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Chemical and microbial storage stability studies and shelf life determinations of commercial Brazilian biodiesels stored in carbon steel containers in subtropical conditions

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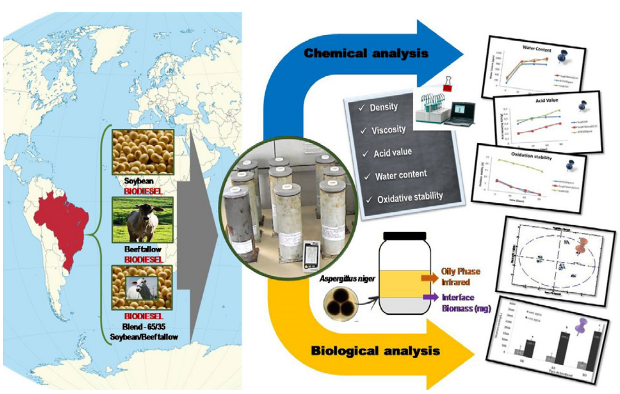
GRAPHICAL ABSTRACT



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ABSTRACT

In the present work long term storage chemical and biological stability of three different commercial Brazilian biodiesel fuels have been studied. Commercial biodiesel fuels from soybean, beef tallow, and blend soybean/beef tallow were initially kept for 60 days in their original containers at the laboratory. Subsequently, the biodiesels were transferred to 1 L carbon steel containers and stored at the laboratory for 90 days exposed to room temperature and humidity. Monthly analyzes of some biodiesel chemical characteristics were conducted. After 90 days, biodiesel samples were sent to be evaluated for their susceptibility to microbial contamination by biomass formation and fuel degradationby FTIR. Results show that after 30 days all biodiesel went out of specification to the water content parameter. Similar result was found for the oxidative stability parameter, except for pure beef tallow biodiesel, which went out of specification after 60 days to the acid value parameter. In terms of microbial contamination, at the end of 60 days, the highest biomass formation occurred in pure soybean biodiesel, followed by blend soybean/beef tallow, and neat beef tallow biodiesels. However, the higher ester carbonyl degradation was observed for 100% beef tallow biodiesel. Thus, in the experimental conditions of this study, the limited shelf life of all studied biodiesels was drastically reduced by the hygroscopicity of the fuel, which acts as a facilitator of other degradative processes, including microbial contamination. The commercial

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soybean biodiesel was considered more vulnerable to long term storage due to its reduced oxidative stability, as well as its higher susceptibility to microbial development. Special care should be addressed by the time that this sort of biodiesel is added to the diesel, unless more robust antioxidant and multipack additives are used, and special handling practices are adopted.

1. Introduction

Biodiesel is a renewable fuel composed of a mixture of fatty acid methyl esters (FAME), which is produced by the transesterification of vegetable oils or animal fat, and alkaline catalysts [1,2]. This fuel can be added to fossil diesel without any damage to the engines. It is also more rapidly degraded and less toxic to the environment than conventional diesel [3]. In Brazil biodiesel has been used since 2005, when it was added to fossil diesel in a proportion of 2%. Since then, this percentage has been increasing, currently reaching 10% [4], which evidences its importance for the Brazilian energy matrix.

Despite its increasing use, and the undeniable environmental benefits, the storage stability of biodiesel is still a matter of great concern. Biodiesel is more susceptible to chemical and biological degradation during long term storage than diesel oil [5–12]. This susceptibility is associated with the chemical composition of the biodiesel and varies considerably depending on the raw material used. Biodiesel obtained from raw materials, such as soybean, in which unsaturated fatty acids predominate, such soybean, for example, is considered to be more susceptible to chemical degradation than biodiesel obtained from beef tallow, in which saturated fatty acids predomite [13–15]. However, other factors, such as the production process and storage conditions, can also influence fuel degradation.

The most common degradative processes for biodiesel are related to humidity and exposure to air and heat. Air humidity tends to induce the incorporation of water, leading to the establishment of hydrolytic degradation processes. The biodiesel hydrolysis alters its physical and chemical characteristics. It may also affect the integrity and stability of the materials which are in contact with the biofuel, such as metallic surfaces, and polymeric materials present in parts and storage structures. In addition, when water contents raises it tends to settle in the bottom of the tanks, thus, favoring microbial development. The action of the oxygen promotes biodiesel oxidation, and the establishment of oxidative processes results in the release of free radicals, and formation of relatively unstable hydroperoxides. These decompose and promote the increase in acidity and polymerization, as well as the formation of gums and sludge, corrosion, turbidity, and varnishing of surfaces, clogging, and leaks [16,17].

The degradation of biodiesel by microbial activity is closely related to the presence of water in the fuel. It occurs mainly through mechanisms such as biomass accumulation, degradation of additives, and production of corrosive metabolites, for instance, organic and inorganic acids (H_2S) [18–20]. In addition, chemical degradation processes can be accelerated by microbial activity [20–27].

Brazil is a country with continental dimensions which has complex distribution and retail fuels chains, and where long distances separate the biodiesel producing regions from refineries where it is added to diesel. In the country, there are at least six biomes, ranging from cold high land regions in the South to hot wet tropical and semi-arid climates in the North and Northeast, respectively. Subtropical weather, however, prevails in most of the economically active and urban regions of the country where the biggest part of diesel consumers is located. This diversity added to the fact that most Brazilian biodiesel plants are concentrated in the Midwest and Southern parts of the country presents an extra logistic challenge to keep the quality of the fuel under control over the distribution, commercialization, and retail chains. Biodiesel should be 100% in line with the specifications so that total quality should be guaranteed until the moment of fuel ignition in the diesel engines. A recent study conducted by INT (National Institute of Technology, Rio de Janeiro, Brazil), however, revealed that approximately 25% of biodiesel shipments reached their distributors out of specifications [28].

Brazilian biodiesel is currently obtained mainly from soybean (79.1%), and beef tallow (16.3%) [29] due to their high availability, and the good suitability of the biodiesel produced [14] to the specifications required by Technical Regulation No. 3/2014, which integrates ANP (Brazilian National Agency of Petroleum, Natural Gas and Biofuels) Resolution No. 45, from 08.25.2014 – DOU 26.8.2014 [30]. Thus, considering the origin of the Brazilian biodiesel, the territorial dimensions of the country, and the complexity of distribution logistics and delivery of biodiesel to the distributors, studies on the evolution of the shelf life and storage stability of biodiesels within the climatic conditions of the country have a fundamental importance. Therefore, the present work had the objective of monitoring physical, chemical, and biological degradative processes suffered by three types of biodiesel commonly sold in Brazil (100% soybean, soybean 65%/beef tallow 35% blend, and 100% beef tallow) under simulated storage conditions.

2. Materials and methods

2.1. Biodiesel samples

In this study three different types of neat biodiesels (B100) were used, which are the most commonly commercialized in the Brazilian market. The first was the 100% soybean (SO) containing TBHQ (2-tert butyl hydroquinone), a commercial antioxidant. The second was 100% beef tallow (BT), and the third was a blend of 65% soybean and 35% beef tallow (BL). Commercial biodiesel volumes were sent by the manufacturers in 100% filled and sealed high-density polyethylene bottles (HDPE).

2.2. Physical and chemical analyzes

2.2.1. Preliminary storage

The received biodiesels were stored in their original conditions of receipt at the laboratory premises for 60 days. These preliminary conditions were established based on market distribution information. Cases in which the addition of biodiesel to diesel was carried out after 60 days of manufacture by the producers were reported. This was especially noted in regions where the receiving and distributing bases were at long distances from the producing centers (e.g. north and northeast regions). After 60 days the HDPE bottles were opened, and biodiesel samples were collected. A set of these samples were sent for physical–chemical characterization analyzes (called time 0 samples) at LACOR-INT (Corrosion and Protection Laboratory at INT, Rio de Janeiro, Brazil) in order to verify if the biodiesel still complied with the parameters established by the ANP 60 days after being received at INT. The physical–chemical parameters analysed were: appearance, water content, oxidation stability, density, viscosity, and acid value. The remaining biodiesels were used for tests in steel carbon containers.

2.2.2. Steel carbon containers tests

After preliminary storage time, for each sample time (30, 60 and 90 days) two sets of four 1L containers of carbon steel AISI 1020 were made for each type of biodiesel. The containers containing a 2.5 cm diameter top hole, they were filled with 800 mL (head space of 20%) of fuel. Each top hole was covered with 08 mm mesh stainless steel shield screens to allow moisture entry, and to minimize impurities. A pre-