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## Analysis of biodiesel yield by nuclear magnetic resonance spectroscopy: an accurate method for truly quantitative test.

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**Abstract** – Transesterification of vegetable oils is the best way to obtain the so called biodiesel. Nuclear magnetic resonance spectroscopy (NMR) was used in this work to perform a fast and accurate analysis of the yield of the transesterification reaction. The analysis routine was optimized, in order to obtain the most exact essay. It was shown that a pulse width of 10.5 micro-seconds and delay interval inter-pulses of at least 10 seconds are necessary to observe true values. By using faster analysis routine, a value from 5 to 10% lower was observed.

Currently, much attention has been paid in the research of agricultural derived fuels, specially ethanol and biodiesel. Both of them have advantages compared with petroleum based corresponding fuels, especially because they are less pollutants and renewable. In Brazil, the well established ethanol industry shows the great potential of that country in producing vegetable derived fuels. The big arable area and weather characteristics can make Brazil a world leader in agricultural based fuels.

Biodiesel is currently prepared by the transesterification reaction of vegetable oils or animal fats. In this process, the tri-glyceride reacts with an alcohol and generates an ester, called biodiesel, and glycerol. In order to optimize the process, it is necessary to have analytical methods that allow a fast and accurate essay to determine the conversion degree in the reaction medium. Ordinarily, techniques like chromatography, near infrared spectroscopy, Raman spectroscopy and <sup>1</sup>H-NMR spectroscopy [1].

Nuclear magnetic resonance spectroscopy needs a very simple sample preparation, only dissolution in deuterated chloroform, and gives qualitative and quantitative information about the sample, like the conversion degree of oil into biodiesel. Moreover, NMR is a fast technique compared with chromatographic methods, allowing one analysis on each ten minutes, approximately.

The aim of this work was develop a routine of NMR analysis that allows a fast and accurate analysis of the reaction medium of transesterification process. For this purpose, mixtures of corn oil and biodiesel with known composition were analyzed, as well as pure samples. It was utilized a spectrometer Varian Inova 400, with a 9.4T magnet, corresponding to 400MHz to <sup>1</sup>H.

In the first step, 90° pulse was determined by varying the pulse width. It was verified that this pulse width is 10.5 micro-seconds for both compounds. After this, by the inversion-recovery method, the longitudinal relaxation time (T<sub>1</sub>) was determined as being 0.47s and 2.35s for corn oil and biodiesel, respectively. These values are important in making quantitative analysis. It is known that in order to obtain a truly quantitative analysis; the delay time between two subsequent pulses must be equal five times the longitudinal relaxation time. If a smaller time interval is used, the tendency is a decrease in the signal of the substance with biggest T<sub>1</sub> value, in other words, the measured conversion degree will be smaller than the true value.

In order to verify the method, mixtures of biodiesel and corn oil with known compositions were analyzed, with an inter-pulse delay of 15s, bigger than the smallest possible value of 11.75s, five times biodiesel's T<sub>1</sub>. In this case, the known and measured values agreed with a linear correlation equal 0.996, indicating that the method is very satisfactory in doing this measurements. When an inter-pulse delay of just 1s was used, the conversion degree measured was from 5 to 10% smaller than the true value.

It was shown that nuclear magnetic resonance is a good tool in analyzing the conversion degree of the transesterifications reaction. It provides a fast and very accurate result. However, an adequate analyses routine must be used in order to obtain truly quantitative measurements.

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