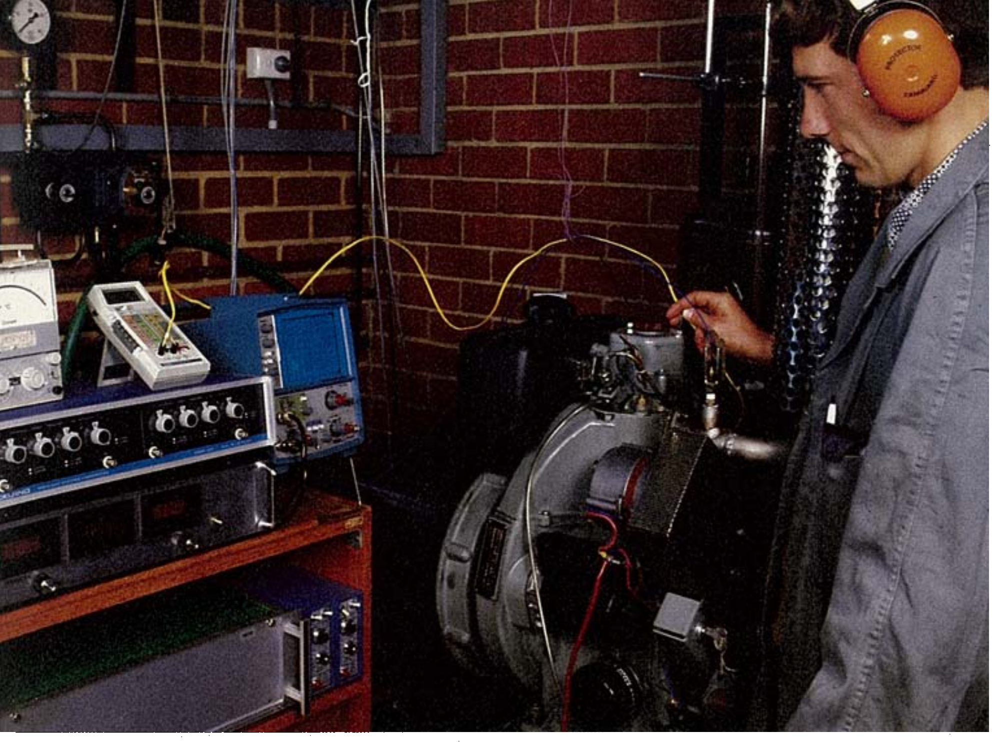


The test set-up for determining fuel quality.

Vegetable oil esters as fuels

One of the diesel engine's greatest assets is its ability to burn a broad range of fuels. Your tolerant diesel will even run on vegetable oil taken straight from the supermarket shelf.

When we couple this with a compression ratio roughly twice that of its petrol-driven counterpart — providing considerably higher efficiency — we can easily see why Rudolph Diesel's brain-child has enjoyed renewed popularity of late.

The practicality of replacing, or at least extending, conventional distillate with vegetable oils has been the subject of 'Project Crop-fuel' — a research program involving several CSIRO Divisions. An article on this work in *Ecos* 27 underlined a number of attractive features of such an enterprise. It is based on a renewable energy source and uses a known technology, and the fuel itself isn't toxic or highly flammable. Initial calculations showed that oilseeds, most likely sunflower, could supply enough fuel to reduce the nation's distillate consumption by about 20% within 5 years.

Economics call the tune, of course, and present abundant crude oil supplies diminish the incentive to pursue the oilseeds alternative. However, as Dr Kevin Harrington of the CSIRO Division of Chemical and Wood Technology points out, price structures are subject to many circumstances, and we may at any time need alternatives at short notice. If that happens, then we may be grateful that we know how to make use of vegetable oils. In a comparatively short time we can start producing diesel fuel in this way.

It's good insurance, thinks Dr Harrington, to iron out all the uncertainties beforehand. That is how he views research into what constitutes the best vegetable oil fuel. His own studies, with those of Dr Ron Johnston of the Division of Energy Technology, seem to indicate that the most desirable fuel may be a sunflower oil ester, a simple chemical modification of the raw oil.

In reaching this conclusion, Dr Harrington has made up 23 different esters of oilseeds, and Dr Johnston has tested their properties in two small diesel engines. In his test, 'methyl sunflower-ate' performed almost indistinguishably from conventional diesel fuel.

We have further substantiation of its suitability as a fuel: staff at the Division of Chemical and Wood Technology have, since late 1982, driven a Gemini diesel sedan 13 000 km on commercial sunflower oil ester. (Esters are normally supplied as solvents to the paint industry.) The unmodified car goes just as well as a conventional one; it starts and accelerates well, and exhaust emissions are low.

Why esters?

Raw vegetable oils will run well enough in engines, but difficulties arise in the longer term. Their viscosity is typically ten times that of distillate, and this has been blamed for build-up of combustion deposits, coking of the injection nozzles, and dilution of the crank-case oil.

Esterifying the oil solves these problems, in large measure, because esters have little more viscosity than distillate. The modified product also has the advantage of dispensing with the acrid smell produced by the breakdown of triglycerides found in raw oil. Instead, glycerol is removed as a by-product, and the exhaust smell is not unpleasant — much like that of a Chinese fish shop, according to one of the Gemini-drivers. Levels of nitrogen oxides and hydrocarbons in the exhaust are also substantially lower with the ester fuel than when regular distillate is used.

Vegetable oils consist mainly of the glycerides of fatty acids, which the plant uses as an energy source during germination. The fatty acid chains of a triglyceride molecule may all be identical, or come in many combinations. It is this variability that gives each vegetable oil — and its esters — a unique set of properties.

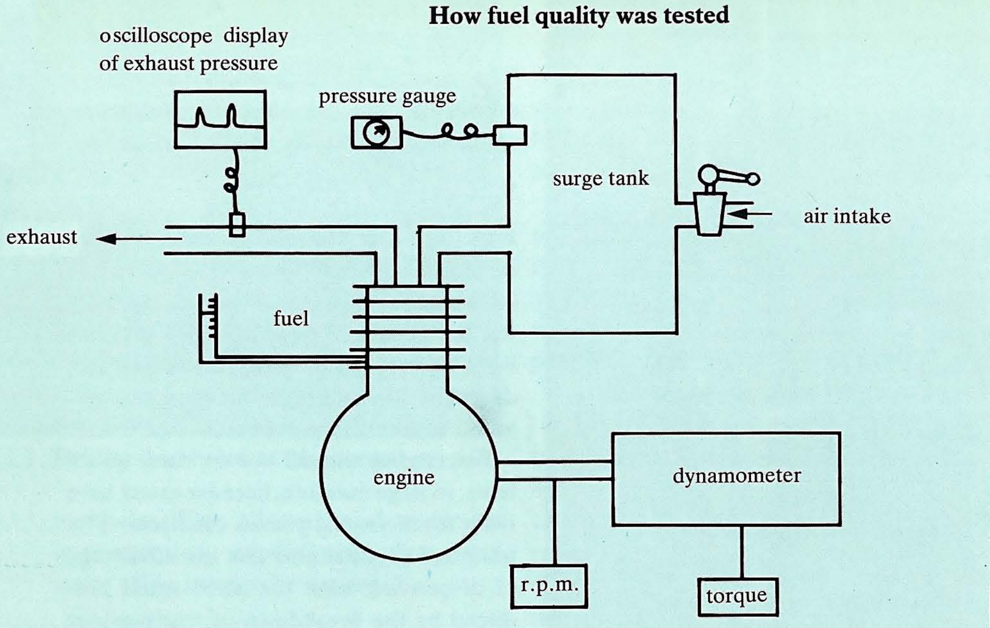
The glycerides can be readily converted to simple esters by reaction with an alcohol — for example, methanol. A catalyst is also needed, and sulfuric acid performs this function well. The product, a mixture of methyl esters, currently costs about $1 per litre in small batches from commercial sources. This is somewhat more costly than the raw oil, but not too expensive when compared with other alternatives to distillate. Dr Harrington thinks the price would be lower if it was manufactured on a larger scale.

Ester tester

The National Energy Research Development and Demonstration Program (NERDDP) supported Dr Harrington's work, in which he prepared experimental quantities — 1 to 2 litres — of various esters. Because of the small quantities available, the researchers had to find a way of determining suitability as a diesel engine fuel that didn't consume much of the precious liquid.

Dr Johnston met the need by reviving a technique first published in 1932, which had apparently fallen into disuse. This

How fuel quality was tested



Air intake to the engine was throttled until it misfired; the air pressure at this point was a measure of the quality of the fuel.

work also received NERDDP support. The test assesses the ignition quality of a fuel by throttling back on the air admitted to the engine until it misfires. The greater the throttling that can be done before misfire, the higher is the quality of the fuel.

We are all familiar with the anti-knock rating of petrol — its 'octane number'. With diesel fuels the equivalent is the 'cetane number'. This indicates how cleanly the fuel will burn and how smoothly the engine will run. Unfortunately, the standard way of measuring the cetane index requires large quantities of fuel.

Dr Johnston calibrated his test arrangement by using fuels of known cetane number in it. Among other practical aspects, he achieved the throttling by letting each engine suck in air from a reservoir tank; the greater the suction an engine was able to set up before it misfired, the better was the fuel. Typically, an engine would misfire several seconds after the reservoir was closed off, when the pressure was three-quarters to one-half of normal atmospheric pressure.

Testing was therefore very rapid, the main consideration being the time taken for one fuel to flush out the last traces of its predecessor (3 minutes or so). Dr Johnston found that 100 mL of fuel was easily enough for him to characterize its ignition quality in the test set-up.

He used two small single-cylinder diesel engines for testing — one a 413-cc direct-injection type, the other a 331-cc indirect-injection unit. The former has fuel injected straight into the cylinder, whereas the latter has it injected into a small chamber at the side. Indirect injection gives somewhat less efficiency, but a cleaner exhaust, and is chosen for diesel cars that have to meet emission-control regulations.

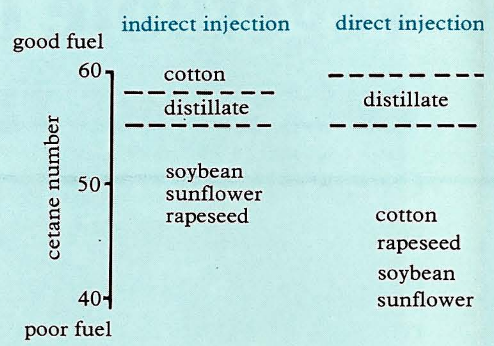
Dr Harrington's ester fuels had been prepared from sunflower oil and commercial fatty acids using five different alcohols: methyl, ethyl, *n*-propyl, *iso*-propyl, and *n*-butyl. The fatty acids were those of sunflower and linseed, and a fairly pure oleic fatty acid. In addition, he made methyl esters from peanut, rapeseed, and castor oils. In all, 23 ester fuels were tested in the two test engines, and four seed oils — cottonseed, soybean, sunflower, and rapeseed — were evaluated also.

The tests showed that a fuel had considerably higher ignition quality when used in the indirect-injection engine. In other words, such engines can tolerate much poorer fuels and still give satisfactory performance.

Furthermore, the esters showed at least a 10-point increase in cetane number over the oil from which they were derived. This quality increase would, in some measure, compensate for the extra cost of ester manufacture.

This chart compares various seed oils for ignition quality in two types of engine: direct-injection and indirect-injection. All except cottonseed oil were considerably worse than distillate. But, as the lower chart shows, esterifying the oils improved matters greatly.

Ignition quality of seed oils . . .



Tests with an ester-fuelled car

Since November 1982, a Holden–Isuzu Gemini sedan has operated as a normal part of the Division of Chemical and Wood Technology's car fleet. An unmodified indirect-injection diesel, it has run exclusively on commercially obtained esterified sunflower oil. Driven in both city and country by ordinary drivers, it has operated reliably and returned 7·1 L per 100 km (39 m.p.g.).

In the only untoward incident, a rubber water hose deteriorated due to ester spillage — esters are good solvents, and can eat through rubber (and dissolve paintwork).

The car started well, ran well, and offered good all-round 'drivability'. On one occasion it suffered a series of power losses after a fuel filter became blocked. This was blamed on thick residue (possibly unreacted mono- and diglycerides) from the fuel drum being added to the car's tank.

The exhaust had a distinct odour — like that from a barbeque plate — but it was not offensive. The Environmental Protection Authority analysed the car's exhaust, and the levels of hydrocarbons, carbon monoxide, and oxides of nitrogen were below standard 'cold urban cycle' limits.

Contamination of engine lubricating oil by oilseed esters has reportedly led to accelerated deterioration of the lubricant in some American experience. However, tests on the Gemini's oil showed it to be in good shape, with only slight contamination.

No fouling of the injector or glow plug was observed at the first inspection (4000 km). The next inspection is planned for 15 000 km, when the cylinder head will be removed for closer observation.

The type of alcohol used in ester formation had very little influence. But the nature of the fatty acid played a significant role. The best ester fuel was derived from a pure oleic fatty acid, followed by those from peanut, sunflower, rape, linseed, and — way below the others — castor oils.

Considering the unmodified seed oils, a consistent ranking for three of them showed up: cottonseed, soybean, and, lastly, sunflower. Rapeseed oil varied in its performance compared with the rest.

Ranking remained generally consistent with each engine type, and at different engine speeds. Dr Johnston takes this as a strong indication that the engine-throttling test provides reliable data. The fact that it produced the same oil-seed ranking other scientists derived using much more protracted testing supports this idea. He believes it has much to offer, particularly in view of its simplicity and speed. He is continuing work with the throttling test, hoping to get a more complete understanding of how rapid laboratory tests relate to longer-term engine performance.

Predictions from chemistry

The engine tests have pleased Dr Harrington, for they confirm his predictions based on general principles of chemical structure.

There is already a wide literature on the hydrocarbon structure of fuels and its relation to their performance in spark-ignition engines. In the case of diesel engines, information is generally lacking on this aspect. However, apparently some data suggest that the properties making for a good (high-octane) petrol are just those that make for poor diesel performance. Dr Harrington has followed this suggestion through and, indeed, the test results conform to the expected inverse pattern. The best ester fuels could be expected to have the following characteristics:

- long, unbranched hydrocarbon chains
- minimum number of double bonds (but too few double bonds can make the fuel a solid, rather than a liquid)
- double bonds should be near the end of the molecule
- no aromatic component (a vegetable oil seldom has such a component, but its glyceryl fraction, when heated, can break down to acrolein, a possible source of aromatics, which perhaps explains why methyl esters perform better than the raw oils)

The exhaust smell is not unpleasant — much like that of a Chinese fish shop.

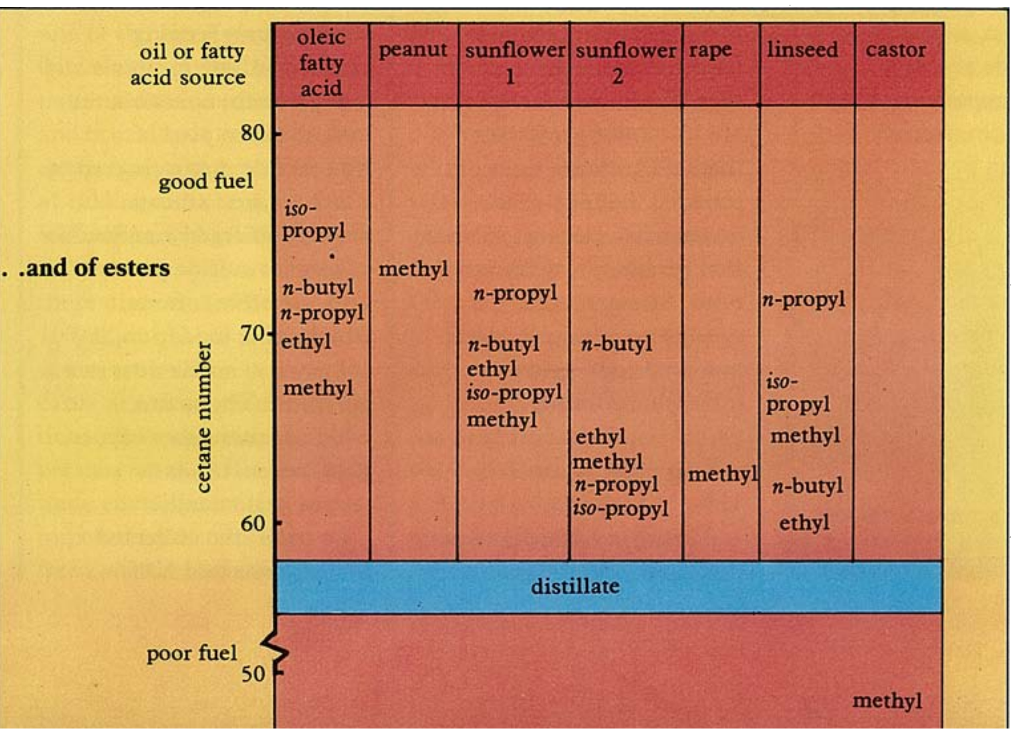
On this basis, the ideal fatty acid would have the structure:

C=CCCCCCCCCCCCCCCCCCOOH

It has a long, unbranched carbon chain with only one double bond, and this is at the end. The double bond is necessary, because without it the substance is a solid with a melting point of 70°C.

The scheme explains why castor oil performs so poorly — its principal component is an unsaturated acid with an hydroxyl side-chain (ricinoleic acid).

The chart shows the ignition qualities (cetane numbers) of various ester fuels determined in an indirect-injection engine. The esters of oleic fatty acid were the best; all except the methyl ester of castor oil were better than distillate.



Dr Harrington hopes these guidelines may be useful to agronomists and geneticists involved in manipulating plants to produce oil with desired chemical properties.

Direct from the seed

Another interest of Dr Harrington's is to reduce the cost of ester fuel by increasing its yield. Instead of esterifying the oil recovered from the seed, he wants to esterify the oil while it is still in the seed.

This has the advantage that the ester is very much less viscous than the oil, and so should be easier to extract. Furthermore, the hull, 30–40% of the total seed weight, has some oil content — about 5% on a dry weight basis — and this would add to the level of recovery (seeds are normally dehulled before processing).

Dr Harrington's experiments have verified that '*in situ* esterification' can raise conversion yields considerably. (The method raised ester yields to more than 40% by weight based on the whole seed, compared with a typically 30% yield when the esters were prepared from the extracted oil.) In addition, the process avoids the dangers and losses associated with the volatile and highly flammable solvent (usually hexane) used to extract the oil.

Of course, the volume of the remaining seed meal plays a large part in the economics of any oilseed operation. Normally the meal is used as stock feed. The meal resulting from *in situ* treatment is unlikely to have suffered deleterious effects, although the presence of the hulls may lower its nutritional value. More study is needed on this aspect.

The last word may be had from Rudolph Diesel himself, who in 1912 said, '. . . the use of vegetable oils for engine fuels may seem insignificant today, but such oils may become, in the course of time, as important as petroleum and the coal-tar products of the present time'.

Andrew Bell

More about the topic

Rapid ranking of diesel ignition quality. R.R.M. Johnston. *Papers, 2nd National Conference on Fuels from Crops, Society of Automotive Engineers Australasia, August 1983.*

Chemical and physical properties of vegetable oil esters and their effect on diesel engine performance. K.J. Harrington. *Papers, 2nd National Conference on Fuels from Crops, Society of Automotive Engineers Australasia, August 1983.*

Diesel fuel from the farm? J. Seymour. *Ecos* No. 27, 1981, 3–10.