

Aging effects on gasoline–ethanol blend properties and composition

Ernane Ribeiro Streva^{a,1}, Vanya Márcia Duarte Pasa^{b,2}, José Ricardo Sodré^{a,*}

^a Pontifical Catholic University of Minas Gerais, Department of Mechanical Engineering, Av. Dom José Gaspar, 500, CEP 30535-610 Belo Horizonte, MG, Brazil

^b Federal University of Minas Gerais, Department of Chemistry, Av. Antônio Carlos, 6627, CEP 31270-901 Belo Horizonte, MG, Brazil

ARTICLE INFO

Article history:

Received 25 January 2010

Received in revised form 26 July 2010

Accepted 30 July 2010

Available online 13 August 2010

Keywords:

Gasoline
Properties
Composition
Aging
Oxidation

ABSTRACT

Blends of 75% gasoline and 25% ethanol (E25) are unique fuels used in Brazil. The natural E25 oxidation process due to aging under atmospheric conditions has been investigated. To evaluate aging effects on the properties of commercially available fuel blends, two samples of regular E25, one sample of regular E25 with additives, and one sample of high octane E25 were tested. The samples were analyzed as new and in aging periods of 30 and 180 days. Fuel density, distillation temperatures T_{10} , T_{50} and T_{90} , motor and research octane number, as well as concentrations of ethanol, oxygen, olefins, total aromatics, benzene and saturates were evaluated. It was observed an increase of fuel density, distillation temperatures, aromatics and oxygen concentration, and a decrease of the concentration of olefins with aging. The results indicate that the use of aged fuel in automotive engines may increase fuel consumption, carbon deposits formation, carbon monoxide and hydrocarbon emissions.

© 2010 Elsevier Ltd. All rights reserved.

1. Introduction

Gasoline is basically made up by hydrocarbons and by low contents of oxygenates. The hydrocarbon components of gasoline are aromatics, olefins and saturates, which are formed by molecular chains of 4–12 carbon atoms. Gasoline also shows low concentrations of sulfur, nitrogen and metals, which introduce molecular instability to the product. This instability is responsible for an oxidation process that starts from production and continues throughout transport and storage, causing gum formation from catalysis reactions of unsaturated hydrocarbons. Anti-oxidizers and metal deactivators are added to gasoline to delay the process of gum formation, but after a period of approximately 2 months the fuel is no longer guaranteed by the distributors to meet the specifications for engine use. Gasoline aging also causes light components evaporation, which can affect engine performance and, mainly, exhaust emissions.

Brazilian gasoline contains 20–25% of ethanol by volume. The ethanol concentration in gasoline is specified within that range by the country's Petroleum National Agency (ANP) and depends on market price and availability. Since 1992 Brazilian gasoline is lead free, thanks to the use of ethanol as anti-knock improver. Three types of gasoline are available in Brazilian gas stations: regular, regular with additives and premium. Regular gasoline is the

most common fuel consumed by Brazilian automotive fleet. Regular gasoline with additives contains special detergent components, and premium gasoline is a fuel with high octane number.

The objective of this work is to analyze aging influence on Brazilian gasoline properties and composition. Four samples of gasoline containing 25% ethanol (E25) were tested: two samples of regular gasoline, one sample of regular gasoline with additives, and one sample of premium gasoline. The samples were tested soon after they were available (day 1), and in aging periods of 30 and 180 days. The 30-days aging period can simulate a typical holidays period, during which a parked vehicle will have aging gasoline in the fuel tank. The 6-month period gives an extrapolation of the aging results. Variations of fuel properties and composition are expected with aging, which can influence engine performance and exhaust emissions.

2. Literature review

Gasoline composition is known to affect its oxidation process. Nagpal et al. [1] studied the olefinic structure of two naphthas produced from different processes using mass spectrometry with gas chromatography. The authors found that the presence of cyclic olefins in gasoline activate gum formation.

Zanier [2] investigated the thermal-oxidative stability of unleaded gasoline using pressure differential scanning calorimetry. The gasoline samples were exposed to 20 bar oxygen pressure and temperatures from 80 to 200 °C, during the aging period of 960 min. As it was concluded by [1], gasoline samples with high amount of olefins and diolefins were shown to be more susceptible to oxidation.

* Corresponding author. Tel.: +55 31 3319 4911; fax: +55 31 3319 4910.

E-mail addresses: estreva@ford.com (E.R. Streva), vanya@ufmg.br (V.M.D. Pasa), ricardo@pucminas.br (J.R. Sodré).

¹ Tel./fax: +55 31 3319 4910.

² Tel.: +55 31 3499 5724; fax: +55 31 3499 5700.

Gouli et al. [3] investigated the use of some oxygenated substitutes for lead as gasoline anti-knock improvers. The authors tested MTBE, p-cresol and the furan derivatives 2-methylfuran, furfurylamine, and furfuryl alcohol. While improving gasoline anti-knock properties, the oxygenated compounds reduced fuel aromatic and olefin content without having any negative effects on properties such as distillation temperatures T_{10} , T_{50} and T_{90} , Reid vapor pressure (RVP) and density. In general, carbon monoxide (CO) and hydrocarbon (HC) emissions were reduced with the use of the oxygenated compounds in gasoline, while carbon dioxide (CO_2) emissions were slightly increased and oxides of nitrogen (NO_x) emissions were dependant on engine load and fuel/air mixture strength.

The effects of ethanol and copper content on gasoline stability were studied by Pereira and Pasa [4]. It was found that the higher the ethanol concentration in gasoline, the higher the fuel density and the lower the gum content. The presence of ethanol in gasoline was proved to have no effect on gum formation, while copper presence accelerated gasoline oxidation process. The oxidized fuel showed higher density than the non-oxidized fuel.

Pereira and Pasa [5] investigated the effects of mono- and diolefins on the stability of automotive gasoline. The authors verified that not all olefins contribute to gum formation. The cyclic olefin cyclohexene and conjugated olefin 2,4-hexadiene were the olefins that most contributed to gum formation. On the contrary, the mono-olefins 1-hexene and 1-heptene and the non-conjugated olefin 1,5-hexadiene did not affect gasoline stability. Increased fuel density with oxidation was attributed to gum formation.

Shatalov and Seregin [6] presented a new method to determine the chemical stability of automotive gasoline. Fuel storage periods of up to 6 months at 77 °C were investigated. The authors found that gum formation is proportional to the oxygen content absorbed by gasoline during storage.

3. Experimental

Two samples of regular E25 ("A" and "B"), one sample of regular E25 with detergent additives, and one sample of high octane number E25, here called premium E25, were tested. The fuel samples analyzed were stored in four production automotive fuel tanks placed in a room with open window to the atmosphere. The fuel tanks were used with their complete set, including the pressure relief system. The samples were exposed to natural variation of atmospheric temperature (18–30 °C), pressure (0.91–0.93 bar) and humidity (32–40%).

The fuel samples were analyzed as new (day 1) and in aging periods of 30 and 180 days, according to the specifications N. 05/2001 established by the Brazilian National Agency for Petroleum, Natural Gas and Biofuels – ANP. Fuel density was measured by a digital density meter. Distillation temperatures were evaluated using a batch distillation unit. Ethanol concentration was determined using a graduated glass test tube and sodium chloride solution. Motor and research octane number, oxygen, benzene, saturates, olefins and total aromatic content were measured by a mid-infrared gasoline analyzer model GS1000. The measured properties and standard methods applied are shown by Table 1.

4. Results and discussion

The variation of the properties and composition of the E25 samples during the aging periods of 30 and 180 days is shown by Figs. 1–8. Fig. 1 shows that the density of all fuel samples increase with aging, as a result of evaporation of the light fractions and gum formation [4,5]. For all E25 samples the maximum density variation during the aging period of 180 days was 0.98%. Gasoline density

Table 1

Measured fuel properties and standard methods applied.

Property	Method
Density (kg/m^3)	ASTM D4052
Distillation temperature T_{10} (°C)	ASTM D86
Distillation temperature T_{50} (°C)	ASTM D86
Distillation temperature T_{90} (°C)	ASTM D86
Ethanol (% v/v)	NBR 13992
Motor octane number	GS 1000
Research octane number	GS 1000
Oxygen (% v/v)	GS 1000
Olefins (% v/v)	GS 1000
Aromatics (% v/v)	GS 1000
Benzene (% v/v)	GS 1000
Saturates (% v/v)	GS 1000

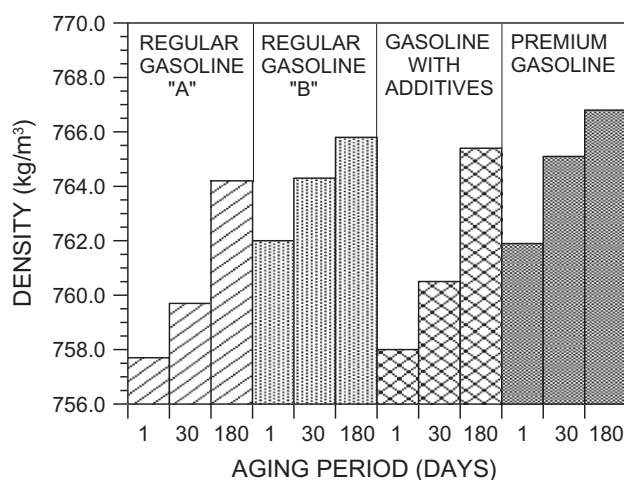


Fig. 1. Variation of E25 density in the aging period.

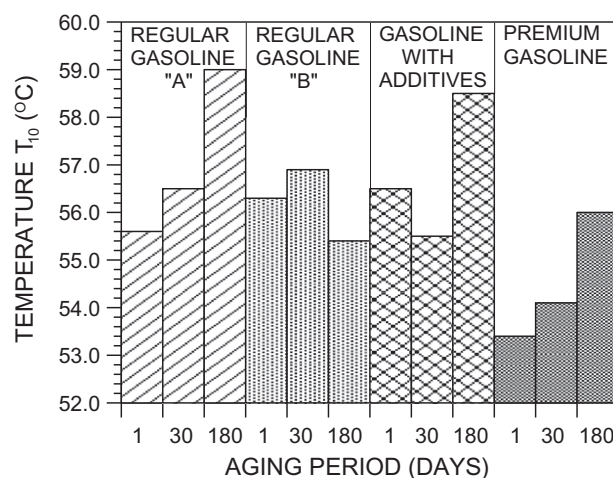


Fig. 2. Variation of E25 distillation temperature T_{10} in the aging period.

is affected by the proportions of its hydrocarbon species and by the carbon-to-hydrogen atoms ratio. In vehicles with electronic fuel injection system a richer mass-based fuel/air mixture could be obtained with increasing fuel density, as the fuel injector displaces constant volumes at a given setting [7]. In that case, increased exhaust hydrocarbons and carbon monoxide emissions would be expected with the use of aged E25, as those pollutants are strongly affected by mixture strength. That is avoided through the use of closed-loop lambda control.

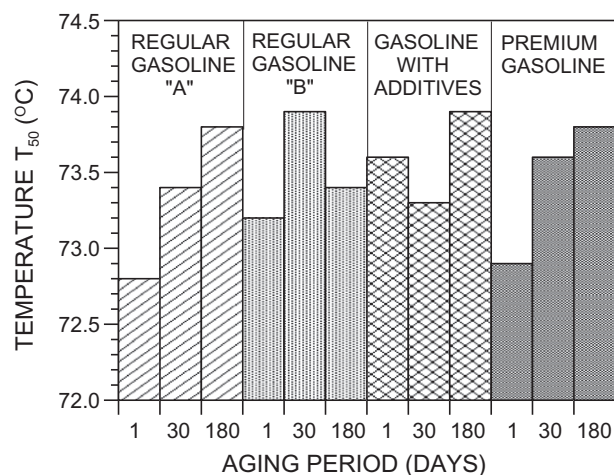


Fig. 3. Variation of E25 distillation temperature T_{50} in the aging period.

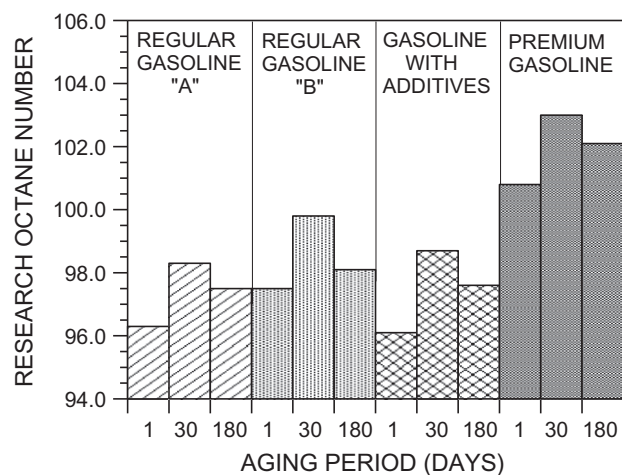


Fig. 6. Variation of E25 research octane number in the aging period.

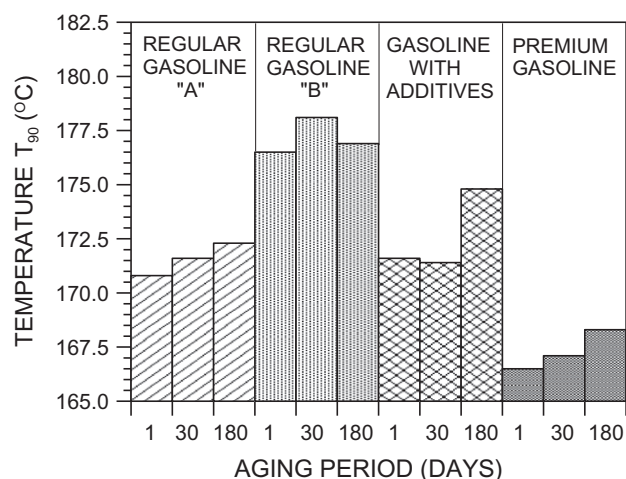


Fig. 4. Variation of E25 distillation temperature T_{90} in the aging period.

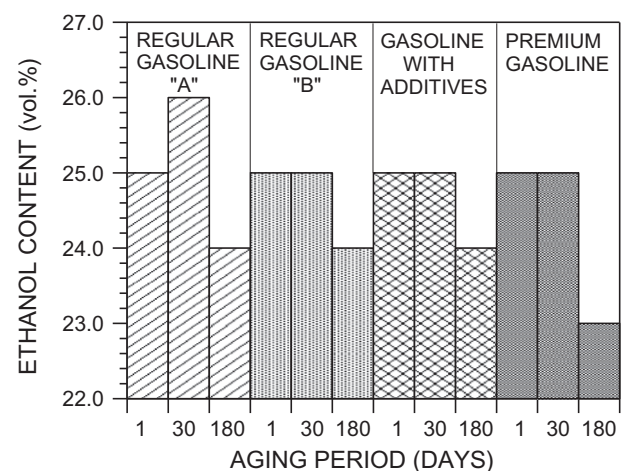


Fig. 7. Variation of ethanol concentration in E25 during the aging period.

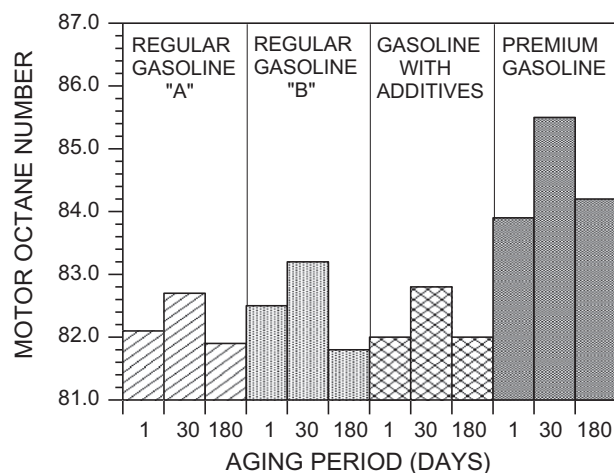


Fig. 5. Variation of E25 motor octane number in the aging period.

Fig. 2 shows increasing distillation temperature T_{10} with fuel aging for all samples, except for the "B" sample of regular E25. The distillation temperature T_{10} influences the volatility of the light

hydrocarbon fractions of gasoline [7]. The increase of temperature T_{10} with fuel aging can incur in more difficult engine cold start and drivability during the warm-up period. In that case, the formation of unburned hydrocarbons in the combustion chamber can be intensified as a result of the injected liquid fuel failing to vaporize.

Similar results as those found for distillation temperature T_{10} (Fig. 2) are seen for distillation temperatures T_{50} (Fig. 3) and T_{90} (Fig. 4), which indicate the volatility of the medium and heavy hydrocarbon fractions of gasoline. The temperature T_{50} influences vehicle drivability for an already warmed engine. Thus, the observed increasing T_{50} value with fuel aging for most of the tested samples (Fig. 3) indicates that a vehicle with a warmed engine fuelled with aged gasoline can present drivability problems. According to Carriconde and Mello [8], increased distillation temperature T_{50} decreases engine output power and increases fuel consumption and acceleration time.

The heavy fractions of gasoline, with distillation temperature above 200 °C, affect fuel consumption of a warmed engine. High distillation temperature T_{90} decreases engine power, while increases specific fuel consumption and acceleration time [8]. High distillation temperature T_{90} can also cause incomplete combustion, due to the low evaporation rate of the heavy hydrocarbon fractions, thus increasing unburned hydrocarbons, deposits and gum formation [7]. Considering the results shown by Fig. 4, those effects are expected from the use of aged gasoline.

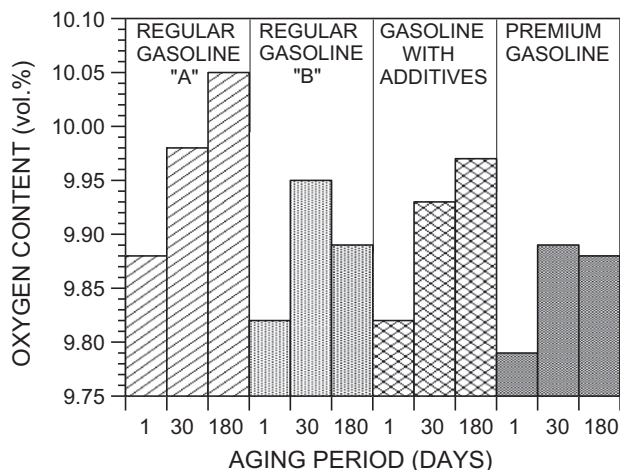


Fig. 8. Variation of oxygen concentration in E25 during the aging period.

Figs. 5 and 6 show that motor and research octane number of the E25 samples present a peculiar trend with fuel aging. Fuel octane number was increased in the first 30 days, but was then reduced at the end of the total aging period of 180 days. The initial loss of the light hydrocarbon fractions through evaporation seems to be beneficial to E25 octane number but then, with decreasing ethanol concentration in the fuel (see Fig. 6), a reverse effect is obtained. Fuel octane number influences engine performance and exhaust emissions. Decreasing octane number increases engine knock and NO_x emissions, mainly for lean fuel–air mixture operation [9].

Fig. 7 shows a reduction of ethanol concentration in the fuel samples with aging. Ethanol is blended to gasoline as an anti-knock improver, in substitution to lead. Thus, decreasing ethanol concentration of the fuel samples in the later stages of the aging period decreases the octane number, as seen in Figs. 5 and 6. Besides, ethanol presence in gasoline helps to reduce exhaust hydrocarbons and carbon monoxide emissions [10,11]. The low variation of ethanol content in the fuel samples during the aging period may be insufficient to cause significant changes on engine emissions.

The increased oxygen concentration in the E25 samples with fuel aging, as shown by Fig. 8, may have a direct relationship with gum formation [6]. However, as gum content has not been measured, a firm conclusion cannot be drawn. Another possibility is that, with fuel aging, oxygen content has been increased due to increasing concentration of other oxygenates that might be present in the fuel, as ethanol showed a different trend (see Fig. 7). Among the samples tested, regular E25 "A" sample and E25 with detergent additives showed continuously increasing oxygen content throughout the whole aging period.

Saturated hydrocarbons, which are stable components and constitute the basis of gasoline, did not show significant changes with fuel aging, as seen in Fig. 9. On the other hand, olefin content in the E25 samples tested shows a significant decrease during the aging period (Fig. 10). That may have been caused by evaporation of light olefins during fuel aging. Olefins are unstable hydrocarbons that, in contact with oxygen, are easily oxidized, forming gum and carbon deposits in the fuel tank, injectors and intake valve. Deposits in the fuel tank can gradually block the fuel filter, causing engine troubles. Deposits in the fuel injectors cause fuel flow reduction, insufficient fuel atomization and, consequently, loss of power and increasing fuel consumption and exhaust HC and CO emissions. Deposits in the intake valves have negative influence on intake air charge, causing loss of power and increased exhaust HC and CO emissions. Hochhauser and Benson [10] found that reducing

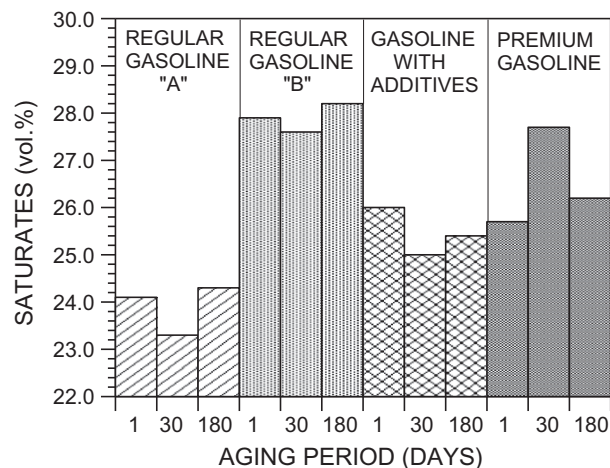


Fig. 9. Variation of saturate concentration in E25 during the aging period.

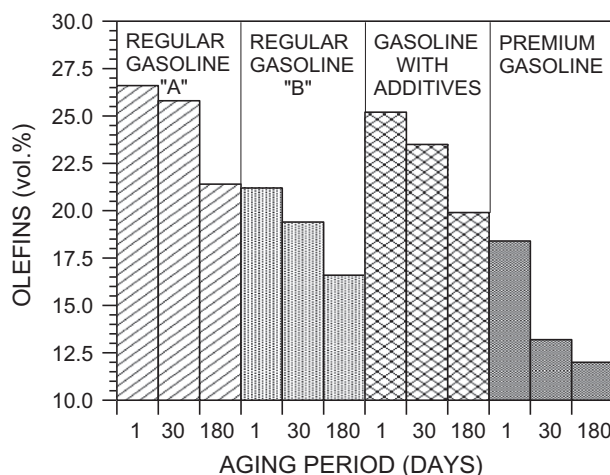


Fig. 10. Variation of olefin concentration in E25 during the aging period.

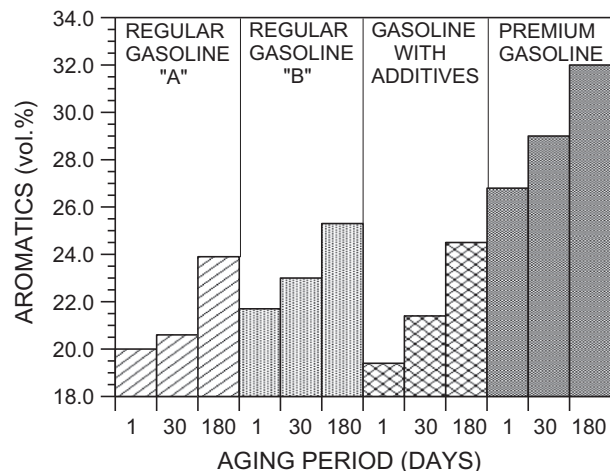


Fig. 11. Variation of aromatic concentration in E25 during the aging period.

the olefin concentration in gasoline from 20% to 5% produced a volumetric fuel economy around 0.2% to 0.6%.

In contrast to olefins behavior (Fig. 10), aromatic content in the E25 samples was increased with aging, as can be observed in

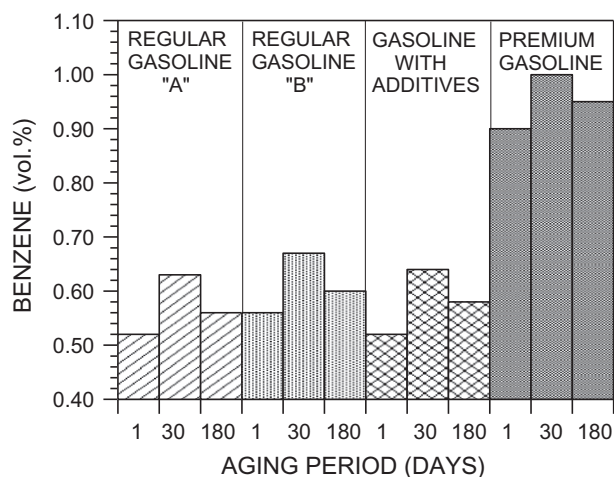


Fig. 12. Variation of benzene concentration in E25 during the aging period.

Fig. 11. The high oxygen concentration in the fuel blends may have accelerated the transformation of olefins into heterocyclic aromatics. Meanwhile, benzene concentration in the fuel blends did not show significant changes in the aging period (Fig. 12). Hochhauser et al. [10] observed that reducing from 45% to 20% the concentration of aromatics in gasoline fuel consumption was decreased by about 3%. Lange et al. [12] realized that CO and HC emissions are lower for low aromatics concentration and high volatility gasoline blended to MTBE. Therefore, the use of aged E25 is expected to increase fuel consumption and emissions of carbon monoxide and hydrocarbons, as the aromatics content is increased.

5. Conclusions

From the results obtained, the following conclusions can be drawn:

- All tested E25 samples showed increasing fuel density through the aging period of 6 months.
- The E25 samples distillation temperatures T_{10} , T_{50} and T_{90} also showed increasing values in the aging period of tests, which can result in difficult cold start and drivability in the warm-up period, deposit formation and increasing hydrocarbons and carbon monoxide emissions.

- E25 aging causes an initial increase of octane number, probably influenced by evaporation of the light fractions, but with further aging the octane number is reduced due to decrease of ethanol content in the fuel.
- Increasing oxygen content and decreasing olefin concentration in the E25 samples were observed with fuel aging.
- In opposition to olefins decrease, aging the E25 samples increased the fuel aromatic content, which can cause higher fuel consumption and also hydrocarbon and carbon monoxide emissions.
- Saturates and benzene concentration did not change significantly with fuel aging.

Acknowledgments

The authors thank Minas Gerais State Research Support Foundation, FAPEMIG, Brazilian National Council for Scientific and Technological Development, CNPq, and Brazilian Coordination for Improvement of High Level Personnel, CAPES, for the financial support to this project.

References

- [1] Nagpal JM, Joshi GC, Rastogi SN. Stability of cracked naphthas from thermal and catalytic processes and their additive response. Part II: composition and effect of olefinic structures. *Fuel* 1995;74:720–4.
- [2] Zanier A. Thermal-oxidative stability of motor gasolines by pressure d.s.c. *Fuel* 1998;77:865–70.
- [3] Gouli S, Lois E, Stournas S. Effects of some oxygenated substitutes on gasoline properties, spark ignition engine performance, and emissions. *Energy Fuel* 1998;12:918–24.
- [4] Pereira RCC, Pasa VMD. Effect of alcohol and copper content on the stability of automotive gasoline. *Energy Fuel* 2005;19:426–32.
- [5] Pereira RCC, Pasa VMD. Effect of mono-olefins and diolefins on the stability of automotive gasoline. *Fuel* 2006;85:1860–5.
- [6] Shatalov KV, Seregin EP. Suitability of automobile gasolines for prolonged storage. *Chem Tech Fuel Oils* 2009;45:373–9.
- [7] Guibet JC, Martin B. *Fuels & engine*. Paris, France: Éditions Technip; 1999.
- [8] Carriconde E, Mello P. Influence of T10%, T50% and T90% distillation points of gasoline on the dynamic performance of otto cycle engines equipped with multipoint electronic fuel injection; Proceedings of the 7th Brazilian congress of engineering and thermal sciences, 2000.
- [9] Hirao O, Pefley RH. *Present and future automotive fuels*. John Wiley and Sons: New York, NY; 1988.
- [10] Hochhauser AM, Benson JD, Burns VR, Gorse RA, Koehl WJ, Painter LJ, et al. Fuel composition effects on automotive fuel economy – auto/oil air quality improvement research program. SAE Tech Paper 930138, 1993.
- [11] Costa RC, Sodré JR. Hydrous ethanol vs. gasoline–ethanol blend: engine performance and emissions. *Fuel* 2010;89:287–93.
- [12] Lange WW, Muller A, Mcarragher JS, Schaefer V. The effect of gasoline composition on exhaust emissions from modern BMW vehicles. SAE Tech Paper 941867, 1994.