Gasoline (petrol) additives – update

In the past I have reported on the quality of fuel in Australia and the potential for unregulated chemicals to enter the fuel market to the detriment of the motorist using the fuel (May 2017, p. 36). Here, I will give an update.

The quality of fuel sold in Australia is regulated by the Fuel Standards Act. The Act sets the levels of various components and performance criteria for gasoline (the preferred industry term for petrol), diesel, LPG, ethanol fuels and biodiesel. The Fuel Standards Act complements vehicle design rules that set performance levels for new vehicles sold in Australia, including emission limits.

The introduction of a standard to lower greenhouse gas emissions comes down to improving fuel economy (km/L). This requires higher efficiency engines, which means increasing the octane of the fuel so that higher compression engines can be used. At the time of writing, it is proposed that the minimum fuel octane will be 95RON (research octane number, premium petrol) rather than the current 91RON for unleaded petrol.

Higher RON can be achieved by more severe refining or using chemical octane boosters. Organometallic additives are very effective but are now banned or opposed by vehicle manufacturers. Widely used octane boosters are alcohols, especially ethanol, and ethers such as methyl tertiary-butyl ether (MTBE). Ethanol is widely used in Australia but has some issues with vehicle compatibility (especially old vehicles) and is not very compatible with petrol (fungible). Although adding ethanol may achieve the 95RON standard, there may be difficulty in obtaining the higher 98RON grades.

Nitrogen compounds such as amines have been used as gasoline additives to reduce deposits on engine intake valves for some years. Currently, there is active interest in using aniline and aniline derivatives in higher concentrations as octane boosters. Adding relatively small quantities of these materials to a gasoline results in large increases in the octane. Prima facie, the aniline additives are five times more effective than ethers such as MTBE in boosting octane. Like all other chemical octane boosters. Organometallic additives are very effective but are now banned or opposed by vehicle manufacturers. Widely used octane boosters are alcohols, especially ethanol, and ethers such as methyl tertiary-butyl ether (MTBE). Ethanol is widely used in Australia but has some issues with vehicle compatibility (especially old vehicles) and is not very compatible with petrol (fungible). Although adding ethanol may achieve the 95RON standard, there may be difficulty in obtaining the higher 98RON grades.

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In evaluating the impact of a gasoline on a lubricating oil, it is important to consider how the gasoline and the components of gasoline contact the lubricating oil.

In an internal combustion engine, gasoline enters the hot combustion chamber as a vapour–air mixture in carburetted engines or is mixed and vaporised in hot air in the combustion chamber in fuel-injected engines. The presence of hot air from prior combustion or the compression process as the piston rises in the cylinder overwhelms any anti-oxidant present in the gasoline. The gasoline is ignited by means of a spark.

Lubricating oil from the sump is carried by the pistons up the cylinder wall. There is always some bypass of the piston and the piston rings; a small amount of lubricating oil is carried into the combustion chamber and clings to the chamber walls, lubricating the piston movement. This oil interacts with the
vaporised gasoline, and the gasoline combustion products and partial combustion products and absorbed materials are carried back into the engine sump by returning oil on the cylinder walls. In this manner, gasoline and gasoline components enter the lubricating oil system and are carried throughout the engine to form varnish and sludge over cooler components remote from the combustion chamber.

Most manufacturers warranty their vehicles for 100,000 km or five years’ operation and since we are concerned with fouling of parts and components that are rarely inspected over this period, it is important that fuel and fuel components do not contribute to excessive fouling. This means that even a small quantity of material that contributes to fouling should be eliminated as far as possible from the fuel system. This could be a major obstacle in developing a high-octane AVGAS from aniline and derivatives.

This problem is in addition to the additives causing swelling of O-ring seals, which may result in fuel leaks.

It is now becoming clear that oxygenates in general can act as octane boosters. The well-researched, demonstrated and commercialised are ethers, particularly MTBE and ETBE, and alcohols, particularly ethanol and potentially butanol, which can be produced from renewable sources. Other oxygenates, such as acetone and esters, are of interest to the racing fuels community but the inclusion in retail gasoline is opposed by the original engine manufacturers.

Methanol, which is opposed by the original engine manufacturers, has been widely used in China where it can be produced from local, low-cost coal. Methanol does not mix well with gasoline and probably to help assist with this problem and maintain access to a low-cost blendstock, there has been a rise in the use of dimethoxy methane (methylal). Methylal can be produced by oxidation of methanol or from methanol and formaldehyde.

Another oxygenate of interest is diethyl carbonate, which delivers good octane (101RON) and, in contrast to ethanol, a low-vapour pressure impact. It seems to be a preferred co-additive to aniline compounds for producing high-octane unleaded AVGAS.

One problem shared by most of these octane-boosting additives is that they are more powerful solvents than pure hydrocarbon gasoline. This property leads them to dissolve into seals (O-rings), which causes the rubber to swell and can result in leaks in the fuel delivery system.

It is important that regulations and regulatory authorities remain in control of additives to gasoline and not inadvertently allow materials into the Australian petrol pool that damage vehicles and engines.

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