Carbon, sulphur and hydrogen in oil refineries

In order to meet new fuels specifications, refineries need to reduce carbon and sulphur contents of petroleum fuels and therefore use more hydrogen. The net result is an increase in global CO_2 emissions.

CARBON CONTENT

Accurately calculating the global carbon balance in oil refinery and petroleum product end-use systems is a challenge of nightmare proportions. All except the lightest of the output streams are of uncertain and variable chemical composition. Oil refining deals with potentially millions of different chemical compounds all mixed up together. Matters are not too difficult up to the six carbons level, the light gasoline region. Beyond six, the number of possible combinations of carbon (linked by single and double bonds in rings and chains) and hydrogen increases exponentially. Then there are the myriad varieties of sulphur and nitrogen compounds commonly present in crude oils. The measurement and tracking of individual compounds through the refining processes, 'refining with tweezers' as it is jokingly called, is clearly impossible. To cap the complexities, where properties of complex pure hydrocarbon compounds have been measured, published data do not always all run in neatly predictable progressions.

Up to the present day, not even the species of the chemical compounds constituting the products have been measured routinely. Speciation is limited to determinations of the PONA (paraffins, olefins, naphthenes, and aromatics species) of some gasolines. There are also some uncertain measures of mono- and poly- aromatics species in some diesel fuels and their components where, depending on the test methods, the values recorded include more or less of the other species attached to the aromatic ring(s).

Physical/performance data on some examples of hydrocarbons in the diesel boiling range					
Hydrocarbon	$C_x:H_y$	Type	Boiling point °C	Density kg/m^3	Cetane Number
Acenaphthylene	$C_{12}H_8$	Diaromatic unsaturated mononaphthene	266	899	0
Acenaphthene	$C_{12}H_{10}$	Diaromatic saturated mononaphthene	279	1024	0
Tetradecyl benzene	$C_{20}H_{34}$	Monoaromatic mononaphthene	359	856	72
Cyclohexyl benzene	$C_{12}H_{16}$	Monoaromatic saturated	236	950	30
n-Octadecane	$C_{18}H_{38}$	Paraffin	316	792	110
n-Hexadecane (Cetane)	$C_{16}H_{34}$	Paraffin	287	773	100
n-Pentadecane	$C_{15}H_{32}$	Paraffin	270	768	95
n-Tridecane	$C_{13}H_{28}$	Paraffin	234	756	50

Source: CRC Handbook of Chemistry & Physics 75th Ann. Ed.1988–89

Petroleum products are specified mainly by measurements of physical characteristics. The available data that define the heaviness of constituents of petroleum energy products are the measures of density and distillation cut points and boiling ranges, augmented by other physical measures that differ between products. The missing chemical measurements prevent the clear appreciation of carbon and hydrogen contents in each batch of product.

Density varies as a consequence both of changes in carbon/hydrogen (and some oxygen and sulphur) ratios, commonly referred to as aromaticity, and from changes in the number of carbon atoms bonded together in the constituent compounds. These physicochemical reasons for the changes in density are important but are unknown in detail in the models used to simulate refineries. The changes in the heating values of the road fuels can and should be accounted for. Fuel economy is generally talked of in terms of litres per 100 km, i.e. in the volumetric terms that the motorist sees. For study purposes though, it is best to work in mass units (so a mass balance can be assured) and adjust the product demands to allow for the mass-based lower heating value (LHV_m) of the fuel.

So is it not possible to do global carbon emission effects studies? Yes, not only is it possible—in fact it could hardly be simpler as long as the study is designed properly. The saviour is the mass balance fundamental that input and output are equal. The changes in input carbon can be calculated precisely. The only other requirement is that the carbon in the not-burned petroleum products does not change between cases. This happens to be true enough when the changes considered are road fuels qualities. What cannot yet be done with any great degree of accuracy is to apportion the carbon emissions between sectors such as refineries, vehicles, homes etc. CONCAWE intends to investigate doing some modelling work on the carbon outputs. Meanwhile, it is necessary to be content with the global CO_2 emission effect, which is actually what counts for sustainability and global warming considerations.

Most of the specifications being tightened, both for gasoline and diesel, tend towards more saturated and paraffinic molecules i.e. a higher hydrogen to carbon ratio. As this ratio deviates increasingly from that in the virgin crude oil fractions, hydrogen addition, and therefore manufacturing, needs to increase.

SULPHUR CONTENT

The physics and chemistry of sulphur compounds are important too. More study is needed before making confident pronouncements on the costs and carbon emissions effects of meeting universal diesel fuel sulphur contents in the region of 10 ppm and below. There is already plenty of experience of operating in this region but it is restricted to gas oils from hydrocrackers (HC), from hydrodesulphurization (HDS) and hydrodearomatization (HDA) units operating on virgin low-sulphur paraffinic gas oils that are undercut (300°C say). The EU diesel pool as a whole relies on the use of deeper virgin cuts, and high demand means high penalties for excluding the gas oils produced by visbreakers, cokers, residue hydrocrackers and cat crackers. Total exclusion of sulphurous and naphthenic crude types 'for ever' from all the EU refineries' crude oil diets also seems unlikely to be sustainable.

Hydroprocessing removes sulphur and increases yields of road fuels, but consumes hydrogen and increases global CO_2 emissions.

In the gas oil cuts, the ever-present sulphur is bonded to carbon atoms in both chains and rings. The sulphur in the chains is the most accessible to desulphurization catalysts but becomes more difficult to reach when in a ring, and much more so when two or possibly three rings are shielding the sulphur. So why not do away with the rings? HDA units add hydrogen and can virtually eliminate polyaromatics and reduce monoaromatics to a point where equilibrium is reached but before hydrocracking of the rings starts to really take off. (Such hydrocracking removes the sulphur but makes products lighter than allowable in diesel.) Hence the rings do not go away but are changed to the saturated naphthene and polynaphthene types.

When treating a gas oil in a desulphurization unit, the most reactive sulphur species are removed first. It follows that the bulk of the sulphur species remaining in a gas oil treated to a level of say 350 ppm sulphur are all fairly refractory and comparatively more difficult to remove. A common option to bridge the gap between the 350 and 50 or 10 ppm level is to add a second HDS unit in series with the existing one. Attacking the least reactive species, necessary to reach such low sulphur levels requires a combination of higher temperature and residence time on the catalyst which must be reflected in the design of such new units. A crucial aspect in the design is catalyst stability i.e. ensure catalyst lives of a practical magnitude. Although process licensors and catalysts manufacturers are working hard on the problem, the outcome remains uncertain so that the precise capital costs associated to such new HDS units remain only a 'best guess'.

As the demand on the desulphurization hardware increase, flexibility and ability to cope with unforeseen technical problems within the refinery decrease. Many refineries may insure against that by 'cherry-picking' crudes and diesel components thereby becoming less consistent in the amounts of diesel they produce.

The practical responses decided on by EU refiners are not yet fully settled for the 350 ppm maximum level following the 1 January 2000 reduction from 500 ppm. Precisely what will be done to the processing hardware to meet the much more challenging reduction to 50 ppm is

shrouded in uncertainty. Any cost study done now on 10 ppm would apportion prospective costs between the 50 ppm measure and a 10 ppm measure before having sufficient knowledge of the hardware developments that is so crucial to assure the reliability of the results.

CHANGES REQUIRE HYDROGEN

Increasing the hydrogen content of fuels beyond what is available in virgin crude fractions inevitably requires hydrogen that therefore has to be manufactured. The standard way of doing this is by partial combustion of hydrocarbons to form a mixture of carbon monoxide and hydrogen followed by the so-called CO-shift reaction with steam where CO is turned into CO_2 while hydrogen is released from the water. In this process the original hydrocarbons act both as feedstock and fuel and all carbon is turned into CO_2.

From a global perspective and assuming that the balance of alternative fuels (such as natural gas) is not affected, additional hydrogen must be made from additional crude oil. Assuming a typical carbon content of 86 per cent mass, each ton of hydrogen manufactured produces 11.5 tons of CO_2.

If this hydrogen is now added to e.g. diesel fuel via hydrotreatment, the CO_2 emissions resulting from usage of this improved fuel decrease both because of its intrinsically higher hydrogen content and its higher heating value.

The net balance is still negative though, reflecting amongst other factors the limited efficiency of the processes involved. We have calculated that a requirement of 0.5 Mt/a additional hydrogen (EU refineries for Auto/Oil I) would result in an additional consumption of 0.41 Mt/a of crude oil for a net global increase of 1.3 Mt/a CO_2 emissions.

Statements that address only a part of the issue, for example, comparisons of the carbon dioxide emissions from vehicles that run on different fuels, can be very misleading. With fuel carbon/hydrogen ratios, as with sulphur removal, there is no such thing as a free lunch in terms of global carbon dioxide emissions.