GASOLINE C MADE WITH HYDROUS ETHANOL

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ABSTRACT

The consumption of ethanol fuel is increasing due to the higher costs of petrol and the increased participation of flex-fuel vehicles in the Brazilian passenger vehicle fleet.

This paper presents some literature information, that Hydrous Ethanol (AEHC, or E100) can be used to make Gasoline C (E22) without water phase separation under typical Brazilian climate.

This might present important improvement in ethanol production energy efficiency, less emission of Green House Gases (GHG), extra electrical energy to sell during the production periods and lower capital investments for the building of new plants.

In Brazil two types of ethanol are used as automotive fuel: AEAC "Anhydrous Ethanol Fuel" with a maximum water content of 0.4% in volume; and AEHC "hydrous Ethanol Fuel" (E100) with a maximum water content of 4.9% in volume. The AEAC is mixed with about 22% in volume with Gasoline A (E0), to make Gasoline C (E22).

The actual AEAC content in gasoline C is determined by legislation. Hydrous ethanol is produced by distillation of the fermented sugar-cane juice, up to a certain point, called the azeotropic point (about 95.6%), when water and alcohol can no longer be separated by fractional distillation.

In order to produce AEAC about the same amount of energy used by the distillation is used by additional processes, the later equipment being of the Molecular Sieve type.

INTRODUCTION

In the quest for diminishing its dependence on foreign petrol, along with its vast agricultural capabilities, Brazil launched the "Pró-Alcool" program giving tax Incentives to alcohol vehicles, after the first petrol cost boom in the 70s.

Nowadays there are two fuel types available at the fuel station for passenger vehicles: E100 (AEHC) that is the derived from simple distillation process and have about 4.9% water content in it [1] and Gasoline C or E25, which is a mixture of 75% Gasoline A and 25% [2] in volume of anhydrous ethanol (AEAC) with a maximum of 0.4% of water.

For emissions tests purposes it is used E22 [2] which has 78% Gasoline A and 22% of AEAC. The gasoline C is made with anhydrous ethanol in order to have a very low temperature for phase separation of less than -30 degrees Celsius.

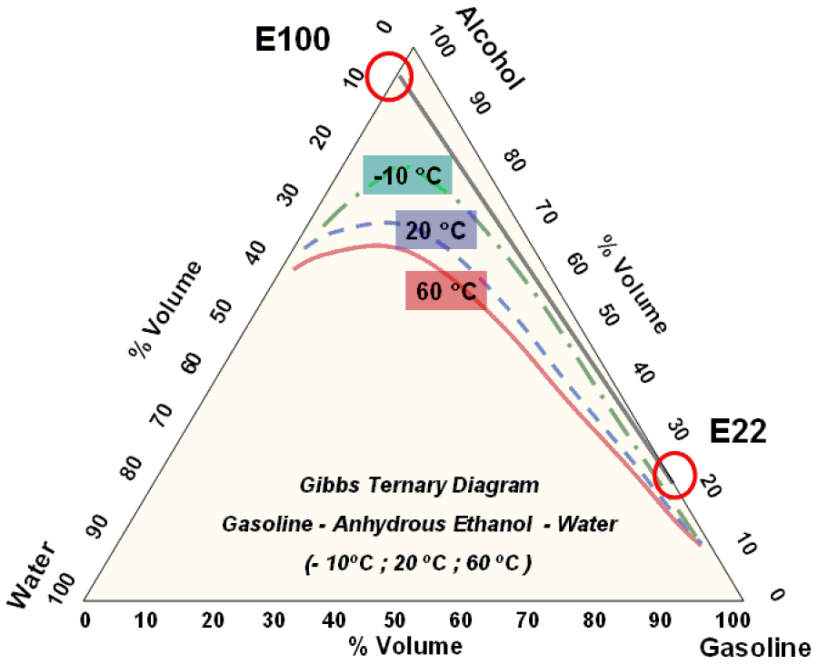

Figure 1: Phase Separation Graph for Gasoline-Ethanol-Water

Water and ethanol are completely miscible with each other forming a stable substance at any temperature.

The same apply to gasoline-ethanol mixtures [12]. But water is not miscible with gasoline, although the addition of ethanol makes gasoline miscible with water at some extent. As shown by the Gibbs Ternary Fuel Diagram shown in figure 1 [12][14][18].

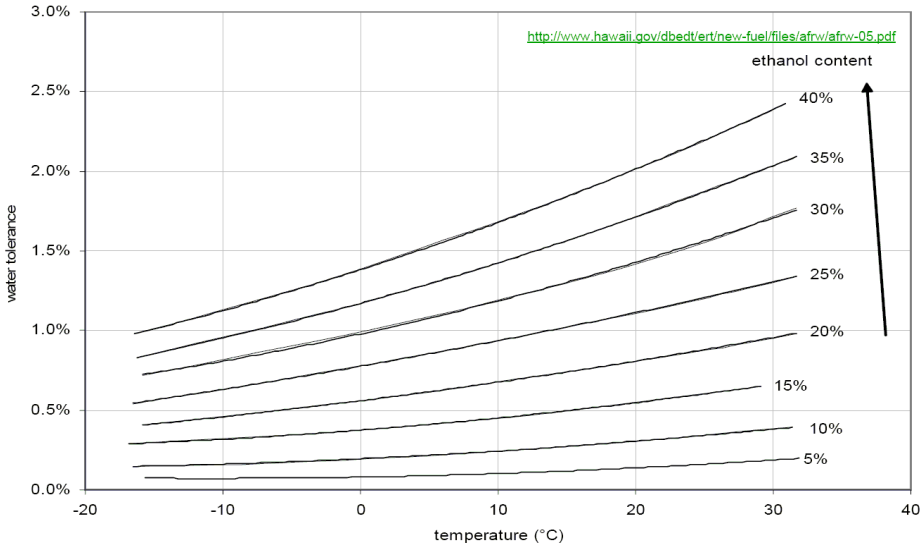

Figure 2: Water tolerance for Gasoline-Ethanol-Water mixtures.

Early studies of ethanol substitution of Lead tetraethyl and methyl tertiary-butyl ether (MTBE) showed that gasoline-ethanol-water mixtures are prone to phase separation at low temperatures [14]. See Figure 2, above.

Climatic conditions in Brazil are such that the lowest recorded temperatures are around -5 degrees Celsius [4]. In fact the last record occurred in São Joaquim (SC) on June 16th, 2008 when the lowest temperature reached -5.4 degrees Celsius. See figure 3. Other low temperatures occurred on June 26th, 2004 in Campos do Jordão (SP) when it reached -5.0 degrees Celcius [4]. . See figure 4.

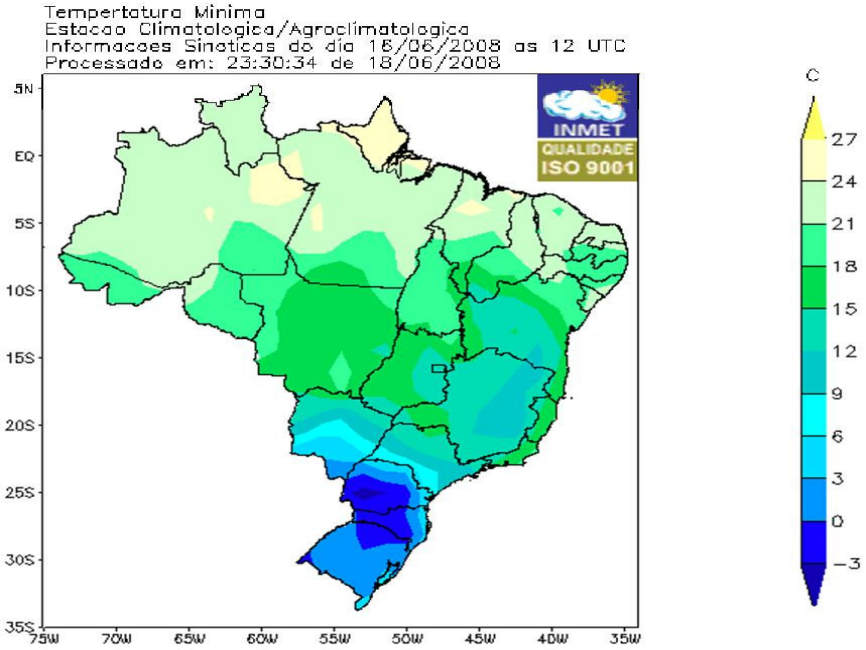

Figure 3: Low temperature record for São Joaquim (SC) in 2008.

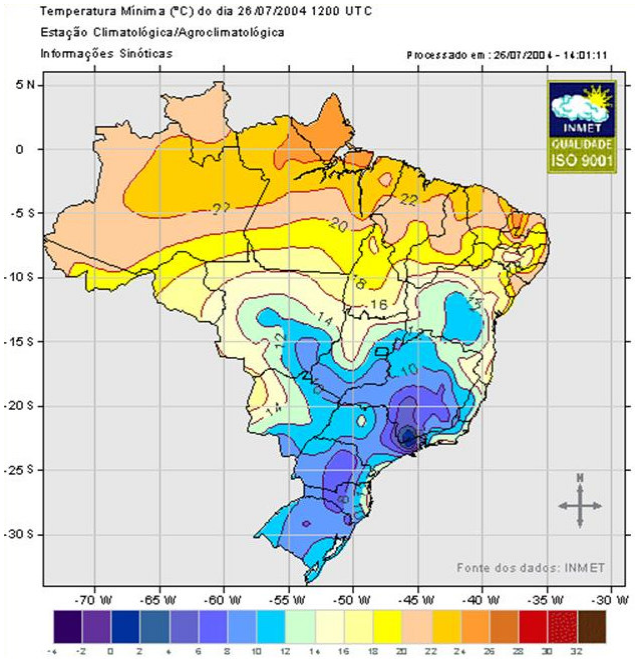

Figure 4: Low temperature record for Campos do Jordão (SP) in 2004.

These low temperatures happen only once a year for only a few hours. Cold chamber simulation of Campos do Jordão low temperature record shows that the fuel line keep 1 or 2 degrees higher than the external temperature due to the bad temperature conduction of fuel. . See figure 5.

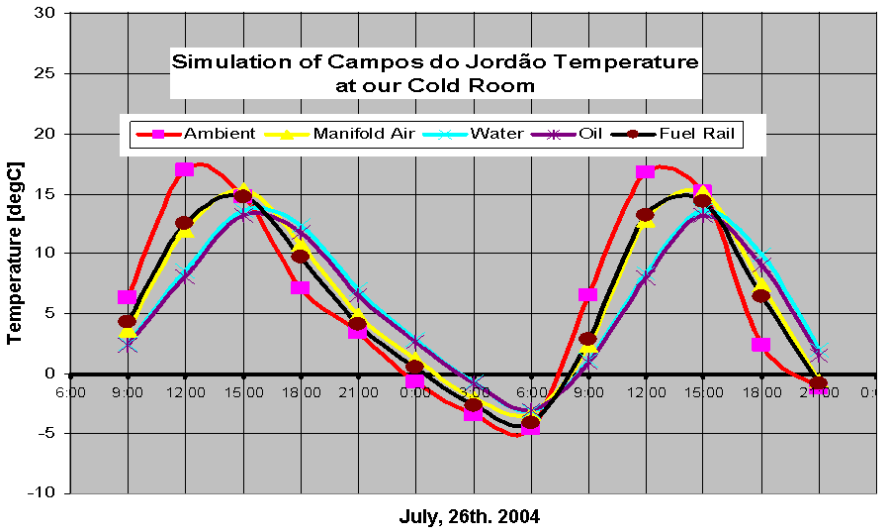

Figure 5: Low temperature simulation in cold chamber.

As the charts show, the low temperatures happen only at specific spots in the country.

This paper will show that it is possible to use gasoline C made with hydrated ethanol (AEHC) with minimum risk of phase separation due to Brazilian climate conditions.

Some advantages of using hydrated ethanol in the formulation of gasoline will explained in the next chapter.

1. ETHANOL PRODUCTION ENERGY

Ethanol is produced by the bacterial fermentation of sugar-cane most up to the point of about 8.5% ethanol concentration [5][11].

Using normal distillation techniques, the produced “beer” can only be purified to approximately 96% which is known as the azeotropic point for water-ethanol distillation. See figure 6.

Once at a 96.4% ethanol/water concentration the vapor from the boiling mixture is also 96.4%. Further distillation is therefore ineffective. This process uses about 2.7 MJ/l of ethanol.[5][13][18]

On the average 1 ton of sugar cane produces about 90 liters of hydrous ethanol (AEHC) and 85 liters of anhydrous ethanol (AEAC). [5]

Every ton of sugar-cane has about 280 Kg of bagasse with 50% moisture and 280 Kg of leaves. They have on the average a 7.5 MJ/Kg Lower Heat Value. [8][9][10]

In order to produce anhydrous ethanol, to be used as a gasoline additive more complex processes are used.

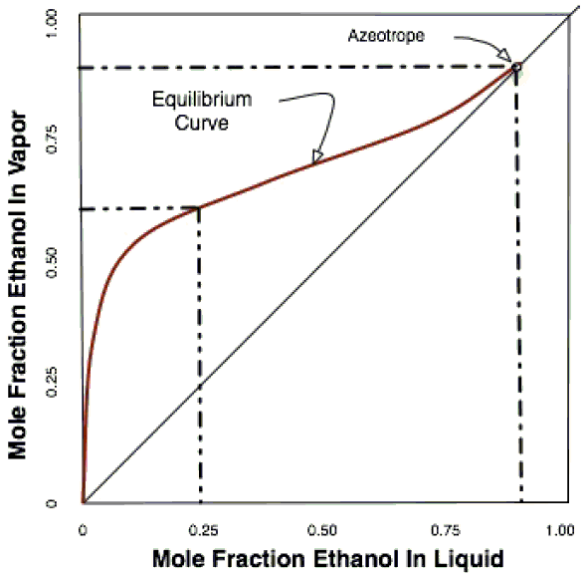

Figure 6. Distillation of ethanol-water mixture.

The most common processes are: a) azeotropic distillation using ciclo-hexane; b) extractive distillation using Mono-ethilene Glicol (MeG) and c) molecular Sieves.

The dehydration using ciclo-hexane is used by about 85% of the ethanol plants and uses about 3.1 MJ/l of anhydrous ethanol. .[5][13][18]

The extractive distillation using Mono-ethilene Glicol (MeG) is used by about 10% of the ethanol plants and uses about 1.4 MJ/l of anhydrous ethanol. [5]

The dehydration using molecular sieves uses a zeolite that is pervious to the water molecules but not for the ethanol molecules. It is used by about 5% of ethanol pants and uses about 1.6 MJ/l of energy. [18]

Considering the weighted average of these three methods the energy consumption to produce AEAC from AEHC is 2.9 MJ/l which compares with the energy needed to produce AEHC.

The saved energy could be used to produce excess electricity which is sold by about R$140,00 per MWh. Or the saved bagasse could be sold by R$13,00/ton.

2. GREEN HOUSE GASES EMISSIONS (GHG)

Regarding Green House Gases emissions for the production of ethanol [5] shows that the production of anhydrous ethanol (AEAC) produces about 436 KgCO2eq/m-3 of ethanol and processed and hydrous ethanol (AEHC) produces 417 KgCO2eq/m-3.

In order to grow one ton of sugar cane it takes from the atmosphere about 1556 KgCO2eq/m-3.
The current yearly production of AEAC to be used for the production of gasoline C is 4.5 billion liters.

Using AEHC the additional avoided GHG emissions could be 85.5 billion KgCO2eq. per year.

3. LABORATORY TESTS

Gasoline C was formulated using hydrated ethanol (AEHC) and the phase separation temperature was measured using a low temperature bath.

E22 was produced by the mixture of 770.9 ml of gasoline A (E0) with 229.1 ml of AEHC. The ethanol as put in becker and the gasoline was poured into it up to the total volume of 1000 ml at 20 degrees Celsius. This fuel was called EH22. As the current ethanol percentage in fuel is 25% EH25 was produced with 260.3 ml of AEHC and 739.7 ml of gasoline A. This mixture was called EH25.

As there are some formulations that use some heavier alcohols to reduce the temperature where phase separation occurs [14][18] it was also produced a EHi22 that is made of 770.9 ml of gasoline A (E0) , 224.1 ml of AEHC and 5 ml of iso-propanol.

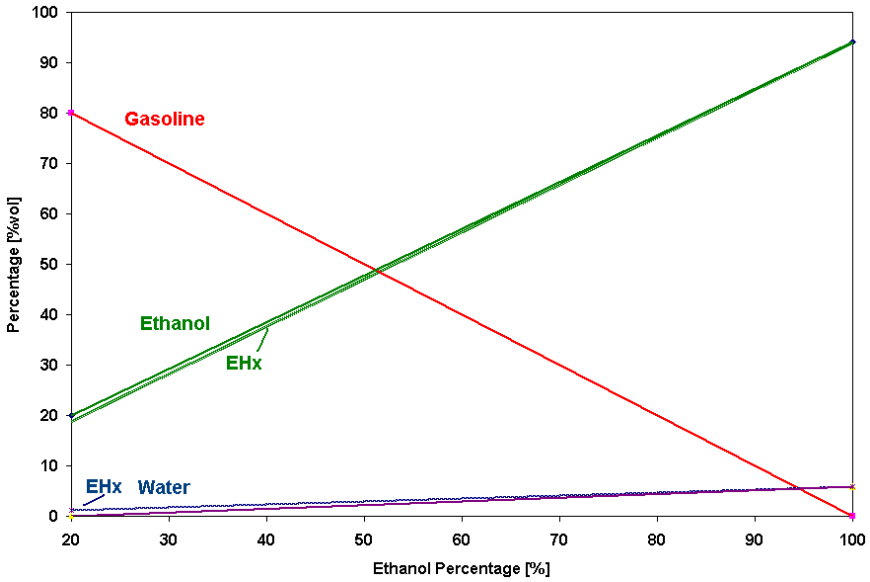

Figure 7: Gasoline, ethanol and water percentages for Exx and EHxx fuels.

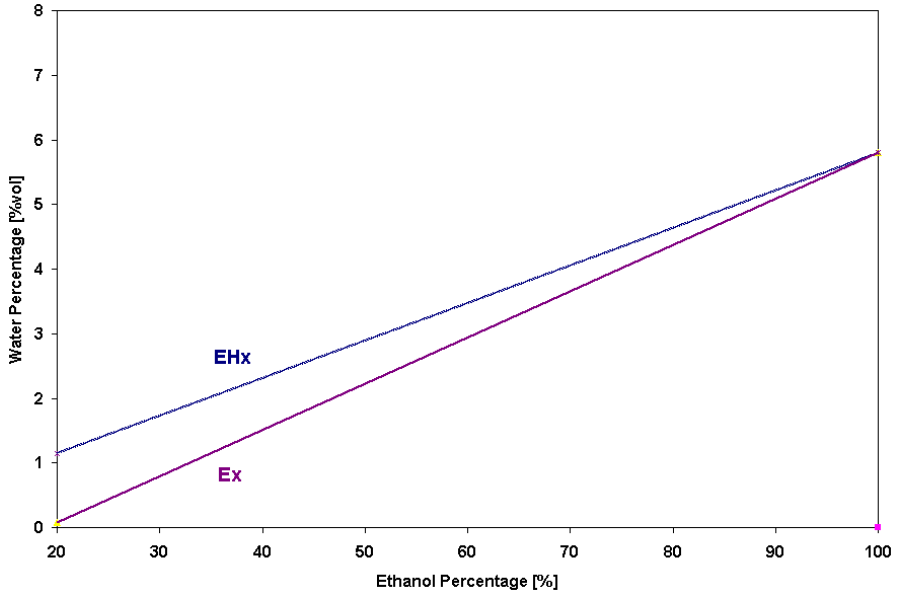

Figure 8: detail of figure 7 above showing water concentrations for Exx and EHxx fuels.

The volume percentage variation of pure ethanol, gasoline and water for a blend between gasoline C (E20 or EH20) and Ethanol (E100) are shown in figure 7. The Figure 8 is the same as figure 7 showing the detail of water percentage. One can see that for the gasoline made using anhydrous ethanol (AEAC) the water content is very low. Also from this figure, one can see that the Gasoline C made with hydrated ethanol (AEHC) has a water content slightly above 1%.

For the sake of reducing the phase separation temperature other alcohols can be isobutanol or tert-butanol (TBA). The phase separation temperature was measured in laboratory per ASTM D 6422 – 99 standards. The results are shown in table 1 below. As can be seen the EH25 mixture has a phase separation temperature of -7 degrees Celsius which is lower than the -5 degrees that sometimes happen in Brazil.

Nowadays there is no denaturant, a substance that is added to make the ethanol fuel tastes bad for human consumption, is added to the ethanol, there are some studies to use TBA or isopropanol as denaturant [ANP].

Phase Separation Temperature [degC]

EH22	-3
EH25	-7
EHi22	-10
E22	< -30

EHi22 has 0.5% volume of iso-propanol

Table 1: Phase separation temperature of some EHxx mixtures.

The addition of 1% TBA or isobutanol makes an EH15 mixture have a phase separation temperature lower than -20 degrees Celsius [18].

4. FUTURE WORK

In the near future it would be interesting to measure and compare the pollutant emissions using E22 and EH22 in order to assess the potential NOx reduction due to increased water content.

Further research of ethanol production energy balance and GHG emissions could lead to better understanding of advantages of using AEHC for the production of Gasoline.

CONCLUSION

The paper showed the feasibility of producing gasoline C using hydrous ethanol for the particular climate in Brazil.

The addition of 0.5-1% of isopropanol, isobutanol or TBA could push the phase separation temperature for EH25 from -7 degrees Celsius to -10 or -20 degrees Celsius.

The avoided energy used for dehydration of hydrous ethanol for the production of anhydrous ethanol could be used to produce electrical energy.

All this point to a cheaper gasoline C and Green House Gases emissions advantages.

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