

Volatilization of benzene from gasoline: the effect of ethanol blends

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Abstract

In this work experiments were performed with vapor collection in columns to assess the evaporation profile of benzene from gasoline-ethanol blend fuels. The vapors from two columns simulating gasoline-contaminated soils (with and without ethanol) were monitored for 77 d. The instrumental analysis was performed by Gas Chromatography (GC) with a Flame Ionization Detector (FID). Compound identification was based on the GC retention times of standard BTX (benzene, toluene and xylenes). The concentration of benzene in the vapor phase decreased by 89.09%, considering the entire experimental period, while the toluene and xylene concentrations were increased by 239.34 and 251.78%, respectively. These results suggest that the benzene evaporation behavior was affected by the interactions among ethanol and other aromatic compounds. These results are particularly important, since ethanol is an alternative to gasoline blends. Furthermore, benzene (a well known carcinogen) was retained in the liquid phase and, in this way, can reach the underground water sources. These findings can point out necessary changes in traditional risk models for soil spills that are based on compound concentrations in the environment.

Keywords: gasoline, ethanol, benzene, BTX, evaporation.



1 Introduction

After the first oil crisis in the 1970s, with growing environmental pollution and the need for clean energy production, several nations around the world developed programs to support the use of alternative fuels, including ethanol and gasohol (which is a gasoline-ethanol blend) as automobile fuels. The main advantages of the ethanol blend fuels are the reduction of greenhouse gas emissions and enhancement of the octane number of gasoline. The ethanol content in Brazilian gasoline ranges from 24 to 25%.

Brazil has two national programs to insert ethanol in its energy matrix. In the first one combustible anhydrous ethyl alcohol (AEAC) is mixed with gasoline in volume percentages varying from 20 to 25%. The mixture volume is established in a law enacted by the government and depends on market and economic variables. In the other program, combustible hydrated ethyl alcohol (AEHC) is sold as fuel to be used in vehicles powered exclusively by ethanol or by flex fuel. Anhydrous ethyl alcohol has been used in the country since 1939 as a gasoline additive with percentages varying from 5 to 25%. As a consequence, Brazilian ethanol production has grown from 31,499 m³ of AEAC and 62,215 m³ of AEHC in 1939/1940 to 8,400,000 m³ of AEAC and 13,900,000 m³ of AEHC in 2007/2008. The technical process utilized in AEAC makes this product very competitive on the domestic and international markets.

Despite the mixture benefits, the presence of ethanol in gasoline can affect the BTX (benzene, toluene and xylenes) volatilization behavior and these compounds can evaporate from spills of underground storage tanks or by accidental releases raising a vapor plume just above the contaminated soil. In the soil spill situation, the rate of evaporation is a function of temperature, wind-speed, atmospheric conditions, solar radiation, dimension of the oil spill and the volatility and diffusion characteristics of the fuel [1].

Compounds with four to six carbon atoms volatilize rapidly. In the gasoline case BTX are the chemicals of greatest concern because of their toxicity and benzene carcinogenic activity [2]. In gasohol the presence of ethanol can modify the dissolution capacity of BTX and increase the groundwater pollution. Some of these changes reported in the literature are variations of free phase measurements in monitoring wells, co-solvency effects that render the BTX dissolution capacity higher in presence of ethanol, preferable biodegradation of ethanol in gasohol plumes, which causes anoxic conditions for BTX degradation [3, 4] and effects of gasohol contamination [5, 6]. Other studies focus on the thermodynamic properties of ethanol and gasoline-blended fuel, behavior of entrapped petroleum products in the subsurface, and soil vapor extractions systems [7-9] or measurements of the vapor pressure enhancement of alcohols-gasoline blends [10]. Thus, despite the well-known harmful effects of BTX in the atmospheric environment, the quantitative analysis of the influence of the ethanol on the evaporation rates of each individual chemical is still lacking in the literature.

The main objective of the present study was the quantitative analysis of the influence of ethanol on the evaporation behavior of BTX, compared to neat gasoline. With this purpose, two columns were prepared and filled with selected

sand. One column was contaminated, with neat gasoline and other with a gasoline-ethanol mixture.

2 Materials and methods

2.1 Samples and solvents

The gasoline samples, without ethanol, were kindly provided by Motors Laboratory of the Alberto Pasqualini refinery – Brazilian Petroleum (REFAP – PETROBRAS). Anhydrous ethanol (25 ml) was mixed with 75 ml of neat gasoline. All reagents and solvents used in this work were of analytical grade. The gasoline samples presents 30.63 (% mass) of aromatics, 11.72 (% mass) of alkanes, 17.90 (% mass) of substituted alkanes, 39.75 (% mass) of other components, and vapor pressure of 51.5 kPa. The BTX standards were purchased from Merck (São Paulo, SP, Brazil) and used with no further treatment.

2.2 Experimental columns

Two plexiglass columns were contaminated with neat gasoline and gasoline-ethanol. The columns present the following characteristics: height: 0.97 m; internal diameter: 0.35 m; total volume: 93.32 L. The columns were filled with 115 kg of washed river sediment with the following characteristics: particle diameters ranging from 0.25 to 0.59 mm, constituted mostly by quartz, uniformity coefficient and coefficient of curvature of 1.08 and 0.89, respectively. A bubbling pressure of a 14.8 centimeter water column was used in this work. The columns were filled with water, from bottom to top to avoid air bubbles and allowed to rest for one week. After this, the columns were left to drain until the water level was 0.5 m high from the base. Initial conditions of the columns were obtained by introducing 1.15 L of neat gasoline in the upper layer of column 1 and the same volume of a gasoline-ethanol mixture (25% v/v of ethanol) in the upper layer of column 2. Oil Red dye (Aldrich 200 mg/L) was added to the gasoline and the gasoline-ethanol mixture in order to monitor the gasoline liquid plume variation. This kind of dye is largely used in laboratory experiments with petroleum hydrocarbons as reported by MacDowell et al. [11]. After the contamination, the columns were closed and the junction between the column body and the cap was sealed with silicon to avoid vapor loss. Gas bags were placed at the top of both columns to collect volatile substances. The Columns were sealed to avoid the influence of the external atmosphere such as wind and pressure variation. The environmental temperature was monitored daily and showed an average value of 20.3 °C.

Plexiglas has previously been used for studies with organic compounds such as the study of biofiltration of BTX [12] and the study of naphthalene bioavailability in a Plexiglass glove box [13]. Baek et al. [14] studied the benzene sorption in sand and conducted a test to verify the influence of Plexiglass® in the results. In a separate experiment concentrations of benzene solution were measured with time for glass and Plexiglass containers under a



closed system. They found that the concentrations of benzene solution in the glass container were lower than those in the Plexiglass container, the greatest difference being 9.8%. This indicates that the use of Plexiglass for the column test would not greatly affect the experimental results on the transport and sorption of benzene in their study.

2.3 Instrumental analysis

The instrumental analysis was performed with a gas chromatograph PerkinElmer (model Autosystem–XL) with flame ionization detection. The samples were injected in the splitless mode. A 30 m Elite column (film thickness 0.25 μm , internal diameter 0.25 mm) was temperature-programmed from 40 $^{\circ}\text{C}$ (held for 10 min) to 220 $^{\circ}\text{C}$ (held for 0 min) at 5 $^{\circ}\text{C}/\text{min}$. The carrier gas (Helium) flux was 1 mL/min. The quality assurance/quality control of analysis was developed on the basis of the ANR Analytical Lab Quality Assurance Manual (August 25, 2006, University of California, USA).

3 Results and discussion

Figure 1 shows the weekly BTX concentration in the neat gasoline and gasoline-ethanol columns, during the sampling period. Although the samples in the present work cannot be classified as soil, these results partially disagree with enhancement of the BTEX (benzene, toluene, ethyl benzene, and xylenes) retention in soil by ethanol reported by Österreicher-Cunha et al. [15] that studied the degradation and distribution processes of ethanol-amended gasoline in tropical soil under unsaturated conditions. Considering that the conditions in the neat gasoline and gasoline-ethanol columns are the same and that some biodegradation occur, the benzene concentration must be higher in the gasoline-ethanol column, since that to Österreicher-Cunha ethanol could delay BTEX degradation because of its constitutive degradation by soil microbiota. However, this was not observed in our results, suggesting that, compared to the biodegradation, co-solvency effects must play a more important role in the reduction of the benzene concentration in the headspace.

In the present work benzene, toluene, and xylenes had their maximum concentrations in the gasoline-ethanol column, at weeks 6, 4, and 11, respectively. Figure 2 shows the relative volatilization of BTX, considering the final and initial times of the entire experimental period where the decrease of the benzene concentration and the increase of the toluene and xylenes volatilization, in the vapor phase can be better observed. Toluene and xylenes shows the highest relative volatilization in the gasoline-ethanol column (239.34 and 257.78%, respectively). These results can be better explained by the cosolvent theory approach.

According Chen et al. [16] the addition of polar organic solvents (such as ethanol) that are completely-miscible or highly-soluble in water to a mixture of hydrocarbons (such as gasoline) and water initiates a cosolvent effect. Water-miscible cosolvents may reduce the net polarity of the oxygene-water

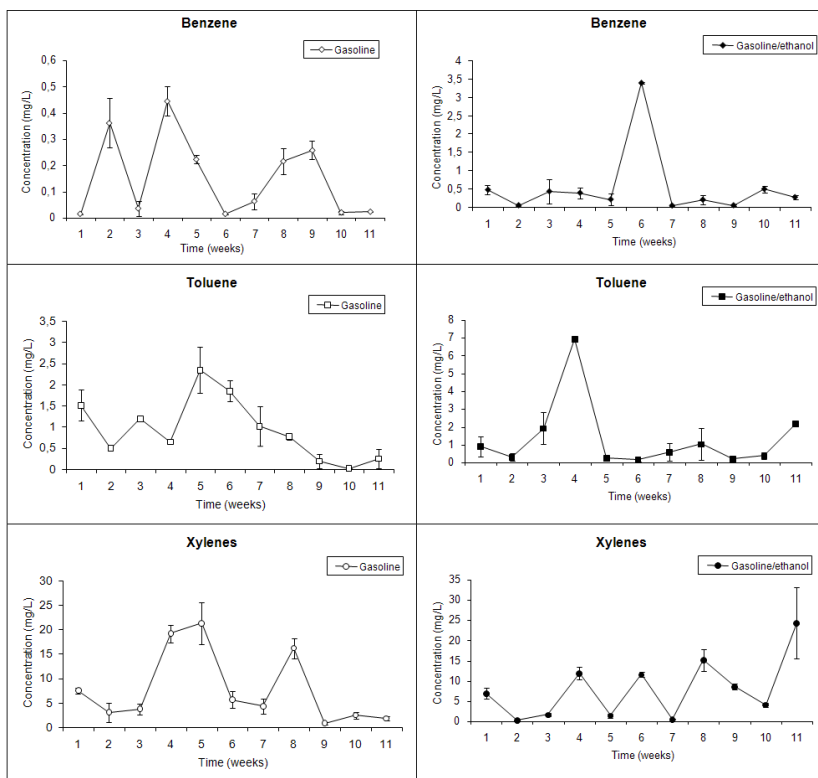


Figure 1: Weekly variation of the benzene concentration in the neat gasoline and gasoline-ethanol columns. Error bars represent \pm standard deviations.

solvent. When a miscible constituent is added to water, it increases the quantity of nonionic organic compounds that can dissolve in the mixed solvent. In this way, while the ethanol increases the water solubility of toluene and xylenes due to the co-solvency effect, the distance among the molecules of those compounds is increased as well their volatilities. Although attractive intermolecular forces are not expected to occur among ethanol and benzene molecules, the decrease of the benzene concentration in the vapor phase of the ethanol-gasoline column should be due to the enhancement of the toluene and xylenes volatility.

Many works have been published regarding the cosolvency promoted by gasoline-ethanol mixtures. According Yu et al. [17] the proportions of BTX in ethanol-amended gasoline are changed due to the cosolvent behavior of ethanol in the presence of an aqueous phase, as well as a reduction in the interfacial tension between the aqueous/nonaqueous phases. The addition of ethanol to the gasoline hydrocarbons can generates a mixture with a boiling point lower than the original compounds. To our knowledge, the present work is the first one reporting measurements of the volatilization of BTX in laboratory sand

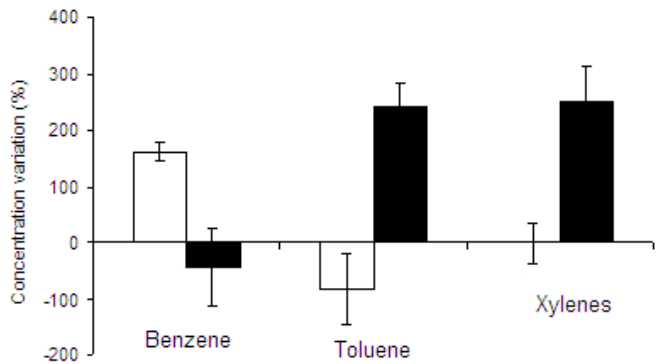


Figure 2: Relative volatilization of benzene toluene and xylenes on the experimental columns, considering the final and initial experimental times. Error bars represent ± standards deviations. Neat gasoline (□); gasoline/ethanol (■).

Table 1: Some physical properties of ethanol and BTX.

Compound	Dipole moment (D)	Density (g cm ⁻³)	Water solubility (mg L ⁻¹)
Ethanol	1.69	1.49	∞
Benzene	0	0.87	175
Toluene	0.37	0.86	535
Xylenes*	0.91	0.61	167

*Average value of the *o*, *m* and *p* isomers.

columns. As such, published results cannot be compared. Pasteris et al. [18] reported similar gas phase concentrations of toluene and *m*-xylene, evaluating the vapor phase transport and biodegradation of gasoline compounds. Those authors studied a large-scale field lysimeter representing a 2.3 m thick sandy unsaturated zone over a gravel aquifer. However, no comparisons were made with gasoline-ethanol fuel.

The co-solvency effects are appreciable among polar (ethanol) and nonionic organic compounds of low polarity (gasoline hydrocarbons). In the present work, the high relative volatilization of toluene and xylenes can be due to the permanent dipole forces that occur among ethanol-toluene and ethanol-xylenes. Table 1 show that toluene and xylenes presents the highest dipole moment.

To Kanai et al. [19] the intermolecular forces are strong enough to allow the chromatographic separation of *meta* and *para* isomers of xylenes.

4 Conclusions

Ethanol may decrease the volatilization of benzene in gasoline-ethanol column. On the other hand, concentrations of toluene and xylenes in the vapor phase of



the gasoline-ethanol column increases drastically. Besides the presence of ethanol, other aspects concerning the BTX volatilization, like adsorption on the sand grains and biodegradation must be addressed.

On the basis of the results of the present study, we can infer that if ethanol promotes the displacement of the contaminant gasoline plume down the contaminated sand, and if benzene is retained in the liquid phase due to the cosolvency effects, a higher concentration of this contaminant can reach the underground water and pose a risk to this important water source.

Acknowledgements

The authors would like to thank CNPq, Pronex Fapergs/CNPq, and University of Caxias do Sul for financial support and REFAP PETROBRAS for the material support.

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