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THE BRAZILIAN EXPERIENCE WITH ETHANOL FUEL: ASPECTS OF PRODUCTION, USE, QUALITY AND DISTRIBUTION LOGISTICS

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Abstract - The reduction in the availability of fossil fuel increased the search for alternative fuel sources (for example, ethanol). In the Brazilian market, light duty vehicles can be fueled with gasohol (18 up to 27.5 %v/v of anhydrous ethanol in gasoline) and/or hydrous ethanol. To minimize the risk of water-induced phase separation of gasoline-ethanol blends, anhydrous ethanol is blended into gasoline at the distribution terminal, rather than distributing it through pipelines. Pure ethanol can be distributed through pipelines or trucks, and in pipeline cases almost all are not exclusive. To monitor the ethanol quality, several fuel sampling points are indicated: storage tanks, pipelines, and ship, if applicable. For these samples, it is important to evaluate the following parameters indicative of product quality: hydrocarbon and water amount, color, conductivity, and acidity. Monitoring ethanol storage, transport and distribution is important to maintain the ethanol quality until the final consumer.

Keywords: Ethanol fuel; Production; Quality; Logistics; Polyduct transport.

INTRODUCTION

The reduction in petroleum reserves, the perspective of supply disruptions, price volatility, as well as environmental issues, have led to the consideration of alternative and renewable liquid fuels to replace conventional petroleum-derived fuels.

Oil remains the world's leading fuel, with 32.6% of global energy consumption. Renewable energy accounts for 3.0% of global energy consumption, but the trend is the growth of its use (BP Statistical Review of World Energy, 2015).

The dominant biofuel in many countries is ethanol, that has been used as blend component in gasoline or as pure fuel, as in Brazil. The main benefit of ethanol is that it can be produced from various renewable raw materials and the life cycle assessment (a tool for evaluating environmental effects of the fuel based on the production, usage and disposal) is an advantage for this fuel compared to fossil fuels (Larsen *et al*., 2009). Ethanol can be produced from biomass such as sugar cane (mainly in Latin America), wheat and sugar beet (mainly in Europe), corn (mainly in the United States), and other grains. The production of ethanol from biomass involves fermentation and distillation, basically.

Global production of ethanol in 2014 was 94 billion liters. Although the United States and Brazil dominated overall volume, Asia experienced particularly high production growth rates (Renewables,

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2015). In Brazil around 56% is hydrous ethanol and 44% is anhydrous ethanol (*Boletim Mensal dos Combustíveis Renováveis*, 2014; Brazilian Energy Balance, 2014).

The US Renewable Fuel Standard (RFS; Subtitle A) of the Energy Independence Security Act (EISA) of 2007 has made it a requirement to increase the production of ethanol and advanced biofuels, starting at 9 billion gallons in 2008, to 36 billion gallons for total renewable biofuels by 2022. Comparing 2000 and 2011, the sources of US gasoline supply (by volume) changed from 1% to 10% for ethanol, which reduced the imported crude oil.

In Europe, Directive 2009/28/EC (RED) requires a 20% share of total energy from renewable sources, and places a mandatory 10% minimum target, to be achieved by all Member States, for the share of biofuels in transport petrol and diesel consumption by 2020. A 10% share on an energy basis represents about a 14% share of road fuels on a volumetric basis (CONCAWE, 2009). At the same time, an amendment was adopted to Directive 98/70/EC1 ("The Fuel Quality Directive") which introduced a mandatory target to achieve by 2020, a 6% reduction in the greenhouse gas intensity of fuels used in road transport. Directive 2009/30/EC sets regular blend maxim at 10%v/v of ethanol (E10), or oxygen maximum content of 3.7 %m/m.

In Brazil, the total area is 850 million hectares and around 0.8% is used for sugar cane production. Nowadays, the sugar cane production is around 72 ton per hectare (635 thousand ton for 2014/2015 production) and ethanol production can reach 7 thousand liters per hectare (1 hectare = 2.47 acres). In 2014, the ethanol production was 28.1 billion liters (*Boletim Mensal dos Combustíveis Renováveis*, 2015). According to the Brazilian Sugarcane Industry Association (UNICA), for the 2012/2013 crop, 53% of the revenue was provided by sugar, 42% by ethanol, 3% by electricity, and 2% by others (Boletim Mensal dos Combustíveis Renováveis, 2014).

Figure 1 shows the location of ethanol plants in Brazil. They are concentrated in the center-south and northeast Brazil.

USE OF ETHANOL IN BRAZIL

The use of ethanol as an automotive fuel is a quite old practice and, in Brazil, since 1931 it has been the target of numerous government measures with respect to its addition to gasoline.

The addition of ethanol to Brazilian gasoline had the initial goal of reducing imports of petroleum derivatives and, in a second moment, solves the problem of ethanol over production due to the falling sugar price in the international market.

The addition of ethanol to Brazilian gasoline was random and the percentage added varied depending on the harvest of ethanol and sugar price on the international market. But in 1979, with the consolidation of ProAlcool (program to motivate the ethanol production and use, started in 1975), the government fixed the addition of 20 %v/v of anhydrous ethanol to gasoline. It is important to point out that, during the four years of the program, vehicles were converted to use neat ethanol and in 1979 the first ethanol powered car, with engine designed to run on neat ethanol, left the assembly lines.

In 2003 production started of flexible fuel vehicles (FFVs) that can operate with any mixture of hydrous ethanol and gasohol (blend of anhydrous ethanol and gasoline). The ethanol content in gasohol, which should be in the range of 18-27.5 % v/v, is fixed by the government and depends on market forces.

In response to these facts, Brazilian ethanol production has grown over the past decades. In 2013 ethanol represented 4.8% of the final energy consumption in Brazil, while gasoline represented 9.4%. In 2013, renewable energy (hydraulic, firewood, sugar cane products, and others) in Brazil represented around 46% of the total primary energy production (258.3×10^6 toe) (Brazilian Energy Balance, 2014).

Figure 2 shows the Brazilian automobile fleet evolution in terms percentage depending on the fuel used. Recently, most new vehicles in Brazil are FFVs. Of the total amount of light vehicle licensing in Brazil, the FFVs accounted for something around 88%.

PRODUCTION PROCESS AND DISTRIBUTION LOGISTICS OF ETHANOL IN BRAZIL

It is known that water can be removed from ethanol only to a certain degree by traditional distillation methods, and then another relatively energy costly process removes the remaining water, a fact that makes anhydrous ethanol approximately 20–25% more energy demanding to produce than the ethanol/water azeotrope (hydrous ethanol) (Larsen *et al.*, 2009).

According to ANP Resolution nº19/2015, anhydrous ethanol (EAC) can have up to 0.4 %v/v of water and hydrous ethanol (EHC) can have up to 4.9 %v/v.

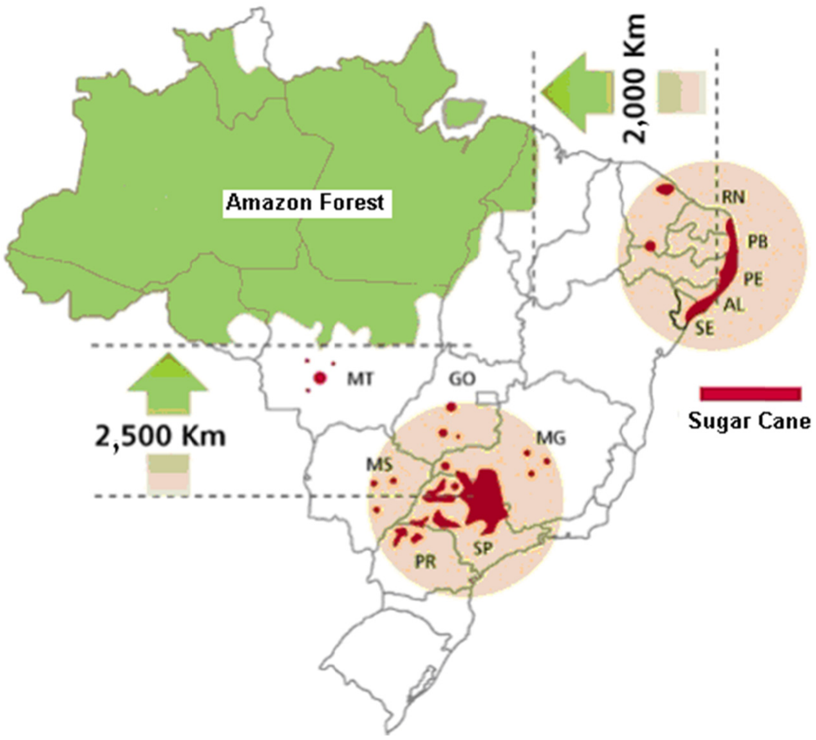


Figure 1: Ethanol plants distribution in Brazil. Source: NIPE-UNICAMP, IBGE and CTC (http://ethanolproducer.com/uploads/posts/web/2013/12/brazilcaneregions_13879047012391.jpg).

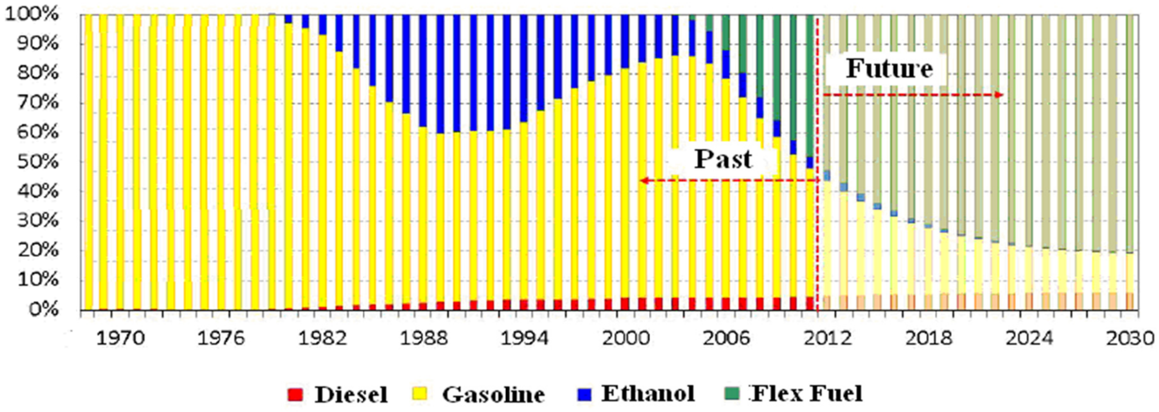


Figure 2: Brazilian automobile fleet evolution depending on the fuel used. Source: ANFAVEA.

Hydrous ethanol is marketed directly to the final consumer, but anhydrous ethanol is mixed with gasoline (known as type A, that does not contain any oxygenate fuel) directly in the trunk at the distribution station, and the product obtained is known as gasoline type C. It is not advisable that gasoline-ethanol blends remain stored in the areas of production and distribution, as they can absorb water from the environment with subsequent phase separation; blending must occur shortly before use (Anton and Steinicke, 2012).

In Brazil, around 90% of ethanol is transported by road, and the remaining 10% is transferred by pipelines or railroad, used as "return freight". Up to now pipelines are not exclusive for ethanol. From the total 7,100 km of pipelines for liquid fuels in the country, around 900 km are used to transfer ethanol.

As to future logistics, Logum Logistics SA (created in March, 2011) is responsible for the construction and operation of the Ethanol Logistics System (logistics, loading, unloading, handling and storage, operation of ports and onshore terminals and waterways) that involves multimodal transport: pipelines, waterways (barges), highways (trucks) and coastal (vessels). Logum (2014) forecasts the creation of pipelines and waterways which will operate in conjunction with the existing distribution system, especially in the central part of the country.

Thus, ethanol quality in the distribution system is routinely required.

ETHANOL QUALITY ASPECTS

For fuels to be useful in the transportation sector, they must have specific physical properties that allow efficient distribution, storage and combustion.

Ethanol storage, transport and distribution monitoring is important to maintain the ethanol quality until the final consumer.

Brazilian Ethanol Specification (ANP Resolution nº 19/2015) presents the parameters that are controlled by the producer/provider/operator, distribution and importer.

Producer/provider/operator and importer are responsible to emit the Quality Certificate, that must contain the results for color and appearance, total acidity, electrical conductivity, density, pH (hydrogen ionic potential), and alcohol, sulfate, iron, sodium, copper, and sulphur content.

Distribution is responsible for emiting the Accordance Bulletin that must contain the results for color and appearance, electrical conductivity, density, pH and alcohol content.

If the ethanol was transferred by pipelines or for imported fuel, the Certificate and the Bulletin must also contain the result for evaporation residue and hydrocarbon content. Otherwise, if the ethanol was transferred by waterway, it must also contain the result for evaporation residue, hydrocarbon, and chloride content. Water, ethanol, and methanol content are required in the case of doubts of quality, or imported fuel.

Petrobras also monitors, in pipelines, ship and trucks, parameters such as color, appearance, electrical conductivity, density, alcohol and hydrocarbon content.

Table 1 lists some ethanol parameters reported in the ANP Resolution, and their relation to fuel quality control. Table 2 shows ethanol characteristics and their effects on the vehicle.

In cases where ethanol is mixed with gasoline, the automotive industry's guiding document towards improved and harmonized market fuel quality is the Worldwide Fuel Charter (2013). Up to 10% by volume of ethanol is permitted by existing regulations, and ethanol should meet the Ethanol Guidelines published by the WWFC Committee (Ethanol Guidelines, 2009).

In the transport system, ethanol can be contaminated by products remaining in the tanks and lines, inadequate operational maneuvers, problems with

Table 1: Ethanol parameters and quality control.

Parameters	Fuel Quality Control
Appearance and color	Transport contamination
Total acidity and electrical conductivity	Production quality and/or transport contamination
Ethanol (or alcohol) content	Transport contamination
Water content	Production quality and/or transport contamination
Methanol content	Transport adulteration
Evaporation residue and hydrocarbons content	Transport contamination
Chloride ion (Cl^-)	Maritime transport contamination
Sulfate ion (SO_4^{-2})	Production quality and maritime transport contamination
Sodium ion (Na^+)	Production quality and maritime transport contamination

Table 2: Ethanol characteristics and their effects at the vehicle.

Parameters	Vehicle Performance	Vehicle Protection
Total acidity and pH		Corrosion
Density and ethanol (or alcohol) content	Drivability (Air/Fuel Ratio)	
Water content	Drivability/fuel consumption	Corrosion
Methanol Content	Fuel consumption (energy content)	
Evaporation Residue		Deposit formation
chloride ion (Cl^-)		Corrosion
Electrical conductivity, sulfate ion (SO_4^{-2}) and sodium ion (Na^+)		Corrosion/Deposit formation
Iron (Fe)		Deposit formation/ Wear
Copper (Cu)		Deposit formation (catalyzes gasoline oxidation)

sealing systems, incorporation of solids due to corrosion of lines, relocation of cargo ships and product adulteration.

To monitor the ethanol quality in this system, several fuel sampling points are indicated: storage tanks, pipelines (at pumping units - beginning, middle and end of pumping ethanol), service station, and ship, if applicable.

Petrobras conducted a follow-up study of ethanol transported by pipelines after 1, 3 and 5 hours and in the final 500 m^3. It was found that the conductivity, water content, hydrocarbons and acidity are higher in the beginning than at 3 hours. The reduction depends on the sample analyzed. Changes in the product quality were not observed during transportation after this period. As noted, the greatest contamination of the ethanol may occur at the start of pumping, as expected, and differences in color are caused by different pollutants or different concentrations.

It is important to mention that anhydrous ethanol in Brazil must receive a dye. In some cases the dye is added by the sugarcane industry and in others by the company responsible for the final product distribution. The anhydrous ethanol with dye cannot be transported by pipeline due to other products pumped in polyducts.

For storage of the ethanol in the production or distribution centers, tanks with floating ceiling and dome are normally used to minimize water absorption and vapor emissions. Another option is to use a fixed ceiling with floating membrane.

Carbon steel for tanks and pipelines works fine with ethanol fuel as long as it does not contain ionic impurities that increase its corrosiveness. Stainless steel is the best material for ethanol tanks, pipelines, and components, but it is expensive compared to most other materials used for fuel tanks and piping. Some carbon steel tanks are coated internally with an epoxy to prevent corrosion over time, but it is necessary to evaluate each epoxy type, because some are not compatible with ethanol. In Brazil, years of practical experience have shown that ethanol can be distributed using these materials without major problems.

Another material commonly found in fuel storage and dispensing is aluminum. When exposed by removal of nickel plating, aluminum was found to be susceptible to widespread pitting. The exposure of the substrate accelerated corrosion due to a combination of galvanic coupling of dissimilar metals and the increased conductivity of the environment (Kass *et al.*, 2012).

If aluminum and magnesium alloys are attacked by alcohol fuel blends, another type of corrosion is observed, called "dry corrosion" (Kruger *et al.*, 2012; Keuken, 2013).

Several studies show the corrosion behavior of several aluminum alloys in ethanol fuels. Kruger *et al.* (2012) investigated this topic by immersion and polarization tests with anhydrous ethanol with water content between 0.05 %v/v and 0.3 %v/v, and temperature in the range between ambient and 80 ºC. They noted that, while high alloyed stainless steels are regarded to be resistant to ethanol fuels of any mixture, for aluminum alloys the addition of water restrains the corrosion. Steels and other metals will corrode if the water content in the fuel mixture is high enough to promote phase separation.

Park *et al.* (2011) examined the effects of dissolved oxygen on the corrosion of aluminum alloy at high temperature (100 ºC) for E20 fuel (a blend of 20 %v/v of anhydrous ethanol in gasoline) by electrochemical tests and surface analyses. They noticed that the water formed by dissolved oxygen in this fuel enhanced the corrosion resistance of the aluminum alloy by promoting the formation of a protective surface film.

Keuken (2013) studied the conductivity of E10 (dry, with 0.2% and 0.5% of water) adding salt water (0.1 to 1.0%, of 3 grams per liter solution). For the same amount of salt water (0.5% to 1.0%, because for low concentrations the salt precipitates out), dry E10 presented higher conductivity than E10 with 0.2 and 0.5% of water. The author concluded that it is necessary to stipulate a minimum water content in fuel ethanol for direct blending of E5, E10 and higher blends to avoid alcoholate (alkoxide) corrosion, and it is also necessary to set a maximum water content for these fuels to ensure that phase separation issues will not occur. It is worth mentioning that E10 and E5, respectively, correspond to blends of 10 %v/v and 5 %v/v of ethanol in gasoline.

Concluding, to guarantee the quality of ethanol, avoiding contamination of the product, it is recommended to: (1) study in detail the history of ethanol batches in order to establish operational procedures for the ethanol transport logistics; (2) dry the storage tanks prior to receiving ethanol; (3) check the current cleaning procedures for storage tanks and, if necessary, establish new standards to prevent water contamination, corrosion products or degradation of coatings of tanks; (4) ensure the integrity of the seal coating and storage tanks; (5) avoid long-time stops of the pumping duct; (6) establish a procedure for passage and maintenance of pig cleaning and separation of products from batches of ethanol and hydrocarbons; (7) avoid chemical injection directly into ethanol and limit their use in products that are transported in front of it; (8) monitor the pipeline inner corrosion.

For maritime transport, usually a dedicated ship is not used for ethanol. So, some cautions are indicated: observe if the paint used in the inner tank is compatible with ethanol; vessels must arrive at the port in the condition "Free for Man" to allow the inspection of each tank vessel; performing "Wall Wash Test" for detection of hydrocarbons, assessment of the color of the wall residue and test chloride; use of inert gas such as nitrogen. If an inert gas with significant amount of CO_2 is used, it will increase ethanol acidity and cause quality problems. Dalmolin *et al.* (2006) showed that increasing the ethanol amount in ethanol-water mixture increases CO_2 solubility.

Regarding storage of small volumes of ethanol for quality analysis, some studies done by Petrobras indicated that storing ethanol in colorless glass vials is not recommended. Keeping two samples of ethanol, one in a bright room and another in the dark, the first one showed corrosivity significantly higher than the second one. The storage in plastic bottles is also not advisable, since this material has a certain permeability and allows absorption of water from the environment.

PREPARATION AND DISTRIBUTION LOGISTICS OF GASOLINE-ETHANOL BLENDS

Logistically, blending ethanol into gasoline at the refineries would be the simplest way to ensure that the finished product met the required specifications. However, the majority of ethanol is blended into gasoline at distribution centers or ethanol production centers (Bechtold *et al.*, 2007). It occurs because gasoline-ethanol blends cannot be distributed via pipeline to avoid increased water content because ethanol is hydroscopic and in all pipeline systems the fuel is inevitably exposed to water. Water is present in existing pipelines because of its very low solubility in the fuels being transported (gasoline for example), and water collects at “low points” in the pipes.

Figure 3 illustrates a polyduct flow carrying gasoline and ethanol. It can be observed how gasoline does not have affinity with water. When the polyduct is not pumping, water tends to flow to the bottom and part of the water is mixed with ethanol and part of the gasoline is mixed with ethanol. The water rich layer is more susceptible to wet corrosion. When pumping restarts, ethanol moves, cleaning the pipeline wall.

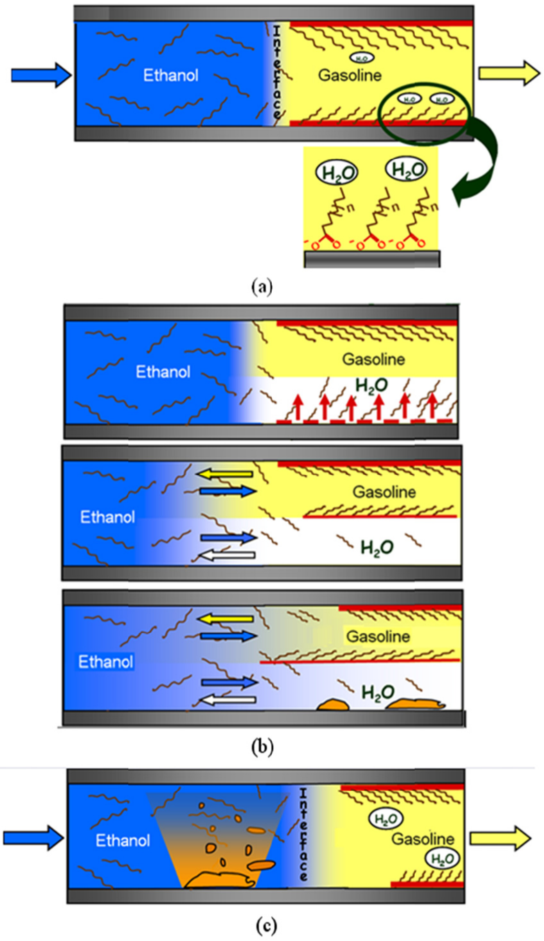


Figure 3: Polyduct transport with the presence of water. (a) polyduct during pumping; (b) polyduct during no pumping; (c) pumping restart.

Due to the high solvency of ethanol, when it is transported by pipelines or stored in metallic tanks, it can drag some impurities (metal deposits, corrosion products) from the inner walls. With this, for pipeline transport of ethanol in systems not exclusive for this product, it is recommended to increase the volume transported to reduce contamination problems. The passage of a sacrifice product prior the ethanol batch is indicated to reduce the losses.

Impurities and water present in the ethanol must be controlled, directly or indirectly. Impurities like corrosion inhibitor (derived from petroleum products) and hydrocarbons affect the ethanol color, iron affects the color and conductivity, and the water content increases the conductivity and decreases ethanol content.

In industry or the distribution process, water is an essential factor for microbial activity. The ethanol-water phase of the tank bottom (as dissolved water condenses, it tends to separate out of the petroleum product, accumulating in tank bottoms and in pipeline low-points) favors the growth of aerobic bacteria colonies, which are detrimental to fuel and to certain components of the fuel handling system.

The two primary types of infrastructure problems caused by microbes are microbiologically influenced corrosion and fouling (Passman, 2013). Some studies show that water increases the corrosion for some metals and, in the case of ethanol solutions, it can decrease.

Passman *et al*. (2009) reported evidence of microbial activity in the aqueous-phase of underground storage tanks containing 10% of ethanol in regular gasoline. However, ethanol can be used as a disinfectant at concentrations higher than 20 %v/v. At these concentrations, it is unlikely that gasoline-ethanol blends will be susceptible to biodeterioration (Source: Mark Bishop´s Chemistry Site).

The primary pillars of microbial contamination control are prevention and remediation. The most commonly recommended is water control. Prevention includes system design, water removal and good cradle-to-grave product stewardship. However, preventing water accumulation in fuel systems is not a trivial process.

To minimize the risk of water-induced phase separation of gasoline-ethanol blends, in Brazil anhydrous ethanol is blended into gasoline at the terminal (directly in the tank truck) prior to shipping to retail service stations rather than distributing it through pipelines.

To ensure a homogeneous mixture the best option is online mixture, on the loading platform in an automated manner, where the proportional volumes to be added are calculated based on product density and temperature. The movement of the tank truck enroute to the service station is sufficient to homogenize the mixture.

EFFECTS OF ETHANOL ADDITION TO GASOLINE

As regards mixtures of ethanol and gasoline, properties that are affected include miscibility, volatility and compatibility with elastomers. Other properties are also affected, but they will not be discussed in this paper.

Miscibility

Ethanol is miscible in water, which means that the two liquids can be mixed in any proportion. In the mixture process, water-water and ethanol-ethanol attractions are broken and ethanol-water attractions are formed (Figure 4). Because the attractions between the particles are so similar, the freedom of movement of the ethanol molecules in water is about the same as their freedom of movement in pure ethanol, and mixture is observed (source: Mark Bishop´s Chemistry Site).

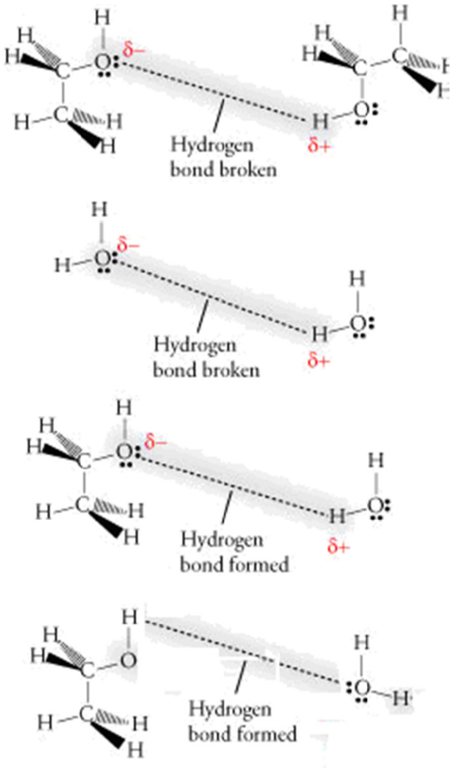


Figure 4: Possible arrangements when ethanol and water molecules are dispersed throughout a solution.

There is a very slight mixing of hydrocarbon and water molecules. The natural tendency toward dispersal does cause some hydrocarbon molecules to pass into the water and some water molecules to pass into the hydrocarbon. New attractions between hydrocarbon and water molecules are formed, but, because the new attractions are very different from the attractions that are broken, they introduce significant changes in the structure of the water.

Anhydrous ethanol is completely miscible with gasoline in any proportion and any temperature. However, the presence of water in the mixture of gasoline-ethanol can cause phase separation problems. The blending problem depends on product temperature, gasoline composition, ethanol content and water content in ethanol. Increasing the amount of ethanol in the mixture decreases the phase separation problem.

The lower the temperature, the lower the water tolerance, so in cold climate conditions, phase separation of ethanol with high water content may occur in gasoline blends. At 21 ºC water solubility in conventional gasoline is around 150 mL×m^{-3} (150 ppm).

In E10, at the same temperature, water solubility is around 5 to 7 L×m^{-3} (5,000 to 7,000 ppm) due to ethanol´s hydroscopic properties; however, at -12 ºC a gasoline-ethanol blend will tolerate approximately 3 L×m^{-3} (3,000 ppm) water. Once the solubility limit is exceeded, phase separation occurs and two phases are formed: an upper gasoline-rich liquid layer and a bottom ethanol-water rich liquid layer (Passman *et al.*, 2009).

Tables 3 and 4 show experimental results of a study conducted by Petrobras that illustrates these statements about the water tolerance and phase separation tendency (indicated by the cloud point) of gasoline-ethanol blends.

Table 3 shows cloud point changes with the amount of hydrous ethanol and the gasoline composition in gasoline-ethanol blends. Increasing the hydrous ethanol fraction decreases the phase separation temperature, and increasing the concentration of aromatics and olefinic hydrocarbons (HCs) also decreases this temperature.

Table 4 shows that, upon increasing the water content in gasoline-ethanol blends by manual addition, the cloud point also increases.

Table 3: Influence of the ethanol content and of the gasoline composition on the cloud point.

Blends, %v/v			**Cloud Point, °C**					
			Gasoline Types					
Gasoline	**Ethanol**	**Water**	**1**	**2**	**3**	**4**	**5**	**6**
88	11.1	0.9	> 35	27	> 35	> 35	> 35	> 35
82	16.7	1.3	> 35	20	27	> 35	22	29
75	23.2	1.8	32	9	16	26	12	19
Gasoline Composition, %v/v:								
Saturated HCs			95.1	59.4	69.2	81.9	66.0	71.8
Aromatic HCs			4.9	27.3	29.8	18.1	25.5	21.2
Olefinic HCs			0.0	13.3	1.0	0.0	8.5	7.0

Table 4: Influence of the water content and of the gasoline composition on the cloud point of gasoline-ethanol blends (E10).

Water, %m/m	**Cloud Point, °C**				
	Gasoline Types				
	1	**2**	**3**	**4**	**5**
0.27	-32	-26	-26	-18	-17
0.41	-8	-2	-2	-2	-8
0.54	11	12	12	14	16
Gasoline Composition, %v/v:					
Saturated HCs	50.6	51.8	49.7	61.8	37.7
Aromatic HCs	31.9	24.7	25.6	21.8	32.2
Olefinic HCs	17.5	23.5	24.7	16.4	28.9

Investigations by the Process Design Center (PDC) led to research work that revised the understanding of water tolerances of ethanol-gasoline mixtures and the conditions under which phase separation occurs. To verify and validate this discovery, covered by international patents WO 2006/137725 A1 and WO 2009/096788 A1, HE Blends BV (a separate entity of PDC) pursued its continuing test programs in Europe, testing vehicles with hydrous blends. The Netherlands experience showed that HE15 (a gasoline-ethanol blend with 15 %v/v of hydrous ethanol) works well between -10 and +30 ºC ambient conditions (Source: PDC and HE Blends).

During the BEST project (Bio Ethanol for Sustainable Transport) more than 10.000 ethanol powered cars were evaluated. HE15 and E10 (a gasoline-ethanol blend with 10 %v/v of anhydrous ethanol in gasoline) showed any negative impact on engines in bench and fleet tests. Another conclusion of this study was that HE15 cannot be mixed with E10 or neat petrol and must have a separate infrastructure. Otherwise there is a risk of water separation in the fuel. In Rotterdam HE15 has been demonstrated and introduced successfully. The hydrous ethanol used to form this fuel has a maximum 6.5 %m/m of water.

The strategy behind this hydrous ethanol is to minimize production costs, because less effort/energy is needed to remove water from the ethanol. Because hydrous ethanol is less expensive and more CO_2 friendly to produce compared to anhydrous ethanol, there are economic and environmental incentives for the presence of water in the fuel blends. However, as mentioned previously, in cold climate conditions, phase separation of ethanol with high water content and gasoline blends may occur.

Volatility

Volatility refers to a fuel’s ability to change from liquid to vapor, and it is commonly measured by the vapor pressure and the distillation curve. These properties can affect proper engine cold starting, vapor lock tendency in older engines without fuel injection (e.g., carbureted engines), and the quality of starting in engines with fuel injection. Vapor pressure is a critical factor in meeting evaporative emission requirements.

Fuels with excessively high vapor pressure may contribute to hot drivability/hot restart problems such as vapor lock. Fuels of too low volatility may contribute to poor cold starts and poor warm up performance in vehicles.

The distillation curve provides insight into the boiling range of the fuel and can be used to predict its operation in engines. The low temperature region of the curve (up to 70 ºC) can be related to the ease of engine starting, engine warm-up, evaporative emissions, and vapor lock (for carbureted vehicles). The middle range of the curve (70-100 ºC) can be related to warm-up, acceleration, and cold-weather performance, while the top range of the curve (above 150 ºC) relates to the propensity for combustion deposits and oil dilution. Industry specifications for gasoline typically emphasize T10, T50, and T90 values from the distillation curves. For ethanol blends with no adjustments made to the base gasoline, these values (especially T50) can vary greatly (Andersen *et al*., 2010a).

Figures 5 to 7 show the experimental results of a study conducted by Petrobras to evaluate aspects of vapor pressure and distillation in gasoline-ethanol blends, using respectively the ASTM methods D5191 and D86. For the blends two base gasolines were used: premium and the standard one (both in accordance with ANP Resolution nº57, 20.10.2011) and two types of ethanol: anhydrous and hydrous (both in accordance with ANP Resolution nº7, 9.2.2011). Anhydrous ethanol was obtained from Sigma-Aldrich and hydrous ethanol from a service station. Premium gasoline presented 5 ppm v/v of sulfur, 46 %v/v of aromatics, <1 %v/v of olefinics, and 53 %v/v of saturated compounds. Standard gasoline presented 850 ppm v/v of sulfur, 26 %v/v of aromatics, 28 %v/v of olefinics, and 46 %v/v of saturated compounds. For studies with hydrous ethanol, it was not possible to evaluate the same amount of blends as with anhydrous ethanol, because a phase separation was observed at laboratory temperature (20 ºC) for blends with hydrous ethanol content below 25 %v/v.

In a mixture, an azeotrope manifests itself as a flat portion of the distillation curve at the boiling temperature of the azeotrope. An azeotrope is a mixture of two or more liquids in a ratio such that the composition of the mixture cannot be changed by simple distillation. This means that the azeotropes of ethanol and hydrocarbons distil at a nearly constant temperature. This phenomenon results in an essentially flat distillation curve in the standard ASTM distillation measurement until the azeotropes of ethanol and hydrocarbons have been eliminated from the liquid. When the ethanol has distilled completely from the liquid, the distillation curve rapidly returns to that of the hydrocarbons (CONCAWE, 2009).

Figure 5 shows that the azeotropes that are formed when gasoline is mixed with ethanol (for ethanol blends from 0-25 %v/v) result in a vapor pressure that is higher than either of the individual components. The literature reports that, beyond 30 %v/v, the vapor pressure drops to equal and below that of gasoline. The observation of a maximum vapor pressure at 5-10 %v/v ethanol is consistent with several studies. The observed difference may reflect the different chemical compositions of the gasoline tested (Andersen *et al*., 2010b). Several authors (Henke *et al*., 2010; Dalmolin *et al*., 2006) provide correlations for calculating the vapor pressure of pure ethanol. For a temperature of 37.8 °C, the vapor pressure of pure ethanol is about 16 kPa.

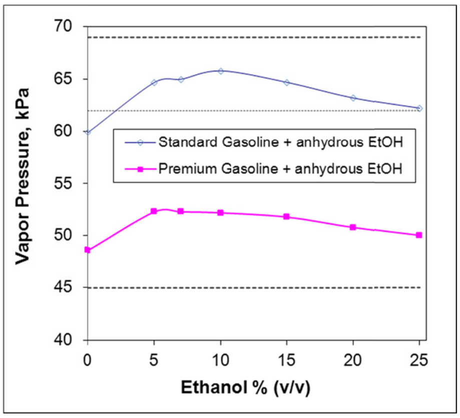


Figure 5: Vapor pressure curves for gasoline-ethanol blends, for a temperature of 37.8 °C.

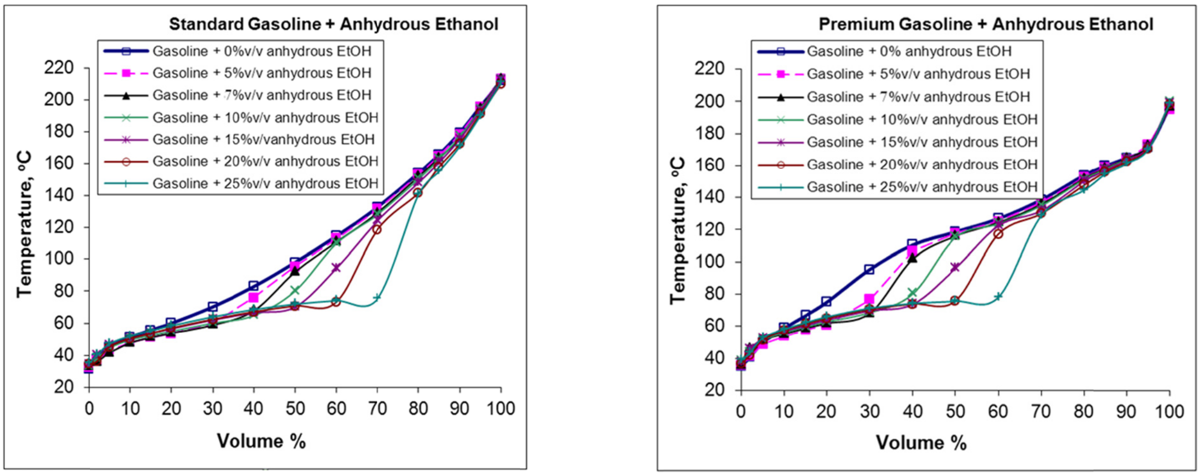
As shown in Figure 6, the addition of small amounts of ethanol (5 to 10 %v/v) gives the largest increase in volatility for approximately the first 30% of the distillation curve. As the fraction of ethanol increases (from 10 to 25 %v/v), there is a substantial decrease in the distillation temperature (increase in volatility) over the middle portion of the distillation curve. It affects the evaporative emissions from a vehicle, because the more volatile the fuel the greater the evaporative losses of the fuel.

The results were compared to available literature data for ethanol (Andersen *et al*., 2010a), and there is good agreement in the change in shape of the distillation curves due to ethanol addition.

Figure 7 shows that, for hydrous ethanol, this decrease is less evident when compared with anhydrous ethanol results, at the same ethanol amount in the blend.

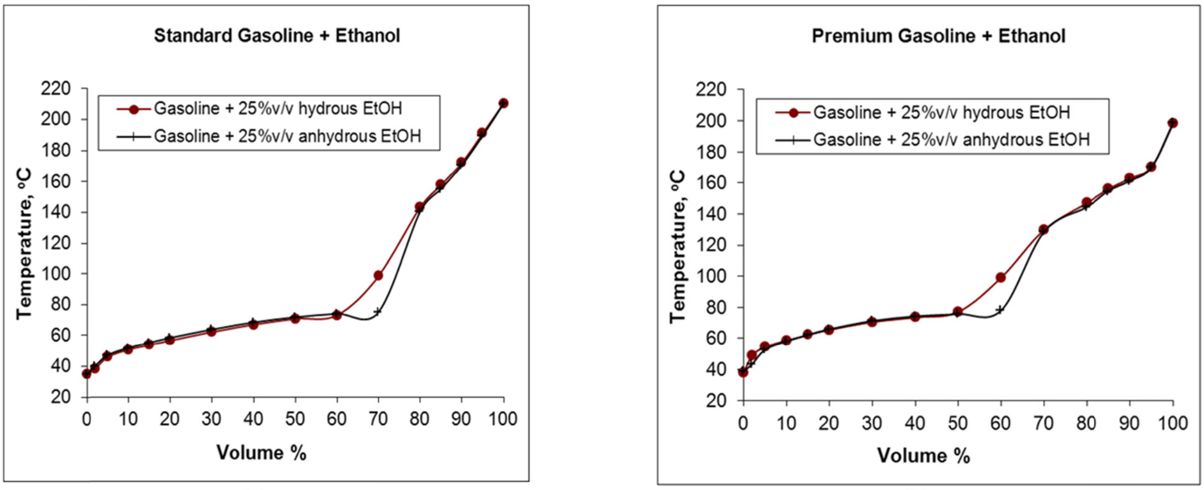
Compatibility with Elastomers

Chemical compatibility refers to changes in the physical, chemical or mechanical properties of a material resulting from thermal-chemical exposure. Moreover, chemical compatibility also means that degradation products, if any, must not contaminate the fuel and impair automotive performance.



(a) (b)

Figure 6: Distillation curves for gasoline-ethanol blends. Standard gasoline (a) and premium gasoline (b), with anhydrous ethanol.



(a) (b)

Figure 7: Distillation curves for gasoline-ethanol blends. Standard gasoline (a) and premium gasoline (b), with hydrous or anhydrous ethanol.

The ethanol compatibility of high-performance fluoroelastomers and nitrile elastomers needs to be evaluated since these materials are considered to be potential alternatives to the current rubber materials used in dispenser seals and o-rings.

A review of pertinent studies has shown that most elastomers exhibit some level of swelling upon exposure to gasoline. The addition of ethanol to gasoline will increase the swelling of most elastomers (except neoprene), and the maximum swelling occurs at ethanol concentrations between 10 %v/v and 25 %v/v. Accompanying the volume increase is a corresponding decrease in the hardness, and the combination of high swelling and increased softening would reduce the effectiveness of the seal (Kass *et al*., 2011).

It is important to point out that the fuel composition affects the results, as reported by Kass *et al.* (2011) and Maciel *et al.* (2013). The former indicated that, for the fuels tested, the aromatic content tends to increase elastomer swelling. The latter studied NBR/PVC blend samples that were exposed to a gasoline rich in olefins (cyclohexene) and observed two times more swelling than for samples exposed to the other fuels, and less extraction of the constituents of the blend and less change in the mechanical properties.

Petrobras conducted a study to evaluate aspects of compatibility with elastomers (nitrile and fluorinated) in gasoline-ethanol blends (three blends: with 25 %v/v of ethanol, 18 %v/v of ethanol, and a fuel representing a mixture of 50 %v/v of gasohol fuel with 50 %v/v of hydrous ethanol). Both elastomers were chosen because they are more impactful on engine operation (nitrile for diaphragms) and sealing function (fluorinated for “O” rings). The base gasoline (gasoline without ethanol) had 324 ppm v/v of sulfur, 26 %v/v of aromatics, 23 %v/v of olefinics, and 51 %v/v of saturated compounds.

The elastomer samples were immersed in each fuel at 60 ºC for 7, 14 and 28 days, and the changes in the weight, hardness, and mechanical properties (traction) studied. In general, the aged samples showed a reduction in the hardness, and an increase in the mass variation, tensile strength and E-modulus. For the hardness, mass variation, tensile strength and E-modulus results, it was observed for all samples that the changes occurred with 7 days of immersion and, after that, the results remained almost unchanged. Maciel *et al*. (2013) indicated that this kind of change occurs by the first day and, after that, remains almost constant.

The mass variation increased after elastomer immersion, more for nitrile elastomers, and less for gasohol - hydrous ethanol blends. Maciel *et al.* (2013) observed that pure ethanol resulted in a decrease in weight, different from the one observed for gasoline samples with ethanol (gasohol).

Comparing the results obtained with nitrile and fluorinated elastomer, the latter showed the best fuel resistance.

CONCLUSIONS

This paper considers some issues related to ethanol: production, quality, use, logistics transportation and the effects of its addition to gasoline on some properties (miscibility, volatility and elastomeric materials compatibility). Procedures are indicated to minimize the risk of water-induced phase separation of gasoline-ethanol blends and to monitor the ethanol quality.

It is important to evaluate the following parameters indicative of ethanol quality: hydrocarbon and water amount, color, conductivity, and acidity.

Monitoring ethanol storage, transport and distribution are important to maintain the ethanol quality until the final consumer.

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