

# RCC Feed-Stream Analysis by $^1\text{H}$ and $^{13}\text{C}$ NMR: Multivariate Prediction of Physical and Chemical Properties

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## Introduction

Over the past few decades  $^1\text{H}$  and  $^{13}\text{C}$  NMR has been widely used to obtain average molecule information on a wide range of petroleum products such as asphaltenes<sup>1</sup>, vacuum gas oils (VGO)<sup>2,3</sup>, and jet fuels<sup>4</sup>. However, NMR parameters are not currently understood and utilized by engineers in charge of unit operations. Detailed NMR information, though extremely rich in quantitative chemical information, is useful only if its variance can be translated into chemical and physical properties that can be applied as control and optimization parameters to improve unit operations. Historically, engineers are familiar with GC derived chemical properties such as aromatics, PONA, olefins in wt% or vol%, as well as distillation properties, viscosity, Conradson carbon, sulfur, density, etc. Some researchers have developed  $^1\text{H}$  NMR methods that derive linear equations that correlate certain proton chemistry functional group concentrations to specific chemical or physical properties<sup>5-7</sup>. However, we have developed more generally applicable multivariate regression methods that allow many chemical and physical property measurements to be derived from the same quantitative  $^1\text{H}$  or  $^{13}\text{C}$  NMR data. In the course of the model development we have also derived magnetic field independent data manipulation methods that allow  $^1\text{H}$  or  $^{13}\text{C}$  NMR derived parameters to be utilized and the X Matrix “spectral” data rather than the spectra themselves. This allows field independent models to be developed as these parameters are calculated directly from the spectrum and are the same regardless of the field strength at which the data was collected. This has implications with respect to calibration transfer between laboratories. In this work we describe the application of these methods on feed-streams to a residual catalytic cracker (RCC), which typically represents the core gasoline and diesel production facilities of a refinery.

## Experimental

**High Field NMR Spectroscopy:**  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra were obtained on both a Varian Unity-300 and a Varian UnityPlus-200 spectrometer, operating at 299.942 and 200.007 MHz for  $^1\text{H}$  and 75.428 and 50.297 MHz for  $^{13}\text{C}$ , respectively. Spectra were obtained neat without addition of lock solvent. Relaxation delay of 4 seconds and an acquisition time of 1.6 seconds were used for  $^1\text{H}$  with an applied 5 degree tip angle pulse. For  $^{13}\text{C}$  NMR a relaxation delay of 9 seconds and an acquisition time of 0.64 seconds were utilized in conjunction with a 45 degree tip angle pulse.

**Low Field NMR Spectroscopy:**  $^1\text{H}$  NMR spectra were obtained on the same samples on a Qualion 60 MHz NMR spectrometer.

**Multivariate Analysis:**  $^1\text{H}$  NMR spectra were processed and then reduced to normalized integral bin spectra (0.1 ppm integration bins from -1 to 10 ppm).  $^{13}\text{C}$  NMR spectra were processed and then reduced to normalized integral bin spectra (1 ppm integration bins from -9.5 to 200.5 ppm). Multivariate analysis was performed using Galactic Grams PLS/IQ. PLS-1 regressions were performed with leave-one-out cross validation. NMR structural parameters and detailed carbon type analyses were performed on all the samples. These parameters were then utilized as the X matrix “spectra” in the regression modeling and calibrations were developed that correlate these carbon NMR parameters to the chemical and physical properties of the RCC feed samples.

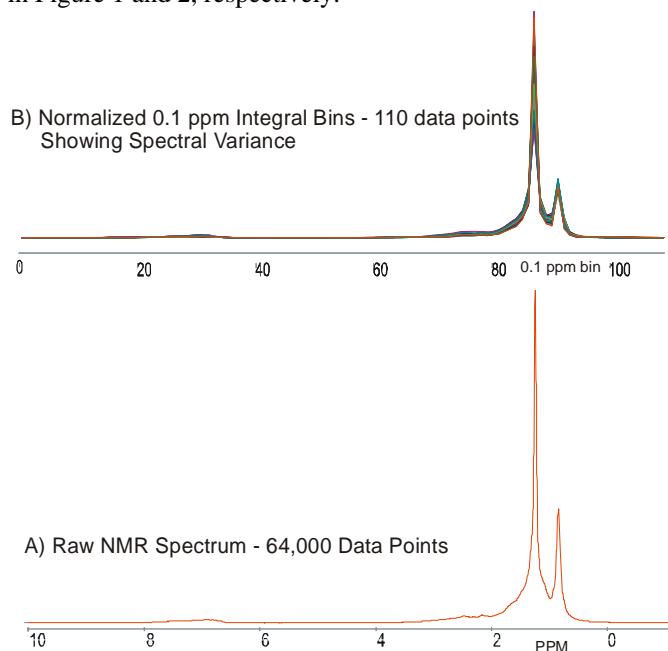
**Samples:** 50 RCC feed samples were analyzed in the laboratory to obtain the various chemical and physical property values for each sample by various ASTM test methods. These samples represent a mixture of VGO and residue/VGO.

## Results and Discussion

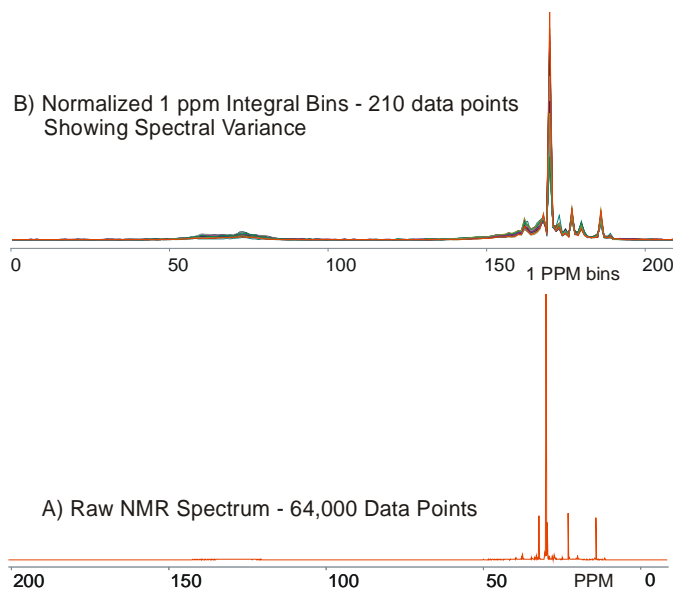
Excellent correlations with chemical and physical properties were obtained with all four sets of NMR data:

- 1)  $^1\text{H}$  NMR at 300 and 200 MHz
- 2)  $^{13}\text{C}$  NMR data at 75 and 50 MHz
- 3)  $^{13}\text{C}$  NMR Carbon Type “Spectra” at 75 and 50 MHz
- 4)  $^1\text{H}$  NMR at 60 MHz

**High Field  $^1\text{H}$  NMR:** Typical  $^1\text{H}$  and  $^{13}\text{C}$  NMR data is shown in Figure 1 and 2, respectively.

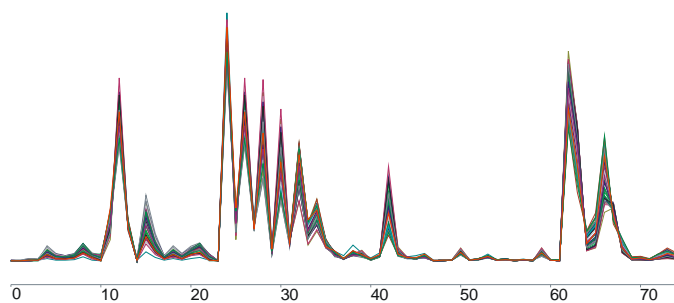


**Figure 1.** Comparison of raw  $^1\text{H}$  NMR data and processed /binned spectrum that is used in the multivariate regression modeling.



**Figure 2.** Comparison of raw  $^{13}\text{C}$  NMR data and processed /binned spectrum that is used in the multivariate regression modeling.

The variance of “spectra” produced by defining the calculated carbon type parameters as data points in a spectrum are shown in Figure 3. The chemical NMR description of the seventy five points in the carbon-type “spectrum” is given in Table 1.1 and Table 1.2. These parameters are calculated independent of the NMR system magnetic field strength and are therefore transferable between laboratories and NMR equipment.



**Figure 3.**  $^{13}\text{C}$  NMR Derived Carbon-Type parameters represented as “spectra” for multivariate regression modeling.

Table 3 shows the regression analysis results obtained on the  $^1\text{H}$  NMR data,  $^{13}\text{C}$  NMR PLS regression results, and the field independent  $^{13}\text{C}$  carbon-type parameter regression results for a series of VGO chemical and physical properties. For each parameter we have shown the  $R^2$  value as well as the SECV (standard error of cross-validation).

**Table 1.1: Carbon Type Parameters Calculated from  $^{13}\text{C}$  NMR Spectra – Points 1-36 of the 75 point “Spectrum”.**

Index	Carbon Type Parameters (%C Unless Otherwise Listed)	Typical Values
1	Ketone carbonyl carbon %c	0.00
2	Aldehyde carbonyl carbon	0.06
3	Carboxylic acids, esters and amides carbonyl carbon	0.00
4	Phenoxy carbon	0.25
5	CH <sub>2</sub> & CH sub aromatic carbon	4.56
6	Naphthenic sub aromatic carbon	2.25
7	CH <sub>3</sub> sub aromatic carbon	1.62
8	Half of internal aromatic carbon	2.23
9	Protonated Internal aromatic C+ 1/2 internal aromatic C	6.09
10	Protonated aromatic carbon	2.68
11	Heteroaromatic other than phenoxy carbon	1.27
12	Methine carbon	15.59
13	Methylene carbon	48.46
14	Methyl carbon	14.93
15	Total carbonyl carbon	0.06
16	Total aromatic carbon	20.96
17	Aliphatic sub aromatic carbon	8.44
18	Methyl-substituted aromatic carbon	1.62
19	CH <sub>2</sub> & CH substituted aromatic carbon	4.56
20	Naphthenic substituted aromatic carbon	2.25
21	Internal aromatic carbon	4.47
22	Peripheral unsubstituted aromatic carbon	6.54
23	Total heteroaromatic carbon	1.52
24	Total olefinic carbon	0.00
25	Total aliphatic carbon	78.98
26	Aliphatic methine carbon (CH)	15.59
27	Aliphatic methylene carbon (CH <sub>2</sub> )	48.46
28	Aliphatic methyl carbon (CH <sub>3</sub> )	14.93
29	Total paraffinic carbon	38.28
30	Paraffinic methine carbon (CH)	2.93
31	Paraffinic methylene carbon (CH <sub>2</sub> )	28.00
32	Paraffinic methyl carbon (CH <sub>3</sub> )	7.35
33	Total naphthenic carbon	40.70
34	Naphthenic methine carbon (CH)	12.66
35	Naphthenic methylene carbon (CH <sub>2</sub> )	20.46
36	Naphthenic methyl carbon (CH <sub>3</sub> )	7.58

Figure 4 shows the regression plots that demonstrate the actual and predicted API-gravity values for the 50 samples in the data set. All three techniques obtain around the same results, although  $^{13}\text{C}$  NMR appears to be slightly superior.

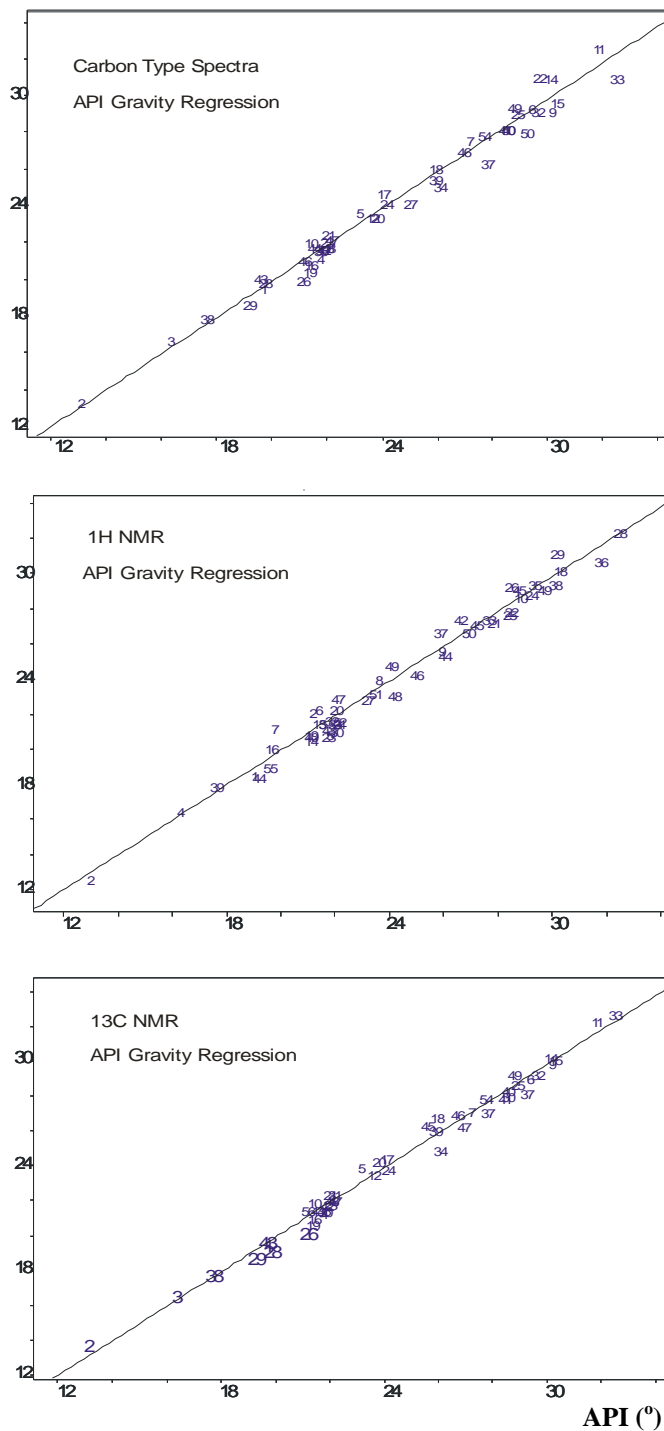
The final dataset that was investigated was one obtained at 60 MHz dataset on a Qualion MRA system that is based on a permanent magnet NMR technology. The results obtained on this platform were very similar to those obtained on the high resolution  $^1\text{H}$  NMR dataset obtained at 300 MHz. Table 4 shows the NMR results obtained on the same parameters described for the high resolution datasets.

**Table 1.2: Carbon Type Parameters Calculated from <sup>13</sup>C NMR Spectra – Points 37-75 of the 75 Point “Spectrum”.**

Index	Carbon Type Parameters (%C Unless Otherwise Listed)	Typical Values
37	Reg1	1.90
38	a'	1.06
39	Reg2	2.42
40	g	1.71
41	Reg3	0.43
42	g'	1.77
43	e	13.29
44	d	2.31
45	Reg4	1.00
46	b'	1.03
47	Reg5	1.42
48	p-Bu	0.04
49	t-Bu	0.13
50	Peak x	0.10
51	b	2.65
52	2-Me	0.23
53	Aromatic a methyl carbon	0.74
54	All other-Me	1.55
55	3-Me	0.40
56	Reg7	0.50
57	p-Pr	0.11
58	t-Pr	0.30
59	4-Me	0.12
60	a	2.62
61	t-Ethyl	0.31
62	p-Ethyl	0.12
63	Linear Paraffin Structure: % Linear Paraffin/Total Paraffin	59.02
64	Waxiness : % Epsilon C/Total Paraffin	34.72
65	Branching Index: %Branching CC/Total Paraffin	9.98
66	Total Branching Content: % C Near Branching C/Total C	14.66
67	C in Branched Environment: % 1-linear paraffin structure	40.98
68	Average Straight Chain Length (C No.)	16.08
69	Methyl branching index	7.31
70	Ethyl branching Index	1.13
71	Propyl branching Index	1.09
72	Butyl branching Index	0.46
73	Total ethyl branching content	2.26
74	Total propyl branching content	3.26
75	Total butyl branching content	1.84

**Table 3: High Resolution NMR Model Performance for VGO Chemical and Physical Properties**

NMR Data Type	<sup>1</sup> H		<sup>13</sup> C		C-Type	
	R <sup>2</sup>	SECV	R <sup>2</sup>	SECV	R <sup>2</sup>	SECV
API Gravity	0.987	0.47 °	0.982	0.61 °	0.98	0.61 °
Total Aromatics	0.949	0.71 wt%	0.975	0.47 wt%	0.976	0.47 wt%
Sulfur	0.97	0.15 wt%	0.985	0.1 wt%	0.977	0.13 wt%
Carbon Aromaticity	0.989	0.46 %C	0.994	0.32 %C	0.998	0.21 %C



**Figure 4.** Actual vs Predicted API gravity plots for regressions performed on <sup>1</sup>H, <sup>13</sup>C, and <sup>13</sup>C Carbon-Type NMR data.

**Table 4: Low Resolution Process NMR Model Performance for VGO Chemical and Physical Properties**

NMR Data Type	<sup>1</sup> H	
	R <sup>2</sup>	SEC V
API Gravity	0.962	0.62 °
Total Aromatics	0.978	0.81 wt%
Sulfur	0.935	0.26 wt%
Carbon Aromaticity	0.965	0.65 wt%

### Conclusions

NMR can be used to rapidly determine physical and chemical properties of RCC feed-streams. Control decisions can be made based on multiple parameter predictions from <sup>1</sup>H, <sup>13</sup>C or C-Type NMR analysis data. Process NMR units can also be utilized for at-line or in-line control of RCC process units.

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