

An aerial photograph of a city, likely San Francisco, showing a dense urban landscape with a prominent highway in the foreground and a hazy skyline of skyscrapers in the background. The text is overlaid on the image.

Air Pollution from Gasoline Powered Vehicles and the Potential Benefits of Ethanol Blending

A Review of Particulate, Nitrogen Oxide, and
Volatile Organic Compound Pollution

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Introduction

Each gallon of hydrocarbon-rich petroleum fuel that is used to power vehicles today produces nearly 20 pounds of carbon dioxide (CO₂), resulting in the annual emission of over 1.5 billion metric tons of CO₂, or roughly 1/3 of the total greenhouse gas emissions in the United States [1]. Efforts to curb climate change effects and reduce the greenhouse gas emissions from the transportation sector have resulted in stricter Corporate Average Fuel Economy Standards (CAFE) and policies such as the Renewable Fuel Standard (RFS) to develop alternative fuels. In addition to CO₂ emissions and its global warming effects, the concerns regarding vehicle emissions include toxic compounds such as carbon monoxide (CO) and nitrogen oxides (NO_x), which have significant epidemiological and environmental consequences. Control of hydrocarbons and CO first began in California in 1966, followed by standards set by the federal government in 1968. The 1970 amendment to the Clean Air Act (CAA) tightened the initial emissions standards and added NO_x as the third major pollutant emitted by vehicle engines [2]. Under the current CAA, the U.S. Environmental Protection Agency (EPA) is required to set standards for six principal air pollutants: ozone, particulate matter, lead, CO, nitrogen dioxide and sulfur dioxide. Airborne pollutants, including both primary tailpipe emissions (e.g. CO) as well as secondary chemical species formed via atmospheric reactions (e.g. ozone), can travel into the respiratory system and through the human body, causing potentially chronic health effects. Ambient and indoor air pollution result in over 5 million deaths a year, globally. In 2013, air pollution was the 4th highest ranking risk factor for death in the world [3]. Although exhaust emissions regulation in the last 50 years has resulted in significantly lower concentrations of toxic airborne pollutants in the United States, an estimated 9,320 deaths in 2013 were attributed to air pollution exceeding the American Thoracic Society (ATS) recommended standards [4]. This statistic is comparable to the 10,076 alcohol-related traffic deaths that occurred in that same year, illustrating that air pollution control remains as a highly relevant national public health concern that necessitates strong policies in parallel to those initiated to reduce CO₂ emissions. This report reviews the recent literature on particulate matter, NO_x, and volatile and semi-volatile organic compounds that result in ozone pollution. Emissions from automobiles are directly linked to fuel composition and engine technology, therefore this report also reviews the key concepts in engine performance (e.g. fuel octane rating, fuel injection technique, etc.). Results from numerous scientific studies are presented to show the current understanding of the sources and potential impacts of emissions from automobiles, focusing on the influences of specific gasoline components and ethanol-gasoline blending.



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1. Fundamentals of Fuel Octane Rating

Since the advent of modern automobiles, the spotlight has been mostly focused on one key feature of its operating fuel - the octane rating. This number quantifies a fuel's capacity to resist auto-ignition when compressed. Vehicles with spark-ignition (SI) internal combustion engines, which run on gasoline, comprise over 90% of the U.S. fleet. SI engines operate by first compressing the fuel-air mixture in the combustion chamber and then, at a carefully determined time, igniting that compressed mixture to transfer chemical energy to mechanical energy. If the fuel auto-ignites before the ignition is initiated by the spark plug, the engine experiences knocking, which can have negative performance effects or even damage the engine (Fig. 1.1). Proper functioning of an SI engine relies on high-octane gasoline fuels, since they have higher anti-knock properties. Automakers design the extent of piston compression of their engines to be compatible with current fuel octane standards. An engine's compression ratio (CR) is the proportion of the cylinder volume at the bottom of the piston stroke to the top of the stroke. CR directly correlates to engine efficiency therefore, extending octane ratings beyond the current minimums can enable automakers to produce engines with better performance and fuel economy.

1.1 History of Octane

Two pure compounds with opposite knocking behavior, n-heptane and isooctane (2,2,4-trimethylpentane), were used to establish the octane scale in 1927. As the name implies, isooctane has superior anti-knock properties and was assigned an octane rating of 100, while n-heptane was assigned a 0 rating. Gasoline and other fuel blends are tested for knock and compared to various mixtures of n-heptane and isooctane. A sample is assigned an octane rating corresponding to the ratio of n-heptane and isooctane required to match its knocking properties. The composition of the mixture that matches the observed knocking of the sample is assigned as the octane rating of that fuel [5]. The Research Octane Number (RON) tests the fuel performance under standard conditions, whereas the Motor Octane Number (MON) simulates more severe operation representative of conditions at high-load or speed. The average of a fuel's RON and MON is referred to as its Anti-Knock Index (AKI). Figure 1.2 shows the trend in fuel AKI, and illustrates the correlation between the rating and engine CR.

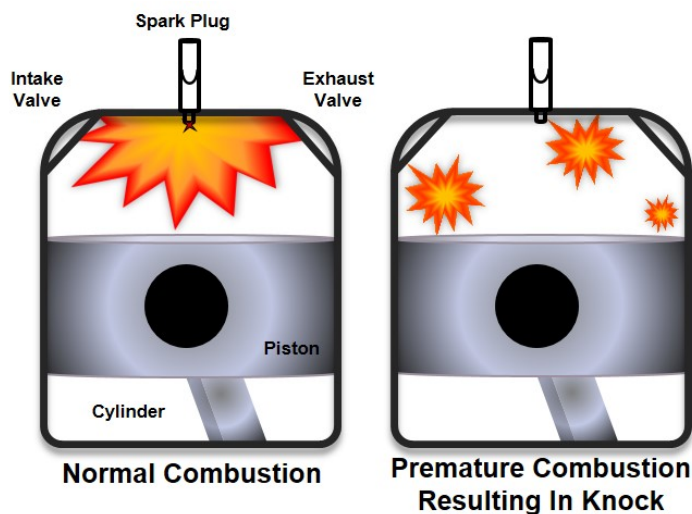


Figure 1.1: Cartoon of internal combustion engine. Under normal operation, the spark plug initiates the propagation of a premixed flame in the combustion chamber. Premature combustion caused by low-octane fuel results in uneven burning, which reduces the power output and can damage valves, pistons, and other engine components.

Today, the AKI federal standard for regular grade gasoline is 87.

Anti-knock agents, also called octane enhancers, are added to gasoline to help meet these federal standards. One of the most widely used octane enhancer for many years was tetra-ethyl-lead (TEL), which at approximately 3 $\frac{1}{2}$ gal gives a 10- to 15-point increase in AKI. As observed in Figure 1.2, lead compounds were phased out of gasoline beginning in 1975. Lead deposits damage the vehicle's catalytic converter, motivating the transition to unleaded gasoline, which increases engine life by as much as 150 % [6]. Lead is also highly toxic for humans; therefore, the transition was both economically and epidemiologically advantageous.

Octane enhancers, such as methyl t-butyl ether (MTBE), were first developed to replace lead. MTBE has both a high AKI rating and causes minimal corrosion to the engine and other parts. However, when gasoline containing MTBE leaks from underground storage tanks, it contaminates the groundwater, resulting in an unpleasant taste and odor in drinking water. This led to limitations on MTBE blending in gasoline, and in certain areas of the country, a total ban on its use. Today, refiners have focused their attention on petroleum refining and blending techniques to increase the concentrations of high-octane hydrocarbons in their gasoline.

1.2 Gasoline Composition

The crude oil that is pumped out of the ground is a complex mixture of several thousand organic compounds. These compounds include:

- straight-chain alkanes (paraffins),
- cycloalkanes (naphtenes),
- aromatic hydrocarbons (aromatics),
- alkenes (olefins).

These are natural constituents of crude oil, but can also be produced in various refining operations.

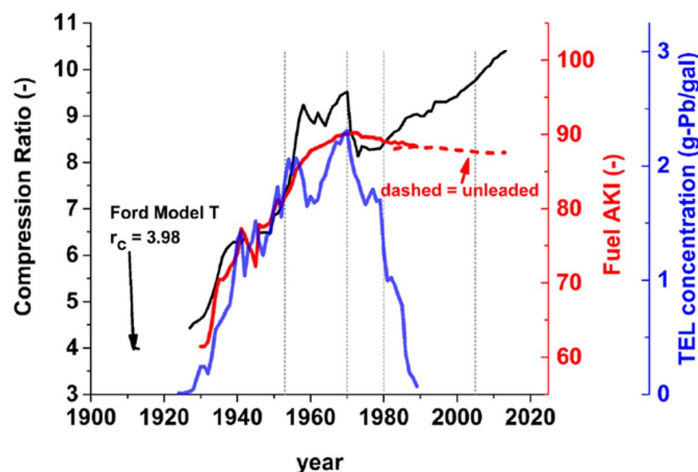


Figure 1.2: Averaged trends in compression ratio (black), fuel AKI (red), and fuel TEL concentration (blue) for the U.S. as a function of year. Plot adapted from Splitter et al. [7].

Techniques such as catalytic cracking and reforming are used to convert lower-demand components to high-demand products or to high-octane streams. By molecular rearrangement or dehydrogenation, catalytic reforming converts low-octane, heavy naphthas into aromatic hydrocarbons, which are added to gasoline components known as reformates. Alkylation and isomerization are also used to convert low-octane straight-chain paraffins to higher-octane branched paraffins, called alkylate, used in premium gasoline blending stocks for its exceptional anti-knock quality.

Some of these solutions have created public health problems of their own. For example, the increased use of benzene and other aromatics has led to concerns over human exposure to known carcinogens. Furthermore, aromatics are known to form polycyclic aromatic hydrocarbons (PAHs), which are precursors to soot and contribute to secondary organic aerosol (SOA) formation. Studies estimate that approximately 3,800 premature mortalities nationwide are due to the aromatics content of gasoline [8]. These health factors, along with an effort to lower the cost of refining, have increased interest in the use of alternative, low-cost, octane boosting oxygenates such as ethanol with RON = 109 [9].

1.3 Ethanol as an Octane Enhancer

Nearly all gasoline in the U.S. now contains 10% ethanol, by volume, sold as E10 [10]. The processes for producing E10 are similar to that of conventional gasoline, although the minimum AKI rating is no longer achieved with refining techniques alone. Refiners deliver a sub-octane fuel (AKI = 84) known as the Blendstock for Oxygenate Blending (BOB) to fuel terminals, where ethanol is blended into the fuel, raising the AKI rating by 2-3 points to meet the standard for regular grade gasoline. The advantageous properties of ethanol have sparked interest in raising the volume beyond 10% to achieve even higher octane rated fuels.

Scientists are actively researching the potential of biofuels in transportation, supporting governmental initiatives to reduce dependence on petroleum-based fuels and lower carbon emissions. Their studies give insights into the consequences of current and proposed ethanol blends not only on the octane rating, but also on emissions of greenhouse gases, particulates, and other toxic pollutants. Research shows that ethanol-gasoline blends have improved combustion processes due to

the oxygen content in ethanol. When compared to E0, ethanol-gasoline blends produce less exhaust emissions [11–17] along with PAH and soot emissions [18, 19]. Ethanol blends reduce combustion temperatures, which discourages nitric oxide production. Furthermore, these blends have faster flame speeds than pure gasoline, enabling complete combustion of the fuel. A review of the literature highlights a general reduction of engine out emissions and a positive effect of alcohol content on thermal efficiency.

Ethanol has been linked to higher evaporative emissions due to its volatility properties. Reid vapor pressure (RVP) and distillation profile of ethanol-gasoline blends are greatly affected by non-ideal mixture behavior. This behavior is a consequence of molecular interactions between the gasoline components and ethanol. Despite the fact that ethanol has a lower RVP than gasoline, blending 10% vol ethanol into gasoline increases the total RVP by about 6 kPa. In ethanol-gasoline blends, the nonpolar hydrocarbon molecules in gasoline interfere with the intermolecular hydrogen bonding between the polar ethanol molecules, and similarly do the ethanol molecules interfere with the hydrocarbons. These interferences with intermolecular bonding allow both types of molecules to more readily escape the liquid as vapor, which is manifested as increased vapor pressures and reduced distillation temperatures. The highest RVP of 68 kPa is observed when 10% vol ethanol is added to the gasoline, followed by a near plateau up to 20% vol. As ethanol content is increased above about 20% vol, RVP of the blend begins to decrease, and above 50% vol ethanol, the RVP becomes less than that of the gasoline [20]. Careful consideration of RVP is an important criteria for controlling evaporative emissions.

High-octane ethanol blends can also enable further engine downsizing and higher CR. Splitter and Szybist [21] demonstrated that E30 fuel improves anti-knock tendencies and high torque capability at stoichiometric conditions. Celik [12] showed that the power obtained from E50 fuel is 29% higher at CR of 10/1 compared to E0 at CR of 6/1. These studies and reviews of alcohol-gasoline blending [22–25] suggest that mid-level alcohol blends can increase vehicle efficiency, in addition to certain emissions advantages. High-octane fuels are essential to the proper functioning of current internal combustion engines and to the potential for future innovations in engine design. Many anti-knock agents that help boost the octane rating of gasoline have significant negative consequences on public health and the environment. Increasing the volume of ethanol blending in gasoline is one potential means to achieve higher octane fuels without the side effects of lead, MTBE, and aromatic hydrocarbons. Furthermore, ethanol blends have been shown to reduce emissions of other harmful pollutants, as discussed in the following chapters.



2. Particulate Pollution

Air pollution exists in both particle and gas phases. Unlike gases, which have defined chemical structures and specific physical properties, particulate matter (PM) come in all shapes and sizes (Fig. 2.1). PM, released from both anthropogenic and natural origins, also vary in their impact on public health and the environment. Once the liquid or solid particles become suspended in the atmosphere, often referred to as aerosols, they can travel into the respiratory system and blood stream, transporting toxic compounds and disrupting normal cell functions. From an environmental standpoint, they are able to scatter and absorb sunlight, which translates to a direct influence on the earth's temperature, climate, and air visibility. Control of PM emissions has developed as one of the main functions of air pollution control agencies. Unlike biogenic PM that can originate from mechanical processes such as sea spray or volcanic activity, anthropogenic PM mainly arises from gas-to-particle chemical conversion and condensation. Therefore, analysis of the composition, origins, and formation mechanisms of anthropogenic PM is a field of active research. Human-made aerosols, which are found in higher concentrations in urban areas, are mainly composed of a carbonaceous nucleus and substances absorbed on its surface, such as polycyclic aromatic hydrocarbons (PAHs), metals, sulfates, and nitrates. Exhaust from the tailpipe of motor vehicles contributes significantly to particulate pollution, since it contains a complex mixture of hundreds of chemicals in the form of precursor gases, as well as particulate carbon. A better understanding of the relationship between fuel composition and exhaust composition can help motivate both technological innovations and policies that enable cleaner energy sources for transportation, particularly relevant for renewable fuel initiatives.

2.1 Health Impact

The size distribution of aerosols is trimodal, including coarse, fine, and ultrafine particles. Coarse particles consist primarily of suspended dust, soil, volcano ash, sea salts, and pollen particles. Fine particles have smaller diameters, generally only a few microns (one-thirtieth the width of a human hair), and are mainly derived from direct emissions of gasoline and diesel engines, coal burning, and industrial processes involving combustion. Ultrafine particles have even smaller diameters, typically less than or equal to 100 nm, but can rapidly grow through coagulation and condensation

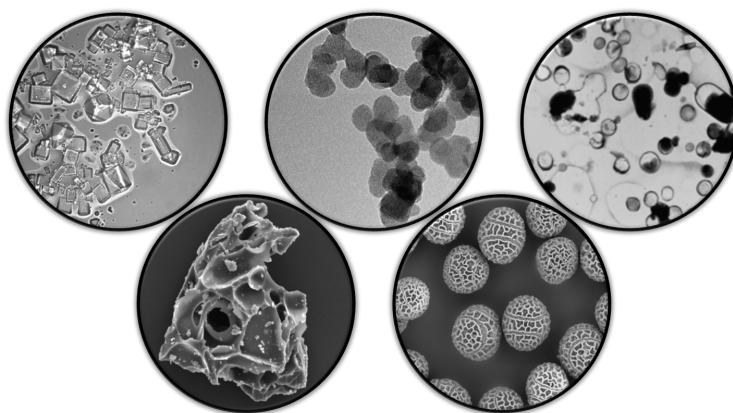


Figure 2.1: Electron microscope images of biogenic and anthropogenic PM, with the approximate dimension of each particle: sea salt (Chere Petty/Univ of Maryland, $\sim 15\mu\text{m}$), soot aggregates (Saffaripour et al. 2015, $\sim 0.5\mu\text{m}$), ammonium sulfate (Casuccio et al. 2002, $\sim 0.5\mu\text{m}$), volcanic ash (Tom Kircher/AVO/UAF-GI, $\sim 50\mu\text{m}$), pollen (Dartmouth E. M. Facility, $\sim 50\mu\text{m}$).

to form larger aggregates, therefore significantly contributing to fine particle exposure as well [26]. Similar to their larger counterparts, ultrafine particles are derived from combustion-related sources, and their emissions depend on specific fuel and engine properties. Once airborne, particles can enter human airways, attach onto surfaces in the respiratory tract and dissolve in body fluids, passing their chemical molecules into the bloodstream and circulating throughout the body. With their small size, fine and ultrafine particles can be breathed more deeply into the lungs and remain suspended for longer periods of time [26]. Public health policy is primarily concerned with the regulation of fine PM, comprised of sulfates, nitrates, ammonium, organic aerosols, and elemental carbon. The main effects associated with exposure to fine PM (referred to as $\text{PM}_{2.5}$) are premature mortality, aggravation of cardiovascular disease, aggravated asthma, acute respiratory symptoms and chronic bronchitis [27]. Nearly 200,000 premature deaths per year in the U.S. are attributed to $\text{PM}_{2.5}$ emissions [28], and the World Health Organization (WHO) estimates 3 million worldwide annual deaths caused by particulate pollution [29]. In 2012, the EPA lowered the primary annual fine particulate standard from $15\mu\text{g}/\text{m}^3$ to $12\mu\text{g}/\text{m}^3$ in an effort to combat these health effects.

2.2 Primary and Secondary Particulate Pollution

PM emissions from automobiles are directly linked to fuel composition and engine technology and are categorized as primary and secondary forms. The emissions that are already particulates at the tailpipe are referred to as primary PM, and those that form from the oxidation of gaseous precursors are secondary PM. The primary form of PM from automobiles, commonly referred to as soot, is composed of both elemental carbon (EC) and organic carbon (OC). EC has a chemical structure similar to graphite and is often interchanged with the term black carbon (BC). The strongest light-absorbing component of soot is BC, which can change the reflectivity of the Earth's surface when it lands on snow. For instance, the accumulation of black carbon aerosols in the Arctic and Himalaya is leading to increased melting of snow and consequent climate change effects [30]. As one of the most prevalent anthropogenic aerosols, soot not only affects global climate but also atmospheric visibility and human health.

In addition to the primary mode, OC can also be emitted as a result of condensation of low vapor

pressure gases onto existing aerosols. Secondary organic aerosols (SOAs) are formed as species such as hydroxyl radicals (OH) oxidize hydrocarbon molecules emitted from combustion. Vehicles typically emit a mixture of hundreds of gases, some of which are SOA precursors, such as single-ring monocyclic aromatics like toluene and xylene [31]. Furthermore, they can emit heavy PAHs, which can rapidly condense onto particles once emitted into the atmosphere, resulting in a higher proportion of these PAHs in smaller, respirable size particles [32]. Research has shown that the SOA fraction of fine organic PM can dominate over the primary organic aerosol fraction in certain areas [31].

Vehicle technology can also impact PM emissions. For instance, new technologies such as the gasoline direct injection (GDI) engines are shown to produce higher particulate emissions than conventional port fuel injection (PFI) engines. GDI engines improve the fuel efficiency of PFI engines by eliminating the throttle that controls the intake air flow into the engine, instead directly injecting the fuel into the cylinder per cycle. GDI-equipped vehicles are being rapidly integrated into the vehicle fleet, from less than 5% in MY2009 to 46% in MY2015 [33]. Although this technique increases efficiency, combustion of locally fuel-rich (Section 3.2) regions in the cylinder results in higher PM emissions [34]. Traditionally, PM emissions have been a concern for diesel engines, but new technologies in gasoline vehicles, along with better understanding of SOA production from gaseous precursors, are widening the focus of this field to both diesel- and gasoline-powered cars.

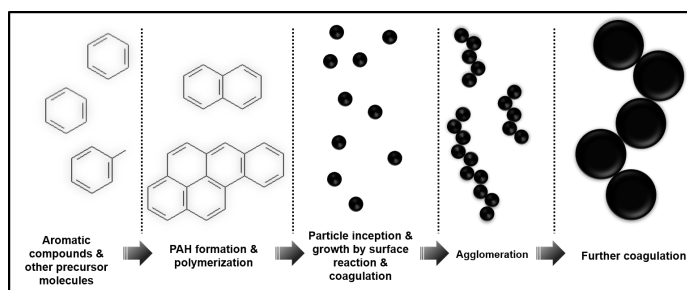


Figure 2.2: A growth mechanism for the formation of particulate carbon, or soot, from coalescence of PAHs.

2.3 The Role of Aromatics

Gasoline is a mixture of several hundred compounds, with varying concentrations based on the sample, including paraffins, olefins, and aromatics. The exact composition of gasoline varies widely, depending on the base crude oil and the refinery processes available, along with product demand and specifications. Aromatic hydrocarbons exhibit high anti-knock properties and can be blended in large volumes to boost the octane value of gasoline. Since the phasing out of toxic octane enhancers such as lead, refiners have used increasing volumes of aromatics to meet anti-knock requirements. Aromatics can be monocyclic, such as benzene and toluene, or polycyclic, such as naphthalene. Exposure to monocyclic aromatics such as benzene is linked to development of leukemia and lymphoma [35]. Several PAHs, found in fuels or produced during combustion, are also toxic and carcinogenic. Although the metabolic activation of PAHs in the body can vary among compounds, they generally convert to oxides and diol epoxides, which are the principal toxic metabolites involved in DNA replication and repair [36].

In addition to their inherent toxicity, PAHs are thought to be the molecular precursors to soot. Although most of the emitted PAHs are formed in the combustion process, higher fuel aromatic content does increase PAH emissions [37]. As shown in Figure 2.2, single-ring aromatics such as benzene can form into PAHs, which then coalesce into nascent soot particles. The growth

process from small molecules such as benzene to larger PAHs involves interaction and recombination reactions among the compounds of the fuel [38]. Although the first aromatic ring may be produced from non-aromatic species [39], higher concentrations of single-ring aromatics in the fuel have been shown to result in higher soot emissions [8]. Additionally, increasing PM emissions are accompanied by increasing PAH emission, of both gaseous and particulate-bound forms [37]. Pandis et al. [40] predicted that approximately 65% of SOAs result from the oxidation of aromatics, 15% from alkanes and 4% from olefins. These predictions are in agreement with that of Grosjean and Seinfeld [41], who also estimated SOA production resulting mostly from aromatics oxidation (58% for aromatics, 21% for alkanes, and 11% for olefins).

Numerous studies have been done to relate aromatic concentration to pollutant formation. Karavalakis et al. [8] studied the effects of aromatics in gasoline on both gaseous and PM emissions in PFI and GDI engines. This study was done on a fleet of seven light-duty gasoline vehicles and three gasoline fuel blends with 15%, 25% and 35% aromatics content, by volume. Their results showed a significant increase in emissions of CO, PM mass and number, and BC with increasing aromatics content for all seven vehicles. This and several other studies [37, 42, 43] illustrate that PM emissions increase with higher aromatic content in gasoline; however, there is currently no effective federal limit on aromatics content in gasoline. California has set limits for reformulated gasoline phase 3 of 25% vol for aromatics. Both the EPA and the California Air Resources Board (CARB) have classified benzene as a human carcinogen, with the federal limit of the percentage of benzene allowed in gasoline set to an average of 0.62% vol.

2.4 Effect of Ethanol Blending

Ethanol has superior anti-knock properties to gasoline, and is currently blended with a sub-octane blendstock to increase the octane rating and produce E10 fuel. Over 90% of gasoline in the U.S. is now blended with ethanol, which has instigated a surge of research and investigation into the efficiency and emissions implications of ethanol-gasoline blending. Storey et al. [19] compared PM emissions of both lean and stoichiometric GDI engines operated with E0, E10, and E20. Between E0 and E10, a 29% reduction of PM mass emissions was shown in the stoichiometric engine and a 42% reduction in the lean operating vehicles, both under the Federal Test Procedure 75 (FTP). Costagliola et al. [44] showed a 30–95% reduction of the number of particulates emitted for ethanol blends ranging from E10–E85. This suggests that the inclusion of more ethanol in the gasoline supply has a potential mitigating effect on PM emissions [18]. In addition to reducing the particle mass and number concentration, ethanol content in the fuel changes the composition of emitted particles. Dutcher et al. [45] showed that BC and particle-bound PAH concentrations decreased with ethanol content, with the greatest drop resulting from the change from E0 to E20. Therefore, ethanol-fuel blending may result in fewer emitted carcinogenic and light-absorbing particles (Fig. 2.3).

The Department of Energy, in collaboration with the EPA, also conducted a study in 2009 to assess the effects of fuel property changes on vehicle emissions. 27 fuels were tested in a fleet of 15 high-sales cars and light trucks from the 2008 model year over the LA92 cycle at 75°F. Four Flexible Fuel Vehicles in the test fleet were also tested on E85 fuel. The data and analysis on emissions properties were published in 2015 [46, 47]. The conclusion with respect to automobile PM emissions was that the most important factor increasing PM emissions is aromatic content, followed by temperature at 90% vol distilled (T90). These findings are in line with previous studies and theoretical combustion science of emission production, since aromatics are known soot precursors. The study also found that ethanol negatively impacted PM, which is a highly controversial and debated result. They attributed this behavior to ethanol's high heat of vaporization, compared to

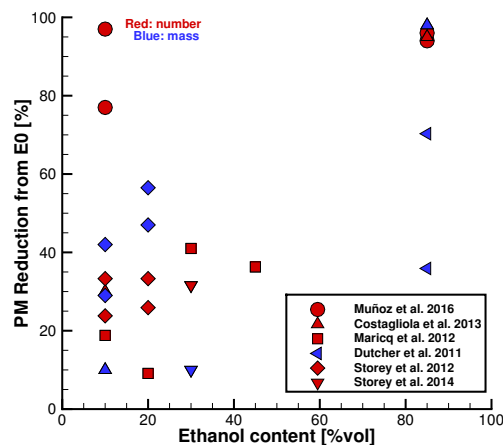


Figure 2.3: Studies showing emissions reductions of various ethanol blend concentrations compared to zero ethanol blends E0, based on total mass or number of particles.

the other hydrocarbons in the fuel. A high heat of vaporization results in lower temperatures after evaporation, making high boiling point aromatics even less likely to evaporate and mix with the air. This results in the production of more PM than would otherwise form without ethanol.

These studies shed light on the complexity of controlling fuel composition for emissions regulation. Clearly, the chemical properties of the base gasoline will affect the properties of the final fuel after blending with ethanol [48]. Although many studies have shown the beneficial effects of ethanol blending on fuel PM emissions, high levels of aromatics in the base mixture can cause conflicting results. A successful regulatory approach may be to control the total aromatic content in the base gasoline mixture, specifically limiting high-boiling point aromatics that contribute to soot formation. Ethanol can also be blended in higher volumes in gasoline to decrease gaseous and particulate emissions and further decrease the relative concentration of aromatics.



3. Nitrogen Oxide Pollution

Nitrogen oxide (NO_x) emissions consist of nitric oxides (NO) and nitrogen dioxides (NO_2). At high temperatures, characteristic of the combustion chamber of engines, nitrogen molecules in air react with oxygen to form NO gas. NO_2 is predominantly formed from the reaction of NO and peroxy radicals, but is rapidly converted back to NO at high-temperature environments containing an abundance of H and O radicals. Much of the NO gas emitted from the tailpipe is oxidized to NO_2 in the atmosphere, therefore exposure to NO_x is often represented by NO_2 concentrations.

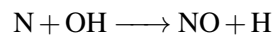
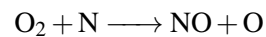
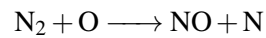
NO_2 is a highly toxic gas that can trigger cell damage and inflammatory processes in the respiratory system [49]. Secondly, ultraviolet radiation from the sun drives the chemical reactions between NO_x and other pollutants, producing ground-level ozone, or smog, which can also trigger serious respiratory problems. In the presence of sulfur dioxide, NO_x react to form acids that fall to the earth with rain, snow, or fog. Acidic droplets can damage forests and vegetation, and disturb the habitats of freshwater organisms. The federal annual mean standard for concentrations of NO_2 in the air, as set by the National Ambient Air Quality Standards (NAAQS), is 0.053 parts per million (ppm). The California standard is set to 0.030 ppm.

Due to the health and environmental consequences of NO_x pollution, regulation of these compounds remain as a major obligation of air quality agencies. In 2015, Volkswagen admitted that 11 million of its vehicles produced NO_x emissions nearly 40 times the permissible levels, resulting in one of the largest consumer class-action settlements in U.S. history. Although this case related to diesel cars, which produce higher amounts of NO_x than gasoline cars, it signifies the importance and relevance of continued NO_x regulation among the U.S. fleet and a continued effort to develop new technologies and fuel-blends which help curb emissions.

3.1 Formation Pathways

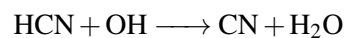
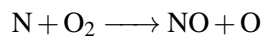
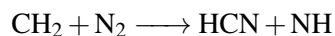
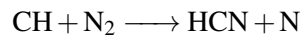
The nitrogen atoms in the formation of NO_x primarily come from the nitrogen in air, which is composed of 78% N_2 . The nitrogen atoms in some fuels (e.g. coal) can also contribute to NO_x emissions, but this is not relevant for most transportation fuels. NO can be formed via a number of reaction mechanisms, the two most significant being thermal and prompt NO formation:

- Thermal NO : This mechanism for NO formation is considered relevant at temperatures above 1,800K where the strong N_2 bond can be broken to initiate the following series of reactions:



This mechanism is the dominant source of NO in fuel-lean and stoichiometric conditions (Section 3.2) [50].

- Prompt NO : This mechanism is responsible for the formation of NO in the colder part of the flame and becomes significant under fuel-rich conditions, since it requires a high concentrations of the hydrocarbon radical species to initiate the sequence of reactions. These reactions first produce cyanonitrene (NCN) and hydrogen cyanide (HCN), which undergo further reactions to form NO [15]:



3.2 Ratio of Air to Fuel

An important operating condition of an engine is the air-fuel ratio, λ . For any combustion process, both fuel and oxidizer are required for a chemical reaction. If the exact right amount of air is supplied to burn off all of the fuel, this proportion of air to fuel is referred to as stoichiometric ($\lambda = 1$). If there is not enough air to burn all of the fuel, the mixture is called fuel-rich ($\lambda < 1$). Lastly, if there is excess air, the mixture is called fuel-lean ($\lambda > 1$). For gasoline, the stoichiometric air-fuel ratio is 14.7. Figure 3.1 shows the emissions associated with each combustion regime.

At higher loads, engines often operate at rich conditions for maximum power. The higher flame speed of ethanol helps in achieving complete combustion for rich mixtures. Most SI engines are designed to operate at stoichiometric or lean conditions and to minimize fuel enrichment, except during short periods of high-load (e.g. acceleration).

The various operating conditions of the engine have respective NO_x emissions. However, these values of NO_x are all well within the capacity of three-way catalytic converters, which convert NO to N_2 in order to meet regulatory standards. He et al. [13] report both engine-out and tailpipe emissions, and showed that catalytic conversion decreases NO_x emissions by up to a factor of 200 (Fig. 3.2b). With a properly functioning three-way catalytic converter, NO_x emissions are typically below 1ppm [51]. Techniques and fuel blends designed to lower engine-out NO_x can reduce the load on the catalytic converter and potentially enable lighter and less expensive catalysts.

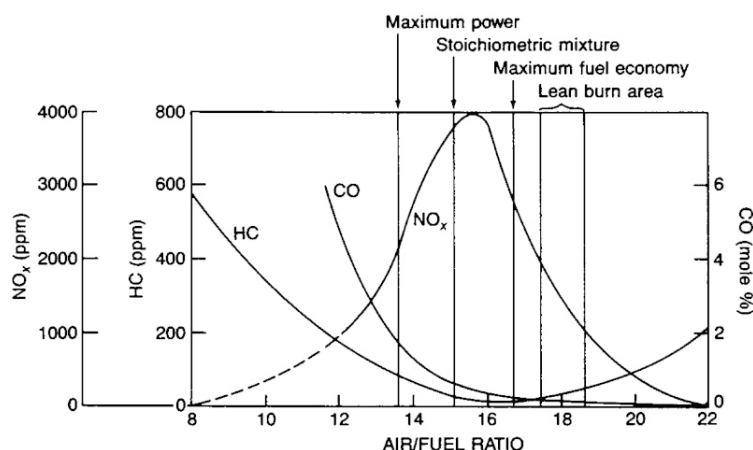


Figure 3.1: Concentrations of HC, CO, and NO_x emissions as a function of air-fuel ratio in a typical gasoline engine. Stoichiometric mixture ($\lambda = 1$) corresponds to an air/fuel ratio of 14.7 [9].

3.3 Effect of Ethanol Blending

Efforts to better characterize the chemical interactions between hydrocarbons, alcohols, and existing engine technologies have resulted in numerous scientific research publications on this subject. These researchers not only investigate the fundamental properties of ethanol-gasoline blends, but also study the effect of different blend concentrations on engine efficiency, greenhouse gas emissions, particulate pollution, and economic cost. There is a sensitivity of emissions testing to engine technology (i.e. direct injection vs. port-fuel injection), operating conditions (i.e. air-fuel ratio λ), mixing of fuel and oxidizer in the combustion chamber, and base-gasoline composition before it is blended with ethanol. Despite the complexity of this subject, key insights into the nature of ethanol-gasoline blends have been developed.

As outlined, the formation of NO is often dependent on high gas temperatures via the thermal NO mechanism. One strategy for reducing NO is to reduce the burned gas temperature. Ethanol blending is shown to be an effective way to reduce the burned gas temperature and consequently NO formation. This behavior is a direct consequence of two key properties of ethanol-gasoline blends. First, ethanol has a higher heat of vaporization than gasoline, which translates to lower compressed gas temperatures during the compression stroke (i.e. charge cooling). This difference in temperature is further increased in the expansion stroke post ignition, which leads to the second key property of ethanol combustion – lower adiabatic flame temperatures, or peak temperatures. Charge cooling and lower temperatures post combustion decrease NO production.

The blended fuel chemical structure also reduces prompt NO formation. This reaction mechanism depends on the presence of hydrocarbon radical species (HC). Alcohols, such as ethanol, are organic compounds in which the hydroxyl functional group ($-\text{OH}$) is bound to a carbon atom. In alcohol flames, the presences of the hydroxyl functional groups act to reduce the level of hydrocarbons produced in the flame, thereby lowering NO formation through the prompt route [22]. Furthermore, the higher flame speed of ethanol-gasoline blends compared to pure gasoline decreases the residence time of the mixture within the prompt-formation region of the flame. Therefore, ethanol blends fundamentally produce less NO_x at the same air-fuel ratio than pure gasoline. Some studies show conflicting results (i.e. increase of NO_x with ethanol blending) [52], illustrating the inherent complexity in these studies created by the wide flexibility in operating parameters and by engine-

specific complications. Furthermore, since ethanol is an oxygenated fuel, during high-load fuel-rich operation, it also effectively increases λ towards stoichiometric conditions where adiabatic flame temperatures are higher. Although this is advantageous for complete combustion of the fuel and enhances the efficiency of the engine, it may increase NO_x emissions compared to the fuel-rich conditions of pure gasoline [53] (Fig. 3.1).

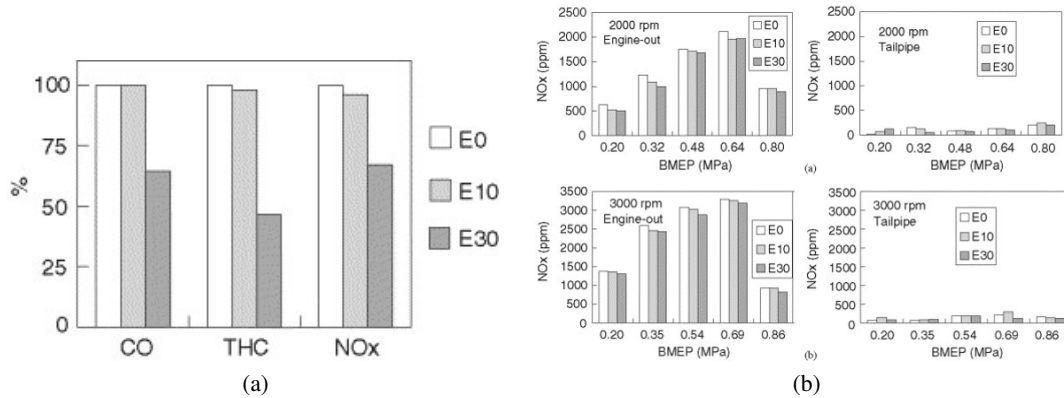


Figure 3.2: (a) Engine-out emissions at idle speed, relative to E0. Plot shows relative emissions versus brake mean effective pressure (BMEP). (b) Ethanol does decrease engine-out NO_x emissions, but tailpipe emissions are similar, due to the catalytic converter. Plot shows emission in parts per million (ppm) versus BMEP [13].

Numerous studies have experimentally investigated the effects of ethanol blending on emissions. Compared to E0, Jung et al. [14] reported a 25% - 45% decrease in NO_x for E85, Canakci et al. [11] reported an 11% decrease for E5 and 15.5% for E10, He et al. [13] reported up to 33% decrease for E30, Celik [12] reported a 33% decrease for E50, and Nakata et al. [16] reported a 25% decrease for E50 and 40% decrease for E100. These studies were performed on common engines such as those in the Toyota Corolla and Honda Civic, and reflect nearly constant load and speed conditions for stoichiometrically operated engines ($\lambda = 1$). Vertin et al. [17] studied the effects of ethanol blending on long-term emissions. For four of the six models tested, the vehicles aged on E0 fuel had higher exhaust emissions compared to vehicles aged on E15 or E20 fuel. The 2009 Honda Odyssey aged using E0 fuel had higher CO and NO_x emissions at 120,000 miles compared to the vehicles aged on E20 with 95% confidence. NO_x emissions from the 2009 Ford Focus aged using E0 fuel were higher than those of E15 at 90,000 miles and E20 at 120,000 miles.

Overall, the effects of ethanol blending are advantageous both for short and long-term NO_x emissions. Catalytic converters today are designed to transform toxic engine-out NO_x emissions, along with other pollutants, to their non-toxic counterparts. Although alcohol-fuel blends inherently enhance the combustion process and reduce NO_x emissions by roughly 30% for mid-level blends, a properly functioning catalytic converter will absorb changes of this scale along with other fluctuations in transient engine operation.



4. Volatile Organic Compound Pollution

Air pollution results from the interaction between emissions and weather. To mitigate the public health consequences of pollution, air quality agencies work to set and enforce emission standards for the most toxic pollutants. It is also important to understand and acknowledge the complex chemistry and interdependence of these pollutants as they react in the atmosphere according to external conditions. For instance, in addition to their inherent toxicity, certain vehicle emissions can react with each other or with biogenic compounds to form secondary pollutants. Organic compounds in the atmosphere are partitioned between gases and aerosols, depending on their vapor pressures and chemical properties. Mostly, organic compounds that have low vapor pressures ($<10^{-11}$ atm) at ambient temperatures exist as aerosols and those with high vapor pressures ($>10^{-5}$ atm) exist in the gas-phase, often termed volatile organic compounds (VOCs) [54]. Essentially, VOCs refer to a large set of compounds that are able to evaporate easily. Aromatics constitute 20-30% of total VOCs in the urban atmosphere [55]. Compounds with intermediate vapor pressures are known as semi-volatile organic compounds (SVOCs). VOCs and SVOCs include pollutants of major concern to public health, such as benzene, toluene, ethylbenzene, xylene, and polycyclic aromatic hydrocarbons (PAHs). Furthermore, they contribute to the formation of ozone and secondary organic aerosols (SOAs).

Almost all of the weather on Earth occurs at the lowest layer of the atmosphere, known as the troposphere. Starting at Earth's surface and spanning up to 20 km above sea level, the troposphere holds nearly 80% of the mass of the atmosphere, comprised of air and water molecules. In this layer are also hundreds of thousands of organic compounds, originating from both biogenic and anthropogenic sources. The chemistry of the urban atmosphere differs from that of the natural troposphere due to the high concentrations of industrial and vehicle emissions such as nitrogen oxides and organic compounds. On a global scale, emissions of VOCs from vegetation are much greater than those from anthropogenic sources [54]. However, in urban areas, vehicular emissions contribute significantly to atmospheric VOC concentrations. Long-range transport strongly influences observed concentrations of ozone and ozone precursors. For example, studies at the west coast of

North America identified the influence of Asian emissions on ozone, hydrocarbons, nitrates, and sulfur concentrations [56].

4.1 Health Concerns and Regulation

Toxic and carcinogenic compounds such as PAHs are SVOCs emitted from vehicle engines and other combustion processes. The World Health Organization (WHO) has classified the PAH Benzo(a)pyrene as a human carcinogen, and numerous other PAHs as probable human carcinogens. PAHs can metabolize to form oxides and diol epoxides, the principal toxic metabolite involved in DNA replication and repair [36]. Exposure to VOCs such as benzene is linked to development of leukemia and lymphoma [35]. Surface ozone is produced by the reaction of VOCs and nitrogen oxides (NO_x) under the influence of sunlight [57, 58]. Ozone is the main component of smog, which can reduce lung function, aggravate asthma and emphysema, and lead to a wide range of respiratory symptoms [59].

Prior to 1966, vehicle manufacturers were not required to meet any exhaust emissions standards, both at the state and federal levels. As concern grew regarding the public health effects of direct and indirect pollution from automobiles, policies emerged to limit emission of the most toxic compounds. Today, the federal standards for Tier 3 vehicles are 4.2 g/mi CO and 0.05 g/mi total NO_x and non-methane hydrocarbon emissions [60]. Prior to emissions control in 1966, unregulated vehicles emitted about 10 g/mi hydrocarbons, 4 g/mi NO_x , and 80 g/mi CO [2]. In California, VOC emissions have decreased by nearly 50 times in the last 50 years (average of 7.5% a year) while fuel usage has tripled in that time [61]. Development of catalytic converters and air pumps that improve combustion efficiency have enabled these tremendous emission cuts. However, the significant health consequences of air pollution today motivate regulatory agencies and automakers to continue to seek innovative solutions to further decrease harmful emissions.

4.2 Ozone Formation

Ozone (O_3) is produced in the atmosphere from the chemical reaction between atomic and molecular oxygen, and any third body molecule (M) such as N_2 . In the troposphere, the oxygen atom required for this reaction is produced from the photo-dissociation of NO_2 to NO, which rapidly reacts with ozone to regenerate NO_2 :



In this reaction path, one ozone molecule is required to regenerate NO_2 , therefore there is a balance between produced and consumed ozone molecules. However, in the presence of hydrocarbons, NO_2 production can circumvent reaction 4.3, and result in the accumulation of ozone. Reaction between the hydroxyl radical (OH) and hydrocarbons generates peroxy radicals (RO_2 , where R is an alkyl group). RO_2 reacts with NO to form NO_2 , which is how the balance between produced and consumed ozone molecules is disrupted and begins to shift towards ozone accumulation.

Reducing anthropogenic VOC and NO_x emissions has been the main method of controlling ground-level ozone in the U.S. It is important to note that although ground-level ozone in the troposphere has harmful effects and requires control, ozone in the upper atmosphere (stratosphere) is beneficial in shielding the planet from excess ultraviolet light.

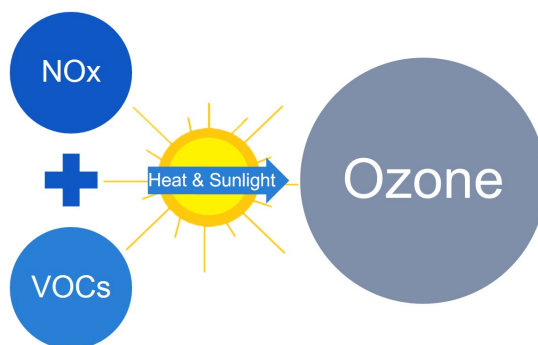


Figure 4.1: Ground-level ozone is not emitted directly into the air, but is formed by photochemical oxidation of NO_x and VOCs, which are emitted from industrial facilities and vehicle exhaust.

4.3 Effect of Ethanol Blending

Costagliola et al. [44] showed a 30–70% reduction in PAH emissions for ethanol blends, and a 50% reduction of benzene and 1,3-butadiene emissions with E85, compared to E0. Hsieh et al. [62] found a 20–80% reduction of hydrocarbon emissions with increasing ethanol content from 5% to 30% vol, compared to pure gasoline. Similarly, Koç et al. [23] found close to 20% and 30% hydrocarbon reductions with E50 and E85 blends. Muñoz et al. [51] concluded that blending of gasoline with ethanol substantially reduced PAH emissions in GDI vehicles. With E10, mean emissions of 2-, 3-, 4-, 5-, and 6-ring PAHs decreased by 67, 77, 74, 88, and 96%. Furthermore, with E85, mean emissions of these PAHs reduced by 85, 82, 91, and 97%. Their research is especially significant due to the recent rapid replacement of PFI vehicles with GDI, which produces more particulates and other harmful emissions. They conclude that pollution consequences from this transition can partly be compensated with ethanol blending, which suppresses particulate and PAH formation. As with particulates, the blending of ethanol in gasoline reduces harmful pollutants resulting from incomplete combustion and lowers the concentration of carcinogenic compounds both in the input fuel and output emissions.



5. Conclusion

Air pollution is a major public health concern, and policy measures are needed to help mitigate its impact from the transportation sector, specially in urban areas. Pollutants derived from vehicular exhaust are not only harmful at a local level, but become airborne and transport their toxic effects more broadly. Furthermore, interactions of PM, NO_x, and VOC emissions with atmospheric factors and other compounds in the air make emissions control a challenging research and regulatory problem.

Clear scientific evidence show that higher concentrations of aromatic hydrocarbons in gasoline result in increased gaseous and particulate pollution. Aromatics, often blended in high concentrations to boost the anti-knock property of the fuel, are found to be precursors of soot. Several monocyclic and polycyclic aromatic hydrocarbons are themselves known carcinogens. Ethanol can also be blended in higher volumes in fuel to decrease gaseous and particulate organic emissions, while also being advantageous both for short and long-term NO_x emissions. Alcohol fuel blends such as mid-level ethanol blends are shown to reduce NO_x production by roughly 30%. When blended into gasoline, ethanol increases the octane rating of the fuel enabling higher efficiency engines and is shown to decrease the emissions of several harmful pollutants.

Emissions from automobiles have a tremendous impact on public health and the environment. The wide scope of impact on both human health and the environment, along with the diverse origins and dispersion qualities of pollution, requires the expertise and collaboration of scientists, medical professionals, and policy makers in order to identify the appropriate mitigation plans. Furthermore, controlling human-made emissions from mobile sources involve automotive manufacturers, oil refiners, and regulatory environmental agencies, who all help to implement the scientific conclusions and policy decisions made to protect public health and the environment.



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