Properties of Brazilian gasoline mixed with hydrated ethanol for flex-fuel technology


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Abstract

In the present work, samples of Brazilian gasoline type C previously mixed with hydrated ethanol at concentrations of 20, 40, 60 and 80 vol.% were analyzed by distillation, octane number, specific mass, pH and conductivity, in order to evaluate the physico-chemical properties for a better comprehension of the effects caused by the flex-fuel technology. The obtained results were compared with the specifications of the ANP – Agência Nacional de Petróleo Gás Natural e Biocombustíveis – that is the federal regulatory agency for monitoring of the quality of fuels in Brazil. It was observed that there exists an ideal concentration of hydrated ethanol for addition in gasoline type C in order to obtain good properties for application in the flex-fuel technology.

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Keywords: Flex-fuel; Hydrated alcohol; Gasoline type C; Octane

1. Introduction

The so-called flex-fuel technology is a synonym of flexibility concerning the use of fuels and gives users a freedom of choice, whether to use only hydrated alcohol or gasoline in their cars, or a mixture of these fuels in any concentration. Actually, about 85% of the cars produced in Brazil are equipped with this technology, and the people can choose the cheaper or available fuel to be used. The flex-fuel technology is based on sensors that detect the concentration of the mixture of gasoline and hydrated alcohol, and the subsequent automatic adjustment of the engine.

In Brazil, the development of the flex-fuel technology deals with the possibility to increase the consumption of alcohol. In general, a gasoline is formed by a complex mixture of paraffins, iso-paraffins, olefins, napthenics and aromatics, with chains containing 4 to 12 atoms of carbon, and the range of ebullition from 30 to 225 °C [1]. Also, gasoline contains some amount of contaminants such as sulfur, oxygen and nitrogen compounds [2,3]. The octane index is a property of gasoline related to the maximum limit in which the fuel and air vapor mixture can be compressed inside the combustion chamber without spontaneous explosion. The hydrated ethanol is a fuel obtained from the sugar cane with purity in the range of 92.6 to 94.7% (degree INPM), which represents ca. 5.3 and 7.4% of water, and boiling point of ca. 78 °C.

The generation of carbon monoxide during the combustion of gasoline is a serious environmental problem in big cities. The addition of ethanol in gasoline decreases the concentration of CO emissions [4]. Thus the application of a mixture of gasoline–alcohol is a very interesting technology, and some countries such as the United States, China, Australia and Japan are planning to employ this flex-fuel technology in the near future.

Mixtures of ethanol-to-gasoline have been used in Brazil since the creation of the National Program of Alcohol (PROALCOOL), in 1975, with proportions of ethanol ranging from 15 to 26 vol.%. The change in the properties of these mixtures leads to the octane increasing, density, vapor pressure and distillation [5]. During the eighties, this national program was finished. In the nineties in Brazil, researches for the application of the “flex-fuel” technology were started, considering the possibility of developing new vehicles replacing the exclusively alcohol vehicles. Although Brazil has a vast alcohol supply infrastructure, alcohol or any mixture of this fuel with gasoline, would represent a differentiation and attractive factor in the consumer market. To alcohol producers, it would mean...
greater flexibility in supplying their fuel, as a consequence of seasonal harvest variations and opportunities in the sugar market. Research work done in Brazil resulted in a technological conception that was superior to the US and other countries. While “flex-fuel” vehicles in the USA were derived from gasoline vehicles, in Brazil advantage was taken of the experience with alcohol vehicles, which have engines with higher compression ratios. Thus, the Brazilian “flex-fuel” concept proved to be better in terms of fuel savings and performance, allowing the use of up to 100% alcohol. The increased interest in the use of alcohol in other countries is stimulating interest in vehicle manufacturers to consider the possibilities of turning Brazil into a production center for “flex-fuel” vehicles, with new opportunities to export this technology.

The aim of the current work is to evaluate the physico-chemical properties of mixtures of Brazilian gasoline type C with different concentrations of hydrated ethanol, in relation to octave, pH, and specific mass, electric conductivity of samples, for application in the flex-fuel technology.

2. Experimental

The gasoline and alcohol samples were obtained directly from a Petrobras station in Natal City at Rio Grande do Norte State, in Brazil. They were mixed in order to obtain the so-called “flex-fuel” samples, in concentrations of 20, 40, 60 and 80 vol.% of hydrated alcohol in gasoline type “C”. The denomination “C” means a commercial gasoline that already contains ca. 25% of anhydrous alcohol. The obtained alcohol-to-gasoline samples were analyzed by distillation, octave, specific mass, pH, and electric conductivity.

The distillations were processed according to ASTM D86 rule [6], using an automatic equipment model ISL-AD86 5G. For the samples, were considered the boiling point relative to 10, 50 and 90% of vapors, the end point and final residue.

The octane number basically of two methods, known as MON (Motor Octane Number) and RON (Research Octane Number), according to ASTM D2699 [7] and ASTM D2700 [8], respectively. The Anti-Detonant-Index (ADI) is the medium value of the two methods (MON + RON)/2 and is related to the resistance of the fuel for detonation. In this work, these properties were determined using an infrared spectrometer PETROSPEC GS-1000 model.

The specific mass of the samples was determined following the ASTM D4052 rule [9], using a digital densimeter Toledo DE-40 model. The electric conductivity of the hydrated alcohol was accomplished according the NBR 10547 Brazilian rule [10]. The test is based in the electric conductivity of the ions present in the solution probably during the alcohol processing. The equipment used for this measure is a digital conductivimeter with temperature control, WALKLAB model from Trans Instruments. To each measurement, the equipment was previously calibrated with a 0.01 mol L\(^{-1}\) KCl solution.

The pH was determined according the Brazilian NBR 10891 [11]. The instrument was a digital B-464 from Micronal, with temperature compensation and equipped with a combined glass electrode of Ag/AgCl with a reference electrolyte and a temperature sensor. The equipment was firstly calibrated with standard solutions of potassium hydrogen phthalate of pH 4.00 and aqueous solution of potassium di-hydrogen phosphate and sodium hydrogen phosphate at pH 7.00.

3. Results and discussion

The results obtained in the analysis accomplished with the gasoline type C and that mixed with hydrated alcohol is given in Table 1. They showed conformity according to the ANP (Agência Nacional do Petróleo, Gás Natural e Biocombustíveis) [12,13]. The amount of anhydrous alcohol in the gasoline type C was determined according the NBR 13992 rule [14], and obtained a value of 26% volume.

The characteristics of distillation have an important effect in its quality, specially related with gasoline containing different solvents on its composition. From the distillation data, information was obtained concerning the volatility and possibility of deposit or residue in the motor. The volatility determines the tendency of a hydrocarbon to produce explosive vapors, affecting the start and heating of a motor. The presence of components of high boiling point can affect mainly the formation of combustion deposits.

Fig. 1 shows the distillation curves of the gasoline type C, and the flex-fuel samples. It is shown that the light, medium and heavy fractions of hydrocarbons are in the temperature range from 35 to 220 °C, which is the limit permitted by ANP. The hydrated alcohol distillates at ca. 75 °C. With respect to the flex-fuel samples, it was observed that the presence of ethanol in the gasoline increases the temperatures of 10% and 50% of the vapors; on the other hand, the temperature relative to 90% of the vapors decreases.

The distillation points that influence the performance of motors are: 10% of vapors, which is related to the starting of the automobile, should be lowered to generate a fast start of the engine with low rotation per minute; 50% of vapors, which represents the heating features, acceleration and economy of the fuel, and lastly, 90% of vapors and end boiling point, which represents the high fraction of hydrocarbons, should be controlled to avoid the formation of deposits inside the engine. These fractions present high molecular compounds including

<table>
<thead>
<tr>
<th>Experiment</th>
<th>Gasoline °C</th>
<th>Flex-fuel alcohol-to-gasoline ANP</th>
</tr>
</thead>
<tbody>
<tr>
<td>T (°C)</td>
<td></td>
<td>A20: 40.0 G80</td>
</tr>
<tr>
<td>Initial</td>
<td>39.0</td>
<td>41.0</td>
</tr>
<tr>
<td>10%</td>
<td>54.0</td>
<td>56.6</td>
</tr>
<tr>
<td>50%</td>
<td>72.5</td>
<td>74.8</td>
</tr>
<tr>
<td>90%</td>
<td>166.7</td>
<td>163.1</td>
</tr>
<tr>
<td>End point</td>
<td>201.6</td>
<td>198.1</td>
</tr>
<tr>
<td>Residue (vol.%)</td>
<td>1.4</td>
<td>1.5</td>
</tr>
</tbody>
</table>

A: hydrated alcohol fuel; G: gasoline type C fuel, and the numbers 20, 40, 60 and 80 are relative to vol.% of fuel. The values are compared with those suggested by ANP.
sulfur. The occurrence of a high percentage of distillation residue can be related to the proportion of these products and to the thermal instability of the obtained fractions at the end of the distillation process. The utilization of gasoline with a high amount of residue contributes to the formation of carbon deposits in the motor.

The mixtures containing 60 and 80% alcohol, respectively, present temperature of vapors of 10 and 90% out of the ANP specification (Table 1), indicating that these two concentrations are not recommended for utilization in the flex-fuel technology. Therefore, the reduction of the higher fractions (90% of volume) would be an indication concerning the deposition of solids in the engine.

Table 2 gives the specific mass, MON, RON and ADI, pH and electric conductivity data, as a function of the amount of hydrated ethanol added to gasoline type C. It is observed that both MON and RON increases with the ethanol concentration in the mixtures. This is due to high value of the Anti-Detonant-Index (ADI) for ethanol of 107.2.

It is observed that there is an increase of the specific mass with the addition of ethanol to gasoline C. The specific mass is a characteristic of the gasoline that relates its total energetic potential. Thus, for high specific masses, a large amount of fuel injected in the engine, for a given volume should have to be considered. Also, a variation in the specific mass led to a consequent variation in the mass of the injected fuel, being impossible in a well balanced air:fuel mixture.

Concerning the electric conductivity of the samples, it was observed that when the ethanol was added to the gasoline type C, this value increased dramatically from 10 μS m⁻¹ for gasoline C, to 180 μS m⁻¹ for the sample A40:G60. For the samples A60:G40 and A80:G20, the values were 180 and 190 μS m⁻¹, respectively, being close to hydrated alcohol, or 200 μS m⁻¹. These results are in agreement with the literature [15].

The control of the electric conductivity and the pH are important parameters to preview some corrosion problems in the engine. As can be visualized in Table 2, these two parameters are in conformity with the ANP specifications, for Brazilian fuels. As can be visualized on this table, at the proportion of 40 vol.% of hydrated ethanol added to the gasoline C, a pH = 7.0 is obtained.

In the flex-fuel vehicles, there is an electronic tool which determines the ideal ethanol-to-gasoline proportion, and the automatic adjustment of the ignition point occurs for a perfect functioning of the engine, altering the time for injection of the fuel and the time for the opening and closing of the valve. For the compensation of the low power detonation for alcohol, the electronic command is adjusted for a better ignition point. A sensor inside the tank is used to detect the alcohol-to-gasoline proportion.

4. Conclusion

The results indicated that the mixtures of hydrated alcohol-to-gasoline increased the octane properties MON, RON and mainly the Anti-Detonant-Index. Also, the specific mass and electric conductivity increased its values with the addition of ethanol. The distillation temperatures increased for the 10 and 50% of vapors and the end point, and decreased for values higher than 50%, reducing significantly the ebullition end point of the sample with 80% ethanol. Concerning the pH values, it was observed that there was a decrease upon ethanol addition. For the A40:G60 and A60:G40 samples, pH values in the range of 7.0–6.9 were obtained, suggesting that the proportion of hydrated ethanol ranging from 40 to 60 vol.% in gasoline C is recommended for vehicles with flex-fuel technology.

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Table 2

<table>
<thead>
<tr>
<th>Property</th>
<th>Gasoline C</th>
<th>Flex-fuel alcohol-to-gasoline</th>
<th>ANP</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>A20:G80</td>
<td>A40:G60</td>
<td>A60:G40</td>
</tr>
<tr>
<td>Specific mass (20 °C kg/m³)</td>
<td>751</td>
<td>762</td>
<td>774</td>
</tr>
<tr>
<td>MON</td>
<td>83.3</td>
<td>85.6</td>
<td>88.1</td>
</tr>
<tr>
<td>ADI</td>
<td>99.4</td>
<td>102.0</td>
<td>103.5</td>
</tr>
<tr>
<td>pH</td>
<td>8.1</td>
<td>7.4</td>
<td>7.0</td>
</tr>
<tr>
<td>Electric conductivity (μS m⁻¹)</td>
<td>10</td>
<td>80</td>
<td>150</td>
</tr>
</tbody>
</table>

A: hydrated alcohol fuel; G: gasoline type C fuel, and the numbers 20, 40, 60 and 80 are relative to vol.% of fuel.

The reported values are compared with those suggested by the ANP.
References