Chemical Analysis of Retail Automotive Gasolines on Romanian Market

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A gasoline quality survey from 48 retail stations belonging to the first top four oil companies present on Romanian market was conducted, in 2013, being investigated for 8 commercial brands the chemical composition (aromatics, olefins, alcohols, ethers, oxygen content), the antiknock resistance, the distillation profile and the vapour pressure, and compared with the limits from 2009/30/EC Directive. The results were interpreted in terms of conformity with standards, impact on engine performance and environment. Full compliance with Fuel Quality Directive requirements for distillation points (E100, E150), vapour pressure, olefins, benzene, oxygen, and ether content was noticed; all but one for aromatics content, in which one brand exceeded with 0.5% the limit, still in the range of apparatus error. The ethers present in gasoline were MTBE (in all the samples), ETBE and TAME (a quarter of all samples) which increased the oxygen content up to the mean of 1.86%. RON for all the tested premium gasolines were compliant, but for regular ones there were a slight difference of 0.1 (94.9, less than limit 95) for 3 out of 4 producers. Regarding MON values, a brand was obviously under the limit whereas other two were close to the correlation method limit (84.8-85). Both density and final distillation point have met the limits of EN 228 transposed in the national standard. No detectable signs of adulteration were reported.

Keywords: gasoline, quality survey, standard conformity, fuel adulteration, spark engine

According to predictions, petroleum based fuels will be the dominant energy source for the next decades in road transportation, 70% of the car fleet in 2030 being still driven by combustion engines [1]. As the share of renewables in overall energy consumption is foreseen to be 15-20% in 2050, the oil companies policy will shape the promotion of biofuels in the quality profile of gasolines [2]. The newcomer countries in European Union (EU) had to comply with more stringent fuel quality standards than the national ones before joining EU. The Romanian gasoline standard [3] has been aligned to European one and to Fuel Quality Directive [4], the latter imposing a set of parameters in Table 1, mandatory for all EU members, focusing on the control and limitation of the fuel impact on people health and environmental pollution.

Gasoline quality in Romania can be evaluated in two stages, before and after joining EU in 2007. During pre-adhesion phase, in 2006 [5], two grades of gasoline have been commercialized on Romanian market, both unleaded, with RON minimum 95, one with sulphur content lower than 50ppm (90.1% from production volume) and the other with sulphur content lower than 10 ppm (9.9%). In 2006 the gasoline survey on 101 samples identified several non-conformities such as: RON mean values were less than limits, *i.e.* 93.9 than minimum required 95, and MON was 84 instead of minimum required 85, higher values of aromatics (39% instead of standard 35%), benzene (1.7% instead of 1%) and sulphur content (74 ppm instead of 50 ppm).

Properties	Directive 2009/ 30/EC
Research Octane Number, RON (min.)	95
Motor Octane Number, MON (min.)	85
Vapour Pressure, VP (kPa, max)	60 (70 - derogation)
Distillation:	
evaporated at 100°C (%v/v, min.), E100	46
evaporated at 150°C (%v/v, min.), E150	75
Olefins (%v/v, max)	18
Aromatics (%v/v, max)	35
Benzene (%v/v, max)	1.0
Oxygen Content (%m/m, max)	3.7
Methanol, (%v/v, max)	3
Ethanol, (%v/v, max)	10
Iso-Propyl Alcohol (%v/v, max)	12
Tert-Butyl Alcohol (%v/v, max)	15
Iso-Butyl Alcohol (%v/v, max)	15
Ethers containing 5 or more carbon atoms per molecule (%v/v, max)	22

Table 1
STANDARD LIMITS OF THE GASOLINE PARAMETERS

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After 2007, Romania revised its fuel quality systems setting up the Fuel Quality Monitoring System, meeting the requirements of EU Directives. Changes appeared in gasoline quality, two grades being sold in 2011, both unleaded, with minimum 95 RON, having 5% biofuel and respectively with minimum RON 98, having 5% biofuel. From a total of 224 gasoline samples only one unleaded sample (min. RON 98) was found as non-compliant at the parameter benzene [6].

The oil companies active on Romanian market also introduced internal standards in surveying fuel quality along the distribution chain: at the exit of oil refinery, in fuel deposits and at fuel stations, in order to avoid any accidental or illegal contamination.

In spite of the evident improvement of gasoline quality in the period 2006-2012, there are still complaints of the customers who believe that gasoline sold in Romania has a lower quality than that sold in other EU countries. Some reasons for lack of trust could be the older memories of the drivers on lower quality of petrol before joining EU, as well as several cases of petrol adulterations presented in justice [7,8].

The fuel quality demand becomes nowadays more difficult to achieve due to EU Directive [4] requirement which have increased the share of oxygenated compound at 3.7%; the formulation of petrol fuel involves the blending with alcohols and ethers asking for a thorough investigation and recomputation of blend properties [9].

The objective of the research work presented in this paper is to perform a small scale, independent quality survey of retail gasoline on the Romanian market, having as main tasks the investigation of standard compliance, the analysis of the non-compliances upon environment and engine performance, as well as the accurate public information.

Experimental part

Composition and fuel test methodologies

A set of gasoline parameters was measured using MID-FTIR spectrometer IROX 2000, Gasoline Analyzer from Grabner Instruments, based on absorption measurements, according to ASTM D 5845, in the range of 2.7 to 15.4 μm [10]. Octane numbers, distillation properties and vapor pressure were determined using factor analysis method or multi-linear regression, based on the correlation between absorbencies and aforementioned properties [11].

There were investigated the following common parameters included in EU Directive [4] and in Romanian standard [3]: RON, MON, VP, evaporated volume at 100°C (E100) and evaporated volume at 150°C (E150), total olefins, total aromatics, benzene, oxygen content, methanol, ethanol, iso-propyl alcohol, tertiary-butyl alcohol, iso-butyl alcohol and ethers with 5 or more carbon atoms. The accuracies of the measurements in mass fractions were 0.5% for ethers and alcohols, 0.2% for benzene, 0.1% for oxygen content, 2% for aromatics and 1.5% for olefins. Additionally, there were measured density and final boiling point (FBP), limited only in Romanian standard [3], which are relevant in terms of engine fuel economy and accumulation of deposits. The accuracy of distillation temperatures is 0.1°C, for pressure reading is 0.1kPa and for density 0.001 g/cm^3.

Survey methodology

The survey methodology was guided after a quality survey of retail biodiesel blends in Michigan [12] and adapted to the specific requirements of petrol fuel.

Gasoline samples were collected at filling stations of four oil companies, national and international ones, whose brand names were kept anonymous. The companies possess over 70% from the total number of filling stations in Romania, namely 2236 [13], and cover more than 95% from customer preferences [14]. Samples were taken randomly from the identified oil companies, called here A, B, C and D, in March-April 2013. Each of the four oil companies (A, B, C, D) sells two types of petrol fuel, a regular grade marked with 1, having RON min.95 (A1, B1, C1, D1) and a premium grade marked with 2 with RON higher than 95, (A2, B2, C2, D2).The total number of samples was 48, from each of 8 commercial brands, being bought 6 samples of the same kind from different filling stations situated in the central area of Romania in the region Brasov - Sibiu.

Results and discussions

Investigation of standard compliance

For simplicity the results of the gasoline measurements were divided on grades and producers the values presented here being the mean calculated value out of 6 samples taken from different stations. In the following charts the dotted lines represent the limits of gasoline parameters from Directive [4] according to table 1 or from national standard, for FBP only [3].

Octane numbers

The Research octane numbers were presented as mean values of the 8 grades in figure 1. It can be noticed that the mean value of the regular grade marked with index 1 is smaller than the mean value of premium grade marked with index 2 (95.25 < 96.85) and the overall mean is 96.05, showing a good agreement with the requirement of the gasoline standard (95).

The mean values of Motor octane numbers of the petrol samples are shown in figure 2. It can be noticed that the mean value of standard grade marked with index 1 is smaller than the mean value of premium grade marked with index 2 (85.12 < 85.6) and the overall mean is 85.36 indicating a good agreement with the requirement of the standard (85), with the exception of the mean value of samples C1, which is smaller than the limit, considering the measurement accuracy (84.5 < 85-0.2).

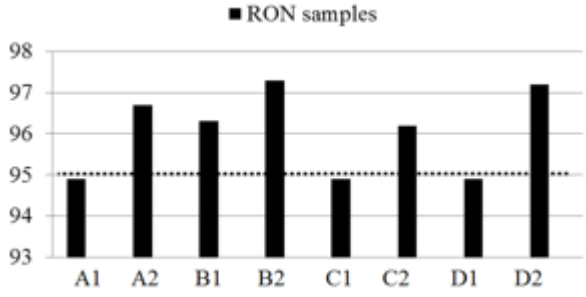

Fig.1. Mean RON of samples

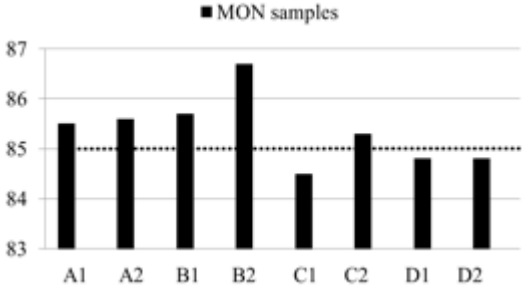

Fig.2. Mean MON of samples

Vapour pressure

Vapour pressure is an indicator of the gasoline volatility, featuring engine operation at cold start and warm-up period. It is constrained into two limits imposed by opposite phenomena: a higher VP provides a rapid cold start of the engine and a lower VP prevents excessive evaporative emissions [14].The Directive 2009/30/EC limits only the maximum value in summer period, admitted to 60 kPa and derogated to 70 kPa for countries with lower temperatures during summer. The overall mean value of VP of the analysed samples was 60.4 kPa, very close to 60 kPa, the maximum value in EU Directive, as illustrated in figure 3. No sample exceeded the maximum derogated value of 70 kPa. The requirements of the national standard [3], 45-90 kPa for transition period, were accomplished.

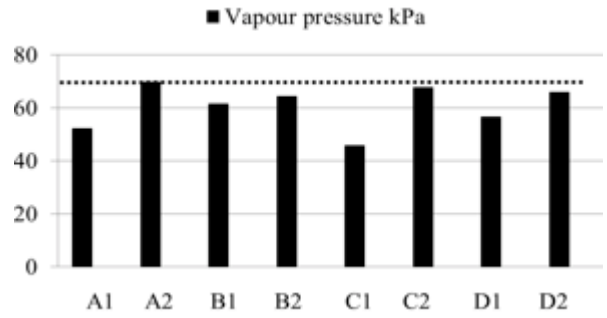

Fig.3. Mean VP of samples

Distillation profiles

The distillation in EU Directive is expressed through minimum imposed values of E100 and E150, illustrated in figures 4 and 5. The minimum percentage of distilled volume is met, both for E100 (46%) and E150 (75%).

The national standard SR EN 228:2012 requires for E 100 a limited range (46-71%) which has been met by all examined samples.

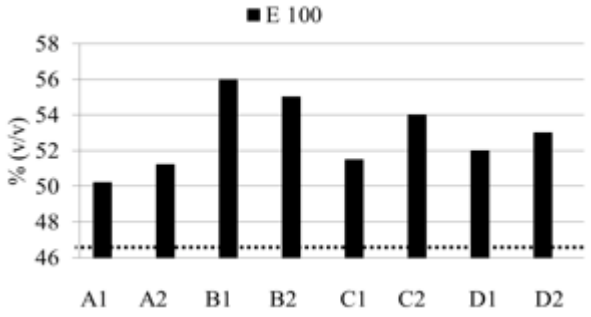

Fig.4. Mean E100 of samples

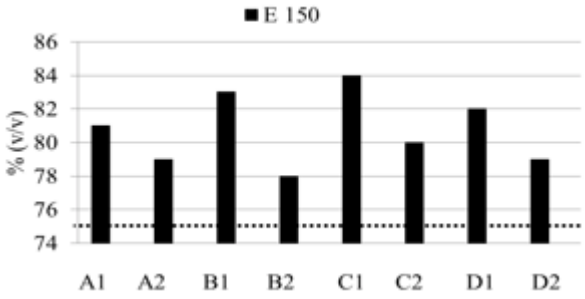

Fig.5. Mean E150 of samples

Olefins

For olefin content, no sample exceeded the maximum of 18% of the standard. The total olefins measured for the samples are represented in figure 6, the overall mean value for 8 types of fuel being 8.16%.That value confirms the general tendency of lowering olefins, thus limiting olefins in evaporative emissions and reducing ozone formation [14].

Aromatics

There is a tendency to lower aromatics which will lead to lower emissions of carbon monoxide (CO) and volatile organic compounds (VOC) in exhaust gas. The distribution of the mean aromatic content for the 8 grades can be seen in figure 7, the overall mean of total aromatics being 33.12%. Only the mean of sample A1 has a slight exceeding of the limit.

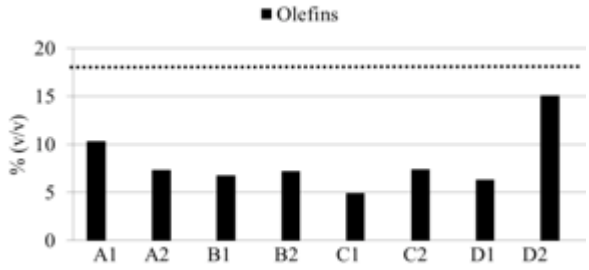

Fig.6. Mean olefin content of samples

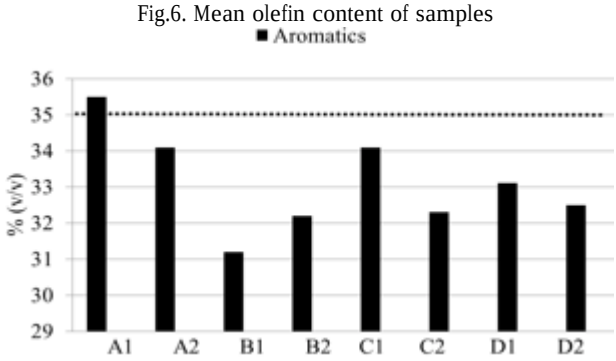

Fig.7. Mean aromatic content of samples

Benzene

One of the aromatic components, benzene, is known as the most harmful compound due to its proven carcinogenicity [15]. It has a distinct limitation in standard, up to 1% concentration in volumes. The limitation of benzene in gasoline will predict lower benzene in evaporative emissions and lower VOC in exhaust gas. The overall mean of benzene content is 0.77% and its distribution is presented in figure 8.

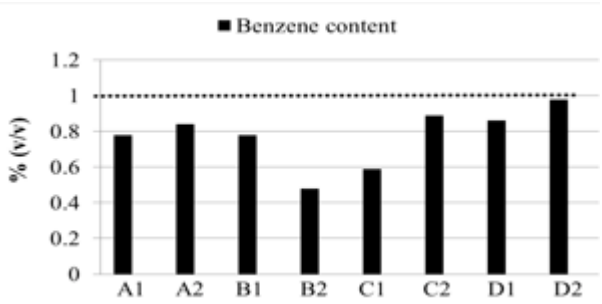

Fig.8. Mean benzene content of samples

Oxygen content

The newcomer in the gasoline composition is oxygen, introduced by the obligations assumed in EU to limit the greenhouse gas emissions with at least 6 % by the end of 2020, mainly by the use of biofuels [4]. For the tested fuels there were found only ethers and no alcohols. The oxygen content was calculated based on the concentration of the measured components, as shown in figure 9. The samples did not exceed the threshold value of 3.7% and the overall mean of all the samples was 1.86%.

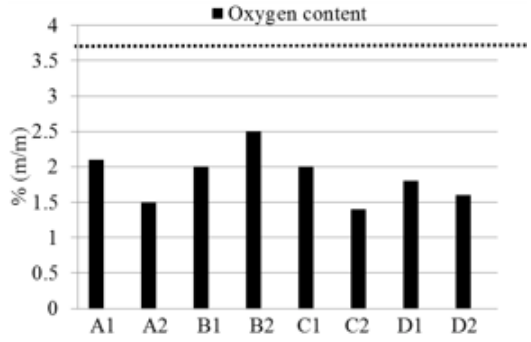

Fig.9. Mean oxygen content of samples

Ethers

The typical ethers which can be used in gasoline as substitution components are MTBE (Methyl Tertiary Butyl Ether), ETBE (Ethyl Tertiary Butyl Ether), TAME (Tertiary Amyl Methyl Ether) and DIPE (Di-Iso Propyl Ether); by means of the variation of ether content, the volatility and distillation profile of the blend can be controlled, ethers being preferred to alcohols. For tested gasolines, the total ether content is revealed in figure 10.

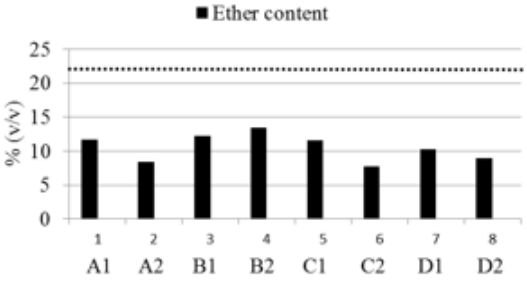

Fig.10. Mean ether content of samples

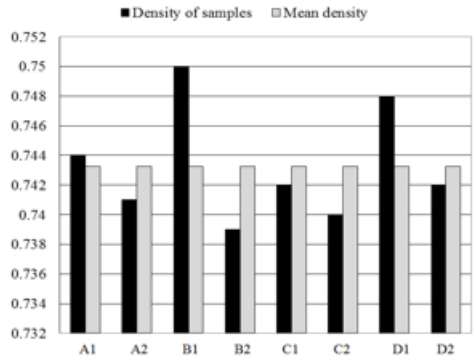

Fig.11. Mean relative density of samples

The most used ether was MTBE, which was found in all the samples. Only two fuels, B1 and C1, have extra ethers in form of ETBE (B1-6.6%v/v and C1- 4.3%v/v) and TAME (B1-1%v/v).The overall mean ether content was 10.6%.

Density

The gasoline density at 15°C is limited in the interval 720-775 kg/m^3 in national standard [3]. As illustrated in figure11, the measured relative densities met the standard range, moreover, the measured range was very narrow (0.739-0.75).

Considering the engine performance, the higher the density of the fuel, the higher the heat released during combustion and the effective power of the engine.

Final Boiling Point

FBP is an indicator of the boiling temperatures of the heaviest hydrocarbons in the petrol, being limited to 210°C in national standard [3]. All the samples have FBP lower than the imposed limit (dotted line) and the overall mean

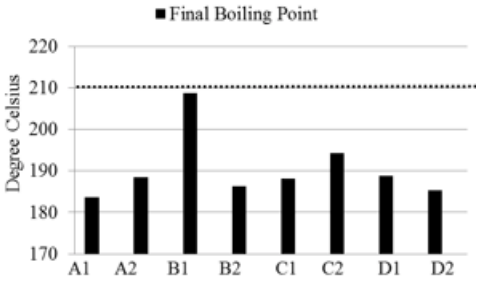

Fig.12. Mean FBP of samples

value of FBP for all tested samples was 190.4°C (fig. 12). The tendency of lowering FBP means lower VOC in the exhaust gas and lower carbon deposits in the combustion chamber, but also less gasoline distilled from one tonne of crude oil.

Analysis of the non-compliances upon environment and engine performance

The non-compliances were detected for octane number, RON being smaller for regular grades A1, C1, D1 (with 94.9 instead of 95). For MON, the only non-compliance is for the gasoline sample C1 (84.5 instead of 85). For aromatics, the mean of sample A1 had a higher content than the limit (35.5% instead of 35%). Considering octane engine requirements, the RON and MON values of several samples are smaller than limits, thus meaning that in some operation modes it is possible to have a very slight tendency to knock. From the environmental point of view a higher aromatic content will produce higher VOC in exhaust gas and atmosphere.

Contamination risk

Fuel can be altered before combustion in spark engine by improper storage, transport and manipulation or accidental or illegal contamination (adulteration). The detection of contamination is difficult as most of the hydrocarbons in contaminants are also present in the composition of automotive gasolines. Nevertheless, there are some parameters sensitive to contamination, such as density, FBP and distillation profile.

Some non-conformities of gasolines must be considered as symptoms for adulteration [16]:

-If relative density is higher than 0.79, it may be suspected contamination with an aromatic product (benzene, toluene, xylene) or diesel fuel;

-If the FBP is higher than 210°C, the petrol could be contaminated with a heavier hydrocarbon which distills at higher temperatures (for example 2% of diesel fuel added to petrol rises the FBP of the blend with 11°C);

-If the distillation profile does not respect the condition of minimum 46% at 100°C, it can be caused by contamination with light hydrocarbons (hexane) or oxygenates (alcohols or ethers) in higher fractions than allowed.

Regarding the tested fuels, taking into account the limits of measurement procedures, the symptoms of contamination were not identified, so there are no clues to indicate any attempt of adulteration.

In amother paper was studied the benzene management in refine gasoline pool [17].

Conclusions

Romanian commitment to EU legislation imposed the meeting of stricter standards and quality evaluation procedures. The distrust of Romanian people on current petrol quality sold in fuels stations is contradicted, in a greater extent, by the results of the present quality survey

performed on 48 fuel stations belonging to the first four oil retailers from the local market, thus being confirmed the efficiency of the Fuel Quality Monitoring System, as indicated in the EU Fuel Quality Monitoring Summary. The analysis of the parameters leads to the following general interpretations:

- The quality parameters met the requirements of the standard,with the exception of few minor non-conformities to octane numbers and aromatic content.
- Fuel relative density varied in a narrow range 0.739-0.750 which means that the injected quantity of fuel in every engine cycle has a very limited dispersion.
-Oxygen content in the fuel was introduced by the use of ethers, the dominant one being MTBE; as the overall oxygen content was not exceeded (1.86 < 3.7%) there is still reserve for adding oxygenates.
- With the overall sample mean of 10.2%, ether content could be doubled (up to 22%), improving also the octane numbers.
- With a minor exceeding (A1), aromatics met the values under 35% and the most harmful component – benzene was kept under the limit of 1%.
- Based on the performed tests, there was no evidence of petrol adulteration.

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