Advanced Gasoline Components for Latin America: Production and Blending Properties of MTBE and ETBE

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Mexico Energy Reform Driving Change

- Gasoline market opens to competition in 2017
- Competitive pressure to reduce costs
- 2008 Biofuels Law mandate renewable fuels
- Lower sulfur specification (NOM-086)
- Continued need to improve air quality, especially in MZs
- Growing need for cleaner-burning octane
  - Low sulfur will cost 1-2 octane points from hydrotreatment
  - Push to reduce aromatics (main contributors to ozone and PM)
  - Engine technology moving towards higher compression and efficiency

Where should PEMEX invest its capital to meet these challenges?
Outline

• MTBE
  – Air quality benefits
  – The norm in most countries around the world

• Ethanol
  – 10 years of experience in the US with corn Ethanol

• ETBE
  – Introduced ETBE in the US in 1992
  – Supplying Japan with ETBE since 2009
  – A superior alternative to ethanol to meet renewable mandates
  – PEMEX has used ETBE and can develop the capacity to produce it in-house

• Lyondell can offer:
  – MTBE, as we have for >20 years
  – ETBE
  – Licensing of technology for campaigning assets between MTBE & ETBE

Continued use of Ethers is the best option for PEMEX & Mexico
MTBE in Mexico: A 23-year Success Story

- Major reduction in key air pollutants since 1992
- No reported groundwater contamination
- Domestic supply by PEMEX and imports have met demand

MTBE helped to clean up the air after Mexico city had the most polluted air in the ‘80s

Source: RAMA database: http://www.aire.df.gob.mx/default.php?opc='aKBh'
Mexico City Air Quality Still Poor
Further Improvement Needed

Ozone and PM10 Exceedances in Mexico City in 2014

O$_3$ and PM10 IMECA NOMs reduced to 95 ppb and 75 $\mu$g/m$^3$

Mexico City Air Exceeded IMECA Standards for Ozone and PM10 >163 days in 2014

Source: RAMA database, REFORMA, December 27, 2014; COFEPRIS.

Villahermosa, Tabasco 26 y 27 de Noviembre del 2015 Hotel Quinta Real
Globally, Ether Blending is the Norm
Exceptions are the US, Brazil & Australia

MTBE is commonly used around the world to improve gasoline specifications
The US Ethanol Experience

10 years of Renewable Fuel Standard (RFS)

- Massive tax subsidies ($66 Billion since 1982) have caused overcapacity and numerous bankruptcies

- Ethanol has substantially increased food prices in the US

- Ethanol has delayed development of advanced biofuels

- Ethanol increases gasoline RVP; US grants 1.0 RVP waiver
  - At same RVP, C4-C5 hydrocarbons must be removed, increasing cost of CBOB

- Ethanol increased air pollution (VOC emissions)
  - Swells elastomers and increases fugitive emissions
  - Increases tailpipe VOC and PM emissions vs. gasoline and MTBE

US corn ethanol has failed to meet the objectives set in 2005

Source: Report Institute of Agriculture, The University of Tennessee, dated October 14, 2015
EPA: Ethanol Increases Fugitive Emissions

- Swelling of gasket materials increases fugitive VOC emissions
- VOC emissions contribute to Ozone and PM formation

Introducing ethanol would reverse Mexico’s air quality improvements

Sources: CRC E-65 report 2004
Ethers Improve Cold-Start Combustion

Which Reduces PM Emissions

- 80% of particulates are formed during the cold start cycle
- High boiling gasoline components (e.g. aromatics) do not completely vaporize and form PM precursors (SOAs)
- Ethers vaporize easily and deliver more heat than alcohols
MTBE improves overall fuel combustion, reducing PM and improving fuel efficiency.
Lower Sulfur, Newer Engines to Boost Octane Demand

• Hydrotreating results in 1-2 unit drop in octane
  – New sulfur specs will increase demand for clean-burning octane
• Auto industry moving to smaller engines with higher compression ratios (CR)
  – Engines are smaller and more fuel efficient but require higher octane
  – 2 point increase in CR requires 7 points more octane and provides 10% more fuel efficiency
• Industry need for clean-burning octane will continue to increase

Ethers offer clean-burning octane for improved fuel efficiency
Ethers are Superior Blending Components

<table>
<thead>
<tr>
<th>Additive</th>
<th>Octane Index</th>
<th>BP °C</th>
<th>Oxygen content wt%</th>
<th>Blending Vapor Pressure (kPa)</th>
<th>Fuel Sensitivity RON - MON</th>
<th>Water Tolerance</th>
</tr>
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<tbody>
<tr>
<td>Gasoline</td>
<td>85</td>
<td>35-220</td>
<td>0.0</td>
<td>60</td>
<td>10</td>
<td>Excellent</td>
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<tr>
<td>MTBE</td>
<td>110</td>
<td>55</td>
<td>18.2</td>
<td>55</td>
<td>17</td>
<td>Excellent</td>
</tr>
<tr>
<td>ETBE</td>
<td>111</td>
<td>67</td>
<td>15.7</td>
<td>28</td>
<td>16</td>
<td>Excellent</td>
</tr>
<tr>
<td>TAME</td>
<td>105</td>
<td>86</td>
<td>15.7</td>
<td>10</td>
<td>14</td>
<td>Excellent</td>
</tr>
<tr>
<td>Ethanol</td>
<td>115</td>
<td>78</td>
<td>34.7</td>
<td>138</td>
<td>34</td>
<td>Very Poor</td>
</tr>
</tbody>
</table>


Ethers provide clean-burning octane without affecting gasoline RVP, distillation properties, sensitivity, water tolerance, or corrosion.
ETBE vs. Ethanol – The Japanese Experience

Japan Enacted Renewable Fuels Mandate in 2009

- Japan evaluated 3, 5, and 10% ethanol (E3 & E10) vs. 8% ETBE
- Stated concerns about ethanol blending included
  - Change in fuel properties (distillation, RVP)
  - Phase separation from water contamination
  - Compatibility with vehicle fuel system materials (gaskets, corrosion)
  - Cost of developing ethanol blending infrastructure
- 3% Ethanol increased running loss emissions by >200% in 1 vehicle
- 8% ETBE decreased running losses by 30% vs. baseline RVP 65 gasoline
- Japan selected ETBE as the preferred bio-fuel in 2007
  - ETBE demand around 3.7% of gasoline in 2017
- Cost of developing Japan’s ethanol distribution and blending infrastructure was estimated at $2.6-4.3 Billion in 2005

Japan chose ETBE to meet renewable fuel mandate since 2009
PEMEX has own Ethers capacity and can produce ETBE as well if Ethanol is to be used.
MTBE & ETBE Production & Use
The Lyondell Experience

• Lyondell produces MTBE and ETBE from HPIB and Raffinate 1 in Houston, France, and the Netherlands
• Lyondell has announced construction of a new world-scale PO/TBA plant in the Gulf Coast (2020 startup)
• HPIB are plants designed to produce MTBE or ETBE in the same equipment
• Lyondell has a commercial design for raffinate 1 to MTBE or ETBE
• In 2009, South American producer retrofitted assets to MTBE/ETBE production.
• PEMEX could convert Tula and Ciudad Madero to ETBE production
  – Cost would be ~1/3 of $58MM required for test ethanol blending project
  – Conversion would increase ethers production by 31KT
  – PEMEX would retain flexibility to blend ETBE or MTBE in same base gasoline

ETBE production by PEMEX less costly than ethanol blending
Summary/Conclusions

- Mexico has been using MTBE for >20 years with great success
- Energy reforms creating opportunities to lower costs
- Biofuels law can create pressure to use local bio-ethanol
  - However, direct ethanol blending has several drawbacks
- Ethers are the best way to add alcohols and butanes to gasoline
- PEMEX could convert local ethanol to ETBE at its refineries
  - Cost of converting to swing ethers production is low
  - Provides flexibility to produce MTBE in case of bad crop year
- Lyondell is committed to continued supply of MTBE to PEMEX
- Lyondell can help PEMEX convert to ETBE production, OR
- Lyondell can convert Mexican ethanol to ETBE starting in 2020

Continued use of Ethers is the best option for Mexico and PEMEX to improve fuel quality and provide cleaner air for the country
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MTBE and ETBE are volatile, partially water soluble, and have only a minimal tendency to adhere to soil particles. Even small volumes can pose a threat to the environment and nearby water resources, if released. Surface spills can reach groundwater through porous soil or cracked surfaces. Underground releases may occur from leaking underground storage tanks. Underground storage tanks should meet all current regulatory requirements (for example, 40 CFR Parts 280 and 281). All efforts should be made to prevent any leaks or spills, and to protect water resources. Where spills are possible, a comprehensive spill response plan should be developed and implemented. If a leak or spill reaches the groundwater, the groundwater may become contaminated. If the groundwater is a source of drinking water, the associated drinking water well(s) could become contaminated. These substances can impart an unpleasant taste and odor to water at very low concentrations.
Back Up
ETBE vs. Ethanol Blending

- Ethanol increases gasoline RVP by ~7kPA; ETBE does not
- Ethanol-blended gasoline had to be reformulated to 65 kPa
  - Volatile components (e.g. butanes) must be removed with ethanol
- 65kPA gasolines compared with 3% ethanol vs. 8% ETBE
  - Ethanol gasoline more sensitive to temperature

Ethers Provide Clean-Burning Octane...

Ethers Allow For More Low Cost Butanes in Gasoline Without Increasing RVP

with minimal reformulation of gasoline
MTBE and ETBE Production

- Nat Gas
- Petroleum
- Biomass

- Methane
- Ethane
- Butane

- Methanol
- Raffinate*
- HPIB**

- MTBE
- ETBE

MTBE and ETBE produced from Raffinate or HPIB in the same equipment

* Mixed butenes from olefin cracker
** High Purity Isobutylene from PO/TBA process
MTBE vs. ETBE Production & Use
The Lyondell Experience

• Changes to MTBE equipment for ETBE production:
  – Larger pumps for ethanol and ETBE
  – Larger reboiler for ethers product (C5) tower
  – Change metallurgy due to higher corrosivity of ethanol
  – Possibly increase trays in product tower
  – Dryer for ethanol recycle and make-up streams to reduce corrosion and DP in reactors

• Changes in operation:
  – Product tower reboiler is prone to fouling in ETBE mode, requiring more frequent cleaning
  – Drying ethanol is recommended to reduce corrosion and reactor plugging
  – Drying ethanol also reduces TBA production
  – ETBE azeotropes with ethanol but not isobutylene
  – Anti-oxidant added to ETBE to improve storage stability (20 ppm)