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Boosting the Octane Rating of Petrol: A Review of the Trends and Impacts on the Environment

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Abstract An important quality of petrol (also called motor spirit or gasoline) is its octane rating (number) which is a measure of how resistant petrol is to the abnormal combustion phenomenon known as knocking (detonation or pinging). Petrol with low octane rating will burn uncontrollably in motor engine resulting loss of power, fuel wastage, and ultimately total engine failure. At the design level, increasing the octane number of petrol meant that the engine compression ratio could be raised to maximized power output. Straight-run motor spirit is characterized by low octane number and was only suitable for the earlier engines with low compression ratios. Latter demands for more powerful engines call for increase in compression ratios of the latter designed engines. The challenge however, was that these latter engines could not run on low quality petrol (with low octane rating). Various additives were sought to boost the octane rating of petrol, and more recently refinery reconfiguration is being given much attention. This work peruses the trends towards boosting the octane quality of petrol, highlighting the impacts of these trends to the sustainability of the environment.

Keywords: *additives, compression ratio, octane rating, petrol, refinery reconfiguration, straight-run motor spirit*

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1. Introduction

In order to appreciate the importance of octane boosting additives on petrol perhaps, a small dose of historical excursion is necessary. Originally, internal combustion engines where developed for cars to run strictly on petrol (motor spirit). Like alcohol spirit, motor spirit was a clean fuel and the main exhaust products were water vapor, carbon dioxide and traces of carbon elements and particles. However, there were two principal problems associated with the use of the pure motor spirit. First, it was a highly refined product that cost a lot to produce. Secondly, with the increase in compression ratio of the latter more powerful engines produced, it becomes very unsatisfactory to run the cars with the available motor spirit. An engine under load would develop a condition known as 'knocking' (pinging or detonation). Providing a solution to this problems, triggered the search for a suitable motor spirit octane boost additives – a substance which when added to the low quality petrol, will boost the octane rating. Benzene, alcohol and latter tetraethyl lead (TEL) etc, were used.

2. Leaded Petrol

Among the early additives that were developed in the 1920s for petrol (motor spirit) used in cars engines was tetraethyl lead (TEL). TEL is cheap and wonderfully effective. It boosts the octane rating of fuel, it also foams a protective coating for valve seats, guides and the upper cylinder and it acts as an efficient lubricant for pumps injectors and other moving parts within the fuel system [1,2].

The combustion of tetra ethyl lead gives lead oxide which is removed from the system by the co-additives of TEL such as organic halide (ethylene dibromide and ethylene dichloride) by converting the lead oxide to lead halides ($PbCl_2$, PbBrCl, and $PbBr_2$) which escape into the air [3,4].

$$2Pb(C_2H_5)_4 + 27O_2 \rightarrow 2PbO_{(S)} + 16CO_{2\,(g)} + 20H_2O_{(g)}$$

$$2C_2H_4Br_2 + 2PbO + 5O_2 \rightarrow 2PbBr_{2(g)} + 4CO_{2(g)} + 4H_2O_{(g)}$$

The release of lead compounds into the air constitutes an environmental pollution. Exposure to lead may result in accumulation in the body organs (i.e. brain), leading to poisoning (plumbism) or even death. The gastrointestinal track, kidneys, and central nervous system are also affected by the presence of lead. Children exposed to lead are at risk of impaired development, lower IQ, shortened attention span, hyperactivity, and mental deterioration, with children under the age of six being at a more substantial risk. Adults usually experience decrease reaction time, loss of memory, nausea, insomnia, anorexia and weakness of the joints when exposed to lead [5,6]. Exposure to lead can result in a wide range of biological effects depending on the level and duration of exposure. Various effects (including risk of high blood pressure and cardiovascular diseases) occur over a broad range of doses, with the developing young and infants being more sensitive than adults [7]. Also, the addition of chemical scavengers (such as organic halides) to inhibit the accumulation of lead in engine; has been linked to halogenated dibenzo-p-dioxins and dibenzofurans in exhaust which may bestow a cancer risk to exposed individuals [8].

By the onset of the 1970s, the negative health impacts of exhaust gases containing lead were well known [9,10]. However, the makers of leaded fuel play-down on this fact stressing that the amount of lead in fuel was insignificant to cause any harm. Thus, they evaded clear evidence that their product was harmful by hiding under the blanket of scientific uncertainty (i.e., incontrovertible proof of causality). This continued until it was discovered that leaded petrol has an additional disadvantage of fast damaging the catalytic converter incorporated in the exhaust system of cars. The use of catalytic converter become largely promoted during the 1980s when it become obvious that many cities in the world were being polluted by emissions from car exhausts [10]. It contains small beads that are coated with metals such as palladium and platinum. Pollutant gases in exhaust, while passing through the converter, are transformed into harmless oxygen, carbon dioxide, and water with the help of these metals acting as catalysts to advance the reactions. It was this latter disadvantage that prompted chemist to introduce the unleaded petrol.

2.1. Unleaded Petrol

A wide spectrum of chemical additives were sought to replace the lubricant and anti-detonation properties of lead in petrol. They included: the organometallics, the aromatics, and oxygenates (ethers and alcohols). Methyl cyclopentadienyl manganese tricarbonyl (MMT), iron pentacarbonyl, and ferrocene (iron dicyclopentadyenil) are commonly used organonometallics, like TEL, they are also metals (Mn and Fe) based. MMT was widely used as lubricant to prevent automotive valve seat recession and also to improve petrol octane rating. Combustion of MMT releases Mn from the tailpipe, primarily as airborne Mn phosphate and sulphate. Manganese, unlike lead which it replaces in petrol, is a normal and essential component of the human diet and the intake from airborne manganese is slight compared to the normal dietary intake. However, manganese can be a neurotoxicant at sufficiently high exposure levels with symptoms such as headache and insomnia, loss of motor control, memory loss, erratic behaviour, and brain cell death [11,12]. The tendency that the use of manganese additives in petrol could increase inhaled manganese exposures is of great concern to public health. There are also indications that MMT like its close cousin – TEL, also affects the emissions control systems of vehicles particularly those with high-density close-coupled (HDCC) catalysts [13]. The above reasons have lead many (including the American Academy of Paediatrics) to called for the phasing out of MMT from petrol. Its use is now banned in Canada and in the state of California as well as in the reformulated gasoline sold in many urban areas of the United States. North America, the European Union, Japan, India, and Indonesia have constantly witness an increasing restriction of the extent to which MMT is used in fuels [14]. This precautionary measure is necessary until a definitive conclusion about risk is established.

The aromatics are volatile organic compounds such as benzene, toluene, ethyl benzene, xylene (BTEX), 1,3-butadiene, and mesitylene (1,3,5-triethyl benzene). Most aromatics are toxic; Benzene and 1, 3-butadiene are extremely toxic pollutant (including carcinogenicity). The amount of Benzene in petrol is therefore, being restricted to 1% volume, while the maximum allowable concentration of aromatics in gasoline is 35% volume.

The Oxygenates appears to be the most favoured additives at present. They contain oxygen in their chemical structures and when applied to petrol, increase the oxygen content of the fuel and improve the efficiency of the combustion process thus, reducing soot, carbon monoxide and nitrogen oxides emissions. Methyl tertiary-butyl ether (MTBE), ethyl tertiary-butyl ether (ETBE), tertiary-amyl methyl ether (TAME), di-isopropyl ether (DIPE), methanol, ethanol, isopropyl alcohol (IPA), and tertiary-butyl alcohol (TBA) are known motor spirit oxygenates.

Among the ethers, MTBE - manufacture by the addition of methanol to the olefin isobutene (2-methyl propene) or the reaction of tertiary butyl alcohol (TBA) with methanol - is the main oxygenate and octane booster of global significance. Its use was much boosted in the 1990s by the implementation of reformulated gasoline (RFG) program which requires gasoline (petrol) to meet a minimum of 2 percent oxygen by weight content [15]. However, the incidence of MTBE contamination of ground waters particularly in the USA led to out-cry for its phase out [16,17]. The State of California has since 2004 phase-out the use of MTBE in gasoline. MTBE has objectionable taste and odour; and it is suspected to be carcinogenic at high dosage [16,17].

Ethyl tertiary-butyl ether (ETBE) has been suggested as substitute for MTBE and has the advantage of low solubility in water. Besides, its higher boiling point and lower vapour pressure enhance the efficiency of producing oxygenated blended gasoline. ETBE is viewed as environmentally friendlier as most of the ethanol use in its production is from bio-ethanol. It is widely used in Europe and in Japan as the preferred bio-fuel [18].

Ethanol –an alcohol – is another extensively used oxygenate. It has an extended record for its use as gasoline blending component, octane booster, and as fuel alternative. With the fall of MTBE from grace, ethanol is seen as fuel for the future. The drive for its use has been compelled by its ease of production from a broad range of agricultural sources, thus can be regarded as sustainable fuel. Critics have often pointed out that the use of land to grow biomass for ethanol production detracts its use for growing foods and may aggravates global food shortage. Also, large investments on modification of the existing infrastructure system are required to make distribution and refueling of ethanol blend fully compactable. Ethanol being hygroscopic cannot be transported in pipelines like petrol, special tank have to be used. The world's largest used of ethanol is in Brazil, where it is being used as an indigenous fuel since the early 1970s. Ethanol use as fuel, is largely been promoted in Europe and in the United States particularly the corn-belt states. There is overwhelming evidence suggesting that the substitution of ethanol for gasoline or its blend with gasoline has helped to reduced photochemical oxidant formation, purged lead and sulphur emission compounds and eliminate carcinogenic hydrocarbons currently produced by aromatic fuel compounds. Thus, offering overall air quality benefits [19,20]. However, alcohol have these problems of "eating up" elastomer fuel lines in older cars and lacking lubricating properties as standard gasoline does [21]. Nevertheless, studies have shown that ethanol blend up to 20% do exhibit physical characteristics which are within the range of variation of petrol [22]. Higher blends of ethanol require vehicles that have been modified or are flex fuel vehicles.

2.1.1. Refinery Reconfiguration

Another perspective to improving octane quality of petrol of increasing interest is refinery reconfiguration. Through reconfiguration, operations such as cracking, reforming, alkylation, isomerisation, olefination, and aromatization are inbuilt into the refining process such that the product hydrocarbons are naturally high blending component for the gasoline pool. A major limitation of this process is the high cost involve in refinery reconfiguration, besides; it may produce hydrocarbons with lots of olefins and aromatics such as toluene, xylene, and benzene. Although, these have high boost on the octane quality of petrol, their health implication must be considered. The presence of olefins in petrol may results in gums and deposits formation which attracts the use of additional additives called antioxidants. It must be emphasized that sufficiently high octane fuel for high compression engines had been similarly achieved since 1913, through thermal cracking process, but since it required added expenditures on plant and equipment, the tight-fisted oil refiners took no delight in it.

2.1.2. Valve Seat Recession

Unleaded petrol has an octane rating of 92 or less while leaded petrol has octane rating of 96 or higher. Besides, leaded petrol has more effective lubricating properties. Modern car engines are designed to suit the use of unleaded petrol. One of the major problem of using unleaded petrol on these older engines is a condition known as 'valve seat recession' (VSR). Without the protective lead coating on the exhaust valve seats, it digs deeper and deeper hole for itself into the cylinder head due to the intense heat and continuous hammering of the valves opening and closing. This results to the breakdown of the engines and will requires expensive overhauling. Modern petrol engines have special harden valve seats which can withstand this harsh environment.

Lead Replacement Petrol (LRP) and aftermarket products that consumers add to automotive fuel - Anti-Wear Additives (AWA) - have been used in these older engines. The additives here may be phosphorous, sodium, potassium or manganese based and is quite satisfactory when use in correct dosing rates in appropriate vehicles. However, no additives provide as much protection as lead. Phosphorous for instance work well at low temperature and loads, but test had shown that protective coating burns off during higher load conditions [21]. Some tested and endorsed lead substitute for preventing valve seat recession by the federation of British historic vehicle clubs (FBHVC) in 1999, included: Miller VSP Plus (manganese based), Red Line Lead Substitute (sodium based), Superblend Zero Lead (potassium based), Castrol Valvemaster & Valvemaster Plus (phosphorus based), Carplan Nitrox 4-Star (potassium based). Since then other AWA have flooded the markets with their producers attesting to their wondrous effectiveness, but the efficiency and environmental impacts of these products still need to be tested by independent bodies.

3. Conclusion

The search for a cheaper and more effective additives than tetraethyl lead is still on however, what is evident is that leaded petrol has been abandon in line with the global spirit of environmental sustainability. And just as leaded petrol, the humankind should rise up to challenge and discontinue the use of any products seen to be detrimental to public health and environment. The lesson from leaded fuel should not be forgotten in hurry, independent studies on the verifications of claims made by the manufacturers of any new additives should be carried out before such products are allowed to be use in the markets. Precautionary measures, rather than incontrovertible proof of causality should be the sine qua non for making regulations to protect public health and environment.

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