CHEMICAL ECONOMICS - PETROL ADDITIVES

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 petrol, diesel, LPG, ethanol fuels and biodiesel. The Fuel Standards Act complements vehicle design rules which sets performance levels for new vehicles sold in Australia which includes emission limits. At present a review of vehicle design rules is underway which will tighten emission standards and extend the emission limits to include greenhouse gas emissions. This harmonises Australian design rules with European design rules.

The revision of the design rules requires a revision of the fuel standards so that the benefits of the new design rules to the motorist will not be compromised by poor quality fuel. One feature of the required fuels is to essentially eliminate sulphur from both petrol and diesel (new limit set at 10ppm sulphur) which would facilitate the introduction of new technologies for nitrogen oxide control (NOx) and particulate emissions from vehicle exhausts.

The introduction of a standard to lower greenhouse 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.

For the motorist, the higher the RON the higher the cost because increasing RON can only be achieved by more severe refining. Furthermore, the new fuel standards will likely decrease the amounts of aromatics and olefins allowed in the fuel. These components are high in octane and the new limits will place further challenges to refiners to achieve the 95RON minimum.

Higher RON can be achieved by using chemical octane boosters. Organo-metallic additives are very effective but are now banned or opposed by vehicle manufacturers. This includes lead compounds, methyl -*cyclo*-pentadiene manganese tri-carbonyl (MMT) and ferrocene.

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). Adding ethanol to petrol results in higher vapour pressure which increases fugitive emissions and separates from petrol in the presence of water, which could be condensation in storage tanks. Although adding ethanol may achieve the 95RON standard there may be difficulty in obtaining the higher 98RON grades.

Widely used in Europe, the Middle East and across Asia is MTBE or, particularly in western Europe and Japan, the ethanol derivative ETBE. Australia does not use MTBE for historical reasons to do with leaking storage tanks contaminating ground water. Compared to other petrol components, MTBE has low toxicity but apparently some people can taste MTBE in potable water at the 20ppb (parts per Billion) level whereas benzene is not detectable below about 150ppb. In my opinion the limiting of ethers on this ground is allowing regulatory authorities to ignore leaking tanks in their jurisdictions.

These ethers are very commonly used in refineries in Asia from where increasing volumes of petrol are being sourced for Australian motorists. By having a low limit on MTBE results in Australia having a boutique fuel standard which can only result in higher fuel costs.

There are several other octane boosting components which may find their way into Australian petrol. One of the drivers is that sometimes chemicals become in excess of demand and can be disposed of by mixing with petrol. Some of these compounds may cause long term damage to vehicles and engines.

The possibility of using furan and substituted furans in petrol are the result of research into producing fuel components from biological sources. Some of these concepts concern the mass production of furans from ligno-cellulosic material feedstock (wood waste etc). Without further treatment these would probably prove be too aggressive in solvent power for seals in vehicles.

Oil major research into the lowering or removal of lead from aviation gasoline is developing high octane petrol formulations containing a diverse range of nitrogen and oxygen containing chemicals. These include toxic and dangerous chemicals such as aniline and aggressive solvents such as diethyl carbonate. Whether or not these could be used in transport vehicle fuels is unknown.

N-methyl aniline (NMA) is mainly used as an intermediate in dye manufacture. It would appear to be being used fairly widely as an octane booster but is alleged to have caused vehicle problems. Because it is not an oxygenate NMA seems to have slipped through several regulatory nets (it is not mentioned in World Wide Fuel Charter which is the auto-industries view of fuels and fuel additives). NMA is permitted in several jurisdictions (e.g. USA) and banned in others (China, Russia). NMA is highly toxic and is easily oxidised forming resins. Where it is permitted it usually has to be in association with detergents and fuel combustion modifiers. Whether or not this solves the issue of gum formation is unknown. Industry sources have indicated that NMA has been used on at least one occasion in Australia.

Acetone is a powerful solvent (lacquer removal - nail polish remover) and widely available from local hardware stores . Acetone's main chemical use is in production of methyl methacrylates (for Perspex etc.) and Bisphenol A (used for polycarbonate polymers) with Asia producing over 1 million tonnes/year from >20 companies. There is currently excess supply over demand.

Although most acetone is made by the chemical industry, acetone could be made by renewable methods. Old fermentation routes, now largely obsolete, are known for co- producing acetone, ethanol and butanol. This technology is being revived by genetic engineering methods to ferment sugars to bio-butanol.

From Internet searches, there appear to be many enthusiastic supporters of acetone for boosting RON to levels of 100 or more. Acetone seems to be widely used by a section of motor enthusiasts who wish to modify and boost performance of road/racing vehicles. This practice is discouraged by other members of this community.

Iso-butanol produced by genetically modified enzymes is being promoted as an alternative to ethanol by Du Pont and BP and several other companies. It has better fungibility than ethanol, does not have the same level of water uptake and a lower impact on vapour pressure. It has been suggested as a co-solvent for ethanol.

Sec-butyl acetate (butac) is an Industrial solvent widely used in lacquer and automotive paint industry. Asia produces over 1 million tonnes/year by over 20 companies. There is currently excess supply over demand. Butac is known to have been used in Vietnam causing vehicle performance problems resulting in its ban.

Whatever the outcome of the Fuel Standards review the Australian motorist is likely to see higher prices for fuel. The demand to increase fuel octane could encourage unscrupulous traders and entrepreneurs to introduce chemicals that although boosting octane cause long term damage to vehicles.

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

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March 2017