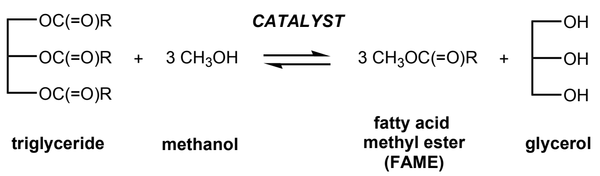
Power to the People

Biofuels

UNIVERSITY OF BATH

Petroleum products and other fossil fuels provide the economies of the world with their main source of organic carbon but this is not sustainable. Reserves are limited and emissions resulting from their use causes major environmental concerns. Biomass currently offers the only sustainable source of organic carbon and, in turn, *biofuels* such as biodiesel and bioethanol offer the only sustainable source of liquid fuels [1]. In addition to representing a renewable resource, biofuels generate significantly lower greenhouse gas emissions than fossil fuels and are potentially CO_2 neutral. In recognition of these advantages, the EU has set a target of 5.75% of all fuel sold to be derived from biological sources by 2010.

A significant proportion of this target will be met by wider utilisation of *biodiesel,* which is obtained by chemical modification of vegetable oils. It is therefore essential to develop more efficient biodiesel production methods in order to improve economic viability and to further reduce its environmental impact.



Scheme 1: *The transesterification of vegetable oil with methanol to yield biodiesel (FAME) and glycerol*

Of course, the use of biomass for fuel is not new and, in some respects, represents a return to the pre-petroleum era of the 19th century. For example, in the mid-1800s, 90% of the US energy and fuel needs were met by biomass. Ironically, about the same time as fossil fuels were becoming the preferred energy source, Rudolph Diesel was demonstrating the use of peanut oil in his new combustion engine. He was quoted as saying:

> "*they [diesel engines] make it certain that motor-power can still be produced from the heat of the sun, which is always available for agricultural purposes, even when all natural stores of solid and liquid fuels are exhausted*" [2].

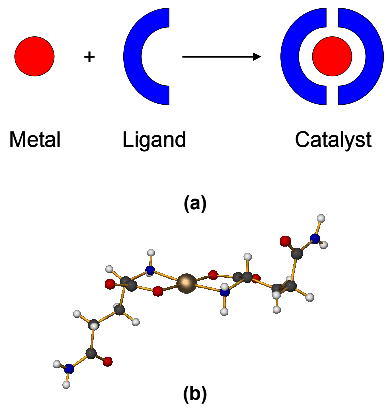


Figure 1: *(a) formation of a metal-based molecular catalyst; (b) a zinc-amino acid biodiesel catalyst*

Today, biodiesel is derived from vegetable oils. These contain *triglycerides,* which are one of the major classes of high energy density liquid molecules generated by biomass. Triglycerides come from a variety of sources including oil palm, soybean and rapeseed. Potential yields of oil per hectare for a range of crops are shown in Table 1. Currently, approximately 20% of rapeseed grown in the EU is used for biodiesel production but increased utilisation of biofuels will require more efficient agricultural methods and the use of new crops. For example, the Chinese tallow tree could yield significantly higher quantities of oil than current crops, and microalgae offer the potential for triglyceride production rates some 200 times higher than terrestrial biomass [1]. Another likely source for the production of these fuels is recycled waste oils obtained from the food trade and meat processing industries. Waste oils are currently expensive to collect and refine, but new legislation severely limits ease of disposal, and secondary usage. As a result the cost of these oils has dropped by over a half and, with the development of better catalyst technology, the use of waste oil for biodiesel production will increase [3].

Oil-producing Crop	Potential Oil Yield (litres per hectare)
Soybean	650
Sunflower	1030
Rapeseed	1220
Chinese Tallow Tree	6270
Algae	72000

Table 1: *Potential yields of some oil-producing crops [1]*

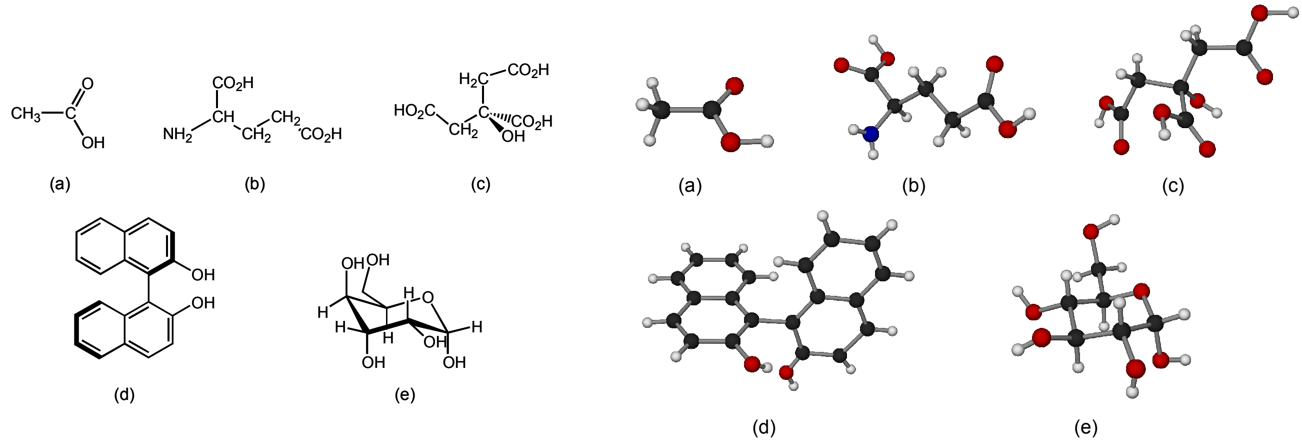


Figure 2: *Some potential ligand precursors (organic scaffolds) for metal-based biodiesel catalysts: (a) acetic acid; (b) glutamic acid; (c) citric acid; (d) 'binol'; (e) glucose.*

Using pure vegetable oil is impractical as a long-term fuel for current diesel engines. Its higher viscosity compared to mineral diesel leads to coking on injectors, carbon deposition on pistons and makes it an unreliable fuel in cold weather [4]. In addition incomplete combustion of vegetable oil can lead to the formation of toxic by-products being formed. These problems can all alleviated by removing the glycerol from the vegetable oil which is achieved by a chemical process called *transesterification*. In this reaction, methanol combines with the triglyceride to give three molecules of biodiesel (in chemical terms called fatty acid methyl esters or FAME for short) and one molecules of glycerol (Scheme 1). This reaction requires a chemical catalyst to work efficiently.

Current industrial catalysts for biodiesel are based on sodium hydroxide (NaOH) or sodium methoxide (NaOMe). These basic catalysts require pre-treatment of the feedstock to remove impurities, water and the free fatty acids (which precludes the use of low quality feed stocks such as waste oils). They also lead to *saponification* (i.e., soap formation) of vegetable oil, which occurs as an undesired side reaction and necessitates lengthy after-process separation procedures [5]. These production steps negate the low price of the catalyst and are energy intensive.

FURTHER INFORMATION

- A website dedicated to this exhibit can be found at http://www.bath.ac.uk/powerttp/
- For more details about our research on clean catalysis visit http://www.bath.ac.uk/chemistry/

It is therefore necessary to develop new environmentally benign, inexpensive and effective catalysts which avoid the costly saponification reaction. A wide range of alternatives have been proposed but to date none are ideal. We are designing new catalysts for transesterification of triglycerides based on environmentally and biologically benign metals such as zinc and titanium combined with a range of naturally occurring organic scaffolds (or ligands) (Figures 1 and 2). The metal centre provides the active site of the catalyst while the ligands control the reactivity of the metal and help to make it soluble in the reaction mixture. By selecting the right combination of metal and ligand we are able to make a range of environmentally friendly transesterification catalysts which in the future will help to make biodiesel production cleaner and more efficient.

REFERENCES

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