Bioalcohols - compounds for Reformulated Gasolines

I. The effect of alcohols on volatility properties of gasolines

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The partial substitution of traditional gasolines with biocompounds is an answer that provides the demand to preserve crude oil resources but also the reducing of poluting emissions produced by automobiles that have significant effect on environmental health. The volatility properties of substituted gasolines with bioalcohols influence the engine running and air pollution by hydrocarbons emissions too. This paper deals the experimental results regarding the substitution effect of two classical gasolines with different composition and properties, with various proportions of 2 to 10% volume of methanol, ethanol, isopropanol (IPA) and tert-butanol (TBA) on the Reid vapor pressure, distillation curves and evaporated percent at 70°C. The experimental results were analyzed by comparison with the values of these properties specified by EN 228 European quality standard of commercial gasolines.

Keywords: gasoline, bioalcohols, volatility properties, experimental

In 20th century and early 21st century, the increasing of energy demand for industry and consumption has lead to excessive utilization of fossil fuels followed by the major consequences on their decreasing. Regarding the crude oil storages decreasing, the percent of 57% is used as fuel for transportation fuel industry [1]. Another important interest is global warming, mainly due to the increasing of carbon dioxide concentration and consequently the transportation is responsible for this. The main dilemma of 21st century is to find an answer of the dispute between the politicies which tend to expand the transportation fuel industry on the one hand and the environmental policies involving the emissions reducing on the other hand [2, 3]. An innovative and challenging way related to the food area is to add various proportions of renewable resources derived biofuels into the fuel engines to reduce the effect of emissions released to the atmosphere. On the European level this idea is encouraged by 30/2003 Directive that focuses on serious utilization of alternative fuels explained by 5.75% from traditional fuels are partially replaced until 2010 and 20% until 2020, respectively [4]. There are various biocompounds that can be used as substitutes of fuel such as: biogas, primary alcohols, vegetable oils, biodiesel, etc. Some of them, such as bioethanol and biodiesel are already known worldwide as alternative energy sources for fuel engines. The international research studies concerning the use of methyl tertiary butyl ether (*MTBE*) and tertiary amyl ethyl ether (*TAME*) as additives for actual gasolines attracts also the interest of other ethers as tertiary butyl ethyl ether (*ETBE*) and tertiary amyl ethyl ether (*TAEE*) for partial substitution of conventional gasolines. The newly research work indicates that *ETBE* is favorable as partially renewable component, because the bioethanol can be used for *ETBE* synthesis and *TAEE* synthesis as well [5, 6].

The pathway followed up to the acceptance of biocompounds on fuel market involves many researches focused on the properties of various biocomponents-gasolines mixtures that firstly emphases advantages and disadvantages of their use into real fuel engines and old type fuel engine, secondly, have to assess the cost of production-distribution network and thirdly have to demonstrate the effect of manufacture, distribution and their use on the environment.

The crude oil resources control by substitution of different proportions of fuels with adequate biocompounds to reduce the enviromental constraints has lead to new challenges. Nowadays, a question in research has appeared: isopropanol and butanol can be used as biocompounds for gasolines reformulation?

The present paper deals with with the experimental work regarding the comparative study between volatility properties of differents blends: isopropanol-gasolines and tert-butanol-gasolines; methanol-gasolines and ethanol-gasolines, respectively.

The experimental study of this paper is part of a larger project refers to elucidate the changes in physico-chemical properties of traditional gasolines substituted with various proportions of primary alcohols and/or ethers.

Experimental part

The volatility properties of gasolines are the main characteristics that influence the performance during engine start-up, acceleration and deceleration time. Moreover, the volatility of gasolines should be limited in order to prevent the vapor lock formation inside engine, the fuel leakage by vaporization and the air pollution by increasing of unburned hydrocarbons emissions. In accordance with the EN 228 European standard and the volatility properties, here are some important properties as the Reid vapor pressure and the distillation curves that calculates the percentage of fuel evaporated at 70°C (*E70*) and the vapor lock index (*VLI*) value [7- 9].

The Reid vapor pressure property is determined at the temperature of 37.8°C by EN 13016 method and is given in kPa.

The distillation properties depend on the type of hydrocarbons and their distribution into gasoline composition and are determined by EN ISO 3405 method. The combustion performances of gasoline and the engine running are related to the characteristics of distillation curve. Thus, the first part of the distillation curve shows the information about the ease engine starting and the

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Table 1
REQUIREMENTS OF VOLATILITY CLASSES ACCORDING TO EN 228 STANDARD [7]

Class	Vapor pressure, kPa	Evaporated at 70°C, E70, % vol.	Evaporated at 100°C, E100, % vol	Evaporated at 150°C, E150, % vol	Final boiling point, °C, max	Distillation residue, % vol, max	VLI (10VP+7E70), Index, max
A	45-60	20 - 48	46 - 71	75	210	2	-
B	45-70	20 - 48	46 - 71	75	210	2	-
C/C1	50-80	22 - 50	46 - 71	75	210	2	C (-) C1 (1050)
D/D1	60-90	22 - 50	46 - 71	75	210	2	D (-) D1 (1150)
E/E1	65-95	22 - 50	46 - 71	75	210	2	E (-) E1 (1200)
F/F1	70-100	22 - 50	46 - 71	75	210	2	F (-) F1 (1250)

Table 2
PHYSICO-CHEMICAL PROPERTIES OF B1 AND B2 BASE GASOLINES SAMPLES

Property	*B1*	*B2*
Aromatics content, % vol	40.3	36.3
Olefins content, % vol	8.60	3.20
Saturated hydrocarbons content, % vol	51.1	60.5
Reid vapor pressure, kPa	56.0	59.8
Density at 20°C, kg/m^3	756	746

Table 3
CHARACTERISATION OF USED ALCOHOLS [10, 11, 12]

Alcohol	Oxygen content, % wt	Boiling temperature, ^{0}C	*RPV*, kPa	Molecular weight, g/mol
Methanol	49.9	64.7	31.7	32.04
Ethanol	34.7	78.3	16.0	46.07
Isopropanol	26.6	82.3	12.6	60.10
Tert-buthanol	21.6	82.3	5.50	74.12

hydrocarbons evaporation, then the middle part shows the details about the engine behaviour on the smooth running, the short trip fuel economy and the fuel consumption, and also the final part of curve indicates the long trip fuel economy, the behavior in the lubricating oil dilution and its deposits on engine block.

The EN 228 standard shows six volatility classes depending on the warm time, summer time and transition time, as shown in table1.

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.

The experimental study was focused on the Reid vapor pressure (*RPV*) and the distillation curves of conventional gasolines and reformulated gasolines by their substitution with various proportions of primary alcohols (between 2-10% vol): methanol, ethanol, isopropanol and tert-butanol.

There have been prepared two types of gasolines without additives, noted *B1* and *B2*. The both samples were obtained by mixing the base components of gasoline such as: the catalytic cracking gasoline, the catalytic reforming gasoline and a isomerization fraction, in this manner: *B1* gasoline sample includes 40% vol catalytic cracking gasoline, 40% vol catalytic reforming gasoline and 20% vol isomerization fraction, *B2* gasoline sample consists of 45% vol catalytic cracking gasoline, 30% vol catalytic reforming gasoline and 25% vol isomerization fraction. The base components provided from the oil refinery were colected in metal containers and kept in fumehood at room temperature. The *B1* and *B2* gasolines samples were prepared using volumetric pipettes and were kept at the same working conditions as base components.

To distinguish the differences between physico-chemical properties, both gasolines were analyzed based on hydrocarbons composition, Reid vapor pressure and density at 20°C. The hydrocarbons composition and the gasolines density were determined by IROX 2000 Fuel Portable Gasoline Analyzer with MID-FTIR provided by Grabner Instruments. The Reid vapor pressure was analyzed by MINIVAP VPS/VPSH Vapor Pressure Tester apparatus. The experimental results are depicted in table 2 and reveal two gasolines samples with different characteristics.

The anhydrous methanol (Rotisolv, purity min 99.9% UV/IR Grade), the anhydrous ethanol (Rotisolv, purity min 99.9% HPLC Gradient Grade), the anhydrous isopropanol (Rotisolv, purity min 99.0% HPLC) and anhydrous tert-butanol (Rotipuran, min 99.5% p.a) were used as starting materials and provided by Carl Roth Company. All alcohols were kept in original containers and were subsequently stored in a refrigerator protected from humidity. The physico- chemical properties of used alcohols are depicted in table 3.

The samples containing 2, 4, 6, 7 and 10% vol alcohol were prepared by using the volumetric method in laboratory at working conditions to avoid gasoline vapors leakage.

The oxygen content was calculated based on the alcohol composition. The results are presented in table 4.

Based on the EN 228 standard the oxygen content of reformulated gasoline with oxygenates is actually limited to max. 2.7% weight [13]. The Reid vapor pressure and the distillation curves were determined for each gasoline. The effect of oxygen content in the reformulated gasolines on the Reid vapor pressures is showed in figure 1 and figure 2.

Table 4
OXYGEN CONTENT OF REFORMULATED GASOLINES WITH ALCOHOLS

	B1 fuel-alcohol blends				
	2% vol	4% vol	6% vol	7% vol	10% vol
MeOH	1.05	2.09	3.14	3.66	5.22
EtOH	0.73	1.45	2.18	2.54	3.62
IPA	0.56	1.11	1.66	1.94	2.77
TBA	0.45	0.90	1.35	1.57	2.24
	B2 fuel-alcohol blends				
	2% vol	4% vol	6% vol	7% vol	10% vol
MeOH	1.17	2.33	3.48	4.05	5.76
EtOH	0.81	1.62	2.42	2.81	4.00
IPA	0.61	1.23	1.81	2.15	3.05
TBA	0.50	1.00	1.50	1.74	2.48

The distillation curves determined by using a MINIDIS Mini-distillation analyzer from Grabner Instruments are illustrated in figures 3-6.

Results and discussions

The effect of Reid vapor pressures on the oxygen content is depicted in the figures 1 and 2 and depends on the pressures of *B1* and *B2* gasolines and those of alcohols. Both base gasolines are placed in the *A* volatility class (summer gasoline) according to the European standard EN 228, but *B2* gasoline is nearly placed to the high limit of *A* volatility class.

For the 2…10% vol methanol addition to gasolines, the Reid vapour pressures values of gasolines-methanol blends increase by increasing of alcohol content. The *B1* gasolines with more than 4% vol. methanol content are placed in the *B* volatility class as all *B2*-methanol blends.

For 2...8% vol. ethanol, the Reid vapor pressures values increase by increasing of oxygen content in the mixture, afterwards decrease up to 10% vol ethanol. The *B1* gasolines with more than 6% vol ethanol are placed in the *B* volatility class as all *B2*-ethanol blends.

For the gasolines reformulated with 2...10% vol isopropanol, the vapor pressures values decrease by increasing of oxygen content and are placed in *A* volatility class (summer time).

In case of 2...8% vol tert-butanol, the vapor pressures values decrease by increasing of oxygen content, and nearly 10% vol *TBA* appear a slowly increasing of vapor pressure. All substituted gasolines with *TBA* are placed in *A* volatility class (summer period).

Lastly, the reformulation of base gasolines with various proportions of methanol and ethanol leads to increasing of Reid vapor pressures and classification of these blends in a higher class of volatility as base gasoline. This must be taken into account in reformulation of commercial gasolines, because practicaly, the gasolines are reformulated with C_4 fraction content for increasing of vapor pressure and this must be avoid or require precaution in case of utilization of these alcohols, mostly for summer gasolines blends which have vapor pressure between 45 and 60 kPa (according to EN 228). Regardless alcohol content for reformulation of gasolines with *IPA* or *TBA*, the vapor pressure decrease and the blends are placed in the same volatility class as base gasoline. This conclusion is adequate because the reformulation of base gasolines with various proportions of *IPA* or *TBA* does not substitute the gasolines reformulation with C4 fraction for increasing of vapor pressure as refiners prefer too. Another positive fact of *IPA* or *TBA* utilization is that can be substituted in high proportions in base gasolines without exceeding the maximum permitted content of oxygen in the mixture. It may use 9-10% vol. *IPA* or 10% vol *TBA* for reformulation with the same characteristics as those of *B1* gasoline and 8-9% vol *IPA* or 10% vol *TBA* for reformulation with the same characteristics as those of *B2* gasoline.

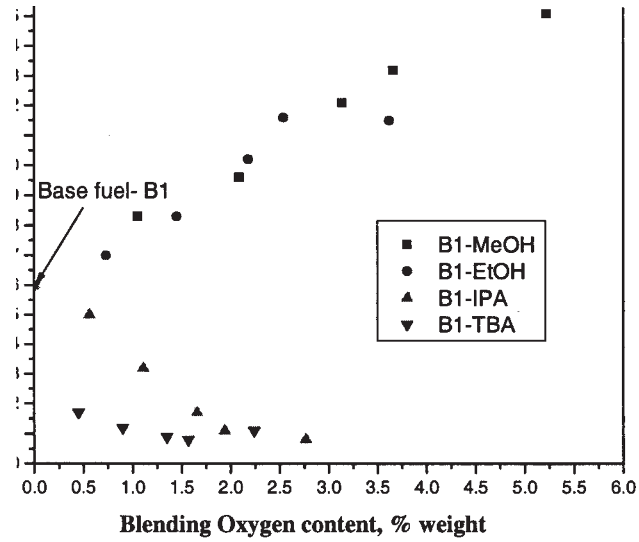

Fig.1 The effect of Reid vapor pressure on the oxygen content for the *B1* gasoline

The gasoline reformulation with various proportions of primary alcohols affects the distillation curves form (fig. 3-6). This means the C_5-C_8 light hydrocarbons (alkanes, alkenes and aromatics) contained in gasolines forms positive azeotropes (minimum-boiling) with the polar compounds as primary alcohols [14]. Depending on the boiling temperature of alcohol (table 3), the azeotropic region is between 35-55°C for methanol, 45-60°C for ethanol and 50-70°C for *IPA* and *TBA*, respectively. The experimental results demonstrate the superior limit of azeotropic region increases by increasing of boiling temperature of alcohols.

Based on the distillation curves of *B1* and *B2* gasoline and reformulated gasoline with various proportion of alcohol were calculated the evaporated at 70°C (*E70*) values depending on the oxygen content (fig 7-8). *E70* values are placed in the positive azeotropic region.

As is seen in figures 7-8, for 10% vol methanol, the *E70* values of gasolines-methanol blends increase by 65.32% than *E70* value of *B1* base gasoline and by 66.40% than *E70* value of *B2* base gasoline.

The *E70* values for blend with 2% vol ethanol increases by 8.87%, respectively with 81.45% for blend with 10% vol, than *E70* value of *B1* base gasoline. For gasoline *B2* - 2% vol. ethanol blends the *E70* values increase with 22.53%

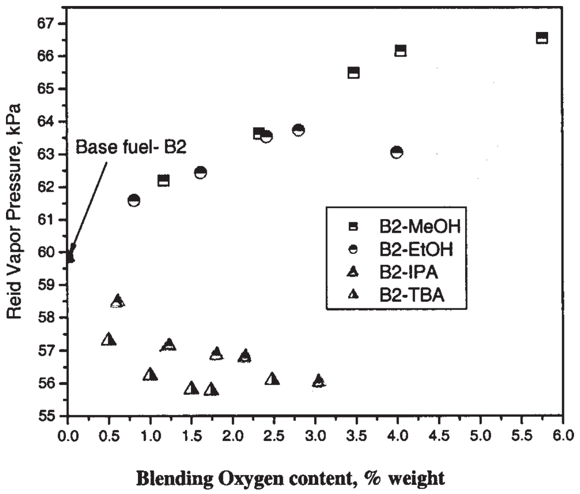

Fig.2. The effect of Reid vapour pressure on the oxygen content for the *B2* gasoline

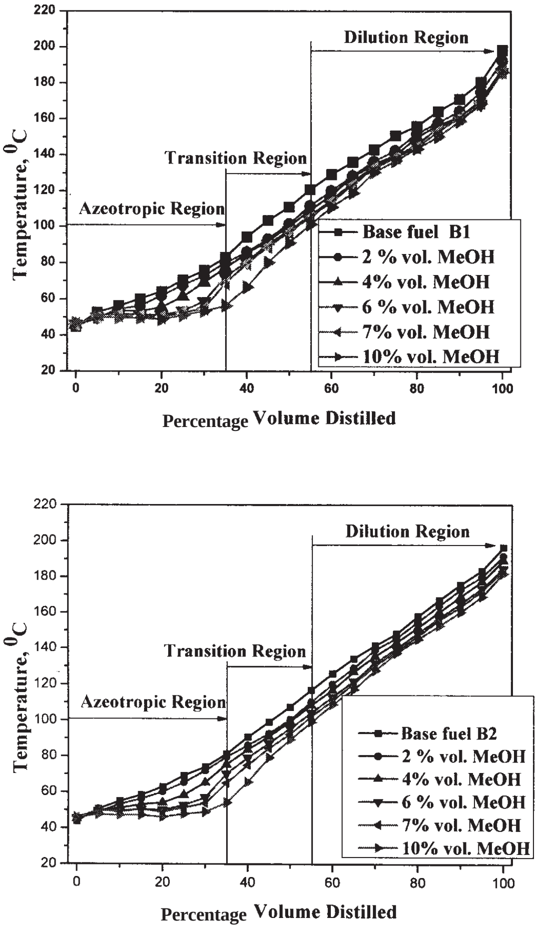

Fig. 3. The distillation curves of reformulated gasolines with various proportions of methanol

and for gasoline *B2* - 10% vol. ethanol, *E70* increase with 82.61% than *E70* value of *B2* base gasoline.

In case of reformulated gasolines with 2, respectively 10% vol isopropanol, the *E70* values increase with 0.81%, respectively with 40.32%, than *E70* value of *B1* base gasoline. In case of gasoline *B2* - 10% vol. isopropanol blend, the *E70* value increase by 54.15% than *E70* value of *B2* base gasoline.

For the *B1* gasoline mixtures substituted with 10% vol *TBA*, the *E70* values increase by 31.05% than *E70* value of B1 base gasoline, and *E70* values increase by 43.1% vol than *E70* value of *B2* base gasoline.

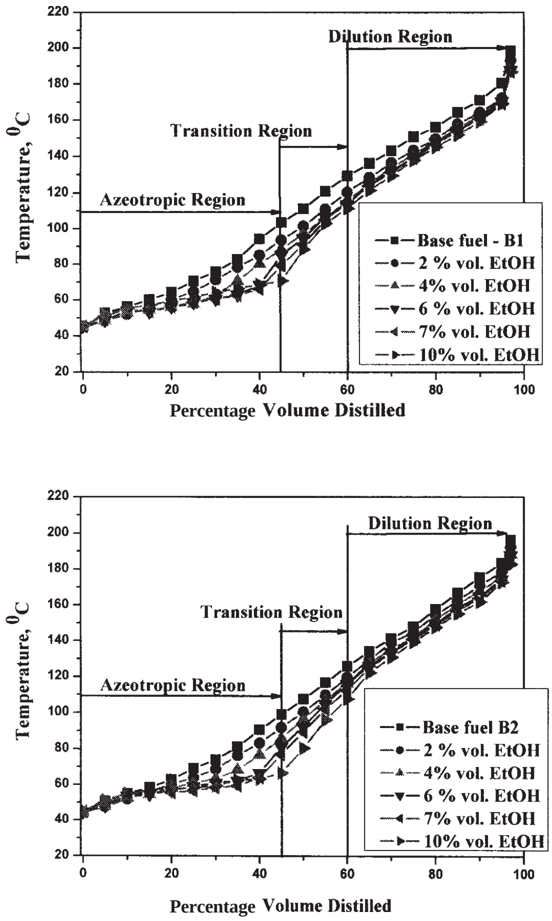

Fig. 4. The distillation curves of reformulated gasolines with various proportions of ethanol

The type of alcohol affects *E70* values of gasoline-alcohols blends in this manner: the substitution effect of gasolines-ethanol blends on *E70* values is clearly than methanol-gasoline blends because the boiling temperature of ethanol is higher than boiling temperature of methanol. In case of reformulation of gasolines with *IPA* and *TBA*, due to the same boiling temperature of both alcohols (table 3), the effect on *E70* value is due to oxygen content and chemical structure of these alcohols.

The base gasoline affects *E70* values of the gasoline – alcohols blends thus: in case of same type and content of alcohol, *E70* values of B2 gasoline-alcohols mixtures are higher than *B1* gasoline-alcohols mixtures because *B2* gasoline has a higher content of saturated hydrocarbons saturated that influences the positive azeotropic region.

In case of reformulated gasolines mixtures with 2…8% vol tert-butanol, the vapor pressures decrease by increasing of the oxygen content; the value of 10% vol *TBA* is a tendency of vapor pressure increasing. From point of view of volatility class, all reformulated gasolines with *TBA* are placed on *A* volatility class (summer time).

Lastly, in case of the reformulation of base gasolines with alcohols proportions of 2...10% vol., the *E70* values increase by increasing of oxygen content. The chemical structure of base gasoline (types of hydrocarbons classes) and the type of alcohol (boiling temperature, oxygen content and chemical structure) influence *E70* values, but the gasolines-alcohols blends do not change the type of volatility class. All blends are placed in A volatility class (summer time) in range of 20-48% vol. according to EN 228.

Based on the experimental results, in second part of our research, will be calculated *VLI* values of reformulated gasolines afterwards the reformulated gasolines and will

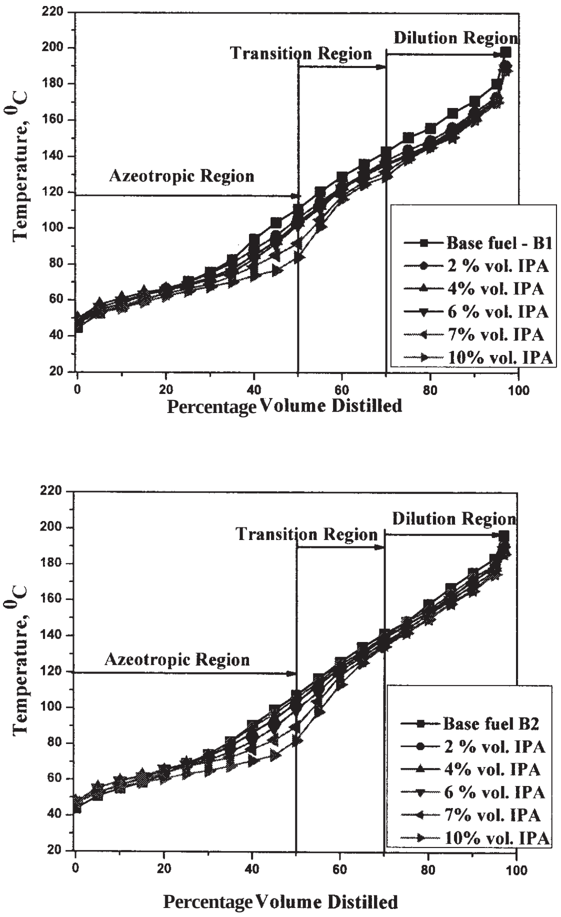

Fig. 5 The distillation curves of reformulated gasolines with various proportions of *IPA*

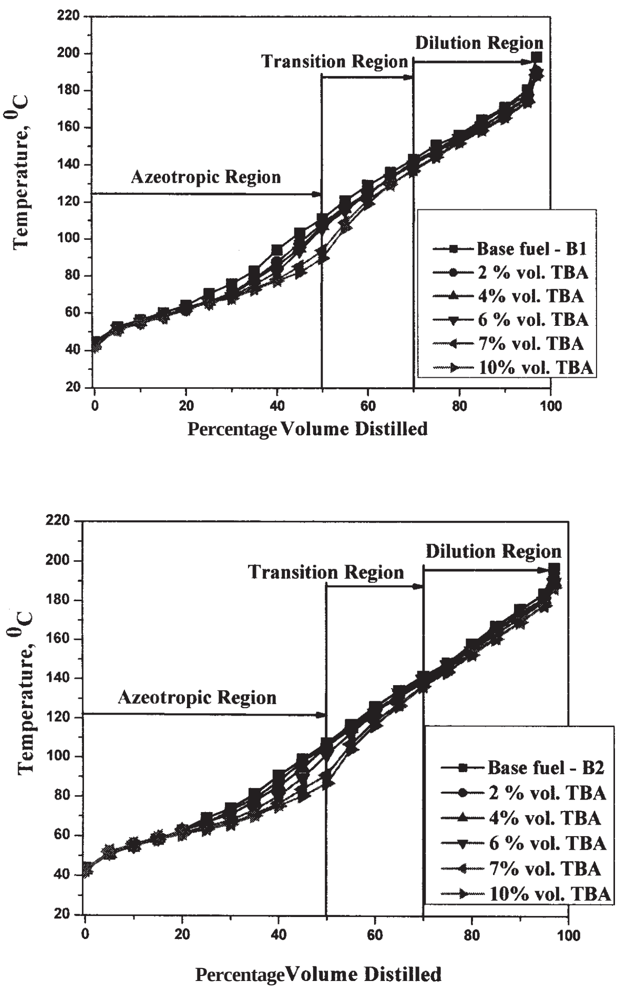

Fig. 6. The distillation curves of reformulated gasolines with various proportions of *TBA*

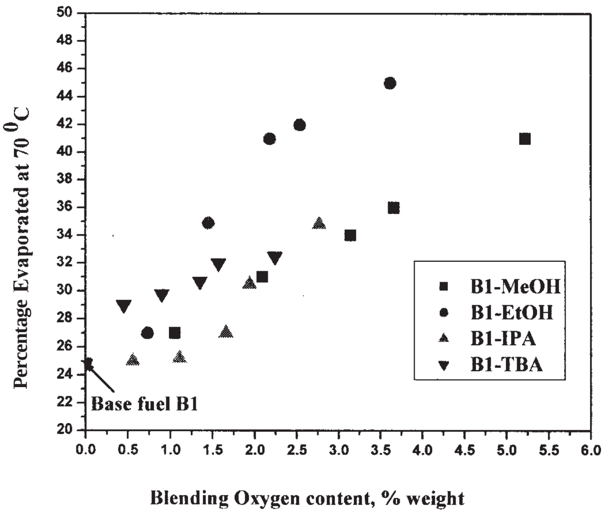

Fig.7. The variation of percentage evaporated at 70°C depending on the oxygen content for B1 gasoline substituted with alcohols

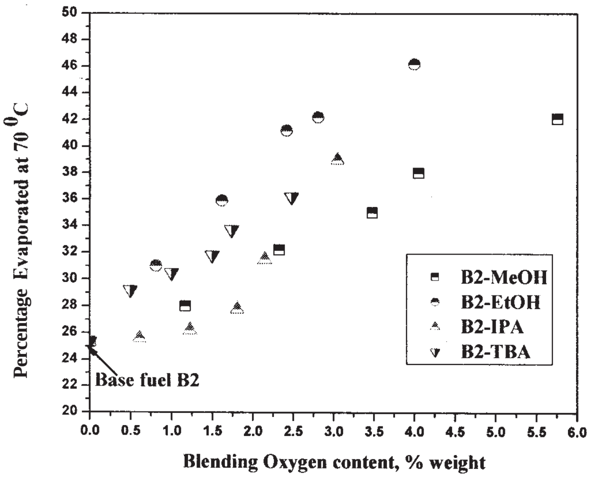

Fig.8. The variation of percentage evaporated at 70°C depending on the oxygen content for B2 gasoline substituted with alcohols

be placed in various volatility classes according to European standard of gasolines. Finally, will be found new equations for prediction of vapor pressure, evaporated percent at 70°C and vapor lock index of the reformulated gasolines with primary alcohols.

Conclusions

The utilization of oxygenates from renewable raw materials in different proportions in base gasolines for saving traditional fuels and also for reducing the polutant emissions becomes gradually a future priority. The experimental study presented in this paper shows the effect of partial substitution of base gasoline with various proportions of alcohols between 2 and 10% vol. on the volatility properties.

The substitution of gasoline in range of 2…10% vol. methanol and ethanol leads to vapor pressure increasing and classification of these blends in higher volatility class than base gasoline.

The experimental study shows *IPA* and *TBA* as promising substitutes compounds of classical gasolines due to the decreasing of the Reid vapor pressure of reformulated gasolines compared with other alcohols as methanol and ethanol. Thus, the C4 fraction is used to improve the vapour pressure of commercial gasolines.

The distillation curves of reformulated gasolines have presented various behaviours compared with base gasoline which shows the presence of positive azeotropes between light hydrocarbons as compounds of gasolines and alcohols. This affects E70 value and showed that all studied blends are placed in the A volatility class (suumer), according to EN 228 standard.

The effect of azeotropic region on the E70 shows an increasing of these values during the increasing of the oxygen content in reformulated gasolines.

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