

ASSESSMENT OF MOISTURE ABSORPTION BY ANHYDROUS ETHANOL UNDER DIFFERENT ENVIRONMENTAL CONDITIONS

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Abstract:

The main use of bioethanol in the world is as a fuel by adding it to gasoline. The addition of ethanol has many purposes, such as increasing gasoline octane number, reducing carbon dioxide emissions by fossil fuels, energy security and environmental sustainability. The suitable bioethanol for mixing in gasoline is the anhydrous one, which must contain up to a maximum of 1% (w/w) of water, according to ASTM D5798-21 [1]. Although it is well known that ethanol is a hygroscopic substance, a complete study addressing the rates of moisture absorption by the ethanol and its evaporation, or showing the influence of the environmental conditions on these factors cannot be found in literature. The assessment of these behaviours is fundamentally relevant for all the ethanol production and distribution chain in order to estimate how long an ethanol batch can be handled keeping the water content, or even to avoid significant loss of ethanol by evaporation, resulting in environmental problems and financial losses. In order to evaluate the ethanol behaviour under different environmental conditions, in this work, as a preliminary study, several environments with different relative humidities and temperatures were simulated in a climatic chamber, and their impact on the moisture absorption rate and/or on the ethanol evaporation were analysed in some anhydrous ethanol samples. It was also evaluated if moisture absorption or ethanol evaporation is the preferential process.

Keywords: ethanol; moisture; absorption; environmental conditions

1 INTRODUCTION

The use of bioethanol as automotive fuel has been considered as a renewable alternative biofuel in the last few years due to many reasons, especially those related to environmental sustainability, energy security, crude oil price volatility and limited availability of the non-renewable fossil fuel.

Brazil started using pure bioethanol as a fuel in internal combustion engines around 1925, and in 1931 the government determined a compulsory blend of at least 5% anhydrous ethanol in gasoline [2]. In 1975, the Brazilian automobile companies, through a government program called “Pro-álcool”, started producing engines running with pure ethanol (hydrated ethanol, containing around 5% w/w of water). Nowadays, Brazil has automobiles, called as flex vehicles, running with ethanol/gasoline blend in any ratio. In 2021, the flex vehicles represented 72.7% of the circulating automotive fleet in the country [3]. Also, Brazil is the second largest ethanol producer in the world, only behind USA. In 2021, U.S. and Brazilian production corresponded to, respectively, 55% and 27% of world production, which amounted 22.5 billion gallons [4].

The main use of bioethanol in the world is as a fuel by adding it to gasoline. The addition of ethanol has the main purpose of increasing gasoline octane number, instead of adding the toxic tetraethyl lead, which is prohibited in most countries. The suitable bioethanol for mixing in gasoline is the anhydrous one, which must contain up to a maximum of 1% (w/w) of water, according to ASTM D5798-21 [1]. In Brazil, the water specification regulated by the National Petroleum Agency (ANP) is limited to 0.4% (w/w), and in the European Union (EU) it is limited to 0.3% (w/w), as defined by the European Committee of Standardization (CEN). Standards from Brazil and USA demand that gasoline must contain up to 27% and 10% or 15% of ethanol, respectively.

It is well known that ethanol is a hygroscopic substance. However, a complete study addressing the rates of moisture absorption by the ethanol and its evaporation, or showing the influence of the environmental conditions on these factors cannot be found in literature. The assessment of these behaviours is fundamentally relevant for all the ethanol production and distribution chain in order to estimate how long an ethanol batch can be handled keeping adequate water content, or even to avoid

significant loss of ethanol by evaporation, resulting in environmental problems and financial losses. This knowledge has special interest not only to the fuel industry, but also to the pharmaceutical and cosmetic ones, for example.

Anhydrous ethanol plants are prevented from moisture raise both by storing the final product in well-sealed containers and by producing it with lower water content than specified by standards, even if it causes some increase in production costs [5]. On the other hand, in all the logistic process involved in anhydrous ethanol transportation before mixing it to gasoline, especially when transferring the ethanol from a container to another, care should be taken in order to avoid moisture raise due to the environment exposure, mainly during a wet day. Studies suggest that gasohol (ethanol blended with gasoline) is a viable fuel for automotive and power equipment, avoiding phase separation and corrosion problems, when the added ethanol contains less than 0.5% of water [6].

In order to evaluate the ethanol behaviour under different environmental conditions, environments with different relative humidities and temperatures were simulated in a climatic chamber, and their impact on the moisture absorption rate and/or on the ethanol evaporation were analysed in some anhydrous ethanol samples. It was also evaluated if moisture absorption or ethanol evaporation is the preferential process. The climatic conditions were precisely controlled and kept constant along a 32 h period test.

2 METHODOLOGY

For the evaluation of evaporation and moisture absorption by the anhydrous bioethanol fuel, it was used a 50 L sample, with $0.477 \pm 0.004\%$ of water, provided by a distillery. The sampling method and the determinations were performed as described in the following topics.

2.1. Sample Preparation

35.00 \pm 0.05 g of anhydrous bioethanol fuel were inserted in a previously weighed 50 mL glass flasks with screw cap sealing. The surface area of the bioethanol fuel in the flask, sample portion which is in direct contact with the environment for vapour exchanges, was $1.52 \times 10^{-3} \text{ m}^2$.

2.2. Sampling

Flasks containing the bioethanol samples were placed in a climatic chamber (Weiss Technik, WK3-340/40) and kept closed during about 15 h waiting for the complete relative humidity and temperature stabilization of the simulated environment. After the stabilization, the flasks were opened and kept static for periods between 5 min and 32 h, and then resealed. Twelve pre-defined time intervals were analysed for two samples, which resulted in 24

flasks placed in the chamber. The climatic conditions simulated by the chamber were maintained constant during the whole period, with fluctuations of less than $\pm 0.25 \text{ }^\circ\text{C}$ and $\pm 1.8 \text{ \%rh}$.

2.3. Climatic Simulation

16 climatic conditions were simulated in the chamber by means of the combination of 04 different temperatures (10 $^\circ\text{C}$, 20 $^\circ\text{C}$, 30 $^\circ\text{C}$ and 40 $^\circ\text{C}$) and 04 different relative humidities (30 \%rh , 50 \%rh , 70 \%rh and 90 \%rh). Inside the chamber, an airstream, which was temperature and humidity conditioned, flowed continuously through the test space by means of its large axial fan located at the rear panel. Both temperature and relative humidity were set and controlled by the software of the equipment. Before starting the tests, the inner space of the chamber was evaluated by means of nine thermometers in order to quantify its temperature stability and uniformity in the range from 10 $^\circ\text{C}$ to 40 $^\circ\text{C}$. The obtained values were used as uncertainty sources of the temperature and relative humidity measurements. The expanded uncertainties of the 16 climatic conditions were 3.5 \%rh and 0.6 $^\circ\text{C}$, with a confidence level of approximately 95%. It is important to point out that the evaporated substances from the samples are not accumulated in the inner of the chamber, since the air is constantly renewed. So, the effect of internal air saturation by ethanol vapor is discarded. All the simulations were performed at atmospheric pressure (101.3 kPa).

2.4. Temperature and Humidity Determination

The standard temperature within the climatic chamber was measured by a platinum resistance thermometer (PRT) of 100 Ω traceable to national standards. The PRT was connected to a digital indicator which was read by a home-made software. In order to keep the confidence of its readings, the resistance of the PRT was constantly checked and adjusted at the ice point. The standard relative humidity within the chamber was calculated for each test by means of the mean values of temperature and dew point temperature of the environmental conditions. The dew point temperatures were measured using a chilled-mirror hygrometer, which is considered as one of the most accurate and reliable methods of measuring dew/frost point temperatures [7]. For all the tests, the temperature and dew point temperature measurements were electronically obtained by means of software at short time intervals and, for the data processing, measurements at 30 s intervals were used. Figure 1 shows the dew-point hygrometer and the climatic chamber used in the experiments.



Figure 1: Dew-point hygrometer and the climatic chamber used in the experiments.

2.5. Moisture Determination

The moisture content of the bioethanol samples removed from the climatic chamber were measured by means of an accurate Karl Fischer coulometric titrator (Metrohm, Titrino 831). The apparatus uses a double platinum electrode, and the electrical current is generated by an electrode without diaphragm. A few drops of Hidranal Coulomat AG analytical solution (approximately 10 drops), which exact mass was weighted in a balance (Mettler Toledo, XS205), were directly injected in the titration vessel with a syringe. The sample analysis from each flask was performed in triplicate. The results are shown as percentage of water in bioethanol sample, given in mass basis (% w/w), and the uncertainties are expressed as Relative Standard Deviation (RSD) from 06 replicates (%).

2.6. Determination of Mass Loss/Gain

This study was conducted by checking the sample weight before and after the period in which it was kept in the chamber. Thus, it was possible to analyse if there was preferably ethanol evaporation or moisture absorption, and to quantify this effect. The flasks had their weights measured once. The results are shown as percentage of weight loss/gain (% w/w), and the uncertainties are expressed as Relative Deviation from the Mean (RDM) from 02 duplicates (%).

2.7. Influence of the Superficial Area on the Moisture Absorption and Ethanol Evaporation

This effect was evaluated by adding the same amount of bioethanol described before (35.00 ± 0.05 g, equivalent to 4.45×10^{-5} m³) into previously weighed glass flasks with different internal areas. The surface areas of bioethanol in these flasks were 0.49, 1.52, 3.32, 4.66 and 6.94×10^{-3} m². The experiment was performed at 20 °C and 50 %rh for a fixed period of 24 h, as described in “Sampling” item.

3 RESULTS AND DISCUSSION

Regarding the analysis of the climatic conditions influence on the samples mass gain/loss, despite of the two competing effects that act inside the chamber, only mass loss was observed in all experiments, which means that evaporation occurs preferably than moisture absorption. Samples mass losses were observed in the first 5 min of sample exposure, especially under higher temperature conditions. At 30 °C and 40 °C, 5 min were enough to cause around 1% of mass loss; while at 10 °C, the same mass loss was reached only after 2 h of exposure.

Tan et al. [8] estimated that pure ethanol would have 40% of its volume as water after 24 h of air exposure, under uncontrolled and unspecified environmental conditions. A semi-quantitative study performed by that group showed a linear moisture absorption rate, at least up to 60 min of observation. However, according to Flores and Conde [9], moisture absorption should not take place up to 2 h of exposure under 25 °C and 40 %rh. These results obtained by Tan and al. and Flores and Conde were not confirmed in our experiments, as shown in the results and discussions below.

As shown in Figure 2, the bioethanol evaporation profile along the 32 h of exposure under any climatic condition presented a slight and positive 2nd order function correlation between the exposed time and mass loss, which means a constant increasing of the evaporation rate. After 32 h of exposure, samples mass loss was greater than 6%, reaching 23% when exposed to 40 °C at 30 %rh.

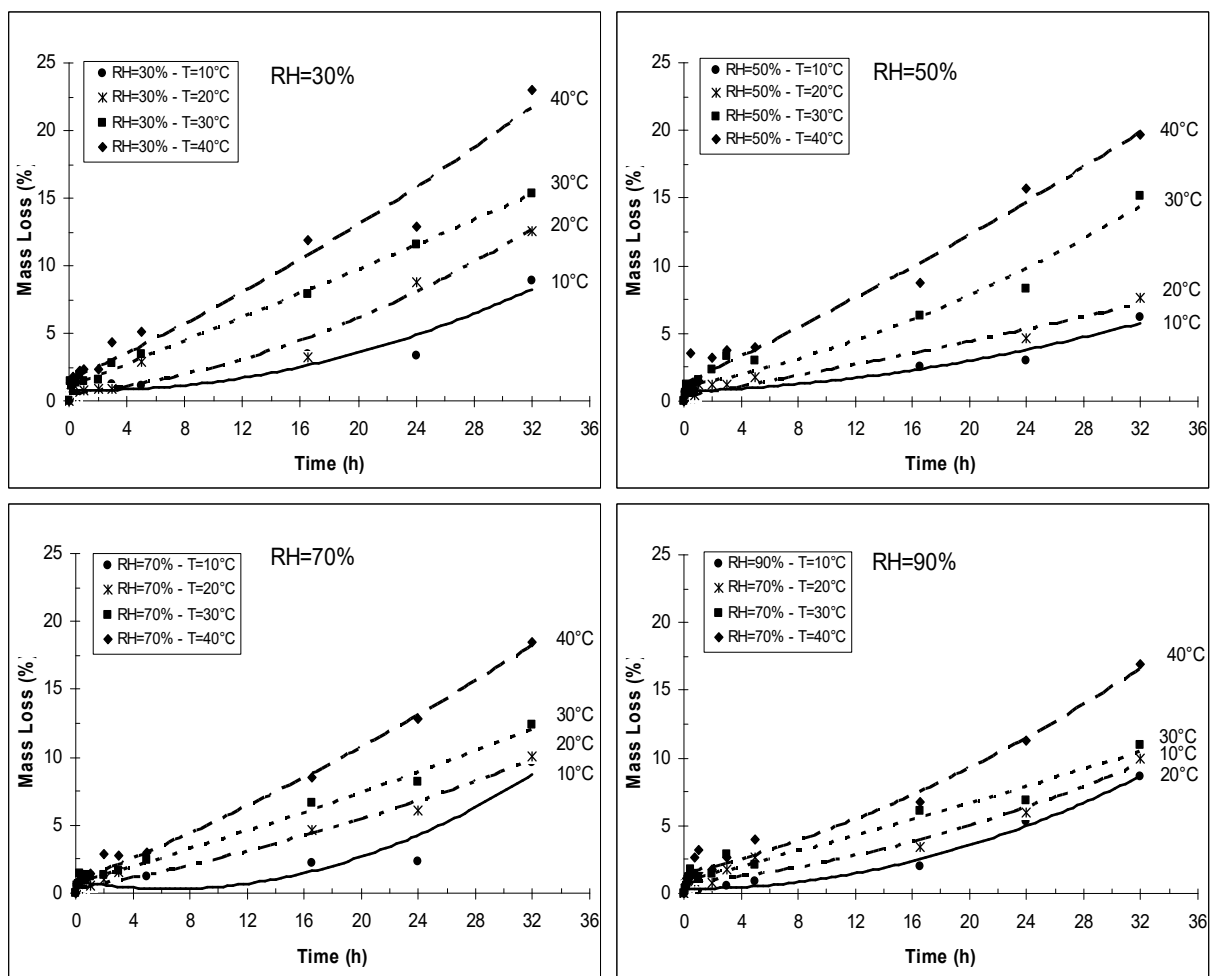


Figure 2: Profile of bioethanol evaporation along 32 h of exposure under different conditions of temperature and relative humidities. The average RDM observed for all the tested conditions was 7%.

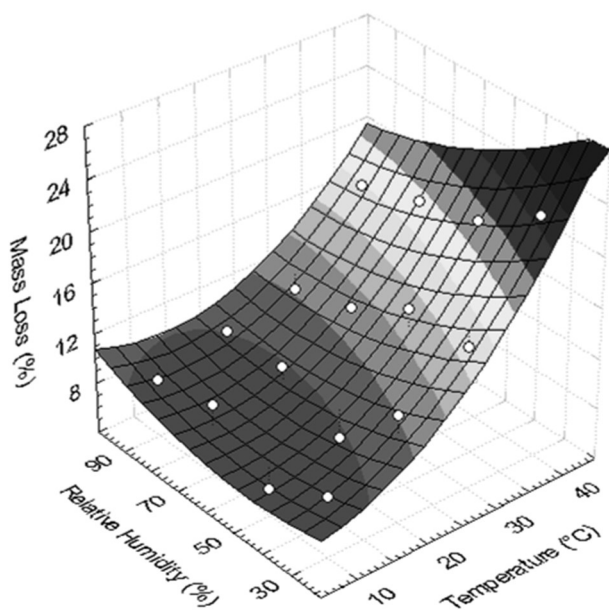


Figure 3: Surface plot demonstrating the effect of relative humidity and temperature on bioethanol evaporation. Mass losses presented herein refer to those obtained at 32 h of exposure. White dots represent the mass loss values determined experimentally.

Both temperature and relative humidity influenced on bioethanol evaporation, although temperature presented a more pronounced effect. For a better demonstration of the simultaneous effect of relative humidity and temperature on the evaporation, a 3D smooth surface plot was prepared, as shown in Figure 3. The mass loss values used to build this figure are those obtained at 32 h of experiment, since these values presented the highest differences. The surface plot is described by a mathematical model, which was analysed by ANOVA (analyses of variance) in order to statistically quantify the influence of temperature and relative humidity on the mass loss. The surface plot, which model explains 94.89% of the variability in mass loss, clearly shows that higher temperatures caused the greatest bioethanol evaporation, especially when associated to lower relative humidities. At lower temperatures, the relative humidity presented much less influence on the evaporation rate. The influence of temperature and relative humidity on the mass loss were estimated with a confidence level of 95%. Statistically, temperature (T) is the quantity that has more influence, providing variation due to the experimental treatment (F-ratio) equals to 154.80.

This value is at least 5 times greater than the variation provided by the relative humidity (RH) and other quantity combinations (RH = 10.30; $T \times T = 10.75$; $T \times RH = 8.20$; $RH \times RH = 1.67$, which is not significant at 95% of confidence level).

3.1. Moisture Absorption

The hygroscopic characteristic of ethanol was observed since the first 5 min of experiment, when independently from the simulated climatic condition, the water content increased from $0.477 \pm 0.004\%$ to at least 0.55%. Even though, under most of the simulated climatic conditions, the tested bioethanol batch could be exposed up to 2 h without exceeding 1% of water content. This water content is the upper limit defined by the ASTM D5798-21 standard, which allows a bioethanol batch to be considered as

“anhydrous” and permitted for mixing in gasoline. The highest moisture absorption rate was observed at 40 °C and 90 %rh. At this condition, the tested bioethanol batch could be exposed only up to 30 min in order to be in accordance with ASTM D5798-21. On the other hand, at 10 °C and 30 %rh or 50 %rh, the bioethanol water content reached only $0.72 \pm 0.04\%$ and $0.86 \pm 0.02\%$, respectively, after 24 h of experiment. Figure 4 clearly shows that both temperature and especially relative humidity positively influenced the water content increasing of the bioethanol, but in order to get an improved demonstration of their simultaneous effect, a 3D smooth surface plot was designed and is shown in Figure 5.

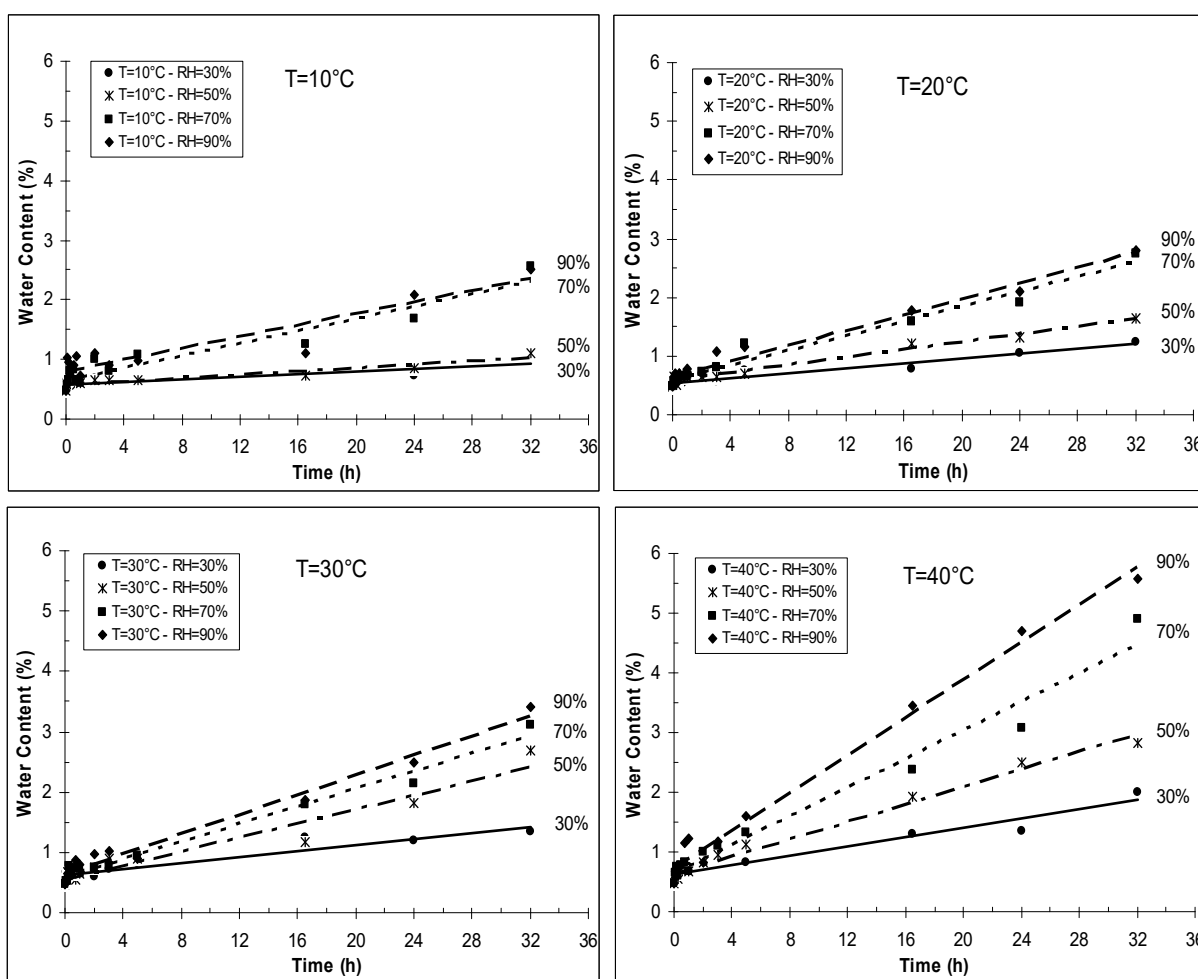


Figure 4: Profile of moisture absorption by bioethanol along 32 h of exposure under different conditions of temperature and relative humidity. The average RSD observed for all the tested conditions was 11%

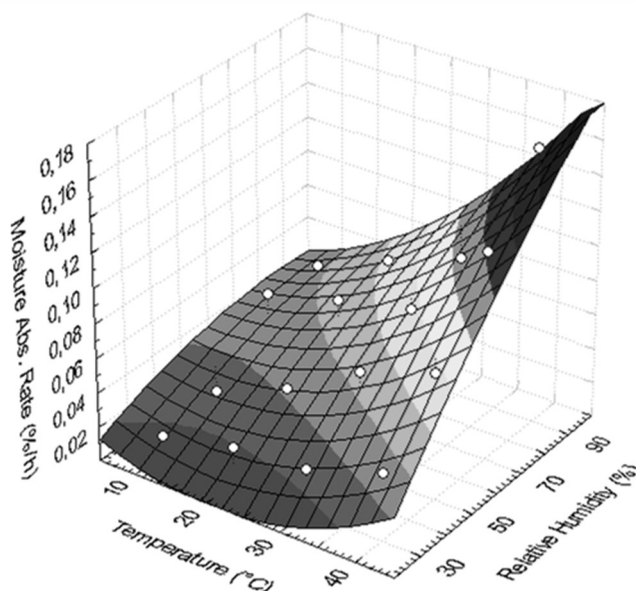


Figure 5: Surface plot demonstrating the effect of temperature and relative humidity on the moisture absorption rate by bioethanol. Mass losses presented herein refer to those obtained at 32 h of exposure. White dots represent the mass loss values determined experimentally.

4 SUMMARY

The results obtained in this work clearly shows that in an environment up to 30 °C, independently of the relative humidity, the bioethanol can be exposed during at least 2 hours and still meet the specification of ASTM D5798-21 regarding the water content (maximum limit defined as 1%). At 40 °C and above, the bioethanol keeps the ASTM specification only up to 30 min.

Regarding the ethanol evaporation (sample mass loss), the experiments show that only 10 min of exposure to any environmental conditions of relative humidity and temperature are enough to cause a mass loss of at least 1%.

It was also observed from the experimental results that there are two competing effects in the bioethanol fuel samples: mass loss by ethanol evaporation and moisture absorption, especially for higher relative humidities. However, the experiments showed that mass loss by ethanol evaporation occurs preferably than moisture absorption. These two phenomena need more detailed investigation, especially at elevated temperatures and relative humidities, since this is a preliminary study.

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