CHEMICAL ECONOMICS - BIODIESEL AND BY-PRODUCTS - GLYCERINE

In a chemical process, if by-products have no or little value then processes should be refined to minimise their production and eliminate waste disposal costs. For many processes by-products are a significant outcome which cannot be eliminated. The essence of many a successful chemical business is maximising the sales revenue from such by-products. The impact of the value of by-products is well illustrated in the production of biodiesel from vegetable oils and fats.

Biodiesel is a mixture of fatty acid methyl esters (FAME) produced by the trans-esterification of oils and fats using methanol. The by-product is glycerine (glycerol).

Regional agricultural considerations tend to determine the source of FAME. In the USA, soybean is a major source, in Europe it is rape (Canola) and in our region palm oil is a major feedstock. Many other seeds can be used if available. Another source in our region is tallow (beef and lamb fat) produced from meatworks.

From seeds, the first step in the process is the milling (crushing of the seed) to produce the vegetable oil and a by-product meal used as cattle feed. So at this first stage, the ultimate production cost of the biodiesel is dependent on three variables - the cost of the seeds (farm economics, seasonal influences), the value of the vegetable oil and its alternate use as a foodstuff, and the value of cattle feed. Clearly the processing margin at the mill will influence the price paid for the vegetable oil for biodiesel.

Oils and fats are tri-glyceride esters of fatty acids. Although many enthusiasts use these oils as diesel fuel, the high viscosity and contaminants make them unsuitable for use as quality biodiesel. The oil produced is trans-esterified with methanol to produce FAME and glycerine. The process removes impurities and reduces the viscosity making the produced FAME a suitable diesel fuel, especially when blended with conventional diesel to produce a blend such as B5 or B20 (5% and 20% blend of biodiesel and petroleum diesel respectively). Higher blends are possible but the use of high levels of FAME is generally not recommended by vehicle manufacturers without changes to engine components such as pumps and injectors.

The inputs are oil and methanol and the outputs are FAME and crude glycerine. Methanol prices are sometimes quite volatile and this volatility has to be accommodated in the process economics.

Refined glycerine has a large demand in food, cosmetics and other high added value industries. There are several grades, with some grades such as Kosher being exclusively produced from vegetable oils. In the early days of biodiesel production, glycerine was a by-product of quite significant value. However, as the biodiesel industry has expanded so as the production of glycerine and this has seen the relative price of glycerine fall.

The fall in the price of glycerine has had a major impact on the production cost of FAME. This is illustrated in the figure which takes account only the feedstock (in this case Canola oil @ $500/t) and methanol costs ($300/t); operating and capital costs are not included.
This figure illustrates the dramatic dependence of the cost of biodiesel production on the achieved value of the by-product glycerine. At current oil prices diesel is traded at about 50c/L which requires crude glycerine prices in excess of $800/t compared to recent prices below $500/t.

The declining profit of bio-fuel operations in the face of declining glycerine prices and the glut of glycerine on the market has sparked research into alternate uses for the glycerine. One is the selective hydrogenation to produce 1,2-propanediol which is a high valued product produced from propylene oxide. This is making some impact on the 1,2-propanediol market but it is not a perfect substitute with preference for some uses still favouring the relatively expensive propylene oxide route. Another idea is the selective hydrogenation to 1,3-propanediol another high valued chemical.

A consequence of poor FAME economics is to promote an alternative approach to bio-diesel so called "green" diesel. In this process the vegetable oil or tallow is treated at high temperature and pressure with hydrogen over a catalyst to hydrogenate and decarboxylate the glycerol esters to produce paraffins and propane. For example a C18 fatty acid ester produces a mix of C17 and C18 paraffins and propane. These products are completely compatible with mineral diesel and LPG (propane). This route avoids the compatibility issues of FAME and conventional diesel as well as avoiding the production of crude glycerine.

Green diesel can be produced in small scale plants producing 100% bio-fuel for blending or use. It can also (with a bit of adaption) be utilised in a conventional refinery hydro-treater producing diesel and directly produce a blend of biodiesel and mineral diesel, e.g. B5 can be produced by hydro-treating conventional gas-oil with 5% vegetable oil or tallow added to the hydro-treater feed. Using a conventional oil refinery process unit avoids the capital cost of building and operating a bio-fuel facility. The economics are almost entirely determined by the price of the vegetable oil relative to that of diesel and LPG.

This route can also be used to produce bio-jet fuel by choosing oils with high C14 and C15 ester content such as coconut oil.

The concept of green diesel has gone further to the concept of bio-refinery in which vegetable oils and tallow are hydro-treated to produce 100% bio-jet, bio-diesel and bio-LPG.
As various jurisdictions legislate for the inclusion of more renewable fuel in the conventional fuel mix, the concept of a bio-refinery is of increasing interests. For example the Italian company ENI has converted its refinery near Venice to produce more that 300,000t/y of 100% renewable fuel.

The major downside for this process is the source of the feedstock. The preferred feed (because of relatively low price as a consequence of high crop yields) is palm oil. This is now being shipped in large parcels to bio-refineries in Europe and around the region for the production of bio-fuels so as to achieve government legislated mandates. This is adding considerably to the demand for palm oil leading to the destruction of tropical rain forests for increased oil production.

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