^{1}H NMR Spectroscopy and Multiple Linear Regression for Prediction of Quantitative Structure-Property Relationships (QSPR) of Diesel Samples

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Abstract: *The most important properties of diesel that determine the quality of this fuel are density, viscosity, cetane number, cetane index, sulfur content, and low-temperature flow properties such as pour point or cold filter plugging point. The cetane number and the cetane index are very important properties because they provide an indication of ignition quality. These properties are primarily dependent upon the composition of diesel, which consists of thousands of individual components such as aromatics, paraffins (normal, branched, cyclic), olefins and oxygenated compounds. There are some standard methods (ASTM, IP OR DIN) to monitoring specifications but all of them are time-consuming and laborious. NMR spectroscopy and multiple linear regression analysis have also been used for predicting fuel properties. In the present work, cetane index and density obtained with NMR data from Brazilian diesel samples were determined directly using proton NMR spectral intensities and were compared with a standard method. NMR data has shown the feasibility of predicting properties of diesel from a single proton spectrum in a very short time though the developed model equations are not universal. Thus, some corrections should be introduced by redoing the multiple regression analysis, and a higher number of samples should be included in the model data set.*

The most important properties of diesel that determine its quality are density, viscosity, cetane number, cetane index, sulfur content, and low-temperature flow properties such as pour point or cold filter plugging point (CFPP).[1,2]

Concerning density, an optimum value is desired because of the effects on engine performance in terms of engine power output and exhaust gas emissions. The cetane number and the cetane index are very important properties because they provide an indication of ignition quality. Similarly, sulfur content has a direct impact on the gas emissions and corrosion of the engine. Thus, all these properties should be measured and controlled so that parameters may be established for defining the quality of this fuel. Such properties are primarily dependent upon the composition of diesel, which consists of thousands of individual components such as aromatics, paraffins (normal, branched, cyclic), olefins and oxygenated compounds.

There are some standard methods (ASTM, IP OR DIN) to monitor specifications but all of them are time-consuming and laborious. Also, many reports describe methods for establishing relationships between properties and composition and for predicting the fuel properties NMR spectroscopy has been also used for predicting fuel properties. However, the ^{1}H NMR spectra of diesel are complex due to the different kinds of hydrocarbons and molecular structures. As these spectra have overlapping signals, and it is not possible to correlate each signal to a specific molecular

structure, they should be divided into regions. These regions are correlated with structural groups (aromatics, naphthenes and paraffins) and then with physicochemical properties.

In the present work, cetane index and density of Brazilian diesel samples from different distribution stations at the Espirito Santo state were determined by directly using proton NMR spectral intensities. The Kapur[3] equations were employed, and the results were compared with those from a standard method based on IR absorption measurement in the range of 2.7-15.4μ. A Fourier Transform spectrometer (IROX DIESEL) obtained by Fuel Monitoring Laboratory from PUC University was used.

For multiple linear regression analysis, the normalized integral intensities of the regions or their combinations were used as "independent variables" and correlated with various properties of the diesel samples, named "dependent variables".

All diesel samples under study were commercial products. They were prepared at 10% in $CDCl_3$ v/v, and the spectra were acquired in a Mercury 200 at ambient temperature. The parameters used for recording free induction decay (FID) signals were the following: ^1H frequency: 200.057 MHz; at: 4s; sw: 4001.6; d1: 0s; nt: 128; pw: 45°; fn: 65536 ; lb:0.3.

The TMS signal was used as reference in 0ppm followed by a second reference in 7.18ppm. The integrals obtained were normalized to a value of 1000. The total time of NMR measurement, including sample and spectrometer preparation, acquiring FID, processing and integration, was typically 30 min per sample.? Table 1 shows some results for cetane index and density.

Table 1. Cetane index and density for Brazilian diesels

Sample	Cetane number			Density (20°C)		
	predicted NMR	measured IROX	difference (%)	predicted NMR	measured IROX	difference (%)
DC 1480/02	45.4	48	5.4	849.6	849.1	0.1
DC 1487/02	46.0	46	0	861.9	854.5	0.9
DC 1491/02	46.2	48	3.7	845.9	846.9	0.1
DC 1499/02	45.7	48	4.8	837.1	841.2	0.5
DC 502/02	45.8	49	6.5	832.9	840.3	0.9

According to these results, good correlation is found for density, but not for cetane index when compared with IROX DIESEL. Indeed, NMR data have shown the feasibility of predicting properties of diesel from a single proton spectrum in a very short time. However, the developed model equations are not universal, and some corrections should be introduced by redoing the multiple regression analysis. Also, a higher number of samples should be included in the model data set.

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