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Determination of biodiesel blend levels in different diesel samples by ^{1}H NMR

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ABSTRACT

The use of ^{1}H NMR to quantify different methyl biodiesels in diesel from different sources is described. Biodiesel samples from soybean and castor oils, which have different fatty acid compositions, and three diesel fuels, which have distinct chemical compositions, were used to prepare biodiesel blends (0.5–30%, v/v). These samples were analyzed by ^{1}H NMR and some relationships of integrals were employed to construct calibration curves. The results indicated that the quantification of biodiesel in diesel by ^{1}H NMR is not affected by either biodiesel or diesel types and thus this technique is especially valuable for such determination.

1. Introduction

The use of alternative fuels has increased due to several factors [1]. Biodiesel is the major substitute for fossil diesel. They have very similar physical properties, which allows the use of pure or blended biodiesel without any modification in the diesel engine or in the existing fuel distribution and storage infrastructure [2,3]. Biodiesel contains insignificant amounts of sulphur and it is biodegradable, non-toxic, and renewable [2,4]. It has a correlation with sustainable development, energy conservation, management, efficiency and environmental preservation [2]. Nevertheless, cold-flow properties, NO_x emissions, oxidative stability, and costs are issues that have to be overcome [5,6]. Moreover, the economical utilization of glycerin, the main co-product of biodiesel, is also an important aspect for the feasible commercialization of this alternative fuel [7].

Biodiesel is basically composed of fatty acid mono-alkyl esters, which are in general obtained through the base-catalyzed transesterification reaction of vegetable oils or animal fats with a short chain alcohol, such as methanol or ethanol [4,8]. It is mostly used in mixtures with fossil diesel but it can also be employed in its pure state. The designation of pure biodiesel is B100 and the mixtures are named by the BXX abbreviation, which indicates the B100 volume (in percent) in the mixture with diesel. Consequently, B2 is constituted by 2% of B100, and 98% of diesel; B5 by 5% of B100 and 95% of diesel [4]. According to the Brazilian law 11.097/2005 of 01/13/2005, B2 became mandatory in 2008, and so will be B5 in 2013. In USA, the utilization of B20 has increased in the last few years [9]. Therefore, the determination of blend levels is one important issue to the quality control of biodiesel due to the increase of biodiesel–diesel blends commercialization [10].

NMR is a versatile spectroscopy method that has become one of the most powerful techniques to elucidate the structure of chemical compounds. In fact, ^{1}H NMR is frequently used to follow the biodiesel synthesis [11–16] and its correlation with NIR was also described for the determination of soybean biodiesel in diesel [9]. As reported by Knothe [9], the peaks of methyl ester moiety (3.6–3.7 ppm), the clusters of peaks (0.8–3.0 ppm) from methylene and terminal methyl protons of the hydrocarbon moieties in biodiesel and diesel, and the olefin protons (5.3–5.4 ppm) in biodiesel were used in order to determine the blend levels.

In the present work, we investigated the usefulness of ^{1}H NMR to determine the blend level of any methyl biodiesel in diesel fuels from different sources. For that, we chose two biodiesel samples (from soybean and castor oils) and three diesel fuels, which were used to prepare biodiesel–diesel blends in the 0.5–30% (v/v) range of concentration and were analyzed by ^{1}H NMR. Biodiesel–diesel blends with known concentrations and B2 commercial samples were also analyzed by ^{1}H NMR to evaluate the effectiveness of ^{1}H NMR for such analyses.

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2. Materials and methods

Methyl biodiesel from castor and soybean oils were kindly provided by Dr. Antonio Moreira dos Santos from São Carlos Engineering School of University of São Paulo (EESC-USP). Nine samples of commercial diesel were acquired in different gas stations in Brazil (São Paulo, Minas Gerais and Tocantins states, as well as Federal District). Both biodiesel and diesel samples were previously ana-

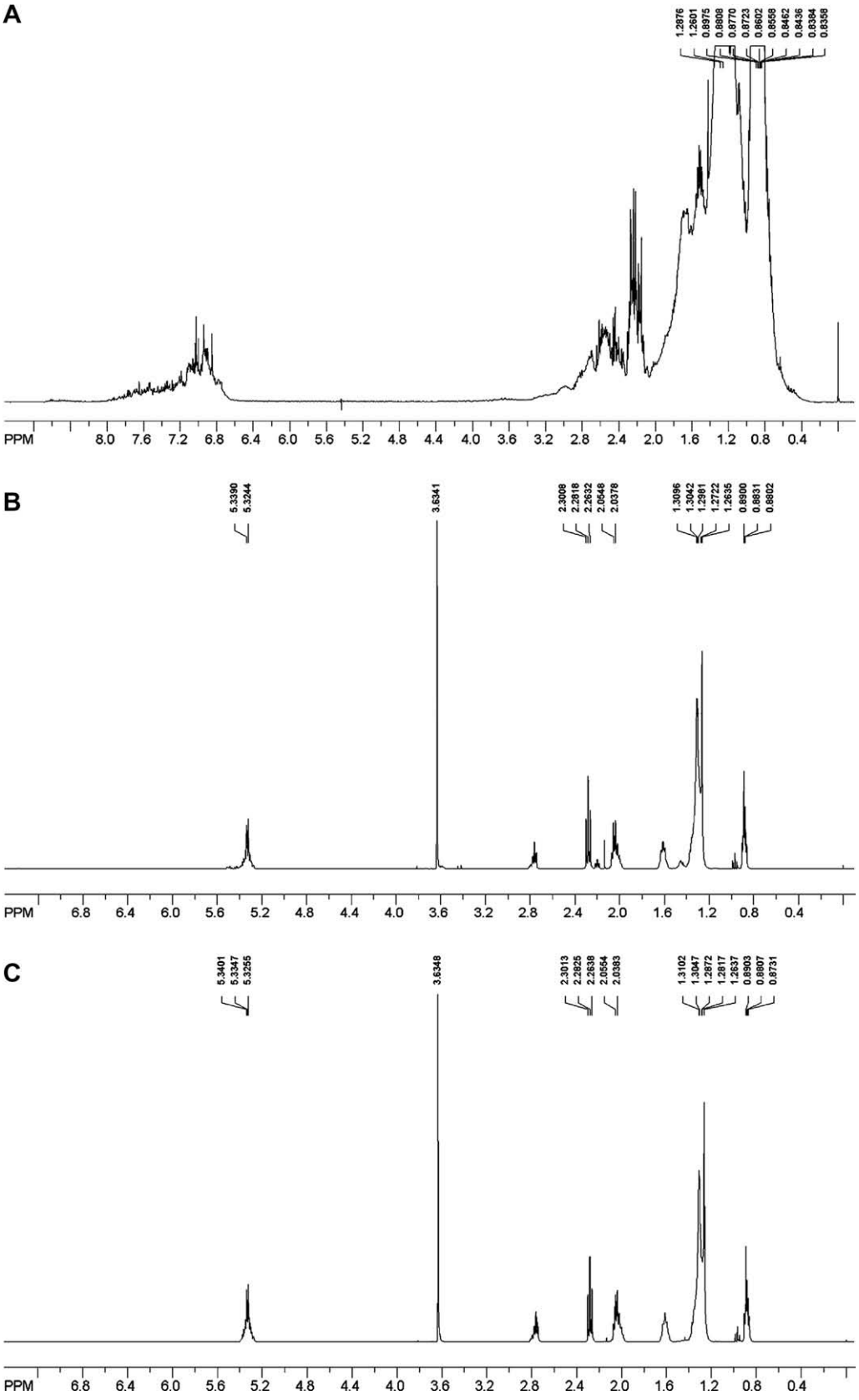

Fig. 1. ^{1}H NMR spectra of diesel - source 1 (A) methyl biodiesel from castor oil (B) and methyl biodiesel from soybean oil (C).