as wet degumming will also enhance the removal of other impurities, thereby reducing the demands on the bleaching earth and minimising bleaching earth consumption.

If gums and soaps are not removed, they can block the surface and the pores of the bleaching earth, reducing its efficiency.

At the adsorbent stage, the bleaching earth adsorbs or decomposes oxidation products such as hydroperoxides, aldehydes, ketones, heterocyclics, polymers, pigments, residual soaps, phosphorous compounds and trace metals.

Natural vs activated

There are differences in the ways natural and acid activated earths perform

Natural bentonite clays act mainly as adsorbents and have a higher cation exchange capacity (CEC) compared with acid-activated bleaching earths.

Acid-activated bleaching earths have adsorbent properties and are solid acid catalysts. The acid catalytic properties allow acid-activated bleaching earths to decompose the primary oxidation products – hydroperoxides – into secondary oxidation products such as aldehydes and ketones, which may then be adsorbed by the bleaching earth.

Residual soaps can be adsorbed onto the exterior surface of the bleaching earth particles and may form a barrier that reduces the performance of the bleaching earth.

Acidic sites on the surface of acid-activated bleaching earths can split the soap, yielding metal cations and free fatty acids. The acidic sites can also crack or protonate pigments so that they are no longer visible. Removal of some of the pigments is cosmetic, but larger pigments need to be removed to prevent them blocking the pores and deactivating the heterogenous catalyst utilised in the hydrogenation process.

While the acid catalytic function of acid-activated bleaching earths is useful for cracking impurities, there is also a downside in that undesirable acid-catalysed isomerisation and polymerisation reactions may occur, depending on the processing conditions at the bleaching stage.

'A wide range of adsorbents can be utilised to produce biofuels including natural and acid-activated clays, activated carbons, zeolites, magnesium silicates and silicas'

Natural bentonites have larger pores than acid-activated bentonite but a lower nitrogen surface area and lower pore volume.

Activated carbons have a high surface area and pore volume, and can have a full range of micro-, meso- and macropores.

Each material has its own advantageous properties.

Different adsorbents

A wide range of adsorbents can be utilised to produce biofuels including natural and acid-activated clays, activated carbons, zeolites, magnesium silicates and silicas. Each adsorbent has its own special properties. Bleaching earths are often formulated from two or more adsorbents to achieve all the desirable functions to remove impurities, while minimising any undesirable side reactions.

The selection of the bleaching earth is very important as some bleaching earths cause the oil to gel when mixed with UCO or waste oils, such that it is impossible to filter the spent bleaching earth from the oil.

It is important to remove chlorides and organochlorines prior to hydrogenation for the HVO process, otherwise the hydrochloric acid produced during hydrogenation could lead to excessive corrosion of the process equipment.

This can be achieved by utilising bleaching earths together with activated carbons, as activated carbons can adsorb both residual chloride and organo-chlorines.

Natural- and acid-activated bleaching earths pre-blended with activated carbon are now increasingly utilised as a cost-effective adsorbent system for refining a wide range of oil qualities and oil types.

For the HVO process, it is necessary to remove those impurities that could adversely affect the performance or lifespan of the heterogenous hydro-treating catalyst by blocking its pores and surfaces. The filtration stage for the spent bleaching earth can be considered as a guard bed that protects the hydrogenation catalyst.

Spent bleaching earth

Spent bleaching earth typically contains about 20-25% residual organic materials. It is therefore beneficial to utilise the spent bleaching earth directly as a fuel – such as in in the cement industry – or the spent bleaching earth oil can be extracted and converted into biofuel.

Fortunately, the hydrogenation process that takes place at high temperature enables removal of residual sulphur as hydrogen sulphide gas, nitrogen as ammonia gas, and oxygen as gaseous water. The sulphur can be beneficially recovered from the hydrogen sulphide. The distillation process following hydrogenation leads to very clean paraffinic fuel with no aromatics or oxygenated products.

Although current biofuels such as sustainable aviation fuel (SAF) can only be viable when they are subsidised or legislated for by governments, the desire for a sustainable future and the efforts to utilise a wide range of waste foodstuffs and agricultural wastes as alternative sources of oil-based feedstocks indicates that biofuels will have increasing importance in the years to come.

Process plant contractors and bleaching earth manufacturers will continue to innovate their products to meet the challenges as sustainable biofuels markets expand. •

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