Nuclear Magnetic Resonance (NMR) Spectroscopy as a Tool for Functional Group Analysis of Real Fuels

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1. INTRODUCTION

Over the past decade, dwindling fossil fuel reserves and environmental concerns have led to a surge in the development and implementation of synthetic alternatives to conventional petroleum derived fuels.[1] For aviation, currently, the use of synthetic paraffinic kerosenes (SPKs), such as Shell-SPK, hydro treated renewable Jet–SPK (HRJ-SPK) and alcohol to jet SPK (ATJ-SPK), in conjunction with archetypal jet fuels (*e.g.* Jet-A) as 'drop-ins' to form blends is being extensively investigated. Presently, the blending ratio is limited to 50 vol% by the revised ASTM protocol D7566, in part, due to a lack of understanding of how these synthetic fuels behave in the aviation turbine combustion process. Currently, engineering performance indicators such as research octane number (RON), motor octane number (MON), cetane number (CN) *etc.* are the legal metrics that relate fuel quality to device operating characteristics. These parameters are measured by approved experimental test procedures. However, alternative fuels, and even their blends, can lie outside the historical experience-base that exists for petroleum-derived gasoline, diesel and aviation fuels. There is now concern that this can manifest in a weakening of the effectiveness of the existing correlations relating the engine performance to the fuel performance indicator as both the fuel identity and the engine design change.[1] Therefore, it is important that new techniques that are capable of reliably characterising fuels emerge. To achieve this, we must understand the fundamental chemical processes that dictate the behaviour of fuels during combustion, rather than simply measuring the outcome (*i.e.* RON, MON, CN *etc*.). It follows that an accurate description of the chemical composition of these fuels on a molecular level will be required for this purpose.

In general, liquid transportation fuels are highly complex mixtures, compromised of an array of hydrocarbon molecules, with biofuels in particular adding a host of oxygenated molecules to the mixture. This complexity severely hinders the precise analysis and characterisation on a molecule-by-molecule basis of such fluids. However, if we consider that all of these molecules are constructed from the same, discrete, pallet of functional groups (*i.e.* -CH_3, -CH_2, CH *etc*.), their analysis is markedly simplified. Previous work by Won *et al.* [2] has shown that global combustion properties of fuel mixtures can accurately be described by the distribution of these functional groups within the fuel. Consequently, if we can quantify this distribution within a given mixture, we can begin to model and predict a range of properties of the fuel. As hydrocarbons form the main constituents of these fuels, quantitative high resolution ^{1}H or ^{13}C nuclear magnetic resonance (NMR) spectroscopy is ideally placed to provide such analyses. NMR spectroscopy is most often applied to the elucidation of single molecule structures, where signals in the NMR spectrum can be assigned to individual ^{1}H or ^{13}C nuclei within a given molecule. This is possible because each of these nuclei experience their own, unique, chemical shift depending on their local magnetic

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environment. For example, -CH_3 groups can be distinguished from -CH_2 groups as these ^{1}H and ^{13}C nuclei resonate in different regions of the spectrum. Furthermore, under the appropriate conditions, the signal observed during the NMR experiment is fully quantitative. We have previously demonstrated that by integrating regions of the NMR spectrum, as opposed to individual signals, we can describe the functional group composition of a variety of fuel mixtures. The purpose of this contribution is to outline the spectroscopic toolbox available in order to maximise the fidelity of these measurements and furthermore, highlight how this can be used to predict properties of real fuels.

EXPERIMENTAL

		Mole % Carbon					
		Aromatic C*H*	C_6H_5-C*H₂*	Paraffinic C*H*	Paraffinic C*H₂*	Paraffinic C*H₂*	Quaternary
TRF	Known	19.7	4.55	2.51	37.77	29.52	5.95
	NMR Derived	19.3	3.88	3.16	37.46	29.16	7.04
	Difference	0.4	0.67	-0.65	0.31	0.36	-1.09
TRF + MCH	Known	12.63	2.92	4.98	47.71	27.6	4.17
	NMR Derived	12.32	2.46	3.61	46.01	29.5	6.08
	Difference	0.31	0.46	1.37	1.7	-1.9	-1.91

Table 1 - A comparison of the known mole % carbon of each defined functional group with that determined by NMR Spectroscopy for TRF and TRF + MCH

In order to accurately predict the properties of a fuel, we require an accurate description of the functional group composition of the mixture. Experimentally, this can be interpreted that we require the following. Firstly, the integral measured for a given functional group must accurately reflect the abundance of that functional group in the mixture *i.e.* the observed signals must be quantitative. Secondly, for any given peak, we must be able to accurately determine the functional groups which contribute to the signal.[3] The latter of these can be addressed by utilising the full range of NMR experiments available and is discussed in more detail below. In order to ensure that the NMR spectra obtained from experiment can be interpreted quantitatively, careful consideration must be given to the parameters used to acquire the data. This is especially pertinent to the recycle delay time, D_1 (the time between scans). Upon placing the sample into the magnet within the NMR spectrometer, a bulk magnetisation vector (M_0) is generated along the z-axis. This magnetisation is then perturbed into the *xy* plane by a 90° radio frequency pulse and allowed to relax. The relaxation is monitored, ultimately giving rise to the observed NMR signal. A typical ^{1}H NMR experiment consists of multiple pulse-observation sequences (scans) and the relaxation time of a ^{1}H nucleus is < 10 seconds. In order for the observed response to relay quantitative data with respect to the sample, it is critical that the bulk magnetisation vector returns to its maximum, M_0, in between scans. If insufficient time is left between scans such that M_0 does not reach its maximum before the next scan *i.e.* D_1 is too short, the integrals measured in the final spectrum are not quantitative.[3] The recycle delay time is a parameter that is frequently and unnecessarily overlooked in the literature, consequently, many of the reported

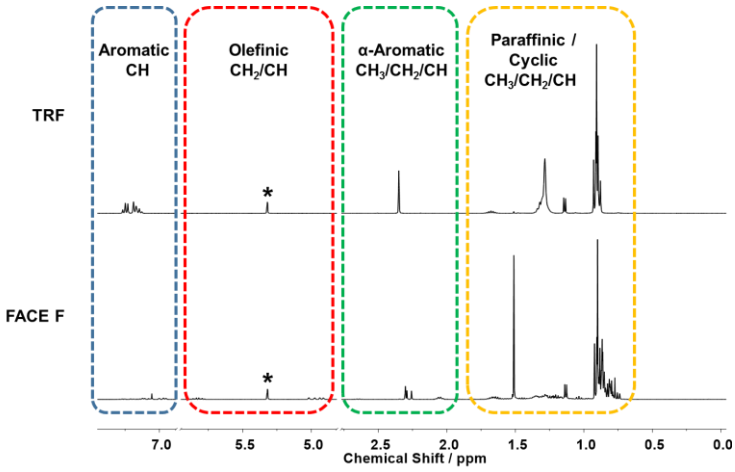

Figure 1- Top: ^{1}H NMR Spectrum of TRF (n-heptane, iso-octane and toluene; 0.50/0.22/0.28) Bottom: ^{1}H NMR Spectrum of FACE F. Both Spectra were collected in CD_2Cl_2 (*) at 400 MHz.

measurements are not truly quantitative.[4] By utilising a delay time of 60 seconds (*c.f.* 5 seconds) with a 90° pulse, we ensured that all of our measurements are fully quantitative.

RESULTS AND DISCUSSION

With the aim of evaluating the fidelity of the NMR method as a means of determining the functional group composition of real fuels, we first studied several primary reference fuels. We have shown that by using only ^{1}H NMR (Figure 1), the mole % carbon of the various functional groups in the toluene reference fuel (TRF, *n*-heptane, *iso*-octane and toluene; 0.50/0.22/0.28) can be measured with a high degree of accuracy (Table 1). This was possible because there was no signal overlap between differing functional groups within these molecules in the NMR spectrum, therefore, we observed discrete signals for each of them. Importantly, this demonstrated that quantitative NMR spectroscopy can be used to describe fuel mixtures in terms of their functional groups was valid.

We next analysed TRF + methyl cyclohexane (*n*-heptane/ *iso*-octane/ toluene and methyl cyclohexane, 0.42/0.20/0.22/0.16) utilising the same methodology. However, the ^{1}H NMR spectrum was not straightforward to interpret as there was significant overlap between the *iso*-octane CH with CH_2 signals from methyl cyclohexane, and between the methyl cyclohexane CH with the *n*-heptane CH_2 signals. This was confirmed using heteronuclear single quantum coherence spectroscopy (HSQC) (Figure 2). In a HSQC spectrum, the ^{1}H spectrum is shown along the *x*-axis while the ^{13}C spectrum is shown along the *y*-axis. In the resulting 2-dimensional spectrum, peaks are observed for any ^{1}H atom covalently bonded to a ^{13}C atom. Importantly, while the observed range of resonances in a ^{1}H spectrum is narrow (~15 ppm), the ^{13}C spectrum is much wider (~200 ppm). Consequently, analysis of the HSQC spectrum allows for the resolution of overlapping ^{1}H signals through correlation with the corresponding ^{13}C signal. Furthermore, the multiplicity of the spin during the experiment can be used to edit the CH_3 and CH signals so that they can be distinguished from the CH_2 signals, which appear then as an opposite phase. Therefore, by using the HSQC experiment, we are able to determine the functional groups that contribute to the signals in the ^{1}H NMR spectrum. Presently however, the signals in the HSQC spectrum cannot be interpreted quantitatively. Therefore, either ^{1}H or ^{13}C NMR must be used as a complementary technique to provide a quantitative functional group analysis. The major drawback of quantitative ^{13}C NMR is that the spectrum takes significantly more time to acquire than the ^{1}H counterpart. This is due both to the longer relaxation time of the ^{13}C nucleus as well as the lower natural abundance, which reduces the sensitivity of the technique. For TRF + methyl cyclohexane, paraffinic CH and CH_2 groups could not be accurately quantified by ^{1}H NMR. Instead, quantitative ^{13}C NMR was used to assign the functional groups present in the TRF + methyl cyclohexane mixture. This was readily implemented because TRF + methyl cyclohexane is composed of four major components.

Our experiments on TRF + methyl cyclohexane showed HSQC spectroscopy to be a powerful tool for identifying overlapping signals in ^{1}H NMR. Therefore, we next investigated how this may be applied to real fuel samples.

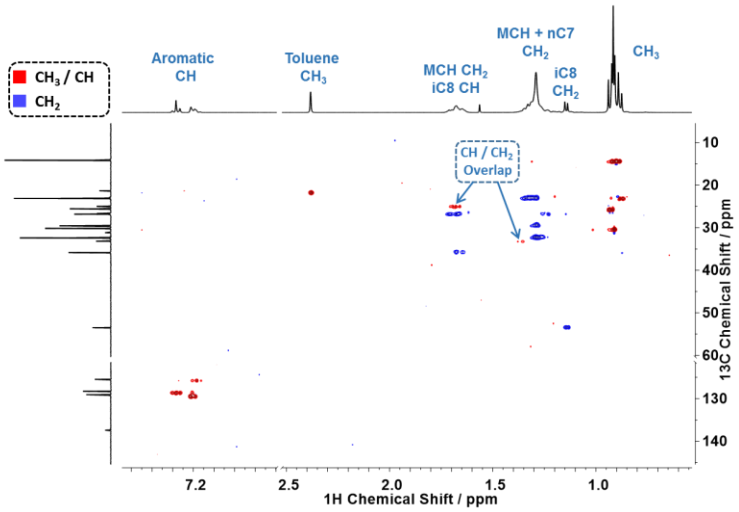

Figure 2 - HSQC Spectrum of TRF + MCH (n-heptane, iso-octane, toluene and methyl cyclohexane, 0.42/0.20/0.22/0.16). $CDCl_3$, 400 MHz.

Based on the experiments discussed above, we have developed a general strategy for the functional group analysis of more complex fuel mixtures. This strategy was tested on exemplar complex fuels such as the FACE gasolines and alternative jet fuels. This paper demonstrates that this methodology is both qualitatively and quantitatively accurate for a very broad range of functional definitions. Firstly, the ^{1}H NMR spectra collected are reliably quantitative. Secondly, we are readily available to identify signal overlap. It is important to note that each real fuel may present a subtly different interpretive challenge in translating the obtained spectra into a functional group identification compared to the analysis of the reference fuels. This is due to the fact the real fuels consist of a significantly higher number of components. Therefore we must consider regions of the ^{1}H spectrum, as opposed to individual signals. In this paper, we demonstrate that HSQC spectroscopy can be used to define the regions of the ^{1}H NMR spectrum which correspond to the quantitative presence of particular functional groups, with little ambiguity. Additionally, we have shown that by making this assignment on a fuel-by-fuel basis, we can significantly improve the fidelity of the technique. For FACE gasolines, we have been able to compare our NMR results with those previously reported from detailed hydrocarbon analysis (DHA). While in general there is a good agreement between the NMR data and DHA, we have found several noteworthy discrepancies, for which it is very difficult to otherwise interpret the NMR data. This highlights the utility and sensitivity of NMR as a technique for the analysis of real fuels. Finally, we show several examples of how this functional group information can be used to predict detailed combustion properties for a selection of real fuels to very high fidelity and accuracy, *e.g.* ignition delay, laminar burning velocity and the maximum soot volume fraction.

CONCLUSION

The current experience-base underpinning our understanding of the combustion processes of petroleum-based gasoline, aviation and diesel fuels does not extend satisfactorily to alternative bio-fuels. Therefore, it is imperative that new techniques are developed which further our understanding of these materials. We have shown that NMR spectroscopy is an effective technique for formulating functional group descriptions of fuel mixtures. In considering fuels as a distribution of functional groups, as opposed to a distribution of molecules (*e.g.* DHA), we have significantly reduced the complexity associated with their characterisation. We have developed models that are capable of predicting key fuel properties using these descriptions of the functional group distributions in fuels. We

envisage these, and similar models, to find utility in guiding the wide scale implementation of alternative fuels and their blends.

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