Understanding How Fuels Behave in Engines

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ABSTRACT
Although the performance of internal combustion engines is mainly set by the design and mode of operation of the engine and its peripheral equipment, differences in fuel composition can sometimes be significant. Understanding the processes that the fuel takes part in is the key to predicting and optimising its effects. Intuition is sometimes an inadequate guide, as illustrated in some examples of fuel behaviour in gasoline and Diesel engines.

Combustion chamber deposits in gasoline engines can increase NOx and hydrocarbon emissions, interfere with valve closure and increase the likelihood of knock. Laboratory experiments have shown that fuel components differ considerably in their deposit forming tendency and this data has been used to develop predictive models for engines. The mechanism by which deposits increase engine octane requirement has been shown in both laboratory and engine experiments to be partly chemical, i.e. they give off active species which induce knock.

The nature of fuel affects both the amount and composition of hydrocarbon emissions from gasoline engines. The main mechanism is trapping of the fuel in the piston top crevice and its partial oxidation during the exhaust stroke. Some of the approaches by various groups to understand and simplify this complicated problem are described. The composition of the exhaust hydrocarbon is responsible, through its effect on catalyst efficiency, for the surprising observation that NOx emissions are lower with aromatic fuels.

Particulate emissions from Diesel engines tend not to increase with fuel aromaticity, in spite of the known propensity of aromatic hydrocarbons to produce soot. It is proposed that the reason for this is a radiative feedback mechanism. Greater sootiness increases the amount of thermal radiation received by the colder, richer regions, raising their temperature and the rate at which the soot is oxidised, tending to reduce the amount finally emitted. Simplified modelling shows that the effect is of sufficient size to produce near fuel independence, and sometimes even an inverse dependence of emissions on the amount of soot initially formed.

INTRODUCTION
The performance of internal combustion engines is mainly set by the design and mode of operation of the engine hardware and its peripheral equipment. Great progress has been made in recent years in increasing fuel efficiency and power and in decreasing emissions. The scope for such improvement offered by changes in fuel composition is much less, but can sometimes be significant. Understanding the processes that the fuel takes part in is the key to predicting and optimising its effects. This paper gives examples of research to understand how fuel behaves in several aspects of both gasoline and Diesel engine operation. The emphasis is on work carried out at Shell Research, and the bias is always towards understanding how changes in the fuel affect the phenomenon. This limited objective often means that a more simplified approach is possible than if the goal were hardware design. Complete descriptions of the engine phenomena are obviously an ultimate goal but a clear understanding of the qualitative aspects of the problem is often lacking in an industry that until relatively late in its development was very largely empirically based. It is obviously important that any specifications for fuel should be based on a correct appreciation of what actually occurs. Intuitive assumptions without proper data or understanding are not always correct, as illustrated below in two examples of the effect on emissions of aromatic content in both gasoline and Diesel fuels.

The first example concerns deposit formation; a phenomenon which is sensitive to fuel quality but has received rather little fundamental investigation in spite of its significant influence on engine design and performance.

COMBUSTION CHAMBER DEPOSITS

Effects on engine performance
Deposits of various types form in many parts of a gasoline engine, usually with detrimental effects, see the extensive reviews by Kalghatgi[1,2]. Deposits in the inlet manifold, injectors and on inlet valves can now be effectively controlled by detergent additives in the fuel. Those in the
combustion chamber are not so easily affected. Although they help to improve fuel economy, they can lead to higher NO\textsubscript{x} and sometimes hydrocarbon emissions. They can cause spark-plug fouling, interfere with valve closure and cause the piston to contact the cylinder head. But the most significant effect is Octane Requirement Increase, ORI, which has to be allowed for in engine design and even then lowers engine efficiency. Typically ORI is 5 octane numbers when it stabilises after 15000 km. The mechanisms responsible are discussed below, but the amount of deposit is always the most important parameter and is rather fuel dependent. Engine studies of deposit formation tend to be protracted and require large quantities of fuel. Laboratory studies can provide a more flexible alternative.

**Lab simulation and fuel effects on deposit formation**

Most of the cylinder deposit is formed when the flame passes close to the cold wall. This process has been studied in a laboratory combustion apparatus (the "quench rig") designed to accentuate this phenomenon[3]. The relative deposition rates correlate well with engine measurements but the laboratory apparatus takes much less time and is more reproducible. A combustible mixture is flowed continuously through a narrow gap (5mm) between two cooled plates and a flame initiated by a spark plug passes through the chamber 10 times a second.

A base propane flame gives no deposit but when heavy, especially aromatic, hydrocarbons are present in the fuel, a viscous brown liquid deposit is formed. This is highly oxygenated, i.e. not a sooty carbonaceous material, and is soluble in methanol. When heated it becomes solid, insoluble in methanol and less oxygenated. It is then physically and compositionally similar to mature engine deposits. The fresh material formed in the laboratory apparatus is therefore believed to be representative of the early stages of deposit formation in engines. When the deposits are thin they build up linearly with time, but there is a removal process; this means that a weakly depositing fuel can actually remove deposit. The deposition rate is less than a molecular monolayer per combustion event, but this is sufficient to give appreciable deposit thickness both in the laboratory simulation and in an engine.

By adding pure hydrocarbons of various structures to a non-depositing base flame, their relative depositing tendencies have been determined. Fig. 1 shows this to increase with molecular weight and with the degree of chemical unsaturation (double bonds, etc.). This agrees with earlier radioactive-labelling experiments of Shore and Ockart[4].

To generalise these results we have built a model of the deposition process[3]. The region close to the wall is cool, contains fuel and oxygen and is supplied with radicals diffusing from the flame. These are ideal conditions for partial oxidation of the fuel and our hypothesis is that the partially oxidised products, being heavier and less volatile because of the oxygen they contain, condense on the wall, where they undergo polymerisation to produce deposits. The chemistry is of course complicated, but we can make a semi-empirical estimate of the number of O atoms introduced for each double bond (2) and aromatic ring (4), etc. which is used to estimate a boiling point of the condensing species. This boiling point is entirely derived from the chemical structure. Simple condensation theory shows that the deposition rate should be exponentially dependent on this parameter. Fig. 2 shows that this is indeed observed in the laboratory apparatus over 4 orders of magnitude in deposition rate.

![Deposition rates for various classes of fuel in the laboratory apparatus, wall temperature 343K.](image)

Because it is a condensation process, the rate of deposition decreases with increasing temperature. In engines, the surface temperature of the deposits increases when they get thicker because of reduced heat transfer to the wall. Consequently, the rate of deposition falls as the deposits grow and eventually the thickness reaches a constant value. A simple semi-empirical treatment[5] of this process allows the deposit masses in an engine to be modelled, at least as far as the relative performance of different fuels. For each molecular component in the gasoline, as analysed by gas chromatography, a nominal boiling point and molecular weight of the condensing species could be calculated from the chemical structure (as in fig 2) and this was used to calculate the deposit build up, assuming the components behave independently in the gas phase and dissolve in each other in the condensed phase. For the sake of practicality, hydrocarbons with similar deposition rates were handled together in one of 18 groupings. Fig. 3 shows that reasonably good agreement between the calculated and measured amount of combustion chamber deposit can be made in this way. Because there are arbitrary parameters in the model, the predictions for different fuels are relative, but the data in the diagram cover three different engines. The deposit thickness was measured at the piston top, but there is a good correlation with the thickness of deposits on the piston head, which are the ones which most affect engine performance.
Although, as is apparent from fig. 2, the polycyclic aromatics are potent deposit formers, they make only a moderate contribution to the deposits formed from a normally formulated gasoline because they are present in fairly small quantities. The same applies for nitrogen and sulphur species, some, but not all of which have high depositing tendencies. The largest contribution in normal gasolines is from the heavier mono-aromatic species.

**Chemical ORI**

Several mechanisms have been proposed to account for the increased propensity of the engine to knock when deposits are present. The volume occupied by the deposits increases the compression ratio, but this is calculated to be only a minor contributor. Thermal effects, particularly the storage of heat from the burnt gas and its release into the end gas in the next cycle is the most usually cited cause. Other mechanisms involving gas motion or fuel evaporation have also been considered but have not received much experimental or theoretical testing. A chemical mechanism, based on the release of active species from the deposits, is of special interest because it offers the possibility of mitigation without complete removal of the deposits. The MIT group[6] found it necessary to include a chemical mechanism in their modelling of engines with deposits. We have recently been able to demonstrate experimentally, in a laboratory apparatus and in an engine, that chemical effects in ORI are significant[7].

The laboratory experiments were carried out in a simple compressed air driven, un lubricated rapid compression machine[7]. This compresses a stoichiometric 80% isoctane/20% heptane - air mixture to 660K and 11.5bar, and the ignition delay is measured. When fresh deposits, transferred from the “quench rig”(described above), were placed on the end wall of the compression cylinder in contact with the autoigniting mixture, the ignition delay was found to be reduced. With successive autoignitions over the same deposit the delay gradually increased back to the value with a clean wall. During this process there was no appreciable change in the amount of deposit, nor presumably in its thermal parameters. Furthermore, there was no significant storage of heat between cycles (because they are several minutes apart) and it can be shown that the deposits caused no change in compression ratio. These results all point towards the reduction in ignition delay being due to a chemical cause, probably the emission of peroxide species from the surface. A mole fraction of di-tert-butyl peroxide of $10^{-7}$ in the gas phase reduced the ignition delay by 10%, comparable to the observed deposit effects, illustrating that not very much active material is required. Each successive autoignition depletes the active material to some extent by evaporation or decomposition, causing the progressive reduction in the effect. Heating the deposits (1hr at 180C) completely destroyed their activity.

The engine experiments[7] demonstrated that the knock limited spark advance (KLSA) of a cylinder in a Toyota 2S- FE bench engine containing deposits can be selectively
increased by blowing hot air through it. In fig 4, the KLSA of untreated cylinders was not affected whereas the KLSA of the treated ones increased by 3 to 4 crank angle degrees. The KLSA returned to its original value after a further 30 minutes running.

This oxidation process occurs under rather complicated conditions. Cold unburnt fuel-air mixture emerges from the crevice as the piston moves down during the power stroke. It is initially close to the wall but will mix with hot burnt gas already in the cylinder. In addition, the temperature falls rapidly as the pressure decreases. During the exhaust stroke the layer of hydrocarbon containing gas on the wall is rolled up in a vortex as the piston rises. The oxidation therefore takes place under conditions where there are large spatial and temporal gradients in temperature and concentration. Turbulent gas motion and heat transfer to the cylinder wall are also controlling. It is not surprising then that the modelling of this phenomenon is difficult, both at a detailed and at an practical level.

A recent semi-empirical model by Eng et al[31] is formulated in a sufficiently fundamental way for it to be used to make some mechanistic inferences. It predicts total (unspecified) hydrocarbon emissions and can account for engine variables such as speed, cylinder temperature and pressure etc. The authors concluded that the hydrocarbon consumption which resulted in CO, CO₂ and H₂O occurred above 1500K. The observed decrease in the extent of oxidation of paraffinic fuels correlated with the diffusion coefficients, implying that diffusive mixing is controlling. Kinetic control still plays some part for the less chemically reactive fuels methane and iso-butene and, although not discussed by Eng et al, aromatics. The work does not address the formation of partial oxidation products.

A more fundamental model of the hydrocarbon oxidation process has been developed by Wu and Hochgreb[10]. They described the detailed kinetics, diffusion and heat transfer occurring in the boundary layer near the cylinder wall by integrating the partial differential equations in time and one spatial dimension. These calculations showed that fuel which entered the cylinder when the temperature was above 1800K was almost completely oxidised, that entering when the temperature had fallen to below about 1100K remained unaffected, and between these values partial oxidation products were formed. The detailed chemistry predicted the speciation of the emitted hydrocarbons quite well. The reduced oxidation of iso-octane over propane was regarded as due to the greater number of steps involved in its oxidation as well as the reduced diffusion coefficient.

These calculations, although idealised by being one dimensional and by treating gas motion only to the extent of including an eddy diffusivity contribution to diffusion, undoubtedly capture the main qualitative features of incylinder hydrocarbon oxidation. They are however large calculations and at Thornton we have attempted to develop simpler empirical models which describe the speciation of the hydrocarbons in the exhaust. The detailed chemistry is retained, since this is essential to describe the multiplicity of products, but the physical conditions are modelled in a much simplified way. There have been several stages in this development[11]; fig. 5 shows some recent results[12] from the latest model built on the understanding arising from the work of Wu and Hochgreb[10]. The boundary layer on the
wall has three layers: the outer one is the hot burnt gas and supplies radicals by diffusion to initiate the chemistry; the middle one (treated as a well-stirred reactor) is where the chemistry occurs; the innermost layer is cool and tends to store intermediate products like alkenes produced in the middle layer, allowing them to escape further oxidation.

Fig. 5 Comparison of observed and predicted exhaust speciation for iso-octane as a fuel. The values are normalised by dividing by the unburnt fuel concentration. Experimental data is from Kaiser et al [13] at φ=0.90 1500rpm part load.

The relative amounts of most partial oxidation products can be fairly well predicted with this simplified model. The exception is ethane which, uniquely, is formed largely by radical-radical reactions. The averaging implicit in simplified models means that absolute radical concentrations, and consequently their recombination rates, are not well modelled. The agreement between observed and predicted CO emissions suggests that its main source under lean conditions is from partial oxidation of trapped hydrocarbons.

Although fuel vapour trapped in the piston top crevice is probably the main source of hydrocarbon emissions in a warmed-up conventional engine, this mechanism may not always be dominant. Liquid fuel effects[9,14] are almost certainly significant when the engine is cold and the processes involved in emissions from direct injection engines have yet to fully elucidated[15].

**NO\textsubscript{X} AROMATICS EFFECT**

The fuel effects on NO\textsubscript{X} emissions are fairly small compared with those due to the design and operation the engine, exhaust catalyst and associated control systems. But it has been observed that decreasing the aromatic content causes a reduction in engine-out NO\textsubscript{X} emission[16]. This is caused in part by the higher flame temperatures of aromatic fuels. But in vehicles with catalysts, lowering aromatic content does not produce as much benefit in the tailpipe emissions and sometimes may even cause an increase[16]. Fig. 6 shows this effect with both model fuels and fully formulated gasolines.

While there is some indication that fuels with low aromatic contents tend to run slightly leaner, the major part of this effect is due to a change in the reductant which reacts with NO on the catalyst[4,17].

Ideally, at stoichiometric conditions the catalyst will cause precisely all of the oxidising gas emitted by the engine, O\textsubscript{2} and NO, to react with the reducing gases H\textsubscript{2}, CO and hydrocarbons. H\textsubscript{2} is unlikely to be present in quantities at near stoichiometric conditions. Laboratory tests with simulated exhaust gas show that CO and most hydrocarbons (including aromatics) are sufficiently reactive to completely reduce both O\textsubscript{2} and NO under normal catalyst operating conditions. However methane (and to a lesser extent ethane) are less reactive and may be left in the gas leaving the catalyst. Consequently, some oxidising gas must also be left; this must be NO which is less reactive than O\textsubscript{2}. Therefore that presence of methane in engine exhaust will be associated with higher NO\textsubscript{X} emissions. The in-cylinder partial oxidation of aliphatic hydrocarbons, described in the previous section, produces quite large quantities of methane. Aromatics, on the other hand, although they are initially less likely to oxidise in the cylinder, tend to produce much less methane when they do so. This is illustrated in fig. 7. The consequent lower NO\textsubscript{X} conversion - and higher NO\textsubscript{X} emission - is shown in fig. 8.

Fig. 6 The NO\textsubscript{X} aromatics effect. Although the engine produces more NO\textsubscript{X} with highly aromatic fuels, the emission after the catalyst is smaller. Stoichiometric operation at 2400rpm part load; engine and fuel details are in LeJeune et al[16].
aliphatic fuels, in line with their sooting propensity observed in atmospheric pressure flames. But the reality is different: when other properties such as density and cetane number are kept constant, several studies[19-22] have found that Diesel soot emissions are almost independent of fuel aromatic content.

Why this should be has not yet been explained; we suggest here that there are mechanisms which increase the soot oxidation rate (tending to reduce emissions) when the initial amount of soot formed is greater. This negative feedback can lead to the near independence on fuel quality observed, and can even cause, under some circumstances, less soot to be emitted for fuels which have a higher soot forming propensity.

In Dec's conceptual model of Diesel combustion[23], the fuel vapour initially premixes with a limited amount of air and burns in this very rich environment, forming large amounts of soot. At a later time in the power stroke the products of this rich combustion mix with the remainder of the air. If the mixing occurs late, the temperature is too low for the soot to oxidise and it is emitted. Anything which raises the temperature of these rich "pockets" will tend to decrease soot emission, and we have identified two possible phenomena. The first is that forming soot in rich combustion products is an exothermic process in many situations, including the current one.

$$\text{CO} + \text{H}_2 \rightarrow \text{C(s)} + \text{H}_2\text{O} \quad \Delta H_{1800\text{K}} = -134 \text{ kJ mol}^{-1}$$

More soot in a pocket leads to higher temperatures. The other is that heating of the rich pockets by radiation from the rest of the burning mixture is greater when they contain more soot.

One would hope that these effects would be included in complete Diesel combustion models which include soot formation and oxidation[24]. But the complexity is such that it is easy to lose qualitative understanding in big models; we have chosen to carry out some simplified calculations. These are illustrative of the orders of magnitude of the quantities involved. An early example of this approach, which seeks to identify and understand the important physical processes rather than to model the detail of particular engines, is the work of Amann et al.[25]

At top dead centre the injected spray is assumed to produce a fuel/air mixture with $\phi=2.8$ at 750K and 38 bar, which represents air compressed by the piston with some heat loss for fuel evaporation, etc. This instantaneously burns adiabatically, but a defined amount of solid carbon is produced, with the remaining gaseous products being in equilibrium with each other. This "pocket" is subsequently modelled using a detailed chemical kinetic scheme which describes the normal post-flame chemistry together with carbon oxidation reactions. The carbon is assumed to be a collection of shrinking spheres of initially 60 nm diameter which react with OH and $\text{O}_2[26]$. The pocket undergoes several other processes. It expands and cools as it follows a pressure history typical of a Diesel power stroke given in ref [27]. It receives energy by thermal radiation as discussed

**RADIATION ENHANCED SOOT OXIDATION**

The aromatic content of Diesel fuel has also been viewed as having a detrimental effect on emissions, in particular the soot component of the particulate emissions. On the face of it, one would expect aromatic fuels to emit more soot than
The pocket mixes with air which started at the same temperature as the pocket and has followed the same pressure history. For any pocket the mixing is assumed to start at some specified time in the power stroke and thereafter the air addition rate is a constant fraction of the current size of the pocket (xx per msec in the current example). In pockets which start to mix with air early when the temperature is high, the H₂ and CO they contain ignites. The pocket temperature then rises sufficiently that all the soot is consumed. The soot in late mixing pockets does not burn and is emitted. The critical mixing time gets later when the amount of soot in the pocket increases because of the higher initial temperature. In fig. 9 the dotted line shows the critical conditions when radiation is neglected. Mixing which starts to the left of the line leads to ignition and complete soot removal.

![Graph showing the critical times for the start of mixing. Pockets which mix to the left of the line ignite. Cases with and without radiation are shown.](image)

**Fig 9** Critical times for the start of mixing. Pockets which mix to the left of the line ignite. Cases with and without radiation are shown.

The pockets exchange radiation with their surroundings. Our treatment is more approximate than established approaches (see citations in ref. [28]). Both loss and gain terms are proportional to the absorption coefficient in the pocket which depends on the amount of soot. The incoming radiation is from other parts of the combustion and the peak temperature and emissivity used are those given in ref. [27]. Because of the T⁴ [29] most of the radiation transfer to the pocket occurs early in the stroke. The solid line in fig 9 shows that when radiation is included, pockets which mix later in the cycle are much more likely to ignite and burn their soot. The radiation effect increases with the amount of soot in the pocket. With extremely high soot loading, shown by the thin solid line in fig. 9., the soot inhibits ignition and even when it occurs soot consumption is not complete.

There will be pockets which mix at various times during the stroke. The distribution of mixing time was represented as an exponential reflecting the expectation that most of the mixing will occur early but that a few pockets will be mixed late. By weighting the unignited regions of fig. 9 with this distribution the amount of soot emitted can be calculated. Fig 10 can be interpreted as the soot emission as a function of the soot propensity of the fuel. When little soot is formed there is the expected linear dependence. But even without radiation the emission becomes less dependent on the initial soot because of the temperature increase caused by soot formation. Inclusion of radiation causes the soot emission to be less than linear at lower soot loadings and demonstrates that the emission can even go through a maximum, with a region where less soot is emitted even though more is initial formed. Typical conversion to soot in the initial rich combustion is of the order of 5% [30], close to the maximum of the curve where the emission is independent of the fuel sooting tendency.

![Graph showing soot emission as a function of soot initially formed. The fraction of carbon emitted is on an arbitrary scale.](image)

**Fig 10** Soot emission as a function of soot initially formed. The fraction of carbon emitted is on an arbitrary scale.

This modelling is very simplistic, especially the mixing model, and many of the parameters are difficult to estimate. It can only hope to illustrate the qualitative features of the phenomenon. Nevertheless, the results indicate that the proposed mechanisms which produce fuel independence of particulate emissions are feasible. More sophisticated modelling of Diesel engine combustion needs to include soot oxidation enhancement due to radiation and to exothermic soot formation.

**CONCLUSIONS**

In an environment as complex as an internal engine there can be benefit in a mechanistic approach. Particularly in respect of the fuel, appreciation of the root causes of a behaviour can ensure that the correct properties are targeted both to mitigate deleterious effects and to contribute to the improvement of the overall performance of the engine through fuel design.

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