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# (E)mission impossible?

**Paul Day, John McNeil and Felix Sirovski** outline their 'minor miracle' – powering diesel engines with an underused by-product

**T**HE worldwide production of glycerine is steadily growing due to forever increasing biodiesel manufacture. For every tonne of biodiesel produced, 100-110 kg of glycerine is obtained as a side product. The world supply of glycerine in 2008 was 3.2m t and the demand is just 0.9m t.

All this has fuelled the search for possible uses for this excess glycerine, which include conversion of glycerine to epichlorohydrin, 1,2-propylene glycol, pyrolysis to hydrogen and its anaerobic digestion. All these applications pale in significance when compared with this one, though – as fuel for diesel engines!

Well any diesel engineer will tell you that this is complete nonsense. Firstly, it is barely combustible. Secondly, it is too viscous. Thirdly, even if somehow you manage to combust it, a lot of toxic acrolein will be produced in the exhaust and the engine will become clogged with polymers.

Nevertheless, here we have purring a standard 40KWh Deutz engine that is fired by glycerine... and the process has been patented not just in the UK but worldwide. Maybe the principle is similar to the one concerning bumblebees; it is said that aerodynamic equations forbid them to fly but, nonetheless, fly they do. So, surely something is wrong with the equations, isn't it?

## standard

Let us look briefly into the operation of the standard diesel engine. A cylinder is filled with air through the intake valve which is then shut and the motion of the piston reduces the volume of air, compressing and heating the air to approximately 600°C. At this time, liquid fuel is injected into the cylinder through a nozzle forming a spray of droplets, which vaporise thanks to energy supplied with hot air. The vaporised fuel auto-ignites due to oxygen and the combustion gases drive the piston downwards, transferring power to the crankshaft.

However, ignition is not immediate; some time lag exists between the start of the fuel injection and the pressure increase due to fuel combustion – the ignition delay, an important characteristic of the fuel. This is split into two parts: physical delay and chemical delay.

The combustion occurs in the gas phase only. As the fuel is a liquid, it needs to be evaporated. The time required to convert liquid to vapour is a physical-delay

component of the total ignition delay.

Combustion is a sequence of chemical reactions in which the vaporised fuel reacts with oxygen. These reactions proceed through a chain mechanism involving free radicals. Once a sufficient concentration of free radicals is reached, rapid oxidation (combustion) occurs. The chemical delay is the time required for the vaporised fuel to ignite.

To initiate the combustion, the oxygen molecule should be split into single atoms. This requires a very high amount of energy, ie, heat. The kinetic energy of the available oxygen atoms and that of the fuel molecules must be sufficient to allow the abstraction of hydrogen atoms from the fuel molecules during in-cylinder collisions, creating an available pool of free radicals; therefore, compression-end gas temperature is the critical parameter (if the temperature is too low, ignition will not occur).

The ignition delay is linked to the diesel fuel property called the cetane number.

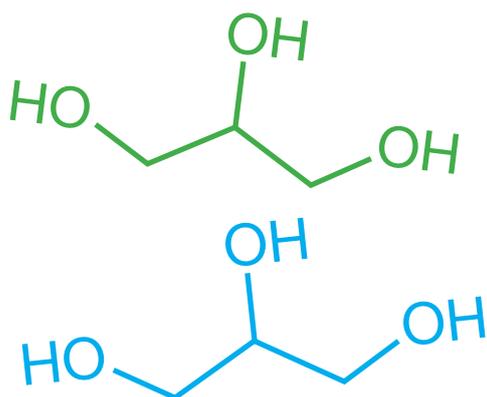
Cetane is an unbranched open chain alkane molecule that ignites very readily under compression as it is quite easy to abstract hydrogen atoms from it and is ascribed the number 100. Alpha-methyl naphthalene is the zero reference, as abstracting hydrogen atoms from an aromatic ring or a methyl group attached to it is not an easy task. The cetane number of any given fuel is derived from the measurement of fuel-ignition delay when using a calibrated test engine; the longer the delay, the lower the cetane number. Fuels for diesel engines commonly have cetane numbers in the range of 38-50. Any fuel with a cetane number below 25 would be classed as 'very low' and very difficult to ignite. Cetane numbers of 25 and below use pilot fuels, typically standard gas oil or compounds such as dimethyl ether, to initiate ignition.

## 'increasing' problems

To increase the compression-end gas temperatures, three methods can be employed, singularly or in combination:

- increasing the compression ratio;
- increasing the mass flow; and
- increasing the inlet air temperature significantly above the ambient.

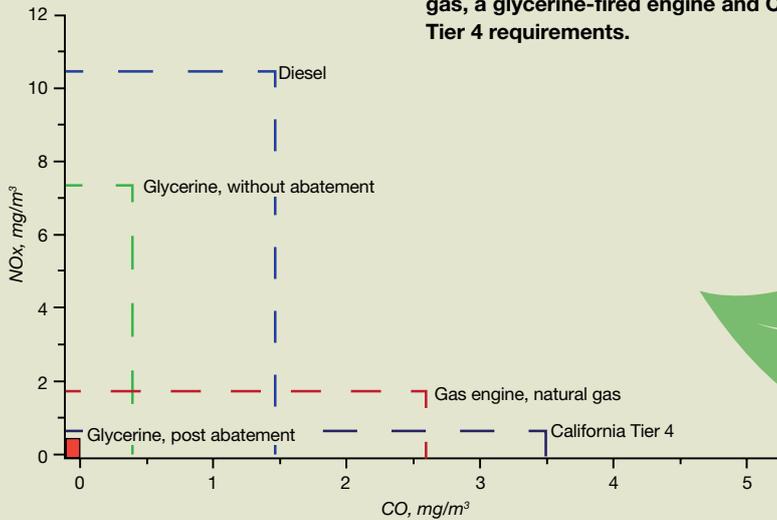
Increasing the compression ratio will increase the end gas temperature and pressure but one can't increase it above a certain limit set by the material strength and engine-design considerations. In plain words, you cannot increase the compression ratio indefinitely





**Emission comparison**

Comparison of emissions for a diesel engine, a gas engine running on natural gas, a glycerine-fired engine and California Tier 4 requirements.



because your engine would become too heavy to operate. Also, the relative end gas temperature increase (per unit of compression ratio) is quite low, thus limiting the temperatures that can practically be achieved.

Increasing the mass flow through the engine at any given compression ratio and engine speed will increase the end gas temperature due to an increased rate of molecular collision with the piston during the compression stroke, leading to increased momentum transfer to the gas.

Increasing the inlet air temperature allows a 'tuneable' end gas temperature. This is due to a normal multiple increase of approximately 3:1 when employing standard compression ratios of between 14-16:1.

The conventional wisdom is that you cannot increase inlet air temperature, as it would result in a drop in power because incoming air will be rarefied and less oxygen will be available. This will lead to increase in emissions because of incomplete combustion. That is what intercoolers are for: they lower the temperature of the inlet air after the turbo, increasing the mass of the charge.

However, if you increase both the inlet air temperature during engine operation from 60°C up to 200°C and its mass flow, this will enable you to combust liquids or gases of any cetane number as long as they have a calorific value. The cetane number constraint is not binding any more. You can even combust petrol if you fancy it.

**simply the best**

Glycerine is better, however. It is possibly the best fuel in the world. So why is it so? First of all, it isn't toxic; actually it is used as a

sweetener in liqueurs. Secondly, it is water soluble; if it's spilled you can just wash it out with water. Thirdly, it's nearly impossible to ignite glycerine under normal conditions; it's quite safe to handle.

True, it's quite viscous, but its viscosity drops dramatically with temperature. At 90°C its viscosity is about 13 centistokes (cSt) - the same as that of fuel oil.

**go compare**

So what about its low calorific value? True, the calorific value of glycerine is not too high, just 16.2 MJ/kg. Compared with 42 MJ/kg of diesel or 37.8 MJ/kg of biodiesel this does not look too impressive. But glycerine is unbelievably dense, denser than water in fact; its density is 1,270 kg/m³. So if you compare calorific values of the three fuels: diesel, biodiesel and glycerine per unit volume, it will be 35.4 MJ/l for diesel, 31.8 MJ/l for biodiesel and 20.6 MJ/l for glycerine. The comparison of prices per 1 MWh also doesn't look too bad, especially if you take into account the renewable obligation certificates (ROC). For 1 MWh produced by burning glycerine, two ROCs are assigned and their current value is about £100 (\$164). In this way, the cost of producing 1 MWh electrical is about £133,

*“ glycerine is... possibly the best fuel in the world. It isn't toxic; it is water soluble; and it's nearly impossible to ignite glycerine under normal conditions ”*

which is lower than with diesel.

There's still the acrolein and other toxic emissions to consider, however. Well acrolein (2-propenal) is ubiquitously present in cooked foods and in the environment. It is formed from carbohydrates, vegetable oils and animal fats, amino acids during the heating of foods, and by combustion of petroleum fuels and biodiesel. Smoking of tobacco products equals or exceeds the total human exposure to acrolein from all other sources. Acrolein and other aldehydes, generally referred to as carbonyls, are the products of incomplete combustion of carbon compounds such as wood, coal gas, gasoline and diesel. Hence they are found in car exhausts, boiler, power and incineration plant effluent exhausts as well as in cigarette smoke. Another chemical reaction responsible for the release of acrolein is the heat-induced dehydration of glycerine.

It is interesting to note that smoke from wood-burning fireplaces contains acrolein in far greater levels than diesel engines: up to 130 mg/m<sup>3</sup> as compared with 0.3-0.4 mg/m<sup>3</sup>. Switching engines from diesel to biodiesel blends does not help matters because acrolein emission is actually increased two or three times.

Switching to glycerine improves emissions quality dramatically, however. Prior to using the standard catalyst abatement, carbon monoxide (CO) measures 63 mg/m<sup>3</sup> compared with 350 mg/m<sup>3</sup> when using diesel, volatile organic compounds (VOCs) measure 24 mg/m<sup>3</sup> [46 mg/m<sup>3</sup> for diesel], nitrogen oxide (NOx) is 2,000 mg/m<sup>3</sup> [2,475 mg/m<sup>3</sup> for diesel] and particulate matter is 0.9 mg/m<sup>3</sup> [19.5 mg/m<sup>3</sup> for diesel].

Post the catalyst, CO in glycerine emissions dropped to zero, acrolein was zero and NOx was 113 mg/m<sup>3</sup>.

The diagram shows the comparison of emissions for a diesel engine, a gas engine running on natural gas, a glycerine-fired engine and California Tier 4 requirements.

### how low can you go?

So why are glycerine emissions so low? Glycerine is a single compound and not a complex blend like diesel is. This makes its combustion chemistry much simpler. Moreover, it already contains 55% oxygen by weight. It is already partly oxidised, hence the relatively low calorific value. On the other hand, this high degree of oxidation is responsible for low emission levels as combustion proceeds at a temperature much higher than that of the normal diesel cycle. This ensures nearly complete destruction of all aldehydes and other carbonyls that might be formed in the process. The virtual absence of any

particulate matter makes the operation of the oxidation catalyst much more efficient and easy.

We would like to add a brief note on the comparison of energy obtained by anaerobic digestion of glycerine (recently one of most popular uses for crude glycerine) and its direct combustion in the engine.

The anaerobic digestion of 1 kg of crude glycerine is quoted to produce biogas with energy content of 11-12 MJ/kg. That is an energy loss of about 25%. Moreover, the efficiency of gas spark-ignited engines is only 22-23% compared with 37-38% efficiency of compression-ignition engines. Thus, the total energy loss is about 60-65%. The figures speak for themselves.

### looking forwards

What does the future hold? The issues hampering the wide rollout of glycerine combustion technology could be divided into two groups. The first is the inability to grasp the technical points behind the innovation, 'not invented here' attitude and the natural resistance to innovation. The second is the absence of fuel-grade glycerine on the market; the pharmaceutical-grade glycerine is too expensive and way over spec for the combustion needs. Also, the existing glycerine-distillation capacities are quite limited.

However, the biodiesel manufacture is not the sole source of glycerine. Back in the 1970s, Israeli scientist Ami-Ben-Amotz developed a patented process of obtaining glycerine from the algae *Dunaliella salina*. However, the production of glycerol was not commercialised due to falling oil prices at the time, linked with the fact that no technology existed to use glycerol as a fuel. This algae is quite peculiar as it thrives in highly saline water ponds, the Dead Sea and the like. The more saline the water, the more glycerine is produced. *D. salina* could accumulate up to 85% of glycerine by dry weight, which it produces to protect itself from the osmotic pressure created by high salt concentration. The presence of the algae is easy to spot when looking at aerial views

of solar salt-production facilities; the ponds tend to be bright red.

The quoted yields could reach 40 t of glycerol per square kilometre per day. With a lower calorific value of approximately 16 MJ/kg, this would equate to approximately 2,300 GJ/ha per annum, which compares very favourably with the average energy yield for oil seed rape (approximately 40 GJ/ha per annum).

The areas where the algae prospers also tend to be totally sustainable, as few other organisms can survive in such highly saline and arid conditions. The culture requires no freshwater or agricultural land, can sequester CO<sub>2</sub> and does not compete with anything else in the food chain.

The glycerol formed within the organism requires no further refinement or chemical modification before use as compared with algal lipids, whose oils required significant modification. The energy required to extract the glycerol can be provided by using the waste heat from embedded glycerol-fuelled power generation. Desalination can also be integrated into the system.

Once extracted the glycerol can be shipped in bulk and could, of course, be used to power the bulk carriers. The environmental consequences of fuel spills into the ocean are minimal. Work is under way on the bulk production of glycerol from algae and it is expected that production of millions of tonnes per annum will be possible within a reasonable time frame.

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**Paul Day** ([paulday@aquafuel.co.uk](mailto:paulday@aquafuel.co.uk)) is the founder and ceo, **John McNeil** ([jmcneil840@aol.com](mailto:jmcneil840@aol.com)) head of engineering and **Felix Sirovski** ([felixsirovski@aquafuel.co.uk](mailto:felixsirovski@aquafuel.co.uk)) head of research of Aquafuel Research ([www.aquafuel.co.uk](http://www.aquafuel.co.uk))

