

South Asia Urban Air Quality Management Briefing Note No. 7

# **Catching Gasoline and Diesel Adulteration**

Adulteration of gasoline and diesel with lower-priced materials is common in South Asia as elsewhere in the world. Some adulterants increase emissions of harmful pollutants from vehicles, worsening urban air pollution. Others do not, although there is often an indirect adverse effect on society through the loss of tax revenue. This note describes the impact of different types of adulteration on air quality and various methods for detection.

dulteration of automotive gasolines and diesel fuels is widespread throughout South Asia. This can result in sub-optimal performance of transportation fuels, and often, but not always, lead to increased tailpipe emissions of harmful pollutants. The Centre for Science and Environment (CSE) recently prepared a report on gasoline and diesel adulteration in Delhi [1], providing a good overview of the scope of the problem and some technical and economic data on the subject. This note reviews typical forms of adulteration, their impact on exhaust emissions, and how adulteration may be detected.

#### **Types of Adulteration**

Financial incentives arising from differential taxes are generally the primary cause of fuel adulteration (see [2] for background). In South Asia, gasoline carries a much higher tax than diesel, which in turn is taxed more than kerosene (see [3] for a discussion on transport fuel taxation). Industrial solvents and recycled lubricants are other materials with little or no tax.

Specific types of adulteration may be broadly classified as follows:

- Blending relatively small amounts of distillate fuels like diesel or kerosene into automotive gasolines.
- Blending variable amounts (as much as 30 percent) of gasoline boiling range hydrocarbons such as industrial solvents into automotive gasolines.
- Blending small amounts of spent waste industrial solvents such as used lubricants — which would be costly to dispose of in an environmentally approved manner — into gasoline and diesel.
- Blending kerosene into diesel, often as much as 20-30 percent.
- Blending small amounts of heavier fuel oils into diesel fuels.

#### Impact on Emissions and Health

Not all forms of adulteration are harmful to public health. Some adulterants increase emissions of harmful pollutants significantly, whereas others have little or no effect on air quality. In some cases health effects are indirect — for example, large scale diversion of rationed kerosene subsidized for household use to the diesel sector does not increase emissions from diesel vehicles, but deprives the poor of kerosene which can otherwise be used for cooking. Lack of availability of subsidized kerosene forces the poor to continue to use biomass and exposes them to high levels of indoor air pollution. In South Asia, indoor air pollution in turn claims far more lives than urban (outdoor) air pollution (for more information see [4]).

Whenever considering the impact of fuel adulteration on air quality, it is important to keep the impact of adulteration in perspective: the effects on emissions of basic engine design and maintenance usually far outweigh those of changes in fuel composition. When engines are out of tune with the specifications set by the manufacturers, or are poorly maintained, they will emit substantially more pollutants — even when operating on fuels that meet all specification requirements — than properly maintained vehicles.

Fuel adulteration can increase the tailpipe emissions of hydrocarbons (HC), carbon monoxide (CO), oxides of nitrogen (NO<sub>x</sub>) and particulate matter (PM). Air toxin emissions — which fall into the category of unregulated emissions — of primary concern are benzene and polyaromatic hydrocarbons (PAHs), both well known carcinogens. Air toxin emissions such as benzene depend mostly on fuel composition and catalyst performance. PAHs in the exhaust are duc primarily to the presence of PAHs in the fuel itself and, in the case of gasoline, in part due to PAH formation by fuel combustion in the engine. Aside from fuel quality, the amounts of pollutants emitted depend on such parameters as the air-to-fuel ratio, engine speed, engine load, operating temperatures, whether the vehicle is equipped with a catalytic converter, and the condition of the catalyst.

#### Gasoline adulteration

Kerosene is more difficult to burn than gasoline, so that its addition results in higher levels of HC, CO and PM emissions even from catalyst-equipped cars. The higher sulfur level of kerosene (for example, the permissible level in India is 0.25 percent by weight as against 0.10 percent for gasoline) can deactivate the catalyst and lower conversion of engine-out pollutants. If too much kerosene is added, octane quality will fall below the octane requirement of the engines and engine knocking can occur. Besides possibly damaging the engine mechanically, knock can increase PM, HC and NO<sub>2</sub> emissions. The latter two are, amongst others, ozone precursors. With gasoline vehicles not equipped with catalysts, the exhaust smell from kerosene is often rather acrid, creating unpleasant conditions in crowded city streets.

When gasoline is adulterated with diesel fuels, the same general effects occur but usually at lower levels of added diesel fuel. Both diesel and kerosene added to gasoline will increase engine deposit formation including in fuel injectors, potentially leading to increased emissions of PM, HC and CO.

Gasoline may also be adulterated with gasoline boiling range solvents such as toluene, xylenes and other aromatics, or light materials such as pentanes and hexanes (rubber solvents) - available at low or zero tax for their normal industrial use. The gasolines in these cases may well continue to meet all specifications. With "judicious" adulteration, the gasoline would not exhibit driveability problems. Larger amounts of toluene and/or mixed xylenes could cause some increase in HC, CO and NO<sub>2</sub> emissions, and significantly increase the level of air toxins especially benzene — in the tailpipe exhaust. The adulterated gasoline itself could also have increased potential human toxicity if frequent skin contact is allowed. Extremely high levels of toluene (45 percent or higher) could cause premature failure of neoprene, styrene butadiene rubber and butyl rubber components in the fuel systems. This has caused vehicle fires in other parts of the world, especially in older vehicles.

Adulteration of gasoline by waste industrial solvents is especially problematic as the adulterants are so varied in composition. Adulterants may contain halogens, silicon, phosphorous or other metallic elements (found in recycled lubricants); these in turn are quite outside the normal gasoline composition range. They will cause increased emissions and may even cause vehicle breakdown by corroding fuel injection systems and carburetters, and by causing deposits on valves, fuel injectors, spark plugs, oxygen sensors and exhaust catalysts. Even low levels of adulterants can be very injurious and costly to the vehicle operator.

For gasoline, any adulterant that changes its volatility can affect driveability. High volatility (resulting from the addition of light hydrocarbons) in hot weather can cause vapor lock and stalling. Low volatility in cold weather can cause starting problems and poor warm-up.

#### **Diesel adulteration**

The blending of kerosene into automotive diesel fuel is widely and legitimately practiced by the oil industry worldwide as a means of adjusting the low temperature operability of the fuel. This practice is not harmful or detrimental to tailpipe emissions, provided the resulting fuel continues to meet engine manufacturers' specifications (especially for viscosity and cetane number). However, high-level adulteration of low sulfur (for example, 0.05 percent) diesel fuel with higher-level sulfur kerosene can cause the fuel to exceed the sulfur maximum.

PAHs and nitrogen-containing PAHs in diesel exhaust arise primarily from a "flow-through" effect from the PAHs in the fuel composition. As a result, the addition of kerosene tends to reduce exhaust PAH emissions because kerosene generally does not contain significant amounts of PAHs.

As a simplified picture, black diesel smoke results from inadequate air/fuel mixing in the cylinder with locally over-rich zones. Higher fuel injection rates, dirty injectors and injection nozzle tip wear through use can lead to locally over-rich zones in the combustion chamber. Overfueling to increase power output, a common phenomenon worldwide, results in higher smoke emissions and lower fuel economy. Dirty injectors are common because injector maintenance is costly in terms of actual repair costs and down-time consequential losses. The addition of heavier fuels increases in-cylinder deposits and fouls injectors.

The addition of heavier fuel oils to diesel is usually easy to detect because the fuel will be darker than normal. Depending on the nature of these heavier fuel oils and the possible presence of additional PAHs, there could be some increase in both exhaust PM and PAH emissions.

## **Tests for Identifying Adulteration**

A number of analytical techniques are available to detect adulteration. In all cases described below, it is important to have good sampling techniques and access to a good petroleum analytical laboratory. Field techniques produce results more quickly but cannot give results that are as detailed or quantitatively accurate as laboratory tests. For the majority of the tests, accurate data on uncontaminated fuels are also a pre-requisite.

## Density

Some field tests can be used to identify some of the more gross adulteration taking place. The most rugged of these is density determination by portable hydrometers. The CSE report shows that, at 15°C, automotive gasoline sold in Delhi typically has a density of 0.74-0.75 kilograms per liter (kg/ 1) and kerosene around 0.79-0.80 kg/l. Diesel fuel has a density in the neighborhood of 0.835-0.855 kg/l. Used properly, good-quality hydrometers could detect significant adulteration if an accurate density on the base gasoline, for example at the shipping terminal, is available. Success with this approach hinges on a good analytical testing regimen with correlation between field hydrometers and laboratory equipment. The use of digital densitometers as per ASTM (American Society for Testing of Materials) D 4052 provides greater accuracy but these are relatively expensive units and need a closely controlled environment not likely to be found in the field at the point of sale.

## Evaporation

Various evaporation techniques such as the ASTM D 381 unwashed gum test will detect very low concentrations (1-2 percent) of diesel fuel in gasoline and fairly low (5 percent) levels of kerosene in gasoline. This is not a field technique.

## Distillation

The ASTM D 86 type of distillation can be useful for detecting kerosene and diesel in gasoline and also significant additions of toluene and mixed xylenes in gasoline. Accurate and complete D 86 distillation data on the uncontaminated fuels would be essential for comparison and some kind of correlative data among the laboratories involved to validate test precision. Judicious blending of, for example, pentanes, hexanes and toluene into automotive gasoline could go undetected by this test since these are normal gasoline constituents.

## Gas chromatography (GC)

GC is a powerful laboratory-based tool for detecting hydrocarbon-based adulterants but requires experienced analysts as well as skilled interpretation of the results. Original GC fingerprints on as many potential base fuels such as automotive gasolines, diesel fuels and kerosene would be essential. Usually there are fairly well established ratios between key gasoline hydrocarbons such as benzene, toluene and the three isomeric xylenes (unless there is a benzenetoluene-xylene extraction plant at the refinery) so that GC could yield very useful data in skilled hands. Some short time duration tests (15 minutes) have been developed for quick fingerprinting of gasolines suspected of being adulterated with kerosene or diesel and these can be easily detected.

#### Ash content determination

Where ash forming contaminants such as silicones and phosphates from waste industrial solvents may be involved, laboratory tests such as ASTM D 482 to measure ash content could yield useful data since neither gasoline nor diesel fuels normally have measurable ash contents. Other options include atomic absorption (AA) or emission spectrography calibrated for trace metals.

#### Markers

Various chemical markers can be used to identify adulteration, such as of kerosene in gasoline. Covert methods include the use of visible dyes which has been successfully applied in industrial countries. However, where visible dyes have been used in South Asia, they have not been effective. More sophisticated methods include invisible dyes which are reacted in field tests with another chemical to produce a color (used in the Philippines) and chemical markers. Chemical markers increase the cost of products: markers must be purchased and added, and detection equipment needs to be bought, operated and maintained.

#### **Steps to Minimize Adulteration**

It goes without saying that an important step in tackling fuel adulteration is reducing incentives for engaging in this commercial malpractice to the extent possible. The incentive in turn depends on the relative benefit (from adding low-priced materials) and cost (from the risk of being caught and fined or having one's business license revoked). The benefit arises from differential taxation, tax evasion and different production costs, and can be reduced but not eliminated. It is also important to bear in mind that fiscal policy has multiple objectives, and reducing fuel adulteration is only one amongst many. As such, concerns about fuel adulteration, however serious, cannot and should not be the sole driver of fiscal policy. The cost depends on the ability of the regulating authorities to detect adulteration, and to impose sufficiently punishing sanctions to deter recurrence of fuel adulteration.

The manner in which retail fuels are distributed has an important bearing on fuel adulteration. For example, having large numbers of small, independent transport truck operators moving fuels from terminals to the point of sale creates an environment conducive to adulteration. Adulteration may also be occurring with the collusion of the retail outlet operator. If government officials are involved in adulteration, establishing a good monitoring and enforcement mechanism becomes all the more difficult. One effective "market-based" approach is the practice in many industrial countries whereby oil companies market at retail and assume responsibility throughout the supply chain to guarantee fuel quality in order to protect their public image and market share.

Even in the best of circumstances, taking and maintaining samples for checking fuel quality is not easy. In South Asia, finding proper sample containers and not being personally harassed at retail outlets while sampling are just two of the very real operational problems to be resolved. The CSE report describes the problems of auditing and sampling retail outlets. These problems are compounded by lack of experience in checking specifically for adulteration.

The Indian Standards test methods being used today are derived mainly from the Institute of Petroleum (IP)/ASTM method equivalents from the early 1990s. Properly executed, they should be able to give acceptable results, even though some results quoted in the CSE report indicates poor precision in some items such as testing for sulfur content. Precision and repeatability could be improved by setting up programs for cross-checking interlaboratory variability. This requires action by the responsible agencies within Government. The first step is recognition of the existence and seriousness of the problem - both from the consumer and environmental perspectives by sufficiently high levels of Government. Given historically high levels of tolerance for fuel adulteration, strong political will needs to be generated before appropriate regulatory and enforcement steps can be taken.

Although there have been calls for more restrictive density specifications to address fuel adulteration, such steps are not advisable. Specifications should be set to ensure satisfactory vehicle operation and limit emissions. Restricting specifications more than necessary would unduly restrict refinery operating flexibility and increase the cost of supplying fuels.

## Conclusions

Identifying and checking fuel adulteration presents a difficult challenge in the face of enormous incentives involved. Yet as vehicle emission standards are progressively tightened in South Asia, fuel quality and vehicle technology are increasingly integrated, so that having fuels that meet the specifications becomes all the more important for meeting the new emission standards. This note shows that

- Adulteration by heavier materials such as addition of waste industrial solvents and kerosene to gasoline or heavier fuel oils to diesel — will at worst destroy fuel injection systems and generally cause deposits on automotive parts, leading to serious increases in tailpipe emissions.
- Adulteration of automotive diesel fuels by kerosene does not have an adverse effect on exhaust emissions, but adversely affect public health by reducing the availability of kerosene for household use to the poor.
- Fuel adulteration has significant financial benefits for those engaged in it. Therefore, anyone investigating it must have the direct protection of local law enforcement agencies in taking field samples. There must also be credible and independent laboratory testing available to achieve any measure of success.

## References

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