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Economics on the Use of Oxygenates

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Abstract. The cost of oxygenating gasoline is analyzed considering spot prices prevailing in the American Coast of the Gulf of Mexico from May to July 2003. We found that it is cheaper to oxygenate gasoline using MTBE rather than EtOH, when unsubsidized EtOH prices are considered. Refineries in countries no subsidizing EtOH, having fluid catalytic cracking units, will find advantageous to use light olefins present in the catalytic gasoline to produce ethers.

Key words: Economics; Oxygenates; Reformulated Gasoline; Ethanol; Methyl tertbutyl ether.

Resumen. Se analizan los costos de oxigenar gasolina al considerar los precios spot prevalecientes en la Costa Estadounidense del Golfo de México de mayo a julio del 2003. Encontramos que resulta más económico oxigenar gasolina usando éter metil terbutílico (MTBE) que etanol (EtOH), cuando los precios no subsidiados del EtOH se consideran. Refinerías de países que no subsidian etanol y que cuentan con unidades de rompimiento catalítico fluido, tienen ventajas al usar las olefinas ligeras de la gasolina catalítica para producir éteres.

Introduction

Oxygenates are used to increase octane number of gasoline and to reduce emissions of carbon monoxide and hydrocarbons. Its use skyrocketed when lead was phased out and later when the 1990 U.S. Clean Air Act was enacted. Originally, U.S. refineries choice of oxygenate was methyl tertbutyl ether (MTBE), but contamination to the underground aquifers by leaks, led some U.S. states to ban its use. However, it has been shown that leaks from other products represented even a higher risk than leaks from gasoline containing MTBE [1]. In Mexico City, to prevent spillages, Petróleos Mexicanos has enforced the installation of double-wall storage tanks in the gasoline stations, fitted with leak detectors installed in between the walls. Banning the use of MTBE is solving the environmental problem at the end of the pipe, instead of at its origin, i.e., the leaking tanks.

Oxygenates have an economic penalty because they are oxidized hydrocarbons, so its heat of combustion is diminished; only compensated partially by its ability to increase octane and to reduce emissions. The following economic analysis compares the economic advantage of using MTBE or ethanol (EtOH). Some other ethers like di-isopropyl, methyl teramylic, ethyl tertbutylic, and ethyl teramylic have the additional advantage of lowering gasoline vapor pressure, so its use allows an increasing butane concentration in gasoline. Butanes are the lowest cost component of gasoline, but the effect of some oxygenates on reducing vapor pressure will not be considered here, as it is a small one. It will also not be considered the economic significance of reducing emissions as it mainly depends on the engine technology, the air-fuel ratio and its tune-up conditions [2]. In fact, an oxygenating

program to be successful must be linked to an Inspection and Maintenance Program [3].

Ethanol has the disadvantage of increasing the Reid Vapor Pressure of an oxygenated gasoline by 6.9 kPa [3], so a more expensive gasoline with a lower RVP has to be employed to reduce vapor emissions.

Economic Evaluation

To make an economic analysis and due to the proximity to Mexico, reference shall be made to the international spot average prices prevailing in the American Coast of the Gulf of Mexico from May 3rd to July 7th 2003 [4]. To evaluate the economic benefit of increasing octane, the price of the octane-liter (\$_{O-L}) is calculated by the difference between premium (P) and regular (R) gasoline prices, divided by 4, to consider their octane difference.

$$\$_{O-L} = \frac{P-R}{4} \quad (1)$$

Let z% be the percent of oxygen weight; y% the oxygenate weight percent and x% the oxygenate volume percent content in gasoline. It shall be here analyzed the cost increment by oxygenating regular gasoline by z%, in relation to prices of oxygenate, gasoline, and octane-liter, on the understanding that for any other level of oxygenation, the cost increase is proportional to the oxygen concentration. No consideration is given to transportation, handling and storage costs of oxygenates, as they vary widely and depend on the location of the gasoline distributor and the oxygenate producer.

Table 1. International average prices from May 3rd to July 7th 2003 in the American Coast of the Gulf of Mexico. (U.S. dollars/L) [4]

MTBE	0.2783
EtOH subsidized	0.1927
EtOH unsubsidized	0.3301
Regular Gasoline (Conventional)	0.2358
Premium Gasoline (Conventional)	0.2448
Regular Gasoline (Reformulated)	0.2480
Premium Gasoline (Reformulated)	0.2747

As in practice, it is easier to prepare solutions by measuring the volume of components than by weighing, but as specifications are given on a weight basis, it is convenient as a first step to transform a blend having $x\%$ by volume of any oxygenate into $y\%$ weight basis. The gasoline density will be denoted by ρ_G and by ρ_O the oxygenate density in kg/L, then:

$$y = \frac{x\rho_O}{x\rho_O + (100-x)\rho_G} = \frac{x\rho_O}{100\rho_G + x(\rho_O - \rho_G)} \quad (2)$$

To transform the $y\%$ weight oxygenate basis into $z\%$ weight oxygen basis in gasoline, $y\%$ is multiplied by a factor F_i , which is, the mass ratio of oxygen to the oxygenate molecule.

$$z = y \cdot F_i \quad (3)$$

Physical-chemical properties of MTBE, EtOH, and gasoline are given in Table 2.

The F_{EtOH} factor here calculated is slightly smaller than 0.3478, reported in the literature⁽⁵⁾. In table 3, equivalent figures are given for a weight oxygen content of 1, 2 and 3% in gasoline to the corresponding values of $y\%$ and $x\%$.

The gasoline cost containing an oxygenate is increased due to a higher intrinsic cost of an oxygenate than gasoline, with the exception of subsidized EtOH; for example MTBE demanded an average price of \$0.2783 U.S.dollars per liter, whereas unsubsidized EtOH had an average price of \$0.3301 U.S. dollars per liter; however an ethanol subsidy of \$0.1374 U.S. dollars per liter, decreased its real average price in the U.S. market to \$0.1927 U.S. dollars per liter, even below the gasoline average price of \$0.2358 U.S. dollars per liter. Due to advances in Industrial Biotechnology, it is expected that cellulose ethanol will be made from crop residues such as wheat straw and corn stover rather than corn-starch derived from corn kernels [6]. It is likely that use of the new technology will decrease ethanol prices.

Oxygenates have a lower heat of combustion than gasoline due to partial oxidation. Therefore, oxygenates as fuel have a lower yield than gasoline. The calculated percentage decrease in fuel economy—yield lost—by the oxygen content of gasoline when EtOH or MTBE are added, have a linear relationship given by their respective eq (4) and eq (5). The

Table 2. Physical-chemical Properties of MTBE, ETOH and gasoline

	MTBE	EtOH	Gasoline
Density, kg/L	0.7424	0.7873	0.7334
Heat of Combustion, kcal/L	6,229	5,063	7,795
Octane number (R+M)/2	110	115	86
Mass ratio of Oxygen to Oxygenate molecule	0.1815	0.35506	

Table 3. Relation among x , y , and $z\%$

OXYGENATE		z% weight of oxygen in gasoline		
		1	2	3
EtOH	y%	2.8164	5.6329	8.4493
	x%	2.8219	5.6547	8.4984
MTBE	y%	5.5096	11.0193	16.5289
	x%	5.5133	11.0340	16.5621

calculated values are based on the heats of combustion of MTBE, EtOH and gasoline as reported in Table 2.

$$Y_{\text{EtOH}} = 9.2131 \cdot O_{\text{EtOH}} \quad (4)$$

$$Y_{\text{MTBE}} = 10.9421 \cdot O_{\text{MTBE}} \quad (5)$$

Where Y_i refers to the fuel economy percent lost by use of the oxygenate, i , and O_i is the oxygen weight percent content of oxygenated gasoline.

It is here assumed that gasoline and the oxygenates behave as ideal solutions, and that octane number is an additive property, in which the octane resulting in a mixture is equal to the sum of the octane-gallon of each component, this is,

$$V_B O_B = \sum_i V_i O_i \quad (6)$$

where the sub indexes B and i refer to the gasoline blend and to each component, respectively. V stands for volume and O for octane number.

The incremental cost per liter of oxygenated gasoline to reach 2.7% oxygen weight by using MTBE or EtOH is summarized in table 4. Figures corresponding to 1% of oxygen weight are also included, as it is the minimal oxygen concentration mandated in Mexico City. There is a considerable controversy over the costs refineries incur in meeting the specifications of reformulated gasoline and oxygenated fuels provisions of the U.S. Clean Air Act. Estimates published by the U.S. National Petroleum Council give a range of 0.783 to 1.85 U.S. dollar cents per liter for the increased cost to produce, deliver and use oxygenated fuels [7]. A study prepared for the U.S. Oxygenated Fuels Association by Lundberg Survey

Table 4. Incremental cost per gallon by oxygenating Regular gasoline with EtOH or MTBE. (U.S. dollar cents/liter of blend)

	EtOH		MTBE	
	2.7 % O		2.7% O	1% O
	Unsubsidized	Subsidized	Unsubsidized	
y%	7.60435	7.60435	2.81643	14.87603
x%	7.64414	7.64414	2.82187	14.90291
incremental cost, U.S. dollar cents/liter of blend.	0.72084	-0.3295	0.2661	0.6334
Octane number increase in blend	2.217	2.217	0.8183	3.577
incremental benefit by oxygenation, U.S. dollar cents/liter of blend.	0.50	0.50	0.1841	0.8048
NET COST, U.S. dollar cents/liter of blend.	0.22221	-0.8282	0.0820	-0.1714

Incorporated indicates that national implementation of reformulated gasoline led to a price increase of 0.764 U.S. dollar cents per liter [8]. US Department of Energy combined market estimation techniques with production cost information to show a 1.03 U.S. dollar cents per liter of premium in the summer and 0.925 U.S. dollar cents per liter of premium in the winter [9]. The average fuel spot prices reported here, give a difference between reformulated and regular gasoline of 1.22 U.S. dollar cents per liter, and a difference between reformulated and premium gasoline of 2.99 U.S. dollar cents per liter.

The intrinsic cost here estimated and reported in Table 4, gives a figure of 0.222 U.S. dollar cents per liter for a 2.7% oxygen content, taking into account unsubsidized EtOH, and a benefit of 0.17 U.S. dollar cents per liter for MTBE. Anyhow, the transportation, storage and handling costs not taken into account here seem to offset the intrinsic costs of the oxygenates in most of the American refineries. However, refineries using isobutylenes or isoamylenes to produce ethers should have a distinctive cost advantage as it is not required to transport and storage olefins, which is precisely the case of the Mexican Refineries that produce MTBE and teramyl-methyl ether (TAME) at the same location.

Discussion

1. For the same oxygen content there is a lesser cost by oxygenating gasoline with MTBE rather than unsubsidized EtOH. Using MTBE, and for 2.7% O in gasoline, there is a net benefit of 0.171 U.S. dollar cents per liter of blend, whereas for 1% O in gasoline, it is 0.063 U.S. dollar cents per liter of blend. The net cost of oxygenating gasoline at the level of 2.7% O is 0.222 U.S. dollar cents per liter of blend for unsubsidized EtOH, and 0.082 U.S. dollar cents per liter of blend when the oxygen content is 1% for unsubsidized EtOH.

2. For MTBE, the benefit obtained by increasing octane number corresponds approximately to 127% of its intrinsic cost.

3. For Mexico, where refineries produce MTBE from the streams coming from the Fluid Catalytic Cracking units, there is a cost advantage as it is not required to meet the expense of transporting olefins, one of the raw materials to produce MTBE. There is an additional environmental advantage of producing MTBE, as the volatile and photo reactive light olefins are removed to produce ethers [10], which otherwise would favor ozone formation, if left in gasoline.

4. The low price of subsidized EtOH makes attractive to mix it with gasoline as it lowers the cost. There is a net benefit of 0.828 U.S. dollar cents per liter of oxygenated gasoline when subsidized EtOH is used to provide a 2.7% oxygen content, whenever intrinsic ethanol costs are only taken into account. However, from the environmental viewpoint, using EtOH to oxygenate gasoline has the disadvantage of increasing by 6.9 kPa the Reid Vapor Pressure (RVP), and consequently increasing evaporative emissions [3], unless a more costly gasoline with a lower RVP is employed.

5. The fuel economy of an oxygenated gasoline with ethanol containing 2.7% weight oxygen is decreased by approximately 2.5%. There is an inverse linear dependence of fuel economy on oxygen content. The car owner will incur in an additional cost of using reformulated gasoline of 0.62 U.S. dollar cents per liter if the oxygenate is unsubsidized EtOH, because of fuel economy lost.

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