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Mutivariate Analysis of ^{1}H and ^{13}C NMR Data of Residual Catalytic Cracker Feed-Streams: NMR Pre-Processing Strategies that Allow the Development of Predictive Models of Physical and Chemical Properties that are Independent of NMR Instrument Magnetic Field Strength

By

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NMR Analyzers

Superconducting NMR Magnet Systems

Permanent Magnet NMR Technology

2nd Generation Process NMR

Application: Steam Cracking Optimization Installed 2000

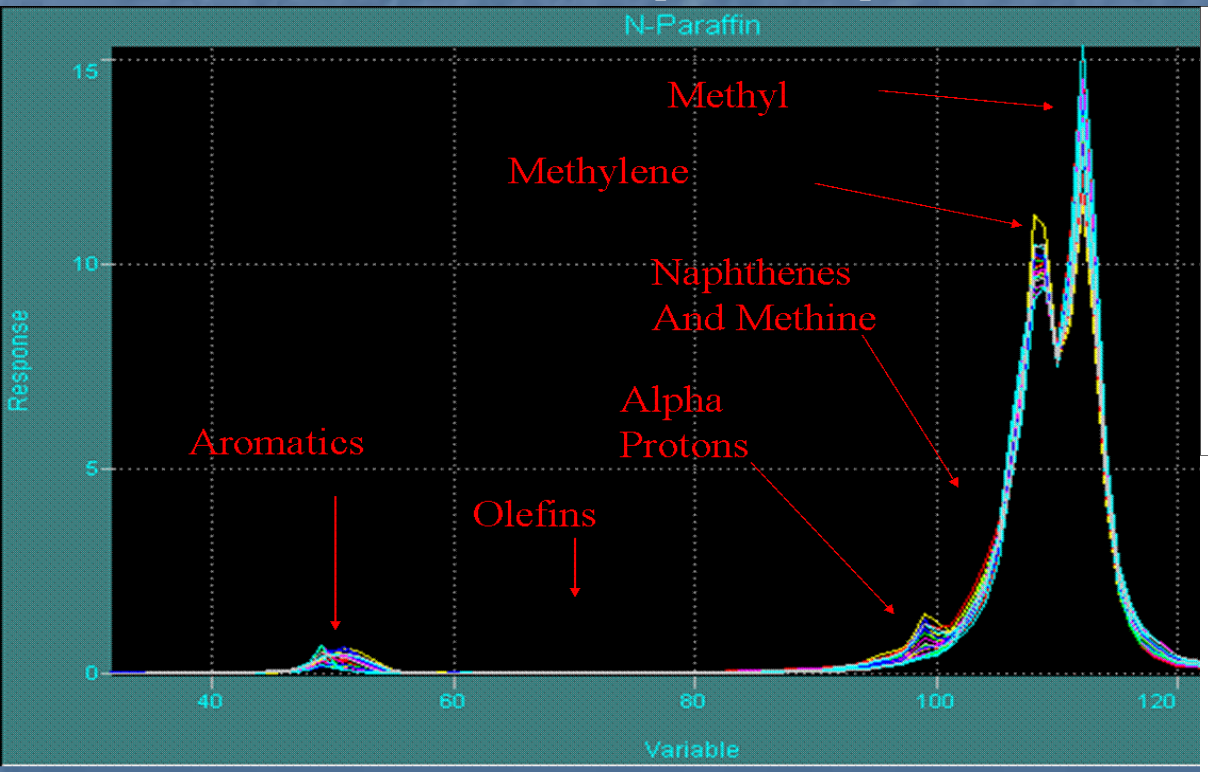
Cracker Facility Capacity: 600,000 Tonnes per Year

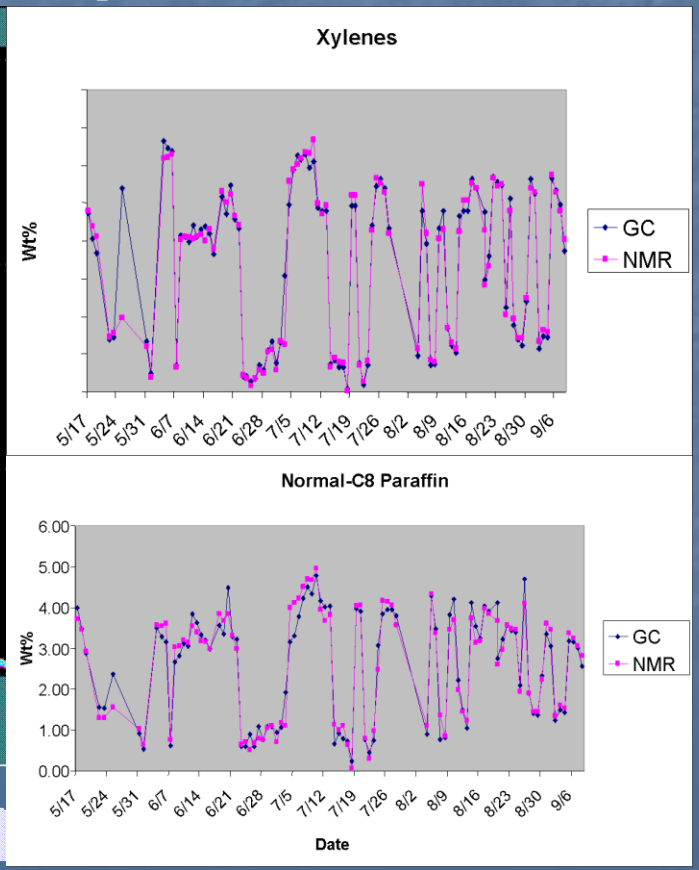
Control Strategy: Feed Forward Detailed Hydrocarbon Analysis to SPYRO Optimization

NMR Analysis: 3-4 Minute Cycle (Single Stream)

NMR PLS Outputs: Naphtha – Detailed PIONA

C4-C10 n-paraffin, i-paraffin, aromatics, naphthenes





Spectral Variability Observed in Naphtha Samples

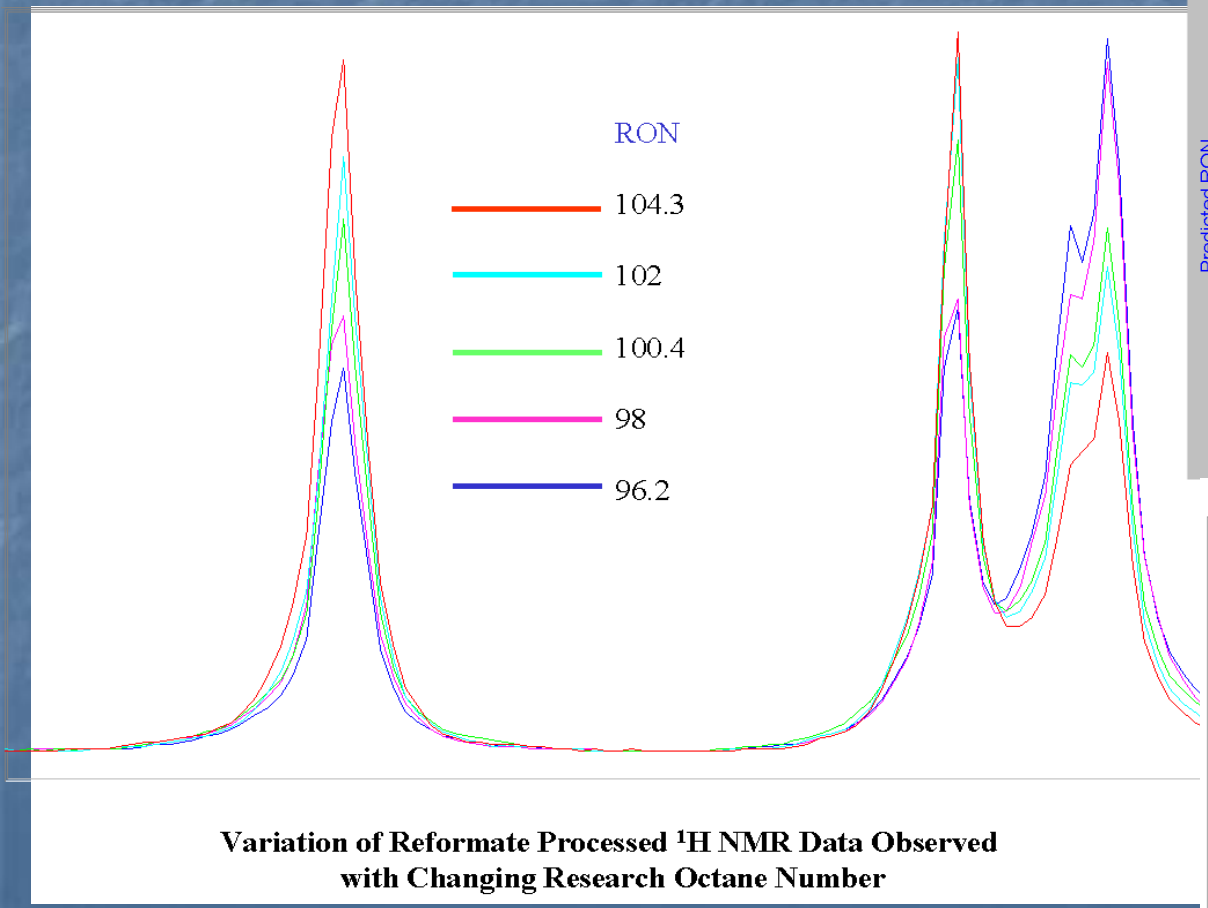
Application: Closed Loop Reformer Control - Installed 1998

Reformer Capacity: 34,000 Barrels per Day

Control Strategy: Control on MON and Benzene Content

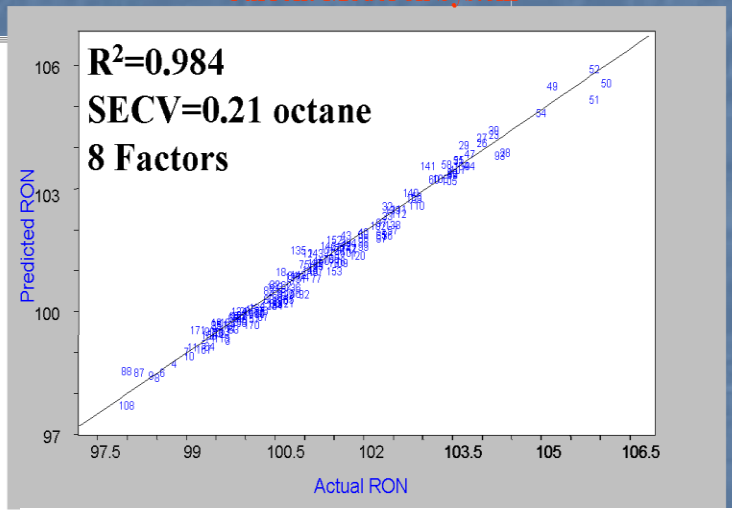
NMR Analysis: 2 Minute Analysis

NMR PLS Outputs: RON, MON, Benzene (Wt%), Total Aromatics (Wt%)

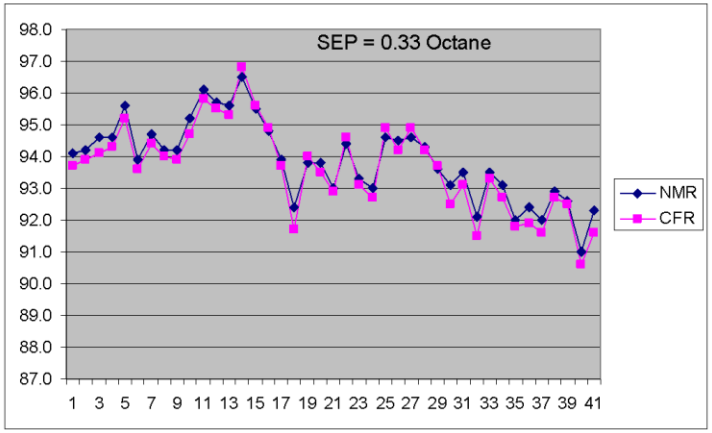


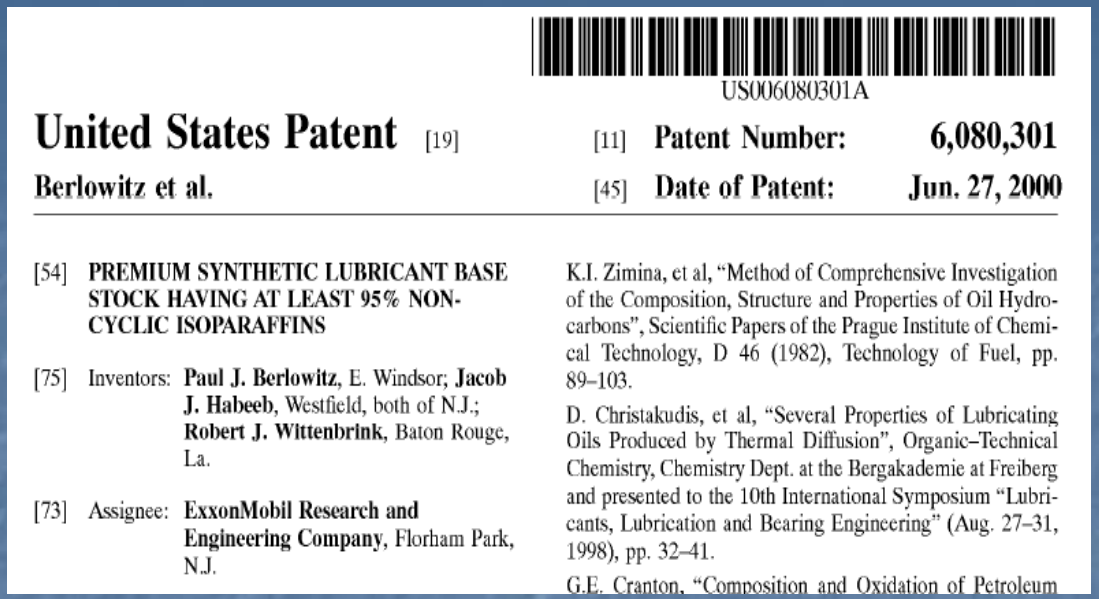
Variation of Reformate Processed ^{1}H NMR Data Observed with Changing Research Octane Number

Current Model on System



NMR Weekly Validation Performance April 2001 – April 2002





US006080301A

United States Patent [19]

Berlowitz et al.

[11] **Patent Number: 6,080,301**

[45] **Date of Patent: Jun. 27, 2000**

[54] **PREMIUM SYNTHETIC LUBRICANT BASE STOCK HAVING AT LEAST 95% NON-CYCLIC ISOPARAFFINS**

[75] Inventors: **Paul J. Berlowitz**, E. Windsor; **Jacob J. Habeeb**, Westfield, both of N.J.; **Robert J. Wittenbrink**, Baton Rouge, La.

[73] Assignee: **ExxonMobil Research and Engineering Company**, Florham Park, N.J.

K.I. Zimina, et al, "Method of Comprehensive Investigation of the Composition, Structure and Properties of Oil Hydrocarbons", Scientific Papers of the Prague Institute of Chemical Technology, D 46 (1982), Technology of Fuel, pp. 89–103.

D. Christakudis, et al, "Several Properties of Lubricating Oils Produced by Thermal Diffusion", Organic–Technical Chemistry, Chemistry Dept. at the Bergakademie at Freiberg and presented to the 10th International Symposium "Lubricants, Lubrication and Bearing Engineering" (Aug. 27–31, 1998), pp. 32–41.

G.E. Cranton, "Composition and Oxidation of Petroleum

Col 4, line 5-14, "with at least 50% of the oil molecules containing at least one branch, at least half of which are methyl branches. At least half, and more preferably at least 75% of the remaining branches are ethyl, with less than 25% and preferably less than 15% of the total number of branches having three or more carbon atoms. The total number of branch carbon atoms is typically less than 25%, preferably less than 20% and more preferably no more than 15% (e.g., 10-15%) of the total number of carbon atoms comprising the hydrocarbon molecules."

Col 12, Line 4-21, "What is claimed is:

1. A lubricant base stock comprising at least 95 wt. % non-cyclic iso-paraffins having a molecular structure in which less than 25% of the total number of carbon atoms of the isoparaffin structure are contained in the branches and less than half of the total iso-paraffin branches contain two or more carbon atoms.

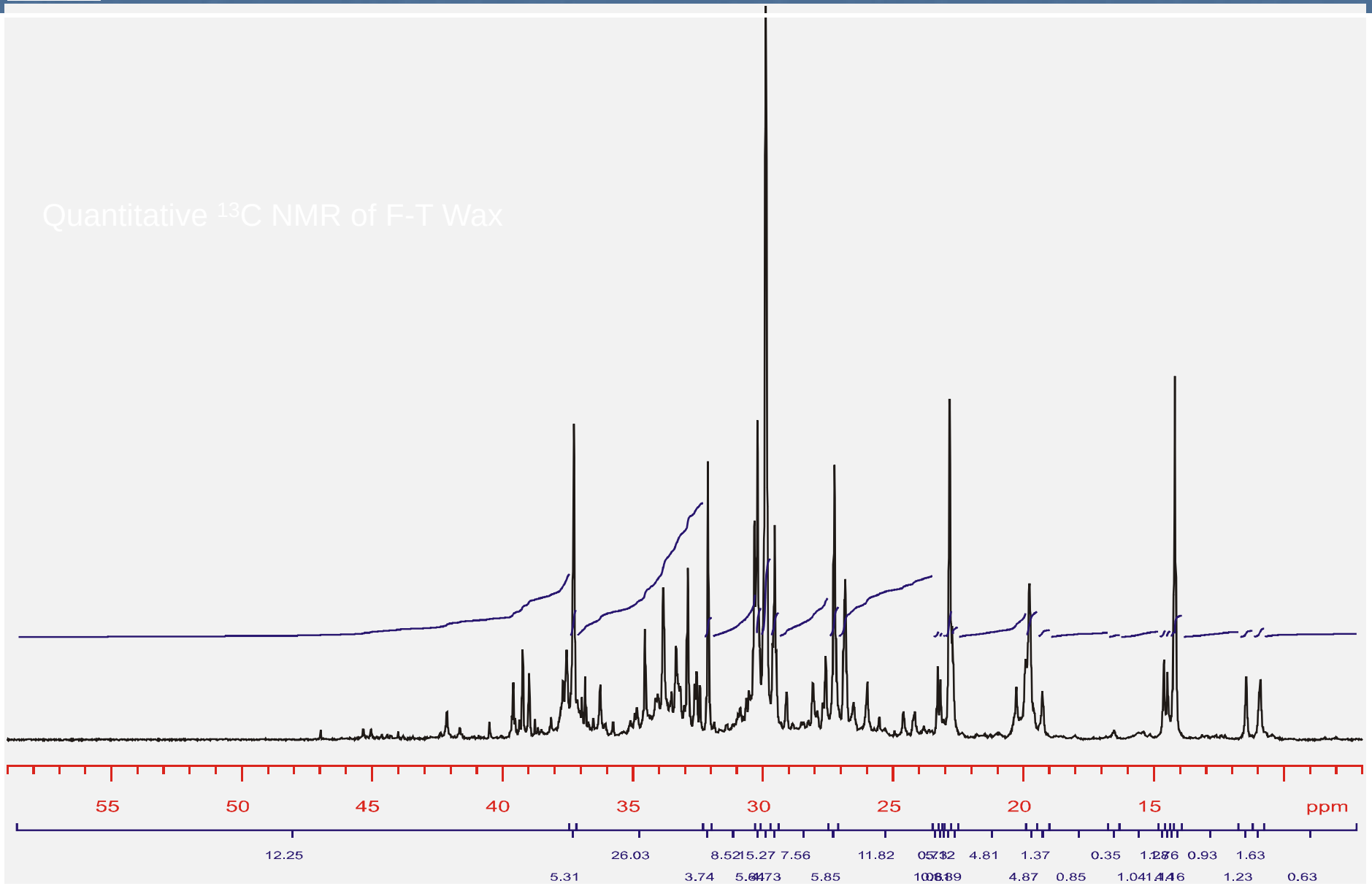
2. A base stock according to claim 1 wherein at least half of the iso-paraffin branches are methyl branches.

3. A base stock according to claim 2 wherein at least half of the remaining, non-methyl branches are ethyl, with less than 25% of the total number of branches having three or more carbon atoms.

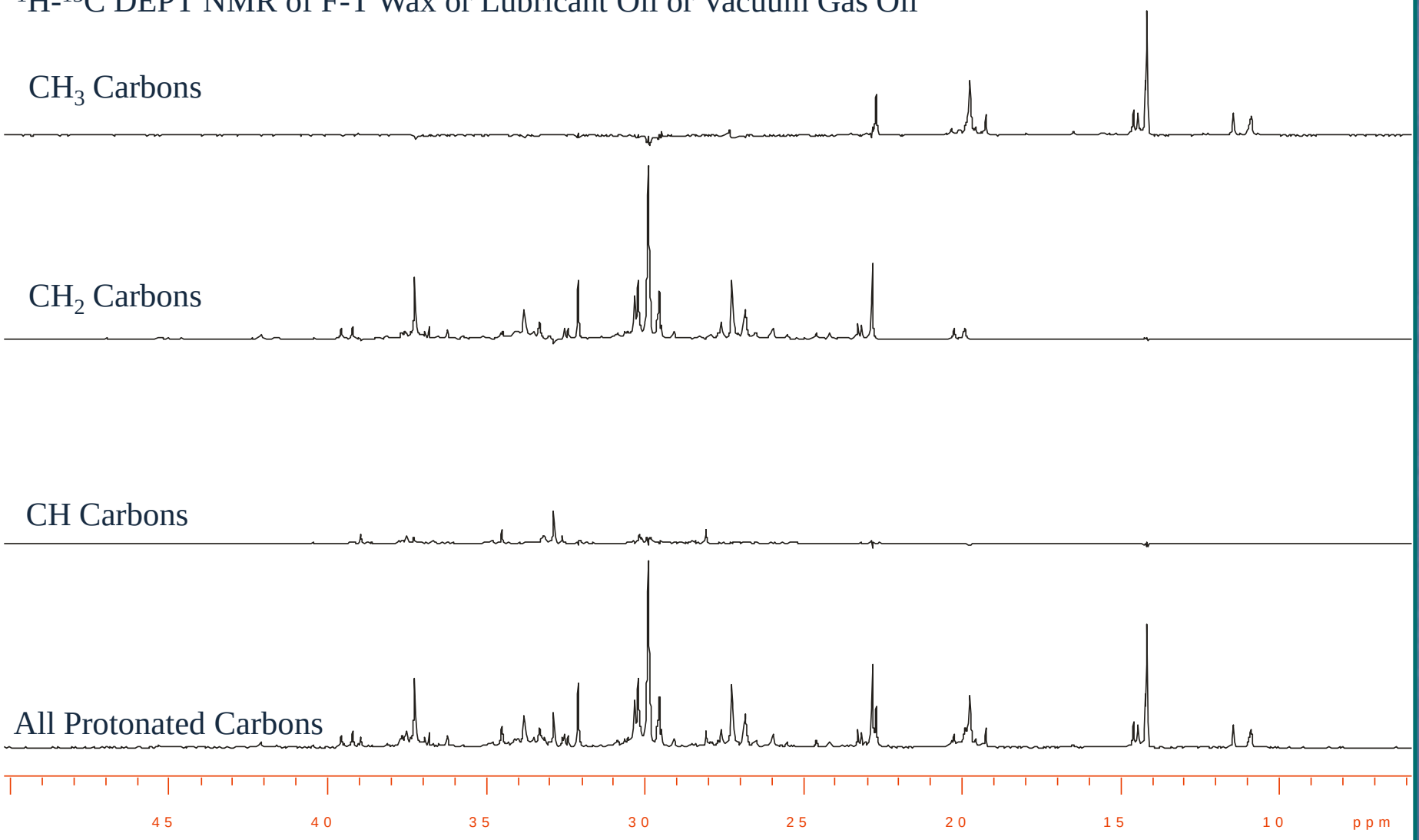
4. A base stock according to claim 3 wherein at least 75% of the non-methyl branches are ethyl.

5. A base stock according to claim 4 wherein of the total number of carbon atoms contained in the iso-paraffin molecule, 10-15% of the carbon atoms are located in the branches."

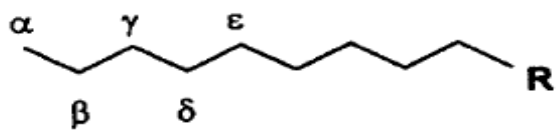
Quantitative ^{13}C NMR of F-T Wax

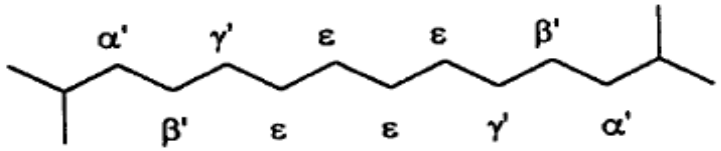


^{1}H-^{13}C DEPT NMR of F-T Wax or Lubricant Oil or Vacuum Gas Oil

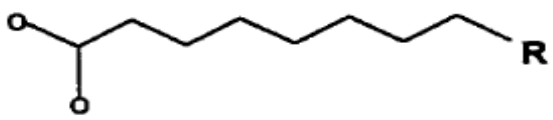


^{13}C NMR Assignments for Various Paraffins Structure Types





P and T Methyl: 22.5 ppm

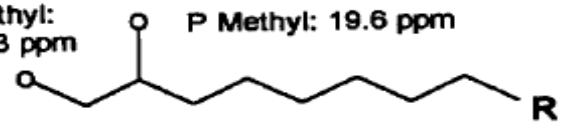


α = 14.0 ppm
β = 22.8 ppm
γ = 32.0 ppm
δ = 29.5 ppm
ε = 29.8 ppm

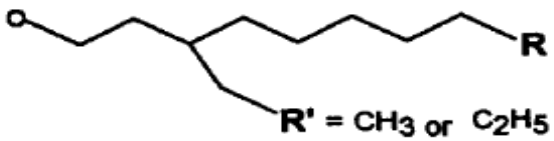
α' = 37.4 ppm
β' = 27.4 ppm
γ' = 30.3 ppm

T Ethyl: 11.3 ppm

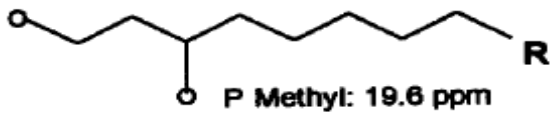
P Methyl: 19.6 ppm



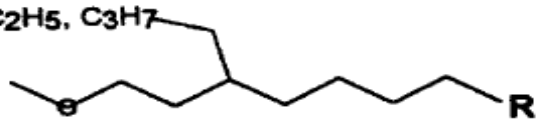
T Propyl: 14.4 ppm



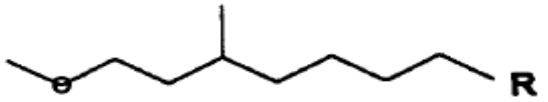
T Propyl: 14.3 ppm



R' = CH3, C2H5, C3H7

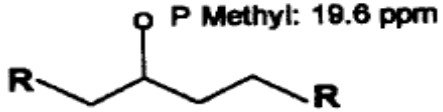


β T Butyl: 23.2 ppm

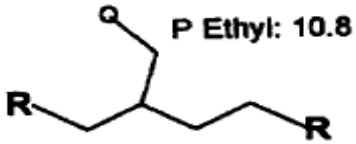


β T Butyl: 23.1 ppm

P Methyl: 19.6 ppm

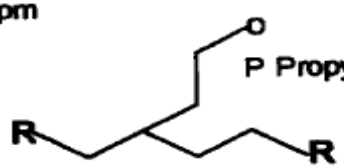


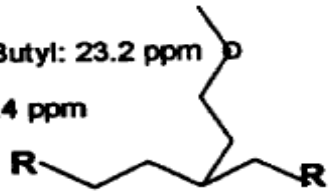
P Ethyl: 10.8 ppm

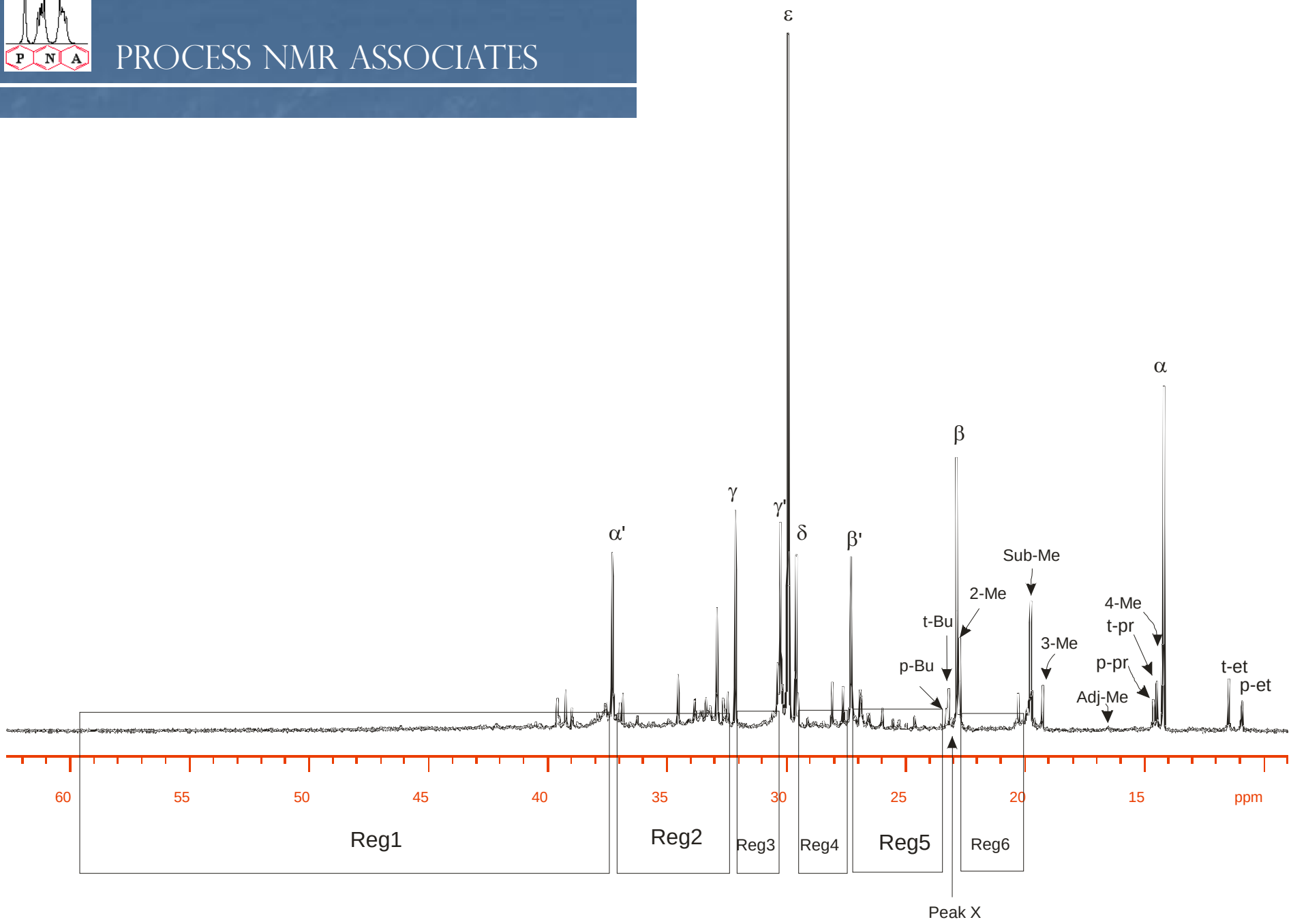


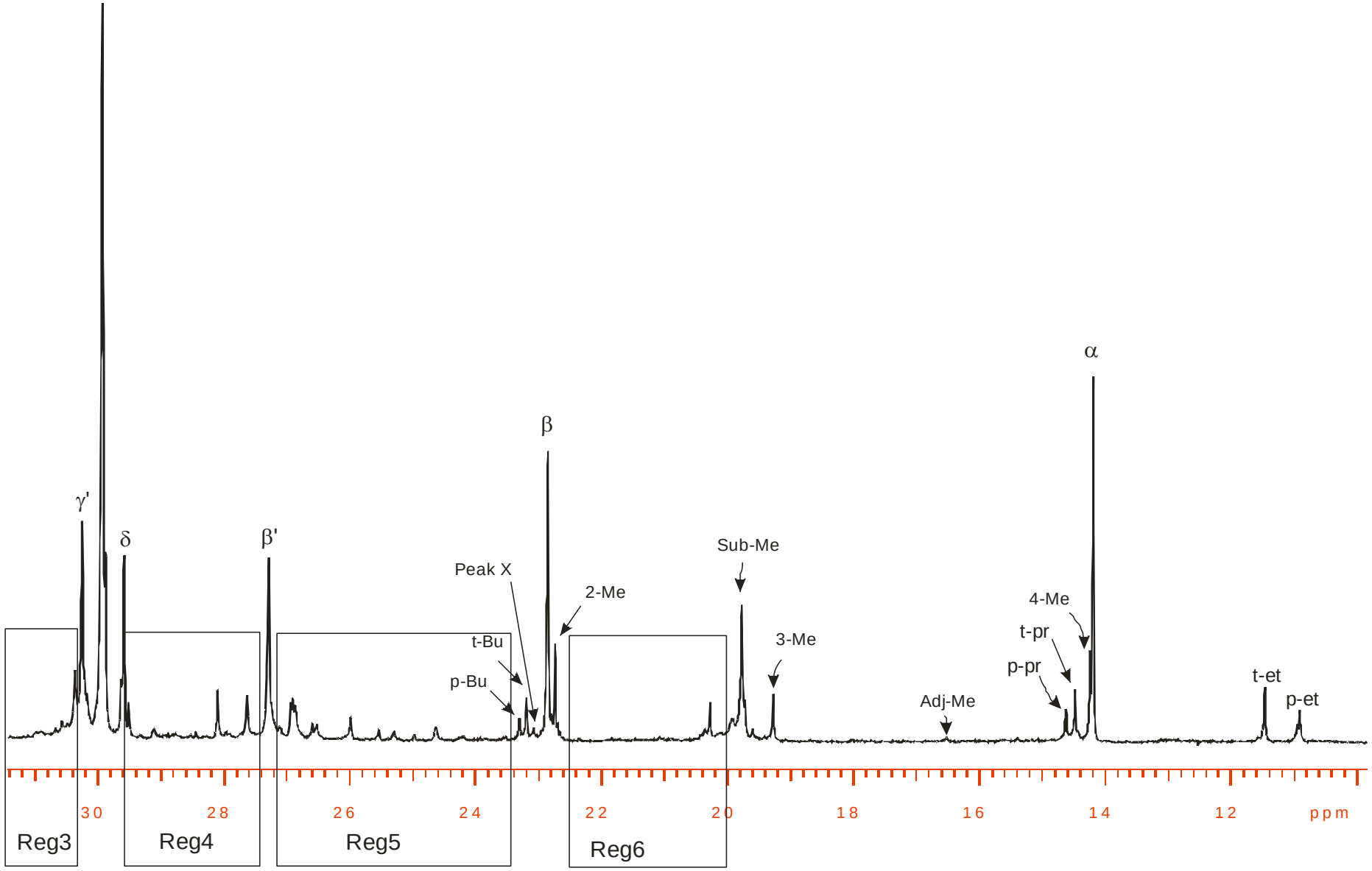
β P Butyl: 23.2 ppm

P Propyl: 14.4 ppm






ε
α
β
γ
γ'
δ
α'
β'
Sub-Me
2-Me
4-Me
t-pr
t-Bu
3-Me
p-pr
p-Bu
Adj-Me
t-et
p-et
60
55
50
45
40
35
30
25
20
15
ppm
Reg1
Reg2
Reg3
Reg4
Reg5
Reg6
Peak X


γ'
δ
β'
Peak X
t-Bu
p-Bu
β
2-Me
Sub-Me
3-Me
Adj-Me
α
4-Me
t-pr
p-pr
t-et
p-et
30
28
26
24
22
20
18
16
14
12
ppm
Reg3
Reg4
Reg5
Reg6

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D35 =(D16+D27+D5+D9+D8)/D32

	A	B	C	D	E	F	G	H	I	J	K	L	M
1	Chemistry	Start	End	Integral									
2	Reg1	54.4217	37.4618	54.2896									
3	Alpha'	37.4618	37.0705	34.087									
4	Reg2	37.0705	32.3322	130.169									
5	Gamma	32.3322	31.9268	18.2366									
6	Reg3	31.9268	30.2863	48.1432									
7	Gamma'	30.2863	30.0879	32.1291									
8	Epsilon	30.0879	29.6998	116.255									
9	Delta	29.6998	29.2858	24.0075									
10	Reg4	29.2858	27.4745	36.5068									
11	Beta'	27.4745	27.0432	34.9705									
12	Reg5	27.0432	23.4808	64.5681		Branch Carbons		Sum of Branches					
13	p-Bu	23.4808	23.2307	5.09098		20.36392		80.79487					
14	t-Bu	23.2307	23.1099	2.99822		11.99288							
15	Peak x	23.1099	23.0236	1.33329									
16	Beta	23.0236	22.739	25.8127									
17	2-Me	22.739	22.4285	6.05213		6.05213							
18	Reg6	22.4285	20.0652	14.8673									
19	Sub-Me	20.0652	19.4701	32.5283		32.5283							
20	3-Me	19.4701	18.944	5.83877		5.83877							
21	Vicinal-Me_1	18.944	16.8802	3.91426		3.91426							
22	Adj-Me	16.8802	16.2764	1.85294		1.85294							
23	Vicinal-Me_2	16.2764	14.8878	4.50949		4.50949							
24	p-Pr	14.8878	14.56	6.12558		18.37674							
25	t-Pr	14.56	14.3875	4.60574		13.81722							
26	4-Me	14.3875	14.3013	2.11832		2.11832							
27	Alpha	14.3013	13.7579	25.9275									
28	Vicinal-Pr	13.7579	11.7913	4.20472		12.61416							
29	t-Ethyl	11.7913	11.2393	4.90747		9.81494							
30	p-Ethyl	11.2393	10.7477	8.67642		17.35284							
31	Vicinal-Ethyl	10.7477	7.02966	3.4342		6.8684							
32	sum			754.7265		161.1469							
33													
34	Parameters Calculated on Percent Basis			Fraction	Per 100C								
35	Linear paraffin structure			0.279	27.86		Linear paraffin structure						
36	Paraffin branching proximity			0.154	15.40		Epsilon Carbon Content						
37	Alpha-Methyl Content			0.034	3.44		Alpha-Methyl Termination						
38	Branching index			0.128	12.83		Carbon CH3 percentage - Gives Number of Branches						
39	Total Branching Index			0.223	22.26		Carbons Located in a Branch - Bu=4C, Pr=3C, Et=2C, Me=1C						

A B C D E F G H I J K L M N O P Q R S T U V Overview Patent 60081

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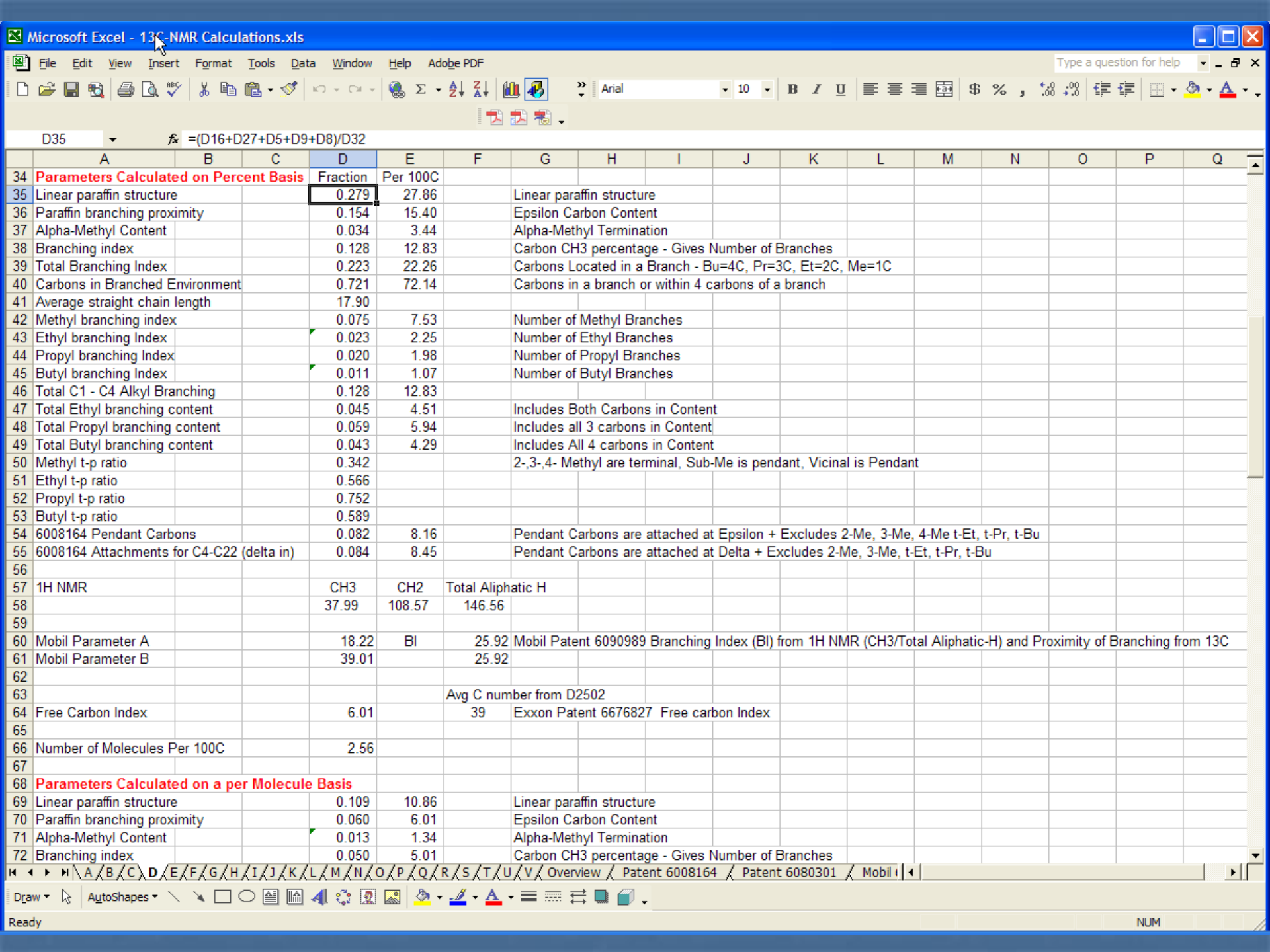

	A	D	E	F	G
34	**Parameters Calculated on Percent Basis**	Fraction	Per 100C		
35	Linear paraffin structure	0.279	27.86		Linear paraffin structure
36	Paraffin branching proximity	0.154	15.40		Epsilon Carbon Content
37	Alpha-Methyl Content	0.034	3.44		Alpha-Methyl Termination
38	Branching index	0.128	12.83		Carbon CH3 percentage - Gives Number of Branches
39	Total Branching Index	0.223	22.26		Carbons Located in a Branch - Bu=4C, Pr=3C, Et=2C, Me=1C
40	Carbons in Branched Environment	0.721	72.14		Carbons in a branch or within 4 carbons of a branch
41	Average straight chain length	17.90			
42	Methyl branching index	0.075	7.53		Number of Methyl Branches
43	Ethyl branching Index	0.023	2.25		Number of Ethyl Branches
44	Propyl branching Index	0.020	1.98		Number of Propyl Branches
45	Butyl branching Index	0.011	1.07		Number of Butyl Branches
46	Total C1 - C4 Alkyl Branching	0.128	12.83		
47	Total Ethyl branching content	0.045	4.51		Includes Both Carbons in Content
48	Total Propyl branching content	0.059	5.94		Includes all 3 carbons in Content
49	Total Butyl branching content	0.043	4.29		Includes All 4 carbons in Content
50	Methyl t-p ratio	0.342			2-,3-,4- Methyl are terminal, Sub-Me is pendant, Vicinal is Pendant
51	Ethyl t-p ratio	0.566			
52	Propyl t-p ratio	0.752			
53	Butyl t-p ratio	0.589			
54	6008164 Pendant Carbons	0.082	8.16		Pendant Carbons are attached at Epsilon + Excludes 2-Me, 3-Me, 4-Me t-Et, t-Pr, t-Bu
55	6008164 Attachments for C4-C22 (delta in)	0.084	8.45		Pendant Carbons are attached at Delta + Excludes 2-Me, 3-Me, t-Et, t-Pr, t-Bu
56					
57	1H NMR	CH3	CH2	Total Aliphatic H	
58		37.99	108.57	146.56	
59					
60	Mobil Parameter A	18.22	BI	25.92	Mobil Patent 6090989 Branching Index (BI) from 1H NMR (CH3/Total Aliphatic-H) and Proximity of Branching from 13C
61	Mobil Parameter B	39.01		25.92	
62					
63				Avg C number from D2502	
64	Free Carbon Index	6.01		39	Exxon Patent 6676827 Free carbon Index
65					
66	Number of Molecules Per 100C	2.56			
67					
68	**Parameters Calculated on a per Molecule Basis**				
69	Linear paraffin structure	0.109	10.86		Linear paraffin structure
70	Paraffin branching proximity	0.060	6.01		Epsilon Carbon Content
71	Alpha-Methyl Content	0.013	1.34		Alpha-Methyl Termination
72	Branching index	0.050	5.01		Carbon CH3 percentage - Gives Number of Branches

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C111

	A	B	C	D	E
108	Parameters Calculated on a per Molecule Basis			Per Molecule	
109	Linear paraffin structure			10.86	
110	Paraffin branching proximity			6.01	
111	Branching index			5.01	
112	Total Branching Index			8.68	
113	Carbons in Branched Environment			28.14	
114	Methyl branching index			2.94	
115	Ethyl branching Index			0.88	
116	Propyl branching Index			0.77	
117	Butyl branching Index			0.42	
118	Total C1 - C4 Alkyl Branching			5.01	
119	Total Ethyl branching content			1.76	
120	Total Propyl branching content			2.32	
121	Total Butyl branching content			1.67	
122	6008164 Pendant Carbons			3.18	
123	6008164 Attachments for C4-C22 (delta in)			3.29	
124	1H NMR CH3 at%			37.99	
125	1H NMR CH2/CH at%			108.57	
126	Branching Index (BI)			25.92	
127	Mobil Parameter A			18.22	
128	Mobil Parameter B			39.01	
129	D2502 Avg Carbon No.			39	
130	Free Carbon Index			6.01	
131	Number of Molecules Per 100C			2.56	
132	Patent 6,008,164				
133	Free carbon Index >3			Yes	
134	Containing Up to 4 Alkyl branches			No	
135	Containing Up to 4 Methyl branches			Yes	
136	Pendant Carbons less Than 4			Yes	
137	Total Attachments			5.01	
138	Attachments for C4-C22			3.29	
139	Methyl Attachments			2.94	
140	Attachments Longer Than Methyl			2.07	
141	Free carbon Index			6.01	
142	Number of Terminal Carbons			1.82	
143	Number of Pendant Carbons			3.18	
144	Average Length of Attachments			1.73	
145	Patent 6,165,949 and 6,080,301				Patent
146					At-Least
147	% Carbon Present in Branches			22.26	< 25%

A B C D E F G H I J K L M N O P Q R S T U V

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Arial 10

D35 =(D16+D27+D5+D9+D8)/D32

	A	B	C	D	E	F	G	H	I	J	K	L	M	N
68	Parameters Calculated on a per Molecule Basis													
69	Linear paraffin structure			0.109	10.86		Linear paraffin structure							
70	Paraffin branching proximity			0.060	6.01		Epsilon Carbon Content							
71	Alpha-Methyl Content			0.013	1.34		Alpha-Methyl Termination							
72	Branching index			0.050	5.01		Carbon CH3 percentage - Gives Number of Branches							
73	Total Branching Index			0.087	8.68		Carbons Located in a Branch - Bu=4C, Pr=3C, Et=2C, Me=1C							
74	Carbons in Branched Environment			0.281	28.14		Carbons in a branch or within 4 carbons of a branch							
75	Methyl branching index			0.029	2.94		Number of Methyl Branches							
76	Ethyl branching Index			0.009	0.88		Number of Ethyl Branches							
77	Propyl branching Index			0.008	0.77		Number of Propyl Branches							
78	Butyl branching Index			0.004	0.42		Number of Butyl Branches							
79	Total C1 - C4 Alkyl Branching			0.050	5.01		Total Number of C1-C4 Branches							
80	Total Ethyl branching content			0.018	1.76		Includes Both Carbons in Content							
81	Total Propyl branching content			0.023	2.32		Includes all 3 carbons in Content							
82	Total Butyl branching content			0.017	1.67		Includes All 4 carbons in Content							
83	6008164 Pendant Carbons			0.032	3.18		Pendant Carbons are attached at Epsilon + Excludes 2-Me, 3-Me, 4-Me t-Et, t-Pr, t-Bu							
84	6008164 Attachments for C4-C22 (delta in)			0.033	3.29		Pendant Carbons are attached at Delta + Excludes 2-Me, 3-Me, t-Et, t-Pr, t-Bu							
85														
86	Parameters Calculated on Percent Basis			Per 100C										
87	Linear paraffin structure			27.86										
88	Paraffin branching proximity			15.40										
89	Branching index			12.83										
90	Total Branching Index			22.26										
91	Carbons in Branched Environment			72.14										
92	Average straight chain length			17.90										
93	Methyl branching index			7.53										
94	Ethyl branching Index			2.25										
95	Propyl branching Index			1.98										
96	Butyl branching Index			1.07										
97	Total C1 - C4 Alkyl Branching			12.83										
98	Total Ethyl branching content			4.51										
99	Total Propyl branching content			5.94										
100	Total Butyl branching content			4.29										
101	Methyl t-p ratio			0.34										
102	Ethyl t-p ratio			0.57										
103	Propyl t-p ratio			0.75										
104	Butyl t-p ratio			0.59										
105	6008164 Pendant Carbons			8.16										
106	6008164 Attachments for C4-C22 (delta in)			8.45										

A B C D E F G H I J K L M N O P Q R S T U V Overview Patent 6008164 Pa

Draw AutoShapes

Ready NUM

Residual Fluidized Catalytic Cracking Feed-stream Analysis

Traditional Analysis – Refractive Index, Distillation, Viscosity Specific Gravity

Calculation – Watson K-Factor

Outcome: aromatic carbon number
aromatic hydrogen number
total hydrogen content

Table 1
Catalytic Cracking Characteristics of Pure Hydrocarbons

Hydrocarbon	Catalytic Cracking
n-Paraffins	Extensive breakdown to C_3 and larger fragments. Product largely in C_3 to C_9 range and contains many branched aliphatics. Few normal α - olefins above C_4.
Isoparaffins	Cracking rate relative to *n*-paraffins increased considerably by presence of tertiary carbon atoms.
Naphthenes	Crack at about same rate as those paraffins with similar numbers of tertiary carbon atoms. Aromatics produced with much hydrogen transfer to unsaturates.
Unsubstituted aromatics	Little reaction; some condensation to biaryls.
Alkyl aromatics (substitutents C_3 or larger)	Entire alkyl group cracked next to ring and removed as olefin. Crack at much higher rate than paraffins.
n-Olefins	Product similar to that from *n*-paraffins but more olefinic.
All olefins	Hydrogen transfer is an important reaction, especially with tertiary olefins. Crack at much higher rate than corresponding paraffins.
Source: Reference No. 7.	

NMR Proposition: Detailed hydrocarbon analysis for kinetic model development

(12) **United States Patent**
Meier et al.

(10) **Patent No.: US 6,275,776 B1**
(45) **Date of Patent: Aug. 14, 2001**

(54) **METHOD FOR CHARACTERIZING RESIDUAL CRUDE OIL AND PETROLEUM FRACTIONS**

(75) Inventors: **Paul F. Meier**; **Dhananjay B. Ghonasgi**, both of Bartlesville, OK (US); **Michael Wardinsky**, Lake Jackson, TX (US)

(73) Assignee: **Phillips Petroleum Company**, Bartlesville, OK (US)

Standard Errors for wt. % Aromatic Carbon

Group	# Samples	Phillips Model	n-d-Method	Total Method
Overall	367	2.31	12.01	7.50

Standard Errors for wt. % Hydrogen (by NMR)

Group	# Samples	Phillips Model	Total Method
Overall	367	0.28	0.78

Standard Errors for wt. % Aromatic Hydrogen

Group	# Samples	Phillips Model
Overall	367	1.78

SUMMARY OF THE INVENTION

According to this invention, the foregoing and other objectives and advantages are achieved in a method for analyzing a mixture of heavy hydrocarbon oils to determine the aromatic carbon content, aromatic hydrogen content, and total hydrogen content of the oil. The method uses three mathematical model equations based on three bulk properties of the oil, and these properties have individual limiting values for infinitely long carbon/hydrogen groups in the liquid state. The petroleum oil properties are refractive index, specific gravity, and the Watson K factor, and the model equations include the respective limiting values.

In a preferred embodiment, the carbon and hydrogen content of oils with boiling points up to 1400° F. is determined from measurements including: refractive index, API gravity, and simulated distillation. The mathematical model equations, which include the limiting value associated with the property, are as follows:

$$C_a = 134.4679[RI - 1.4750] - 20.4858[K - 12.5] \quad \text{EQ. (1)}$$

$$H_a = 333.471[RI - 1.4750]^2 - 6.687[K - 12.5] \quad \text{EQ. (2)}$$

$$H = -20.77[Sp.Gr. - 0.8510] + 0.58[K - 12.5] + 14. \quad \text{EQ. (3)}$$

where:

C_a=wt. % aromatic carbon

H_a=wt. % aromatic hydrogen

H=wt. % total hydrogen

K=Watson K factor, i.e.,$[(VABP(F)+460)^{1/3}]/Sp.Gr.$

RI=refractive index at 68° F.

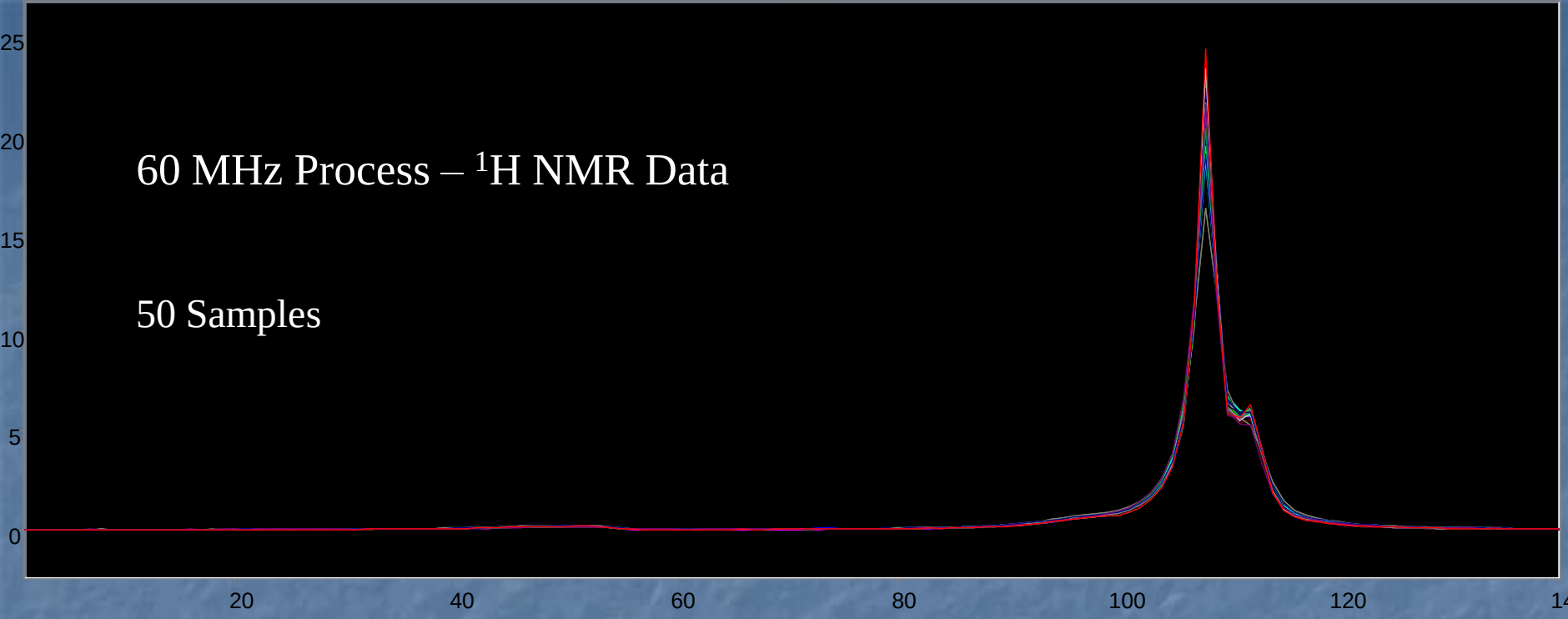
SpGr.=specific gravity, density of oil at 60° F. relative to water at 60° F., and

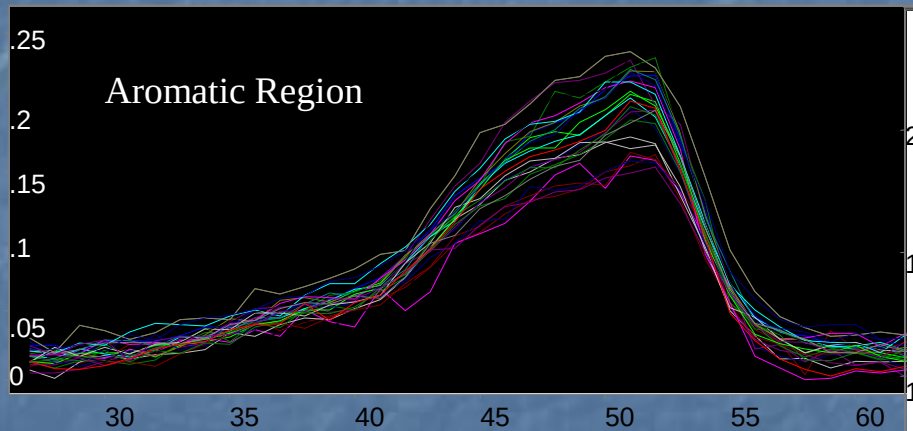
VABP = volume average of distillation curve boiling points at % off

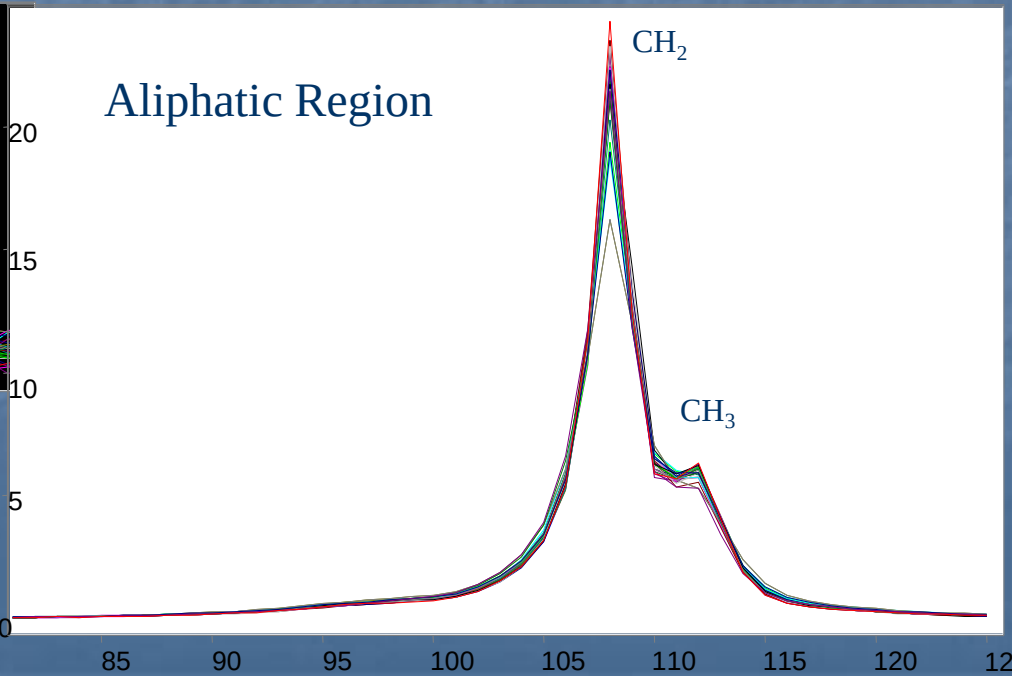
= [10% + 30% + 50% + 70% + 90%]/5

60 MHz Process – ^{1}H NMR Data

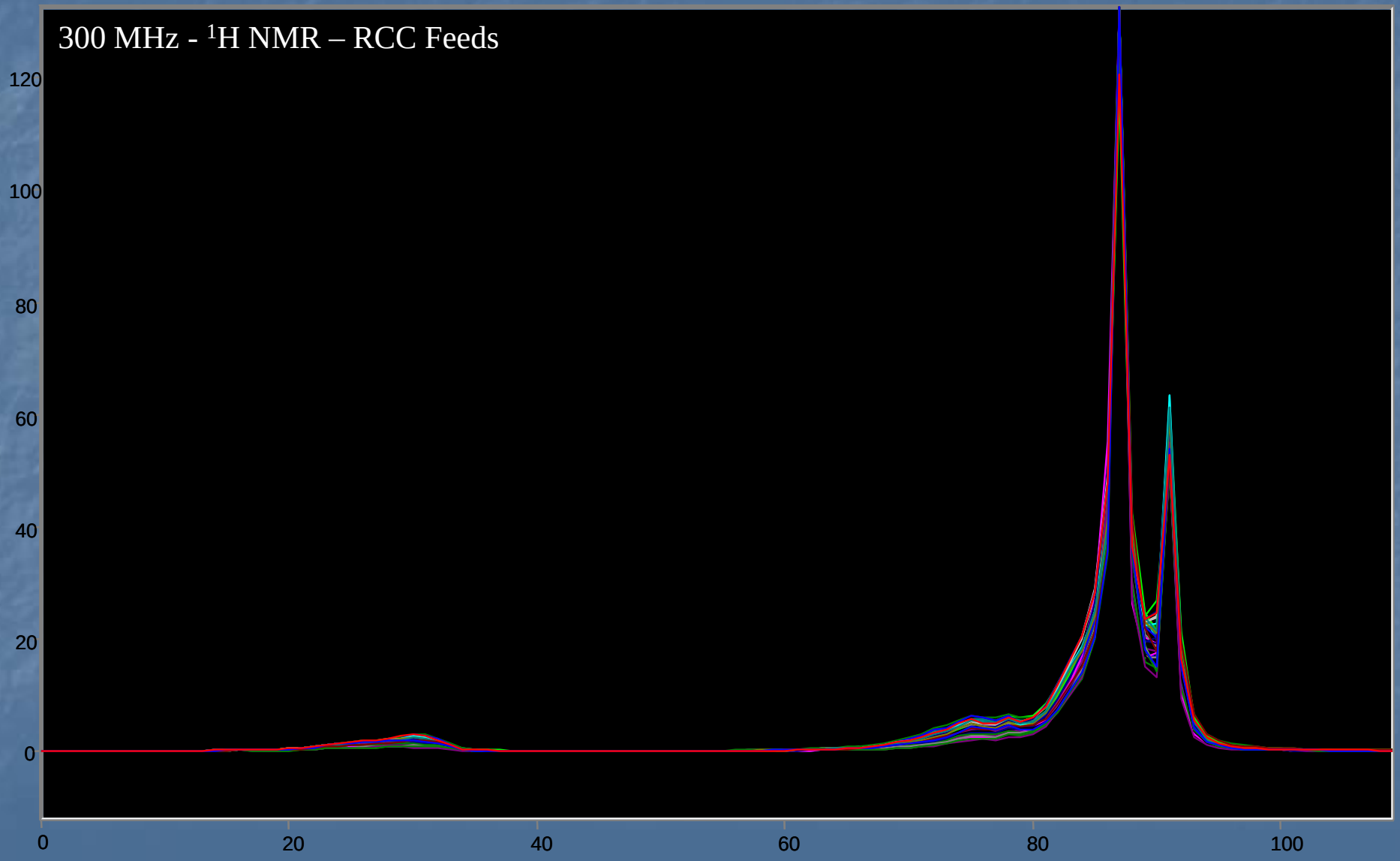
50 Samples

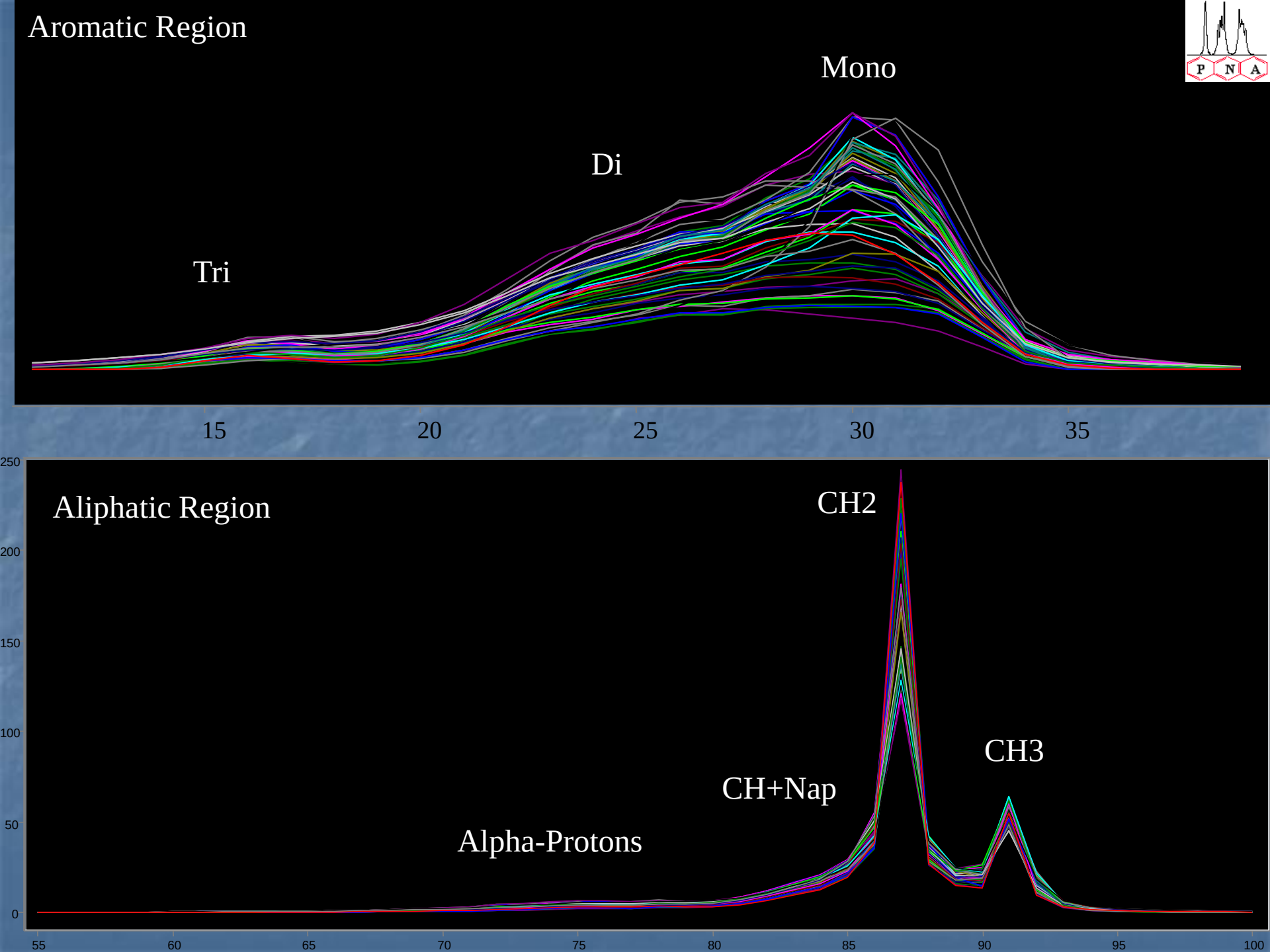




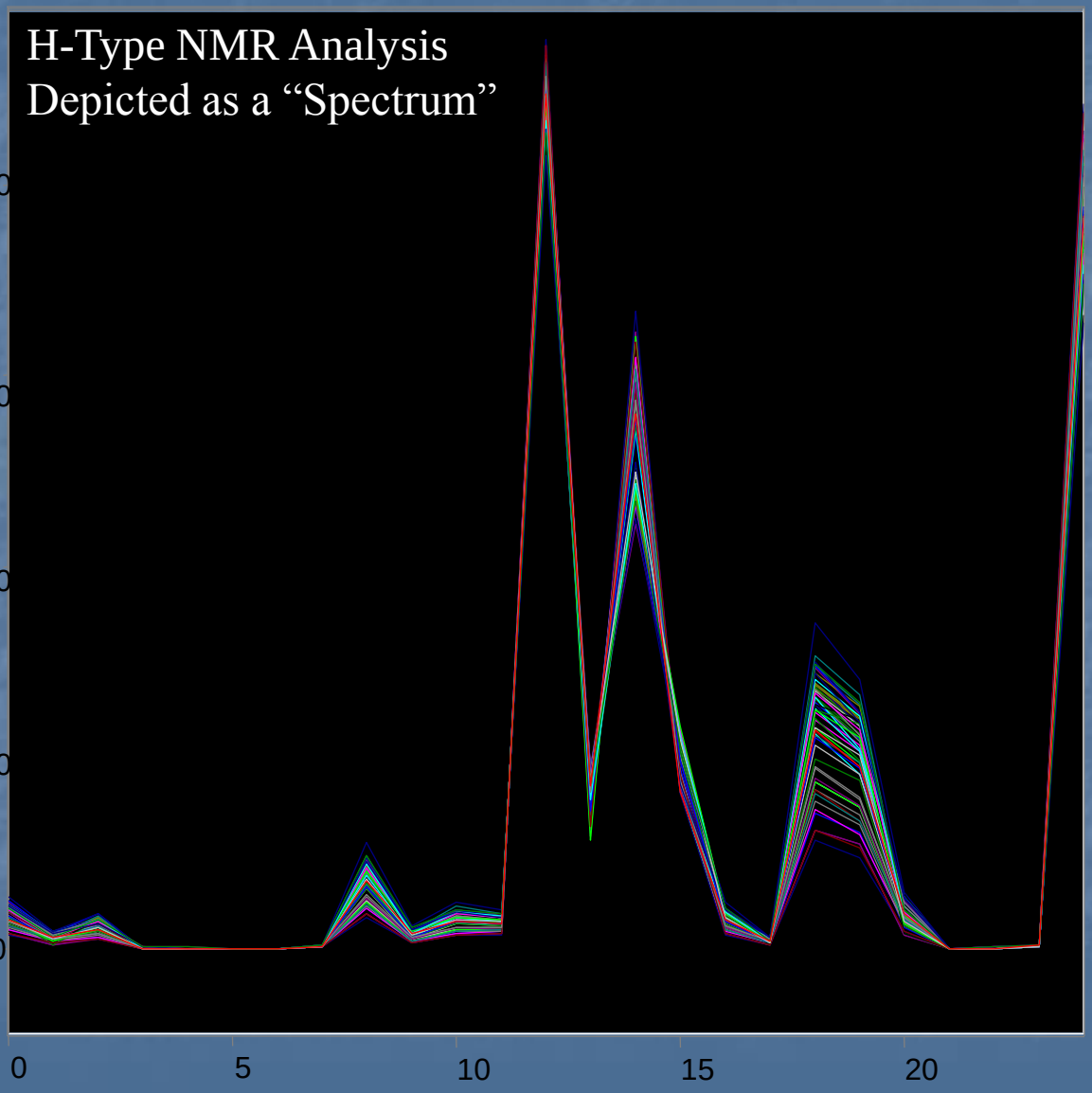


PROCESS NMR ASSOCIATES

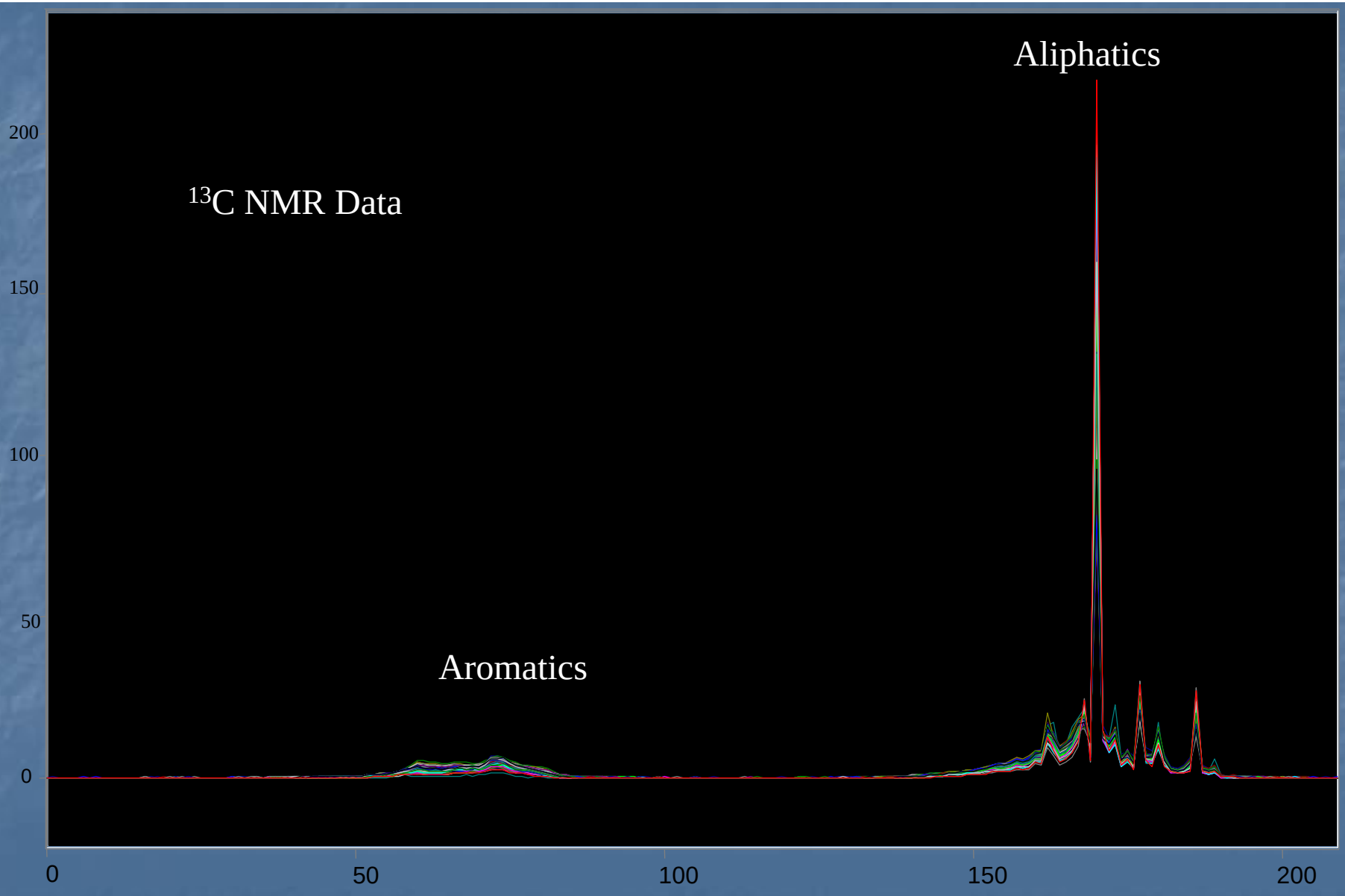



Aromatic Region
Mono
Di
Tri
15
20
25
30
35
Aliphatic Region
CH2
CH3
CH+Nap
Alpha-Protons
250
200
150
100
50
0
55
60
65
70
75
80
85
90
95
100

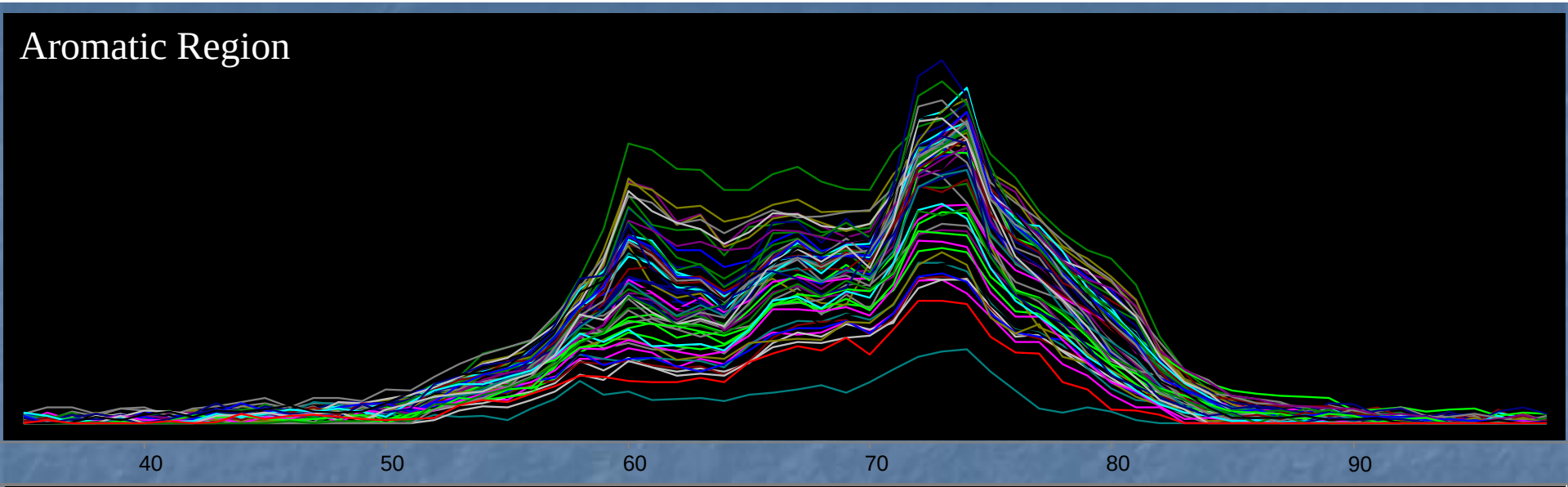
PROCESS NMR ASSOCIATES



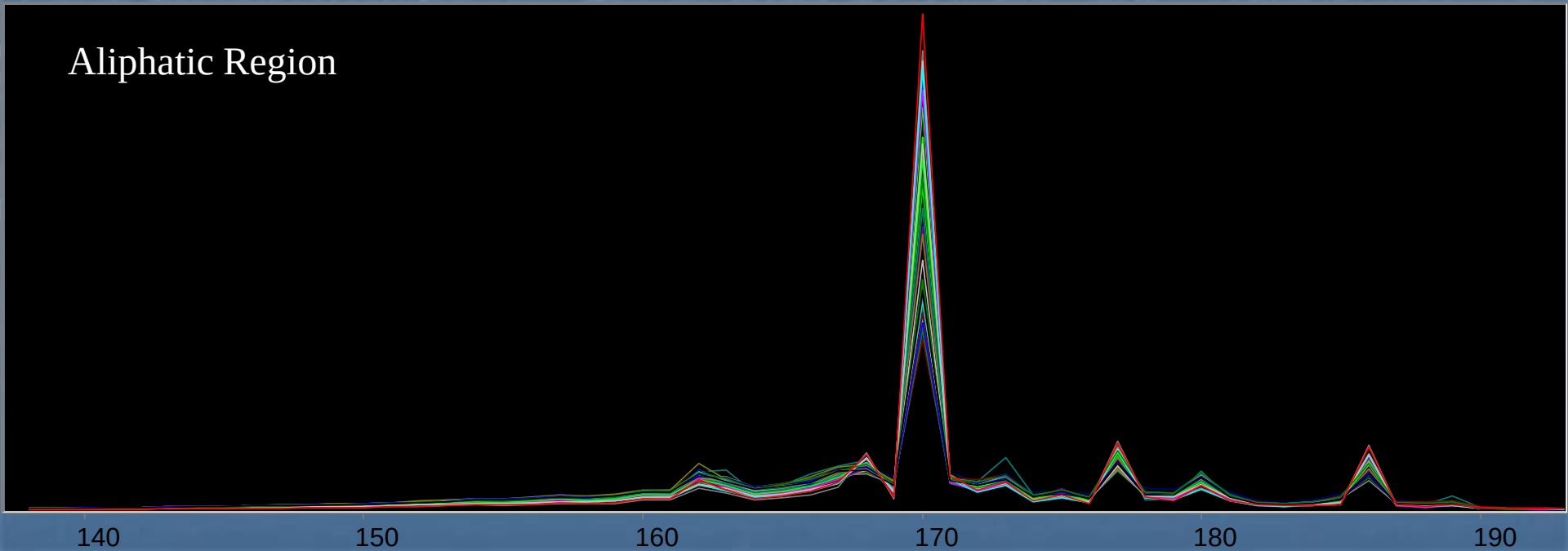
Parameter	1H - Type Analysis
1	Total aromatic
2	Diaromatic+ protons
3	Monoaromatic protons
4	Total olefinic
5	R**H**C=CH_2
6	R**H**C=C**H**R
7	RHC=C$\mathbf{H}_2$
8	Oxygenates protons
9	Total α protons to aromatics
10	a-CH to aromatics
11	a-CH_2 to aromatics
12	a-CH_3 to aromatics
13	Saturates
14	Paraffinic CH
15	Paraffinic CH_3
16	Paraffinic CH_3
17	Substituted aromatic carbon
18	Bridgehead carbons
19	Total aromatics (wt %)
20	Mono aromatics (wt %)
21	Di+ aromatics (wt %)
22	Benzene (wt %)
23	Olefin functions (wt %)
24	Oxygenates (wt %)
25	Saturates (wt %)


Aliphatics
^{13}C NMR Data
Aromatics
200
150
100
50
0
0
50
100
150
200

Aromatic Region



Aliphatic Region

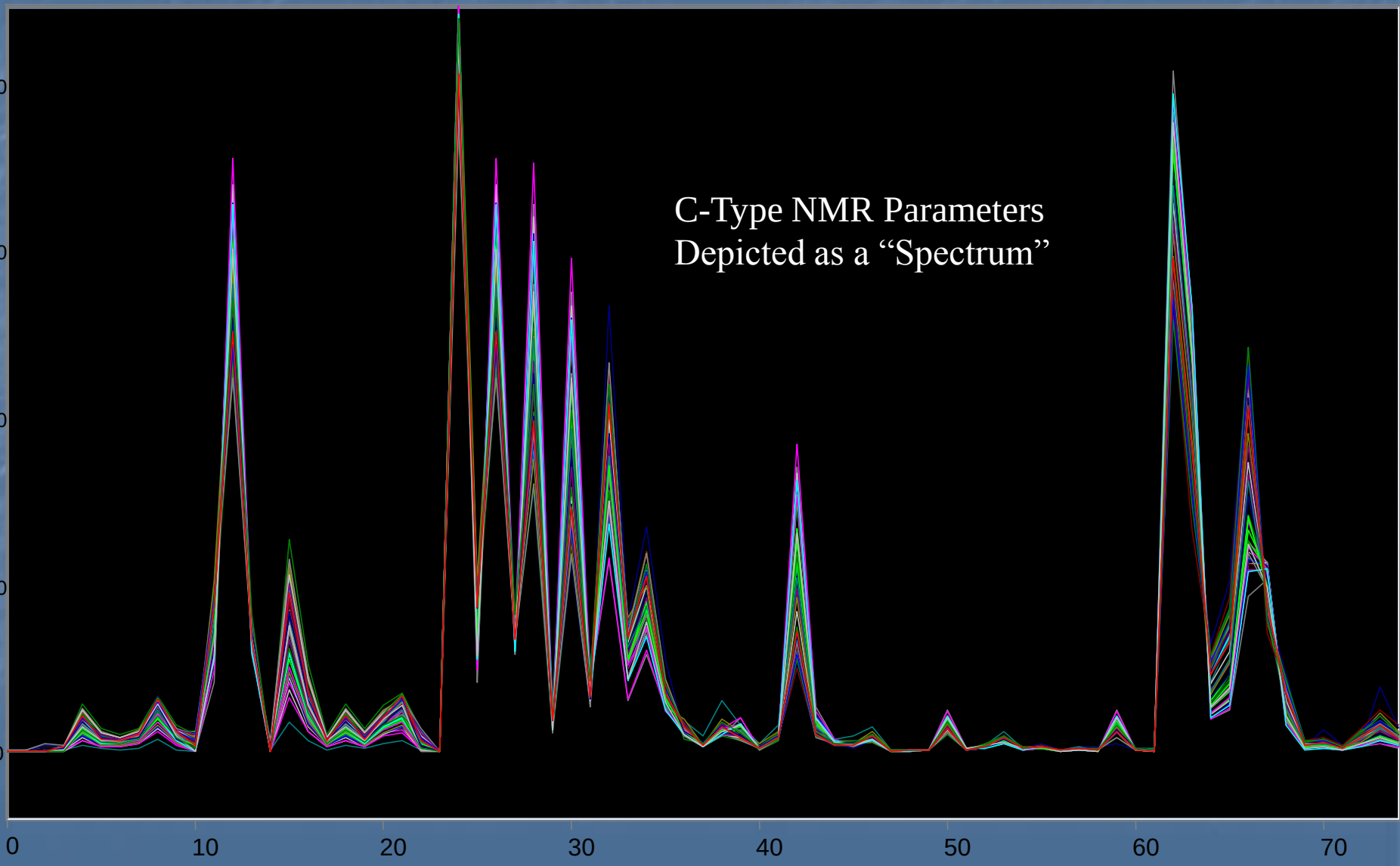


Calculated C-Type Parameters

Index	Carbon Type Parameters (%C Unless Otherwise Listed)
1	Ketone carbonyl carbon
2	Aldehyde carbonyl carbon
3	Carboxylic acids, esters and amides carbonyl carbon
4	Phenoxy carbon
5	CH2 & CH subsituted aromatic carbon
6	Naphthenic sub aromatic carbon
7	CH3 substituted aromatic carbon
8	Half of internal Aromatic Carbon
9	Protonated Internal aromatic C
10	Protonated Aromatic Carbon
11	Heteroaromatic other than phenoxy carbon
12	Methine carbon
13	Methylene carbon
14	Methyl carbon
15	Total carbonyl carbon
16	Total aromatic carbon
17	Aliphatic sub aromatic carbon
18	Methyl-substituted aromatic carbon
19	CH2 & CH substituted aromatic carbon
20	Naphthenic substituted aromatic carbon
21	Internal aromatic carbon
22	Peripheral unsubstituted aromatic carbon
23	Total heteroaromatic carbon
24	Total olefinic carbon
25	Total aliphatic carbon

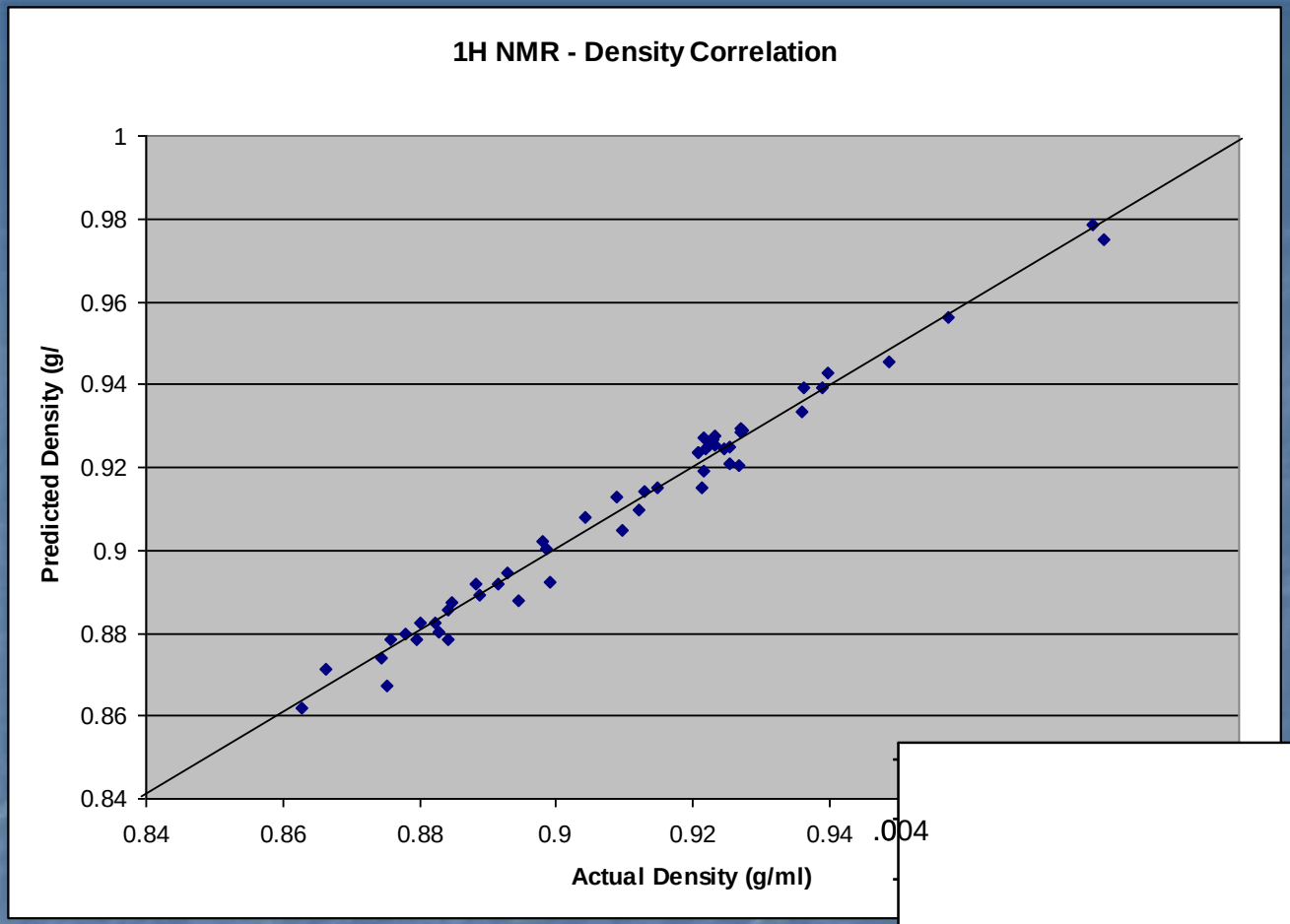
Index	Carbon Type Parameters (%C Unless Otherwise Listed)
26	Aliphatic methine carbon (CH)
27	Aliphatic methylene carbon (CH2)
28	Aliphatic methyl carbon (CH3)
29	Total paraffinic carbon
30	Paraffinic methine carbon (CH)
31	Paraffinic methylene carbon (CH2)
32	Paraffinic methyl carbon (CH3)
33	Total naphthenic carbon
34	Naphthenic methine carbon (CH)
35	Naphthenic methylene carbon (CH2)
36	Naphthenic methyl carbon (CH3)
37	Reg1
38	α'
39	Reg2
40	γ
41	Reg3
42	γ’
43	ε
44	δ
45	Reg4
46	β'
47	Reg5
48	pendant-Bu
49	terminal-Bu
50	Peak x

Index	Carbon Type Parameters (%C Unless Otherwise Listed)
51	β
52	2-Me Substitution
53	Aromatic α methyl carbon
54	All other-Me
55	3-Methyl
56	Reg7
57	pendant-Pr
58	terminal-Pr
59	4-Methyl
60	α
61	terminal-Ethyl
62	pendant-Ethyl
63	Linear Paraffin Structure: % Linear Paraffin/Total Paraffin
64	Waxiness : % Epsilon C/Total Paraffin
65	Branching Index: %Branching CC/Total Paraffin
66	Total Branching Content: % C Near Branching C/Total C
67	C in Branched Environment: % 1-linear paraffin structure
68	Average Straight Chain Length (C No.)
69	Methyl branching index
70	Ethyl branching Index
71	Propyl branching Index
72	Butyl branching Index
73	Total ethyl branching content
74	Total propyl branching content
75	Total butyl branching content

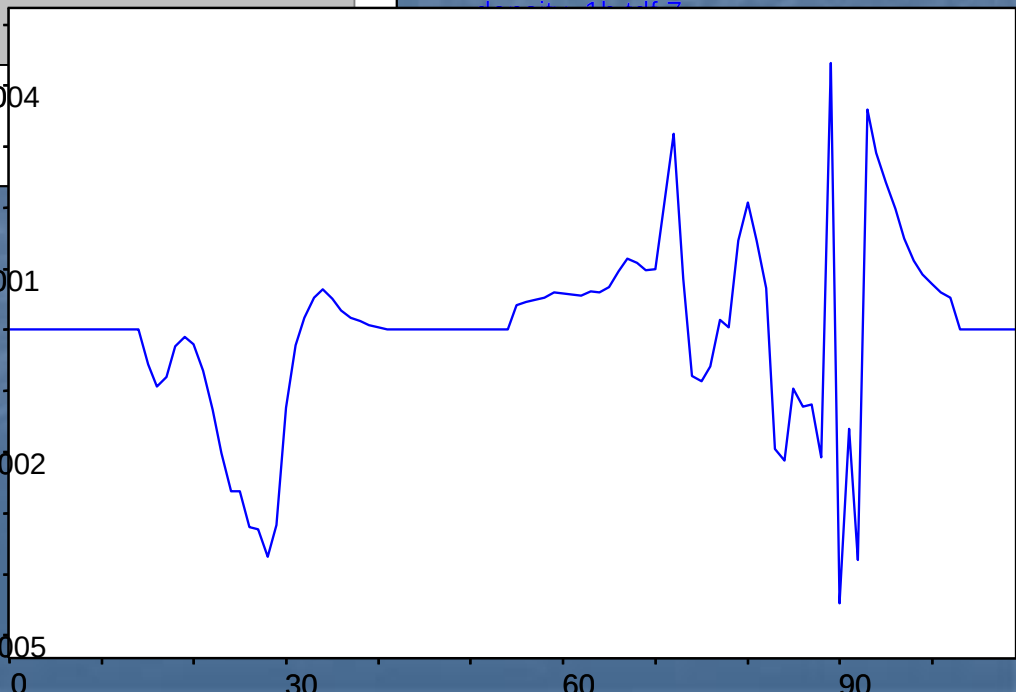

C-Type NMR Parameters
Depicted as a “Spectrum”
80
60
40
20
0
0
10
20
30
40
50
60
70

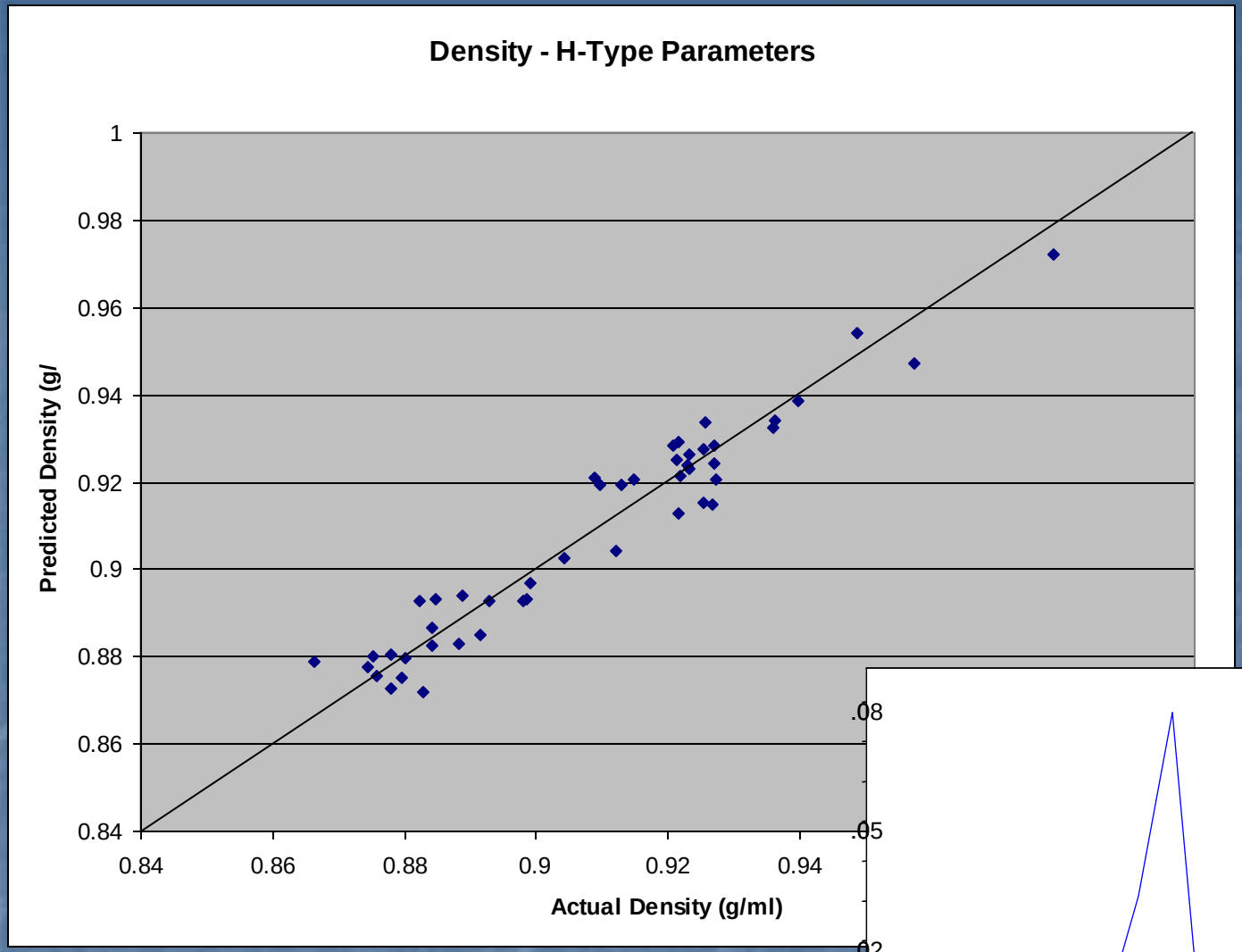
Summary of RCC Feed NMR Analysis – Correlations to Physical/Chemical Properties

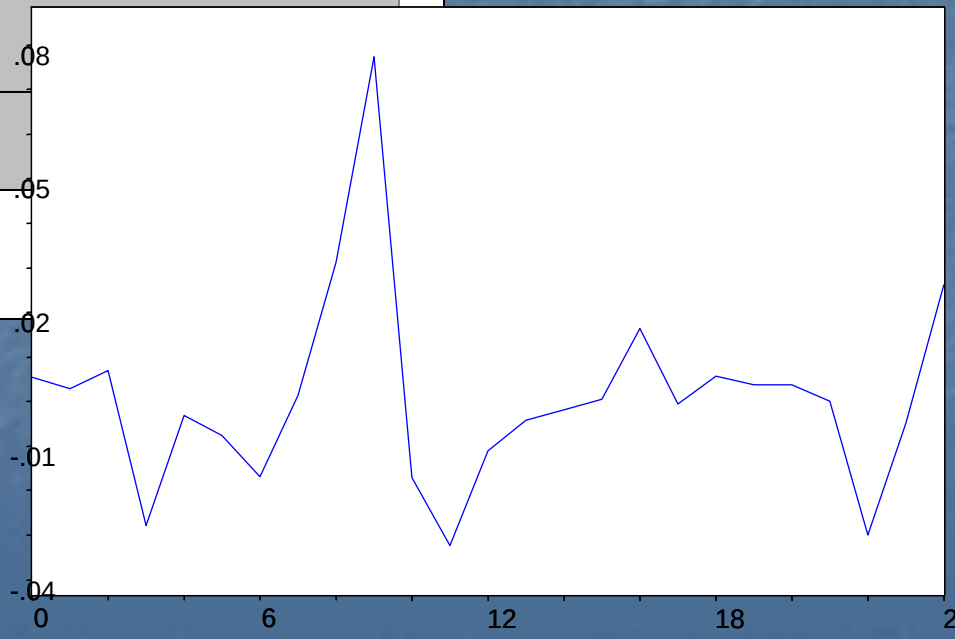
Resonance Frequency	60 MHz Proton	300 MHz Proton		75 MHz Carbon-13	
Parameter	1H NMR 0.1 ppm Bin	1H NMR 0.1 ppm Bin	H-Type Spectrum	13C NMR 1 ppm Bin	C-Type Spectrum
Density at 15°C	0.961	0.983	0.924	0.982	0.974
Viscosity Index	-	0.951	-	0.935	-
MCRT	0.940	0.952	0.727	0.931	0.875
SULPHUR	0.931	0.964	0.855	0.979	0.962
Carbon Aromaticity	0.958	0.951	0.926	0.998	0.997
HYDROGEN	0.925	0.914	0.819	0.922	0.862
Total Aromatics	0.936	0.946	0.904	0.965	0.941
Monoaromatics	0.930	0.941	0.912	0.954	0.897
Diaromatics	0.927	0.945	0.866	0.951	0.897
TriAromatics	0.941	0.911	0.862	0.939	0.863
Tetra+ aromatics	0.913	0.921	0.656	0.912	0.934



^{1}H NMR Correlation to Density

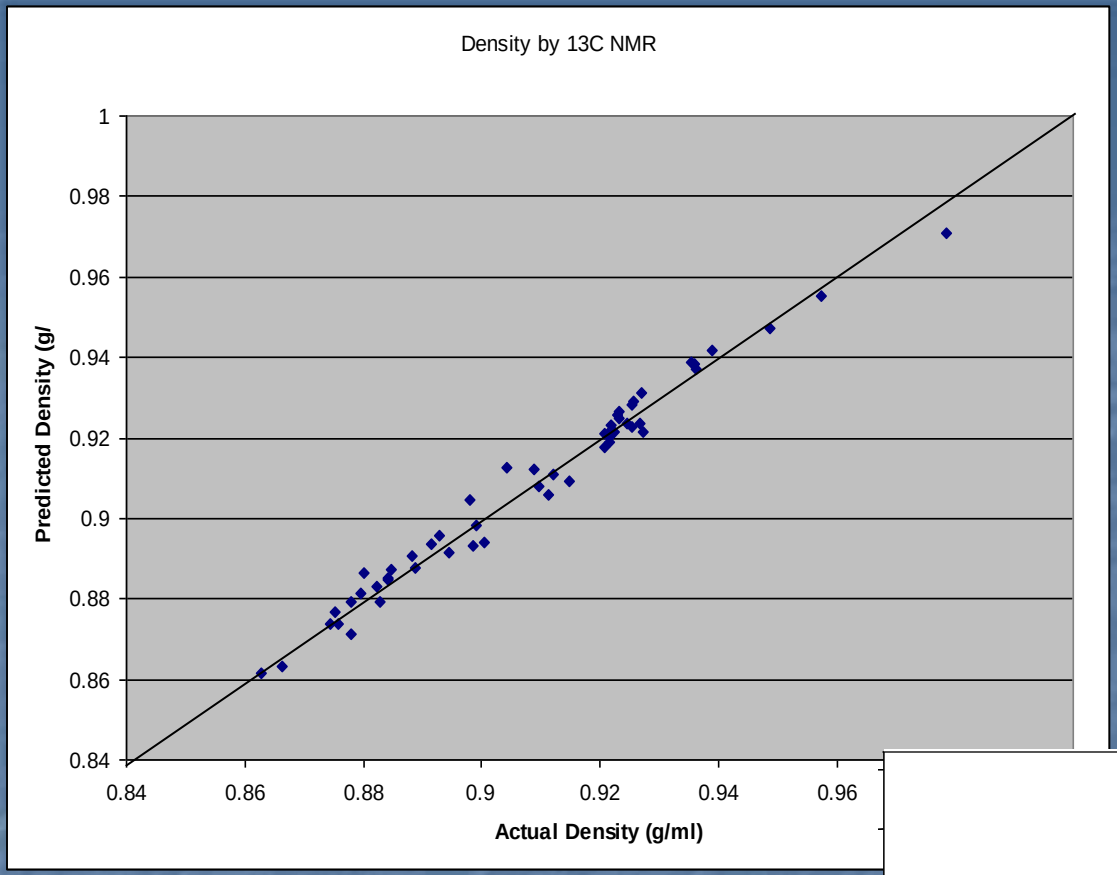


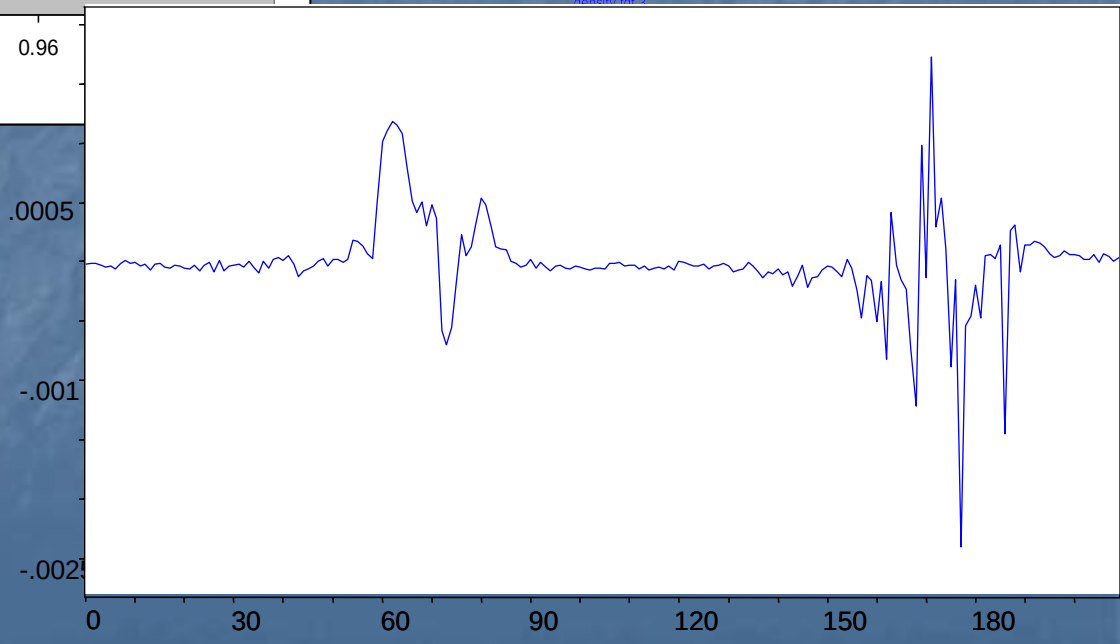


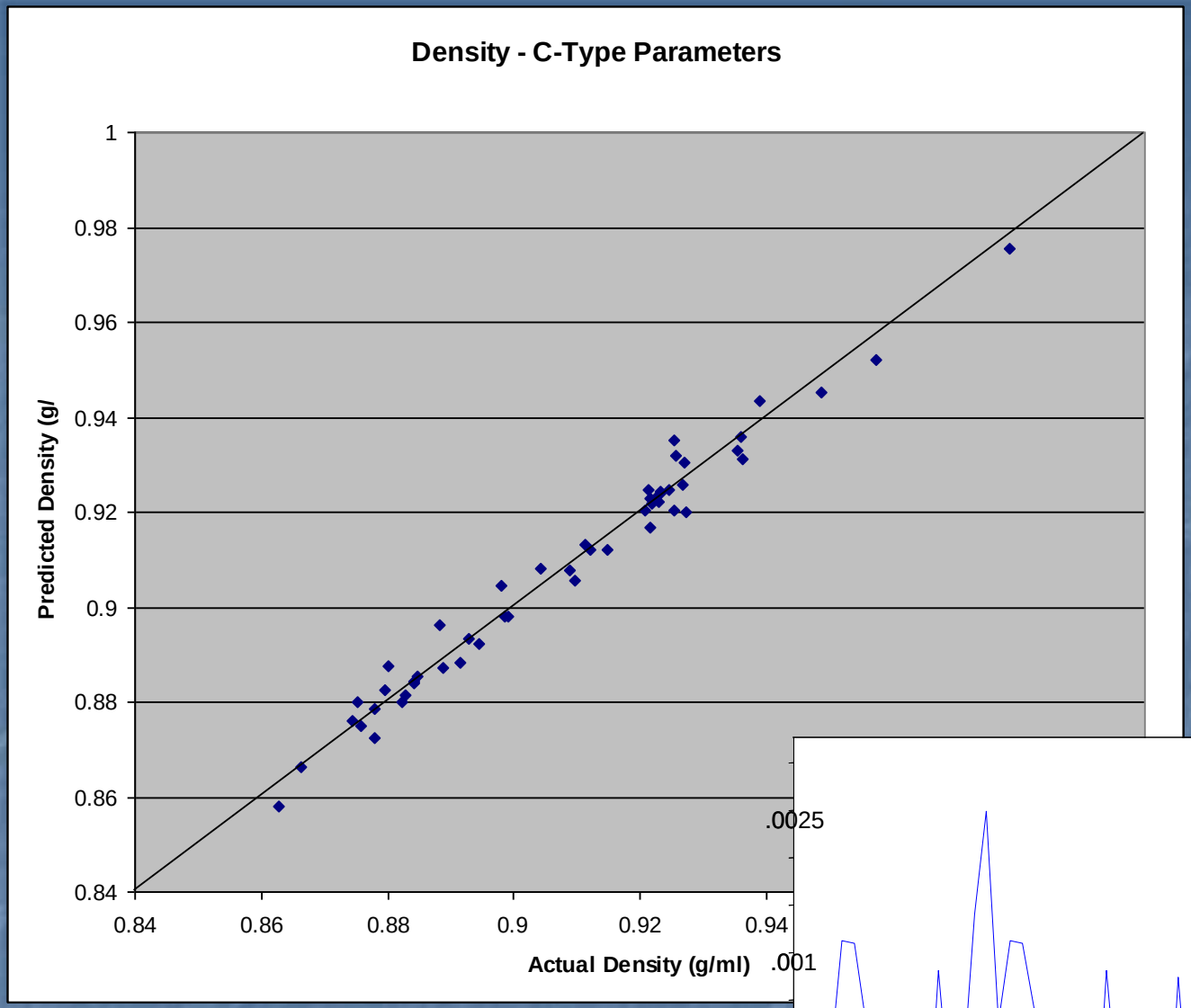


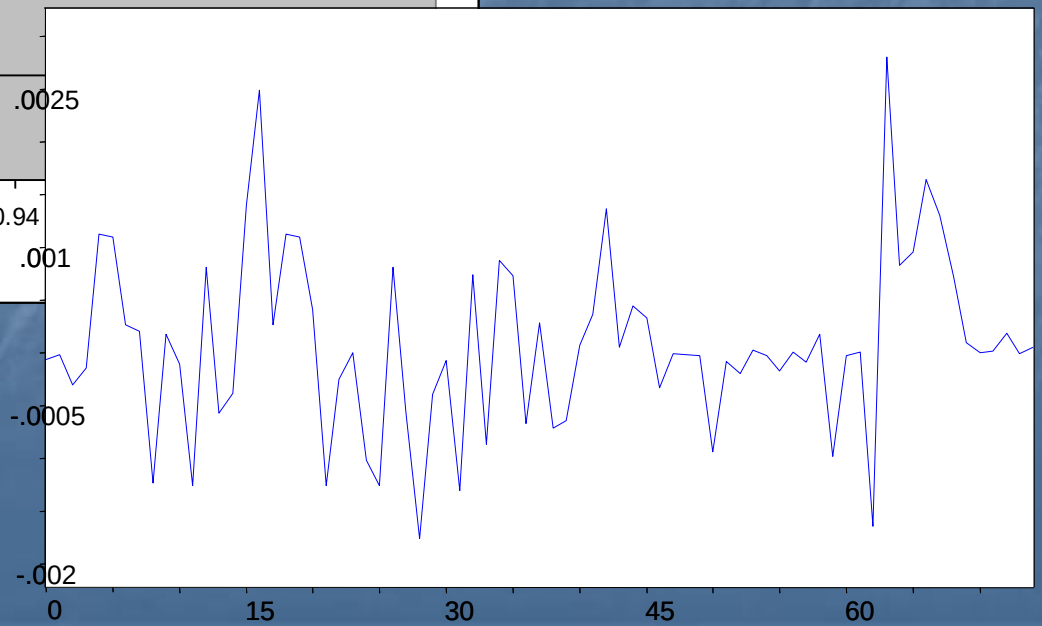
Density Correlation with
Proton Type Parameters

^{13}C NMR Correlation to Density

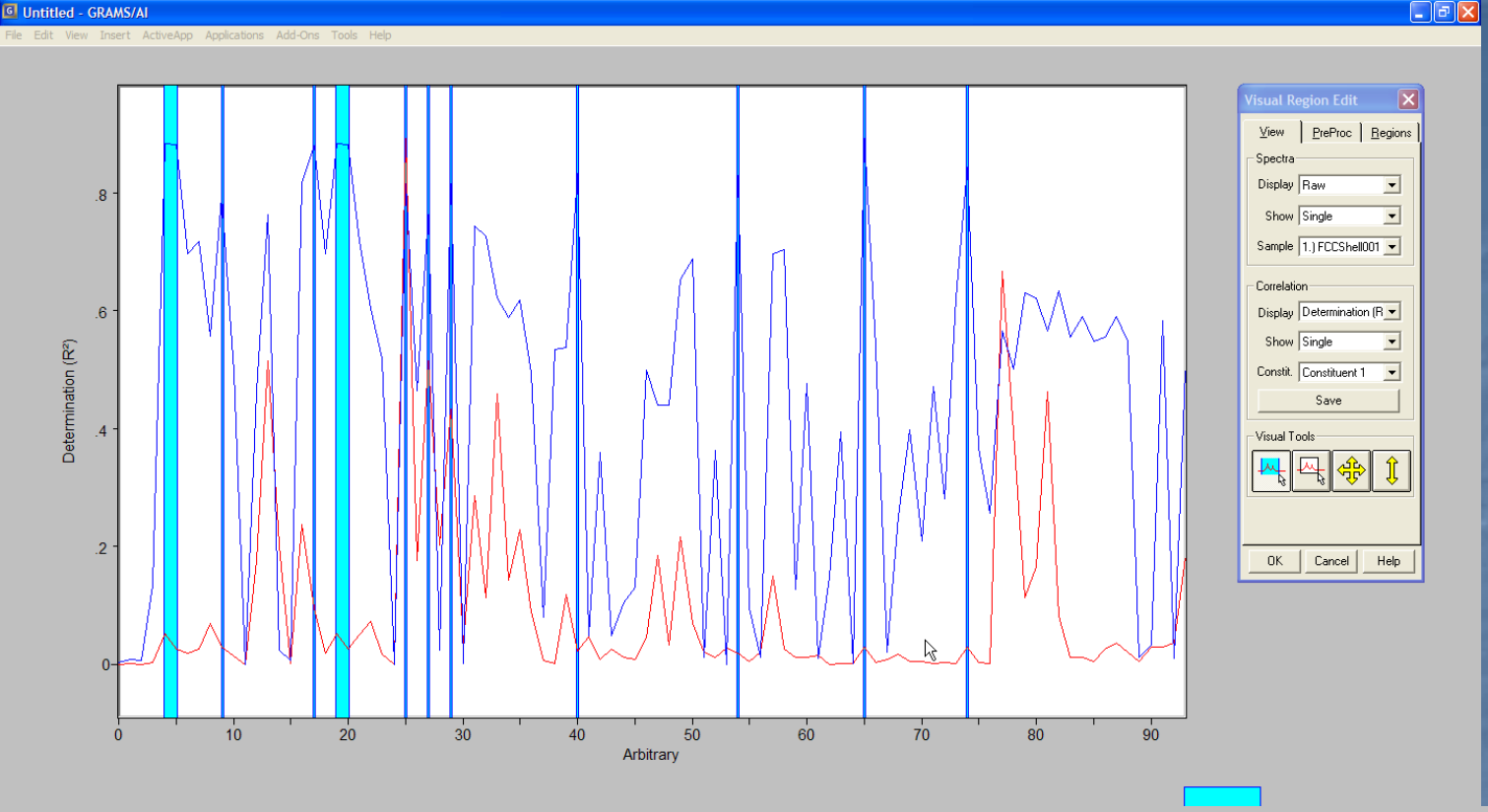


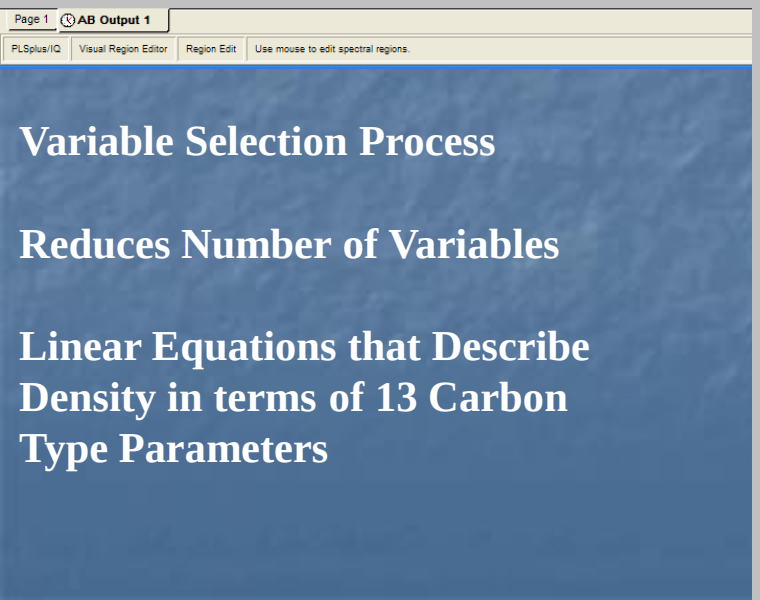






Density Correlation with Carbon Type Parameters

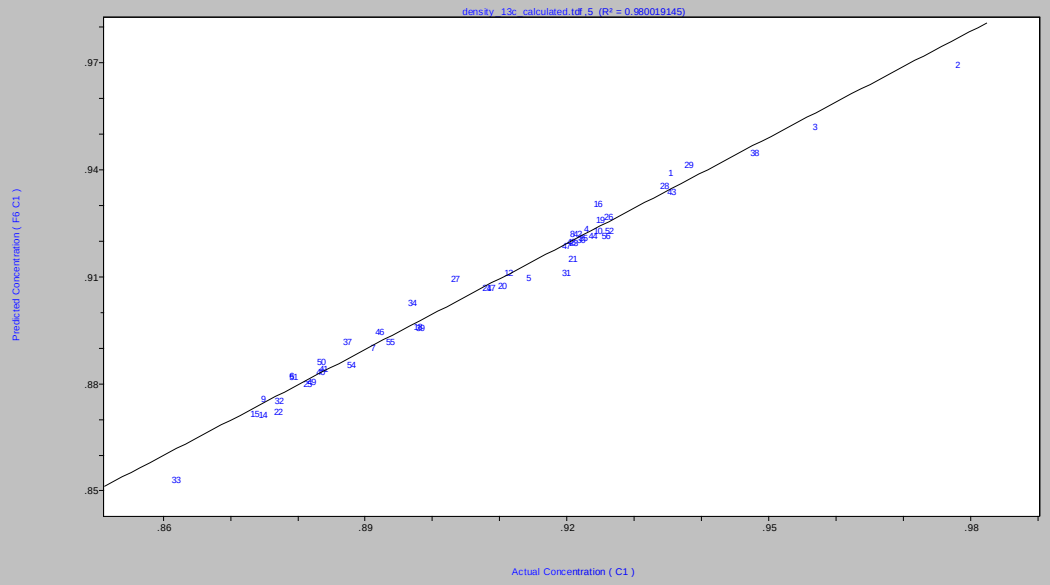




Variable Selection Process

Reduces Number of Variables

Linear Equations that Describe Density in terms of 13 Carbon Type Parameters

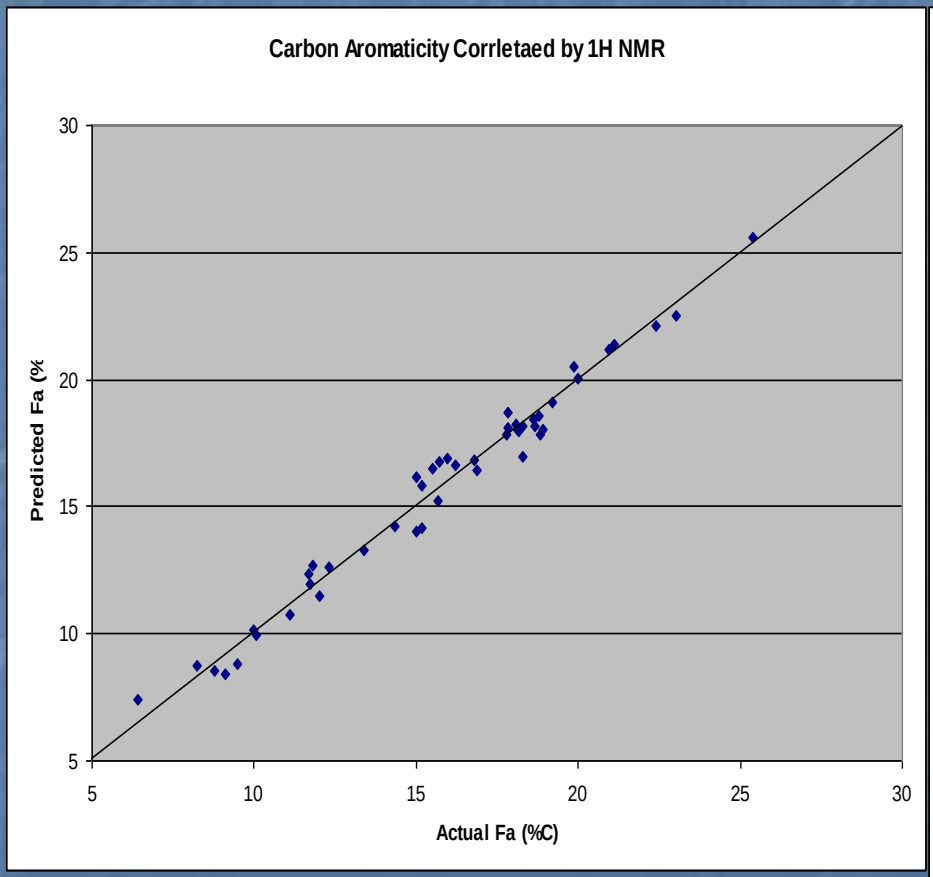


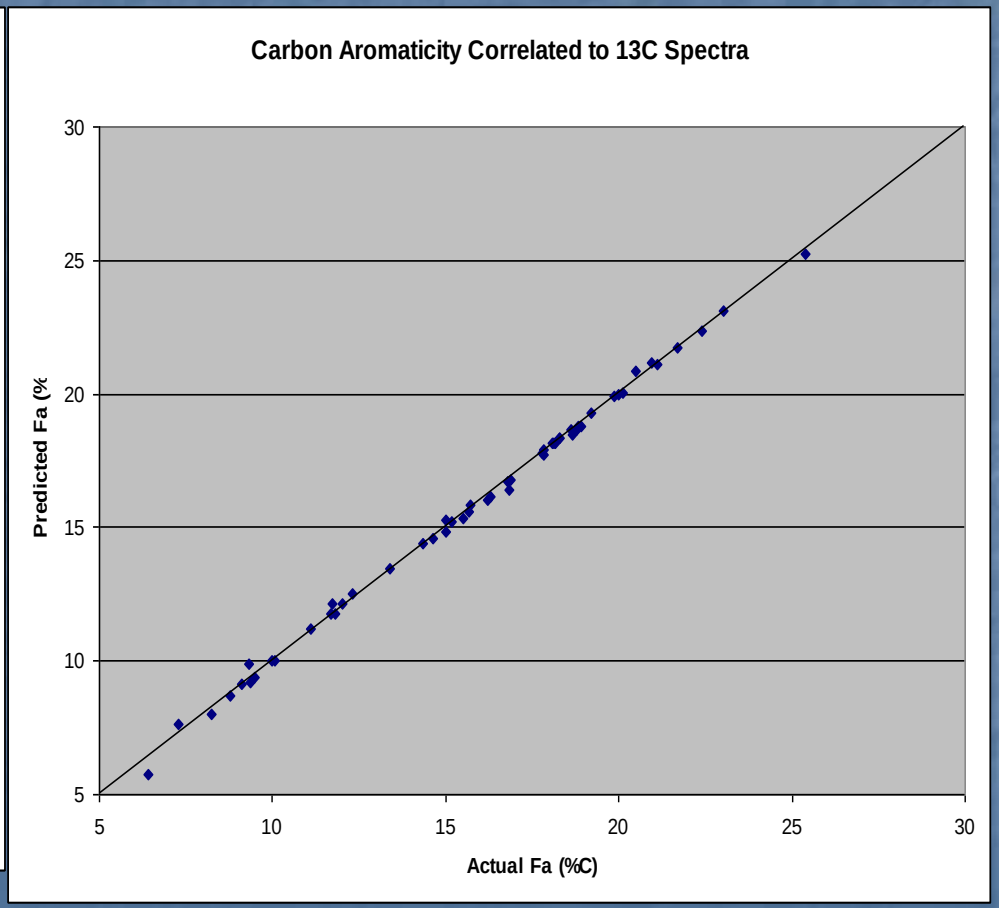
Correlation of ^{1}H and ^{13}C NMR Spectra to ^{13}C Derived Parameters

13C Parameter	1H NMR	13C NMR
Total aromatic carbon	0.980	0.996
Aliphatic substituted aromatic carbon	0.962	0.999
Methyl-substituted aromatic carbon	0.970	0.994
CH2 & CH substituted aromatic carbon	0.935	0.996
Naphthenic substituted aromatic carbon	0.973	0.996
Internal aromatic carbon	0.949	0.994
Peripheral unsubstituted aromatic carbon	0.950	0.996
Total heteroaromatic carbon	0.275	0.976
Total aliphatic carbon	0.952	0.997
Aliphatic methine carbon (CH)	0.932	0.999
Aliphatic methylene carbon (CH2)	0.976	1.000
Aliphatic methyl carbon (CH3)	0.610	0.996
Total paraffinic carbon	0.984	0.995
P methine carbon (CH)	0.876	0.940
P methylene carbon (CH2)	0.987	0.998
P methyl carbon (CH3)	0.810	0.960
Total naphthenic carbon	0.964	0.989
N methine carbon (CH)	0.927	0.996
N methylene carbon (CH2)	0.957	0.987
N methyl carbon (CH3)	0.809	0.966
N methine/N methylene ratio	0.085	0.878
Mole fraction bridgehead aromatic C	0.448	0.899
Aromatic carbons per aromatic group	0.697	0.895

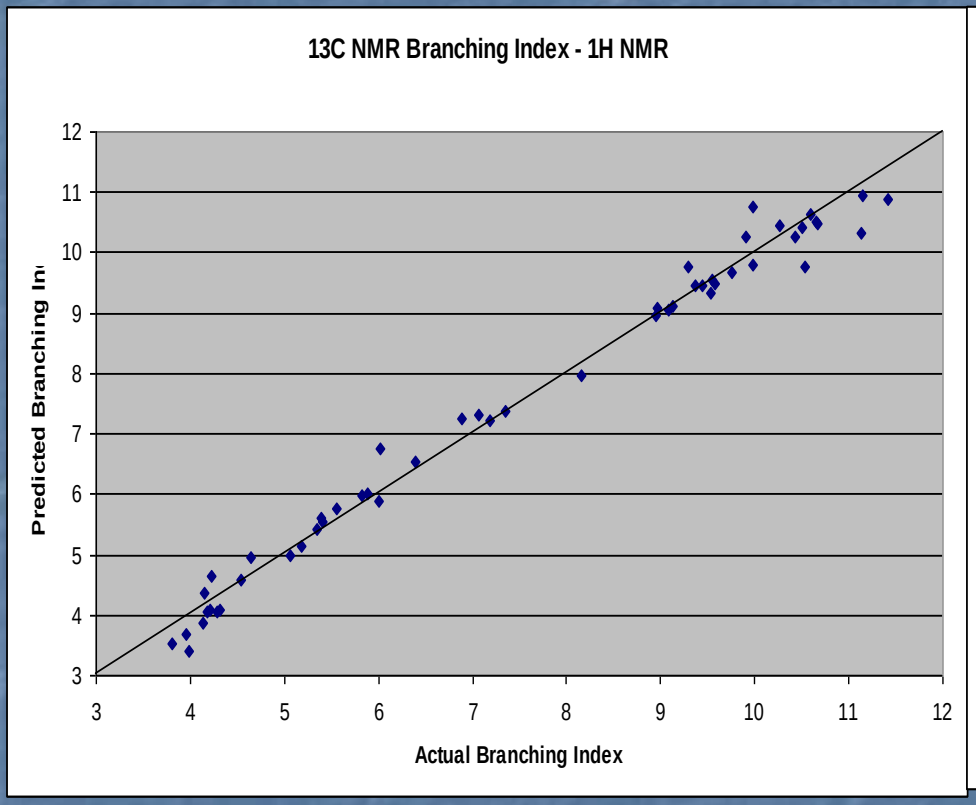
13C Parameter	1H NMR	13C NMR
Cluster number (=aromatic cluster size)	0.941	0.995
Aliphatic substitutions per cluster	0.087	0.906
Methyl-substitutions per cluster	0.379	0.909
CH2 & CH substitutions per cluster	0.063	0.899
Naphthenic substitutions per cluster	0.227	0.910
Heteroatoms per cluster	0.032	0.926
Naphthenic CH3 per cluster	0.449	0.906
# of naphthenic ring carbons per cluster	0.524	0.924
Naphthenic rings per cluster	0.317	0.939
# of paraffinic carbons per cluster	0.892	0.934
Average chain length of paraffinic substitutions	0.913	0.932
Linear paraffin structure	0.972	0.976
Waxiness : e/total paraffin	0.977	0.983
Branching index	0.973	0.972
Total branching content	0.964	0.972
Carbons in branched environment	0.972	0.976
Average straight chain length	0.967	0.986
Methyl branching index	0.972	0.962
Ethyl branching Index	0.945	0.945
Propyl branching Index	0.919	0.932
Butyl branching Index	0.919	0.951
Total ethyl branching content	0.946	0.946
Total propyl branching content	0.919	0.933
Total butyl branching content	0.917	0.950

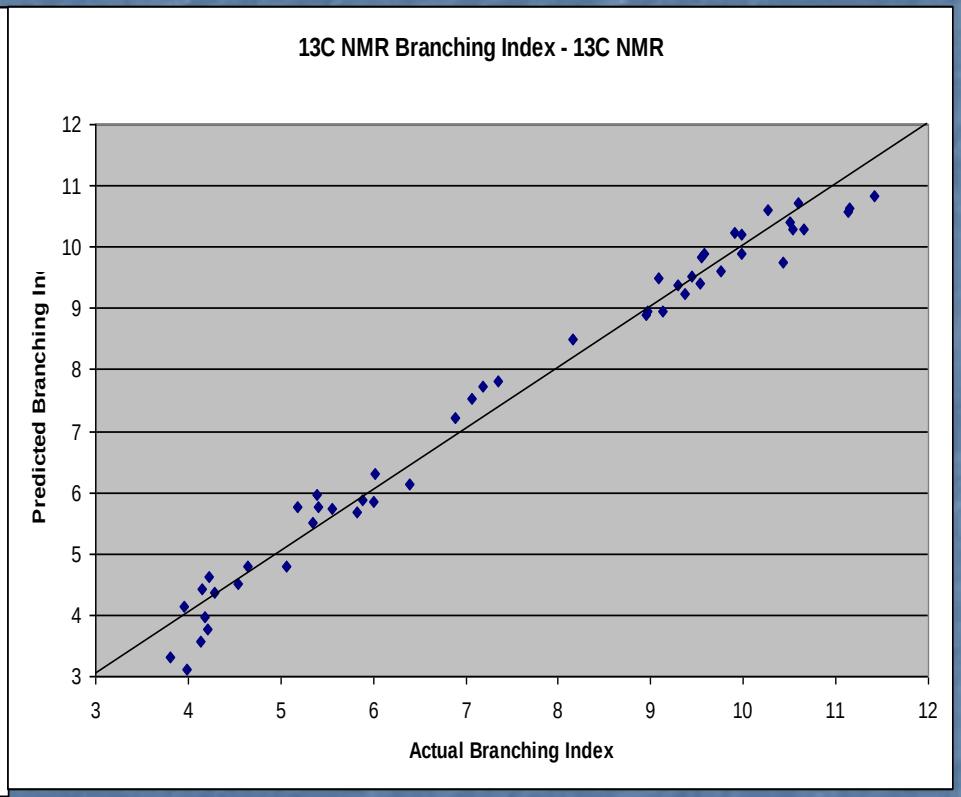
^{1}H and ^{13}C NMR Correlation to Carbon Aromaticity





^{1}H and ^{13}C NMR Correlation to Branching Index





Branching Carbons/Total Paraffinic Carbons

Summary

Chemical and Physical Properties of RCC Feed-Streams can be determined by ^{1}H NMR (at 60 and 300 MHz) and by ^{13}C NMR

H-Type and C-Type Parameters do not provide as good a correlation as is observed by full spectrum regression. We assume that this is due to loss of resolved chemical shift information when the spectrum is reduced to larger integral areas.
However, these approaches allow transfer of calibration models between NMR instruments at different magnetic fields.

^{1}H NMR can be combined with PLS regression modeling to provide detailed carbon type analysis for RCC Feeds

Regression analysis of ^{13}C NMR data can be utilized to fully automate the prediction of ^{13}C NMR type analysis : reducing the necessity for considerable knowledge and analysis time on the part of the analyst.

Other Work

Similar analysis has been performed on:
Crude Oil - TBP, Density, Water
Canadian Syncrude - Olefins, Density, Distillation
Vacuum Residues – Distillation, Density, ^{13}C Parameters
Naphtha – Density, PIONA, Distillation
Gasoline – Octane, Benzene, Oxygenates, Distillation, Aromatics
Kerosene – Distillation, Smoke Point
Jet Fuel – Cloud Point, Freeze Point, Distillation, Density
Diesel – Density, Cloud point, Flash, Distillation, Cetane Index
Reformate – Octanes, Benzene, Aromatics
Alkylate – Octane, Distillation
Lubricant Oil and Intermediates – Pour, VI, Distillation, ^{13}C Parameters
FT-Waxes – ^{13}C Parameters
VGO – FCC Feeds (Same as RCC Feeds)
Biodiesel and Diesel/Biodiesel Blends
Edible Oils – Fatty Acid Distributions