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Refineries and Fuel Alcohol

The following article is the 60th in a series of articles written by IRI Advisory Board member George Unzelman, president of HyOx, Inc.

Aromatics On The Front Burner

Aromatics have become one of the focal points with respect to gasoline reformulation. In the last decade the concentration of this class of hydrocarbons, all based on the benzene ring, has increased from about 22 volume percent to 32 volume percent in the U.S. gasoline pool. The rise in gasoline aromatics was no surprise to knowledgeable people associated with petroleum processing. Also in the 1990 decade it will be no surprise to this writer when aromatics in gasoline are reduced.

In the late 1970s the major environmental move with respect to gasoline composition was to eliminate lead antiknocks. The logical and most technically sound substitute for lead at the time was to increase aromatic hydrocarbons and, by so doing, the industry retained some semblance of gasoline octane quality for the unleaded grades as the phasedown progressed. There is ample evidence that industry observers and forecasters knew that lead removal would create new problems. In fact the aromatic content of today's gasoline can be rather accurately predicted from an Ethyl Corporation paper given Oct. 16, 1979. One paragraph reads as follows:

"Certainly, aromatics will be significant replacement for antiknocks. This will have an impact on the availability and cost of aromatics now going to the petrochemical industry. The amount of additional aromatics required will depend on the volume and octane levels of the various grades of gasoline, the use of high-octane blending stocks from alkylation and isomerization processing units, and the use of alcohols and ethers."

By extrapolating data from that paper and converting Research octane to $(R+M)/2$, those projected average aromatic levels closely track today's U.S. gasoline. Many of the same forecasters also pointed out the potential health hazards involved in substituting aromatics for lead in gasoline. Since that time benzene has become one of the major hydrocarbon targets for environmental concern. Further, studies of exhaust emissions have shown that benzene can be manufactured in the internal combustion engine from heavier gasoline aromatics. While most of the aromatics are combusted in the engine or destroyed in the catalytic converter, some escape through the tailpipe. The concentration of benzene in the tailpipe emissions can be blamed on both the original benzene content in gasoline before combustion and the amount of benzene formed in the engine from the breakdown of heavier aromatics.

Therefore benzene concerns are twofold from the environmental viewpoint. The amount contained in gasoline that can contribute to evaporative emissions is subject to some human exposure. Also the small amount from the tailpipe that, not only is exposed to the freeway driver, but ultimately is a potential hydrocarbon to take part in the photochemical reaction to form smog.

However it is not surprising that the opposing viewpoints on the dangers of benzene are at extreme ends of the scale. Edwin G. Rothschild, Energy/Environmental Policy Director of Citizen Action commented in *USA Today* under the heading Gas Fumes Are Hazardous to Your Health:

"Every time we fill up our automobiles with gasoline, we are inhaling vapors that contain cancer-causing benzene..."

We are also exposed to benzene in the air we breathe. This is because benzene is emitted from our car's tailpipe from the combustion of gasoline containing benzene and other so-called aromatic hydrocarbons..."

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Congress is considering President Bush's clean air proposal which contains provisions that would require the use of cleaner-burning fuels. Unfortunately, the oil and auto industries have succeeded in persuading some members of Congress to scuttle this proposal."

Charles J. DiBona, president of the American Petroleum Institute, countered Rothschild under the heading Pumping Gas is Little Risk to Health. Some of his comments follow:

"The Citizen Action accusation that gasoline self-service is risky is irresponsible rhetoric. Let's look at the facts: Benzene is present in gasoline at levels far below the U.S. Consumer Product Safety Commission's product-labeling limit. Both the Health Effects Institute and the Environmental Protection Agency have extensively studied the question of danger to consumers from filling their own gas tanks. They have found no scientific evidence of any adverse human health effects from the limited exposure you get from pumping your own gasoline...

People using self-service pumps are typically exposed to low levels of vapors for only a few minutes a week, a level that does not subject them to increased risk of cancer or to other dangers...

Everyone, including oil companies, has a responsibility to reduce exposure that leads to serious risks. The socially responsible course of action is to assess risks accurately and reduce the risks according to how serious they are..."

The bottom line is that both viewpoints carry a measure of truth. Benzene is a known carcinogen and exposure to this chemical should be minimized. Benzene is present naturally in crude oil to varying degrees but is also formed at the refinery in the naphtha reforming process. There is more benzene in gasoline today than there was 30 years ago but it is in quite low concentration. Depending on the makeup of a particular marketed gasoline, benzene concentration can range from 1 to 5 volume percent. The U.S. average is about 1.5 volume percent. The technology exists, with new processing, to reduce benzene concentration and still maintain marketed octane quality. Also, processing capabilities exist, such as etherification, etc., to eventually facilitate lower overall aromatic content and still maintain marketed octane quality. However, all aromatics cannot be eliminated from U.S. gasoline unless some "super engine" is evolved that does not recognize octane requirement. Aromatics are the key hydrocarbons contributing octane quality to finished gasoline. The sad truth is that if the etherification options had been available to petroleum-refiner planners during the early stages of the push for lead removal (1970-1980), the aromatic content of gasoline would probably be lower today.

In the final analysis, the state of California will very likely place some restriction on the benzene content of gasoline. Eventually EPA will probably follow the example for the U.S. It is indeed fortunate that the ethers have become an attractive option for refiners to increase the octane quality of gasoline. Therefore these oxygenated compounds provide the best opportunity to reduce total aromatics in reformulated gasolines and improve overall air quality. Whether they will admit it or not, today both the environmentalists and the oil industry are sighting in on the same target with respect to gasoline aromatics, the oil industry with research to implement reformulated gasolines and the environmentalists with rhetoric.
