

MOTOR GASOLINES

Chevron Products Company

TECHNICAL REVIEW



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Introduction

Although the petroleum industry was almost 50 years old when the first Model T rolled off Henry Ford's production line in 1908, gasoline and the automobile grew up together. The industry was born in August, 1859, near Titusville, Pennsylvania, when a drilling effort financed by Edwin Drake hit crude oil at a depth of 70 feet. The major product in the early years wasn't gasoline; it was lamp oil, called *coal oil* or *kerosene*.¹ People were reading more and wanted better light than that provided by candles and whale oil lamps. The natural gasoline in crude oil was a surplus by-product. Being too volatile to use in lamps, it was burned at the refineries, dumped or converted to a gaseous fuel for gas lights.

The development of the electric light and the astonishing growth of the automobile in the first decades of the 20th century turned the industry's focus from kerosene to gasoline. In 1911 gasoline sales exceeded sales of kerosene for the first time. The simple engines in the first cars would run on almost any liquid that burned. But as the demand for power increased and the engines became more sophisticated, gasoline was recognized as the right fuel for the spark-ignition internal combustion engine.²

Drivers obtain the performance they expect only when the characteristics of the fuel match the fuel requirements of the engine. As a result, the gasoline engine and its fuel matured as mutually-dependent partners. An engine was not designed without considering the gasolines available in the market place. And gasoline was not made without considering the requirements of the engines in which it would be burned. The partnership became a triumvirate in the last decades of the 20th Century as environmental considerations began to change both engine design and gasoline characteristics.

This review collects information about all three members of the triumvirate in one place. As befits Chevron's sponsorship, the major focus is on gasoline – its performance, characteristics, refining and testing, and safe use. But significant space is devoted to the operation of modern engines and to the impact of environmental regulation on both engines and fuels. Numerous cross references emphasize how interconnected these topics are. We hope readers will find the review a source of valuable and accurate information, whether they read it from cover to cover or zero in on an area of interest.

¹ Both the names *coal oil* and *kerosene* were holdovers from the previous decades when lamp oil was distilled from coal. Kerosene, a corruption of the Greek words for *wax* and *oil*, was one American company's brand name for coal oil.

² Petroleum Panorama, The Oil and Gas Journal, 57 (5), January 28, 1959.

Introduction

When most drivers think about gasoline, it is to remember to fill up and maybe to check the price. Because gasoline almost always performs well, drivers forget what a sophisticated product it is. More thought would reveal a demanding set of performance expectations:

- An engine which starts easily when cold, warms up rapidly and runs smoothly under all conditions.
- An engine which delivers adequate power without knocking.
- A vehicle which provides good fuel economy and generates low emissions.
- Gasoline which does not add to engine deposits or contaminate or corrode the fuel system.

While proper vehicle design and maintenance are necessary, gasoline plays an important role in meeting these expectations.

This chapter discusses how gasoline's characteristics affect driving performance.

Volatility

Driveability is the term used to describe how an engine starts, warms up and runs. It is the assessment of a vehicle's response to the accelerator, relative to what the driver expects. Driveability problems include: hard starting, backfiring, rough idle, poor throttle response and stalling (at idle, under load or when decelerating).

The key gasoline characteristic for good driveability is *volatility* – the gasoline's tendency to vaporize. Volatility is important because liquids and solids don't burn; only vapors burn. When a liquid appears to be burning, actually it is the invisible vapor above the surface that is burning. This rule holds true in the combustion chamber of an engine; gasoline must be vaporized before it can burn. In cold weather, gasoline is blended to vaporize easily. This allows an engine to start quickly and run smoothly until it is warm. In warm weather, gasoline is blended to vaporize less easily to prevent vapor lock and minimize evaporation, which contributes to air pollution.

It is important to note that there is no single best volatility for gasoline. Volatility must be adjusted for the altitude and seasonal temperature of the location where the gasoline will be used. Later, this chapter will explain how the gasoline specification addresses this requirement.

Three properties are used to measure gasoline volatility: *vapor pressure*, *distillation profile* and *vapor-liquid ratio*. A fourth property, *driveability index*, is calculated from the distillation profile.

VAPOR PRESSURE

For those materials that can exist as a vapor, some vapor is present even when the material is in its liquid or solid state. A material's *vapor pressure* is the pressure exerted by the vapor when the vapor is in equilibrium with the liquid or solid. The vapor pressure of gasoline is measured at a temperature of 100°F (38.8°C) and a pressure of one atmosphere, and expressed as pounds per square inch (psi) or kilopascals (kPa).

Vapor Pressure

Vapor pressure is the single most important property for *cold-start* and *warmup driveability*. (*Cold-start* means that the engine is at ambient temperature, not that the ambient temperature is cold.) When the gasoline's vapor pressure is low, the engine may have to be cranked a long time before it starts. When it is extremely low, the engine may not start at all. Engines with port fuel injection (*see p. 46*) appear to start more readily with low vapor pressure fuel than carbureted engines.

Distillation Profile

Gasoline is a mixture of hundreds of hydrocarbons, many of which have different boiling points (*see p. 24*). Thus gasoline boils or *distills* over a range of temperatures, unlike a pure compound, water for instance, that boils at a single temperature. A gasoline's *distillation profile* is the set of increasing temperatures at which it evaporates for a fixed series of increasing volume percentages – 5%, 10%, 20%, 30%, etc. – under specific conditions (*see p. 34*). (Alternatively, it may be the set of increasing evaporation volume percents for a fixed series of increasing temperatures.) Figure 1-1 shows the distillation profiles of average conventional summer and winter gasolines.

Various ranges of a distillation profile have been correlated with specific aspects of gasoline performance.

Front-end volatility is adjusted to provide:

- easy cold starting
- easy hot starting
- freedom from vapor lock
- low evaporation and running-loss emissions

Midrange volatility is adjusted to provide:

- rapid warmup and smooth running
- good short-trip fuel economy
- good power and acceleration
- protection against carburetor icing and hot stalling

Tail-end volatility is adjusted to provide:

- good fuel economy after engine warmup
- freedom from engine deposits
- minimal fuel dilution of crankcase oil
- minimal volatile organic compound (VOC) exhaust emissions (*see p. 15*)

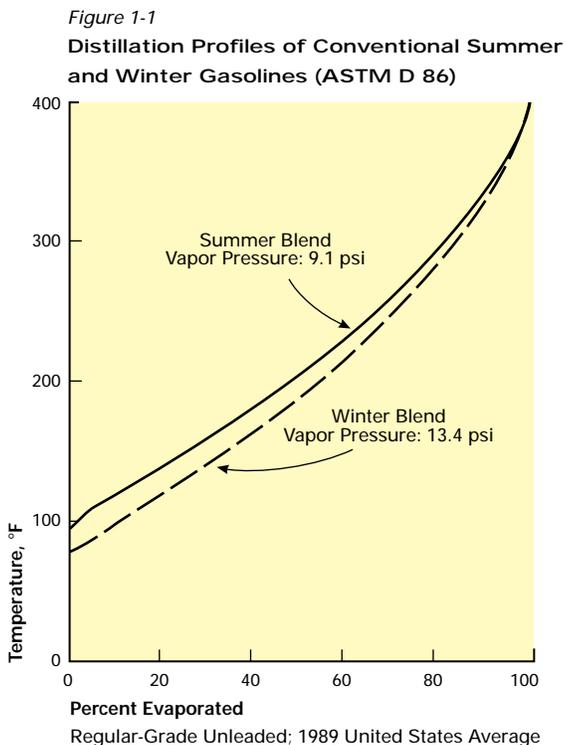


Figure 1-2 graphically illustrates these correlations. The temperature range is approximate; the exact range depends on the conditions that exist in the location where the vehicle is driven.

Vapor-Liquid Ratio

The vapor locking tendency of a gasoline is influenced both by the temperatures at the front end of its distillation profile and by its vapor pressure. But the property that correlates best with vapor lock is the temperature at which the gasoline forms a vapor-liquid ratio of twenty (V/L=20) – the temperature at which it exists as twenty volumes of vapor in equilibrium with one volume of liquid at atmospheric pressure. This correlation was developed for vehicles with suction-type fuel pumps and carburetors. How well it applies to later-model fuel-injected cars with pressurized fuel systems is not known.

Driveability Index

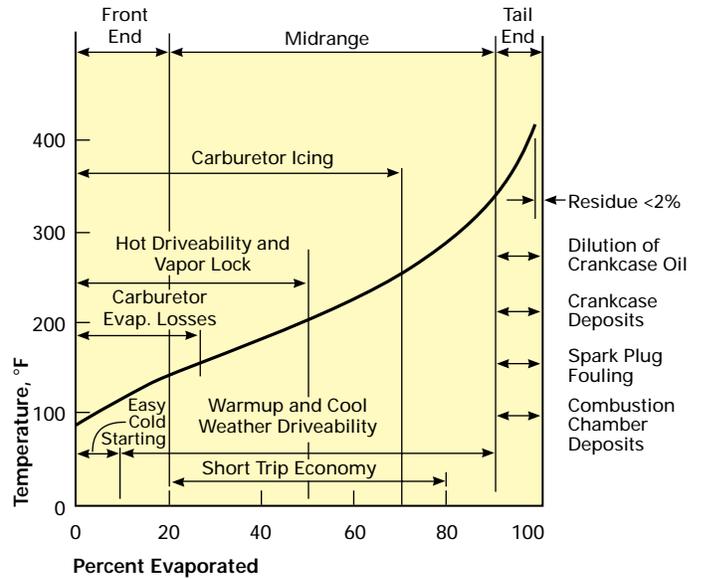
While each range of the distillation profile is important, the gasoline represented by the entire profile is what the engine must distribute, vaporize and burn. To predict cold-start and warmup driveability, a *driveability index (DI)* has been developed using the temperatures in degrees Fahrenheit for the evaporated percentages of 10% (T₁₀), 50% (T₅₀) and 90% (T₉₀):

$$DI = 1.5(T_{10}) + 3.0(T_{50}) + (T_{90})$$

The DI varies with gasoline grade and season; the normal range is 850 to 1300. Lower values of DI generally result in better cold-start and warmup performance, but once good driveability is achieved, there is no benefit to further lowering the DI.

The equation was developed using data for conventional gasolines and has not been proven to be applicable to oxygenated gasolines. Work continues to improve the DI equation and to make it universally applicable.

Figure 1-2
Correlation of Distillation Profile Ranges (ASTM D 86) with Gasoline Performance



VAPOR LOCK

Vapor lock occurs when excessive gasoline vapor accumulates somewhere in the fuel system – fuel pump, fuel line, carburetor, or fuel injector – and reduces or interrupts the fuel supply to the engine. When the fuel supply is reduced, the air-fuel ratio becomes too *fuel lean* (too much air for the amount of fuel), which may cause loss of power, surging or backfiring. When the fuel supply is interrupted, the engine stops and may be difficult to restart until the fuel system has cooled and the vapor recondensed.

Overheated fuel is the main cause of vapor lock. Fuel temperature depends on the air temperature, how hard the vehicle is working, how well the fuel system is isolated from the heat of the engine and how effectively the fuel system is cooled.

Figure 1-3a
ASTM D 4814 Vapor Pressure and Distillation Class Requirements

Gasoline Volatility Class	Vapor Pressure, psi; Maximum	Distillation Temperature, °F			
		10% Evap.; Maximum	50% Evap.	90% Evap.; Maximum	End Point; Maximum
AA	7.8	158	170-250	374	437
A	9.0	158	170-250	374	437
B	10.0	149	170-245	374	437
C	11.5	140	170-240	365	437
D	13.5	131	150-235	365	437
E	15.0	122	150-230	365	437

CARBURETOR ICING

Carburetor icing occurs when the intake air is chilled below the freezing point of water by evaporation of the gasoline in the carburetor. The ice forms on the throttle blade and in the venturi and can interrupt carburetion, causing the engine to stall.

Icing can be acute when the air is moist (70% or higher relative humidity) and the ambient temperature is between 35°F and 55°F (2°C and 13°C). These weather conditions are common during the fall, winter and spring in many parts of the country and they can last well into the summer in some coastal regions. Carburetor icing is not a problem when the intake air temperature is below freezing because then the air is too dry.

The extent of carburetor icing does not depend on the weather alone. It also involves carburetor and vehicle design and the mechanical condition of the engine – in particular, those components that affect warmup time, like thermostats, automatic chokes, intake air heaters, and heat risers. And it also involves gasoline volatility. The 70% evaporated temperature in the distillation profile is a good index of the tendency of a gasoline to cause carburetor icing – the lower this temperature, the more severe the icing.

Carburetor icing is not as big a problem as it used to be. For emission control reasons, most carbureted engines since the late-1960s have been equipped with intake air heating systems, which generally eliminate carburetor icing. The problem will be reduced further as vehicles with carburetors are replaced by fuel injected vehicles.

Gasoline volatility not only affects a vehicle’s driveability, but also its VOC emissions – both evaporative and exhaust emissions (see p. 15). Because of this relationship, the federal government and some states limit gasoline volatility to control the aspect of air quality affected by hydrocarbon emissions. ASTM incorporates federal volatility regulations into the gasoline specification as they are promulgated.

Fluctuating volatility requirements make gasoline manufacture and distribution a complex process. A refiner producing gasoline for a multi-state area may have to make gasolines with several different volatilities and change the volatility from month-to-month. And each gasoline has to be kept separate while it is shipped to the appropriate location.

Figure 1-3b
ASTM D 4814 Vapor Lock Protection Class Requirements

Vapor Lock Protection Class	Vapor-Liquid Ratio (V/L) Temperature, °F	Vapor-Liquid Ratio (V/L); Maximum
1	140	20
2	133	20
3	124	20
4	116	20
5	105	20
6	95	20

Volatility Specifications

The gasoline specification, ASTM D 4814 (see p. 31), controls the volatility of gasoline by setting limits for the vapor pressure, distillation profile and vapor-liquid ratio properties. The specification employs six vapor pressure/distillation profile classes (Figure 1-3a) and six vapor-liquid ratio classes (Figure 1-3b). The specification assigns one vapor pressure/distillation profile class and one vapor-liquid ratio class each month to each geographical area (state or portion of a state) in the United States based on altitude and the expected ambient temperature range.

ASTM D 4814 does not include a DI requirement. Several organizations have proposed various DI limits, but none had been approved as of 1996.

Antiknock Performance

Knock-free engine performance is as important as good driveability. *Octane number* is a measure of a gasoline's antiknock performance – its ability to resist knocking as it burns in the combustion chamber. There are two laboratory test methods to measure the octane number of a gasoline (*see p.33*). One yields the *Research octane number (RON)*, the other, the *Motor octane number (MON)*. RON correlates best with low speed, mild-knocking conditions; MON correlates best with high-speed and high-temperature knocking conditions and with part-throttle operation. For a given gasoline, RON is always greater than MON. The difference between the two is called the *sensitivity* of the gasoline.

Because RON and MON are measured in a single cylinder laboratory engine, they do not completely predict antiknock performance in multicylinder engines. There is a procedure to measure the antiknock performance of a gasoline in vehicles (*see p. 33*). The resulting value is called *Road octane number (RdON)*. Since vehicle testing is more involved than laboratory testing, there have been a number of attempts to predict RdON from RON and MON. The equations take the form:

$$\text{RdON} = a(\text{RON}) + b(\text{MON}) + c$$

A good approximation for RdON sets $a=b=0.5$ and $c=0$, yielding $(\text{RON} + \text{MON})/2$, commonly written $(\text{R}+\text{M})/2$. This is called the *Antiknock Index (AKI)*. The Federal Trade Commission requires dispensing pumps to be labeled (*posted*) with the gasoline's AKI.¹ Owner's manuals also must indicate the octane requirement of vehicles² by AKI.

Neither the AKI nor the several other single-value indices that have been developed work for all vehicles. The performance of some vehicles correlates better with RON or MON alone than with a combination of the two. And for a given vehicle, the correlation can vary with driving conditions.³

As the formula indicates, gasolines with the same AKI can have different RONs and MONs. This may explain why a vehicle knocks with some fill ups of the same brand but not with others; or why it knocks with one brand of gasoline but not with another. Of course, for a comparison to be valid, the vehicle must be operated under identical conditions, which is not easy for the typical driver.

Generally, three grades of unleaded gasoline with different AKIs are available in the United States – regular, midgrade and premium. At sea level, the posted AKI for regular-grade is usually 87 and for midgrade, 89. The AKI of premium-grade varies more, ranging from 91 to 94.

KNOCKING

Knocking or pinging is the sound of abnormal combustion. Normal combustion in a spark-ignition internal combustion engine is initiated by a spark. The flame front fans out from the spark plug and travels across the combustion chamber rapidly and smoothly until almost all the fuel is consumed. When combustion is abnormal, the last part of the unburned mixture ignites spontaneously (*autoignites*) and burns very rapidly, causing the pressure in the cylinder to rise rapidly*. This creates the characteristic knocking or pinging sound.

Occasional light knocking doesn't hurt an engine. However, heavy or prolonged knocking can result in:

- Objectionable noise
- Loss of power
- Overheating of engine parts
- Knock-induced surface ignition (*see p. 42*)
- Engine damage

Knock occurs because the gasoline's antiknock rating (octane number) is below the antiknock requirement of the engine at that moment. Generally, the situation involves high load conditions, like hard acceleration or climbing a grade.

*Knocking due to autoignition is called *spark knock*. Other types of abnormal combustion related more to engine conditions than gasoline characteristics are discussed on p. 42.

¹ The gasoline being dispensed must have an antiknock index equal to or greater than the posted value.

² Older owner's manuals of some foreign cars specify RON; some more recent ones specify both RON and AKI.

³ See p. 52 for the variables which affect an engine's octane requirement.

HEATING VALUE

The *heating value* (also referred to as *energy content*) of gasoline is its heat of combustion – the heat released when a known quantity of fuel is burned under specific conditions. In the United States, the heating value is usually expressed as British thermal units (Btu) per pound or per gallon at 60°F. [The international metric (SI) units are kilojoules per kilogram or per cubic meter at 15°C.] For *gross heating value*, the water produced by the combustion is assumed to be recondensed to a liquid. For the lower *net heating value*, the water is assumed to remain a gas. Since all engines exhaust water as a gas, the net heating value is the appropriate value for comparing different fuels.

Since gasoline is sold by volume, it is customary to express gasoline heating values per unit volume, specifically, Btu per gallon. This is the value which correlates with fuel economy because fuel economy is also expressed per unit volume (miles per gallon).

The densities of the hydrocarbons in gasoline vary over a much wider range than their heating values per unit weight. Consequently, compositional changes that result in density changes are accompanied by changes in heating value per unit volume. If the density of a conventional gasoline decreases, its heating value per unit volume also decreases.

Adding oxygenates to conventional gasoline also decreases the heating value. Oxygenates have lower heating values than hydrocarbons on either a unit weight or unit volume basis. The amount of decrease depends on the amounts and identities of the oxygenates.

The posted AKIs are lower in the Rocky Mountain states. These *altitude gasolines* historically provided the same antiknock performance as higher-AKI gasolines at sea level. The octane requirement of older-model engines decreases as air pressure (barometric pressure) decreases. Barometric pressure is lower at higher elevations.

Since 1984, vehicles have been equipped with more sophisticated control systems, including sensors to measure, and engine management computers to adjust for, changes in air temperature and barometric pressure (*see p. 49*). These vehicles are designed to have the same AKI requirement at all elevations and the owner's manuals specify the same AKI gasoline at all elevations.

It is difficult for a driver to know whether a gasoline has the antiknock performance the engine requires when the engine is equipped with a knock sensor system. These systems, which temporarily retard spark timing to eliminate knocking, are installed on many late-model engines (*see p. 50*). Retarding the spark reduces power and acceleration. The knock sensor responds so quickly that the driver never notices the knock. Loss of power and acceleration will be the only clues that the antiknock quality of the gasoline does not meet the vehicle's octane requirement.

Using gasoline with an antiknock rating higher than that required to prevent knock or to prevent spark retardation by the knock sensor will not improve a vehicle's performance.

Power

The power an engine develops depends on its design. In general, the more air an engine can process, the more power it can produce. Major design considerations for power are the displacement of the engine, the compression ratio, and the presence of a supercharger or turbocharger. Other factors affecting power are the number of valves per cylinder, valve timing, and spark timing (*see Chapter 5*). Because different grades of gasoline have essentially the same heating value, they all provide the same power as long as their antiknock performance meets the engine's requirement.

Fuel Economy

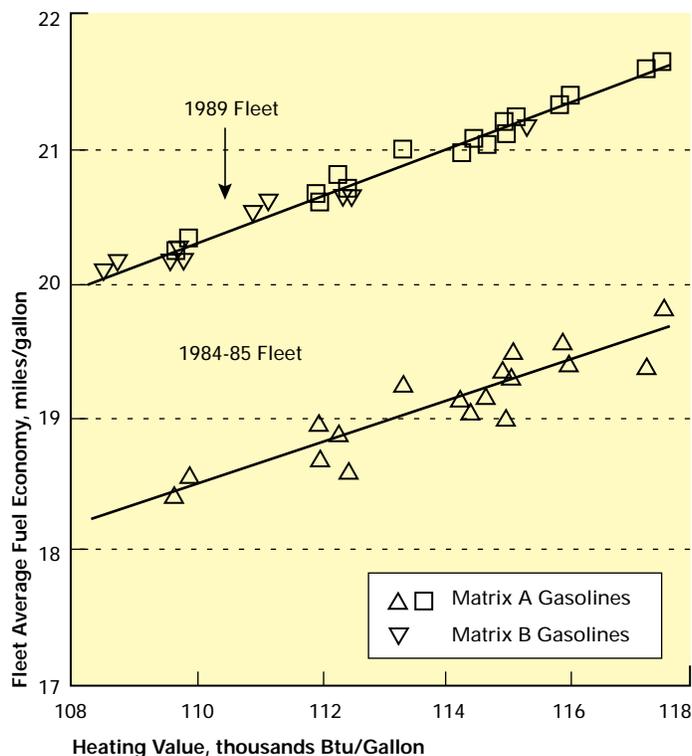
Fuel economy is usually expressed as the number of miles traveled on one gallon of gasoline – miles per gallon (mpg). Many drivers calculate it by counting the miles driven between fill ups. Driving on the road is not a good way to determine how fuel economy is affected by gasoline composition because it is difficult to control the many other factors that are involved (*see below*). A more-accurate determination is possible under controlled laboratory conditions. Vehicles are mounted on a chassis dynamometer in a temperature controlled space and driven through a specified operating cycle (*see p. 16*). The weight or volume of the gasoline consumed during the cycle may be measured or it may be calculated from the weight fraction of carbon compounds in the vehicle's exhaust.

Figure 1-4 shows that the average fuel economies of two fleets of vehicles are proportional to the heating values of the gasolines tested.⁴ This is the relationship predicted by combustion theory. The newer fleet was composed of 1989 model-year cars; the older fleet of 1984-1985 model-year cars. The test involved two different sets of gasolines (Matrix A and Matrix B) which varied in aromatics content, olefins content, oxygen content, oxygenate type, and several other properties. This result shows that heating values can be used as surrogates for actual fuel economy measurements when considering the effect of gasoline composition on fuel economy.

Conventional fuels have always varied in heating value. One cause is the formulation differences among batches and among refiners. A survey of 1990-1991 conventional gasolines found that the heating value of summer gasolines varied over an eight percent range.⁵ The heating value also varies by grade and by season. On average, the heating value of premium-grade gasoline is about 0.7% higher than regular-grade because premium-grade, in general, contains more aromatic hydrocarbons – the class of hydrocarbons with the highest densities. The heating value of winter gasoline is about 1.5% lower than summer gasoline because winter gasoline contains more volatile, less dense hydrocarbons.

Oxygenated gasolines, which are required in some areas of the United States (*see p. 36*), have lower heating values because the heating values of the oxygenate components are lower than those of the hydrocarbons they displace. The percent decrease in heating value is close to the mass percent oxygen in the gasoline. For example, gasoline in carbon monoxide nonattainment areas must be oxygenated to a minimum of 2.7 mass % oxygen during four or five winter months.⁶ As a result, its heating value is about 2.7% lower than conventional gasoline. Federal reformulated gasoline and California Phase 2 reformulated gasoline must be oxygenated year round to an average oxygen content of about 2 mass %. As a result, their heating values are about 2% lower than that of conventional gasoline. In addition, California Phase 2 reformulated gasoline sets some limits on distillation temperatures and aromatics content, which have the secondary effect of lowering the density of the fuel. This reduces the heating value by about another 1%.

Figure 1-4
Relationship between Fleet Average Fuel Economy and Heating Value



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⁴ Albert M. Hochhauser et. al., *Fuel Composition Effects on Automotive Fuel Economy – Auto/Oil Air Quality Improvement Research Program*, Paper No. 930138, Society of Automotive Engineers, March 1993.

⁵ California Air Resources Board, *Survey of California Gasolines*, Sacramento, California, 1991.

⁶ *Nonattainment area* is an EPA designation for an area where an air pollutant, carbon monoxide in this case, exceeds the limit established by the National Ambient Air Quality Standards more often than allowed.

The gasolines which produced the result displayed in Figure 1-4 were specially formulated to span a wide range of compositions. The compositional variations were much greater than those that separate conventional and reformulated commercial gasolines. Thus, the result provides solid evidence that reformulated gasoline does not exert some unusual effect on fuel economy. Individual drivers have reported decreases of 10%, 15% and even 20% in fuel economy when they began using reformulated gasoline. Not surprisingly, many of the claims are anecdotal. Few drivers keep continuous fuel-economy records, so they don't have a good fuel-economy baseline for the gasoline they previously used. Even with a baseline, a fuel-economy value based on the consumption of a single tankful of gasoline can be misleading. Drivers interested in the fuel economy should average the result over several tanks of gasoline or, better yet, over several months of driving.

Factors Affecting Fuel Economy

Fuel economy is affected by a vehicle's size, weight, aerodynamics, fuel delivery system, engine type and transmission type. These values remain constant for a specific vehicle.

Figure 1-5
Estimates of Fuel Economy Reductions Caused by Various Factors

Factor	Conditions	Percent Reduction in Fuel Economy	
		Average	Maximum
Temperature	20°F vs. 77°F	5.3	13
Idling/Warmup	Winter vs. summer	Variable with Driver	20
Defroster	Extreme use	Analogous to air conditioning on some vehicles	
Head wind	20 mph	2.3	6
Uphill driving	7% grade	1.9	25
Poor road conditions	Gravel, curves, slush, snow, etc.	4.3	50
Congested traffic	20 mph vs. 27 mph average speed	10.6	15
Highway speed	70 mph vs. 55 mph	N/A	25
Acceleration rate	"Hard" vs. "easy"	11.8	20
Wheel alignment	0.5 inch	<1	10
Tire type	Non-radial	<1	4
Tire pressure	15 psi vs. 26 psi	3.3	6
Air conditioning	Extreme heat	21%	N/A
Windows	Open vs. closed	Unknown, but likely small	

Office of Mobile Sources, United States Environmental Protection Agency, *Fuel Economy Impact Analysis of RFG*, August 1995 (Document EPA 420-F095-003).

There also are many variable factors. As mentioned, the heating value of the gasoline is one. In addition, fuel economy is affected by weather conditions, air conditioner use, road conditions, the route driven, driving speed and driving style. And it is affected by the mechanical condition of the car – engine tune, wheel alignment and tire pressure. Some of these non-gasoline factors have the potential to cause substantial changes in fuel economy. Figure 1-5 is a list of average and maximum effects published by the United States Environmental Protection Agency (EPA).

Winter-related factors can combine to lower fuel economy 20% compared to the summer. Rain or snow on the road offers more resistance to the tires. It may also require the driver to slow for safety to a less fuel-efficient speed. In cold weather, a richer air-fuel mixture is required to start and warmup the engine. And much of the warmup is done at idle because of the need to defog or defrost the windows. Also, in many vehicles, the air conditioner is operated to assist defogging. More energy is required to overcome the resistance created by the higher viscosities of cold lubricants – engine oil, transmission fluid, and differential lubricant.

Short trips are worse for fuel economy than long trips because a cold engine uses more fuel than a warm engine and because of the energy required to overcome the resistance of cold lubricants.

Traffic jams and bumper-to-bumper driving exact a heavy toll on fuel economy.

Fuel Economy Road Test

The results of a Wisconsin on-road fuel economy test demonstrate that some of the above factors can have a much bigger effect on fuel economy than a few percent change in gasoline heating value.⁷

The test was designed to minimize all factors affecting fuel economy except gasoline composition. Vehicles were driven over the same route of 100 miles of urban and suburban roads. The fuel economy of each vehicle on the route was measured four times for each gasoline: once in the morning and afternoon of the same day, and again in the morning and afternoon of a day a week later. Some vehicles were driven by the same driver all four times. Other vehicles were driven at different times by two drivers. When the results for the two weeks were compared, most of the fuel economies in the second week were lower. The differences were greater than 10% for a quarter of the car-fuel combinations. Two factors that probably contributed to the week-to-week differences were the driver change and a weather change. Ambient temperatures were lower in the second week; in some cases, noontime temperatures were as much as 30°F cooler.

The gasolines used in the Wisconsin test were commercial gasolines – a conventional gasoline and federal reformulated gasolines (federal RFGs) oxygenated with MTBE, ETBE or ethanol. When the results for all the road tests of all the vehicles were combined, the average fuel economy of the three oxygenated federal RFG gasolines was 2.8% lower than the average fuel economy of the conventional gasoline – a value much less than the 10% week-to-week difference for some of the car-fuel combinations, but right in the range predicted by the differences in the gasolines' heating values.

Other Performance Factors

Both federal and California regulations require that some gasolines be oxygenated. Using oxygenated gasoline leans the air-fuel mixture of carbureted engines and fuel injected engines without a closed-loop feedback system. Fuel leaning can cause some degradation in driveability, depending on the engine's calibration (*see p. 39*).

Without additives, deposits form throughout an engine's intake system – in the fuel injectors, carburetor, intake manifold, intake ports and on the intake valves. Deposits can be very deleterious to engine performance – degrading driveability, decreasing power and fuel economy and increasing emissions (*see p. 53*).

⁷ *On-Road Study of the Effects of Reformulated Gasoline on Motor Vehicle Fuel Economy in Southeastern Wisconsin*, Wisconsin Department of Natural Resources, March 1995.

THE BEGINNING

Smog is the common term for the forms of air pollution involving haze and oxidants, such as ozone. Smog was identified as a serious problem in the Los Angeles basin in the 1950s. As university scientists and government health agencies investigated the problem, they found that vehicle emissions were a significant source of smog precursors. Acting on this information, the California Legislature established emissions limits for 1966 model cars. Federal legislation to reduce vehicular emissions, as part of a greater air quality program, was initiated with the adoption of the Clean Air Act of 1963. The first Federal limits for exhaust emissions from gasoline-powered cars were implemented starting with the 1968 model year.

Introduction

Today it is almost impossible to discuss gasoline or gasoline-powered vehicles without considering air quality. A number of areas in the United States fail to meet one or more federal air quality standards. In some of these areas, vehicles are responsible for more than half of the problem emissions.

This chapter explains who regulates emissions, and how and why. It also explains which emissions come from vehicles and how they are formed. Finally it explains how emissions are affected by gasoline characteristics and how gasoline is being reformulated to reduce emissions.

The explanations are complicated because they involve complex regulations and complex science. Sometimes complete accuracy is sacrificed to keep this review as short and simple as possible. The number of acronyms is unavoidable; both government regulation and science use them heavily.

Progress

Are the efforts of adding pollution control systems to vehicles and reformulating gasoline paying off in better air quality? The answer is yes. Urban air quality has improved dramatically over the last twenty years. To illustrate, Figure 2-1 shows the declining trend lines for the maximum hourly concentrations of three air pollutants – ozone, carbon monoxide, and nitrogen dioxide – in California. The fact that these decreases are not uniform from year-to-year may indicate the impact of meteorological fluctuations on ambient pollutant concentrations.

The improvement in urban air quality is primarily due to significant advances in emissions control technologies that have been applied to the various sources. For example, today a new model passenger car emits less than 5% of the volatile organic compounds and carbon monoxide and only about 10% of the oxides of nitrogen emitted by a vehicle built before emissions controls began to be used. Similarly impressive improvements have been achieved for certain stationary sources such as refineries and power plants.

It's too soon to have definitive results, but early findings indicate the introductions of federal Phase I reformulated gasoline and California Phase 2 reformulated gasoline, both of which are predicted to reduce emissions another 15%, are significantly improving air quality.

Legislation

The Clean Air Act of 1963 initiated the federal government's regulation of air pollution. It was amended in 1967, 1970, 1977, and, most recently, in 1990. The stated purpose of the Act is "... to protect and enhance the quality of the Nation's air resources" As the purpose suggests, the act addresses a wide range of air pollution issues, not just vehicle emissions.

One purpose of the Act was to "... encourage cooperative activities by the States and local governments for the prevention and control of air pollution"

However, the Act forbids states from setting separate vehicle emissions standards. This restriction was included so that auto manufacturers would not have to produce cars with different emissions control systems to meet different state standards. The restriction was waived for California. Because of its more severe smog levels and its long history of working to control vehicle emissions, California is allowed to establish its own regulations for controlling vehicle emissions, subject to federal approval. Under certain circumstances, other states are allowed to require the sale of new vehicles that meet the more stringent California standards.

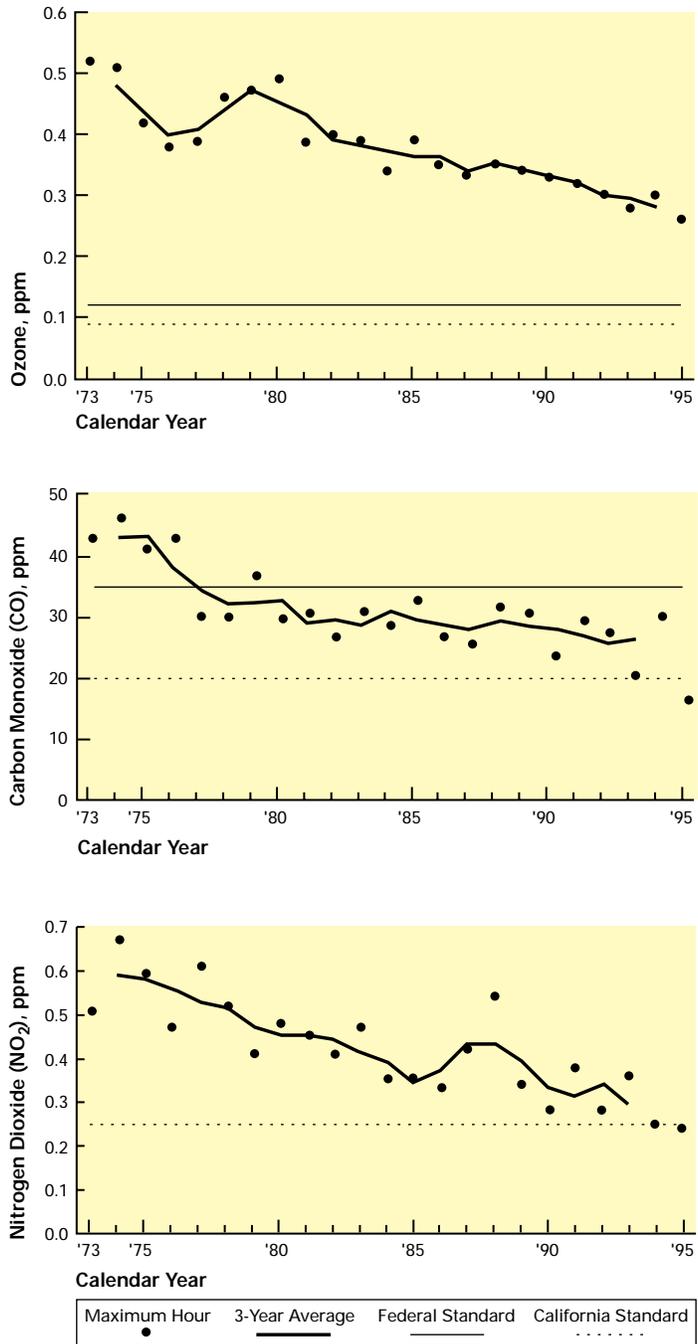
Administration/Regulation

Laws are not administered by the body that adopts them. The Congress or state legislature assigns the administrative responsibility to a governmental agency. The 1970 amendments of the Clean Air Act created the United States Environmental Protection Agency (EPA) and made it responsible for implementing the requirements of the Act and its amendments. California’s laws covering vehicle emissions are administered by the California Air Resources Board (California ARB), which was established by the legislature in 1969.

While some laws contain a lot of detail, they can’t address all the issues surrounding their application in our complex industrial society. The agency administering the law has the responsibility to write regulations which will make the legislative intent a reality. Title 40 of the Code of Federal Regulations contains the EPA regulations concerning the protection of the environment.

The states, as Congress intended, do much of the work to carry out the provisions of the Clean Air Act and its amendments. State and local air pollution agencies hold hearings, write regulations (based on guidance from the EPA), issue permits, monitor pollution, issue notices of violations and levy fines. It is appropriate for the states to take the lead because state and local agencies need to select and enforce pollution control strategies that make sense for their region. Geography, weather conditions, housing patterns, regional traffic patterns and the nature of local industry all influence pollution levels.¹

Figure 2-1
Maximum Hourly Pollutant Levels in California
1973-1995



Reprinted with permission from CVS News, July 1996

¹ The Plain English Guide to the Clean Air Act, U.S. Environmental Protection Agency, EPA 400-K-93-001, April 1993.

The Clean Air Act and its amendments "... set deadlines for the EPA, states, local governments and businesses to reduce air pollution." Each state is required to develop a plan which explains the actions it will take to meet or maintain the air quality standards set by the EPA. A state implementation plan (SIP) is a collection of the regulations the state will use. The EPA must approve each state's SIP. The EPA assists the states by providing scientific research, expert studies, engineering designs, and money to support clean air programs.

Air Quality Standards

Air pollutants are natural and artificial airborne substances which are introduced into the environment in a sufficient concentration to have a measurable effect on humans, animals, vegetation, or building materials. From a regulatory standpoint, substances become air pollutants when the EPA says they are. As part of the

Figure 2-2
Ambient Air Quality Standards

Criteria Pollutant	Averaging Time	Maximum Average Concentration	
		Federal Standard	California Standard
Ozone; ppm	1 - Hour	0.12	0.09
Carbon Monoxide (CO); ppm	1 - Hour	35	20
	8 - Hour	9	9
Nitrogen Dioxide (NO ₂); ppm	1 - Hour	-	0.25
	Annual	0.053	-
Sulfur Dioxide (SO ₂); ppm	1 - Hour	-	0.25
	24 - Hour	0.14	0.05
	Annual	0.03	-
Suspended Particulate Matter (PM ₁₀); µg/m ³	24 - Hour	150	50
	Annual	50	30
Lead; µg/m ³	30 - Day	-	1.5
	Quarterly	1.5	-
Sulfates; µg/m ³	24 - Hour	-	25

process, the Clean Air Act requires the EPA to issue a *criteria document* for each pollutant that documents its adverse effects. Regulated pollutants therefore are referred to as *criteria pollutants*. The EPA uses the information in the criteria documents to set National Ambient Air Quality Standards (NAAQS) at levels that protect the public health and welfare. Figure 2-2 lists the criteria pollutants and the federal and California standards, which in most cases are more stringent. Some of the criteria pollutants, like carbon monoxide, are *primary pollutants*, which are emitted directly by identifiable sources. Others, like ozone, are *secondary pollutants*, which are formed by reactions in the atmosphere. And others, like particulates, are of mixed origin.

Air Pollutants²

Ozone Ground-level³ ozone is formed by the interaction of reactive organic gases, oxides of nitrogen (NO_x), and sunlight. The role of sunlight explains why the highest concentrations of ozone in the atmosphere occur in the summer months and why there is a diurnal pattern to the concentrations, with higher concentrations occurring in the afternoon and lower concentrations at night.

"[Ozone] damages lung tissue, reduces lung function, and sensitizes the lungs to other irritants." "[It is] responsible each year for agricultural crop yield loss in the U.S. of several billion dollars and causes noticeable [leaf] damage in many crops and species of trees."⁴

² Paul Degobert, *Automobiles and Pollution*, Society of Automotive Engineers, Warrendale, PA, 1995.
³ In the stratosphere, a layer of ozone partially shields the earth from solar ultra-violet radiation. Stratospheric ozone is formed by a different mechanism than ground-level ozone.
⁴ *National Air Quality and Emission Trends Report*, 1992. Office of Air Quality Planning and Standards, U. S. Environmental Protection Agency, EPA 454/R-93-031, October 1993.

Reactive Organic Gases (ROGs)⁵ ROGs are not a criteria pollutant, though some specific ROGs are classified as toxics (*see below*). Their importance stems from their role in forming ozone. All hydrocarbons except methane and ethane are ROGs, which explains why so much effort is directed toward reducing hydrocarbon emissions from vehicles and stationary sources.

The EPA estimates that, nationwide, about equal quantities of VOC emissions come from man-made and natural sources. Gasoline engines accounted for about 26% of the man-made VOC emissions in 1994, the latest year for which data are available (*Figure 2-3*).

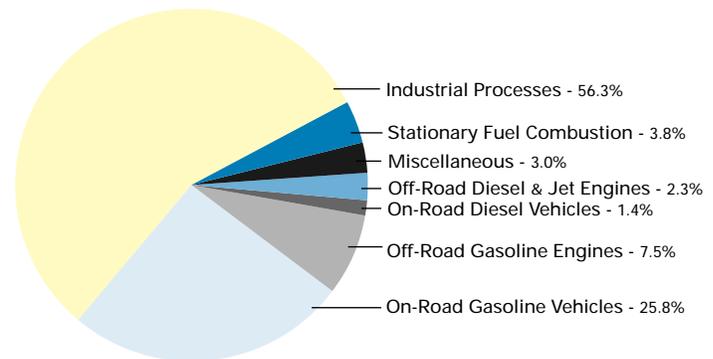
Not all hydrocarbons contribute equally to ozone formation. Their reactivity depends on their chemical structure and the atmospheric conditions to which they are subjected. Under most conditions, olefins and aromatics are more reactive than paraffins.

The toxicity of organics depends on their structure. Most hydrocarbons are nontoxic at low concentrations. Some low-molecular-weight aldehydes are carcinogens and some monocyclic and *polycyclic aromatic hydrocarbons (PAH)*⁶ are suspected or known carcinogens.

Carbon Monoxide (CO) CO is primarily generated by combustion processes. The EPA estimates gasoline engines are responsible for almost 75% of the man-made CO emissions (*Figure 2-4*). One reason is that engines that run on variable air-fuel mixtures are harder to control than stationary sources running on fixed mixtures. CO's toxicity stems from its ability to reduce the oxygen-carrying capacity of the blood by preferentially bonding to hemoglobin.

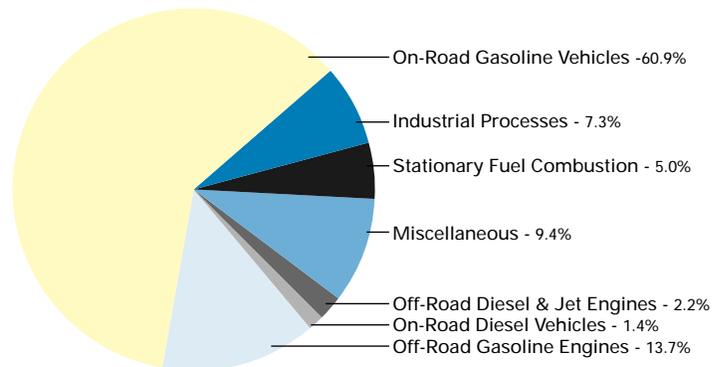
Nitrogen Dioxide (NO₂) The air quality standard applies only to NO₂, but where emissions are concerned, NO and NO₂ are usually analyzed simultaneously and expressed as NO_x. Most (90%) of the NO_x emissions are man-made. The EPA estimates that gasoline engines generate about 24% of the man-made NO_x emissions (*Figure 2-5*).

Figure 2-3
Emissions Sources:
1994 National Man-Made VOC Emissions
23,175,000 Short Tons



US EPA National Air Pollution Emissions Trends

Figure 2-4
Emissions Sources:
1994 National Man-Made CO Emissions
98,016,000 Short Tons



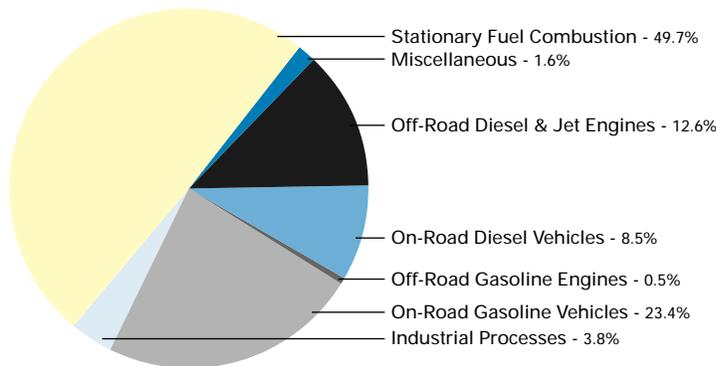
US EPA National Air Pollution Emissions Trends

⁵ ROGs is the preferred term when discussing ozone production. But when focus is on emissions, the term *volatile organic compounds (VOCs)* is more common. This review will use both terms. The primary difference between ROGs and VOCs is that the latter includes methane and ethane, which do not participate in ozone formation and, therefore, are not ROGs. Another term which is sometimes used is *non-methane organic gases (NMOGs)*.

⁶ Also called *polycyclic aromatic matter (POM)*, or *polynuclear aromatics (PNA)*.

While NO is nontoxic by itself, it contributes to ozone formation. “NO₂ can irritate the lungs and lower resistance to respiratory infection In some western areas, NO_x is an important precursor to particulate concentrations.”⁷

Figure 2-5
Emissions Sources:
1994 National Man-Made NO_x Emissions
23,616,000 Short Tons (as NO₂)



US EPA National Air Pollution Emissions Trends

Sulfur Dioxide (SO₂) SO₂ is primarily produced from the combustion of fuels containing sulfur. Facilities (*stationary sources*) that burn fuel oil and coal are the major source. On-road and off-road engine fuels are estimated to be the source of less than 3% of the total SO₂ emissions. SO₂ is a moderate lung irritant. It and NO_x are major precursors to acidic deposition (acid rain).

Particulate Matter (PM₁₀) PM₁₀ is particulate matter with particle size less than 10 microns (0.0004 inch). The EPA estimates fugitive dust from roads accounts for about two-thirds of the total. Less than 2% is attributed to on-road and off-road engines, but the percentage is higher in urban areas where there is less dust and more combustion sources. Particulates from engines include primary carbon particles (mainly from diesel engines) and secondary sulfate and nitrate aerosols formed by SO₂ and NO_x.

Lead Once the primary source of air-borne lead was vehicles burning gasoline containing lead alkyl antiknock additives. Now it is point sources, like smelters and battery plants. The total national lead emissions decreased sharply from 1970 to 1994 as sales of unleaded gasoline replaced leaded gasoline and as the lead content in leaded gasoline was phased down. The sale of gasoline containing lead or lead additives for on-road use was prohibited in the United States in January 1996. Excessive exposure to lead may cause neurological impairments such as seizures, mental retardation and/or behavioral disorders. Fetuses, infants and children are especially susceptible to low doses of lead. The hazardous threshold for blood lead poisoning is still being disputed.

Toxic Organics The Clean Air Act Amendments of 1990 classified the following as *toxic air pollutants* related to gasoline and gasoline vehicles: benzene, polycyclic organic matter (POM), acetaldehyde, formaldehyde, and 1,3-butadiene. The EPA calculates that the five toxic organics combined comprise 3.8% of total VOC emissions; about 70% of that amount is benzene. 1,3-Butadiene, formaldehyde, and acetaldehyde are not present in gasoline; they are formed during combustion. Benzene is a known human carcinogen. Although some POMs are carcinogens, the POM content of gasoline and gasoline exhaust is so low as to be difficult to measure. The aldehydes are eye and throat irritants. Formaldehyde is a suspected human carcinogen.

⁷ *National Air Quality and Emission Trends Report, 1992*. Office of Air Quality Planning and Standards, U. S. Environmental Protection Agency, EPA 454/R-93-031, October 1993.

Vehicle Emissions: Sources⁸

When fuel is burned with the correct amount of air in a gasoline-powered engine, the gases which are left are predominantly water vapor, carbon dioxide and nitrogen – all of which are benign, although carbon dioxide is a greenhouse gas. However, deviations from this ideal combustion lead to the production of some VOCs, CO, NO_x and PM₁₀.⁹

Gasoline-powered vehicles tend to be the greatest emitters of CO, and substantial emitters of VOCs and NO_x, but only modest emitters of PM₁₀. Diesel-powered vehicles, on the other hand, are substantial emitters of PM₁₀ and NO_x, but only small emitters of CO and VOCs. (See Figures 2-3, 2-4 and 2-5.)

Exhaust VOCs Exhaust VOC emissions consist primarily of unburned hydrocarbons, but partially-burned oxygen-containing compounds such as aldehydes are also present. Although, in any reasonably operating vehicle, the vast majority of the fuel is burned before the combustion gases exit the engine, a small fraction – typically 1% to 5% – manages, for a variety of reasons, to escape unburned. Factors that influence the amount of VOC emissions include engine design, operating temperature, air-fuel ratio (A/F), presence of fuel system deposits, and the condition of the engine and its controls. If the vehicle has some significant malfunction that inhibits proper ignition or combustion, like a bad spark plug, the VOC emissions can be many times higher than normal.

Evaporative VOCs Exhaust gases are not the only source of VOC emissions from gasoline-fueled vehicles. The EPA has estimated that more than half the VOCs emitted from gasoline vehicles in 1990 was *evaporative emissions*. Evaporative VOC emissions are quite different from exhaust VOC emissions in their composition. They contain no combustion products and their composition is weighted heavily towards the lowest boiling components of gasoline because gasoline vapor is a main source.

Gasoline vapor escapes from the typical vehicle by a variety of mechanisms. Sources include the fuel tank, carburetor (on vehicles that use them), and intake manifold. Liquid gasoline can also permeate through elastomeric fuel hoses and leak or seep from fuel system components or connections.¹⁰ Factors that influence the amount of evaporative emissions include fuel system design (see p. 47), component integrity, fuel system and ambient temperatures and gasoline vapor pressure (see p. 2).

Carbon Monoxide CO is the primary product of incomplete combustion of fuel. The main factor influencing its production is the A/F. If the mixture is *fuel rich*, i.e., has insufficient air (O₂) to convert all of the fuel carbon to carbon dioxide (CO₂), the exhaust will contain a high level of CO. Fuel rich operation can result either by design or by accident. By design, virtually all vehicles employ momentary enrichment to aid vehicle starting, with greater (or longer) enrichment at

⁸ A significant amount of emissions-related information may be obtained via the EPA's World Wide Web site at <http://www.epa.gov/OMSWWW/>.

⁹ For a detailed discussion of pollutant formation and control in gasoline engines, see J. B. Heywood, *Internal Combustion Engine Fundamentals*, McGraw-Hill, 1988.

¹⁰ In these cases the composition of the evaporative VOCs will be characteristic of the whole gasoline.

colder ambient temperatures. Enrichment also is used commonly under high power demand, partly to increase power output and partly to help prevent permanently damaging the convertor catalyst by overheating.

By accident, a vehicle can operate fuel rich due to a malfunction of the fuel supply or control system. The causes are many, but include: (1) deterioration or failure of components like a carburetor or oxygen sensor, (2) deposits formed over time in fuel injectors or carburetors by poor-quality gasoline, or (3) maintenance deficiencies such as maladjustment or neglect.

Oxides of Nitrogen NO_x is produced by a different mechanism than that for CO and exhaust VOCs. Whereas the latter are products of incomplete combustion, NO_x is produced when combustion is robust. It is generated by reactions of nitrogen and oxygen which occur at high temperatures. Nitrogen is always present in the combustion chamber because air is 80% nitrogen. The production of NO_x is increased by the presence of excess oxygen, which occurs under fuel lean conditions, and especially by higher combustion temperatures. Thus, NO_x is affected by the A/F and by engine design factors which influence temperature, such as compression ratio, spark timing, and cooling system performance. Combustion chamber deposits generally are believed to have a modest insulating effect, thus raising combustion temperatures and increasing NO_x emissions slightly.

Vehicle Emissions: Limits

The Clean Air Act required the EPA to set limits for exhaust emissions from gasoline-powered cars starting with the 1968 model year. The limits applied to CO and hydrocarbons (HC). Limits for NO_x were added starting with the 1973 model

year. Figure 2-6 shows how the federal limits for passenger cars, expressed as grams per mile (g/mile), have been tightened over the years. California has a separate set of passenger car limits which were initially applied to the 1966 model year and which typically have preceded the federal limits by a couple of years. There are other federal and California limits for other gasoline vehicles: light-duty trucks, heavy-duty trucks and buses. Chapter 5 describes the variety of emission control devices and strategies employed to reduce the emissions from gasoline-powered vehicles.

Exhaust emissions are very dependent on how a vehicle is operated. In order to standardize the test conditions, the EPA requires that exhaust emissions be measured while the vehicle is *driven* according to a specified speed-time *cycle* on a dynamometer. Two cycles are currently used: the Federal Test Procedure Cycle (FTP 75) and the Highway Fuel Economy Test Cycle (HWFET). The former simulates a 7.5-mile urban route with a cold start, frequent stops, and an average speed of 19.6 mph. The latter simulates a 10.2-mile highway route with a warm engine and an average speed of 48.6 mph.

Figure 2-6
Federal Passenger Car Exhaust Emission Standards

Model Year	Maximum Emissions; g/mile (FTP-75 Cycle)		
	Carbon Monoxide (CO)	Hydrocarbons (HC)	Oxides of Nitrogen (NO_x)
Pre-Control (Estimated)	84	10.6	4.1
1968 - 69	51	6.3	-
1970 - 71	34	4.1	-
1972	28	3.0	-
1973 - 74	28	3.0	3.1
1975 - 76	15	1.5	3.1
1977 - 79	15	1.5	2.0
1980	7.0	0.41	2.0
1981	3.4 ^a	0.41	1.0
1994	3.4	0.25 ^b	0.4

^a 1981-82 model years allowed 7.0 g/mile with waiver.

^b Non-methane hydrocarbons.

Inspection and Maintenance

In addition to establishing emission limits for new vehicles, the EPA has long recognized the importance of making sure that vehicles in use continue to function as they were designed. The emission control systems of a modern gasoline-powered vehicle are complex (*see Chapter 5*). To deliver the intended emissions performance, all of the systems must function properly. A single defect can hurt the effectiveness of several subsystems, thus greatly increasing emissions. For example, a fault which causes the engine to operate fuel rich will not only increase production of CO and HC in the engine, but will drastically reduce the ability of the catalyst to eliminate these pollutants, thus increasing their emissions by a factor of perhaps 10 or more. When this happens, one “broken” vehicle can pollute as much as ten properly functioning vehicles! Thus, regular inspection of the engine and its emissions controls, plus prompt and effective repair of any defects, is as important to clean air as requiring the controls initially.

In 1983, the EPA oversaw the introduction of *Inspection and Maintenance (I/M)* programs in a number of states with air quality problems. These mandatory programs, often referred to as *smog inspections*, subject a vehicle to a set of inspections to detect if the emissions control systems are defective or have been tampered with. The inspections may be conducted at state-run facilities or at privately-owned shops. Most involve a visual check of the vehicle for obviously broken, damaged or missing emissions control components and some type of measurement of emissions from the vehicle’s tailpipe. If the vehicle fails any of the tests, the owner is usually required to have the affected items repaired, subject to certain cost limits. The 1990 Clean Air Act Amendments require a number of regions in the United States to implement more stringent I/M programs.¹¹

Vehicle Emissions: Gasoline Effects

The vehicle emission control systems described in Chapter 5 are a much more effective way to reduce emissions than changing the characteristics of gasoline. But changes in gasoline properties and composition can make a difference. The explanations here apply chiefly to vehicles built since 1985.

Sulfur Sulfur in the fuel becomes sulfur oxides in the exhaust, which temporarily poison the three-way catalyst. Reducing gasoline’s sulfur content increases converter efficiency and decreases VOC, CO, NO_x, and toxics emissions.

Reducing the sulfur content also reduces the direct emission of sulfur dioxide and sulfates – criteria pollutants, but gasoline engines are not a major source of these pollutants.

FUEL ECONOMY AND EMISSIONS

Fuel economy is measured as miles per gallon; emissions are measured as grams per mile. There is no direct relationship between the two. While intuition suggests that an engine burning more fuel per mile would produce more emissions per mile, it is not true. The emissions from an engine on a gram/mile basis mostly depend on an engine’s design and its state of tune. Furthermore, most of the emissions produced by the engine are destroyed by the catalytic converter. Large-engine passenger vehicles can burn twice as much fuel per mile as small-engine vehicles, yet both meet the same emissions limits.

In another example, converting from conventional gasoline to oxygenated reformulated gasoline decreases fuel economy by about 3%. So, after the conversion, a vehicle will burn slightly more gasoline to travel a mile. However, the weight of pollutants in the exhaust is less because the reformulated gasoline is designed to reduce the formation of pollutants in the combustion chamber (*see p. 19*). Thus emissions per mile are lower even though slightly more gasoline is consumed. California Phase 2 reformulated gasoline provides an additional emissions benefit because its lower sulfur content improves the efficiency of the catalytic converter relative to high-sulfur-content fuel.

¹¹ Detailed information regarding Inspection and Maintenance programs can be obtained from the U.S. Environmental Protection Agency, Office of Mobile Sources, National Vehicle and Fuel Emission Laboratory, 2565 Plymouth Road, Ann Arbor, Michigan 48105. Regulations regarding I/M programs can be found in Code of Federal Regulations, Volume 40, Part 51 (40 CFR ‘51), subpart S.

Oxygenates As explained earlier, CO is the result of incomplete combustion and its formation is very dependent on the A/F. Increasing the oxygen content of gasoline by adding oxygenates has the same effect as increasing the amount of combustion air, i.e., making the air-fuel mixture more fuel lean. The result is more oxygen in the combustion chamber, more complete combustion and less formation of carbon monoxide. The beneficial effect may be limited to pre-1990 vehicles with less effective A/F control systems. Some research found that added oxygenates had no effect on CO emissions from newer vehicles.

Oxygenates also tend to reduce VOC emissions, significantly increase aldehyde emissions and, in many cases, increase NO_x emissions. The NO_x increases may occur because oxygenated gasolines put more oxygen into the combustion chamber in open-loop operation. As explained previously, NO_x formation is increased by excess oxygen and higher combustion temperatures. The potential relationship between oxygen and increased NO_x caused California to limit the oxygen content of Phase 2 reformulated gasoline to 2.2 mass %. Initially the EPA also limited the oxygen content of Federal reformulated gasoline, but removed the limit in 1996. Since CO emissions are a wintertime issue, the requirement that summertime reformulated gasoline contain oxygen is the subject of considerable controversy.

Olefins Increasing and decreasing olefins both provide benefits. Gasoline with a higher olefins content tends to give lower VOC emissions because olefins burn more easily and more completely than the other classes of hydrocarbons in gasoline. Gasoline with a lower olefins content tends to decrease NO_x formation and the amount of olefins in the evaporative emissions, which is desirable because olefins are more reactive than paraffins and naphthenes for ozone formation. For reformulated gasolines, the choice is to decrease olefins.

Aromatics Decreasing the total aromatics content of gasoline decreases the amount of benzene in exhaust VOC emissions because larger aromatic molecules are partly converted to benzene during combustion or in the catalytic convertor.

Decreasing aromatics also tends to reduce CO and total exhaust VOC emissions, but the effects are variable and complex. This may be because the aromatic compounds in gasoline are so diverse.

Benzene Decreasing the benzene content of gasoline reduces the amount of benzene in both evaporative and exhaust VOC emissions.

Vapor Pressure Decreasing the vapor pressure of gasoline reduces evaporative VOC emissions.

Distillation Profile Temperatures Gasoline containing significant amounts of high boiling components tends to give high VOC emissions. High boiling components are more difficult to vaporize, especially in a cold engine, making complete combustion more difficult. Thus placing limits on the distillation profile can lower VOC emissions.

Reformulated Gasolines (RFGs)

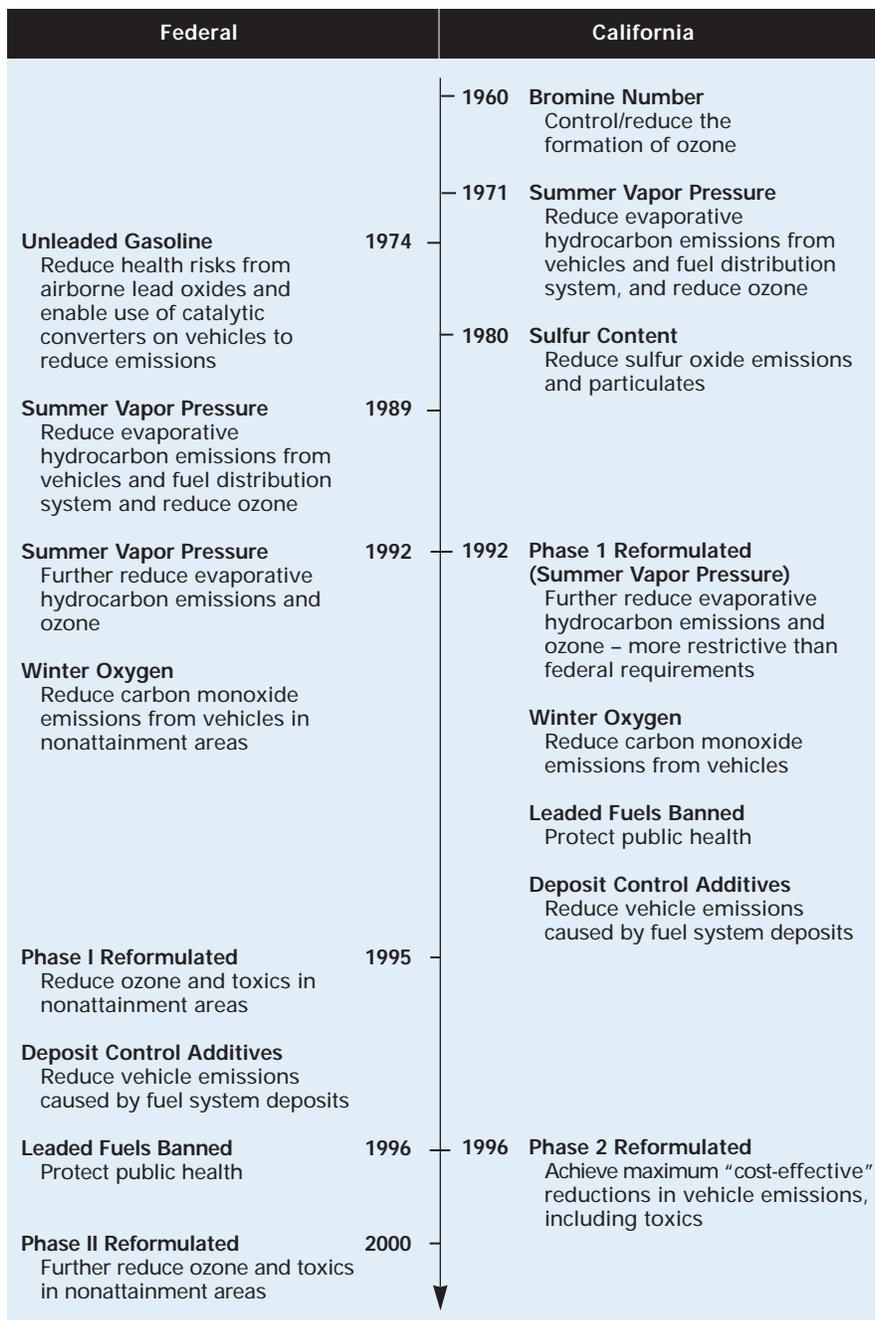
Acting on the above relationships, the EPA and the California ARB in the last 35 years have established a number of regulations to control gasoline properties to reduce emissions from gasoline-fueled vehicles. The chronology is shown in Figure 2-7.

The most significant changes occurred in the 1990s. In 1992, the EPA required the maximum vapor pressure of summertime gasoline be decreased to reduce evaporative VOC emissions. They *capped* (placed an upper limit on) vapor pressure at 7.8 psi in ozone nonattainment areas in the southern states, where average summer temperatures are highest, and at 9.0 psi elsewhere.

In 1992 California Phase 1 RFG was required throughout California. The Phase 1 RFG regulations capped summertime vapor pressure at 7.8 psi for the entire state, not just for ozone nonattainment areas, and forbade the use of lead-containing additives. They also made the use of deposit control additives mandatory, on the basis that engine intake system deposits increase emissions (*see page 55*).

1992 also saw implementation of the EPA’s Winter Oxygenate program, which requires the addition of oxygenates to gasoline sold in the 39 areas of the country that have not attained the National Ambient Air Quality Standard for CO. Gasoline in these areas must contain 2.7 wt% oxygen minimum, averaged over the high CO months. The four or five applicable winter months vary from area to area.

Figure 2-7
Chronology of United States Gasoline Regulations



Federal RFG was mandated by the Clean Air Act Amendments of 1990. Federal Phase I RFG was introduced in 1995. It must be used in the nine extreme or severe ozone nonattainment areas across the country.¹² Less severe nonattainment areas may *opt-in* to the program. A few characteristics of federal Phase I RFG are fixed. The average benzene content must be less than 1 vol % and the average year-round oxygen content must be greater than 2.1 mass %. Otherwise the general approach is to set vehicle emission reduction targets, rather than property or composition limits. The EPA provided refiners with two equations which relate gasoline composition to vehicle emissions – a *Simple Model* and a *Complex Model*. As the names indicate, the Simple Model involves fewer gasoline characteristics than the Complex Model. The Simple Model only may be used from 1995 through 1997. It requires the refiner to adjust gasoline composition to reduce average toxics by 16.5%, relative to 1990 baseline gasoline. In lieu of a VOC target, it limits average summertime vapor pressure to 8.1 psi in the Northern states and to 7.2 psi in the Southern states.

The Complex Model is optional from 1995 through 1997 and mandatory beginning in 1998. It requires the refiner to adjust gasoline composition to meet VOC, toxics, and NO_x limits. Federal Phase II RFG will be introduced in 2000. It continues the Phase I limits on benzene and oxygen content and the use of the Complex Model, but requires greater reductions in VOCs, toxics, and NO_x. Figure 2-8 summarizes the emissions reductions which must be achieved for gasolines formulated under the Phase I and Phase II programs. Decreasing vapor pressure, benzene content, and sulfur content are the primary strategies refiners are expected to use to meet the Phase I Complex Model and Phase II emission limits.

Beginning in 1995, all motor gasolines in the United States were required to contain a deposit control additive, on the basis that engine intake system deposits increase emissions.

In 1996, Phase 2 RFG, also known as *Cleaner Burning Gasoline*, was required throughout California. California ARB's initial regulations for Phase 2 RFG provided a recipe that controlled eight parameters of volatility and composition. The recipe set maximum limits for summertime vapor pressure and benzene, total aromatics, olefins and sulfur contents. It also placed limits on the distillation profile temperatures for the 50% and 90% evaporated points and required a minimum oxygen content year-round.

Later the Phase 2 RFG regulations were revised to allow refiners to choose between the original recipe and a mathematical model – the *Predictive Model* – similar to the federal Complex Model. The intent was to reduce the cost of producing Phase 2 RFG by giving refiners more flexibility. Refiners may use an alternative recipe if the Predictive Model indicates its emissions will be equal to or lower than those of ARB's original recipe. When the Predictive Model is used, the eight parameters are limited to values (*cap limits*) higher than the limits in the original recipe, but still quite restrictive. No gasoline sold in California may have

a parameter with a value exceeding its cap limit. Oxygen addition is not mandatory in the summertime if the model is used, except in areas where the federal RFG program also applies. The California ARB predicts Phase 2 RFG will reduce VOC emissions by 17%, CO and NO_x emissions by 11%, and organic toxics by 44%, relative to Phase 1 RFG. This is equivalent to removing 3.5 million cars from California's roads!

Figure 2-8

Reductions in Vehicle Emissions for Federal Phase I and Phase II Reformulated Gasoline Programs

	Effective Date	Reduction in Emissions, % (Averaged Standard, Compared to 1990 Baseline Refinery Gasoline)		
		VOC	Toxics	NO _x
Phase I				
Simple Model	1995	Vapor Pressure Limits ≥17.1 ^b , ≥36.6 ^c	≥16.5	No Increase ≥1.5
Complex Model	1998 ^a			
Phase II				
Complex Model	2000	≥27.4 ^b , ≥29.0 ^c	≥21.5	≥6.8

^a Optional 1995-1997; mandatory starting in 1998.

^b Northern States

^c Southern States

3 · GASOLINE REFINING AND TESTING

Introduction

Technology exists to make gasoline from coal, shale oil, tar sands and exotic sources like recycled plastics and rubber tires. But these processes are complicated and expensive. Petroleum crude, also called *crude oil* or *crude*, is still the most economical source of gasoline.

The first step of gasoline refining isolates the gasoline naturally present in crude, much as the first refiners did. Then, in more complex steps, non-gasoline components of crude are converted into gasoline and gasoline molecules are rearranged to improve their characteristics. Understanding the various conversion steps requires knowing something about the hydrocarbon building blocks that make up gasoline and crude. So this chapter first discusses the composition of gasoline and the nature of hydrocarbons. Then it explains the various refining steps and how the resulting products are blended to create a finished gasoline. Finally it describes the gasoline specification properties and the tests used to measure them.

Composition

There are two ways to describe a material – by its chemical composition or by its properties. Both viewpoints can be instructive. Gasoline is a complex mixture of hundreds of hydrocarbons. The hydrocarbons vary by class – paraffins, olefins, naphthenes, and aromatics – and, within each class, by size. The mixture of hydrocarbons (and oxygenates) in a gasoline determines its physical property and engine performance characteristics.

Gasoline is manufactured to meet the property limits of the specifications and regulations, not to achieve a specific distribution of hydrocarbons by class and size. But, to varying degrees, the property limits define chemical composition. Consider, for example, gasoline volatility. Chapter 1 explains that gasoline boils over a range of temperatures – its distillation profile – and that the gasoline specification limits this range. Each individual hydrocarbon boils at a specific temperature called its *boiling point* and, in general, the boiling point increases with molecular size. Consequently, requiring a distillation profile is equivalent to requiring a population of hydrocarbons with a range of sizes. The temperature limits of the distillation profile exclude smaller hydrocarbons with lower boiling points and larger hydrocarbons with higher boiling points.

The most common way to characterize the size of a molecule is *molecular weight*. For a hydrocarbon, an alternate way is carbon number – the number of carbons in its molecular structure. Butane, for example, has a molecular weight of 58 grams per gram-mole (g/mole) and a carbon number of 4 (C₄); benzene has a molecular weight of 78 g/mole and a carbon number of 6 (C₆).

Figure 3-1
Gasoline Carbon Number
Distribution

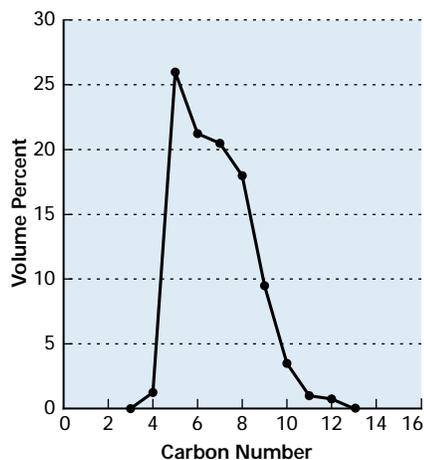


Figure 3-1 shows the carbon number distribution of a typical gasoline. Note that the range of sizes runs from C₄ to C₁₂ with the most prevalent size, C₅, and the average size, C_{6.8}. Figure 3-2 shows, as expected, that the cumulative carbon number distribution parallels the distillation profile.

Octane is another example of how property limits define chemical limits. Figure 3-3 illustrates how Research octane number (RON) varies with class for hydrocarbons of the same carbon number. So, an octane limit requires greater representation of some classes and less of others. But octane differentiation goes beyond class. Different isomers of the same hydrocarbon can have different octanes. The RON of isooctane (2,2,4-trimethylpentane) is 100 by definition, while the RON of normal octane is less than zero. Other properties, such as volatility, also are influenced by isomer structure.

With the advent of air pollution regulations, property specifications have been supplemented by some composition specifications. As noted in Chapter 2, the first gasoline-related air pollution regulation limited the amount of olefins in gasoline sold in Southern California by establishing a Bromine Number maximum specification. More recent regulations limit the amounts of both olefins and aromatics in reformulated gasolines.

Gasolines contain small amounts – less than 0.1 volume % – of compounds with sulfur, nitrogen and oxygen atoms in their structures (excluding added oxygenates). Even though these compounds also are composed primarily of carbon and hydrogen atoms, they are not classed as hydrocarbons because of the presence of the other atoms. The compounds either originate in the crude or are formed by the refining processes. Refining destroys many nitrogen- and, particularly, sulfur-containing compounds (*see below*), but some survive. Reducing the sulfur content of gasoline is required by California Phase 2 RFG regulations and will be a major tool in complying with federal Phase II RFG regulations.

Figure 3-2
Distillation Profile vs. Cumulative Carbon Number Distribution

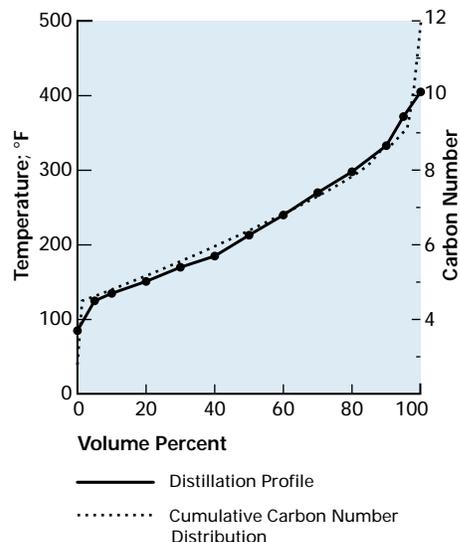
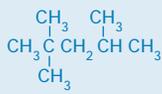
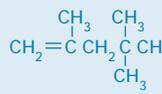
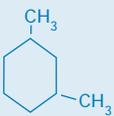
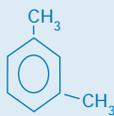
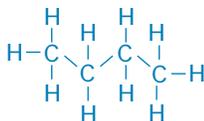
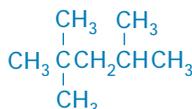
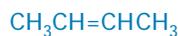
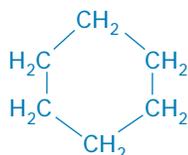


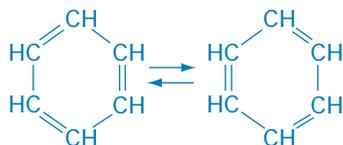
Figure 3-3

Research Octane Number (RON) Varies with Hydrocarbon Structure

Compound	n-Hexane	1-Hexene	Cyclohexane	Benzene
Formula	C ₆ H ₁₄	C ₆ H ₁₂	C ₆ H ₁₂	C ₆ H ₆
Structure	CH ₃ (CH ₂) ₄ CH ₃	CH ₂ =CH(CH ₂) ₃ CH ₃		
RON	25	76	83	123 (est.)
Compound	2,2,4-Trimethylpentane (Isooctane)	2,4,4-Trimethyl-1-pentene (Isooctene)	Cis 1,3- dimethyl-cyclohexane	1,3-Dimethylbenzene
Formula	C ₈ H ₁₈	C ₈ H ₁₆	C ₈ H ₁₆	C ₈ H ₁₀
Structure				
RON	100	106	72	118

Butane**Structural Isomers****2-Butene****Cyclohexane**

Shorthand

Benzene

Shorthand

ABOUT HYDROCARBONS

Hydrocarbons are organic compounds composed entirely of carbon and hydrogen atoms. Each of the four major classes of hydrocarbons – paraffins, olefins, naphthenes and aromatics – represents a family of individual hydrocarbons that share some structural feature. The classes differ in the ratio of hydrogen to carbon atoms and how the atoms are arranged.

Paraffins Paraffins have the general formula C_nH_{2n+2} , where “n” is the number of carbon atoms. The carbon atoms in paraffins are joined by single bonds and are arranged in a “zig-zag” pattern, but the molecules usually are represented by a shorthand linear structure.

It is possible for paraffins with four or more carbon atoms to exist as two or more distinct compounds, which have the same number of carbon and hydrogen atoms. These compounds, called *structural isomers*, differ in the arrangement of the carbon atoms. Normal octane (*n-octane*) and isooctane are two examples of eight-carbon structural isomers. Isooctane is the common name for 2,2,4-trimethylpentane, which specifies the branching pattern of the three methyl groups on a pentane backbone.

Olefins Olefins (C_nH_{2n}) are similar to paraffins, but have two fewer hydrogen atoms and contain at least one double bond between carbon atoms. They rarely occur naturally in crude oil, but are formed during refining. Like paraffins, olefins with four or more carbons can exist as structural isomers.

Naphthenes In naphthenes, also called *cycloparaffins*, some of the carbon atoms are arranged in a ring. The naphthenes in gasoline have rings of five and six carbon atoms. Naphthenes have the same general formula as olefins, C_nH_{2n} . As with the normal paraffins, the carbon atoms in cycloparaffins naturally arrange themselves in a zig-zag pattern, but the molecule is usually drawn as the planar structure, usually in a shorthand notation which indicates the bonds, but omits the carbon and hydrogen atoms.

Aromatics Like naphthenes, some of the carbon atoms in aromatics are arranged in a ring, but they are joined by *aromatic* bonds, not single bonds. The structure can be envisioned as an average of two discrete cyclohexatriene molecules, as it was thought to be in the early days of organic chemistry. However, the aromatic bond character is now known to be distributed evenly around the ring. The shorthand representation for a monocyclic aromatic ring is a hexagon with a circle representing the aromatic bonds.

Aromatic rings always contain six carbons; in polycyclic aromatics, like naphthalene, some of the carbons are shared by two or more rings.

Refining

Raw Material

As it comes out of the ground, petroleum crude can be as thin and light-colored as apple cider or as thick and black as melted tar. Thin crudes have high American Petroleum Institute (API) gravities and, therefore, are called *high-gravity* crudes; conversely, thick crudes are *low-gravity* crudes. High-gravity crudes contain more natural gasoline and their lower sulfur and nitrogen contents make them easier to refine. However, modern refining processes are capable of turning low-gravity crudes into high-value products like gasoline. Refining low-gravity crudes requires more complex and expensive processing equipment, more processing steps, and more energy and, therefore, costs more. The price difference between high-gravity and low-gravity crudes reflects the refining cost difference.

All crudes are composed primarily of hydrocarbons of the paraffinic, naphthenic, and aromatic classes. Each class contains a very broad range of molecular weights.

Processes

Today's refinery is a complex combination of interdependent processing units, the result of a fascinating intertwining of advances in chemistry, engineering and metallurgy. It all started with the simple physical separation process called *distillation*.

Distillation In the late 1800s, crude was separated into different products by boiling. Distillation works because crudes are composed of hydrocarbons with a broad range of molecular weights and, therefore, a broad range of boiling points. Each product was assigned a temperature range and the product was obtained by condensing the vapor that boiled off in this range at atmospheric pressure (*atmospheric distillation*). The earliest crude stills were simple pot stills consisting of a container where crude was heated and a condenser to condense the vapor. Later, distillation became a continuous process with a pump to provide crude flow, a furnace to heat the crude, and a distillation column to separate the different boiling *cuts*.

In a distillation column, the vapor of the lowest boiling hydrocarbons – propane and butane – rises to the top. The *straight run* gasoline, kerosene, and diesel fuel cuts are drawn off at successively lower positions in the column (*see Figure 3-4*)¹. Hydrocarbons with boiling points higher than diesel fuel aren't vaporized; they remain in liquid form and fall to the bottom of the column (*atmospheric bottoms*).

Initially, atmospheric bottoms was used for paving and sealing. Later it was found that it could yield higher-value products like lubricating oil and paraffin wax when it was distilled in a vacuum. *Vacuum distillation* requires sturdier stills to withstand the pressure differential and more sophisticated control systems.

The limits of distillation as the sole refining process were quickly recognized: Because the yield of each product is determined by the quantity of the hydrocarbons in its boiling range in the crude, distillation couldn't produce enough gasoline to meet the demand. And it was producing higher boiling material for which there was no market.

CONTINUOUS PROCESSING

The change from a batch to a continuous flow process was a major step in the evolution of petroleum refining. Today, almost all processes are continuous flow, because it would be impossible for a modern refinery to process the volume of crude it does using batch processes.

¹ Straight run products are those isolated from crude by simple distillation.

DENSITY AND GRAVITY

Density (ρ) is the mass of a unit volume of material at a selected temperature. For example, the density of water is 0.9990 grams per cubic centimeter (g/cm³) at 15.67°C (60°F). *Relative density* (RD) – also called *specific gravity* – is the ratio of the density of the material at a selected temperature to the density of a reference material at a selected temperature. For the relative density of petroleum crudes and products in the United States, the reference material is water and both temperatures are 60°F.

$$RD (60/60^\circ\text{F}) = \frac{\rho_{\text{sample}} (60^\circ\text{F})}{\rho_{\text{water}} (60^\circ\text{F})}$$

The United States petroleum industry often uses API gravity instead of relative density. The following equation relates API gravity, in degrees API (°API), to relative density.

$$^\circ\text{API} = \frac{141.5}{RD (60/60^\circ\text{F})} - 131.5$$

While API gravity measurements may be made on liquids at temperatures other than 60°F, the result is always converted to the value at 60°F, the standard temperature. As the above formula indicates, API gravity is inversely proportional to relative density: API gravity increases as relative density decreases. Thus, a high gravity crude has a lower density than a low gravity crude.

Cracking The discovery that hydrocarbons with higher boiling points (the larger ones left in the distillation bottoms) could be broken down (*cracked*) into lower-boiling hydrocarbons by subjecting them to very high temperatures offered a way to correct the mismatch between supply and demand. This process – *thermal cracking* – was used to increase gasoline production starting in 1913. It is the nature of thermal cracking to make a lot of olefins, which have higher octane, but may cause engine deposits. By today's standards, the quality and performance of this early cracked gasoline was low, but it was sufficient for the engines of the day.

Eventually heat was supplemented by a *catalyst*, transforming thermal cracking into *catalytic cracking*. A catalyst is a material that speeds up or otherwise facilitates a chemical reaction without undergoing a permanent chemical change itself. Catalytic cracking produces gasoline of higher quality than thermal cracking. There are many variations on catalytic cracking, but *fluid catalytic cracking* (FCC) is the heart of gasoline production in most modern refineries. The term comes from the practice of *fluidizing* the solid catalyst so that it can be continuously cycled from the reaction section of the cracker to the catalyst regeneration section and back again. The FCC process also produces building blocks for other essential refinery processes, like alkylation.

Hydrocracking is similar to catalytic cracking in that it utilizes a catalyst, but the catalyst is in a hydrogen atmosphere. Hydrocracking can break down hydrocarbons that are resistant to catalytic cracking alone. It more commonly is used to produce diesel fuel than gasoline.

The next group of processes increase a refinery's octane pool. While these processes predate the regulation of antiknock additives, they became more important as lead was phased out of gasoline. Without antiknock additives, the only way to produce high octane gasolines is to use inherently high-octane hydrocarbons or to use oxygenates, which also have high octane values² (see Figure 3.3).

Reforming The *reforming* process literally *re-forms* the feed, converting straight-chain paraffins into aromatics. For example, reforming cyclizes normal heptane (RON = 0) and then abstracts hydrogen to produce toluene (RON = 120). The hydrogen by-product is almost as important as the octane upgrade. Hydrogen is an essential ingredient for processes like hydrocracking and hydrofining. Refineries often have a hydrogen deficit, which has to be made up by making hydrogen from natural gas (methane) or other hydrogen-rich feeds.

Alkylation *Alkylation* combines small, gaseous hydrocarbons with boiling points too low for use in gasoline to form liquid hydrocarbons. The feed, which comes from the FCC unit, includes C₄ hydrocarbons like isobutanes and butylenes and sometimes C₃ and C₅ paraffins and olefins. The principal products are high-octane isomers of trimethylpentane like isooctane (RON = 100). Alkylation is a key process for producing reformulated gasolines because the contents of the other classes of high-octane hydrocarbons – olefins and aromatics – are limited by regulation.

Polymerization Another combination process is the polymerization of olefins, typically the C₃ olefin, propylene, into a series of larger olefins differing in molecular weight by three carbon atoms – C₆, C₉, C₁₂, etc. Polymerization is a

² A manganese-based antiknock additive is not widely used in the United States at this time (1996) (see p. 30).

less-favored process than alkylation because the products are also olefins, which may have to be converted to paraffins before they are blended into gasoline.

Isomerization *Isomerization* increases a refinery's octane pool by converting straight-chain (typically C₅ and C₆) paraffins into their branched isomers. For a given carbon number, branched isomers have higher octane values than the corresponding straight chain isomer.

Hydrotreating *Hydrotreating* is a generic term for a range of processes that use hydrogen with an appropriate catalyst to remove impurities from a refinery stream. The processes run the gamut from mild, selective hydrotreating to remove highly reactive olefins to heavy hydrotreating to convert aromatics to naphthenes.

Sulfur removal, or *desulfurization*, is an example of a hydrotreating process. The lower sulfur limits for reformulated gasoline may require the desulfurization of a significant proportion of FCC gasoline. There are also processing reasons to desulfurize refinery streams. In reforming, excess sulfur in the feed deactivates the catalyst. In FCC, excess sulfur in the feed results in high levels of sulfur in the FCC gasoline and greater production of sulfur dioxide during catalyst regeneration.

The Modern Refinery

The schematic layout of a modern, fully integrated refinery is shown in Figure 3-4. Crude oil is fed to the distillation column where straight run light and heavy gasoline, jet and diesel are separated at atmospheric pressure. Whereas straight-run jet and diesel are usually acceptable as is, the straight run gasolines typically require more processing to convert them into gasoline blending components. The straight run light gasoline may be isomerized to increase octane, or hydrotreated to convert benzene to cyclohexane so that the final gasoline blend will meet a benzene specification limit, or both. The straight run heavy gasoline is hydrotreated to remove sulfur and then reformed to improve octane and generate hydrogen for the hydrotreaters.

The bottoms from the atmospheric column is vacuum distilled to obtain *gas oils* for FCC or hydrocracker feed. The gas oils are hydrotreated to reduce sulfur and nitrogen to levels which will not interfere with the FCC process. Even though the feed was substantially desulfurized, the FCC product must be *sweetened* to convert reactive sulfur compounds (*mercaptans*) to more innocuous ones, otherwise the gasoline blend will be odorous and unstable. Alternatively, in California and other areas with tight restrictions on the sulfur content of finished gasoline, the FCC product must be further desulfurized.

Previously, the *vacuum resid* might have been used as low-value, high-sulfur fuel oil for onshore power generation or marine fuel. Now, to remain competitive, refiners wring as much high-value product as possible from every barrel of crude. As a result, the vacuum resid is sent to a *resid conversion* unit, such as a resid cracker, solvent extraction unit or coker. These units produce more transportation fuel or gasoil, leaving an irreducible minimum of resid or coke. The resid-derived streams require further processing and/or treating before they can be blended into light fuels like gasoline or diesel.

Processing Changes Required by Air Pollution Regulations

The balance among the various processes in a refinery is dynamic, responding both to external and internal developments. The impact of air pollution regulations (*see Figure 2-7*) on refinery operations is a good example. The requirement for unleaded gasoline and the gradual increase of its sales roughly paralleled the gradual phase-down of lead in leaded gasoline. Both these trends increased the need for higher octane components. In response, refiners produced more reformate, FCC gasoline, alkylate, and oxygenates, roughly in this order. Later, tighter and tighter vapor pressure limits reduced the amount of butane which could be added to gasoline in the summer. This resulted in excess butane, and, since butane has good octane, further increased the need for higher octane components. A solution which solved both problems was to use butane to make alkylate. The requirements for oxygenated gasoline helped the octane shortfall, because oxygenates have high octanes. The need for oxygenates prompted some refiners to add units to make MTBE and other ethers. Most recently, the advent of California Phase 2 reformulated gasoline placed new restrictions on olefins, aromatics, heavy ends, and sulfur. This required more hydrotreating, alkylation and cracking capability. The investment to make all these changes through 1996 is in the tens of billions of dollars, nearly equaling the capitalization of the refining industry at the beginning of the reformulated gasoline era.

Blending

Despite the diversity and ingenuity of the processes within a modern petroleum refinery, no single stream meets all the requirements of gasoline. Thus, the final step in gasoline manufacture is blending the various streams into a finished product. It is not uncommon for the finished gasoline to be made up of six or more streams (*see Figure 3-4*). Sometimes, to provide more flexibility, a stream is distilled into several fractions and each fraction is used as a separate blending component, for example FCC light and FCC heavy gasoline.

Several factors make this flexibility critical:

- The requirements of the gasoline specification (ASTM D 4814) and the regulatory requirements are complex.
- Different marketing locations served by the refinery may have different performance and regulatory specifications (*see Chapters 1 and 2*).
- A blend must satisfy multiple internal inventory and economic requirements.

To obtain an ontest blend, on time, every time, refiners use computerized blending programs to generate an optimized blend recipe. A computer program integrates all the performance, regulatory, economic, and inventory requirements.

Gasoline Additives

Additives are gasoline-soluble chemicals that are mixed with gasoline to enhance certain performance characteristics or to provide characteristics not inherent in the gasoline. Typically, they are derived from petroleum-based raw materials and their function and chemistry are highly specialized. They produce the desired effect at the parts-per-million (ppm) concentration range. (One ppm is 0.0001 mass percent.)

Metal deactivators are *chelating agents* – chemical compounds which capture specific metal ions. The more-active metals, like copper and zinc, effectively catalyze the oxidation of gasoline. These metals are not used in most gasoline distribution and vehicle fuel systems. However, when they are present, metal deactivators inhibit their catalytic activity.

Demulsifiers are polyglycol derivatives. An *emulsion* is a stable mixture of two mutually insoluble materials. A gasoline-water emulsion can be formed when gasoline passes through the high-shear field of a centrifugal pump if the gasoline is contaminated with free water. Demulsifiers improve the water separating characteristics of gasoline by preventing the formation of stable emulsions.

Antiknock compounds are lead alkyls – tetraethyl lead (TEL) and tetramethyl lead (TML)- and methylcyclopentadienyl manganese tricarbonyl (MMT). Antiknock compounds increase the antiknock quality of gasoline. Because the amount of additive needed is small, they are a lower cost method of increasing octane than changing gasoline chemistry. Gasoline containing tetraethyl lead was first marketed in 1923. The average concentration of lead in gasoline gradually was increased until it reached a maximum of about 2.5 grams per gallon (*g/gal.*) in the late 1960s. After that, a series of events resulted in the use of less lead: new refining processes which produced higher octane gasoline components, steady growth in the population of vehicles requiring unleaded gasoline, and EPA regulations requiring the reduction of the lead content of gasoline in phased steps beginning in 1979. The EPA completely banned the addition of lead additives to onroad gasoline in 1996 and the amount of incidental lead may not exceed 0.05 g/gal.

MMT was commercialized in 1959 and was used in gasoline alone or in combination with the lead alkyls. The Clean Air Act Amendments of 1977 banned the use of manganese antiknock additives in *unleaded* gasoline unless the EPA granted a waiver. MMT continued to be extensively used in unleaded gasoline in Canada. In 1996, after several waiver requests and court actions by the manufacturer, the courts ordered the EPA to grant a waiver for MMT. Its use is limited to a maximum of 0.031 g/gal. California regulations continue to ban the addition of manganese to gasoline.

MMT's future is clouded: Its use in gasoline is opposed by environmental groups and the automobile manufacturers. Gasoline containing MMT leaves significant red-orange deposits on spark plugs, catalytic converters, oxygen sensors and combustion chamber walls. The manufacturer has developed a large body of data to support its claim that MMT in gasoline does not reduce performance or increase emissions. The auto manufacturers have expressed concerns about shortened catalyst, oxygen sensor, and spark plug life and interference with the performance of the new on-board diagnostic system (*OBD-II*; see p. 51). They are also concerned about meeting future low emission limits with MMT in the fuel. Some new vehicle owner's manuals recommend against using gasoline containing MMT. Very little MMT is being used in U.S. gasoline at this time (1996). An effort is underway in Canada, which the manufacturer is opposing, to have the government ban MMT in unleaded gasoline.

Deposit control additives. See Chapter 5.

Anti-icing additives are surfactants, alcohols, and glycols. They prevent ice formation in the carburetor and fuel system (*see p. 4*). The need for this additive is disappearing as older-model vehicles with carburetors are replaced by vehicles with fuel injection systems.

Dyes are oil-soluble solids and liquids used to visually distinguish batches, grades, or applications of gasoline products. For example, gasoline for general aviation, which is manufactured to different and more exacting requirements, is dyed blue to distinguish it from motor gasoline for safety reasons.

Markers are a means of distinguishing specific batches of gasoline without providing an obvious visual clue. A refiner may add a marker to their gasoline so it can be identified as it moves through the distribution system.

Drag reducers are high-molecular-weight polymers that improve the fluid flow characteristics of low-viscosity petroleum products. As energy costs have increased, pipelines have sought more efficient ways to ship products. Drag reducers lower pumping costs by reducing friction between the flowing gasoline and the walls of the pipe.

Specifications

It has been critical to the successful development of gasoline and gasoline-powered vehicles to have consensus among refiners, vehicle manufacturers, and other interested parties on the characteristics of gasoline necessary for satisfactory performance and reliable operation. This consensus is reached under the auspices of the American Society for Testing and Materials (ASTM).

ASTM Committee D-2 on Petroleum Products and Lubricants is responsible for gasoline specifications and test methods. A large number of groups are interested in and/or affected by the specifications. Their viewpoints are brought to the D-2 forum by representatives who also are members of ASTM:

- Individual refiners
- American Petroleum Institute (API), an association of petroleum refiners
- Petroleum marketing organizations
- Vehicle and engine manufacturers
- American Automobile Manufacturers Association (AAMA), an association of United States vehicle manufacturers
- Governmental regulatory agencies like the United States Environmental Protection Agency
- Society of Automotive Engineers (SAE)
- Coordinating Research Council (CRC), an organization that directs, through committee action, engineering and environmental studies on the interaction between automotive equipment and petroleum products.

The ASTM specification for gasoline, D 4814 – *Standard Specification for Automotive Spark-Ignition Engine Fuel*, is widely recognized². It has been written into federal regulations and most state specifications for gasoline.

Figure 3-5
ASTM D 4814 Properties

Property	Intent
Schedule of Seasonal and Geographic Volatility Classes, which includes: Vapor Pressure/Distillation Class Vapor Lock Protection Class	To insure good driveability (<i>see Chapter 1</i>).
Solvent Washed Gum Content	To protect against the presence of gums formed by oxidation which can contribute to fuel system deposits.
Oxidation Stability	To protect against the formation of additional gum by air oxidation during storage.
Water Tolerance	To protect against the phase separation of dissolved water at colder temperatures. Not usually a problem for hydrocarbon blends, but can be for some oxygenated blends (<i>see p. 39</i>).
Sulfur Content	To protect against engine wear, deterioration of engine oil, corrosion of exhaust system parts and a temporary reduction in the efficiency of the convertor catalyst.
Copper Strip Test	To protect against corrosion of fuel system parts due to reactive sulfur compounds.
Lead Content	To insure that unleaded gasolines are free of lead.

D 4814 specifies nine gasoline properties (*Figure 3-5*). These do not include octane number or antiknock index, which are set by gasoline refiners and marketers “based on their perception of the technical and competitive needs in the market.”³

D 4814 references over 30 other ASTM methods that describe how to sample gasoline and how to run specific tests. These associated methods are essential. Specifying a property has no value unless everyone measuring the property uses the same procedure and, for a given material, gets the same answer within the defined precision. D 4814 also contains four appendices including one which discusses the significance of specifications and another which summarizes EPA’s gasoline regulations.

EPA and some states set additional standards for gasoline. These are not included in D 4814 unless they involve properties traditionally covered by the method, e.g., vapor pressure, in which case ASTM revises D 4814 to conform to the regulations.

Each gasoline refiner, each pipeline that ships gasoline, and even the automobile manufacturers may set additional internal specifications beyond ASTM D 4814, or may set more stringent limits for the D 4814 properties. But, except in the case of internal refining specifications, these limits will not prevail unless all interested parties recognize their value.

Test Methods

Vapor Pressure

ASTM D 323 – *Test Method for Vapor Pressure of Petroleum Products (Reid Method)*⁴

ASTM D 5190 – *Test Method for Vapor Pressure of Petroleum Products (Automatic Method)*

ASTM D 5191 – *Test Method for Vapor Pressure of Petroleum Products (Mini Method)*

² The hyphenated suffix associated with the method number indicates the year the method was last updated and the version within the year, e.g., D 4814-96a.

³ ASTM D 4814

⁴ D 323 cannot be used to measure the vapor pressure of gasoline containing ethanol and, therefore, no longer is recognized by D 4814.

ASTM D 4953 – *Test Method for Vapor Pressure of Gasoline and Gasoline-Oxygenate Blends (Dry Method)*

In all four methods, a chilled fixed volume of gasoline is placed in a test chamber and heated to 38.8°C (100°F). Then the pressure developed by gasoline vapors is measured in units of pounds per square inch (psi). The methods differ in the design of the apparatus, including the design of the test chamber. D 323 yields *Reid vapor pressure (RVP)*, the other methods yield *Dry Vapor Pressure Equivalent (DVPE)*.

Octane

ASTM D 2699 – *Standard Test Method for Research Octane Number of Spark-Ignition Engine Fuel.*

ASTM D 2700 – *Standard Test Method for Motor Octane Number of Spark-Ignition Engine Fuel.*

Both these test methods employ a CRC single-cylinder, variable compression, knock-test engine. The engine is operated under different test conditions of speed, mixture temperature, and spark advance for each method. The compression ratio of the test engine is adjusted to produce a knock of standardized intensity for the test gasoline – the gasoline being rated. Then the primary reference fuel whose knock intensity matches that of the test gasoline at the set compression ratio is identified. The octane number of the reference fuel is the octane number of the test gasoline.

The series of primary reference fuels are blends of normal heptane (octane number defined equal to 0) and isooctane (octane number defined equal to 100). The octane number of each primary reference fuel is equal to the volume percent of isooctane it contains.

Chapter 1 discusses the significance of Research octane number (RON) and Motor octane number (MON) and how they are used to define the antiknock quality of gasoline.

Road Octane Number (RdON)

Generally, RdON is determined by the Modified Uniontown Procedure, CRC Designation F-28. In this procedure, a test vehicle is operated on a series of primary reference fuels of increasing octane number under maximum-throttle acceleration⁵. The basic timing is advanced for each reference fuel until *trace knock* – the lowest knock level detected by the ear of the person rating the fuel – is detected. The plot of basic spark timing versus RON provides a *primary reference curve* for the test car. Then the car is operated on the gasoline to be rated until the spark advance needed to cause trace knock under maximum throttle acceleration is found. The octane number associated with that spark timing advance in the primary reference curve is the RdON of the test gasoline.

Because of the numerous variables involved, 10 to 15 test vehicles, usually different models, must be used for a statistically significant determination. The final RdON of the test gasoline is the average of RdONs of the individual vehicles.

⁵ This test can not be run on modern vehicles whose timing is regulated by an engine control module (see p. 49).

Distillation Profile

ASTM D 86 – *Test Method for Distillation of Petroleum Products*

A 100 ml sample is placed in a round bottom flask and heated at a rate specified for samples with its vapor pressure characteristics. Temperatures are recorded when the first drop is collected (initial boiling point), at recovered volumes of 5 ml, 10 ml, every subsequent 10 ml interval to 90 ml, 95 ml and at the end of the test (end point). For gasoline samples, the temperatures associated with each incremental volume percent recovered are converted to temperatures for each incremental volume percent evaporated by correcting for any sample loss during the test.

Vapor-Liquid Ratio (V/L)

ASTM D 2533 – *Test Method for Vapor-Liquid Ratio of Spark-Ignition Engine Fuels*

ASTM D 5188 – *Test Method for Vapor-Liquid Ratio Temperature Determination of Fuels (Evacuated Chamber Method)*

ASTM D 4814, Appendix X2 – Three methods – a computer method, linear equation method, and nomograph method – for estimating V/L from vapor pressure and distillation test results (not applicable for oxygenated gasolines).

In D 2533, a measured volume of liquid fuel at 32°F is introduced into a glass buret filled with glycerol (non-oxygenated fuel) or mercury (all fuels). The buret is heated to the desired temperature and the volume of vapor in equilibrium with the liquid is recorded after the pressure of the system has been adjusted to the desired pressure, usually one atmosphere (760 mm Hg). If the temperature corresponding to a given vapor-liquid ratio is desired – usually $V/L = 20$ – the vapor-liquid ratio is determined at several temperatures, the results plotted, and the temperature at the desired vapor-liquid ratio is read from the plot.

In D 5188, a calculated volume of air-saturated sample (all fuels) at 32°F is introduced into an evacuated, thermostatically-controlled test chamber of known volume. The sample volume is calculated to obtain the desired vapor-liquid ratio in the chamber. After injection, the chamber temperature is adjusted until a stable chamber pressure of 101.3 kPa (760 mm Hg) is achieved.

API Gravity (See p. 26)

ASTM D 1298 – *Standard Practice for Density, Relative Density (Specific Gravity), or API Gravity of Crude Petroleum and Liquid Petroleum Products by Hydrometer Method*

ASTM D 4052 – *Test Method for Density and Relative Density of Liquids by Digital Density Meter*

For D 1298, the sample is placed in a cylinder and the appropriate hydrometer is lowered into the sample. After temperature equilibrium has been reached, the sample temperature and hydrometer scale reading are recorded. The Petroleum Measurement Tables are used to convert the recorded value to the value at 60°F.

For D 4052, about 0.7 ml “of liquid sample is introduced into an oscillating sample tube and the change in oscillating frequency caused by the change in the mass of the tube is used in conjunction with calibration data to determine the density of the sample.”⁶

Solvent Washed Gum Content

ASTM D 381 – *Test Method for Existent Gum in Fuels by Jet Evaporation*

Fifty milliliters of gasoline are evaporated under controlled conditions of temperature (about 310°F) and air flow for 30 minutes. The residue is weighed before and after extraction with n-heptane and the result reported as milligrams per 100 ml.

Potential Gum

Chevron Method based on ASTM D 873 – *Test Method for Oxidation Stability of Aviation Fuels (Potential Residue Method)*, which combines ASTM D 525 – *Test Method for Oxidation Stability of Gasoline (Induction Period Method)* and ASTM D 381 – *Test Method for Existent Gum in Fuels by Jet Evaporation*.

One hundred milliliters of gasoline free of deposit control additive is oxidized for four hours at 212°F in a bomb initially charged with 100 psi of oxygen. After this treatment, the amount of insoluble gum is collected by filtration and measured and the soluble gum is isolated by ASTM D 381 and measured. The total insoluble and soluble gum is reported as potential gum in units of milligrams per 100 ml.

⁶ ASTM D 4052

4 · OXYGENATED GASOLINE

Introduction

In the 1990s, air quality regulations required gasolines in some parts of the United States to be oxygenated either in the winter or year-round – gasolines in carbon monoxide (CO) nonattainment areas and federal Phase I and California Phase 2 reformulated gasolines (RFG) (*see pps. 19 and 20*). But oxygenated gasoline is not new. Oxygenates – primarily ethanol (ethyl alcohol or grain alcohol) – have been added to gasoline for decades. Widespread use of ethanol in the United States began in 1978 when a Nebraska group marketed gasoline containing 10% ethanol as *gasohol*. The program was a means to increase gasoline availability during the oil embargo. Later, the *gasohol* name was abandoned, but the use continued. By 1992, eight percent of all the gasoline sold in the United States contained ethanol. Much of the blend was marketed in the midwestern states, the same region where the bulk of ethanol is produced.

Chemistry

Oxygenated gasoline is a mixture of conventional hydrocarbon-based gasoline and one or more oxygenates. Oxygenates are combustible liquids which are made up of carbon, hydrogen, and oxygen. All the current oxygenates belong to one of two classes of organic molecules: alcohols and ethers.¹ In alcohols, a hydrocarbon group and a hydrogen atom are bonded to an oxygen atom: R-O-H, where “R”

¹ The word *ether* reminds many people of the anesthetic. While the anesthetic is commonly called *ether*, its correct chemical name is diethyl ether (CH₃CH₂OCH₂CH₃). It is not used as a gasoline oxygenate because it is too volatile.

Figure 4-1

Information about Oxygenates For Gasoline

Name	Formula	Structure	Oxygen Content, mass %	Blending Research Octane Number (RON) ¹	Maximum Concentration Approved by EPA ²	
					Mass % Oxygen	Volume % Oxygenate
Ethanol (EtOH)	C ₂ H ₆ O	CH ₃ CH ₂ OH	34.73	129	(3.70) ³	10.0
Methyl <i>Tertiary</i> -Butyl Ether (MTBE)	C ₅ H ₁₂ O	$\begin{array}{c} \text{CH}_3 \\ \\ \text{CH}_3\text{O}-\text{C}-\text{CH}_3 \\ \\ \text{CH}_3 \end{array}$	18.15	118	(2.74)	15.0
Ethyl <i>Tertiary</i> -Butyl Ether (ETBE)	C ₆ H ₁₄ O	$\begin{array}{c} \text{CH}_3 \\ \\ \text{CH}_3\text{CH}_2\text{O}-\text{C}-\text{CH}_3 \\ \\ \text{CH}_3 \end{array}$	15.66	119	2.70	(17.1)
<i>Tertiary</i> -Amyl Methyl Ether (TAME)	C ₆ H ₁₄ O	$\begin{array}{c} \text{CH}_3 \\ \\ \text{CH}_3\text{O}-\text{C}-\text{CH}_2\text{CH}_3 \\ \\ \text{CH}_3 \end{array}$	15.66	112	2.70	(16.6)

¹ RON of the pure compound which is consistent with the RON of the oxygenate-gasoline mixture obtained by blending.

² Values in () calculated from limit using known relative density of the oxygenate and 0.74 relative density of gasoline (60/60°F)

³ For pure, undenatured ethanol.

represents the hydrocarbon group. All alcohols contain the “OH” atom pair. In ethers, two hydrocarbon groups are bonded to an oxygen atom; the groups may be the same or different: R-O-R or R-O-R’.

Use

The EPA regulates which oxygenates can be added to gasoline and in what amounts (*see sidebar on p. 38*).

The most widely used oxygenates are ethanol, methyl *tertiary*-butyl ether (MTBE) and *tertiary*-amyl methyl ether (TAME). Ethyl *tertiary*-butyl ether (ETBE) may be used more in the future. Figure 4-1 summarizes some information about these oxygenates. Note that, on a volume basis, each ether has a different maximum concentration because each has a different oxygen content and relative density.

Figure 4-2 gives the ranges of oxygenate use – in terms of oxygen

content of the gasoline – required by the emission regulations. The regulations do not require a specific oxygenate. Any oxygenate use conforming with the EPA’s Substantially Similar or Waiver conditions is acceptable. Different gasoline brands in the same area tend to contain the same oxygenate, but uniformity is not required. Here are a few of the many factors that determine a refiner’s oxygenate choice:

- What are the economics? Ethanol can be more economic than the ethers because there is a federal excise tax exemption for its use, and about one-third of the states also offer a tax exemption or other incentive. These incentives are designed to encourage the development of an agriculturally-based fuel ethanol industry.
- What is the availability? The bulk of the ethanol is produced in the midwest. Some ether plants are located in or adjacent to refineries and use refinery streams as feed.
- What is the best blending location? At refineries, ethers usually are used because ethanol blends can not be shipped by pipeline. It is hard to keep pipelines dry, and water in the pipeline will reduce the ethanol content of the gasoline (*see below*). The water tolerance of ethers is similar to that of gasoline.

Figure 4-2

Oxygen Content Required by United States Emissions Regulations

Regulation	Oxygen Content, mass %		
	Average	Minimum	Maximum ¹
CO Nonattainment Areas ² (4 or 5 Winter Months)			
California		1.8	2.2
Other States		2.7	3.5
Federal RFG ^{3,4}			
Simple Model			
Phase I	≥2.1	1.5	4.0 ^{5,6}
Complex Model			
Phase I	≥2.1	1.5	4.0 ⁵
Phase II	≥2.1	1.5	4.0 ⁵
California Phase 2 RFG ²			
Summer			
Flat Limit		1.8	2.2
Predictive Model		None ⁷	2.7
Winter			
Flat Limit		1.8	2.2
Predictive Model		1.8	2.7

¹ Regardless of this limit, specific oxygenates may not exceed their Substantially Similar or Waiver limits. For example, the Substantially Similar maximum limit for ethers like MTBE is 2.7 mass % oxygen (2.9 mass % in CO nonattainment areas in the winter).

² Per gallon limits.

³ Average limits.

⁴ CO nonattainment area oxygen limits take precedence over RFG oxygen limits in CO nonattainment areas in the winter.

⁵ Upper limit of valid range for oxygen content variable in model.

⁶ States have option to decrease to 3.2 mass %.

⁷ Value controlled by Predictive Model except in federal RFG areas in California where the 1.5 mass % limit applies.

OXYGENATE REGULATION AND THE SUBSTANTIALLY SIMILAR RULE

The Clean Air Act Amendments of 1977 control the use of oxygenates in unleaded gasoline. The purpose is to ensure that oxygenate use won't contribute to emission control system failures that could result in increased emissions. The regulations which the EPA developed to implement the law prohibit the introduction or increase in concentration of a fuel or fuel additive which is not *substantially similar* to any fuel or fuel additive utilized in the certification of any 1975 or subsequent model year vehicle.

In 1981, the EPA issued the Substantially Similar ruling that recognized that the use of certain types of oxygenates was safe below a specified oxygen content. The rule, as revised in 1991, allows aliphatic alcohols (excluding methanol) and/or ethers to be blended into gasoline up to a concentration that would result in 2.7 mass % oxygen in the blend. The rule requires the finished blend to possess all the physical and chemical characteristics of an unleaded gasoline specified by ASTM D 4814-88 for at least one of the seasonal and geographic volatility classes.

The EPA regulations also created a process by which a waiver could be granted for an oxygenate recipe which the applicant had demonstrated would not cause or contribute to the failure of any emission control device or system. The EPA has granted waivers for concentrations of ethanol in gasoline up to 10 vol %. (The mass % oxygen content of this blend depends on the density of the gasoline; it is 3.7 mass % for pure ethanol added to gasoline with the typical relative density of 0.74 at 60/60°F; it is 3.5 mass % for a mixture of 90 vol % gasoline and 10 vol % denatured ethanol.) The EPA also has ruled that gasolines containing up to 2.0 vol % MTBE which are subsequently blended with 10 vol % ethanol (4.0 mass % oxygen total for pure ethanol) do not violate the ethanol waiver. This was to assure an adequate supply of base gasoline for blending with ethanol.

The EPA also has granted waivers for blends of gasoline and gasoline-grade *tertiary*-butyl alcohol (TBA) up to 3.5 mass % oxygen content (16 vol % TBA) and for various blends of methanol and gasoline-grade TBA or other higher-molecular-weight alcohols (cosolvents).

At terminals, standard practice is to blend ethanol with gasoline in the tank truck which will deliver the blend to the service station. Terminal blending involves more operating and capital expense than refinery blending. Also, because oxygenates raise octane, a low-octane conventional gasoline is needed, if the resulting oxygenated gasoline is to have the AKI commonly available in the area.

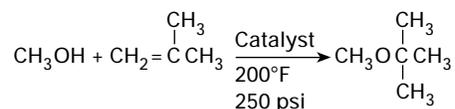
Oxygenates may be used in areas of the country where they are not required as long as EPA's concentration limits are observed. Since all oxygenates are more expensive than the conventional gasoline they displace, ethanol's tax incentives make it the only one likely to be used near its concentration limit. The other oxygenates will be used at lower concentrations (1-7 vol %) only when the octane of the gasoline needs enhancement and when adding oxygenates is the most economic solution.

The information available to the retail consumer about the oxygenate composition of the gasoline varies. There is no federal labeling regulation; this is an area controlled by state regulations. Some states require dispenser labels for oxygenated gasolines in CO nonattainment areas and RFG gasolines. A typical label reads: *The gasoline dispensed from this pump is oxygenated and will reduce carbon monoxide pollution from motor vehicles.* Some labels, like this one, do not provide any information on which oxygenate(s) the blend contains; others do. Few, if any, states require labeling for gasolines containing low levels of oxygenate added to increase octane. A national association of state Weights and Measures agencies that are responsible for dispenser calibration and labeling issued a revised standard guideline for dispenser labeling in 1996.

Sources

Ethanol can be synthesized from petroleum by hydrating ethylene, but most of it (94% in 1993) is derived from the fermentation of carbohydrates, principally corn. The process involves distillation to separate it from the fermentation residues, dehydration to remove the water which codistills with the alcohol and, for fuel ethanol, the addition of a noxious or toxic material (denaturing) to make it unfit for human consumption.

MTBE is derived from methanol and isobutylene. A catalyst is used to assist the reaction.



Most methanol is produced from natural gas (*methane*). Isobutylene is obtained from petroleum, either as a byproduct of the refining process or from butane. While it is made from methanol, MTBE is a different material with different properties. It doesn't have methanol's corrosivity and toxicity defects (*see sidebar*).

The other ethers are made by the similar processes. ETBE is derived from ethanol and isobutylene. TAME is derived from methanol and isoamylenes.

Performance Issues

Fuel Leaning Oxygenated gasoline leans the air-fuel mixture of carbureted engines and fuel injected engines which don't have an electronic control module (ECM) (*see p. 49*). Engines with ECMs become fuel lean when the ECM is not controlling – when the engine is cold or the vehicle is being accelerated rapidly. The rest of the time, the ECM adjusts the air-fuel ratio to compensate for the oxygen in the fuel. If a carburetor is set to provide a very fuel rich mixture, fuel leaning might improve performance. Otherwise, fuel leaning can degrade driveability; the extent depends on the engine's calibration.

Ethanol has a higher heat of vaporization than ethers. Some of the degradation in driveability of gasoline oxygenated with ethanol can be attributed to the additional heat needed to vaporize the fuel.

Volatility Adding ethanol to a conventional gasoline not designed for alcohol blending can produce a blend which is too volatile. Ethanol can increase the vapor pressure 1.0 psi for a conventional gasoline with a vapor pressure of 9.0 psi. This increase, coupled with the corresponding reduction in mid-range distillation properties, lowers the V/L=20 temperature, reducing vapor lock protection. Blend volatility is increased only slightly by MTBE and not at all by ETBE and TAME.

Ethanol is not the oxygenate of choice for summer RFGs. The volatility increase makes it more difficult to meet the very tight vapor pressure limits of these gasolines.

Water Tolerance Conventional gasoline, depending on its aromatic content, can dissolve up to 150 parts per million (ppm) water at 70°F. Oxygenating gasoline with ethers can increase water solubility to 600 ppm. Contacting either conventional gasoline or ether-oxygenated gasoline with additional water will not affect the properties of the gasoline.

Cooling water-saturated blends turns them hazy because some of the water becomes insoluble. However, the water that is released does not contain much ether and there is not enough water to cause performance problems.

The situation is different for gasoline oxygenated with 10 vol % ethanol. The gasoline-alcohol blend can dissolve more water (6000–7000 ppm at 70°F). When this blend is cooled, both the water and **some of the ethanol** become insoluble. Contacting the blend with more water also draws ethanol from the blend. The result, in both cases, is two layers of liquid: an upper ethanol-deficient gasoline layer and a lower ethanol-rich (up to 75% ethanol) water layer. The process is called *phase separation* and it occurs because ethanol is completely soluble in water, but only marginally soluble in hydrocarbons. After phase separation, the gasoline layer will have a lower octane number and may knock in an engine. The engine will not run on the water layer.

METHANOL IS NOT ETHANOL

Ethanol and methanol should not be confused; they are different compounds. While limited amounts of gasoline oxygenated with methanol and its cosolvents have been available in the past, its use in the future is likely to be minimal.

- Gasoline oxygenated with methanol is more corrosive towards fuel system metals and accelerates deterioration of elastomers.
- Gasoline oxygenated with methanol is not approved by many vehicle owner's manuals.
- Adding methanol to gasoline significantly increases the vapor pressure of the blend – an undesirable effect in this era of more stringent volatility controls.
- Methanol, unlike ethanol, is toxic.

The potential for phase separation requires that gasoline oxygenated with ethanol not be exposed to water during its distribution or use in a vehicle. Because of this requirement, gasoline oxygenated with ethanol is not transported in pipelines, which sometimes contain water. This requirement also means that extra care should be taken when gasoline oxygenated with ethanol is used as a fuel for boat engines.

Material Compatibility Some fuel system metal components will rust or corrode in the presence of water or acidic compounds. The additional water dissolved in oxygenated gasolines does not cause rusting or corrosion, but water from the phase separation of gasoline oxygenated with ethanol will, given time.

Oxygenates can swell and soften natural and some synthetic rubbers (elastomers). Oxygenated gasolines affect elastomers less; the extent of which also depends on the hydrocarbon chemistry of the gasoline, particularly the aromatics content. The effect is of potential concern because fuel systems contain elastomers in hoses, connectors ('O'-rings), valves and diaphragms. The elastomeric materials used in today's vehicles have been selected to be compatible with oxygenated gasolines. Owners manuals approve the use of gasoline oxygenated with 10 vol % ethanol or 15 vol % MTBE. (The compatibility of the other ethers is the same as that of MTBE.)

Automobile manufacturers upgraded their fuel system elastomers at different times. Elastomers in pre-1975 vehicles may be sensitive to oxygenated and high-aromatics gasolines. Elastomers in 1975 to 1980 vehicles were upgraded, but not to the same extent as in later models.²

Chevron's experience is that there is not a significant compatibility problem between oxygenated gasolines and elastomers in older cars. There was not an increase in problems when oxygenated gasoline was introduced in 39 metropolitan areas in the winter of 1992. This held true for the western states, which tend to have more older cars in their vehicle populations and for areas where different oxygenates were used (MTBE throughout California; ethanol in Portland, Oregon and Seattle/Tacoma, Washington).

Fuel Economy The effect of oxygenated gasoline on fuel economy is discussed on p. 7.

Introduction

Understanding the performance of a gasoline-powered vehicle not only requires knowing something about gasoline but knowing something about the engine and some related systems.¹

It is useful to regard an engine as a set of interconnected systems. Four of the systems of a gasoline-powered engine will be covered here – the air, fuel, exhaust and control systems. The *air system* delivers the intake air-fuel mixture to the engine. The *fuel system* provides for gasoline storage in the vehicle, delivers gasoline to the intake air system and mixes the air and gasoline in the correct proportion so the mixture burns well in the engine. The *exhaust system* routes the combustion gases to the atmosphere. In modern vehicles, a complex, computerized *control system* balances the often conflicting goals of high power, good fuel economy and low emissions.

Combustion Cycle

Gasoline-powered automotive engines are internal combustion, spark-ignition engines that burn fuel in an enclosed chamber – the *cylinder* – that is integral to the engine. (Diesel-powered engines also are internal combustion engines, but they don't involve spark-ignition; the fuel ignites spontaneously at the higher pressures and temperatures at which the engine operates.) The engine's power is generated by the rapid expansion of gases formed by the combustion of a compressed air-fuel mixture. Most automotive engines are reciprocating-piston type devices in which a *piston* slides back and forth in a cylinder. Power from the motion of the piston is transmitted through a connecting rod to a crankshaft, which is coupled to the drive wheels via a drivetrain.

Most automotive gasoline engines operate in a *four-stroke cycle*. For a piston engine, each stroke is one motion of the piston, either up or down. A piston that is all the way at the top of its travel, relative to the cylinder head, is at *top dead center (TDC)*. Conversely, a piston that is all the way at the bottom of its travel is at *bottom dead center (BDC)*. The four strokes occur over two complete revolutions (720°) of crankshaft rotation. *Valves* are used to control gas flow into or out of the cylinder volume above the piston. This volume is called the *combustion chamber*. The *compression ratio* of an engine is the ratio between the volume in the combustion chamber when the piston is at BDC and the volume in the chamber when the piston is at TDC. The *swept volume* of a cylinder is the region above the piston at BDC but below the piston top when it is at TDC. The engine's *displacement* is the total swept volume of all the cylinders.

¹ Some of the information in this chapter was drawn from the vehicle references listed in the *Sources of More Information* on p. 65.

ABNORMAL COMBUSTION PHENOMENA

Chapter 1 described knocking – *spark knocking* – involving the autoignition of the air-fuel mixture ahead of the flame front. But other abnormal combustion phenomena occur. *Surface ignition* involves the ignition of the air-fuel mixture by a hot spot rather than by the spark. Potential ignition sources include: glowing combustion chamber deposits, sharp edges or burrs in the combustion chamber or an overheated spark plug electrode. Heavy, prolonged spark knock can generate hot spots which produce surface ignition.

The hot spot ignites a portion of the mixture before it would normally start to burn. This may occur either before or after spark ignition. Surface ignition before the spark is called *preignition*. Surface ignition after the spark is *postignition*. When preignition occurs, ignition timing is lost and the upward movement of the piston is opposed by the high pressure generated by the early combustion. This results in engine roughness, power loss, and severe localized heating of the piston crown. If it is prolonged, the localized heating can burn a hole in the piston.

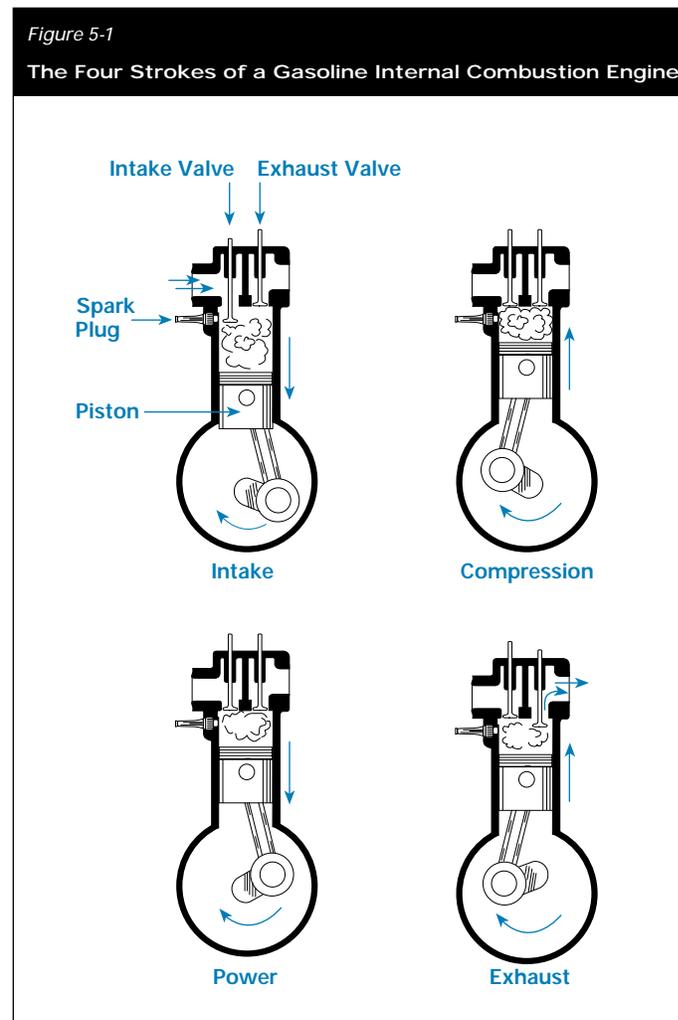
When preignition is caused by a hot spot generated by prolonged, heavy spark knock, it is known as *knock-induced preignition*. It has the same adverse effect on engine operation as preignition from other sources. **Knock-induced preignition is the most damaging side effect of spark knock.**

Postignition reduces the combustion time, and the loss of combustion control can cause knock, engine roughness and reduced power output. The extent of its effect depends on its location in the combustion chamber and the time in the cycle that it occurs.

Run-on is the phenomenon where the engine continues to run after the ignition switch is turned off. It also is referred to as *after-running* or *dieseling*. The engine runs noisily and the exhaust smells bad. Run-on is usually caused by *compression ignition* – where the air-fuel mixture is autoignited by the general high temperature of the combustion chamber – but it can also be caused by surface ignition. The incidence of run-on is decreased or eliminated as the octane quality, especially RON, of the gasoline is increased. Another important run-on factor is idle speed. This is why many carbureted engines are equipped with an idle stop (*anti-dieseling*) solenoid. Run-on is not a problem with fuel injected engines because fuel cannot be delivered to the combustion chamber when the ignition switch is turned off.

Figure 5-1 pictorially summarizes the four strokes – intake, compression, power and exhaust. The first downward motion of the piston in the four-stroke cycle – the *intake stroke* – draws the air-fuel mixture into the combustion chamber through the open intake valves. As the piston reverses direction and begins to move back up, the intake valves close. This upward motion of the piston is the *compression stroke*. Compression raises the pressure and temperature of the mixture. Near the top of the compression stroke, the spark plug produces a spark, igniting the mixture. The mixture burns and expands, which drives the piston downward for the third or *power stroke*. As the piston passes BDC and begins to move back up again, the exhaust valves open, beginning the *exhaust stroke*. The upward motion of the piston pushes the burned gases out of the engine into the exhaust manifold and eventually out the exhaust pipe.

For combustion to occur, the fuel must be in the vapor state (*see p. 1*). In addition, the relative amounts of air and fuel vapor are very important. In the ideal mixture for complete combustion of gasoline – the *stoichiometric mixture* – the ratio of air



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mass to fuel mass is 14.7:1. A mixture with less air and more fuel is *fuel rich*, and a ratio with more air and less fuel is *fuel lean*.

Control of the air-fuel ratio (A/F) is a critical element of good emissions performance. Since CO and VOC increase under fuel rich operation while NO_x emissions rise during fuel lean operation, most modern vehicles strive to maintain the stoichiometric A/F. The *Control* section (below) describes how this is accomplished.

Engine Structure

Engines generally are separated into two distinct pieces, the cylinder head and the block (*Figure 5-2*). The *head*, or top of the modern vehicle engine, controls the gas flow through the engine and also holds the spark plugs. Poppet *intake valves* and *exhaust valves* allow for precisely timed intake and exhaust flows. Spring-closed poppet valves can be opened and closed very quickly, an essential feature for optimum performance at high engine speeds. The valve seats are hardened to withstand the high temperatures of the combustion gases and to prevent abrasion due to valve contact and rotation. The movement of the valves is controlled by means of a shaft with elliptical lobes on it called a *camshaft*. As the camshaft rotates, the lobes push against the rocker arms to open the valves against spring pressure either directly or via pushrods. Engines with a camshaft mounted in the head above the valves are of an *overhead cam (OHC)* design, and engines with the camshafts mounted below the valves, on the block, are of a *pushrod* design. Pushrods transmit the valve opening force from the tappets, which ride on the camshaft lobes, up to the rocker arms. If each cylinder head has two camshafts overhead, the engine is a *dual overhead cam (DOHC)* design. An overhead camshaft is driven off the crankshaft by either a timing belt or a timing chain; a block-mounted camshaft is driven by either a timing chain or a gear.

Engines typically have one to three intake valves and one or two exhaust valves per cylinder (*Figure 5-3*). An engine with two intake and two exhaust valves per cylinder is of a *four-valve head* design. More valves per cylinder are preferred for better breathing. Usually the exhaust valves are slightly smaller in diameter than the intake valves. It is easier to push out exhaust gases pressurized above atmospheric pressure, than to draw in air-fuel mixture at atmospheric pressure.

The *block*, or bottom of the engine, contains the power-producing mechanical components. Cylinders in the block contain the engine's pistons. Typically each piston has at least three rings mounted in grooves in its perimeter to create a seal for the combustion chamber. The top of the piston is the surface that the

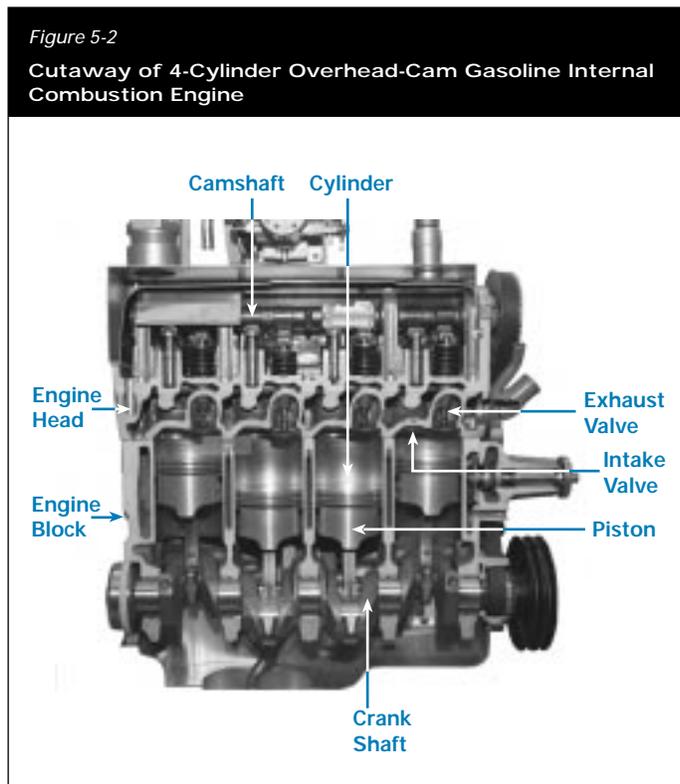
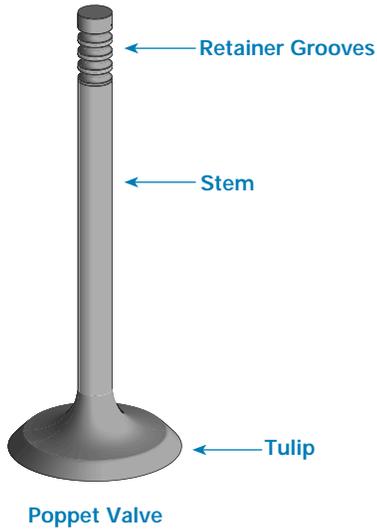


Figure 5-3
Poppet Valve



expanding combustion gases push against. Each piston is supported by a *wrist pin*, which is attached to a *connecting rod*. All of the connecting rods are attached to the engine's *crankshaft*. As the air-fuel mixture ignites and expands, it forces the piston down, which moves the connecting rod and turns the crankshaft. The crankshaft is mounted at the bottom of the engine in a volume called the *crankcase*. The oil pan forms the bottom of the crankcase. Oil is drawn from here by the oil pump and distributed throughout the engine, including the valve train in the head.

Passenger car engines may have as few as three cylinders or as many as 12. Engines with fewer than eight cylinders often will have them in a row – an *in-line* configuration. Engines with six or more cylinders usually have two rows, or banks, of cylinders, arranged with the central axis of the cylinders in each bank at an angle to the other bank. These are usually termed “V” engines (e.g., V-6).

Engine design is one way to reduce emissions. When there is an understanding of how pollutants are created, changes often can be implemented to minimize them at the source. For example, exhaust VOC emissions can be reduced by careful mechanical design of the combustion chamber and the air and fuel intake systems.

Air System

Air is drawn into the engine through the *intake system*. An *air filter* is used to keep dust and contaminants (e.g., insects) out of the engine. To control engine speed, a *throttle* is mounted in the air intake. This is simply a disk attached to a shaft to block air flow into the engine. The *accelerator pedal* is mechanically linked to the throttle. Depressing the accelerator pedal tilts the disk, reducing the blocked area and allowing more air to enter the engine. With more air, the engine can use more fuel and produce more power to accelerate, climb a hill or maintain a higher cruising speed.

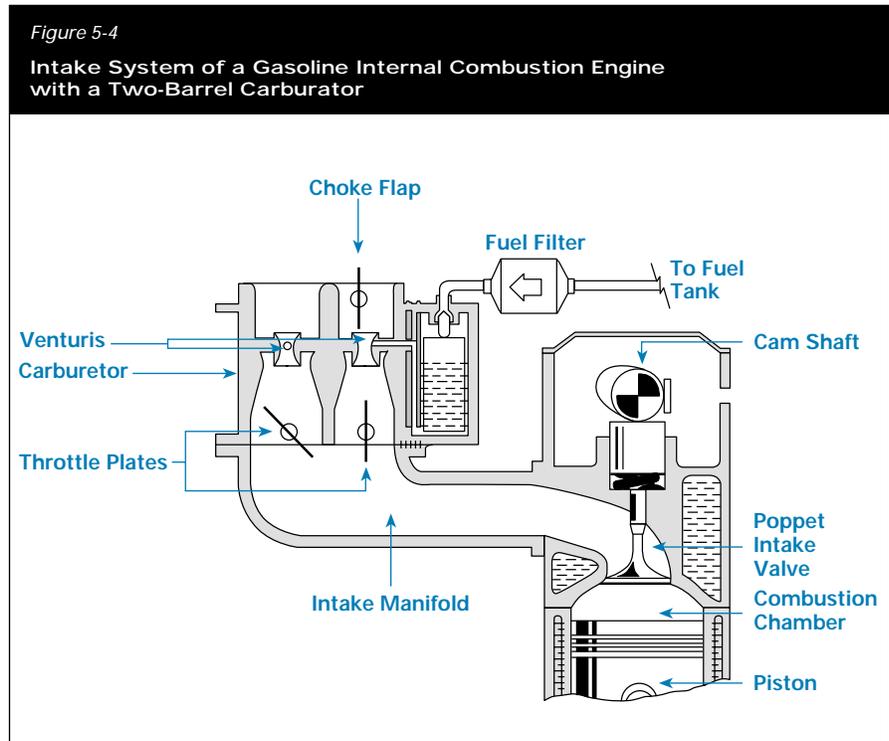
An engine that uses intake air at atmospheric pressure is said to be *naturally aspirated*. The amount of air a naturally aspirated engine can use is limited by the local air density (barometric pressure) and pressure losses in the intake system. To get more air into an engine, small compressors are sometimes used to pressurize the intake air. If the compressor is driven off the engine crankshaft, it is called a *supercharger*. Superchargers usually are belt driven, either directly or through a clutch. Positive displacement superchargers are generally used on small and medium displacement engines in which the balance between supercharger size and increase in engine power is acceptable. Another way to power the compressor is to put it on a common shaft with a turbine driven by the engine's exhaust gas. This arrangement is called *turbocharging*. Turbochargers are more compact than superchargers and can be used on all sizes of engines. To maintain boost pressure at a relatively constant amount over a wide range of engine speeds, some sort of pressure regulator is needed. A wastegate is the typical solution. The wastegate opens to divert some of the exhaust flow around the turbine when boost pressure is at the desired level.

Fuel System

Carburetors

In the intake system, air is mixed with a small amount of vaporized gasoline to produce a homogeneous air-fuel mixture. Many different devices have been used for this purpose; historically, the carburetor was the most common (Figure 5-4). A carburetor employs a venturi to discharge the correct amount of fuel into the intake air stream. A *venturi* is a converging-diverging nozzle. The diameter of the nozzle decreases to a minimum at the throat and then increases to the discharge end. As air passes through the venturi, its velocity increases up to the narrowest portion (throat) because the flow area decreases. As the air velocity increases, its pressure decreases, creating a vacuum that draws fuel out of the carburetor's fuel bowl through a tiny orifice called a *jet*. Additional jets are used to enrich the mixture during acceleration and to supply sufficient fuel at idle. A *choke flap* is used to enrich the mixture when the engine is cold by reducing the amount of air available to the engine. The choke is located above the venturi and the throttle is located below the venturi on *downdraft carburetors*.

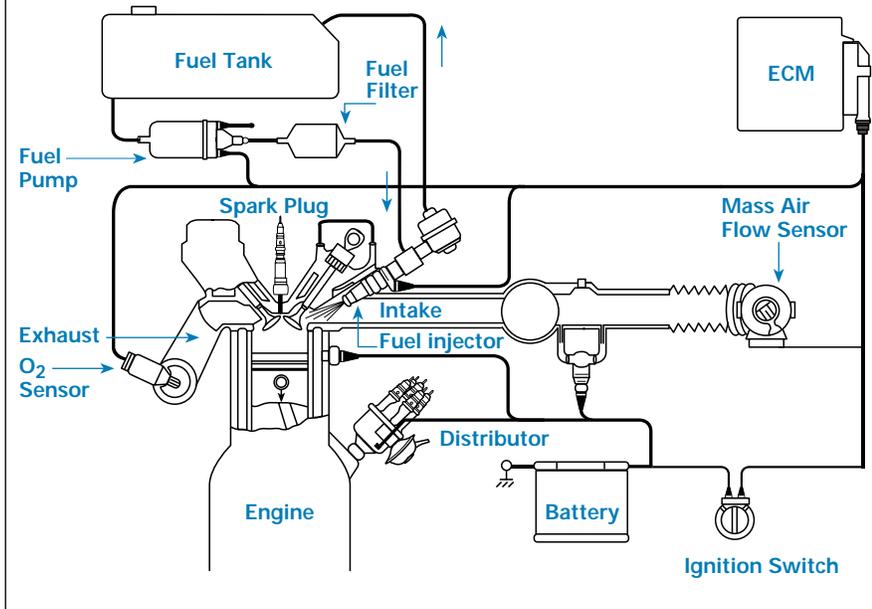
Typically a carburetor has two venturis staged together, one located slightly downstream of the other. This arrangement produces a higher vacuum with less overall pressure loss than a single larger venturi. A *two-barrel carburetor* on an in-line engine has two sets of staged venturis located side by side to provide greater air and fuel flow for more power. ("V" engines require *four-barrel carburetors*.) One set of venturis is usually larger than the other. The smaller set is used alone at low loads; both sets are used at medium and high loads. Carburetors have been replaced by fuel injectors on new vehicles sold in the United States because carburetors do not control fuel flow precisely enough to meet federal exhaust emission requirements. In part this is because they are volume-flow based and difficult to calibrate for all of the vehicle's operating conditions.



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Figure 5-5

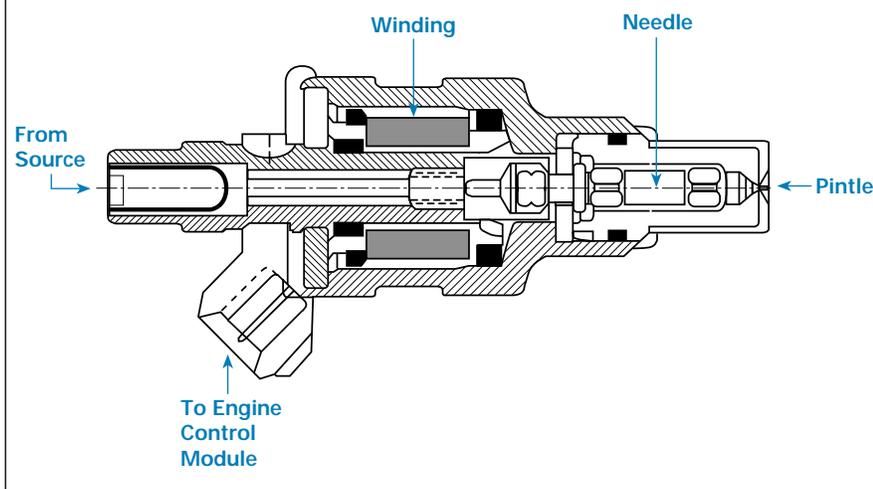
Fuel and Control Systems for a Port-Fuel-Injected (PFI) Gasoline Internal Combustion Engine



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Figure 5-6

Section View of Fuel Injector for a Gasoline Internal Combustion Engine



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Injectors

To overcome the carburetor's limitations, engine builders switched to *fuel injectors*. Fuel injection systems can be categorized into two broad groups depending on where the injectors are located. A system that has the injector in the throttle body, mounted on the air intake manifold, is called a *throttle body injection (TBI)* system. A system that uses one injector at the intake port of each cylinder, where it sprays on the intake valves, is called a *port fuel injection (PFI)* system (Figure 5-5). To enrich the mixture during cold starts, an additional cold start injector may be used. This injector provides additional fuel to the intake air for a short period of time while the engine warms up.

An electrically powered *fuel pump* provides fuel at low pressure (30-50 psi) to either the central injection unit or the individual port injectors. A *fuel filter* is installed in the line after the pump to remove particulate matter from the fuel and prevent injector clogging. A diaphragm *pressure regulator* maintains pressure and routes excess fuel back to the fuel tank.

Fuel injectors meter the amount of fuel delivered to the inlet air (Figure 5-6). When the injector is off, the spring keeps the needle against the seat, preventing fuel flow. Energizing a solenoid winding pulls the needle back against spring pressure (it moves only about 0.006 in.), allowing fuel to flow through the annular passage around the needle and out through the injector tip. The needle tip, the *pintle*, is designed to break up the liquid fuel into a fine spray to promote rapid formation of vapor and enhance the mixing of fuel and air.

Several strategies are used to time fuel injection. Some older throttle body injectors and PFI systems inject fuel almost continuously, much like a carburetor. Intermittent injection systems fire the injectors simultaneously to deliver the same quantity of fuel to each cylinder. These systems sometimes deliver fuel twice per cycle. Sequential injection systems fire injectors sequentially at the same crankshaft angle on each cycle. Fuel quantity is metered by controlling the time the injector is open (*pulse width*).

Storage

A vehicle has a fuel tank for on-board fuel storage. Modern fuel tanks are sized to provide a vehicle range of between 275 and 400 miles. Most fuel tanks are made of steel, which can be corroded rapidly by water in combination with organic acids from the gasoline. As protection, tanks are lined with a corrosion resistant material, commonly a plating of a tin-lead (*terneplate*) or zinc-nickel alloy. Organic coatings also have been used. Mercedes introduced an all-aluminum tank in 1991, and Volkswagon pioneered the use of a plastic fuel tank in 1976. Plastics can be formed in complex shapes to increase fuel storage capacity. A significant problem with plastic tanks is their permeability to fuel vapor. High-density polyethylene tanks must be lined with a low-permeability material or the vehicle's evaporative emissions will be too high (*see p. 15*).

Evaporative Emissions Control Systems have been employed on all gasoline passenger cars sold in California since 1970 and in the United States since 1971. They collect vapor evolved by the gasoline in the fuel tank and introduce it into the engine later. The heart of the system is a canister containing activated carbon. It is located in the line through which the tank *breathes* – drawing in air from the atmosphere when gasoline is consumed or the tank temperature drops and emitting air when the tank temperature rises. The activated carbon absorbs gasoline vapor in the emitted air like a sponge absorbs water, preventing the vapor from reaching the atmosphere. The canister also is connected to the engine's intake system by the *purge control valve*, which is opened at certain times to allow the accumulated vapors to be purged from the canister and burned in the engine. For the system to work, the canister must be the tank's only vent to the atmosphere. The filler tube must be sealed by a functional, properly tightened gas cap.

Other sources of fuel-related emissions, such as those resulting from fuel leaks or seepage, and from gasoline permeation through hoses, are best controlled through proper component design and choice of hose, fuel tank, and gasket materials, as well as prompt repair of defective components.

Exhaust System

Combustion gases are routed out of the engine by the exhaust system. It has four parts – exhaust manifold, exhaust pipe, catalytic converter, and muffler. The *exhaust manifold* collects exhaust gases from several cylinders and combines them into one flow stream. The *exhaust pipe* runs from the exhaust manifold underneath the vehicle to the rear. The *catalytic convertor* and *muffler*, which reduces engine noise, are mounted in the exhaust pipe.

Catalytic Converter

A catalytic converter may be the most important emissions control device on a vehicle. They have been installed on gasoline-powered vehicles since 1975. It uses catalysts containing precious metals such as platinum and rhodium to convert pollutants in the engine exhaust into nonpolluting compounds. The first catalysts were oxidation catalysts. As the name indicates, they were designed to oxidize CO and VOCs in the exhaust into carbon dioxide and water. To work properly, it requires excess oxygen in the exhaust, which can be achieved either by operating the engine lean or by injecting air directly into the exhaust stream between the engine and the catalyst. *Three-way catalysts*, introduced about 1980 and now used almost exclusively, perform the oxidation function described above, but also reduce NO_x into nitrogen and oxygen. Since excess oxygen interferes with the reduction reaction, the three-way catalyst performs best when the A/F is very near the stoichiometric value. Thus, careful control of A/F is doubly important on modern cars, first, to minimize the formation of CO and VOCs in the engine, and, second, to assure that the catalytic converter operates at maximum efficiency.

Exhaust Gas Recirculation

Exhaust Gas Recirculation (EGR) is a strategy employed on many modern gasoline engines to reduce NO_x emissions. The principle is relatively simple. Exhaust gas, being already burned, is essentially inert. If some of this exhaust gas is introduced into the intake manifold (recirculated) along with air and fuel, it won't participate in the combustion reactions. However, the exhaust gas can absorb some of the heat produced, thereby lowering the cylinder temperature. Since NO_x production is favored strongly by higher temperatures, EGR reduces NO_x emissions substantially. The mechanics of EGR involve appropriate piping between the engine's exhaust and inlet systems and a control valve to regulate the amount of exhaust that is recirculated. When implemented properly, EGR can increase fuel economy under cruise conditions.

Positive Crankcase Ventilation

Positive Crankcase Ventilation (PCV) was one of the first techniques employed to reduce unburned VOC emissions from gasoline-powered vehicles. It was required initially on California vehicles in 1961. Since the gases in the combustion chamber are under high pressure while combustion is taking place, a small fraction leaks past the rings that seal the gap between the piston and the cylinder wall. These *blow-by gases* end up in the crankcase. They are a mixture of unburned fuel, air and combustion products. As the blow-by gases accumulate in the crankcase, they must be vented to avoid pressurizing the crankcase, which would force oil out of the engine. PCV systems consist of tubing and a control valve that meters the flow of the blow-by gases from the crankcase back into the engine's intake system, from which they are drawn into the cylinders and burned. Prior to the use of PCV, blow-by was vented to the atmosphere, providing a significant source of VOCs.

Control Systems

Fuel Control

To meet the often conflicting goals of high power, good fuel economy and low emissions, engine designers have had to develop high speed, computerized engine control systems. Sensors monitor various conditions and an *electronic control module (ECM)* collects the information and uses it to determine a response to the driver's input. Figure 5-7 lists the conditions the ECM may monitor in newer vehicles and the functions it may control.

One of the ECM's most important functions is air-fuel mixture control. The air-fuel mixture must be kept very close to stoichiometric for optimum performance of the three-way catalyst. The amount of air in the mixture is determined by throttle position and engine speed; the ECM must command the injectors to provide the corresponding amount of fuel. It does this based on input from a sensor in the intake manifold that measures the mass of intake air and feedback from the oxygen sensor that measures the amount of oxygen in the engine exhaust. When the ECM is using these and other inputs to control the amount of fuel, it is described as operating in a closed-loop mode. When an engine is cold-started, the ECM is in the open loop mode – it is not controlling engine operations because the oxygen sensor is not warm enough to be operational. After a few minutes when the ECM detects that the oxygen sensor is operating, it switches to the closed-loop mode.

Under steady state conditions, closed loop control based on direct oxygen sensor input works fine, but it breaks down under transient conditions. When the driver suddenly opens the throttle to accelerate, there is a delay before the feedback from the oxygen sensor reflects the new situation: It takes time for the fuel mixture to be burned in the engine, for the oxygen sensor to measure the oxygen content of the exhaust and for the ECM to command the injectors to inject more fuel. During the delay, the air-fuel mixture would be fuel lean, which could cause driveability and emissions problems. Therefore, under transient conditions, “the ECM uses an anticipatory control strategy that uses engine load and RPM to determine the approximate fuel requirement.”² The ECM consults a data table (*map*) in its memory to determine the amount of fuel to inject for the transient

Figure 5-7

Conditions Monitored and Functions Controlled By the Electronic Control Module (ECM)

Conditions That May Be Monitored	Functions That May Be Controlled
<ul style="list-style-type: none"> • Mass flow of intake air* • Intake manifold air pressure • Intake manifold air temperature • Throttle position • Angular rate of change of throttle position • Engine speed • Camshaft or crankshaft position • Quantity of oxygen in the exhaust • Spark knock • Engine coolant temperature • Vehicle speed • Gear selection • Transmission controller • State of air conditioner 	<ul style="list-style-type: none"> • Mass of fuel injected for steady state, accelerating and enrichment conditions • Idle speed • Cold start injector, if equipped • Evaporative emissions control system (e.g., when to purge the charcoal canister) • Amount of exhaust gas recirculation (EGR) • Spark timing • Amount of boost for turbocharged vehicles • Input to the Automatic Braking System (ABS) computer for traction control • Transmission shift points

* Measuring the mass of the intake air eliminates the need to compensate for the change of air density with altitude.

² Ronald K. Jurgen, Editor-in-chief, *Automotive Electronics Handbook*, McGraw-Hill, Inc., New York, 1995.

combination of engine load and RPM. The map is developed by the engine manufacturer by system modeling and engine testing.

Because of production variations among engines, changes due to wear and aging and variations in fuel characteristics, the factory installed map can't represent the best answer. So the ECM is equipped with an adaptive learning feature which enables it to use oxygen sensor input to generate a second engine load/RPM map for the specific current conditions. This second map is continually being updated. The the next time the engine reaches the same load/RPM operating point, the anticipatory control value will be closer to the correct value for the specific engine and fuel.

There are several special situations which require different fuel control strategies. An engine needs extra fuel – *mixture enrichment* – for starting, for hard acceleration and at wide open throttle (WOT). When the engine is cold, fuel vaporizes more slowly. So extra fuel is needed to ensure that combustion will occur (A/F=13:1 for optimum startability). Some injector systems use an additional cold-start injector to provide the extra fuel. The cold-start injector typically operates for only a few seconds until a stable idle is achieved. Other designs simply program the port fuel injectors to inject more fuel.

Another form of mixture enrichment, called *commanded enrichment*, is used under hard acceleration and at WOT in order to keep the gas temperatures in the combustion chamber from becoming too hot. This helps reduce the potential for knocking and avoids overheating the catalytic converter. EPA concerns about excessive hydrocarbon and carbon monoxide emissions while a vehicle is under hard acceleration may end the use of commanded enrichment.

Idle is a common operating condition, especially in city driving. To reduce fuel consumption, it should be as slow as possible. Idle control is usually accomplished by adjusting the size of the air-fuel mixture, although it also can be controlled by adjusting the ignition timing.

Knock Control

Most new cars come equipped with a device called a *knock-sensor* that detects knock and provides a signal to the ECM. To eliminate the knock, the ECM retards the engine's timing, that is, it fires the spark plug later in the compression stroke. This reduces the peak cylinder pressure and, as a result, the tendency for autoignition. The downside of timing retardation is a decrease in power. When knock is sensed in a turbocharged engine, the ECM also decreases the amount of boost to further reduce peak cylinder pressure. Boost reduction significantly decreases power. Loss of power due to the ECM's knock-elimination strategies can be prevented by using a gasoline with a higher AKI.

On-Board Diagnostics (OBD)

Now the EPA requires new vehicles to be able to detect faults in certain emissions-critical equipment: catalyst, oxygen sensor and engine misfire. When a defect is detected, the ECM turns on a *malfunction indicator light (MIL)* – often the "check engine" light – on the dashboard and stores a fault code in computer memory. The code, which can be retrieved by a repair technician with the proper equipment, helps the technician identify the faulty component.

California began requiring a second generation OBD system – *OBD-II* – in 1994, with full implementation early in the next decade. The purpose is "to detect and aid in the diagnosis of malfunction of vehicle emission control and emissions-related components and systems." Figure 5-8 lists the OBD-II monitoring requirements. These measures, while somewhat costly and difficult to engineer, should substantially reduce the number of vehicles on the road with poorly running engines or defective emissions control systems.

Figure 5-8

Systems That California Requires the Second-Generation On-Board Diagnostic Analyzer (OBD-II) to Monitor for Malfunction

- Overall catalyst system efficiency
- Evaporative control system leakage (fuel tank vapor space and vapor lines)
- Ignition misfire
- Secondary air injection system operation
- Fuel delivery system effect on emissions
- Oxygen sensor performance
- EGR system flow rate
- Electronic powertrain components that can affect emissions or are used for emission diagnostic strategies
- Air conditioning system refrigerant loss

OCTANE NUMBER REQUIREMENT AND OCTANE REQUIREMENT INCREASE

The *octane number requirement (ONR)* of an engine is defined as the octane number of the reference fuel that will give *trace knock* under the most severe speed and load conditions. Trace knock is the knock intensity that is just audible to the trained technician. ONR usually is reported as an AKI value.

The ONR of an engine is determined with either a primary or a full-boiling reference fuel series. The primary series is the same group of isooctane-normal heptane blends used to measure RON and MON (see p. 33). A full-boiling reference fuel series is a group of commercial-like gasolines blended from normal refinery components in one-RON increments.

The ONR of an engine is usually determined by making a series of maximum-throttle or part-throttle accelerations at standard spark timing—using primary or full-boiling reference fuels which are successively lower in octane number—until trace knock occurs. The AKI of that fuel is the ONR of the engine. The ONR of different engines varies considerably and as much as a ten-octane-number range in ONR can be obtained for vehicles with the same engine model.

The ONR of an engine is influenced by its operating conditions. The effects of some of the more significant of these are listed in Figure 5-9. Mechanical problems, such as a malfunctioning exhaust gas recirculation (EGR) valve, and electrical problems, such as advanced spark timing, can increase ONR.

The ONR test procedure has become more complicated with the introduction of knock sensors and sophisticated engine control systems. Not only are spark timing, transmission shift points and enrichment strategies – all of which strongly affect an engine’s ONR – controlled by the engine’s ECM, but adaptive learning may cause the ECM to vary its responses from driver to driver and fuel to fuel. Before each reference fuel is evaluated, the vehicle must be driven through a cycle to stabilize the ECM. It also is important to test fuels in order of decreasing RON, to maintain the same rate of throttle movement and to avoid heavy knock conditions.

When an engine is brand new, its ONR is determined by its design and assembly. Generally, it will not knock when operated on a gasoline with the AKI recommended by the automobile manufacturer. However, an engine’s ONR can increase dramatically during the first several thousand miles. This effect, called *octane requirement increase (ORI)*, is caused by the buildup of carbonaceous deposits in the engine’s combustion chambers.

It generally takes 10,000 to 15,000 miles for a vehicle to reach equilibrium deposit levels and maximum ORI. On the average, ORI is about 5 AKI numbers, but the ORI of individual engines can vary from 1 to over 13 numbers. Thus, an engine may not knock when it is new, but after it reaches equilibrium, a higher octane grade of gasoline may be required to prevent knocking.

Combustion chamber deposits increase ONR in two ways. They increase the combustion temperature both by transferring more heat to the incoming mixture and slowing the transfer of heat from the combustion gases (thermal insulation). They increase the compression ratio because their bulk volume reduces the volume of the combustion chamber at TDC. The increase in compression ratio has a much smaller effect on ORI than the heating effect.

Research has shown that precursors for combustion chamber deposits come from the fuel, some fuel additives and the engine oil, and that certain fuel and engine oil components form more deposits than others. So far, the only quick, effective means of removing these deposits is to treat the gasoline with an aftermarket deposit control additive concentrate based on polyether amine chemistry. The treat level is 10 to 20 times higher than that in service station gasolines. At this elevated concentration, one tankful of gasoline can decrease ORI 30 to 40%. Periodic treatment is required because the deposits reform with additional driving and the ONR gradually returns to the previous equilibrium level.

Figure 5-9
Average Effect of Some Variables on Engine Octane Number Requirement (ONR)

Variable	Change in Variable	Change in ONR, AKI Number
Compression Ratio	+1 ^a	+3 to +5
Air-Fuel Ratio	+1 ^b	+2
Spark Advance	+1°	+0.5 to +0.8
Ambient Temperature	+10°F ^c	+0.5
Absolute Humidity	+10 grains/lb	-0.3
Altitude	+1000 ft	-1.5 ^d
Combustion Chamber Deposits		+1 to +13 ^e

a In range 8:1 to 11:1

b Fuel leaning

c In range 160°F to 180°F

d For newer engines the change is almost zero because the ECM leans the air-fuel mixture and advances the spark timing as altitude increases.

e Change depends on engine design, fuel, lubricant and operating conditions.

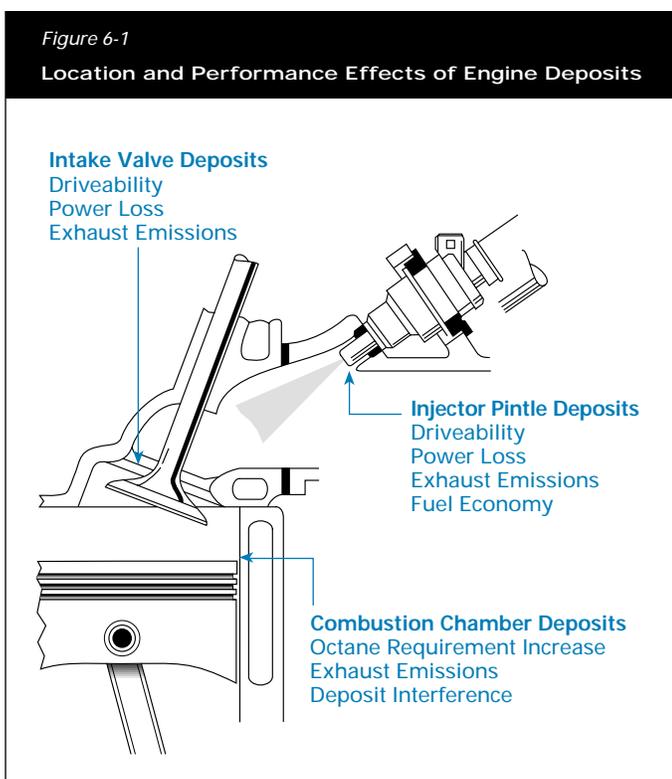
Introduction

Almost without exception, commercial gasolines would build up deposits on the components of an engine's intake system over time if they weren't additized. A number of additives have been developed which prevent and/or remove intake system deposits. Unfortunately, some of them increase combustion chamber deposits, solving one problem, but creating another. Since all base gasolines are formulated to the same regulated specifications (*see p. 31*), the performance of the deposit control additive is one of the few features that differentiates one brand of gasoline from another.

Engine Deposits and Performance

The schematic in Figure 6-1 shows the critical areas of deposit formation and the associated performance impacts.

Fuel Injectors and Carburetors Fuel injectors are designed to accurately meter fuel to the engine and to deliver it in a precise pattern of fine droplets. Because the fuel passages are small, injectors are highly sensitive to small amounts of deposits in the critical regions where the fuel is metered and atomized. These deposits can reduce fuel flow and alter the spray pattern, degrading driveability, decreasing power and fuel economy and increasing emissions. Deposits cause similar problems for carbureted engines because carburetors also use a number of small channels and orifices to meter fuel.



Port fuel injector (PFI) deposits are believed to form during the *hot soak* period after the engine has been turned off. The stationary gasoline trapped in the injector is exposed to a higher temperature for a longer time than the gasoline which flowed through the injector when the engine was running. The heat degrades the gasoline, initiating deposit formation.

Intake Valves and Ports Intake valves and ports are subject to more deposit build up than fuel injectors because they operate at higher temperatures. Heavy valve and port deposits reduce maximum engine power because they restrict air flow. Intake valve deposits also have been shown to affect exhaust emissions, particularly VOCs and NO_x (*Figure 6-2*). In some very sensitive modern fuel-injected engines, low levels of intake valve deposits can degrade cold start and warm-up driveability (*see p. 2*). Other valve deposit problems include valve sticking in very cold weather – because deposits interfere with the valve stem sliding in its guide – and burned valves – because severe deposits prevent the valve from seating properly.

Combustion Chamber When an engine is brand new, its octane number requirement (ONR) is determined by its design and the quality of its manufacture. Generally, it will not knock when operated on gasoline with the antiknock quality prescribed by the manufacturer. However, the engine's ONR increases as combustion chamber deposits form during the first several thousand miles of operation (*see p. 52*). If the increase is large enough, the recommended gasoline AKI may not prevent knocking or, if the vehicle is equipped with a knock sensor, the loss of power which accompanies knock suppression (*see p. 50*).

Combustion chamber deposit interference (CCDI) is a new problem that has occurred in a few modern engines. It is the result of physical contact between deposits located on the piston top and cylinder head and is manifested as a very loud banging sound when the engine is cold. CCDI is limited to the engines which have been designed, primarily to reduce emissions, to have minimal clearance –1 millimeter or less – between some areas of the piston top and the cylinder head (*squish* areas) when the piston is at top dead center. Deposits contribute to CCDI, but poor control of manufacturing tolerances in the susceptible engines also can be a factor. CCDI occurs primarily at cold-start. The interference and the telltale sound disappear as the engine warms up and the thermal expansion of the various engine components increases the clearance between the piston top and head at top dead center.

Historical Development of Deposit Control Additives¹

Carburetor Detergent This class of additives consists of relatively inexpensive low-molecular-weight surfactants used at low concentrations. When introduced in 1954, they were effective in preventing and, in many cases, removing deposits from carburetor throttle bodies. However, they could not handle deposits in other parts of the carburetor, like the air bleeds, or in the rest of the engine intake system. The introduction of PCV and EGR emission control systems in the 1960s and 1970s increased deposit levels in the whole intake system (*see p. 48*). As a result, carburetor detergents were not as effective as they were in the simpler 1950s vehicles.

Detergent-Dispersants This class of additives consists of polybutene succinimides. Additives with similar chemistry had been used widely as engine oil dispersants before the chemistry was applied to gasoline in 1968. Detergent-dispersants are used at concentrations three to five times higher than carburetor detergents. Their performance is sometimes improved by using them in combination with a petroleum carrier oil. They provide keep-clean performance for the intake manifold and intake ports. But they don't control intake valve deposits and have poor carburetor and fuel injector cleanup performance.

Deposit Control (DC) Additives The first additive of this class was introduced in 1970. It was based on polybutene amine chemistry and was used in combination with a carrier oil. While they have to be used at higher concentrations than detergent-dispersants, DC additives provide benefits throughout the engine intake

PERFORMANCE CATEGORIES

There are two performance categories for deposit control additives: *keep-clean* and *cleanup*. *Keep-clean* indicates that when additized fuel is tested in a clean engine, the part of interest still will be relatively clean at the end of the test. *Cleanup* indicates that when additized fuel is tested in an engine where deposits have been built up on the part of interest (by previously running the engine on a lower quality gasoline), the deposits on the part will be significantly reduced at the end of the test. *Cleanup* performance is more demanding than *keep-clean* performance.

¹ L. M. Gibbs, *Gasoline Additives – When and Why*, Paper No. 902104, Society of Automotive Engineers, October 1990.

system. They clean up – and keep clean – the throttle body and upper areas of the carburetor, fuel injectors, intake manifold, intake ports, and intake valves.

Lead salts are a combustion catalyst for carbon, so the shift to unleaded gasoline changed the nature of combustion chamber deposits. When the first generation DC additives were used in unleaded gasoline, they continued to control intake system deposits, but increased combustion chamber deposits. In response, a second generation DC additive designed specifically for use with unleaded gasoline was developed and introduced in 1980. It was based on new polyether amine chemistry, which provides excellent deposit control performance throughout the intake system without contributing to combustion chamber deposits or causing any other adverse side effects.

No Harm and Compatibility

DC additives are used at concentrations which are twenty to fifty times higher than the concentrations of other gasoline additives (*see p. 28*). At these higher concentrations, they have the potential to affect gasoline properties, fuel system materials and engine oils. So DC additives are tested for the absence of negative attributes (*no harm*) as well as for the positive attribute of controlling deposits. The additized fuel must be fully compatible with the elastomers and metals it will contact. Also it must have good water tolerance and not contribute to spark plug fouling or crankcase sludge formation.

Emissions

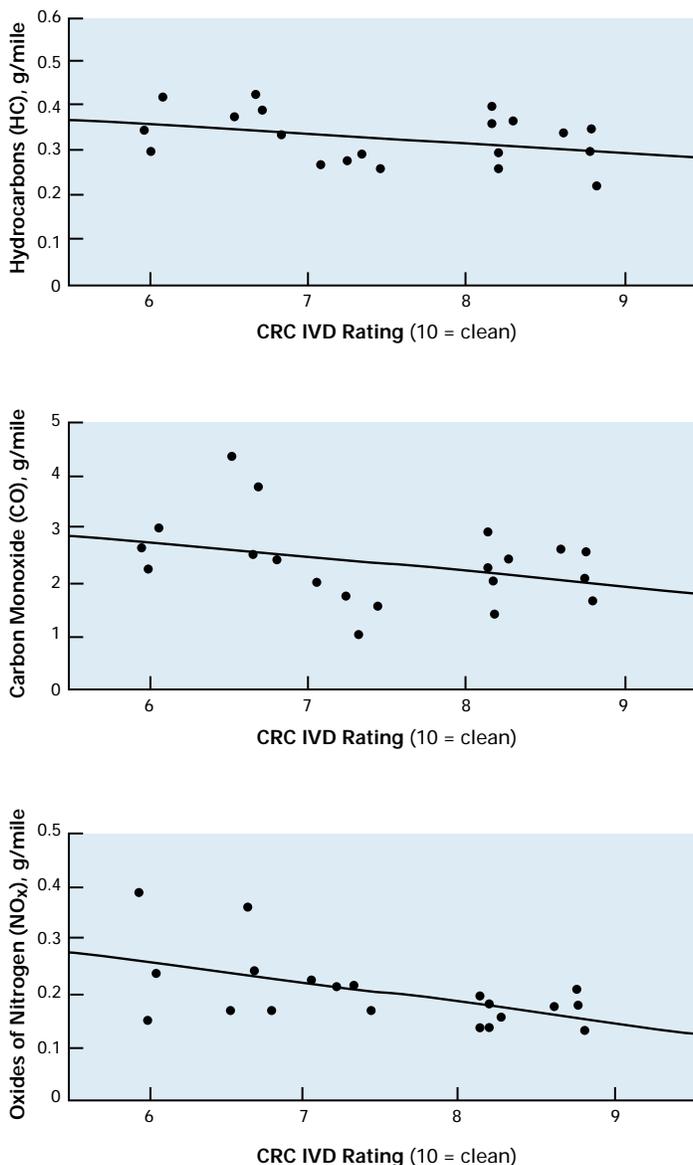
At some level, carburetor, injector, intake port and valve and combustion chamber deposits all increase engine emissions (*see Chapter 2*). For example, Figure 6-2 illustrates that hydrocarbon, CO and NO_x tailpipe emissions all are lower when intake valves are cleaner.

Required Additive Use

Because of this relationship between decreased deposits and decreased emissions, all motor gasoline sold in the United States must contain an additive which provides a minimum level of deposit control performance. This requirement was established by the Clean Air Act Amendments of 1990 and became effective in January 1995. A similar requirement has been in effect in California since January 1992. Additive manufacturers are required

Figure 6-2

Intake Valve Deposits (IVD) Increase Tailpipe Emissions



Emissions were measured by Federal Test Procedure Cycle (FTP 75), results are average results for a 20-car fleet.

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ADDITIVE CERTIFICATION TESTS

The fuel injector keep-clean test was developed by the Coordinating Research Council (CRC) (see p. 31) and established as ASTM D 5598 – *Test Method For Evaluating Unleaded Automotive Spark-Ignition Engine Fuel for Electronic Port Fuel Injector Fouling*. The method uses a 1985-1987 model Chrysler vehicle equipped with a 2.2-liter 4-cylinder turbocharged engine. After the vehicle has been operated through over 720 one-hour cycles for a total of 10,000 miles, no injector may have greater than a 5% flow restriction.

The intake valve keep-clean test was adapted from one developed by BMW and the Southwest Research Institute and established as ASTM D 5500 – *Test Method for Vehicle Evaluation of Unleaded Automotive Spark-Ignition Engine Fuel for Intake Valve Deposit Formation*. The method uses a 1985 model BMW 318i vehicle. After the vehicle has been operated through a cycle of mixed city, suburban and highway driving for 10,000 miles, the average intake valve deposit weight must not exceed 100 mg per valve.

to obtain EPA certification for their additives. The certification request must include documentation of the additive's effectiveness in specified fuel injector keep-clean and intake valve keep-clean tests (see sidebar) and the additive concentration at which this performance is achieved. Certification may be obtained for use nationwide, for use in specific areas of the United States, or for use with particular types of gasoline. Nationwide certification requires using a test gasoline which meets ASTM D 4814, but has a greater tendency to form deposits than the average gasoline.

Gasoline formulators must add a certified deposit control additive to their gasoline at the certification concentration level or higher. Over some range, higher concentrations often provide improved performance; for instance, changing keep-clean performance to cleanup performance. Historically, some gasoline brands have provided much higher deposit control performance than the certification performance required by the EPA. For competitive reasons, they probably will continue to do so.

Aftermarket Additives²

Engine deposits are affected by engine design, driving conditions, gasoline base fuel quality, and gasoline additives. While all gasoline must contain a deposit control additive, some additives are less effective than others or are used at concentrations which are less effective. In addition, some engine designs form heavier deposits than others, and some engine designs are extremely sensitive to deposits which do form. Aftermarket deposit control additives are available which can clean up deposits which have formed due to these circumstances. Treating one tankful of gasoline with the aftermarket additive is often sufficient. However, additive chemistry and dosage play large roles in determining the effectiveness of the product. Polyether amine-based aftermarket additives have been shown to be particularly effective at providing both excellent intake system and combustion chamber deposit cleanup.

² *Aftermarket additives* are additives intended to be added by the customer to a gasoline (or oil) which already is in the customer's vehicle.

QUESTIONS AND ANSWERS

What is gasoline?

Gasoline is the fuel designed for spark-ignition internal combustion engines. *Conventional gasoline* is a mixture of compounds, called *hydrocarbons*, derived from petroleum crude plus a small amount of a few additives to improve its stability, control deposit formation in engines, and modify other characteristics.

What is oxygenated gasoline?

Oxygenated gasoline is conventional gasoline to which oxygenates have been added to increase octane and/or, as required by regulation, to reduce emissions. Oxygenated gasoline is required during winter in those metropolitan areas which do not meet the federal air quality standard for carbon monoxide (*carbon monoxide nonattainment areas*). Reformulated gasolines are also oxygenated during the winter and may be oxygenated year-round. The common oxygenates are *ethanol* and *methyl tertiary-butyl ether (MTBE)*. Other ethers which may be used are *tertiary-amyl methyl ether (TAME)* and *ethyl tertiary-butyl ether (ETBE)*.

Will oxygenated gasoline perform as well as conventional gasoline in my vehicle?

Oxygenated gasoline will perform as well in modern vehicles with engine control systems which adjust the air-fuel ratio. Oxygenated gasoline may cause some driveability problems in carbureted cars and fuel injected cars without engine control systems because they result in an air-fuel mixture which is more *fuel lean*. Oxygenated gasoline reduces fuel economy, on average, by 2-3%. The odor of gasoline oxygenated with MTBE or the other ethers differs from that of conventional gasoline.

What is reformulated gasoline (RFG)?

Reformulated gasoline (RFG) is a gasoline blended to reduce evaporative and exhaust emissions from vehicles. The characteristics of the gasoline are specified by regulation, either directly or by a model which relates gasoline characteristics to emissions. The federal government and the State of California have somewhat different regulations for RFG. Federal RFG is required in those metropolitan areas which do not meet the federal air quality standard for ozone (*ozone nonattainment areas*). California RFG is required throughout the state. Reformulated gasoline is always oxygenated during the winter and may be oxygenated year-round.

Will RFG perform as well as conventional gasoline in my vehicle?

If the RFG is oxygenated, the answer for the performance of oxygenated gasoline applies. Oxygenated RFG will reduce fuel economy, on average, by 2-3%. Regulations require RFG to have a low vapor pressure during the summer, which could make starting a cold engine more difficult on unseasonably cold days in the spring.

If RFG has a lower fuel economy and more gasoline is needed to go the same number of miles, doesn't this counteract some of the emissions benefit of RFG?

The emissions benefits of RFGs were determined by testing them in fleets of actual vehicles. The test vehicles saw the same fuel economy penalty that your car sees. Since the emissions are measured in units of *grams per mile*, the emissions benefit for RFG already includes any effect of the fuel economy penalty.

Why did my fuel economy drop much more than 2-3% when I began using RFG?

The 2-3% fuel economy penalty for RFG was determined by extensive laboratory testing and has been validated by independent organizations like the California State Automobile Association. The penalty also is in line with the decrease in the heating value of RFG compared to non-oxygenated conventional gasoline. A decrease in fuel economy much greater than 2-3% probably is the result of a mistuned engine or of comparing fuel economy results obtained under different driving and/or weather conditions.

Why did Chevron put a warning label on its dispensers when it introduced RFG in California?

The label warned the owners of older or high-mileage vehicles that testing indicated that California RFG may cause some fuel system parts, particularly those older or worn fuel system parts in a very small percentage of older or high-mileage vehicles, to fail. The parts of concern were parts containing *elastomers* – synthetic rubber-like materials – like ‘O’-rings, hoses, valves and diaphragms. Chevron did not expect RFG to “attack” or otherwise damage the parts. Our concern arose because the properties of RFG differ somewhat from those of conventional gasoline and as some older elastomers tried to adjust to the property change, leaks or other failures might occur. When RFG reached the market place, we learned that the concern was not justified. There is no credible evidence that fuel system leaks or vehicle fires increased after RFG was introduced.

What is knocking?

Spark knock is the sound of abnormal combustion. When combustion in a spark-ignition internal combustion engine is initiated by a spark, the flame front should fan out from the spark plug and travel across the combustion chamber rapidly and smoothly. If the last part of the air-fuel mixture ignites spontaneously (*autoignites*) before the flame front arrives, the sudden jump in the pressure in the cylinder creates the characteristic knocking or pinging sound. Knocking occurs because the octane of the gasoline is below the antiknock requirement of the engine **at that moment**.

Can knocking harm my engine?

Occasional light knocking won’t harm an engine. Heavy or prolonged knocking can result in loss of power, overheating of parts in the cylinder and engine damage.

What is octane?

Octane number is a measure of the antiknock quality of gasoline – the ability of the gasoline to resist knocking when it is burned in an engine. There are two laboratory tests to measure octane which are run in a single-cylinder engine operated under different conditions: *Research octane number (RON)* and *Motor octane number (MON)*. The octane number posted on gasoline dispensers in service stations is the *antiknock index (AKI)* – the average of RON and MON $[(RON + MON)/2]$, usually abbreviated $(R + M)/2$. The AKI was chosen as the posted value because experience showed it to be the best indicator of the antiknock performance of gasoline in the majority of vehicles.

What octane gasoline should I use in my vehicle?

For starters, use a gasoline with the AKI recommended by your owner’s manual. (The owner’s manuals for some older foreign cars recommend an RON value instead of an AKI value. A rule of thumb is that the RON of a gasoline equals the AKI + 5.) Using gasoline with an antiknock rating higher than that required to prevent knock will not improve a vehicle’s performance, including its power, unless the vehicle is equipped with a knock sensor (*see below*).

There are two reasons why your vehicle might knock on a gasoline with the AKI recommended by the owner’s manual. 1) The engine is at the upper end of the octane requirement range. The octane requirement of each engine in vehicles of the same make and model is a little different because of variations in manufacturing tolerances. 2) The octane requirement of the engine increased more than usual because the equilibrium level of the combustion chamber deposits is higher than usual.

Leaded gasoline is no longer available in the United States because it was completely banned from on-road gasoline in 1996. Driving around town or at normal highway speeds with unleaded gasoline will not result in exhaust valve seat recession. Exhaust valve seat recession may occur with unleaded gasoline at higher engine operating temperatures generated by an extended period of high-speed or up-hill driving or towing a heavy load. If a trip is going to involve one or more of these situations and your pre-1971 vehicle hasn't been equipped with metal alloy exhaust valve seats, consider adding a *lead substitute aftermarket additive* to the gasoline in your tank during the trip. Consult your engine manufacturer before using the additive.

What can I do to get better fuel economy?

Good fuel economy is a combination of good vehicle maintenance and sensible driving. Maintenance factors which contribute to good fuel economy are a properly tuned engine, a clean air filter, aligned and balanced front wheels, and tires with the correct air pressure. Since mistuned engines also result in higher emissions, the onboard diagnostic system in a modern car will alert you to an engine problem.

Sensible driving involves smooth, steady acceleration rather than “jackrabbit” starts; driving at moderate rather than high speeds on the highway; not carrying a heavy load, using a luggage rack, or towing a trailer unnecessarily; not using the air conditioner or defroster excessively, and not idling the engine when it could be turned off.

Some factors which reduce fuel economy are beyond your control: water, slush, or snow on the road, head winds, driving up hill, and driving in stop-and-go traffic.

Will premium gasoline give better fuel economy than regular? Will one brand of gasoline give better mileage than another?

Gasolines with higher heating values give better fuel economy. Differences can exist, but they will be small compared to the benefits to be derived from the maintenance and driving tips in the above answer.

Traditionally, premium has had a slightly higher heating value than regular, and, thus, provided slightly better fuel economy. The difference – less than 1% better – is not large enough to offset premium's higher cost. The difference is likely to be less or nonexistent between grades of reformulated gasoline.

There can be differences in heating value among batches of gasoline from the same refinery or among brands of gasoline from different refineries because of compositional differences. The differences are small and there is no practical way for the consumer to identify the gasoline with a higher heating value.

How long can I store gasoline without it going bad?

Gasoline stored in a tightly closed container in a cool place will stay good for at least one year. It is better if the container or gas tank is almost (95%) full. If the container or gas tank will be in the direct sun or will be heated above 80°F much of the time, add an aftermarket fuel stabilizer to the gasoline when you first buy it. Gasoline-oil blends for two-stroke cycle engines stored under the proper conditions will keep as well as gasoline itself.

Can I use motor gasoline in my airplane?

Chevron recognizes that some older planes are certified [Supplemental Type Certificate (STC)] to use motor gasoline. The gasoline must meet the requirements of the gasoline specification (ASTM D 4814) and must not contain ethanol. Chevron strongly recommends AGAINST using motor gasoline in place of aviation gasoline. Aviation gasoline is made to different standards and, because of the serious consequences of engine failure, is distributed with extra attention to purity and cleanliness. In addition, the pilot will not always know whether the gasoline is oxygenated and, if so, what oxygenate it contains. And motor gasoline deposit control additives have not been approved for use in aviation fuels

HANDLING GASOLINE SAFELY

Introduction

Gasoline is dangerous. First, and foremost, it is highly flammable – it is easy to ignite and it burns explosively. Second, exposure to gasoline liquid or vapor can cause adverse health effects.

All companies are required to develop and make available safety information on their products. You may obtain a Material Safety Data Sheet (MSDS) for Chevron gasoline by calling 1-800-689-3998. The MSDS provides detailed information on the hazards associated with gasoline and the appropriate responses.

Chevron's MSDS for gasoline contains the following human health warnings:

DANGER!

- Harmful or fatal if swallowed – can enter lungs and cause damage.
- Vapor harmful.
- Long-term exposure to vapor has caused cancer in laboratory animals.
- May cause eye and skin irritation.
- Extremely flammable.
- Keep out of reach of children.

Filling a Container

There have been several fires at service stations when customers placed metal containers on plastic bed liners in pickup trucks while filling the containers with gasoline. Filling a container is a special situation that requires extra precautions:

- Use only an UL-approved plastic or metal container.
- Shut off the vehicle's engine.
- Place the container **on the ground** a safe distance from the vehicle, other customers, and traffic. Don't fill a container in or on a car or truck.
- Keep the nozzle in contact with the container during filling.
- Manually control the nozzle valve; do not latch it open.¹
- Do not smoke.
- Avoid breathing gasoline fumes.

Flowing gasoline generates a static electric charge that builds up on the gasoline in the receiving container. If the charge isn't given an opportunity

¹ If the nozzle is fitted with a fume-recycling device, the filler-spout seal must be compressed to activate the dispenser.

to dissipate, it could jump from the container to the metal spout of the dispenser nozzle as a static spark. If a spark occurs near the open mouth of the container where the concentration of gasoline vapor and air is in the flammable range, it could ignite the gasoline.

Putting the container on the ground and keeping the nozzle in contact with the container help dissipate the static charge. The charge will dissipate more slowly from a container being filled on an insulating surface – carpet in the trunk of a car and on the bed of a utility vehicle or the plastic bed liner of a pickup truck. Placing the container on the ground has the secondary benefit that an accidental spill won't contaminate the vehicle.

Fill the container only about 95% full. This leaves room for gasoline to expand if it warms up in storage. Without an air space, expansion will force liquid gasoline out of the container or distort the container.

Transporting Gasoline

Before putting a container of gasoline in the trunk of a vehicle or the back of a pickup, tighten the cap of the container and the cap of the air vent, if there is one. Wipe the outside of the container to remove any liquid gasoline or gasoline residue. Secure the container in the trunk or pickup so turns or road vibrations won't cause it to slide around or tip over. Do not leave a container of gasoline in direct sun on a hot day, or in the trunk of a car that is in direct sun on a hot day. Heating the gasoline will build up pressure in the container.

Storing and Handling Gasoline

To avoid a fire, keep the gasoline away from any ignition source (flame or spark) and any ignition source away from the gasoline. There should not be an appliance pilot light or igniter within 50 feet of where gasoline is stored or handled. Gasoline fumes, which are invisible and heavier than air, can travel along floor for some distance when they are not dispersed by air currents. If ignited, the fumes become a fuse that brings the flame back to the liquid gasoline source.

To avoid eye and skin contact, wear safety glasses and gasoline-resistant gloves².

For both fire and health considerations, it is best to handle gasoline outdoors. Ignition sources are less prevalent and the fumes are diluted and dispersed more quickly.

First Aid

Eye Contact: Flush eyes immediately with fresh water for at least 15 minutes while holding the eyelids open. Remove contact lenses, if worn. No additional first aid should be necessary. However, if irritation persists, see a doctor.

Skin Contact: Wash skin thoroughly with soap and water. Remove and wash contaminated clothing. See a doctor if irritation is severe.

Inhalation: If respiratory irritation or nervous systems effects (headache, dizziness) occur, move the person to fresh air. If any of these effects continue, see a doctor.

Ingestion: If swallowed, give water or milk to drink and telephone for medical advice. DO NOT make the person vomit unless directed to do so by medical personnel. If medical advice cannot be obtained, then take the person to the nearest medical emergency treatment center or hospital.

Emergency Information: Call your local Poison Control Center or Chevron Emergency Information Center at (800) 231-0623 (24 hours).

Using Gasoline

Gasoline should be used only as an engine fuel. It should not be used as a solvent, cleaner, barbecue starter or for any other non-engine use.

Occasionally, students propose science projects involving gasoline. Chevron strongly recommends AGAINST student projects requiring the handling of gasoline. The risks are too great for people not completely familiar with the hazards. Gasoline should never be brought into the living space of a house or taken to school.

Disposing of Gasoline

Do not dispose of gasoline by pouring it onto the ground or into a sewer, street drain, or stream or river. These actions are environmentally harmful and may result in a fire or explosion.

Excess gasoline in good condition can be added to the fuel tank of a gasoline-powered car or truck. (Don't dispose of gasoline/oil mixtures for two-stroke cycle engines this way.) Use a funnel with a flexible stem to direct the gasoline past the flap valve in the filler tube of newer vehicles. The funnel will help prevent gasoline from being spilled on the vehicle. Oxygenated gasoline can damage the finish of some vehicles. Flexible stem funnels are available at some auto supply stores.

It's not as easy to get rid of gasoline that has deteriorated. There are organizations that will help dispose of gasoline in an environmentally responsible way. Finding the best option may take some searching. Sources of information are your community's fire department, recycling center, and hazardous waste disposal center. Check the government pages of your phone book to locate these organizations. Commercial organizations are listed in the Yellow Pages under *Environmental & Ecological Services* and *Oils, Waste*. You may have to pay for the disposal, but the cost should be weighed against the cost of repairing an engine damaged by bad gasoline.

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Office of Mobil Sources
United States Environmental Protection Agency
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401 M Street SW
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(202) 233-9000
<http://www.epa.gov/omswww/>

California Air Resources Board
P.O. Box 2815
Sacramento, CA 95814
(916) 322-2990
<http://www.arb.ca.gov/html/homepage.htm>

Vehicles

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Federal Regulations

Fuels and Energy Division
Office of Mobile Sources
United States Environmental Protection Agency
Mail Code: 6406J
401 M Street SW
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<http://www.epa.gov/omswww/>

Code of Federal Regulations, Title 40 – Protection of Environment
Part 51 – *Requirements For Preparation, Adoption, and Submittal of Implementation Plans*
Subpart S – *Inspection/Maintenance Program Requirements*
Part 79 – *Registration of Fuels and Fuel Additives*
Part 80 – *Regulation of Fuels and Fuel Additives*
Part 85 – *Control of Air Pollution From Motor Vehicles and Motor Vehicle Engines*
Part 86 – *Control of Air Pollution From New and In-use Motor Vehicles and New and In-use Motor Vehicle Engines: Certification and Test Procedures*

National Vehicles and Fuel Emission Laboratory
Office of Mobile Sources
United States Environmental Protection Agency
2565 Plymouth Road
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California Regulations

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<http://www.arb.ca.gov/html/homepage.htm>

A B B R E V I A T I O N S

°F	degrees Fahrenheit, the unit of temperature in the United States customary system
°C	degrees Centigrade, the unit of temperature in the metric (SI) system
°API	degrees American Petroleum Institute, the unit of gravity in the API system
ABS	automatic braking system
A/F	air-fuel ratio
AKI	antiknock index, the average of the Research and Motor octane numbers [(RON + MON)/2, which is simplified to (R + M)/2]
API	American Petroleum Institute
ARB	(California) Air Resources Board
ASTM	American Society for Testing and Materials
BDC	bottom dead center, lowest position of piston in a cylinder, relative to the cylinder head
C _n	carbon number of hydrocarbon whose molecule contains “n” carbon atoms
CCDI	combustion chamber deposit interference
CFR	Code of federal regulations
CO	carbon monoxide
CO ₂	carbon dioxide
CRC	Coordinating Research Council
DI	driveability index
DOHC	double overhead cam
DVPE	dry vapor pressure equivalent, the value of vapor pressure obtained by a specific method
ECM	engine control module
EGR	exhaust gas recirculation
EPA	(United States) Environmental Protection Agency
ETBE	ethyl <i>tertiary</i> -butyl ether
EtOH	ethanol
FTP 75	federal test procedure cycle, a dynamometer emissions test cycle
HC	hydrocarbon
HWFET	highway fuel economy test cycle, a dynamometer emissions test cycle
I/M	inspection and maintenance program: program to check condition and performance of a vehicle’s emission systems
kPa	kilopascal, a unit of pressure in the metric (SI) system
MMT	methylcyclopentadienyl manganese tricarbonyl, an antiknock compound
MON	Motor octane number
MTBE	methyl <i>tertiary</i> -butyl ether
NAAQS	national ambient air quality standard

NMOG	non-methane organic gases
NO	nitric oxide
NO₂	nitrogen dioxide
NO_x	oxides of nitrogen
OBD	On-board diagnostics: the ability of engine control module to analyze and diagnose emission system malfunctions
OHC	overhead cam
ONR	octane number requirement (of an engine)
ORI	octane requirement increase (of an engine)
PAH	polynuclear aromatic hydrocarbons, aromatic hydrocarbons with several fused rings
PCV	positive crankcase ventilation
PFI	port fuel injector
PM₁₀	particulate matter with a particle size less than 10 microns
PNA	polynuclear aromatics
POM	polycyclic organic matter
psi	pounds per square inch, a unit of pressure in the United States customary system
RdON	road octane number
RFG	reformulated gasoline
RD	relative density
ROG	reactive organic gases
RON	Research octane number
SI	Système International d'Unités (International System of Units), metric system of measurement
SIP	state implementation plan, a plan to improve air quality
SO₂	sulfur dioxide
SO_x	sulfur oxides
STC	Supplemental Type Certificate, a certificate which can be purchased for some older planes that allows the use of motor gasoline in place of aviation gasoline.
T_v	distillation profile temperature at "v" volume percent evaporated
TAME	<i>tertiary</i> -amyl methyl ether
TBA	<i>tertiary</i> -butyl alcohol
TBI	throttle body injector
TDC	top dead center, highest position of piston in a cylinder, relative to the cylinder head
TEL	tetraethyl lead, an antiknock compound
TML	tetramethyl lead, an antiknock compound
V_t	distillation profile volume percent evaporated at "t" temperature
V/L	vapor-liquid ratio
VOCs	volatile organic compounds
WOT	wide open throttle