Influence of Ethanol on Vapor Pressure of Refinery Components and Commercial Type Gasoline Blends

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Abstract: *European member states have to comply with the Directive 2009/30/EC, which mandates the use of biofuels in motor fuels. Bioethanol is one of the possible renewable fuels that can be used. However, in Mediterranean member states with higher climate temperatures during summer, the production of gasoline with bioethanol as an oxygenate blending component will face increased volatility problems. This study examines the impact of ethanol addition (from 0.5 to 10% v/v) on vapor pressure of refinery streams used for gasoline blends and on commercial motor gasoline fuels. The addition of ethanol in small proportions increased the vapor pressure of the final gasolines tested. The change in vapor pressure was measured (expressed) using delta VP – ΔRVP. The ΔRVP was calculated in each blending component, in an attempt to identify the impact of the refinery stream composition on the change of vapor pressure due to the ethanol addition. The more volatile winter grade samples showed a lower increase in delta vapor pressure compared to the less volatile summer grade fuels. Thus, the addition of ethanol up to 5% v/v into gasoline led to increased vapor pressure of blends. Samples with higher content in olefinic and aromatic hydrocarbons had higher increase in the vapor pressure. Moreover, gasolines containing TAME in their composition revealed a smaller increase in vapor pressure, compared to gasolines that did not contain ethers in their composition. The results of the present research showed that when ethanol is added in gasoline, the change of vapor pressure will be significant and must be taken into account, especially for commercial gasolines which are subjected to ethanol addition and they should meet the specifications set by EN 228:2012 standard.*

Keywords: *Gasoline, ethanol vapor pressure, refinery components*

I. Introduction

Increased worldwide interest in reducing reliance on petroleum-based fuels and improving air quality has prompted broadened use of alternative, renewable fuels, including gasoline blended with various oxygenates. One of the crucial measures envisaged by the EU policies in the field of energy and transport is the promotion of biofuels use in order to increase their market penetration in response to the need for energy supply security and implementation of the Kyoto protocol. [1 – 3] At the moment, ethanol and biodiesel are the only biofuels available in sufficient quantity that can allow the achievement of this target. According to the Directive 2003/30/EC and the EN 228 Standard, alcohol such as bioethanol is to be used as blending component in gasoline in the European Union. [4]

These biocomponents were introduced in order to reduce the percentage of the aromatic hydrocarbons, attributing on the one side to the antiknock index permitting a higher compression rate in internal combustion engine and on the other side they have a significant environmental impact. The member states of the European Union are obliged by the European Commission to blend gasoline with alcohols and ethers so as to encounter the negative effects of aromatic hydrocarbons and organolead compounds. These compounds are toxic and are charged with high level of regulated emissions such as carbon monoxide (CO), carbon dioxide (CO2) and hydrocarbons (HC) emissions.[5] Ethanol blended with gasoline generally results in lower hydrocarbon and carbon monoxide emissions from engines operating richer than stoichiometry. [6] So, the enleanment affect of the ethanol reduced overall hydrocarbon and carbon monoxide emissions while increasing NOx emissions from engines without feedback controls. Depending on the engine type and duty cycle, ethanol blends may produce increased NOx emissions compared with the emissions of petroleum-gasoline used in an unmodified engine. Engines designed to meet stringent emission regulations have not demonstrated additional reductions in HC and CO emissions or increases in NOx emissions when using ethanol blends. However, more testing is required to confirm the interaction between emission reduction strategies and ethanol blends. [7]

Vapor pressure (DVPE) is a key fuel variable for evaporative emissions. The effect of vapor pressure is strongly non-linear. The ethanol blends with final DVPE around 75 kPa gave considerably higher evaporative emissions than the lower volatility fuels. Differences between fuels with DVPE in the range 60-70 kPa were

small. [8] As well as, higher DVPE levels of ethanol/gasoline blends can also increase evaporative emissions unless they are properly controlled by the on vehicle systems.[9] Ethanol presence in gasoline had a significant role in evaporative emissions - Volatile Organic Compounds (VOC's). [10 – 12]

Ethanol is to be used as fuel additive up to 10 % v/v as a maximum percentage according to the EN 228:2012 Standard. A significant property for gasoline is its volatility as expressed through the profile of the distillation characteristics and the vapor pressure. Gasoline evaporates in a wide thermal region from 30°C to 210°C, since it is a mixture of components and the distillation curve should be in "linearity" to the Standard Distillation Curve [S-plot]. [13] Additionally, vapor pressure defines the volatility, showing the tendency of the lighter hydrocarbons by affecting the front-end volatility of the gasoline, which in turn is related to cold-start problems, determining the vapor lock index and simultaneously, the excessive losses of evaporates. Ethanol forms azeotropes with the hydrocarbons typically comprising gasoline. An azeotrope is a mixture of two or more liquids in such a ratio that the composition of the mixture cannot be changed by simple distillation. This means that the azeotropes of ethanol and hydrocarbons distil at a nearly constant temperature. This phenomenon results in an essentially flat distillation curve in the standard ASTM distillation measurement until the azeotropes of ethanol and hydrocarbons have been eliminated from the liquid. When the ethanol has distilled completely from the liquid, the distillation curve rapidly returns to that of the hydrocarbon-only gasoline. [9] The azeotropic behavior which was appeared when ethanol was mixed with gasoline is called as minimum azeotrope and is a positive deviation from Raoult's Law, reducing the gradient of the distillation curve resulting to a plateau of the curve around 70 °C, where the ethanol evaporates. [9, 14] Thus, while the vapor pressure of ethanol is 17.2 kPa, when it is mixed with gasoline, the vapor pressure of the final fuel considerably increases leading to vapor lock problems and excessive losses of fuel. [12]

The vapor pressure of mixtures of gasoline with oxygenates such as methanol or ethanol was increased. The maximum increase was denoted in the range of 5-10% v/v ethanol addition. [12, 15] The total elevation was characteristic of the additive. However, the existence and location of the peak was of interest for designing blended fuels for maximum performance and minimal environmental impact.[12, 15] Also, the RVPs of dual alcohol blends containing ethanol and 1-butanol in equal volume proportions lie approximately midway between those of the two single alcohol blends containing the same total alcohol volume concentration. Thus, the vapor pressure of dual alcohol blend can be approximated as the simple volumetric average of two single alcohol blends. [15]

A solution to encounter the increased volatility may be the common presence of ethanol and co-solvent as ETBE. Bioethanol and bio-ETBE (47% renewable fuel) are octane number boosters and their common presence in gasoline may be beneficial. [6] ETBE inhibits the elevation of gasoline volatility enhancing the addition of lighter costless products as butane, reacting as a stabilizer for ethanol-gasoline blends as regards the volatility as expressed by RVP. [6, 16] Another alternative suggestion approaching the before-mentioned statement may be the addition of the azeotropic mixture of ethanol/ETBE in gasoline. The azeotropic ETBE/ethanol mixture may be a possible oxygenated additive for the formulation of eurosuper-type gasolines. It was noticed that gasolines with azeotropic additives show lower vapor pressures than gasolines formulated with ethanol, and therefore low levels of volatile organic compounds, similarly to highly pure ETBE. Moreover, the use of the azeotropic mixture containing ethanol and ETBE in its formulation is environmentally attractive in industrialized countries due to the need to reduce carbon dioxide emissions. [17]

The impact of ethanol addition on vapor pressure of gasoline has been extensively studied, but there are data on the literature available only for final gasolines. Gasoline is prepared by blending the various refinery components at the proper quantities. Gasoline blending components have different compositions and different properties. Due to this different composition the addition of ethanol is expected to have different impact on each blending component. The objectives of this study were to determine the influence of ethanol addition in pure refinery gasoline blending components on Reid vapor pressure. The change of vapor pressure (delta-VP) due to ethanol addition on refinery components was examined, to determine the forces between ethanol and different type of hydrocarbons, which prevailed in refinery components. Consequently, blends were prepared by simulating commercial fuels, in order to investigate the effect of ethanol addition on volatility change of fuels, as clearly expressed by the change in vapor pressur values (Δ-VP).

II. Materials And Methods

The interpretation of volatility properties, according to the quality standard of commercial gasoline in Europe, is made on the basis of values of vapor pressure, which corresponds to the classic Reid Vapor Pressure (RVP). The aim of this experimental research was to determine the vapor pressure of gasoline blending components, and the fuels derived by blending these components with ethanol. The ethanol was added by 0.5% v/v step in the range of 0 – 2% v/v ethanol addition and then, by 1% v/v step, in the range of 2 – 10% v/v ethanol addition. The measurements were realized by the standardized method EN13106-1 and they were expressed in kPa.

Eight refinery blending components were used in order to determine the influence of ethanol addition on the vapor pressure of different types of hydrocarbons. The samples were supplied by Hellenic Petroleum SA, Aspropirgos Refinery, and Motor Oil SA, Corinth Refinery. The main properties of the refinery blending components are given in Table 1.

Table 1. Main properties of the refinery blending components

Properties	Units	Ref	Alk	Isom-1	Isom-2	FCC-1	FCC-2	LSR	TAME	Method
Density at 15 °C	kg/m^3	827.9	697.1	669.8	651.5	744.0	720.7	661.6	729.0	EN ISO 12185
Vapor Pressure at 37.8 °C	kPa	35.8	49.7	84.6	92.6	24.9	48.4	88.8	89.3	EN ISO 13016-1
RON		102.2	98.4	86.4	85.3	92.6	93.2	77.1	99.7	EN ISO 5164
MON		91.7	91.3	82.2	82.6	82.2	82.5	75.3	89.7	EN ISO 5163
Aromatics	% v/v	76.95	3.00	7.30	0.32	21.09	12.94	1.81	29.45	EN ISO 22854
Benzene	% v/v	0.73	0.14	0.20	0.13	0.77	0.32	1.79	0.49	EN ISO 22854
Olefins	% v/v					25.43	32.31		13.51	EN ISO 22854
n Parafins	% v/v	3.93	2.60	9.16	8.02	15.49	13.83	41.10	18.53	EN ISO 22854
iso Parafins	% v/v	17.22	89.71	72.21	82.38	23.23	20.75	43.13	17.81	EN ISO 22854
Naphthenes	% v/v	0.68	1.00	11.33	9.28	14.70	15.15	13.82	0.49	EN ISO 22854
TAME	% v/v								20.68	EN ISO 22854
Oxygen	% m/m								3.25	EN ISO 22854

The refinery fractions examined thoroughly were:

Reformate (Ref): This component is the product of heavy naphtha catalytic reforming. The naphthenes and paraffins are mainly converted to aromatics over platinum base catalyst. Side products may be produced such as LPG and hydrogen. The composition of Refomate fraction includes a high content of aromatic hydrocarbons. As a result, this fraction has excellent octane rating characteristics showing high RON and MON values and low volatility.

Catalytic Cracking Naphtha (FCC): This component is the product of Fluid Catalytic Cracking Unit. This unit breaks down the heavier and complex hydrocarbon molecules to simpler and lighter molecules by using heat and in the presence of zeolite based catalyst. Heavy hydrocarbons of vacuum gasoil (VGO) are converted into lighter and more valuable products, such as products in the range of gasoline (C5 – C10 hydrocarbons) and some middle distillate components. Other side products are gaseous olefinic hydrocarbons (mainly C3 and C4). FCC naphtha has a moderate octane rating due to high olefins content and a moderate aromatics level. In the present work, two different FCC samples were examined. FCC-1 is heavy catalytic cracking naphtha including mainly C6 – C9 hydrocarbons with a high olefin content showing very low volatility. FCC-2 is full range catalytic cracking naphtha with increased olefins content. This fraction contains mainly C5 – C9 hydrocarbons showing good octane characteristics and average volatility.

Isomerate (Isom): This component is the product of conversion of normal paraffins as included in light naphtha to isoparaffins. The composition of light naphtha contains a very low percentage of aromatics and a negligible percentage of olefins. The isomerate fraction examined contains mainly C5 and C6 isoparaffins. As regards its properties, Isomerate has low octane numbers (RON, MON) and high volatility. During the experiment procedure, two different batches of Isomerate were used and they were called as Isom-1 and Isom-2. In the first case Isom-1 was blended with about 10% Reformate in the Refinery in order to reduce the high vapor pressure of the pure isoparaffinic product (stabilized sample), and then, Isom-2 was a pure product as received from the Isomerization unit of Refinery. Light Naphtha (LSR): This component is hydrotreated light naphtha which is used mainly as feedstock for Isomerization units, or it may be used as blending component for finished gasoline. It is a volatile component containing mainly C5 and C6 normal paraffins and isoparaffins with low aromatics content, but with the total of them being the toxic benzene. Regarding its properties, LSR has low octane numbers.

Alkylate (Alk): This component is the product of the alkylation unit of refinery. This fraction comes from the chemical reaction between isobutane and light olefinic C3 and C4 hydrocarbons. All the procedure is carried out under a strong acid catalyst (sulfuric or hydrofluoric catalyst), giving highly branched chains but low aromatics, producing mainly isoparaffins with carbon numbers in the range C7 – C8. As regards alkylate properties, it has a high-octane value (excellent RON and MON). Alkylate is regarded as a high quality blending component due to the absence of aromatic and olefinic hydrocarbons. Also, it has an intermediate volatility.

TAME: This component is the product of the tert-amyl methyl ether (TAME) production unit. TAME is the product of reaction of active C5 isoolefins (isoamylenes) with methanol. C5 fraction is the light fraction of the FCC naphtha. The final product examined contains the fraction of C5 that has not reacted (C5 Raffinate), and a percentage of Reformate that has been added in the Refinery in order to reduce the vapor pressure of the

product. In the current work, the product used component contains about 20% m/m TAME. The addition of Reformate increases the content of aromatics. The presence of C5 fraction justifies its volatility. It is a volatile component with very high octane numbers. Apart from the refinery samples, fuel grade bioethanol was used in this series of experiments. The bioethanol sample used was "dry" with very low water content, and it was denatured with ETBE.

Table 2. Compositions of binary blends

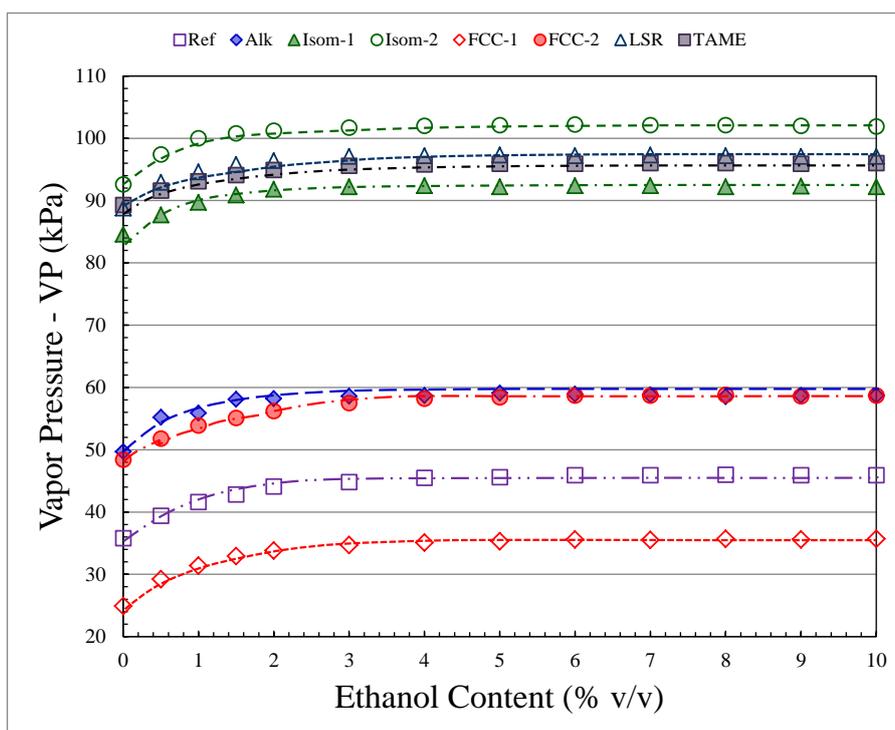| Name	Composition	Vapor Pressure at 37.8°C (kPa)
Blend 1	25% Alk + 75% Isom-1	69.1
Blend 2	50% Alk + 50% Isom-1	58.0
Blend 3	75% Alk + 25% Isom-1	48.8
Blend 4	25% Ref+ 75% Isom-1	65.7
Blend 5	50% Ref + 50% Isom-1	54.5
Blend 6	75% Ref + 25% Isom-1	42.7
Blend 7	25% FCC-2 + 75% Ref	32.1
Blend 8	50% FCC-2 + 50% Ref	33.2
Blend 9	75% FCC-2 + 25% Ref	37.8
Blend 10	25% FCC-2 + 75% Isom-1	67.7
Blend 11	50% FCC-2 + 50% Isom-1	58.1
Blend 12	75% FCC-2+ 25% Isom-1	49.1

Figure 1: Impact of ethanol addition on vapor pressure (RVP) of refinery blending components

III.   Results And Discussion

A. Refinery Blending Components

Vapor pressure is a property of fuel which was measured according to EN 13106-1 test method by employing the Grabner VPxpert apparatus. The Grabner VPxpert instrument function is based on a triple step expansion technique for the determination of the vapor pressure. In the set of experiments this instrument was employed for the measurement of the vapor pressure of refinery fractions and their blends containing ethanol.

The refinery components used have different values in their vapor pressures as displayed in Table 1. This behavior has to do with its composition. The less volatile component was the heavier FCC naphtha sample (FCC-1). FCC-1 composition contains mainly C6 – C9 hydrocarbons. The lower volatility of FCC-1 may be explained by the absence of the very volatile C5 and lighter hydrocarbons resulting in a low vapor pressure

value for this sample. Also, the whole FCC naphtha sample (FCC-2) was examined containing about 19% v/v C5 and lighter hydrocarbons. FCC-2 showed a significantly higher vapor pressure compared to FCC-1 sample. Also, Reformate sample has low vapor pressure since it contains a low percentage of 2% v/v C5 and lighter hydrocarbons. In contrast, the more volatile component of the examined components was Isom-2. Isom-2 composition includes over 80% v/v C5 and C6 isoparaffins. Additionally, the fraction Isom-1 had a lower vapor pressure compared to Isom-2, due to the addition of Reformate in the Refinery. Consequently, LSR is a very volatile component, since its composition includes 41.5% v/v C5 and lighter hydrocarbons. Finally, the Alkylate refinery fraction has an intermediate volatility justified by the presence of about 17.5% v/v C5 and lighter hydrocarbons, in the form of mainly isoparaffins.

Table 3. Composition of commercial like gasoline samples

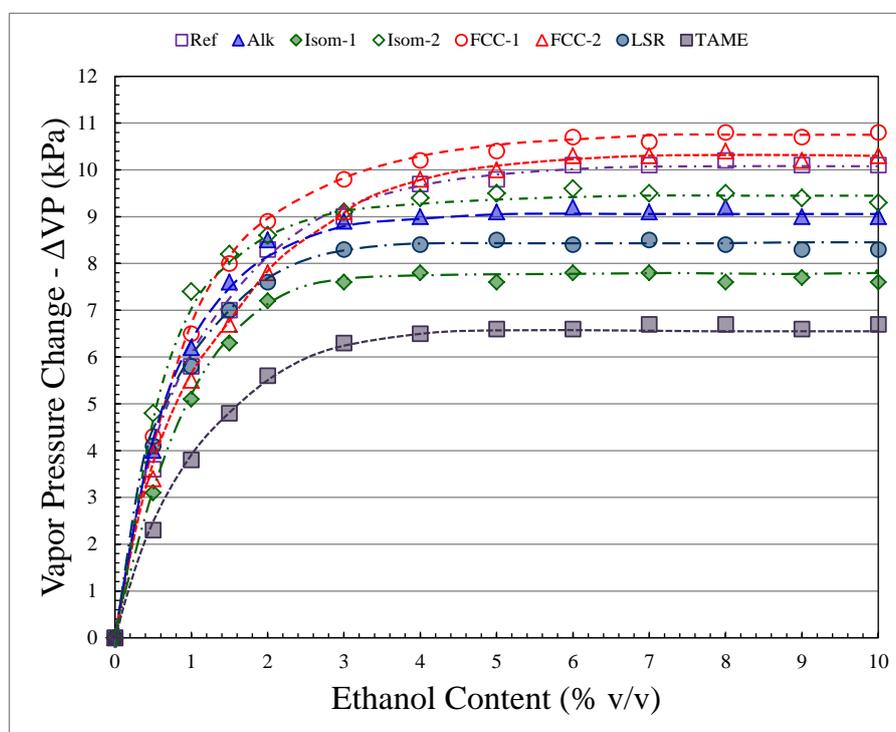| Properties	Units	G1	G2	G3	G4	G5	G6	G7	G8	G9	G10	G11	G12	Test Method
Density at 15 °C	kg/m³	743.1	730.3	745.6	730.4	725.6	720.6	729.9	730.5	717.2	713.3	726.2	724.2	EN ISO 12185
Vapor Pressure at 37.8 °C	kPa	43.8	50.7	54.1	53.9	52.3	51.9	59.9	61.3	63.7	70.5	69.4	70.0	EN ISO 13016-1
RON		95.5	93.5	96.2	94.7	93	92.9	94.6	95.5	91.7	90.8	94.3	94.8	EN ISO 5164
MON		87.7	85.4	86.7	86.2	84.8	84.7	86	84.5	83.9	83.4	86	86.3	EN ISO 5163
Aromatics	% v/v	32.94	27.85	34.81	27.71	25.92	22.99	29.67	29.87	22.16	22.09	28.98	27.71	EN ISO 22854
Benzene	% v/v	0.42	0.61	0.56	0.55	0.45	0.35	0.56	0.54	0.50	0.50	0.53	0.53	EN ISO 22854
Olefins	% v/v	9.69	6.46	10.41	7.79	9.69	11.31	7.87	7.27	9.69	8.08	6.60	7.95	EN ISO 22854
n Parafins	% v/v	8.07	12.33	6.69	8.49	10.52	9.42	7.91	6.81	12.38	12.48	7.60	6.94	EN ISO 22854
iso Parafins	% v/v	39.28	43.68	24.55	37.27	42.45	44.08	30.75	30.46	43.74	45.44	33.20	28.73	EN ISO 22854
Naphthenes	% v/v	7.72	7.72	6.11	6.70	9.42	10.02	6.43	5.18	10.08	10.40	6.26	5.66	EN ISO 22854
TAME	% v/v			6.20	4.14			6.20	7.24			6.20	8.27	EN ISO 22854
Oxygen	% m/m			1.01	0.68			1.03	1.20			1.03	1.38	EN ISO 22855

Figure 2: Impact of ethanol addition on vapor pressure change (ΔVP) of refinery blending components

It was observed that the addition of ethanol in the refinery components resulted into an increase in the vapor pressure of the blend. As shown in Fig. 1, the maximum vapor pressure was measured in the range of 4-

5% v/v ethanol. After the maximum value, a stabilization of vapor pressure was remarked. This change in vapor pressure is caused by ethanol intermolecular interactions that occur via hydrogen bonds as developed by the electronegativity between oxygen and hydrogen, leading to polarization of the bond. So, bond polarization gives ethanol a permanent dipole moment, leading to electrostatic interactions among molecules. These interactions were strong at a specific concentration in each ethanol – refinery component blend. [18] Except for hydrogen bond interactions there are other weaker interactions such as van der Waals interactions among hydrocarbons. Van der Waals interactions develop between opposite charged components as non polar compounds (low boiling point hydro-carbons) and polar compounds such as ethanol. These interactions contribute to drive earlier the ethanol from liquid to gas phase elevating the vapor pressure of blends by forming minimum boiling azeotropes due to a deviation from Raoult's law. All these interactions contribute to a deviation from the ideal linear blending vapor pressure of gasoline ethanol mixtures [9] In an ethanol addition percentage higher than 5% v/v, the vapor pressure stabilized since ethanol molecules remained in liquid phase and they didn't form minimum azeotropes with low boiling point hydrocarbons. [18] Thus, a negligible difference was recorded remaining at the same values of pressure. The vapor pressure of refinery components is displayed in Figure 1. The higher values were noticed for Isom-1 and Isom-2. LSR and TAME were following. These components have a high percentage of parafinnic hydrocarbons in their composition. The heavier components such as FCC-2, Reformate and FCC-1 followed.

In order to estimate the change of vapor pressure by ethanol addition, it was decided to present the difference of the vapor pressure of the samples containing ethanol from the vapor pressure of the pure component using delta VP, or ΔVP. The ΔVP changes are displayed in Fig. 2.
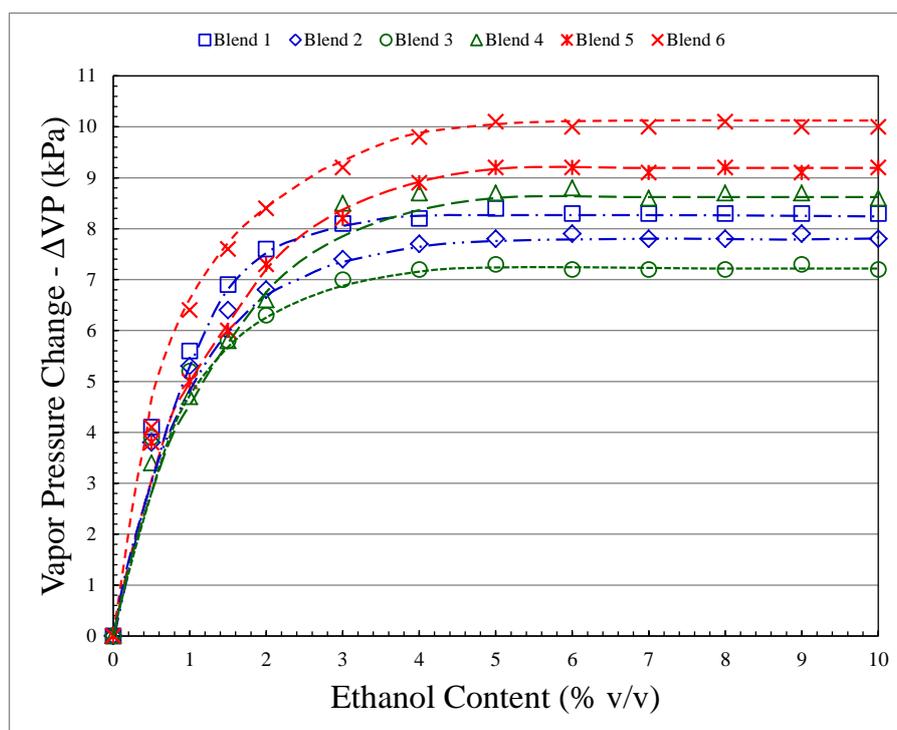

Figure 3: Impact of ethanol addition on vapor pressure change (ΔVP) of binary blends B1 – B6

The maximum vapor pressure change was denoted at 5 – 10% ethanol addition and the corresponding change was over than 7 kPa (1 psi) reaching values at 10 kPa. As shown in Fig. 2, lower values of vapor pressure change were recorded for lighter components such as Isomerate fractions. Particularly, the maximum change for Isom-1 (stabilized sample) was 9.5 kPa and for Isom-2 (the pure Isomerate component) was at 7.6 kPa. For alkylate component at 9.4 kPa. This behavior may be justified by the fact that both Isomerate and Alkylate components mainly contain isoparaffins. Isoparaffins are molecules with low polarization. Thus, a similar interaction with ethanol molecules is expected, leading to a similar increase in the vapor pressure value. As regards LSR, the main difference with Isomerate fraction is the percentage of normal paraffins to isoparaffins. Especially, in the case of LSR the ratio of normal to iso paraffins is near 1÷1, while in the case of Isomearate this ratio is about 1/10. For Light Naphtha (LSR) a quite lower value of ΔRVP was noticed reaching 8.5 kPa. In addition, the highest increase of vapor pressure was at 10.4 kPa and it was recorded for the heavier components of FCC Naphtha (FCC-1) and then for FCC-2 and Reformate which was at 9.4 kPa. [6, 10, 19]

B. Binary Blends

The continuation of work included the preparation of binary blends where ethanol was added in the range of 0.5 – 10% v/v so as to assess the molecular interactions between different types of hydrocarbons and ethanol. All the blends prepared and measured are presented in Table 2. For the preparation of binary blends the whole FCC fraction (FCC-2) and the Isom-1 (stabilized sample) were used as blending components. The volatility change was expressed by ΔVP.
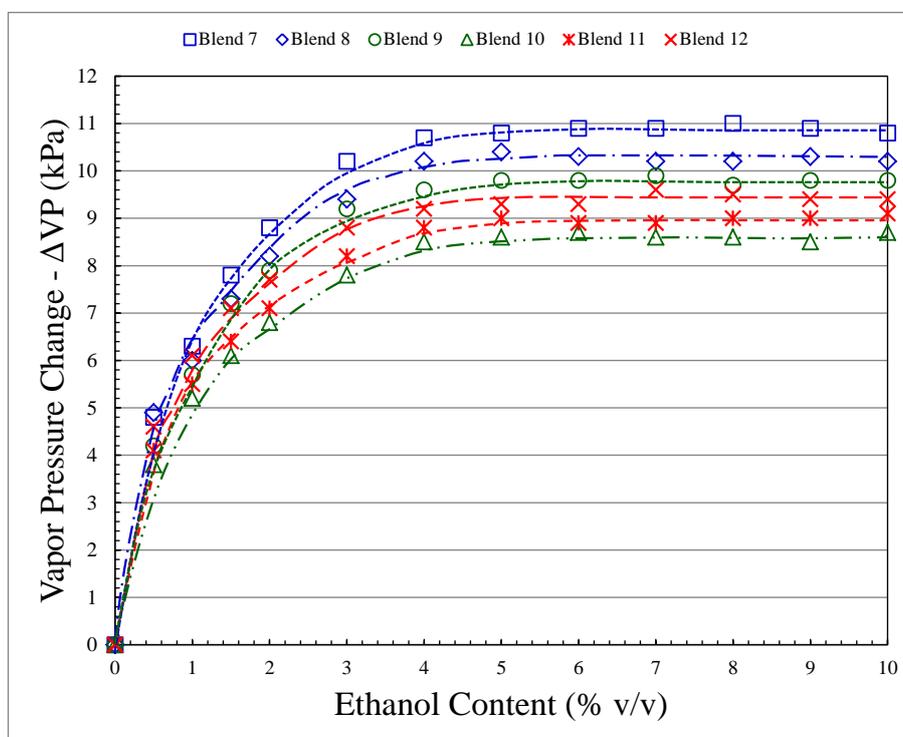

Figure 4: Impact of ethanol addition on vapor pressure change (ΔVP) of binary blends B7 – B12

As depicted in Fig. 3 and Fig. 4, the maximum increase of vapor pressure for binary blends was depicted at 5% v/v ethanol addition and for Blend 6, Blend 10 and Blend 8 showing a change of 11.1, 10.4 and 9.6 kPa respectively. Close values were recorded for Blend 12, Blend 11 with ΔRVP values recorded at 10, and 9.3 kPa. Lower values were recorded for blends: Blend 1, Blend 2, Blend 3, Blend 9 reaching a change of 8.6, 8.6, 8.1, 8.0 kPa respectively. Even lower change was noticed for Blend 4 at 5.2 kPa. These measurements revealed that the van der Waals forces between polar hydrocarbons (such as olefins and aromatics in FCC and Reformate fractions) and ethanol are rather strong due to the available electrons (π-electrons) leading to an increase of vapor pressure. [6, 10, 19] In binary system with paraffinic components as Alkylate and Isomerate fractions, a smaller increase of RVP was noticed at 5% v/v ethanol addition. Specifically, Blend 1 and Blend 2 yielded a change of 8.6 kPa respectively. The presence of Isomerate and Alkylate fraction in blends increased the paraffinic character of the fuel, revealing a moderate increase of delta vapor pressure. The more polar hydrocarbons (aromatics, olefins) formed easier strong minimal azeotropes with ethanol, increasing thus the vapor pressure. Aromatics have available six electrons while in FCC fraction one-pair of electrons (π- bond) is available. In contrast, in paraffinic hydrocarbons, σ-bonds are created with no available electrons a fact that affects the interactions between hydrocarbons and ethanol molecules and may justify the lower increase of vapor pressure. [6, 10, 19]

C. Commercial Gasoline Blends

Consequently, twelve multicomponent blends were prepared so as to simulate the behavior of commercial gasoline. Seven summer grade fuels or Class A and five winter grade fuels or Class C were prepared. This classification was in accordance with their vapor pressure. The blends prepared are given in Table 3 and the composition of these blends is shown in Table 4. In these samples ethanol was added from 0.5 to 10% v/v. A higher percentage of volatile components such as Isomerate and LSR contributes to a higher vapor pressure value, which is needed for cold climates, which require a more volatile fuel in order to achieve ignition at low temperatures.
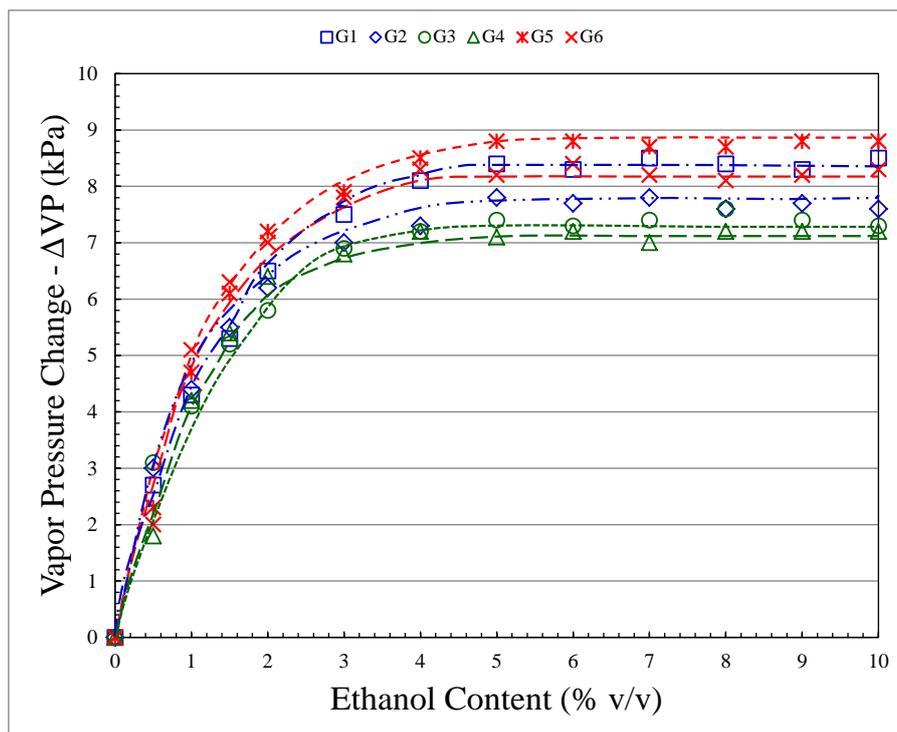
Figure 5: Impact of ethanol addition on vapor pressure change (ΔVP) of commercial type gasolines G1 – G6

The composition of G1 corresponds to a low volatility summer grade (Class A) fuel according to the volatility classification of EN 228 (45 – 60 kPa). This fuel had the lower volatility. The ethanol addition at 5% v/v led to an increase in vapor pressure of 8.6 kPa. This vapor pressure change may be explained by the presence of Reformate and FCC in significant amounts of 35% v/v and 30% v/v respectively. The addition of 5% v/v ethanol led to an increase of vapor pressure at 19.6%.(Fig.4)

In G2 gasoline composition, the polar (olefinic and aromatic) hydrocarbons content was reduced. In G2 composition, LSR refinery fraction was added (15% v/v) and the alkylate concentration increased to 15% v/v. The vapor pressure of gasoline G2 was higher than G1 due to the presence of more volatile compounds (LSR). The 5% v/v ethanol addition led to an increase of the vapor pressure at 7.8 kPa or 15.4% vapor pressure change. According to published works similar percentages of ethanol addition (4-5% v/v) drove to the maximum vapor pressure change. In higher percentages of ethanol addition a stabilization of vapor pressure followed (Fig.5, Fig. 6). [18] It was noticed that the reduction of polar compounds led to a direct decrease of vapor pressure change in the same percentage of 5% v/v ethanol addition.

Additionally, gasoline blends G3, G4, G5, G6 are classified as summer grade fuels. G3 sample is low in paraffinic hydrocarbons including a high percentage of TAME. G4 sample has higher content of paraffinic hydrocarbons including Isom-1, LSR, Alkylate fraction and a lower content of olefinic and aromatic hydrocarbons. G5 and G6 have higher paraffinic hydrocarbons content, with low aromatic content and rather high olefinic hydrocarbons content. The higher vapor pressure increase was measured in samples G5 and G6 with delta vapor pressure measured at 7.9 and 8.2 kPa or 15.1% and 15.8% respectively. In samples G3 and G4 the maximum vapor pressure change was at 7.1 kPa for both samples that corresponds to 13.9% and 13.4% respectively. Another significant difference between G3, G4 and G5, G6 fuels is that G3 and G4 samples contain TAME, while G5 and G6 do not. (Fig. 5) According to the bibliography, some ethers may form azeotropes with ethanol.

The formation of such azeotropes may reduce the ethanol molecules that are available for the interactions with small molecular weight hydrocarbons. The less available ethanol and the less the interactions of ethanol and hydrocarbons may result in a smaller vapor pressure change. [9, 17]

The gasoline samples G7, G8, G9, G10, G11, G12 simulate winter grade fuel. As shown in Table 3, the percentage of volatile compounds was rather high. The winter grade fuels should have a vapor pressure in the range of 60 – 80 kPa, according to the EN 228:2012. G9 and G10 gasolines do not contain any TAME in their composition, while the other 4 samples have significant content of TAME in their composition. At 5% v/v ethanol addition, the increase in the vapor pressure for the winter grade fuels was from 6.5 to 7.8 kPa, while for summer grade fuels this change was in a higher range of 7.1 – 8.8 kPa. The lower increase of delta vapor pressure was denoted for samples G11 at 6.5 kPa, and for G12 at 6.1 kPa. These samples contain Isomerate (Isom-1) in high percentages, low percentages of polar components (FCC and Reformate) and high percentage

of TAME. As mentioned in the previous paragraph, ethers like TAME may form azeotropes with ethanol, and thus, may reduce the amount of minimum boiling azeotropes that are formed between hydrocarbons and ethanol molecules. [17] Samples G7 and G8 which also contain TAME in high percentage, revealed a same behavior as samples G11 and G12, with slightly higher delta vapor pressure values, at 6.4 and 7.1 kPa or 10.7% and 11,6% change. The higher increase of delta vapor pressure was measured for G9 with ΔVP at 7.8 kPa or 12.2% increase and G10 with ΔVP at 6.7 kPa or 9.5% increase. Gasoline G9 had a higher content in polar FCC component (FCC-2) compared to G10. In turn, gasoline G10 had a higher content of non polar components such as Isomerate and LSR compared to G9 sample. For this reason gasoline G10 showed a smaller change of vapor pressure due to the addition of the ethanol (Fig. 6).
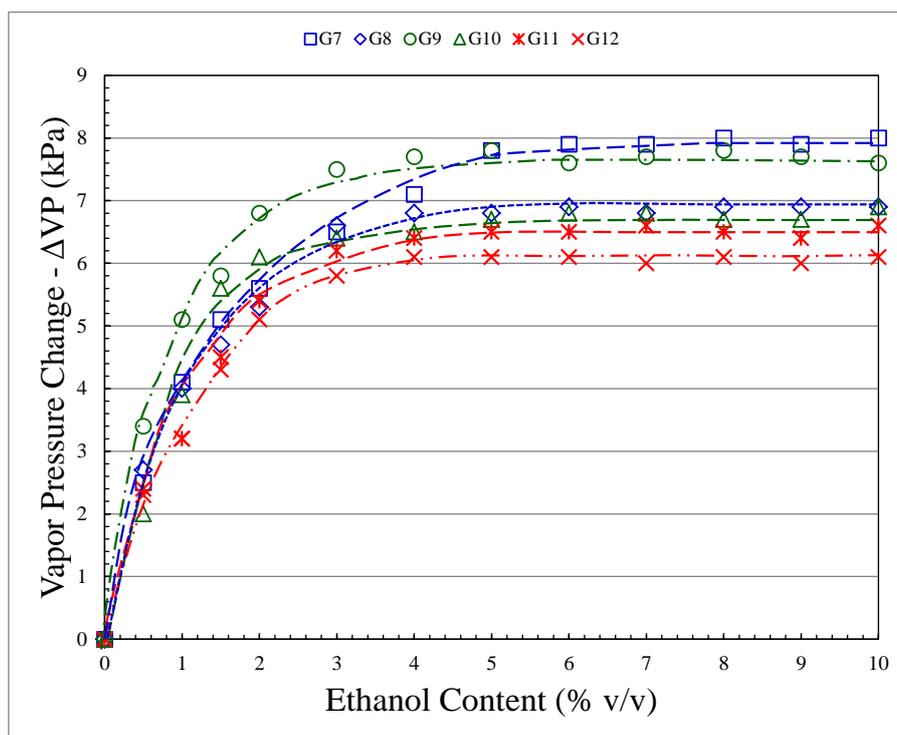

Figure 6: Impact of ethanol addition on vapor pressure change (ΔVP) of commercial type gasolines G7 – G12

IV. Conclusion

European member states have to comply with the Directive 2009/30/EC, which mandates the use of biofuels in motor fuels. As result, blending of bioethanol into automotive petrol is obligatory. Ethanol addition significantly affects the properties of motor fuels such as volatility as expressed in the present work through the vapor pressure or ΔRVP change. In all samples vapor pressure was measured according to EN 13016 test method at 37.8 °C (100 °F). The objective of this study was to determine the influence of ethanol addition (from 0.5 to 10% v/v) on vapor pressure of refinery streams used for gasoline blending and also, in blends that simulate commercial motor gasoline fuels. Results showed that the composition of the fuel had impact on the vapor pressure increase. The more polar blending components as Reformate and FCC Naphtha, which contain the higher concentrations of aromatic and olefinic hydrocarbons, had the higher relative increase in their vapor pressure. Paraffinic components like Isomerate and Alkylate revealed a slightly less increase in their vapor pressure due to the addition of ethanol. Less volatile components led to a more significant vapor pressure change. As well as, the refinery components that contain tert amyl methyl ether (TAME) revealed the smaller relative increase of vapor pressure when ethanol was added in these samples. Ethers such as TAME can form azeotropes with ethanol and as a result, may reduce the available ethanol to form minimum boiling azeotropes with the small weight hydrocarbons of gasoline. All the before-mentioned assumptions must be taken under consideration in the case of commercial gasolines which should meet the specifications set by EN 228:2012 standard.

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