Advanced Gasoline Components for Latin America; Production, Blending, and Environmental Properties of MTBE and ETBE.

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Abstract

This article reviews the production of MTBE and ETBE from High Purity Isobutylene (HPIB) or mixed butenes (e.g. Raffinate 1), the fuel blending properties of MTBE and ETBE to alcohols, and the cost, performance, and environmental benefits of blending ethers instead of alcohols into gasoline. Mexico has achieved remarkable air quality improvements in the past 20 years by blending MTBE into its gasoline. Global experience over the past 35 years confirms that *tert*-butyl ethers are the cleanest and simplest way to incorporate methanol, ethanol, and butanes into fully fungible and highly stable gasoline while boosting octane for optimal driving performance and air quality improvements.

Introduction

Outside of Brazil and Colombia, MTBE has been the main octane blending component for gasoline in Latin America for over 20 years.[1] Mexico, Venezuela, and Chile were the largest importers of MTBE from the United States in 2013, according to the US Energy Information Administration.[2] The benefits of MTBE on air quality have been the most dramatic in Mexico City, which the United Nations Environment Programme (UNEP) declared "the most polluted on the planet" in 1992.[3] Since PEMEX started adding MTBE to metropolitan zone (MZ) gasoline in 1993, ozone (O3) levels in Mexico City have decreased by 53%, carbon monoxide (CO) levels by 86%, and particulate matter (PM10) by 32% despite a near doubling of the number of vehicles on the road, Figure 1.[4] In 2007, Japan chose to use 7% ETBE instead of ethanol as primary biofuel for the 60 million passenger cars running on gasoline.[5]

Meanwhile European ETBE consumption increased from 200 to 3,700 Kilotons per year from 2003 to 2010[6] and global MTBE consumption has increased from 15 to 20 Million tons since 2007, driven primarily by Asian demand growth. Europe has long been a leader in fuel quality and air quality standards and other regions often look to Europe to drive future developments. MTBE has been used in the region for over 40 years and has enabled the lowering of key specifications including sulfur, benzene, olefins, RVP, and aromatics, resulting in considerable emissions reduction. ETBE is also used extensively to fulfill national bio-fuels mandates and achieve CO_2 reduction targets. Both fuel ethers are used in the most common gasoline grades (RON 95 / 98) offered in EU member states; these are fully aligned with the EURO emission standards for vehicles (currently EURO VI). In 2009, the European Union increased the limit for fuel ethers in gasoline from 15 vol. % to 22% vol. %.[7]

Unlike in the United States, where the US EPA failed to fully enforce its 1986 regulation on Leaking Undergrounds Storage Tanks (LUSTs), Mexico authorities developed strict new standards[8] for double-hulled USTs with interstitial leak detection and PEMEX replaced all single-hulled USTs in 1993 and 1994 at its gasoline stations. This protects Mexico's groundwater supplies from leaks of all gasolines, including, potentially, ethanol-blended gasolines which pose an even greater water contamination threat than MTBE.

Consequently, Mexico has avoided the groundwater contamination problems that eventually led 25 of the 50 States in the U.S. to restrict or ban MTBE as a gasoline additive. The States that banned MTBE were mainly corn-growing States interested in promoting the use of ethanol as an octane alternative in gasoline. As a result of the 2008 Biofuels Law,[9] PEMEX is now facing similar calls, from both domestic and US ethanol suppliers,[10] to instead blend ethanol into gasoline despite a 23 year record of success of reducing air pollution with high-quality MTBE-blended gasoline. So PEMEX and Mexico are now faced with the choice of making significant capital investments to upgrade its refining and distribution system to accommodate volatile and water-sensitive ethanol blends or to continue utilizing ethers as clean-burning octane components for its gasoline.

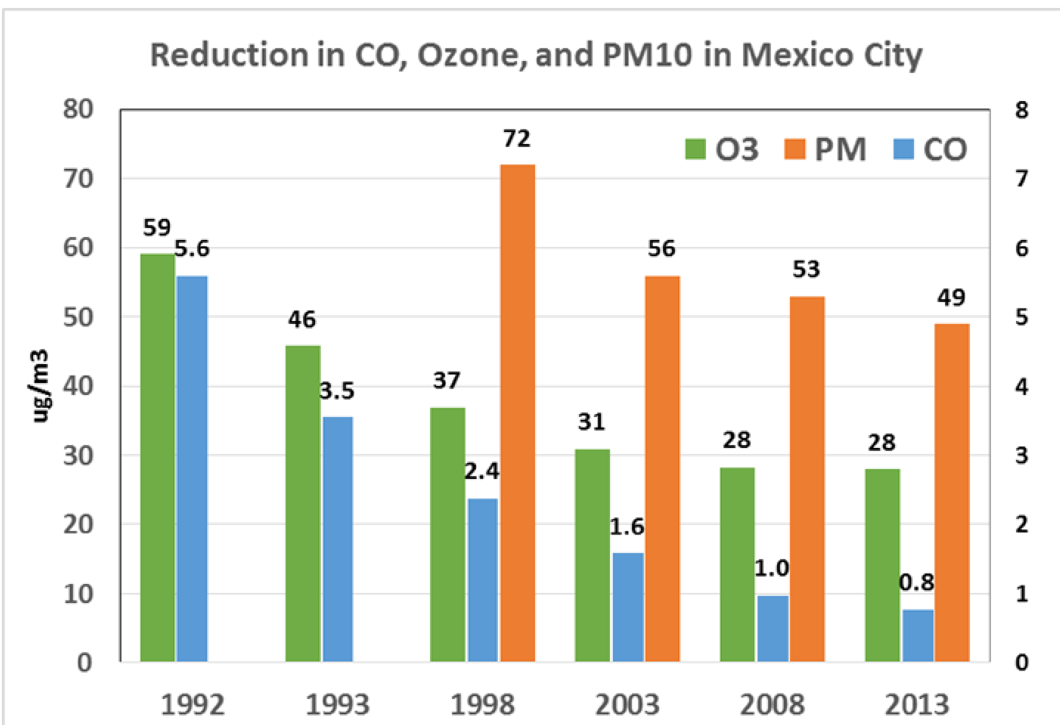

Figure 1: Reduction in the Air Pollutants Carbon Monoxide (CO), Ozone, and Particulate Matter (PM10) in the Valley of Mexico following the adoption by PEMEX of MTBE as an oxygenated gasoline component in 1992. Red Automática de Monitoreo Atmosférico (**RAMA**) database.

Despite Mexico's remarkable air quality improvements since the adoption of MTBE in 1992, the air quality in Mexico City and other Metropolitan Zones is still considered poor during the winter months when particulate matter (PM10) and ozone levels increase, Figure 2. This is in part due to the continued migration of people from rural to metropolitan zones, an increase in car

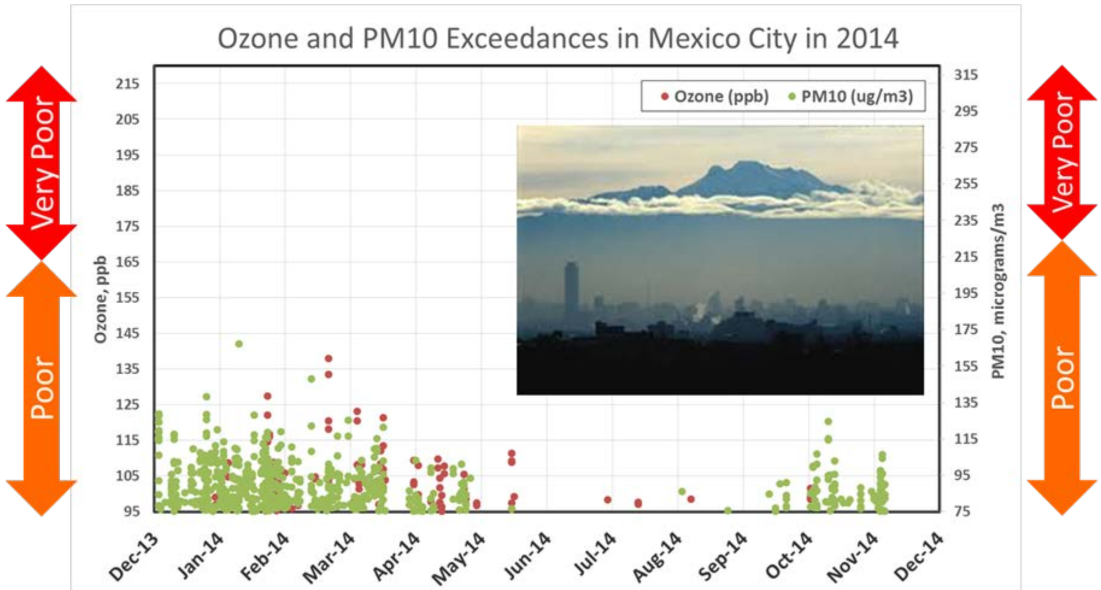

Figure 2: Ozone and PM10 levels in the Mexico Valley exceeded safe IMECA standards 163 days in 2014. Red Automática de Monitoreo Atmosférico (**RAMA**) database.

ownership per capita,[11] and also to the Mexico City's Valley's unique altitude and topography, which tends to trap pollutants in the Metropolitan Zone.[12] This phenomenon is exacerbated in the winter months due to weak synoptic winds and higher exhaust emissions caused by colder ambient temperatures. Also contributing to unhealthy air episodes was the historical use of high sulfur fuels (>80ppm), an older vehicle fleet, and poor maintenance of vehicles. All these factors contribute to incomplete combustion of gasoline in engines and inefficient removal of pollutants (CO, VOCs, PM, SOAs) from exhaust gases due to reversible poisoning of the catalytic converters by sulfur.

Air pollution, especially particulate matter (PM10 and PM2.5), was believed to be responsible for 15,000 premature deaths in Mexico City in 2008 when the average PM10 concentration was 53 µg/m3.[13] The average PM10 level 5 years later was still 49 µg/m3. Therefore, it is vitally important that Mexico continue to improve the quality of its gasoline by setting fuel specifications that will further reduce vehicular emissions of PM and ozone precursors (VOCs). This includes further reductions in allowable sulfur, aromatics, and by selecting high-octane, cleanest-burning oxygenated components that reduce fugitive and tailpipe emissions of hydrocarbons, precursors to secondary organic aerosols (SOAs), and particulate matter.

In 2017, Mexico will begin privatizing its energy sector and the Mexican gasoline market will be open to foreign suppliers for the first time since 1938, when the energy sector was nationalized. Meanwhile the Comisión Reguladora de Energía (CRE) is working with interested parties to update the specification for gasoline (NOM-086) and has recently published a one-year interim specification (NOM-EM-005-CRE-2015).[14] This interim specification does not allow the blending of methanol or addition of metallic octane additives but allows ethanol or ethers to be blended into gasoline to meet the 1.0-2.7 wt. % oxygen requirements in metropolitan zones. CRE, PEMEX, and other stakeholders will continue to negotiate the new fuel specification in 2016 which will then be in effect for 5 years. The challenge for PEMEX and other stakeholders in Mexico is to decide whether they will invest much more capital for ethanol production and distribution of ethanol blends like the US did 10 years ago or continue successfully using ethers as it has for 23 years. Since land, water, and energy will have to be diverted from food production to fuel ethanol production, this becomes a very important policy decision that could have widespread consequences on food and gasoline prices, automobile design and drivability, and air quality in Mexico's metropolitan zones.

Ethanol vs. ETBE Blending; the US vs. Japanese Experience

It has been ten years since the United States replaced MTBE and the Reformulated Gasoline (RFG) program with an ethanol-blending mandate in the form of the Renewable Fuel Standard (RFS). It is noteworthy that the US EPA did not federally ban MTBE although 25 of the 50 individual States did, either because of groundwater contamination issues (e.g. California) or because it benefitted local farmers in their states who could grow corn for ethanol production. Most of the 25 states that banned MTBE were corn-growing states that were not part of the RFG program (i.e. did not use MTBE in gasoline).

Therefore, based on the greatly expanded use of MTBE in the global gasoline markets, it appears that the de-selection of MTBE in the United States was primarily driven by the EPA's failure to enforce minimum standards for Underground Storage Tanks (USTs) and by agricultural states that saw an opportunity to mandate the use of ethanol as a renewable fuel. The state MTBE restrictions had little or nothing to do with doubts about the substantial air quality benefits from MTBE use, or its toxicity risks, which are negligible, especially when compared to other gasoline components.[15]

Congress first established the Renewable Fuels Standard (i.e. ethanol mandate) with the enactment of the Energy Policy Act of 2005 (EPAct, P.L. 109-58). This initial RFS (referred to as RFS1) mandated that a minimum of 4 billion gallons (15,141 KKL) of ethanol be used in 2006, rising to 7.5 billion gallons (28,390 KKL) by 2012. Two years later, the Energy Independence and Security Act of 2007 (EISA, P.L. 110-140) greatly expanded the biofuel mandate volumes and extended the date through 2022. The expanded RFS (referred to as RFS2) required the annual use of 9 billion gallons of biofuels (mostly ethanol) in 2008, rising to 36 billion gallons in 2022, with at least 16 billion gallons from cellulosic biofuels, and a cap of 15 billion gallons for corn-starch ethanol.[16]

The promised benefits of ethanol in reducing GHG emissions and improving air quality have been the subject of controversy. Even the non-partisan U.S. Congressional Research Service has questioned whether they have materialized and admits the RFS has resulted in unintended consequences.[14] These include higher food prices, a boom and bust ethanol industry that is now looking to export its product,[8] and, as gasoline demand in the US decreased, a need to blend more than 10 % ethanol to meet the increasing volumes mandated by the RFS (blend wall). As a result, opposition to the RFS and ethanol use in the US has been mounting. Twelve automotive manufacturers have opposed any further increase above 10 vol. % ethanol in gasoline over concerns about corrosion of automotive components and swelling of gaskets and have threatened to void warranties if E15 is used in their automobiles.[17] Earlier this year, a bipartisan bill was also introduced in the US Senate to repeal the corn ethanol mandate in the Renewable Fuel Standard.[18]

In 2006, the Japanese government began evaluating both ethanol and ETBE to meet the anticipated requirements of their renewable fuels mandate. Based on extensive research on the economic and environmental impacts of both oxygenates, the Japanese government approved both E3 and ETBE8, but all the major refiners in Japan chose to adopt ETBE instead of ethanol. Stated concerns about ethanol blends included the changes in fuel distillation properties and RVP, its potential to cause phase separation if water is present in the distribution system, and incompatibility with some fuel component systems.[19,20]

The relative effects of ethanol and ETBE blending on fuel Reid Vapor Pressure (RVP) were described in two studies[21],[22] by the Japanese Petroleum Energy Center (PEC) and the Advanced Technology and Research Institute (ATRI) and are illustrated in Figures 3 and 4. When ethanol was

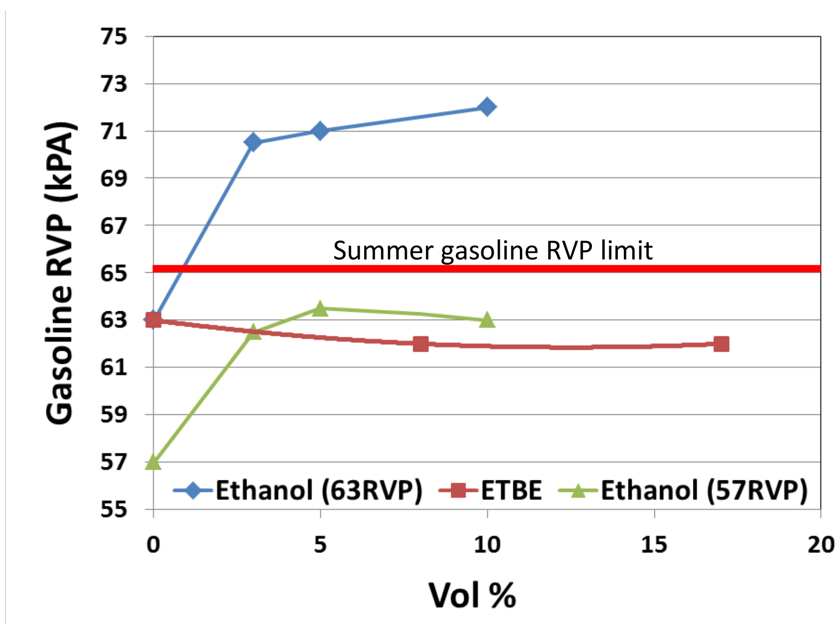

Figure 3: Effect of Ethanol and ETBE on the RVP of Blendstocks for Oxygenated Blending (BOB). Ethanol BOB RVP must be reduced by 6-10 kPA for finished gasoline to meet summer specification. In contrast, the same base gasoline can be used with ETBE.

added to a base gasoline with an RVP of 63 kPA, it caused a 7-8 kPA increase in the fuel RVP. In contrast, addition of 8 and 17% ETBE caused a slight drop in RVP to 62 kPA. Therefore, in order to formulate a final fuel that meets the summer season RVP with ethanol, the RVP of the base fuel had to be lowered to 57 kPA. This is typically achieved by removing low-cost butanes and pentanes from gasoline blending operations, thereby increasing the cost of the base gasoline. This lower cost butane or pentane must then be replaced by additional gasoline at the higher gasoline market price.

The study also looked at the impact of 3% ethanol and 8% ETBE on the vehicles' fuel system VOC emissions as Hot Soak Losses (HSL) and Diurnal Breathing Losses (DBL) of 62-63 kPA test gasolines, Figure 4. Adding 3% ethanol to gasoline increased diurnal VOC breathing losses almost 300% and

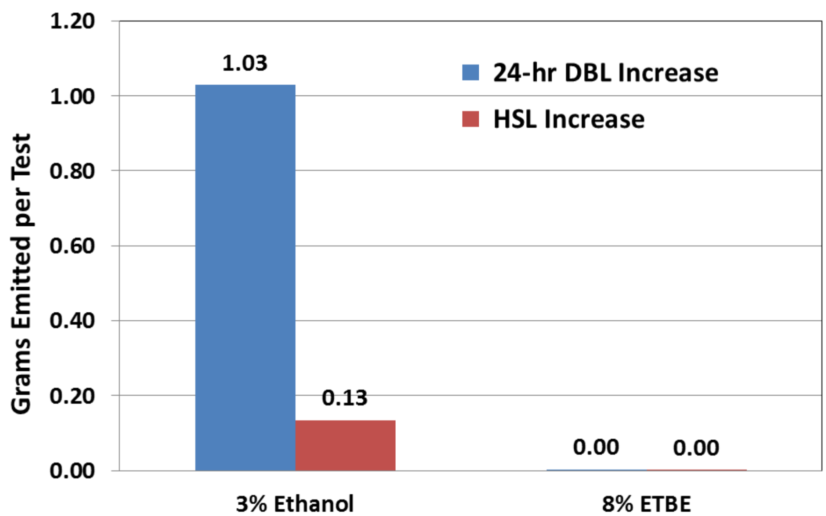

Figure 4: Effect of 3% Ethanol and 8% ETBE on Fugitive Emissions from Vehicle Fuel Systems.

Hot Soak VOC losses by 236%. In contrast, adding 8% ETBE had essentially no effect on permeation VOC losses. Fugitive VOC losses from a vehicle's fuel system can contribute very significantly to air pollution in the form of increased ozone levels concentrations of respirable particulate matter, as is discussed later.

This detrimental effect of ethanol was also documented in two permeation studies[23,24] conducted by the Coordinating Research Council (CRC) for the U.S. EPA and California's Air Resources Board (CARB). The first study,[21] conducted in 2004, compared fugitive VOC emissions from 10 vehicle fuel systems. The study evaluated VOC permeation at 30°C and 40°C using non-oxygenated gasoline, and gasoline with 5.5 vol. % ethanol or 11 vol. % MTBE (both ~ 2 wt.% oxygen). The three fuels were also matched by RVP, T10, T50, and T90, and had similar aromatic contents.

The study recorded VOC permeation from the vehicle's fuel system under static conditions at two temperatures and a diurnal test over many days of fuel exposure and after several weeks of acclimation. Compared to the MTBE or non-oxygenated fuels, the static tests showed a very significant increase in permeated VOCs for ethanol-blended gasoline at both temperatures. At

30°C, the ethanol-blended fuel emitted 84% more VOCs than the MTBE-blended fuel and 78% more at 40°C. The MTBE-blended fuel had the lowest fugitive VOC emissions of the three fuels, with 14% and 12% fewer emissions than non-oxygenated gasoline, Figure 5.

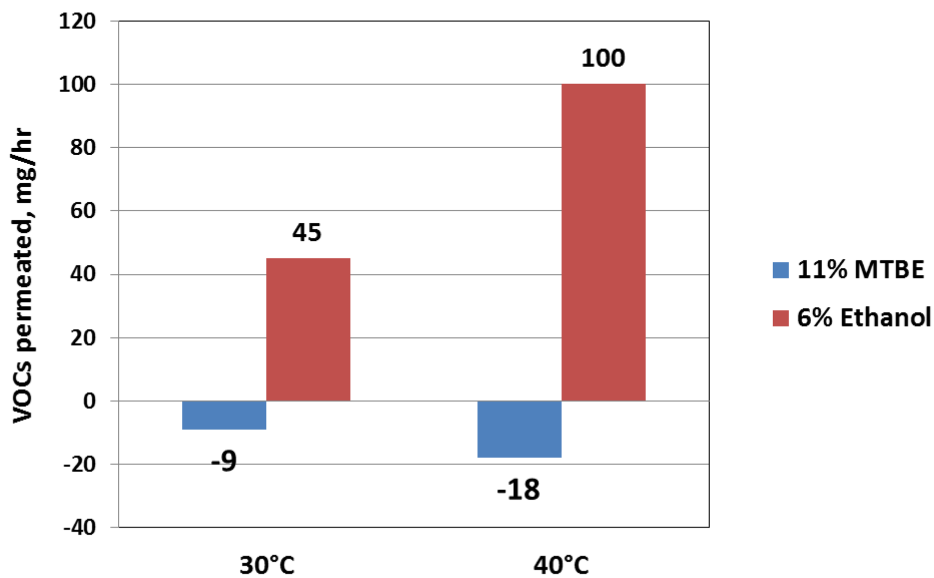

Figure 5: Average (10 vehicles) effect of adding 5.5% ethanol and 11% MTBE on static fugitive VOC emissions from gasoline compared to similar gasoline without oxygenates.

The diurnal tests simulate daily operation of the vehicle, with a cycle from 18°C to 40°C and back to 18°C which are temperatures typical for gasoline to experience in a fuel system. The VOC emissions in the diurnal test showed the same pattern as in the static tests, with MTBE-blended gasoline showing the lowest emission, non-oxygenated gasoline emitting 13% more VOCs, and ethanol-blended gasoline emitting 65% more VOCs. The VOC emissions were speciated and their ozone forming potential calculated (from Maximum Incremental reactivities in grams O3/gram VOC). These studies demonstrate that ethers such as MTBE and ETBE in gasoline blends do not increase fugitive VOC emissions from vehicles whereas ethanol (or alcohol) blends cause a very significant increase in VOC permeation losses from the vehicle fuel systems during and after operation. These large increases in VOC permeation losses will result in increased air pollution in the form of ozone and particulate matter.

Environmental Impacts of Increased Permeation with Ethanol

Based on the difference in diurnal VOC emissions between MTBE and ethanol-blended gasolines, the reactivity of the emitted VOCs, and the number of vehicles in the Mexico City Federal District,[9] it is possible to estimate the effect of switching from 11% MTBE to 6% ethanol on ozone pollution. This analysis shows that switching from MTBE to ethanol in gasoline could result in an added 11 Kilotons of ozone per year to the atmosphere in the Mexico Valley, Figure 6. Even assuming a much slower growth rate (2.7% AGR) of the number of vehicles from 2015 to 2020, ozone produced from increased fugitive emissions of VOCs could reach 12.5 Kilotons by 2020.

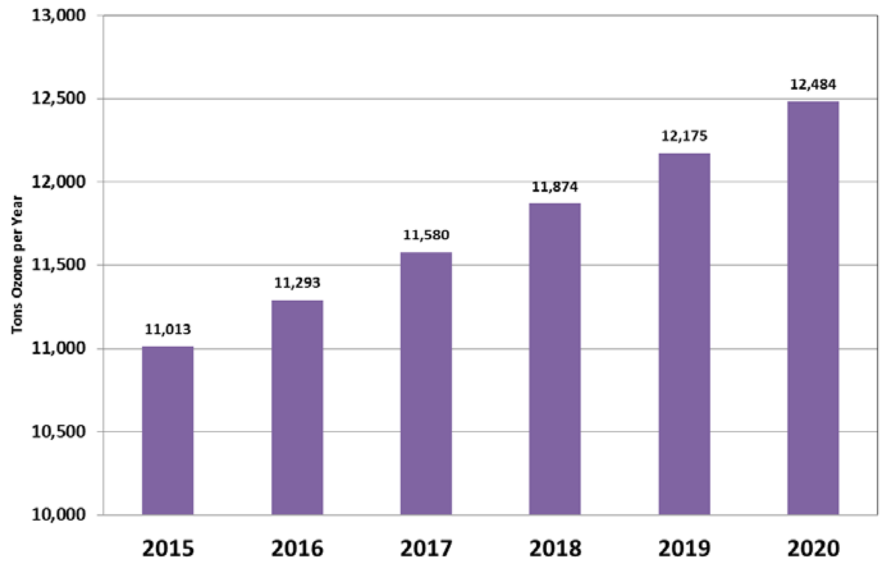

Figure 6: Estimated Increase in Ozone From Vehicular Fugitive Emissions in Mexico DF if 11% MTBE Were Replaced by 6% Ethanol. CRC E65 Report "Fuel Permeation from Automotive Systems."

This possible result clearly would be deleterious to air quality. The impact on incremental PM formation is difficult to estimate but would also be negative, since some of the top VOCs emitted when ethanol is added to gasoline included C7-10 aromatics, which are known SOA and PM precursors.[21,25,26]

The impact of ethanol vs. ethers on tailpipe emissions of hydrocarbons and PM is more difficult to quantify, since very few studies comparing the two have been published.[27] However, it can be inferred from the thermochemical properties of alcohol-hydrocarbon blends[28] and the known effect of alcohols on the distillation properties of gasoline.[29] Approximately 80% of the vehicles' tailpipe PM is emitted under cold-start engine conditions, before the Engine Control Unit (ECU) oxygen sensor reaches its operating temperature, and the higher boiling components of gasoline incompletely vaporize and are emitted as either SOAs precursors or PM.[30]

Under constant-speed, running conditions, both ETBE and ethanol were shown to decrease PM emissions from a lean-burn SIDI engine.[26] This decrease was attributed to a decrease in the aromatic content of the fuels formulated to the same RON with oxygenated ETBE and Ethanol in the hot mode (10.15) cycle. The particle number also correlated strongly to the T90 (temperature at which 90% of the fuel is evaporated) of the fuel, which was affected by the distillation properties of ETBE and Ethanol. This correlation between PM emissions and fuel T90 was particular strong in the cold mode (11) test cycle. The authors observed that when ethanol was used as the blending component, the T50 of the gasoline decreased due to azeotrope formation with gasoline hydrocarbon components. Therefore, heavier gasoline fractions were required were required to maintain T50 within specification, resulting in a higher T90 and increased PM emissions, especially in the cold mode.

So while ethanol was as effective as increasing RON as ETBE, which is necessary to replace aromatics in the fuel, it's tendency to lower T50 by forming azeotropes resulted an increase in T90 which negated the benefit of removing aromatics. Ethers like MTBE and ETBE do not form azeotropes with other gasoline components and do not depress T50 nearly as much as ethanol. In addition, alcohols and their blends with gasoline have significantly higher enthalpies (heats) of vaporization than ethers or gasoline hydrocarbons.

The latent heat of vaporization of a fuel refers to the energy required to vaporize the entire fuel and has been linked to the potential for PM formation.[29] The heat of vaporization of ethanol/isooctane mixtures increases linearly with ethanol content from 300 KJ/Kg for pure isooctane to 920 KJ/Kg for pure ethanol. This effect of increasing ethanol content on PM formation (both mass and number) was demonstrated in a GDI engine during cold-start as well as running (warm) conditions. The base fuel was identical in all cases so PM increased as a result of increasing ethanol content despite a reduction in the aromatic content of the ethanol/gasoline blends.

The more heat is required to vaporize gasoline and the less heat is generated during combustion, the more PM will be produced and emitted, especially during cold start conditions. Aromatics are the highest boiling components in gasoline and are very efficient SoA and PM precursors. Alcohols have high heats of vaporization and lower energy contents than ethers or other gasoline components so they are detrimental to complete fuel vaporization especially under cold-start conditions, Figure 7-8. Ethers, on the other hand, vaporize readily and deliver more

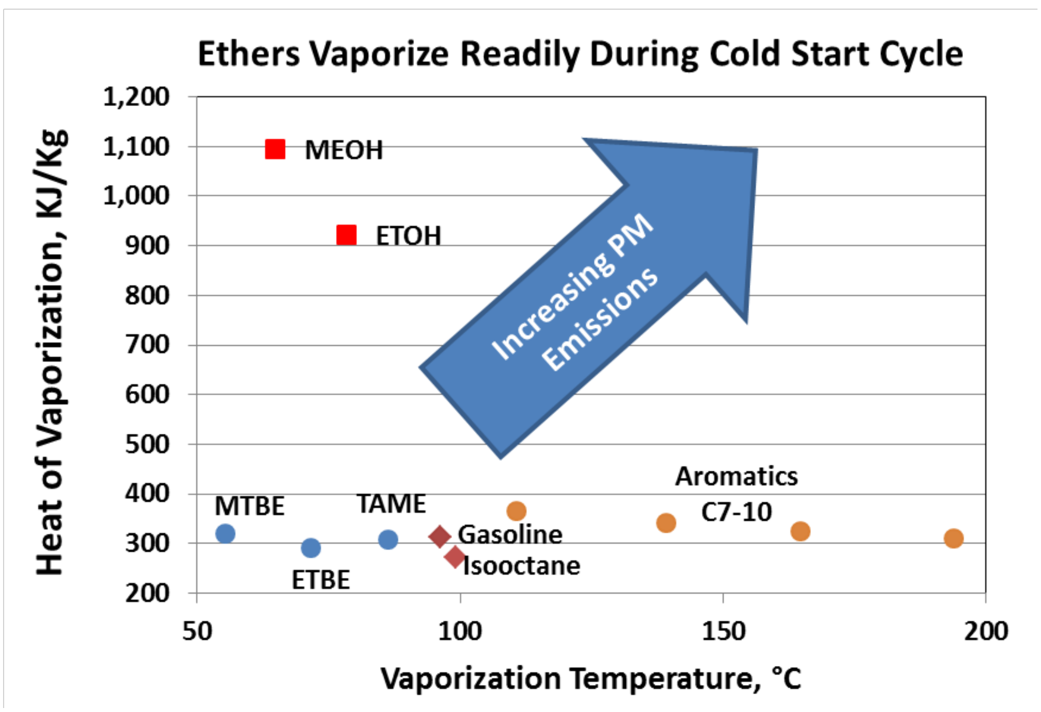

Figure 7: Heat of Vaporization vs. Boiling Point of Common Gasoline Blending Components. Aromatics do not completely vaporize under cold-start conditions, increasing hydrocarbon and particulate emissions and reducing fuel efficiency.

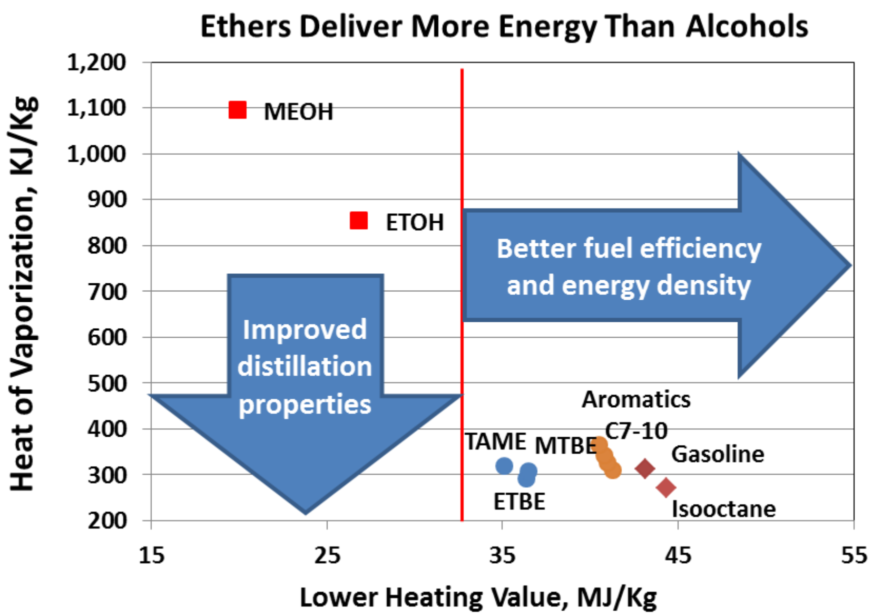

Figure 8: Heat of Vaporization vs. Lower Heating Value of Common Gasoline Blending Components. Alcohols require more heat to vaporize and contain less energy than ethers and other gasoline components. This reduces fuel efficiency and increases tailpipe emissions.

heat during cold start conditions, effectively reducing PM formation compared to regular gasoline and especially ethanol-blended gasoline. Both alcohols and ethers boil at lowers temperatures compared to other gasoline components, but ethers improve vaporization of gasoline components and provide significantly more energy to the combustion process than alcohols, Figures 7-8.

In addition, incomplete combustion of fuel is likely to result in lower fuel efficiency, especially if the unburned portion includes high-energy components such as aromatics. Ethers provide the right balance of volatility, oxygen content, and energy density to facilitate complete gasoline combustion, especially under cold-start conditions before the fuel-air ratio can be properly adjusted by the ECU. These properties were demonstrated in a recent study and are illustrated in Figure 9, which shows the effect of increasing amounts of MTBE in gasoline on PM emissions and fuel efficiency in a modern Gas Direct Injection (GDi) engine.[31]

Incomplete fuel combustion can be exacerbated at the high altitude of the Mexico City Valley since the oxygen content is ~25% lower than at sea level. Therefore, fuel components such as MTBE and ETBE that provide high octane, good vaporization properties, intermediate oxygen content, and good energy content are expected to have beneficial effects on fuel efficiency and PM reduction in both conventional PFi and modern high compression engines operating under these conditions. MTBE and ETBE provide the optimal balance of properties for clean and efficient gasoline combustion, without the increase in fugitive VOC and tailpipe PM emissions observed when alcohols are used.

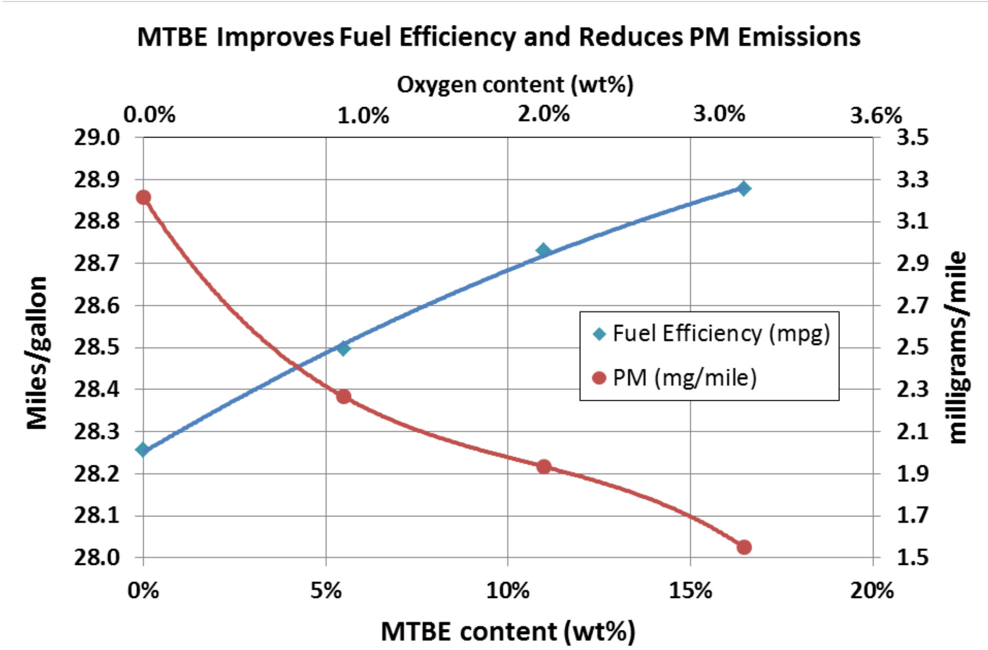

Figure 9: Effect of increasing MTBE Content on PM Emissions and Fuel Efficiency in a Modern Gasoline Direct Injection (GDi) Engine under NDEC and FTP-75 Protocols.

Cost Considerations

PEMEX has been considering using methanol and ethanol instead of MTBE imports in an attempt to reduce the cost of blended gasoline. Methanol is not approved for use as a fuel blending component in Mexico or other advanced nations because of its detrimental environmental impact and damage to automotive components.[32] Global automotive manufacturers oppose the use of methanol in the Global Fuel Charter: "Methanol is an aggressive material that can cause corrosion of metallic components of fuel systems and the degradation of plastics and elastomers." Its water sensitivity is so high that a higher alcohol such as tert-butanol must be added to prevent phase separation, effectively negating any cost advantage over blending MTBE. Methanol also negatively impacts fuel sensitivity to water, distillation properties, vapor pressure, and cold start combustion efficiency, resulting in increased emissions of PM, VOCs, and formaldehyde.

For over two decades, Mexico has been incorporating inexpensive methanol in its gasoline as MTBE and TAME, which is the preferred way to benefit from its low cost without its negative side-effects. In the 1990s the US EPA approved methanol/tert-butanol blends and ARCO marketed a 50/50 blend as Oxinol.[33] However, this fuel component was inferior and less cost-effective than MTBE and was never embraced by US refiners.

MTBE continues to be an attractive blend component for octane when blending export gasoline from the USGC or for blending locally in Mexico or other Latin American countries. In October 2015, MTBE traded around 170 cents/gal (USGC FOB basis), approximately 40 cents/gal higher than regular gasoline. However, MTBE's high octane (110 AKI) relative to gasoline (87 AKI) currently provides about 80 cents/gal blending advantage meaning the MTBE market price is significantly below the theoretical blend value for blending MTBE into gasoline. Often times, the octane benefit of MTBE can provide more than 100 cents/gal upgrade value versus regular gasoline price, and MTBE has consistently traded at prices well below its theoretical blend value.

Ethanol blending is permitted in many countries including in Mexico in the recently promulgated NOM-EM-005-CRE-2015 up to the 2.7 wt. % oxygen limit, which corresponds to 7.8 vol. % Ethanol, 14.9 vol. % MTBE, or 17.2 vol. % ETBE. Because of their lower oxygen content compared to alcohols, PEMEX can take advantage of more MTBE and ETBE volume than ethanol without exceeding the 2.7 wt. % oxygen limit. In October 2015, corn-based US ethanol also traded around 170 cents/gal (USGC FOB basis). Ethanol has slightly higher octane than MTBE at 116 AKI. However, the additional octane benefit is more than offset by ethanol's much higher blending RVP (138 KPA). Blending ethers either has no effect on gasoline RVP (in the case of MTBE) or reduces it (in the case of ETBE), since MTBE has the same RVP as typical gasoline (54 KPA) and ETBE has lower RVP (28 KPA). So, unlike adding ethanol, adding either MTBE or ETBE to a Blendstock for Oxygenated Blending (BOB) allows the refiner to increase its octane without having to remove lighter components such as inexpensive butanes. In the current low-crude market, ethanol provides no economic incentive versus MTBE. As mentioned, both ethanol and MTBE are priced at similar levels of 170 cents/gal in the USGC. MTBE price is highly correlated to gasoline and crude prices, whereas ethanol price is tied to crop conditions, weather, and government mandates and subsidies.

In summary, while both MTBE and ethanol provide octane benefits to gasoline, there is no variable cost benefit to using ethanol instead of MTBE particularly if the low crude environment persists. Beyond variable cost, the most important costs to consider, in regards to ethanol blending, are the significant capital costs associated with new distribution, storage, and blending equipment due to corrosion[34] and phase separation[35,36] issues associated with ethanol. The total cost of converting Mexico's current infrastructure to handle ethanol can be estimated from a 2007 report from the Japan's New Energy and Industrial Technology Development Organization (NEDO),[18] which estimated the cost of converting Japan's fuel distribution and refineries for ethanol blending at $2.6-4.3 Billion in 2005. According to the Japanese Automotive Manufacturers Association (JAMA), there were 70 million automobiles in Japan vs. an estimated 42 Million in Mexico today. Adjusting for inflation and the number of vehicles, we estimate that it could cost Mexico between US$1.90 and $3.14 Billion to upgrade its infrastructure for ethanol blending nationally.

An alternative for PEMEX to consider if the use of ethanol were to be mandated is to convert existing MTBE and TAME capacity to ETBE. Producing ETBE would be a more cost-effective way to incorporate domestically produced ethanol into the gasoline pool. Mexican ethanol from Veracruz and Tamaulipas can be transported to Ciudad Madero, Cadereyta, or Tula refineries and converted to ETBE in existing MTBE or TAME production assets with minimal capital investment Figure 10.

The following paragraph describes in general terms the modifications needed to convert MTBE capacity to also enable production of ETBE. Additional details are available in the form of a

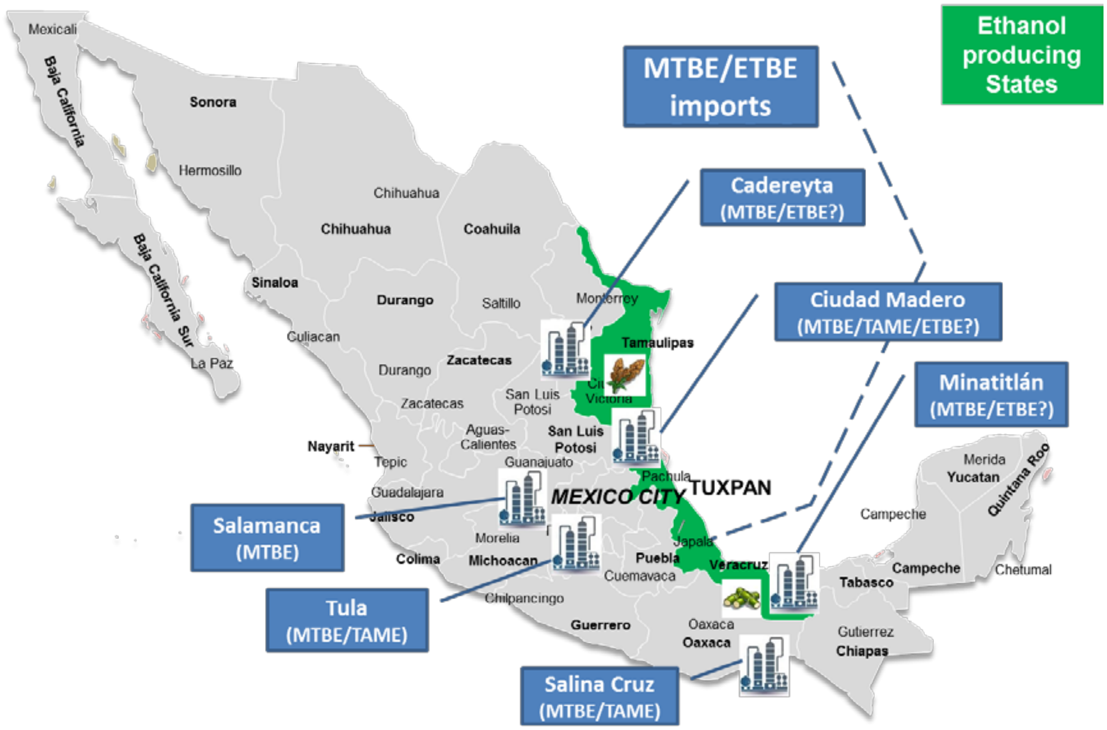

Figure 10: Domestic Ethanol from Veracruz and Tamaulipas could be converted to ETBE at local refineries with minimal capital investment compared to converting the current gasoline distribution system to handle ethanol blending at terminals and running refineries at higher severity.

complete technology package which was successfully implemented in 2009 in South America and has been in operation at three Lyondell manufacturing sites since 1992.

MTBE and ETBE Production

LyondellBasell has been the leading global producer of MTBE and ETBE since the US EPA mandated the use of 15% MTBE in winter gasoline in 1992 and 11% MTBE nationwide in 1995. LyondellBasell alternates between MTBE and ETBE production at its Houston, Fos-sur-Mer (France), and Rotterdam plants and has announced 900 Kilotons of new TBA (tert-butanol) and derivatives capacity in the Gulf Coast starting in 2019. Feedstocks for MTBE and ETBE production include high purity isobutylene (HPIB) from TBA dehydration or Raffinate 1 (mixed butenes) from petroleum refining or olefin crackers and either methanol from shale gas or ethanol from biomass, Figure 11.

In 1992, LyondellBasell also developed an engineering design to produce either MTBE or ETBE from Raffinate 1. This design was successfully implemented by an MTBE producer in South America with Lyondell's assistance in 2009. The producer has been alternating between MTBE and ETBE production in the same equipment for the past 6 years. PEMEX currently produces 540 kilotons per year of MTBE and TAME at several of its refineries and could potentially modify its ether units in Cadereyta or Ciudad Madero to alternate between MTBE and ETBE production from

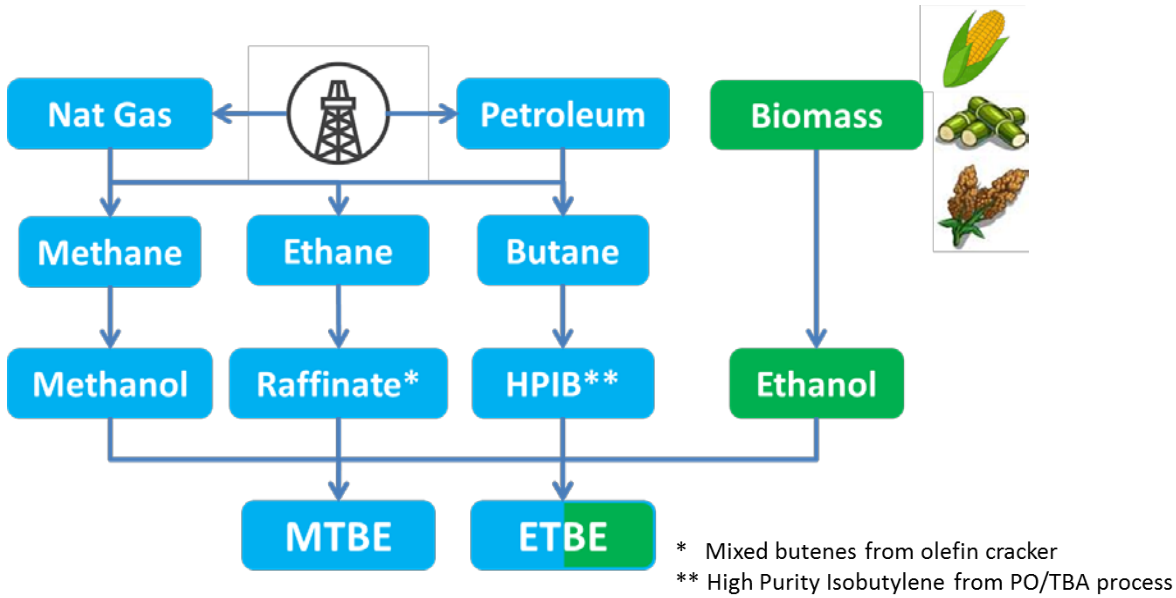

Figure 11: Raw materials and intermediates in the production of MTBE and ETBE. Main crops for bioethanol include corn, sugarcane, and sorghum.

locally-produced sugarcane or sorghum ethanol. A grassroots MTBE/ETBE unit could also be builtat the Minatitlán refinery to convert ethanol to ETBE and methanol to MTBE. This could allow PEMEX to incorporate bio-ethanol from Veracruz and Tamaulipas into gasoline as ETBE without investing in a separate distribution system or having to make refinery adjustments to accommodate the higher vapor pressure (RVP) caused by ethanol.

MTBE/ETBE Process Considerations

PEMEX currently produces MTBE and TAME at all its refineries, except Minatitlán. The two largest MTBE units are at Tula (95 KT per year capacity) and C. Madero (99 KT per year). Cadereyta produces another 43 KTy of MTBE and is located close to sorghum ethanol production in Tamaulipas. These three units combined have enough potential ETBE capacity to consume the 97KT of domestic ethanol PEMEX currently has under contract and still have room for 52KTy of MTBE production.

The engineering and process changes required to produce ETBE in a unit designed for MTBE production are relatively minor. For example, the conversion ETBE service with a refinery mixed C4s feedstock may include the following scope, assuming campaigning between MTBE and ETBE:

I. Scope for the conversion
(1) Adding or modifying alcohol pumps/motors for higher capacities (for feed and recycle)
(2) Adding or modifying ether pumps/motors for higher capacities
(3) Adding capacity to reactor coolers
(4) New C4 wash column (the existing column more likely inadequate)
(5) Adding wash column pumps/motors

(6) Corrosion monitoring devices on the ethanol pipe from OSBL to ISBL
(7) Adding ethanol dehydration package
(8) Two ETBE product inhibitor injection systems
(9) Additional cooling and heating utilities, and power supplies
(10) Ethanol receiving/storage with pumps/motors (no needed for ETBE only)
(11) ETBE product storage with pumps/motors (not needed for ETBE only)
(12) ETBE off-spec storage with pumps/motors (not needed for ETBE only)

The ISBL scope items from (1) through (7) above may be estimated at $10.0MM TIC (Total Installed Cost) for a 100 KTA ETBE plant South Central America, 2015. Items from (8) to (11) are OSBL scope the TIC of which is dependent on the logistics conditions at the plant site.

II. Possible additional scope pending review of existing equipment capacities in MTBE service
(1) Adding capacity to debutanizer overhead condensers
(2) Adding capacity to debutanizer reboilers

These minor process modifications would require significantly less capital than the $58 million PEMEX estimates will be needed to upgrade its infrastructure to handle and blend ethanol for this test program, along with refinery adjustments at Ciudad Madero and Minatitlán.[37] Switching to ETBE production at Tula and Ciudad Madero alone would also add 31 KT of ethers capacity at these two refineries and eliminate the need for separate ethanol transportation and blending at gasoline terminals or separate pumps and storage tanks at retail gasoline stations.

The loss of MTBE capacity for ETBE production could easily and affordably be met by Gulf Coast imports. The LyondellBasell Governing Board recently approved construction of world-scale PO/TBA plant in the Gulf Coast to be completed in 2019.[38] This facility will also include a new ethers unit capable of producing more than 1,000 KT of MTBE or ETBE. LyondellBasell will have capacity to support an increase in requirements for MTBE or ETBE to PEMEX beginning in 2020 and help PEMEX and Mexico meet the requirements of the 2008 Biofuels law as it currently does for Japan and increased demand for clean-burning, high octane fuel components as it has for decades.

Trends in Clean-burning Octane Demand

Lastly, it is important to consider current and future trends in the demand for clean-burning octane and in engine design. Reductions in sulfur and aromatic contents are likely to continue to further improve air quality. This will increase worldwide demand for clean-burning, high-octane blending components like MTBE and ETBE to replace the olefins lost during hydrodesulfurization and aromatics, which are responsible for most of the ozone and PM pollution. At the same time, high-compression GDi engines are anticipated to become the fastest growing technology over the next 10 years, due to their smaller size and higher fuel efficiency compared to port fuel-injected (PFi) engines.[39] These engines require higher octane gasolines than PFi engines because their higher compression ratios can increase chamber pressures, temperatures, and knocking.

At the same oxygen content, MTBE and ETBE provide significantly more volume, energy, and octane than methanol and ethanol, Figure 13. Both MTBE and ETBE provide more octane than 17% aromatics at permitted levels (2.7 wt%) oxygen, and ETBE provides almost as much energy on an equivalent volume basis. Unlike aromatics and alcohols, however, MTBE and ETBE improve gasoline combustion, reduce fugitive VOC emissions and tailpipe emissions of hydrocarbons and particulate matter, which improves both air quality and fuel efficiency. Unlike alcohols, MTBE and ETBE are fully compatible with automotive components and will not cause corrosion or phase separation in Mexico's gasoline distribution infrastructure.

Given the anticipated increase in demand for clean-burning octane components globally, we believe that continuing to use MTBE and ETBE will deliver the greatest return. Ethers provide more fuel volume and energy compared to alcohols at the same oxygen content and more octane than aromatics at the same volume content. The cost of converting existing MTBE capacity to dual production (MTBE/ETBE) or even building a grassroots unit is a fraction of the cost of developing a separate distribution infrastructure to blend ethanol. The return will be significantly greater blending flexibility and capacity, lower refinery operating costs, and cleaner air.

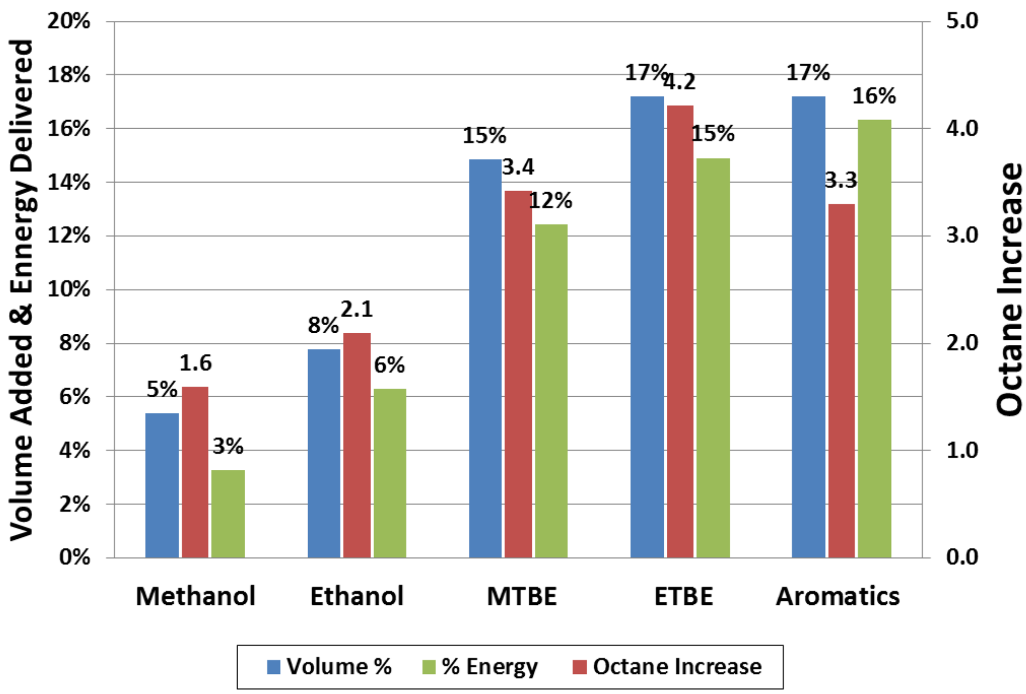

Figure 13: Comparison of the octane, volume, and energy contribution of alcohols vs. ethers at the same oxygen content (2.7 wt. %) and aromatics on the same volume basis as ETBE (17 wt. %).

Conclusions

The cost, energy, and environmental benefits of incorporating ETBE and MTBE into gasoline instead of alcohols are undeniable. Ethers are more compatible with gasoline, with automotive components, PEMEX's current refinery operations, and Mexico's gasoline distribution system. Ethers do not increase gasoline vapor pressure (RVP), cause corrosion, phase separation, or increase fugitive and tailpipe VOC and PM emissions like alcohols do. Ethers provide clean-burning octane whose demand will continue to increase as sulfur and aromatic levels continue to be reduced and more fuel-efficient engines with higher compression ratios take market share away from older, less efficient engines.

We believe that with a timely and relatively minor investment in its ethers production assets and with Lyondell's continued supply of MTBE and technological assistance, PEMEX can maintain its position as the leading supplier of advanced fuels to the Mexican market. PEMEX's choice of MTBE in 1992 has resulted in much cleaner air for all Mexicans. Investing in MTBE and ETBE will help PEMEX meet future demand for clean burning octane, continue to improve air quality nationwide, and help meet the requirements of the 2008 Biofuels law.

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