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A Review of Applications of NMR Spectroscopy in the Petroleum Industry

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Nuclear Magnetic Resonance (NMR) spectroscopy has been applied to petroleum chemistry since the first days of its commercial existence. Petroleum companies such as Texaco and Marathon were among the first to use ^1H NMR to provide detailed information on the hydrocarbon chemistry of raw petroleum and its various products. The literature associated with almost 60 years of applications is large and cannot be accommodated in a single book chapter. However, there have been numerous reviews of petroleum NMR applications as well as a number of excellent articles and book chapters that cover the literature up to the early 1990s [1-6]. Since then, there have been no definitive books or review chapters published though the utilization of NMR throughout the petroleum chemistry research arena has been widespread. In this chapter we will concentrate on the applications that have been developed over the past two decades and how NMR technology has developed to encompass the entire scope of petroleum chemistry from down-hole exploration tools to online refinery process analysis.

NMR continues to be an exceedingly useful tool to study the proton and carbon chemistry of many petroleum derived products and raw materials. We will discuss liquid and solid-state NMR applications and also the application of NMR to raw materials previously not considered as petroleum. In this period of alternative energy awareness it is important to include many alternative energy applications such as coal-to-liquids, gas-to-liquids, bio-fuels, biomass conversion, etc. The synthetic fuel products produced by these processes will become increasingly the focus of research and analysis and NMR offers a unique perspective on the chemistry of these products. Rather than go into a detailed description of NMR spectroscopy theory a brief description of current NMR technology will be provided along with an overview of how the various technology platforms are being used to provide detailed physical and chemical information on a broad range of petroleum related materials.

NMR Spectroscopy

NMR is a radiofrequency spectroscopy that is based on the electromagnetic manipulation of nuclear spins. As a fall-out from the development of radar technology in World War II scientists utilized radio frequency (RF) spectrometers and permanent magnet systems to confirm the presence of nuclear magnetic moments and in doing so produced a spectroscopy that has become one of the principal tools for hydrocarbon chemical analysis. Though many nuclei in the periodic table are NMR active, the petroleum analysis field is dominated by the application to ^1H and ^{13}C nuclei. Other nuclei of interest to petroleum chemists, particularly in the catalytic research area, are ^2H , ^{29}Si , ^{27}Al , ^{31}P , ^{11}B , ^{23}Na , and ^{15}N .

The physical basis of the NMR technique is the interaction of nuclear magnetic moment of certain nuclei with applied magnetic fields. The nuclear magnetism arises from the fact that the nucleus contains an odd number of nucleons (protons and neutrons). When these nuclei are placed in a strong magnetic field, provided by a superconducting solenoid magnet or a permanent magnet, each nuclear spin aligns with the applied field and precesses around it with a unique frequency, called the Larmor frequency, directly proportional to the applied field. If the precessing spins are irradiated at a resonance frequency corresponding to their particular precession frequency (radiofrequency energy range - 100 kHz to 900 MHz depending on the

magnetic field strength) there is a resonant adsorption of the applied radiofrequency energy. This energy adsorption, at the Larmor frequency, causes the magnetic moments of the nucleus under observation to move out of alignment with the applied external magnetic field and when the radiofrequency pulse is turned off the spins are restored to equilibrium alignment.

The rates at which this realignment with the applied magnetic field occurs are referred to as relaxation times [7]. The rate at which the spins align along the magnetic field axis is referred to as spin-lattice relaxation time (T_1) and the rate at which spin coherence is lost in the perpendicular plane of the laboratory magnetic field is referred to as the spin-spin relaxation time (T_2). The values of these relaxation times contain inherent information about the interactions of the nuclear spins with their physical and chemical environment. Differences in T_1 and T_2 are indicative of molecular structure, chemistry, and intermolecular interactions. Relative differences in the absolute value and the distribution of T_1 or T_2 values can be utilized to great advantage when observing NMR-active nuclei in molecules present in a complex mixture such as petroleum related materials. Of note are the T_1 and T_2 differences observed between hydrocarbons and water due to the higher diffusion rates of water. Also of interest are the shorter proton T_2 times found in asphaltenes and heavy residue samples due to the high molecular weight and paramagnetic content with metals such as vanadium being present.

The precession of the spins as they re-align with the applied magnetic field generates a voltage in the NMR probe coil within which the sample is situated. The ^1H and ^{13}C nuclei in different chemical environments on a petroleum derived molecule have different electronic environments that affect the precession frequency of the nucleus which leads to a dispersion of signals that yield chemical information about the proton producing that signal. These electronically induced signal dispersions are called chemical shifts and they allow chemists to observe and quantify various chemical functionalities and determine absolute molecular structure. The voltage generated in the coil contains a dispersion of frequencies related to the chemical makeup of the sample. This voltage is collected by the NMR spectrometer through an analog-to-digital converter and stored as the raw data of the NMR analysis. This stored signal is called the free induction decay (FID). In low field (Time Domain) TD-NMR the FID is typically the final result of the experiment. In high field, high-resolution NMR the Fourier transformation of the FID yields a frequency spectrum that contains resonance peaks corresponding to protons or carbons in different chemical environments. The areas under the peaks are quantitative to the amount of ^1H or ^{13}C present as that chemical type. Integration of the peaks and subsequent manipulations and calculations yield quantitative proton and carbon type analyses as well as average molecule representations.

Further description of the NMR phenomenon and the experimental developments in multinuclear and multidimensional NMR are beyond the scope of this review but can be found in the extensive NMR literature [8-11]. Tables I and II show the basic chemical shifts observed for ^1H and ^{13}C NMR nuclei, respectively.

NMR Technology Background

It is important to briefly describe the NMR technologies that are currently available for the analyst to study petroleum chemistry and production processes. Contrary to conventional perception NMR technology is robust, relatively easy to execute, and can be relatively inexpensive to implement. While NMR manufacturers and users have always driven the technology to higher and higher magnetic field strengths requiring superconducting magnet technologies, for much of petroleum chemistry extra high magnetic field strengths are overkill

due to the complex mixture nature of petroleum samples which means the spectra consist many hundreds if not thousands of unresolved peaks. Critical and complete information can be

Table I: ^1H Chemical shift ranges for various proton types present in petroleum

Description	Start (ppm)	End (ppm)
Triaromatic CH	9	8
Diaromatic CH	8	7.25
Monoaromatic CH	7.25	6.4
Total Aromatic H	9	6.4
Olefinic CH/CH ₂	6.4	4.5
CH ₂ Alpha to 2 Aromatics	4.5	3.4
Alpha-CH	3.4	2.8
Alpha-CH ₂	2.8	2.4
Alpha-CH ₃	2.4	2
Beta Paraffinic CH/CH ₂ and Naphthenic CH/CH ₂	2	1.28
Epsilon CH ₂ (Long Chain)	1.28	1.24
Paraffinic CH ₂ and Beta CH ₃	1.24	1
CH ₃ (Gamma)	0.95	0.5
Total Aliphatic H	4.5	0.5

Table II : ^{13}C chemical shift ranges for carbon types present in petroleum

Description	start (ppm)	end (ppm)
Carbonyl	215	190
Carboxyl	190	160
Phenolic Carbon	160	150
CH ₂ /CH Substituted Aromatic Carbon	150	138
Naphthene Substituted Aromatic Carbon	138	135
Methyl Substituted Aromatic Carbon	135	133
Internal Aromatic Carbon	133	129.5
Internal + Protonated Aromatic Carbon	129.5	124
Protonated Aromatic Carbon	124	120
Heteroaromatic Carbon	120	90
Methine Carbon	60	37
Methylene Carbon	37	22.5
Alpha Methyl Carbon	22.5	20
Methyl Carbon	20	0.5

obtained for lower magnetic field instruments operating at or below 400 MHz. In fact, for solid-state ^{13}C NMR operating at frequencies at or below 200 MHz has particular advantages that will be described later. Developments in permanent magnet technology, spectrometer design, and materials have also enabled the development of compact NMR systems that can be utilized for

online process control or for mobile NMR analysis. There are several types of NMR instrumentation that are utilized in petroleum chemistry studies and each will be described briefly in the coming sections along with applications which are performed with each type.

Low Resolution NMR - also known as Time-Domain NMR (TD-NMR).

These instruments are the smallest, lowest cost implementation of NMR technology and are serviced by several commercial companies such as Bruker, Oxford Instruments, Magritek, and Process NMR Associates. They are based on small permanent magnet systems that produce relatively inhomogeneous fields at strengths of 0.04-1.47 Tesla (corresponding to ^1H resonance frequencies of 2-60 MHz). Depending on the manufacturer and the applications desired the instrumentation costs between \$25-\$60K. The magnetic field produced by these small magnet systems is inhomogeneous and only very basic NMR data can be obtained related to total hydrogen content or relaxation times of protons in the sample. Relaxation times, T_1 and T_2 , are time constants that can be determined from multi-pulse NMR experiments that are related to molecular mobility, viscosity, and paramagnetic nuclear interactions. The relaxation times can also be used to determine water content in oil or oil content in water. Obviously, these parameters are of interest to petroleum chemists as these relaxation times can be attributed to chemical and physical properties of petroleum materials such as molecular size, asphaltene content, wax content, vanadium content of heavy ends, hydrogen content of all streams undergoing further processing, and water content of crude oils. Figure 1 shows a typical bench-top TD-NMR system. Typical NMR data produced by such a system is shown in Figure 2. Instruments of this type have been used extensively in down-hole tools operated by oil exploration and production companies. Excellent overviews of TD-NMR technology utilized for down-hole analysis have been published by these companies [12-13] and the patent literature is filled with new instrument designs and applications. Over the past decade developments in multi-pulse sequences and mathematical algorithms (such as one- and two-dimensional Laplace inversions) have allowed distributions of relaxation times to be determined as well as the correlation between T_1 and T_2 , or T_2 and diffusion coefficients[14-15]. These new developments have opened up new avenues of research to discern chemical and physical differences between petroleum samples.



Figure 1: Typical TD-NMR Bench-top Spectrometer operating at 20 MHz, comprises a digital spectrometer (left), which is USB connected to a small computer. The 10 mm magnet system (right) weighs 8.5 kg and is 16x16x16 cm in dimension.

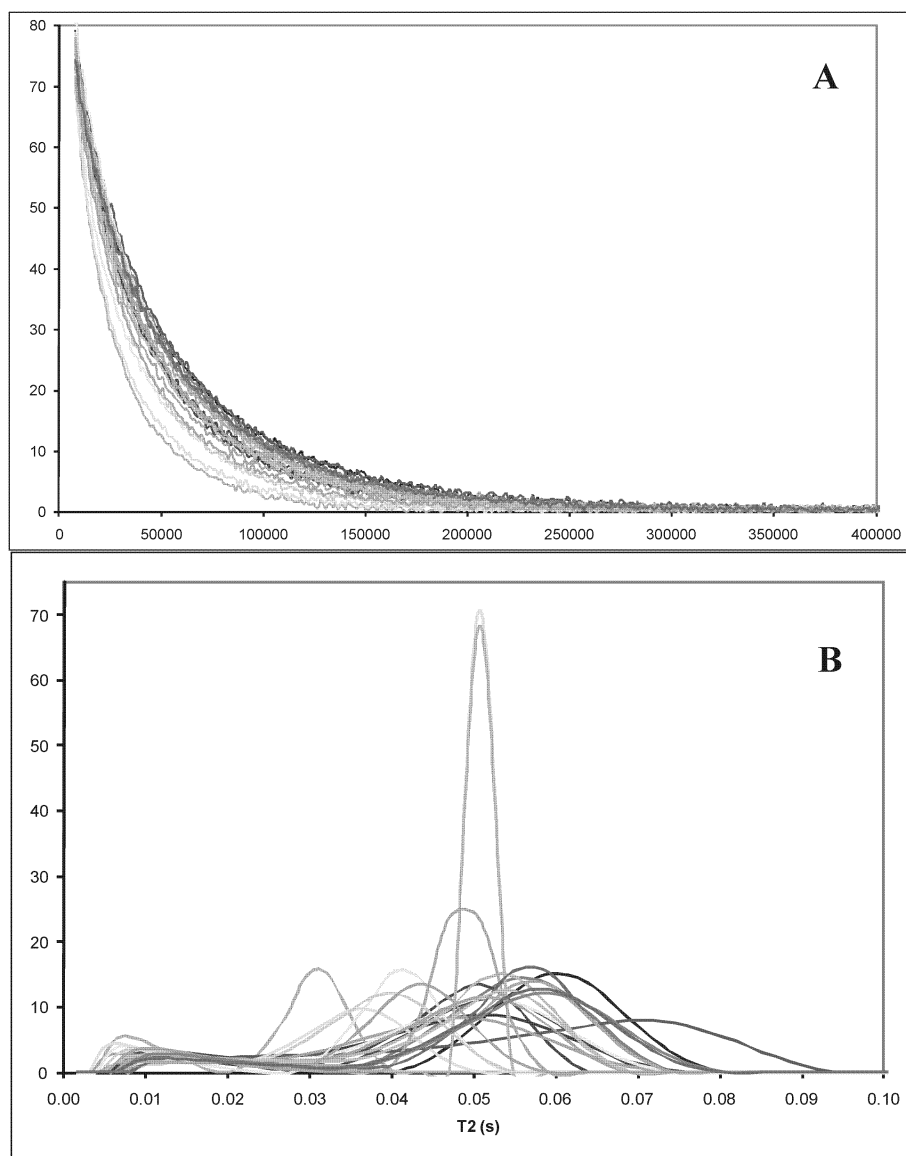


Figure 2: (A) T_2 Relaxation Curves (A) from CPMG experiments on a 20 MHz TD-NMR instrument, (B) Calculated T_2 Distributions obtained from inverse Laplace transformation, for fluid catalytic cracker (FCC) Feeds showing differences in heavy/light component concentrations as well as viscosity and paramagnetic content.

High Resolution NMR at Low Magnetic Fields – Process NMR Instrumentation

This instrumentation was developed in the 1990's and is based on arrays of NdFeB permanent magnets that allow for the production of an intermediate magnetic field strength (1.47T), high basic field homogeneity, and tight magnet temperature control. Mechanical and electrical shim systems allow high resolution NMR data to be obtained at a resolution of around 0.025 ppm and a ^1H resonance frequency of 60 MHz. Currently there is only one manufacturer of this type of NMR instrumentation. The magnet itself is fully shielded (has no external fringe field), is stable, and field mountable in chemical plants and refineries. Laboratory versions of the instrument cost around \$80,000 while field mountable systems cost \$200-\$450K depending on the application and the number of streams to be analyzed and their sample handling

requirements. On-line process control applications involve correlation of ^1H NMR spectral variability with chemical and physical properties of interest to engineers for continuous quality assessment or feed-forward and feed-back process control and optimization of refining processes. Laboratory configurations of the instrument are available for at-line analysis and laboratory based application development. A Qualion 60 MHz NMR system is shown in Figure 3. This spectrometer is available in a laboratory configuration and as a fully certified online instrument housed in an explosion-proof housing.

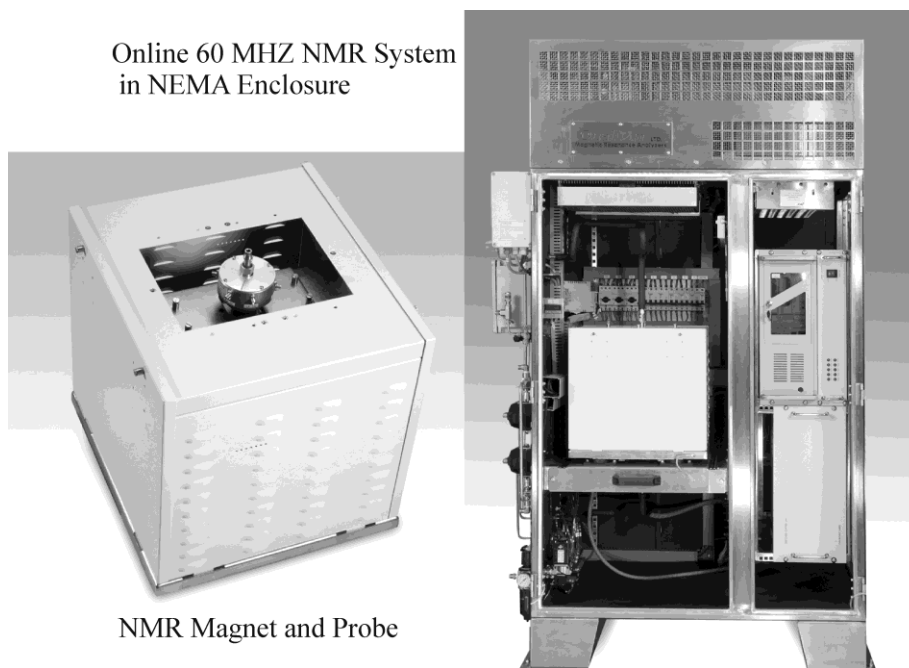


Figure 3: 60 MHz High Resolution Process NMR Spectrometer

Typical ^1H NMR spectra of finished gasoline product obtained on such an instrument are shown in Figure 4 with a description of the proton chemistry observed. At the present time there are approximately 25 process NMR systems online at various refineries around the world.

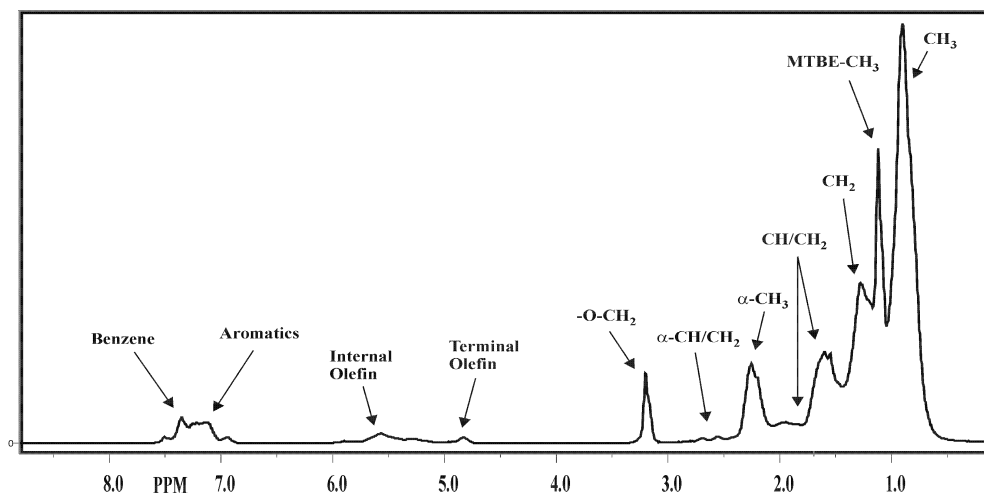


Figure 4: 60 MHz ^1H NMR of a finished gasoline obtained on a process NMR unit.

High Field (>200 MHz) NMR Instrumentation for Liquid and Solid-State NMR Analysis

The NMR instrumentation utilized to derive detailed multinuclear hydrocarbon information is based on superconducting magnet technologies that allow high resolution NMR to be obtained at resonance frequencies of 200 – 1000 MHz for ^1H , and 50 - 250 MHz for ^{13}C . The cryogenically cooled magnet solenoids are immersed in liquid helium (fill frequency of 3 months to 1 year) and further insulated by a jacket of liquid nitrogen (fill frequency 10-14 days). As the magnetic field strength increases, the instrument price rises from \$200K to as much as \$4,000K. With increasing magnetic field strength the experimental sensitivity increases meaning that experiments take less time and the spectral resolution improves yielding higher resolving power between different types of ^1H or ^{13}C chemistry. However, in the authors experience, instrumentation with field strengths of 7-11.7 Tesla (^1H resonances frequencies of 300-500 MHz) is adequate for most liquid-state petroleum applications as the higher resolving power at very high fields does not provide any extra discernment of detailed chemistry. In the case of solid-state NMR experiments (typically performing ^{13}C NMR analysis on carbonaceous materials) field strengths of 2.35-4.7 Tesla (^1H resonance frequency of 100-200 MHz) are optimal for quantitative and qualitative experiments as they allow slower magic angle spinning speeds to be used while avoiding overlap of aromatic carbon spinning sidebands with aliphatic carbons. Solid-state NMR instrumentation is essentially laboratory based and very few implementations of the technology have been applied anywhere outside the typical research center laboratory environment. As a comparison of the higher resolution of ^1H NMR experiments performed on superconducting NMR systems compared to the 60 MHz NMR systems several spectra of a diesel fuel is shown from the two spectrometers in Figure 5. More peaks are resolved at 300 MHz but the overall chemistry can be seen to be the same. Examples of the corresponding ^{13}C NMR spectra of gasoline and diesel are shown in Figure 6.

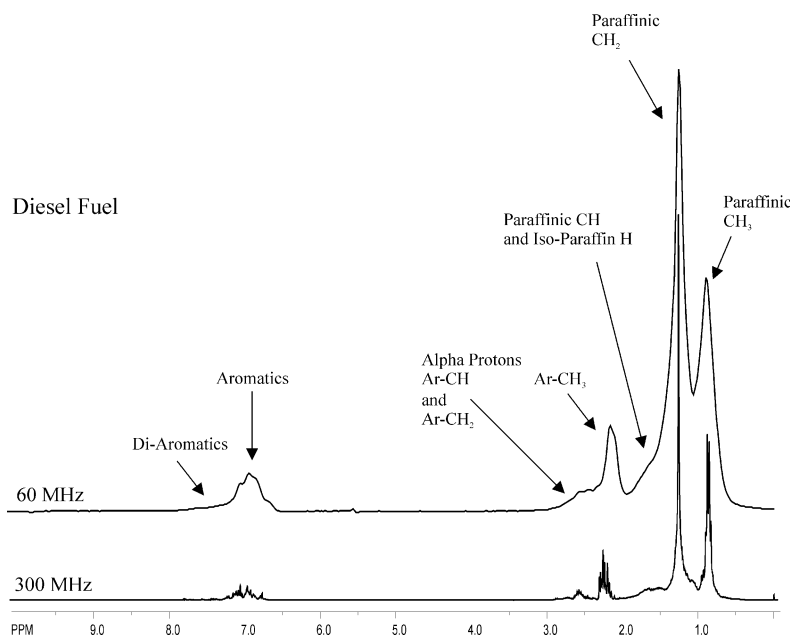


Figure 5: ^1H NMR of diesel fuel at different resonance frequencies - 60 MHz process NMR and 300 MHz superconducting NMR. Observed proton chemistry is indicated on the spectrum.

As described in previous reviews high resolution/high field NMR instrumentation also brings the entire range of NMR experiments to bear on petroleum chemistry. Multidimensional NMR experiments such as correlation spectroscopy (COSY) and hetero-nuclear correlation (HETCOR), can yield important information about ^1H - ^1H and ^1H - ^{13}C connectivity on petroleum molecules. This can be a very important tool to allow analysis and quantification of difficult to observe chemical functionality in NMR spectra of complex mixtures when NMR signals are highly overlapped. As an example, the identification of conjugated di-olefins is made possible by ^1H - ^1H COSY experiments where the olefin chemical shift range can be used to show the presence of protons that are adjacent to each other on conjugated olefin double bonds [16]. An example of a COSY result obtained on a coker naphtha is shown in Figure 7.

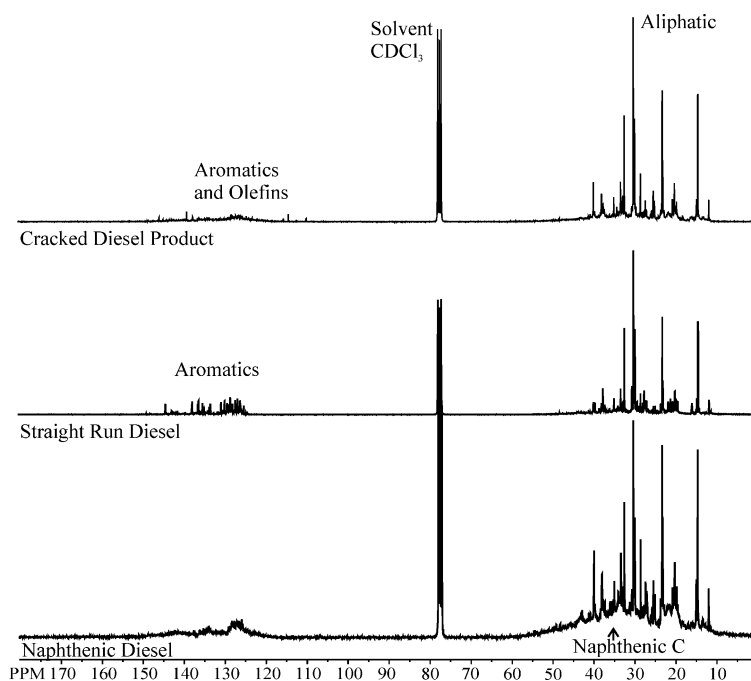


Figure 6: Quantitative ^{13}C NMR on 3 diesel fuels from different refinery processes. Cracked diesel shows the presence of olefinic carbon, straight run diesel showing a narrow distribution of aromatics, and naphthenic diesel showing a typical "hump" in the aliphatic carbon region. This "hump" can be quantified to calculate the fraction of naphthenic and paraffinic carbons.

Another useful ^1H - ^{13}C NMR technique known as Distortionless Enhancement by Polarization Transfer (DEPT), allows the discernment between methyl (CH_3), methylene (CH_2), methane (CH), and quaternary carbons. This technique is a vital component in the analysis of hydrocarbon branching, as well as providing data crucial to the calculation of aromatic ring system sizes and average molecule descriptions. An example of a DEPT NMR result is shown in Figure 8. Comparison of the signal intensity observed in the aromatic CH region of both the DEPT and quantitative ^{13}C spectra of heavy petroleum materials, compared to the signal intensity of methylenes in a known weight of a standard material (such as 1500 Mw Polyethyleneglycol (PEG-1500)), can allow the calculation of the mole fraction of bridgehead aromatic carbons to be calculated. This then facilitates the further calculation of average aromatic ring size and many average molecule parameters. In conjunction with carbon type analysis these average molecule parameters describe the petroleum product in such a way that

differences due to chemical and physical property variation as well as refinery processing can be observed and understood.

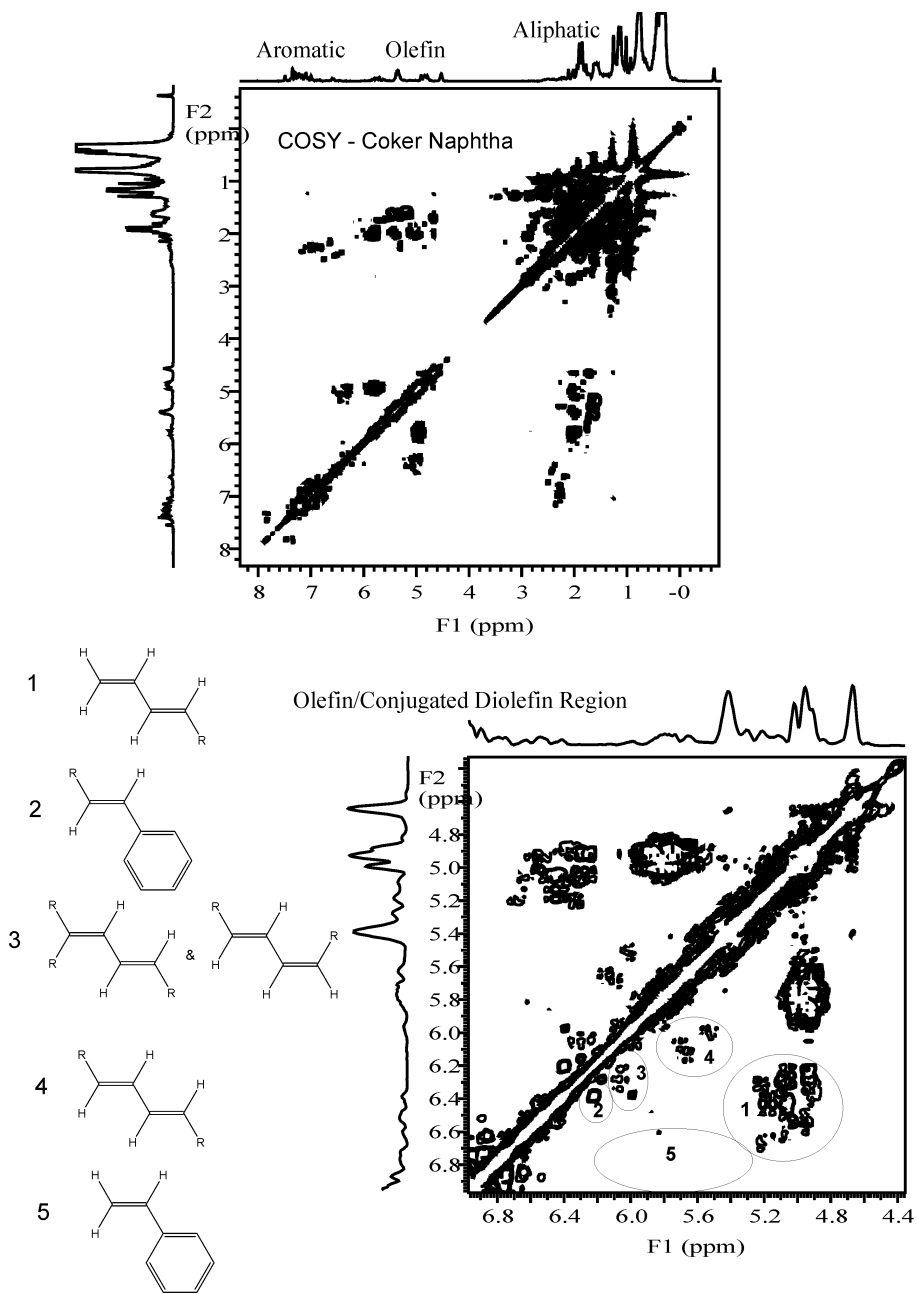


Figure 7: ^1H - ^1H COSY (Correlation Spectroscopy) of a coker naphtha stream. Correlation of olefinic protons with adjacent olefin and aromatic protons yields a distribution of conjugated diolefins that can then be quantified in the 1-dimensional NMR spectrum.

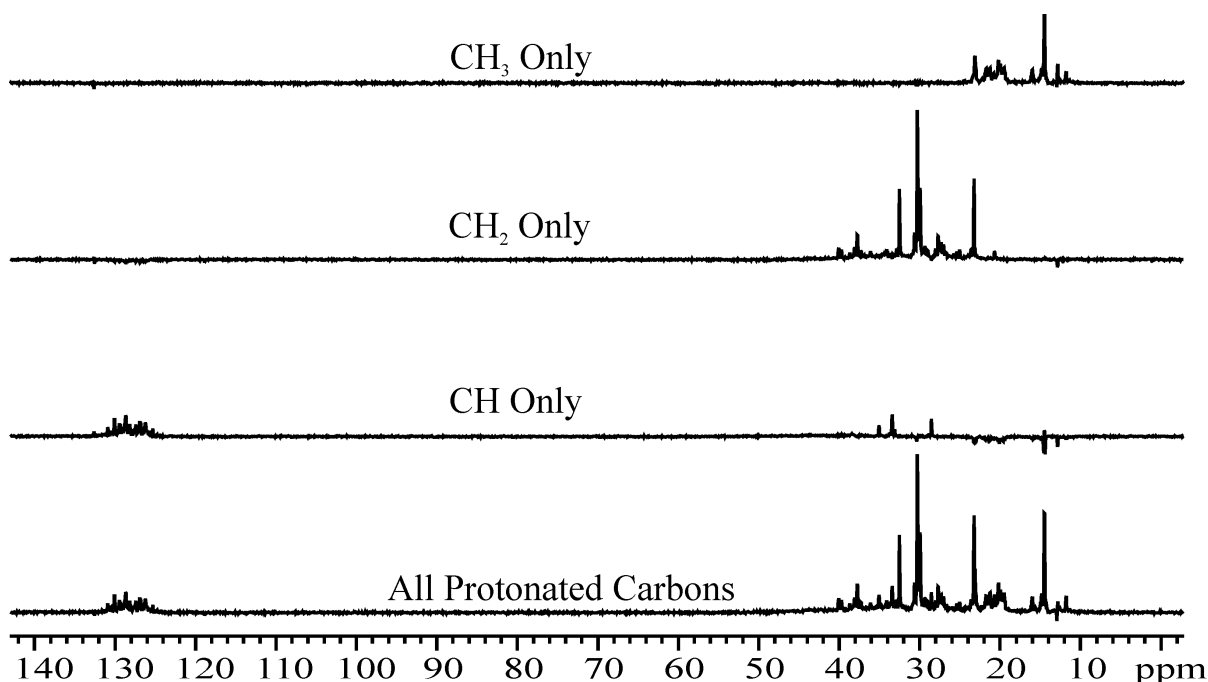


Figure 8: ^1H - ^{13}C DEPT NMR of a diesel fuel showing the calculated sub-spectra for CH_3 , CH_2 , and CH carbons - quaternary carbons are not observed. Comparison of DEPT results with the quantitative ^{13}C single pulse excitation spectrum allows quaternary carbons to be identified and quantified.

Solid-state ^1H and ^{13}C NMR is widely utilized to study heavy petroleum solids such as asphaltenes, coal, shale, bitumen, engine deposits, soots, biomass, refinery coke, refinery residues and tars, catalyst cokes, gums, lignites, humics, soils, etc. Figure 9 shows a few example spectra obtained by solid-state ^{13}C NMR with cross-polarization. Carbon type analysis as well as average molecule parameters can be derived from integration or deconvolution of these spectra. Of particular interest is the carbon aromaticity, phenolic and carboxylic content, as well as the average aromatic cluster size. These techniques involve higher powered RF pulses and specialized NMR probes. In solid samples the molecules are not tumbling rapidly as they do in the liquid-state. This means that inter-nuclear spin-spin interactions (dipolar couplings), and orientation dependent interactions between static electronic environments and the magnetic field (chemical shift anisotropy) cause severe broadening of the NMR peaks leading to peaks that are several kHz wide and from which little detailed chemical information can be obtained. The higher power levels are required to adequately excite the broad spectral range of NMR signals and to adequately decouple ^1H from ^{13}C in the gated acquisition of ^{13}C FIDs. The probes are designed to allow high power operation and to rapidly spin the solid samples at a “magic angle” orientation about the applied magnetic field. In the case of ^1H and ^{13}C NMR experiments, the mathematical derivations of the dipole-dipole coupling and chemical shift anisotropy contain a sample orientation related multiplication factor of $(3\cos^2\theta-1)$. When the sample is oriented at $54^\circ44'$ with respect to the applied magnetic field, and spun rapidly (3-50 kHz), the broadening interactions are averaged away and high resolution isotropic resonances are obtained. An artifact of the solid-state MAS experiment is that in the case of larger chemical shift anisotropy carbons (such as aromatic or carboxylic carbons) spinning sidebands are observed in the spectrum at modulo the spinning frequency. Along with the isotropic resonances these sideband peaks must

be quantified as part of the signal intensity from these carbon types. Application of this technique to ^{13}C has been very successful over the years, though ^1H is still challenging due to the extremely strong dipole-dipole interaction that cannot be removed by slower magic angle spinning speeds and homonuclear decoupling schemes. The magic angle spinning probes employ high tolerance ceramics and air drive/bearing systems that spin cylindrical ceramic rotors containing the sample. These rotors can be 1.5 mm to 14 mm in diameter and be spun at rates of 40-50 kHz and 2-3 kHz, respectively.

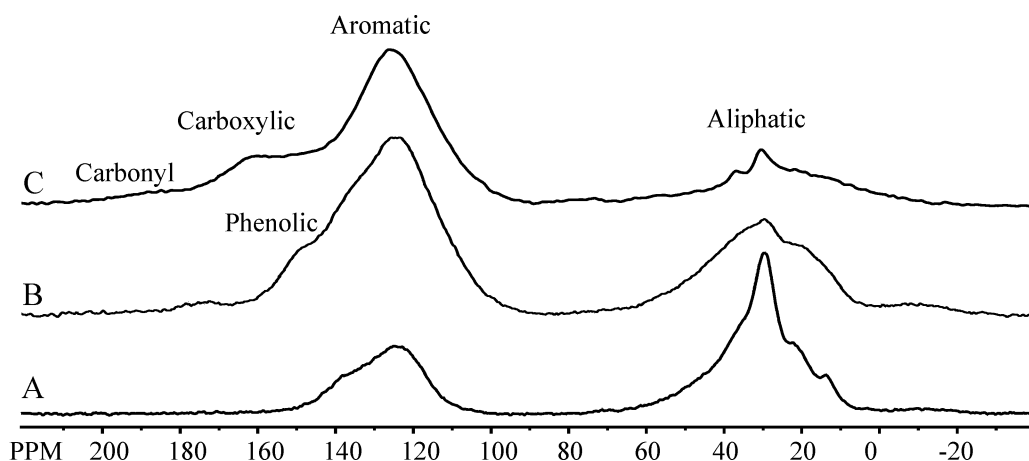


Figure 9: Solid-state ^{13}C cross polarization spectra obtained with magic angle spinning and high power inverse-gated decoupling - A) petroleum precipitated asphaltene, B) Illinois No. 6 coal, and C) gasoline engine combustion chamber deposit

Applications – Low Field NMR (2-30 MHz)

The first and most obvious application of low field NMR to petroleum characterization was the early development in the 1950s of a continuous wave NMR analyzer that observes an absorptive NMR signal by sweeping through a range of radio frequencies, typically centered around 20 MHz. The strength of the NMR absorption could be calibrated with the use of standard materials (such as pure toluene or dodecane) to yield an absolute weight% hydrogen content value. ASTM methods were developed utilizing this technology – D3701 [17] for the hydrogen content analysis of aviation turbine fuels, and D4808 [18] for the hydrogen content analysis of light and middle distillates, gas oils and residua. However, the NMR technology and methodology that was utilized in the development of these methods is now obsolete as low field bench-top instrumentation has moved from frequency sweeping where single frequencies are sequentially irradiated, to pulsed radio frequency technology where a broadband range of radio frequencies are simultaneously excited. In the 1990's an effort was undertaken to develop an ASTM method based on current pulsed NMR technology to replace the previous obsolete methods. The product of that development was ASTM D7171 (Standard Test Method for Hydrogen Content of Middle Distillate Petroleum Products by Low-Resolution Pulsed Nuclear Magnetic Resonance Spectroscopy) [19]. This method yields the same information as the previous methods and allows the utilization of modern spectrometers [20]. Variations of the method utilizing deuterated solvents have also been developed to allow analysis of sample limited quantities of petroleum materials or particularly heavy petroleum products that are

difficult to handle and introduce into the spectrometer for analysis. These test methods involve the NMR signal intensity measurement of known weights of a series of standards (pure petroleum components such as dodecane which is 15.386 wt% H) compared to the signal intensity of a known weight of the unknown petroleum sample. Direct comparison of the intensity after adjustment for sample weight yields the weight% hydrogen of the sample. The utilization of TD-NMR in a refinery has been limited predominantly to hydrogen content analysis alone and the technology is confined to the laboratory and has yet to migrate to online application.

By far the most prevalent utilization of NMR in the exploration industry is in well logging where NMR incorporated into down-hole tools yields quantitative information on the presence of water and oil mixtures as well as the viscosity of the formation liquids as well as the porosity of the formation [12-15]. Discernment of water from hydrocarbon is relatively straightforward as the diffusion coefficient of water is considerably greater than that of hydrocarbons which leads to considerable differences in relaxation behavior. These applications developed from strong research efforts into a combination of rugged instrument design for high pressure and temperature operation, unilateral magnet designs, and the development of one- and two-dimensional Laplace inversion algorithms applied to multi-pulse NMR experimental data. Numerous articles have been published on the subject and it is currently an active area of development. By a combination of T_1 , T_2 , diffusion, and hydrogen index measurements, in combination with the density, temperature and pressure of the fluids, it is possible to identify the fluid type, formation porosity and permeability, water saturation level, oil viscosity and gas content. These analyses are performed on dead crudes (degassed) and live crudes (pressurized samples containing gas). Much emphasis is placed on the discrimination of different distributions of T_1 and T_2 relaxation times as well as the inter-dependence of the relaxation profiles with each other by means of two-dimensional T_1 - T_2 , T_2 -Diffusion, and T_1 -diffusion. It is an obvious extension of this approach that 3-dimensional T_2 - T_1 -D relaxometry is plausible to find added dimensions of variability in NMR derived data. The distributions and relaxation phenomena allow the separation and quantification of overlapping fluid signals such as those arising from heavy oil hydrocarbons and capillary bound and clay-bound water. T_2 measurements are obtained from CPMG (Carr-Purcell-Meiboom-Gill) echo experiments. T_1 measurement is obtained from inversion recovery or 90-tau-90 experiments, and diffusion coefficients are derived from a series of echo experiments with pulsed field gradients applied during the echo-delay (PGSE - pulsed gradient solid echo). Two-dimensional correlations of these relaxation and diffusion parameters are obtained by T_1 or T_2 encoding before the observation experiment is performed [21-28]. Figure 10 shows how a CPMG combined with PFG can generate 2D T_2 -D rate data that yields information on porosity and heavy oil molecular weight distributions.

Another area of development for low field NMR is the application to bitumen exploration and processing particularly in the tar sand fields of Alberta [29]. The TD-NMR tools developed for well logging have been applied successfully to the estimation of bitumen content in cores taken in the field, and to the viscosity of bitumen which is vital for successful recovery and processing operations [30]. Oil sands require multiple stages of processing before they are finally refined. Water-in-oil stability can prove to be a difficult processing issue as it is required that processing produces a complete separation of bitumen, water, and solids (such as clay) before refining. TD-NMR is well suited to the study of water-in-bitumen emulsions and the effect of

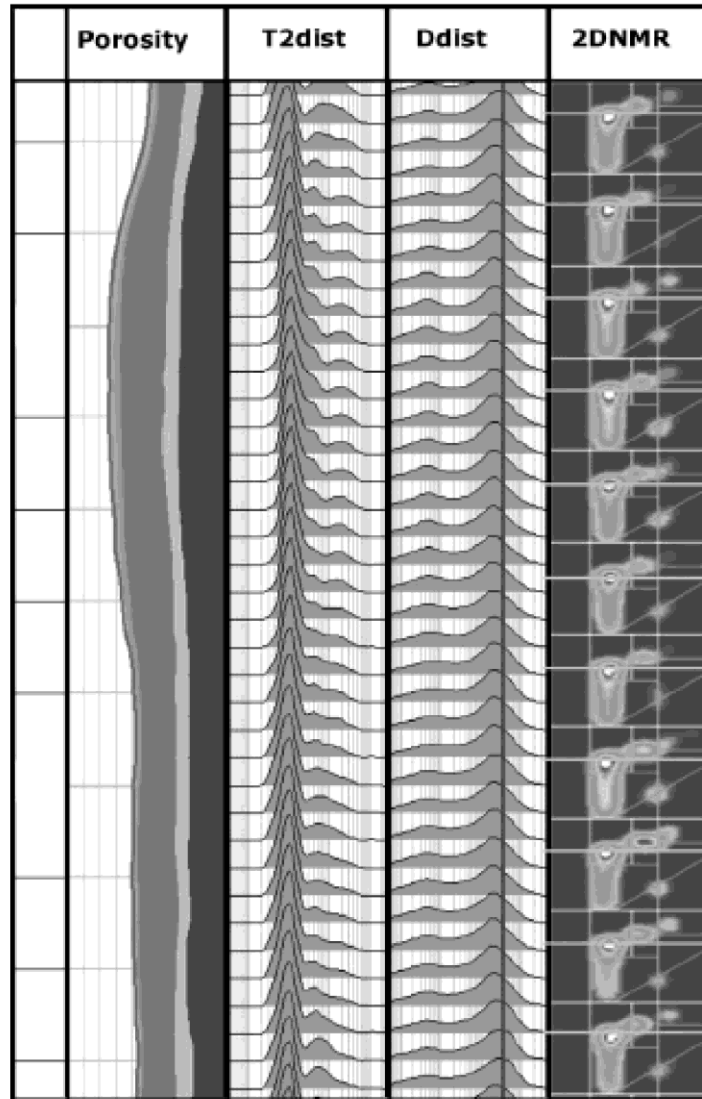


Figure 10: 2D NMR log obtained from the field. Shows T_2 - D plot as well as the projections of the T_2 (Track 2) and D (Track 3) distributions. Track 1 shows the volume ratio of different fluid components. (From Ref 22 - © Elsevier)

processing conditions and addition of demulsifiers and naphtha on phase stability and drop-size distributions present in these mixtures. Asphaltene precipitation and flocculation as well as their rate dependence on asphaltene concentrations can be observed. NMR can also provide the relative quantity of solvent and water in bitumen froths and bitumen-solvent mixtures [31-32]. Figure 11 shows an example of a T_2 distribution obtained on an Alberta tar sand compared to the T_2 distributions of bulk water and bitumen. Bulk water has a long T_2 of around 2 seconds while the viscosity and paramagnetic content of bulk bitumen leads to a distribution of short T_2 relaxation times on the order of 0.1-3 ms. In a tar sand sample water is trapped in the pores of the sand and thus is interacting with the pore structures which leads to shortened T_2 times compared to bulk water. From the plot shown here it is possible to determine the relative intensities of the water and bitumen components.

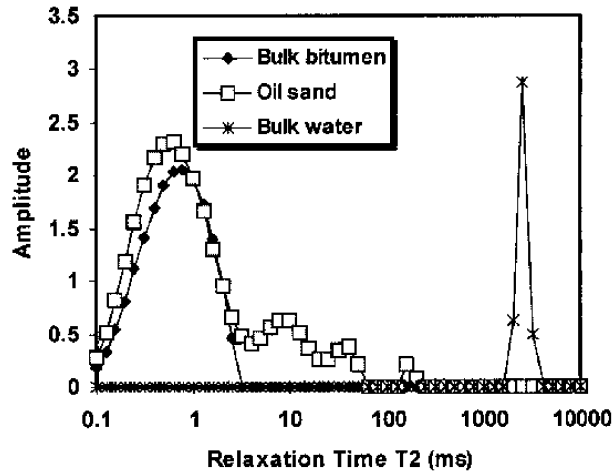


Figure 11: T_2 distribution for an Alberta oil sand compared to the distribution from bulk water and bulk bitumen. (From Ref 29 - © Wiley)

Figure 12 shows a plot of NMR calculated water content versus the actual Dean Stark water measurement on the samples. The effect of processing conditions on the viscosity of the bitumen products is another vital parameter. Finally, the processing of process water will be an obvious extension of the application of TD-NMR technology to bitumen processing. NMR analysis of the hydrocarbon content of waste water and the characterization of tailings is an area that is being explored [33].

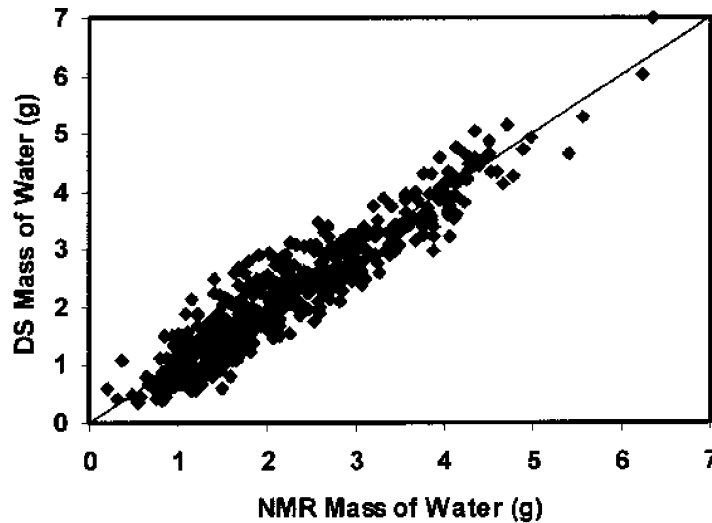


Figure 12: NMR predicted water content from T_2 distributions obtained by CPMG and Laplace inversion versus Dean Stark water content of a Alberta Oil Sand Ores. (From Ref 29 - © Wiley)

The effect of temperature on bitumen softening is a field of interest to civil engineers who wish to determine the role of bitumen chemistry on the mechanical properties and durability of asphalt layers on road construction [34]. NMR based melting curves can be used to determine

the correct bitumen to use in road construction in areas with different freeze-thaw and winter-summer temperature variations.

Australian coal researchers have developed a methodology to determine the hydrogen, carbon and moisture content of coal. This approach involves the characterization of each coal as a signal intensity surface obtained by performing a 30 step T_1 encoding (the t_1 dimension) of a pulse sequence that consists of an FID + 4 spin echoes (the t_2 dimension). The resulting 3D signal intensity surfaces were fit as a combination of 5 relaxation decays of exponential and Gaussian character. The relative contents of five identified proton components correlated to two types of water (interacting with clays and organic phase), as well as three types of organic protons (a rigid organic phase (80% of protons), mobile aliphatic phase organics, and a high aromatic organic phase). The T_2 value of the rigid organic phase is affected greatly by chemical and physical changes caused by coalification making this parameter a good indicator of coal rank [35]. From this quantification it was possible to determine the water, hydrogen, and carbon content of the coals. Taking the NMR analysis a step further they introduced a temperature dependent aspect to the experiment by obtaining the NMR parameters at a series of temperatures. Figure 13 shows a plot a typical signal surface obtained from the experimental measurement as well as a plot of the relationship between the 5 components and the amplitude surface for each of the 275 coal samples analyzed.

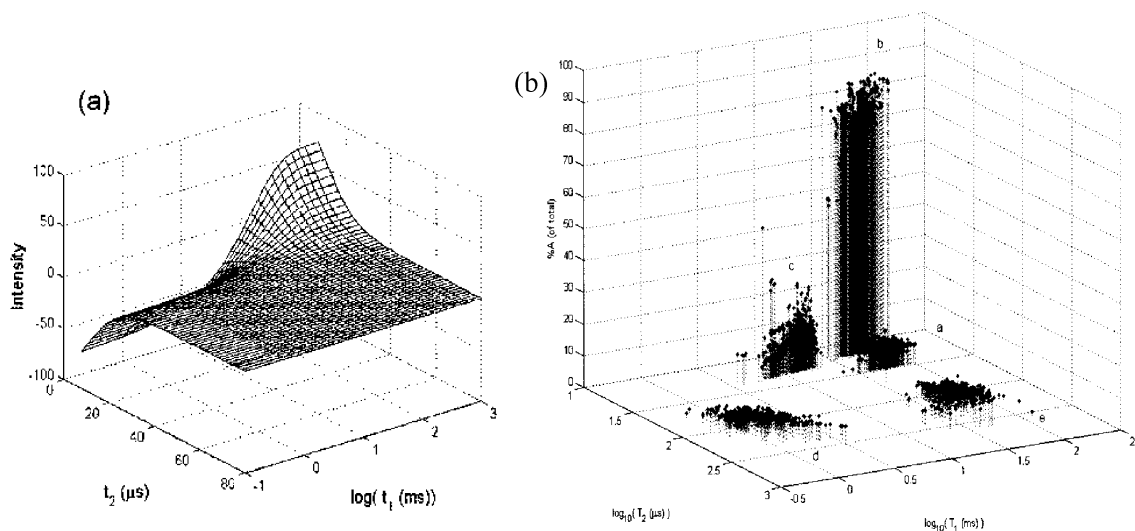


Figure 13: Coal TD-NMR analysis (a) Signal amplitude surface obtained by inversion recovery encoding of an FID + 4 echoes sequence, and (b) the 5 NMR relaxation components for 275 coal samples that can be obtained from fitting the signal surfaces from each coal. (From Ref 35 - © Elsevier)

The five calculated NMR parameters obtained at different temperatures were then utilized as a “coal NMR spectrum” (not a spectrum in the traditional sense) and a partial least squares regression was used to establish a correlation between the NMR relaxation “spectrum” and traditional coal parameters. Good correlations were obtained for wt% moisture, wt% volatile matter, wt% hydrogen, wt% carbon, Wt% oxygen, gross specific energy, petrographic composition (vitrinite and intertinite vol%), and reflectance [36]. These analyses will be directly applicable to other carbonaceous solids such as kerogen, shale, coke, and various deposits.

Online process control utilizing TD-NMR real-time analysis of refinery streams is currently not in practice but will soon be a reality thanks to the reduction in cost of basic NMR

instrumentation capable of performing these measurements. Several companies are developing NMR platforms that can perform real time hydrogen-analysis and T_2 - T_1 -Diffusion distribution analysis for analysis of heavy oils, bitumen, crude oils and heavy refinery streams [37]. Use of such systems has been ongoing in the petrochemical industry where TD-NMR has been utilized for polyolefin analysis since the late 1980s [38-40].

Applications – High Resolution, Low Field NMR (30-60 MHz)

High resolution NMR performed at frequencies of 30-60 MHz have been carried out in NMR studies of petroleum starting in the early 1950's. However, as NMR superconducting magnet technology emerged in the 1960s (200 MHz systems) then improved to 300+ MHz during the 1970's-1980's the number of studies at 60 MHz decreased as continuous wave 60 MHz instruments such as the Varian EM-360 or JEOL FX-60 were replaced. In the early 1990's a new permanent magnet/electrical shimming technology was developed that yielded small (60 kg), high homogeneity, inherently shielded, stable NMR magnet systems ideal for online process NMR and laboratory based application development. In 1995, a 53 MHz NMR analyzer was placed on a fuel gas stream from a Texaco refinery's cogeneration unit in Los Angeles [41]. The analyzer measured BTU, specific gravity, methane content, hydrogen content, olefinic H, and hydrocarbon content; the NMR compared favorably with the GC analysis utilized prior to the NMR installation. Unlike the GC, the process NMR did not require component speciation to determine BTU and specific gravity. Rather, the BTU was calculated directly from the C-H bond types observed in the ^1H NMR spectrum. The following year a process NMR system was installed on a Stratco Alkylation unit at the same refinery. The NMR response of the acid/hydrocarbon emulsion was used to calculate sulfuric acid strength (wt%). This was done by correlation of the varying acid peak position (relative to the stationary chemical shift values for covalent CH protons on the acid soluble oils and hydrocarbons in the emulsion) with titrated acid strength values [42]. A further development allowed ^1H NMR analysis of the spent acid to provide acid strength, acid soluble oil content, and water content. Figure 14 shows the ^1H NMR spectra obtained on spent acid in the third settler of a train of refinery alkylation units. Acid strength is a vital number for control as low acid strength leads to runaway polymerization of the butane leading to process shutdown and major clean-up operations.

Since 1994, on-line process NMR applications have involved partial least-squares (PLS) regression modeling, where the entire (or partial) NMR spectral variability is regressed against chemical and physical parameter values obtained from primary testing methods (typically ASTM test methods). An early version of the process NMR equipment operating at 42 MHz was used to correlate ^1H NMR response to MTBE (methyl tertiary butyl ether) content in gasoline [43]. Meanwhile Texaco researchers developed a number of PLS regression correlations for a wide range of gasolines between ^1H NMR and a number of chemical and physical properties such as ASTM research octane (ASTM D2699), motor octane (ASTM D2700), distillation values (ASTM D86 - T5, T10, T50, T90, T95), benzene content (D3606), aromatic content (ASTM D1319 and D5769), olefin content (by Supercritical Fluid Chromatography (SFC) and ASTM D1319), oxygenate content (MTBE or Ethanol – by ASTM D5599), and density (ASTM D4052) [44]. An Australian refinery is currently utilizing NMR to certify gasoline entering the gasoline pool [45].

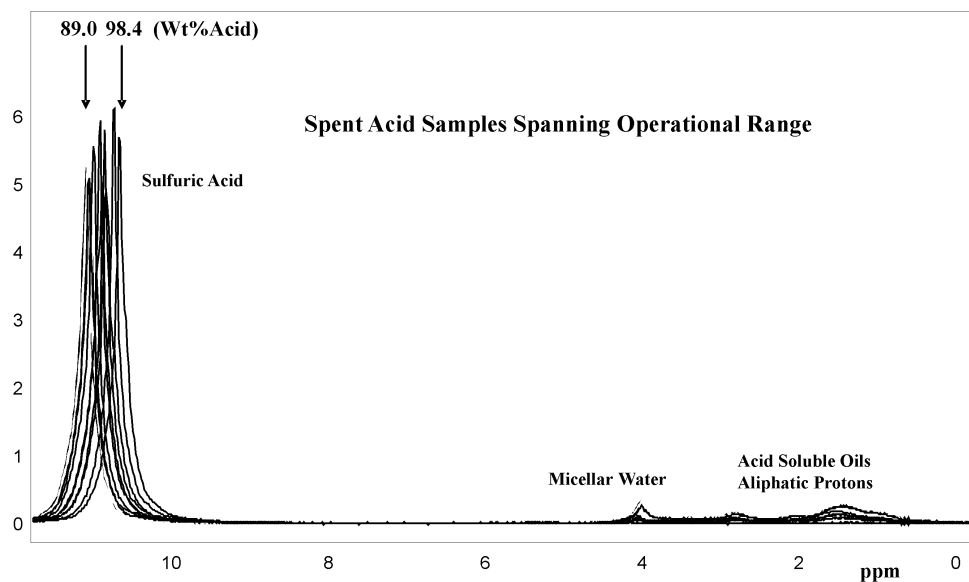


Figure 14: Online ^1H NMR analysis of the spent acid present in a settler of a refinery alkylation unit.

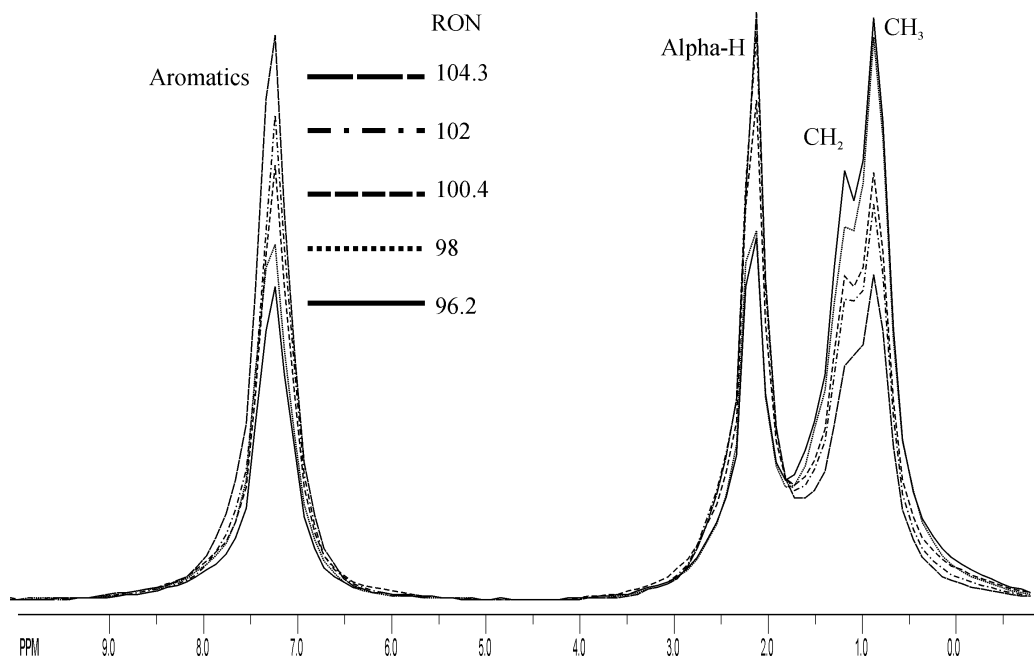


Figure 15: ^1H NMR spectra of reformates with different research octane numbers.

A UK refinery is using full spectrum PLS analysis of ^1H NMR spectra to control a reformer unit where the NMR predicts ASTM research octane (ASTM D2699), motor octane (ASTM D2700), benzene content (D3606), and aromatic content (ASTM D5769). Figure 15 shows an example of stacked 60 MHz ^1H NMR data obtained on reformate samples with different research octane numbers. The ^1H spectra have been converted into 140 x 0.1 ppm integral bins - this is a process whereby the entire spectrum from 12 to -2 ppm is integrated every

0.1 ppm. This is a resolution deduction which improves the signal to noise ratio of the data and allows various normalizations to be performed to avoid issues with density changes and presence of contaminants in the analysis streams.

Perhaps the most challenging PLS-regression analysis has been between ^1H spectral variability and GC-PINA (Gas Chromatography - Paraffins, Iso-Paraffins, Naphthenes, Aromatics) analysis with speciation of each hydrocarbon type into C_4 through C_{10} carbon number distribution. This analysis was applied to naphtha analysis and was utilized for feed forward control of ethylene and propylene cracking units [46-47]. Another application included the analysis of an NMR to monitor and control a cracker used to process both naphtha condensates and diesel range material [48]. Figure 16 shows typical spectral response of naphthas at 60 MHz as well as an example of real time PINA data utilized for control.

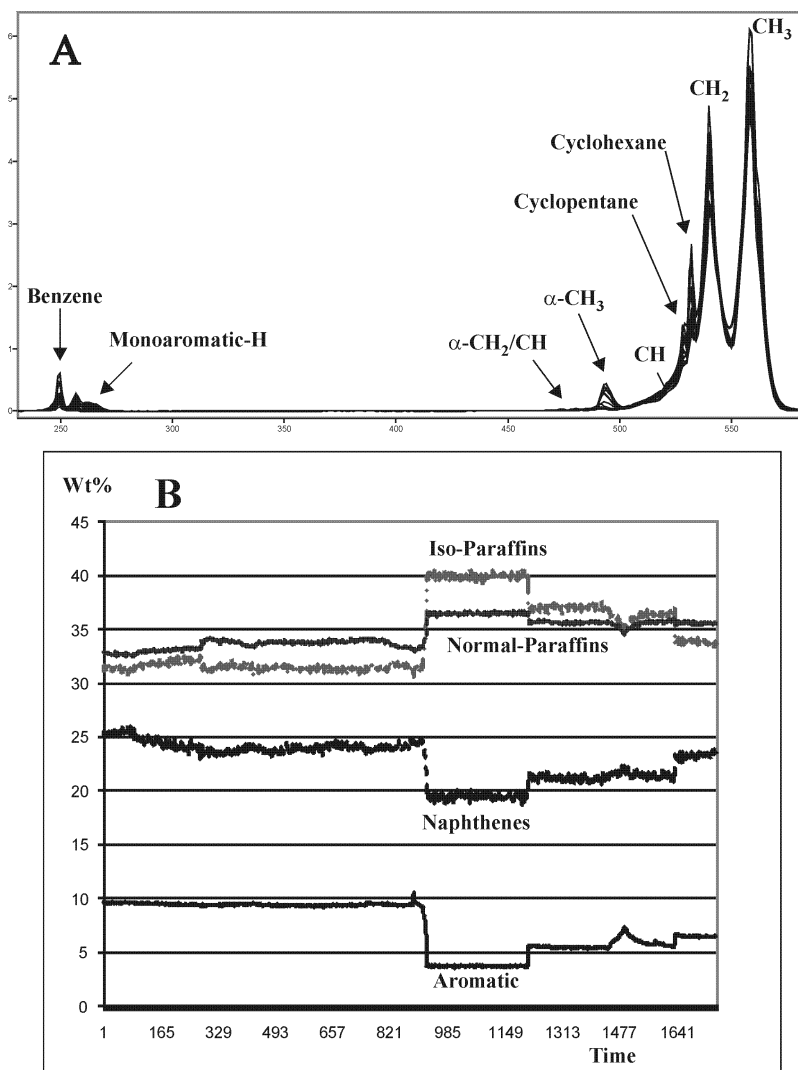


Figure 16: Process ^1H NMR PLS Prediction of naphtha PINA analysis (A) Typical NMR spectral variation, and (B) 4 days of online predictions showing chemical component variation.

Another challenging application is the NMR crude oil assay which involves regression analysis of ^1H NMR against true boiling point and density data on crude oils. Crude oil blending applications have been studied as have feed-forward control of refinery crude units. In one application a Caribbean refinery performed a complete optimization project on a crude unit monitoring the true boiling point of the crude feed as well as the distillation (ASTM D86), freeze point (ASTM D2386), and flash point (ASTM D93) of the kerosene product, and the distillation (ASTM D86) values of the naphtha product [49]. Other applications have been installed online for crude unit product analysis. The streams analyzed by chemometric predictions vary depending on the control strategy and the economics of the refinery. Some installations analyze naphtha, kerosene, diesel, and gas oils. Others concentrate heavily on crude unit diesel as well as hydro-treated diesel streams, or cracked cycle oils that are routed to the same analyzer [50-51]. In the analysis of diesel the ^1H NMR can predict the cold flow properties, distillation points (D86 or D2887 Simulated Distillation), density, aromatics content, olefin content, and cetane index (or cetane number) of the diesel stream. In a further application of the technology the customer is receiving carbon number distributions obtained from simulated distillation data to better predict the cut points of the diesel product in order to avoid inclusion of dibenzothiophene in the diesel product, ensuring the diesel meets ultra low sulfur specifications.

A European refiner has applied online NMR analysis to a base oil manufacturing process [52]. ^{13}C NMR based NMR parameters (aromatic carbon content % (Fa), naphthenic carbon content % (Fn), and paraffinic carbon content % (Fp)) were regressed against the online ^1H NMR spectra to obtain an excellent correlation allowing ^{13}C NMR parameters to be predicted by ^1H NMR analysis. The refractive index, simulated distillation, density, and viscosity index were predicted for the vacuum gas oil feedstream, the intermediate raffinate and the final base oil product. Online application of these three ^{13}C NMR parameters and the other physical property measurements has also been ongoing at several online NMR installations on FCC feed streams. Online ^1H NMR analysis of light cycle oils and cracked spirits is also found at the above mentioned FCC installations.

Applications: High Resolution, High Field NMR (200-600 MHz) Liquid-State Analysis

In the more familiar arena of high resolution NMR in which commercial spectrometers operating at 200-600 MHz are utilized to observe ^1H and ^{13}C NMR the approach to the chemical information present in an NMR spectrum varies widely depending on the researcher. There are several approaches that can yield useful information that informs the researcher about sample to sample variability of the petroleum material under observation, or informs one of the changes that have occurred to chemical and macromolecular properties during petroleum processing. ^1H NMR parameters are derived predominantly by liquid-state NMR due to the paucity of data that has emerged from solid-state ^1H NMR experiments that are still plagued by poor resolution. ^{13}C NMR parameters are obtained for liquid-state NMR experiments and solid-state magic angle spinning experiments. Quantitative conditions can be obtained in ^1H NMR studies by utilizing appropriate relaxation delays between the accumulating pulses. For liquid-state ^{13}C NMR experiments it is important that relaxation agents such as Chromium (III) Acetylacetonate be used in the deuterated solvents (usually CDCl_3 or a $\text{CDCl}_3\text{-CS}_2$ combination) in which the petroleum samples are dissolved. The relaxation agents reduce the ^{13}C relaxation rates from paramagnetic interactions, and thereby shorten the required relaxation delays between pulses, allowing rapid signal accumulation and timely experimental results. Inverse gated decoupling is also a requirement to avoid nuclear overhauser effects (NOE) that cause carbons with different

protons to be enhanced to different degrees rendering the data non-quantitative from one carbon type to another throughout the entire sample chemistry. This decoupling simply means that the ^1H decoupling is only applied during the FID acquisition.

Table III: Proton Types Obtained from ^1H NMR Analysis

Sample
Total Aromatic-H %
Total Aliphatic-H %
Total Olefinic-H % - can be further broken down into internal and terminal olefin
Alpha-H % - ^1H on carbons alpha to aromatic rings - can be broken into CH_3 and CH_2/CH
Epsilon-CH, % - Methylenes distanced from chain terminals and branches.
Beta - CH/CH_2 % - Paraffinic CH_2 and CH other than alpha and Epsilon
Total Aliphatic CH/CH_2 %
Gamma - Methyl CH_3
Alpha- CH_3 %, Alpha- CH_2 %, Alpha-CH %, CH_2 Alpha to 2 Aromatic Rings %
Monoaromatic-H % Diaromatic-H % Triaromatic+-H %
Aliphatic CH_3 to CH_2/CH Ratio
Mono/PNA Aromatic Ratio

Table IV: Carbon Fraction Parameters obtained from quantitative ^{13}C NMR

NMR Carbon Fraction	Description
Fa^{CO}	Fraction of Carbonyl (%) sp2 - aldehydes and ketones
Fa^{COO}	Fraction of Carboxyl (%) sp2 - acids, esters, amides
Fa^{P}	Fraction of phenolic carbon (ar-C-OH) (%) sp2
Fa^{S}	Fraction of substituted aromatic carbon (%) sp2
$\text{Fa}^{\text{B}} + \text{Fa}^{\text{H}}$	Fraction of combined bridgehead and protonated aromatic carbon (%) sp2
Fa^{N}	Fraction of non-protonated aromatic carbon (%) sp2
Fa^{C}	Fraction of sp2 carbon present as carbonyl and carboxyl (%) sp2
Fa'	Fraction of aromatic carbon (%) sp2
Fa	Fraction of sp2 carbon (Aromatics and Carboxyl/Carbonyl) (%) sp2
Fa^{L}	Fraction of sp3 (aliphatic) carbon sp2
Fa^{B}	Fraction of bridgehead aromatic carbon sp2
Fa^{H}	Fraction of protonated aromatic carbon sp2
Fa^{O}	Fraction of Ether Type Carbon (sp3 carbon adjacent to O)
$\text{Fa}^{\text{L-amine}}$	Fraction of Amine Carbon (sp3 carbon adjacent to N)
$\text{Fa}^{\text{L-CH/CH}_2}$	Fraction of CH and CH_2 in naphthenics and paraffins (sp3)
$\text{Fa}^{\text{L-Arom-CH}_3}$	Fraction of CH_3 attached to Aromatics (sp3)
$\text{Fa}^{\text{L-Aliphatic-CH}_3}$	Fraction of CH_3 attached to paraffins or naphthenes (sp3)

One approach is to determine the ^1H and ^{13}C NMR molecular parameters directly from the spectrum. Typical ^1H and ^{13}C derived chemistry parameters are given in Table III and Table IV. Another approach is to calculate average structural parameters that describe the “average” chemistry of the sample as an idealized single molecule. Typical average structural parameters for liquid- and solid-state NMR studies are shown in Table V. The basis for these tables are the exhaustive data tables presented in the book by Boduszynski and Altgelt [53-54]. The derivation and use of these parameters as descriptors of the true chemistry of the sample is rather

questionable and open to much interpretation leading to academic on the calculation methodologies and meaning of the NMR derived parameters [55-56]. NMR analysis does not yield the distribution and skewness of the ^1H or ^{13}C chemistry distributions around the calculated average. NMR cannot determine the true molecular speciation or the distribution of the entire petroleum mixture.

Table V: Typical Structural Parameters for Average Molecule Descriptions

Symbols	Definition - Determination of Calculation
M_W	Average Molecular Weight (by LD-MS)
C_{ar}	Total Aromatic Carbons (by ^{13}C NMR)
C_{al}	Total Aliphatic Carbons (by ^{13}C NMR)
C_{us}	Unsubstituted Aromatic Carbons (by ^1H NMR)
C_s	Alkyl-Substituted Aromatic Carbons Except CH_3 (by ^{13}C NMR)
C_{CH_3}	Methyl-Substituted Aromatic Carbons (by ^{13}C NMR)
C_{sub}	Alkyl-Substituted Aromatic Carbons ($C_{sub} = C_s + C_{\text{CH}_3}$)
C_p	Peripheral Aromatic Carbons ($C_p = C_{us} + C_{sub}$)
C_h	carbons attached to Heteroatoms (by ^{13}C NMR)
C_{int}	Internal Quaternary Aromatic Carbons ($C_{int} = 6 + C_{ar} - 2C_p$)
C_{ext}	External Quaternary Aromatic Carbons ($C_{ext} = C_{ar} - (C_p + C_h + C_{int})$)
F_a	Aromaticity ($f_a = C_{ar}/(C_{ar} + C_{al})$)
R_a	Aromatic Ring Number ($R_a = ((C_{ar} - C_p)/2) + 1$)
n	Average Length of Alkyl Side Chains ($n = C_{al}/C_{sub}$)
CI	Condensation Index ($CI = (C_{int} + C_{ext})/C_{ar}$)

From Reference 94 - © American Chemical Society

The average molecule description is always limited by the many assumptions that are made in the calculations. For example, in many experiments one has to assume that all aliphatic carbons are in groups that are attached to aromatic rings. This has to be done because NMR cannot discern between free paraffin molecules and alkyl carbons on substituted aromatic molecules. The NMR spectrum informs the researcher that there are alpha protons (CH , CH_2 , and CH_3 groups attached to aromatic rings), it does not inform you of the breakdown of the molecular distribution that would link the signals in the aliphatic region to those particular pendant groups. As such it is recommended that researchers follow changes in chemistry observed directly from the spectrum. Average molecule parameters can be used as an alternate method to follow gross chemistry trends with processing changes, and should not be used to represent the true changes to ^1H or ^{13}C chemistry.

Another approach is the reduction of ^1H NMR spectral data into NMR molecular parameters followed by regression analyses that derive predictive equations for the calculation of physical and chemical parameters of interest for the petroleum product being analyzed. Cookson

and Smith published a series of papers on composition-property correlations for diesel and kerosene fuel based upon a general equation derived from a combination of HPLC data and standard ^{13}C molecular parameters [57-59]:

$$P = a_1[n] + a_2[\text{BC}] + a_3[\text{Ar}] \quad (1)$$

Where P is the fuel property value, and [n], [BC], and [Ar] are the weight fractions of n-alkanes, branched plus cyclic saturates, and aromatics, respectively. These values are obtained from HPLC data processed with response factors estimated from ^{13}C NMR results on the same sample [60]. The coefficients a_1 , a_2 , and a_3 are determined from multiple linear regression analysis. It was also found that a four parameter model containing separate coefficients for monoaromatic and diaromatic content marginally improved the property predictions.

In a further development studies were published for composition-property relations based solely on ^{13}C NMR data that fit the following type of equation [61]:

$$P = a_1C_n + a_2C_{\text{ar}} + c \quad (2)$$

Where C_n is the % n-alkyl carbon, and C_{ar} is the % aromatic carbon. Jet fuel properties predicted included: smoke point, aromatic content, hydrogen content, heat of combustion, freeze point, and inverse specific gravity. For diesel the predicted properties were: pour point, cloud point, hydrogen content, aniline point, diesel index, cetane index, and inverse specific gravity. Figure 17 shows examples of calculated versus actual quality properties for jet and diesel fuels derived from ^{13}C analysis alone utilizing equation (2). The property predictions were further improved by developing models for jet and diesel fuels with variable boiling ranges [62]. In these analyses equation 2 was utilized in conjunction with GC simulated distillation data to provide an equation that accommodates the effects of variations in boiling range:

$$P = a_1C_n + a_2C_{\text{ar}} + \sum b_i T_i + k \quad (3)$$

where T_i represents a series of temperatures at which a specific weight % of the fuel has boiled, and coefficients a_1 , a_2 , b_i , and k are determined by multiple linear regression. Table VI shows the coefficients obtained for property prediction of jet and diesel fuels.

In another series of papers spread over the past decade researchers at Indian Oil Corporation have utilized a ^1H NMR methodology whereby intensity data from chemical shift regions correlating to different hydrogen types are regressed against property parameters obtained from primary testing methods. As an example, the various hydrocarbon types (total aromatics, olefins, and oxygenates) in motor gasoline were obtained by NMR correlated to gas chromatography (GC - ASTM D-5580 and D-4815) and fluorescent indicator absorption (FIA – ASTM D-1319) test methods [63]. It is advantageous when working with refinery engineers that NMR results be converted to gas chromatography values given in Wt% or Vol%. ^1H and ^{13}C NMR values for aromatics yield numbers that are much different than an engineer would expect when he deals with GC values for control and property evaluation. Also the fact that NMR yields hydrocarbon types in terms of nuclear percentages rather than by molecular type means that there is a disconnect between what NMR defines as aromatic and what is defined as aromatic by GC.

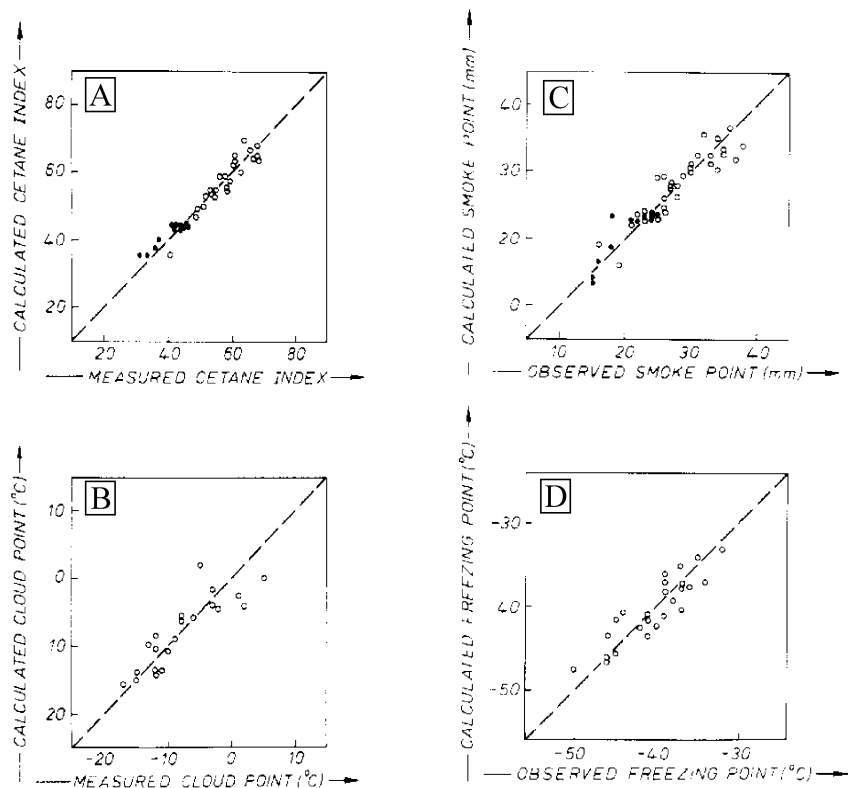


Figure 17: Plots of measured versus calculated values of (A) cetane index, (B) cloud point of diesel fuels, and the (C) smoke point, (D) freezing point of jet fuels (o = petroleum • = synfuel) based on Equation (2). (From Ref 61 - © American Chemical Society)

Table VI: Statistical data for composition-property relations based on Equation (3) for variable boiling range fuels*

Property	a_1	a_2	b_1	b_2	k	r.m.s.d.e	adj R^2
Jet Fuels							
Smoke Point (mm)	29.3	-74.7	-0.065	-0.045	43.4	1.6	0.94
Aromatics Content (vol%)	-4.8	121.0	0.072	0.015	-11.9	2.1	0.94
Hydrogen Content (wt%)	2.35	-4.89	-0.006	-0.006	16.2	0.13	0.94
Density (g cm^{-3})	-0.137	0.0386	0.0005	0.0004	0.6577	0.008	0.91
Freezing Point ($^{\circ}\text{C}$)	81.1	53.6	0.255	0.338	-206.2	2.5	0.93
Diesel Fuels							
Cloud Point ($^{\circ}\text{C}$)	33.2	-12.3	0.154	0.422	-189.4	2.8	0.92
Pour Point ($^{\circ}\text{C}$)	29.3	-24.5	0.192	0.389	-186.4	3.7	0.87
Aniline Point ($^{\circ}\text{C}$)	55.6	-67.7	0.078	0.073	18.7	3.0	0.94
Hydrogen Content (wt%)	2.41	-5.62	-0.003	-0.002	14.48	0.13	0.95
Density (g cm^{-3})	-0.157	0.0655	0.0003	0.0001	0.7652	0.008	0.92
Cetane Index (AP)	52.0	-71.4	0.094	0.066	3.7	2.2	0.96
Cetane Index (BP)	55.1	-25.1	0.002	0.046	22.8	2.5	0.95
Cetane Number	49.1	-32.4	0.061	0.025	24.3	2.2	0.95

* Model: $P = a_1C_n + a_2C_{ar} + b_1T_{10} + b_2T_{90} + k$

(From Ref 62 - © Elsevier)

As an example of the disparity between GC and NMR analysis of aromatics, dodecylbenzene is considered 100% aromatic by GC, while to NMR it is 21.7% aromatic (5H on aromatic ring / 23H on aliphatic chain). By obtaining GC or FIA data and then correlating ^1H NMR spectral variability to those values the ^1H NMR can yield GC values in wt% for the hydrocarbon types of interest. In order to do this directly from the observed ^1H NMR chemical types the Indian Oil Company researchers integrated the spectrum into 8 distinct regions yielding relative intensity data on aromatics (region A, 6.5-8.0 ppm), olefins (region U, 4.5-6.2 ppm), oxygenates (region O, 3.0-3.5 ppm), alpha-CH₂/CH (region B, 2.45-3.0 ppm), alpha-CH₃ (region C, 2.05-2.45 ppm), CH/CH₂ in naphthenes, normal and iso-paraffins (region E, 1.4-2.05 ppm), CH₂ in long alkyl chains (region G, 1.05-1.4 ppm), and methyls (region H, 0.5-1.05 ppm). The calculation of chemical and physical properties is performed on a carbon basis. This means that the ^1H NMR data must be converted to represent the relative number of carbons in each carbon type (T_C) as well as the relative molecular weights of each carbon type group (T_W). An estimation of the substituted aromatic carbon (Ar_s) (and in some cases the bridgehead aromatic carbons (Ar_b)) must be derived from the alpha-proton (2.05-3.0 ppm) and aromatic proton (7.4-9.0 ppm) regions of the spectrum. The proton intensity data is reduced to carbon type values by dividing each integral value by the number of protons attached to each carbon type (see Eq.(4)). The group molecular weights are obtained by multiplying the calculated carbon number values by the molecular weight of the group (12 for C, 13 for CH, 14 for CH₂, and 15 for CH₃), as follows:

$$T_C = A/1 + 1.12U + B/2 + C/3 + E/2 + F/1 + G/2 + H/3 + \text{Ar}_q + O/2 \quad (5)$$

where Ar_q = substituted aromatic carbon - calculated indirectly through alpha-H = $(B/2 + C/3)$. Substituting for Ar_q and multiplying by the M_w of each carbon type T_W is obtained:

$$T_W = 13(A+F) + 14B + 10C + 7(E+G) + 5H + 14.36U + 7O \quad (6)$$

Now that we have the total group molecular weight we can calculate the wt% of the individual components. For example, to calculate total aromatics (A_W) the group molecular weight is calculated as:

$$A_W = 13(A/1) + 14n(B/2) + 15(C/3) + 12(B/2) + 12(C/3) = 13A + 7nB + 9C + 6B \quad (7)$$

$$\text{Total Aromatic Content (Wt\%)} = 100 \times A_W/T_W \quad (8)$$

Figure 18 shows the correlations between NMR calculated total aromatics in gasolines and the Wt% values obtained on the same samples by FIA and GC separations methods.

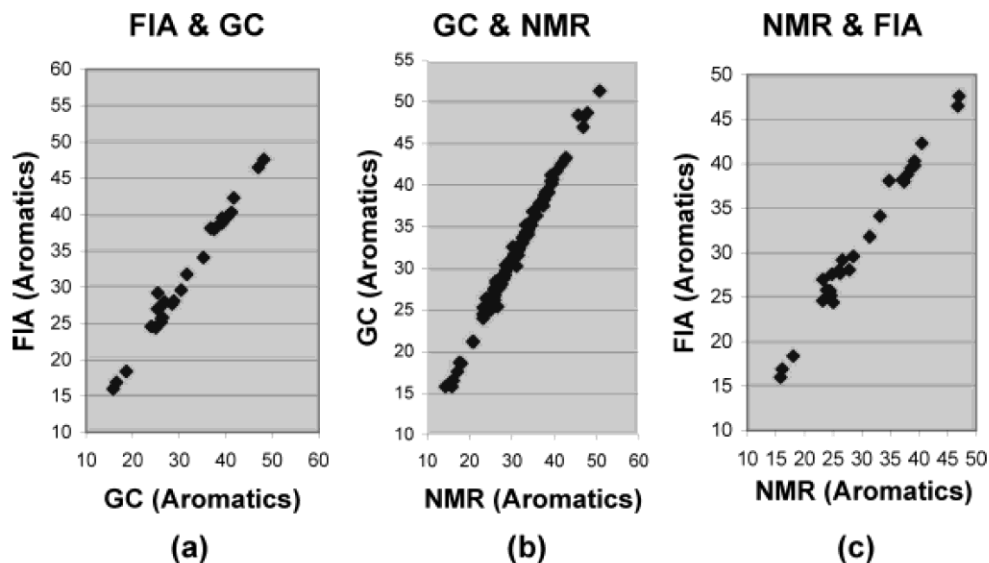


Figure 18: Plots of the correlation between GC and FIA analysis methods and the calculated value of total aromatics from Equation (8), units are wt% - (Ref 63 - © American Chemical Society).

For gasoline range material various predictive equations based on this approach have been developed for PONA [64,65,67], benzene and total aromatics [66,67], oxygenates [67-69], and octane number [70]. Total aromatic content was estimated for aviation turbine fuels by ^1H NMR [71]. A number of papers were published on this approach to estimation of properties of middle distillates and diesel fuels to yield the following parameter estimations:

- Total aromatics and the mono- and di-plus aromatics distribution by ^1H and multidimensional NMR [72]
- Bromine number (ASTM D-1159) by ^1H and ^{13}C NMR [73]
- Total Aromatics by ^1H NMR – comparison with mass spectrometry [74]

The technique was extended to vacuum gas oil (VGO) fractions [75], as well as feedstocks to both FCC (Fluid Catalytic Cracker) and RFCC (Residual Fluid Catalytic Cracker) [76], in which total aromatic content by open column chromatography (ASTM D-2549) was calculated according to the previous methodology. Other important process control information was also derived from the ^1H and ^{13}C NMR with respect to alkyl chain lengths, aromatic substitution patterns, and degree of substitution, allowing estimates to be calculated for the product profile, yield pattern and expected coking tendency of the feed.

In a modified approach the Indian research group has applied multiple linear regression (MLR) to develop predictive equations based on 18 integrals representing specific proton types in the ^1H NMR spectrum. The integrals were stored as a “modified spectrum” and “spectrum” was regressed against various chemical and physical properties for diesel samples. The regression analyses produced regressions statistical correlations with $R^2 > 0.99$ [77]. Figure 19 shows the correlations obtained between NMR calculated values and a number of chemical and physical property laboratory test methods. The equations that the calculations are based on are shown in Table VII.

Table VII: Property correlation equations calculated by MLR from 18 ^1H NMR integral regions

Property	Model Equation	R ²	Std Error
Density	$5.092(\text{A}+\text{B}) + 2.537(\text{H}+\text{I}) + 1.732(\text{J}) + 1.083(\text{L}) + 4.279(\text{M}) + 1.704(\text{O}) + 0.830(\text{P}) + 2.380(\text{Q}) + 0.426(\text{R})$	0.998	1.11
Viscosity	$-0.097(\text{D}+\text{E}+\text{F}+\text{G}) - 0.438(\text{H}) + 0.333(\text{I}) - 0.0446(\text{L}) + 0.0073(\text{P}) + 0.091(\text{Q}) - 0.0245(\text{R})$	0.998	0.09
Cetane Number	$-0.272(\text{A}+\text{B}+\text{C}+\text{D}) + 0.570(\text{H}+\text{I}) + 0.653(\text{J}) - 0.712(\text{L}) + 3.001(\text{M}) - 0.408(\text{N}) + 0.0886(\text{P}) + 0.152(\text{R})$	0.998	0.4
Cetane Index	$-0.713(\text{C}+\text{D}) + 0.528(\text{K}) - 1.268(\text{M}) + 0.075(\text{P}) + 0.240(\text{Q})$	0.998	0.27
Sulfur	$11.01(\text{A}+\text{B}+\text{C}+\text{D}+\text{E}+\text{F}+\text{G}) + 37.46(\text{H}+\text{I}) - 43.8(\text{J}) - 9.959(\text{L}) - 5.065(\text{M}) + 1.358(\text{P}) - 12.639(\text{Q}) + 2.864(\text{R})$	0.992	24
%Vol up to 350°C	$0.72(\text{A}+\text{B}+\text{C}+\text{D}+\text{E}+\text{F}+\text{G}) + 1.052(\text{J}) - 0.916(\text{K}) + 0.437(\text{L}) - 5.065(\text{M}) + 0.719(\text{O}) + 0.031(\text{P}) - 0.434(\text{Q}) + 0.215(\text{R})$	0.992	0.63
FBP	$-3.249(\text{C}+\text{D}) - 2.903(\text{E}+\text{F}+\text{G}) + 3.661(\text{K}) + 7.828(\text{M}) + 0.453(\text{P}) + 1.771(\text{Q}) + 0.146(\text{R})$	0.998	1.46

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A similar approach, employing partial least-squares (PLS) regression was taken by another group that obtained 12 integral values from the ^1H NMR spectra of Colombian crude oils. These were regressed against crude properties to yield a true boiling point prediction of the product fractions (yield of naphtha, jet A, diesel, gas oil, and residue), sulfur content, nitrogen content, waxes, micro-Conradson residue (MCR), asphaltene content (nC₇ insolubles), Nickel, Vanadium [78]. A full spectrum approach was taken by Edwards and Kim, where integrated spectra (integral binned every 0.1 ppm from 12 to -2 ppm), and “spectra” created from hydrogen and carbon molecular and structural parameters calculated from both ^1H and ^{13}C data, for both diesel and VGO samples, were correlated to diesel and vacuum gas oil parameters with PLS regression [79]. In this study PLS regression models were developed that allowed 34 detailed ^{13}C NMR parameters to be calculated from ^1H NMR spectra thus drastically reducing the time involved in obtaining detailed carbon type analysis.

In other applications of multivariate analysis and neural networks to NMR analysis of gasoline a ^1H NMR method was developed to identify gasoline adulterated by solvents by both principal component analysis (PCA) and hierarchical cluster analysis (HCA) [80], and a method was demonstrated for obtaining octane numbers from ^{13}C NMR spectra and neural networks [81]. Staying on the topic of correlation of ^1H NMR structural parameters to the concentration of hydrocarbon groups (Paraffinic +Naphthenic %, and Aromatic %) of heavy oils such as tail oil, catalytic slurry oil, catalytic heavy tar, and waxy oil taken from various refinery processes. One can also develop relationships directly from the NMR spectrum by fitting plots of relative proton content (%H) of various proton types in the spectrum versus chromatographic column test results to determine alicyclic and paraffin hydrocarbon content (P+N) and aromatic hydrocarbon content (A) [82].

Many examples can be found of molecular and structural parameters derived from both ^1H and ^{13}C NMR applied to the study of processing changes in heavy oils, bitumen, and heavy refinery streams. Many of these papers contain similar approaches with regard to molecular representations and molecular and structural parameter calculation from the ^1H and ^{13}C data. However, on close examination many papers use different chemical shift ranges, assume conflicting or different chemistry in the ranges chosen, miss some chemistry types entirely, and utilize different calculation approaches. Some researchers fully describe the calculation process they have utilized, and others do not reveal how the calculations are performed at all. With the

growing importance of these NMR derived parameters in heavy petroleum processing, a consistency of approach, a standard method development process, and even a final “master spreadsheet” for the calculations should be considered, perhaps within the auspices of standard testing organizations such as ASTM, IP, or API. The advantage of NMR for many of these analyses is that it is a direct experimental technique that yields chemically rich information even on heavy petroleum streams that can only be approached with difficulty by chromatography or mass spectrometry to obtain reliable chemical information. The issue that hinders NMR from

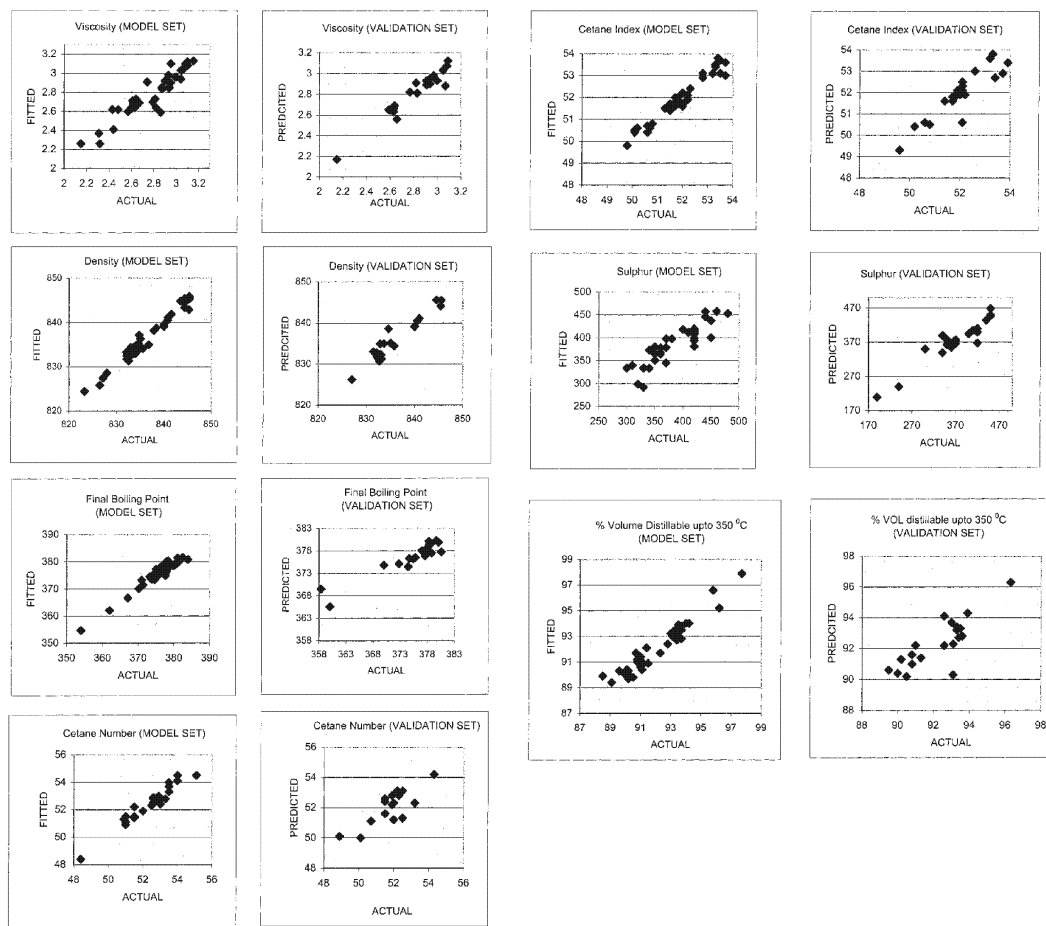


Figure 19: Correlation between NMR calculated chemical and physical properties of diesel and the laboratory experimental value for a validation set of samples. (Ref 76 - © American Chemical Society)

developing into a more widely applicable technique is the absence of official regulation of NMR methodology and experimental execution. In the petroleum industry especially, NMR operates outside the realms of standard test methods and standard operating procedures. This has become a weakness in the development and implementation of NMR technology to routine petroleum sample analysis. In high resolution NMR analysis of petroleum products the only standard test method is ASTM D5292-99 (Standard Test Method for Aromatic Carbon Contents of Hydrocarbon Oils by High Resolution Nuclear Magnetic Resonance Spectroscopy) [83]. This standard method represents the simplest ^{13}C NMR analysis – in the future, it too will face problems as there is a push towards synthetic crudes and fuels where olefin content will be high

and aromaticity numbers will need to be developed that discern between aromatic and olefinic carbon the signals of which overlap heavily in the ^{13}C spectrum- this will require combined ^1H and ^{13}C as well as 2D heteronuclear approaches that allow identification of olefinic carbons. This is routine methodology that needs to be developed and standardized so that it can be equally implemented by interested testing parties. The molecular and structural parameters described previously must be standardized so that they can be implemented with confidence in the areas of refinery control [84-86], bitumen processing [87-90], and asphaltene chemical analysis [91-99]. For these heavy petroleum fractions in particular there is a need to develop uniform methodologies to calculate the average aromatic ring sizes from which the remainder of the average molecule parameters are derived in ^{13}C NMR analysis. A number of combination methodologies utilizing quantitative ^{13}C NMR and DEPT-45 experiments holds promise to allow consistent analysis of overlapping protonated and bridgehead aromatic carbons in the 110-129.5 ppm region of the spectrum. Many researchers have published results indicating that DEPT experiments can be used to obtain semi-quantitative NMR parameters that can be consistently calculated [84,90,99-108]. Average molecule parameters derived from ^{13}C and ^1H NMR are utilized to monitor processing effects on aromatic ring size and the length of aliphatic substitutions. Figure 20 shows typical data obtained from a series of hydrodemetallization (HDM) reactions at different temperatures. NMR was used to monitor average molecule parameters such as C_{int} (internal aromatic carbon, sometimes called bridgehead aromatic carbon), f_a (carbon aromaticity), C_{sub} (number of alkyl attachments per aromatic ring system, and n (alkyl side chain). Variation in these values can be attributed to changes from conversion of catacondensed to pericondensed aromatic ring systems or vice-versa, reduction in ring sizes due to removal of heteroatoms from the aromatic structures, cracking of alkyl side chains leading to shorter attachments and fewer substitutions on the rings.

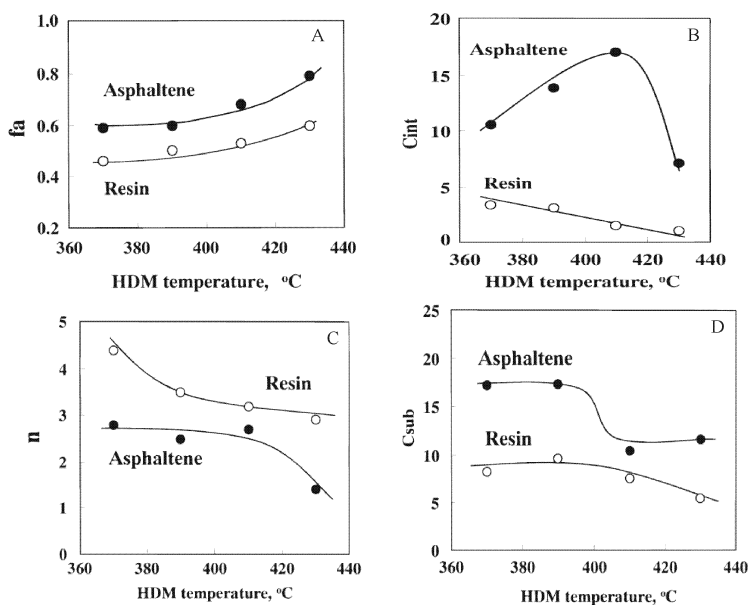


Figure 20: Effect of temperature and HDM reactor conditions on asphaltene and resin average molecule structural parameters calculated from ^1H and ^{13}C NMR. (From Ref 94 - © American Chemical Society)

The same NMR approaches that are utilized to envision changes in aromatic and aliphatic chemistry in heavy oils and bitumens are utilized in the study of lubricant base oils. Some approaches are simplistic, such as the utilization of pulsed field gradients (PFG) in NMR echo and DOSY (diffusion ordered spectroscopy) experiments to discern between high and low molecular weight components in a base oil mixture via their self-diffusion coefficients. The experimental results can be related to the kinematic viscosity and pressure viscosity coefficients of the base oil at different operational temperatures [109-110]. PFG applied to a series of lubricant base stocks showed a good correlation with kinematic viscosity as shown in Figure 21. The effect of hydrotreating and de-waxing operations can be readily observed by either structural or molecular parameters from ^1H and ^{13}C NMR [111]. Oxidative stability test results performed on pure or additized base oils can also be related to NMR derived parameters [112-113]. In all these studies important information is derived from ^{13}C derived values of F_a , F_p , and F_n , average

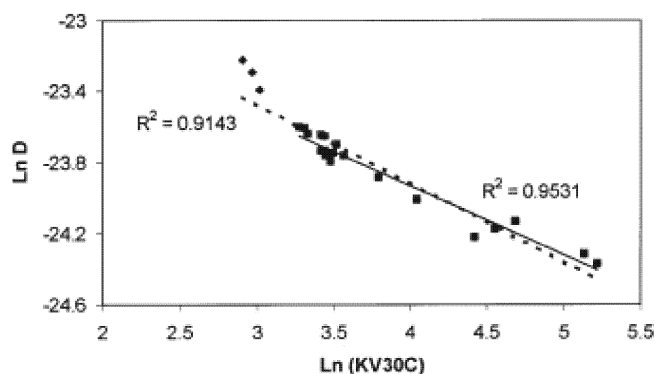


Figure 21: Diffusion coefficients derived from ^1H PFG-NMR show excellent correlation with kinematic viscosity at 30°C. (From Ref 109 - © American Chemical Society).

chain length, alkyl substitution, aromatic carbon distribution, iso-paraffin content, branching index. In studies of thermo-oxidative and physical property behavior directional changes in the values of these NMR parameters yield informative chemical correlations that can be used to formulate lubricants mixtures and additized products, or to optimize the base oil manufacturing process. A few examples are: 1) higher branching leads to lower oxidation stability, 2) increases in average alkyl chain length lead to increase viscosity, 3) branching index and naphthenic content increase while normal paraffin content and aromatic content decrease increasing severity of the hydrogenation process, 4) aromatic carbon decrease and saturated carbon increase leads to an increase in viscosity index during hydrogenation, 5) average chain length of paraffinic base oils decreases with hydrogenation while it increases in aromatic extracts [111]. Details of the ^{13}C NMR assignments for base oils produced by different manufacturing processes as well as those for hydrocracked base stocks can be found in articles by Sarpal et al. [114-115]. ^{13}C NMR is uniquely suited to analyze branching structures of iso-paraffins. Approaches to the analysis involve utilization of DEPT experiments to identify either CH carbons at branching points as well as CH_3 carbons whose chemical shift varies depending on the proximity of a molecule termination or a branching point. Figure 22 shows the peaks in the aliphatic region of the ^{13}C NMR spectrum that are associated with CH_3 chemistry, while Table VIII shows the chemical shifts of various CH branching points.

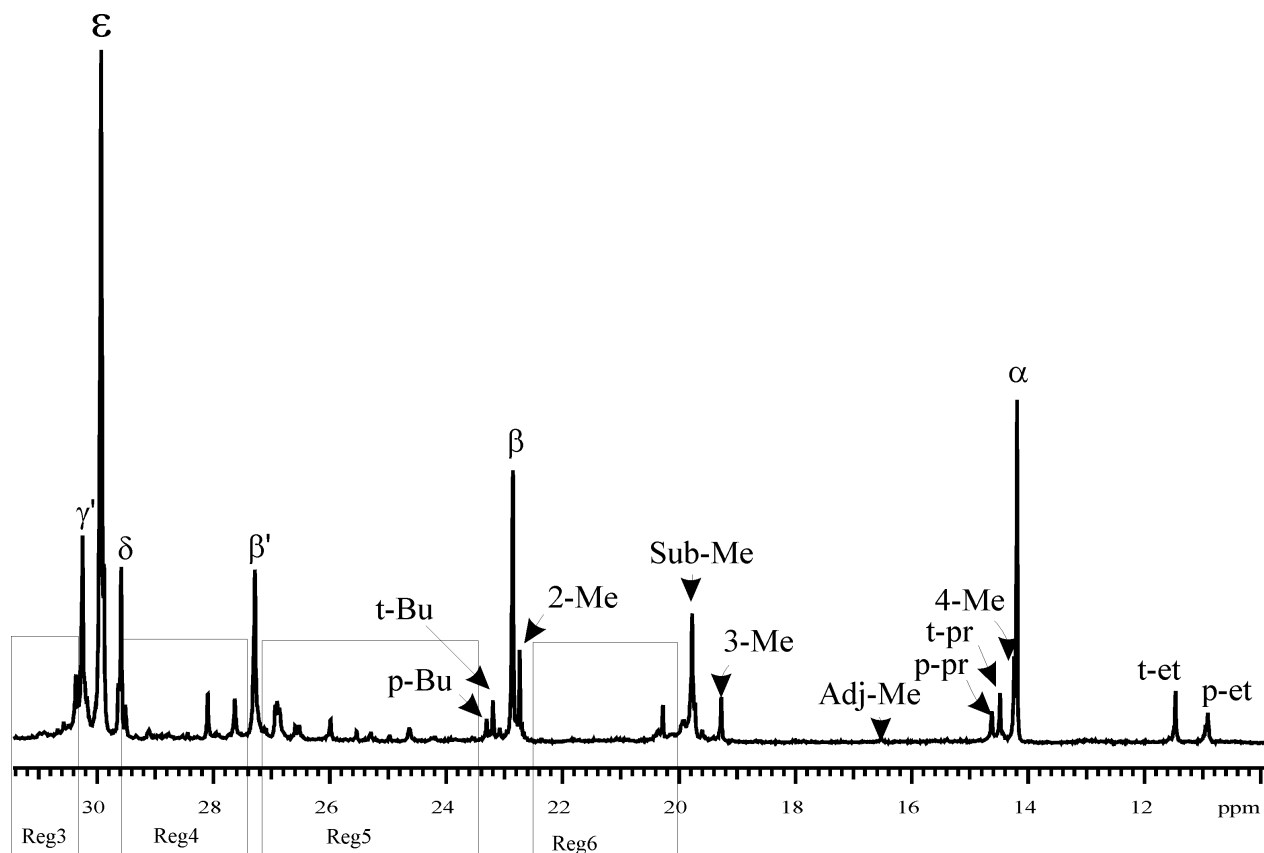


Figure 22: Identification of peaks associated with various pendant and terminal methyl carbons in the aliphatic carbon region of the spectrum. Also identified are the α , β , γ , δ , ϵ resonances due to carbons in linear regions of a paraffin chain, as well as β' and γ' resonances which are methylenes 2 and 3 carbons away from a branch point.

Table VIII: Chemical Shift Assignments of Methine Carbons in Paraffinic Branches

Group	Chemical Shift (ppm)	Corresponding branching of isoparaffins
CH-a	28.00-29.00	2-methyl branching
CH-b	32.75-32.90	4-methyl branching
CH-c	32.90-33.15	8- or inner methyl branching
CH-d	33.15-33.25	7-methyl branching
CH-e	33.25-33.45	3-methyl branching
CH-f	33.45-33.60	7- or inner ethyl branching
CH-g	34.50-34.80	5-,6-methyl, 4-,5-, 6-ethyl branching
CH-h	39.00-39.50	3-ethyl branching

From Ref 120 - © American Chemical Society

Another area of interest is the application of ^{13}C NMR to Fischer-Tropsch base stocks. The fact that these waxes are almost entirely paraffinic makes assignment and quantification of most branching types straightforward. In particular ExxonMobil[116], Chevron [117], and Mobil [118] have been very active in defining products by way of ^{13}C detailed branching calculations. One of the concepts developed is the “free carbon index” (FCI) which is a measure of linear

paraffin chain character – defined as the number of carbons more than four carbons removed from a terminal methyl group and more than 3 carbons removed from a branching point (ϵ carbons).

$$\text{FCI} = 100 \times (\epsilon \text{ carbons}) / \text{average carbon number}$$

where average carbon number is obtained from GC analysis (ASTM D-2502). As an example of how NMR is being used to define the properties of a lube stock product range we can take an excerpt from the example ExxonMobil patent which describes the product in terms of NMR branching character:

- 1) “.... at least about 75 wt% iso-paraffins”
- 2) “FCI typically in the range of 4 to 12, preferably less than 10”
- 3) “A further Criterion which differentiates these materials structurally from polyalphaolefins is the branch length....at least 75% of the branches, as determined by NMR, are methyls and the population of ethyl, propyl and butyls falls sharply with increasing molecular weight to the point where no more than 5% are butyls. Typically the ratio of “free carbons” to end methyl is in the range of 2.5 to 4.0”
- 4) “...basestocks have, on average, from 2.0 to 4.5 side chains per molecule.”

This approach to defining and patenting products in terms of branching carbon distributions indicates that petroleum product manufacturers should be routinely performing ^{13}C NMR analysis on everything they produce to prove that their products are either different from their competitors or establish the detailed branching details in order to prove “prior art” when those products are patented by a competitor. This approach is not solely performed in the lubricant oil area of Fischer Tropsch products, it has also expanded into diesel fuel product descriptions by ^{13}C NMR branching values [119-120]. In the case of the ExxonMobil descriptions of diesel fuel analysis the ^{13}C detailed branching values were regressed in order to yield predictive equations for cetane number, cold filter plugging point, cloud point, and pour point.

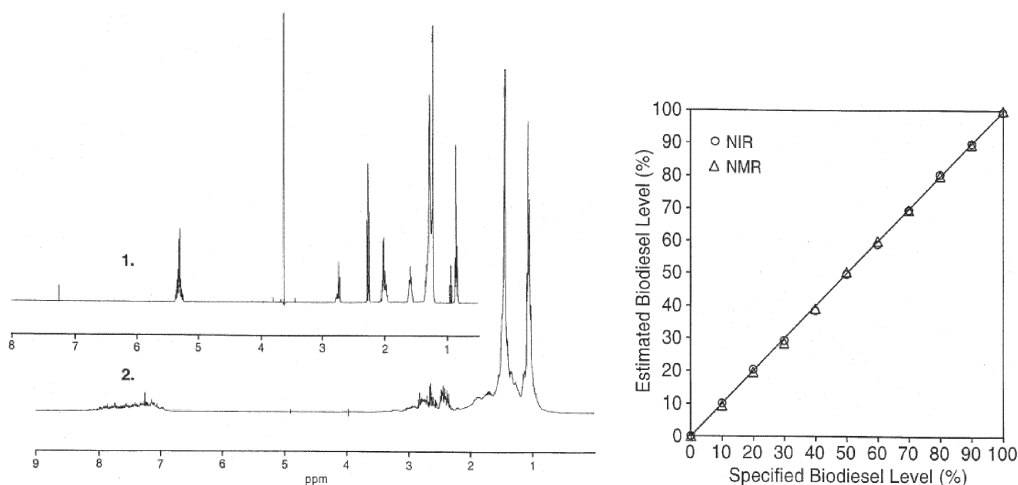


Figure 23: ^1H NMR spectra of FAME biodiesel from soybeans (1) and petroleum derived diesel (2) along with the plot of the NMR and NIR predicted biodiesel blend content versus actual blend concentration (vol%). (From Ref 124 - © AOCS Press)

Another area of utility for NMR is in biofuels production, quality assessment, and blending operations. Reaction monitoring in biorefineries will be an area where the chemical specificity of NMR will be invaluable. At the moment NMR is considered the primary method for analysis of esterification reactions used to produce fatty acid methyl esters (FAME) from vegetable oils [121-124]. Other techniques are utilized for real time monitoring but these techniques (NIR, FT-IR, Raman) are calibrated with ^1H NMR data. NMR will also play a role in the study of biodiesel stability during storage and the effect of air exposure on the unsaturated fatty acids present in the biodiesel [125]. Figure 23 shows the ^1H NMR spectra of FAME and conventional diesel as well as the excellent correlation between NMR calculated FAME content on a series of calibrated blends.

NMR allows methods to be developed that monitor types of unsaturation and the relative concentrations as samples are exposed to different techniques (NIR, FT-IR, Raman) are calibrated with ^1H NMR data. NMR will also play a role in the study of biodiesel stability during storage and the effect of air exposure on the unsaturated fatty acids present in the biodiesel [125]. Figure 23 shows typical ^1H NMR of diesel and biodiesel as well as a calibration of biodiesel content in diesel by NMR. NMR allows methods to be developed that monitor types of unsaturation and the relative concentrations as samples are exposed to different storage conditions with respect to temperature, presence of light and air, presence of metal, etc. In the U.S. the commercialization of B20 (20% biodiesel / 80% petroleum-derived diesel) has begun, and in Europe and Brazil B2 blends are being developed. ^1H NMR is an ideal method for monitoring the blend ratio during production and throughout the distribution network. PLS models were evaluated and found to produce adequate prediction capability [126]. 60 MHz NMR instrumentation would be ideal for many biofuel applications and has sufficient resolution to allow real-time reaction monitoring and ready observation of biodiesel in diesel.

Applications: High Field NMR (200-600 MHz) Solid-State Analysis

Solid-state ^{13}C NMR is the predominant analysis performed in the characterization of petroleum macromolecules which are too large and insoluble to be analyzed in solvent solutions. ^1H NMR of carbonaceous solid materials does not yield reasonable results due to the large dipole-dipole interactions that require extremely high spinning speeds to average. For many years researchers attempted to utilize fast spinning and multipulse decoupling techniques but in general the results are disappointing and very little useful information is obtained.

^{13}C NMR has been found to be very useful in the study of carbonaceous solids and two approaches are typically taken experimentally - cross polarization (CP) and single pulse excitation (SPE), both performed with magic angle spinning (MAS). The SPE experiment is also known as Bloch decay (BD). Initially most work was performed using CP-MAS because it has a number of time saving advantages over SPE-MAS. The CP technique utilizes a polarization transfer experiment whereby the magnetization is initially excited by a 90° pulse on the protons in the sample and that magnetization is transferred from the protons to the ^{13}C coupled to those protons during a thermal mixing period called a "contact time". After an optimized contact time the mixing pulses are turned off and the ^{13}C NMR signal is collected while the protons are decoupled. This experiment has the advantage that a considerable sensitivity enhancement is gained and the experiment is performed on the T_1 time scale of the ^1H in the sample which are considerably shorter than those of ^{13}C allowing for faster acquisition of NMR spectra. The

technique also has disadvantages in that quantitation is made difficult due to the different rates at which the polarization occurs from protons to carbons in different chemical and motional environments. Molecular motion modulates the H-C dipole contact through which the polarization occurs so that faster motion leads to less efficient transfer. Also inter-nuclear C-H distances also effect the rate of polarization transfer and any carbon that is further than 7 Angstroms from a proton will not be observed at all. In carbonaceous materials with extended aromatic structures this leads to non-observation of a large amount of aromatic material. In general this leads to SPE-MAS yielding higher aromaticity (fa) values than CP-MAS experiments. SPE-MAS also has issues with quantitation due to the long T_1 times associated with quaternary carbons and other carbon types found in petroleum. The main issue is the amount of time involved in acquisition of ^{13}C SPE-MAS experiments which can be considerable. The instrumentation that one employs in performing these experiments also dictates which experiment the researcher will have to employ. Aromatic and carboxylic carbons have a considerably large chemical shift anisotropy (CSA) which leads to the fact that these carbon types yield an isotropic NMR peak that is surrounded by progressively smaller spinning sidebands due to the incomplete averaging of the CSA by magic angle spinning. These spinning sidebands are inherently part of the aromatic signal and must be integrated and accounted for in the various structural parameter calculations. The CSA scales with increasing NMR magnet strength. Thus, in the case of a 200 MHz NMR spectrometer the sample must be spun at 7 kHz in order for the first spinning side band to be beyond the aliphatic region and thus able to be properly quantified. At 400 MHz the MAS speed required for avoidance of MAS sideband overlap with aliphatic carbon signals is 14 kHz, and at 600 MHz it is 21 kHz. Interestingly, at 60 MHz the MAS requirement is only 2.1 kHz which means that lower magnetic field instrumentation at 60 MHz is ideal for ^{13}C CP-MAS experimentation. Lower sensitivity at 60 MHz (15 MHz for ^{13}C) field strength can be overcome by using larger sample rotors of 10-14 mm (which can easily spin at 2.1 kHz). This is an important issue as at spinning speeds above 7 kHz the C-H dipolar coupling through which the CP experiment works begins to be averaged by the MAS and thus the experiment becomes less quantitative when performed on a high field NMR instrument. If lower MAS speeds are used the overlap of sidebands with isotropic carbon peaks becomes a considerable quantitation problem. To avoid this issue researchers perform only SPE-MAS experiments at higher fields where they have good sensitivity from the higher field magnet systems. However, due to the necessity to spin at 14 -21 kHz the sample rotors used are much smaller in diameter (4 mm) and some of the sensitivity gain is lost due to less sample being analyzed. SPE-MAS does have the advantage that all carbon is potentially observed and if long relaxation delays are used the data yields results that are considered more representative than those obtained by CP-MAS.

The seminal paper describing the acquisition and calculation of average molecule and carbon type structural parameters was written by Solum, Pugmire and Grant [127]. The experiments and processing/calculation methodology described has been used by many research groups as the basis for subsequent solid-state ^{13}C analysis of solid carbonaceous materials such as coal [127-138], kerogen [139-143], peat and lignites [144], refinery coke and residues [145-147], catalyst coke [148-149], bitumen and pitch [150-151], soots and combustion deposits [152-157]. An excellent overview of the ^{13}C NMR methodology to determine the carbon skeletal structure of carbonaceous materials is presented by Solum et al in a study of soot [152 see Appendix]. A combination of three different experiments is required to obtain datasets from which structural parameters can be derived.

- 1) Variable Contact Time(VCT) CP-MAS experiment - a series of 20 contact times varied from 100 μ s to 20 ms the analysis of which allows the aromaticity of the sample to be determined independent of the contact time.
- 2) Dipolar-dephased CP-MAS in which a series timings for a delay and echo that are inserted after the mixing pulses are turned off and the decoupling is turned on. This experiment yields a decaying NMR signal that is fit to both Gaussian and Lorentzian decays (protonated and non-protonated carbon signals respectively) to yield a fraction of aromatic and aliphatic carbons that decay with a Gaussian behavior (parameter M_{0G}). As protonated carbons decay with Gaussian behavior this allows the relative amount of protonated and non-protonated aromatic (or aliphatic) carbons to be calculated.
- 3) A high signal-to-noise CP-MAS NMR obtained with a 2 ms contact time. This experiment is used to accurately determine the various integral intensity values for the different carbon types observed in the spectrum. Table IX shows the ^{13}C chemical and structural average molecule

Table IX: Solid-State ^{13}C NMR Parameters: Chemical Shift Ranges Utilized, Parameter Descriptions, and Calculations

Parameter	Shift Range (ppm)	Description	Calculation
F_a	90-240	Carbon Aromaticity	
F_a'	90-165	Aromaticity - not including Carboxyl/Carbonyl	$F_a' = F_a - F_a^C$
F_a^C	165-240	Carboxylic and Carbonyl Carbon	
F_a^{CO}	185-240	Carbonyl - Ketone, Aldehyde	
F_a^{COO}	165-185	Carboxylic - Acid, Ester, Amide	
F_a^P	150-165	Phenolic Aromatic Carbon	
F_a^S	135-150	Alkyl-Substituted Aromatic Carbons	
F_a^H	90-165	Protonated Aromatic Carbon	DD Aromatic - $F_a^H = F_a' M_{0G}$
F_a^N	90-165	Non-Protonated Aromatic Carbon	$F_a^N = F_a' - F_a^H$
F_a^B	90-165	Bridgehead Aromatic Carbon	$f_a^B = F_a^N - F_a^P - F_a^S$
F_{al}	0-50	Total Aliphatic Carbon	
F_{al}^O	50-90	Oxygenated Aliphatic Carbon	
F_{al}^H	22-50	Protonated Aliphatic Methylene and Methine	DD Aliphatic - $F_{al}^H = f_{al} M_{0G}$
F_{al}^*	0-22	Methyl Carbons	$F_{al}^* = F_{al} - F_{al}^H$
X_b		Mole fraction of Bridgehead Carbons	$X_b = F_a^B / F_a'$
C		Carbons per Aromatic Cluster	See Figure 24 - C is calculated from X_b
$\sigma + 1$		Average Number of Alkyl Attachments	$\sigma + 1 = (F_a^P + F_a^S) \times C / F_a'$
P_o		Fraction of Intact Bridges and Loops	$P_o = (F_a^P + F_a^S - F_{al}^*) / (F_a^P + F_a^S)$
B.L.		Bridge and Loop Alkyl Attachments	$B.L. = P_o (\sigma + 1)$
S.C.		Terminal Alkyl Side Chains	$S.C. = (\sigma + 1) - B.L.$
M_w		Average Molecular Weight of a Cluster	$M_w = 12.01 C / (F_a' \times \%C/100) \quad \%C \text{ from Elemental}$
M_T		Average Molecular Weight of Attachments	$M_T = (M_w - 13M_{0G}C - 12(1-M_{0G})C) / (\sigma + 1)$

parameters that can be calculated by a combination of the three experiments. Figure 24 shows the plot of the mole fraction of bridgehead aromatics (X_b) versus C , where C is the number of carbons per aromatic cluster. X_b is obtained from the various integral intensity calculations. This parameter is the starting point for the average molecule structural parameter calculations. Using the plot of X_b vs C the value of C is derived. Having reduced the carbon fraction parameters to a 100 carbon basis it is then possible to calculate how many aromatic cluster there are per 100 carbons (Fa'/C). The rest of the calculated structural parameters are a logical progression from this obtaining this value.

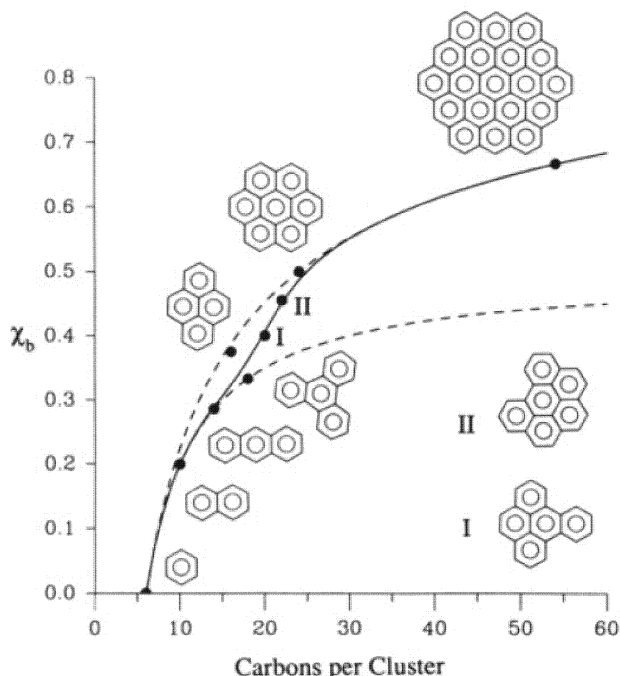


Figure 24: Mole Fraction of Bridgehead aromatic carbon (X_b) versus the average number of carbons per aromatic cluster (C). Utilized in the calculation of average molecular structural parameters for carbonaceous materials by solid-state ^{13}C NMR. (From Ref 127 - © American Chemical Society).

Table X: ^{13}C Carbon Types in Coal Utilized in Calculations to Correlate to Coal Liquefaction Yields

Hydrocarbon gas (HC (wt%)) $= 0.33(\text{CH}_2 + \text{CH}_3)\% + 6.15$	$25 < \text{CH}_2 + \text{CH}_3 < 45$
CO_x gas (O_{CO_x} (wt%)) $= 1.43(\text{C}=\text{O} + \text{COOH})\% - 1.45$	$2 < \text{C}=\text{O} + \text{COOH} < 5.5$
Water ($\text{O}_{\text{H}_2\text{O}}$ (wt%)) $= 2.03(\text{Ar}-\text{O}-\text{OCH}_3)\% - 10.84$	$6 < \text{Ar}-\text{O}-\text{OCH}_3 < 12$
Oil (wt%) $= 0.86 \text{CH}_2\% + 27.5$	$20 < \text{CH}_2 < 35$
Residue (wt%) $= 122.0fa - 49.2$	$0.5 < fa < 0.7$

From Ref 138 - © Elsevier

The utility of these solid-state ^{13}C parameters is clear for coal analysis and the delineation between coal and petroleum chemistry is becoming less distinct with the advent of coal derived synthetic fuels from coal-liquefaction and gasification-Fischer Tropsch processes. ^{13}C NMR is being utilized to predict coal liquefaction reactivity with Table X showing the correlations between coal carbon structure and liquefaction product yields of hydrocarbon gas, CO_x gas, water, oil, and residue.

As alternate energy sources are investigated the analysis of organic sedimentary solids other than coal is increasing. Type I, II, and III kerogens were studied directly by solid-state ^{13}C NMR and the hydrogen-rich Type II and II kerogens were found to have increasing f_a' , decreasing $f_a^S/(\sigma+1)$, decreasing attachment chain length, increasing values of C, and decreasing F_a^C , with increasing thermal maturity. Example ^{13}C spectra for a range of kerogen materials is shown in Figure 25. The ^{13}C NMR structural parameters obtained on this broad kerogen dataset is shown in Table XI demonstrating the large differences that are observable in the NMR derived parameters.

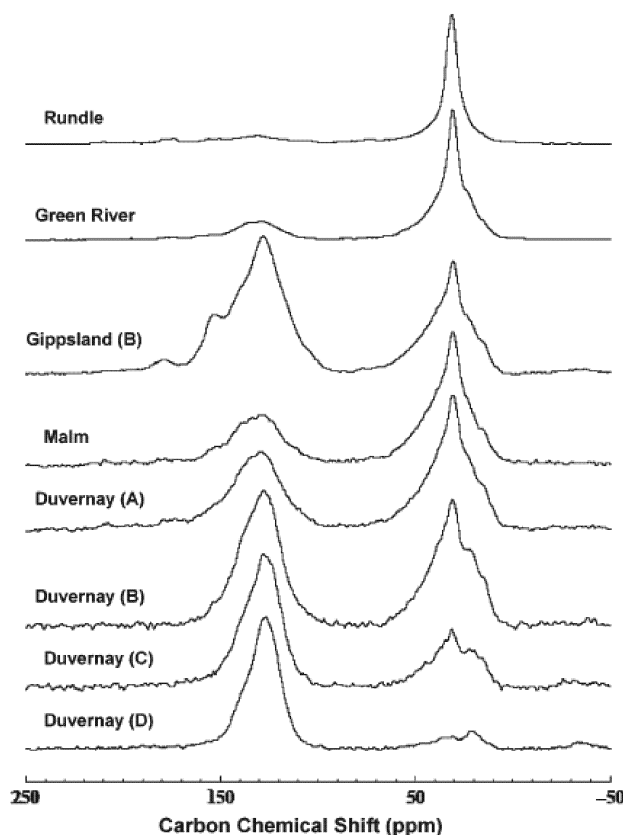


Figure 25: Solid-state ^{13}C CP-MAS NMR spectra of a wide range of kerogens spanning a range of organic matter types and thermal maturation. (From Ref. 139 - © American Chemical Society)

Table XI: Solid-State ^{13}C NMR Average Molecule Lattice Parameters for Kerogen and Lower Limit Estimate for Organic Oxygen ($F_a^C + 0.5(F_a^P + F_{al}^O) \times 100$)

sample	C	FAA	Cn'	$fa^C + 0.5(fa^P + fa^O)$ (x100)
Green River	16	0.40	10.3	7.0
Rundle	10	0.42	15.0	11.0
Duvernay (A)	12	0.43	4.5	12.0
Duvernay (B)	19	0.32	3.8	4.5
Duvernay (C)	19	0.30	3.4	6.0
Duvernay (D)	20	0.24	1.1	4.5
Oxford Clay	13	0.40	12.5	11.2
Paradox	17	0.29	6.1	4.1
Malm	13	0.40	7.2	11.5
Draupne	17	0.36	7.6	5.8
Bakken	12	0.27	8.2	5.4
Monterey	12	0.28	15.0	7.5
Gippsland (A)	15	0.37	2.3	10.0
Gippsland (B)	14	0.31	3.1	5.5
Proprietary (A)	16	0.35	3.4	10.2
Proprietary (B)	19	0.26	1.6	3.6
Proprietary (C)	18	0.15	1.8	1.2
Fruitland	14	0.32	3.8	7.9

↓ = thermal maturity sequence A= immature B-C = oil window, D = post-mature

(From Ref 139 - © American Chemical Society)

Conclusion

NMR spectroscopy has provided detailed chemical information on the proton and carbon chemistry of petroleum materials for over 60 years. NMR analysis will help researchers and engineers meet the future challenges involved in online process control, alternative energy exploration and production, and improved petroleum product quality. Developments in Field Programmable Gate Array FPGA electronics is currently leading to the development of cheaper and smaller NMR instrumentation platforms which combined with improved automated data processing and chemometric analysis software will place NMR in the hands of many more researchers as an increasingly routine analyzer.

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