Techniques used for the determination of renewable contents present in diesel oil

https://doi.org/10.56238/sevened2024.003-008

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ABSTRACT

The determination of the renewable content present in diesel is of great importance for the monitoring of the fuel quality and inspection by the fuel regulation agencies, being necessary to know the techniques used for this purpose. In this article, a systematic review was developed to study the techniques used to determine the presence of renewable content in diesel. The results of the study showed that there are some techniques that are used in this determination, such as: mid-infrared spectroscopy, measurement of the amount of radiocarbon C14, FTIR spectroscopy along with the use of chemometric techniques and others that will be addressed in this study.

Keywords: Biodiesel, Determination techniques, Mass Spectrometry with Accelerators, Spectroscopy FTIR, Mid-infrared spectroscopy.

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INTRODUCTION

In the modern world, renewable energy is a significant source of energy that can be used by society to perform its tasks sustainably. In its life cycle, renewable energy assumes great importance, because both in the area of transportation and in other areas in which this energy has an influence, scholars believe that with less harmful agents for the environment, greater benefits, both for government agents, businessmen and for society as a whole.

The traditional production of biofuels, regulated by the ANP, uses important plants in the structuring line, highlighting also the use of animal fat, in addition to the addition of vegetable oils, soybean being one of the best known, in addition to others, such as, "dendê, sunflower, babaçu, peanut, bean, and jatropha, by alkaline transesterification, but can also be obtained by cracking and esterification. (Empresa de Pesquisa Energética - EPE,2022). In order to determine the biodiesel content in diesel the ANP uses the analysis through the mid-infrared spectroscopy (FTIR) that needs several samples, besides requiring a complex calibration that is not performed by several research institutions.

Biodiesel is a renewable fuel produced from renewable sources of vegetable oils or animal fats, such as soybean oil, palm oil, sunflower oil, animal fat, among others. Biodiesel can be used in diesel engines as a total or partial substitute for conventional diesel derived from petroleum, offering significant environmental and economic benefits. Among the types of biodiesels we have the Hydrotreated Vegetable Oil (HVO), also called green diesel or renewable diesel, which has a chemical composition similar to diesel from fossil origin, but comes from renewable raw material, Its composition is similar to the diesel derived from petroleum and can be mixed with mineral diesel in any proportion, including full replacement (Brazilian Institute of Oil and Gas - 2022).

The use of biofuels is extremely applicable due to its contribution to the preservation of the environment, contributing to the reduction of environmental pollution, and is also a renewable energy option to replace or mitigate the market for petroleum products in the future. In relation to fuel blends of renewable content and diesel there are specific analytical techniques used to determine the biodiesel content in blends with conventional diesel. These techniques are important to ensure that the blend of biodiesel and conventional diesel meets established quality standards and to avoid performance problems or engine damage.The objective of this paper was to identify and evaluate the techniques that are used to determine the percentage of renewable content present in diesel fuel of fossil origin .

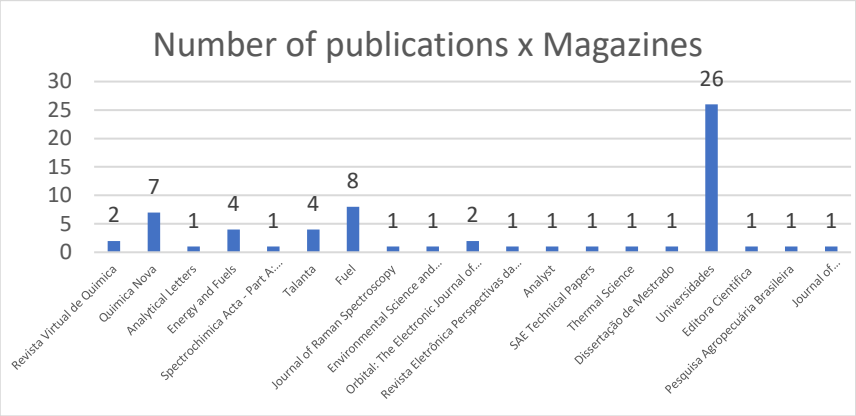
MATERIALS AND METHODS

The research was conducted by means of a systematic review of national and international publications that study the techniques used to determine the content of renewable contents present in

diesel oil, from 2008 to 2023. All the research was carried out in reference sites with consolidated studies. International and national periodicals and repositories showed the studies about the techniques for determining the content of renewable contents present in diesel oil.

The systematic review is characterized as an investigation in which the focus of studies is based on the recovery and careful analysis of academic productions already published on the subject to be researched. Being that these studies have importance in testing hypotheses aiming the survey, analysis, evaluation and to understand a particular phenomenon studied, in addition to systematize and synthesize the research already conducted in the field studied (Donato et al, 2019).In this process of systematic review, we used the databases Mendeley, Google Scholar and Dimensios to survey the articles to be studied, then their selection was made through the impact factor of the journal, were also organized into groups considering the year of publication in the period 2008 to 2023. After data collection and selection of the material, sixty-five articles were kept, all searched with the descriptors "renewable content prediction in diesel", "biodiesel in diesel", "biodiesel prediction techniques", "HVO prediction in diesel" "HVO prediction techniques".

Figure 1: Number of publications x journals



Source: Elaborated by the authors (2023).

In Figure 1 we have the relationship between the number of publications by journals, it is noted that universities publish a large number of articles on the subject. The journal Fuel published a large number of articles on the analytical techniques used to determine the content of renewable contents present in diesel.

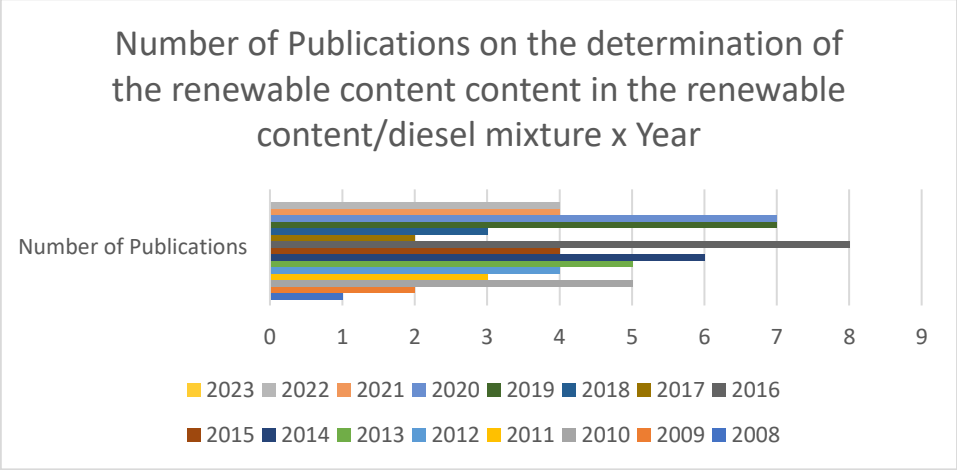
RESULTS

The research and studies conducted with the techniques for determining the content of renewable content present in diesel fuel have shown great importance due to the use of renewable content in fossil fuels and the determination of this content is very important in the quality of blends. The articles selected for this study expressly present in their abstracts the discussion on these

techniques used to determine the content of renewable contents in diesel.

In this article, the data collected from a survey of the databases and repositories that contain these studies will be presented, and presented through a bibliographical study. One of the most important discoveries was the fact that a large number of studies were carried out at universities. The evolution of research in the selected period can be understood from the following graph:

Figure 2: Number of publications on the determination of renewable content in diesel blends x year



Source: Elaborated by the authors (2023).

According to the analysis of figure 2, we have that in the year 2016 was published the largest number of articles on the subject and it is noted that in the year 2022 four articles were selected for this study showing that there is a need to increase research on the subject which is of great importance for the energy future of the world.The scientific literature presents reports on the use of infrared spectroscopy (IR) to monitor the transesterification of vegetable oils with methanol and ethanol, determining the conversion rate of this reaction. Because diesel and biodiesel have different chemical functions, the IR spectra of these fuels contain specific bands. This technique can also be used to quantify the percentage of biodiesel present in biodiesel:diesel blends .(Guarieiro , 2008)

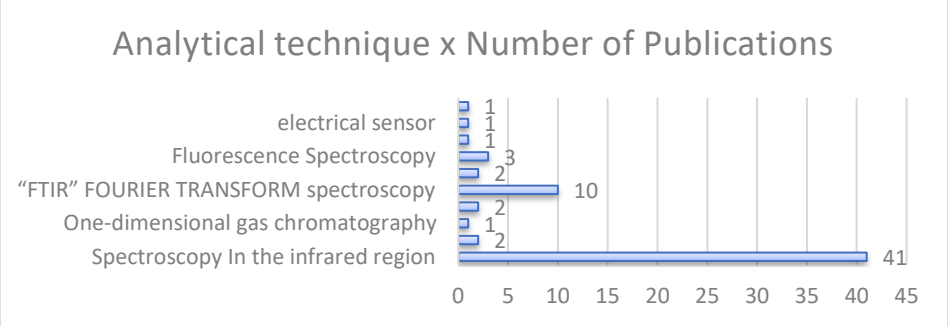
Articles were searched that contemplate other techniques for the quantification of biodiesel content present in diesel , among them we have , Raman spectroscopy which is used as a tool to classify fuel blends and quantify the biodiesel contents and to identify and quantify the blends of diesel and biodiesel, being performed the analysis through Raman spectroscopy based on partial least squares regression (PLS). In this method, biodiesel mainly shows three characteristic Raman regions corresponding to the spectroscopy of diesel . (Liu *et al*., 2019)

Regarding the determination of the HVO content in the HVO/diesel blend,it is known to be a very difficult function, because when mixing the two fuels we get as a result a mixture of the same or very similar hydrocarbons.Common analytical methods like infrared region spectroscopy do not perform the exact differentiation of hydrocarbons belonging to HVO from hydrocarbons belonging to

fossil fuels.(Vrtiska et al , 2016)

The techniques are based on the measurement of C14 (carbon 14) and have two main groups which are: accelerator mass spectrometry (AMS) and liquid scintillation counting (LSC), however these methods have a good accuracy, but are time and cost intensive. (VRTIŠKA et al , 2016). FTIR spectroscopy along with the use of chemometric techniques which are partial least squares regression (PLS) and principal component regression (PCR) are being used to determine the HVO content in HVO/diesel and can also be used in the quantification of FAME biodiesel in diesel.(Santos et al ,2022)

Figure 3: Number of publications x analytical technique



Source: Elaborated by the authors (2023).

Figure 3 shows that the technique with greater use for quantifying the content of renewable content present in diesel is the Spectroscopy in the infrared region because it is used in the analysis of blends of biodiesel FAME and diesel that have different chemical components. Another widely used technique is the "FTIR" FOURIER TRANSFORM spectroscopy that can be used both for the determination of the content of FAME biodiesel present in diesel and for the determination of the content of hydrotreated vegetable oil present in diesel. The results that will be exposed, through table 1, refer to the techniques that are currently used to identify the content of renewable content present in diesel and that were identified in the systematic review.

Table 1. *Comparison between the techniques used to determine the content of renewable content present in Diesel*

Fuel Blending	**Technique Used**	Technique Evaluation _ Used
HVO /DIESEL	Measurement of the amount of radiocarbon C14	Relatively good accuracy, but they are very time-consuming and expensive
HVO / DIESEL **BIODIESEL / DIESEL**	FOURIER TRANSFORM spectroscopy "FTIR" together with the use of chemometric techniques	Best predictive capability of all. The maximum error of the HVO content prediction did not exceed 0.25% by weight
BIODIESEL / DIESEL	Infrared (IR) spectroscopy	Spectroscopy in the mid-infrared region is a suitable technique for the quantification of biodiesel in diesel blends because the carbonyl function of methyl or ethyl esters of biodiesel is a single,
		thin band and absorbs in a distinct region of the infrared spectrum of diesel(Dantas,2019)
BIODIESEL / DIESEL	Raman spectroscopy based on partial least squares (PLS) regression	Raman spectroscopy combined with PCA and PLS could identify and quantify fuels and biofuels
BIODIESEL / DIESEL	COLORIMETRIC TEST	Applying Student's t-test it was concluded that the methods can be considered statistically equivalent. Therefore, it was confirmed that the colorimetric assay for hydroxamic acid is suitable for detecting and quantifying the biodiesel content in biodiesel/diesel blends and can also be easily adapted for field analysis.
BIODIESEL / DIESEL	3D total spectrofluorimetry in combination with Principal Component Analysis (PCA)	With the use of Total Fluorescence Spectroscopy together with PCA one can determine adulteration of diesel by high amounts of biodiesel
BIODIESEL / DIESEL	Chromatography	This method was validated and showed selectivity; adequate linearity (r>0.99) without lack of fit and heteroscedasticity; adequate values according to MAPA of intermediate precision and repeatability (less than 5.0 and 4.8, respectively), of error evaluated intraday and interday (less than 4.8 and 4.9, respectively) of limits of quantification (52.62 µg/g) and detection (15.95 µg/g); and robustness. 100 of these diesel oil samples (18 non-compliant and 82 compliant).(Brouck,2012)

The results presented in Table 1 show that the techniques used to determine the content of

renewable content present in diesel are defined basically for differentiation between diesel and biodiesel FAME because in this case there is a mixture between hydrocarbons and the carbonyl function of methyl or ethyl esters of biodiesel which is a single band, In relation to the differentiation between HVO and diesel is used the measurement of the amount of C14 radiocarbon in the sample through the counting of liquid scintillation or accelerator mass spectrometry (AMS) that present good results but have disadvantages in relation to the high time used to perform the tests and the high cost of analyzing a sample. Analyzing the table we have that the FTIR spectroscopy along with the use of chemometric techniques has been a process with high potential to be the most applied in the quantification of the contents of renewable content present in diesel, because this process has a lower cost per sample, besides having a reduction in the time for performing the tests and being reduced the amount of sample to be used in the tests.

One-dimensional gas chromatography is basically used when there are mixtures of FAME biodiesel with diesel because mixtures are formed between hydrocarbons and the carbonyl function of the methyl or ethyl esters of biodiesel and that in the chromatography by the process of separation of the components are more evident by the difference of these elements.(Brouck,2012)

MAIN CONCLUSIONS

The systematic review performed to determine the techniques that are being used to determine the content of renewable content present in diesel was very important, because through this investigation we found the articles that dealt with this being possible, thus, bring the most commonly used methods currently and be able to verify in the literature how these researches are found. It was verified in this study that the analytical technique involving the Spectroscopy In the infrared region is the most used in the analysis of blends of biodiesel FAME and diesel.In relation to the determination of the HVO content in diesel it was noted that mass spectrometry with accelerators is the most widely used, because it has less time in sample preparation and requires a smaller number of samples, but it was found that as the cost and time required for the tests are high, it was evident that the FTIR spectroscopy technique combined with the use of chemometric techniques begins to be widely used because the efficiency in the results is excellent and the cost compared to other techniques is much lower. What makes this work, among others, a differential.

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