A PRIMER ON PETROL OXYGENATES

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ACELA

europe sustainable fuels DRIVING CLEANER MOBILITY WITH FUEL ETHERS

Intro: Add names SF, ACFA, ACELA

MEX case study + parallels to African metropolitan areas

Economic benefits of using ethers: new section

Air quality models: MOVES or Copert -> integrated? Copert is EU and MOVES: rest of the world

+ Toxstrategies on carcinogenicity and IARC (include link to announcement, what is IARC, earlier assessments ECHA etc)

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The fuel ether industry is pleased to present a 'Primer on petrol oxygenates'. This report was prepared at the request of the Specification Group of the African Refiners Association (ARA) to serve as reference document on oxygenates.

With increasing pressure to improve air quality in many parts of the World, including in Africa, improving fuel quality remains a priority for regulatory agencies.
Oxygenates, and particularly fuel ethers, are high-octane petrol blending components that help reduce overall emissions of both CO_2 and air pollutants. Additionally, the implementation of high-quality fuels goes hand in hand with the introduction of modern vehicles with improved engine technology, which provide a positive contribution to the economic development of a certain area.

This report includes an overview of the different types of oxygenates in common use. While the list of oxygenates used in fuels is long, this report focuses on the most widely used oxygenates, especially alcohols and fuel ethers. Other oxygenates, while mentioned, are not discussed in detail.

This report aims to provide ARDA members with an overview of the impact that oxygenates, and especially fuel ethers have on vehicle performance, the environment and the economy. It also describes the various regulations affecting their use, including differences in fuel specifications. The report also highlights the key physical and blending properties of oxygenates and their value in formulating high-quality petrol.

OXYGENATES BY TYPE

Petrol (gasoline) is a complex mixture of refinery hydrocarbon streams, additives, and in many cases, oxygenated blending components. The final composition must meet critical specifications and efficiency characteristics for optimal performance in a variety of engine and vehicle types and technologies. Fuel composition and quality also have a direct impact on vehicular emissions, both evaporative and exhaust, which impact air quality, fuel efficiency, and greenhouse gas (GHG) emissions.

Oxygenates are organic compounds which contain one or more oxygen atoms. Oxygenates enhance octane and improve the combustion of other petrol components. Only two types of oxygenates are commonly used as petrol blending components: alcohols and ethers. Oxygenates use in petrol goes back to the 1970s, when refiners sought to replace lead with less toxic octane boosters and increase petrol volumes. In fuel, the most commonly found oxygenates are: methanol (MeOH), ethanol (EtOH), methyl tertiary butyl ether (MTBE), ethyl tertiary butyl ether (ETBE), tertiary amyl methyl ether (TAME) and tert-amyl ethyl ether (TAEE). This paper will focus on those most widely used oxygenates, their blending properties, environmental and health impacts as well as their transportation and storage practices.

Other oxygenates, belonging to the group commonly called non-traditional gasoline additives (NTGAs), include substances such as secondary butyl acetate (SBA), acetone and methylal (dimethoxymethane). They have been sporadically used as octane enhancers, mainly due to the loopholes in the regulations. NTGAs include such substances as butyl acetate (SBA), acetone and methylal acetate. The effects of NTGAs on engine and fuel distribution components have not been extensively studied, but in 2006, the use of acetone in petrol caused massive vehicle breakdowns in Ho Chi Minh City and led to bans on the use of NTGAs in many petrol specifications.

Table 1: Oxygenates suitable for petrol blending

Formula	Name	Abbreviation
CH_3OH	methanol	MeOH
CH_3CH_2OH	ethanol	EtOH
$(CH_3)_2CHOH$	isopropyl alcohol	IPA
$(CH_3)_3COH$	*tert*-butyl alcohol	TBA
$(CH_3)_2CHCH_2OH$	isobutyl alcohol	IBA
$CH_3CH_2CH_2CHOH$	*n*-butanol	nBA
$(CH_3)_3COCH_3$	methyl *tert*-butyl ether	MTBE
$(CH_3)_3COC_2H_5$	ethyl tert-butyl ether	ETBE
$(CH_3)_2(C_2H_5)COCH_3$	tert-amyl methyl ether	TAME
$(CH_3)_2(C_2H_5)COC_2H_5$	tert-amyl ethyl ether	TAEE
$(CH_3)_2CHOCH(CH_3)_2$	di-isopropyl ether	DIPE

Source: Ullman's encyclopaedia of industrial chemistry, p.10

ALCOHOLS

While the use of alcohols as fuels and fuel components goes back to the 1850s, interest in alcohols as fuels became more widespread in the 1970s because of oil embargos, rising oil prices, and – more recently – lower Greenhouse Gas Emissions (GHG).

The alcohols used as transport fuels include methanol, ethanol, and butanols, all of which can be produced from renewable biomass or petrochemical feedstocks.[1] Alcohols are added to petrol to increase octane and, when produced from biomass, to reduce GHG emissions.

Fuel ethanol (ethyl alcohol or bioethanol) is produced by fermenting biomass. According to a 2018 USDA study[2], the most common feedstocks to produce ethanol for fuels are corn and sugarcane. Ethanol from petroleum feedstocks is not used in petrol because it does not contribute to reductions in CO_2 or benefit from favourable governmental incentives.

Methanol (methyl alcohol) is a building block of several products and can be used as an alternative fuel in vehicles. Methanol can be produced from natural gas, coal, biomass or landfill gas. There are a variety of technologies used to produce methanol. In fuels, methanol is generally used as a neat product because of the need to use co-solvents when blended with petrol. Bio-methanol can be blended with petrol or used to produce bio-methyl tertiary butyl ether (bio-MTBE), bio-dimethyl ether (bio-DME), or synthetic biofuels (source: USDA).

Butanols - Tertiary-butanol (t-butanol or TBA), n-Butanol and isobutanol have various applications, including as octane boosters for petrol. TBA is a co-product in the production of propylene oxide and is also manufactured by the catalytic hydration of isobutylene. Dehydrating TBA is one of the methods to produce isobutylene, which is then used to produce MTBE. The direct blending of TBA and methanol in petrol is now limited, because MTBE provides higher octane and better compatibility with petrol and vehicle components.

FUEL ETHERS

Fuel ethers are valuable blending components for petrol. The most common include: methyl tertiary butyl ether (MTBE), ethyl tertiary butyl ether (ETBE), tertiary amyl methyl ether (TAME), tert-amyl ethyl ether (TAEE) and diisopropyl ether (DIPE).

Fuel ethers have been blended in petrol since the 1970s, with substantial growth in the 1980s caused by the phase-out of lead. The two most commonly used fuel ethers are MTBE and ETBE. These fuel ethers are made by reacting isobutylene with methanol or ethanol. Desirable properties of fuel ethers include high octane, negligible sulphur content, low blending vapour pressure (BRVP) compared to both petrol and alcohols, and lower oxygen content compared to alcohols.

MTBE's high-octane properties, low boiling temperature and moderate blending vapour pressure (55 kPa), help refiners upgrade lower quality refinery streams. MTBE is also used to upgrade regular octane petrol to higher "premium" grade and to meet the petrol specifications in many countries. The oxygen content of MTBE allows the production of cleaner-burning petrol, which reduces exhaust emissions of volatile organic compounds that are precursors to ozone and particulate matter (PM), the two main components of smog. MTBE also replaces aromatic compounds in petrol, which results in lower evaporative and exhaust emissions of toxics (BTEX) and smog precursors.

ETBE also has a low blending vapour pressure (28 kPa), which helps reduce petrol vapour pressure and evaporative emissions of smog precursors and toxic air contaminants (BTEX). Unlike ethanol, ETBE can also be blended into petrol at the refinery and then shipped to the final destination point by pipelines. Ethanol, because of its corrosivity and tendency to phase separate when water is present, must be transported separately to terminals and blended close to the distribution centres. The key blending properties of ETBE are its high octane, low blending vapour pressure, and very low sulphur content. ETBE also delivers greater GHG reduction benefits than the contained ethanol.

1 *Review and qualitative assessment of Clean Octane Options for Gasoline, HART Energy Consulting, December 2007,*

2 *Bob Flach, Sabine Lieberz, Jennifer Lappin and Sophie Bolla, EU Biofuels Annual 2018, USDA, 7 March 2019 https://gain.fas.usda.gov/Recent%20GAIN%20Publications/Biofuels%20Annual_The%20Hague_EU-28_7-3-2018.pdf*

PHYSICAL AND BLENDING PROPERTIES OF OXYGENATES

Oxygenates are typically used to replace tetra-ethyl lead (TEL), aromatic streams such as reformate that contain BTEX (benzene, toluene, ethylbenzene and xylenes), and olefins and other octane boosters that contribute disproportionately to air pollution. Oxygenates also contribute to a reduction in sulphur, which poisons the catalysts in three-way catalytic converters (TWCC) resulting in greater exhaust emissions of air pollutants. Most oxygenates improve the combustion of other petrol components, thereby reducing Carbon Monoxide (CO) emissions and partially combusted hydrocarbons and improving fuel efficiency. Alcohols, however, behave differently from ethers when blended in petrol, due to their different solubility properties and compatibility with the hydrocarbon components of petrol. Most notably, alcohols increase the gasoline vapour pressure (RVP) and permeation, resulting in increased exhaust and evaporative emissions of ozone and PM precursors. Alcohols also change the distillation characteristics of gasoline. Ethers, on the other hand, lower gasoline vapour pressure, reduce evaporative emissions, and lower exhaust emissions of PM, VOCs, and toxics compared to alcohols.

The oxygenates most widely used are MTBE, ETBE and ethyl alcohol. This chapter describes and compares the blending properties of fuel ethers and alcohols.

COMPARISON OF PROPERTIES OF OXYGENATES

The hydroxyl (-OH) group in alcohols results in strong hydrogen bonding and polarity that are quantified by their Hansen solubility parameters and illustrated in Figure 1. Because of this, alcohols have greater affinity for water than petrol and, when all three are present, will separate into two phases; under certain conditions of temperature and alcohol/water concentrations the phase comprised mostly of hydrocarbons and the lower (denser) phase comprised predominantly of ethanol and water.

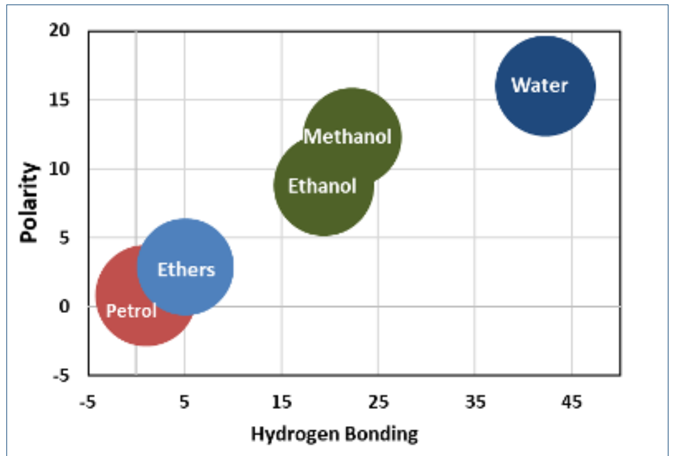


Figure 1: Hansen Solubility Parameter (MPa$^{0.5}$) plot showing the difference between petrol, ethers, and alcohols.

The organic phase is gasoline with lower octane due to the depletion of ethanol and the lower phase, although combustible, can cause sever engine damage if it is allowed to enter the engine.

Ethers, on the other hand, have limited water solubility and remain in the hydrocarbon phase in the presence of water. This imparts greater stability to the finished petrol, allowing it to be shipped from the refinery to the final distribution points by all modes of transportation, including pipelines, barges, and sea-going vessels. Ether-blended petrol is also more compatible with elastomers and plastics found in the distribution and storage infrastructure and vehicles. Unlike alcohol-blended petrol, they are also non-corrosive and resistant to biological fermentation and oxidation.

Another consequence of the high polarity and hydrogen-bonding properties of alcohols is their non-linear blending properties, high blending vapour pressures, and tendency to form azeotropes with close-boiling hydrocarbons, including toxic aromatics such as benzene, toluene, ethylbenzene, and xylenes (BTEX). This results in a lowering of T50 (increase in volatility), an increase in RVP ranging from ~7 kPa for higher volatility blends to ~15 kPa for lower volatility (< 62 kPa blendstocks).[3] These changes require a reformulation of the Blendstocks for Oxygenate Blending (BOBs) for ethanol blending or changes in the specifications for fuels containing 5-15% v/v ethanol.

These changes in petrol properties can be attenuated by co-blending ethers and alcohols. For example, adding ETBE to an ethanol-blended petrol was shown to result in lower RVP and improved petrol stability than petrol without ETBE.[4] This blending approach has been implemented in France, where all blendstocks for ethanol blending contain bio-ETBE. This allows additional renewable ethanol to be incorporated into petrol as ETBE while mitigating the impact of direct ethanol blending at the terminals. It also lowers the overall cost of the petrol, since more butanes can be left in the blendstock when ETBE is present. The ETBE-containing blendstock can also be transported via pipeline to terminals without the risk of phase separation.

Another important consideration when selecting oxygenates is their energy content, which is directly correlated to the amount of oxygen present in the blend component. The graph below shows the correlation between oxygen content and energy density of some oxygenated petrol blendstocks as listed by both EN228 (European Petrol standard) and the EU Fuel Quality Directive.

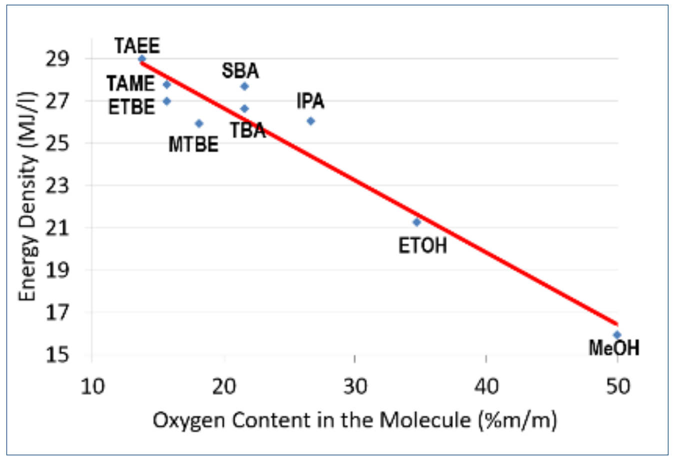


Figure 2: Correlation Oxygen Content - Energy Density of some Oxygenated Petrol Blend-stocks

All oxygenates have a lower energy content than petrol (ACEA: 33.7 MJ/litre), but some alcohols have a significantly lower energy density than ethers. Higher alcohols such as IPA, SBA, and TBA also have a higher energy density than ethanol or methanol. Thus, as the alcohol content increases, the amount of chemical energy available for combustion decreases. Since the energy content of ethanol is roughly 33% lower than petrol, petrol blended with 10% v/v ethanol will contain ~3% less energy and produce lower mileage than unoxygenated petrol. Again, this impact can be mitigated by blending ethanol as ETBE, since it provides 6 MJ/L higher energy density than ethanol.

European technical specifications (EN228) prescribe a range for petrol density (720-775 kg/m3), while the EU Directive (Fuel Quality Directive - FQD) does not include density among those listed in Annex I, since not considered environmentally relevant. The lower the actual density of petrol sold, the lower the energy contained in that litre of petrol (even if the petrol would not contain any oxygen) and, in turn, the lower the distance the vehicle will be able to run on that litre of fuel.

The comparison of physical and blending properties of fuel ethers and alcohols is listed in the tables below.

Table 2. Physical and blending properties of ethers (Source: Ullmann's Encyclopedia, p.13)

	MTBE	ETBE	TAME	TAEE	DIPE
CAS Number	1634-04-4	637-92-3	994-05-8	919-94-8	108-20-3
Molecular mass	88	102	102	116	102
Oxygen, wt.%	18.2	15.7	15.7	13.8	15.7
Solubility in water, g/L @25ºC	42	12	20	4.5	20
Boiling point, °C	55	72	86	102	68
RVP* blending, kPa	55	28	10	9	34
Density, kg/L	0.74	0.75	0.77	0.77	0.73
Stoichiometric air/fuel ratio	11.73	12.15	12.15	12.57	12.15
Net Energy Density, MJ/L	26	27	28	29	27
RON, blending	117	119	110	108	110
MON, blending	102	103	99	95	99

Table 3. Physical and blending properties of alcohols (Source: Ullmann's Encyclopedia, p.13)

	MeOH	EtOH	IPA	TBA	IBA	nBA
CAS Number	67-56-1	64-17-5	67-63-0	75-65-0	78-83-1	71-36-3
Molecular mass	32	46	60	74	74	74
Oxygen, wt.%	50.0	34.8	26.7	21.6	21.6	21.6
Boiling point, °C	65	78	82	83	108	117
Density, kg/L	0.8	0.79	0.79	0.78	0.8	0.81
Stoichiometric air/fuel ratio	6.46	8.98	10.33	11.16	11.16	11.16
Net Energy Density, MJ/L	16	21	25	27	27	27
RVP*, neat, kPa	31.7	17.3	12.4	11.7	4.1	2.8
RVP* blending, kPa	414	117.3	96.6	60.7	34.5	44.2
RON, blending	133	130	121	109	105	94
MON, blending	99	96	96	93	92	81

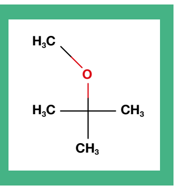
** Reid Vapor Pressure*

3 *Memorandum from Robert McCormick of National Renewable Energy Laboratory to Kristy Moore, Vice President, Renewable Fuels Association, 26 March 2012.*

4 *D. Karonis et. al., SAE Int. J. Fuels Lubr., 2008-01-2503, Vol. 1, Issue 1.*

MTBE

- Name: tert-butyl methyl ether, MTBE
- EC Number: 216-653-1
- CAS Number: 1634-04-4
- Molecular formula: C5H12O



MTBE is a volatile, colourless liquid, with an odour similar to terpene. It has a boiling point of 55.2ºC and freezing point of -109ºC. MTBE is flammable and is soluble in other ethers, hydrocarbons, and alcohols. MTBE is only sparingly soluble in water (4.2 wt.%). MTBE is produced by acid-catalysed condensation of methanol and isobutylene. MTBE is almost exclusively used to increase the octane and oxygen content of petrol.

The research octane number (RON) of MTBE is between 115-135, and the motor octane number (MON) between 98-110, depending on the base petrol blendstock. This range has been determined by a large number of experimental data obtained when formulating petrol.

The 2016 SAE paper 'Blending Octane Evaluation of Fuel Ethers: A Literature Review' indicates that the RON level of MTBE is 117 and of MON is 102. Blending octane numbers of petrol are sensitive to the composition and octane numbers of the base petrol.

According to the MTBE Handbook, which takes into consideration some of the studies, a 15% v/v of MTBE represents a reasonable concentration of MTBE in petrol in terms of octane number increase, change in fuel stoichiometry, and commercial availability of MTBE. The high-octane properties of MTBE are particularly effective in upgrading low-octane unleaded petrol components such as naphtha and natural gasoline.

The boiling point of MTBE is low, which provides higher front-end octane numbers (FEON) to petrol. FEON is the octane number of a petrol fraction which boils below 100 degrees Celsius. This is an important element in cold-start conditions, when the low-boiling components of petrol get a chance to vaporize. MTBE is very effective in boosting the front-end octane and gives very high FEON numbers (135 RON). The FEON of MTBE is higher than that of butane, reformate, alkylate, and aromatics. FEON also increases engine efficiency during the low-speed acceleration stage.[5]

Among the properties that influence the performance of petrol are Reid Vapour Pressure (RVP) and distillation profile. In many countries, including the US and members of the European Union, the RVP is kept low to reduce evaporative VOC emissions which lead to ground-level ozone.

Adding MTBE to petrol may affect its RVP, depending on the RVP of the blendstock. For example, blending 15 wt.% MTBE in a 63kPA blendstock decreases the RVP of the finished petrol by approximately 2 kPa (Figure 3). Hence, there is no need to remove butane with MTBE and, depending on the RVP limit of the finished petrol, additional butane can be added to the blend to reduce cost. This is one of several advantages of ethers over alcohols.

Figure 3 illustrates how ethanol and methanol both increase the volatility (RVP) of petrol. Adding ethanol to petrol causes an RVP increase ranging from 7 to 12 kPa depending on the RVP of the Blendstock for Oxygenate Blending (BOB). The RVP increase from 1.0 vol. % methanol is of the order of 15 kPa and increases to 20 kPa at 2.0 v/v methanol. This makes alcohols less useful than ethers for formulating low RVP petrol for ozone non-attainment areas. This also requires the refiners to remove additional butanes and pentanes when producing BOBs for alcohol blending, which increases cost. The RVP impacts of different oxygenates are compared in Figure 3.

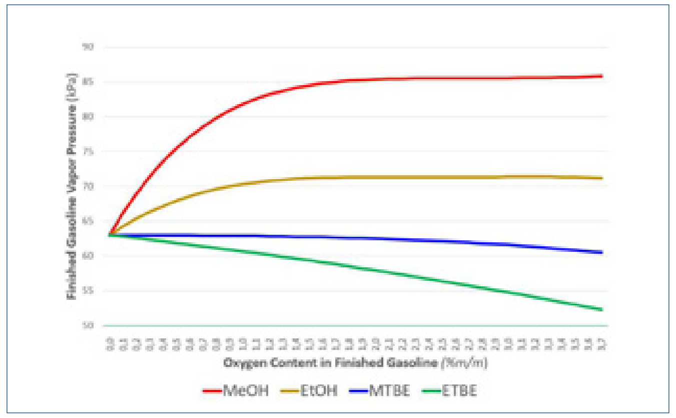
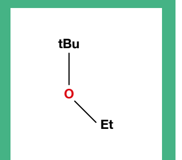


Figure 3: Effect of oxygenates concentration on vapour pressure of petrol a) ETBE; b) MTBE; c) EtOH; d) MeOH.

MTBE boils in the same temperature range as other light refinery components. MTBE is soluble in any ratio with petrol. In contrast with alcohols, MTBE does not form azeotropes with other hydrocarbon components or depress the distillation curve (T50) of the finished petrol.

ETBE

- Name: Ethyl tert-Butyl Ether (ETBE)
- EC Number: 211-309-7
- EC Name: 2-ethoxy-2-methylpropane
- CAS Number: 637-92-3
- Molecular formula: C6H14O



Ethyl tertiary-butyl ether (ETBE) is a flammable liquid with a boiling point of 72º C. ETBE is produced by the acid-catalysed condensation of isobutylene and bio-ethanol. The blending vapour pressure of ETBE is 27.6 kPa, which is significantly lower than

5 *Handbook of MTBE and Other Gasoline Oxygenates. Halim Hamid Mohammed, Ashraf Ali March 11, 2004, CRC Press, p. 41.*

that of ethanol. The blending octane of ETBE is 119 RON and 103 MON. The effect of ETBE on the distillation characteristics is similar to MTBE. ETBE blends linearly with petrol and does not form azeotropes.

ETBE offers advantageous physical and chemical properties compared to ethanol for petrol blending including:

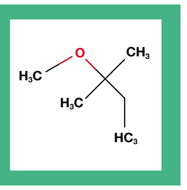
- significantly lower blending volatility
- no significant distortion of the distillation curve
- better tolerance of wet distribution systems
- lower octane sensitivity (RON-MON)
- improved materials compatibility

Blending ETBE with petrol for ethanol blending also imparts the following benefits:

- Lower RVP, which leaves room for more light components,
- Reduced water sensitivity,
- Better compatibility with seals and gaskets,
- Octane sensitivity (RON – MON) in line with finished petrol specifications requirements.

TAME

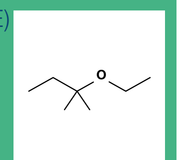
- Name: tert-amyl methyl ether (TAME)
- EC Number: 216-653-1
- CAS Number: 994-05-8
- Molecular formula: C6H14O



The boiling point of TAME (86ºC) is higher than that of MTBE, ETBE, ethanol and methanol. It has a very low RVP of 10.4 kPa, a RON of 110, and MON of 99. TAME is used in petrol similarly to MTBE, ETBE or ethanol. Typically, 1-10% TAME is blended in petrol.[6]
It is produced by the acid-catalysed condensation of tert-amylenes with methanol. Around 97% purity TAME is produced from this mixed refinery stream.

TAEE

- Display Name: tert-amyl ethyl ether (TAEE)
- EC Number: 618-804-0
- EC Name: tert-amyl ethyl ether
- CAS Number: 919-94-8
- Molecular formula: C7H16O

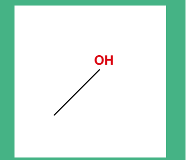


Among fuel ethers, TAEE has the highest boiling point of 102 degrees Celsius and the lowest blending BRVP of 9 kPA. The octane rating of TAEE is 108 RON and 95 MON. The freezing point is -20 degrees Celsius.

It is produced by the acid-catalysed condensation of tert-amylenes with ethanol.

METHANOL

- Display Name: Methanol
- EC Number:200-659-6
- EC Name: Methanol
- CAS Number: 67-56-1
- Molecular formula: CH4O



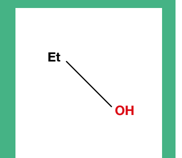
Methanol is a volatile flammable liquid, produced from synthesis gas (CO/H2). The feedstock for production is either natural gas or renewable feedstock such as landfill gas, biomass, captured CO_2 or municipal waste. Methanol is used in the production of MTBE, but it is sometimes used on its own as an octane enhancer. However, its use is limited or prohibited in many countries due to its effect on petrol volatility and corrosivity.

Direct blending of methanol requires co-solvents such as tert-butanol or isopropanol, due to its inherent incompatibility with hydrocarbons and affinity for water. This can lead to phase separation when water is present, resulting in a low-octane hydrocarbon phase and a methanol-rich aqueous phase. Methanol also has an oxygen content of nearly 50%. Therefore, its stoichiometric property of air / fuel ratio and energy density are very different to that of other petrol components. This limits methanol's utility as a petrol blending component and explains why it is only used in areas where MTBE is not available and cannot be produced.

The octane value of methanol is 133 RON and 99 MON. The high-octane rating helps in reduction of the engine knock and results in better fuel efficiency, if the compression ratio of the car is adjusted. While there are efficiency benefits of methanol, its energy density is around 50% that of petrol, which means that the range a vehicle can travel on a tank of fuel is reduced.

ETHANOL

- Display Name: Ethanol
- EC Number: 200-578-6
- EC Name: Ethanol
- CAS Number: 64-17-5
- Molecular formula: C2H6O



Ethanol, also known as ethyl alcohol is a clear, colourless, flammable liquid. Ethanol can be synthesized by the acid-catalysed hydration of ethylene or by conventional biomass fermentation and distillation. Feedstocks for the production of ethanol includes a biomass derivative such as sugar (from sugar beet or sugarcane), grain (corn, wheat, etc.), or cellulosic material (including wood and biowaste)[7].

6 *European Union Risk Assessment Report, TAME, European Commission https://www.fuelethers.eu/assets/uploads/2018/10/TAME_-_EU_Risk_Assessment_Report_-_2006.pdf*

7 *Octane Enhancers, Ullman Encyclopedia of Industrial Chemistry, Marco Di Girolamo, Maura Brianti and Mario Marchionna*

Prior to blending with Petrol ethanol is denatured with gasoline to prevent human consumption. Ethanol is most often added to petrol to increase octane and to extend domestic petrol supplies.

Ethanol is most commonly added to petrol in quantities no higher than 10%, with the exception of E85, a mixture of 85% ethanol and 15% petrol). Ethanol blends above 10% requires dedicated engines and fuel distribution systems. Petrol with a concentration of 10% ethanol can also cause material compatibility problems for certain fuel system components (seals, injection pumps).

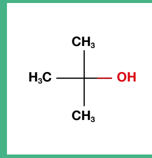
With a RON number of 130 and a MON of 96, the addition of ethanol to petrol has greater effect on Research Octane Number (RON) than on MON.

There is a significant increase in RVP resulting from even a small addition of ethanol to petrol. This is an interesting property of alcohols, as the RVP of pure alcohols is lower than those of most petrol components. The low vapour pressure of fuel grade ethanol is caused by attractive forces between the ethanol molecules called hydrogen bonding. Hydrogen bonding causes alcohols to have a greater tendency to stay in the liquids state than their low molecular weight would predict. However, when blended into petrol at relatively low concentrations the other components disrupt this hydrogen bonding causing the ethanol and other volatile components to evaporate. This raises the vapour pressure of the blend and increases evaporative emissions from the fuel.

Another undesirable property of ethanol is its low energy content, which is 33% lower than that of gasoline. This is due to its relatively high oxygen content. Oxygen cannot burn and release energy like carbon and hydrogen so the higher the oxygen content, the lower the energy available for combustion. Hence, the higher the ethanol content in petrol, the lower the efficiency of the fuel. At 10% ethanol, the available energy in the fuel is reduced by 3.3% which results in fewer kilometers driven per litre of fuel.

TERT-BUTANOL

- EC / List name: 2-methylpropan-2-ol
- IUPAC name: 2-methylpropan-2-ol
- EC number 200-889-7
- CAS number: 75-65-0
- Index number: 603-005-00-1
- Molecular formula: C4H10O



Tertiary-butanol (t-butanol or TBA) is a co-product from the manufacture of propylene oxide. TBA was commercialized as a fuel component in the past but is now dehydrated to produce isobutene for the production of MTBE.
In the 1980s ARCO Chemical commercialized two TBA-based fuel additives, Arconol™ and Oxinol™ 50, a 50/50 blend of TBA and methanol. The products were eventually discontinued because refiners preferred to use MTBE.

HEALTH AND ENVIRONMENTAL IMPACT OF OXYGENATES

In the regulatory and toxicological evaluation of substances, the terms hazard and risk are often used. Understanding the difference between a hazard and a risk of a substance is key for the regulator. A hazard is property that can inherently cause harm, independently from the application, whereas risk is the potential for a hazard to cause harm, which is dependent on the application and exposure level.

RISK = HAZARD x EXPOSURE

In other words, a chemical will not cause harm to humans or the environment unless they are exposed to a sufficient amount of that chemical to cause harm. The risks associated with chemicals can be eliminated, or at least greatly reduced, by reducing exposure and selecting fuel components that have low inherent toxicities.

The use of oxygenates generally improves fuel quality by increasing octane and replacing more toxic components such as lead and BTEX (benzene, toluene, ethylbenzene and xylenes), reducing sulphur, and improving combustion. However, the net impact on evaporative and exhaust emissions and air quality depends on the oxygenate, other fuel components, and the type of engine and vehicle used. MTBE was the first oxygenate to be selected by refiners over ethanol and other alternatives to replace lead as an octane booster in the 1980s. The ban on the use of some organometallic octane boosters such as lead coincided with the introduction of the three-way catalytic converter (TWCC), which is an important technology to reduce exhaust emissions of CO, NO_x, and carcinogenic combustion products such as aldehydes. Lead, manganese, and sulphur all reduce the ability of the TWCC to convert NO_x to nitrogen and partially combusted organics (e.g. VOCs, butadiene, CO, and aldehydes) to CO_2.

The introduction of MTBE, the TWCC, electronic control modules (ECM) to regulate air to fuel ratio, evaporative control technologies, and reductions in sulphur and BTEX content have all contributed to significant reductions in criteria air pollutant concentrations, especially in large urban areas. Carbon monoxide pollution, once a significant problem, was virtually eliminated by the combined use of MTBE and the ECM. Properly functioning TWCCs have also contributed to significant decreases in NO_x, particulate matter (PM10 and PM2.5), and volatile organic compounds which react in the atmosphere to form ozone and PM. The two main components of smog.

In Mexico City, the most polluted city in the world in 1992,[8] replacing TEL with MTBE contributed to an 82% decrease in ambient CO concentrations, a 53% decrease in ozone, and a 32% decrease in PM10 between 1993 and 2014, despite a tripling of the population and vehicle fleet and slow adoption of low-sulphur standards. In the United States, similar reductions were achieved until 2005, when the Renewable Fuel Standard (RFS) mandated the use of 10% ethanol in petrol. This mandate and several State bans on the use of MTBE led to its deselection in the US and Canada, but Mexico and other Latin American, Asian, and European countries continue to use it instead of, or in addition to, ethanol. After a multi-year analysis of available options, Japan chose ETBE over ethanol in 2009 to meet its renewable fuels mandate, and France has chosen a flexible hybrid approach where both ETBE and ethanol are used.

It is noteworthy that most countries that have mandated ethanol use in petrol did so for reasons other than air quality. The US Congress justified the RFS and the ethanol mandate by claiming.
it would reduce imports crude oil imports and CO_2 emissions. Since then, shale gas and crude production have made the US a net exporter of natural gas and crude oil, and the ethanol mandate and costly Renewable Identification Number (RIN) tax system used to subsidize its use have become increasingly controversial. The Association of Fuel and Petroleum Manufacturers (AFPM) have called for a repeal of the RFS, as have several non-governmental organizations (NGOs), concerned over the impact of fuel ethanol production on groundwater contamination due to fertilizer runoff, land use, and loss of bio-diversity. China, the leading producer of MTBE in the world, announced a national ethanol programme in 2017 to eliminate a large surplus of ageing corn but has since announced that it will not implement E10 nationwide due to the competition with food.

Ethers are generally preferred over alcohols due to their superior compatibility with other petrol components, vehicle components, distribution infrastructure, and greater reduction of vehicular emissions and air pollutants.

The US Environmental Agency (EPA) and other regulatory bodies have conducted or funded numerous studies to compare the impact of ethers and alcohols on overall emissions and air quality. The US EPA has combined this knowledge in an emissions model called MOVES 2014a that can predict the impact of fuel components on vehicular emissions. The MOVES model is currently used by the US EPA and State air regulators to estimate the impact of fleet, fuel, and infrastructure changes on air emissions and comply with federal air quality targets.

This chapter summarizes the key findings from these studies and compares the impact of ethers and alcohols on vehicular emissions. This chapter also summarizes a few toxicological properties of oxygenates, although they are generally less toxic than the petrol components they are replacing. So, it is fair to say that the use of oxygenates generally reduces the overall toxicity of petrol and that it is their impact on vehicular performance, emissions, and air quality that is the most important consideration for refiners and regulators alike.

TOXICOLOGY

Table no 4 shows the EU hazard classification of typical petrol components according to the harmonised classification and labelling (CLP00) approved by the European Union. The information below is on pure compounds, and this is not how components and oxygenates are encountered in fuel applications. They are rather encountered as one component of the complex mixture of hydrocarbons found in fuels, and human exposure to the fuels is limited to the potential vapour phase environments of these compounds that are closely linked to fuel transportation, refuelling at stations, and possible exhaust emissions from vehicles. Oxygenates might have a direct exposure associated with occupational fuel blending operations.

8 According to the World Health Organization

Table 4. EU hazard classification of typical petrol components

MTBE	Highly flammable liquid and vapour and causes skin irritation.	
ETBE	A highly flammable liquid and vapour and may cause drowsiness or dizziness.	
TAME	Highly flammable liquid and vapour is harmful if swallowed and may cause drowsiness or dizziness.	
TAEE	A highly flammable liquid and vapour.	
Methanol	Toxic if swallowed, is toxic in contact with skin, is toxic if inhaled, causes damage to organs and is a highly flammable liquid and vapour. Additionally, the classification provided by companies to ECHA in REACH registrations identifies that this substance is suspected of causing cancer.	
Ethanol	A highly flammable liquid and vapour. Additionally, the classification provided by companies to ECHA in REACH registrations identifies that this substance causes damage to organs, is toxic if swallowed, is toxic in contact with skin, is toxic if inhaled, causes serious eye damage and causes skin irritation.	
Tert-butanol (TBA)	A highly flammable liquid and vapour, causes serious eye irritation, is harmful if inhaled and may cause respiratory irritation.	

Source: ECHA (European Commission), Substance information

Extensive and robust inhalation toxicity testing (sub-chronic, neurotoxicity, developmental, reproductive, immunotoxicity, genotoxicity) has been undertaken that has been conducted on petrol vapour condensate fractions (GVC) of a series of unleaded petrol each blended with an oxygenate of interest (MTBE, ETBE, EtOH, etc.). These toxicity studies were designed to examine the worst-case real-world exposures to oxygenates contained in unleaded petrol.

The series of GVC toxicity studies of petrol containing various oxygenates was directly structured to reflect realistic human exposure scenarios. That series of tests, implemented under the US EPA health effect test rule for the Clean Air Act, was sponsored by the manufacturers of fuel oxygenates and coordinated by the American Petroleum Institute. Most of the findings of these studies were published as a Special Issue of Regulatory Toxicology and Pharmacology in 2014 (RTP Vol 70, Issue 2, Supplement, pp. S1-S96). That wide spectrum of endpoint toxicity testing concluded that the findings "demonstrate a wide margin of safety between various high-end exposure scenarios and the no observed adverse effect levels (NOAEL) demonstrated in the hazard screening studies reported in this issue." In fact, the study findings largely demonstrated that the toxicity of various oxygenate containing petrol GVCs, when exposed to animals under worst-case vapour emission exposures (GVC), was not differentiated from the toxicity of GVC from unleaded petrol alone. Thus, as the above quote summarizes, exposures to petrol containing oxygenates do not pose significant health risks under conditions of typical human exposure scenarios.

1. Health assessment of gasoline and fuel oxygenate vapours: Generation and characterization of test materials
2. Health assessment of gasoline and fuel oxygenate vapours: Subchronic inhalation toxicity
3. Health assessment of gasoline and fuel oxygenate vapours: Micronucleus and sister chromatid exchange evaluations
4. Health assessment of gasoline and fuel oxygenate vapours: Neurotoxicity evaluation
5. Health assessment of gasoline and fuel oxygenate vapours: Immunotoxicity evaluation
6. Health assessment of gasoline and fuel oxygenate vapours: Reproductive toxicity assessment
7. Health assessment of gasoline and fuel oxygenate vapours: Developmental toxicity in mice
8. Health assessment of gasoline and fuel oxygenate vapours: Developmental toxicity in rats
9. Gasoline risk management: A compendium of regulations, standards, and industry practices
10. Alternative Tier 2 health effects testing requirements for gasoline and oxygenated gasolines

Link to the open source documents: https://www.sciencedirect.com/journal/regulatory-toxicology-and-pharmacology/vol/70/issue/2/suppl/S

ALCOHOLS

Ethanol is a flammable substance that is not considered toxic to living organisms (source: ECHA). Ethanol occurs in nature and most organisms are able to metabolize it. Ethanol is readily biodegradable and does not bio-accumulate in soil or living organisms. Spillage onto soil results in evaporation into the air and dilution by soil or water. Ethanol is a VOC. Ethanol is slightly toxic to the green algae chlorella vulgaris. The International Agency for Research on Cancer (IARC) has classified ethanol as a known human carcinogen (Group 1) when ingested. The IARC evaluation was based however on chronic alcohol abuse in humans, a vastly different exposure scenario than exposure as a fuel additive. The ethanol in petrol is not considered toxic to humans, since its inhalation exposure is below levels capable of producing an acute or chronic response.

Methanol is toxic when inhaled or ingested. It also causes damage to organs. Human methanol poisoning is noted only in abuse scenarios, with exposure vastly higher than in fuels. Overall, methanol in petrol is not considered toxic to humans, as supported by the GVC studies. Methanol is readily biodegradable and does not harm aquatic life or the environment, according to ECHA's classification. Methanol is not classified as Persistent, Bioaccumulative and Toxic (PBT) or very Persistent and Very Bioaccumulative (vPvB).

FUEL ETHERS

MTBE, ETBE, TAME and TAEE are flammable liquids with low acute toxicities. They can be moderately irritating to the skin, eyes and respiratory system but are not sensitizers. Ecotoxicological assessments of MTBE show different results: according to ECHA Risk Assessment (200), MTBE is inherently biodegradable under certain conditions in an aquatic aerobic environment, although the agency also concludes, that under other test conditions no biodegradation is observed.

The available data indicates a low potential for bioaccumulation which means MTBE is not expected to bioconcentrate or accumulate in biota.
Additionally, according to the EU framework for Substances of Very High Concern, MTBE is not considered as Persistent, Bioaccumulative and Toxic (PBT) or as very Persistent and Very Bioaccumulative (vPvB).

The authors of the risk assessments of MTBE (2001), ETBE (2002) and TAME (2008) concluded that their use in petrol has no detrimental impact on human health, the atmosphere, or the environment. They are not classified as carcinogens, mutagens, or reproductive toxins. It should it be noted that MTBE in groundwater has been identified as a past environmental problem, due to leaking underground fuel tanks in the US. However, current tank technology has largely eliminated this concern. After extensive industry testing to evaluate this issue, the United States Environmental Protection Agency (EPA) took no further action on health risks associated with such exposures (described in special issue; see Swick et al, RTP 70: S3-S12, 2014). For further risk limitation measures check section 7.

Further assessments have been performed at international level: a vast amount of information about MTBE is available, as this substance has been thoroughly tested and evaluated, with the first health screening conducted in 1969. The International Agency for Research on Cancer (IARC) has determined that MTBE is not classifiable as a human carcinogen (Group 3) based on extensive research.

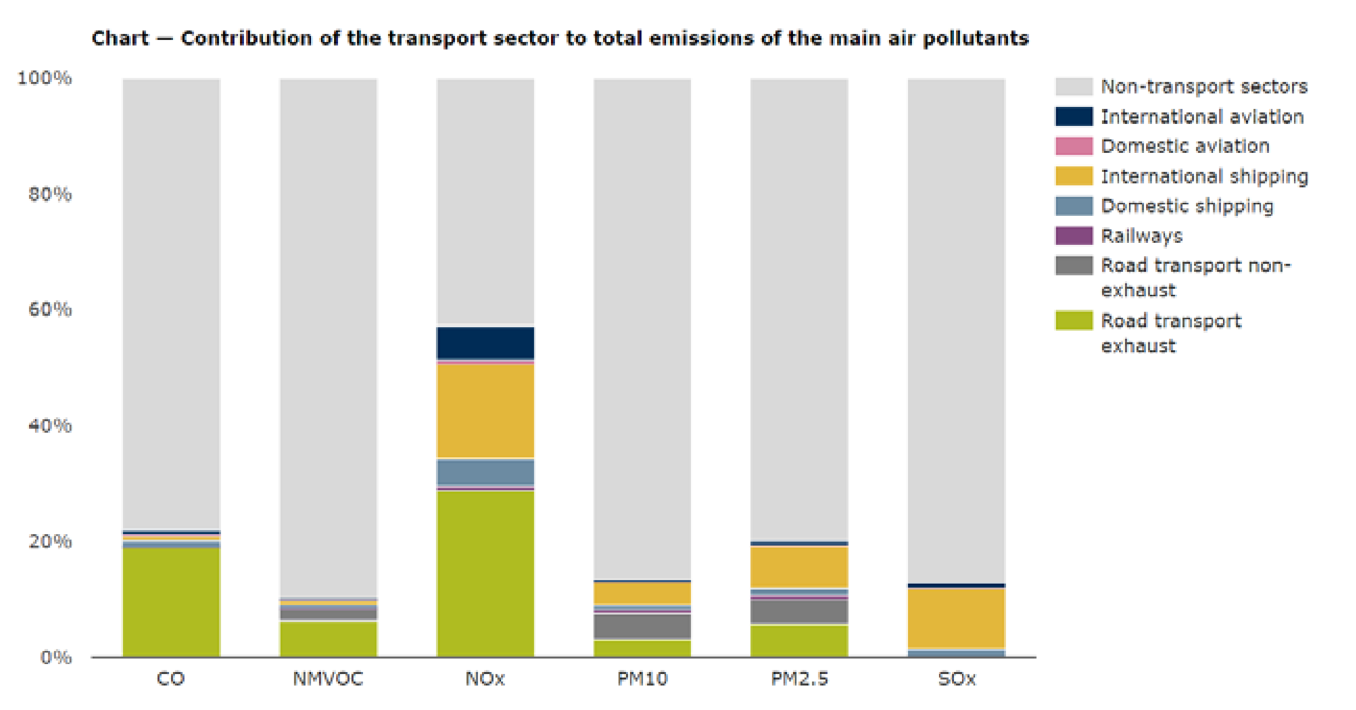
There is a vast amount of health information available on the potential health risks associated with worst-case human exposures to petrol vapours (GVCs) containing a wide range of oxygenates (list) indicates a "wide margin of safety". The data on MTBE is more extensive in that the comprehensive animal carcinogenicity testing has been conducted with this agent, indicating MTBE is not a human carcinogen.

AIR QUALITY IMPACTS OF OXYGENATES

Any discussion about the air quality impact of oxygenates needs to be put into the context of the full petrol mixture and all emission mechanisms. However, traditionally, the emission measurement system for transport has focused on tailpipe emissions and less so on evaporative emissions which account for the majority of vehicular emissions.
The most common air pollutants associated with transportation are: ozone and its precursors (Volatile Organic Compounds or VOCs), Carbon Monoxide (CO), Nitrogen Oxides (NO_x), Particulate Matter (PM10, PM2.5), Sulphur Dioxide (SO_2), and Toxics Organics including aldehydes, benzene and other aromatics, and 1,3-butadiene.

According to the Global Environmental Outlook (GEO) 6 report, "Growth in urbanization, industrialization, motorization and the emission of mineral dust from deserts have increased outdoor pollution in Africa". The transboundary transport, dispersion and eventual deposition of pollutants also contribute to raised outdoor pollution levels in the region. Especially for urban areas, the observed trend in levels of outdoor pollution requires the implementation of transport solutions that include setting standards for the condition of road vehicles and investing in sustainable mass transport systems".

Figure 4: Contribution of the transport sector to total emissions of the main pollutants.



Source: GEO 6 Report

TYPES OF EMISSIONS

There are several types of emissions associated with production and use of fuels:

1. EMISSIONS RELATED TO PRODUCTION AND DISTRIBUTION OF FUELS.

These emissions are mostly relevant to greenhouse gas (CO_2) accounting for biofuels and the transport of ethanol to terminals and distribution centres. Fuel ethers do not require a separate distribution and storage infrastructure, so emissions from this additional transport mode (mainly rail and trucks) are non-existent.

2. EMISSIONS RELATED TO VEHICLES

a. Exhaust Emissions - While the vast amount of petrol is burned in the combustion engine, some of it escapes intact or only partially combusted. The level of emissions depends on the engine, temperature, air-fuel ratio, if fuel system deposits exist, and if the car is equipped with a well-functioning catalytic converter. For example, the majority of PM emissions occur during the cold-start cycle of the engine. There are many standardized test methods for measuring exhaust emissions, and most studies focus on them.

b. Evaporative emissions - Exhaust gases are not the only type of emissions. VOCs can also be released to the environment because of changes in daily temperatures, leaks, or permeation through elastomeric and plastic components in the fuel tank and distribution system. These emissions can occur via the fuel tank, fuel hoses, cap, or vapour canister. According to the HART Energy study, published in 2007, nearly 50% of VOCs emitted by petrol cars come from evaporation. However, this depends greatly on the vehicle's emission control technology, the age and condition of the vehicle, and the vapour pressure of the petrol. Fuel composition also plays an important role. In particular, ethanol has been shown to significantly increase evaporative emission both form increased RVP and increased permeation. One of the problems with measuring evaporative emissions is that it can take 4-6 weeks of acclimation to the new fuel before evaporative emissions stabilize. Consequently, there are relatively few sound test protocols and reliable studies on evaporative emissions compared to exhaust emissions.

CRITERIA AIR POLLUTANTS

Most regulatory agencies set national ambient air quality standards that define air quality based on the local and regional ambient concentration of several air pollutants.

There are several such frameworks in Africa, including the *"National Framework for Air Quality Management in the Republic of South Africa"*[9], *"Lusaka Agreement (2008) - Southern African Development Community (SADC) Regional Policy Framework on Air Pollution"*[10], *"Eastern Africa Regional Framework Agreement on Air Pollution (Nairobi Agreement-2008)"*[11].

Note that carbon dioxide is not a criteria pollutant because it is not toxic or a precursor to other criteria pollutants (e.g. VOCs are precursors to ozone and PM). It is only a concern because it is a greenhouse gas and, as such, may contribute to increasing global temperatures. But it does not inherently pose a health risk in polluted urban areas.

Volatile Organic Compounds (VOC). While VOCs play a critical role in ground-level ozone formation, they are not themselves criteria pollutants. Regulatory agencies do not set ambient VOC concentrations but instead monitor and set limits on VOCs' main atmospheric by-product, ozone.

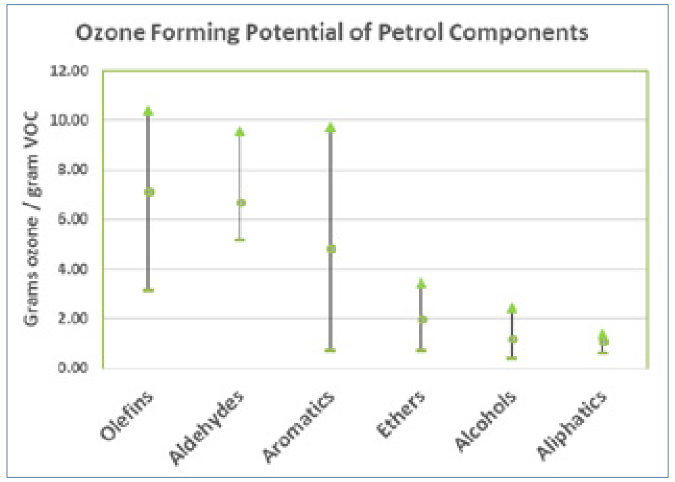
9 https://cer.org.za/wp-content/uploads/2018/10/National-Environmental-Management-Air-Quality-Act-39-2004-the-2017-National-20181026-GGN-41996-01144.pdf https://www.loc.gov/law/help/air-pollution/southafrica.php

10 https://www.york.ac.uk/media/sei/documents/publications/gapforum/Final_circulated_Lusaka_Agreement.pdf

11 https://www.york.ac.uk/media/sei/documents/publications/gapforum/Eastern_Africa_Air_Pollution_Agreement.pdf

The science of ozone formation from VOCs is well understood and the yield of ozone from most petrol components and combustion by-products has been quantified by testing under controlled conditions. The Maximum Incremental Reactivity (MIR) (MIR) scale measures the incremental weight of ozone formed when a gram of VOC is introduced in a test chamber that contains a standard mixture of VOCs, light, and NO_x. The results have been tabulated by William Carter, Professor Emeritus at UC Riverside[12] The figure below illustrates the MIR of common petrol components and combustion by-products.

Figure 5: Ozone Forming Potential of Petrol Components



It is because olefins and aromatics contribute disproportionately to ozone (and PM) formation that their content is often limited in petrol specifications. Aldehydes are common exhaust gases that are not only toxic but produce high levels of ozone as well when they react further in the atmosphere. Ethers, alcohols, and aliphatic hydrocarbons (e.g. alkylate and isoalkanes) produce relatively little ozone, so they are preferred components in reformulated petrol for ozone non-attainment areas.

Ozone. Ground-level ozone is one of the main components of smog and it is formed by reaction of sunlight, volatile organic compounds, and NO_x. Ozone has damaging effect on lungs and has been linked to asthma. The World Health Organization warns that *"excessive ozone in the air can have a marked effect on human health. It can cause breathing problems, trigger asthma, reduce lung function and cause lung diseases."*[13]

Exhaust VOCs are virtually eliminated by well-functioning TWCCs but evaporative VOC emissions are more difficult to control, especially in older vehicles. In modern vehicles, the main way to control VOC emissions and, ultimately, ozone is to improve evaporative emission controls and reduce petrol vapour pressure. The sulphur and metallic content of petrol can also affect the efficacy of the TWCC catalysts in converting exhaust VOCs and

12 https://intra.engr.ucr.edu/~carter/SAPRC/

13 https://www.afro.who.int/health-topics/air-pollution

toxics to CO_2. Therefore, regulatory agencies set strict limits on sulphur content and prohibit the use of lead and other organometallics (e.g. MMT, ferrocene) altogether. This includes the development of the African fuel standards Afri 4,5 and 6 that require a decrease of sulphur in petrol and diesel.

Because alcohols increase petrol vapour pressure and permeation of other petrol components through plastic tanks and elastomeric tubing and gaskets, they also increase VOC emissions, even when RVP is controlled. This has led the Mexican Commission on Energy Regulation (CRE) to prohibit the use of ethanol-blended petrol in major metropolitan areas in their NOM-016 petrol specification and restrict the allowable use of ethanol to 5.8 vol.% in the rest of the country. Mexico also does not grant an RVP waiver to ethanol-blended gasoline as some countries do to reduce air pollution. The Mexican Institute of Petroleum (IMP) has stated that a 1 psi RVP waiver alone would increase VOC emissions from vehicles by 19%. This number is corroborated by other regulatory agencies such as the US EPA.

Particulate Matter (PM10 and PM 2.5). PM10 is composed of particles whose diameter is less than 10 microns, while PM 2.5 contains particles with an average diameter of less than 2.5 microns. The primary component of PM 2.5 is black carbon, which has adverse impact on health. According to WHO, it can cause asthma, respiratory problems, low birth weights, heart attacks, lung cancer and premature death[14].

PM forms by the reaction of secondary organic aerosols (SOAs) with NO_x and SO_x in the atmosphere. SOAs are produced when reactive petrol components such as aromatics and olefins do not combust completely in the engine. This occurs mostly in the cold-start phase of the engine cycle and is exacerbated by the presence of alcohols, which have a charge-cooling effect and a lower heat of combustion compared to ethers or other hydrocarbons. PM can also form when reactive VOCs evaporate from the vehicle and react in the atmosphere.

The science of PM formation is not as developed as that of ozone formation, but studies sponsored by the US EPA and conducted by the Coordinating Research Council[15] and Toyota Motor Corp[16] show that petrol components with unsaturation (primarily aromatics and olefins) contribute disproportionately to PM formation and that the use of ethanol can also be detrimental, because it prevents their complete volatilization and combustion.[17]

14 WHO: https://www.who.int/news-room/fact-sheets/detail/ambient-(outdoor)-air-quality-and-health

15 EPAct/V2/E-89 Assessing the Effect of Five Gasoline Properties on Exhaust Emissions from Light-Duty Vehicles Certified to Tier 2 Standards

16 Ben Amara, A., Tahtouh, T., Ubrich, E., Starck, L. et al., "Critical Analysis of PM Index and Other Fuel Indices: Impact of Gasoline Fuel Volatility and Chemical Composition," SAE Technical Paper 2018-01-1741, 2018, doi:10.4271/2018-01-1741.

17 Butler, A., Sobotowski, R., Hoffman, G., and Machiele, P., "Influence of Fuel PM Index and Ethanol Content on Particulate Emissions from Light-Duty Gasoline Vehicles," SAE Technical Paper 2015-01-1072, 2015, doi:10.4271/2015-01-1072.

Carbon Monoxide (CO). CO is emitted when carbon in fuel is not completely oxidized. CO is toxic to humans and animals, and in very high dosages can be fatal. Around 18% of all CO emissions in Europe come from transport[18].The advent of the ECM or ECU (electronic control unit) as it is also known, to control fuel/air ratio has significantly reduced ambient CO concentrations to the point where CO levels are well below harmful levels, even in polluted urban areas. Well-functioning TWCCs also help in reducing CO by converting it to CO_2.

Nitrogen Oxides (NO_x) is a term used to describe different pollutants (NO_2 and NO), which contain nitrogen and oxygen. NO_x is formed in the combustion process. NO is an ozone precursor, while NO_2 can cause respiratory problems and is a precursor to particulate matter. Most polluted urban areas are NO_x-limited, which means that an increase in NO_x does not result in an increase in ozone. Therefore, most regulatory measures to reduce ozone formation focus on reducing VOC emissions instead of NO_x. The NO_x level is nonetheless monitored and controlled to minimize its direct impact on public health and indirect impact on PM formation. Reducing the fuel sulfur content and avoiding the use of organometallics are also important in controlling NO_x, since they poison the catalysts in TWCCs. Well-functioning TWCCs convert NO_x back to harmless nitrogen gas.

Sulphur Dioxide (SO_2). Sulphur Dioxide comes primarily from combustion of fuels containing sulphur. Emissions of SO_2 cause cardiovascular and respiratory illnesses. SO_x also reacts with water in the atmosphere to produce sulfuric acid (acid rain).

Lead. While tetraethyl lead (TEL) has been banned in most of the world. It is still used in a handful of remaining countries and in aviation gasoline for piston aircraft (AVGAS). Lead exposure leads to neurological impairments: seizures, mental delays and behavioural disorders. Lead is particularly toxic to infants and children.

Toxics. The so called Toxic Organic Pollutants include a list of pollutants which cause or may cause cancer or other serious health effects, such as reproductive effects or birth defects, or adverse environmental and ecological effects. The US EPA[19] identifies 187 hazardous air pollutants, out of which 30 are identified by the US as posing a threat in urban areas. This includes such substances as benzene, some aromatic hydrocarbons (toluene, ethylbenzene, and xylenes), aldehydes (esp. formaldehyde and acetaldehyde), and 1,3-butadiene.

Changes in petrol properties and composition can help in reducing vehicle emissions. The air quality implications need to be considered by the refiner in the cost-benefit analysis of which octane enhancer to use.

18 https://www.eea.europa.eu/data-and-maps/indicators/transport-emissions-of-air-pollutants-8/transport-emissions-of-air-pollutants-6

19 EPA https://www.epa.gov/urban-air-toxics/urban-air-toxic-pollutants

ETHANOL AND AIR QUALITY

There are many studies[20] available regarding the impact of ethanol on air quality. While blending pure ethanol has an impact on the reduction of some of the air pollutants such as CO, it also increases pollution of others. According to a 2017 study published by Alberto Salvo, an economist at the National University of Singapore, and Franz Geiger, a physical chemist at North-western University in Evanston, Illinois, the introduction of E20 in Brazil has led to an increase in ozone emissions in Sao Paolo.[21] A study developed by Robert K. Niven from the School of Aerospace, Civil and Mechanical Engineering, University of New South Wales in Australia suggests that if compared to zero ethanol in petrol, around 10% of ethanol by volume in petrol has the following effect on air quality:

- Generally, ethanol produces lower tailpipe emissions of total HCs and CO than petrol which does not contain ethanol.
- Causes a significant to substantial increase in emissions of toxics such as acetaldehyde (ethanal), and an increase of formaldehyde.
- Reduces emissions of 1,3-butadiene, benzene, toluene and xylene emissions and PM emissions when compared to petrol with no ethanol.
- Causes an increase in NO_x emissions, though here results are mixed.

20 https://www.researchgate.net/publication/222381005_Ethanol_in_gasoline_Environmental_impacts_and_sustainability_review_article

21 Ethanol-Blended Gasoline Policy and Ozone Pollution in Sao Paulo, 2017, https://papers.ssrn.com/sol3/papers.cfm?abstract_id=3190811

The US Environmental Protection Agency (EPA) suggests what while some studies suggest a reduction in exhaust CO, 1,3-butadiene and benzene, others do not. Inconsistencies across studies can result from differences in vehicle emission control technologies, fuel composition, test cycle, and age of vehicles.[22] The EPA outlines a reduction in emissions of benzene and 1,3-butadiene, increases in formaldehyde, and very large increases in acetaldehyde for E85.

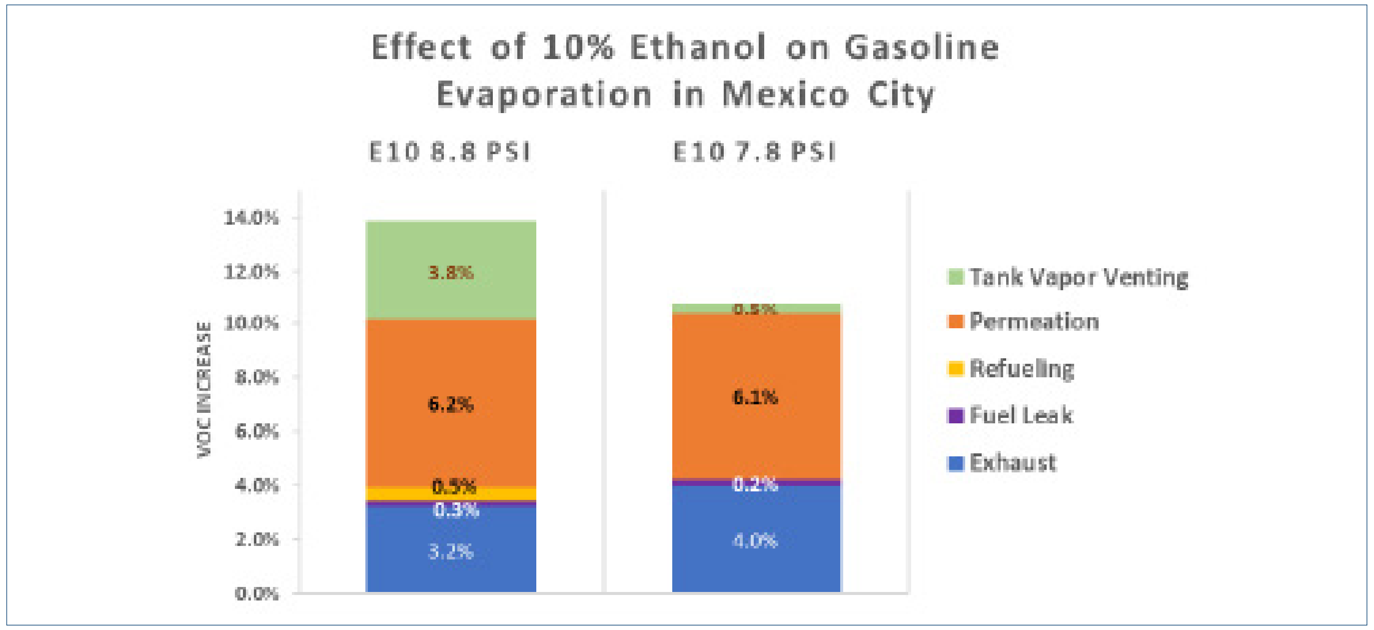
The EPA's study also directs attention to the so-called upstream emissions related to production and distribution of ethanol. They key pollutants come from the energy needed to sustain production operations. This includes emissions of PM, CO, NO_x, SO_x and VOC. As ethanol cannot be transported by a pipeline, there are also emissions related to the distribution of this fuel. At the same time however, EPA notes that usage of ethanol at the refinery can result in reduced emissions at this level.

While the addition of ethanol to petrol may reduce exhaust emissions of CO and VOCs, it significantly increases evaporative emissions of VOCs though a combination of permeation, tank vapour venting and refuelling. The magnitude of these increases varies with gasoline RVP and the vehicle's emission control technology. However, even in vehicles equipped with EURO IV control technology, evaporative VOC emissions exceed exhaust emissions as illustrated in Figure 6.[23] This can lead to significant increases in ozone and PM pollution especially in polluted urban environments. This is exacerbated in countries where E10 is granted an RVP waiver which results in increased tank vapor venting.

22 U. S. Environmental Protection Agency, AIR QUALITY IMPACTS OF INCREASED USE OF ETHANOL UNDER THE UNITED STATES' ENERGY INDEPENDENCE AND SECURITY ACT

23 Koupal, John; Palacios, Cynthia. Atmospheric Environment, Volume 201, p. 41-49

Figure 6. Effect of 10% ethanol on exhaust and evaporative emissions from vehicles equipped with EURO IV emission control technologies (baseline is same fuel with 10% MTBE).



METHANOL AND AIR QUALITY

A study conducted in 2012 by the US Environmental Protection Agency, examined pollution from vehicles fuelled with methanol or methanol-gasoline blend. The results suggest that blended fuel does not generally show any significant changes relative to base-line emission rates of pollutants. The Federal Test Procedure showed an increase in emissions of formaldehyde.[24] However, the representations of the methanol industry suggest that methanol provides a decrease in NO_x and VOC[25] emissions. Methanol as a fuel is mostly used in China. Studies conducted by Chinese researchers suggest that total emissions of VOCs and BTEX (benzene, toluene, ethylbenzene, p, m, o-xylene) from all vehicles fuelled with methanol/petrol blends were lower than those from vehicles fuelled with only petrol[26].

A 2013 study published in the journal Fuel, compared the exhaust and evaporative emissions from base gasoline (M0) and the same gasoline splash-blended with 15% methanol (M15). 26 The test results showed that compared with M0, exhaust THC and CO emissions from a EURO IV passenger car fuelled with M15 decreased by 16% and 7% while the NOX increased by 85%. The formaldehyde emitted from M15 fuelling passenger car was almost twice that from M0.

For the evaporative emissions, diurnal losses were far greater than hot losses and were the main contributor to the evaporative emissions. Evaporative VOC emissions from M15 increased by 63%. Criteria pollutants such as carbonyls and VOCs increased by 19% and 23%. Moreover, methanol emissions from M15-fueling car were 128 times higher than that from gasoline.

It is important to note that the relatively new vehicle (17K miles) was not acclimated to the M15 fuel for any significant amount of time so the study likely underestimated the potential impact of methanol on permeation, evaporative emissions, especially in older vehicles with EURO IV or older emission control technologies.

It is also worth noting that the global car manufacturing industry, in the latest Worldwide Fuel Charter[27], is calling to ban pure methanol as a fuel for cars. *"Methanol is not allowed, due its nature of being an aggressive material that can cause corrosion of metallic components of fuel systems and the degradation of plastics and elastomers."*[28]

FUEL ETHER'S EFFECT ON AIR QUALITY

By raising the oxygen content of petrol, fuel ethers enable a more complete combustion of fuel, resulting in improved vehicle performance and fuel efficiency, lower exhaust emissions and improved air quality. With fuel ethers, more petrol is burned inside the engine rather than expelled through the exhaust system into the atmosphere, allowing for cleaner-running engines. In addition, ethers do not increase RVP or permeation of VOCs like alcohols do so evaporative emissions also decrease.

Several emissions models have been developed based on the results of numerous laboratory and on-road studies. The US EPA first developed the COMPLEX model in 1990 which is still used by refiners to demonstrate a fuel's compliance with the Clean Air Act. However, COMPLEX does not differentiate between oxygenates and does not account for permeation effects or particulate formation. Based on additional studies on evaporative emissions and particulate formation COMPLEX was supplanted by PREDICTIVE and, ultimately by the MOVES 2014A model.

MOVES Mexico is an updated version of the US Environment Protection Agency's MOVES2014a model that estimates the effect of fuel composition on vehicle pollutants.
Unlike previous models, it accurately estimates evaporative emissions of VOCs and exhaust PM emissions based on different vehicle emission control technologies and fuel compositions. MOVES Mexico also differentiates between alcohols and ether oxygenates which most models, including MOVES 2014a and its predecessors (COMPLEX and PREDICTIVE) cannot do.

Nonetheless, the COMPLEX model is easy to use and does provide information on the impact of changes in fuel formulation on exhaust and evaporative emissions. For example, Colombia produces two base unoxygenated gasolines for ethanol blending, regular and premium. The base gasolines have octane numbers (AKI) of 81.5 and 87 and are finished with 10% ethanol at the terminals to produce oxygenated gasolines with octane numbers of 84 and 89 AKI and the properties listed in Table 5.

These properties are the variables used by COMPLEX to estimate the emissions of VOCs, NOx, and air toxics produced by these fuels and to compare them to a reference fuel. This model can also be used to compare fuels with different components or components levels so it is very useful in comparing fuels with different compositions and oxygenates.

24 Peter A. Gabele, James O. Baugh, Frank Black, and Richard Snow, Journal of the Air Pollution Control Association 35:1168-1175 (1985)

25 https://methanolfuels.org/about-methanol/environment/

26 Peipei Dai, Yunshan Ge, Yongming Lin, Sheng Su, Bin Liang, Fuel, 113, 2013, 10-16

27 https://www.acea.be/publications/article/position-paper-methanol-as-a-gasoline-blending-component

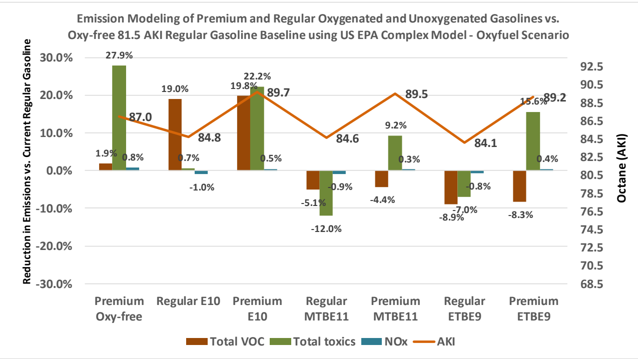
28 See footnote 27

Table 5: Composition of Colombian Gasolines and Input Properties for COMPLEX Model Emissions Modeling.

	Regular Oxy-free	Premium Oxy-free	Regular E10	Premium E10
MTBE (wt% oxygen)	0.0	0.0	0.0	0.0
ETBE (wt% oxygen)	0.0	0.0	0.0	0.0
Ethanol (wt% oxygen)	0.0	0.0	3.5	3.5
OXYGEN (wt%)	0.0	0.0	3.5	3.5
SULFUR (ppm)	100.0	100.0	89.9	89.9
Octane (AKI)	81.5	87.0	84.8	89.7
RVP (psi)	8.0	8.0	9.3	9.3
E200 (%)	41.0	41.0	51.1	51.1
E300 (%)	83	83	93	93
AROMATICS (vol%)	28	35	22	28
OLEFINS (vol%)	0.0	0.0	0.0	0.0
BENZENE (vol%)	1.0	2.0	0.8	1.6

Emissions from these gasolines were compared to a US reference fuel and the results normalized to the Regular Oxy-free gasoline which is the emissions baseline in the following graph. Blends where the ethanol was replaced with 11% MTBE or 9% ETBE were also evaluated and are included in the graph.

	Premium Oxy-free	Regular E10	Premium E10	Regular MTBE11	Premium MTBE11	Regular ETBE9	Premium ETBE9
Total VOC	1.9%	19.0%	19.8%	-5.1%	-4.4%	-8.9%	-8.3%
Total toxics	27.9%	0.7%	22.2%	-12.0%	9.2%	-7.0%	15.6%
NOx	0.8%	-1.0%	0.5%	-0.9%	0.3%	-0.8%	0.4%
AKI	87.0	84.8	89.7	84.6	89.5	84.1	89.2



The results show that adding Oxyfuels (MTBE or ETBE) to the base gasolines results in significant reduction in emissions. Replacing ethanol results in even greater reductions, mainly because E10 fuels are granted a 1.3 psi RVP waiver which is not required for Oxyfuel blended gasolines.

MTBE reduces emissions of:

- VOCs by 5-6% vs. base gasolines and 24-25% vs. E10 gasolines
- Toxics by 12-17% vs. base gasolines and 13% vs. E10 gasolines
- NO_x emissions were relatively unaffected by formulation changes

ETBE reduces emissions of:

- VOCs by 9-10% vs. base gasolines and 28% vs. E10 gasolines
- Toxics by 7-12% vs. base gasolines and 7-8% vs. E10 gasolines
- NO_x emissions were relatively unaffected by formulation changes

A similar computer-based study, conducted with the COPERT4 model provides another estimation of how fuel-ethers perform in comparison to other fuel components, such as ethanol. The simulation, which was developed with support and inputs from the EU, compares gasoline evaporative emissions, defined as all the VOCs emitted by the vehicle itself and not deriving from fuel combustion.

Five different scenarios have been developed assuming the following different gasoline compositions

- Basecase (B1): pure hydrocarbon gasoline in compliance with EN228, i.e. no oxygenates;
- Ethanol 1 (E1): finished gasoline (in compliance with EN228) containing 5 % v/v of ethanol (Smart Blending[29]);
- Ethanol 2 (E2): finished gasoline with 5 % v/v of ethanol according to the alcohol RVP waiver (case comparable to Splash Blending[30]);
- ETBE 1 (ETBE1): finished gasoline in compliance with EN228 with 11 % v/v (E5 equivalent) of ETBE (Smart Blending);
- ETBE 2 (ETBE2): finished gasoline with 11 % v/v (E5 equivalent) of ETBE (Splash Blending);

The key element for the above scenarios is the vapour pressure of the summer grade gasoline that has been fixed in line with to Fuel Quality Directive (Directive 98/70/EC as amended by Directive 2009/30/EC).

For the COPERT simulations these other aspects have been considered: five years intervals from 2015 to 2030; EU-27 Member States (no information available from Croatia); the entire vehicle fleet (from pre-Euro to Euro 6); only the Euro 6 cars (and later) since in 2030 it should be the dominant technology.

The simulations results show that:

1. For the base case, the total evaporative emissions decrease by about 20% from 2015 to 2030 when all petrol cars are considered, due to the fleet renewal, while, on the opposite, the evaporative losses increase a lot in the Euro-6 case due to the combined effect of population growth and degradation;
2. The use of ethanol significantly worsens air quality with a strong increase of the total emissions with respect to the base case for both smart blending E1 (up to 40%) and waiver case E2 (up to 60%);
3. The use of ETBE, both in smart and splash blending, allows to slightly decrease the total emissions (up to 5%) compared to the base case.

As general conclusion of COPERT simulations, ETBE represents the best bio-component to blend in gasoline in terms of total volatile emissions savings for both the entire vehicle fleet and Euro-6 cars.

29 Smart Blending: Blendstock for Oxygenate Blending (BOB) plus oxygenated compound

30 Splash Blending: finished gasoline in compliance with EN228 plus oxygenated compound

In the case of the entire car fleet, blending ETBE instead of ethanol would reduce total VOC emissions by 50,000 to 80,000 tonnes/year (24 to 38%).

Furthermore, these simulations highlight how the use of ETBE as gasoline blending bio-component (in case of smart blending) would reduce the evaporative emissions of 24% in 2015 and 26% in 2020 with respect to the ethanol addition (same energy content).

In summary, the results of several models all show the same trends; that blending oxyfuels with gasoline reduces pollution significantly whereas blending ethanol increase air pollution in most cases.

Direct and indirect effect of adding fuel ethers to petrol

	How?	How much?
Direct effect	Oxygen allows more complete fuel combustion.	• Fuel ethers reduce CO emissions by same % as their content in gasoline • Each 1 or 2% of fuel ether typically leads to a 1% reduction in total hydrocarbon emissions.
Indirect effect	High octane and other properties allow to dilute other, less desirable, components in the gasoline pool.	• Fuel ethers have significantly lower ozone forming potential compared to conventional gasoline blending components (e.g. aromatics, naphtha).

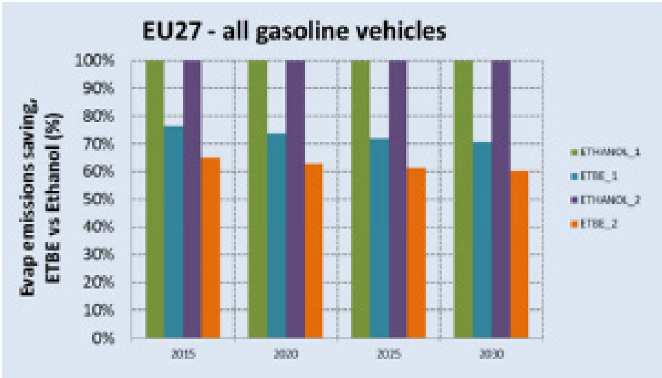


Figure 7: EU 27- all gasoline vehicles.
Evaporative emissions saving, ETBE vs ethanol.

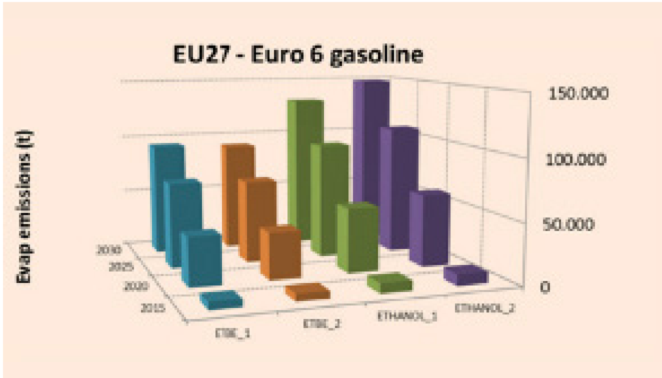


Figure 9: EU 27 - Euro 6 gasoline, evaporative emissions of ETBE and ethanol

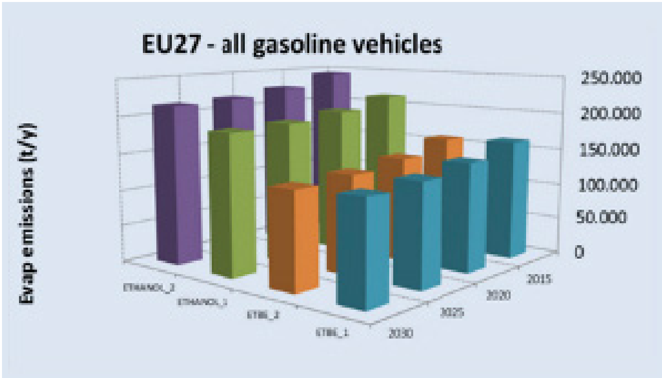


Figure 8: EU 27 - all gasoline vehicles,
Evaporative emissions of ethanol and ETBE

PARTICULATE EMISSIONS

As noted in Better Fuel for Cleaner Air, "Emissions of particulate matter (PM) are of increasing concern amongst health researchers, with linkages between adverse health effects and particulate exposure being demonstrated at increasingly lower levels of particulates in the atmosphere."

A 2011 study from the California Air Resources Board (CARB) evaluated the possible type of oxygenate effect on PM emissions in four vehicles as illustrated in Chart 1. As shown in Chart 1, the CARB Phase 2 Cert fuel made with 11%v/v MTBE produced significantly lower PM mass emission than the matched clean fuel made with 6%v/v ethanol which both provides 2.1 wt.% oxygen in gasoline. The other key fuel properties such as aromatic content and T90 were held relatively constant. The average PM emissions with the MTBE blend was about 50+ % lower than the matched ethanol blend.[31]

Furthermore, a PM emissions study, published in the International Journal of Automotive Technology, was conducted with increasing amounts of MTBE blending in the fuels using two GDI vehicles (EURO 5 emission equivalent vehicles). The average PM emissions results are shown in the following Chart 2. The MTBE blends appear to generate significantly less PM emission compared to the oxy-free base fuel. Much of the reduction can be explained by the cleaner base fuel that was possible to use thanks to MTBE high-octane properties which enabled a significantly lower aromatic content and a T90 temperature when compared to the base fuel.[32]

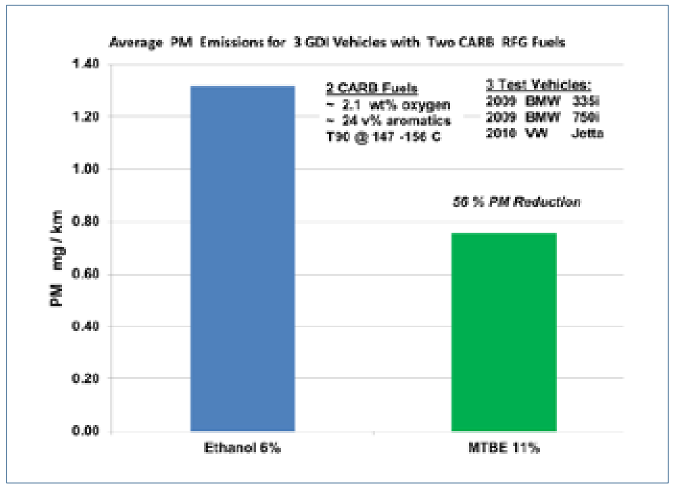


Figure 10: Average PM emissions for 3 GDI vehicles with two CARB RFG Fuels

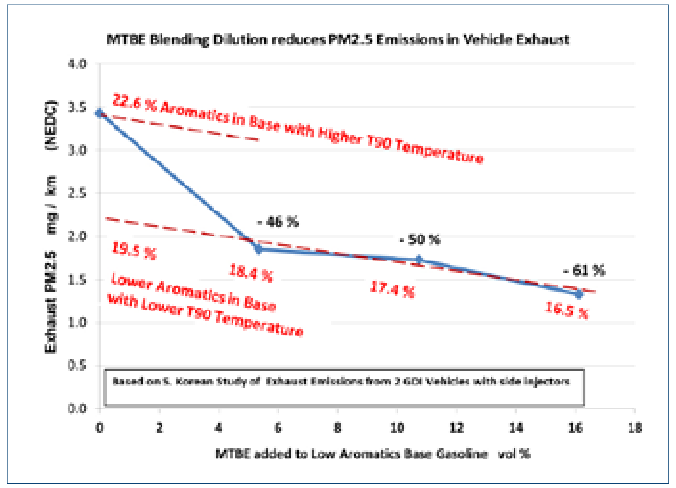


Figure 11: MTBE blending dilution reduces PM 2.5 in vehicle exhaust

31 "Review of Fuel Effects on PM Emissions," p 88, appendix p, lev iii pm, Technical Support Document Development of Particulate Matter Mass Standards for Future Light-Duty Vehicles, Staff of California Air Resources Board, December 7, 2011

32 "Influence of Oxygenate Content on Particulate Matter Emission in Gasoline Direct Injection Engine," Oh, C. and Cha, .G, International Journal of Automotive Technology, V.14,No,6 pp. 829-836 (2013)

GREENHOUSE GAS REDUCTION POTENTIAL OF OXYGENATES

GHG EMISSIONS REDUCTION POTENTIAL OF OXYGENATES

The GHG impact of any biofuel is a trade-off between the CO_2 reduction achieved by using biofuels and the GHGs that are generated in the production process, transportation, and any changes resulting from the reformulation of the finished petrol.

The latter is often overlooked in lifecycle analyses (LCAs) but can have a significant impact on the actual GHG reduction benefit of biofuel use. For example, the use of ethanol requires reformulation of the base petrol blend which impacts the well to wheels CO_2 impact of the fuel. Also, the energy content of the fuel must be accounted for since modern engines adjust the fuel to air ratio to be stoichiometric. In other words, while oxygenate use in older vehicles could result in higher fuel efficiency by improving combustion, the energy density of the final fuel is more directly correlated to fuel efficiency in modern vehicles.

In addition, ethanol blending with petrol requires a separate storage, transport, and blending infrastructure than oxyfuels due to its hygroscopicity and potential to phase separate in the presence of water. The energy and GHG impacts of this separate supply chain must be accounted for in any LCA analysis in order to derive meaningful results.

It is also important to note that significant GHG reductions from petrol use can be achieved simply by replacing energy-intensive components such as reformate with less energy-intensive components such a MTBE and naphtha.

Other considerations need to be taken into account to properly evaluate the contribution of GHG emission reduction, including whether the feedstock is first generation or advanced. The typical and default values for biofuels if produced with no net carbon emissions from land-use change are listed in Annex V of the Renewable Energy Directive agreed by the EU in 2018.

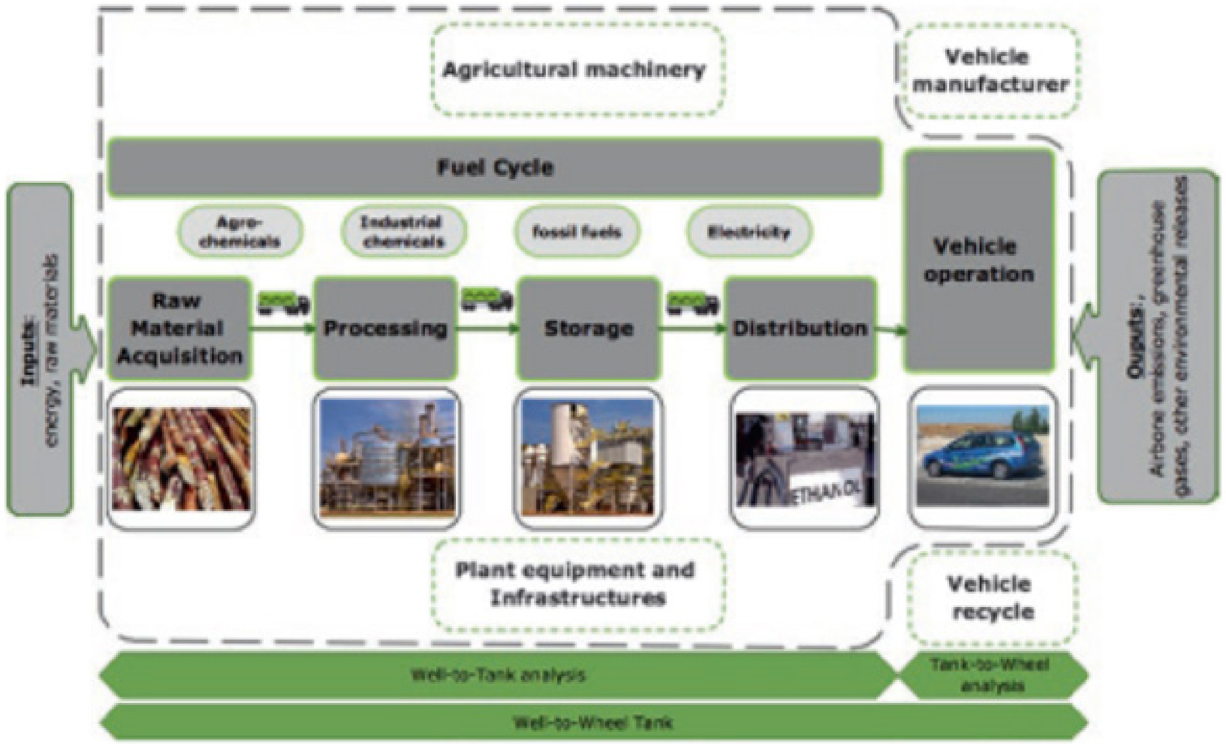


Figure 12. https://www.researchgate.net/publication/326382547_The_Effect_of_Biofuel_Production_on_Greenhouse_Gas_Emission_Reductions_Holistic_Perspectives_for_Policy-making/figures

GHG EMISSIONS AND ETHANOL

According to the study conducted by the Argonne National Laboratory[33], the life cycle of corn-based ethanol instead of petrol would reduce GHG emissions by 34%, while cellulosic ethanol could reduce it between 51% - 88%. The calculations take into consideration land-use change emissions (LUC).

33 Michael Wang, Jeongwoo Han, Jennifer B Dunn, Hao Cai and Amgad Elgowainy. *Well-to-wheels energy use and greenhouse gas emissions of ethanol from corn, sugarcane and cellulosic biomass for US use* https://iopscience.iop.org/article/10.1088/1748-9326/7/4/045905/pdf

WTW GHG emission reductions	Corn	Sugarcane	Corn stover	Switchgrass	Miscanthus
Including LUC emissions	19–48% (34%)	40–62% (51%)	90–103% (96%)	77–97% (88%)	101–115% (108%)
Excluding LUC emissions	29–57% (44%)	66–71% (68%)	89–102% (94%)	79–98% (89%)	88–102% (95%)

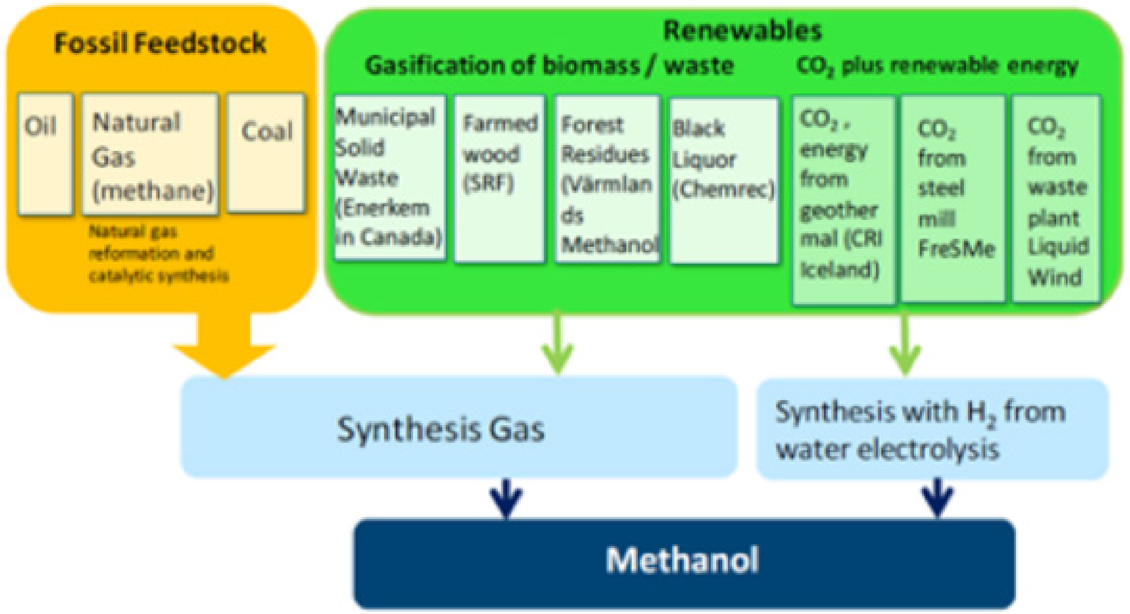
Table 5: WTW GHG emission reductions for five ethanol pathways (relative to WTW GHG emissions for petroleum petrol), Source: Well-to-wheels energy use and greenhouse gas emissions of ethanol from corn, sugarcane and cellulosic biomass for US use.

However, these reductions are for the pure fuels, not the blends most commonly sold, namely E10 or E6. For E10 based on corn ethanol, the maximum GHG reduction vs. gasoline is 3.4%, but this savings is further eroded by a number of petrol production and supply chain impacts that, in some cases, reduces the GHG savings of E10 to zero versus conventional gasoline.

GHG EMISSIONS AND METHANOL

As methanol can be produced from different feedstocks, its impact on GHG emission reduction will also vary. The default values for the production of renewable methanol are defined in Annex V of the EU Renewable Energy Directive (2018).

Figure 13: Overview and examples of feedstocks used to produce methanol[34]



34 SUMMETH – Sustainable Marine Methanol Deliverable D5.1 Expected benefits, strategies, and implementation of methanol as a marine fuel for the smaller vessel fleet

FUEL ETHERS AND GHG EMISSIONS REDUCTION

The bio-ethers ETBE and TAEE have been shown to offer GHG additional savings compared to the bio-ethanol used in their manufacture. Indeed, the energy saved thanks to fuel ethers' high-octane level and reduced volatility offsets the extra processing step required to convert bio-ethanol into bio-ether.
Studies carried out by Hart Energy Consulting and CE Delft (1,2), using their own in-house modelling systems showed that ETBE offered an additional CO_2 benefit over direct ethanol blending. The studies support the following conclusions:

Blending ethers into petrol is more energy efficient (and therefore reduces CO_2 emissions) than blending ethanol into petrol. Pure ethanol blending requires a base petrol that has a lower RVP compared to a base petrol in which ETBE is blended. Producing a lower RVP base petrol increases energy consumption in a refinery because the base petrol requires more processing in order to compensate for the higher RVP of the ethanol.

Ethanol in the form of ETBE allows for more efficient transport from the source to the pump compared to ethanol, which reduces CO_2 emissions.

ETBE decreases crude oil and reduces refinery energy consumption for crude oil processing and octane production, thus reducing CO_2 emissions.

ETBE typically offers an additional saving of 24kg of CO_2-equivalent/GJ of ethanol.

While the CO_2 reduction is small compared to the total refinery footprint, it is significant when considering the greenhouse savings obtained by using ETBE instead of ethanol.

Another way oxyfuels reduce the GHG impact of petrol is by replacing high-energy components such as reformate with lower-energy components such as naphtha and oxyfuels. Even non-bio MTBE contributes to significant reductions in CO_2 yield from petrol as is illustrated in Figure 14.

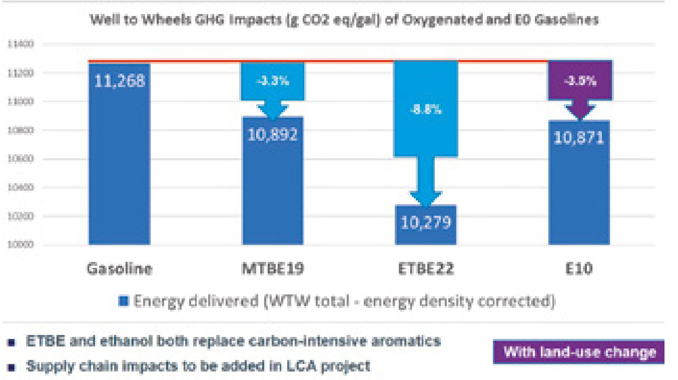


Figure 14. Wells to Wheel GHG impacts of various petrol blends using bio-ethanol (incl. land use change) and oxyfuels at the same oxygen level.

It is noteworthy that MTBE and ETBE both deliver greater CO_2 reduction benefits than ethanol at the same oxygen level (2.7 wt.%). This is without adding the higher energy supply chain impacts of transporting ethanol separately to the terminals for blending.

Hart Energy Consulting has also completed a follow-up study on TAEE, which shows that this is a general benefit for bio-ethers.

REGULATIONS AND SPECIFICATIONS

Oxygenates have been used to improve engine performance for over 30 years. However, usage of oxygenates in petrol goes back to the 1920s when the search for an additive began. Ethanol started to be blended in petrol as early as 1930s. MTBE was first added to petrol in Italy in 1973. By 1979, MTBE became popular to extend petrol production in the United States and elsewhere (Arab oil embargo) and to replace lead.

In 1990s the US Clean Air Act amendments required usage of oxygenates in reformulated petrol. The 1992 winter oxygenates programme required 2.7% oxygen by weight (i.e. 15% of MTBE), and the 1995 Reformulated Gasoline Phase I required 2% of oxygen by weight in 28 metropolitan areas. Petrol producers chose MTBE over ethanol to meet the oxygen demand because of its low cost and superior blending properties.

In 2005, the US Congress passed the renewable fuel standard (RFS) that mandated the use of 10% ethanol in gasoline. This led to the phaseout of MTBE use in the US. The RFS remains unpopular with refiners and environmentalists due to its detrimental impact on petrol cost and air and water pollution.

In Europe, the Fuel Quality Directive (98/70/EC) established a minimum allowance for fuel ethers at a level of 15% by volume. At the same time, the ongoing debate and new mandates for biofuels in petrol, set targets of 2% in 2005, 5,75% in 2010, 10% (cap on first gen of biofuels) in 2020 and 14% of renewable share in transport in 2030 (cap on first generation of biofuels and mandate for advanced biofuels included). These targets, supported by national mandates and subsidies, stimulated the development of bio-ethers, and the growth of ETBE in Europe since the early 2000s.

In Asia, MTBE began to be widely produced and consumed in the 1990s in Saudi Arabia, South Korea, and China and is commonly imported in Taiwan, Thailand, and Indonesia. Japan chose ETBE over ethanol in 2009 to meet its renewable fuel targets because of the lower cost of implementation and superior air quality impacts.[35]

35 https://www.fuelethers.eu/assets/uploads/2018/10/2011-03-23_Overview_of_the_Asian_fuel_ethers_market_and_opportunities_for_Europe.pdf

GLOBAL MANDATES & LIMITATIONS

EUROPE

The European Union is a global leader in setting standards aimed at reduction of pollution from fuels. The legislation put forward in the past 30 year has dramatically improved European petrol and removed from the market the most toxic components such as lead.

Environmental fuel specifications are considered by the European Commission to be an important element of cost-effective measures to reduce air pollution and protect human health. Prior to this, there were no common legally binding fuel quality requirements for environmental protection for transport fuels in the EU. In particular, high levels of lead and sulphur emitted from fuels were raising environmental and health concerns among the European Community. The first fuel specifications included a ban on lead and limits on benzene and aromatics in petrol. The legislation was amended in 2003 to include additional environmental specifications such as reduction in sulphur. High sulphur fuels have now been completely replaced by low sulphur ones as per table below, as of 1 January 2009. The last amendment of the Fuel Quality Directive (FQD) took place in 2009 and focused on reduction of the GHG emissions from fuels use and introduction of the target for GHG intensity of fuels. The Directive also further limited the use of aromatics in petrol to help improve air quality in Europe and introduced a limitation on the use of the organometallic additive MMT to 6 mg per liter starting in 2011 to 2 mg per liter from 2014 on. In 2011 a derogation (waiver) for vapor pressure for the blending of ethanol in petrol has been introduced. In 2015, the Directive was further amended to add biofuel provisions.

Fuel Quality Directive guards the technical specifications of fuels in Europe

The Fuel Quality Directive sets technical specifications for fuels to be used with positive ignition and compression-ignition engines as well as establishes a target for reduction of life cycle greenhouse gas emissions[36].

The Directive compels Member States to ensure that petrol available at their markets is compliant with technical specifications set out in Annex I of the Directive.

36 https://eur-lex.europa.eu/legal-content/EN/TXT/?qid=1531839131701&uri=CELEX:01998L0070-20151005

Table 6: Environmental specifications for market fuels to be used for vehicles equipped with positive-ignition engines (Annex I of the Fuel Quality Directive)

Parameter (1)	Limits (2)	
	Minimum	Maximum
Research octane number (RON)	95 (3)	—
Motor octane number (MON)	85	—
Vapour pressure, summer period (4)	—	60,0 (5) kPa
Distillation:		
— percentage evaporated at 100 °C	46,0 % v/v	—
— percentage evaporated at 150 °C	75,0 % v/v	—
Hydrocarbon analysis:		
— olefins	—	18,0 % v/v
— aromatics	—	35,0 % v/v
— benzene	—	1,0 % v/v
Oxygen content		3,7 % m/m
Oxygenates		
— Methanol		3,0 % v/v
— Ethanol (stabilising agents may be necessary)		10,0 % v/v
— Iso-propyl alcohol	—	12,0 % v/v
— Tert-butyl alcohol	—	15,0 % v/v
— Iso-butyl alcohol	—	15,0 % v/v
— Ethers containing five or more carbon atoms per molecule	—	22,0 % v/v
— Other oxygenates (6)	—	15,0 % v/v
Sulphur content	—	10,0 mg/kg
Lead content	—	0,005 g/l

Annex I of FQD specifies fuel properties as the minimum Research Octane Number, the maximum limitation on of the vapour pressure and the maximum olefinic and aromatic contents. The Directive also specifies the maximum oxygen content at 3,7% m/m. At the time, it sets the maximum level of methanol (3% v/v), ethanol (10% v/v) and fuel ethers (22% v/v).

The Fuel Quality Directive also compels fuel suppliers to reduce the greenhouse gas intensity of the fuel mix they supply by 6% in 2020 compared to 2010.

Article 9 of the Fuel Quality Directive 98/70/EC relating to the quality of petrol and fuels, Member States include an obligationto report on the quality of fuels sold in their markets. Hence, there is a wide variety of information about the fuel quality available in the public domain, with reports going back in time to 2001. The information included in these reports covers a variety of specific issues, including the feasibility of increasing the maximum permitted biofuel content of petrol, the use of metallic additives other than MMT in fuels, cost-benefit and impact analysis of a reduction in the maximum permitted vapour pressure for petrol for the summer period below 60 kPa among others[37].

The Commission's 2009 amendment of the Fuel Quality Directive introduced a possibility to waive the vapour pressure during the summer period (Article 3(4) and (5)). The Directive allows two types of derogations: a bioethanol waiver which increase the maximum vapour pressure of petrol blended with bioethanol and low ambient summer temperatures. As petrol contains volatile organic components including benzene, they can evaporate from liquid petrol at ambient temperature. VOCs have a particularly negative effect on air pollution as they contribute to formation of ground level polluting ozone. The vapour pressure of a liquid VOC is a measure of how easy liquid evaporate. A fuel ability to vaporize is referred as volatility and more volatile components evaporate at lower temperatures and less volatile at higher. For instance, a 2%v/v to 10%v/v blend of ethanol can increase the vapour pressure to 72.4-75.8 kPa. This is key as the higher vapour pressure the higher emissions of hydrocarbons which can be observed when petrol is stored or fuelled into the car's tank and when the car is on the move[38].

Member States of the EU have implemented different monitoring system for fuel quality. They range from simple sampling from a range of retail fuel stations through analysis at refinery level to random sampling across the distribution chain[39].

CEN Standardization and Fuel Quality

The European Committee for Standardization (CEN) is responsible for developing and defining voluntary standards at European level and has been recognized by the European Union and the European Free Trade Association (EFTA) for its role. CEN developed voluntary industry standards EN228 for unleaded petrol. They include further specifications in addition to these introduced by the Fuel Quality Directive.

37 https://eur-lex.europa.eu/legal-content/EN/TXT/?qid=1531839131701&uri=CELEX:01998L0070-20151005

38 European Commission, Guidance note on notifications of exemptions from the vapour pressure requirements for petrol pursuant to Article 3(4) and (5) of Directive 98/70/EC relating to the quality of petrol and diesel fuels https://ec.europa.eu/clima/sites/clima/files/transport/fuel/docs/guidance_note_vapour_pressure_en.pdf

39 COM/2006/0186 - Report from the Commission - Quality of petrol and diesel fuel used for road transport in the European Union - Third annual report (Reporting year 2004)

AMERICAS

The United States of America

The use of oxygenates in petrol was approved by the EPA in 1982 up to 11% volume and up to 15% volume in 1988.

The US winter oxygenates gasoline programme was introduced in early 1990s in order to reduce exhaust emissions of Carbon Monoxide (CO). This set a requirement of 2.7% v/v (or 15% of MTBE/ 7.4% v/v of ethanol) of oxygen. The 1994 reformulated gasoline (RFG) program was designed to reduce the emissions of VOCs, Toxics and NO_x. The programme set a min, 2.1% oxygen (11.7 % v/v or 5.8% v/v of ethanol). The major of petrol producers chose to blend MTBE rather than ethanol because of its superior blending properties and compatibility with the existing gasoline distribution system. MTBE production also allowed refiners to utilize mixed butenes and incorporate more of this abundant and inexpensive chemical into gasoline as MTBE.

The Energy Policy Act of 2005 passed by the US Congress removed the oxygenate requirement for reformulated gasoline and introduced a renewable fuel standard mandating the use of 10 vol.% ethanol. This act was justified based on the premise that ethanol would decrease the US dependence on foreign oil and reduce emissions of greenhouse gases. This led to refiners to switch from MTBE to ethanol in the US. Since then, MTBE has not been used in significant quantities in the US but has been exported instead.

EPA has not set a national standard for MTBE, although some states have set their own limits. California is the only state with a complete ban of MTBE because of groundwater contamination issues caused by leaking underground storage tanks (LUSTs) in the 1990s. Since 2015, all underground storage tanks in the United States have been upgraded to stricter standards to prevent leaks and provide for early detection and strengthen maintenance standards. However, several states filed lawsuits against petrol producers for the cost of environmental remediation, some of which are still being settled. Consequently, the current United States production is exported, principally to Mexico, Chile, Venezuela, and Asia[40].

40 *IHS Markit, Gasoline Octane Improvers/Oxygenates, 2017, https://ihsmarkit.com/products/gasoline-octane-improvers-chemical-economics-handbook.html*

Blending biofuels in the US is a relatively a recent development. In 2007, the Energy Policy Act (EISA) established a mandate for biofuels in domestic petrol. The legislation also allows an exemption known as the Small Refinery Act (SRE) program. In July 2019, EPA proposed increasing the volume of biofuels which refiners must blend to 20.04 billion gallons (roughly 75 bn of litres) in 2020. The new mandate includes 15 billion gallons (56 bn litres) of first generation of biofuels and 5.04 billion (19 bn litres) of advanced biofuels (i.e. form agricultural wastes). The mandate for cellulosic fuel has been set at 540 Elements of the Renewable Fuel Standard of 2005 are being challenged by the Association of Fuel and Petrochemical Manufacturers Association (AFPM) and environmentalist groups on the grounds that it increases the cost of gasoline and both air and water pollution. The US EPA has also been granting temporary exemptions from the renewable volume obligation (RVOs) to small refineries who demonstrate disproportionate economic hardship.

MEXICO

Fuels in Mexico are regulated by standard NOM-016-CRE-2016. The 2016 specification sets a 30 ppm sulphur limit, with a per-batch limit of 80 ppm sulphur. The new standard sets the octane levels for regular and premium petrol. The maximum oxygen level is set at 2.7% by weight and a minimum of 1.0 wt% oxygen is required in the major metropolitan zones of Mexico City, Guadalajara, and Monterrey. The standard allows the use of MTBE, ETBE, and TAME. Use of ethanol is prohibited in Mexico City, Guadalajara and Monterrey Metropolitan Zones (MZs) and limited to 5.8 vol. % in the rest of the country. E6 gasoline is subject to the same vapor pressure limits as other gasolines. The Mexican Institute of Petroleum and the Commission on Energy Regulation (CRE) set these strict limits on ethanol blending because of its detrimental impact on VOC emissions and air pollution.

In 2017, The Commission on Energy Regulation (CRE) passed amendments to NOM-016 allowing ethanol up to 10 vol.% outside of Metropolitan Zones and granting E10 gasoline waivers for oxygen (up to 3.5wt%) and RVP (1 psi). These amendments were passed outside of the normal regulatory process, were declared unconstitutional by the Mexico Supreme Court in January 2020 and repealed by CRE on September 18, 2020.

Table 7. Selected petrol specification in Mexico per region[41]

Property	Mexico City Metropolitan Region	Guadalajara & Monterrey Metropolitan Regions	Rest of the country	
	Premium and Regular		Premium	Regular
Aromatics (maximum % vol)	25.0	32.0	32.0	Inform
Olefins (maximum % vol)	10.0	11.9	12.5	Inform
Benzene (maximum % vol)	1.0		2.0	
Sulfur (ppm)	30 (annual average), 80 (maximum per batch)			
Oxygen (maximum % mass)	1.0-2.7		2.7	

Table 8. Octane levels in Mexico: Current standards

Property	Premium gasoline	Regular gasoline
Octane number (RON)	94	Inform
Octane number (MON)	Inform	82
Octane index ((RON+MON)/2)	91	87

Table 9. Vapour specifications in Mexico

		Volatility Class			
Property	Unit	AA	A	B	C
Vapor pressure	kPa (lb/in2)	54 (7.8)	62 (9.0)	69 (10.0)	79 (11.5)
Distillation temperatures:	°C				
10% (Maximum)		70	70	65	60
50%		77-121	77-121	77-118	77-116
90% (Maximum)		190	190	190	185
Final boil (Maximum)		225	225	225	225
Distillation residue (maximum)	% Volume	2	2	2	2

NOM-016 sets a strict, year-round RVP limit of 7.8 psi (AA) in Mexico City and Guadalajara to minimize evaporative VOC emissions. These populated urban areas are particularly susceptible to ozone and PM due to their altitude, topography, large populations, and large number of older vehicles.

RVP limits in Monterrey MX and the rest of the country are adjusted seasonally to reflect changes in ambient temperatures and allow for more light components to be blended in petrol.

41 "Transport policy: https://www.transportpolicy.net/standard/mexico-fuels-diesel-and-gasoline/

ASIA

MTBE use started in Asia in the 1990s, with China as one of the early adopters. The fuel specifications were mostly based on oxygen at 2.7%wt max based on the US success in reducing air pollution with reformulated gasoline containing MTBE. The Chinese developed their own MTBE production technologies with small capacities.
In Asia/Pacific the main driving force for usage of fuel ethers was the need to improve air quality by improving fuel quality. MTBE begun to be commonly imported in Taiwan, Thailand, Indonesia, and largely produced and consumed in Saudi Arabia, South Korea.

Nowadays most of Asia allow MTBE, except for Australia/NZ with 1 vol.% limit, and the Philippines, with an ethanol mandate and a 2 vol.% limit on MTBE.

Notes:

1. *Refiners and fuel importers may choose to comply with the maximum (flat) limit, or the averaging limit coupled with a cap limit. Refiners and importers may also certify alternative specification by using the CARB PREDICTIVE model to demonstrate that emissions are equivalent to those of a gasoline meeting the flat limits or the averaging limits plus cap values.*
2. *Applicable to markets requiring Euro 4, Euro 5 heavy duty, US EPA Tier 2 or 2007/2010 Heavy Duty On-Highway or equivalent emission standards.*
3. *Applies on December 31, 2011.*
4. *CAA specifies a limit of 62.1 kPa (9 psi) for any gasoline sold during the high ozone season (Jun. 1 to Sept. 15). More stringent volatility (summer RVP) requirements are set for RFG, which vary by the region and month, and range from 48.3-62.1 kPa (7-9 psi). EPA provides a 1.0-psi RVP allowance for gasoline containing ethanol at 9 to 10 volume percent.*
5. *47.6 kPa (6.9 psi) applies when a producer is using the CaRFG3 Predictive Model to certify a final blend NOT containing ethanol; otherwise, the 48.2-kPa (7.00 psi) limit applies.*
6. *1.8% winter minimum applies from Nov. 1 to Feb. 29 in the South Coast Area and Imperial County.*
7. *If the gasoline contains 3.5 % > ethanol ≤ 10%, the maximum oxygen content cap is 3.7 %*
8. *Guangdong sets all-year RVP limit as 60 kPa; Guangxi, and Hainan must comply with summer RVP limits year round*
9. *Fuel quality specification for regular/ premium gasoline*

MIDDLE EAST

The main driving force for oxygenates in Middle East was the need to replace the lost octane from lead removal. The Middle East has been developing quite rapidly in the past years and with this there is a visible increase in consumption and production of petrol. The fuel quality standards are quite diverse in Middle Eastern states. In fact, only 5 out of 11 Middle Eastern countries have implemented Euro 5 standards. Two of them have Euro 4 in place and the rest Euro 2 or lower. Middle East, following China, North East Asia and South East Asia is one of the biggest producers of fuel ethers.

Example of fuel specification in China

Table 10: Gasoline fuel standards comparison

Source: ICCT policy update

Fuel Property	China V	China VIA	China VIB	Beijing VI
Research Octane (RON), min.	95-89	95-89	95-89	95-89
Motor Octane (MON), min.	90-84	90-84	90-84	90-84
Anti-Knock Index (AKI), min.	84-87-90	84-87-90	84-87-90	84-87-90
Aromatics, vol%, max.	40	35	35	35
Olefin, vol%, max.	24	18	15	15
Benzene, vol%, max.	1	0.8	0.8	0.8
Sulfur, ppm, max.	10	10	10	10
Washed Gum Content, g/m³, max.	5	5	5	5
Density 15C, kg/m³	720-775 (20°C)	720-775 (20°C)	720-775 (20°C)	720-775 (20°C)
RVP, kPa	45-85	45-85	45-85	47-80
	Winter (Nov-Apr)	Winter (Nov-Apr)	Winter (Nov-Apr)	Winter (Nov-Mar)
	40-65[7]	40-65[7]	40-65[8]	42-62
	Summer (May-Oct)	Summer (May-Oct)	Summer (May-Oct)	Summer (May-Aug)
				45-70
				Spring/ Fall (Mar-May/Sep-Nov)
Lead, mg/l, max.	5	5	5	5
Manganese, mg/liter, max.	2	2	2	2
Oxygen, % m/m	2.7 (max.)	2.7 (max.)	2.7 (max.)	2.7 (max.)

NS = Not specified; NA = Not available; ND = Nondetectable; NAP = Not applicable

PRODUCTION OF OXYGENATES

ALCOHOLS

Alcohols used as transport fuels include methanol, ethanol, and butanols, all of which can be produced from renewable biomass or petrochemical feedstocks and processes.[42]

Renewable ethanol (ethyl alcohol or bioethanol) is produced by fermenting biomass. According to a 2018 USDA study[43], the most common feedstocks to produce ethanol for fuels are corn and sugarcane. Use of 'synthetic' ethanol from petroleum feedstocks is very limited because it is no eligible renewable credits or other tax benefits.

Ethanol can be synthesized by the hydration of ethylene with acid catalysts or by conventional biomass fermentation and distillation. The feedstock for production of ethanol includes a variety of organic feedstocks such as sugar (from sugar beet or sugarcane), grain (corn, wheat, etc.), or cellulosic material (including wood and biowaste)[44]. In Europe, ethanol is produced mostly from locally available sugar beet, feed wheat, barley and corn. In the US and China, the main feedstock is corn and in Brazil, one of the biggest producers of ethanol in the world, sugarcane[45]. Production of ethanol from cellulose and hemicellulose is still limited[46]. In 2017, EU produced 0.41 million tonnes (dry matter equivalent) of cellulosic ethanol. 1.81 million tonnes were produced from sugars and 11.41 million tonnes from cereals.[47]

It is added to petrol in quantities not higher than 10%, with the exception of mixture E85 (85% of ethanol and 15% of petrol). Ethanol mixture above 10% requires dedicated engines. Petrol with concentration of 10%+ ethanol can also cause material compatibility problems for certain fuel system components (seals, injection pumps).

42 Review and qualitative assessment of Clean Octane Options for Gasoline, HART Energy Consulting, December 2007,

43 Bob Flach, Sabine Lieberz, Jennifer Lappin and Sophie Bolla, EU Biofuels Annual 2018, USDA, 7 March 2019 https://gain.fas.usda.gov/Recent%20GAIN%20Publications/Biofuels%20Annual_The%20Hague_EU-28_7-3-2018.pdf

44 Octane Enhancers, Ullmann's Encyclopedia of Industrial Chemistry, Marco Di Girolamo, Maura Brianti and Mario Marchionna

45 Handbook of MTBE and other octane enhancers, 2004

46 US Office of Energy Efficiency and Renewable Energy, https://www.energy.gov/eere/bioenergy/biofuels-basics

47 EPure statistics: https://www.epure.org/media/1763/180905-def-data-epure-statistics-2017-designed-version.pdf

Methanol is produced from natural gas, coal, biomass or landfill gas. There are a variety of technologies used to produce methanol. In fuels, methanol is generally used as a neat product because of the need to use co-solvents when blended with petrol. Bio-methanol can be blended with petrol or used to produce bio-MTBE, bio-DME, or synthetic biofuels (source: USDA).

Methanol is produced from synthesis gas (CO/H_2). The feedstock for production is either natural gas or renewable feedstock such as landfill gas, biomass, captured CO_2 or municipal waste. Methanol is used in the production of MTBE, but it is sometimes used on its own as an octane enhancer. However, its use is limited or prohibited in many countries due to its effect on petrol volatility and corrosivity.

Tertiary-butanol (t-butanol or TBA) is a co-product in the manufacture of propylene oxide. In the 1980s ARCO Chemical commercialized two TBA-based fuel additives, Arconol™ and Oxinol™ 50, a 50/50 blend of TBA and methanol. It was a mixture of t-butanol and methanol. The products were eventually discontinued because refiners preferred to use MTBE.

Fuel ethers are produced by the reaction of olefins (i.e. butenes or isobutylenes) and alcohol (i.e. methanol or ethanol) over a bed of acidic resin. Both pure isobutylene (from TBA dehydration) and mixed butenes are used to produce MTBE. Only the isobutylene portion of mixed butenes reacts with the alcohol. The alcohols used can be from either petrochemical feedstocks (primarily natural gas) or agricultural feedstocks (e.g. cane sugar, starch, agricultural and forestry waste).

- MTBE is produced by reacting isobutene with methanol over the surface of an acidic resin beads.
- ETBE is similarly manufactured by the reaction of isobutylene and ethanol.
- TAME is obtained by the liquid phase reaction of methanol and two isoamylenes. Around 97% of TAME is produced as part of the mixed refinery stream.
- TAEE is produced from isoamylenes, as it is the case of TAME, but in reaction with ethanol.

The reactions occur in either a liquid or gas-liquid phase reactor which contains an acidic ion exchange resin or sulphuric acid and can take place at a temperature of 50-90 °C with a pressure of 20 bar. Consequently, the resulted mixture is distilled in order to obtain a high purity product (>95%).

SUPPLY CHAIN & INFRASTRUCTURE

ALCOHOLS

Ethanol plants are usually located near the bio-feedstock production source, which are not typically near fuel refineries.

On the input side, first generation ethanol plants use wheat or corn as the primary feedstock and produces ethanol and other by-products such as distillers grains. Depending on the cost and availability of the local feedstock, some producers may import corn and wheat for ethanol production.

On the output side, the primary product of the plant is ethanol, which is blended with petrol at different percentages and sold to consumers. Thus, fuel refiners and blenders are the major purchasers of ethanol.

One of the main challenges faced by the ethanol producers is ethanol's high affinity for water. Thus, they cannot use the current most efficient means of liquid ingredients transportation in the petrol supply chain, which are the pipelines. Consequently, to avoid potential contact with water, ethanol must be blended at the terminal and then transported via rail and delivery trucks to retail service stations.

Storage and blending challenges arise as well, due to special facility and equipment installation, or adjustment of the old ones, that would help preventing water contamination and mitigate the potential impacts of corrosion and biodegradation. All the above-mentioned requirements involve high costs and time management. Therefore, ethanol producers consider infrastructure as a significant determinant in plant location. A diversified distribution network as well as accessibility to utility services (i.e. natural gas, electric power or water) comprise the basic components needed to produce ethanol.

Methanol suffers from the same distribution limitations as ethanol, being hygroscopic, soluble in water, and readily biodegradable. In most cases, it must be transported separately from gasoline to the blending terminals to prevent phase separation. The finished fuel is then moved in tanker trucks to the retail stations.

FUEL ETHERS

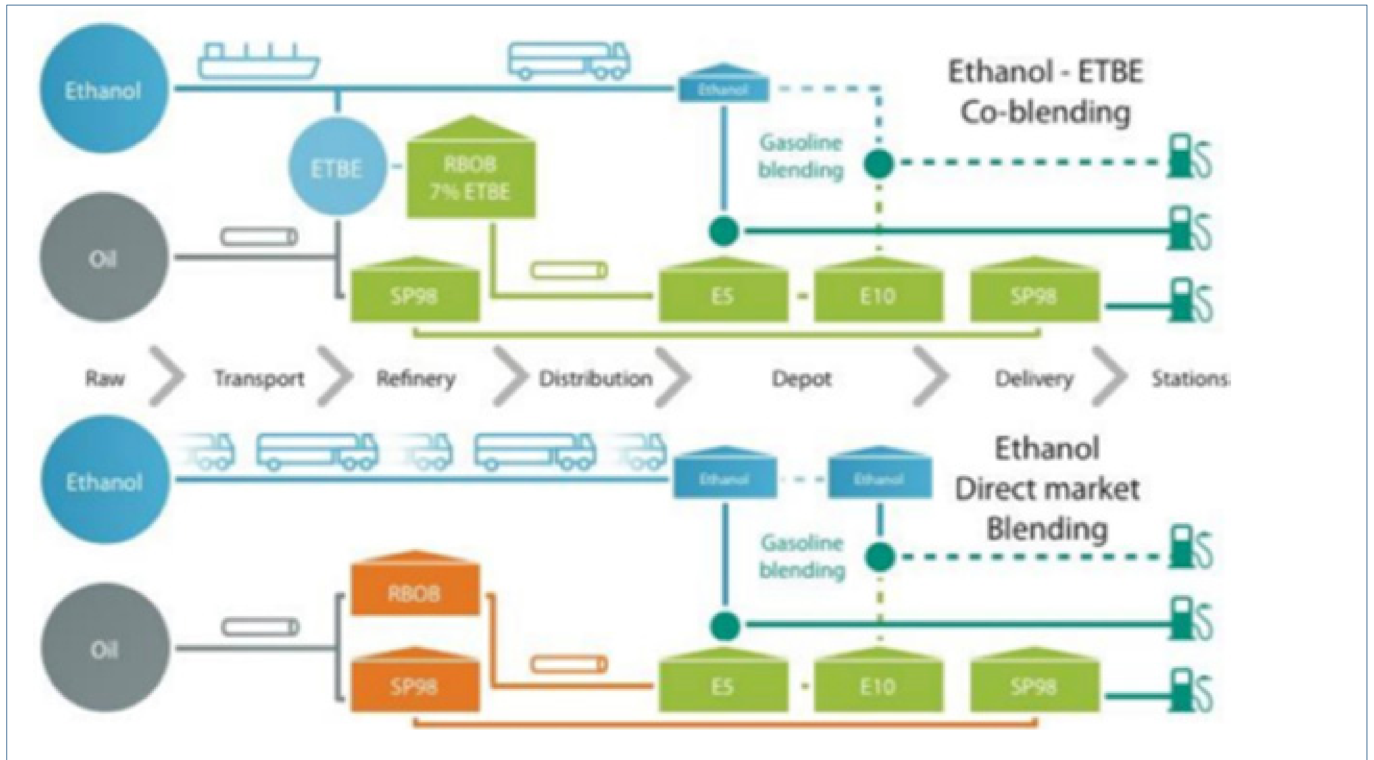
As fuel ethers were originally produced from petrochemical and renewable feedstocks, Oxyfuel production facilities are usually co-located with refineries or petrochemical plants that are linked to sources of petroleum and natural gas.

Unlike alcohols, fuel ethers have relatively low water solubility which allows the transportation of the finished gasoline in barges, vessels, or pipelines without the risk of phase separation or changes in the product specifications and fit-for-purpose properties. This provides cost and logistical advantages to alcohol-blended fuels.

Today, MTBE is still produced predominantly from natgas and petroleum derived methanol and isobutylene, although biomass-derived methanol can also be used. Isobutylene is produced from a variety of feedstocks including mixed butene streams from fluid catalytic crackers, refinery butenes, or isobutane. Isobutane is converted to isobutylene by two main processes, either dehydrogenation or conversion to tert-butanol in the PO/TBA process followed by dehydration. Thus, MTBE is still a popular and cost-effective way to upgrade abundant natural gas liquids and petroleum feedstocks into a clean-burning, high octane product.

ETBE can be produced in the same equipment as MTBE by replacing methanol by ethanol. Essentially all the ETBE produced today use bio-ethanol from a variety of feedstocks including sugarcane, corn, wheat and sugar- beets. Bio-ethanol is transported to the refiners and petrochemical plants where it is combined with isobutylene. Bio-ETBE is then blended into petrol at the refinery or on sea-going vessels and shipped to the destination via pipelines and any other suitable mode of petrol transport. Hence, oxyfuels offer a significant cost advantage over alcohols since they do not requires a separate storage, blending and transportation infrastructure.

Figure 15: ETBE supply chain



Source: LyondellBasell

GLOBAL SUPPLY AND DEMAND

Petrol demand is highly dependent on its price. The price in turn reflects producers' costs and consumers' willingness to pay. Therefore, changes in the crude oil price are the primary driver of petrol price. The price for crude oil supply is strongly influenced by the the Organization of the Petroleum Exporting Countries (OPEC) production decisions. Among other determinants of the petrol price are government taxes, refining costs, marketing and distribution[48].

The use of fuel ethers as blending components in petrol, improves the quality of transport fuel and reduces exhaust emissions. Oxyfuels also extend the available supply of petrol and provide higher blend value than reformate or alkylate, the two main high-octane components of conventional gasoline.

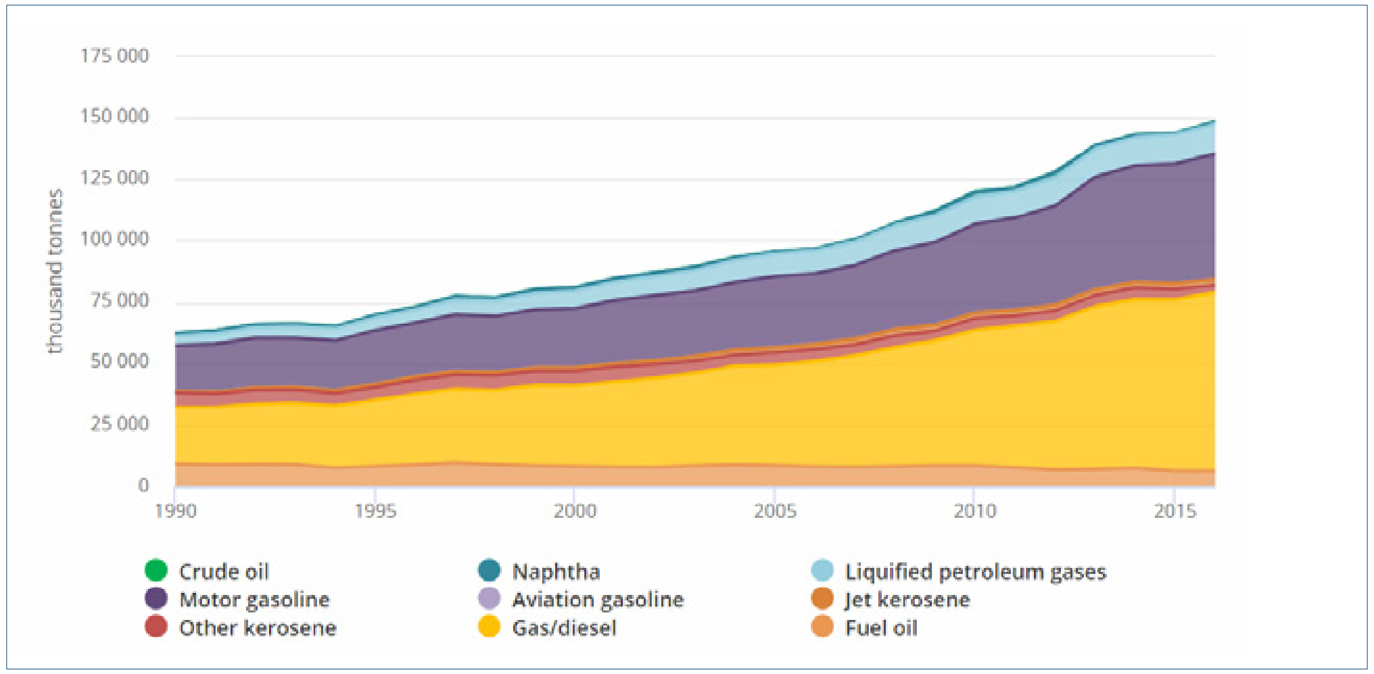
As the demand for mobility and standard of living in Africa continues to grow, so will the demand for higher quality petrol.

For this reason, it is imperative that regulations allow for their use to lower costs and improve fuel and air quality.

Thus, the global demand for ethers continues to grow with petrol demand despite fuel efficiency and EV effects.

48 EIA: https://www.eia.gov/energyexplained/index.php?page=gasoline_factors_affecting_prices

Figure 16: Final consumption of oil and oil products in Africa, 1990-2016 [49]



Source: IEA

49 IEA: https://www.iea.org/statistics/?country=AFRICA&year=2016&category=Oil&indicator=OilProductsCons&mode=chart&- dataTable=O

BEST PRACTICES FOR USE, STORAGE, TRANSPORTATION AND BLENDING

CONTAINMENT, HANDLING AND SAFETY PRACTICES

STORAGE AND TRANSPORT OF FUEL ETHERS

With regards to storage of fuel ethers, recommendation is to use internal floating roofs operating at atmospheric pressure or fix-head tanks with vapour management system. It is also recommended to have diking outside storage tanks to contain any spills and nearby water supply in case of fire. As to the unloading stations, it is recommended to install instruments which can warn for potential overfilling and automatic devices able to shut off the flow if overfilling is imminent. The loading racks ought to be 150 feet from equipment or tanks[50].

50 White Paper on MTBE for the government of Australia, 2015, Stratas Advisors, p.73

Best practices for transfer of fuel ethers:

- Personnel to have protective clothing
- Fire protection procedure should be put in place
- MTBE or ETBE - dedicated unloading systems are recommended. Lines should be free of water, and cleared with petrol
- Safety showers and eye washing stations
- Tools used should not produce any sparks as the product is flammable
- Unloading block valve
- The hose used should be accordion like, made of stainless steel and double-braided
- Grounding connectors are recommended
- Nitrogen supply with pressure regulator and check valve.

Best practices for marine transport of fuel ethers:

- Ensure material compatibility
- Contact with water should be avoided
- Ensure that the ships are equipped with alcohol-resistant fire foams
- Monitoring of the vented marine transport is key to ensure acceptable vapour exposure

UNDERGROUND STORAGE TANKS

The California UST legislation study recommends several good practices which can help in ensuring save storage of MTBE, and with it any liquid product at the station:

- The UST needs to have a double walled system or if the tank is single wallet, a secondary containment should be installed.
- Usage of appropriate material to prevent corrosion, and if there is a possibility for the corrosion to occur, the tank should have cathodic protection to mitigate the risk.
- The UST should be equipped in a leak detection system which can alert about the leak.
- Regular monitoring of the tank as well as local monitoring of soil should take place.
- Finally, the report recommends registration of the UST system with the local authorities.

There are several regulations governing storage of liquid fuels, providing requirements for the Underground Storage Tanks and for monitoring of groundwater both in the US and in Europe. The European regulations are regulatory revised and adequately enforced, which has played an important role in having good standards for USTs in the past 30 years.

Worth noting is that the revisions of the UST requirements in the US came after the reported detection of MTBE in California in the early 90s. Main reason were leaking USTs. This suggests that regular revisions of the legislations, proper implementation and regular checks of the status of USTs is key in ensuring safety of storage of petrol. Main requirements for USTs in Germany, the Netherlands and the US are listed below.

Requirements for UST in Germany and the Netherlands

Germany	The Netherlands
Single-walled tanks are not allowed for water-soluble liquids. **Double-walled tanks mandatory** for water-endangering liquids. **Leakage tracing equipment mandatory** Double-walled pipes + leakage tracing equipment or in case of single-walled pipes: Suction line + downward to tank. Inspection of the UST / pipe by authorized expert (every 2.5 / 5 years).	Tanks and pipes **must be resistant to the stored product** for a minimum period **of 15 years.** For light oil a **vapor return** 'stage I' is **compulsory**. At the filling point it is necessary to **indicate which type of overfill is installed.** At each filling point it must be clearly stated what the **net content of the tank** is as well as for which product that tank is destined.

Requirements for UST in the US

United States of America
As of 1998 all UST systems must include corrosion, **spill and overfill protection.** As stated in the Resource Conservation and Recovery Act (RCRA), **required notification of all gasoline UST system to authorities.** Owners / operators to notify **tank existence, releases** (suspected and confirmed), **corrective action plan and prior to closure / change-in-service.** **Requirements for leak detection:** monthly monitoring; inventory control and tank tightness testing every 5 years for old and new tanks.

FUTURE OUTLOOK

FUEL ETHERS

Today, fuel ethers are used almost everywhere in the globe except for the US, Canada, and Australia (New Zealand). Several recent developments have positively impacted the outlook for MTBE and ETBE globally, including China's reversal on their E10 program and the revival of ETBE and bio-MTBE in Europe.

Overall, the growth of fuel ethers globally is expected to track with global petrol demand, especially in developing countries. Significant growth is expected in South East Asia, the Middle East, and Africa. The compatibility of fuel ethers with the gasoline production and distribution infrastructure, vehicle components, and their superior blending properties and blend value will continue to make them important components in gasoline.

In more developed countries where food and water supplies are abundant and CO_2 concerns are higher, bio-ETBE is expected to become the oxyfuel of choice over MTBE and ethanol. Bio-MTBE may also become popular, but only if the production of bio-methanol increases substantially.

ETHANOL

According to the OECD-FAO report on Agricultural Outlook 2018 -2027, the production of ethanol globally is to increase by around 14% (from 120 bn L in 2017 to nearly 131 bn L by 2027). The main producers of ethanol will be the US, Brazil (nearly 50% of the production), China, and the EU.

China has announced they will no longer implement E10 nationally stating supply issues and competition with food. Ethanol and the Renewable Fuels Standard in the United States is facing increasing opposition from both the refiners concerned about the cost of the fuel and environmental and non-governmental organizations concerned about its impact on air and water quality.

Future growth in ethanol use is also limited by the 33% decrease in energy content compared to gasoline, competition with food for land and water, concerns about land use change deforestation and biodiversity, and the now well recognized impacts on air quality and groundwater pollution form fertilizer runoff.

METHANOL

According to the Global Methanol Market 2019-2027, the compound global methanol growth yearly rate will be at 5.42% between 2019 - 2027.[51] According to the report "The methanol market also faces challenges such as unstable methanol prices, economic slowdown hindering the demand for methanol and strict regulations & policies." The report lists key drives for the growth of the methanol market such as rising acceptance of the Methanol to Olefins (MTO) technology, rise in petrochemicals' demand, need for methanol in transportation fuels (of note, the report includes market segmentation based on derivatives and end-users. (Derivatives: formaldehyde, gasoline, DME, acetic acid, MTBE & TAME and others& end-users: automotive, electronics, paints & coatings, construction and others).

A report issued by Global Data points that Russia, Iran and the US will be the key drivers for global methanol industry growth in 2019 - 2030. They are to constitute nearly 64% of the global methanol capacity additions.

Direct-blending of methanol into petrol is expected to remain low due to regulatory limits, and the global availability of MTBE as a superior blendstock.

51 Global Methanol Market 2019-2027, https://www.researchandmarkets.com/reports/4791833/global-methanol-market-2019-2027?utm_source=BW&utm_medium=PressRelease&utm_code=jftkjm&utm_campaign=1273706+-+Global+Methanol+Market+Outlook+Report+2019-2027%3a+Projecting+a+CAGR+of+5.42%25+During+the+Forecast+Period&utm_exec=joca220prd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