

Impact of Simultaneous ETBE and Ethanol Addition on Motor Gasoline Properties

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ABSTRACT

This study examines the impact of ETBE and ethanol addition on the main properties of motor gasoline. European Union mandates the use of biofuels in all transport fuels, according to the 2003/30/EC Directive. The addition of ethanol, a known octane enhancing component, in small proportions significantly increases the vapor pressure of the final gasoline, exceeding the maximum specification limits. ETBE (ethyl tert-butyl ether) is on the other hand an excellent but expensive octane enhancing component with beneficial impact on vapor pressure of the final gasoline. This paper examines the ability of ETBE to act as a stabilizer in gasoline – ethanol blends. Two gasoline samples with different chemical compositions and characteristics were prepared by blending basic refinery components. In each sample, ETBE was added in concentrations of 2, 4, and 6 % V/V respectively. In each of these ETBE – gasoline blends, ethanol was added in concentrations from 1 to 6 % V/V in 1% steps. The properties measured were composition, density, distillation characteristics, vapor pressure and octane numbers (RON and MON). In all cases, the addition of ETBE and ethanol had positive effect on octane numbers. The vapor pressure was increased due to ethanol addition, but the blends with ETBE had lower vapor pressures compared to the blends without ETBE. The higher the ETBE concentration, the lower the increase in vapor pressure of the final blend (0.4 to 2.7 kPa, depending on ETBE and ethanol content). Therefore, the use of ETBE as stabilizer can contribute to the introduction of bioethanol in motor gasoline, especially in the warmer EU countries of the Mediterranean Region.

INTRODUCTION

BIOFUELS AND DIRECTIVE 30/2003/EC – The Commission of the European Union is focused on the sustainable development of the Member States, in parallel with the protection of the environment. The transport section is accounting almost 30% of the total energy consumed within the member states, and remains almost 100% dependent on oil. The Commission White Paper 'European transport policy for

2010: time to decide' expects CO₂ emissions from transport to rise by 50 % between 1990 and 2010, to around 1,113 million tones, the main responsibility resting with road transport, which accounts for 84 % of transport-related CO₂ emissions. From an ecological point of view, the White Paper therefore calls for dependence on oil (currently 98 %) in the transport sector to be reduced by using alternative fuels such as biofuels. Therefore, in order to fulfill the requirements of the Kyoto Protocol for CO₂ emissions reduction, and increase the dependency on imported oil, European Union has issued Directive 2003/30/EC, on the promotion of the use of biofuels or other renewable fuels for transport. [1] Directive 2003/30/EC requires that all Member States should ensure that a minimum proportion of biofuels and other renewable fuels will be placed on their markets, and, to that effect, shall set national indicative targets. The reference value for these targets of 2 %, calculated on the basis of energy content, of all motor gasoline and diesel for transport purposes has been set since December 31st 2005. This reference target value shall be 5.75 %, of all motor gasoline and diesel for transport purposes placed on their markets by December 31st 2010.

Total energy consumption in the transport sector in the 25 EU member states accounts to 354,942 million tones of oil equivalent (mtoe) (2005), which is 31.3% of the total inland energy consumption. Motor gasoline consumption for the same period was 113,205 mtoe, accounting to 31.9% of total energy consumption in the transport sector. [2]

According to the Directive 2003/30/EC bioethanol and bio-ETBE, (ETBE produced from the reaction of bioethanol with isobutylene) are two of the possible biofuels that can be used as blending components in motor gasoline. European Standard EN 228 is also including both components as two of the possible oxygenated components that can be added in motor gasoline, because they are high octane number components.

GASOLINE AND OXYGENATES BLENDS – The stringent environmental standards and fuel economy

regulations have enforced changes in the specifications of the gasoline fuels. Lead phase out due to environmental and toxicological reasons resulted into the utilization of oxygenated compounds as octane enhancers. MTBE and ethanol were the two oxygenates mostly used as blending components for the production of premium unleaded gasoline. Oxygenates have high molecular oxygen content and are either alcohols or ethers. The purpose of the addition of oxygenates in gasoline is to assist in fuel combustion, leading to lower emissions of carbon monoxide (CO) and hydrocarbons (HC) due to the presence of additional oxygen atoms. They also have higher octane ratings than gasoline and are blended with low octane gasoline basestocks to meet the octane requirements. [3]

Ethanol was first used as a motor vehicle fuel in 1908, but remained a small niche fuel favored by racers for many years. [4] As from the 1970s, several events occurred that led to the introduction of ethanol into the commercial gasoline market, especially in the United States. Energy security concerns brought about by the Arab oil embargo spurred Congress to enact tax incentives to encourage the production of alternative fuels. Around the same time, concerns about environmental impacts associated with gasoline began to emerge. The banning of lead in gasoline created a demand for blending agents, like ethanol, with high octane value. Ethanol demand further increased after Congress passed legislation requiring the use of oxygenates in gasoline to reduce harmful emissions from mobile sources. Global warming, generally considered to be the next major environmental front, may further boost the demand for ethanol. Ethanol, being a renewable fuel, produces less greenhouse gases emissions than gasoline. [5]

ETBE is an oxygenated fuel that can be blended with gasoline to make it burn more cleanly and thus improve overall air quality. ETBE is produced by the reaction of ethanol with isobutylene. The advantage of the use of ETBE as a blending component lies in eliminating many of the historical impediments such as increased volatility of gasoline and incompatibility with gasoline pipelines limiting the broader use of ethanol. As ETBE can be blended at the refinery level, it can be economically transported to areas that previously had not been able to utilize ethanol. ETBE conforms to the overall goals of reducing the health impacts of motor gasoline: during the synthesis of ETBE, the excess butanes are utilized in the refining industry. These butanes can be converted to isobutylene which, when combined with ethanol, produce an environmentally friendly octane booster (ETBE). [6, 7]

Octane Number – One of ethanol's positive attributes, and one of the main reasons it is blended into gasoline, is its ability to increase the octane number of the gasoline to which it is added. Generally speaking, the addition of 10 % V/V ethanol will increase the octane of the gasoline to which it is added by 2 to 3 (R+M)/2

octane numbers. [8] However, the actual octane increase is dependent upon the octane of the base fuel and, to a lesser degree, its composition. The octane increase is more pronounced for research octane than for motor octane.

Ethanol's blending octane number is 129 for Research Octane Number (RON) and 96 for Motor Octane Number (MON) resulting in an Antiknock Index, or blending octane of 112.5 (R+M)/2.

The octane numbers for ETBE are relatively high and therefore ETBE can be used to improve the octane rating of gasoline. The blending octane numbers of ETBE is 119 for research method and 103 for motor method resulting in an Antiknock Index, or blending octane of 111 (R+M)/2.

Octane sensitivity, which is the difference between RON and MON (Sensitivity = RON–MON) should be as low as possible, a value of 10 or below being the requirement for the regular unleaded gasoline according to EN 228 Standard. ETBE has better sensitivity compared to ethanol (16 for ETBE, 33 for ethanol). This parameter is critical for refinery blenders, and may help them overcome problems of formulating gasoline with acceptable sensitivity limits.

Volatility – Gasoline is metered in liquid form, through the fuel injectors, atomized and mixed with air before entering the cylinders. It is very important that a fuel's tendency to evaporate is controlled to certain standards. A fuel's ability to vaporize, or change from liquid to vapor, is referred to as its volatility and is an extremely important characteristic of gasoline. It is well known that fuel volatility can affect several areas of vehicle performance. [9, 10]

The main terms for the expression of gasoline volatility are the distillation profile and the vapor pressure.

The distillation test is used to determine fuel volatility across the entire boiling range of gasoline. Gasoline consists of a variety of chemical components that evaporate at different temperatures. More volatile components evaporate at lower temperatures, less volatile ones at higher temperatures. The distillation curve and especially the front end volatility T_{10} , T_{20} and T_{50} recovery points may be lowered by 12 °C or more if ethanol is added in motor gasoline. If the base gasoline has a low T_{50} , the addition of ethanol could drop the T_{50} significantly. This, in turn, could result in poorer hot weather driveability and increase evaporative emission losses. The T_{50} of gasoline is also a major factor in calculating driveability index. Unlike alcohols, ETBE and other ethers have no azeotropic effects on the distillation curve of gasoline. Therefore, ETBE blends into gasoline in a smooth, predictable fashion much like any other hydrocarbon that boils in the same temperature range. Because of its favorable boiling point (73 °C), ETBE will normally reduce the mid-range temperatures of the

gasoline's distillation curve. This provides added flexibility in producing high octane and/or low vapor pressure premium gasoline.

Table 1. Base refinery components properties

Properties	Reformate	FCC Gasoline	Alkylate	Isomerase	Specification Limits (EN 228)	Test Method
RON	103.0	93.1	94.0	85.4	95 min	EN ISO 5164
MON	92.6	80.6	91.9	83.3	85 min	EN ISO 5163
Density (kg/m ³ , 15 °C)	820.2	726.3	706.2	650.0	720 – 775	EN ISO 12185
Sulfur (mg/kg)	0	120	5	10	50 max	EN ISO 20846
Composition (% V/V)						prEN 14517
Parafins	24.1	37.5	98.3	94.0		
Olefins	0.0	30.0	0.0	0.0	18 max	
Naphthenes	0.3	10.8	0.9	6.0		
Aromatics	75.6	21.7	0.8	0.0	35 max	
Benzene (% V/V)	3.7	0.9	0.3	0.0	1 max	prEN 14517
Vapor Pressure (kPa)	45.2	55.9	49.6	92.4	45 – 60 summer 50 – 80 winter	EN 13016-1
Distillation (°C)						EN ISO 3405
IBP	41.1	37.4	36.2	28.0		
10%	74.2	53.1	89.1	40.1		
50%	127.9	99.6	107.3	49.2		
90%	165.1	159.4	136.2	62.1		
FBP	204.3	195.2	208.9	76.2		

The vapor pressure of a fuel must be high enough to provide ease of starting the engine but not so high as to contribute to vapor lock or excessive evaporative emissions. The historically used “Reid Method” has been replaced by simpler test methods, but remains the reference, since all new methods can be correlated with the results of the Reid method.

The vapor pressure of ethanol is only 17.2 kPa. However, when ethanol is added to gasoline at low levels, a non-ideal mixture is formed resulting in a fuel with a higher vapor pressure than either liquid by itself. For example, a gasoline with a 69 kPa vapor pressure, when blended with ethanol at the 2 % V/V to 10 % V/V range, would typically increase within 72.4 to 75.8 kPa vapor pressure ranges. The exact increase is dependent upon the vapor pressure and composition of the base fuel. Lower aromatic fuels tend to exhibit a slightly greater vapor pressure increase. [11, 12]

The blending Vapor Pressure of pure ETBE is 28 kPa, well below that of finished gasoline, thus allowing the use of more light hydrocarbons, typically butane during gasoline blending. Some polar contaminants of commercial ETBE, such as ethanol, blend non-ideally in hydrocarbons such as gasoline, and thereby generate vapor pressure increases much higher than reflected by their true vapor pressure. Therefore, it is important to keep these contaminants to a reasonably low level in commercial ETBE in order to maximize its vapor pressure benefit to gasoline.

This paper presents experimental data from ternary blends of gasoline, ethanol and ETBE. The main idea is

the investigation of ETBE as a stabilizing component that can reduce the vapor pressure of the gasoline – ethanol blends.

EXPERIMENTAL SECTION

BLENDING COMPONENTS – In order to investigate the impact of simultaneous ethanol and ETBE addition on the properties of unleaded motor gasoline, the main refinery components blended in the refineries to produce marketed products were collected. The blending components were provided by Hellenic Petroleum, Aspropirgos Refinery. Each of the blending components was analyzed regarding volatility characteristics, octane rating, and composition. All test methods were carried out according to the official ISO and EN methods described in EN 228 standard. The properties of the blending components are given in Table 1. Reformate has the higher octane numbers, due to its very high aromatics content. The only component that contains sulfur, exceeding the 2009 specification limit of 10 mg/kg, is the FCC Gasoline which contains 120 mg/kg sulfur.

BASE FUELS FORMULATION – The blending components were blended in different proportions, in order to produce unleaded gasoline samples with different compositions, reflecting the average quality of gasoline marketed in Greece within the year. Two gasoline blends were prepared and analyzed according to the official ISO and EN test methods. The properties of the 2 base fuels are given in Tables 2 and 3. The gasoline blends were prepared in order to represent a winter grade (Blend I) and a summer grade gasoline

(Blend II). Blend I has higher octane number, but due to its high percentage of reformat used in this blending, the benzene content was exceeding the EN 228

specification limits (1 % V/V). Blend II exceeds the maximum sulfur content of 50 mg/kg according to EN 228 standard.

Table 2. Properties of Blend I base fuel and its blends with ETBE

Properties	Blend I	Blend I-2	Blend I-4	Blend I-6	Specification Limits (EN 228)	Test Method
RON	92.5	93.2	93.8	94.3	95 min	EN ISO 5164
MON	84.2	84.6	84.8	85.1	85 min	EN ISO 5163
Density (kg/m ³ , 15 °C)	737.2	737.2	737.2	737.2	720 – 775	EN ISO 12185
Sulfur (mg/kg)	46	45	45	45	50 max	EN ISO 20846
Composition (% V/V)						prEN 14517
Parafins	50.9	49.5	48.9	47.8		
Olefins	12.0	11.8	11.5	11.3	18 max	
Naphthenes	5.7	5.6	5.5	5.4		
Aromatics	31.4	30.8	30.1	29.5	35 max	
Benzene (% V/V)	1.50	1.47	1.44	1.41	1 max	prEN 14517
Oxygen (% m/m)		0.31	0.63	0.94	2.7 max	prEN 13132
Vapor Pressure (kPa)	55.2	54.0	53.0	52.5	45 – 60 summer 50 – 80 winter	EN 13016-1
Distillation (°C)						EN ISO 3405
IBP	39.1	37.7	38.5	38.6		
10%	58.2	58.8	59.3	60.0		
50%	99.0	98.6	97.8	97.8		
90%	157.2	157.2	155.6	157.9		
FBP	186.0	186.2	187.0	187.2	210 max	
E70 (% V/V)	24.0	24.9	26.7	24.2	20 – 48 summer 22 – 50 winter	
E100 (% V/V)	50.4	51.7	50.8	52.1	46 – 71	
E150 (% V/V)	84.5	86.4	86.6	85.9	75 min	
ETBE (% V/V)		2.0	4.0	6.0		

Table 3. Properties of Blend II base fuel and its blends with ETBE

Properties	Blend II	Blend II-2	Blend II-4	Blend II-6	Specification Limits (EN 228)	Test Method
RON	94.0	94.6	95.1	95.6	95 min	EN ISO 5164
MON	84.1	84.5	84.7	85.0	85 min	EN ISO 5163
Density (kg/m ³ , 15 °C)	715.5	715.9	716.3	716.7	720 – 775	EN ISO 12185
Sulfur (mg/kg)	54	52	52	52	50 max	EN ISO 20846
Composition (% V/V)						prEN 14517
Parafins	58.6	57.4	56.3	55.1		
Olefins	13.5	13.2	13.0	12.7	18 max	
Naphthenes	6.8	6.7	6.5	6.4		
Aromatics	21.1	20.7	20.3	19.8	35 max	
Benzene (% V/V)	0.99	0.97	0.95	0.93	1 max	prEN 14517
Oxygen (% m/m)		0.32	0.65	0.97	2.7 max	prEN 13132
Vapor Pressure (kPa)	62.2	61.2	60.8	60.4	45 – 60 summer 50 – 80 winter	EN 13016-1
Distillation (°C)						EN ISO 3405
IBP	35.8	34.4	35.2	35.3		
10%	52.5	53.1	53.6	54.3		
50%	79.4	79.0	78.5	78.2		
90%	151.6	149.8	148.2	150.5		
FBP	186.4	184.6	184.4	184.6	210 max	
E70 (% V/V)	39.7	39.8	39.8	39.1	20 – 48 summer 22 – 50 winter	
E100 (% V/V)	65.9	66.5	67.5	67.5	46 – 71	
E150 (% V/V)	89.5	90.2	90.5	89.7	75 min	
ETBE (% V/V)		2.0	4.0	6.0		