

The use of oxygenated hydrocarbons in gasoline and their contribution to reducing urban air pollution

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Abstract - One of the most significant advances to occur in automotive fuel technology over the past ten years has been the use of oxygenated hydrocarbons in the production of gasoline. Whereas ten years ago essentially all transportation fuel was 100% petroleum-based, today it is safe to say that over 40% of all cars in West Europe and 25% of those in the United States, or roughly 100 million cars, are being driven on gasolines containing oxygenates.

This paper will briefly review the underlying reasons for oxygenated fuel use, the types and characteristics of the most common oxygenates, environmental benefits resulting from their use, and the outlook for the future.

INTRODUCTION

The current use of oxygenates began in the latter half of the 1970s when crude oil shortages developed and the search for alternative fuels began in earnest. Methanol, which could be produced from coal, and bio-ethanol from agricultural feedstocks were extensively evaluated as replacements for petroleum-based motor fuel. While neat alcohol use was blocked by the need for a separate fuel distribution system and specially designed vehicles, commercial blending of alcohols in gasoline began in 1979 in West Germany and in 1981 in the United States. Separately, Brazil embarked on a monumental program to convert all motor fuel to either neat ethanol or a 20% ethanol / gasoline blend.

OXYGENATE USE

Today, oxygenates are used by refiners not so much as a crude oil supplement but as an important and much needed source of octane. Octane demand has increased dramatically due to removal of lead anti-knock compounds from gasoline. Allowed lead levels in leaded gasoline are being reduced as recent medical evidence shows that current automotive lead emissions are a serious and costly health hazard (Refs. 1-4)

The United States has phased out lead use down to the 0.026 g/l* level. West European countries have reduced lead levels to 0.15 g/l with the significant exceptions of France, Italy, Spain, and Portugal which currently allow lead up to 0.4 g/l. Reductions in these countries are expected as pressures mount to harmonize standards by 1992. In fact, Italy has already announced their intention of reducing lead to 0.15 g/l by 1991 (Ref. 5). In several urban areas, where higher lead levels are still allowed, the concentration of lead in the atmosphere currently exceeds the limit set by the EEC in 1982 (2 micrograms / cubic meter annual average) (Ref. 6).

Unleaded gasoline is another big factor driving octane demand. This is now being introduced in Europe to allow the reduction of vehicle exhaust emissions by means of catalytic converters. Unleaded gasoline introduction is proceeding in varying degrees in West European countries (Table 1). In the United States, with 80% of the market being unleaded, most of the increase in octane demand has already occurred. Octane demand is, however, increasing further by the introduction of higher octane premium unleaded grades.

* 1 g/l = 1 kg m⁻³.

Table 1 - Lead Use in Gasoline - by country

Country / Area	Maximum Lead Allowed in Leaded Gasoline	Unleaded Gasoline Per cent Of Total Market
Europe:		
France	0.40 g/l	<1
Portugal		<1
Spain		<1
Italy	0.30 g/l Apr '89 0.15 g/l June '91	
* Austria		29
Belgium		<1
* Denmark		30
* Finland		<1
Greece		<1
Ireland		<1
Luxemburg	0.15 g/l	<1
* Netherlands		20
* Norway		18
* Sweden		28
* Switzerland		27
* United Kingdom		<1
* West Germany		27
United States	0.026 g/l	80
Japan	-	100

(* Denotes countries which currently have tax incentives for unleaded gasoline.)

In West Europe, octane demand will continue to grow rapidly, with most of the increase coming in the Mediterranean countries. Fig. 1 shows projected octane demand in motor octane number of the clear gasoline pool (MON* clear) for Northern and Southern Europe.

The most common oxygenates used today are Methyl Tertiary Butyl Ether (MTBE) (IUPAC nomenclature: 2-methoxy-2-methylpropane). Methanol / Tertiary Butyl Alcohol (TBA) (IUPAC nomenclature: 2-methyl-2-propanol blends and Ethanol. MTBE is widely used in both Europe and the United States while Ethanol is confined to the American States that subsidise

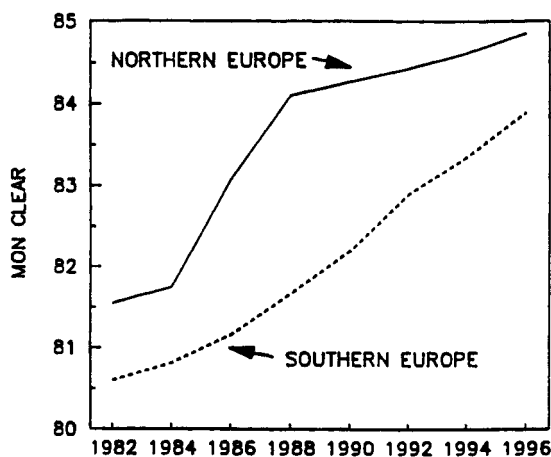


Fig. 1 Octane demand European refining industry

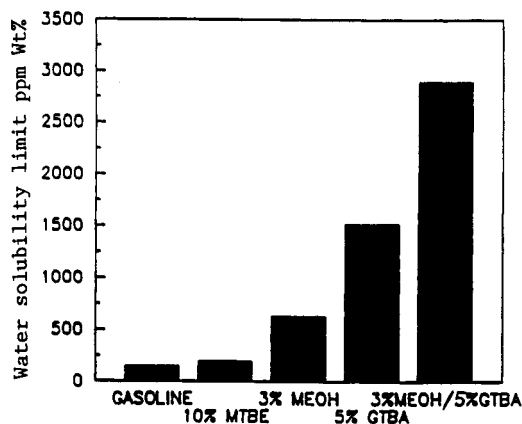


Fig. 2 Water tolerance of selected oxygenates (at 0°C)

* MON = Refer to GLOSSARY OF TERMS at the end of document.

**Table 2 - Typical Properties of Commonly Used Oxygenates
(Compared To Gasoline)**

	Blending Octanes		Blending RVP / Bar	Blending Density / g cm ⁻³	Distillation / °C	Oxygen Content / Wt %
	Ron*	Mon				
MTBE	118	101	0.55	0.740	51-74	18
TBA	109	94	0.70	0.755	74-95	22
Methanol / TBA	121	97	2.30	0.774	74-84	40
Gasoline	92-98	82-88	0.6-1.1	0.74-0.78	28-215	0

agricultural Ethanol production. The most significant use of Methanol / TBA blends today is in Austria and West Germany. Volumetric concentrations used are typically 0 - 15 % for MTBE, 3 - 5 % for methanol, 3 - 7 % for TBA, and 5 - 10 % for ethanol. MTBE is the most commonly used oxygenate and enjoys the fastest growth due to its superior blending properties and greater physical similarity to gasoline hydrocarbons.

SELECTED PROPERTIES OF OXYGENATES

The key property of any oxygenate is its octane blending value (Table 2). This can vary according to the composition of the gasoline components with which it is blended. Other important properties include vapour pressure, distillation, specific gravity, oxygen content and, for alcohols, the water solubility properties.

Methanol practically cannot be blended without a higher alcohol "cosolvent" such as TBA, IBA, SBA, or IPA (isobutyl alcohol, sec-butyl alcohol and isopropyl alcohol: IUPAC nomenclature 2-methyl-1-propanol, 2-butanol and 2-propanol). Otherwise, methanol would be extracted as soon as the gasoline came in contact with water, which is a common occurrence in most distribution systems. Cosolvent alcohols increase the water solubility of gasolines containing methanol and increase the equilibrium concentration of methanol in the gasoline phase, should the solubility be exceeded (Fig. 2 and 3).

The solubility of water in gasolines containing ethanol is usually high enough not to require a cosolvent. For any alcohol use in gasoline extensive precautions must be taken by refiners to avoid any excessive contact with water during the manufacture or distribution of the product.

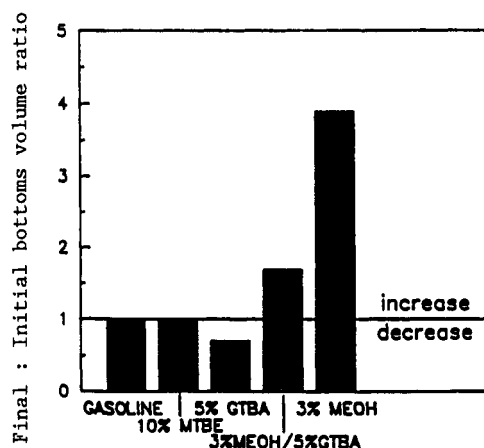


Fig. 3 Single water extraction test data with fuels containing oxygenates

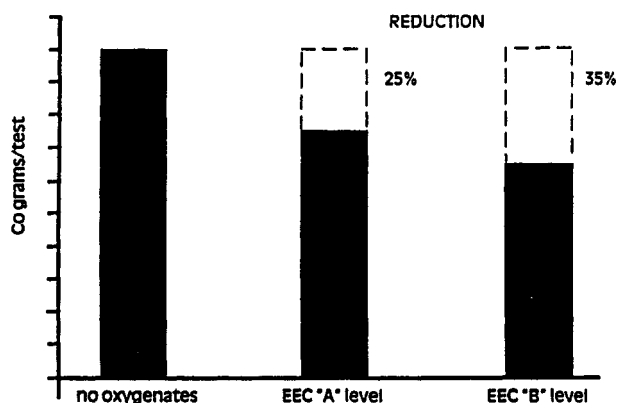


Fig. 4 CO-exhaust emission reduction with oxygenates

* Ron = Refer to GLOSSARY OF TERMS at the end of document.

ENVIRONMENTAL BENEFITS

While oxygenates initially were considered as a crude oil supplement and today are mainly used for their octane value, future use will be strongly environmentally driven. Perhaps the most important benefit of using oxygenates, even today, is the contribution they make to reducing air pollution.

Oxygenates have a positive environmental impact in four major areas:

1. Lead use can be reduced due to the octane contribution.
2. Vehicle carbon monoxide emissions are reduced by 25 - 30%.
3. Vehicle benzene emissions are reduced by 15 - 20%.
4. The photochemical reactivity of evaporated hydrocarbons are reduced.

Carbon Monoxide - Motor vehicles typically account for over 90% of the carbon monoxide in urban atmospheres. Approximately 75% of the total pollutants found in motor vehicle exhaust are, in fact, CO (Refs. 7-9).

Due to the leaning effect on the engine air to fuel ratio, oxygenates reduce vehicle CO emissions by roughly 25% when used at the 2.5 weight % oxygen level (Fig. 4). This reduction is basically a function of oxygen content and is independent of oxygenate type (Refs. 10-13). For some engines, hydrocarbon exhaust emissions are also reduced. NOx emissions, on average, remain unchanged (Fig. 5) (Ref. 14-18).

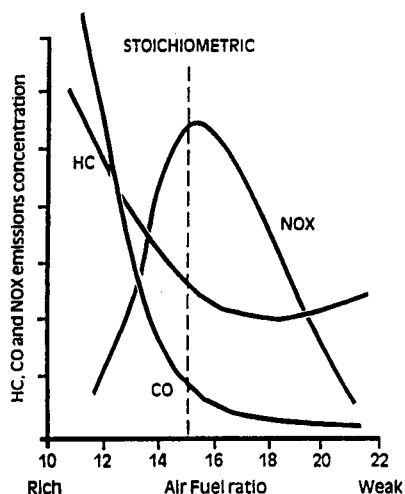


Fig. 5 Exhaust emissions vs Air-Fuel ratio

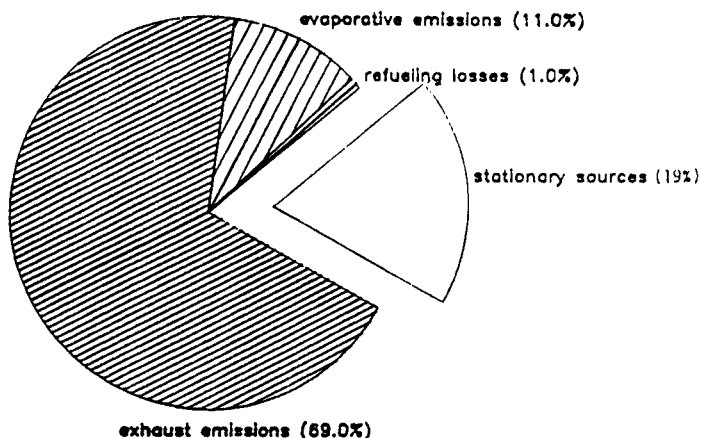


Fig. 6 Sources of atmospheric benzene (West Germany)

In the United States, several States are developing legislation that will mandate a minimum level of oxygen in all gasolines sold in market regions that currently exceed federal CO standards (Refs. 19-20). Colorado and Arizona already have legislation in place requiring all gasoline to contain a minimum of 2 weight % oxygen during the winter months, when CO levels are their highest.

The higher emissions of the European car population compared to those of the United States make the CO reducing properties of oxygenates even more significant here. For the same percentage reduction, the total quantity of CO reduced can be far greater in Europe and other regions which have less restrictive emission controls.

Benzene - As lead is removed from gasoline, a major environmental concern is that refiners will increase reforming severity to make up for lost octane. This would result in increased amounts of aromatics in gasoline, including benzene which is a known carcinogen (Refs. 21-22). Current EEC legislation sets a maximum benzene level of 5 volume % in unleaded gasoline (Ref. 23). Lower levels of 3 volume %, or less, are currently being considered in West Germany. California is now proposing to reduce the average benzene content to 0.6 volume % in the early 1990s.

Typically, 80 to 90 % of all benzene found in the atmosphere comes from gasoline powered motor vehicles (Fig. 6). For European vehicles, 85% of the the total benzene emitted is from the exhaust. Evaporative and refuelling losses make up the remainder (Ref. 24).

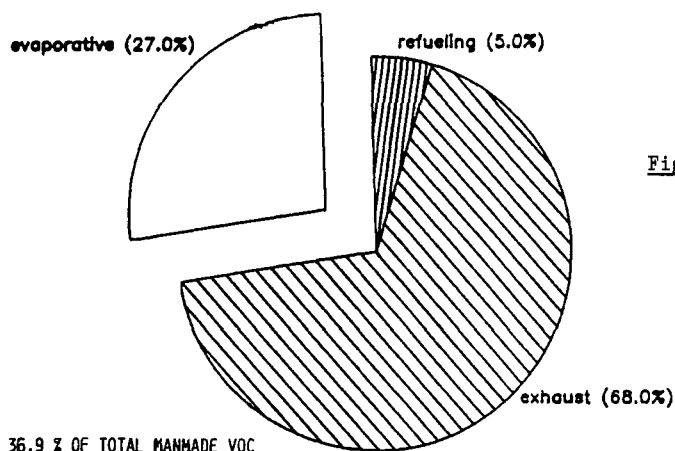


Fig. 7 VOC emissions from gasoline vehicles (Western Europe)

Even with no benzene in a gasoline other aromatics, such as toluene, have been found to increase motor vehicle benzene emissions (Ref. 25).

Oxygenates used instead of reformates to provide octane can significantly reduce benzene emissions. For example, MTBE used at 10 volume % can reduce aromatic levels by as much as 6 volume per cent. This can result in a 12 % reduction of benzene in the vehicle exhaust, regardless of whether or not the vehicle is equipped with a catalyst.

Photochemical Pollution - In addition to the exhaust emission reductions, oxygenates can also produce benefits with regard to vehicles' evaporative emissions. In West Europe 27% of VOC (volatile organic compounds) emitted from gasoline powered motor vehicles is in the form of evaporated fuel (Fig. 7) (Ref. 26). This relative contribution will increase as stricter exhaust emission legislation comes into effect. Of all the components used in gasoline, a comparison between studies that rank atmospheric reactivity of individual compounds shows oxygenates to have some of the lowest oxidation rates (Ref. 27).

Since oxygenates displace other hydrocarbons in the fuel vapour phase, the implications are that evaporative emissions from gasolines blended with oxygenates will probably contribute to a reduction in smog build-up in the atmosphere (Ref. 28).

CONCLUSION

Oxygenated compounds have an important role to play in the transportation fuel sector, offering:

1. A reduced dependency on imported crude oil.
2. A cost effective source of octane, which is required to produce low-lead and unleaded gasoline.
3. Significant reductions in several key motor vehicle pollutants.

The use of oxygenates in gasoline will continue to grow driven by octane demand, particularly in Europe, and for environmental reasons, particularly in the United States.

GLOSSARY OF TERMS

MTBE - METHYL TERTIARY BUTYL ETHER (2-METHOXY-2-METHYLPROPANE)	RON - RESEARCH OCTANE NUMBER (AGTM D-2700)
TBA - TERTIARY BUTYL ALCOHOL (2-METHYL-2 PROPANOL)	MON - MOTOR OCTANE NUMBER (ASTM D-2700)
MEOH - METHANOL (METHYL ALCOHOL)	RVP - REID VAPOR PRESSURE (EN12)
IBA - ISOBUTYL ALCOHOL (2-METHYL-1-PROPANOL)	EEC - EUROPEAN ECONOMIC COMMUNITY
SBA - SEC-BUTYL ALCOHOL (2-BUTANOL)	VOC - VOLATILE ORGANIC COMPOUNDS
IPA - ISOPROPYL ALCOHOL (2-PROPANOL)	

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