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The Use of FRP with Alcohol-Containing Fuels

ABSTRACT

There will be increasing use of alcohols and other oxygenated compounds, such as MTBE and TAME, for enhancing the octane value of gasoline. In some cases, alcohols, such as methanol, may be used as a direct fuel. In recognition of this, many standards relating to the storage, handling, or containment of petroleum products containing oxygenates have been adopted, such as UL 1361. FRP has had a long history of successful use in containment of gasoline, but introduction of alcohols coupled with increased levels of reformates makes the fuels more aggressive toward FRP. Designing resins for this purpose is now very demanding, especially in view of stringent standards required to prevent leaking from underground tanks and secondary containment vessels. This paper discusses the trends in gasoline production as well as recently completed testing for candidate resins. Of special interest is the good performance observed for novolac-based vinyl esters and high-crosslink-density polyesters.

INTRODUCTION

Although FRP has been long used for storage and containment of petroleum fuels, the phase-out of lead from gasoline coupled with changes in economics of refinery operations has resulted in fuels which can be increasingly aggressive. This stems from the need to maintain gasoline octane requirements which are necessary to meet goals of national automobile efficiency achieved largely through use of high engine compression ratios.

Gasolines now contain more aromatic compounds due to increased reliance on refinery hydrocracking and reforming operations. Many gasolines now also significantly contain oxygenated compounds to meet necessary octane requirements. These oxygenates are principally composed of aliphatic ethers such as MTBE or TAME, but have also included various alcohols such as methanol and ethanol. These additives not only improve octane values, but also reduce net emissions of hydrocarbons and carbon monoxide.

It is estimated that today only 2% of the total gasoline pool contains oxygenates. However, the 1990 amendments to the Clean Air Act have mandated the use of cleaner-burning fuels in 41 cities that exceed federal ambient air standards for carbon monoxide. By October 15, 1992, gasoline sold in these areas must contain 2.7% oxygen by weight. This could affect 25–30% of the U.S. gasoline pool. Considerable refinery expansions are underway to provide the increased amount of oxygenates.

It is thus important for the FRP industry to constantly monitor the contemporary and future trends associated with gasoline supply so that composites can resist these fuels, especially since failures of storage facilities can represent serious environmental consequences. The need for resistance to oxygenated fuels is now well recognized in standards adopted by government and product evaluation organizations such as Underwriters Laboratories. Additionally, RCRA requirements now place stringent standards on secondary containment and leak detection systems for storage of petroleum fuels and other chemicals.

A good deal of data exist on the resistance of FRP to alcohol-fuel blends as well as to other candidate oxygenated additives. However, much of the data represent a potpourri of temperature and other test conditions from a variety of laboratories. There was thus felt to be a need for better comparative evaluation of resins used in these applications. Accordingly, ASTM C-581 full immersion testing was started about a year ago to consistently compare various resins when exposed to some of the most aggressive fluids, as well as to accelerated temperature (100°F) associated with Standard 1316 of Underwriters Laboratory. Since the entire UL approval process is lengthy and expensive, it is hoped these results are useful to fabricators and end users.

Resins tested included a variety of Bis-A epoxy vinyl esters, epoxy novolac vinyl esters, isophthalic polyesters, and high crosslink density polyesters. Special attention was given to the high crosslink density polyesters because of their attractive costs, as well as due to their historic use in Europe for alcohol containing fuels, coupled with recent successful use by U.S. fabricators. Results confirmed the good resistance of high performance vinyl esters as well as the high crosslink density polyesters.

Testing of gasoline-containing liquids is quite hazardous, so the initial scope was limited for safety purposes. Results of the testing will serve to guide future experiments incorporating other resins, cure systems, and alternate fuels. The current work has generated nearly 2,500 distinct data points, which require a great deal of time for proper statistical analysis. However, key results and conclusions are presented for preliminary purposes.

THE NEED FOR HIGH OCTANE FUELS

The fuel-air mixture in each engine should ideally burn smoothly and evenly following timed ignition by the spark plug. However, with an improper fuel, problems can arise. As the spreading flame front sweeps across the combustion chamber, the yet unburned portion of the fuel (sometimes called end gas) becomes so heated upon compression that it auto-ignites and detonates in an instant. This results in "knocking" which produces objectionable noise, engine wear, loss of efficiency, and waste of fuel. The chemical mechanism associated with knocking is complex,

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but it relates to a series of pyrolysis and oxidation reactions which occur as the temperature of the fuel-air mixture is progressively increased. Unstable hydrocarbons are thus formed, which are prone to auto-ignition and instantaneous detonation. Apart from the obvious deleterious effects on the engine and fuel economy, unburned hydrocarbons can ultimately escape to the atmosphere despite use of modern emission control systems. These hydrocarbons then contribute to photochemical smog, along with other adverse environmental effects.

Gasoline is a mixture of various paraffin, olefin, naphthenes (saturated cyclics), and aromatic hydrocarbons which collectively boil in the 85–400°F range. Quite often gasoline content is controlled in refineries on the basis of "PONA" analysis (paraffins, olefins, naphthenes, aromatics). It has long been recognized that the chemical structure of these hydrocarbons largely determines their tendency to cause knocking. Straight-chain paraffins are much more knock-prone than branched chained paraffins. Likewise, naphthenes are more likely to induce knocking than aromatics.

There are some exceptions to these general rules. A notable one is for simple alkanes, such as methane, ethane, propane, and butane. All of these have relatively high anti-knocking tendencies, but with the exception of butane, they are too volatile for use in conventional gasoline. Since butane is readily available and relatively cheap, refiners try to incorporate as much butane into the gasoline as possible. However, the limitation is the resultant vapor pressure of the gasoline, which is customarily measured and reported as Reid vapor pressure. The standards on Reid vapor pressure will vary with the season or geographical markets. To overcome the volatility restrictions, aliphatic ethers derivable from butane (e.g., MTBE) have been introduced, as will be discussed later on.

Another category of compounds which display good anti-knocking properties involves so-called oxygenates which are within (or reasonably close) to the boiling range of gasoline. The compounds are principally the alcohol homologs of the simple alkanes, such as methanol or ethanol. Other recently introduced oxygenates which display excellent properties include various ethers made from C-4 and C-5 olefins reacted with methanol or ethanol. An example is methyl tertiary-butyl ether (MTBE) made from isobutylene and methanol.

Details on why these oxygenates serve to improve anti-knock properties is beyond the scope of this paper. However, a significant side benefit is that oxygenated fuel additives are very clean burning, largely due to the fact that since they already contain oxygen, less air is stoiciometrically required to complete the total combustion. The clean burning nature of these oxygenates not only reduces hydrocarbon emissions, but carbon monoxide as well.

The knocking tendency for gasoline is measured on an "octane scale," which is used worldwide. Since highly branched paraffins are far less prone to knocking than straight chain paraffins, a value of zero was long ago assigned to *n*-heptane while a value of 100 was arbitrarily assigned to isooctane. The so-called motor octane number (MON) is thus a measure of the volumetric percentage of isooctane required in a blend with *n*-heptane to match the behavior of a particular gasoline being tested.

Throughout the years other tests and indices of anti-knocking properties have been developed. A common one is the so-called Research octane number (RON) which is measured under less severe conditions. The difference between MON and RON is sometimes called the "sensitivity," which is a rough index of how sensitive (in terms of anti-knock performance) the fuel becomes upon more severe engine operating conditions, such as higher speed. Generally, olefins and aromatics impart much more sensitivity to the gasoline than do paraffins. Other octane ratings have been developed to obtain a better indication of how the automobile will perform over a wide range of speeds, loads, and weather conditions. This index is called the road octane number (RdON). The RdON is approximately equal to the average of the MON and RON values. Therefore, it is rather common to see candidate fuels indexed to the value (MON + RON)/2.

Some typical comparative octane values are as follows for major gasoline components or octane enhancers:

	(MON + RON)/2
Hydrocarbons	
Toluene	105
Motor Alkylate	92
Methane	131
Ethane	109
Propane	105
N-butane	93
Isobutane	99
Oxygenates	
Methanol	118
Ethanol	107
Tertiary-butyl Alcohol (TBA)	99
Methyltertiary-butyl Ether (MTBE)	108
Tertiary-amyl Methyl Ether (TAME)	105

An automobile engine can be ideally represented by the air-standard Otto cycle. The net work and efficiency is directly proportional to the compression ratio. Early vintage automobiles operated at 5:1 compression ratio, whereas modern engines are in a 10:1 or higher range. As the compression ratio is increased, the need for higher octane value of the fuel increases. The cost and availability of high octane fuels is thus quite important in achieving goals of national fuel efficiency. Indeed, the U.S. Department of Transportation has issued regulations mandating a staged increase in minimum combined fleet economy for each manufacturer. This mandate was 18 miles/gallon in 1978, but is now over 27 miles/gallon. These regulations present opportunities for FRP not only in accommodating storage of high octane fuels, but also for fabrication of lighter weight automotive structural composites.

THE SIGNIFICANCE OF THE PHASE-OUT OF LEAD

In the 1920s, considerable research was begun to investigate chemical additives which would be effective in improving gasoline octane ratings. Perhaps 150 such compounds were discovered, but by far the most effective were various alkyl-lead compounds, most significantly, tetraethyl lead (TEL) and tetramethyl lead (TML). Remarkably, no alternate small concentration additives have since been discovered which favorably compare with the effectiveness or cost of the various lead alkylates. In the 1970s, a manganese derivative was tried as a substitute, but it was banned when it was shown to affect catalytic converters.

The obvious problems with lead alkylates are environment and health effects, especially in view of the nation's ever-increasing appetite for gasoline. Health problems can occur not only from the lead per se, but also from various halogenated scavengers used in conjunction with TEL or TML to reduce accumulation of inorganic lead compounds on spark plugs and exhaust valves. These scavengers were most commonly ethylene dichloride (EDC) and ethylene dibromide (EDB). Moreover, lead is a poison to oxidation catalysts used in catalytic converters which have been used in automobiles ever since the tightening of hydrocarbon emission standards.

In the early 1970s, it was estimated that gasoline contained about 2 gms of lead per gallon. In order to reduce emissions of lead compounds, the U.S. Environmental Protection Agency ordered a gradual decrease in the average lead content of all gasolines. The EPA mandate initially required a lead phasedown to 0.5 grams per gallon by January 1, 1979, although the phasedown was postponed several times due to lack of reforming (and other unit operation) capacities within refineries to establish a high enough octane pool to meet demand. Lack of reforming capacity greatly contributed to the infamous gasoline lines of the 1970s.

Currently, as most people know, lead has been phased out altogether for automotive gasoline. This continues to place demands on refineries for meeting octane requirements, which becomes increasingly difficult in view of the relative scarcity of premium crude petroleum feedstocks.

REFINING OPERATIONS

Refineries rely on a number of basic processes to produce gasoline. These principally include distillation, cracking, and hydrocracking. Distillation is the first step in the refining of crude oil, but the gasoline yield (called straight-run gasoline) is normally of low quality especially with the types of crudes now available.

Cracking involves treatment of the heavier fractions to pyrolyze them into lower-boiling ones. Modern cracking is accomplished catalytically, quite often by fluidized bed processes. Fluid catalytically cracked (FCC) gasolines have RON values of 92–94, and as such make good blendstocks. Hydrocracking involves cracking in the presence of added hydrogen. Although hydrocracking is expensive, it is a versatile process to maximize the gasoline yield or to vary the yield of gasoline versus other refinery products, such as fuel oil. There is a trend in modern refineries to employ increasingly severe conditions of temperatures and pressures in hydrocracking and various hydrotreatment processes. Nevertheless, whenever hydrocracked stocks constitute a high proportion of finished gasoline, they must be subjected to an octane improvement process call reforming, since they lack the high octane olefins present in catalytically cracked blending stocks.

Reforming is the major process in the refinery to increase octane values. The resulting octane number improvement stems mainly from cracking of low octane heavy paraffins into lighter, highly branched paraffins and olefins. Depending on the type of catalysts and operating conditions, different reactions occur. Usually for best overall economics, the conditions are selected not only to treat the paraffinic constituents, but also to abstract hydrogen from naphthene constituents and to remove hydrogen from heavier aromatics. The resulting aromatics are rich in benzene, toluene, and xylene (called BTX fractions), which are excellent contributors to octane values. Reforming is a workhorse process in refineries to increase the octane pool, although other processes are used. Examples include alkylation, polymerization, isomerization and hydrotreating.

In the old days when lead was permissible as an anti-knock additive, there was less demand placed on reforming to meet octane requirements since it was quite simple to merely add TEL or TML to boost the octane number. The octane number of the reformate increases as operating conditions are made more severe through higher temperatures and increases in reaction time. However, increasing the severity of reforming decreases the yield. This is because the more severe conditions convert more of the feedstock to light hydrocarbon gases. Moreover, the BTX fractions are more dense which shrinks the volume of liquid product. Reduced yield to meet higher octane requirements by conventional reforming is thus a major reason why oxygenated additives are now considered.

OXYGENATED ADDITIVES

Refinery operations and costs can become very complicated, but it has largely been economic considerations which have motivated the trends toward use of oxygenated components as a supplement to octane enhancement.

Methanol, for example, has a very high octane number, and despite sophisticated processing steps it can be made from low grade feedstocks. Usually methanol is made catalytically at high pressure from synthesis gas (CO and H_2) obtained from high temperature steam reforming of natural gas. For some of the more conventional uses of methanol, e.g., solvents, the cost of doing this is justified. However, in a refinery the methanol can be made from synthesis gas resulting from the partial oxidation of heavy feedstocks which otherwise could be next to worthless. It can also theoretically be made from gasification of petroleum coke, which results when very heavy feedstocks are carbonized to obtain the "bottom of the barrel." Petroleum coke has some markets in metallurgical processing and for use in making anodes for aluminum production. However, many refineries will simply stockpile petroleum coke because it cannot be sold.

The methanol can alternatively be used to make aliphatic ethers from light olefins using ion exchange type catalysts. The ethers are added to gasoline at typical levels of 7% by volume and include:

- methyl-tertiary-butyl ether (MTBE)—made from methanol and isobutylene
- tertiary-amyl-methyl ether (TAME)—made from methanol and isoamylene
- ethyl tertiary-butyl ether (ETBE)—made from ethanol and isobutylene, although this is a product feasible only if refiners have access to ethanol

Refiners can readily produce the olefins required to make these ethers. A common method for making isobutylene is from butane dehydrogenation, although other processes can be used such as fluid cat cracking and pyrolysis. As previously mentioned, butane itself is a good octane component but its use is restricted by vapor pressure limitations. Since the ethers are in the proper boiling range they essentially represent economical ways for refiners to extend the octane pool, with the side benefit that these ethers reduce automotive emissions.

MTBE performs very nicely in gasoline and seems to improve engine efficiency in the low-speed acceleration phase. However, when it was first introduced in 1979, it was not without controversy and involved waivers to the Clean Air Act since at the time it was new and not fully tested. EPA interpretative rulings finally allowed use of aliphatic ethers provided total oxygen content of the fuel did not exceed 2% and the final fuel conformed to other ASTM specifications. This upper limit was later extended.

Current domestic MTBE production capacity is about 400,000 barrels per day, but demand is expected to double over the next four to five years. Numerous plant expansions have been announced. It is expected that MTBE and similar ethers will not be exceptionally aggressive to FRP, at least much less so than from other candidate octane boosters such as methanol and ethanol. Test results thus far indicate this is true. However, with the strong apparent trends toward use of these ethers it is necessary for the FRP industry to continue with testing and to be very up-to-date on the gasoline production scenario.

ALCOHOLS AS GASOLINE ADDITIVES

During the gasoline shortage of the 1970s, ethanol was added to gasoline to meet the octane requirements and to extend the volumetric production. This mixture came to be marketed as "gasohol," although the term may since have lost its original meaning. Since ethanol has a good octane value, the gasohol blends work nicely.

Most ethanol is derived from grain, usually when it is in surplus and with much of the cost of alcohol production subsidized through tax credits. It is doubtful whether grain derived alcohol will have a significant impact on future energy demands. Although grain alcohol may appear to take advantage of solar energy, studies often indicate that the energy to grow grain (fertilizers, harvesting, etc.) exceed the energy in the net product. Nevertheless, grain alcohol is currently used as an octane supplement in many areas,