

Effect of Oxygenated Compounds in Formulated Type EURO Gasolines

M. Petre^{*}, R.E. Dragomir^{**}, P. Roșca^{***}

^{*}Department of Chemical Engineering, Faculty of Petroleum Refining and Petrochemistry, Petroleum-Gas University of Ploiesti, 100680, Ploiesti, Phone: (040) 721527037, E-mail: mpetre@upg-ploiesti.ro

^{**} Department of Petroleum Engineering and Petrochemistry, Faculty of Petroleum Refining and Petrochemistry, Petroleum-Gas University of Ploiesti, 100680, Ploiesti, Phone: (040) 722794700, E-mail: ralued@yahoo.uk

^{***} Department of Petroleum Engineering and Petrochemistry, Faculty of Petroleum Refining and Petrochemistry, Petroleum-Gas University of Ploiesti, 100680, Ploiesti, Phone: (040) 723699482 E-mail: proasca@upg-ploiesti.ro

Abstract: This paper presents an experimental study regarding the effect of replacing aromatic compounds and partially olephinics from a catalytic cracking gasoline with oxygenated compounds (ethanol and ethyl tert-butyl ether (*ETBE*)), in motor octane number (MON) and research octane number (RON). For this study, there has been chosen two types of catalytic cracking gasolines, similar with conventional gasoline. The first type of gasoline that contains 46.6 % volume aromatic hydrocarbons has the MON 83.6 and the RON 95.7. And the second type contains 33.6% volume aromatic hydrocarbons, has the MON 83.2 and the RON 94.4. Although imposed by quality requirements, decreasing the content of aromatic hydrocarbons has the effect of reducing the RON to the lowest limit stipulated in the EN 228 quality standard. In order to compensate the octane loss, 2, 4, 6, 8, 10% volume ethanol has been added, and the conclusion was that, in the case of both gasolines a slight increase in the MON, and a significant impact on the RON. Adding 5, 10, 15, 20% volume *ETBE*, has a more significant effect on the MON of both gasolines, with an average of 1.1 octanes. After performing the experimental study, we came to the conclusion that by increasing the ethanol or *ETBE* content, the olephinic content of both gasolines is reduced, which is a positive thing, because these reformulated gasolines respect the new quality standards imposed.

Keywords: gasoline, oxygenated compounds, aromatic compounds, motor octane number, research octane number

1. Introduction

The increase of the petroleum fuel oils amount necessary for transport, their unique character, and their non-uniform distribution throughout the Globe, as well as the restrictions imposed by preserving the environment, have quickened the research developed regarding obtaining and utilizing new sources of unconventional oil fuels, that should allow, if not totally, the partial substitution of conventional gasolines and diesel fuels.

At present time, on a world wide level, researchers elaborate, at the industrial scale the following variants for total or partial substitution of conventional gasoline with oxygenated organic compounds: fueling motor engines with pure alcohols (methanol, ethanol, tert-butanol, etc.); the development of fueling motor vehicles with alcohol mixtures, in different proportions; the utilization alcohol or ether type oxygenated organic compounds in mixture with the motor vehicle gasolines; alcohol conversion (methanol, ethanol) and vegetable oils in synthetic gasolines.

On one hand, the quality of engine fuels is in constant change, especially when it comes to the sulphur content, aromatic and olephinic hydrocarbons. In table 1 we may see the presented synthesis regarding the evolution of the quality of engine fuels [3, 4]. Reaching the EURO quality standards has been a constant provocation that determined the modification of refining schemas, the increase of the

role of hydro treating processes, the introduction of gasoline reformulation (isomerization, alkylation), the utilization of high-quality catalysts and the change of mixture recipes.

TABLE 1 Evolution of the gasolines quality in the European Union

	EN 228 1993 EURO II	Dir. 98/70- 2000 EN 228: 1999 EURO III	Dir. 98/70 2005 EURO IV	Dir. 98/70 2009 EURO V
Sulphur, ppm max	500	150	50 (10)	10
Aromatics, %max. vol	-	42	35	30
Olefins, %max. vol	-	18	18	14
Gasoline, %max. vol	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

As it can be observed, from the data presented in table 1, we can expect in 2009 for a new stage regarding the quality of engine fuels. The reduction of aromatic and

olephinic hydrocarbon content will lead to the decrease of the MON and of the RON. A way for compensating the octane loss is the partial substitution of gasolines with oxygenated compounds.

Introducing a certain content of oxygenated compounds in motor vehicle engine fuels is compulsory, being imposed by the quality standards in use. The EU 30/2003 directive proposes the substitution of conventional engine fuels with 5.75% alternative fuels until 31 December 2010, respectively with 20% alternative fuels until the year 2020 [5]. This ensures a durable energetic development and increases the national security level in terms of energy by decreasing pressure on traditional sources of fossil fuel.

In this paper we present an experimental study regarding the effect of adding varied proportions of ethanol and *ETBE*, on the octane number of two catalytic cracking gasolines. Our attention has been drawn towards these two oxygenated compounds, because ethanol can be obtained from regenerative raw material and *ETBE* through the conversion of bio-ethanol.

2. Experimental study

Conventional engine fuel represents a mixture of gasolines obtained through raw material processing and through technological processes. Using several components in processing the conventional gasolines is compulsory for ensuring the necessary conditions imposed by the quality standards in use. The catalytic cracking gasolines represents more than 50% of the content of conventional engine fuels, so we may consider it a basic component of the reformulated gasolines, and through its features, it influences the quality of the final mixture. Having this in mind, for the experimental study developed throughout this paper, we have chosen two catalytic cracking gasolines with different contents of aromatic hydrocarbons, having different octane numbers, as we may see in table 2. The properties of the catalytic cracking gasolines and of their mixture with oxygenated compounds are determined with a IROX 2000 Portable Gasoline Analysis with MID-FTIR instrument.

The properties of ethanol and of *ETBE* that have a strong influence over their mixtures with gasolines are shown in table 3 [6].

In order to study the effect of substituting the catalytic cracking gasolines with *ETBE* mixtures with 5, 10, 15, 20% volume *ETBE* and 2, 4, 6, 8, 10% volume ethanol from each gasoline have been prepared and the content of aromatic and olephinic hydrocarbons have been experimentally determined. Results have been shown in Fig. 1 and 2.

In diagrams shown in Fig. 1 and 2, we may observe the decrease in aromatics and olephinics contents, proportional with the increase of each amount of oxygenated compound added in the mixture.

TABLE 2. The properties of the catalytic cracking gasoline

Properties	Gasoline A		Gasoline B	
	% volume	% weight	% volume	% weight
benzene	0.83	0.95	0.84	0.97
toluene	8.7	9.8	4.7	5.4
m-xilene	5.8	6.5	5.9	6.7
o-xilene	1.9	2.2	1.9	2.2
p-xilene	2.1	2.4	2.4	2.7
Propel-benzene	3.3	3.7	2.6	2.9
2-ethyltoluene	3.3	3.8	2.4	2.8
3-ethyltoluene	4.7	5.3	4.5	5.1
4-ethyltoluene	2.4	2.7	1.9	2.2
mesitilen	2.7	3	2.6	3
pseudocumen	5.4	6.2	5.6	6.5
isoduren	2.7	3.1	2.3	2.7
Total aromatics	46.6	53.3	33.6	38.8
Total olephinics	21.8	20.6	23.5	22.5
Total saturated	31.6	26.1	42.9	38.7
MON	83.6		83.2	
RON	95.7		94.4	

TABLE 3. The properties of the ethanol and of the *ETBE*

	Oxygen, % wt.	RON	MON
Ethanol	34.8	130	96
ETBE	15.7	118	101

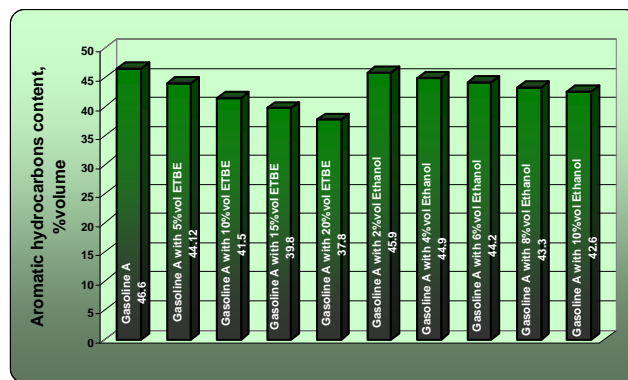


Figure 1. The *ETBE* and ethanol effect on aromatic hydrocarbons content of mixtures with catalytic cracking type A gasoline.

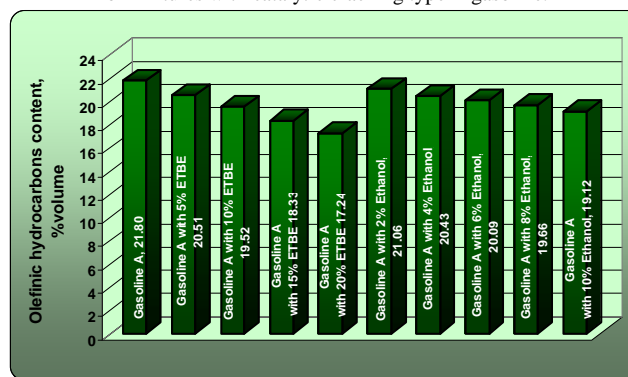


Figure 2. The *ETBE* and ethanol effect on olephinic hydrocarbons content of mixtures with catalytic cracking type A gasoline.

In the case of type A gasoline, regardless of the *ETBE* or ethanol added ratio, we can not obtain the minimum amount indicated in the quality standards for engine fuel type EURO IV (maximum 35% volume), although in the case of substituting 20% volume from this gasoline with *ETBE*, we may observe a decrease with 8% volume in the content of aromatic hydrocarbons from the gasoline's basic composition. Also, only through substituting 20% volume of this gasoline with *ETBE*, one can obtain the olefinic hydrocarbon content lower than the minimum amount indicated for engine fuel type EURO IV (maximum 18% volume).

In the case of type A catalytic cracking gasoline mixtures with the proportions of oxygenated compounds stipulated above, octane numbers have been determined and graphical representations in Fig. 3 and 4 have been drawn.

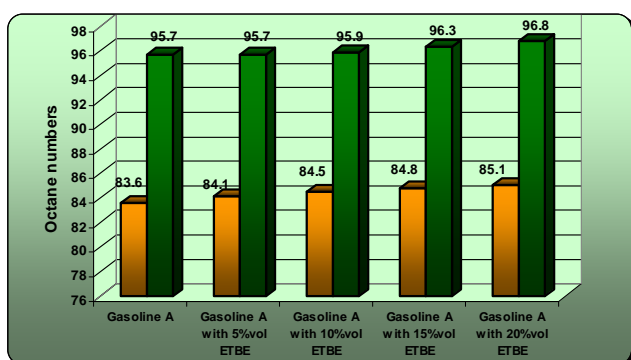


Figure 3. The *ETBE* effect on octane numbers of mixtures with type A catalytic cracking gasoline.

In the graphic presented in Figure 3 we can observe an increase in the octane numbers once with the increase of *ETBE* content. For a content of 20% volume *ETBE*, the MON of the mixture with type A catalytic cracking gasoline has reached over the minimum value stipulated in the EN228 standard. This is explained with the help of the high motor octane number of the *ETBE*.

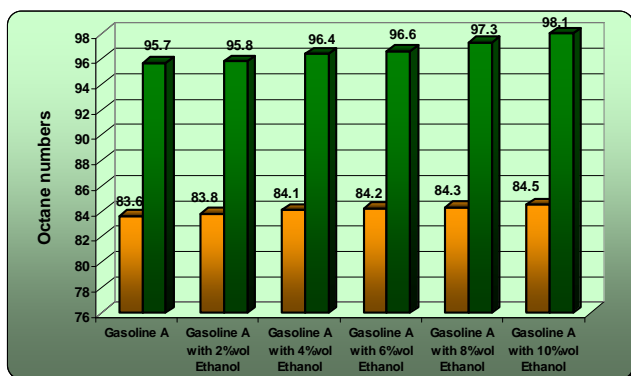


Figure 4. The ethanol effect on octane numbers of mixtures with type A catalytic cracking gasoline.

In the graphic presented in Figure 4 we can observe an increase in the octane numbers proportional with the increase of ethanol content. For a content of 10% volume ethanol, the RON of the mixture with type A catalytic cracking gasoline has increased with 2.4 octanes, higher

than the minimum value stipulated in EN228 standard. This is explained with the help of the high RON of the ethanol. We must take into account the differentiated increase of RON and MON octane numbers proportionally with the addition ratio and the type of oxygenated compound used in this process. Regarding the same addition ratio one can observe higher increases in the RON when substituting gasoline with ethanol, while the increase of the MON remains at a constant level. Although apparently similar increases in the octane numbers are obtained at lower ratios of added ethanol, using large amounts of *ETBE* presents many advantages because it allows the reduction of aromatics and olefinics content from the gasoline preserving and even slightly increasing the RON and the MON.

In the development of the experimental study type B catalytic cracking mixtures have been prepared, with the same amounts of *ETBE* and ethanol as in the case of type A gasoline, and the aromatic and olefinic hydrocarbons content has been experimentally determined. Results have been graphically represented in Figures 5 and 6.

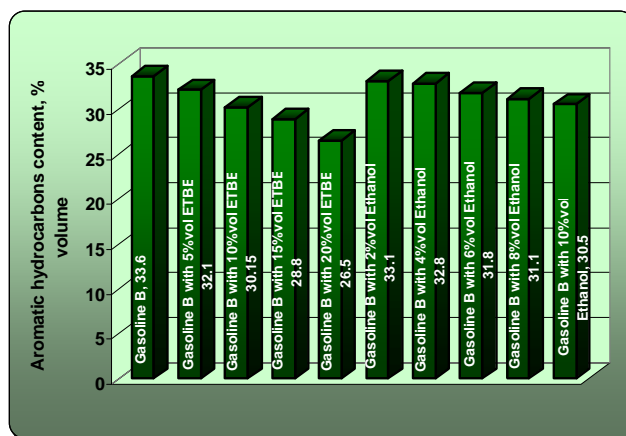


Figure 5. The *ETBE* and ethanol effect on aromatic hydrocarbons content of mixtures with catalytic cracking type B gasoline.

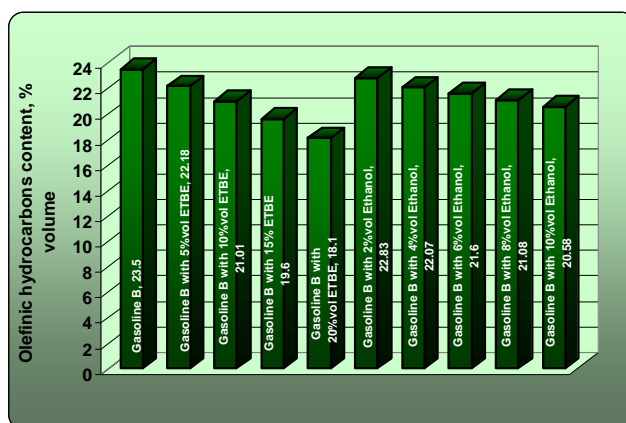


Figure 6. The *ETBE* and ethanol effect on olefinic hydrocarbons content of mixtures with catalytic cracking type B gasoline.

In the graphics presented in Fig. 5 and 6 we can observe the decrease in the content of aromatic and olefinic hydrocarbons, with the increase of the content of each oxygenated compound added in the mixture as in the

case of type A gasoline. In the case of type B gasoline that has lower aromatics and higher olefinic content, by substituting more than 10% volume gasoline with *ETBE*, we can observe a decrease in aromatic hydrocarbons content under the lowest accepted level indicated in the case of the engine fuel type EURO V (maximum 30% volume). Regarding the olefinic hydrocarbon content, regardless of the added *ETBE* or ethanol ratio, we can not obtain the lowest content stipulated for the engine fuel type EURO IV (maximum 18% volume).

In the case of type B catalytic cracking gasoline mixtures with the proportions of oxygenated compounds stipulated above, octane numbers have been determined and graphical representations in Fig. 7 and 8 have been drawn.

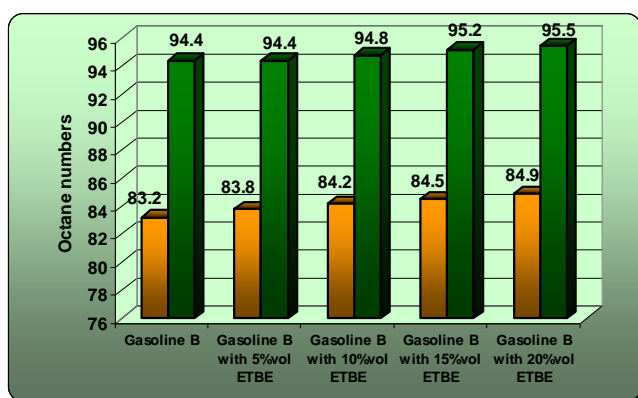


Figure 7. The *ETBE* effect on octane numbers of mixtures with type B catalytic cracking gasoline.

In the graphic presented in Figure 7 one can once again observe an increase in the octane numbers proportional with the increase of *ETBE* content.

For a content of 20 % volume *ETBE*, the MON of the mixture with type A catalytic cracking gasoline has increased close to the minimum value stipulated in EN228 standard. For a content of 15% volume *ETBE*, the RON increases above the minimum value stipulated in EN228 standard.

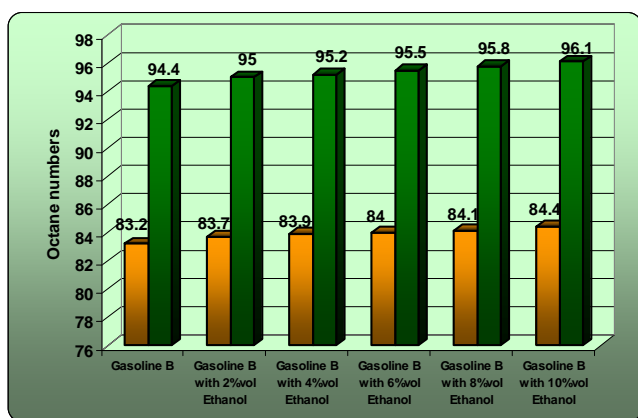


Figure 8 The ethanol effect on octane numbers of mixtures with type B catalytic cracking gasoline

In the graphic presented in Fig. 8 one can observe an increase in the octane numbers proportional with the increase of ethanol content.

For a content of 10 % volume ethanol, the MON of the mixture with type B catalytic cracking gasoline has increased by 1.2 octanes, but does not reach the minimum value stipulated in EN228 standard. Instead, the RON increased by 1.7 octanes through the substitution of 10 % volume from type B gasoline. This is possible due to the ethanol's high RON.

3. Conclusions

The study presented in this paper has confirmed that by substituting catalytic cracking gasolines with different ratios of oxygenated compounds, we can reduce the aromatic and olefinic hydrocarbons content of conventional engine fuels and in the same time we can compensate or even slightly increase a part of the octane loss. But, in the case of catalytic cracking gasoline with an initial content of over 40% volume aromatic hydrocarbons, even substituting it with high amounts of oxygenated compounds, does not meet the demands of reaching the amount of aromatics imposed by the present or future quality standards. Even if we can compensate the decrease in the MON by using *ETBE* and in the RON by using ethanol, does not mean it is the only solution, how much more so that the increase in oxygenated compounds entails the increase in the oxygen amount of their mixture with gasolines. We must not forget the fact that the EN228 standard restricts the total amount of oxygen from the gasolines to 2.7% weight, value which is already surpassed at 17% volume *ETBE* or in the case of 8% volume ethanol. In the case of a catalytic cracking gasoline, with an initial aromatic hydrocarbons content of maximum 35% volume, as in the case of type B gasoline, which comprises the quality conditions imposed by the present EURO IV standard, it is easy to reduce its content of aromatic hydrocarbons to the maximum value demanded by the EURO V standard, by substituting it with moderate *ETBE* amounts (approximately 10% volume).

Regarding the decrease of olefinic hydrocarbons content from catalytic cracking gasolines, substituting them with *ETBE* seems like an acceptable solution.

When it comes to conventional gasolines, the added oxygenated compounds can not meet all of the quality restrictions demanded by the future engine fuels quality standards, and this imposes orientation towards other octane components that present a low content of aromatic and olefinic hydrocarbons.

At the end of this experimental study and after the previous conclusions, we may assert that in order to reduce the content of aromatic and olefinic hydrocarbons to the maximum levels demanded by the EURO V engine fuels, we must combine solutions liked to the optimization of component production in the case of conventional gasolines by partially substituting them with *ETBE* in various proportions. A solution regarding compensating the octane loss seems to be the partial substitution of conventional engine fuels with mixtures of ethanol and *ETBE* produced through experiments.

The present study will be continued through further research concerning the effect of ethanol and *ETBE* mixtures or other ethers, on the reduction of undesirable hydrocarbons content, and also on the increase in octane numbers of partially substituted gasolines with oxygenated compounds.

AKNOWLEDGMENT

The present study has been performed using the apparatus from the "Engine Fuels Quality Testing" laboratory of the Faculty of Petroleum Refining and Petrochemistry, apparatus that we have been able to acquire with the help of funds received from **Module IV CEEEX-45/2006 Contract**.

REFERENCES

1. Onutu I., Rosca P., Matei V., Asigurarea specificatiilor de calitate si ecologice prin reformularea combustibililor de tip benzine auto, Simpozion Icechim, **2003**.
2. Rock K., Korpelshoek M., Bioethers impact on the gasoline pool, Biofuels, **2007**, pp. 9-15.
3. Debuisschert, Q., Domergue, B., Pucci, A., Watipont, L., ERTC Annual Meeting, 17 November **2004**, pp. 12-15, www.Axens.net.
4. Directive 98/70/EC of the European Parliament and of the Council of 13 October **1998** relating to the quality of petrol and diesel fuels and amending Council Directive 93/12/EC.
5. Directive 2003/30/EC of the European Parliament and of the Council of 8 May **2003** on the promotion of the use of biofuels or other renewable fuels for transport.
6. Alcohols/Ethers as oxygenates in diesel fuel: Properties of blended fuels and evaluation of practical experiences, IEA Advanced motor fuels, annex XXVI final report, Tec TransEnergy Consulting, Report TEC 3/**2005**.