The search continues to find catalysts that can handle high free fatty acids (FFAs) as well as triglycerides, do not require a process for their recovery, and produce high purity or no glycerol by-product

Heterogeneous catalysts – a step change in biodiesel processing

by Brian Warshaw

Despite well-known disadvantages, the majority of biodiesel is still produced using base catalysts such as sodium and potassium hydroxides dissolved in methyl alcohol.

This is partly due to a long historic usage, and partly because they are inexpensive to obtain and prepare. But this mood is changing with the increased use of more effective base catalysts such as the methylates or methoxides; and the progressive availability of porous solid, or heterogeneous catalysts that are coming out of the laboratory as commercial products, proving to be viable alternatives.

In general, the traditional base catalysts, being homogenous, and in liquid form, suffer a disadvantage in that they are difficult to recover and recycle, as well as leaving trace amounts in the product. Heterogeneous catalysts can be retained in place, remain available for reuse, and do not contaminate the Fatty Acid Methyl Ester (FAME) or Vegetable Oil Methyl Ester (VOME) biodiesel.

According to Michael Markolwitz, responsible for worldwide marketing of sodium and potassium methoxides at Evonik Degussa, two-thirds of currently operating large facilities can use these products.

Typically these are the plants with an annual capacity of between 50,000 and 300,000 tonnes, in which the methoxides would replace the use of the corresponding hydroxides plus methanol, as the base catalyst.

Although not alone in manufacturing the methylates, it is little wonder that with such a large potential market, Evonik Degussa is pursuing an aggressive marketing policy.

Currently the products NM30 (sodium methylate solution), and KM32 (potassium methylate solution) are manufactured in Germany at Niederkassel-Lülsdorf near Cologne; but at the end of March 2009 it is opening a 60,000 tonnes plant in Mobil, Alabama, US, which will serve the North American Free Trade Area.

Evonik Degussa supplies its NM30 as a ready to use solution of 30% sodium methylate in methanol. Used with rapeseed oil in a ratio of 1 tonne to 17 or 18 kg of catalyst, the resultant rapeseed oil methyl ester is separated from the glycerol, and the catalyst is neutralised at the end of the process. The KM32 solution is primarily used to process waste cooking oils.

Markolwitz explains that NM30 has two major advantages over the traditional use of hydroxides. The mixing of sodium hydroxide with methanol produces an exothermic reaction and both dedicated equipment and staff to do this, whereas the alkoxide NM30 is supplied in an ISO container that is emptied into a local storage tank, and from that moment is safely handled in a closed system.

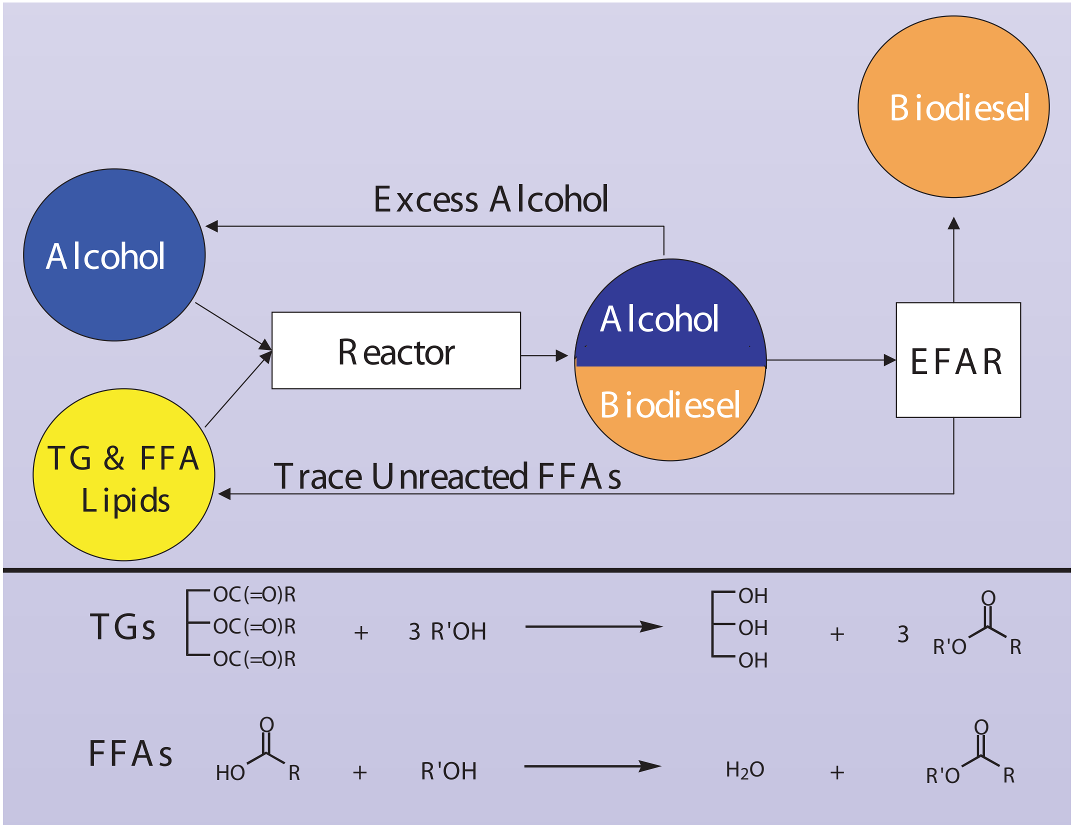
Another disadvantage is of soaking the hydroxide in methanol, so that it is impossible to prevent a percentage of water being formed, and this water disturbs the transesterification process. The inclusion of water causes a loss in FAME yield, and according to the experience of some customers who have changed from hydroxides to alkoxides, this can be as high as 25%.

Technology for the next generation of biodiesel

Perhaps the best known of the relatively new solid catalytic processes is the fixed-bed, heterogeneous system to produce VOME and glycerol from vegetable oil and methanol, developed by the Institut Français du Pétrole (IFP), and designed and commercialised by its subsidiary, Axens.

The latest version of the process is the Esterfip-H, which uses a heterogeneous catalyst described as a spinel mixed oxide of two non-noble metals that necessitates the catalyst being neither recovered from the product nor subjected to aqueous

The Mcgyan process: a continuous reactor



Source: McNeff Research Consultants

treatment. The first Esterfip process using a homogeneous process was started in 1992, followed by the Esterfip-H process, which was commissioned in Q1 2006 for Sofiproteol at Sete in France.

Whereas Axens uses a catalyst comprising a combination of zinc and aluminium metal oxide pellets, the Mcgyan process uses a porous solid zirconium oxide based catalyst.

A Cat's eye view

Later, in June this year, when the 3 million gallon a year (11.36 million litres) Ever Cat Fuels refinery at Anoka, Minnesota, has produced its first biodiesel, McNeff Research Consultants will be pushing ahead with the licensing of the process.

The initial oil feedstock will come from corn waste, the residue from a local ethanol processing plant. This will be combined with alcohol, and passed through the tube reactor. The particles packed into the reactor are chemically and thermally stable, which allows them to be operated at high temperatures and pressures without any loss in conversion efficiency over long periods of use, and enabling the catalytic conversion of the triglycerides and FFAs into FAME.

Two processes remain to be completed. First, the separation of alcohol from the biodiesel; and then a final polish in the Easy Fatty Acid Removal vessel, where biodiesel is separated to storage, and traces of unreacted FFAs removed. The FFAs and the alcohol are returned to their respective tanks, and reused in the continuous process cycle. Heat from the liquid leaving the reactor is exchanged with the liquid entering the reactor, thereby reducing the energy requirement of the process.

During the initial development a piloting of the process, methanol, ethanol, and propanol were each

Source: Ever Cat Fuels

Aerial view of Ever Cat Fuels facility

successfully tested and found to be suitable alcohols. As too, were 20 oils, fats, and greases, including refined algae oil. Ever Cat has concluded an agreement with Great River Energy to cooperatively develop a production system to process algae, which has a high FFA content in the oil.

The Mcgyan process is a catalytic conversion where water does not play a role. This is fairly rare.

The cost of the Ever Cat biodiesel facility has been contained within the planned \$5 million (€4 million) that included the purchase of the three-acre (1.2 hectare) site, a 9,000 square feet (836 m^2) production building, eight large, and four small tanks, a truck loading unit, and site infrastructure. When it was planned, Ever Cat anticipated a ten-fold production expansion once the process had been proved at scale, and contiguous to the site is a further 4.87 acre (2 hectare) parcel of land.

One heterogeneous catalyst serves all processes

Catilin has completed 18 months of tests on its T300 catalyst

With food-based feedstock oils costing around two-thirds of the end product, it is not surprising that Catilin, based in Iowa, USA, has focused on developing a catalyst that will inclusively process the less expensive oil materials; the high FFAs, and algal oils.

Although there is little independent information on oil yields that can be obtained from algae, some sources have suggested that this could be almost 1,000 m^3 per hectare. The company's T300 catalyst has very high catalytic activity that allows its use at standard operating conditions. It is granular, has an average particle size of 35 microns, and a density greater than two grammes per millilitre to ensure easy separation from the FAME and glycerine. The catalyst does not contain metals, and is non-toxic, thereby eliminating disposal problems. Catilin has now completed 18 months of laboratory and pilot plant tests.

According to the company, the catalyst can be reused many times, and can be deployed in existing production facilities since a fixed bed reactor is not required.

The catalyst operates at temperatures similar to that used by the hydroxides, averaging 68°C, and at one atmosphere pressure. The conversion through the reactor takes typically one hour, and the retention time will determine the ratio of catalyst to oil.

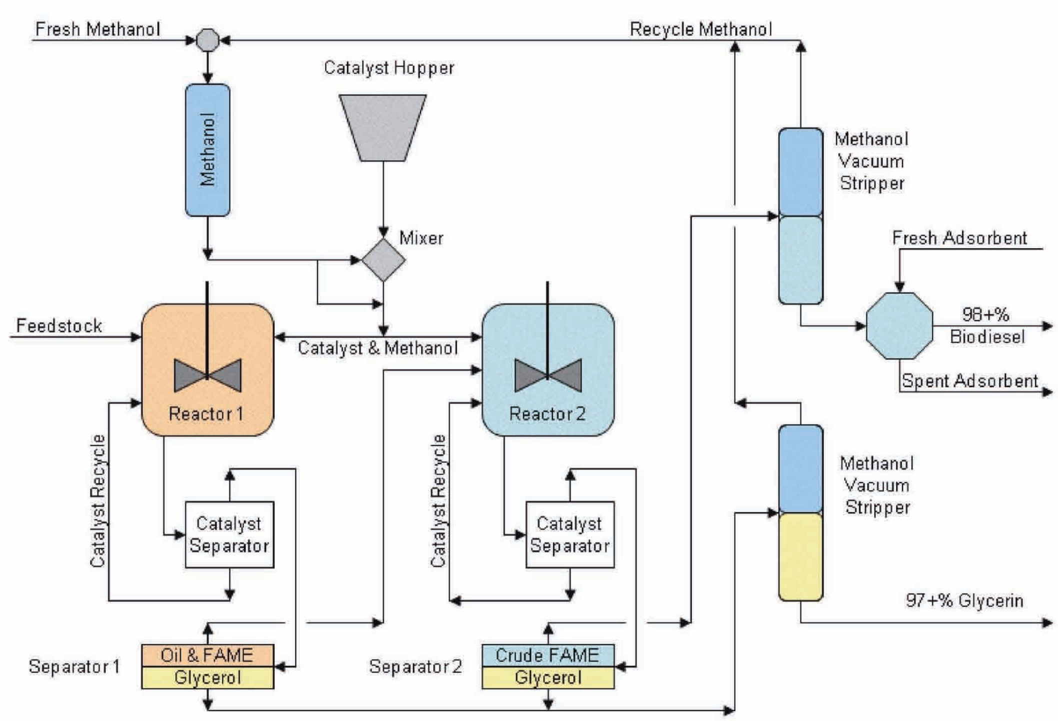
After combining the feedstock, methanol, and catalyst in the reactor, they are subject to continuous stirring, thereby retaining the catalyst in suspension. Egressing the first-stage reactor, the fluid comprises unconverted oil, FAME, glycerine, methanol, and catalyst. A separator recovers the catalyst and recycles it back to the reactor. The remaining semi-processed oil and methanol is reprocessed in a parallel reactor where the purity of the methyl ether and glycerine is increased. Following separation, the methanol is stripped and returned to the start of the process, and the glycerine sent to storage. The biodiesel is absorbent dried, and ready for use.

In pilot trials, the biodiesel produced with the T300 catalyst and refined, bleached, and deodorised soyabean oil complied with the requirements of ASTM D6751-08, and the European Standard EN 14214, including the ASTM 6217, and EN 116 cold filtration tests.

The commercialisation of new porous solid heterogeneous catalysts in biodiesel production is just three years old so other companies are likely to come out with similar offerings.

For the time being research in this area is clearly aimed at developing solid catalysts with high surface areas that can neutralise acids and produce the biodiesel in a single step.

Catilin process flow diagram



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