BULETINUL Universităţii Petrol – Gaze din Ploieşti	Vol. LXI No. 4/2009	19 - 30	Seria Tehnică

The Oxygenates Compounds Type Alcohols and Ethers as Reformulated Gasoline Substitutes

Mihaela Petre, Paul Rosca, Raluca-Elena Dragomir, Oana Mihai

Universitatea Petrol – Gaze din Ploieşti, Bd. Bucureşti nr. 39, Ploieşti
e-mail: mpetre@upg-ploiesti.ro

Abstract

The partial substitution of gasolines with different loadings of alcohols and/or ethers represented recently the target of many discussions within scientific research area being as an alternative for both the reducing of fuel consumption from nonrenewable sources and a path to reduce the pollutant emissions of vehicles.

This paper consists of two parts. The first part presents the European legislation regarding the gasoline reformulation, a theoretical study concerning the physical and chemical properties of following alcohols: methanol (MeOH), ethanol (EtOH), isopropanol (IPA), tert-butyl alcohol (TBA) and ethers as: methyl tert-butyl ether (MTBE), tert-amyl methyl ether (TAME), ethyl tert-butyl ether (ETBE), tert-amyl ethyl ether (TAEE) and the properties of reformulated gasolines and the standardized analysis methods.

Based on the experimental study, in the second part is illustrated the loading effect of 2, 4, 6, 7, 10% volume of gasoline with oxygenates type alcohols on the motor and research octane numbers, the density at 20°C, the distillation curves and Reid vapor pressure of these reformulated gasolines.

Key words: *alcohols, ethers, gasolines, substitution, properties*

The Requirements of European Legislation Regarding the Reformulation of Gasolines

In the 21st century one of the greatest challenges is the reconciliation between the human activities and the environment. From these, the road and urban transport have a negative impact that gradually tends to be perceived as such in Romania.

Currently, related to the aim by EU factors regarding the environment-transport relationship, the advanced studies are carried out. It is emphasized the importance of a sustainable environmental policy development in the transport area to reduce its impact on the environment [1, 2].

The fuel quality is specified in the Directive by assessment of certain properties (Table 1). The limitation of certain fuel properties is closely related to the decreasing of emissions to the level which do not influence the environment and public health.

The values of fuel properties and their physical and chemical measurements are done in Europe according to the standards: EN 228 for gasoline fuel and EN 590 for diesel fuel. According to the quality standard of gasoline, the last mentioned table notes the requirement about the reducing of aromatic hydrocarbons and olefins content, but a new challenge appears for manufacturers: the decreasing of MON and RON values. This means the refineries develop other processes to produce new compounds able to satisfy the specifications of commercial gasoline [3]. One way to equalize the loss of octane compounds is the partial replacement of gasolines with oxygenates.

Table 1. The development of fuel quality in UE

Properties	1993 EURO II	1999 EURO III	2005 EURO IV	2009 EURO V
Sulfur, ppm max	500	150	50 (10)	10
Aromatics, % vol. max	-	42	35	30
Olefins, % vol. max	-	18	18	14
Benzene, % vol. max	5.0	1.0	1.0	1.0
Oxygen, wt % max	-	2.7	2.7	2.7
RVP, kPa	35-100	90	60	60
RON/MON min	95/85	95/85	95/85	95/85

The loading of oxygenates content into the gasolines composition is also required by legislation. The Directive 30/2003 EU requires the substitution of conventional fuels with alternative fuels with 5.75% until 31 December 2010 and 20% until 2020, respectively.

As UE country, Romania joined to the 30/2003 Directive and adopted many laws regarding to realize its stipulations. As consequence in May 2007 appears many additionals of 1844/2005 Directive regarding the promotion of biofuels and other renewable fuels for transport. Thus, it provided the bringing of biofuels and conventional fuels mixtures on the market and from July 1, 2009 the gasoline has a minimum content of biofuel - 4% volume [4].

This UE ambitious work plan cooperated with proposed goals by Kyoto Protocol regarding the reducing of greenhouse gases by 5% during period 2008-2012 compared with their levels in 1990 [5], were the focus of many scientific discussions and also for manufacturers of vehicles. The experience of some countries such as USA, Brazil, France, Sweden, Germany and Austria regarding the development and application of new automotive fuels showed the increasing of bioethanol and biodiesel content can combine the requirements of both directives. After discussions more than two years, the European forum has revised the legislation regarding application of biofuels by the introduction of Directive 2009/28/EC–Renewable Energy Sources, entering into force on 25 June 2009 and Directive 2009/30/EC–Fuel Quality Directive [6, 7].

The Fuel Oxygenates as Partial Compounds of Commercial Gasolines

The fuel oxygenates improve the efficiency of gasoline hydrocarbons combustion and reduce the emissions of carbon monoxide. Also, due to reduced volatility compared with the constituent hydrocarbons of refinery gasoline, oxygenates contributes to reduce the emissions of volatile organic compounds.

The fuel oxygenates are compounds containing the oxygen atom in the chain of carbon and hydrogen atoms. Actually, the fuel oxygenates are blended into gasoline in two forms: alcohols or ethers.

Among the alcohols used as loading into the formulation of commercial gasolines are the following: MeOH (methanol), EtOH (ethanol), IPA (isopropanol), TBA (tert-butyl alcohol), and IBA (2-methylpropyl alcohol). In Table 2 are included some physical and chemical properties of alcohols.

The main used ethers as substitutes for gasolines are: MTBE (methyl tert-butyl ether), TAME (tert-amyl methyl ether), ETBE (ethyl tert-butyl ether), TAEE (tert-amyl ethyl ether). Among the ethers, the MTBE is the most used oxygenate compound, followed by ETBE and TAME. In Table 3 are included some physical and chemical properties of ethers.

Table 2. The physical and chemical properties of fuel oxygenates type alcohols as partial substitutes compounds of commercial gasoline [8...11]

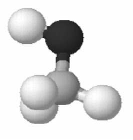
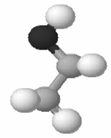
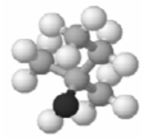
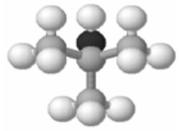
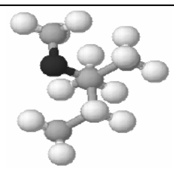
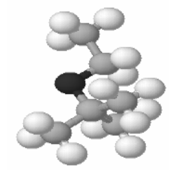
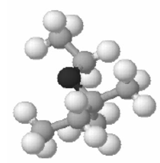
Alcohol	**MeOH**	**EtOH**	**IPA**	**TBA**
CAS number	67-56-1	64-17-5	67-63-0	75-65-0
Structural formula				
Chemical formula	CH_3OH	CH_3CH_2OH	$CH_3CHOHCH_3$	$(CH_3)_3COH$
Molecular weight, g/mol	32.04	46.07	60.10	74.12
Density (at 20 C), g/cm^3	0.7918	0.789	0.786	0.7808
Boiling temperature, ºC	64.7	78.3	82.3	82.3
RVP, kPa	31.7	16.0	12.6	5.5
Oxygen, % wt	49.9	34.7	26.6	21.6
Solubility in water,	miscible	miscible	miscible	miscible
Blending RON/MON	122-133/92	121-130/96	117-118/95-98	105-109/94-95

Table 3. The physical and chemical properties of fuel oxygenates type ethers as partial substitutes compounds of commercial gasoline [8...11]

Ether	**MTBE**	**TAME**	**ETBE**	**TAEE**
CAS number	1634-04-4	994-05-8	637-92-3	919-94-8
Structural formula				
Chemical formula	$CH_3-O-C(CH_3)$	$C_2H_5-C(CH_3)_2-O-CH_3$	$(CH3)_3COCH_2CH_3$	$CH_3CH_2C(CH_3)_2OCH_2CH_3$
Molecular weight, g/mol	88.15	102.18	102.18	116.20
Density, g/cm^3	0.741	0.764	0.7519	0.750
Boiling temperature, C	55.2	86.3	72.2	102
RVP, kPa	55	10	28	NA (not available)
Oxygen, % wt	18.15	15.7	15.66	15.66
Solubility in water,	4.8 g/100 g	1.2 g/100 g	1.2 g/100 g	NA
Blending RON/MON	115-118/101	109-112/98-99	117-119/102-103	NA

The important difference between alcohols and ethers structure is the presence of the hidroxyl group in alcohols structure and missing in ether structure. The lack of hydrogen bonding into the ethers structure determine the decreasing of boiling temperature with 80ºC compared with the alcohol with the same number of carbon atoms. Another effect of hydrogen bonding lack is the ethers have lower density than alcohols in liquid phase.

Among the oxygenates compounds type ethers, MTBE as a substitute of commercial gasoline compensates the loss of octanes due to the prohibition of the tetra-ethyl lead (TEL) as additive for gasolines for the past 20 years in USA. Then, the automotive industry has used MTBE as an oxygenate additive in gasoline, saying that MTBE not only can enhance the octane number, but also reduce the exhaust gases emissions. Additionally, the MTBE addition into unleaded gasoline with 15% can reduce the CO emissions by 10-15%, NO_x emissions by 1.0-1.7% and the total hydrocarbon emissions by 10-20% [12].

Over 85% of reformulated gasolines contain MTBE because of its low cost and its physical and chemical properties that indicate a low vapor pressure, the total miscibility with gasoline, the boiling point and the development of fuel consuming [13]. However, MTBE is 30 times more soluble in water than the hydrocarbon constituents in gasoline. This unwanted property gradually showed in case of leakage of reformulated gasoline with MTBE additive from underground storage tanks or automotive tanks, the ether with a high mobility infiltrates through soil up to the ground water and can contaminate it. According to the US legislation, the concentration of MTBE in water must be below 20-40 g/L to avoid the taste and odor problems [14]. Since 2001 in USA, the problems regarding the environment and human health have led to the prohibition of MTBE utilisation in gasoline [15]. Europe disagres the USA point of view regarding the MTBE usage. Many studies effectuated by specialists lead to the conclusion that the advantages of consuming of reformulated gasoline with MTBE are more obvious than the disadvantage created by the possibility of leakages from storage tanks, from both point of views- the improvement of fuel quality and the reducing of exhaust emissions [16…18].

Following these discussions was not prohibit its use as a oxygenate component in gasoline, but recommended to avoid the leakages from storage tanks by applying of additional measures where the price could be partially covered by introduction of additional taxes regarding fuels that contain it [11].

On international plan the idea of specialists regarding the possibility of MTBE usage is different, the social stress of some scientific groups have led to increasing of research and testing studies and the development of other fuel oxygenates which provide good quality of reformulated gasolines and reduce the exhaust emissions, respectively. The first solution offered by the researchers and accepted by both the refinery enginers and users was back to use the ethanol. The history of the ethanol usage blended with gasoline started during the First World War and continued during the Second World War, then followed by falling it. The back to use the ethanol held with the crude oil crisis in ‘70 years, being considered as a substitute of gasoline.

The ethanol improves the properties regarding the combustion of gasoline and reduce the harmfulness of exhaust emissions [19, 20]. With the reducing of greenhouse emissions and global warming, the ethanol as alternative component of gasoline has become the focus of scientists of whole world [21, 22].

The enthusiasm of researches to promote the biofuels were located mainly the ethanol as biosubstitute of gasolines. Today, the ethanol is produced from different renewable raw materials, using effective and reasonable methods [23]. The research regarding the development of raw materials other than the agricultural feedstocks for obtain bioethanol is focused on the utilisation of forestry and municipal solid wastes as raw materials [24].

The recent studies regarding the application of higher alcohols in the gasoline reformulation has shown some unexpected results. Both the propanol and butanol can be obtained from the same sources as the ethanol by using the fermentation processes with lower yields and higher recovery cost. Although seems to be a non economic method, the application of bioalcohols in gasoline has more favorable effects than the ethanol [25]. The biobutanol have the advantage of small consumption as fuel (have same energy density as classical gasoline: 26-27 MJ/liter biobutanol, 32-33 MJ/liter gasoline, MON value is 94, the low oxygen content in molecule and can be blended with high proportion in gasoline (up to 16%), very low vapor pressure (VOC emissions are reduced) and the affinity to water is much less than ethanol [26, 27].

From 1990s the role of ether as gasoline substitutes increased because of their vapor pressure less than that of ethanol, which has the effect of reducing concentrations of VOC in exhaust gases [28]. The ozone layer level and its role in global warming process are directly related to the exhaust gases. In the actual time of climate changes, the ethers compounds play an important role in the projects related to the use of renewable raw materials.

Compared with the ethanol, the ethers such as TAME, ETBE and TAEE have another important advantage: the lower solubility in water [29, 30]. Because the ETBE and TAEE are considered the semi renewable compounds, being obtained from bioethanol, offers it a great advantage compared to TAME or MTBE, which are obtained from methanol derived from natural gas.

The international legislative requirements regarding the reducing of exhaust emissions, the oil crisis and the need to reduce the fuel consumption have increased the role of oxygenates in gasoline reformulation.

The Properties of Reformulated Gasolines. The Standardized Methods

On international plan, the gasolines quality is identified by testing of some properties, by the analysis methods referred to the standards: EN-CEN (European Committee for Standardization), ISO (International Organization for Standardization), JIS (Japanese Industrial Standards), ASTM International (formerly American Society for Testing and Materials) and other standards with national application (Table 4).

The fuel producers are required by national legislation to provide the quality of products by analysis reports that shows the testing of same properties by same analytical methods referred to the European standards. The European standard regarding the fuels quality up to 5% volume ethanol, EN 228:2004 standard was adopted by the Romanian Association for Standardization, named as „SR EN 228:2004, Automotive fuels. Unleaded gasoline. Requirements and testing methods"[31].

The fuel quality specifications and the testing methods are continually modified based on the legislative requirements and technological progress. The standard EN 228 was recently revised (2009) regarding the increasing of bioethanol content from 5% vol to 10% vol., the content of other oxygenates, the oxygen content from 2.7% to 3.7% mass and the change of vapor pressure for summer time [33].

As in the previous presentation, by the standards based on the number of qualities that the fuel must be have and by the analysis methods, is showed the complexity of these products and the effort of manufacturers to get them at the desired quality level but obtaining the least pollutant emissions often ignored by the fuel users. In terms of fuel user is important the vehicle is easy starting in cold season, starts quickly, runs easily, if the engine has sufficient power and operate without shocks, are not deposits and corrosion in the distribution system of engine, and finally, if the fuel is cheaper.

Are showed below some of most important characteristics of gasoline and how affect the vehicle performance and also some differences between the testing way and calculation, function of the specific standards.

The volatility of fuel shows the easy way which the fuel vapors are formed in the starting conditions of engine in cold time. In the warm period, the volatility of gasoline mixture should be lower to avoid the formation of vapor plugs, the problems regarding the fuel injection system, to avoid the fuel evaporation and to increase the hydrocarbons emissions. The Reid vapor pressure values are between 60-90 kPa for winter time and 45-60 kPa for summer time.

Table 4. Comparaison between the characteristics of automotive fuels and their analysis methods on international plan [32]

Caracteristic property	**Unit**	**Analysis method**			
		Romania	ISO/EN	ASTM	JIS
Density at 15 °C	kg/m^3	SR EN ISO 3675:03, SR EN ISO 12185:03	EN ISO 3675 EN ISO 12185	ASTM D 4052 ASTM D 1298	K 2249
Octane number COR COM		SR EN ISO 5164:06 SR EN ISO 5163:06	EN ISO 5164 EN ISO 5163	ASTM D 2699 ASTM D 2700	K 2280 K 2280-96
Lead content	mg/l	SR EN 237:05		ASTM D 3237	K 2255
Benzene content	% (v/v)	SR EN 12177:01, SR EN 14517-05	EN 238 EN 14157	ASTM D 3606, ASTM D 5580	K 2536
Content of: Olefins Aromatics	% (v/v)	SR EN 14517-05, SR EN 12177:01,	EN 14517	ASTM D 3606 ASTM D 1319	K 2536
Distillation: E70, E100, E150, End Point, Residue	% (v/v)	SR EN ISO 3405:03	EN ISO 3405	-	-
Distillation T10, T50, T90, End Point, Residue	ºC	-	-	ASTM D 86	K 2254
Vapor pressure	kPa	SR EN 13016	EN 13016	ASTM D 5191 ASTM D 6378	K 2258
Sulfur content	mg/kg	SR EN ISO 20846, SR EN ISO 20884	ISO 20846 ISO 20884	ASTM D 2622, ASTM D 5453	K 2541
Stability to oxidation	min	SR EN ISO 7536:01 SR ISO 7536:99	EN ISO 7536	ASTM D 525	K 2287
Cooper strip corrosion		SR EN ISO 2160-03	EN ISO 2160	ASTM D 130	K 2513
Gum content (solvents washed)	mg/100ml	SR EN ISO 6246:00	EN ISO 6246	ASTM D 381	K 2261
Volatility index, VLI		calculus	calculus	-	-
Driveability index, DI		-	-	calculus	-
Appearance		Visual test	Visual test	ASTM D 4176	-
Oxygen content	% (m/m)	SR EN 13132:00 SR EN 13132:01	EN 13132	D 4814	K 2536
Oxygenates content	% (v/v)	SR EN 13132:00 SR EN 13132:01	EN 13132	D 4814	K 2536

According to the European Standard EN 228, the used properties for showing the volatility of reformulated gasoline are: the Reid vapor pressure, the distillation curve, the vapor/liquid ratio and vapor lock index (*VLI*). *The fuel vapor pressure* must be high enough to provide an easy starting of engine, but not too high to contribute at the appearance of vapor loop or evaporating of excess emissions.

The Reid vapor pressure of gasoline is measured at a temperature of 37.8ºC and atmospheric pressure and is expressed in kPa. The vapor pressure measurement can be performed by a variety of laboratory procedures and analysis equipments.

The distillation curve is a graph of the boiling temperature variation function of % volume distilled (evaporated). The gasoline includes a variety of chemical compounds evaporated at different temperatures. The volatile components are evaporated at lower temperatures and the least volatile components are evaporated at high temperatures.

The different zones of the distillation curve can be related to the performance and operation of engine:

- the initial zone must give: easy starting in cold and warm period, the avoidance of vapor plugs, low emissions;
- the middle zone should provide: easy starting, the fuel economy at short trip, the good engine power;
- the final zone must be give: the fuel economy at long road, eliminate the deposits on the engine, the minimum dilution of lubricating oil, low emissions of VOC.

According to EN 228 standard, based on the distillation curve are obtained the following values: the percentage of evaporated fuel at temperature of 70ºC (*E70*), at temperature of 100°C (*E100*) and 150ºC (*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.

Based on the percentage of evaporated fuel at temperature of 70ºC (E70) and the Reid vapor pressure, is calculated the fuel quantity indicating a tendency of fuel to form vapor plugs and is noted *VLI (*vapor lock index)*:*

$$VLI = 10 \cdot VP + 7 \cdot E70 \qquad (1)$$

According to the ASTM 4814 American standard, the used properties to show the volatility of reformulated gasoline are: the Reid vapor pressure, the distillation curve, the vapor/liquid ratio and the driveability index (*DI*).

Comparatively with the European standard and based on the distillation curve, the American standard shows: the temperature corresponding to 10% evaporated (T10), the temperature corresponding to 50% evaporated (T50), the temperature corresponding to the evaporation of 90% fuel (T90), the temperature corresponding to the final boiling point and the residue content. These values are specified in the standard function of the volatility class of gasoline. Based on the T10, T50, T90 temperatures from D-86 distillation curve of conventional gasoline can be calculated the driveability index (*DI*), according to equation:

$$DI = 1.5 \cdot T_{10} + 3 \cdot T_{50} + 1 \cdot T_{90} \qquad (2)$$

The relation of driveability index for reformulated gasolines with oxygenated compounds is shown below (3):

$$DI = 1.5 \cdot T10 + 3 \cdot T50 + 1 \cdot T90 + 11 \cdot \%wt\ Oxy \qquad (3)$$

where: $\%wt\ Oxy$ is weight % of oxygen content from oxygenated compounds.

Based on the vapor pressures, the profile of distillation curve and the driveability index, in the USA are six classes of volatility.

The tendency of gasolines to form the vapor plugs depends on temperature (vapor pressure) and on the starting zone of distillation curve. The temperature of 20% volume of vapor fuel in equilibrium with 1% volume of liquid fuel at atmospheric pressure represents the unit that shows the formation of vapor plugs during the starting of engine.

For each class of volatility, depending on the values of this work report are six classes of protection against the vapor plugs formation. The temperature at which V/L ratio = 20 depends on the summer or winter time and is between 35 and 60ºC. The higher values indicate the protection against to the vapor plugs. For reformulated gasolines blended with alcohols (ethanol), the values of this study must be adjusted.

The octane number denotes the detonation performances of gasoline. There are the two laboratory tests which determines the octane numbers: The first test which is conducted on a single cylinder engine under the medium detonation and speed conditions and is named the *research octane number (RON)* and a second test which is performing on the same type of engine, but under high speed and high temperature detonation conditions and is named the *motor octane number (MON).* The difference between RON and MON is called the *gasoline sensitivity.* The American standard requires a different measure of octane number, called *pump octane number* or *anti-knock index (AKI)* and is calculated as the average between RON and MON.

The Experimental Study of the Important Properties of Gasolines Substituted with Different Loadings of Lower Alcohols

To emphasize the effect of classical gasoline substitution with different loadings of alcohols was prepared a mixture containing 40% vol catalytic cracking gasoline, 40% vol catalytic reforming gasoline and 20% vol isomerization component. The proportions of 2, 4, 6, 7, 10% vol. of this gasoline have been replaced by methanol (MeOH), ethanol (EtOH), isopropyl alcohol (IPA) and tert-buthanol (TBA), respectively. For each gasoline-alcohol mixture were experimentally determined: the motor and research octane numbers, the distillation curves and the Reid vapor pressure.

The experimental study regarding the influence of alcohol content and type of alcohol on the octane numbers was achieved with IROX 2000 Fuel Analyzer Portable Gasoline Analysis with MID-FTIR from our laboratory facilities and the results are presented in Fig. 1.

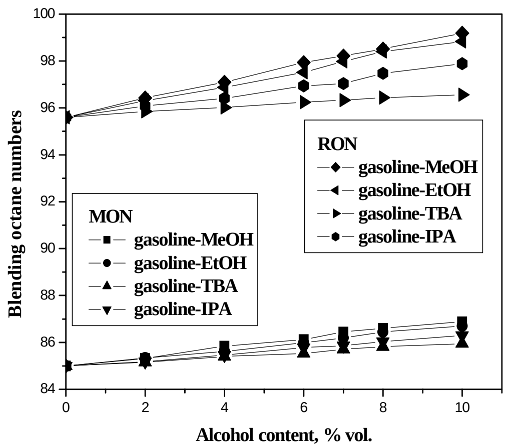


Fig.1. The influence of type and alcohol content on the octane numbers of reformulated gasoline

The figure 1 shows that:

- the octane numbers of reformulated gasoline with alcohols depends on the octane numbers of the alcohols mixture and therefore with the increasing of alcohol content increases the octane numbers of the reformulated gasoline compared to the classical gasoline;
- the research octane numbers of gasoline-alcohols mixtures increase in the following way: methanol> ethanol> IPA> TBA;
- the motor octane numbers of gasoline-alcohols mixtures increase in the order: methanol> ethanol> TBA> IPA.

The MINIDIS mini-distillation analyzer were experimentally determined the distillation curves for all mixtures of classical gasoline substituted with different proportions of alcohol, but in Fig. 2 and 3 are presented only the experimental results of methanol-gasoline mixtures and the comparison between the distillation curves of reformulated gasoline with 10% volume of each type of alcohol.

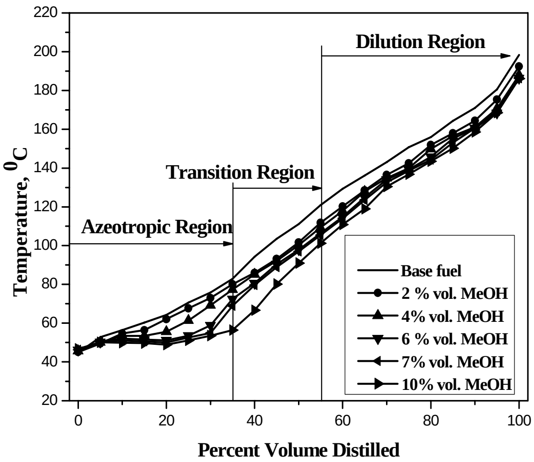


Fig. 2. The influence of methanol content
on the distillation curves of reformulated gasolines

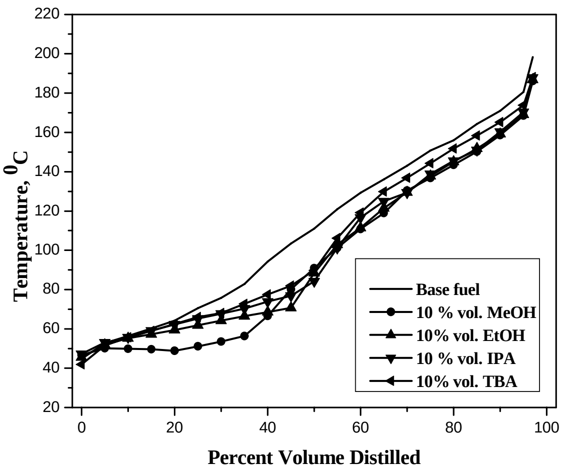


Fig. 3. The Influence of type alcohol on the position of zone
of azeotropes formation between alcohols and some components of base gasoline

The distillation curves of the gasolines-alcohols mixtures show the presence of three zones: the azeotropic zone with minimum boiling temperature between some components of base gasoline with alcohols, the transition zone and the final zone. Each zone has different effects regarding the engine operation. In the case of reformulated gasolines with alcohols, the decreasing of boiling temperatures of the beginning zone of the curve, due to the formation of azeotropes, leads to some negative effects in engine operation: the increasing of vapor lock and the evaporation loss emissions.

In the Fig. 3 is observed the azeotropic zone is extended from 0-35% vol. distilled for gasoline-methanol mixtures, up to 0-50% vol. distilled in the gasoline-isopropanol mixtures due to the increasing of normal boiling temperature of alcohol. This affects the transition zone of the distillation curve and has direct effect to rapid warm-up and smooth running, good short-trip fuel economy and good power and acceleration.

For each gasoline-alcohol mixtures were also determined the vapor pressures by using MINIVAP VPS/VPSH equipment from our laboratory. The experimental results are plotted in the Fig. 4.

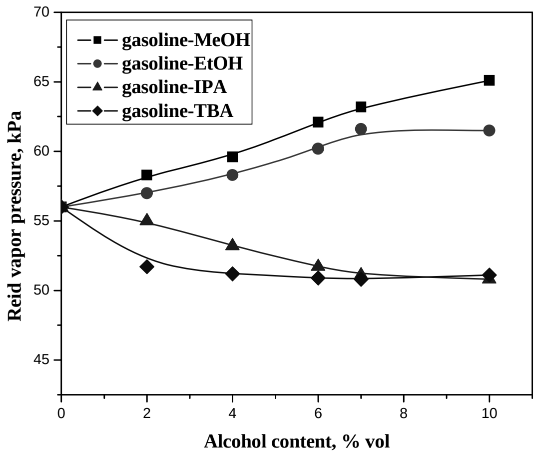


Fig. 4. The influence of alcohol content
on the Reid vapor pressure of reformulated gasoline

The data from Fig. 4 shows:
- in the methanol case, the vapor pressure of mixtures increase compared to that of the base gasoline with the increasing of % volume of alcohol;
- in the ethanol case, the vapor pressure of mixtures increase compared to that of the base gasoline with the increasing of % volume of alcohol up to 8%, and then it decrease;
- in the isopropanol and tert-butanol, the vapor pressure of gasoline mixtures decrease compared to that of base gasoline with the increasing of alcohol content.

It showed that the Reid vapor pressures values of gasoline mixtures with more than 5% volume methanol loading and also the gasoline mixtures with more than 7% volume ethanol loading are within the limits 60-90 kPa for winter time and the gasoline-IPA and gasoline-TBA mixtures are between 45-60 kPa in the summer time, respectively.

Conclusions

The partial substitution of gasolines with different loadings of oxygenates was the target of many research studies and discussions of international/national organizations. Over the time, the scientific world, the fuel producers and fuel users have expressed different ideas regarding the advantages and disadvantages of use of alcohols or ethers as partially or completely substitutes of classical fuels.

The present experimental study showed the requirement of reformulation of gasolines with oxygenates such as alcohols and ethers, their influence on some properties regarding the detonation and their volatility.

The octane numbers of reformulated gasolines with alcohols increases with the loading of alcohol content compared to those of the base gasoline.

Regarding the distillation curves of reformulated gasolines is concluded that due to the increasing of the normal boiling temperature of alcohol, the azeotropic zone is extends from 0-35% distilled volume for gasolines-methanol mixtures up to 0-50% distilled volume for the gasolines-isopropanol mixtures.

The Reid vapor pressures values of gasolines mixtures with 5% volume methanol loading and gasolines mixtures with more than 7% volume ethanol loading are for winter time and the vapor pressures values for the gasoline-IPA mixtures and gasoline-TBA mixtures are for summer time.

ACKNOWLEDGEMENT
The present study has been performed by the fundings received from CNCSIS/UEFISCSU 1291/2008 Project.

References

1. * * * *Progress Report on the Sustainable Development Strategy* 2007*,* Communication from the commission to the Council and European Parliament, Brussels, 22.10.2007, COM (2007) 642 final, http://ec.europa.eu.
2. * * * *A sustainable future for transport: Towards an integrated, technology-led and user friendly system*, Communication from the commission, Brussels, COM (2009) 279/4.
3. Rock K., Korpelshoek M. - Bioethers impact on the gasoline pool*, Biofuels,* 2007, pp. 9-15.
4. * * * *Contextul național privind biocarburanții, în acord cu normele UE*, Faza 1 - Perioada de desfasurare: sept. 2007-dec. 2007, www.icia.ro/Documents.../jtkwv_Raport%20etapa%201.pdf.
5. * * * *Kyoto Protocol to the United Nations framework convention on climate change*, United Nation, 1998, http://unfccc.int/resource/docs.
6. * * * *Newsletter by the European Renewable Energy Council* (EREC), May-June-July 2009, http://www.erec.org.
7. Rose, K.D. - *Overview of European legislation Impacting Vehicles and Fuels*, (CONCAWE), http://www.pecj.or.jp/japanese/overseas/euro/japan-eu_2nd/pdf/0325_09032501-KDR-Overview-of-European-Legislation-K-D-Rose.pdf.
8. Lesnik, B. - Physical and Chemical Properties of the Fuel Oxygenates, *U.S. Environmental Protection Agency*, *ASTSWMO State Symposium on Fuel Oxygenates*, October 21, 2002.
9. Nylund, N.-O., Aakko, P., Niemi, S., Paanu, T., Berg, R. - *Alcohols/ethers as oxygenates in diesel fuel: properties of blended fuels and evaluation of practical experiences,* IEA Advanced motor fuels and evaluation of practical experiences, IEA Advanced Motor Fuel, Annex XXVI Final Report, 27.12.2005.
10. www.efoa.org/oxygen.
11. Ashraf, M. A., Hamid, H. - *Blending properties of MTBE and other oxygenates in gasoline*, http://books.google.ro/books.
12. Song, C.-L., Zhang, W.-M., Pei, Y.-Q., Fan, G.-L., Xu, G.-P. - Comparative effects of MTBE and ethanol additions into gasoline on exhaust emissions, *Atmospheric Environment*, **40**, 2006, pp. 1957–1970.
13. Zhang, Z.Y., K.H., Ajay, K.R. - Determination of adsorption and kinetic parameters for methyl tert-butyl ether sythesis from tert-bytyl alcohol and methanol*, Journal of Catalysis*, 2001, p. 209–221.
14. Kinner, N. E., Fate - *Transport and Remediation of MTBE*, Bedrock Bioremediation Center, April 23, 2001, http://epw.senate.gov/107th/kinner.pdf.
15. Poulopoulos, S. G., Philippopoulos, C. J. - Comparison between methyl tertiary butyl ether and ethanol as oxygenate additives: The influence on the exhaust emmisions, *7th International Conference on Environmental Science and Technology*, Ermoupolis, Greece – Sept. 2001.
16. Tavlarides, V., Poulopoulos, S. G., Philippopoulos, C. J. - MTBE Addition in Gasoline: The Effect on Automotive Exhaust Emissions, *Tech. Chron. Sci. J. TCG*, V, 2000, No. 1-2.

17. Zervas, E., Montagne, X., Lahaye, J. - Impact of Fuel Composition on the Emission of Regulated Pollutants and Specific Hydrocarbons from a SI Engine, *Tech. Chron. Sci. J. TCG,* V, 2004, No. 1-2.
18. Osman M.M., Matar M.S., Koreish S. - Effect of methyl tertiary butyl ether (MTBE) as a gasoline additive on engine performance and exhaust emissions, *Fuel Sci. Technol. INT'L* 11 (10), 1993, pp.1331-1343.
19. Aakko, P., Nylund, N.-O. - *Technical view on biofuels for transportation-Focus on ethanol end-use aspects,* Research Report, PRO3/5100/03 06.05.2004.
20. He, B.-Q., Wang, J.-X., Hao, J-M., Yan, X.-G., Xiao, J.-H. - A study on emission characteristics of an EFI engine with ethanol blended gasoline fuels*, Atmospheric Environment,* **37**, 2003, pp. 949–957.
21. E I A - *Energy Information Administration*, http://www.eia.doe.gov/kids/milestones/ ethanol.html.
22. Szklo, A., Schaeffer R., Delgado, F. - Can one say ethanol is a real threat to gasoline?, *Energy Policy*, **35**, 2007, pp. 5411–5421.
23. * * * *Biofuels for transportation, Global Potential and Implications for Sustainable Agriculture and Energy in the 21st Century*, Summary, June 2006, www.worldwatch.org/pubs/biofuels.
24. * * * *Sustainable biofuels: prospects and challenges*, The Royal Society, 2008, http:// royalsociety.org/displaypagedoc.asp?id=28914.
25. Brekke, K. - Butanol-An Energy Alternative?, *Ethanol Today*, March 2007, pp. 36-39.
26. Ramey, D. - Butanol: The Other Alternative Fuel, *Agricultural Biofuels: Technology, Sustainability and Profitability*, pp. 137-147, http://nabc.cals.cornell.edu/pubs/nabc_19/ NABC19_5Plenary2_Ramey.pdf.
27. Arnold, F.-H. - The Race for New Biofuels*, Engineering &Science*, No. 2, 2008, pp. 12-19.
28. Basell, L. - *The current and future role of bio-ETBE in the EU, Feature Article*, August 2008, Volume 1, Issue 4, 3388-V1-0908.
29. Pumphrey, J.A., Brand, J.I, Scheller, W.A. - Vapour pressure measurements and predictions for alcohols–gasoline blends*, Fuel,* **79**, 2000, pp. 1405-11.
30. Catalun˜a, S. R, Menezes, E.W., Samios, D., Piatnicki, C.M.S. - Effect of additives on the antiknock properties and Reid vapor pressure of gasoline*, Fuel,* **84**, 2005, p.951-959.
31. Greabu, A. - Standardizare şi integrare europeana. Referenţiale pentru evaluarea conformităţii produselor şi serviciilor. Specificaţii de produs şi standarde*, Standardizarea*, Iunie, 2007, pp. 1-7.
32. * * * *Worldwide Fuel Charter*, September 2006, Fourth Edition.
33. Dixson-Declève, S., Szalkowska, U. - Biofuel Standards & Quality Needs, *2nd International Conference on Biofuels Standards*, Brussels, March 19-20, 2009, http://ec.europa.eu/energy/renewables/events.

Compuşii oxigenaţi de tip alcooli şi eteri ca substituenţi ai benzinei reformulate

Rezumat

Cerinţele legislative mondiale privind reducerea emisiilor poluante eşapate, criza petrolului şi nevoia de a reduce consumul de carburanţi au crescut rolul compuşilor oxigenaţi în reformularea benzinelor auto.
În prima parte a lucrării s-au prezentat cele mai importante proprietăţi fizico-chimice ale alcoolilor şi eterilor, un studiu de literatură privind efectul utilizării acestor compuşi asupra unor proprietăţi ale benzinelor reformulate şi modul cum acestea influenţeaza performanţele vehiculelor, precum şi unele deosebiri între modul de testare sau calcul a unor mărimi, în funcţie de standardele care le specifică.
În partea a doua a lucrării s-a exemplificat, prin rezultate experimentale efectul substituirii parţiale unei benzine clasice cu proportii de 2, 4, 6, 7, 10 %vol de metanol, etanol, isopropil alcool şi tert-butanol. Pentru fiecare amestec de benzină-alcool s-au determinat: cifrele octanice motor şi de cercetare, densitatea la 20ºC, curbele de distilare şi presiunea de vapori Reid.