Antioxidants Efficiency for Methyl Soy and Cottom Biodiesel Blend and Diesel S-10/Biodiesel Mixture (B-15) Kept Stored in Steel Canisters for 30 days

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ABSTRAT

The decay of the oxidative stability index (OSI) of samples of fatty acid methyl biodiesel produced from soybean and cotton oils in the proportion of 96% of soy and 4% of cotton oil kept stored in containers of steel over 30 days was monitored as well as the efficiency of three commercial antioxidant products added at a dosage of 500ppm were determined. Diesel S10-biodiesel mixtures in the proportion of 15% (B15) were prepared and the evolution of the modified oxidative stability index (OSI) was also monitored. To start with all samples of biodiesel after the addition of the three antioxidant additives at concentrations of 500 ppm showed an immediate significant increase in OSI for average values above 12h required by the ANP. However, only one antioxidant product was able to maintain the OSI level above 12h for 10 days of storage only (i.e., providing a short-term protection only). Similar trend was observed with reference to B15 mixture studied and just one product was able to maintain the B15 OSI level above 20h for 10 days of storage only. None of the antioxidants were capable to provide neither medium nor long term protection for the fuels studied.

KEYWORDS

Oxidation stability; storage stability; antioxidants performance; biodiesel; B15 diesel-biodiesel blend

INTRODUCTION

Among the advantages and attractions of biodiesel, we highlight the fact that it is practically free of sulfur and aromatic compounds, which make its combustion cleaner and without the formation of SO_2 emissions - the main responsible for acid rain, as well as 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, we can consider biodiesel a natural and attractive substitute for mineral diesel because it causes less impact on the environment. Added to its economic and strategic advantages, there is, therefore, the growing use of biodiesel for vehicular applications in diesel cycle engines, particularly in devoloping countries like Brazil. (OLIVEIRA; COELHO, 2017).

In 2020, 6.4 billion liters of biodiesel were consumed in Brazil, about 10% of mineral diesel consumption, which makes us one of the world leaders in adding biodiesel to diesel. According to the Brazilian Combustibles Agency (ANP), biodiesel can be defined as a renewable fuel obtained from a chemical process called transesterification. Through this process, the triglycerides present in oils and animal fats react with a primary alcohol, methanol or ethanol, generating two products: the ester and the glycerin. Pure biodiesel can be labelled internationally as B100 whilst the nomenclature BX is used to designate the percentage of biodiesel contained in the commercialized diesel blend, where X is the volume percentage of the biodiesel in the blend (KUSS et al., 2015). It should be noted that the Brazilian Energy Policy Council (CNPE) decided on 11/29/2021 to maintain the 10% biodiesel content added to road diesel until the end of 2022, with a forecast to have its content increased annually by 1% up to 15%. According to the Ministry of Mines and

Energy (MME), this measure has with the objective of preserving the interests of society, reconciling measures to contain the price of diesel with the maintenance of the National Biofuels Policy, providing predictability, transparency, legal and regulatory security to the sector. Despite the undeniable strategic, environmental and social benefits of biodiesel, its degradation potential is a matter of great concern.

Given its large continental dimensions and its relative economic strength, Brazil has a considerable fuel distribution and commercialization (resale and retail) network. In 2018, we had 156 distribution companies, 407 transport/dealer/retail companies (TRRs) for direct service to large industrial, urban and rural consumers and 40,662 fuel service stations spread from North to South of the country (SINDICOM, 2019), capable of guarantee the supply of diesel throughout the territory. A matter of great concern, especially in continental countries such as Brazil, which have complex fuel distribution and retail chains and biodiesel production regions concentrated in the South and Midwest, concerns the long distances traveled by biodiesel between producing regions to the primary and secondary distribution bases where it is added to mineral diesel. In addition, Brazil has six terrestrial biomes with a diversity of microclimates that vary significantly, involving: a) the lands of the Pampa Gaucho and the cold highlands in the South; b) the lands of the Pantanal in the extreme west of the Central-West Region; c) the fertile lands of the Cerrado that go from the Center-West to Maranhão; d) the humid and hot tropical regions of the North Region, such as the Amazon; e) the semi-arid and wild regions of the Caatinga in the heart of the Northeast. Finally, we can highlight the subtropical climate that prevails in the Atlantic Forest Biome, involving the states of São Paulo, Minas Gerais, Rio de Janeiro and Espirito Santo and the coastal region, where the most economically active and urban areas of the country and the majority of vehicle diesel consumers are located. It should also be noted that, depending on the time of year and the location of the distribution bases and refineries, biodiesel may remain in transit through long road and river modals, culminating in long storage time in the most remote regions before being added to mineral diesel. While in regions close to refineries and large distribution bases and consumption areas, its storage time may not exceed 10 days, biodiesel can take between 20/30/45 days to be added to mineral diesel, notably in remote areas and/or relatively low handling and consumption and even and 90 days in far remote regions like the Amazon region.

It is well reported in the literature that interactions of atmospheric agents such as oxygen and air temperature, and others, like humidity tend to introduce problems in the quality of stored biodiesel (KNOTHE, 2007). This is particularly notable in countries like Brazil, where limited shelf-life of stored biodiesel have been reported (CAVALCANTI et al, 2018). More recently, premature clogging of filters in heavy-load vehicles and metropolitan buses; increase in the number of early stops due to clogging of filters and injector breakage in vehicles; blockages and pumps breaks at gas stations resellers; accelerated clogging of filters, blocking of pumps, wear and breakage of parts, in addition to sudden stops of machinery, have been reported by the market to ANP in 2020. Among the degradation processes capable of negatively impact the quality of biodiesel, emphasis should be given to the degradation by oxidation, induced by its contact with oxygen in the air, which can be catalyzed by the conjugated action of oxygen, temperature and by contact with metals (CAVALCANTI et al., 2016).

Degradation by oxidation takes as its starting point the triglycerides present in vegetable oils and animal fats. It is a complex process, composed of three stages: initiation, propagation and termination steps (PULLEN; SAEED, 2012). The first one is relatively slow and characterized by the removal of hydrogen from the fatty acid to form a carbon-based free radical. In the second stage, the propagation step occurs, involving the reaction between the radicals formed in the previous stage, with oxygen producing hydroperoxides. Finally, the termination stage begins when the hydroperoxides that accumulated in high concentration begin to combine with each other and with the free radicals generated by the initiation. At this stage, the rate of peroxide degradation exceeds the rate of peroxide formation. The hydroperoxides produced together with other degradation products can be converted into aldehydes, alcohols or short-chain acids or polymerized (PULLEN; SAEED, 2012).

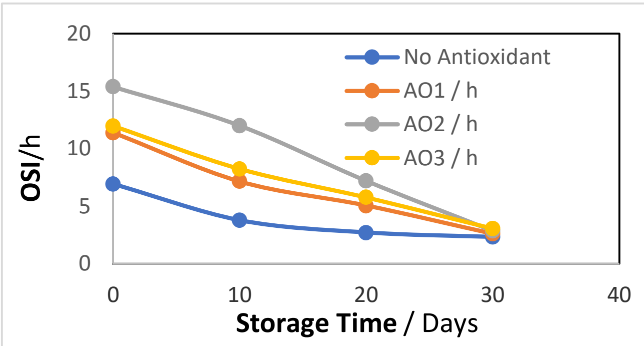
The tendency to oxidation can be ranked in the laboratory through a series of tests, with the Accelerated Oxidative Stability Test or the Rancimat Test being the most widely accepted by the market. It is used as a reference test for the purpose of evaluating the oxidative stability of biodiesel by the analysis methods EN 15751:2014. It is also known as the modified Rancimat method that make it also possible to determine the oxidation stability index (OSI) of diesel-biodiesel blends. In general, storage stability studies are carried out in glass PEAD bottles or PEAD containers. Due to the reported interference of contact with metals, the present studies were carried out in carbon steel containers with access to open air, as seen in practice the processes of loss of stability in fuel storage systems in supply bases and refineries. The need for studies to evaluate the short, medium and long-term storage shelf-life and efficiency of antioxidant products available in the national market are the main driving force of the present work.

METHODOLOGY

In the present work, the analytical method EN 15751:2014 for determination of the Oxidative Stability Index (OSI) was used. In all experiments a measurement uncertainty of ±1.3h was found. Previous INT studies demonstrate significant drops OSI values of biodiesel and diesel-biodiesel blend samples that were kept stored in steel containers subject to the action of atmospheric weathering (i.e., the effects of oxygen in the air, temperature and relative humidity). Carbon steel containers with a capacity of 1 L were used, with 800 mL of each container being filled with the fuels, were left aside for 30 days at the corridor of the INT laboratory and had their temperature and relative humidity locally monitored. After 10, 20 and 30 days, containers were opened in triplicate and the evolution of the oxidative stability index (OSI) was monitored. It should be noted that this parameter reflects the antioxidant reserve existing in a certain type of biodiesel or diesel-biodiesel mixtures. It can also be used to evaluate the efficiency of the added antioxidant products.

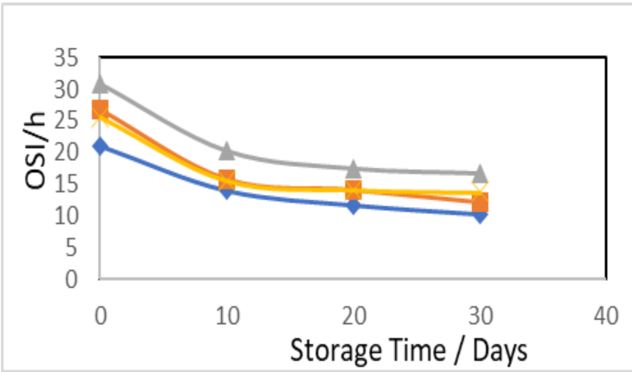
RESULTS AND DISCUSSION

Figure 1 shows the results concerning the biodiesel OSI decay, in which only product AO2



(500 ppm) was able to attend the 12h requirement established by ANP however for ten days of storage only.

Figure 2 shows the results concerning the B15 OSI decay, in which only product AO2 (500 ppm) was able to attend the proposed 20h requirement by European Standardization Bodies



however, for ten days of storage only.

CONCLUSIONS

Based on the results achieved, it was found that:

1) all samples of biodiesel (B100So96Co4) after the addition of the three antioxidant aditives at concentration of 500 ppm showed an immediate significant increase in OSI average values above 12h required by the ANP. However, throughout the storage tests in which only one antioxidant product was kept, it was able to maintain the level above 12h for only 10 days of storage;

2) all B15 samples studied containing the three antioxidant additives at concentrations of 500 ppm showed an immediate significant increase in the OSI for mean values above 20h. However, during the storage tests in which only a sample of B15 containing antioxidant product at the concentration studied was maintained, it was able to maintain the level above 20h for only 10 days of storage;

3) among the three comercial antioxidants evaluated at a concentration of 500 ppm, all were able to maintain a shelf life of biodiesel samples but for only 10 days, exhibiting what is called a very short-term storage stability,

4) it is recommended that for deliveries destined to remote regions, with long and complex logistics, as well as to low-turn distribution centers where medium and long storage times are observed and relatively empty tanks predominate studies that evaluate the antioxidante efficiency with increasing antioxidant dosimetry and variable concentrations should be carried out.

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