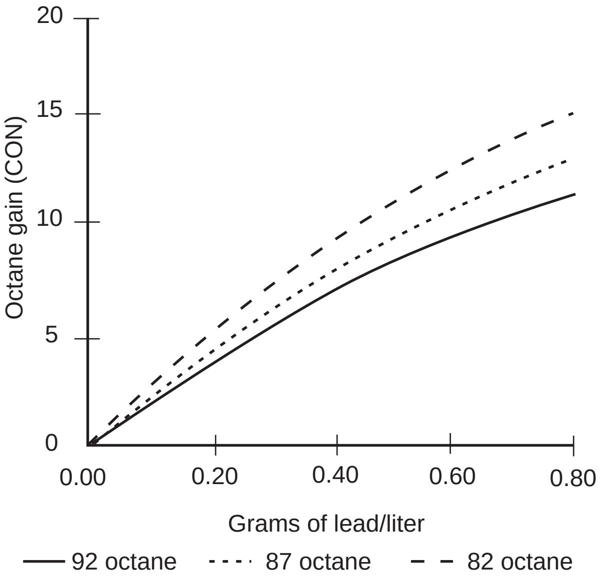
Removal of Lead from Gasoline: Technical Considerations

The Effects of Lead in Gasoline

Refiners add tetraethyl lead (TEL) and tetra- methyl lead (TML) to gasoline to increase octane. In most situations, adding lead is the least expensive means of providing incremental octane to meet gasoline specifications. At sufficiently high levels, addition of lead can increase octane as much as 10 to 15 control octane numbers (Figure 1). Lead susceptibility (the gasoline's propensity to increase in octane with lead addition) is a function of the gasoline's composition and blending properties. In general, the higher a base gasoline's clear octane (before lead addition), the lower is its lead susceptibility. Lead addition is subject to decreasing returns to scale: each increment of lead added to a gasoline blend provides a smaller octane boost than the previous increment. Thus, the marginal cost of octane from lead addition increases as the lead level increases.

Figure 1. Octane Improvement from Addition of Lead: 92, 87, and 82 Octane (CON) Gasolines



In addition to its octane benefit, TEL also provides engine lubrication benefits. Lead in gasoline prevents the wear of engine parts (valve seat recession) under severe driving conditions such as prolonged high speed, towing, and hilly terrain for vehicles—typically older models—manufactured with soft valve seats. Consequently, a mandate for lead removal is often accompanied by requirements for gasoline additives designed to prevent valve seat recession. Sodium-based additives, for example, can be blended into gasoline for this purpose.[1]

Gasoline Octane Number

Octane number is a measure of a gasoline's propensity to knock (ignite prematurely, before the piston reaches the top of the stroke) in standard test engines. The higher a gasoline's octane is, the better is its antiknock performance. Gasolines have two octane ratings. The *research octane number* (RON) measures antiknock performance at low engine speeds; the *motor octane number* (MON) measures antiknock performance at high engine speeds. For any gasoline, RON is higher than MON, usually by 8 to 12 numbers. The difference between the two is called octane sensitivity. Most countries set specifications (minimum levels) for both RON and MON by gasoline grade. The United States, however, sets specifications for the *control octane number* (CON), the arithmetic average of RON and MON.

Oil-Refining Processes

Oil refineries transform crude oils into numerous coproducts. Refined coproducts fall into four broad categories in the order of increasing specific gravity and decreasing volatility: liquefied petroleum gas (LPG) and refinery gases; gasoline; distillate (kerosene, jet fuel, diesel fuel, and heating oil); and residual oil (fuel oil, bunker oil, and asphalt). In virtually all situations, light products—gasoline and distillate—are the most valuable, and heavy products (residual oil) are the least valuable. The following main oil refining processes play key roles in gasoline production.

1. *Crude distillation* splits crude oil into discrete fractions suitable for further processing. It is the indispensable process in any refinery, the precursor for all others. Of the many crude fractions produced in the crude distillation unit, two, *light naphtha* and *medium to heavy naphtha,* are especially important in gasoline blending. Both are in the gasoline boiling range, and both have low octane, making them unattractive as gasoline blendstocks.

Light naphtha (boiling range, 15°–70°C) has three alternative dispositions: (a) direct blending to gasoline in small proportions; (b) direct blending in larger proportions (as present in the crude oil mix), with attendant addition of lead to the gasoline pool; or (c) upgrading by isomerization followed by blending.

Medium and heavy naphtha (boiling range, 160°–375°F) is the primary feed to catalytic reforming, the workhorse of the upgrading process.

2. *Conversion processes* convert heavy feeds into lighter materials for further processing or direct blending. *Fluid catalytic cracking* (FCC) is the most important conversion process. The FCC unit is the heart of a conversion refinery, the most important single determinant of the refinery's profit margin. The FCC unit converts heavy refinery streams, in the residual oil range, into a spectrum of lighter, more valuable refinery streams, including (a) a moderate-quality, high-octane gasoline blendstock (91–93 RON clear) called *FCC gasoline*; and (b) refinery gases, which may be sold or used as feed to alkylation and oxygenate production.

3. *Upgrading processes* improve the octane of crude fractions already in the gasoline boiling range.

Catalytic reforming is the most important and most universal upgrading process for gasoline manufacture. In most refineries, reforming is the primary source of additional octane. Reforming upgrades heavy naphtha (35–55 RON clear) to a prime gasoline blendstock, called *reformate*. The refiner can vary the octane level of reformate over a wide range (90–102 RON clear) by controlling the "severity" of the reformer, primarily by dropping pressure or increasing temperature, or both. No other refining process allows the refiner comparable control of blendstock octane. The combination of high-octane blendstock and operating flexibility usually makes reforming the process of choice for controlling octane level and producing incremental octane-barrels in response to lead phase-out. However, reformate is high in aromatics and benzene: the higher the reformer severity, the higher the aromatics and benzene content. (For example, increasing reformer severity from 90 to 100 RON increases the aromatics content of reformate by roughly 15 percentage points.)

Isomerization upgrades light naphtha (70–78 RON) to *isomerate,* a high-quality, moderate-octane blendstock (85–90 RON).

Alkylation combines light olefins (propylene, n-butenes, and isobutene), which are produced mainly by the FCC unit, and isobutane, coming from hydrocracking, FCC, reforming or straight-run, and NG processing, to form *alkylate,* a high-quality, high-octane blendstock (92–97 RON). Alkylation can be employed only in refineries with an FCC unit.

Polymerization converts light olefins (propylene and butenes) to form polygasoline, an olefinic, high-octane blendstock (97 RON). This process relies on the same olefin feeds as alkylation and can be employed only in refineries with an FCC unit. Polymerization increases the olefin content of gasoline;

- *Etherification processes* produce oxygenate blendstocks such as methylterbutylether (MTBE), ETBE, TAME and DIPE. Of these blendstocks, MTBE is the most widely used. It has exceptionally high octane (115 RON) and other desirable blending properties as well. In the refinery, MTBE is produced using purchased methanol and isobutene produced mainly by the FCC unit. As with alkylation, refinery-based etherification can be employed only in refineries with an FCC unit.
- *Blending* mixes blendstocks and additives to produce finished products that meet specifications. Merchant MTBE, for example, can be purchased on world oil markets. Because of its high octane, blending merchant MTBE is a

common method of adding octane to gasoline without capital investment. Certain gasoline additives such as MMT and DurAlt are also known to increase gasoline octane.

Refinery Categories

Refineries can be categorized into two main groups (see Table 1).

- *Skimming* refineries are relatively simple, comprising crude distillation, treating, upgrading (catalytic reforming in hydroskimming refineries only), and blending. Skimming refineries produce refined products in proportions determined mainly by the proportions of boiling-range fractions in the crude oil mix. For example, a skimming refinery's gasoline output can be no greater than the aggregate volume of the crude oil fractions in the gasoline boiling range (about 60°–400°F).
- *Conversion* refineries are relatively complex, comprising crude distillation, treating, upgrading (at least catalytic reforming and usually other processes as well), conversion (at least one conversion process and often more than one), and blending. Conversion refineries produce more light products and less heavy products than is indicated by the distribution of boiling range fractions in the crude oil mix. Some deep conversion refineries produce an all-light product slate containing no residual oil products. Conversion refineries shift the product slate toward light products by cracking (converting) heavy crude oil fractions into gasoline blendstocks, distillate blendstocks, and refinery gases. Conversion refineries offer more options for lead removal than skimming refineries.

Technical Options for Replacing Lead in Gasoline

Various technical options are available for replacing lead when it is removed from a gasoline pool:

- Increasing the octane of reformate by increasing reformer severity (within the limits of sustainable operations). In some instances, achieving the necessary increase in reformer severity will call for revamping and modernizing the reformer.
- Increasing refinery production of high-octane blendstocks—FCC gasoline, reformate, isomerate, alkylate, polygasoline, and ethers (MTBE)—by increasing the utilization of existing process units and, if necessary, expanding or revamping existing process units or adding new units. As noted above, alkylate, polygasoline, and ethers can be produced only in conversion refineries. Increasing their production from existing units calls for increasing the output of the refinery's FCC unit;
- Reducing the volume of light naphtha in the gasoline pool, by (a) increasing the volume of light naphtha upgraded to isomerate; (b) increasing the volume of light naphtha sold to the petrochemical sector; or (c) reforming a part (the higher boiling range materials) of he light naphtha stream.
- Blending high-octane blendstocks, such as merchant MTBE, or octane enhancing additives, such as MMT—into the gasoline pool.
- Blending additional butanes into the gasoline pool. (This, however, will increase the volatility of gasoline.)

These technical options may be applied in any combination that is technically feasible in a given refinery. Each refinery has its own capital stock

Table 1. Refinery Categories and Processes

	Skimming		*Conversion*		
Process	*Topping*	*Hydroskimming*	*Coking*	*Catalytic cracking*	*Deep conversion*
Crude distillation	•	•	•	•	•
Treating	•	•	•	•	•
Blending	•	•	•	•	•
Upgrading		•	•	• •	• •
Conversion			•	• •	• • •
Oxygenate production				•	•

and cost structure and faces a unique set of costs and technical requirements when it seeks to remove lead from its gasoline pool. Determining the optimal combination of technical options, therefore, calls for detailed refinery analysis.

The Cost of Lead Phase-Out

The cost of lead phase-out depends on a number of factors, including: the initial lead concentration in gasoline, the processing capabilities of the refinery, planned refinery modernization or modification to meet evolving product demands, and limits on other gasoline properties (e.g., volatility, aromatics, and benzene).

The cost of lead removal is generally in the range of US$0.02–$0.03 / liter of gasoline with initial lead levels of 0.6 g / liter or more and about US$ 0.01–$0.02 / liter for initial lead levels of about 0.15 g / liter. Complex refineries with conversion capacity tend to have lower lead removal costs than do technically less-advanced refineries with limited process options. Refinery modernization, therefore, generally facilitates the phase-out of lead.

Analysis of Lead Phase-Out

Analyzing lead phase-out alternatives can be carried out by a combination of detailed engineering analysis and refinery modeling. This approach exploits detailed information that engineers can develop regarding the refinery of interest and makes it possible to assess numerous alternatives for lead removal and their effects on refinery economics and gasoline quality. Refiners customarily rely on refinery models (linear programming models configured to represent their operations) to optimize refining and blending operations and as planning tools to assess the necessary changes in operations, the required process additions, and the blendstock or additive purchases needed to phase lead out of gasoline.

Modeling provides a quick and relatively inexpensive method of assessing the economic and technical aspects of lead reduction, such as: (a) alternative technical approaches for lead phase-out, including process upgrading, process additions, changes in operating procedures, and the use of purchased high-octane blendstocks or additives; (b) cumulative refining costs; (c) investment requirements; (d) changes in gasoline composition; and (e) the potential costs and investment requirements of other constraints on refinery operations, such as limits on certain gasoline properties (e.g., aromatics content, benzene content, and volatility). Refinery analysis generally consists of the following steps:

- *Development of technical data on the refinery*. Actual process capacities and yields (and the potential for upgrading), crude oil slate, product slate, lead use, gasoline grade splits, prices for crude oil and refined products, and product specifications for the time period of interest are established.
- *Development of crude oil assays*. If not already incorporated in the refinery model, distillation curves for the crude oils processed by the refinery are constructed.
- *Adjustment of capital costs and required rates of return*. The costs of new process capacity are adjusted and incorporated in the refinery model, along with the rate of return used to annualize capital costs, to reflect the economic conditions faced by the refinery of interest.
- *Calibration of the refinery model*. The refinery model is configured so as to yield reasonable values for key measures of refinery operations: marginal refining costs at observed product volumes, marginal costs of meeting product specifications, gasoline blend recipes, lead use, and capacity utilization of various refining processes. The calibration case serves as the base for comparing the results of subsequent "lead reduction" cases. A well-calibrated refinery model increases confidence in the results of subsequent model runs.
- *Evaluation of various lead reduction cases for the projected product slate*. Once the refinery model is calibrated to represent baseline operations, further model runs are made to assess the feasibility and cost of progressively lower lead limits for gasoline. These model runs are designed to evaluate the effects of various approaches for reducing lead use on refinery operations, such as changes in operating severity, the addition of new process capacity (reforming, pen-hex isomerization, and so on), and the use of additives.

Note

1. One such additive is Lubrizol's Powershield 8164. At the recommended concentration of 0.7 grams per liter (g/l), bulk blending of Lubrizol's additive in gasoline costs about US$0.003 per liter.

Sources

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