

# Review of Market for Octane Enhancers

## Final Report

*J.E. Sinor Consultants, Inc.  
Niwot, Colorado*



**NREL**

**National Renewable Energy Laboratory**

1617 Cole Boulevard  
Golden, Colorado 80401-3393

NREL is a U.S. Department of Energy Laboratory  
Operated by Midwest Research Institute • Battelle • Bechtel

Contract No. DE-AC36-99-GO10337

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NREL Technical Monitor: K. Ibsen

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## **INTRODUCTION AND MARKET SETTING**

### **THE USE OF BLENDING AGENTS**

Crude oil is easily separated into its principal products (gasoline, distillate fuels, and residual fuels) by simple distillation. However, neither the amounts nor the quality of these natural products matches demand. Whereas the potential yield of gasoline directly from crude oil is less than 20%, the demand is about 50%. The heavy material must be converted to lighter material; at the same time, the octane number of many refinery streams must be improved. The naphtha fraction, which boils at 0°–210°C, is used to make gasoline. Virgin naphtha can be used directly as gasoline, except that its octane value is too low (78 research octane number [RON], 75 motor octane number [MON]). Before lead was banned, enough tetraethyl lead could be added to raise the octane number to acceptable levels. Today, octane requirements must be achieved by changing the chemical composition of the straight-run gasoline fraction.

Catalytic reforming is the chief process used to increase the octane of gasoline components. The feed to a reforming process is naphtha (usually virgin naphtha) boiling at 80°–210°C. Reformers generate highly aromatic, high-octane product streams that can have RON values higher than 100 and MON values of 90. Other chemical reaction processes used to raise octane number include alkylation and isomerization.

The alternative to chemical rearrangements for achieving the necessary increase in octane number is to use an octane-enhancing blending agent. Blending agents are gasoline components that are used at levels as high as 20% and that are not natural components of crude oil. Currently most blending agents are oxygenated compounds, comprising ethers such as methyl tertiary butyl ether (MTBE) and alcohols such as ethanol. Although they are widely used today, both MTBE and ethanol have disadvantages, and neither is likely to be able to satisfy all future needs for octane enhancement. This leaves a continuing market opening for new, high-octane blending agents. The major question addressed by this study is whether an aromatic compound, such as might be obtained as a by-product of lignin processing, could satisfy a part of the continuing need for octane enhancement in most U.S. refineries.

### **THE PETROLEUM REFINING INDUSTRY**

The number of refineries continues to decline slowly; the remaining ones operate at higher capacity and with greater efficiency. For U.S. refiners the 1990s were characterized by low product margins and low profitability (1). Cash operating margins were low, as was return on equity (about 5%). Part of the reason is the cost of regulation. U.S. refineries spent about \$30 billion during the 1990s to comply with government mandates (largely environmental).

Refineries also have to deal with the economic impacts of variable crude prices, crude quality variability, and low marketing and transport profit margins. Consequently, there is a need for increased flexibility, increased throughputs, higher conversions, greater process efficiency, operating cost reductions, and greater reliability. In general, low prices over a long stretch during the 1990s prompted domestic refiners to pursue greater value from their fixed assets while reducing operating costs and improving efficiency. The use of blending agents with desirable properties and prices can assist refiners in all these areas by avoiding the need for new capital investment and environmental control costs.

Table 1 provides data on the distillation and downstream charge capacity of U.S. refineries over the past 10 years. Table 2 shows the potential relative mix of products from downstream processing over the past decade, based on the production capacity of U.S. operable refineries.

### **PETROLEUM MARKET TRENDS AND STATISTICS**

The supply of refined petroleum products has increased by more than 3 million bbl/d since 1970 (see Table 3). In 1998 more than 18 million bbl/d of refined petroleum products were supplied in the United States. U.S. refiners rely on domestic and foreign producers for crude oil inputs, and for some unfinished

TABLE 1

**DISTILLATION AND DOWNSTREAM CHARGE CAPACITY**  
(Thousand Barrels per Stream Day)

Year	Atmospheric	Vacuum	Thermal	Catalytic Cracking		Catalytic	Catalytic	Catalytic	Fuels
	Crude Oil			Cracking	Fresh				
	Distillation	Distillation	Cracking			cracking		treating	asphalting
1987	16,460	6,935	1,928	5,251	466	1,189	3,805	9,083	230
1988	16,825	7,198	2,080	5,424	381	1,202	3,891	9,170	240
1989	16,568	7,225	2,073	5,324	326	1,238	3,911	9,440	245
1990	16,507	7,245	2,108	5,441	314	1,282	3,896	9,537	279
1991	16,557	7,276	2,158	5,559	304	1,308	3,926	9,676	271
1992	16,633	7,172	2,100	5,608	280	1,363	3,907	9,644	276
1993	15,935	6,892	2,082	5,540	244	1,397	3,728	9,677	269
1994	15,904	6,892	2,107	5,586	191	1,376	3,875	10,616	261
1995	16,326	7,248	2,123	5,583	169	1,386	3,867	10,916	251
1996	16,287	7,349	2,050	5,595	155	1,388	3,727	11,041	275
1998	16,936	7,537	2,046	5,919	153	1,552	3,779	11,461	318

Source: *Petroleum Supply Annual 1998, Volume 1*. U.S. Department of Energy, June 1999.

TABLE 2

**CAPACITY FOR SELECTED REFINERY UNIT PRODUCTS**  
(Thousand Barrels per Stream Day)

Year	Alkylates	Aromatics	Asphalt	Isomers	Lubricants	Marketable	Hydrogen	Sulfur
			and			Petroleum		(short
			Road Oil			Coke	(MMcfd)	tons/day)
1987	974	287	788	326	250	364	2,569	23,806
1988	993	289	788	465	232	368	2,418	27,639
1989	1,015	290	823	469	230	333	2,501	28,369
1990	1,030	290	844	456	232	341	2,607	24,202
1991	1,077	292	866	490	229	367	2,527	23,875
1992	1,095	290	812	494	217	356	2,644	23,811
1993	1,083	286	814	499	217	393	2,674	25,940
1994	1,086	278	793	499	213	410	2,940	24,554
1995	1,105	285	846	502	217	427	3,139	24,885
1996	1,120	288	872	577	244	458	3,052	26,466
1998	1,171	302	845	666	233	441	3,104	26,423

Source: *Petroleum Supply Annual 1998, Volume 1*. U.S. Department of Energy, June 1999.

TABLE 3

**OVERVIEW OF PETROLEUM SUPPLY**  
(Million Barrels per Day)

Year	Field Production			Imports	Petroleum Products Supplied
	Total Domestic*	Crude Oil	Natural Gas Plant Liquids		
1984	10.554	8.879	1.630	5.437	15.726
1985	10.636	8.971	1.609	5.067	15.726
1986	10.289	8.680	1.551	6.224	16.281
1987	10.008	8.349	1.595	6.678	16.665
1988	9.818	8.140	1.625	7.402	17.283
1989	9.219	7.613	1.546	8.061	17.325
1990	8.994	7.355	1.559	8.018	16.988
1991	9.168	7.417	1.659	7.627	16.714
1992	8.996	7.171	1.697	7.888	17.033
1993	8.836	6.847	1.736	8.62	17.237
1994	8.645	6.662	1.727	8.996	17.718
1995	8.626	6.560	1.762	8.835	17.725
1996	8.607	6.465	1.830	9.478	18.309
1997	8.611	6.452	1.817	10.162	18.620
1998	8.392	6.252	1.759	10.708	18.917

\*Includes crude oil, natural gas plant liquids, and other liquids. Beginning in 1993, fuel ethanol blended into finished motor gasoline and oxygenate production from merchant MTBE plants are also included.

Source: *Petroleum Supply Annual 1998*. U.S. Department of Energy, Energy Information Administration, July 1999.

feedstocks (primarily motor and aviation gasoline blending components) and refined products. Over the past 10 years imports of crude have risen steadily (Table 3).

Refiners have been able to add refining capacity and keep pace with demand. As long as capacity can meet demand, refiners will import crude oil rather than refined products.

Projections indicate that, although distillation capacity will increase to some degree at U.S. refineries, U.S. petroleum imports could continue to rise if oil prices remain low. More importantly, increases in the level of imports will be affected by domestic production, which is declining. The import situation will be exacerbated by increasing environmental restraints and costs, which greatly inhibit the construction of new facilities to expand refinery distillation capacity. However, imports of refined products depend on competition in the marketplace between domestic and foreign refiners, as well as on capacity.

## REFINERY PRODUCTS

About 90% of the crude oil entering a refinery is converted to fuel products, including gasoline; distillate fuel oil (diesel fuel, home heating oil, industrial fuel); jet fuel (kerosene and naphtha types); residual fuel oil (bunker fuel, boiler fuel); kerosene; liquefied petroleum gases (propane, ethane, butane); and coke.

Another category of petroleum products includes the non-fuel products, represented by asphalt and road oil, lubricants, naphtha solvents, waxes, non-fuel coke, and miscellaneous products. The third and smallest category includes petrochemicals and petrochemical feedstocks such as naphtha; ethane; propane; butane; ethylene; propylene; butylene; benzene, toluene, xylene (BTX); and others. Some compounds, such as toluene, can become product components in all three market sectors. Many have relatively high octane values and may be used as octane enhancers.

The annual supply of refined products to consumers is derived from a combination of a small amount of field production (natural gas liquids, hydrocarbon [HC] liquids, blending components), products generated at refineries, imported refined products, and stocks on hand. Refinery production is dominated by gasoline production (more than 46%).

Distillate and residual fuels compose the next largest share (about 25% of refinery production). Trends in the quantity of petroleum products (refinery output plus field production plus stocks, including imports) over the past 5 years are shown in Table 4.

The principal classes of refining products, along with their typical boiling ranges and uses, are shown in Table 5.

TABLE 4

**SUPPLY OF U.S. REFINED PRODUCTS**  
(Million Barrels)

	<u>1997</u>	<u>1996</u>	<u>1995</u>	<u>1994</u>	<u>1993</u>
Natural Gas Liquids and LRG	101.6	92.6	101.2	108.0	117.1
Finished Products					
Gasoline	210.2	197.6	204.8	217.4	228.4
Special Naphthas	2.11	1.9	2.0	2.2	2.5
Kerosene	6.3	7.0	7.2	8.0	4.1
Distillate Fuel	134.8	126.7	130.2	145.2	140.9
Residual Fuel	41.8	45.9	37.2	41.9	44.2
Kerosene Jet Fuel	39.8	39.8	39.5	45.6	38.0
Naphtha Jet Fuel	1.7	0.08	0.60	1.2	2.4
Unfinished Oils	88.7	87.9	86.5	91.3	88.4
Other Refined Products*	60.1	58.4	59.8	63.0	58.9
Total	687.0	657.7	667.9	723.9	724.8

\*Lubricants, waxes, petroleum coke, asphalt/road oil, miscellaneous products.

Source: *Petroleum Supply Annual, 1996*. U.S. Department of Energy,  
Energy Information Administration, June 1997.

TABLE 5

**MAJOR PETROLEUM PRODUCTS**

<u>Product</u>	<u>Boiling Range (°C)</u>	<u>Uses</u>
Low Octane Gasoline	0 - 200	gasoline, solvents
High Octane Gasoline	0 - 200	high octane gasoline
Liquid Petroleum Gas	-160 - 0	fuel gas, bottled gas, petrochemical feedstock
Diesel Fuels	175 - 370	fuel for diesel engines
Jet Fuel	65 - 290 (military) 175 - 290 (commercial)	gas turbine (jet) engines
Distillate Fuel Oil	175 - 370	residential and commercial heating
Residual Fuel Oil	260 - 650	electrical generation, large steam plant, marine fuel
Lubricating Oils	650+	automobile, aircraft, marine engines; refrigeration, electrical transformers, heavy machinery lubrication
Asphalt	nonvolatile	coatings, paving
Coke	nonvolatile	fuel, electrode manufacture

## CHANGING FUEL SPECIFICATIONS

### GASOLINE COMPOSITION

In the United States there is no single national specification for conventional gasoline properties other than octane level and lead content for gasoline sold in areas that are in compliance with National Ambient Air Quality Standards (NAAQS). The former American Automobile Manufacturer's Association (AAMA) published an "AAMA Gasoline Specification." The American Society for Testing and Materials (ASTM) maintains several standards such as levels of manganese, peroxides, water, and gum, but does not address fuel composition for gasoline properties.

### OTHER GASOLINE REQUIREMENTS

To satisfy high-performance automotive engines, gasoline must meet exacting specifications, some of which are varied according to location and based on temperatures or altitudes.

Octane is probably the single most recognized measure of gasoline quality. The octane value of gasolines must be posted on service station dispensers. The other requirements are not as well known.

#### Volatility

The properties of a gasoline that control its ability to evaporate are also critical to good vehicle operation. In an Otto cycle engine, the fuel must be in the vapor state for combustion to take place. The volatility or vaporization characteristics of a gasoline are defined by three ASTM tests: Reid vapor pressure (RVP) (ASTM D323), the distillation curve (D86), and the vapor/liquid ratio (V/L) (D2533) at a given temperature.

Distillation data may be expressed in two ways: the percent evaporated at a given temperature ( $E_{xxx}$ ); or the temperature for a given percent evaporation ( $T_{yy}$ ). Because  $E_{xxx}$  values blend linearly, these are generally preferred by refiners and blenders. Gasoline performance specifications have been reported in both ways. ASTM specifications generally prefer the  $T_{yy}$  format.

The V/L ratio tests measure the amount of vapor formed from a given volume of liquid at a given temperature at atmospheric pressure. A common measure for specifying gasoline is the temperature at which the V/L ratio is 20 ( $T_{V/L=20}$ ). Although V/L can be measured experimentally, the test is difficult and time consuming, and techniques have been developed to calculate it from RVP and D86 values.

When designing fuel volatility targets, gasoline blenders must strike a balance between various driveability performance characteristics. Driveability refers to the ability of a car to start easily, accelerate and idle smoothly, and respond to changes in throttle position. Too much volatility is as problematic as too little. Targets must be matched to local ambient temperature conditions. Volatility requirements, like octane, are strong functions of vehicle design.

To control evaporative emissions, various state and federal regulations limit the allowable RVP of gasoline by season and location. Any blending component with an RVP higher than about 7 psi could face market limitations.

#### Startability

To achieve combustion in an Otto cycle engine, the air/fuel ratio in the combustion chamber must be near stoichiometric. Unfortunately, when the engine is first started, the walls of the combustion chamber and the intake manifold are not hot enough to vaporize much fuel. Therefore, the vehicle is designed to meter extra fuel and less air to the engine upon startup so there is adequate vapor in the engine to support combustion. The ability of a fuel to achieve good starting can be correlated with RVP and a measure of the front end of the distillation curve, either  $E_{70}$  or  $T_{10}$ .

## Vapor Lock

At the other end of the spectrum from starting is vapor lock, which results from too much volatility. Vapor lock occurs when too much fuel evaporates and starves the engine or provides too much fuel to the engine. It occurs on days that are warmer than usual and when the car has reached full operating temperatures.

## Warmup

Warmup refers to the period of operation that begins immediately after the car has started and continues until the engine has reached normal operating temperatures, usually after 10 minutes or so of operation.

From the fuel's perspective, the middle of the distillation curve plays the largest role in achieving good warmup performance. Under the vehicle operating regime, the front end of the fuel totally evaporates. The back end of the fuel, or heaviest molecules, have trouble evaporating. The molecules boiling at about 100°–150°C are the most important during warmup.

The most common expression for controlling driveability is the driveability index (DI), which has the form:

$$DI = 1.5T_{10} + 3T_{50} + T_{90}$$

Generally, fuels that have values of DI below 570 when T is in °C (1,200 when T is in °F) provide good warmup driveability performance. During a load increase the more volatile components of the fuel (the front end) will vaporize preferentially and enter the engine. The various natural fractions in a fuel will have different octane ratings.

Such a fuel (composed of natural boiling fractions) is unlikely to give an acceptable engine performance, as the fractions that boil at 45°–105°C have a low RON. A useful concept here is the  $\Delta$  octane number (ON). This is the difference between the knock rating of the whole gasoline, and the knock rating of the gasoline boiling below 100°C. The lower the  $\Delta$  ON, the better the transient performance of the gasoline in avoiding knock.

## Back-End Volatility

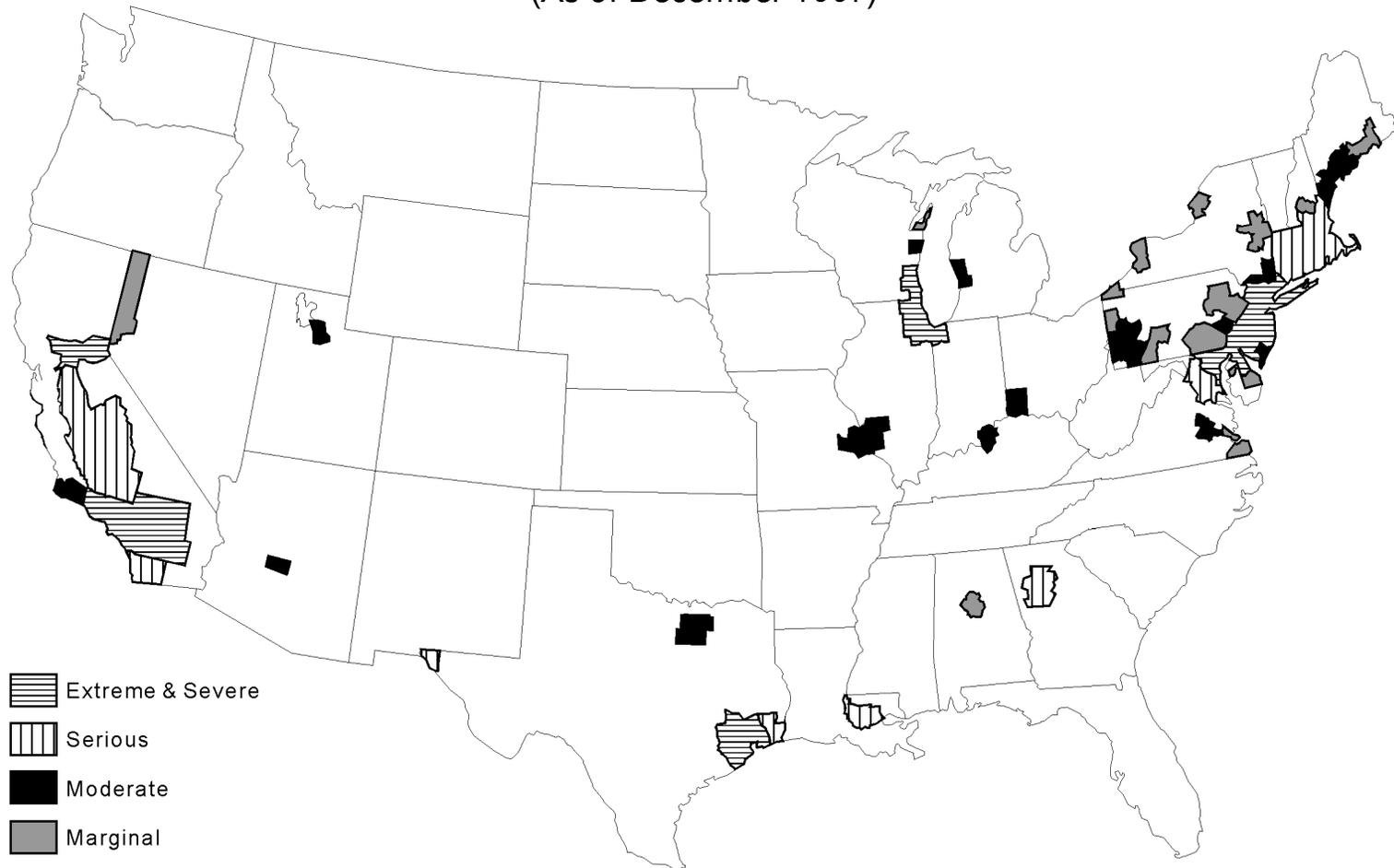
The portion of the gasoline that boils at temperatures higher than 150°C is called the back end. Molecules in this region have high energy density and contribute significantly to fuel economy. Too much material in this boiling range, however, can cause problems because it is hard to volatilize and tends to accumulate on the walls of the cylinder when the engine is cold. From there it can be washed into the oil sump and dilute the oil. Generally, as the engine heats up this material evaporates. However, if there are too many back ends in the gasoline, some may not boil off and the performance of the lubricant may be degraded. Heavy molecules, such as those with more than 12 carbon atoms, may contribute to combustion chamber deposits. Condensed ring aromatics are particularly effective contributors to these deposits. Vehicle volatility requirements are strong functions of ambient temperatures.

## FEDERAL PHASE II REFORMULATED GASOLINE

The Clean Air Act Amendments of 1990 provide that only reformulated gasoline (RFG) may be sold in nine areas of the country classified as extreme or severe for ozone pollution (Figure 1). Other areas that have a lesser degree of nonattainment have been allowed to opt into the RFG program. Including both the required areas and the opt-in areas, as much as 50% of the gasoline sold in the United States was originally expected to be RFG. Phase I began January 1, 1995; Phase II began January 1, 2000. The U.S. Environmental Protection Agency (EPA) expected the Phase I program to achieve a 15%–17% reduction in volatile organic compounds (VOCs) and toxic emissions from motor vehicles compared

FIGURE 1

CLASSIFIED OZONE NONATTAINMENT AREAS  
(As of December 1997)



- Extreme & Severe
- Serious
- Moderate
- Marginal

(Transitional & Incomplete Data Areas Not Included)

SOURCE: THE CLEAN FUELS REPORT

with 1990. Phase II will reduce VOCs by 25%–29%, toxics emissions by 20%–22%, and nitrogen oxides (NO<sub>x</sub>) by 5%–7%. All reductions are relative to the average 1990 U.S. baseline quality.

All RFG must contain at least 2.0% oxygen by weight, a maximum of 1.0% benzene by volume, and must not contain heavy metals. Sulfur, T<sub>90</sub>E, and olefins content are not reduced, but may not be higher than a refiner's 1990 average. The aromatic HC content cannot exceed 25% by volume on average. A summary of the regulation is given in Table 6.

TABLE 6

**U.S. REFORMULATED GASOLINE REQUIREMENTS**

**Fixed Specification Requirements**

Parameter

Benzene, %v/v max	1.0
Oxygen, %m	2.0 - 2.7
Heavy Metals	none without an EPA waiver
T90E, Sulfur, Olefins	average no greater than refiner's 1990 average
Detergent Additives	compulsory

**Phase II (2000 onward) Complex Model**

(All emission reductions are relative to 1990 baseline quality)

<u>Parameters</u>	<u>VOC</u>		<u>Toxics</u>	<u>NOx</u>
	<u>(% reduction) (min)</u>		<u>(% reduction)</u>	<u>(% reduction)</u>
Region	1 (south)	2 (north)	all	all
Batches	27.5	25.9	20.0	5.5
Average	29.0	27.4	21.5	6.8

**Statutory Baseline Parameters - 1990 Average Quantity**

Gravity	59.1
Benzene	1.6%v
Aromatics	28.6%v
Olefins	10.8%v
Sulfur	338 ppm
Distillation	
T50	97°C
T90	167°C
E93C	46%v
RVP	8.7 psi
BEE, Benzene Exhaust Emissions, g/mile =	$1.884 + (0.949 \times \%benzene) +$
0.113 (%aromatics - %benzene)	

Source: 17

Refiners are now required to use a complex model, a set of equations correlating a gasoline's properties to its emissions characteristics, for certification.

Supplies of conventional gasoline are also regulated to prevent any increase in emissions (the so-called "anti-dumping" rule). Aromatics and benzene are controlled by means of a formula (benzene exhaust emissions, see footnote in Table 6). Emissions of benzene, toxics, and NO<sub>x</sub> are not allowed to exceed 1990 values, and VOC emissions are controlled by regional RVP limits. Baseline (1990) conventional gasolines cannot exceed the limits shown in Table 7.

In California, only California reformulated gasoline (CaRFG) may be sold. In 1999 gasoline production in the United States was about 7.85 million bbl/d, of which 19.5% was considered to meet federal RFG standards and 12% to meet CaRFG standards. In September 1998 the EPA expanded its definition of areas that would be allowed to opt in, potentially allowing as many as 80 more air quality areas across the country to opt into the RFG program. The American Petroleum Institute (API) and the National Petroleum Refiners Association (NPRA) filed suit. In January 2000 the U.S. Court of Appeals for the D.C. Circuit handed down a decision in API and NPRA versus EPA, overturning EPA's allowance of additional areas to opt into the RFG program. The court ruled that "Congress provided for opt-in only for [nonattainment] areas classified as Marginal, Moderate, Serious or Severe. It meant what it said."

TABLE 7

**MAXIMUM ALLOWED COMPOSITIONAL LIMITS  
FOR BASE GASOLINE**

<u>Generic Certification</u>	<u>T<sub>90</sub>, °C</u>	<u>Olefins, %v</u>	<u>Aromatics, %v</u>
National	180	18.7	41.2
PADD I	181	22.2	42.5
PADD II	178	14.4	38.3
PADD III	181	18.2	39.5
PADD IV	173	19.4	31.15
PADD V	178	11.5	44.2

PADD = Petroleum Administration for Defense District

Source: 17

**EPA'S NEW TIER II SPECIFICATION FOR SULFUR CONTENT**

In May 1999 the Clinton Administration released proposed rules regulating Tier II vehicle emissions and sulfur content in gasoline. The rule will slash the average sulfur content of all gasoline by 90%. The EPA issued its Notice of Final Rulemaking in December 1999.

## Sulfur in Gasoline

As seen in Table 8, the EPA has put forth a phased-in approach for limiting sulfur content in RFG and conventional gasoline in three ways:

- Individual refineries must produce gasoline with an average sulfur content of no more than 30 ppm beginning January 1, 2005.
- Refiners and importers must meet “corporate-pool” average sulfur content levels of 120 ppm beginning January 1, 2004, and 90 ppm beginning January 1, 2005.
- Each gallon of conventional gasoline and RFG must not exceed the per-gallon caps of 300 ppm beginning October 1, 2003, and dropping to 80 ppm January 1, 2006.

An averaging, banking, and trading program will be available for fuels produced with less than 150 ppm beginning in 2000. Levels higher than 30 ppm can be sold through 2004 and 2005 if the refiner has accumulated enough of these credits.

TABLE 8

### NEW SULFUR LIMITS IN GASOLINE

	For the Average Period Beginning:		
	<u>January 1, 2004</u>	<u>January 1, 2005</u>	<u>January 1, 2006+</u>
Refinery/Importer Average (ppm)	--	30	30
Corporate Pool Average (ppm)	120 *	90 *	per-gal. cap applies
Per-Gallon Cap (ppm)	300 **	300	80

\*If a refiner obtained sulfur credits by earlier-than-required sulfur reductions, the credits could be used to sell some gasoline containing more than 30 ppm sulfur, but in no case could these corporate pool averages be exceeded.

\*\*This per-gallon cap must be met beginning October 1, 2003.

Source: EPA

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## Flexibility for Small Refiners

Domestic and foreign refiners that employ no more than 1500 people corporation-wide will have 4 more years to comply with the proposed rule (until January 1, 2008). Table 9 provides a brief summary of the small refiner sulfur standards, which are directly tied to the individual refinery baseline sulfur levels.

## Geographic Phase-In Area

The EPA also defined a Geographic Phase-In Area (GPA), consisting of states that have somewhat less urgent environmental need in the near term for reductions in ozone precursors and whose emissions are less important in terms of ozone transport concerns. This area includes Alaska and some states in the Great Plains and Rocky Mountains (Figure 2).

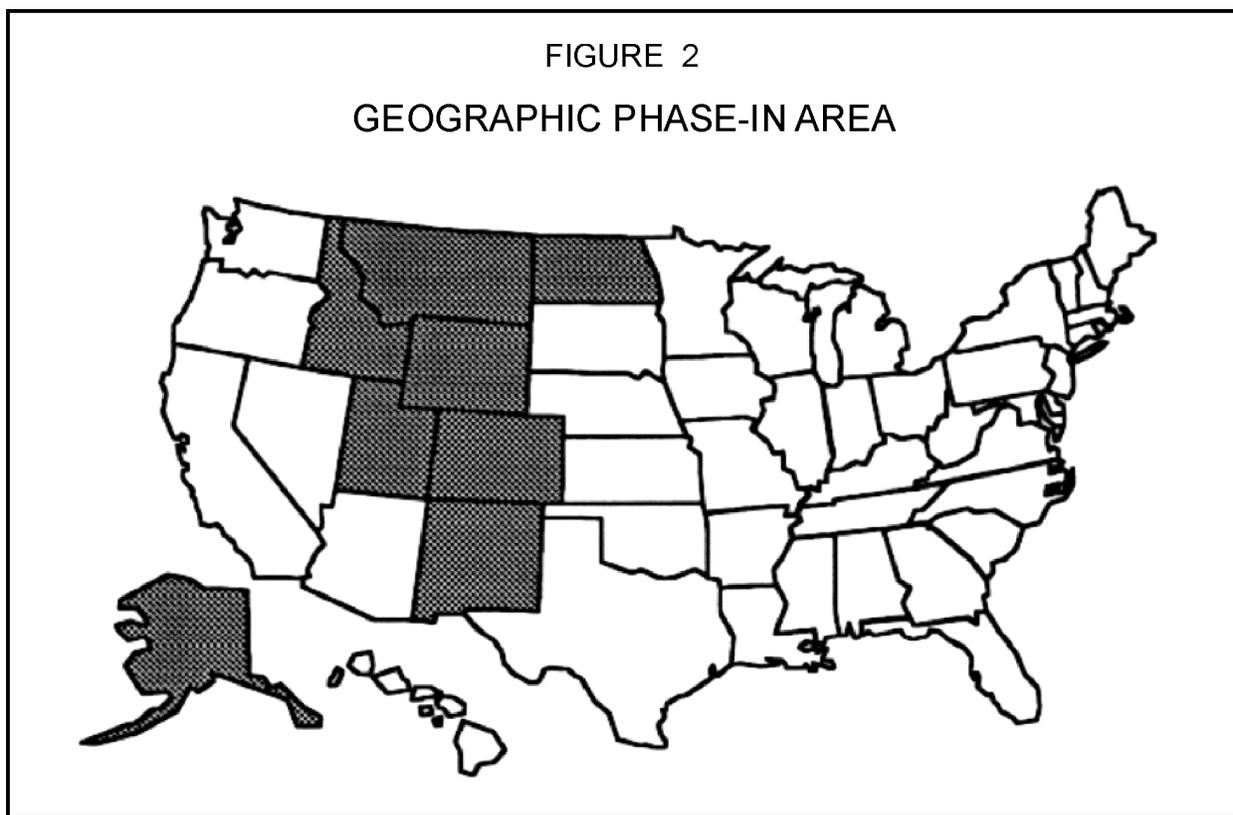
The refining industry in the GPA is dominated by relatively low-capacity, geographically isolated refineries, many of which are owned by independent companies. Such refineries face special challenges in complying with the national program requirements by 2004. They are therefore being given 1 more year to comply, compared to the rest of the country.

TABLE 9

**SMALL REFINER SULFUR STANDARDS**

<u>Refinery's Baseline Sulfur Level (ppm)</u>	<u>Sulfur Standards (ppm) That Apply During 2004-2007</u>
0 to 30	Refinery average: 30 Cap: 80
31 to 80	Refinery average: no requirement Cap: 80
81 to 200	Refinery average: baseline level Cap: factor of 2 above the baseline
201 and Above	Refinery average: 200 ppm or 50% or baseline, whichever is higher, but in no event greater than 300 ppm Cap: factor of 1.5 above baseline level

Source: EPA



The GPA provision covers all gasoline produced or imported for use in the GPA, whether refined there or brought in by pipeline, truck, rail, etc. Refineries and importers must meet a 150-ppm average and a 300-ppm cap for all gasoline produced or imported for the GPA under this program beginning January 1, 2004. However, if a refinery's or importer's 1997–1998 average sulfur level is less than 150 ppm, that refinery's or importer's gasoline has a standard of its baseline plus 30 ppm but in no case greater than 150 ppm (Table 10). For example, a refinery with a baseline of 100 ppm would have a sulfur standard of 130 ppm for its GPA gasoline, a refinery with a baseline sulfur level of 140 ppm would have a standard of 150 ppm for its GPA gasoline, and a refinery with a baseline of 200 ppm would have a standard of 150 ppm for its GPA gasoline. The temporary provisions for the GPA apply for 3 years, 2004 through 2006.

Gasoline produced by refiners subject to the small refiner standards is not subject to the GPA provision. Gasoline produced by such refiners can be sold nationwide, including in the GPA.

TABLE 10

**GASOLINE SULFUR STANDARDS FOR THE GEOGRAPHIC PHASE-IN AREA**  
(Excludes Small Refiners)

<u>Compliance As Of:</u>	<u>2004</u>	<u>2005</u>	<u>2006</u>	<u>2007</u>
Refinery GPA Gasoline Average <sup>1</sup> , ppm	150	150	150	30
Corporate Pool Average <sup>2</sup> , ppm	120	90	not applicable	cap applies
Per-Gallon Cap <sup>3</sup> , ppm	300	300	300	80

<sup>1</sup>The standard for GPA gasoline is the more stringent of 150 ppm or the refinery 1997-1998 baseline plus 30 ppm.

<sup>2</sup>Applies only to refiners/importers that sell <50% of their gasoline outside the GPA.

<sup>3</sup>In 2004 both GPA and non-GPA gasoline may have a sulfur content as high as 350 in which case the refinery or importer becomes subject to a correspondingly more stringent cap standard in 2005.

Source: EPA website

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### **Diesel Fuel Quality**

The EPA is also seeking to implement new diesel fuel quality standards that would match the sulfur standards for gasoline. However, the adopted regulation has not addressed the issue of sulfur level in diesel fuel. Refiners say that trying to force diesel to meet the same 30-ppm sulfur standard expected for gasoline in 2004 will impose huge additional capital requirements well in advance of probable EPA emissions requirements for light-trucks and sport utility vehicles (SUVs), or possible new standards on heavy-duty diesels.

Varying industry estimates of the incremental cost of desulfurizing diesel to 30 ppm sulfur are \$0.05–\$0.15/gal. Refiners say they will need at least 4 years to plan for and execute desulfurization projects. Although there are some cost savings (“secondary efficiencies”) of planning for and executing refining investments for simultaneous desulfurization of both gasoline and diesel, they are not nearly enough to overcome the initial high capital costs of desulfurizing both streams in advance of actual EPA diesel emissions requirements. A concern voiced by automakers during the discussion of the EPA proposal was that, unless ultra-low sulfur diesel fuels are legislated, the Tier II standard is not feasible for diesel

vehicles. The EPA said it would address this issue in a separate rule. A Notice of Proposed Rulemaking for diesel fuel is expected in early Spring 2000.

## **REACTIONS TO THE NEW SULFUR STANDARD**

The NPRA said complying with the new sulfur standard will cost refiners \$3 billion–\$5 billion and add \$0.03–\$0.05/gal to the cost of gasoline. According to the EPA the rule should add only \$0.01–\$0.02/gal.

The EPA and automakers have claimed the sulfur content of gasoline interferes with catalytic converters on cars. The average gasoline sulfur content now is about 330 ppm.

NPRA and API had argued for two higher, regional gasoline sulfur standards, which they said reflect the nation's varied air quality needs. They said that, under the EPA rule, gasoline sulfur levels would be reduced nationwide to the extremely low levels now required in California, which has the nation's worst air quality. That means all consumers, even those who live in areas where air quality is good, would pay for this costlier-to-manufacture fuel.

The refining industry's plan also would make additional sulfur reductions, if needed, to the 90% reduction level in the EPA proposal, but later to allow for the implementation of new, more cost-effective refinery processing technology. EPA's unnecessarily rapid schedule could prevent refiners from using potentially more cost-effective, but commercially unproven, sulfur reduction technology, say NPRA and API. U.S. refiners warn that a hasty push to desulfurize gasoline and diesel without a thorough analysis of emissions standards requirements, consumer demand, and capital constraints, could lead to costly stranded investments.

### **Treatment Required**

In any case, pretreating cat cracker (FCC) feedstocks will likely be required for both gasoline and diesel desulfurization, but post-treatment of streams will be necessary also if both streams must achieve ultra-low sulfur levels. Certain refiners can already produce ultra-low sulfur diesel. Others have announced a commitment to achieve the 30-ppm sulfur target.

No diesel engine technology today needs ultra-low sulfur. Heavy-duty diesel engines will not need reduced sulfur to meet 2004 EPA standards. Needs of advanced engines and vehicle technology—heavy- and light-duty—are still to be defined.

### **Need for the New Rule**

Some of the sharpest criticism of the sulfur rule has been directed to the EPA's stated justification—that it is needed to help states meet the new NAAQS for ozone and particulate matter (PM). In the May 13 *Federal Register* notice first announcing the proposal, the EPA said that without the sulfur rule, "in 2007 approximately 80 million Americans will be living in areas that are in nonattainment for the [new] 8-hour ozone NAAQS," and that its models project that "102 areas with about 55 million people will be in nonattainment with the new PM<sub>2.5</sub> NAAQS by 2010."

The problem with these references to the new NAAQS is that they were remanded by the U.S. Circuit Court of Appeals in Washington on May 14, 1999. Since then, the EPA has gone to great lengths to say its Tier II standards are not grounded only in the new NAAQS.

Some opponents of the sulfur reductions also say the requirement will lead to an increased need for oxygenates in gasoline because the desulfurization process reduces octane levels. But MTBE, one of the two most common oxygenates, has come under fire, especially in California. In late March, California Governor Davis announced that he would phase out MTBE because it contaminates groundwater. Ethanol, the other widely used oxygenate, is produced primarily in the Midwest, where the grains used in its manufacture are grown.

## CHANGES PROPOSED BY THE AUTOMOBILE MANUFACTURERS

Automakers are generally in favor of the sulfur cuts, which they say would make it much easier for them to reduce emissions and meet new requirements. Sulfur poisons catalytic converters, making them much less efficient at removing NO<sub>x</sub> and other pollutants.

The Association of International Automobile Manufacturers (AIAM) said, "AIAM supports the need for a 30-ppm [sulfur level in] gasoline . . . However, we need to recognize that further improvements will be necessary to achieve maximum reductions from current technology and to enable advanced technologies in the developmental stage."

According to the AIAM, "[We] feel strongly that the EPA [emission-reduction] rules should not have the unintended consequence of freezing advanced fuel-efficient technologies out of the US market."

Automakers laud the EPA's new rule, but say they will need a further reduction in sulfur to 0–5 ppm to achieve NO<sub>x</sub> emissions reductions and fuel-efficiency goals. The alliance said a joint industry-government initiative has found that the most promising new technology to achieve fuel-efficiency goals would require near-zero sulfur fuel.

The Partnership for a New Generation of Vehicles (PNGV) has found that four-stroke direct-injection engines are the best for meeting fuel-efficiency goals during the next 10 years. But this type of "lean burn" engine would make NO<sub>x</sub> tailpipe emissions targets difficult to meet. NO<sub>x</sub>-adsorber catalysts are extremely sensitive to sulfur, and their efficiency degrades quickly when not operated with near-zero sulfur fuels.

The EPA has not commented on the auto industry's request for near-zero sulfur content in gasoline. Such a fuel would be a "Category Four" fuel under the revised World-Wide Fuel Charter released at the end of 1998. Three automobile groups developed the Charter: the now defunct AAMA, the Association des Constructeurs Europeen d'Automobiles and the Japanese Automobile Manufacturers Association. Also supporting the Charter are endorsements from the American, European, and Japanese automakers, and from the worldwide Engine Manufacturers Association and the automaker associations of Canada, South Korea, China, and South Africa.

The objective of the global fuels harmonization effort is to develop common, worldwide recommendations for "quality fuels," taking into consideration customer requirements and vehicle emissions technologies that will in turn benefit customers and all other affected parties, the automakers said.

The Charter establishes three categories of unleaded gasoline and diesel fuel:

- Category 1: Markets with no or minimal requirements for emission controls; based primarily on fundamental vehicle and engine performance concerns.
- Category 2: Markets with stringent requirements for emission control or other market demands. For example, markets requiring U.S. Tier zero or Tier I, EU-Stage 1 or 2, or equivalent emission levels.
- Category 3: Markets with advanced requirements for emissions control or other market demands. For example, markets requiring U.S. California LEV, ULEV, or EU-Stage 3 or 4 or equivalent emission levels.

The Charter specifications for Categories 1, 2, and 3 gasoline are listed in Tables 11, 12, and 13, respectively.

Although the Charter specifications are intended for worldwide use, automakers acknowledge that national standards may differ. "Where national requirements are more severe than these recommendations, those national limits have to be met," automakers said.

Refiners reacted sharply to the Charter, saying the proposed specifications lack the necessary scientific justification and are internally inconsistent. Although automakers cannot force the acceptance of Charter fuels, government agencies could require fuels that more closely resemble the Charter. An opportunity could arise if automakers added a Charter fuel message to car owner's manuals, encouraging customers to use higher quality Charter fuels.

### Aromatic Fuel Components in Gasoline

As seen in Tables 11, 12, and 13, the maximum allowable aromatics levels for Categories 1, 2, and 3 are 50%, 40%, and 35%, respectively. Although aromatic compounds are generally considered to be environmentally undesirable, reducing aromatics levels is extremely expensive, requiring large quantities of hydrogen. Therefore, little actual reduction in aromatics is being proposed in the World-Wide Fuels Charter. The 35% level is approximately the current aromatics content of U.S. gasoline.

TABLE 11

**CATEGORY 1 UNLEADED GASOLINE**  
**Markets with No or Minimal Requirements for Emissions Control;**  
**Based Primarily on Fundamental Vehicle/Engine Performance Concerns**

Properties	Units	Limit	
		Minimum	Maximum
91 RON Research Octane Number	-	91.0	-
Motor Octane Number	-	82.0	-
95 RON Research Octane Number	-	95.0	-
Motor Octane Number	-	85.0	-
98 RON Research Octane Number	-	98.0	-
Motor Octane Number	-	88.0	-
Oxidation Stability	minutes	360	-
Sulfur Content	% m/m	-	0.10
Lead Content	g/l	-	0.013
Manganese Content	g/l	-	-
Oxygen Content	% m/m	-	2.7
Aromatics	% v/v	-	50.0
Benzene Content	% v/v	-	5.0
Volatility			
Unwashed Gums	mg/100 ml	-	70
Washed Gums	mg/100 ml	-	5
Density	kg/m <sup>3</sup>	715	780
Copper Corrosion	merit		class 1
Appearance			clear and bright
Carburetor Cleanliness	merit	8.0	-
Fuel Injector Cleanliness	% flow loss	-	10
Intake Valve Cleanliness I	merit	9.0	-

Source: World Refining, January/February 1999

TABLE 12

**CATEGORY 2 UNLEADED GASOLINE**  
**Markets with Stringent Requirements for Emission Control**  
**or Other Market Demands**

<u>Properties</u>	<u>Units</u>	<u>Limit</u>	
		<u>Minimum</u>	<u>Maximum</u>
91 RON Research Octane Number	-	91.0	-
Motor Octane Number	-	82.5	-
95 RON Research Octane Number	-	95.0	-
Motor Octane Number	-	85.0	-
98 RON Research Octane Number	-	98.0	-
Motor Octane Number	-	88.0	-
Oxidation Stability	min/tes	480	-
Sulfur Content	% m/m	-	0.02
Lead Content	g/l	non-detectable	
Phosphorus Content	g/l	non-detectable	
Manganese Content	g/l	non-detectable	
Silicon	g/kg	non-detectable	
Oxygen Content	% m/m	-	2.7
Olefins Content	% v/v	-	20.0
Aromatics Content	% v/v	-	40.0
Benzene Content	% v/v	-	2.5
Volatility			
Sediment	mg/l	-	1
Unwashed Gums	mg/100 ml	-	70
Washed Gums	mg/100 ml	-	5
Density	kg/m <sup>3</sup>	715	770
Copper Corrosion	merit	class 1	
Appearance		clear and bright	
Fuel Injector Cleanliness	% flow loss	-	5
Intake Valve Sticking	pass/fail	pass	
Intake Valve Cleanliness			
Method 1 (CEC F-05-A-93), or	avg. mg/valve	-	50
Method 2 (ASTM D 5500), or	avg. mg/valve	-	100
Method 3 (ASTM D 6201)	avg. mg/valve	-	90
Combustion Chamber Deposits			
Method 1 (ASTM D 6201), or	%		140
Method 2 (CEC-F-20-A-98)	mg/engine		3,500

Source: World Refining, January/February 1999

TABLE 13

**CATEGORY 3 UNLEADED GASOLINE**  
**Markets with Advanced Requirements for Emissions Control**  
**or Other Market Demands**

<u>Properties</u>	<u>Units</u>	<u>Limit</u>	
		<u>Minimum</u>	<u>Maximum</u>
91 RON Research Octane Number	-	91.0	-
Motor Octane Number	-	82.5	-
95 RON Research Octane Number	-	95.0	-
Motor Octane Number	-	85.0	-
98 RON Research Octane Number	-	98.0	-
Motor Octane Number	-	88.0	-
Oxidation Stability	minutes	480	-
Sulfur Content	% m/m	-	0.003
Lead Content	g/l	non-detectable	
Phosphorus Content	g/l	non-detectable	
Manganese Content	g/l	non-detectable	
Silicon	g/kg	non-detectable	
Oxygen Content	% m/m	-	2.7
Olefins Content	% v/v	-	10.0
Aromatics Content	% v/v	-	35.0
Benzene Content	% v/v	-	1.0
Volatility			
Sediment	mg/l	-	1
Unwashed Gums	mg/100 ml	-	30
Washed Gums	mg/100 ml	-	5
Density	kg/m <sup>3</sup>	715	770
Copper Corrosion	merit	class 1	
Appearance		clear and bright	
Fuel Injector Cleanliness II	% flow loss	-	5
Intake Valve Sticking	pass/fail	pass	
Intake Valve Cleanliness			
Method 1 (CEC F-05-93), or	avg. mg/valve	-	30
Method 2 (ASTM D 5500), or	avg. mg/valve	-	50
Method 3 (ASTM D 6201)	avg. mg/valve	-	50
Combustion Chamber Deposits			
Method 1 (ASTM D 6201), or	%	-	140
Method 2 (CEC-F-20-A-98)	mg/engine	-	2,500

Source: World Refining, January/February 1999

## CALIFORNIA'S PHASE III SPECIFICATION FOR GASOLINE

In December 1999 the California Air Resources Board (CARB) approved new specifications for gasoline that cut the allowable sulfur content even further. The new Phase III CARB rule calls for the sulfur content of gasoline to be reduced to 15 ppm on average, with a flat limit of 20 ppm (Table 14). The allowable benzene content is reduced from 0.8 vol% to 0.7 vol%.

TABLE 14

### CALIFORNIA PROPOSED PHASE III SPECIFICATIONS FOR GASOLINE

Property	Flat Limits		Averaging Limits		Cap Limits	
	Phase 2	Phase 3	Phase 2	Phase 3	Phase 2	Phase 3
Reid Vapor Pressure, lb/in <sup>2</sup> (warmer months only)	7.00	7.00 or 6.90 <sup>a</sup>	NA <sup>b</sup>	NA	7.00	6.40-7.20
Sulfur Content, ppm by weight	40	20	30	15	80	60, 30 <sup>c</sup>
Benzene, vol.%	1.0	0.8	0.8	0.7	1.2	1.1
Aromatics, vol.%	25.0	25.0	22.0	22.0	30.0	35.0
Olefins Content, vol.%	6.0	6.0	4.0	4.0	10.0	10.0
T <sub>50</sub> , °F	210	213	200	203	220	220
T <sub>90</sub> , °F	300	305	290	295	330	330
Oxygen, vol.%	1.8-2.2	1.8-2.2	NA	NA	1.8-3.5 0-3.5	1.8-3.7 <sup>d</sup> 0-3.7
Driveability Index (max)	none	1,225	NA	NA		NA

<sup>a</sup>Equal to 6.9 psi if using the evaporative element of the Predictive Model.

<sup>b</sup>Not applicable.

<sup>c</sup>60 ppm (wt) will apply December 31, 2002; 30 ppm (wt) will apply December 31, 2004.

<sup>d</sup>Allow 3.7 for gasoline containing no more than 10 vol.% ethanol.

<sup>e</sup>Driveability Index =  $1.5 \cdot T_{10} + 3 \cdot T_{50} + T_{90} + 20$  (wt.% oxygen).

Source: California Air Resources Board

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Because the new rule eliminates the option for refiners to use MTBE in the future, some relaxation of other parameters was allowed, to partially compensate for the loss in octane and in product volume (particularly mid-distillate volume) when MTBE is prohibited. The T<sub>50</sub> and T<sub>90</sub> distillation temperatures cap limits have been relaxed slightly and the aromatics HC cap increased slightly to allow refiners more flexibility in using various refinery HC streams to meet volume and octane requirements. Although the cap limit for aromatics is increased from 30% to 35%, the average and flat limit values remain at 22% and 25%, respectively.

No gasoline with aromatic content higher than 35% can be sold. No gasoline with aromatic HC content higher than 25% can be sold unless it:

- Is part of a refiner's overall average of 25% or less.
- Has been certified as a low-PM alternative gasoline formulation by calculation using the California Predictive Model.
- Has been certified as an alternative gasoline formulation based on automotive test results.

If a refiner chooses to certify gasoline as an alternative formulation under either of the last two options, the required overall average aromatics content drops from 25% to 22%.

CARB proposes adding a new specification for driveability index to preserve vehicle driveability and to ensure that compliance with advanced emission standards is not hampered by increases in the cap levels for the distillation temperatures. Adverse vehicle driveability can result in increased emissions. The staff is proposing that the DI be less than 1,225. The DI equation in this case is defined as:

$$DI=1.5T_{10}+3T_{50}+T_{90}+20^* \text{ (wt\% oxygen)}$$

## **PHASE-OUT OF MTBE**

Unlike the HCs that constitute conventional gasoline, MTBE is soluble in water. When conventional gasoline leaks from underground storage tanks it seeps downward until it finds the groundwater level, and floats on that surface. It is detectable only in that thin film at the hydrostatic surface. MTBE, however, dissolves in the water and becomes dispersed in minute but detectable concentrations throughout the groundwater column.

In March 1999 California's Governor Davis issued an executive order for removing MTBE from gasoline in California by no later than December 31, 2002. Other states are likely to follow suit. In October 1999 the order was relaxed to removal "as soon as possible." However, the December 31, 2002, deadline remains in regulations proposed by CARB in December 1999.

In July 1999 the EPA, responding to the recommendations for a "Blue Ribbon Advisory Panel" on MTBE, said it would work toward national elimination of the oxygenate requirements for RFG, opening the way for phase-out of MTBE. Some 269,000 bbl/d of MTBE were being added to gasoline at its peak. Because MTBE is a major contributor to octane levels in gasoline, its removal will cause refiners to take expensive measures to replace the lost octane values. Ethanol is a potential source for replacing both oxygen and octane value, but its high vapor pressure makes it undesirable as a blendstock. A low-vapor-pressure, high-octane blending component is needed to cancel out the vapor pressure effect of ethanol.

## REQUIRED PROPERTIES OF FUEL BLENDING COMPONENTS

There are in today's U.S. marketplace, in addition to regular, mid-grade or intermediate, and premium gasolines, federal and California RFGs; non-reformulated or conventional; and low-RVP. All these can be oxygenated. To achieve market acceptance, an octane enhancer must be compatible with all these types.

### PERFORMANCE CRITERIA

For many years AAMA conducted surveys of gasolines obtained from service stations in more than 20 U.S. cities. About 800 samples each year were analyzed by an independent contractor for all the chemical and physical properties found in the AAMA Gasoline Specification.

Colucci et al. (2) used a computer model to calculate a score for every gasoline sample in the AAMA survey. This model has a performance component and an emissions component. The performance characteristics of the gasoline samples were obtained by comparing their properties to a set of performance evaluation criteria based on the AAMA Gasoline Specification (Table 15).

The parameter  $T_{95}$  acts as a measure of the high boiling, primarily aromatic components of gasoline, which are the primary precursors in forming fuel injector and engine deposits. Octane quality is important in preventing engine knock. Driveability index is a critical property for cold-start and warm-up driveability performance, and for reducing HC emissions. The traditional equation was modified to account for the adverse effect of ethanol (because of its high heat of vaporization compared with gasoline). The equation used is given at the bottom of Table 15.

The maximum performance score was set at 100 points, and the points given to each criterion are shown in Table 15.

### GASOLINE EMISSIONS CRITERIA

With the introduction of federal and California RFGs, came the use of models for calculating vehicle emissions based on the gasoline's chemical and physical properties. Colucci et al. used the Federal Complex Model and the California Predictive Model to calculate the emissions of HC, CO, NO<sub>x</sub>, and toxics. The California model was used only for gasolines obtained in California. The complex model was used for all non-California gasoline samples (conventional and RFG).

Both models contain review criteria (see Table 16) that place limits on critical fuel properties. A sample that exceeds any limit receives a zero score.

The maximum emissions score for a sample was set at 100 points. For summer samples, the 100 possible points were divided as follows: HC - 35, NO<sub>x</sub> - 35 (both are involved in ozone production), CO - 0, toxics - 30. For winter, the division was: HC - 20, NO<sub>x</sub> - 20, CO - 30, toxics - 30.

Evaporative emissions were not included in the calculations. The effect on the emission score was minimal because evaporative emissions are essentially only HCs; they have no effect on CO and NO<sub>x</sub> emissions, and only a minimal effect on toxics.

### COMPARISON OF GASOLINES BY TYPE

As shown in Figure 3, the total score for CaRFG was highest, followed by federal RFG and conventional. Figure 3 shows that gasoline reformulation, to the extent it has been done for California, improves emissions and fuel performance.

The total and performance scores for the low-RVP gasolines are considerably less than those for all other gasoline types. This is due to the generally higher driveability index associated with low-RVP gasolines.

TABLE 15

**PERFORMANCE EVALUATION CRITERIA**

<u>Group</u>	<u>Parameter</u>	<u>Limits</u>	<u>Points</u>
Contaminants	Lead-g/gal	Pb<0.01	5
		0.01≤Pb<0.05	0
		Pb≥0.05	-10
	Manganese-g/gal	Mn>0.001	-10
		otherwise	0
	Peroxides-ppm	p<1.0	5
		1.0≤p<3.0	0
		3.0≤p<6.0	-5
		p≥6.0	-10
	Water-ppm	w<350	5
		350≤w<500	0
		500≤w<1,000	-5
w≥1,000		-10	
Deposit Control	Unwashed Gum-mg/100 ml	UG<70 mg/100 ml	5
		otherwise	0
	Washed Gum-mg/100 ml	WG<5 mg/100 ml	5
		otherwise	0
	T95°F	T95<345	5
		345≤T95<375	0
T95≥375	-5		
Distillation	RVP-psi	Meet AAMA Spec	5
	T50°F	otherwise	0
	T90°F		
Sulfur	Sulfur-ppm	S≤80	10
		80<S≤150	5
		150<S≤500	0
		S>500	-10
Octane-(R+M)/2	Regular	O≥88	10
		87≤O88	5
		O<87	0
	Midgrade	O≥90	10
		89≤O<90	5
		O<89	0
	Premium	O≥92	10
		91≤O<92	5
		O<91	0
Driveability Index	Driveability Index Compared to AAMA Spec	DI -100 to -20	35
		DI -20 to -5	20
		DI -5 to +5	10
		DI +5 to +20	0
		DI +20 to +40	-10
		DI +40 to +60	-20
		DI >+60	-35

Note:  $DI=1.5*T_{10}+3.0*T_{50}+1.0*T_{90}+7.0*\text{vol.}\% \text{ ethanol}$

Source: 2

TABLE 16

**EMISSIONS EVALUATION CRITERIA****California Predictive Model Review Criteria**

<u>Parameter</u>	<u>Upper Limits</u>	<u>Comments</u>
RVP, psi	7.3	applied to summer season only
T50, °C	107	
T90, °C	168	
Aromatics, %	32.7	
Olefins, %	12.5	
Oxygen, wt. %	2.8	
Sulfur, ppm	105	
Benzene, %	1.41	

If any parameter exceeds the Predictive Model upper limit, fuel fails.

**Federal Complex Model Review Criteria**

<u>Parameter</u>	<u>RFG Limits</u>	<u>Conventional Limits</u>	<u>Comments</u>
Oxygen, wt. %	0 - 4.1	0 - 4.1	
Sulfur, ppm	0 - 525	0 - 1,025	
RVP, psi	6.1 - 10.3	6.1 - 10.3	upper limit, summer only
E <sub>93C</sub> , %	27.6 - 72.5	27.6 - 72.5	
E <sub>149C</sub> , %	68.9 - 100	68.9 - 100	
Aromatics, %	7.3 - 57.7	0 - 57.7	
Olefins, %	0 - 27.5	0 - 32.5	
Benzene, %	0 - 2.21	0 - 5.11	

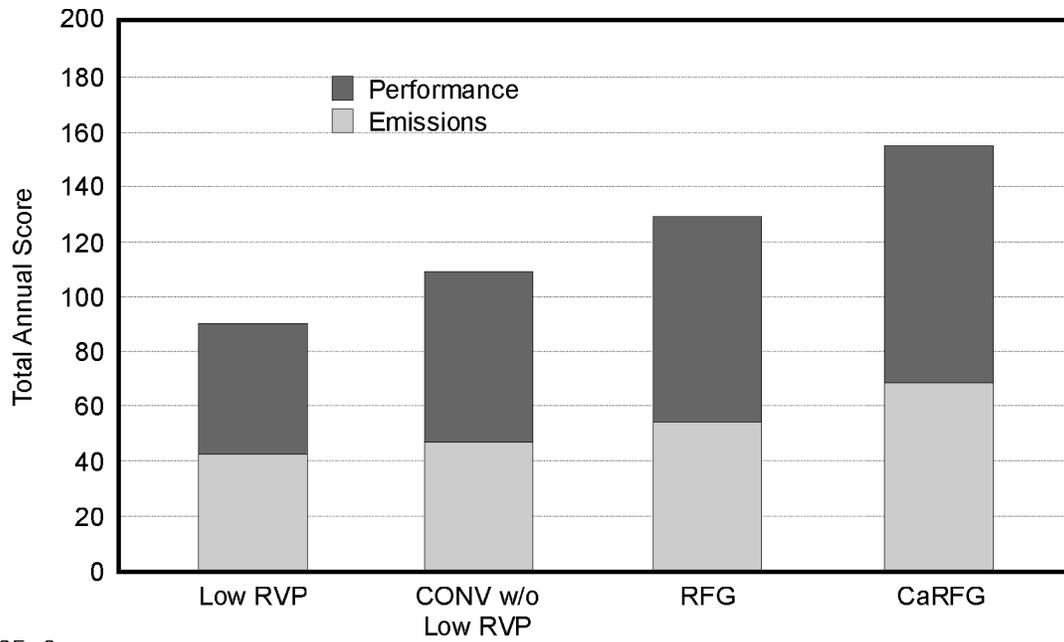
If any parameter lies outside the Complex Model limits, fuel fails.

Source: 2

**APPLICATION TO OCTANE ENHANCERS**

Tables 15 and 16 indicate the most important performance and emissions criteria for gasoline and give a set of relative weightings to apply to each. Figure 3 shows how different gasolines compare when using these weighting factors in 1996. The same approach could be used to compare two gasolines—one with and one without a lignin-derived octane enhancer. If the use of such an enhancer significantly lowered the total score, the product would be difficult to sell in tomorrow's markets.

FIGURE 3  
1996 TOTAL SCORES BY FUEL TYPE



SOURCE: 2

## FEDERAL TIER II AND LEV II EMISSION STANDARDS FOR LIGHT-DUTY VEHICLES

### TIER II REPORT TO CONGRESS AND FINAL RULEMAKING

In July 1998 the EPA generally outlined the need for tighter tailpipe emission standards and the feasibility of emission-control technologies in its Tier II Report to Congress. A proposed rule was published in the *Federal Register* May 13, 1999, and the Notice of Final Rulemaking was signed on December 21, 1999. The new rule sets much more stringent exhaust emission standards beginning in 2004. It also offers a more concrete process by which automakers must achieve tailpipe emission reductions, building on the National Low Emission Vehicle (NLEV) program, and adding requirements for heavier light-duty vehicles (LDVs), that is, SUVs.

The regulation grants automakers flexibility in implementing Tier II standards by allowing NO<sub>x</sub> emissions as high as 0.2 grams per mile (g/mi) as long as the averages emitted per mile across a fleet are less than 0.07 g/mi.

### RELATIONSHIP TO THE NATIONAL AMBIENT AIR QUALITY STANDARDS

The need for reduced levels of sulfur in gasoline comes about because automakers say there is no other feasible method of reaching the low levels of tailpipe emissions required under the Tier II emission standards for LDVs (sulfur poisons auto emission catalysts). The Tier II standards were released at the same time as and in conjunction with the sulfur-in-gasoline rule. The new tailpipe standards are said to be necessary to meet the new NAAQS for ozone and PM issued by the EPA in 1997. However, on May 14, 1999, the U.S. Court of Appeals remanded those standards, saying that the EPA had overstepped its authority. Thus, at the time of writing, it is unclear whether either NAAQS will prevail. If not, the Tier II tailpipe standards, discussed later, may have to be revised.

### FEDERAL TIER II STANDARDS FOR LIGHT-DUTY VEHICLES

The Tier II standards apply to new LDVs, which are classified into the following categories (see Table 17):

1. Passenger cars
2. Light light-duty trucks (LLDT), at less than 6,000 pounds gross vehicle weight rating (GVWR)
3. Heavy light-duty trucks (HLDT), at more than 6,000 pounds GVWR
4. Medium-duty passenger vehicles (MDPV), a new class of vehicles introduced by this rule that includes SUVs and passenger vans rated at 8,500–10,000 pounds GVWR

The program focuses on emissions of ozone-forming pollutants including:

- NO<sub>x</sub>
- Non-Methane Organic Gases (NMOG)
- PM

The same set of federal standards, expressed in grams per mile of pollutants emitted, applies to all passenger cars, light trucks, and MDPVs, regardless of the vehicle or engine size. Under this approach, which reflects the EPA's concern with increasing market share and emissions from minivans and SUVs, larger vehicles will have to use cleaner engine and emission control technologies than do vehicles with small engines. The same requirements will apply to all vehicles regardless of the fuel, that is, gasoline and diesel-fueled vehicles will be certified to the same emission standard.

TABLE 17

**LIGHT-DUTY VEHICLES AND TRUCKS;  
CATEGORY CHARACTERISTICS**

	<u>Characteristics</u>
LDV	A passenger car or passenger car derivative seating 12 passengers or less.
Light LDT (LLDT)	Any LDT rated at up through 6,000 lbs GVWR. Includes LDT1 and LDT2.
Heavy LDT (HLDT)	Any LDT rated at greater than 6,000 lbs GVWR, but not more than 8,500 lbs GVWR. Includes LDT3 and LDT4.
Medium-Duty Passenger Vehicle (MDPV)	A passenger vehicle (SUV or van) rated at 8,500 to 10,000 GVWR.

Source: 18

**Nitrogen Oxides**

The Tier II standards will limit new vehicle NO<sub>x</sub> levels to an average of 0.07 g/mi. The Tier II standards must be met over a full useful vehicle life of 120,000 miles. For comparison, the Tier I standards establish NO<sub>x</sub> limits of 1.0 g/mi for diesel cars and 0.4 g/mi for gasoline cars over 50,000 miles of vehicle life. Higher limits apply to heavier vehicles.

For new passenger cars and LLDTs, the Tier II NO<sub>x</sub> standards will begin to take effect in 2004. The standards will be fully phased in by 2007. For HLDTs and MDPVs, the Tier II standards will be phased in beginning in 2008, with full compliance in 2009.

**Carbon Monoxide**

Carbon monoxide standards have been aligned for all LDVs and LDTs. The CO standards (see Table 18) are essentially the same as those for the NLEV program for LDVs and LLDTs. These standards will harmonize with California LEV II CO standards except at California's SULEV level (EPA Bin 2). Bins applicable during the interim programs will include CO values from the NLEV program for LDV/LLDTs and from the California LEV I program for HLDTs.

**Formaldehyde Standards**

Similar to the approach to CO standards, EPA is aligning all Tier II LDVs and LDTs under the formaldehyde standards from the NLEV program or California LEV II program. HLDTs, which are not subject to the NLEV program, will become subject to federal formaldehyde standards for the first time.

The HCCO standards are primarily of concern for methanol and compressed natural gas-fueled vehicles, because formaldehyde is likely to be produced when methanol or methane is not completely burned in

TABLE 18

**FINAL TIER 2 LIGHT-DUTY FULL USEFUL LIFE EXHAUST EMISSION STANDARDS**  
(Grams Per Mile)

<u>Bin #</u>	<u>NOx</u>	<u>NMOG</u>	<u>CO</u>	<u>HCHO</u>	<u>PM</u>	<u>Comments</u>
10	0.6	0.156/0.230	4.2/6.4	0.018/0.027	0.08	a,b,c,d
9	0.3	0.090/0.180	4.2	0.018	0.06	a,b,e
The above temporary bins expire in 2006 (for LDVs and LLDTs) and 2008 (for HLDTs)						
8	0.20	0.125/0.156	4.2	0.018	0.02	b,f
7	0.15	0.090	4.2	0.018	0.02	
6	0.10	0.090	4.2	0.018	0.01	
5	0.07	0.090	4.2	0.018	0.01	
4	0.04	0.070	2.1	0.011	0.01	
3	0.03	0.055	2.1	0.011	0.01	
2	0.02	0.010	2.1	0.004	0.01	
1	0.00	0.000	0.0	0.000	0.00	

- a. Bin deleted at end of 2006 model year (2008 for HLDTs).
- b. The higher temporary NMOG, CO and HCHO values apply only to HLDTs and expire after 2008.
- c. There is an additional temporary higher bin restricted to MDPVs.
- d. Optional temporary NMOG standard of 0.280 g/mi applies for qualifying LDT4s and MDPVs only.
- e. Optional temporary NMOG standard of 0.130 g/mi applies for qualifying LDT2s only.
- f. Higher temporary NMOG standard is deleted at end of 2008 model year.

Source: 18

the engine. HLDTs are not included under the NLEV program and will therefore not face formaldehyde standards in 2001 as LDVs and LLDTs will (1999 in the Northeast). The EPA is including formaldehyde standards for HLDTs under the Tier II program and under the interim programs.

**Particulate Matter Standards**

For Tier II vehicles, the PM bin values are designed such that PM should consistently be 0.01 g/mi or lower. To provide manufacturers with flexibility, there is a 0.02 g/mi PM standard for vehicles that certify to the highest Tier II bins. The EPA anticipates that low-sulfur diesel fuel will be available by 2007 to enable diesel vehicles to use advanced diesel technologies and meet these PM standards.

For the interim standards there is a PM standard of 0.06 g/mi for the highest bins. The PM standard is 0.08 g/mi for Bin 10. For HLDTs, manufacturers will likely have to use advanced diesel technologies, which require low-sulfur diesel fuel, to attain the interim standards. Such fuels will probably not be widely available until 2006 or 2007. PM standards are primarily a concern for diesel-cycle vehicles, but they also apply to gasoline and other Otto-cycle vehicles.

## Non-Methane Organic Carbon Limits

The NMOG limits in the Tier II standards vary depending on which sets of emission standards manufacturers use to comply with the average NO<sub>x</sub> standard (see Tables 18 and 19).

### Useful Life

The useful life of a vehicle is the period of time, in terms of years and miles, during which a manufacturer is formally responsible for the vehicle's emissions performance. For LDVs and LDTs, there have historically been both "full useful life" values, approximating the average life of the vehicle on the road, and "intermediate useful life" values, representing about half the vehicle's life. The EPA is finalizing several changes to the useful life provisions for LDVs and LDTs. The new rule equalizes full useful life values for all Tier II LDVs and LDTs at 120,000 miles. Current data indicate that passenger cars are driven approximately 120,000 miles in their first 10 years. Trucks are driven farther. Former regulatory useful lives were 10 years/100,000 miles for LDV/LLDTs and 11 years/120,000 miles for HLDTs.

Intermediate useful life values, where applicable, will remain at 5 years or 50,000 miles, whichever occurs first. If manufacturers elect to certify Tier II vehicles for 150,000 miles to gain additional NO<sub>x</sub> credits, the useful life of those vehicles will be 15 years and 150,000 miles.

TABLE 19

### LIGHT-DUTY INTERMEDIATE USEFUL LIFE (50,000 MILE) EXHAUST EMISSION STANDARDS (Grams Per Mile)

<u>Bin #</u>	<u>NO<sub>x</sub></u>	<u>NMOG</u>	<u>CO</u>	<u>HCHO</u>	<u>PM</u>	<u>Comments</u>
10	0.4	0.125/0.160	3.4/4.4	0.015/0.018	--	a,b,c,d,f,h
9	0.2	0.075/0.140	3.4	0.015	--	a,b,e,h
The above temporary bins expire in 2006 (for LDVs and LLDTs) and 2008 (for HLDTs)						
8	0.14	0.100/0.125	3.4	0.015	--	b,g,h
7	0.11	0.075	3.4	0.015	--	h
6	0.08	0.075	3.4	0.015	--	h
5	0.05	0.075	3.4	0.015	--	h

- a. Bin deleted at end of 2006 model year (2008 for HLDTs).
- b. The higher temporary NMOG, CO and HCHO values apply only to HLDTs and expire in 2008.
- c. There is an additional higher temporary bin restricted to MDPVs.
- d. Optional temporary NMOG standard of 0.195 g/mi applies for qualifying LDT4s and MDPVs only.
- e. Optional temporary NMOG standard of 0.100 g/mi applies for qualifying LDT2s only.
- f. Intermediate life standards are optional for diesels certified to bin 10.
- g. Higher temporary NMOG value deleted at end of 2008 model year.
- h. Intermediate life standards are optional for any test group certified to a 150,000 mile useful life (if credits are not claimed).

Source: 18

## **Supplemental Federal Test Procedure**

Supplemental Federal Test Procedure (SFTP) standards require manufacturers to control emissions from vehicles when operated at high rates of speed and acceleration (the US06 test cycle) and when operated under high ambient temperatures with air conditioning loads (the SC03 test cycle). The light-duty SFTP requirements begin a 3-year phase-in for model-year 2000. For HLDTs, SFTP requirements begin a similar phase-in for 2002. SFTP standards do not apply to diesel-fueled LDT2s and HLDTs.

## **Certification Bins and Phase-In Schedule**

For new passenger cars and LLDTs, the Tier II NO<sub>x</sub> standards will be phased in beginning in 2004, with the standards to be fully phased in by 2007. For HLDTs the rule provides a three-step phase-in program. In 2004 a limit of 0.6 g/mi NO<sub>x</sub> will be implemented. A standard of 0.2 g/mi will be phased in at 25% in 2004, 50% in 2005, 75% in 2006, and 100% in 2007. In the final step, 50% of these vehicles would meet the 0.07 standard in 2008; the rest will comply in 2009.

Manufacturers have a choice of certifying their vehicles to any of 10 certification bins shown in Tables 18 and 19. Three temporary bins, scheduled to expire at the end of 2006 model-year (2008 for HLDTs), allow some flexibility for manufacturers to certify diesel vehicles during the transitional period. Diesel engines are ultimately expected to require advanced emission controls, such as particulate filters and lean NO<sub>x</sub> catalysts, to be able to meet the standards.

Having additional bins provides an incentive for manufacturers to produce vehicles emitting less than 0.07 g/mi of NO<sub>x</sub> because manufacturers would have some vehicles (especially larger LDTs) that they might find more cost effective to certify to levels higher than the 0.07 g/mi average standard. However, to do this they would have to offset those vehicles in the NO<sub>x</sub> averaging system with vehicles certified lower than 0.07 g/mi.

There is no fleet average standard for PM emissions. The PM standards for the certification bins range from 0 (Bin 1, zero emission vehicle), through 0.01 g/mi (Bins 2-6), to 0.02 (Bins 7 and 8). The current Tier I PM standard for diesel cars is 0.08 g/mi.

## **CALIFORNIA LEV II EMISSIONS STANDARDS**

CARB is adopting LEV II standards to take effect for model year 2004 LDVs and medium-duty vehicles. These standards, shown in Table 20, have a single category that applies to all passenger cars, SUVs, and LDTs as heavy as 8,500 pounds gross vehicle weight (GVW) (weight of vehicle plus load). Two other categories apply to medium-duty vehicles as heavy as 14,000 pounds GVW. These standards represent the maximum allowable exhaust emissions for the intermediate and full useful life of the vehicles.

TABLE 20

**LEV II EXHAUST EMISSION STANDARDS FOR 2004+  
LEVs, ULEVs AND SULEVs  
(Passenger Car, Light-Duty Truck, and Medium-Duty Vehicle Classes)**

<u>Vehicle Type</u>	<u>Durability Vehicle Basis (mi)</u>	<u>Vehicle Emission Category</u>	<u>NMOG (g/mi)</u>	<u>Carbon Monoxide (g/mi)</u>	<u>Oxides of Nitrogen (g/mi)</u>	<u>Formal- dehyde (g/mi)</u>	<u>Particulate from Diesel Vehicles (g/mi)</u>
All PCs;	50,000	LEV	0.075	3.4	0.05	0.015	n/a
LDTs <8,500 lbs GVW		ULEV	0.040	1.7	0.05	0.008	n/a
Vehicles in this category	120,000	LEV	0.090	4.2	0.07	0.018	0.01
are tested at their loaded		ULEV	0.055	2.1	0.07	0.011	0.01
vehicle weight		SULEV	0.010	1.0	0.02	0.004	0.01
	150,000	LEV	0.090	4.2	0.07	0.018	0.01
	(optional)	ULEV	0.055	2.1	0.07	0.011	0.01
		SULEV	0.010	1.0	0.02	0.004	0.01
MDVs	120,000	LEV	0.195	6.4	0.2	0.032	0.12
8,501 - 10,000 lbs GVW		ULEV	0.143	6.4	0.2	0.016	0.06
Vehicles in this category		SULEV	0.100	3.2	0.1	0.008	0.06
are tested at their adjusted	150,000	LEV	0.195	6.4	0.2	0.032	0.12
loaded vehicle weight	(Optional)	ULEV	0.143	6.4	0.2	0.016	0.06
		SULEV	0.100	3.2	0.1	0.008	0.06
MDVs	120,000	LEV	0.230	7.3	0.4	0.040	0.12
10,001 - 14,000 lbs GVW		ULEV	0.167	7.3	0.4	0.021	0.06
Vehicles in this category		SULEV	0.117	3.7	0.2	0.010	0.06
are tested at their adjusted	150,000	LEV	0.230	7.3	0.4	0.040	0.12
loaded vehicle weight	(Optional)	ULEV	0.167	7.3	0.4	0.021	0.06
		SULEV	0.117	3.7	0.2	0.010	0.06

Source: California Air Resources Board

## SUMMARY

The new Tier II emission standards are extremely stringent and unlikely to be economically feasible without some type of low-sulfur fuel. Hydrodesulfurization will tend to saturate the aromatic fraction of gasoline and reduce the ON. Thus, an increased need for aromatic octane enhancers can be forecast. In California and in the federally mandated RFG areas, however, the limit on aromatics content may restrict the market potential for aromatic octane enhancers.

## EFFECTS OF CHANGING AUTOMOTIVE TECHNOLOGY

Three potentially major changes in automotive technology could affect future need for high-octane fuel:

- The adoption of gasoline direct-injection (GDI) engines
- A shift from gasoline to diesel engines
- The success of fuel cell vehicles

The effects of these changes are discussed in the following sections.

### GASOLINE DIRECT-INJECTION ENGINES

This technology is already well on its way to capturing a significant market share. The GDI engine, also known as the direct-injection, spark-ignition (DISI) engine, was pioneered by Mitsubishi and other Japanese manufacturers. It should allow a gasoline-fueled engine to approach diesel engine efficiencies more closely than has been possible. The low-load efficiency is much higher than in the typical spark-ignition (SI) gasoline engine. Mitsubishi even claims that the efficiency of the DISI engine can surpass that of the diesel engine.

The increased fuel efficiency of a DISI engine arises from three major sources:

- A higher compression ratio can be used (Mitsubishi uses 12.5 compared to typical values of 9 to 11 for naturally aspirated SI engines and 17 for diesel engines).
- Lean mixtures can be used under low-load conditions (40:1 air/fuel ratio instead of stoichiometric 14.6:1).
- Throttling losses are reduced under low-load conditions.

These factors make conventional diesel engines more efficient than conventional gasoline engines. On the other hand, the DISI engine is capable of higher output (power) than a same-size diesel engine. Mitsubishi achieves this through a dual-mode operating procedure. For low-load conditions, fuel is injected late in the compression stroke, as in a diesel engine. Ultra-lean combustion is achieved, as in a diesel engine, by the formation of a stratified charge mixture. But under high-load conditions, fuel is injected during the intake stroke, which forms a homogeneous air/fuel mixture as in a conventional gasoline engine, leading to higher power output than a conventional diesel engine.

The chief barrier to DISI technology is that many observers do not believe expected US Tier II emission standards can be achieved for NO<sub>x</sub>, even by using high exhaust gas recirculation (EGR) rates. Much research is being devoted to developing a lean-burn NO<sub>x</sub> catalyst to solve this problem.

Mitsubishi has built more than 500,000 GDI engines, and expects all its Japanese-market engines to be DISI in the year 2000. Other Japanese manufacturers predict the same by 2005. Mitsubishi says that its engine offers 25%–40% better fuel efficiency during idling and under varying speed conditions in Japan. Nissan is also offering GDI engines for the Japanese market.

The differently tuned European version is claimed to provide a 25% better fuel efficiency at higher speeds. Last year, Renault's Megane Coupe became available with the first commercially available European car engine with direct gasoline injection. The company claims fuel consumption is reduced by 20% without compromising emissions performance. The problem of the high sulfur content of European gasoline (compared with Japanese fuel) was tackled by greatly increasing the EGR to 25%.

Volkswagen AG is preparing to introduce GDI engines in Europe soon (3). The Volkswagen GDI engines are said to approach the thermal efficiency of VW's vaunted TDI turbodiesels—often said to be the most efficient engines in production.

With DISI engines, high-octane fuels will lose some of the advantage of having a high ON because operation at low-load (which has the greatest effect on average miles per gallon) is accomplished with high excess air and stratified charge and is not as limited by the ON. Also, DISI engines running in the stoichiometric mode at high load can operate at higher compression ratios than conventional gasoline engines because of the cooling effect of direct liquid injection. Fuels with high ONs will still have an advantage, although reduced compared to the current situation. For example, the efficiency advantage of an increase in compression ratio from 15 to 16 is less than half that of an increase from 10 to 11.

## **A SHIFT FROM GASOLINE TO DIESEL ENGINES**

As a result of breakthroughs in fuel injection technology, European automakers are marketing diesel-powered cars that are peppier, cleaner, quieter, and more efficient than ever. These vehicles constitute one of the fastest-growing segments of Western Europe's auto market. Their share is expected to increase to one-third by 2003 (4). Behind this turn of events is a new generation of electronically controlled, high-pressure fuel-injection systems combined with new "common-rail" technology. This promises to make diesel engines as quiet and smooth as gasoline engines, while offering much greater fuel economy. Thus, diesel represents the industry's best hope of cutting carbon dioxide emissions.

Common-rail technology, by improving combustion, dramatically reduces the levels of emissions and noise. The common-rail system has a continuously running high-pressure pump that sends fuel into a pipeline running along the top of the engine (hence the term common rail) at up to 1,400 atmospheres pressure. Because the pump is not driven by the engine, the injection pressure can be optimized irrespective of engine speed. In addition, computer control of the fuel injection makes several small "pilot" injections possible, achieving precise control over the combustion process.

In the United States the PNGV has focused on small diesel-type engines as a key technology. The PNGV initiative is a joint industry-government research effort aimed at producing by 2004 cars that have roughly triple the gas-mileage efficiency—about 80 miles per gallon—of today's models.

If ultra-low sulfur diesel fuel or other types of zero-sulfur fuels (such as dimethyl ether or Fischer-Tropsch liquids) become available, the small diesel engine (now referred to as the compression ignition direct injection or CIDI engine) could displace the gasoline engine and eliminate the need for octane improvers.

## **THE SUCCESS OF FUEL CELL VEHICLES**

Over the longer term, fuel cells could offer the automobile industry near-zero emission vehicles with long range, good performance and rapid refueling. Fuel cells generate electricity directly from a chemical reaction between hydrogen and oxygen, triggered by a catalyst. The required hydrogen can be either carried on the vehicle as a compressed gas, or extracted ("reformed") from a fuel, such as gasoline, methanol, ethanol, or propane, carried onboard the vehicle. The electricity produced is used to power a traction motor that drives the wheels. Current research is focused on improving fuel cell size, lowering costs, and developing efficient, compact, and responsive onboard fuel reformers that would provide the needed hydrogen.

A high ON is of no value to a fuel being fed to a reformer to make hydrogen.

Several companies, including General Motors (GM), Ford Motor Company, and DaimlerChrysler AG, have said they will have fuel cell vehicles ready to manufacture by 2004.

Ford, DaimlerChrysler, and Ballard Power Systems have announced a partnership with three oil companies—Texaco, Atlantic Richfield and Shell Oil—as well as the State of California, to put a demonstration fleet of fuel-cell-powered vehicles on the road starting in 2000.

Ford and DaimlerChrysler each have invested hundreds of millions of dollars in a fuel cell research and development partnership with each other and Ballard. Although GM has bought fuel cells from Ballard, GM and Toyota plan to develop their own automotive fuel cell systems.

Fuel cell vehicles remain prohibitively expensive, and reducing their cost to that of a comparable car powered by an internal-combustion engine is viewed as key to their acceptance. But DaimlerChrysler has said that its first fuel-cell-powered Mercedes-Benz cars will come to market at about the same price as conventionally powered vehicles (5). The cars will be introduced at prices 10%–15% higher than comparable vehicles with internal combustion engines. But at that level, government incentives would push the final price down to the same level as today's gasoline engines—or lower.

The federal government offers a 10% tax credit on the purchase price of an electric vehicle, to a maximum of \$4,000. The law includes fuel cells in the definition of electric power. In addition, some state and local governments, including New York and air quality management districts in California, offer more incentives.

## **SUMMARY**

The shift to gasoline direct injection engines is almost certain to occur, and has, in fact, begun. This technology makes it possible to get the same performance with a somewhat lower octane-number gasoline. However, the effect on total octane needs should be relatively minor.

A shift from gasoline to diesel engines is under way in Europe, but this may or may not happen in the United States. The key positive factor in Europe is that prices for gasoline are much higher than for diesel fuel. The key negative factors in the United States are the difficulty in meeting NO<sub>x</sub> emission standards and the potential designation of diesel exhaust as a carcinogen. Any fractional change of market share from gasoline to diesel totally eliminates the need for octane enhancement in that fraction. This would have major market repercussions for octane enhancers from lignin by-products.

Similarly, any market share picked up by fuel cell vehicles becomes a market with zero need for octane enhancement. The future for fuel cell vehicles is highly speculative, and substantial penetration of the market in less than 15 to 20 years seems unlikely.

## COMPETITION FROM AROMATICS IN GASOLINE

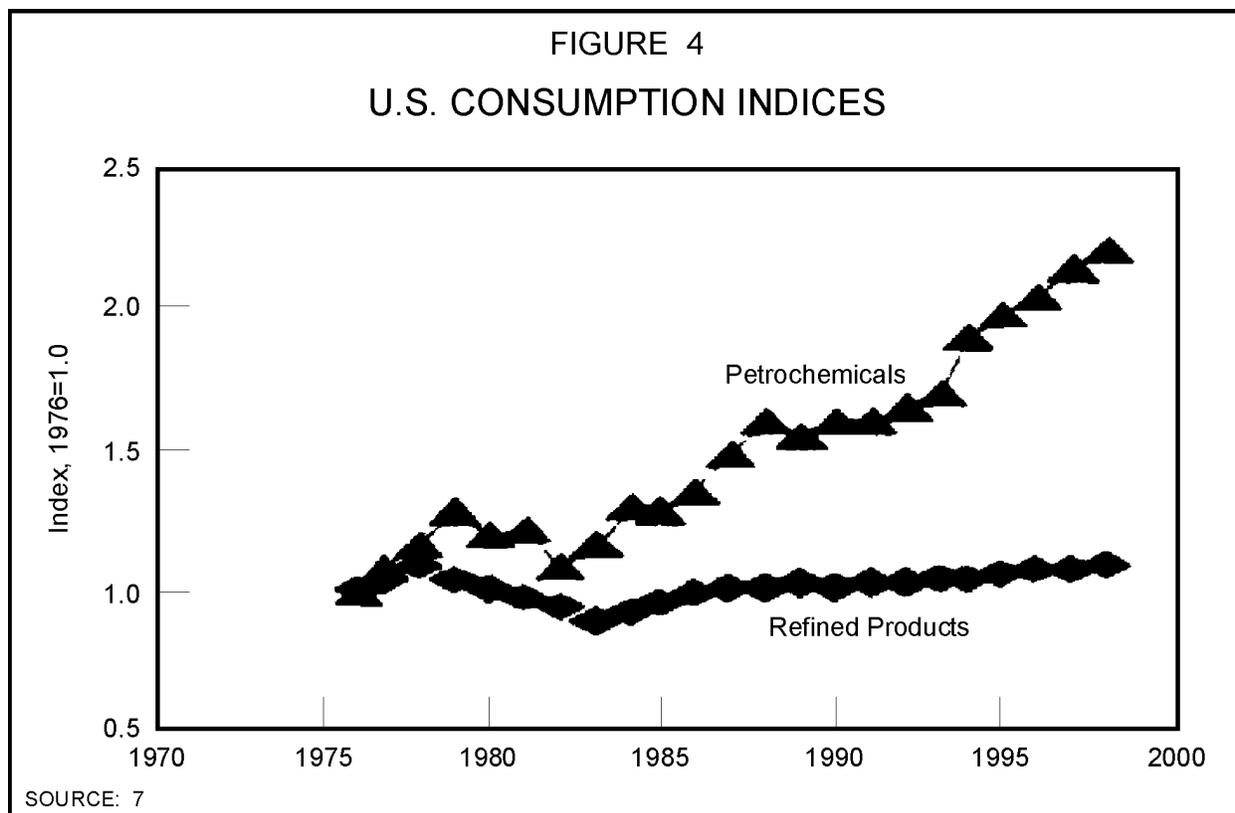
### SOURCES AND SUPPLY OF BTX AROMATICS

Benzene (B), toluene (T), and mixed xylenes (X) are referred to as BTX chemicals. They are used on a large scale as petrochemical feedstocks. Because they are often produced together in the same process, they can be considered as a group. However, BTX as such is not an article of commerce. The BTX aromatics are derived from the gasoline fraction of petroleum products produced by the catalytic reforming of naphtha. In the past they could be added back to gasoline to raise the octane number. However, there are now limits on the amount of benzene allowed in gasoline (1%), and it cannot be considered as an octane enhancer.

An aromatic octane enhancer derived from lignin by-products would be a gasoline blending component rather than a gasoline additive. Thus, it must compete with petroleum-derived aromatic blending components. These compounds move back and forth between the gasoline markets and the petrochemicals markets as supply and demand fluctuate.

Essentially every refinery in the world has numerous streams that contain benzene, xylene, ethylene, propylene, etc. Figure 4 compares the relative growth rates of refined product consumption in the United States with that of all petrochemicals. The graph shows that although demand for refined products has hardly grown, the need for petrochemicals has more than doubled.

Reformate, the product of catalytic reforming, has a high octane rating, mostly because of the BTX components. Any BTX needed for chemical use or intended for sale to other refineries as an octane enhancer, is separated from the reformate stream before it is blended into the gasoline pool. On the whole, perhaps only 15% of the BTX produced in refinery reformate streams is separated and sold or used separately.



## BTX Recovery

The complexity of separating and purifying individual BTX components from crude BTX depends on the amount and kind of other components present. If the amount is small enough, simple distillation is sufficient. If not, liquid-liquid extraction or extractive distillation with a polar solvent is used to separate the slightly polar aromatics from the nonpolar, nonaromatic HCs.

In some refineries BTX production may be important enough to support its own reforming facilities and should not be considered as simply a gasoline by-product (6). The consumption of BTX in the petrochemical market is in the approximate proportions 67:5:28, respectively. However, no process makes BTX in these proportions. Consequently, toluene is usually in excess supply and sells for a lower price than benzene or xylene. Thus, commercial processes are used to convert toluene to benzene and xylenes. Much of the separated toluene returns to the gasoline pool as an octane enhancer for blending.

Petrochemical profitability cycles have historically not correlated with refinery profitability, contributing to large movements of aromatics back and forth between the two markets.

## Toluene

There are an estimated 23 producers of toluene in the United States, with total production capacity of 1.9 billion gal/yr (this does not include the 85%–90% of toluene left in the reformate stream from which it is derived and blended directly into the gasoline pool). Toluene is also derived as a by-product of styrene production.

Toluene has a wide range of end uses. Its main use (other than gasoline blending) is as an HC solvent. Toluene is also a feedstock for a number of derivatives, including benzene and xylenes. Of the toluene that is separated, about 75%–80% is used for chemicals or solvents. The remainder is blended back into gasoline as an octane enhancer.

The ON  $(R + M)/2$  of catalytic reformates is typically 88.9–94.5, depending on severity of the reforming operation. Toluene has a blending octane number (BON) of 103 to 106.

Toluene is, therefore, a valuable blending component, particularly in unleaded premium gasolines. Although reformates are not extracted solely to generate a high-octane blending stock, the toluene coproduced when xylenes and benzene are extracted for use in chemicals, and that exceeds demands for use in chemicals, has a ready market as a blending component for gasoline.

As a blending component in automotive fuels, toluene has two chief advantages. First, it has a high ON compared to regular and premium unleaded gasolines. Second, its relatively low volatility permits it to be incorporated into gasoline blends of other available and less expensive materials, such as *n*-butane, with relatively high volatility. Toluene demand has been increasing at about 3% per year.

## Mixed Xylenes Fraction

There are three isomers of xylene: orthoxylene, metaxylene, and paraxylene. Orthoxylene is used mostly to make phthalic anhydride. Paraxylene is used mostly to make polyethylene terephthalate. Metaxylene is used to make isophthalic acid, but much of it returns to the gasoline pool.

If a refiner operates a reformer above 100 to 102 RON (depending on the feed), mixed xylenes can be produced without extraction. The mixed xylenes stream in a refinery contains ethyl benzene as well as the three xylene isomers in approximately the following proportions (21) :

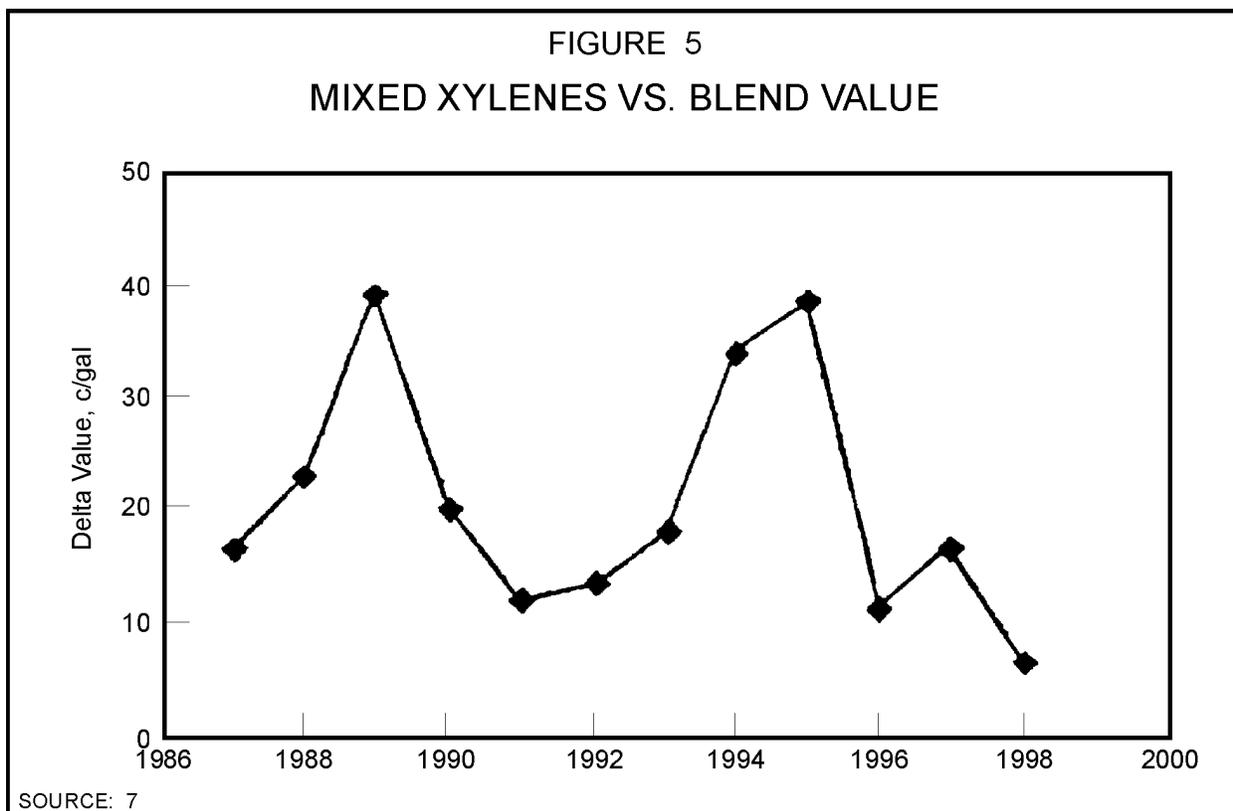
- o-xylene            22%
- m-xylene           40%

- p-xylene 18%
- ethyl benzene 20%

There are about 21 U.S. producers of mixed xylenes, with total productive capacity of more than 13 billion lb/yr. Mixed xylenes are extracted from the gasoline blending pools at refineries. Also, they can be produced by disproportionation of toluene.

A refiner selling mixed xylenes is selling into the “middle” of a manufacturing chain. Most paraxylene producers also have catalytic reformers and are simply using the mixed xylene as added feedstock to an isomerization/purification system. Thus, a mixed xylene seller is in a “last in, first out” situation. However, mixed xylene sales volume can be significant: domestic consumption of mixed xylene is roughly 25% of paraxylene consumption.

The differential between the selling price of mixed xylenes and the blend value has moved from a few cents to as much as \$0.40 over the past 15 years (Figure 5). Thus, a refiner who built a unit specifically to manufacture mixed xylenes would have to either sell the product at gasoline blending value some of the time or else only operate part-time. Benzene, toluene, and xylenes are all excellent high-octane blending components. Thus, to the extent that aromatics are allowed in gasoline, there will always be BTX available for octane enhancement. A lignin by-product will have to compete directly with the BTX products on price unless some advantage other than octane can be claimed.



## Catalytic Reforming

Reforming is a platinum-catalyzed, high-temperature, vapor-phase process that converts a relatively nonaromatic C<sub>6</sub>-C<sub>12</sub> HC mixture (naphtha) to an aromatic reformate. The octane rating of the reformate is directly related to its aromatic content, which is high when the reformer is operated at high severity (high temperatures, low space velocity). Some cracking to light products also occurs, and this increases at high severity. A typical reformate contains BTX in the proportions 19:49:32, respectively, although these proportions can be varied somewhat by tailoring the feed composition and operating conditions (6).

Reformer feed is normally straight run naphtha boiling at 80°–210°C. The aromatic content of these naphthas is quite low, as is the ON.

## Other Sources of BTX

The historical source of BTX is from coal pyrolysis. Another source is the pyrolysis gasoline produced as a by-product of manufacturing ethylene.

A new approach is a process to convert C<sub>2</sub> to C<sub>6</sub> light paraffins into aromatics by using a modified zeolite catalyst.

The Mobil methanol-to-gasoline process converts methanol into gasoline containing about 50% aromatics by using a ZSM-5 catalyst.

## PETROCHEMICAL MARKETS

Table 21 shows historical U.S. prices for commercial-grade toluene from 1976 to 1995. The minimum price for the toluene used in chemicals is set by its value in unleaded gasoline, which is the principal use. The ceiling price is set by the relative values of benzene and toluene. When the value of benzene is such that the differential between benzene and toluene exceeds the cost of converting toluene to benzene, the price of toluene is set by its value for the conversion to benzene. A differential of \$91/ton (about \$0.30/gal) is generally needed to make the conversion of toluene to benzene economically attractive (7).

In the refining industry, refined products will generally move. If not, a price cut of \$0.01–\$0.02/gal will make them move. By comparison, many petrochemicals are like refining solvents. Normal heptane, for example, may carry a posted price more than double that of gasoline. However, just because a refiner can produce a tank of normal heptane meeting all the specifications, there is no guarantee that he can sell it.

A number of factors influence the aromatics market. The product chain from the refinery to the consumer is long and there are many markets. Thus, growth rates depend on numerous unrelated events. The most profitable year for paraxylene in decades was probably caused by a poor cotton crop in India. Demand for styrene, and therefore benzene, plummeted when McDonald's stopped using polystyrene boxes.

Prices are not always transparent. Using historical recorded prices does not always lead to meaningful analysis. There are few market participants, especially in aromatics, and individual companies have tremendous market presence. On the U.S. mainland, Amoco has more than 40% of the paraxylene capacity. There are only three other paraxylene purchasers in the United States.

A company making an intermediate aromatic product is frequently selling to a buyer who also makes the same product. If the market is oversupplied, a nonintegrated producer may not have buyers. Thus, marketing requires ongoing development and strong technical support. The low-cost producer is not necessarily the winner. Small yield differences, which are critical in refining, are meaningless here. The cost to reach the market may be more critical than the cost of production.

TABLE 21

**UNITED STATES TOLUENE,  
COMMERCIAL-GRADE DCI  
HISTORICAL SPOT PRICES**

<u>Year</u>	<u>Spot, \$/Metric Ton</u>	
	<u>High</u>	<u>Low</u>
1995	225.9936	225.0208
1994	247.6080	245.8144
1993	229.2160	226.9664
1992	257.5184	253.9312
1991	278.5248	272.1712
1990	348.2624	334.4304
1989	286.2768	280.5616
1988	272.9008	264.2976
1987	231.6480	227.2096
1986	208.7568	203.6800
1985	336.0416	330.9040
1984	309.1680	304.2432
1983	330.4784	326.3136
1982	369.9376	363.6752
1981	402.0096	396.8416
1980	389.6976	383.7392
1979	359.0544	345.2832
1978	176.6240	173.6448
1977	154.9488	150.8752
1976	167.0784	162.8832

---

The recent price history for BTX aromatics is given in Table 22. Purchasing agents are forecasting price increases through the year 2000 (Figure 6). *Purchasing Magazine's* index of aromatic chemicals prices (based on prices in December 1983 being equal to 100) is projected to increase from a mid-1999 value of 60 to around 67 in 2000.

### **Outlook for Mixed Xylenes**

There are significant petrochemical markets for para and ortho xylene, intermediates in the production of polyester fibers, film, and resins.

Consumption of polyester fiber and bottle resins has resulted in an outstanding 8% growth rate for mixed xylenes. Despite strong increases in demand, the industry has managed to overbuild capacity.

The long-term forecast has mixed xylenes demand increasing 5%–6% versus historical growth rates of 8% because of the maturing of the polyester market.

### **Forecast for Aromatics Feedstock**

Most of the official naphtha statistics generally exclude naphtha reformed in a refinery to produce aromatics, gasoline, and hydrogen. Refiners classify the naphtha as an intermediate and do not report it

TABLE 22

**AROMATICS PRICE HISTORY**  
(\$/gal)

	<u>Contract</u>	<u>Spot</u>
<b>Toluene</b>		
1999	0.94	0.81
1998	0.90	0.89
1997	0.96	1.02
1996	0.91	0.96
1995	1.05	1.15
<b>Benzene</b>		
1999	0.70	0.72
1998	0.90	0.90
1997	1.05	1.05
1996	1.00	0.95
1995	1.12	1.12
<b>Mixed Xylenes</b>		
1999	0.75	0.92
1998	0.90	0.87
1997	1.03	1.04
1996	1.03	1.03
1995	1.36	1.53

as a finished product. Naphtha produced in a refinery and used in an olefins cracker is more often reported in the naphtha statistics. Similarly, the naphtha produced and sold to stand-alone aromatics or fertilizer operations is also generally reported.

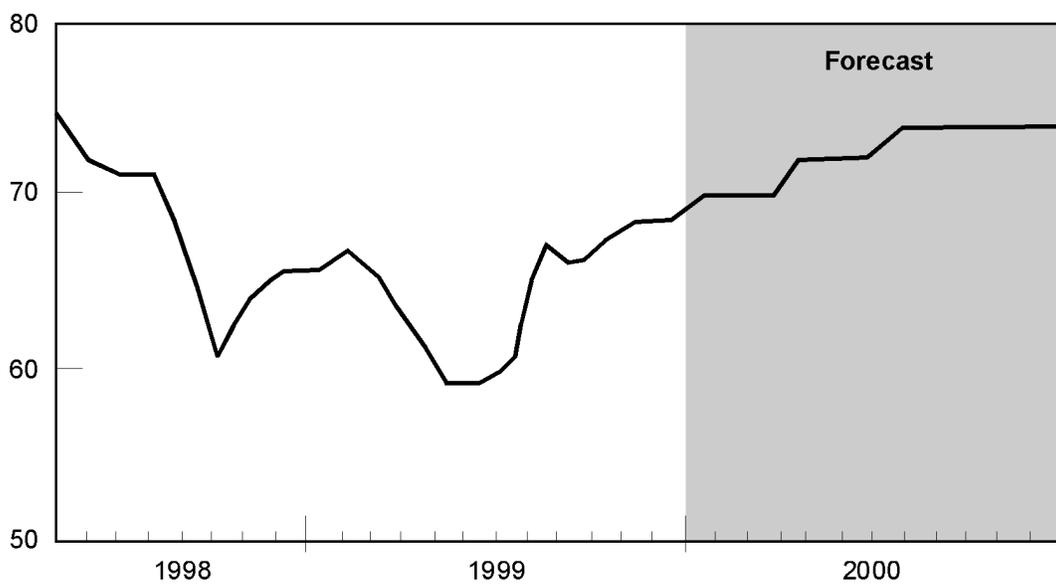
The combined growth in olefins and aromatics production will require a rapidly increasing naphtha supply. However, the rapid increase in condensate production in the Middle East will result in increasing supplies of naphtha. Some of the condensate will be processed in the Middle East, thereby increasing naphtha exports.

Naphtha trade as a percentage of reported production is about 20% (8). There is some trade in aromatic naphtha, but most naphtha trade is feed for olefins plants.

### SUMMARY

Large quantities of BTX and other high-octane aromatic compounds are consumed by the petrochemicals industry. Depending on relative prices, these materials move back and forth between the gasoline market and the petrochemicals market. Because toluene and xylene both have excellent blending properties and are widely available, they are likely to be first choice for enhancing octane in situations where aromatic enhancers are allowable.

FIGURE 6  
FORECAST FOR AROMATICS PRICE INDEX



SOURCE: 16

Demand for BTX in the petrochemicals industry is increasing, but so is the supply of naphtha feedstock from which BTX is derived. Therefore, pricing should remain relatively stable with respect to crude oil. A biomass-derived octane enhancer would have to compete in price with crude-oil-derived octane boosters.

## TRANSPORTATION AND DISTRIBUTION

### SHIPMENT AND STORAGE

The logistics of getting an aromatic octane enhancer (for convenience called OCTAlig) from the producers to the consumers will in many ways be similar to the situation for ethanol. In both cases the product must, for economic reasons, be manufactured in an agricultural location near its feedstock source(s) and then transported to some point in the gasoline distribution system where it can be blended into a gasoline stream. The most likely point for this blending is the refinery, but transportation costs may dictate blending at large terminals that have the proper blending facilities and are located closer to the source of OCTAlig.

Based on the similarity of circumstances regarding ethanol, OCTAlig could be delivered by a combination of marine cargo and railcar shipments.

The product would typically be shipped to larger terminals, where it would later be removed for delivery by transport truck to final destination terminals. A survey of terminal operators indicated that 62% could offer new product storage in 6 months or less (9).

### MARINE CARGOES

Larger plants located on navigable waters could ship some of their OCTAlig via marine cargo, typically by shipping the product down the Mississippi via 10,000-barrel river barges. For refineries not on the Mississippi River system the product would be staged at a terminal facility in New Orleans, Louisiana, until enough is accumulated to warrant shipment. Such shipments would fill one compartment of an ocean-going vessel. Shipments could be as small as 1 million gallons, but would more likely be 4 to 6 million gallons (a 3-month supply for a 100,000 bbl/d refinery).

Once staged in New Orleans and loaded onto ships, the product could go to any coastal terminal or refinery. The entire process requires slightly more time than rail shipments. It could also go overseas to markets less hostile to aromatics.

The cost of moving product by marine cargo does not present major economic incentives over rail. The cost of barge movement from the plant to New Orleans and a terminaling fee to amass product before loading the ship make total marine cargo movement costs nearly the same as or more than rail. The main benefit of marine cargoes accrues to the destination terminal, which in many cases will prefer single shipments of large quantities as opposed to the more time-consuming task of spotting, inspecting, and unloading railcars (9).

### RAIL SHIPMENTS

If the OCTAlig plants are landlocked, only rail shipments are viable. Plants making fewer than 80 million gal/yr are also not likely to ship by marine cargo because the required volume cannot be rapidly amassed for such shipments. Consequently, most OCTAlig plants would be limited to rail shipments.

Rail shipments typically consist of one or more 30,000-gal railcars typically loaded at approximately 29,000 gal. Transit time from Midwestern ethanol plants to various coastal markets is 2–3 weeks. Considering time to return the railcar to the plant, one complete turnaround could take 4–6 weeks. Using the average of 5 weeks, one can assess how many railcars would be required.

Typical rail costs for shipping ethanol from the Midwest to California are \$0.14–\$0.17/gal, depending on the plant of origin and market destination (9). Shipping costs for OCTAlig are assumed to be the same.

## STORAGE AND DISTRIBUTION

Unlike ethanol, OCTAlig could be blended into gasoline at the refinery. However, it could also be blended at a destination terminal. Terminals vary widely in their degree of flexibility to handle new or additional products such as OCTAlig. Blending at terminals is usually accomplished in one of three ways.

**Tank Blending:** OCTAlig and gasoline could be blended in one or more terminal tanks. A few terminals in the Midwest, especially those with recirculation capability (in-tank devices to recirculate/stir the product) have distributed ethanol blends in this manner. This is the least preferred method available because the blend could encounter excessive moisture, which could result in the ethanol phase separating from the blend. Also, terminal tankage is not routinely equipped with recirculation/mixing devices.

**Top-Off Blending:** OCTAlig and gasoline are injected separately into the transport truck and the agitation from loading and transport blends the fuel. Volumes are controlled by preset meters activated by loading cards. This could be done in a single terminal (i.e., one loading rack) or by loading the ethanol at one terminal and the gasoline at another (terminals must be close together). This method was successfully used for ethanol throughout the Midwest for a number of years and is still used at some terminals.

**In-Line/Injection Blending:** This is the preferred method. The blending agent and gasoline are blended in-stream before the meter and a single finished product is metered. This method eliminates the potential for blending errors and provides better quality control. It also provides greater reporting ease for program compliance.

## PRICING AND COST CONSIDERATIONS

### PRICING BY COMPARISON TO ETHANOL

A detailed cost analysis is beyond the scope of this study. However, the situation for OCTAlig would be substantially similar to that of ethanol. Ethanol has traditionally been priced on one of three bases:

- Profit margin improvement (lower cost than gasoline)
- Octane value
- Oxygenate value for oxygenated gasoline

During the 1980s, ethanol was sold largely by pricing it so that, net of tax credits, it was slightly cheaper than gasoline. This allowed blenders to improve their margins and/or lower their total product cost (9). As state tax credits diminished and ethanol began to achieve more widespread acceptability, it began to be priced more for its octane value. This involves two approaches. In some cases a refinery might make a suboctane gasoline so that, when blended with ethanol at the terminal it would meet the required octane specification. The second and more common method is to add ethanol to unleaded regular, selling the resulting blend as mid-grade, and/or blending unleaded regular with a small amount of premium and ethanol to achieve the octane requirement of a premium-grade product. More recently a large portion of ethanol produced has been sold for its value as an oxygenate to comply with the oxygen requirements of oxygenated fuel and RFG programs.

The Renewable Fuels Association estimates that in 1998 approximately 650 million gallons of ethanol were used to meet oxygen standards. Based on 1998 production figures, about 740 million gallons were sold into the octane market. When gasoline prices are low, the absence of state tax credits precludes the use of ethanol solely as a product extender or margin improver.

Although ethanol is priced based on its octane and/or oxygenate values, its production costs are dictated by the unrelated price of corn. Similarly, the cost of producing OCTAlig will be unrelated to the cost of gasoline. Production costs do not have a major impact on pricing decisions because product must be priced to compete based on its value to the end user. Production costs do, however, have an impact on production volume. Large, well-financed plants can alter their production to market conditions and often have contractual agreements for pricing and volume. During down cycles in market prices, smaller plants will typically operate as long as their net plant price exceeds cash production costs. Although this typically results in selling most product at a price that does not cover debt service and amortization, it may allow some payment toward debt service. Once sales prices fall to a level that does not allow a gross margin above cash production costs, smaller plants will typically shut down temporarily.

Most ethanol sold into current oxygenate markets is supplied by large producers with some product supplemented by smaller plants. A large portion of this product is sold based on contracts or long-term commitments. However, Congress is now debating whether to relax the requirements for oxygen in gasoline (10). This could eliminate a large part of the current market for ethanol.

The octane enhancement market represents the current lowest price use of fuel-grade ethanol. The octane market can be divided into two distinct groups: states with state tax credits and those without. Product sold in states with tax credits sells at higher prices because the blender can recoup higher costs through the tax credit. Only a few states with tax credits remain.

Where ethanol is priced primarily for its value as an oxygenate, the price is driven by the price of gasoline. These prices are set based on the value of product at the terminal. Transportation costs do not figure into the pricing equation because price is based on value to the blender. However, ethanol producers must consider transportation costs when determining whether to meet the necessary market price. In the case modeled in Reference 9, the cost of shipping ethanol to the California market is \$0.14–\$0.17/gal of ethanol. Also, the use of a central breakout terminal will result in handling charges of \$0.25–\$0.70/bbl (\$0.006–\$0.017/gal), depending on the type of storage/throughput agreement and volumes involved. In most cases there will also be the cost of transporting the ethanol from the central breakout terminal to the

destination terminal and a throughput charge at the destination terminal (in the case of third-party terminals and throughput agreements). However, these later charges are experienced in all other markets and are not particularly relevant. Thus, from the Midwest to California handling costs will be \$0.146–\$0.187/gal of ethanol. Similar distances and costs could be involved with transporting and delivering OCTAlig. If shorter distances are involved, costs would be proportionally lower.

Given the uncertainty of projecting gasoline prices, projecting prices for OCTAlig becomes equally difficult. However, producers would likely redirect production for as little as \$0.05 incremental margin per gallon of ethanol if it were for a market involving long-term commitments (9). Consequently, ethanol could be drawn to California from the Midwest octane market for this margin improvement plus transportation (\$0.196–\$0.237/gal of ethanol).

Again, the lowest valued ethanol markets are the octane enhancement markets in states without state tax credits. The ethanol octane blend market in the Midwest has traditionally been priced at the rack price of unleaded plus \$0.54/gal (the value of the federal motor fuels excise tax credit). Although the formula of unleaded plus \$0.54/gal somewhat undervalues the octane value of ethanol, it is the traditional pricing mechanism and the one currently used. To induce blenders to use ethanol, a blend margin incentive, traditionally provided by the unleaded price plus \$0.54, must be provided. This incentive is estimated to be \$0.05/gal. Based on January 2000 prices for octane blending components (see Table 23), the blending value for aromatics is \$0.007–\$0.009/octane gal. Thus, if OCTAlig had an ON of 106, its theoretical octane premium would be \$0.14–\$0.19/gal, but if a \$0.05 incentive is needed, the realizable price might be \$0.09–\$0.14 /gal over unleaded regular gasoline price.

Ethanol sells at a discount to its octane blend value, at least partly because of its unfavorable effect on gasoline vapor pressure.

## **PRICING BASED ON REFINERY OPERATIONS**

The value of an octane barrel (i.e., the value in excess of the price of a barrel of regular gasoline that a refiner would pay for a barrel of gasoline blending component having a blending octane number one number higher than the refinery's average output) is highly variable, depending on each refinery's configuration and its normal feedstock.

To increase the ON of its gasoline, a refinery has three major process options (11):

- Catalytic reforming of the naphtha
- Alkylation of olefins
- Isomerization of paraffins

Different refiners will have different best options, but the value of a purchased octane enhancer will be the saving to the refinery resulting from not having to add capacity for one of these processes. Basically, the value to most refineries is whatever the refinery saves in not having to run the reformer or expand reformer capacity. Studies have shown this value to be \$0.30–\$0.60/octane bbl (\$0.0071–\$0.0143/octane gal) (5). The value of an octane barrel is also highly influenced by the vapor pressure and other characteristics. If the octane enhancer also contains oxygen, additional value might be obtained.

TABLE 23

**PRICES OF FUELS AND COMPONENTS, JANUARY 2000**

	<u>Octane<sup>1</sup></u>	<u>01/20/00</u>	<u>01/21/99</u>
<b>Incremental Octane (\$/gal) (U.S. Gulf Coast prices, spot, barge)</b>			
MTBE	110	\$0.92	\$0.47
n-Butane	91	0.73	0.27
Isobutane	121	0.71	0.28
Ethanol <sup>2</sup>	113	0.58	0.49
Benzene	101	1.29	0.72
Toluene	103	0.94	0.53
Xylene	106	1.02	0.56
Methanol <sup>3</sup>	115	0.28	0.22
<b>Spot Gasoline (\$/gal)</b>			
Unleaded Regular Houston		\$0.736	\$0.3260
Unleaded Premium Houston		0.7760	0.3490
<b>Wholesale Rack Gasoline (\$/gal)</b>			
Regular (RFG), Houston		\$0.7706	\$0.3461
Mid-grade (RFG), Houston		0.8075	0.4024
Premium (RFG), Houston		0.8638	0.4575
<b>Crude Oil</b>			
WTI--Gulf Coast Spot		\$29.68	\$12.38
Futures, Apr-00		26.98	

<sup>1</sup>Octane blending values will vary with gasoline blendstock.

<sup>2</sup>Minus 54 ¢/gal incentive.

<sup>3</sup>Methanol must be blended with cosolvent alcohol to be used as gasoline additive.

Source: 19

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February 2000 market data for U.S. refineries include (12):

- World crude oil price: \$26.22/bbl
- West Texas Intermediate crude: \$27.25/bbl
- Product value, 6 months futures \$29.04/bbl
- Refinery spot price for gasoline, Gulf Coast \$0.725/gal
- Pump price for gasoline ex tax \$0.936/gal
- Retail price at pump, U.S. average \$1.34/gal
- Six-month futures crack spread \$4.48/bbl

Toluene with a BON of  $(R+M)/2 = 112$  should have a premium value of \$0.17–\$0.34/gal for a refinery with an average octane pool of 88. Based on current refinery spot prices, this would result in a refinery value of \$0.89–\$1.07/gal for toluene or another octane enhancer with the same BON. For reference, the recent market price for toluene (Table 23) is about \$0.94/gal.

For 2020, the U.S. Department of Energy's *Annual Energy Outlook* (13) projects a base-case price of \$22.04/bbl of crude oil. If the refinery margin (crack spread) stays at \$4.48, the product value will be \$26.52. Applying the same ratio between 2000 and 2020 prices for gasoline, we calculate a refinery spot price of \$0.66/gal. The value of a BON = 112 octane enhancer then becomes \$0.83–\$1.00/gal.

## MARKET PROJECTIONS

### CURRENT MARKET PRICES FOR GASOLINE AND COMPONENTS

World oil prices have swung violently during the past year. Prices for crude oil, gasoline, and octane-enhancing blend components are given in Table 23 with a comparison between January 1999 and January 2000 prices. In most cases the difference is a factor of 2 or more. The exceptions are methanol and ethanol, which have markets other than the transportation fuels market.

### POTENTIAL BACKLASH FROM MTBE PHASE-OUT

Anticipating the phase-out of MTBE, air regulators want to ensure refiners produce gasoline that continues to achieve current levels of air toxic emission reductions. Regulators at the Northeast states for Coordinated Air Use Management (NESCAUM) are asking the EPA to revise the gasoline standards to reflect real-world, rather than statutory, emissions reductions.

The Clean Air Act Amendments of 1990 sought toxic emissions reductions of 16.5% from Phase I RFG and 21.5% from Phase II RFG. According to NESCAUM, the use of Phase I RFG actually reduces air toxics 35%, and conventional gasoline now being sold in the region cuts such emissions 13%.

The EPA must revise the Phase II RFG performance standard for toxics to ensure that the 1998 annual average in the Northeast—a 35% reduction in toxic emissions—continues to be achieved after January 1, 2000, NESCAUM said, “In addition, toxic air emissions from conventional gasoline sold in the Northeast have declined 13 percent since 1990, and those emission benefits should also be preserved through additional federal regulation.

“As MTBE is reduced or eliminated from the fuel supply, gasoline producers will add other compounds with known and unknown public health risks to make up the lost volume and octane provided by MTBE,” NESCAUM pointed out. “The most economical near-term option available to refiners supplying the Northeast RFG market may be to increase levels of aromatic compounds including benzene, toluene and xylene.”

That has been the experience in Maine, which opted out of the RFG program in response to rising concerns over MTBE-contaminated groundwater. The fuel properties reported by Maine’s gasoline suppliers and distributors show a 50% decrease in MTBE use and a corresponding 70% increase in aromatics over the levels of aromatics present in RFG sold in Maine during 1997. “We are adamant that air toxic reductions of 35 percent be maintained,” stressed NESCAUM. “As we grant refiners more flexibility, they have to ensure what they replace MTBE with does not hurt air quality.”

If any new regulations on air toxics are passed, they would not necessarily specifically target aromatics because the RFG rules are based on performance; they do not mandate a specific composition.

When MTBE is removed from the gasoline pool, the refinery must replace:

- The lost volume (11%)
- The lost octane value
- The lost nega-toxic value
- The lost oxygen value (unless the regulations are changed)

The nega-toxic value is described as follows. The widespread use of MTBE came about as a means of adding required oxygenates to the gasoline in certain areas. To add enough oxygen to satisfy regulations, refiners had to blend in 11% MTBE. This displaced 11% of the original gasoline containing benzene and other air toxics and resulted in lower overall emissions of air toxics. Thus, just as a barrel of MTBE may be described as containing so many octane barrels, it may also be described as containing so many negative toxic, or nega-toxic barrels. That is the amount (in percentage points) by which toxic emissions are reduced when pure MTBE is burned instead of the original gasoline blend. Because blending

characteristics are unlikely to be linear, the value of any blending component in terms of octane barrels or of nega-toxic barrels should be determined by measuring the blend at the actual blend compositions to be sold rather than by using pure component values.

If an aromatic compound with nega-toxic values could be found, it should be acceptable within the composition limits described earlier.

## **COMPETITION WITH ETHANOL**

If MTBE is to be totally phased out, which appears likely, the additional effect of gasoline desulfurization will almost certainly create a nearly nationwide shortage of octane. The ethanol industry sees this as a tremendous opportunity for increased sales of ethanol as an octane enhancer. On a volume basis, ethanol contains more oxygen than MTBE. The current 2 wt% oxygen requirement for RFG can be met by using 5.7 vol% denatured ethanol instead of 11 vol% MTBE.

Adding 5.7% ethanol to unleaded regular gasoline should raise the octane index,  $(RON + MON)/2$ , by about 1.5 octane numbers. If OCTAlig has the same anti-knock rating as xylene it would take about 7% OCTAlig to produce the same 1.5 increase in octane index.

If MTBE (4.3 billion gal/yr) is totally replaced by ethanol, 2.2 billion gallons of ethanol would be required in addition to that already being used. Total U.S. ethanol production capacity is about 1.5 to 1.8 billion gal/yr, so the production capacity would be more than doubled. However, ethanol demand is unlikely to reach that point chiefly because:

- Refiners have other means of making up at least part of the octane deficit.
- Transportation costs are too high for ethanol to be competitive in some parts of the country.

One approach taken by ethanol market analysts (9) is to assume that for gasoline sold outside the federal RFG areas ethanol would be used only to supply the extra octane needed for premium and mid-grade gasolines. These grades put the greatest octane requirement on the gasoline pool. They account for about 30% (15% each) of total gasoline sales (14). Even at this level, the potential market for octane enhancers with suitable characteristics is much larger than the amount of OCTAlig that would be produced under any reasonable scenario.

Corn-based ethanol has three major disadvantages in the marketplace:

- It is high priced.
- It is water soluble and cannot be shipped in ordinary petroleum product pipelines.
- It raises the RVP when added to gasoline.

For OCTAlig to compete with or displace ethanol in the octane market, it would have to be significantly superior to ethanol in one or more of these characteristics. For the last two items, OCTAlig may have an advantage, but until samples are produced and adequately tested in gasoline blends, this will remain unknown as will the price.

## **MARKET CAP IMPOSED BY AROMATICS LIMITS**

On the surface, an aromatic blending component cannot be added to gasoline. As pointed out in Table 6, the average (1990 baseline) historical level of aromatics in gasoline was 28.6%, and the federal RFG Phase II rules place a 25% limit on aromatic HC content. Also, the anti-dumping provision will probably prohibit refiners from increasing the aromatic levels in their non-RFG gasolines. Thus a refinery could apparently only add an aromatic blending component if it first removed an aromatic fraction on a one-for-one basis. This could only be justified if OCTAlig were far superior to the aromatics now in gasoline. This may not be achievable.

However, if gasoline is desulfurized with current hydrotreating technologies, the aromatics content will be lowered in all gasoline. This provides a window for introducing an aromatic product. As one example,

Bavaro (15) estimated that desulfurization from 300 ppm to 30 ppm via FCC hydrotreating would result in 1.7% lower aromatics in the product. Using xylene as the model aromatic, this would suggest a loss of about 0.5 ON.

If OCTAlig has the same octane rating as xylene (107 octane), 1.7% could be blended to help remedy the octane loss without exceeding the original aromatics content in the gasoline. For a 100,000-bbl/d refinery, this amounts to 1,700 bbl/d or 26 million gal/yr. Total U.S. gasoline production is about 8.4 million bbl/d (14). Thus, the total theoretically possible market for OCTAlig would be 142,800 bbl/d or 2.2 billion gal/yr. This can be compared to the current total U.S. ethanol production capacity of 1.5 to 1.8 billion gal/yr.

If a refinery has room under its aromatics cap, more than 1.7% OCTAlig could conceivably be used as an octane booster to change regular gasoline to mid-grade, or mid-grade to premium at a blending terminal.

#### **Note on Octane Value of Aromatics**

The weighted average ON for a mixed xylenes stream added to a 90-octane gasoline is 107 octane. That is based on the following blending ONs for the individual compounds (see Reference 20):

- o-xylene = 101 RON, 86.8 MON
- m-xylene = 119 RON, 101 MON
- p-xylene = 116 RON, 96 MON
- e-benzene = 124 RON, 107 MON
- average (RON + MON)/2 = 107

BONs are highly dependent on the composition of the base gasoline and on the percentage blended. Aromatics typically have strong deviations from linearity when blending, and the blending differential varies greatly from compound to compound

The average BON for mixed xylenes, using the data from API Project 45 (Reference 22), would be about 126. Using this number, only about 3.4% xylenes would be needed to match the effect of 5.7% ethanol. This would increase the value of the xylenes. However, the blending values in API 45 were determined by adding 20% of the test compound to a 60-octane base, which is not representative of a modern refinery gasoline stream. Therefore, using a high number such as 126 for OCTAlig does not seem justified unless some data are available to substantiate such a value.

## **SUMMARY**

### **FUEL COMPOSITION REQUIREMENTS**

Certain specific compositional requirements for gasoline limit the level of aromatic compounds in gasoline. For federal Phase II RFG, the limits are 1% benzene and 25% by volume total aromatics. In California, the Phase III RFG specification is an average of 22% aromatics or less. For non-RFG gasoline, the aromatic content is limited to the refinery's 1990 baseline level.

### **FUEL PERFORMANCE REQUIREMENTS**

To be completely accepted, an octane enhancer would have to demonstrate the following characteristics when blended into gasoline:

- No increase in volatility
- No decrease in startability
- No increase in driveability index
- No residue on distillation at 200°C
- No increase in temperature at 90% distilled point
- No increase in emissions of CO, NO<sub>x</sub>, NMOG, and particulates

### **EPA'S NEW SPECIFICATION FOR SULFUR CONTENT**

The sulfur-in-gasoline rule, issued in December 1999, greatly reduces the amount of sulfur allowed in gasoline by January 1, 2005. The most logical way for a refinery to reduce the sulfur level of its product is to hydrotreat either the products or the reformer feedstock, or both. This process will reduce the average aromatics content of gasoline by about 1.7% and opens the door for introducing 1.7% of an aromatic octane enhancer.

### **NEED FOR OCTANE**

The predicted phase-out of MTBE, used as an oxygenate and an octane enhancer, will result in a nationwide shortage of octane. Although ethanol could be used more widely as an octane enhancer, its high vapor pressure and its solubility in water are undesirable characteristics in the market for gasoline blending agents.

### **FEDERAL TIER II AND CALIFORNIA LEV-II EMISSION STANDARDS**

These new emission control regulations for LDVs greatly reduce the allowable emissions of NO<sub>x</sub>, NMOG, and particulates. The same standards, in terms of g/mi pollutant emitted, will apply to all LDVs regardless of size, including the largest pickup trucks and SUVs. The automakers say that these standards can be achieved only if virtually sulfur-free gasoline is available.

### **CHANGING AUTOMOTIVE TECHNOLOGY**

Three potentially major changes in automotive technology could affect the future need for high-octane fuel:

- GDI engines
- A shift from gasoline to diesel engines
- Fuel cell vehicles

GDI engines do not require as high an ON as conventional engines. Although GDI engines are predicted to win a large market share in the future, the effect on octane requirement is relatively small.

A large shift from gasoline to diesel would eliminate the need for high-octane fuels. Although this may occur in Europe, it is considered unlikely in the United States.

Fuel cell vehicles likewise would eliminate the need for octane enhancers. Fuel cells may succeed in the marketplace in 15–20 years.

### **COMPETITION FROM AROMATICS IN GASOLINE**

Benzene, toluene, and xylene are high-octane components of gasoline and are important feedstocks in the petrochemicals markets. BTX moves back and forth between the gasoline and petrochemicals markets depending on small price changes. Because BTX is widely available and an excellent octane enhancer, an aromatic lignin-derived octane enhancer (OCTAlig) would have to compete directly with BTX.

### **COMPETITION FROM ETHANOL**

Ethanol is expected to capture a significant share of the future market for octane enhancers. However, ethanol has two unfavorable characteristics for blending into gasoline:

- It increases the vapor pressure of gasoline.
- Its solubility in water prohibits its use in pipeline and conventional blending tanks.

For these reasons ethanol sells at a discount with respect to its theoretical value as an octane increaser. OCTAlig would not be subject to this penalty, but it would suffer some of the same high transportation and distribution costs because production plants are located far from refinery sites.

### **COST AND PRICING CONSIDERATIONS**

One conventional way for a refinery to meet increased octane requirements is to increase catalytic reformer capacity or operating severity. Thus, the value of a purchased octane enhancer can be calculated as being equal to the saving from not having to add reforming capacity. Using this method we estimate the value of OCTAlig (hypothetical octane index of 112) delivered to the refinery to be \$0.17–\$0.34/gal higher than the price for unleaded regular. Assuming transportation costs similar to ethanol (say \$0.16/gal) yields a netback price at the OCTAlig production plant of \$0.01–\$0.18/gal higher than the price of unleaded regular gasoline. Shorter transportation distances could change these numbers to \$0.09–\$0.26.

### **PRICE PROJECTION TO 2020**

The Energy Information Administration's *Annual Energy Outlook for 2000* gives a reference case projected oil price of \$22.04/bbl for 2020 (compared to \$26.22 in January 2000). Depending on assumptions for refinery operation margins, a 112-octane OCTAlig would be worth \$0.83–\$1.00/gal at the refinery. This yields a netback price at the production plant of \$0.57–\$1.00, depending on distance.

### **MARKET PROJECTION**

The future required desulfurization of gasoline will probably reduce average aromatics levels in gasoline by 1.7% and create a loss of 0.5 ONs. This opens the window for introducing an aromatic octane blending agent without increasing the historical aromatics content. If OCTAlig has the same octane rating as xylene, 1.7% could be blended to remedy the octane loss without exceeding the original aromatics content in gasoline. On this basis, the total theoretical U.S. market for OCTAlig could be 142,800 bbl/d or 2.2 billion gal/yr. This can be compared to the current total U.S. production capacity for ethanol of 1.5–1.8 billion gal/yr.

If OCTAlig proves to have nega-toxics value, it could have much wider applicability by substituting for aromatics in gasoline at levels much higher than 1.7%.

## CONCLUSIONS AND RECOMMENDATIONS

There is continuing pressure on petroleum refiners to generally reduce the amount of aromatics in gasoline. In California there is an explicit average limit of 22 vol%. However, some aromatics will always be allowed in gasoline if they have the right characteristics. Federal EPA specifications for RFG under the complex model will, in theory, allow aromatics as high as 50%, provided automotive emissions will meet all statutory requirements.

Refiners must first meet federal Phase II and California Phase III regulations, which will reduce the level of aromatics in gasoline. They will then later have to meet the new federal limits on sulfur. Meeting the sulfur caps will cause an unintentional reduction in aromatics and loss of octane number. The expected simultaneous phase-out of MTBE from the gasoline pool will create increased nationwide demand for octane. This clearly opens the door for an aromatic blending agent to replace the lost octane value by bringing the aromatics content back to the allowable level.

We conclude that pursuit of an octane enhancer derived from lignin should not be dropped just because it is aromatic. Although being aromatic does raise a yellow caution flag, it is not by any means a prohibitive situation. The most important key will be the effect the new product has on air toxics emissions when burned in internal combustion engines. If the resulting emissions are less than would be produced by increasing the level of the aromatics already in the gasoline, the new product can be said to have a negative value, and should be readily acceptable at levels that do not exceed the original aromatics content.

The potential market volume under such a scenario could be 2 billion gal/yr. Because there is a clear need for a product to replace the octane that will be lost as a result of both desulfurization and MTBE phase-out, we recommend that work continue in this area. This report presents numerous criteria by which candidate materials can be evaluated.

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