



Evaluation of the density, volatility and anti-knock rating physical-chemical properties of alternative butanol/gasoline fuel blends

Luiz Filipe Paiva Brandão^{1,2} and Paulo Anselmo Ziani Suarez^{2*}

¹Agência Nacional do Petróleo, Gás Natural e Biocombustíveis, SGAN 603, Módulo H, 70830-030, Brasília, Distrito Federal, Brazil. ²Laboratório de Materiais e Combustíveis, Instituto de Química, Universidade de Brasília, Brasília, Distrito Federal, Brazil. *Author for correspondence. E-mail: psuarez@unb.br

ABSTRACT. Butanol, popularly known as butyl alcohol, has been recently recognized by researchers from around the world as a promising component for use in blends with gasoline, because of its very similar physical-chemical properties. In this study, butan-1-ol (*n*-butanol) and 2-methylpropan-1-ol (isobutanol) were blended with pure gasoline in proportions of up to 30% mass. The blends density, volatility and anti-knock rating were experimentally determined and compared with Brazilian commercial gasoline specifications. The results showed that the blends properties kept a strong dependency on the linear or branched butanol molecular structure and with the interaction effects of its hydroxyl groups. In the blends, a polynomial increase in density was observed, with a consequent volatility reduction, affecting the vapor pressure and distillation curve, especially for specified 50 and 90% evaporated temperatures (T50 and T90). Minor effects were observed at the T10 and FBP curve extremes. Octane rating and anti-knock index gains were observed, with noted increase of MON for 2-methylpropan-1-ol based blends. At the tested butanol content range, blends characteristics presented satisfactory compatibility with Brazilian gasoline specifications.

Keywords: alcohols; oxygenates; quality; specification.

Avaliação das propriedades físico-químicas de densidade, volatilidade e poder antidetonante de misturas combustíveis alternativas butanol/gasolina

RESUMO. O butanol, popularmente conhecido como álcool butílico, tem sido recentemente reconhecido por pesquisadores de todo o mundo como um promissor componente para uso em misturas com a gasolina, em razão de suas propriedades físico-químicas muito similares. Neste estudo, o butan-1-ol (*n*-butanol) e o 2-metilpropan-1-ol (isobutanol) foram misturados com gasolina pura em proporções de até 30% em massa. A massa específica, volatilidade e o poder antidetonante foram determinados experimentalmente e comparados com especificações da gasolina comercial brasileira. Os resultados mostraram que as propriedades das misturas mantiveram forte dependência com a estrutura molecular do butanol, linear ou ramificada e com os efeitos de interação de seus grupos hidroxilas. Nas misturas, um aumento polinomial na massa específica foi observado, com uma consequente redução da volatilidade, afetando a pressão de vapor e a curva de destilação, especialmente nas temperaturas especificadas de 50 e 90% evaporados (T50 e T90). Menores efeitos foram observados para o T10 e PFE nos extremos da curva. Ganhos de octanagem e índice antidetonante foram observados, com notável aumento de MON para as misturas preparadas com o 2-metilpropan-1-ol. Na faixa de concentração de butanol testada, as características apresentaram satisfatória compatibilidade com as especificações brasileiras da gasolina.

Palavras-chave: álcoois; oxigenados; qualidade; especificação.

Introduction

The use of oxygenated compounds as fuels has been investigated for more than a century (Kumar, Cho, Park, & Moon, 2013) and some countries like Brazil and United States of America currently use ethanol as liquid fuel in large scale. For instance, in Brazil, anhydrous ethanol is blended with gasoline (from 18 to 27% vol according to the ethanol availability) and hydrated ethanol (94.5% vol) is used

directly in modified flex/fueled vehicles. More recently, the use of butanol as fuel has attracted growing interest from researchers around the world. Butanol (C₄H₁₀O, 74.1216 g mol⁻¹) is an alcohol with four carbons and with one functional hydroxyl group (OH) in its structure, existing as four isomers: butan-1-ol (*n*-butanol), butan-2-ol (*sec*-butanol), 2-methylpropan-1-ol (*iso*-butanol) and 2-methylpropan-2-ol (*tert*-butanol). Despite their

related similar energy content, these isomers have different physical-chemical properties due to their structural differences (Jin, Yao, Liu, Lee, & Ji, 2011).

Like ethanol, butanol can be produced both by petrochemical or fermentative route. Indeed, among the existing processes, petrochemical hydroformylation and Acetone-Butanol-Ethanol fermentation (ABE) are the most used (Brito & Martins, 2017; Rochón, Ferrari, & Lareo, 2017; Yang, Kuitinen, Vepsäläinen, Zhang, & Pappinen, 2017). It is worth mentioning that nowadays almost all butanol in the world is produced from petroleum derivatives by hydroformylation, also known as 'oxo synthesis or oxo process' (Clarke, 2005; Franke, Selent, & Borner, 2012; Pospech, Fleischer, Franke, Buchholz, & Beller, 2013; Uyttebroeck, Hecke, & Vanbroekhoven, 2015). However, improvements and developments in bioprocess technologies and genetic engineering is contributing to increase the economic competitiveness of the fermentation process for biobutanol production from biomass (Rodrigues, 2011; Jin et al., 2011). Other less common routes, such as catalytic conversion, have attracted recent interest in research and industry, especially for butanol production ability from ethanol as a raw material (Ogo, Onda, & Yanagisawa, 2011; Riittonen et al., 2012; Dowson, Haddow, Lee, Wingad, & Wass, 2013; Sun & Wang, 2014; Wu et al., 2017).

When compared with ethanol, the main advantage of butanol is its fuel properties, which have a great similarity to those of gasoline. In addition, butanol has traditionally been recognized by the industry and researchers as a product that can be transported through the same petroleum products pipeline infrastructure and is compatible with the technology of conventional vehicle engines, reducing the need for new investment (Kolodziej & Scheib, 2012; Mariano et al., 2013).

Density is a property that affects engine performance, or more specifically, the injection pump, which measures the fuel supplied to the system. For this reason, it is directly related to the mass of fuel injected within the combustion chamber and also with its energy content. It is a property often considered in volume correction calculations in the fuel market, based on a change of temperature (Rand, 2010; Deng et al., 2013; Oliveira, Filho, & Afonso, 2013; Muzíková, Šimálek, Pospíšil, & Šebor, 2014; Dikio, Bahadur, & Ebenso, 2016).

Volatility measures the tendency of a fuel to vaporize under a given condition. It is a feature of paramount importance for any liquid fuel, because it

is closely related to the engine performance in terms of cold start, acceleration and power. Distillation is one of the most important quality indexes for evaluating the evaporation rate of liquid fuels at different temperatures; it is useful to determine the boiling range of a fuel and the content of light and heavy components (Li, Yu, Wang, & Wang, 2015). The vapor pressure is another important property used to measure the lightweight fuel vaporization trend in gasoline.

The anti-knock rating is related to the ability of a fuel to resist to compression without detonating, under a given condition. The maximum performance is obtained when the fuel-air mixture is evenly burned inside the combustion chamber, until all the fuel is consumed. However, in real situations, undesirable pre-flame reactions involving unburnt end gases can result in the formation of molecules or species that can spontaneously auto-ignite before the flame front arrives, causing abnormal combustion (engine knocking). Alcohols and other oxygenates slow the progress of the auto-ignition reaction due to the formation of a radical species and the production of unsaturated hydrocarbons. Alcohols also have a higher latent heat of vaporization than gasoline, resulting in additional cooling of the combustion chamber supplied by evaporation of the alcohols (Totten, Westbrook, & Shah, 2003).

The motor octane number (MON) and research octane number (RON) are the most common standard tests to measure the octane quality of a fuel and used to calculate the anti-knock index (AKI) from the arithmetic mean of their values. A fuel with a high octane number improves energy efficiency in an engine, providing higher compression ratios, representing gains in fuel economy, power and torque, whereas a fuel with a low octane number is more prone to suffer from pre-ignition problems (Albahri, 2003; Anderson, Kramer, Mueller, & Wallington, 2010; Yates, Bell, & Swarts, 2010; Westbrook, Pitz, Mehl, & Curran, 2011; Hu, Tiang, Zhang, Li, & Huang, 2017).

In this context, several experimental and theoretical studies regarding butanol/gasoline blends have recently been published, most of them targeted to evaluate their combustion, performance and emissions in Otto engines (Masum, Masjuki, Kalam, Palash, & Habibullah, 2015; Yanai, Bryden, Dev, Reader, & Zheng, 2017; Elfasakhany, 2016; Li et al., 2017; Yusof et al., 2017). However, few attempts have been made regarding quality and specification criteria. In this paper, butan-1-ol/gasoline and 2-methylpropan-1-ol/gasoline blends

were prepared and evaluated in terms of the density, volatility (distillation and dry vapor pressure equivalent - DVPE) and anti-knock rating (MON, RON and AKI), which represent three key features of a fuel intended for use in spark ignition engines. Measured values were also compared with Brazilian specification for commercial gasoline, established by National Agency of Petroleum, Natural Gas and Biofuels (ANP), the regulatory body in Brazil.

Material and methods

Preparation of butanol/gasoline blends

A total of 24 butanol/gasoline blends were prepared using pure gasoline provided by Total Distribuidora S.A., Brasilia, state Distrito Federal, Brazil, as fuel matrices, and analytical grade butan-1-ol and 2-methylpropan-1-ol standards (min. 99.0%), purchased from Vetec, Brazil, as oxygenated compounds were used as received. Pre-calculated masses of the butanol standards and respective fuel were individually weighted and, after that, mixed in 500 mL amber glass flasks positioned on an electronic Bel semi-analytical balance (resolution ± 0.01 g), which resulted in butanol contents from 2.5 to 30.0% mass. This testing interval was defined considering typical oxygenated concentrations adopted in Brazil (Portaria Mapa n^o 75/2015), United States (ASTM D7862) and Europe (EN 228) for use in commercial blends with gasoline, thus providing better comparison parameters. In the present paper, tables and graphs are reported in mass % terms. After preparation, all the samples were refrigerated at approximately 4°C to avoid volatile compound losses.

Physical-chemical characterization

Density, distillation and vapor pressure characteristics were respectively determined according to the ASTM D4052, ASTM D86 and ASTM D5191 standard methods, also used by ANP for commercial gasoline regulation. Density was determined at 20°C in an automatic Anton Paar DMA 4500, which measures changes in a glass U-tube oscillation frequency (T), caused by the sample, compared to the calibration data, according to Equation 1.

$$T = 2\pi \sqrt{\frac{\rho V_c + m_c}{K}} \quad (1)$$

where:

ρ is the sample density, V_c is the U-tube internal volume, m_c is the mass of the empty tube and K a U-tube specific constant.

Temperatures were measured by densimeter with resolution of $\pm 0.01^\circ\text{C}$. About 3 mL of each sample was manually injected into the densimeter, until the U-tube was completely filled. Analyzes were performed in triplicate.

The Dry Vapor Pressure Equivalent (DVPE) of blends was determined in a Grabner Instruments MINIVAP VPS, according to ASTM D5191 standard method. For the test, the sample was aspirated and introduced into a test chamber, thermostatically controlled at 37.8°C (100 F) with the vapor-liquid maintained at 4:1 ratio. DVPE results, in kilopascals (kPa), were automatically calculated by the chamber's total pressure (sample + air dissolved partial pressures), according to Equation 2. Analyzes were performed in triplicate.

$$DVPE(kPa) = 0.965 P_{tot} - A \quad (2)$$

where:

P_{tot} is the total vapor pressure in kPa and A is a 3.78 kPa constant value.

An automatic Normalab NDI 450 distiller was used for the volatility tests, according to the ASTM D86 standard method. Firstly, exact 100 mL of the sample was measured in a Normalab graduated glass cylinder and immediately transferred into a distillation flask. Then, the same glass cylinder was positioned at the condenser tube outlet for distillation product collection. The system was heated at a 4 to 5 mL min⁻¹ rate and the distillation temperatures were registered by a calibrated PT100 type thermocouple.

Motor octane number (MON), research octane number (RON) and anti-knock index (AKI) analyzes were estimated in a portable analyzer, PetroSpec GS-1000 plus VOC. This equipment performs the analysis based on medium infrared in spectral region of 400-4000 cm⁻¹ and uses a multivariate technique (multiple linear regression - MLR). Analyzes were performed by comparing the gasoline based blends spectra to those from a factory reference database.

Results and discussion

Density

Densities measured for analytical grade butan-1-ol (809.8 kg m⁻³) and 2-methylpropan-1-ol (802.4 kg m⁻³) standards were higher than the respective value for pure gasoline (728.12 kg m⁻³). Blends densities were progressively, but not linearly, increased, reaching values of up to 750.75 kg m⁻³ for butan-1-ol blends and up to 746.89 kg m⁻³ for 2-

methylpropan-1-ol blends, respectively, corresponding to percentage increases of 3.1 and 2.6% compared to that of pure gasoline, as depicted in Figure 1.

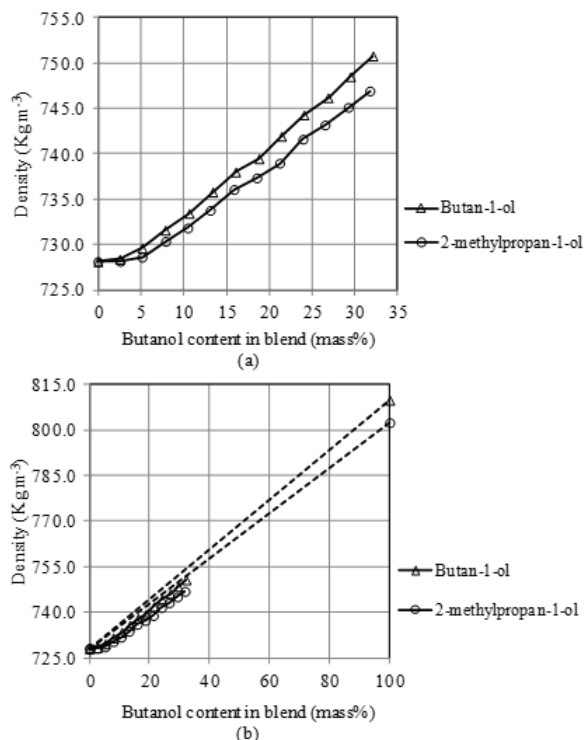


Figure 1. (a) Density curves behavior in function of the butanol content in blends. Brazilian legislation does not set density limits for commercial gasoline. (b) Comparison of the experimental density curves with reference dashed straight lines connecting density values of pure gasoline to those of each butanol pure standard.

In Figure 1a it is possible to identify two different regions: blends with up to 5.0% mass butanol content (with less slope) and those higher than 5.0% mass (with more slope). For lower concentrations, once butanol was added to blends, the synergistic interaction between the hydroxyl groups tended to be weakened by the greater amount of other hydrocarbon compounds that surround butanol molecules, producing, as reported, only discrete increases in density values. Thus, when increasing butanol content, the interactions between hydroxyl groups become more effective and the influence of hydrogen bonds in the overall interaction forces, more intense.

Both density curves were better fitted to a second order polynomial function, with determination coefficients (R^2) higher than 0.994. The steeper slope of butan-1-ol curve is associated with the higher packaging capacity of the linear butan-1-ol structure. Along the curve, it is possible to observe

the intensification of the differences between butan-1-ol and 2-methylpropan-1-ol, due to the packaging effect, resulting in the consequent distancing between curves.

Muzíková et al. (2014) and Li et al. (2015) evaluated, respectively, the variations in the density of blends of butan-1-ol and 2-methylpropan-1-ol in gasoline and showed a curve with linear behavior. We believe the difference between the result here presented and those reported in aforementioned references is only because, in our study, more samples were tested with smaller butanol content increment.

Figure 1b allows a better visualization of the influence of the butanol-hydrocarbon components interactions over the final density values. As can be depicted in Figure 1b, it is possible to observe slight deviations on the experimental curves compared to the straight lines adopted as reference, demonstrating that the blends final densities are, in fact, affected by extra molecular interactions and are not only the result of a simple average of blends components combinations. Such interaction effects are better discussed below.

Beyond the butanol content in blends, three main factors were considered determinants for the density results, related to the interactions between butanol and hydrocarbons: (a) linear or branched structure of butanol, (b) van der Waals forces or hydrogen bonds and (c) the hydrocarbon composition of fuel. The structure of butanol shows a close relationship with the packaging capacity of the molecules, with each other and with the hydrocarbons. Hydrogen bonds, stronger than van der Waals forces, act with a tendency to join molecules, increasing density, however OH interactions strength depend, above all, on the blends butanol content. Among the hydrocarbons, van der Waals forces have little effect on the density final value. The size, structure and composition of the matrix hydrocarbons, as well as the presence of heteroatoms, show a direct contribution to the blends density, explained by its solvation capacity to minimize butanol OH hydrogen bonds strength in blends.

Volatility

The measured vapor pressure for pure gasoline was 50.1 kPa, considerably higher than those of butan-1-ol (0.9 kPa) and 2-methylpropan-1-ol (2.0 kPa) pure standards. Such differences in volatility can be mainly attributed to the strong effects of the butanol hydrogen bonds, also extended

to the blends. The blends vapor pressure was reduced by up to 18.1% and more intensely for 2-methylpropan-1-ol blends, due to the less packaging capacity of the branched isomer structures, resulting in greater volatility. In Figure 2, it is possible to observe a quite similar DVPE decay behavior for both isomers, which resulted in the final values of 41.0 and 41.8 kPa for blends prepared with 30% mass of butan-1-ol and 2-methylpropan-1-ol, respectively. Despite this reduction, all blends presented DVPE values below the maximum limit of 69.0 kPa specified in Brazil for a commercial gasoline.

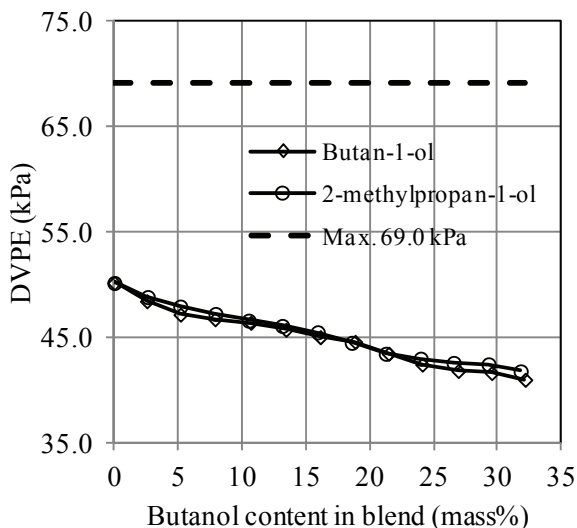


Figure 2. DVPE curves in function of the butanol content in blends. The dashed line at 69.0 kPa refers to the Brazilian specification limit for commercial gasoline.

Figure 3 shows the distillation curves at atmospheric pressure for selected blends (10.0, 20.0 and 30.0% mass) and the curve obtained for pure gasoline. The distillation temperature corresponding to a gasoline X% evaporated volume (TX) is a direct function of its chemical composition.

For comparative reasons, pure gasoline curve (Δ) was adopted as reference. Basically, three important ranges could be observed in the distillation curves: 1) initial, which precedes the butanol evaporation, 2) transition, when butanol is distilled from the flask and 3) final, when the remaining hydrocarbons are distilled.

In Figure 3, it is possible to observe a distillation temperature increase between T10 and T40 (T50 and T60, depending on the blend butanol content) compared to those registered on the pure gasoline curve, which suggests a heavier composition TX fraction. In fact, the higher butanol density, compared to pure gasoline, increases the mass/volume ratio and, thus, reduces

the blends volatility. In the distillation test, this meant a higher temperature required to evaporate a given blend percentage volume, represented by the curves elevation (Y axis) in relation to that of pure gasoline. For blends containing 10% mass of butanol the elevation was more discreet. At the 30% mass, this elevation extended until near the point T60 and T50, for butan-1-ol and 2-methylpropan-1-ol blends, respectively, which shows that both the lightweight and medium-weight gasoline fractions were altered by butanol. Already in other advanced distillation TX temperatures, the inverse occurs, that is, the blend distillation temperature was reduced in relation to what was observed for pure gasoline.

Deviations observed for blends curves in relation to pure gasoline, points to the formation of a plateau in the distillation curves central region, a phenomenon that can be attributed to the capacity of butanol to form an azeotrope-like compound with some components of gasoline, thus behaving more closely to a pure substance in relation to the boiling point. In the case of pure gasoline, the temperature variation between 40 and 80% evaporated (T40 to T80) was 45°C, whereas for blends with 30% mass of butanol, this variation, in the same range, was only 15°C. This shows that azeotropic shifts respond proportionally to the butanol content in blend.

In the course of the distillation, the blend composition was varied and gasoline lighter hydrocarbons were continuously distilled from the flask, resulting in a progressively heavier and less volatile blend. This situation evolved until the blend became as lightweight (or as heavy-weight) as pure gasoline. This distillation stage, identified by the curves crossover in Figure 3, is directly related to the butanol boiling point. The crosses of butan-1-ol and 2-methylpropan-1-ol blends at different curves points can be justified by the different boiling points of the isomers, so that higher boiling points result in later curves crossings.

At a given distillation stage, blends reaches the azeotropic composition and temperature, when the curve flattening becomes more pronounced in the central region. At this moment, the temperature remains little altered until the azeotropic-like compound is totally distilled from the flask. A rapid increase in the evaporated percentage volume, however, was observed, which extended to T70, T80 and T90 for blends with 10, 20 and 30% mass of butanol, respectively. Once the azeotrope has been completely evaporated from the system, gasoline hydrocarbons remaining in the flask evaporate at their respective boiling points, which can be seen as a transition region, when there is a sudden increase

(inflection) in the distillation curve. This increase in temperature (reduction of the blend evaporation rate) occurs because of the lower volatility of the heavy-weight hydrocarbons that are distilled in this

range, relative to the azeotrope. Blends with a higher butanol proportion presented a more abrupt inflection and a greater reflex at the curve final portion, after 90% evaporated (T90).

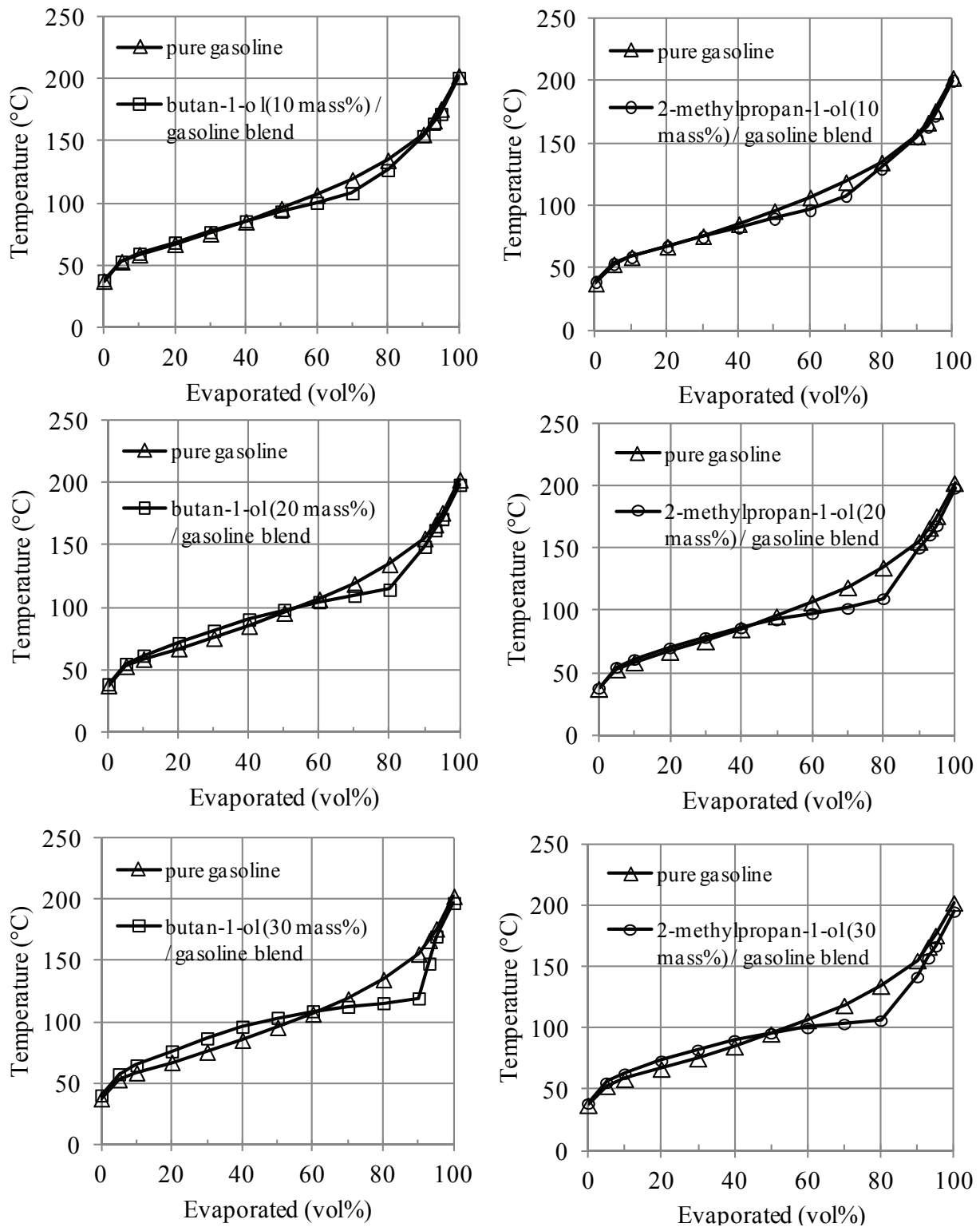


Figure 3. Comparison of the distillation curves of pure gasoline (Δ) and blends containing 10, 20 and 30% mass of butan-1-ol (□) and 2-methylpropan-1-ol (○).

Octane rating

Figure 4 shows the blends MON behavior as a function of the butanol content. The MON values increased almost horizontally for butan-1-ol blends, whereas for 2-methylpropan-1-ol, the increase was quite steep, following a parabolic pattern. As result, the addition of 2.5% mass of 2-methylpropan-1-ol in the blend was sufficient to produce an MON increase of 1.4 octane versus just 0.2 octane with the addition of the same butan-1-ol percentage.

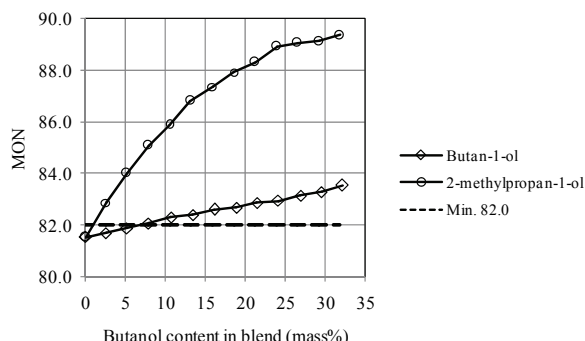


Figure 4. Motor octane number (MON) as a function of butanol content in pure gasoline. The dashed line indicates the ANP specification (min. 82.0) for Brazilian commercial gasoline.

The MON curves result from a summation of combustion inhibiting factors. The strong steric effects of butanol branched carbon chains make it difficult to interact with oxygen and, consequently, make the combustion reaction less favorable when compared to the corresponding linear isomers. Also in terms of the branched structure, the stabilization effects (Schobert, 1990), concerning the possibility of radical formation on the 2-methylpropan-1-ol tertiary carbon, should be considered.

The synergistic effects between the butanol OH groups require more heat from the combustion chamber for the blends vaporization, which also makes the blends more resistant to detonation. These effects were predominant in blends with a 2-methylpropan-1-ol content up to about 22.5% mass, from which no significant MON gain was observed. From this point, it is possible that such effects no longer affected the kinetics of the combustion so significantly, although the proportion of butanol had been increased.

The MON increase for butan-1-ol blends can be almost exclusively associated to the interactions between butanol OH groups, since that for the linear structure the steric hindrance is not so restrictive and the formation of tertiary radicals in the combustion reaction is limited. In this case, because they respond directly to the oxygen content, MON values grow moderately and linearly to the butanol content increase in blends.

Research octane number (RON) curves in Figure 5 showed a non-linear pattern close to a polynomial function with no significant differences between both isomers blends. In this case, 2-methylpropan-1-ol blends did not show the same gain observed for MON.

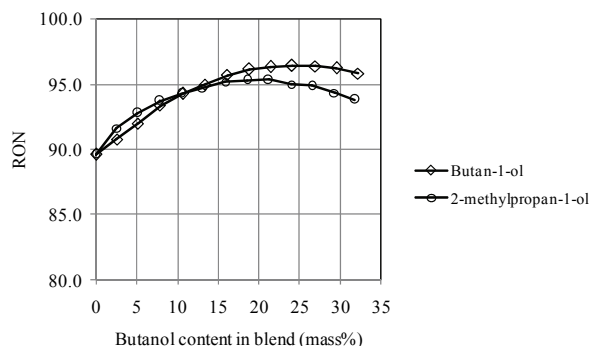


Figure 5. Research octane number (RON) as a function of the butanol content in pure gasoline. Not specified by ANP.

A higher RON gain was observed for 2-methylpropan-1-ol blends, as observed in the initial curve region, demonstrating that the sum of effects caused by 2-methylpropan-1-ol still overlap with that of butan-1-ol. However, as the butanol content in the blend increases, the hydrogen bonds appear to become stronger and more prevalent among the more unblocked linear chains of butan-1-ol, progressing to cross-curves when blends reach about 10% mass of butanol.

As observed in Figure 6, resulting AKI values were higher for 2-methylpropan-1-ol blends compared to those of butan-1-ol blends, which can be attributed to the extraordinary MON increase achieved by the branched butanol isomer. For both blends types, non-linear AKI curves were obtained revealing some AKI tendency to stabilization and even reducing for blends prepared with butanol contents higher than 22.5% mass, approximately.

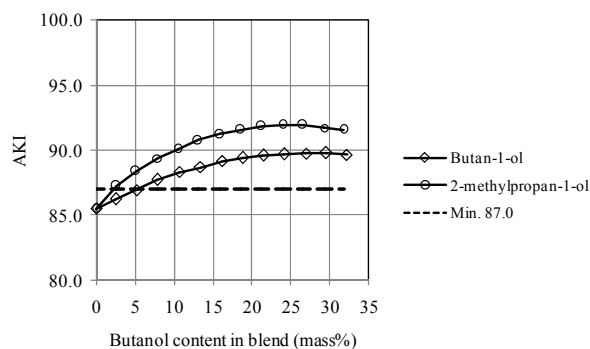


Figure 6. Anti-knock index (AKI) versus butanol content in pure gasoline. The dashed line indicates the ANP specification (min. 87.0) for Brazilian commercial gasoline.

Practically all tested blends reached octane and AKI values higher than those ANP limits for commercial gasoline, except for two blends produced with butan-1-ol contents of 2.5 and 5.0% mass. Anti-knock gains obtained from 2-methylpropan-1-ol blends were comparable to those of a commercial high-octane gasoline, demonstrating the great potential of this branched alcohol as an octane booster.

Conclusion

Better butanol/gasoline blend characteristics were achieved by using 2-methylpropan-1-ol isomer, which had softer impacts over the gasoline's original density and volatility, besides providing higher octane gains compared to the butan-1-ol blends. The different effects exercised by butanol isomers were evidenced by the experimental curves deviations, becoming more evident with the progressive increase of the butanol content in blends. Because of its individual particularities, butanol isomers can be used for an adjustment of one or other fuel characteristics.

Presented results showed that the effects of butanol on gasoline are advantageous and well tolerated by the hydrocarbon matrix. However, curves tendencies observed for density, distillation, MON, RON and AKI showed that butanol contents beyond 30% mass may result in some drawbacks related to blends being too dense and intense volatility reduction (mainly medium and high-weight fractions) and low (or none) octane gain compared to other blends with lower butanol contents.

This study also opens an opportunity for the investigation of ethanol/butanol blends as a way to minimize undesirable characteristics of ethanol. We are currently studying other properties of butanol/gasoline blends in order to evaluate the overall feasibility of ethanol, partial or total, substitution in commercial fuel blends in the Brazilian market.

Acknowledgements

The authors thank *Agência Nacional do Petróleo, Gás Natural e Biocombustíveis* (ANP), *Coordenação de Aperfeiçoamento de Pessoal de Nível Superior* (Capes), *Conselho Nacional de Desenvolvimento Científico e Tecnológico* (CNPq) and *Fundação de Apoio a Pesquisa do Distrito Federal* (FAPDF) for partial financial support. The authors are in debt with Distribuidora Total S.A. for gently providing of pure gasoline. PAZS thanks CNPq for his research fellowship.

References

- Albahri, T. A. (2003). Structural group contribution method for predicting the octane number of pure hydrocarbon liquids. *Industrial & Engineering Chemical Research*, 42(3), 657-662. doi: 10.1021/ic020306+
- Anderson, J. E., Kramer, U., Mueller, S. A., & Wallington, T. J. (2010). Octane numbers of ethanol- and methanol-gasoline blends estimated from molar concentrations. *Energy & Fuels*, 24(12), 6576-6585. doi: 10.1021/ef101125c
- Brito, M., & Martins, F. (2017). Life cycle assessment of butanol production. *Fuel*, 208, 476-482. doi: 10.1016/j.fuel.2017.07.050
- Clarke, M. L. (2005). Branched selective hydroformylation: a useful tool for organic synthesis. *Current Organic Chemistry*, 9(7), 701-718. doi: 10.2174/1385272053764980
- Deng, B., Fu, J., Zhang, D., Yang, J., Feng, R., Liu, J., ... Liu, X. (2013). The heat release analysis of bio-butanol/gasoline blends on a high speed SI (spark ignition) engine. *Energy*, 60, 230-241. doi: 10.1016/j.energy.2013.07.055
- Dikio, E. D., Bahadur, I., & Ebenso, E. E. (2016). Intermolecular interactions between 2-methyl-2-butanol and petroleum ether at different temperatures: density, viscosity and refractive index measurements. *Journal of Molecular Liquids*, 219, 795-800. doi: 10.1016/j.molliq.2016.04.041
- Dowson, G. R. M., Haddow, M. F., Lee, J., Wingad, R. L., & Wass, D. F. (2013). Catalytic conversion of ethanol into an advanced biofuel: unprecedented selectivity for n-butanol. *Angewandte Chemie International Edition*, 52, 9005-9008. doi: 10.1002/anie.201303723
- Elfasakhany, A. (2016). Experimental study of dual n-butanol and iso-butanol additives on spark-ignition engine performance and emissions. *Fuel*, 163, 166-174. doi: 10.1016/j.fuel.2015.09.059
- Franke, R., Selent, D., & Borner, A. (2012). Applied hydroformylation. *Chemical Reviews*, 112(11), 5675-5732. doi: 10.1021/cr3001803
- Hu, E., Tiang, H., Zhang, X., Li, X., & Huang, Z. (2017). Explosion characteristics of n-butanol/iso-octane-air mixtures. *Fuel*, 188, 90-97. doi: 10.1016/j.fuel.2016.10.002
- Jin, C., Yao, M., Liu, H., Lee, C. F., & Ji, J. (2011). Progress in the production and application of n-butanol as a biofuel. *Renewable Sustainable Energy Reviews*, 15(8), 4080-4106. doi: 10.1016/j.rser.2011.06.001
- Kolodziej, R., & Scheib, J. (2012). Bio-isobutanol: the next generation biofuel. *Hydrocarbon Processing*, 91, 9, 79-85.
- Kumar, S., Cho, J. H., Park, J., & Moon, I. (2013). Advances in diesel-alcohol blends and their effects on the performance and emissions of diesel engines. *Renewable Sustainable Energy Reviews*, 22, 46-72. doi: 10.1016/j.rser.2013.01.017

- Li, Y., Meng, L., Nithyanandan, K., Lee, T. H., Lin, Y., Lee, C. F., & Liao, S. (2017). Experimental investigation of a spark ignition engine fueled with acetone-butanol-ethanol and gasoline blends. *Energy*, *121*, 43-54. doi: 10.1016/j.energy.2016.12.111
- Li, Y., Yu, Y., Wang, Z., & Wang, J. (2015). Physical and Chemical properties of isobutanol-gasoline blends. *Environmental Progress & Sustainable Energy*, *34*(3), 908-914. doi: 10.1002/ep.12061
- Mariano, A. P., Dias, M. O. S., Junqueira, T. L., Cunha, M. P., Bonomi, A., & Filho, R. M. (2013). Butanol production in a first-generation Brazilian sugarcane biorefinery: Technical aspects and economics of greenfield projects. *Bioresource Technology*, *135*, 316-323. doi: 10.1016/j.biortech.2012.09.109
- Masum, B. M., Masjuki, H. H., Kalam, M. A., Palash, S. M., & Habibullah, M. (2015). Effect of alcohol-gasoline blends optimization on fuel properties, performance and emissions of a SI engine. *Journal of Cleaner Production*, *86*, 230-237. doi: 10.1016/j.jclepro.2014.08.032
- Muzíková, Z., Šimálek, P., Pospíšil, M., & Šebor, G. (2014). Density, viscosity and water phase stability of 1-butanol-gasoline blends. *Journal of Fuels*, *2014*, 1-7. doi: 10.1155/2014/459287
- Ogo, S., Onda, A., & Yanagisawa, K. (2011). Selective synthesis of 1-butanol from ethanol over strontium phosphate hydroxyapatite catalysts. *Applied Catalysis A: General*, *402*(1-2), 188-195. doi: 10.1016/j.apcata.2011.06.006
- Oliveira, B. M., Filho, J. M. M., & Afonso, J. C. (2013). A densidade e a evolução do densímetro. *Revista Brasileira de Ensino de Física*, *35*(1), 1601-1610. doi: 10.1590/S1806-11172013000100024
- Pospech, J., Fleischer, I., Franke, R., Buchholz, S., & Beller, M. (2013). Alternative metals for homogeneous catalyzed hydroformylation reactions. *Angewandte Chemie International Edition*, *52*(10), 2852-2872. doi: 10.1002/anie.201208330
- Rand, S. J. (2010). *Significance of tests for petroleum products* (8th ed.). Newburyport, MA: ASTM International.
- Riittonen, T., Toukoniitty, E., Madnani, D. K., Leino, A., Kordas, K., Szabo, M., ... Mikkola, J. (2012). One-Pot liquid-phase catalytic conversion of ethanol to 1-butanol over aluminium oxide—the effect of the active metal on the selectivity. *Catalysts*, *2*(4), 68-84. doi: 10.3390/catal2010068
- Rochón, E., Ferrari, M. D., & Lareo, C. (2017). Integrated ABE fermentation-gas stripping process for enhanced butanol production from sugarcane-sweet sorghum juices. *Biomass and Bioenergy*, *98*, 153-160. doi: 10.1016/j.biombioe.2017.01.011
- Rodrigues, J. A. R. (2011). Do engenho à biorrefinaria. A usina de açúcar como empreendimento industrial para a geração de produtos bioquímicos e biocombustíveis. *Química Nova*, *34*(7), 1242-1254. doi: 10.1590/S0100-40422011000700024
- Schobert, H. H. (1990). *The chemistry of hydrocarbon fuels*. Cornwall, GB: Butterworth & Co. Ltda.
- Sun, J., & Wang, Y. (2014). Recent advances in catalytic conversion of ethanol to chemicals. *ACS Catalysis*, *4*(4), 1078-1090. doi: 10.1021/cs4011343
- Totten, G. E., Westbrook, S. R., & Shah, R. J. (2003). *Fuels and lubricants handbook: technology, properties, performance and testing*. Conshohocken, PA: ASTM International.
- Uyttenbroeck, M., Hecke, W. V., & Vanbroekhoven, K. (2015). Sustainability metrics of 1-butanol. *Catalysis Today*, *239*, 7-10. doi: 10.1016/j.cattod.2013.10.094
- Westbrook, C. K., Pitz, W. J., Mehl, M., & Curran, H. J. (2011). Detailed chemical kinetic reaction mechanisms for primary reference fuels for diesel cetane number and spark-ignition octane number. *Proceedings of the Combustion Institute*, *33*(1), 185-192. doi: 10.1016/j.proci.2010.05.087
- Wu, X., Fang, G., Liang, Z., Leng, W., Xu, K., Jiang, D., ... Li, X. (2017). Catalytic upgrading of ethanol to n-butanol over M-CeO₂/AC (M = Cu, Fe, Co, Ni and Pd) catalysts. *Catalysis Communications*, *100*, 15-18. doi: 10.1016/j.catcom.2017.06.016
- Yanai, T., Bryden, G., Dev, S., Reader, G. T., & Zheng, M. (2017). Investigation of ignition characteristics and performance of a neat n-butanol direct injection compression ignition engine at a low load. *Fuel*, *208*, 137-148. doi: 10.1016/j.fuel.2017.06.096
- Yang, M., Kuittinen, S., Vepsäläinen, J., Zhang, J., & Pappinen, A. (2017). Enhanced acetone-butanol-ethanol production from lignocellulosic hydrolysates by using starchy slurry as supplement. *Bioresource Technology*, *243*, 126-134. doi: 10.1016/j.biortech.2017.06.021
- Yates, A., Bell, A., & Swarts, A. (2010). Insights relating to the autoignition characteristics of alcohol fuels. *Fuel*, *89*(1), 83-93. doi: 10.1016/j.fuel.2009.06.037
- Yusof, M. N. A. M., Zulkifli, N. W. M., Masjuki, H. H., Harith, M. H., Syahir, A. Z., Kalam, M. A., ... Khuong, L. S. (2017). Performance and emission characteristics of a spark ignition engine fuelled with butanol isomer-gasoline blends. *Transportation Research Part D*, *57*, 23-38. doi: 10.1016/j.trd.2017.09.004

Received on September 19, 2017.

Accepted on October 16, 2017.

License information: This is an open-access article distributed under the terms of the Creative Commons Attribution License, which permits unrestricted use, distribution, and reproduction in any medium, provided the original work is properly cited.