Supplementary Information (SI) for Analytical Methods.

Predictive Model for the Determination of the Hydrotreated Vegetable Oil (HVO) Content in HVO/Fossil Diesel Blends using Gas Chromatography coupled to Mass Spectrometry and Multivariate Analysis

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Preparation of Biodiesel

Biodiesel synthesis was carried out with commercial soybean oil (soya brand). The transesterification reaction occurred via the methyl route using basic homogeneous catalysis and a 1:6 molar ratio of oil/methyl alcohol. Excess alcohol was added to favor the reaction, which is one of the relevant factors for obtaining a good yield in the reaction. The catalyst used in the reaction was potassium hydroxide (KOH), at a concentration of 1% based on the mass of oil.

Using a fume hood, 1.0 g of potassium hydroxide (KOH), brand (Vetec, grade PA), was dissolved in a 100 mL beaker, with the aid of stirring until the KOH was completely dissolved. In this step, the methoxide is formed. of potassium.

100 mL of commercial soybean oil were added to a 250 mL round-bottom flask, with subsequent addition of a magnetic stirrer. Subsequently, the round-bottom flask was heated in a water bath to a temperature of 45ºC, when the previously prepared potassium methoxide solution was added. Then, the reaction mixture was kept heated at 45ºC under strong stirring with reflux for one hour.

The reaction mixture was transferred to a separation funnel and left to rest for 24 hours, when the formation of two phases was observed: the upper one, containing biodiesel, and the lower one, containing glycerol, soaps and excess base and alcohol. The lower phase was collected in a 100mL beaker and taken to the waste disposal site.

25 mL of 10% hydrochloric acid aqueous solution were added to the funnel containing the remaining phase, leaving to rest for 15 minutes. The aqueous phase was removed and the washing process was repeated with another 25 mL of 10% hydrochloric acid. Then, washing was carried out twice with 20 mL of saturated NaCl solution and once with distilled water. The absence of basic catalyst was confirmed by measuring the pH of the last washing water, which must be neutral;

To dry the biodiesel, the solution obtained was transferred to a Erlenmeyer flask and anhydrous Na2SO4 (desiccating agent) was added and waited 15 minutes. Afterwards, the mixture was filtered and the fraction obtained (biodiesel) was transferred to a beaker, so that its volume could be measured. The biodiesel obtained had a clean appearance and no turbidity.

Method to distinguish Diesel, biodiesel and vegetable oil

Mattos, 2019 developed a methodology to identify and quantify diesel, biodiesel and vegetable oil. This result was added to the supplementary material for information purposes. (DE MATOS, Tais Santana et al. Determination of the biodiesel content on biodiesel/diesel blends and their adulteration with vegetable oil by high-performance liquid chromatography. **Energy & Fuels**, v. 33, n. 11, p. 11310-11317, 2019.)

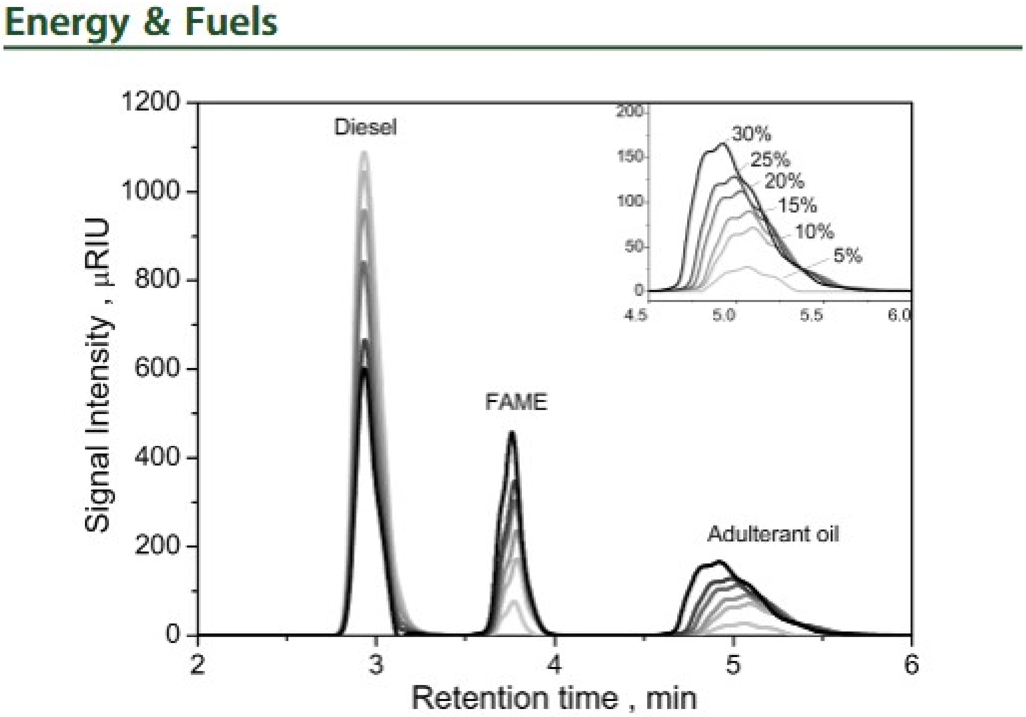

Figure 1: Chromatograms obtained by NP-HPLC-RI of biodiesel/diesel blends adulterated with soybean oil to plot calibration curves (5.0 to 30.0% vol). The inset shows the adulterant oil peak, and the difference concentrations tested.

The methodology developed by Matos cannot identify diesel and biodiesel samples.

Initial tests in the development of the methodology

As a preliminary analysis, a standard sample of 1 to 30 carbon atoms was injected. The chromatogram (below) of a standard sample containing hydrocarbon mixtures of 7 to 30 carbon atoms when subjected to chromatographic separation. For the sake of better visualization of the range of hydrocarbons that make up fossil diesel and HVO, the software that controls the CG was adjusted to observe the separation from the hydrocarbon with 13 carbon atoms. With this, it is possible to observe the separation of the homologous series starting with tridecane and ending with triacontane. Furthermore, the retention times for each peak can be observed, which serve as a comparison parameter for real samples of diesel oil and HVO.

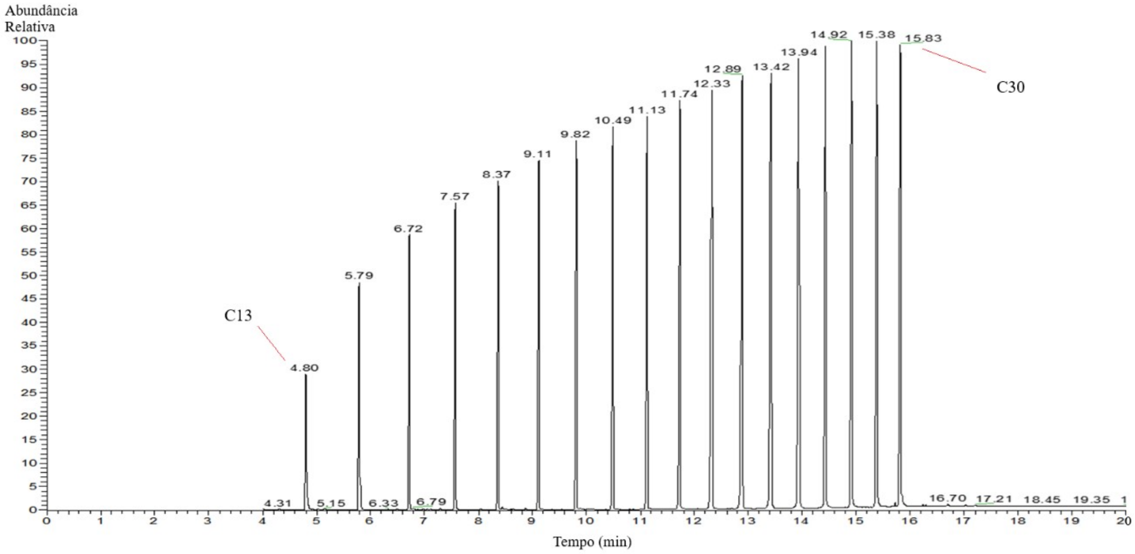

Fig. 2. Homologous series of hydrocarbons from C12-C30

Chromatographic profile in a ternary sample of diesel and biodiesel (B12)

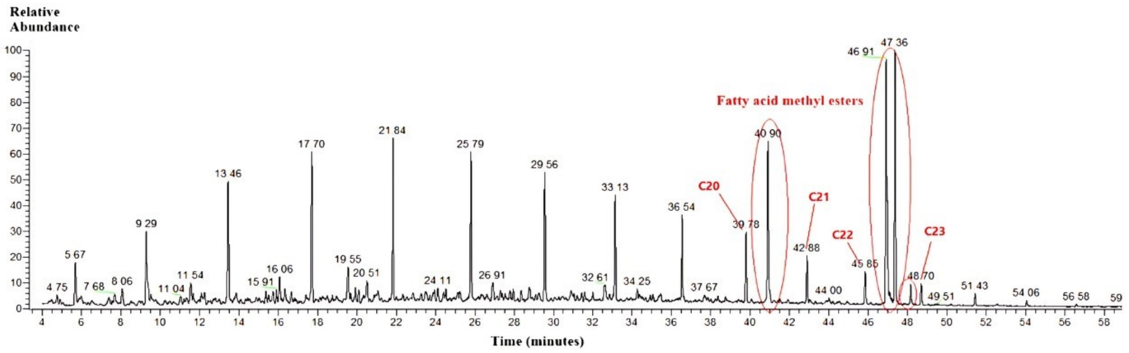

Fig. 3 Chromatographic profile in a ternary sample of diesel and biodiesel (B12)

References

Matos, Tais Santana et al. Determination of the biodiesel content on biodiesel/diesel blends and their adulteration with vegetable oil by high-performance liquid chromatography. Energy & Fuels, v. 33, n. 11, p. 11310-11317, 2019.) http://dx.doi.org/10.1021/acs.energyfuels.9b03133.