The Effect of Bio-ethers on the Volatility Properties of Oxygenated Gasoline

MIHAELA NEAGU PETRE1*, PAUL ROSCA, RALUCA-ELENA DRAGOMIR

Petroleum- Gas University of Ploiesti, Faculty of Petroleum Refining and Petrochemistry, 39 Bucuresti Blv., Ploiesti, Romania

One way to reduce the vented pollutant emissions from vehicles and also to extend the raw material base is to use oxygenated bio compounds as substitutes of some parts of conventional gasoline. The volatility properties of substituted gasoline with bio-ethers influence both the vehicle engine running and hydrocarbon losses by evaporation. A study regarding the effect of substituting two types of classical gasoline with different compositions and properties with the proportion varying between 4 to 15% vol. of methyl tert-butyl ether (MTBE), tert-amyl methyl ether (TAME) and bio- ethyl tert-butyl ether (bio-ETBE) on the Reid vapour pressure, on the distillation curves and vapour lock index is presented in this paper. The experimental results were interpreted by comparison with the values of these specified properties by commercial gasoline quality European standard, EN 228. In the commercial gasoline formulation it has become very useful to establish some relation for calculating the Reid vapour pressure of the evaporated percentage at the temperature of 70°C (E70) and vapour index (VLI), so that the screening in the volatility classes be quickly predicted. Because the literature doesn't present such calculation relation, in the final part of this paper we suggest some empirical relation by means of which this properties are determined depending on base gasoline characteristics, on type and ratio of used ether addition in the formulation recipe.

Keywords: gasoline, bio-ethers, volatility properties, calculation relations

The use of oxygenated compounds for auto - gasoline reformulation in order to improve their quality and reduce carbon monoxide and unburned hydrocarbon emissions are a common practice. Introducing some oxygen percentage in auto – gasoline is obligatory in all the EU countries. The revised Fuel Quality directive 2003/30/EC has recently been adopted, that being a constitutive part of the EU Climate Change and Energy Package, adopted by the EU in April 2009 [1].

The gradual reduction of life cycle GHG emissions per energy unit from fuels and energy supplied from transport by 6% until 2020 as compared to the level in 2010 is required by this directive.

Another requirement of the directive is to increase the share of oxygenated compounds, as well as the total oxygen content to reach 3.5% weight. At car manufacturers' demand the oxygen content will be maintained at the maximum 2.7% weight, at least until 2013. The role of oxygenated compounds ether type (with five or more carbon atoms in molecule) in auto-gasoline formulation will be decisive because their content will be increased from 15 to 22% vol.

The MTBE (methyl *tert*-butil ether; 2-methoxy-2methylpropane) is the most produced oxygenated compound in the EU and US. In the '90s, the MTBE market has seen a significant increase. In 1999, the consumption was over 20 million tons/year, almost double than in 1992. The MTBE introduction in gasoline has a double role, the first one being to enhance its octane number and the second one being to reduce the exhaust gases emissions (by 10 – 15% the CO emissions, 1.0 - 1.7% NO_x and by 10 - 20% the total hydrocarbon emissions) [2].

Despite these multiple advantages, its popularity has declined dramatically as a result of one harmful property, which is its high solubility in water and the possibility to contaminate drinking water. The intensive usage and underground storage tanks of MTBE raised environmental pollution issues at least in the US, this leading to a negative perception coming from the public and finally its being forbidden starting with 2005.

Europe does not fully share the views of the US on using MTBE. Many studies and debates have concluded that the benefits of using reformulated gasoline with MTBE, both in terms of improving fuel quality and of reducing emissions into the atmosphere, are more obvious than the disadvantage created by leakage from storage tanks [3-6].

The role of MTBE increased considerable after the introduction in 2004 of the European Standard EN 228, which specifies the reduction of aromatic hydrocarbon content from 42 to 35% vol. At that time the MTBE was the appropriate oxygenated compound that could compensate the octane loss.

There are over 50 plants in Europe, with production capacities of ethers ranging from 15.000 tons to 600.000 tons/year. While in 2006 they produced mostly MTBE (and some TAME), starting with 2008 the interest for ETBE (ethyl *tert*-butyl ether; 2-ethoxy-2-methylpropane) has increased [7]. The ETBE is considered to be semi-renewable because it can be produced by the etherification of isobutene, from mixture of C_4 isomers with bio-ethanol [8].

Over 63% ⁴ of the etherification plants from Europe have been converted into bio-ETBE plants Only one plant in Germany produces *tert*-amyl ethyl ether (TAEE; 2-ethoxy-2-methylbutane) and has a capacity of 160 t/year) [7]. Most of these plants are in Germany, France and Spain. The costs for converting an MTBE unit into an ETBE unit (revamping costs) are very low [8].

The interest for producing tert-alkyl ethers is growing, because producing the reformulated gasoline is a requirement with respect to EURO standards and also contributes to the reduction of pollution. The most

^{*} email: mpetre@upg-ploiesti.ro; Tel. +40 721 527 037

important pollutants resulted from internal combustion engines are carbon monoxide, unburned hydrocarbons, nitrogen oxides and material particles. The reformulated types of gasoline with oxygenated compounds contain less aromatic hydrocarbons such as benzene, toluene, xylenes. All in all, these types of gasoline have a lower content of reactive hydrocarbons and a lower tendency of releasing unburned (or partially oxidized) hydrocarbons [9].

The studies performed on the car engines using various types of gasoline with low content of aromatic hydrocarbons indicated a decrease of carbon monoxide emissions by 12.5 – 13% weight, of NMHC (non-methane hydrocarbons) by 12% and a significant decrease of benzene emissions [10]. However, some studies showed that an increase of formaldehyde and acetaldehyde concentration resulted in emissions from types of gasoline burning with reformulated MTBE and ETBE [11-13].

The use of oxygenated compounds as substitutes of a part of vehicle gasoline influences the volatility, density, octane rating, combustion enthalpy, fuel consumption and level of vented gas emissions [14].

The present tendency to especially reduce the vapour pressure is justified by the connection between this and hydrocarbon losses by evaporation. The ethanol or methanol mixed with gasoline has the tendency to increase the Reid vapour pressure, and thus hydrocarbon losses by evaporation. From this point of view, more favorable are IPA (isopropanol) and TBA (tert-butanol) because these two compounds can decrease the Reid vapour pressure of reformulated gasoline [15]. As far as the hydrocarbon emissions and vapour pressure are concerned, the ethers appear to be more attractive [14, 16].

A comparative study of the volatility properties (distillation curves, Reid vapour pressure and vapour lock index) between one type of reformulated non-oxygenated gasoline, compared to the same properties of an oxygenated type of gasoline with 4, 7, 10 and 15 % (v/v) ethers is presented in this paper.

We chose, as oxygenated compounds, the ethers produced by the Romanian industry today and which are used as substituents for commercial types of gasoline, MTBE and TAME, as well as an ether which is to be obtained and used soon. Depending on the bio-ethanol production stage, the present units for etherification can be easily converted to produce bio-ETBE. The experimental study of volatility properties and the results' interpretation in terms of the influence of ether type and its content on them will show the benefits of using bio-ETBE as substitute of present gasoline.

The experimental study described in this paper is part of a larger project through which we try to explain the changes of the physico-chemical properties of conventional gasoline when this is substituted with primary alcohols and/or ethers in different proportions.

Experimental part

Methods

The distillation curves, Reid vapour pressure (RVP), octane numbers, basic chemical composition of conventional and reformulated gasoline were verified in this study, using the top of the range equipment in our laboratory as well as standardized work methods.

IROX 2000 Fuel Portable Gasoline Analyzer with MID-FTIR from Grabner Instruments was used for establishing the chemical composition and octane number of gasoline. The tests were carried out according to the following standards: ASTM 5845 (specific oxygenated compounds), ASTM D 6277 correlated with EN 238 (specific aromatic hydrocarbons), ASTM D 1319 (total aromatic, olefin and saturated hydrocarbons, oxygenated compounds), ASTM D 2699 and D 2700 for RON and MON.

For determining the Reid vapor pressure a MINIVAP VSP/ VPSH Vapor Pressure Tester device by ASTM D 5191 standard was used. The gasoline distillation was made according to ASTM D 86 or EN ISO 3405 standards, using a MINIDIS Mini – distillation analyzer from Grabner Instruments.

Materials

The effects of the oxygenated compounds content (MTBE, TAME, ETBE) in gasoline, was evaluated for a base gasoline composition noted as GasA. The basic fuel coming from the oil refinery contains 43% reformate, 22% isomerate and 35% FCC naphta (v/v). The samples were prepared by volumetric methods in the laboratory, avoiding the gasoline vapours leakage. The samples contain 4, 7, 10 and 15% vol. ethers. The physico-chemical properties and octane numbers for GasA and ethers are shown in table 1 and table 2.

The anhydrous methyl *tert*-butil ether (MTBE) for synthesis/Merck, *tert*-amyl methyl ether (TAME) by min. 97% purity/ Aldrich, ethyl *tert*-butyl ether (ETBE) for synthesis/Merck were used as starting materials. All ethers were kept in original containers and were subsequently stored in a refrigerator protected from humidity.

Results and discussions

Volatility properties of gasoline oxygenated with ethers

The volatility is the property that shows how easily a fuel can evaporate in the engine. This can be expressed using vapour pressure and distillation curves. The level of emissions of volatile compounds in the gasoline supply system and in the combustion when starting the engine on cold days and in continuous operation on hot days is significantly influenced by the vapour pressure [21].

The type of hydrocarbons and their distribution into gasoline composition influences the distillation curves of gasoline which is related to the combustion performances of gasoline and the engine running. The information about ease engine starting and the hydrocarbons evaporation are indicated by the first part of distillation curve. The middle

 Table 1

 PHYSICO-CHEMICAL CHARACTERISTICS

 AND OCTANE NUMBERS OF GasA

Physicochemical characteristics	GasA
Specific mass at 25°C (kg/m3)	755
Vapor pressure at 37.8 °C (kPa)	55.9
Research octane number - RON	95.0
motor octane number - MON	85.0
Antiknock index AKI=(RON+MON)/2	90.0
Aromatics (vol%)	38.1
Olefinics (vol%)	12.9
Saturated (vol%)	49.0
Evaporated % at 70°C	33.0
Evaporated % at 100°C	51.5
Evaporated % at 150°C	78.0
Final boiling point (°C)	190.4

Ether	MTBE	TAME	ETBE		
CAS number	1634-04-4	994-05-8	637-92-3		
Structural formula					
Chemical formula	$CH_3 = O = C(CH_3)_3$	$C_2H_5 - C(CH_3)_2 - O - CH_3$	(CH3) ₃ COCH ₂ CH ₃		
Molecular weight, g/mol	88.15	102.18	102.18		
Density, g/cm ³	0.741	0.764	0.7519		
Normal Boiling temperature, C	55.09	86.30	72.86		
RVP, kPa	55.2	10	28		
Oxygen, % wt	18.15	15.7	15.66		
Solubility in water,	4.8 g/100 g	1.2 g∕100 g	1.2 g/100 g		
Blending RON/MON	115-118/101	109-112/98-99	117-119/102-103		

 Table 2

 PHYSICAL AND CHEMICAL PROPERTIES OF FUEL OXYGENATES TYPE ETHERS AS PARTIAL

 SUBSTITUTES COMPOUNDS OF COMMERCIAL GASOLINE [17-20]

part of distillation curve gives details about engine behaviour on smooth running, the short trip fuel economy and the fuel consumption. The long trip fuel economy, the behavior in the lubricating oil dilution and its deposits on engine block are indicated by the last part of distillation curve.

The volatility properties are dealt within terms of EN 228 international standard. According to EN 228 standard, based on the distillation curve the following values are obtained: the percentage of evaporated fuel at a temperature of 70°C (*E70*), at a temperature of 100°C (*E100*) and 150°C (*E150*), the final point of distillation and the residue content of gasoline. The limits which can vary these quantities are specifics for the volatility classes of gasoline. The European standard regarding the quality gasoline provides six classes of volatility based on summer, winter and transition period.

The tendency of fuel to form vapor plugs, noted *VLI* (vapour lock index), is calculated with relation:

$$VLI = 10 . VP + 7 . E70$$
 (1)

based on the percentage of evaporated fuel at 70°C (E70) and Reid vapor pressure.

In terms of volatility classes, the *A* volatility class (with *RPV* for summer time 45-60 kPa) and the D/D1 volatility class (with *RPV* for winter time 60-90 kPa) have more practical applicability.

Distillation curves

According to the EN 228 standard, the distillation curves can be interpreted through the representative values of evaporated percentages of fuel at various temperatures: 70°C (*E*70), 100°C (*E*100) and 150°C (*E*150). The distillation curves of oxygenated gasoline compared with the one of the base gasoline are shown in figures 1-3. Based on the experimental setup, representative values for the distillation of GasA as well as for these oxygenated types



Fig. 1. The influence of MTBE over the distillation curves of gasoline-MTBE blends.





of gasoline with 4, 7, 10 and 15% vol. ethers have been obtained from their distillation (figs. 4-6).

The vaporized percentage increases in the presence of MTBE and decreases in the presence of TAME or ETBE (fig.



Fig. 3. The influence of ETBE over the distillation curves of gasoline-ETBE blends



Fig. 4. The influence of ethers over the percent evaporated at 70°C

4) at a temperature of 70° C (*E70*). This behavior is justified by the boiling temperatures of ethers (table 2) and their effect on the hydrocarbon volatility from the first part of the distillation curve. The introduction of MTBE, with the lowest boiling temperature (55.09°C) from all studied ethers, allows an easier evaporation of its mixtures with hydrocarbons from 70° C zone of gasoline distillated curves.

Thus, for gasoline with 15% MTBE, the evaporated percent increases by 10% than the base gasoline GasA. Instead, the TAME which has the boiling temperature 86.3°C will have as effect a decrease of percentage that can evaporate at this temperature. For example, in the case of the gasoline oxygenated with 15% vol. TAME, the decrease is by 5%. As previously explained, because of fact that ETBE has a boiling temperature (72.86°C) near 70°C it has a minor effect on the *E70*. More specifically, at the gasoline oxygenated with 15% vol. ETBE, a decrease by only 3% of evaporating at 70°C occurs.

The effect of the ethers on the evaporated percentage at 70°C is directly proportional with the content of oxygenated compound added to the gasoline (fig. 4).

In terms of engine running, the gasoline oxygenated with MTBE enhances cold start of vehicles by increasing the fuel evaporation in the first zone of the distillation curve, but without raising too much problems with the appearance of vapor plugs. The gasoline oxygenated with TAME, even if this evaporates more difficultly, can be supplementary additivated with C_4 fraction to correct this deficiency.

The evaporation at 100°C increases in the presence of ethers with the boiling temperature lower than 100°C as



Fig. 5. The influence of ethers over the percent evaporated at $100^{\circ}C$



Fig. 6. The influence of ethers over the percent evaporated at $150^{\circ}C$

MTBE, ETBE or TAME. As shown in figure 5, the ethers influence on the *E100* increasing, in the following order: MTBE>ETBE>TAME. The introduction of 15% vol. MTBE in the base gasoline leads to an increase by 10.5% of the evaporated. The same content of ETBE, added to gasoline increase by 6% of the evaporated percentage. The effect of the TAME, due to its boiling temperature of 86.3°C, is an increase by only 3.5% the evaporated at a temperature of 100°C. From the point of view of engine gasoline behaviour, the value *E100* indicates the behavior at the vehicle starting, the fuel economy for short distance and the fuel consumption. The gasoline oxygenated with MTBE, ETBE or TAME means that they offer to the vehicle easier starting and smaller fuel consumption, due the evaporation much more than conventional gasoline at the 100°C.

The evaporated percentages at the 150°C (*E150*), from the gasoline oxygenated with the studied ethers, increase with the increase of each ether content (fig. 6). From point of view of these types of gasoline behaviour in the vehicle engine, at 150°C, the effect is favorable because the increase of fuel economy for short distance, enhances the lubricating oil dilution and reduces the deposits on the engine.

In conclusion, MTBE favors the evaporation on the all distillation curve of oxygenated gasoline. ETBE, although slightly affects the evaporation at 70°C, has the advantage that favors the evaporation on the middle and last part of the distillation curve. TAME disadvantages the evaporation at 70°C, but advantages the evaporation at 100 and 150°C temperature.

According to the EN 228 standard, the representative values of the evaporated percentages from the fuel at



The vapor lock index (VLI) for ether contents: Ether Volatility class 0% vol 4% vol 7% vol 10% vol 15% vol MTBE 790 815.60 826.88 841.11 860.19 A TAME 790 752.50 707.70 775.00 736.70 Α ETBE 790 774.00 759.00 746.50 725.00 Α

certain temperatures: *E70, E100* and *E150*, place the studied gasoline in the volatility category A, corresponding to summer gasoline.

The interpretation of volatility properties, according to the quality standard of commercialized gasoline in Europe, is also made on the basis of values of Reid vapor pressure. Our experimental research was to determinate the vapor pressures at the temperature of 37.8° C for base gasoline GasA and for those obtained by its oxygenation with 4 – 15% vol. ethers, by the standardized method ASTM D 5191. The results, expressed in kPa, for the base gasoline and for the oxygenated ones with ethers, are presented in the figure 7.

As seen, the introduction of ethers in the gasoline influences the vapor pressures of gasoline. The presence of MTBE leads to a slightly increase of vapor pressure of oxygenated gasoline. In the presence of the TAME and ETBE, whatever their content, the vapor pressures of oxygenated gasoline are lower than those of GasA gasoline. The decrease of vapor pressure is more accentuated with increase of the ethers content. The decreasing a vapor pressure of fuel by adding the oxygenated compounds is a positive, because the losses of evaporated hydrocarbons are smaller during refueling and from the vehicle fueling system.

According to the volatility classes of gasoline, in terms of vapor pressure, the EN 228 standard places the oxygenated gasoline with ethers, in the class A, corresponding to the summer season. The addition of C_4 fraction to oxygenated gasoline increase the vapor pressure values to the cold season level. Such flexibility in the use of gasoline oxygenated with ethers, especially of those with ETBE, gives them a favorite place in the commercial gasoline producers options.

At the end of the interpretation of volatility properties of gasoline oxygenated with ethers, based on experimental data, with equation (1), we have been able to calculate the vapor lock index (*VLI*). Knowing *VLI*, besides other volatility properties, allows a complete and correct positioning in the volatility classes of gasoline, according to the EN 228 standard.

As shown (table 3), VLI of gasoline oxygenated with MTBE are higher than GasA gasoline, due to both *E70* values

Fig. 7. The influence of the ethers on the vapor pressures of oxygenated gasoline

Table 3VLI INDEX AND VOLATILITY CLASSOF GASOLINE OXYGENATED WITH
ETHERS

and vapor pressures, influenced upwards by almost all concentration range of tested ethers in this paper. In the case of gasoline oxygenated with TAME and ETBE, *VLI* decrease with the increase of ether content, the decrease occurring due to both lower values of evaporated percentage at the temperature by 70°C (*E70*) and lower vapor pressure. No matter the ether type and its content, *VLI* of oxygenated gasoline is kept in the volatility class A, as base gasoline GasA.

Proposals on mathematical correlation of volatility with physico-chemical properties of ethers and base gasoline

The vapor index *VLI* has been calculated in the present paper with equation (1), indicated by the quality standard of commercial types of gasoline in Europe EN 228, which came into force in 2004. The equation (1) is valid for both non-oxygenated and oxygenated types of gasoline with primary alcohols or ethers. As previously seen, for using this equation, is need to obtain experimentally the distillation curves and Reid vapor pressure for various types of gasoline. The experiments involve top of the range equipment and time, which vehicle fuels producers do not always have at hand. Our purpose, based on the experimental data that we have obtained, is to find mathematical correlations for calculating the Reid vapor pressures and the evaporated percentage at a temperature of 70°C, correlations based only on base gasoline characteristics and type and content of ethers [22].

A large number of experimental data, included in a database should be useful to provide the opportunities for the validation of our proposed correlations. For now, based on the experimental data obtained for a synthetic gasoline, we can only propose an empirical equation, with application in the range of 4-15% vol. ethers. From the effect of ethers on the analysis and interpretation of changes occurring in the distillation curves and the oxygenated gasoline vapor pressure, we believe that, both, physical and chemical properties of gasoline oxygenates and base gasoline are decisive factors.

The graphic representation of the volatility experimental results (*E70* values from figures 4-6 and Reid vapors pressure from fig. 7) showed a second order polynomial

Table 4 COEFFICIENTS OF REGRESSION EQUATION AND REGRESSION QUALITY

Coet	fficients of the sec	Analysis of regression quality				
Reid vapor pressures						
Oxygenated compounds	A	B ₁	B ₂ R		SD	
MTBE	55.99773	0.00228	0.02149			
TAME	55.87498	-0.25175	-0.00403	-0.00403 0.99939 0		
ETBE	56.00968	-0.22545	22545 0.0006529 0.99980 0.0		0.02437	
	Evaporated percentage a 70°C temperature					
	A	<i>B</i> ₁	B ₂	R	SD	
MTBE	33.09996	0.82693	-0.01351	0.99693	0.28113	
TAME	32.9939	-0.38173	0.00326	0.99940	0.02010	
ETBE	33.05937	-0.34475	0.00927	0.99222	0.15023	

(2)

variation according to the content (% vol.) of oxygenated compounds. The equation is: $Y = A + B_1 X + B_2 X^2$

Y is the Reid pressure vapor (in kPa) or evaporated percentage at 70, 100 and 150°C of the gasoline oxygenated with ethers:

X- ether content (in % vol.);

A, B_{v} , B_{z} - constants whose values depend on the basic gasoline properties and physico-chemical properties of pure ethers.

The experimental data regression of the Reid vapor pressures *RPV* and the *E70* values recorded from the distillation curves of the investigated types of gasoline are showed in table 4.

The data from table 4 show a good quality of the regression, the determination coefficient R tends to 1, and the standard deviation SD to 0. Normally, the coefficient A of the polynomial equation for the vapor pressure calculation is very close to the vapor pressure of the base gasoline (55.9 kPa) and the coefficient A of the equation used to calculate the evaporated percentage at a 70°C temperature is E70 for Gas A (33 %vol.). Coefficients B_1 and B_2 are correlated with vapor pressure, boiling temperature, molecular weight and oxygen content (% weight) of the ethers.

The following specific correlation for Reid pressure vapor of gasoline reformulated with MTBE, TAME and ETBE have been obtained:

$$RPV = RPV_{b} + \frac{\% VOxy}{8 \cdot RPV_{MTBE}} + \frac{(\% VOxy)^{2}}{17 \cdot RPV_{MTBE}}$$

formixtures gasoline-MTBE (3)

$$RPV = RPV_b - \frac{\% v Oxy}{0.4 \cdot RPV_{TAME}} - \frac{(\% v Oxy)^2}{25 \cdot RPV_{TAME}}$$

for mixtures gasoline - TAME (4)

$$RPV = RPV_b - \frac{\%vOxy}{0.2 \cdot RPV_{ETBE}} - \frac{(\%vOxy)^2}{15 \cdot RPV_{ETBE}}$$

for mixtures gasoline - ETBE (5)

where:

RPV_b - Reid vapor pressure of base gasoline, kPa;

 $RPV_{\mbox{\tiny MTBE}}$, $RPV_{\mbox{\tiny bTAME}}$, $RPV_{\mbox{\tiny ETBE}}$ - Reid vapor pressure of pure ethers, kPa;

%vOxy - volume percent of ether in oxygenated gasoline. The following specific correlations for calculating the percentage of evaporated volume at a 70°C on distillation curve (E70) for gasoline reformulated with MTBE, TAME and ETBE have been obtained:

$$E_{70} = E_{70b} + \left(\frac{M_{MTBE}}{2 \cdot t_{MTBE}}\right) \cdot \% v Oxy - \left(\frac{0.4 \cdot t_{MTBE}}{M_{MTBE}} \cdot \% w O\right) \cdot (\% v Oxy)^2 -$$
for mixtures gasoline – MTBE (6)

$$E_{70} = E_{70h} - \left(\frac{M_{TAME}}{3 \cdot t_{TAME}}\right) \cdot \% v Oxy + \left(\frac{0.06 \cdot t_{TAME}}{M_{TAME} \cdot \% w O}\right) \cdot (\% v Oxy)^2 -$$
for mixtures gasoline - TAME (7)

$$E_{70} = E_{70b} - \left(\frac{M_{ETBE}}{4 \cdot t_{ETBE}}\right) \cdot \% v Oxy + \left(\frac{0.2 \cdot t_{ETBE}}{M_{ETBE}} \cdot \% w O\right) \cdot (\% v Oxy)^2 -$$
for mixtures gasoline - ETBE (8)

where:

 E_{70b} - evaporated percentage at 70°C of base gasoline; ^{270b} Evaporated percentage at 10°C of blace gasoline;
 ⁹wOxy- volume percent of ether in oxygenated gasoline;
 ¹t_{AME}, t_{TAME}, t_{ETBE}- boiling temperature of pure ether, °C;
 ¹M_{MTBE}, M_{TAME}, M_{ETBE}- molecular weight of pure ether,
 ⁹wO- oxygen weight percent in pure ether.

All new correlations are valid for gasoline oxygenated with 4-15% volume of each type of ether.

For checking relations 3-8 the vapor pressures and evaporated percentage at 70°C for all mixtures gasolineethers have been calculated and have been presented comparatively with the experimental results in table 5. The average absolute relative deviation (AARD %) between the experimental values and the calculated ones has also been calculated using the relation:

$$AARD\% = \frac{1}{n} \sum_{i=1}^{n} \left| \frac{M_{calc} - M_{exp}}{M_{exp}} \right| \cdot 100$$
 (9)

where:

 M_{calc} , M_{exp} - calculated unit (e.g. Reid vapor pressure, percentage evaporated at 70°C or vapor index (VLI)); n - number of points.

Volatility	RPV	RPV	ARD	E70	E70	ARD	ΓŸL1	VLI	ARD
properties	exp	calc	%	exp	cale	%	exp	calc	%
MTBE,					I <u> </u>				
%νОҳу									
4	56.01	55.93	0.1497	36.50	35.98	1.4251	815.6	811.12	0.5493
7	56.09	55.97	0,2138	38.00	37.93	0.1961	826.88	825.16	0.2081
10	56.11	56.03	0.1457	40.00	39.62	0.9419	841.11	837.65	0.4108
15	56.27	56.17	0.6094	42.50	41.90	1,4074	860.19	855.05	0.5975
AARD%			0.2797		t <u></u> -	0.9926	:	<u> </u>	0.4414
TAME,							F		
%vOxv									
4	54.75	54.54	0,3947	31.50	31.47	0.0813	775.00	765.67	1.2037
7	53.90	53.65	0.4564	30.50	30,40	0.3421	752.50	749.31	0.4240
10	53.02	52.70	0.5966	29.50	29.38	0.4187	736.70	732.64	0.5517
15	51,17	50.95	0.4310	28.00	27.81	0.6889	707.70	704.15	0.5016
AARD%		1	0.4697			0.3827			0.6702
ETBE,									
%vOxy									
4	55.14	54.85	0.5266	32.00	31.74	0.8068	774.00	768.79	0.6735
7	54.47	54.23	0.4345	31.00	30.68	1.0239	759.00	755.10	0.5134
10	53.80	53.58	0.4086	30.50	29.96	1.7637	746.50	741.40	0.6835
15	52.78	52.39	0.7527	30.00	29.12	2.9178	725.00	718.51	0.8956
AARD%		<u> </u>	0.5306		1	1.6280		J	0.6915

Table 5
COMPARISON BETWEEN CALCULATED VOLATILITY PROPERTIES AND EXPERIMENTAL ONES FOR
GASOLINE GasA OXYGENATED WITH ETHERS

Equations 3-8 proposed by the authors to calculate the properties of gasoline and volatile ethers mixtures, are validated by the data presented in table 5, since they find a good correlation between property values and the calculated volatility achieved by the experimental tests. Thus, between calculated Reid pressure vapors and the experimental ones, the highest average absolute relative deviation is 0.53% for gasoline substituted with ETBE, and the lowest one is 0.28% for gasoline substituted with MTBE. By comparing the calculated values of the evaporated percentage at 70°C with the experimental ones, one can notice that the highest average absolute relative deviation is 1.63% for gasoline substituted with ETBE, and the lowest one is 0.38% for gasoline substituted with TAME. For the volatility index calculated with equation (1), based on experimental data and those obtained by calculating with equation 3-8, the highest average absolute relative deviation is 0.69% for gasoline substituted with ETBE, and the lowest one is 0.44% for gasoline substituted with MTBE.

Conclusions

The European directives on auto fuels quality impose intensive usage of oxygenated compounds resulted from renewable raw materials, in order to save conventional fuels and to reduce pollutant emissions. The experimental results presented in the paper come to show the effect of partial substitution of classical gasoline with ratios of ethers between 4 and 15% volume on volatility properties.

The conventional gasoline substitution with ratios between 4 and 15 % volume MTBE leads to the light increase of Reid vapor pressure, and in the case of gasoline oxygenated with TAME or ETBE, no matter the ether content, the Reid vapor pressure decreases. According to volatility classes of vehicle gasoline, due to the pressure vapors, standard EN 228 places gasoline oxygenated with ethers in class A, corresponding to summer season. The pressure vapor can be increased to values corresponding to the cold season by adding C_{4} fraction. The substitution of gasoline with various ether proportions has a good influence in distillation curves, which has been proved by the values of evaporated percentage at 70°C, 100°C and 150°C. The VLI vapor index calculated from experimental data increases compared to the base gasoline for all oxygenated gasoline, but keep the fuel in A class corresponding to the summer season.

The Reid vapor pressures and the evaporated pressures at 70°C experimentally obtained for gasoline oxygenated with ratios of 4 to 15% vol. of MTBE, TAME or ETBE vary to second order polynomial functions in accordance with the ether volume percentage used for formulating these mixtures. Empirical relations for predicting the pressure vapor and the evaporated percentage at 70°C (*E70*) have been proposed for the oxygenated gasoline, based on experimental determinations of *RPV* and *E70* of base gasoline and the physico-chemical properties of pure ethers. The differences between the experimental and predicted results show a good average absolute relative deviation value (*AARD* %), which is between 0.28% and 1.63%. The obtained relations may represent useful tools for estimating the volatility properties of gasoline oxygenated with ethers.

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