Automotive fuels and internal combustion engines: a chemical perspective

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Commercial transportation fuels are complex mixtures containing hundreds or thousands of chemical components, whose composition has evolved considerably during the past 100 years. In conjunction with concurrent engine advancements, automotive fuel composition has been fine-tuned to balance efficiency and power demands while minimizing emissions. Pollutant emissions from internal combustion engines (ICE), which arise from non-ideal combustion, have been dramatically reduced in the past four decades. Emissions depend both on the engine operating parameters (*e.g.* engine temperature, speed, load, A/F ratio, and spark timing) and the fuel. These emissions result from complex processes involving interactions between the fuel and engine parameters. Vehicle emissions are comprised of volatile organic compounds (VOCs), CO, nitrogen oxides (NO_x), and particulate matter (PM). VOCs and NO_x form photochemical smog in urban atmospheres, and CO and PM may have adverse health impacts. Engine hardware and operating conditions, after-treatment catalysts, and fuel composition all affect the amount and composition of emissions leaving the vehicle tailpipe. While engine and after-treatment effects are generally larger than fuel effects, engine and after-treatment hardware can require specific fuel properties. Consequently, the best prospects for achieving the highest efficiency and lowest emissions lie with optimizing the entire fuel–engine–after-treatment system. This review provides a chemical perspective on the production, combustion, and environmental aspects of automotive fuels. We hope this review will be of interest to workers in the fields of chemical kinetics, fluid dynamics of reacting flows, atmospheric chemistry, automotive catalysts, fuel science, and governmental regulations.

Introduction

The vast majority of motor vehicles used around the world rely on *four-stroke* internal combustion engines. These engines contain a reciprocating piston within a cylinder, two classes of valves (intake and exhaust), and a spark plug in the case of a spark-ignition (SI) engine. Diesel engines do not have a spark

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plug, and instead rely on autoignition of the fuel. In a four-stroke SI engine, the air–fuel mixture is drawn into the cylinder during the *intake stroke* when the piston moves from the top to the bottom of its travel with the intake valve open. After the intake valve closes, the piston compresses the intake charge by a factor of approximately 10 (the *compression ratio* is the ratio by which the charge is compressed) during the *compression stroke* into a small volume (combustion chamber) between the piston top and the top of the cylinder. In the traditional pre-mixed SI engine, the spark then ignites the flammable mixture and a flame passes smoothly across the combustion chamber at a velocity governed by the turbulent flame speed. In a diesel engine, the fuel is injected directly into either the cylinder or a pre-chamber and the fuel burns primarily as a diffusion flame attached to the fuel injector. The burning fuel increases the gas temperature, raising the pressure in the combustion chamber, which causes the piston to be driven down during the *expansion stroke*, generating power to propel the vehicle. When the piston approaches the bottom of its travel, the exhaust valve opens and the exhaust gases are pushed by the rising piston through the exhaust manifold, through any included after-treatment devices, and out the exhaust pipe into the atmosphere during the *exhaust stroke*. The details of SI and diesel engine operation are not discussed here, but are available elsewhere.[1] In this review, the source and composition of automotive fuels are discussed. After examining fuel issues, combustion in internal combustion engines is explored, including a detailed discussion of the chemistry associated with VOC, NO_x, CO, and PM emissions. The effect of fuel composition on catalytic exhaust after-treatment is then examined, followed by a discussion of the atmospheric chemistry relevant to ICE operation. Finally, we describe the chemical issues associated with likely future automotive fuels.

Crude oil composition

More than 95% of the world's transportation fuel comes from fossil fuels. Gasoline (petrol) and diesel, the predominant transportation fuels, are primarily derived from crude oil. Crude oil is a highly complex mixture derived from organic matter deposited with sediment millions of years ago that has been transformed.[2] The most common petroleum source rocks contain organic matter derived from photosynthetic marine microscopic organisms, called plankton, which floated near the surfaces of ancient oceans. Some petroleum and appreciable amounts of gas are derived from land plant material. In both cases, anaerobic microbial and diagenetic processes convert this primary organic matter into kerogen. When buried to great depths and heated, petroleum is generated from kerogen and expelled from the source rocks. The presence of biogenic markers provides compelling evidence of the biological origin of crude oil.[3] Contrary to common perception, oil is not produced from vast pockets of pooled liquids. Once expelled from source statra, oil and gas, driven by buoyancy and capillary pressure, migrate through tiny, water-filled pore spaces and fractures. This upwards migration may be stopped by a layer of impervious or non-porous rock and become trapped. Large reserves of producible oil occur only when it is trapped in a large, subsurface structure of highly permeable rock much like water that is trapped in a sponge.

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Oil deposits exist in many locations and originated with varied organic precursors that were subjected to different temperature and pressure histories. Hence, it is not surprising that crude oil has physical properties (viscosity and density) and chemical composition (hydrocarbon distribution, oxygen, nitrogen, and sulfur, and heavy metal content) that vary greatly depending upon location.

After the crude oil is recovered from below the ground or ocean floor, it is conveyed *via* pipeline or tanker to a refinery, where it is converted into useful products. The first step involves separation based on volatility, carried out by distillation. The lightest fraction consists of dissolved gases (liquified petroleum gas, or LPG) that span the carbon range C_2–C_4. Gasoline-range material encompasses the range $\approx C_4$–C_{12}, while diesel covers $\approx C_{10}$–C_{24}. As Fig. 1 shows, 2/3 of each barrel refined in the United States ends up as gasoline or diesel. The ratio is different in other parts of the world, reflecting differing demands. However, as shown by Fig. 2, the initial unprocessed crude has a molecular weight distribution

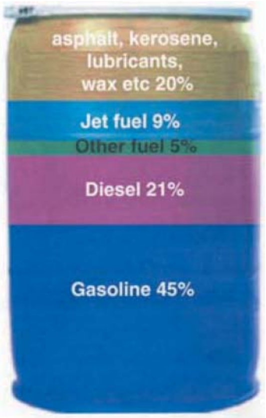


Fig. 1 End uses for typical barrel of oil in the United States. Source: American Petroleum Institute (API).

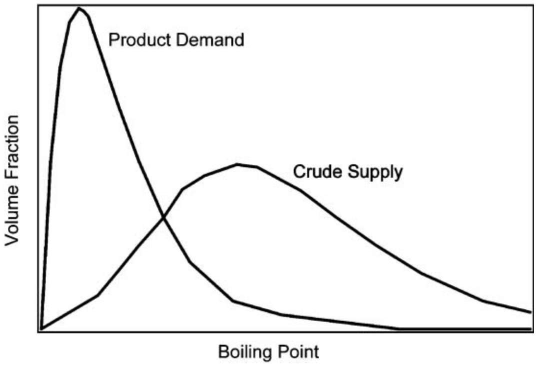


Fig. 2 Boiling point distribution of unprocessed crude compared to the product demand, demonstrating the large degree of refining required to meet product demand.

skewed to heavier products. Refinery processes that transform lower value, heavy material into lighter products are required to meet the transportation fuel demand.[4] These processes include:

Catalytic cracking—breaking apart of heavy molecules, most often in a reactor employing a fluidized catalyst bed.

Hydrocracking—catalytic cracking of heavy molecules with the addition of hydrogen to extend catalyst life.

Coking—a severe thermal cracking (free-radical-mediated) process.

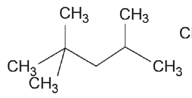
Meeting the demands of commercial fuel requires more than just volatility modifications, however. The fuel produced from crude distillation performs poorly in conventional engines, and must be blended with other refinery streams to meet performance and regulatory specifications. Details of these conversion processes will be described below following a discussion of spark ignition and diesel engines.

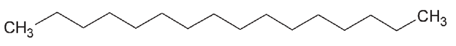
Spark-ignited engine operation

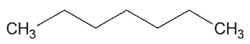
Port fuel injected (PFI) engines are the most commonly used spark ignition (SI) engine in current vehicles. In certain markets, a very small number of direct-injected spark ignition (DISI) engines have been introduced. Both use gasoline fuel. In PFI engines, fuel is injected into the intake port near the closed intake valve, producing a well mixed fuel–air charge in the combustion chamber. This is the most commonly used engine type in current vehicles. These engines are typically operated with a stoichiometric fuel–air ratio, which is the ratio that permits complete conversion of the fuel and oxygen in the intake charge to form CO_2 and H_2O. As a result of the premixed combustion, it produces very low particulate emissions. The levels of other emissions directly leaving the engine are relatively high, and compliance with regulated emission standards relies on the effectiveness of the three-way catalyst, which reduces emissions by 95–99% as discussed in more detail below.

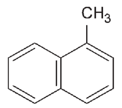
In DISI engines, the fuel is injected directly into the combustion chamber. At higher load, the fuel is injected during the intake stroke to form a nearly homogeneous fuel–air mixture at the time of ignition. At lower load, the injection timing can be delayed until the compression stroke to produce a "stratified" fuel mixture. This mixture is ideally uniform, premixed, and stoichiometric near the center, and devoid of fuel near the cylinder walls. This spatial localization translates into a faster burn and allows the engine to be run more fuel-lean overall than PFI engines, providing improved fuel economy and better performance during transient acceleration/deceleration. In practice, however, it is difficult to realize this idealized mixing, and fuel-rich and lean regions result, leading to reduced benefits. Additionally, because this engine injects fuel droplets directly into the combustion chamber, particulate emissions are increased substantially relative to PFI engines.[5] Like PFI engines, DISI engines rely on catalytic devices to significantly reduce engine-out concentrations of regulated emissions.

For gasoline, the primary performance criterion is knock resistance, defined by the fuel's octane number. Engine knock is a condition where a fraction of the unburned fuel mixture spontaneously ignites before it can be consumed by the flame generated from the spark plug. The resulting mini-explosions can cause significant engine damage. Engine knock has historically limited the performance and efficiency of spark-ignited engines, and much work has been done to minimize knock through hardware modifications and chemical upgrading of the fuel. The octane number of a fuel is measured using a single cylinder, variable compression ratio, knock testing engine. The compression ratio of the engine is adjusted to give knock of a standard intensity. The engine is then run using reference fuels which are mixtures of n-heptane and iso-octane (2,2,4-trimethylpentane). The octane number of n-heptane is defined as 0 while that of iso-octane is 100. The octane number of the test fuel is defined as the volume percent of iso-octane in the reference fuel giving the same knock as the test fuel.


iso-octane, octane number = 100


n-hexadecane (cetane), cetane number = 100


n-heptane, octane number = 0


1-methyl napthalene, cetane number = 0

Two octane numbers are routinely used to specify the knock resistance of a fuel—the research and motor octane numbers (RON and MON, respectively). RON is measured at a lower operating speed and intake air temperature than MON. The latter is most representative of aggressive, high-load driving and in practice usefully defines ignition quality for aircraft and racing engines. RON, on the other hand, appears to be a better descriptor of ignition quality for modern automobiles.[6] In Europe and Japan, fuel at the pump is denoted by its RON (typical values are 90 and 95 for Japan and Europe, respectively), whereas in North America a linear average of the two ((R + M)/2) is displayed (typical values are 87–92).

Historically, metallic anti-knock additives such as tetraethyl lead (TEL) were added to gasoline to increase its octane number. The mechanism behind TEL's antiknock performance involves its decomposition to form lead oxide particles in the unburned gas prior to arrival of the flame. These particles scavenge radicals formed from low temperature oxidation reactions of the fuel, thereby inhibiting preflame chain branching reactions that lead to autoignition and hence knock. At one time TEL was ubiquitous in gasoline, but its use has been eliminated in most of the world. This is due to concerns over the health impacts of lead, and its interference with exhaust after-treatment catalysts, for example due to physical coating of the catalyst and formation of an inactive alloy with Pd. Efforts to phase out the use of lead additives are continuing.

The virgin naphtha distilled from crude oil is comprised of three main types of hydrocarbons: paraffins (alkanes), naphthenes (cycloalkanes), and aromatics. Olefins, which are not naturally present in crude oil, are produced by cracking processes in the refinery, and are valuable gasoline components because of their high octane number and flame speed. The catalytic transformations that provide streams to upgrade the gasoline include:

Alkylation—reaction of a C_3/C_4 alkane with a C_3/C_4 olefin to yield a high octane iso-paraffin.

Isomerization—catalytic conversion of n-paraffins to iso-paraffins.

Reformation—conversion of paraffins and cyclo-paraffins to branched paraffins and aromatics *via* dehydrogenation/dehydrocyclization.

The streams are carefully blended to meet octane and other product specifications. Where possible, performance-based specifications are used (*e.g.*, for oxidation stability), but in other cases the composition of the fuel is specified.

Fuel specifications place restrictions on volatility to ensure good vehicle operation and to limit evaporative emissions. The volatility of gasoline is adjusted seasonally, and is higher during winter in cold climates to promote starting of cold vehicles. In addition, the vapor pressure is controlled to maintain a fuel-rich, *i.e.*, non-explosive, mixture in the gas tank.

Compositional constraints on gasoline can also be specified and are motivated by air quality considerations. Air quality is affected by local meteorology and pollutants from stationary and mobile sources. Consequently, studies focusing on improving air quality must consider all related factors. If it is determined that improvements from mobile-source emissions are cost-effective compared to other alternatives, modifications to the vehicle-fuel system may be appropriate.

Fuel composition changes mostly are driven by the requirements of engine or after-treatment hardware to meet air quality requirements. Of the fuel's compositional constraints, lead is the most important. As described above, this is due to health concerns and the irreversible poisoning of catalytic converters. Compositional constraints on sulfur have also been specified to address after-treatment effectiveness. The effect of sulfur on catalytic converter effectiveness is much smaller than lead and is generally reversible, with the extent of reversibility depending on pollutant and drive cycle. Sulfur levels have been reduced during the past decade. For example, the sulfur limit for European gasoline was 1000 ppm in 1993, and was lowered to 150 ppm in 2000. Fuels at or below 10 ppm are already being introduced in Europe, and by 2009 all European gasoline will be at this level. Similar reductions are occurring in other parts of the world. Concerns over health effects have also led to reductions in the level of benzene, which is now capped at 1% in Europe and in U.S. reformulated gasoline (RFG). Performance and product quality considerations also are reflected in fuel specifications. Where possible they are expressed as performance requirements, for example laboratory tests are used to evaluate fuel stability and gum formation. Limitations on the concentration of aromatics and olefins are also included in some areas. Oxygenates may be added to gasoline and are controlled through maximum limits, and in some cases minimum limits. Vapor pressure reductions can reduce evaporative emissions. Collectively, lead, sulfur, and vapor pressure are the fuel variables that have had the greatest impact on reducing emissions.

In the following sections, CO, NO_x, and HC emissions from PFI engines are discussed. Regulated emissions from DISI engines[7] and fuel effects[8,9] are presented and discussed elsewhere.

The major emissions from gasoline engines can be classified as either products of incomplete combustion or species formed at high temperature in the cylinder. The primary incomplete combustion products include carbon monoxide (CO) and unburned or partially-burned fuel, usually denoted as hydrocarbon (HC) or volatile organic compounds (VOC). Engine-out CO levels are normally quite low, and are reduced to very low levels by exhaust catalysts. Lean-burn gasoline engines can have higher CO levels than stoichiometric engines since the lower burned gas temperatures contribute to slower flame propagation, and combustion may not progress to completion.

Oxides of sulfur and nitrogen are also formed during combustion and constitute significant emission challenges. Sulfur oxides (primarily SO_2, collectively denoted SO_x) are formed from combustion of sulfur-containing molecules in the fuel. SO_2 reduces the conversion efficiency of 3-way gasoline catalysts and is a more severe poison for advanced NO_x after-treatment systems (discussed below). As mentioned above, this has motivated the substantial reductions in fuel sulfur realized in recent decades. Nitrogen oxide (primarily NO and NO_2, or NO_x) emissions come from two sources—oxidation of fuel-bound nitrogen and high temperature oxidation of atmospheric nitrogen in the combustion chamber. Although some nitrogen is present in the fuel, the vast majority of NO_x emissions come from oxidation of atmospheric nitrogen initiated *via* reaction with O atoms, $O + N_2 = NO + N$, followed by $N + O_2 = NO + O$, and $N + OH = NO + H$ (see ref. 1, section 11.2 and refs. therein). This is known as the Zeldovich mechanism after its discoverer.[10] Oxygen atoms are produced by the unimolecular thermal decomposition of molecular oxygen, and hence the formation of NO increases sharply with temperature. Reducing the burned gas temperature is an effective means to limit NO_x emissions. One commonly employed strategy, termed exhaust gas recirculation (EGR), involves recirculating a fraction (5–30%) of the exhaust gas to the intake manifold. The dilution effect, combined with replacement of air with the exhaust gases CO_2 and H_2O which have higher heat capacities, leads to lower combustion temperatures and hence reduced NO formation. Unfortunately, there is no free lunch: EGR increases soot production, decreases thermal efficiency, and can cause misfire

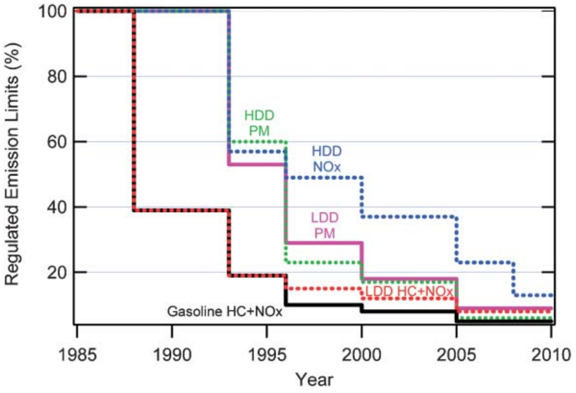


Fig. 3 Regulated emission levels *vs* time for European vehicles, normalized to 1985 levels. HDD = heavy duty diesel, LDD = light duty diesel. From reference 12.

at excessive levels. As usual, fine control is required to balance effects.

HC, CO, and NO_x emissions from motor vehicles have been regulated for five decades, being first introduced in California in the 1960s.[11] As shown in Fig. 3 for the case of Europe, tremendous improvements have been realized over the past 20 years and are continuing.

Emissions caused by evaporation of unburned fuel into the atmosphere make-up roughly one third of total gasoline vehicle HC emissions and are also regulated. These emissions occur while the vehicle is parked, during refueling,[13] while the engine is running, and immediately after the engine is turned off while the vehicle fuel system is still warm. On modern vehicles these emissions are controlled by venting vapors to a carbon canister onboard the vehicle, with the vapors later purged from the canister and burned in the engine. In most cases, control is based on the total mass of HC emissions. However, the California Air Resources Board (CARB) has also adopted regulations which require control of automotive vehicle exhaust based on its reactivity in generating photochemical smog in the urban atmosphere (see below).

Exhaust HC species differ in their ability to contribute to smog formation. The concentrations of major and many minor exhaust hydrocarbon species must be measured accurately and their sources within the engine understood to facilitate control of the exhaust mass and reactivity. A detailed understanding is particularly challenging since the composition of evaporative emissions differs significantly from exhaust emissions, and both differ significantly from fuel composition. For example, olefins have a very high ability to form smog. Therefore, reducing olefins emitted from the vehicle is beneficial. However, simply lowering the fuel olefin levels may not yield the expected reduction since olefins are formed during the combustion process by reactions that depend on operating conditions and fuel composition, as discussed below. By contrast, methane is essentially unreactive in the atmosphere. Methane emissions are not subject to governmental control in the US but are controlled in Europe. While the differing atmospheric reactivity of various hydrocarbons is well-established, changes to the overall fuel composition are not considered to have had a large effect on air quality in California. Rather, it has been reductions in the total amount of HC emissions that have the largest effect. Since HC and NO_x levels both affect atmospheric ozone levels, much research has been carried out to identify effective ozone reduction strategies. While there have been large emission reductions from new vehicles, it is also important to reduce the number of "high-emitters," *i.e.*, engines that have not been properly maintained, which represent a small fraction of vehicles while accounting for a highly disproportionate fraction of vehicle HC and CO emissions.[14]

Sources of organic emissions from SI engines

The following discussion briefly examines selected sources of the emissions leaving the exhaust port of an SI engine (engine-out emissions). The engine-out emissions provide information about the combustion processes in the engine and exhaust system and are the gases that are fed into the catalyst for after-treatment. Catalytic converters will be discussed in a later section.

Organic emissions are a complex mixture of unburned fuel and products of incomplete fuel combustion, consisting primarily of olefins, smaller amounts of aldehydes, and some CO. The mass distribution of these species in the exhaust is a function of the engine design, fuel composition, and the engine operating conditions such as spark timing, EGR levels, *etc.*[15] Engine effects are not detailed here but are discussed in ref. 15.

Following ignition by the spark plug, a flame front propagates smoothly across the engine cylinder at a velocity determined by the turbulent flame speed. This process is generally very efficient with little HC fuel escaping combustion during near-stoichiometric operation. However, unburned fuel and fuel-derived organic combustion products representing ~1–2% of the HC mass in the initial fuel mixture are present in the engine-out exhaust. These emissions are subsequently reduced by 95–99% by the exhaust catalyst. This section examines briefly some of the sources of these emissions, which are discussed in detail elsewhere.[15–17]

Crevice volumes—For all operating conditions, a major source of HC emissions is unburned fuel (~5–7% of the intake charge) stored in crevice volumes within the cylinder, particularly around the piston rings.[17] The flame cannot propagate through narrow entrances into crevice volumes and the stored fuel remains unburned. Fuel leaves the crevices during the expansion stroke and a large fraction of the stored HC is converted to CO or CO_2 in the hot burned gases within the cylinder and exhaust system. The remaining organic emissions (20–40% of the fuel stored in a crevice) consist of unburned fuel and organic products of partial combustion. Burn-up of stored HCs within the exhaust system is very important in determining the amounts of specific product species that are emitted.[18]

Wall wetting by fuel—Another important HC source arises from liquid fuel striking the cool walls of the combustion chamber during cold engine start-up. This produces a fuel film, which does not evaporate and burn during flame passage but does evaporate later in the combustion cycle when the cylinder gases are cooling, providing increased HC emission. The HC emissions from wall wetting disappear when the engine is fully warm.[19]

Absorption of fuel in oil layers—A third potential source of HC emissions results from gaseous fuel dissolving in oil layers or oil-soaked deposits within the cylinder during the intake and compression strokes. The dissolved fuel is shielded from the flame and desorbs during the expansion stroke. While the possibility that such an effect can occur in an engine has been demonstrated unambiguously, the actual magnitude of the effect is likely to be small during warmed-up operation.[20]

Effect of fuel structure on HC emissions

Many studies have been performed to investigate fuel effects on emissions using gasoline blends with varying properties. However, a wider range of fuel effects can be illustrated by considering pure compound fuels. While the fuel structure effects on HC emissions are small for vehicles with advanced after-treatment, these studies provide valuable insight into the combustion process within the engine, and permit identification of strategies to optimize performance.

Experiments have been performed in which a fully warm engine was run on single-component HC test fuels, both gaseous and liquid. The engine was operated at 1500 rpm, medium load (3.8 bar IMEP), and $\phi = 0.9$ (ϕ is the actual fuel/air ratio divided by the stoichiometric ratio). The liquid fuels were introduced into the engine by a fuel injector located in the intake port. Select experiments with liquid fuel injection farther upstream in a heated section of the intake manifold yielded identical results, indicating that mixture preparation/volatility effects are small. The gaseous fuels were mixed with air upstream of the intake manifold to promote good mixing.[15] Fig. 4 presents the total engine-out HC emissions for eight fuels as a percentage of the total carbon mass present in the intake charge (*e.g.*, 1.4% of the initial iso-octane fuel exits the exhaust as unburned HC species). The total emissions vary greatly with fuel structure. Two factors have been identified for this large variation: diffusion and reactivity. Diffusion of fuel molecules from boundary layers near the cylinder wall into the hot core gas causing partial oxidation of this fuel may be a significant source of burn-up of HC species exiting crevices during the expansion stroke. Thus, higher molecular weight fuels, which diffuse more slowly, tend to exhibit higher emissions.[15,21] However, this cannot be the only mechanism causing the observed changes. As seen in Fig. 4, there are much higher emissions when the engine is run on methane than when run on ethylene. This is contrary to a simple diffusion hypothesis since methane diffuses faster than ethylene. The increased emissions using methane fuel presumably result from its lower reactivity and slower oxidation. Thus, a combination of chemical kinetic reactivity plus diffusion is required to understand the observed variations.

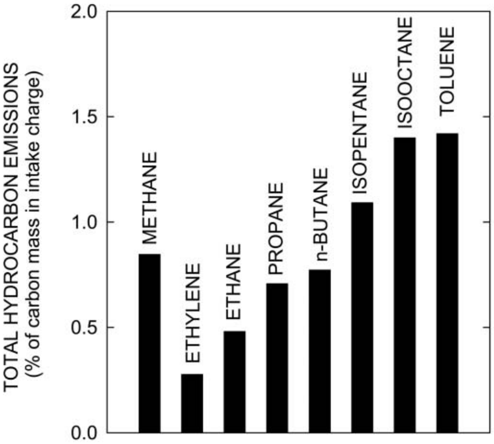


Fig. 4 Engine-out emissions for single component fuels as a percentage of the total carbon in the intake charge. Operating conditions: 1500 rpm, 3.8 bar IMEP, MBT spark timing, $\phi = 0.9$, 90 °C coolant temp, and 73 °C oil temp. See ref. 15 for more details.

Fuel structure is also critical in determining the specific HC product species that are exhausted from the engine. As an example, for iso-octane fuel (2,2,4 trimethylpentane) unburned iso-octane represents approximately 46% of the total carbon mass emission at the engine operating condition of Fig. 4.[15] The remainder of the emissions consist primarily of olefins (isobutene [22.9%], propylene [9%], and dimethyl pentenes [4%]). Each of these olefins is a β-scission decomposition product (*i.e.*, formed by breaking of a C–C bond one removed from the radical site) of one of the iso-octyl radicals formed by hydrogen atom abstraction from fuel molecules as unburned fuel/air flows out of crevice volumes and is partially oxidized.[15] This is a typical decomposition process for paraffin fuel components. The remainder of the emissions consists primarily of small amounts of methane [1.7%] and unsaturated HCs (*i.e.*, ethylene [3.5%], acetylene [2%], and 1,3-butadiene [0.5%]). The amounts of the decomposition products in the exhaust relative to unburned fuel vary with engine operating conditions. If a change in the operating condition increases the temperature of the exhaust system (*e.g.* increased engine speed or retarded spark timing), the contribution of olefinic decomposition products in the engine-out exhaust will increase relative to that of the unburned fuel. Aromatic and olefinic fuel species produce different ratios of partial oxidation products to fuel in the exhaust than paraffins, but still tend to form HC product species which are characteristic of the fuel structure.[15]

In summary, the HC species composition of the engine-out exhaust for a fully warm PFI engine depends both on the structure of the fuel molecule and on the engine operating parameters (*e.g.* engine temperature, speed, load, A/F ratio, and spark timing).[15,22] A multi-component gasoline fuel will produce emissions which are related to the sum of those expected from the individual fuel species in the gasoline.[23,24] DISI engines also have emissions which depend on fuel structure but exhibit different dependence on operating parameters.[7,25]

Effect of a catalyst on emissions

Exhaust catalysts are highly effective devices used to reduce the engine-out hydrocarbon, CO, and NO_x mass emissions to levels meeting government standards for SI vehicles. Automotive catalytic converters typically consist of one or more ceramic monolithic honeycomb substrates wrapped with a mounting material and contained in a metal can. The monolith surface is coated with alumina, other high surface area oxides such as ceria or zirconia, and precious metals such as Pt, Rh, and Pd. The precious metals provide catalytic reduction/oxidation of the pollutants in the exhaust gas, while the oxides can improve catalytic efficiency by storing and giving up oxygen as engine operating conditions change.

These catalysts are very efficient after the catalyst has reached its optimum operating temperature (light-off). Oxidation catalysts were introduced in the mid-1970s to control HC and CO emissions. When more stringent NO_x control was mandated, a new type of catalyst was required that could oxidize CO and HC to CO_2 and H_2O while simultaneously reducing NO_x to N_2 and O_2. This type of catalyst is designated "three-way" because it reduces the tailpipe concentrations of the three regulated emissions; CO, HC, and NO_x. To meet the requirement of simultaneously oxidizing CO and HC while reducing NO_x, the engine must be operated at the stoichiometric air/fuel (A/F) ratio, requiring careful feedback control using an on-board exhaust gas sensor. The overall conversion efficiency is improved somewhat by causing the A/F ratio to oscillate by ~2–3% around the stoichiometric A/F. At high levels, sulfur can affect the conversion efficiency of three-way catalysts. However, for modern vehicles at current European and US sulfur levels the effect is small. The result is a device that achieves impressive performance. For example, three-way catalysts permit vehicles to reach California SULEV (super-low-emission-vehicle) non-methane HC emission levels of 0.01 g per mile. Advanced NO_x after-treatment catalysts for lean DISI vehicles are more sensitive to fuel sulfur levels.

A substantial fraction of the mass emissions during the mandated US Federal Test Procedure (and other governmental test protocols) occurs in the first ~20 s for modern vehicles and ~120 s for older vehicles. This is the time during a cold start before the catalyst system reaches the light-off temperature. Thus, it is critical to reduce the time to light-off and much effort has been expended to achieve this goal. Strategies include placing catalysts closer to the exhaust port where gases are hotter, reducing catalyst mass to achieve faster temperature rise, and setting engine operating conditions to achieve higher exhaust temperature and leaner air–fuel mixtures during cold-start. "Cold-start" emissions come directly from the engine-out exhaust and depend on fuel composition and engine operating conditions.[26] Smaller amounts of regulated emissions continue to be emitted throughout vehicle operation, which are also important. The vehicle catalyst must meet emissions standards for 120,000 miles of operation, and catalyst durability is also a crucial design consideration.

The exhaust catalyst is effective in removing most hydrocarbons with the exception of methane, which is more difficult to remove catalytically. Thus, the tailpipe (after catalyst) emissions contain a larger fraction of methane than is present in the gas leaving the engine combustion chamber. Methane is unreactive in urban areas and tailpipe HC emissions standards in the US exclude methane. The air quality impact of methane emissions from vehicles is essentially negligible.[27]

The efficiency with which specific HC species in the exhaust are removed by the warmed-up catalyst has been measured for several catalyst formulations as a function of fuel to air (F/A) ratio near stoichiometric.[28] Data for a Pt/Rh catalyst formulation are presented in Fig. 5. This figure shows that for conditions slightly rich of stoichiometric F/A the conversion efficiency for different classes of hydrocarbons is olefins > aromatics > paraffins. In addition, the conversion efficiency of all species decreases as the fuel mixture becomes fuel-rich with the alkane efficiencies decreasing faster than the olefins which in turn decrease faster than the aromatics for this formulation. At stoichiometric F/A, the efficiencies are approximately: olefins (99%); aromatics (~98%); and paraffins (90–95% depending on the specific species and catalyst). Methane efficiencies tend to be less than 75% depending on catalyst formulation. The automotive catalyst is normally very efficient at removing pollutants from the exhaust gas stream, provided the F/A is maintained close to stoichiometric.

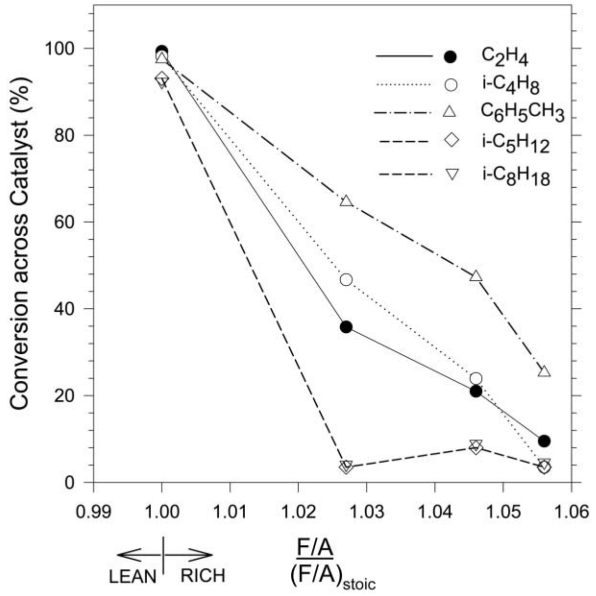


Fig. 5 Conversion efficiency for selected HC species over a Pt/Rh three-way catalyst, taken from ref. 28. Fuel lean and rich ratios are indicated.

However, under certain circumstances, catalysts can contribute to pollutants. For example, in the process of reducing NO_x some N_2O is formed and escapes through the tailpipe. N_2O is a greenhouse gas. N_2O emissions from the on-road vehicle fleet have a global warming impact which is approximately 1–3% of that of CO_2 emitted from vehicles. NH_3 can be formed under fuel-rich conditions as well as occasional instances of "rotten egg" odor resulting from conversion of SO_2 into H_2S. The latter is avoided through the addition of sulfur scavengers to the catalyst formulation, as well as providing fuels with an appropriate sulfur level for the vehicle. Engine operating parameters and catalyst formulations need to be selected to maximize their intended function and minimize unwanted processes.

While advanced gasoline engines that employ lean fuel/air mixtures to improve combustion efficiency generate lower levels of engine-out NO_x, after-treatment catalysts are not yet available that effectively convert NO_x to N_2 in exhaust streams that contain residual O_2. One of the leading candidates for lean

NO_x after-treatment is the NO_x trap,[29] which stores NO_x on the catalyst during routine operation and periodically provides conditions that reduce the NO_x to N_2. However, the materials that effectively store NO_x also store SO_x, leading to an effective poisoning of the catalyst. While the sulfur can be removed *via* catalyst regeneration, the high temperatures employed degrade the life of catalyst. One of the main challenges to generating lean NO_x after-treatment is the development of sulfur-tolerant catalysts.

Diesel engines

While diesel engines are often popular choices based on their durability, cost effectiveness, and high torque, the primary advantages of diesel engines over SI engines are their improved fuel economy and resulting lower (approximately 20–30%) CO_2 emissions.[30] These improvements result from several factors, the most important being increased compression ratio and the fact that the diesel engines operate lean and unthrottled (*i.e.*, with no imposed restrictions on air entering the cylinder) even at light load.[1] Modern diesel engines typically use direct injection of fuel into the engine cylinder. This fuel auto-ignites and does not require a spark. A higher compression ratio is required to obtain the compression temperature necessary to achieve autoignition and the rate of fuel burning is controlled by the rate of fuel flow through the injector. Thus, a flame does not propagate across the combustion chamber as occurs in a SI engine but burns largely as a diffusion flame attached to the fuel injector. This mode of combustion can generate high particulate matter (soot) and NO_x emissions as will be discussed below. Because autoignition starts the combustion event, the fuel's ignition properties and chemical composition are different from SI engine fuel, which is blended to be resistant to autoignition (or knock). Diesel fuel is blended to ignite easily at the engine compression temperature. Because knock is not a problem in properly adjusted diesel engines, higher compression ratios can be used.

With diesel fuel, ignition quality is also the main performance criterion. Diesel fuel ignitability is specified by its cetane number (CN) which, like octane number, is measured in a stationary engine and specified by comparison to reference fuels. Whereas gasoline must be resistant to autoignition, diesel fuel is required to autoignite readily. This is because combustion proceeds without spark ignition, *i.e.*, burning must commence spontaneously as the fuel is injected into a gas mixture that has been heated adiabatically by piston compression. Whereas gasoline ignition quality is dictated by performance at severe, high load conditions, diesel ignition quality is most critical under cold start and light load conditions—the fuel must ignite easily enough to allow start-up and smooth running under cold conditions.

Originally, the cetane number of a fuel was defined as the volume percent of n-hexadecane (cetane) in a blend of n-hexadecane and 1-methylnaphthalene that gave the same ignition delay as the test fuel when run in a standard test engine. Cetane ignites very readily and is assigned a cetane number (CN) of 100, whereas 1-methylnaphthalene is very resistant to ignition and is assigned a CN of 0. In recent times, toxicity concerns with 1-methylnaphthalene have prompted its replacement by heptamethylnonane (CN = 15). Additionally, the high cost of these pure components has spurred the development of full boiling-range secondary reference fuels with carefully controlled properties. Two such reference fuels with CN = 19 and 76 are commonly utilized, and the same linear blending relationship outlined for the pure components is used to assign the CN of the test fuel. Diesel fuels generally have cetane numbers between 40–55. The US average is CN $\sim$ 45, while Europe and Japan have CN $>$ 50. In some cases ignition promoters, called cetane improvers, are added to aid fuel autoignition. Most commonly the cetane improvers are alkyl nitrates such as 2-ethylhexyl nitrate, which have weak internal bonds that rupture readily at high temperature, thereby assisting autoignition. Typical concentrations are up to 1000 ppm, but levels up to 2000–5000 ppm by weight can be used. Organic peroxides have also been used in some cases but are generally less effective and more costly.

As with gasoline, the diesel-range fuel produced through crude distillation contains paraffins, naphthenes, and aromatics. The major refinery upgrading processes are aimed at reducing the concentration of sulfur and converting heavier molecules into diesel *via* catalytic cracking and hydrocracking (described earlier). Typically, the cost of converting heavier molecules into diesel is greater than the cost of converting heavier molecules into gasoline.

High levels of sulfur interfere with catalytic exhaust after-treatment devices that can dramatically lower NO_x and PM emissions from vehicles. High sulfur levels can also contribute directly to particulate matter (PM) emissions, but with low-sulfur fuels the effect is small compared to other PM sources.

The concentration of aromatic species is also controlled in some diesel fuel specifications. Although the effects of fuel changes on emissions are relatively small compared to improvements brought about by advanced engine technology, lower aromatics brings about small reductions in NO_x emissions. The higher NO_x formation tendency of aromatics is attributed to their higher adiabatic flame temperature. In addition, 2-ring and 3-ring polynuclear aromatic hydrocarbons (PAHs) have been shown to contribute to increased soot formation, reflecting the role of multi-ring aromatics as soot precursors during combustion. The relationship between aromatics and soot is discussed in more detail below.

The volatility of diesel fuel is also controlled. The initial boiling point is specified to provide a fuel-lean (non-ignitable) mixture in the fuel tank. Diesel's higher molecular weight also contributes to poorer low temperature performance, in particular due to wax formation with highly n-paraffinic fuels, which can plug fuel lines and filters. To this end, cold flow additives are sometimes added to diesel to improve performance.

While the primary regulated emissions from diesel engines are similar to those from SI engines (*e.g.* organics, CO, and NO_x), there are differences in degree. Exhaust CO and HC emissions are lower in diesel engines and can be converted to H_2O and CO_2 with an exhaust oxidation catalyst. Engine out NO_x levels are lower for diesel engines than their stoichiometric gasoline counterparts reflecting the somewhat lower combustion temperatures in the diesel engine. However, tailpipe-out NO_x emissions are higher from diesels reflecting difficulties in reducing NO_x to N_2 in the highly oxidizing environment of diesel exhaust, which typically contains approximately 8% O_2. Meeting future NO_x emission targets is a formidable technical challenge. As with gasoline, diesel fuel nitrogen levels are very low, and most of the engine-out NO_x comes from oxidation of atmospheric nitrogen.

Diesel exhaust contains more PM than gasoline exhaust. The higher particulate emissions arise from the nature of the diffusion flame and result from combustion of liquid fuel droplets near the fuel injector. Although most of the particulates are burned by the excess O_2 in the cylinder before leaving the engine, some survive and leave the exhaust as small particles. Control of particulate emissions is a significant issue for diesel engines.

Fuel properties can affect PM emissions, although the effects are generally small relative to engine and after-treatment variables (such as diesel particulate traps which are discussed below). Addition of oxygenated organic species such as dimethoxymethane to conventional diesel fuel has been shown to give some reduction in particulate emissions[31] as can the use of reformulated diesel fuels (*e.g.*, Fischer–Tropsch diesel fuel). The mechanism behind reduced PM includes both physical (improved fuel/air mixing from enhanced fuel vaporization) and chemical (decreased production of species that are precursors to soot) factors. Often, the source of the improvement is difficult to isolate. For example, many of the oxygenates added to diesel are more volatile than the fuel itself and hence promote improved fuel/air mixing. Similar improvements can be realized with non-oxygenated fuels *via* hardware modifications such as high pressure fuel injection systems, in particular those capable of multiple injections per engine cycle. A direct chemical role of the oxygenates, *e.g.*, the formation of combustion intermediates that scavenge soot precursors, has not been identified. Fuel physical and chemical properties also affect PM emissions. Many studies have shown that high molecular weight fuel components are difficult to vaporize and thus undergo combustion in regions that are fuel (carbon) rich, leading to increased soot formation. Thus, lighter boiling fuel or improved mixture formation can contribute to lower PM formation. Density is another property that has been linked to PM formation, and can affect engine performance in a number of ways. Well controlled engine studies[32] showed physical interactions with the fuel injection system which influenced the calibrations through the electronic control unit. Density and boiling range may also affect mixture formation, although over the range of realistic diesel fuels this effect is small.[33] In addition, density changes may reflect chemical changes in the fuel which influence the combustion. Recent studies[34] with detailed analytical characterization of the fuel[35] have shown that naphthenes and aromatics contribute to PM formation, with aromatics about twice as potent as naphthenes. Similarly, multi-ring naphthene/aromatics are more potent than their single-ring analogues. This reflects a key step in PM formation, which is transformation of small fuel oxidation products into aromatic rings, followed by multi-ring aromatic formation, particle inception, and oxidation. Fuel molecules that already possess or are readily converted to these seed molecules will lead to enhanced PM formation.

The recent development of diesel particulate traps that can filter solid particles from the exhaust and subsequently burn them constitutes a significant advance in emissions control. This technology is highly effective at reducing exhaust PM to very low levels and is much more effective than incremental changes in fuel. PM traps have been introduced commercially and seem likely to become more widely used in areas where PM emissions are a concern.

Advanced internal combustion engines

There is presently considerable effort devoted to developing engines with improved efficiency and emissions. In the short term, improved versions of gasoline and diesel engines are being developed that will yield higher efficiency and lower emissions. These rely on increasingly sophisticated mechanical and computerized control of the combustion process, allowing the engines to operate with more optimal fuel/air mixtures, combustion timing, *etc*. Standard methods for increasing the efficiency of gasoline engines include raising the compression ratio or turbocharging,[1] both of which require higher octane fuels. Practically, this necessitates higher levels of aromatics, olefins, and/or highly branched paraffins in the fuel. Lean DISI engines are another approach to improving fuel efficiency. More recently, the use of high EGR levels to reduce throttling losses has been shown to be effective.

Innovative strategies are being introduced to target specific problems. For example, several automakers have developed schemes for producing a volatile fuel on-board a vehicle to reduce cold start emissions.[36] The volatile fuel improves fuel/air mixing and reduces fuel condensation on the cylinder walls, leading to fewer HC emissions during the time before catalyst light-off. Simultaneously, further reductions in sulfur levels could help to facilitate advanced NO_x after-treatment such as NO_x storage catalysts, though alternative after-treatment systems based on selective catalytic reduction (SCR) with urea can reduce NO_x emissions to very low levels and are not as sulfur-sensitive. For conventional diesel engines, automakers are requesting higher cetane numbers to improve cold start feasibility and emissions (*e.g.*, white smoke, the mixture of unburned or partially burned fuel and water vapor). However, studies[32,34] have shown that higher CN contributes to higher PM in modern, warmed-up engines. Additionally, present-day vehicles with high-pressure direct-injection fuel systems are less sensitive to CN differences than older vehicles.

Significant improvements in fuel economy can be achieved through vehicle hybridization. Hybrid vehicles achieve part of their efficiency benefits by limiting the amount of time the engine spends operating at idle and other low power conditions, which are the most inefficient part of the operating cycle. In addition, hybrids can capture a portion of the energy losses that accompany braking. Potentially, hybrids could also ease fuel startup requirements, for example permitting lower cetane numbers for light duty diesel engines or reducing HC and CO emissions from gasoline engines.

One promising recent development is the homogeneous charge compression ignition (HCCI) engine, which operates *via* principles that are a combination of gasoline and diesel engines.[37,38] Like a spark-ignition engine, the HCCI engine operates with a premixed intake charge; like the diesel, it operates at a very lean fuel–air ratio, and combustion begins *via* compression ignition. This engine exhibits diesel-like efficiency and very low NO_x emissions because the combustion temperature is very low. However, at low loads, the HC and CO emissions can be high because the combustion process does not go to completion.[37,38] Particulate emissions are reduced relative to a diesel engine because of the more complete mixing, but they may not be negligible.[38] Control of emissions by adjusting engine calibrations is the subject of current research. Although these engines may need to operate in normal diesel mode at high loads, there may be opportunities for fuel optimization, and many studies are under way in this area. Early results indicate that HCCI operation with diesel fuels may benefit from lower CN fuel than current diesel. Fuel volatility may be a factor in ensuring good mixture preparation, and fuel composition factors are also being studied.

One of the significant challenges facing the development and commercialization of practical HCCI engines is combustion control. Unlike gasoline or diesel engines, where combustion is initiated by a spark or fuel injection timing respectively, HCCI ignition is determined by fuel autoignition kinetics. When the mixture is compressed to the suitable temperature and pressure, the fuel will ignite spontaneously. Unfortunately, this may not always coincide with the timing that provides optimal efficiency and emissions. Moreover, at high load, the burn rate cannot be restrained and the excessively fast heat release generates significant combustion noise. This limitation presently precludes HCCI operation at high load without significant compromises in other areas.

Because ignition is determined by the fuel kinetics, fuel structure effects can be significant. By far the most important property is ignitability, which is related to a fuel's octane or cetane number. Because the temperature, pressure, and time history of the octane and cetane tests differs from that in an HCCI engine, none of the conventional ignitability parameters RON, MON, or CN are accurate predictors of HCCI ignition. The definition of a suitable HCCI ignition metric is the focus of ongoing research. However, studies to date indicate that the optimal fuel ignitability will likely lie somewhere between today's diesel and gasoline fuels, *i.e.*, either a low octane gasoline or low cetane diesel. Recent results[39] suggest that at constant ignitability and volatility, fuel composition effects (*e.g.*, aromatics level) may be less important with HCCI compared to conventional diesel or gasoline operation. While it is too early to tell, the most likely scenario is that if HCCI engines are introduced into the market place, they will be designed to operate on market fuel. However, the opportunity exists to gradually shift to a fuel optimally formulated for advanced engines. The evolution of fuels is discussed in the Future Automotive Fuels section below.

Atmospheric chemistry

As mentioned earlier, air quality concerns have motivated the studies on fuel/engine/after-treatment effects on emissions. An essential element of these studies is an understanding of the atmospheric fate of species emitted from vehicles. The atmosphere is a giant photochemical reactor operating at temperatures of 200–300 K and pressures $\leqslant$ 760 Torr. It contains 21% oxygen by volume and is a highly oxidizing environment. ICE exhaust components released into the atmosphere are oxidized in a complex series of reactions giving increasingly polar and less volatile products. Eventually they are either oxidized completely, *e.g.*, the oxidation of methane into CO_2 and H_2O, or are converted into partially oxidized species, which are removed *via* wet and/or dry deposition to the Earth's surface, *e.g.*, the oxidation of NO_2 into HNO_3. The oxidation reactions are initiated principally by reaction with OH radicals, although reaction with ozone, NO_3 radicals, and Cl atoms also play a role. Photolysis can be an important loss process in the lower atmosphere for compounds which absorb at wavelengths $>$ 300 nm.

The driving force for most of the chemistry that occurs in the atmosphere is the formation of hydroxyl (OH) radicals *via* photolysis of ozone to form $O(^1D)$ atoms which react with water vapor to give two OH radicals. The atmospheric lifetimes of many pollutants are determined by their reactivity towards OH radicals. While the OH radical concentration in the atmosphere varies with location, time of day, season, and meteorological conditions, the global 24 hour average is approximately 1×10^6 cm^{-3}. The atmospheric lifetime of most vehicle emissions can be estimated from their reactivity with OH radicals. For example, CO, toluene and undecane (n-$C_{11}H_{24}$) have rate constants for reaction with OH radicals under ambient conditions of 2.4×10^{-13}, 5.6×10^{-12}, and 1.4×10^{-11} cm^3 $molecule^{-1}$ s^{-1} and hence have atmospheric lifetimes of approximately 50, 2, and 1 days, respectively.

Oxidation reactions occurring in the atmosphere have similarities to those in combustion systems. However, there is one obvious and important difference: temperature. In the atmosphere the temperature is 200–300 K while in combustion systems the peak temperatures are typically 1500–2500 K. The different temperature regimes have two key ramifications. First, at high temperatures more reaction channels become kinetically available, and in particular the importance of decomposition processes increases. Decomposition *via* C–C beta-scission is a major loss mechanism for alkyl radicals during high temperature combustion. In contrast, addition of O_2 to give peroxy radicals (RO_2) is essentially the sole loss mechanism for alkyl radicals in the atmosphere. RO_2 radicals react in the atmosphere to give a great variety of aldehydes, ketones, and other oxygenated organics. In contrast, in combustion the formation of large oxygenated compounds is limited. Formaldehyde is present at significant concentration in automobile exhaust and is formed from methyl and ethyl radicals which cannot undergo further beta-scission reactions. The chemistry associated with engine knock (autoignition) takes place at moderately elevated temperatures (600–1100 K) in the presence of excess oxygen. At these temperatures, knock chemistry depends in great measure on RO_2 reactions that bear a similarity to atmospheric chemistry (although NO_x reactions are much less important since little NO_x is present at low temperatures). However, decomposition reactions (to form alkenes) and rearrangements of RO_2 radicals become important.[40] At the much higher temperatures encountered (1500–2500 K) during the main flame propagation process, the importance of alkyl radical decomposition processes increases. Decomposition *via* beta-scission becomes a major loss mechanism for alkyl radicals during high temperature combustion as discussed earlier. In addition, more radical species can be involved as chain carriers in flame combustion than in atmospheric processes. Thus, the atmospheric oxidation of alkanes is initiated *via* reaction with OH radicals. Oxidation of fuel during flame propagation is initiated primarily by reaction with OH during lean or stoichiometric operation but can also involve reactions with other high-temperature reactive species such as O and H atoms as well as thermal decomposition depending on the A/F ratio.

The atmospheric degradation reactions that remove pollutants from the air have unwanted side effects. The degradation products and intermediates can lead directly, or indirectly, to adverse environmental impacts. Emissions from internal combustion engines contribute to the photochemical smog present in many large-scale metropolitan areas. On a time scale of hours in the presence of sunlight, atmospheric chemical reactions convert vehicle emissions and exhaust into a mixture of oxidants such as ozone and peroxyacetyl nitrate (PAN = $CH_3C(O)O_2NO_2$) that is generically known as photochemical smog. As indicated in Fig. 6, the key ingredients for the formation of photochemical smog are VOCs, NO_x, and sunlight.

The chemistry is initiated by reaction of OH radicals with VOCs to give alkyl radicals (R) which, in one atmosphere of air, add O_2 rapidly (within 10^{-7} s) to give peroxy radicals, RO_2. The dominant fate of RO_2 radicals in urban air is reaction with NO which occurs with a rate constant of approximately 1×10^{-11} cm^3 molecule^{-1} s^{-1} under ambient conditions. Typical NO levels in polluted urban air are 10–100 ppb and the lifetime of RO_2 radicals is approximately 0.1–1.0 s. Alkoxy radicals, RO, have an atmospheric lifetime typically of the order of 0.01–0.10 ms and undergo isomerization, decomposition *via* C–C bond scission, or reaction with O_2 to give carbonyl containing compounds which in turn can react with OH radicals to generate more peroxy radicals. The reaction of RO_2 with NO generates NO_2 which is a brown colored gas and absorbs at 400–450 nm. The NO_2 photolysis rate, J_{NO2}, in the lower atmosphere (troposphere) depends on the cloud cover and is typically in the range (0.3–1) $\times 10^{-2}$ s^{-1}, giving a lifetime of NO_2 of several minutes. Photolysis of NO_2 gives O atoms and regenerates NO which reacts with more RO_2 radicals to form more NO_2. In one atmosphere of air, O atoms add O_2 with an effective bimolecular rate constant of 1.5×10^{-14} cm^3 molecule^{-1} s^{-1}, $[O_2] = 5.2 \times 10^{18}$ cm^{-3}, and O atoms have a lifetime of 13 ms with respect to conversion into ozone.

Fig. 6 provides a highly simplified picture of photochemical ozone formation. It does not include the processes which limit ozone formation such as the formation of nitric acid and organic nitrates. The addition reaction of OH radicals with NO_2 gives HNO_3. Nitric acid does not participate in gas phase ozone forming reactions and is removed by wet and dry deposition. Formation of HNO_3 is a major loss mechanism for atmospheric NO_x and limits the formation of ozone. Organic nitrates, $RONO_2$, are formed as minor, but important products, in the reaction of RO_2 radicals with NO. Acyl peroxy nitrates (*e.g.*, $CH_3C(O)OONO_2$) are formed *via* the association reaction of NO_2 and acyl peroxy radicals (*e.g.*, $CH_3C(O)O_2$). $RONO_2$ and $RC(O)OONO_2$ species tend to be less reactive than their parent hydrocarbons and serve as sinks for radicals and NO_x in urban air. Acyl peroxy nitrates such as PAN, $C_2H_5C(O)OONO_2$ commonly known as peroxy propionyl nitrate or PPN, and $C_6H_5C(O)OONO_2$ commonly known as peroxy benzoyl nitrate or PBzN are phytotoxic (toxic towards plants). They are also powerful lacrymators and are responsible for the eye irritation associated with air pollution. Concentrations of PAN in urban air typically exceed those of PPN and PBzN by factors of approximately 10 and 100, respectively, reflecting the source strengths of the corresponding aldehyde precursors.

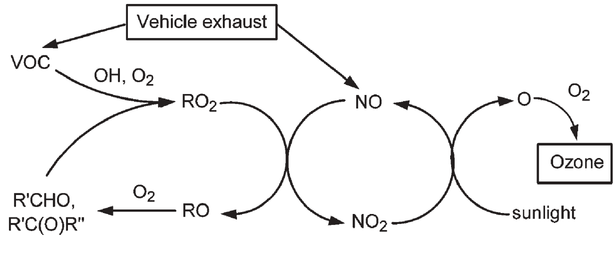


Fig. 6 Photochemical production of ozone.

VOCs have different kinetic and mechanistic reactivities and hence differ in their ability to contribute to photochemical ozone formation. Kinetic reactivity refers to the rate of reaction with OH radicals, O_3, and NO_3 radicals (and hence rate at which RO_2 radicals are generated). Mechanistic reactivity refers to the reactivity of the oxidation products of the VOC (their ability to generate more RO_2 and OH radicals and their ability to act as sinks for radicals and NO_x). Compounds which react rapidly with OH radicals and give products which also promote ozone formation (*e.g.*, alkenes) will produce more ozone within urban air masses than compounds which react slowly (*e.g.*, CH_4) or give products which suppress further ozone formation (*e.g.*, C_6H_5CHO).

Scales have been developed to provide a quantitative ranking of the ability of different VOCs to contribute to ozone formation. The "maximum incremental reactivity" (MIR) scale was developed by Carter[41] (and is used by the California Air Resources Board and the U.S.E.P.A.) and the "photochemical ozone creation potential" (POCP) scale was developed by Derwent *et al.*[42] These scales are based upon computer models of urban or regional air chemistry. The models include the atmospheric chemistry of individual VOCs, meteorological data, emissions inventories, and simulate the formation of photochemical smog. In the maximum incremental reactivity scale the effect on the predicted maximum ozone concentration for a small change in emission of a given VOC is computed and the result is reported in units of moles of O_3 formed per mole of VOC added. In the POCP scale the integrated effect on ozone along a multi-day modeled trajectory of adding a given amount of VOC in the scenario relative to adding the same mass of ethylene VOC is computed. The POCP for ethylene is defined as 100.

POCPs for selected VOCs in ICE exhaust are given in Table 1. As seen from the table, there are large differences in the POCPs of different VOCs. The negative value for benzaldehyde reflects the ability of one of its oxidation products, the phenoxy radical, to react with NO_2 giving nitrophenols thereby removing radicals and NO_x from the

Table 1 Photochemical ozone creation potential (POCP) values for selected VOCs[43,44]

VOC	POCP
Ethane, C_2H_6	8.8
Propane, C_3H_8	18.3
n-Butane, n-C_4H_{10}	36.3
n-Pentane, n-C_5H_{12}	36.6
2,2-Dimethylpropane, $C(CH_3)_4$	20.3
n-Hexane, $CH_3(CH_2)_4CH_3$	45.6
n-Octane, $CH_3(CH_2)_6CH_3$	40.1
Ethylene, $CH_2{=}CH_2$	100.0*
Propene, $CH_3CH{=}CH_2$	105.4
trans-2-butene, $CH_3CH{=}CHCH_3$	110.7
Acetylene, $CH{\equiv}CH$	9.9
Formaldehyde, HCHO	47.1
Acetaldehyde, CH_3CHO	55.0
Acetone, CH_3COCH_3	7.5
Butanone, $C_2H_5COCH_3$	35.3
Methanol, CH_3OH	16.5
Ethanol, C_2H_5OH	39.7
Dimethyl ether, CH_3OCH_3	19.8
Methyl *tert*-butyl ether, $CH_3OC(CH_3)_3$	17.8
Ethyl *tert*-butyl ether, $C_2H_5OC(CH_3)_3$	27.0
Benzene, C_6H_6	20.3
Toluene, $C_6H_5CH_3$	51.0
1,3,5-Trimethylbenzene, $C_6H_3(CH_3)_3$	108.2
Benzaldehyde, C_6H_5CHO	−10.4

system. The low POCPs of ethane, acetylene, acetone, and benzene reflect their low reactivity towards OH radicals.

Future automotive fuels

Fossil-fuel-derived gasoline and diesel are likely to dominate transportation fuels for at least the next 20 years. This projection is based on three factors. First, contrary to some popular belief, there are substantial (>40 years supply) reserves of conventional oil, unconventional oil, and other fossil fuels (coal, gas) that can be converted at modest cost into gasoline or diesel. Furthermore, with history as a guide, it seems likely that additional finds and advances in extraction technology will make significant contributions to future reserves. Second, gasoline and diesel are unrivalled in their energy density, low cost, and ease of use. Third, the sheer magnitude (approximately 750,000,000 conventional vehicles in current global fleet, 55,000,000 vehicles manufactured in 2004, 2.5 trillion liters gasoline equivalent annual global transportation fuel use) and durability (vehicles 10–20 years, refineries > 30 years) of the existing infrastructure render substantial short term changes in the global fuel market unlikely.

Changes in automotive fuels are more likely to be evolutionary than revolutionary. The availability of low sulfur fuels is likely to increase as lower emission vehicles spread more widely throughout the world. As our understanding of the factors impacting emissions and their associated impact on the environment improves we may see a focus on modifying the chemical composition of fuel, but the broad composition of gasoline and diesel fuel is unlikely to change substantially. Compressed natural gas (CH_4) and liquefied petroleum gas (C_3H_8 and C_4H_{10}) are likely to see continued use in niche markets but because of availability, infrastructure, low energy-density, and difficulty-of-handling considerations, are unlikely to find substantial increase in use.

Gas-to-liquids (GTL, or Fischer–Tropsch) technology, which converts methane to liquid hydrocarbons, may present a practical alternative to transporting remote natural gas *via* pipeline or tanker. Both gasoline and diesel range GTL fuels can be produced, but diesel volumes will likely exceed those of gasoline initially. Pure GTL fuels are typically comprised of n-and iso-paraffins, with very small levels of naphthenes, aromatics, and sulfur. As such, their combustion properties can differ from conventional fuels. As one example, the octane and cetane numbers of pure GTL fuels are well outside the range of conventional fuels. For this reason, and those related to distribution of small volumes of these fuels, GTL fuels will likely be incorporated as blend components into conventional fuels.

Looking to the future, biofuels may make a contribution to the automotive fuel pool. Possible biofuels include ethanol derived from fermentation of biomass, biodiesel synthesized by transesterification of vegetable oils and animal fats, and Fischer–Tropsch diesel derived from biomass gasification (known as BTL, for biomass-to-liquids). Biofuels have certain desirable combustion properties. For example, ethanol has octane numbers higher than conventional gasoline, and ethanol addition to gasoline provides an octane boost. However, oxygenated fuels such as ethanol (and to a lesser extent biodiesel) have a lower energy density than conventional fuels. As with GTL, BTL fuels are highly paraffinic, and BTL diesel can provide a cetane boost to conventional diesel. As with GTL fuels, pure biofuels have properties outside the range of conventional fuels, will be available in small volumes, and will likely be utilized as blend components.

Looking further ahead, hydrogen or electricity may become the automotive fuel of choice. Hydrogen as a fuel for internal combustion engines can provide advantages based on its unique combustion properties. For example, hydrogen flames burn very fast and flame propagation is possible with very lean mixtures. These properties, together with high knock resistance, make hydrogen a desirable fuel for advanced ICEs. Most of the interest with hydrogen, however, is not related to its combustion properties, but rather to its use in conjunction with a fuel cell. Fuel cell vehicles have received considerable attention due to their potential to be much more efficient than gasoline vehicles on the road today. However, there are formidable technical challenges to be overcome before H_2 will see mass use as a transportation fuel. These include: high cost and environmental impacts associated with H_2 production and distribution; low energy density, which makes storing sufficient H_2 on a vehicle difficult; safety; cost; and durability.

Electricity (*i.e.*, electric battery powered vehicles) has the same appeal as hydrogen as well as its own challenges (principally the development of cheap, robust, high energy density, rapidly rechargeable batteries). There is significant room for improvement in internal combustion engines, and advanced engines may have well-to-wheel efficiencies on par with H_2 fuel cell or electric vehicles.

Concluding thoughts

In the future, transportation will continue to play a central role in the world's economic growth and prosperity. The fuels and engines we use today reflect over a century of innovation and technological development. The efficiency with which fuels are processed and delivered to service station pumps is impressive. Fuel composition has evolved to optimally balance performance, environmental, and cost considerations. Notably, the phase-out of lead anti-knock additives and reductions in sulfur, when coupled with engine and after-treatment hardware advances, have yielded significant benefits. The composition of gasoline and diesel leaving a refinery reflects a sophisticated optimization of refinery processes to maximize overall efficiency. The results are impressive—the thermal efficiency for gasoline and diesel production is 85–92%. Stated alternatively, for every 100 Joules of crude oil that enters the refinery, approximately 90 Joules leaves the refinery as highly upgraded fuel.[45]

Today's engines have realized significant improvements in efficiency, emissions, reliability, and durability. Hardware developments such as sophisticated fuel injection equipment, EGR, turbocharging, and complex engine control strategies have made significant contributions to the development of compact and powerful engines. During the past thirty years, after-treatment devices have played an essential role in significantly reducing vehicle emissions. Oxidation and three-way catalysts have proved to be effective emission control devices. PM traps are performing well in real world service. Together with these advances, research into the atmospheric fate and reactions of hydrocarbons, NO_x, and their relationship to tropospheric ozone, has provided the understanding necessary to assess the impact on the atmosphere of IC engine operation.

Despite these accomplishments, many challenges remain for the scientific and engineering community. Further improvements in efficiency and emissions are required and will necessitate optimization of the entire fuel/engine/after-treatment system.

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