Techniques Used for Determining the Hydrotreated Vegetable Oil Presence in Diesel

Fabio de Sousa Santos[1,2*], Marcelo A. Moret[1,2], Lilian Lefol Nani Guarieiro[1]
[1]SENAI CIMATEC University Center; [2]Computer Modeling and Industrial Technology Program; Salvador, Bahia, Brazil

Determining HVO content in diesel is essential for fuel quality control and other important aspects, so studying the techniques used for this purpose is necessary. In this article, the authors did a systematic review to determine the techniques used to define HVO in diesel and the efficiency of each technique. The results of the study showed that the use of techniques that are based on measuring the amount of C14 radiocarbon in the sample have good efficiency, but concerning the cost and time used to perform the exams, FTIR spectroscopy together with the use of Chemometric techniques is an excellent alternative for the study.
Keywords: HVO. Determination Techniques. Liquid Cinstillation. Mass Spectrometry with Accelerators. FTIR Spectroscopy.

Introduction

Renewable energy is an essential energy source that humans can use to carry out their activities sustainably. In its life cycle, renewable energies are of great importance because both in the area of transport and in other areas in which this energy has influence, scholars believe that, with a lower presence of agents harmful to the environment, more incredible benefits, both for government agents, entrepreneurs, and for society as a whole. The traditional production of biofuels, regulated by the ANP, uses essential plants in the structuring line, also highlighting the use of animal fat, in addition to the addition of vegetable oils, soybean, one of the best known, in addition to others, such as "the palm, sunflower, babassu, peanut, bean, and jatropha, through alkaline transesterification, but it can be obtained by cracking and esterification as well [1].

Hydrotreated vegetable Oil (HVO), also called green diesel or renewable diesel, has a chemical composition similar to fossil-based diesel oil; however, it comes from renewable raw materials. This biofuel can be produced from the hydrotreatment of vegetable oils or animal fats, from the synthesis of molecules from synthesis gas obtained by the gasification of organic waste, and by the fermentation of sugar cane, among other processes. Its composition is similar to petroleum-derived diesel, so it can be mixed with mineral diesel in any proportion, even as a complete replacement [2].

The chemical process of producing HVO is carried out through hydrotreatment (HDT). Through it, the raw material reacts with hydrogen gas under controlled conditions of pressure and temperature to produce a fuel similar to fossil diesel. A range of technologies for its preparation, that is, different raw materials, can be used, both of animal and vegetable origin [3]. In addition to these factors, Kalnes and colleagues [4] list the classification of HVO as a "second generation of biofuels" since it comes from the green chemistry process, according to the authors as mentioned earlier. Furthermore, the HVO already has production in other countries, facilitating learning and placement in the national territory without significant obstacles in its production. The differential issue between biofuel and green diesel is the number of hydrogen molecules [1].

The use of biofuels is highly likely due to their contribution to preserving the environment, reducing environmental pollution, and being a renewable energy option to replace or mitigate the market of petroleum products in the future.

Received on 25 September 2022; revised 16 November 2022.
Address for correspondence: Fabio de Sousa Santos. Rua Professor Viegas,186 - Condomínio Mirabeau Sampaio, Block B.apto 012 - Salvador - BA, Brazil. Zipcode: 40301-075. E-mail: fabiosousasantos4@gmail.com or fabio11@ba.estudante.senai.br. DOI 10.34178/jbth.v5i4.261.

J Bioeng. Tech. Health 2022;5(4):341-345

Among the renewable sources, the most favorable is certainly HVO, as it has immense advantages compared to biodiesel, such as a more significant amount of energy density, lower NOx emission, superior storage properties, and production without the presence of glycerol., in addition to being a fuel that can fully replace diesel without any engine modification [5].

This article aimed to identify and evaluate the techniques used to determine the percentage of HVO-type renewable content in diesel fuel of fossil origin. This study will present the fuel mixtures and techniques that can be used to determine HVO inserted in diesel oil. In addition, the efficiency of the techniques used to determine the HVO present in diesel will be evaluated. From this perspective, this work was supported by theoretical references in the scope of determination of the HVO content present in diesel to identify these techniques and evaluate their efficiency in this process.

Materials and Methods

The research was carried out through a systematic review of the period between 2007 and 2022 of national and international publications that study the techniques used to determine the HVO content in diesel oil.

We made a methodological choice of investigation for the survey of the studies carried out. All searches took place on reference sites with consolidated studies. With few studies in Brazil, international journals and repositories dominate the research on the techniques to determine the HVO content present in diesel oil.

The systematic review represents an investigation focused on the recovery and careful analysis of literary productions already carried out on the proposed theme. These studies test hypotheses to raise, analyze, evaluate, and understand a given phenomenon studied, systematizing and synthesizing the research already carried out in the studied field [13]. In this systematic review process, the software dimension and read cube were used to survey the articles to be studied. Then their selection took place through the impact factor of the periodical. They were also organized into groups considering the year of publication from 2007 to 2022. After data collection and material selection, twenty-eight articles were kept, all of which were searched using the descriptors “prediction of HVO (Hydrotreated vegetable Oil) in diesel”, “HVO (Hydrotreated vegetable Oil) in diesel”, “techniques for prediction of HVO (Hydrotreated vegetable Oil)”. In this research, some techniques were found that are used to determine the HVO content present in diesel.

Results and Discussion

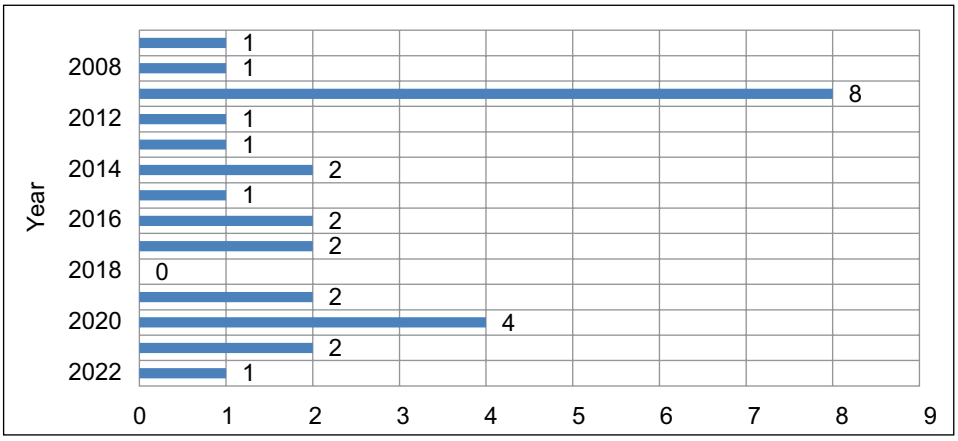
Research and studies carried out with the techniques to determine the HVO content in diesel oil have shown significant relevance due to their applications for the evolution of renewable contents about fossil fuels. The articles selected for this study expressly present in their abstracts the discussion about these techniques used to determine the HVO content in diesel.

Thus, in this writing, data collected from a survey carried out in a virtual environment from banks and repositories that host these studies are presented in the light of a bibliographic study. One of the most important revelations that we can point out is the low academic production in Brazil, which highlights the importance of this writing. Figure 1 presents the evolution of the research in the selected period.

The scientific literature presents reports on using infrared (IR) spectroscopy to monitor the transesterification of vegetable oils with methanol and ethanol, determining the conversion rate of this reaction. As diesel and biodiesel have different chemical functions, the infrared spectra of these fuels contain specific bands. Therefore, this technique can also quantify the percentage of biodiesel in biodiesel: diesel mixtures [6].

Determining the HVO content in the HVO/ diesel mixture is a challenging task, as the two fuels are a mixture of the same or very similar hydrocarbons.

Figure 1. Number of publications on the determination of the HVO content in the HVO/diesel mixture x year.



Source: Authors.

Moreover, standard analytical methods differentiate hydrocarbons belonging to HVO from hydrocarbons belonging to fossil fuels [7].

To determine the HVO present in diesel, we have that can be based on the measurement of the number of radiocarbon C14 in the sample. The methods based on the measurement of C14 (carbon 14) can be divided into two main groups, which are: accelerator mass spectrometry (AMS) and the other is liquid scintillation counting (LSC); however, both methods have relatively good accuracy but are very time-consuming and expensive[7]. Liquid Scintillation Counting is a radiocarbon dating technique that was popular in the 1960s. In this method, the sample is in liquid form, and a scintillator is added. This scintillator produces a flash of light when it interacts with a beta particle. A vial with a sample is passed between two photomultipliers, and only when both devices register the flash of light is a count made. Accelerator mass spectrometry (EMA) is a modern method of radiocarbon dating that is considered the most efficient way of measuring the radiocarbon content of a sample. In this method, the carbon 14 content is directly measured to the carbon 12 and 13 present. The method does not count beta particles but the number of carbon atoms in the sample and the proportion of isotopes [8,9]. Another technique currently used is FTIR spectroscopy, combined with chemometric techniques that are partial least squares regression (PLS) and principal components regression (PCR), which are used to determine the HVO content in HVO/ diesel. This technique, developed by Dan Vrtiška and Pavel Šimáčˇek from the University of Chemistry and Technology, Department of Petroleum Technology and Alternative Fuels, is a methodology for determining the content of hydrotreated vegetable oil (HVO) present in Diesel using Fourier transform infrared spectroscopy (FTIR) and chemometric analysis for some fuel mixtures existing in Europe [7]. The results in Table 1 refer to the techniques currently used to identify the HVO content present in diesel, in addition to informing the efficiency of these techniques used.

The results in Table 1 show that the techniques used to determine the HVO content present in diesel have excellent efficiency. However, liquid scintillation counting and accelerator mass spectrometry (AMS) has disadvantages concerning the high time used. Furthermore, to perform the exams and the high cost of analyzing a sample. Therefore, FTIR spectroscopy, combined with chemometric techniques, is a process that has great potential to become the most used in the determination of contents. Mainly the HVO is present in diesel because, in this process, we have a lower cost per sample. In addition, the time for carrying out the tests is

Table 1. Comparison between the techniques used to determine the HVO content present in diesel.

Fuel Blend	Technique Used	Limit of Detection	Efficiency of Technique	Ref.
HVO /DIESEL	Measurement of the amount of C14 radiocarbon in the sample using accelerator mass spectrometry (AMS)	47000	Relatively good accuracy but they are very time-consuming and expensive	[7,10]
HVO / DIESEL	Measurement of the amount of C14 radiocarbon in the sample using scintillation counting _ _ net (LSC)	47000	Relatively good but they are very time-consuming and expensive	[7,10]
HVO / DIESEL	FTIR spectroscopy, together with the use of chemometrics techniques	-	Best predictive ability of all. The maximum error of the prediction of the HVO content did not exceed 0.25% by weight	[7]

DL = Detection Limit (AP = 1950 DC).

shorter, and the amount of sample used is reduced. Determining the fraction biogenic based on the measurement of the carbon 14 content is possible in different ways. The measurement directly from the carbon 14 activity of fuels liquids by scintillation counter _ net (LSC) is fast but overloaded by some disadvantages. For example, the color of fuels causes different quenching properties in the scintillation cocktail and affects _ The measurement efficiency [11]. The disadvantages of the AMS measurement technique are sample preparation, combustion, and graphitization, while the time of a _ regular AMS measurement is fixed. Nevertheless, the AMS 14C measurement technique is excellent for determining the biological base content in fuel mixtures, even _ below 1.0 m/m % [12].

Conclusion

The systematic review carried out to determine the techniques used to determine the HVO content present in diesel was very important because, through this investigation, we found the articles that dealt with this being possible, thus, bringing the procedural definition of each technique and power. Evaluate the efficiency of each of these. It was noted in the study that the technique involving mass spectrometry with accelerators (EMA) is the most effectively used because it has a shorter time in sample preparation and requires a smaller number of samples. However, it was found that as the cost and the time required to perform the exams were high, it became evident that the FTIR spectroscopy technique and the use of chemometric techniques began to gain great visibility because the efficiency in the results was excellent. The cost concerning other techniques is much lower. In addition to these factors, there is no short-term reduction in the costs of exams performed by the techniques of mass spectrometry with accelerators (EMA) and liquid scintillation counting, which, in addition to this fact, take longer to perform. What makes this work, in addition to others, a differential?

References

1. Renewable fuels for use in Diesel cycle engines. Energy Research Company – ERC, 2020. Available at: https://www.epe.gov.br/sites-pt/publicacoes-dados-abertos/publicacoes/PublicacoesArquivos/publicacao-467/NT_Combustiveis_renovaveis_em_%20motores_ciclo_Diesel.pdf Accessed on July 15, 2022.
2. What is green diesel or renewable diesel? Brazilian Institute of Oil and Gas – BIO, 2021. Available at: https://www.ibp.org.br/noticias/o-que-e-diesel-verde-ou-diesel-renovavel/. Accessed on July 15, 2022.
3. Zeman P et al. Hydrotreated vegetable oil as a fuel from waste materials. Catalysts 2019;9(4):337.
4. Kalnes T, Marker T, Shonnard DR. Green diesel: A second generation biofuel. International Journal of Chemical Reactor Engineering 2007;5(1).
5. da Costa RBR et al. Experimental assessment of renewable diesel fuels (HVO/Farnesane) and bioethanol on dual-fuel mode. Energy Conversion and Management 2022;258:115554.
6. Guarieiro LLN et al. Analytical methodology to quantify the biodiesel content in the biodiesel: Diesel blend using infrared spectroscopy. New Chemistry 2008;31:421-426.
7. Vrtiska D, Šimácek P. Prediction of HVO content in HVO/diesel blends using FTIR and chemometric methods. Fuel 2016;174:225-234.
8. Olanrewaju F et al. An improved heat release rate (HRR) model for the analysis of combustion behaviour of diesel, GTL, and HVO diesel. In: SAE Technical Paper Series. SAE International 2020.
9. Bowman S. Radiocarbon dating. University of California Press, 1990.
10. Beta Analytic detection capabilities and limits. Beta Analytic,2020. Available at https://www.radiocarbon.com/portugues/radiocarbono-laboratorio.htm, Accessed July 12, 2022.
11. Doll CG et al. Analysis of fuel using the direct LSC method determination of bio-originated fuel in the presence of quenching. Applied Radiation and Isotopes 2017;122:215-221.
12. Varga T et al. High-precision biogenic fraction analyses of liquid fuels by 14C AMS at HEKAL. Radiocarbon 2018;60(5):1317-1325.
13. Donato H, Donato M. Stages for undertaking a systematic review. Acta Medica Portuguesa 2019;32(3):227-235.