Storage stability of B10 and B15 binary vehicular diesel mixtures and B15 ternary diesel blends containing 5% HVO

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ABSTRACT

The new environmental guidelines require the development of less polluting energy matrices produced from renewable sources. In the case of liquid fuels, biofuels represent a sustainable energy alternative to replace fossil fuels, including in this context biofuels produced from vegetable and animal oils, such as biodiesel (FAME) and renewable diesel, such as hydro treated vegetable oil (HVO), which exhibit properties very similar to mineral diesel, and allow their application in diesel cycle internal combustion engines without adaptations. In this study, the storage stability of the following fuel mixtures was evaluated: i) diesel oil + 10% biodiesel - B10; ii) diesel oil + 15% biodiesel - B15 and iii) diesel oil + 15% biodiesel + 5% HVO - B15HVO5. The evolution of the oxidative stability index (OSI), dissolved water content and specific mass of the binary mixtures B10 and B15 and ternary B15HVO5, mentioned above, which remained stored for 60 days in steel containers, left outdoors, according to INT's own methodology, were evaluated [1]. Regarding oxidative stability, the effect of adding 5% HVO to the B15 mixture was positive, increasing the OSI of the B15 mixture from 27.03h to 31.77h. This initial OSI value remained above the limit value (OSI>20h) recommended by DIN EN 590:2022 for only 45 days of storage. Regarding water content, the three mixtures presented an evolution of results within the ANP specification (<500ppm), as well as regarding specific mass, which remained within the range specified by ANP, throughout the storage period of 60 days.

INTRODUCTION

It is worth noting that Brazil signed the Paris Agreement in 2015, committing to reduce its greenhouse gas emissions by up to 37% by 2025 (compared to levels emitted in 2005), extending this target to 43% by 2030 [2]. One of the recognized viable ways to achieve these targets is the gradual replacement of fossil diesel with biodiesel. Among the advantages and attractions of biodiesel, we highlight that it is practically free of sulphur and aromatic compounds, which make its combustion cleaner and without the formation of SO_2 and biodegradable mainly responsible for acid rain, with emissions with lower CO_2 content, added to the fact that it is a non-toxic and biodegradable fuel. Therefore, when compared to mineral diesel oil, such as diesel A S10, we can consider biodiesel a natural substitute as it causes less impact on the environment. In addition to its economic and strategic advantages, the use of biodiesel for vehicle applications in diesel cycle engines is therefore growing. In the case of vehicle diesel, 14% biodiesel is currently added to diesel A S10. Although the undeniable benefits of biodiesel are strategic, environmental and social, which validate it as a natural substitute for mineral diesel, its instability with regards to its high tendency to oxidation, high hygroscopicity and potential for degradation are issues that require great attention. In addition, the particularity of the Brazilian case - a country of large continental dimensions, which involves complex transportation and handling operations - is of utmost importance. In this case, it is extremely important to know the shelf life of the biodiesel that will be added to diesel A S10. Findings of loss of stability over time in storage, as well as incidences of residue formation problems (sludge) have been reported by the market [3] and make preserving its quality throughout the entire commercialization chain a major challenge, that is, from its production to its addition to mineral diesel and subsequent combustion in the engine.

Green diesel, also known as renewable diesel, is defined as a biofuel composed of paraffinic hydrocarbons produced from alternative routes such as hydro treatment of vegetable oils, fermentation, oligomerization, Fischer-Tropsh/synthesis gas from biomass, hydrothermolysis, etc. from which it is possible to generate paraffinic hydrocarbons as a final product. In 2021, through ANP RESOLUTION No. 842, products of this nature were regulated by ANP for use as vehicle diesel [4]. It is worth noting that paraffinic hydrocarbons are linear chain compounds, are free of aromatics, oxygen and sulphur, and have a high cetane index. This reduces the problems of sludge formation that occur with biodiesel and the other instability problems reported above [5]. In the HVO production process, hydrogen is used to remove oxygen from the triglyceride (vegetable oil) and given its compositional nature as reported above, the harmful effects of ester-type fuels such as biodiesel are not observed, such as oxidation, increased NOx emissions, deposit formation, storage stability problems, faster aging of engine oil or poor cold properties.

In this context, HVO emerges as a promising alternative, as a synthetic liquid biofuel that can be mixed with diesel and is already being used internationally, both pure and in binary and ternary mixtures [6]. Given this promising scenario, in addition to studying conventional Bx mixtures (mineral diesel type A S10 + biodiesel), the present study chose to evaluate the behaviour of a mixture containing HVO.

As highlighted by Wahnfried [7], solutions such as the addition of second-generation biofuels, such as HVO, may prove attractive in reducing stability and sludge formation problems and benefiting the achievement of environmental goals and improving the quality of commercial vehicle diesel.

Studies conducted by de Souza and D'Ávilla [8] revealed that HVO exhibits superior oxidative stability to biodiesel, concluding that the addition of HVO can be beneficial in 10% biodiesel (B10) blends. Therefore, we will evaluate whether the addition of 5% HVO will also be beneficial in a 15% biodiesel (B15) blend and how this evolves over time in storage. First, however, it is important to define what we understand by storage stability in this work. Storage stability can be defined as the ability of the liquid fuel to maintain its physical and chemical properties in the face of its interactions with the environment over different storage periods, properties that need to be preserved until the final moment of combustion in the diesel engine [9].

In general, storage stability studies are conducted either in glass bottles closed, accelerated with temperature, according to standardized methodologies such as the one reported above by Souza and D'Ávilla [8] or involving exposure to the natural environment, such as the one conducted by do Amaral, B. E., de Rezende, D. B., & Pasa, V. M. D. [10] in which they exposed glass bottles in an open environment (roof of the building).

In this work, we will be conducting under conditions not accelerated by temperature, however stored in steel containers exposed to the open air, as is seen in practice in the processes of loss of stability in fuel storage systems at supply bases, monitoring the evolution of the oxidative stability index (OSI), the dissolved water content and the specific mass of the mixtures over time.

METODOLOGY

The present storage stability work was conducted for 60 days from March 2023 until April 2023. Samples of diesel A S10 supplied by Vibra were used to formulate the mixtures. Biodiesel was supplied by GRANOL (95% soy/5% cotton) accompanied by a quality certificate issued in accordance with the requirements of ANP Resolution No. 45 of 2014 in force. HVO was supplied by PREEMAB of Sweden, with a quality certificate issued in accordance with EN 590:2013.

The following formulations were studied:
i) Diesel oil S10 + 10% biodiesel - B10
ii) Diesel oil S10 + 15% biodiesel - B15
iii) Diesel oil S10 + 15% biodiesel + 5% HVO - B15HVO5

Twenty-four one litre capacity AISI 1020 carbon steel containers were assembled on a table outside the laboratory, as seen in Figure 1. Each container was filled with 800 mL of the abovementioned mixtures, using nylon screw caps as illustrated below. Each cap had a 1-inch diameter hole containing stainless steel protective screens with 0.8 mm mesh in order to allow the eventual entry of moisture and not external impurities.

Figure 1 – View of the experimental set up at lab corridor

The mixtures were subjected to analyses of oxidative stability, water content and specific mass every 15 days, at the time of the beginning of the storage tests, hereinafter referred to as T0, as well as after 15, 30, 45 and 60 days of storage, identified as T15, T30, T45 and T60. It is worth mentioning that the local temperature and relative humidity were monitored throughout the planned 60 days of exposure.

In the first case, oxidative stability determinations were carried out in accordance with EN 15571:2014, also known as the modified Rancimat Method, in which 7g of Bx mixture samples are placed in the reaction vessel, under a constant flow of oxygen (10 L.h-1) and a temperature of 110ºC, with the aim of determining the oxidative stability index (OSI), also known as the induction period (IP), which reflects the antioxidant capacity still present in the Bx mixtures. Regarding the determination of water content and specific mass, the test methods EN ISO 12937 and ASTM D4052 were adopted, respectively.

RESULTS

When setting up the experiment - moment T0, the following oxidative stability values were obtained: a) IEO = 32.45h for mixture B10; b) IEO = 27.03h for mixture B15 and c) IEO = 31.77h for the ternary mixture, first observing the beneficial effect of adding 5% HVO, increasing the IEO of mixture B15 from 27.03h to 31.77h. It is worth noting that all the results of the Oxidative Stability Index (OSI) obtained at moment T0 were found to be in agreement with the requirements of the DIN EN 590:2022 which establishes a minimum IEO limit of 20h. Table 1 below illustrates the results of the oxidative stability tests over time, relating to the binary and ternary B10 and B15 mixtures containing 5% HVO stored for a period of 60 days.

Table 1 – Oxidative stability over time

Mixtures	OSI (h) T15 days	OSI (h) T30 days	OSI (h) T45 days	OSI (h) T60 days
B10	29,07	25,67	19,07	12,07
B15	21,43	14,58	11,52	8,32
B15 + 5% HVO	27,66	23,24	19,24	12,55

Analyzing the results presented in Table 1, we can observe the decline of OSI values, commonly observed over the storage time, with a less intense decrease being verified in the B15HVO5 mixture, which remained with an OSI above the DIN EN 590:2022 20 h limit up to 45 days of storage. In other words, the addition of 5% HVO was also beneficial, as it allowed for a longer shelf life. Regarding the B15 mixture without the addition of HVO, we can see that the shelf life was shortened to 15 days.

Regarding water content, the three mixtures presented results in accordance with the limit <500ppm specified by ANP Resolution No. 968, of April 30, 2024, as well as regarding specific mass, which remained practically unchanged in the range of 815.00 to 850.00 kg/m3, throughout the storage period.

Finally, no sludge or residues were observed at the bottom of the steel containers.

CONCLUSIONS

Based on these results, greater storage stability was observed in the B15 mixture containing 5% HVO, whose presence significantly increased the oxidative stability index to a value above the 20-hour limit required by the ANP. Despite the addition of 5% HVO, in order to achieve a shelf life of 60 days, exhibiting an OSI above 20 hours, throughout this storage period, new formulations or higher concentrations of antioxidant additives are necessary. In other words, 5% HVO was not enough to guarantee a stable shelf life for a B15 mixture containing 15% of 100% biodiesel rich in unsaturations, such as the 95% soybean + 5% cotton used in this study.

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