Physical-Chemical Properties Analyses of Methanol-Ethanol Blends for Flex-Fueled Engines Applications

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ABSTRACT

Ethanol is predominantly utilized in the Brazilian flex-fueled fleet as hydrated ethyl alcohol fuel (HEAF). However, suspect fuel, which often involves the addition of anhydrous ethanol, methanol, or water to hydrated ethanol, poses significant concerns. The molecular structure differences between methanol and ethanol result in distinct variations in combustion behavior, specifically, methanol exhibits a higher heat of vaporization and lower energy content per volume compared to ethanol. These differences lead to considerably altered combustion events characterized by increased temperature and pressure, creating a highly corrosive environment due to both the elevated conditions and the chemical properties of methanol. Such changes underscore the risks associated with suspect fuel, which can adversely affect vehicle performance, fuel economy, and engine durability. This research aims to conduct a comprehensive analysis of the physical-chemical properties of ethanol and methanol, proposing a method to create a blended fuel that achieves a reasonable balance to mimic the behavior of pure hydrated ethanol, thereby minimizing detection through standard fuel field tests.

Keywords: Combustion, Methanol, Suspect Ethanol, Flex-Fuel, Fuel Properties

INTRODUCTION

Ethanol has emerged as a cornerstone of Brazil's flex-fueled vehicle market, serving as a sustainable alternative to traditional fossil fuels [1,3]. The Brazilian government has actively promoted the use of hydrated ethyl alcohol fuel (HEAF) as part of its commitment to reduce greenhouse gas (GHG) emissions and fostering energy independence. With a significant portion of the national fleet capable of running on ethanol, it has become integral to the country's transportation sector. However, the increasing reliance on ethanol has also brought to light the challenges associated with fuel quality and integrity.

One of the most pressing issues facing the Brazilian fuel market is suspect fuel. This practice, which often involves the illicit addition of anhydrous ethanol, methanol, or water to hydrated ethanol [8], poses significant risks to both consumers and the automotive industry. Suspect fuel can lead to compromised fuel quality, resulting in adverse effects on vehicle performance, fuel economy, and engine durability. As such, understanding the implications of suspect fuel is critical for ensuring the reliability and efficiency of Brazil's flex-fueled fleet.

The chemical properties of ethanol and methanol play a pivotal role in their combustion behavior [3]. Ethanol (C_2H_5OH) and methanol (CH_3OH) differ not only in their molecular structures, but also in their physical and chemical characteristics [5]. Methanol, for instance, exhibits a higher heat of vaporization and lower energy content per volume compared to ethanol. These differences can lead to significantly altered combustion events, characterized by increased temperature and pressure. Such conditions create a highly corrosive environment within the engine, exacerbating wear and tear and potentially leading to catastrophic failures.

This research aims to conduct a comprehensive analysis of the physical-chemical properties of ethanol and methanol and the effects of suspect by proposing a method to create a blended fuel that achieves a reasonable balance to mimic the behavior of pure hydrated ethanol. The findings of this research will not only contribute to a better understanding of suspect fuel but also provide valuable insights for regulatory measures aimed at ensuring fuel quality and protecting consumers [8].

METHODS

MATERIALS – The study utilized commercially available HEAF and anhydrous methanol, both sourced from reputable suppliers. The ethanol used was 96.2% purity, while the methanol was of analytical grade. All chemicals were handled in accordance with safety protocols, and appropriate personal protective equipment (PPE) was worn during the experiments.

PREPARATION OF FUEL MIXTURES – To create a series of fuel blends, various proportions of ethanol to methanol were prepared. The following proportions were selected for analysis: 100% ethanol (control), 21% ethanol and 73% methanol, 30% ethanol and 67% methanol and 8.5% ethanol and 88% methanol, the complementary volume was used water. Each mixture was prepared by volumetrically measuring the components using calibrated glassware and then mixing them thoroughly in a clean container. The mixtures were made in a temperature-controlled environment at 20ºC, in order to maintain and control the properties of the mixtures during analysis.

CHARACTERIZATION OF PHYSICAL-CHEMICAL PROPERTIES – In order to understand the behavior of fuel mixtures, four physical-chemical properties of extreme importance for engine operation were analyzed. The pH, electrical conductivity, alcoholic content and specific mass, all of which have a direct impact on engine tuning and calibration [9].

The mentioned characteristics play an important role in the functioning of the engine, and their use outside the established parameters can harm some components and the functionality of the engine.

pH indicates the presence of acids or bases in the fuel, which can cause corrosion in tanks, pipes, and engine components. Acidic fuels can damage the fuel system and reduce the lifespan of the equipment. Additionally, pH is an indicator of fuel quality. Fuels with pH outside the ideal range can affect combustion efficiency and engine performance. Measuring pH can help identify fuel contamination by water or other contaminants. The presence of water, for example, can alter pH and lead to the formation of emulsions, which can impair fuel performance. pH can also affect combustion efficiency and overall engine performance, as fuels with pH outside the ideal range can result in power loss and increased fuel consumption.

For this characteristic, each ethanol-methanol blend mixture was measured with a pH meter Digimed DM22. The pH meter should be calibrated using standard buffer solutions with known pH values, rinse the pH electrode with distilled water in order to avoid cross-contamination between samples, immerse the pH electrode in the solution to be tested and allow it to stabilize for 1 minute. Once stabilized, the pH meter will display the pH value of the solution.

Electrical conductivity can indicate the presence of contaminants, such as water from public supply or impurities, in the fuel. Water, for example, has a much higher conductivity than most fuels, and its presence can be detected through this measurement. Additionally, fuels with high conductivity may be more prone to corrosion of tanks and fuel systems. Measuring conductivity helps identify fuels that may cause damage to equipment. Electrical conductivity can also affect combustion efficiency and engine performance, as fuels with inadequate conductivity can result in combustion problems and loss of efficiency. Finally, fuels with high conductivity can increase the risk of sparks and ignition, posing a safety risk.

It was determined with a conductivity meter Tecnal/model Tec-4MP. Measurements were taken in μS/m to evaluate conductivity characteristics, using the following procedure: before taking measurements, the conductivity meter should be calibrated using standard solutions with known conductivity values, rinse the conductivity cell (electrodes) with distilled water to remove any contaminants and avoid cross-contamination between samples, immerse the conductivity cell in the solution to be tested (make sure that the electrodes are fully submerged and do not touch the bottom of the container), allow the reading to stabilize, which may take a few seconds.

Alcoholic content can affect the quality and performance of the fuel, as fuels with inadequate alcoholic content can cause combustion problems, such as engine failures and increased emissions. Furthermore, the alcohol content can influence the energy efficiency of the fuel, as fuels with very high alcoholic content may have lower calorific value, affecting engine efficiency. The proportion of alcohol in the fuel can also impact engine performance, including power, throttle response and vehicle fuel economy.

This characteristic was measured using an Anton Paar DMA35 densimeter, which is specifically designed for liquid density measurements. The measurement procedure is as follows: first, calibrate the densimeter with standard solutions of known densities. Next, insert the tip of the densimeter into the liquid sample and activate the device to draw the sample into the measuring tube. After insertion, allow a brief period for the reading to stabilize. The density of the liquid will then be displayed on the densimeter scale, and based on this density, the device will calculate and return the alcohol content value.

Specific mass is a critical indicator of fuel quality, once specific mass values outside the expected range may suggest contamination or suspect. Furthermore, specific mass is essential for calculating the energy content of the fuel, because, generally, fuels with a higher specific mass contain more energy per unit volume, which is vital for optimizing engine efficiency. Additionally, specific mass can affect combustion efficiency and overall engine performance, as fuels with inappropriate specific gravity may lead to combustion issues and power loss.

The same Anton Paar DMA35 densimeter was utilized following this procedure: prior to measurement, the densimeter must be calibrated using liquids of known density. Insert the tip of the densimeter into the liquid sample and activate the device to draw the sample into the measuring tube. After insertion, wait a few moments for the reading to stabilize. The density of the liquid will be displayed on the densimeter scale, and the measured value will be provided in kg/m³.

The four characteristics above were chosen because they are widely used by the ANP through rapid analysis kits to check whether fuel has been suspected [7]. In addition, the characteristics mentioned above have a direct impact on the operation of the engine, such as acceleration of the corrosive process, engine performance, emissions control and energy efficiency.

RESULTS

The results obtained from the study on creating a balanced mixture of methanol and hydrated ethanol revealed significant information that could impact the fuel market in Brazil. The research demonstrated that it is feasible to formulate a mixture that not only achieves a balance between the two fuels but also maintains the desirable characteristics of pure HEAF [4].

Mixture 1 – The initial solution was prepared using 100 ml of hydrated ethanol. The first component added was water, totaling 25 ml, which was introduced in increments of 5 ml, repeated five times. For the methanol, the addition was staggered: it began with five increments of 5 ml each, followed by two increments of 10 ml, then 15 ml, and subsequently seven increments of 20 ml. This was followed by a single addition of 40 ml, and finally, five more increments of 20 ml, resulting in a total of 340 ml of methanol added. With each addition, the four properties of interest were monitored. It was observed that each component contributed differently to the behavior of the mixture. The final mixture exhibited a 365% increase to achieve the physical-chemical properties specified by ANP [2].

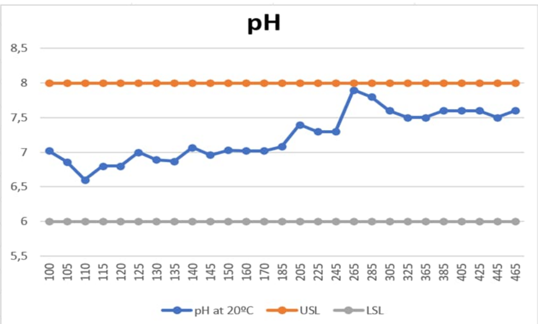

Figure 1 – pH – Mixture 1

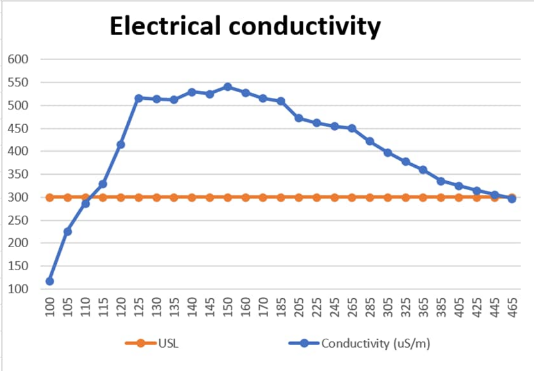

Figure 2 – Electrical conductivity – Mixture 1

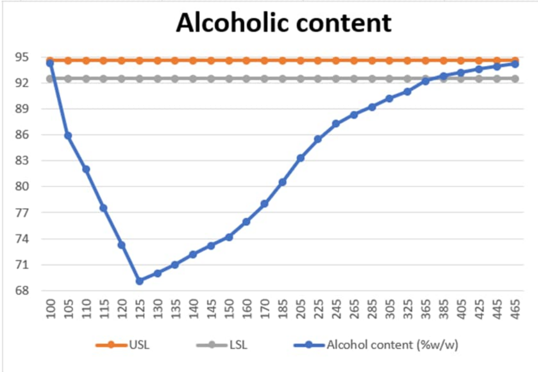

Figure 3 – Alcoholic content – Mixture 1

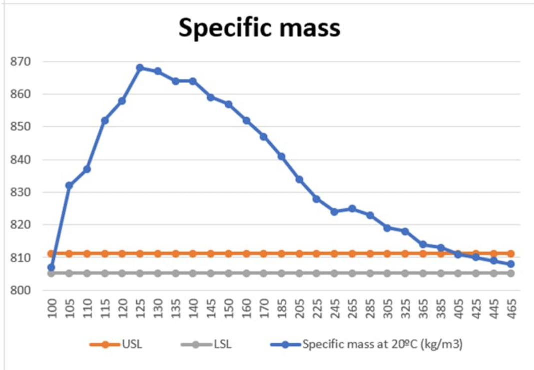

Figure 4 – Specific mass – Mixture 1

Mixture 2 – The initial solution was prepared using 100 ml of hydrated ethanol. The first component added was water, totaling 10 ml, which was introduced in increments of 5 ml, repeated twice. For the methanol, the addition was staggered: it began with two increments of 5 ml each, followed by two increments of 10 ml, then three increments of 20 ml. This was followed by two additional increments of 10 ml each, and finally, five increments of 20 ml each, culminating in a final addition of 10 ml, resulting in a total of 220 ml of methanol added. With each addition, the four properties of interest were monitored. It was observed that each component influenced the behavior of the mixture differently. Also aiming to achieve the physical-chemical properties specified by ANP [2], the final mixture exhibited a 230% increase in volume.

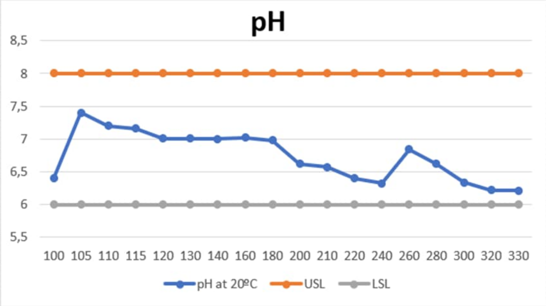

Figure 5 – pH variation – Mixture 2

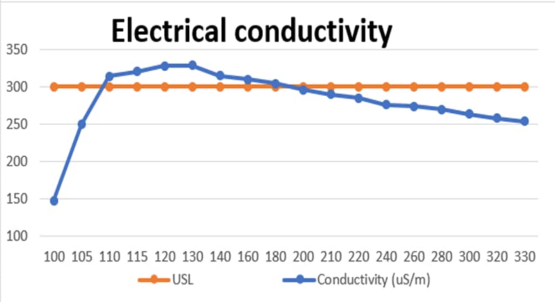

Figure 6 – Electrical conductivity – Mixture 2

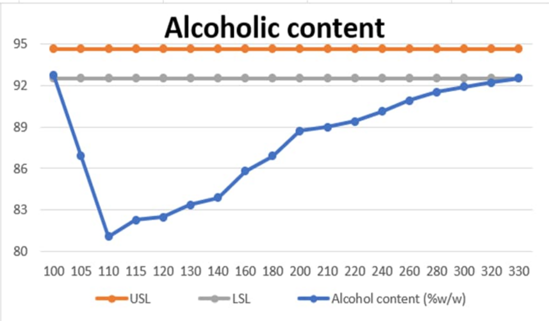

Figure 7 – Alcoholic content – Mixture 2

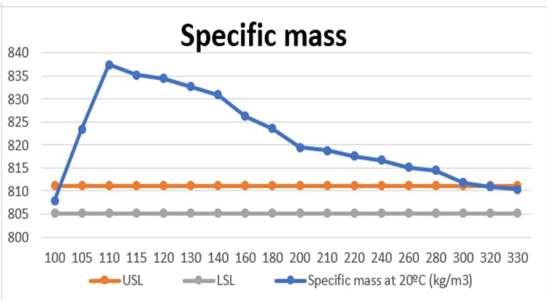

Figure 8 – Specific mass – Mixture 2

Mixture 3 – The initial solution was prepared using 100 ml of hydrated ethanol. The first component added was water, totaling 40 ml, which was introduced in increments of 10 ml, repeated four times. For the methanol, the addition was staggered: it began with four increments of 10 ml each, followed by six increments of 40 ml each, then three increments of 80 ml, and finally, thirteen increments of 40 ml, resulting in a total of 1,040 ml of methanol added. With each addition, the four properties of interest were monitored. It was observed that each component contributed differently to the behavior of the mixture. The final mixture exhibited an increase of 1,080% to achieve the physical-chemical properties specified by ANP [2].

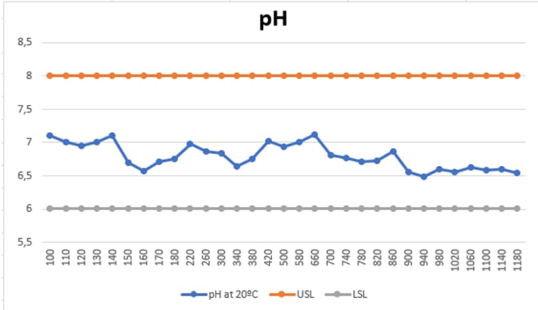

Figure 9 – pH variation – Mixture 3

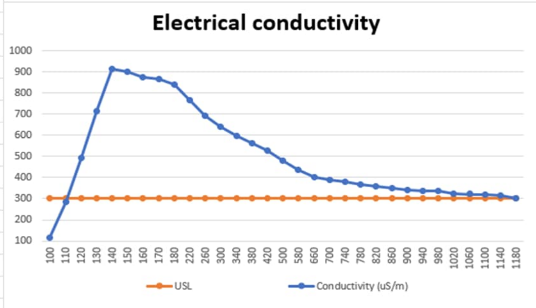

Figure 10 – Electrical conductivity – Mixture 3

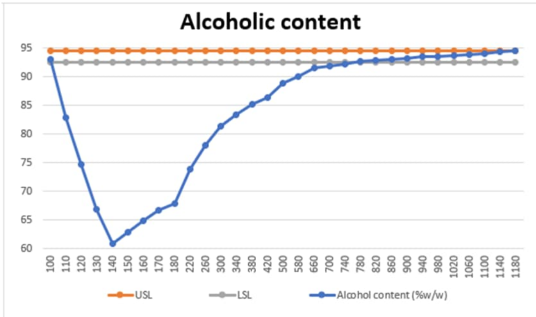

Figure 11 – Alcoholic content – Mixture 3

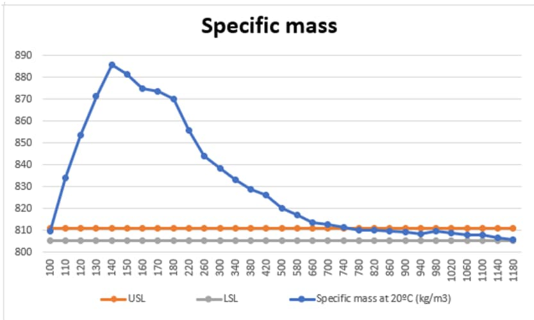

Figure 12 – Specific mass – Mixture 3

DISCUSSION

The study aimed to investigate the potential for creating a balanced mixture of methanol and HEAF that closely resembles the physical-chemical characteristics of pure HEAF. Given the increasing concerns surrounding suspect fuel and its implications for vehicle performance, fuel economy, and engine durability, this research is particularly relevant in the context of Brazil's flex-fueled vehicle market.

Through a systematic approach, three blends of methanol and HEAF were prepared analyzing their physical-chemical properties, including pH, electrical conductivity, alcoholic content and specific mass. The results demonstrated that it is indeed feasible to formulate a mixture that achieves a balance between the two fuels while maintaining the desirable characteristics of HEAF [3, 6].

One of the key findings of this research was the significant impact of the methanol-to-ethanol ratio on the physical-chemical properties of the fuel mixtures. As the proportion of methanol increased, notable changes were observed, which are critical factors influencing fuel flow and atomization in combustion engines. The study identified specific ratios, especially those around 73%, 67% and 88% methanol, that yielded mixtures with properties closely aligned with those of pure HEAF.

The implications of these findings extend beyond the laboratory by developing a method to create a blended HEAF/methanol fuel that mimics the behavior of pure regular HEAF which deceives all engine diagnosis systems and in-field fuel probing/testing from regulatory agencies. The findings underscore the potential for such blends to serve as potential alternatives in the face of suspect fuel challenges [1, 3].

Future works should focus on the long-term effects of using these blended fuels in various engine types and under different operating conditions, mainly the combustion behavior and increased corrosion investigating the complexities of fuel composition and its impact on engine performance, in-vehicle fuel economy and durability.

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Diego Cruz has a degree in Production Engineering from Centro Universitario Fundação Santo André and a MBA in Industrial Management from Fundação Getúlio Vargas. He has more than 15 years' experience in failure analysis and industrial processes (forming, machining and heat treatment) working in national and multinational companies in the auto parts and automotive segments. Currently as Materials Engineer at General Motors, he worked in GMSA Fastening Laboratory, analyzing bolted joints and developing tightening processes, and is now responsible for failure analysis on powertrain components.

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