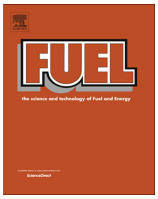
Fuel xxx (2015) xxx–xxx

Contents lists available at ScienceDirect

Fuel

journal homepage: www.elsevier.com/locate/fuel



# NMR in the time domain: A new methodology to detect adulteration of diesel oil with kerosene

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UNCORRECTED PROOF

ARTICLE INFO

*Article history:*
Received 10 July 2015
Received in revised form 17 October 2015
Accepted 19 October 2015
Available online xxxx

*Keywords:*
Diesel oil
Adulteration
Low-field NMR

ABSTRACT

Petroleum products such as LPG (cooking gas), kerosene, gasoline, diesel oil, among others, are obtained from the refining of crude oil. Among these, the diesel has great importance in the Brazilian road system where fuel consumption leads the rankings in the road sector in Brazil. The high consumption (approximately 50% of total) makes this fuel target to adulteration by irregular products like kerosene, which has low cost and good miscibility with the fuel. Adulteration causes irreparable damage to the car, such as sudden drops in engine, difficulties in starting, increased fuel consumption, degradation of machine performance and environmental harm as emissions of particulate matter during the combustion. This study proposes a new methodology, the nuclear magnetic resonance in the time domain (TD-NMR) to detect the adulteration of four commercial diesel oils with kerosene. Results of the study show that the diesel oil has a transverse relaxation time ($T_2$) around 0.67 s, while the adulterant kerosene is 1.33 s, and the adulterated samples in the range of 5–100% presented $T_2$ between 0.67 and 1.33 s. The TD-NMR methodology proposed showed excellent agreement with quantification of adulterant content detected by mid-infrared (MIR) which is the standard technique to detect non-compliance of fuel.

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## 1. Introduction

Petroleum is composed primarily of a mixture of hydrocarbons and small amounts of nitrogen, sulfur and oxygen [1]. The National Agency of Petroleum, Natural Gas and Biofuels (ANP) defines oil as any liquid hydrocarbon in its natural state, such as crude oil and condensate, § 1 of art. 6 of Law N. 9478 of August 6 1997 [2].

Petroleum products such as LPG (cooking gas), kerosene, gasoline, diesel oil, among others, are obtained from the refining of crude oil. Such compounds are produced from the distillation of oil, and are distinguished by the boiling point of the chemical compounds distributed in a narrow temperature range. Diesel oil, for instance, has a boiling point of 125 °C and 328 °C, and is hence part of the medium distillates [1,3]. Diesel is of most importance for the road transport, so much so that in 2013 it led the fuel consumption ranking in the Brazilian road sector with about 50% [4].

In Europe, diesel is sold with percentages between 2% and 10% biodiesel [5]. In Brazil, the fuel sold should obey ANP parameters and specifications including: color, biodiesel content, flash point, viscosity, among others. Such parameters should be determined in accordance with official test methods, specified by Resolution N. 50 of 12.23.2013 [6] in Brazil. Among these specifications is the biodiesel content that according to Law N. 13.033 of 24 September 2014, all diesel sold in Brazil after November 1, 2014 should contain 7% (v/v) biodiesel [7].

Diesel can be marketed as road fuel or sea fuel. The first is classified as A when the fuel is obtained by means of refining without the addition of biodiesel, and B when it is obtained by refining with the addition of biodiesel according to the content prescribed by law [8]. Regarding the sulfur content, diesel oils A and B are presented as diesel B S10 and S10 for fuels with a maximum sulfur content of 10 mg/kg or diesel S500 and BS 500, for fuels containing maximum sulfur of 500 mg/kg. The marketing of diesel oil B S10 is mandatory in cities and metropolitan regions, while diesel BS 500 is mandatory in all national territory except for the previously cited cases [6].

The rate of non-compliance of diesel linked to its consumption has grown between 2011 and 2012 in Brazil. Note that nonconformities are oil features and properties in disagreement with ANP Resolution N. 50 of 12.23.2013. Nonconformity inherent in fuel adulteration causes almost irreparable damage in the car, such as sudden drops in engine, difficulties in starting, increased fuel consumption and increased emissions of particulates and exhaust gases [9,10]. For example, diesel with large amount of sulfur can

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http://dx.doi.org/10.1016/j.fuel.2015.10.078
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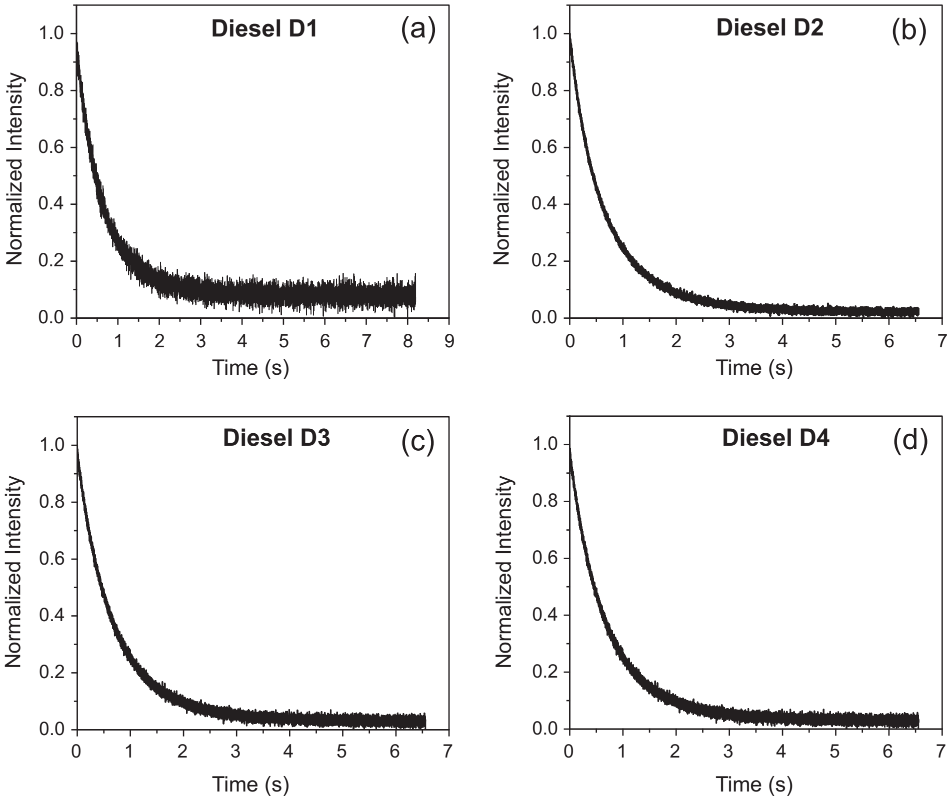

**Fig. 1.** Normalized signal decay curves over time for CPMG experiments for diesel oils D1 (a), D2 (b), D3 (c) and D4 (d) without the addition of adulterant (kerosene). It is possible to observe an exponential behavior of the intensity of the normalized signal over time for all samples.

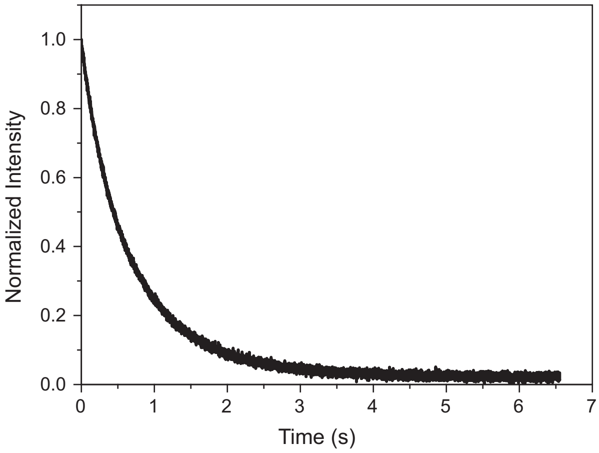

**Fig. 2.** Decay curves of the normalized intensity obtained by CPMG for kerosene adulterant. It is possible to observe an exponential behavior of the intensity of the normalized signal over time.

lead to oxidation and reaction with water vapor and the consequent formation of sulfuric acid. Sulfur or others adulterant as kerosene can cause severe effect on engine performance and environmental problem associated to increase in emission of particulate material, acid rain, corrosion of engine and clogging of nozzles [9,10].

Fuel adulteration normally occurs by adding a cheaper product with good miscibility with the fuel. Such fraud aims at illegal profit. The most common adulterants of diesel fuel are kerosene, biodiesel and residual oils [11–13]. In this study we used the kerosene due to its excellent miscibility with the fuel and availability.

The literature provides several techniques for analyzing diesel, such as spectroscopy in the region of the infrared [14–17] and visible ultraviolet [18], mass spectrometry [19–21], spectrofluometry [8,11] and nuclear magnetic resonance of high resolution [22].

Gaydou and colleagues tested the ability to detect the adulteration of blends of diesel/biodiesel with vegetable oil by NIR (4430–10000 $cm^{-1}$ with resolution of 4 $cm^{-1}$) and MIR (650–4000 $cm^{-1}$ with resolution 4 $cm^{-1}$) and associated the information obtained for these techniques with chemometrics. In certain concentrations, the isolated techniques were successful to detect adulteration, however, the simultaneous use has great potential to be linked to the use of chemometry [15]. On the other hand, Fernandes and colleagues evaluated the use of the range between the visible and NIR region, separately and simultaneously, to determine the content of biodiesel in diesel/biodiesel blends using chemometric models. The concentration of biodiesel varied between 5% and 50% (v/v) and the band used was around 530 nm. Results show that it is possible to determine biodiesel in diesel when the two regions are analyzed [18].

Corgozinho and colleagues developed an analytical method for identifying and quantifying residual oil in diesel samples with 2% biodiesel (B2) using spectrofluometry (340–800 nm) with chemometric methods. Adulteration was done in a range between 0.5% and 25% in increments of 0.5% residual oil. The study was successful and the technique associated with chemometrics could classify samples B2 and adulterated, diesel and quantify the residual oil in samples [8]. Divya and Mishra developed a method to determine the percentage of kerosene fraction in diesel (v/v) by means of fluorescence excitation–emission and multivariate calibration models. Concentration of the kerosene fractions added to diesel varied from 0% to 100% (v/v), though the method was not successful in identifying those samples with kerosene percentages between 1% and 10% [13].

Please cite this article in press as: Cunha DA et al. NMR in the time domain: A new methodology to detect adulteration of diesel oil with kerosene. Fuel (2015), http://dx.doi.org/10.1016/j.fuel.2015.10.078

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