The focus on aromatics in automotive fuels specifications

Can further reductions in aromatic hydrocarbons be environmentally justified?

Over the years, and particularly in the past decade, European motor fuel specifications have changed dramatically. This has followed a general trend, supported mainly by concerns about the effect of road traffic on urban air quality. The USA, and more specifically California, have led the world with regard to gasoline, while diesel has attracted considerable attention in Europe due to its much larger share of the personal car market.

Beside sulphur reduction, these changes have been mainly targeted towards aromatic hydrocarbons, with an initial focus on benzene in gasoline. Exposure of workers and the public at large to benzene, an acknowledged category 1 carcinogen, has caused particular concern and justified drastic reduction measures. Benzene can be released into the atmosphere through evaporative emissions from gasoline storage (fixed or mobile) or through vehicle tailpipe emissions. The former are directly related to the benzene content of the fuel while the latter are also influenced by the total aromatics content of the fuel.

The reduction of the benzene content of gasoline to below 1% in 2000, together with the introduction of increasingly efficient catalytic emissions control systems on vehicles, has essentially solved the exhaust emissions problem. Other measures, including vapour recovery systems and reduction of the vapour pressure of gasolines, particularly in summer, have curtailed emissions of benzene and, more generally, of volatile hydrocarbons from both bulk and on-board storage.

Other aromatic compounds, such as toluene, xylenes or ethylbenzene are not such a direct concern, but their effect on vehicle emissions of benzene and other pollutants has been the focus of attention. Increasingly effective exhaust after-treatment systems and the introduction of lower sulphur fuels have already dramatically reduced these effects and are set to further do so. Nevertheless a 42% v/v total aromatics limit in gasoline was introduced in 2000 and a further reduction to 35% from 2005 is already foreseen in the legislation.

In the case of automotive diesel, early work in the USA suggested a link between regulated emissions and total aromatics content of the fuel. Later work, however, showed the importance of density and demonstrated that polyaromatics have more effect than monoaromatics. Polyaromatics have also come under scrutiny because of the carcinogenic nature of some of these compounds, leading to a polyaromatics limit of 11% m/m in European automotive diesel from 2000. Recent CONCAWE work[1] showed that, for older technology vehicles, the quality of the fuel has a discernible effect on exhaust emissions of a marker polyaromatic compound, but that this virtually disappears with more modern technology engines and/or when an oxidation catalyst is installed.

Also from 2000 the minimum cetane number of automotive diesel was increased from 49 to 51 while the maximum density was reduced to 845 kg/m^3. These two new limits indirectly control the level of total aromatics in the fuel.

Consequences for the refiners and beyond

Aromatic hydrocarbons are an integral part of motor fuels. The problem of reducing their concentration in the commercial blends is of a different nature for gasoline and diesel.

Aromatics are desirable to meet the performance criteria of gasolines, where they provide the bulk of the octane rating, the fundamental quality for a spark-ignited engine. Aromatics are actually ‘made’ by refineries in order to meet their octane target.

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[1] *CONCAWE Review Volume 10, Number 1 (April 2001)*

In diesel, aromatics are part of the package of molecules found in the relevant virgin crude oil cuts and are also produced in catalytic and thermal cracking of heavier cuts. They are not particularly needed and have, in fact, a detrimental effect on cetane quality. Removing them is a question of cost but also of energy consumption with the corollary increase in CO_2 emissions.

Aromatics in gasoline: the quest for octane

The octane quality of the fuel is the property that allows a spark-ignited engine to run efficiently by permitting a high compression ratio[2]. The demand for octane has increased over the years particularly in Europe where more power was sought from smaller engines and a higher emphasis was placed on fuel economy. The current European standard grade has a minimum requirement of 95 RON, 85 MON.

Octane is related to the molecular composition of the fuel. Straight chain paraffins and naphthenes (saturated cyclic hydrocarbons) have poor octane ratings whereas aromatics, branched paraffins and olefins, have high octane values. Oxygenated compounds such as alcohols and ethers generally have very high blending octanes. MON is generally lower than RON and the difference (called sensitivity) is highest with unsaturated and oxygenated molecules.

Addition of an organic lead compound was, in the past, an alternative way to boost the octane rating by typically 3–4 points. The elimination of lead, both on health grounds and to enable the use of 3-way exhaust catalysts, has removed this option. The use of alternative metal-based additives such as MMT (methylcyclopentadienyl manganese tricarbonyl) or Ferrocene is not widespread in Europe and there is continued controversy on their possible effects on engines and after-treatment systems. The whole of the octane requirement therefore has to stem from the molecular composition of the gasoline.

The molecular ‘cocktail’ of virgin gasolines (known as ‘naphthas’) is such that their octane rating is generally very low, typically 65–75. The traditional solution has been to ‘reform’ the naphthas, a process whereby paraffins are cyclized and cyclic molecules are dehydrogenated to aromatics. Reforming is therefore an essential source of hydrogen (and in many refineries the only one), a commodity in increasing demand for hydrotreating of various streams, particularly gasoils. Most reformates are produced with RON values between 98 and 102 and contain between 60% and 75% aromatics. This includes the benzene present in the virgin streams and that formed from ‘precursor’ molecules such as cyclohexane. The lighter naphtha fractions can also be improved by isomerization, turning straight chains into branched paraffins.

Large volumes of the world’s gasoline are produced via catalytic cracking of heavier cuts such as vacuum distillates and atmospheric residues. These ‘cracked gasolines’ are strongly unsaturated, containing aromatics (including some benzene) and large amounts of olefins. Their octane rating is relatively high, typically 91–93 RON, although not high enough for the modern European premium grades especially in view of their high sensitivity. Catalytic crackers also produce significant quantities of mixed C3 and C4 hydrocarbons. These, and particularly the C4 fraction, can be combined by alkylation to form C7 and C8 hydrocarbons.

In terms of volumes, only reformates and cracked naphthas have the potential to provide the bulk of the demand at the required octane level. The sources of isoparaffins are limited and such components as isomerates and alkylates, although important, can only play a supporting role when it comes to producing the large volumes of gasoline required by the market. Oxygenates such as alcohols or ethers generally have favourable octane properties and have, in recent years, assumed an important role in gasoline manufacture, principally in the form of MTBE (methyl tertiary butyl ether).

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[2] *Octane rating is a performance property measured by comparison of the self-ignition tendency of a fuel with that of two reference compounds in a standard test engine. Two different sets of testing conditions are used resulting in a RON (Research Octane Number) and a MON (Motor Octane Number) rating, with MON generally lower than RON. The ‘road octane number’, (RON+MON)/2, is used as a single specification in the USA whereas both numbers are specified separately in Europe.*

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The elimination of most of the benzene had a relatively limited impact on octane because the benzene concentrations were relatively low to start with (about 3% v/v average for Europe) and because benzene could be at least partially replaced by heavier aromatics. The reduction was achieved by a combination of measures involving not making the benzene by eliminating the precursors from the reformer feed and/or changing the crude diet. Where this was not sufficient or not desirable, benzene was physically separated from the bulk of the reformate and either sold to the petrochemical industry or hydrogenated. It must be noted that the initial concerns over benzene overproduction never materialized as most of the benzene originally found in gasolines is now not made in the first place.

The residual benzene now comes more or less in equal parts from reformate and from cracked gasolines. Any further reduction of the benzene specification would require addressing the problem of removing benzene from both streams. At this level the options are limited. Solvent extraction of reformates, although applied on a limited scale for the production of individual aromatics, has not been used specifically for the purpose of removing benzene from gasoline. This could be envisaged but would be very capital- and energy-intensive. The full-range cracked gasoline is often split into two or three cuts to provide optimum blending flexibility and, more recently, sulphur removal. Benzene can be concentrated in the 'heart-cut', a stream that is sometimes hydrotreated and reformed because of its comparatively low octane. In this way the bulk of the benzene can be concentrated in the reformate and dealt with accordingly. Directionally though, this entails replacing olefinic by aromatic octane and is therefore limited by the total aromatics specification.

Reduction of total aromatics in gasoline is a particularly thorny problem for a refiner as it requires a strategy for replacing the octane deficit by using other suitable molecules. The above short inventory of possible options shows that the number of candidates is limited. When the other limits on olefins, sulphur, oxygen content are factored in, the feeling is increasingly that we may 'run out of molecules' to formulate our gasolines.

Branched paraffins are the preferred compounds but their availability is very limited and they cannot play much more than a supporting role when it comes to producing the large volumes required by the market. Oxygenates are widely available but supply would in no way be sufficient to make up a major aromatics shortfall. In any case their use is currently limited by a maximum allowable oxygen content of 2.7% m/m. Ethers, particularly MTBE, have also caused concern in relation to potential contamination of underground water.

At the 35% aromatics level, the combined pressures of benzene reduction, virtually complete sulphur removal and olefins limitation will stretch the octane producing capability of the refineries to the limit. Any further reduction of the total aromatics, besides having no environmental justification, would require a complete rethink of the way gasoline is manufactured and require massive investments.

It is also worth noting that the growing demand for isoparaffins for gasoline manufacture is having an effect on the availability of light naphtha, the traditional bulk feedstock for light olefins production. A CONCAWE study on the consequences of reducing total aromatics from 42% to 35% suggested an increase of the density of petrochemical naphtha from 690 to 710 kg/m^3. Such a change can have far-reaching consequences. Higher feed density generally equates to lower olefin yields and proportionally higher production of pyrolysis gasoline i.e. mainly aromatics that may not match the demand. Portions of these heavier streams also traditionally find their way back into the refinery blends where they are increasingly unwanted. The increased value of C4 olefins as alkylation feed also introduces an extra 'front' in the competition of fuels and petrochemicals for appropriate feedstocks.

Aromatics in diesel

Although there is no total aromatics limit as such in EU diesel, the amount is effectively constrained through the combination of the density, distillation and cetane specifications. Currently at 51 the European cetane number specification is the world's highest. Tightening of tail-end distillation limits as well as the need for ultra-deep desulphurization also pushes refiners towards selecting lighter fractions for the diesel pool.

In practice the current specifications allow the use of only small amounts of simply desulphurized cracked gasoils in diesel blends. This is even more the case at the 10 ppm sulphur level, as ultra-deep desulphurization of cracked stocks is difficult to achieve in standard or modified hydrodesulphurization plants. Turning cracked gasoil into suitable diesel components requires deep hydrogenation either in a purpose-built plant or as part of the feed stream to a hydrocracker. As a consequence EU diesel is, already today, largely blended from virgin and deeply hydrogenated streams. This is set to become even more so in the future. This constrains the production volumes in a context of increasing demand for diesel and jet fuel. While development of a sizeable distillate deficit for the whole region is likely, it will be mostly filled from outside sources such as Russia and the Middle East. European refiners are unlikely to enjoy sufficient margins to justify massive yield investments but they will have a strong incentive to maximize diesel and jet production from their existing facilities. As a result the relatively light, low aromatic distillate fractions favoured as petrochemical feed, are likely to become more desirable to the refiners for their fuel business.

In addition to the implicit limit on total aromatics discussed above, the content of di+ aromatics in European diesel has also been limited to 11% m/m since January 2000. The polyaromatics content of a virgin gasoil is highly dependent on the origin of the crude. Cracked stocks generally have high levels of polyaromatics but this is also very variable. Hydrotreating converts part of the polyaromatic content to monoaromatics, the conversion rate depending on the operating conditions (modern plants operating at higher pressure and lower temperature achieve higher conversion rates). The current European market average is around 5% m/m but this conceals a large disparity between individual situations. Further sulphur reductions will somewhat reduce this number but a significant reduction would require specific processing steps involving deep hydrogenation.

The bottom line

The European refining industry has achieved great improvements in the quality of road fuels and is actively working towards meeting the 2005 specifications and towards the virtual elimination of sulphur by the end of the decade. This has already required, and will require further large investments, while resulting in additional CO_2 emissions.

As long as the spark ignition engine has a sizeable share of the vehicle market, aromatics will play a vital role in providing both the quantity and high-octane quality of the required fuel. Any further reduction of the aromatics content of motor fuels would require further in-depth changes in the way streams are processed and selected in the refinery. This would invariably translate into extra costs and extra energy use, i.e. extra CO_2 emissions from the refinery.

The indications are that, at the level already legislated and with the advent of advanced engines and after-treatment technologies, further reductions of the aromatics content of road fuels would afford minimal benefits in terms of emissions reduction and air quality improvement.