Solid-State ^{13}C NMR Applied to Petroleum Related Materials:

Combustion Deposits, Asphaltenes, Residues, Kerogen, Shale, Bitumen, Coal, the Works

By
John C Edwards, Ph.D.
Process NMR Associates, Danbury, CT USA

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Problems Caused by Engine Deposits

Combustion Chamber Deposits (CCDs)

Increased Emissions
Fuel Economy Decrease
Octane Requirememt Increase (Manifested by Knocking)
Physical Contact of Piston with Cylinder Head

Intake Valve Deposits (IVDs)

Cold Start Stalling, Rough Idle, Hesitation
Valve Sticking
Increased Emissions

Crankcase Sludge and Varnish

Loss of Oil Flow
Filter Plugging
Increased Wear
Loss of Lubricity
Catastrophic Engine Failure

4 Automotive Engine Dynamometer Testing Conditions

2.2L PFI Turbo

Test Conditions: 90 Hour Test

Condition	Time	Speed	Load
#	min	rpm	N-m (ft-lb)
1	6	1800	33 (25)
2	12	2650	61 (45)

5.0L SPFI

Test Conditions: 90 Hour Test

Condition	Time	Speed	Load
#	sec	rpm	N-m (ft-lb)
1	30	850	0
2	90	1800	33 (25)
3	90	2100	54 (40)
4	30	3000	230 (170)
5	300	2650	41 (30)

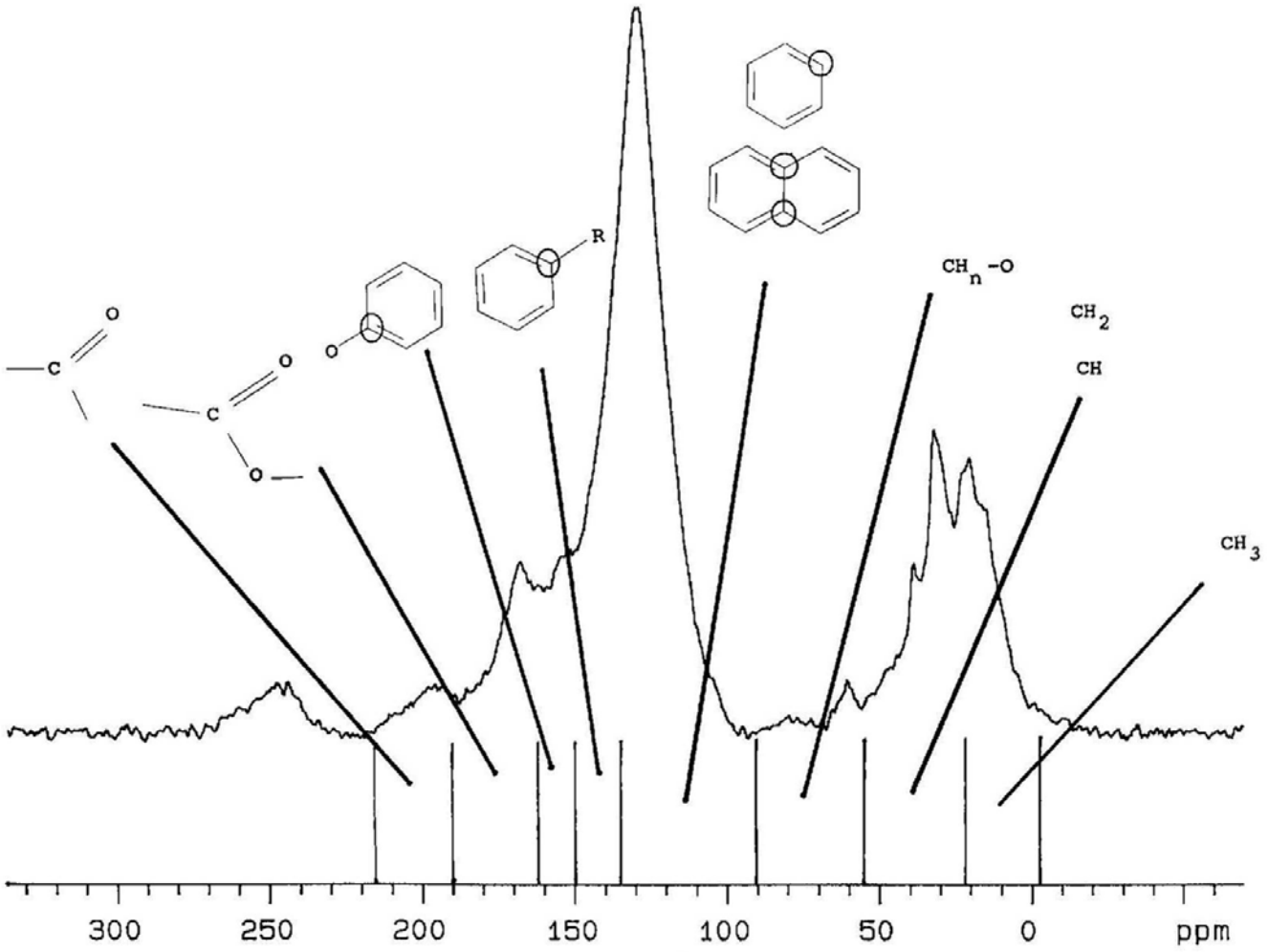
Parameters Measured : Weight and Thickness of Deposit

Objectives

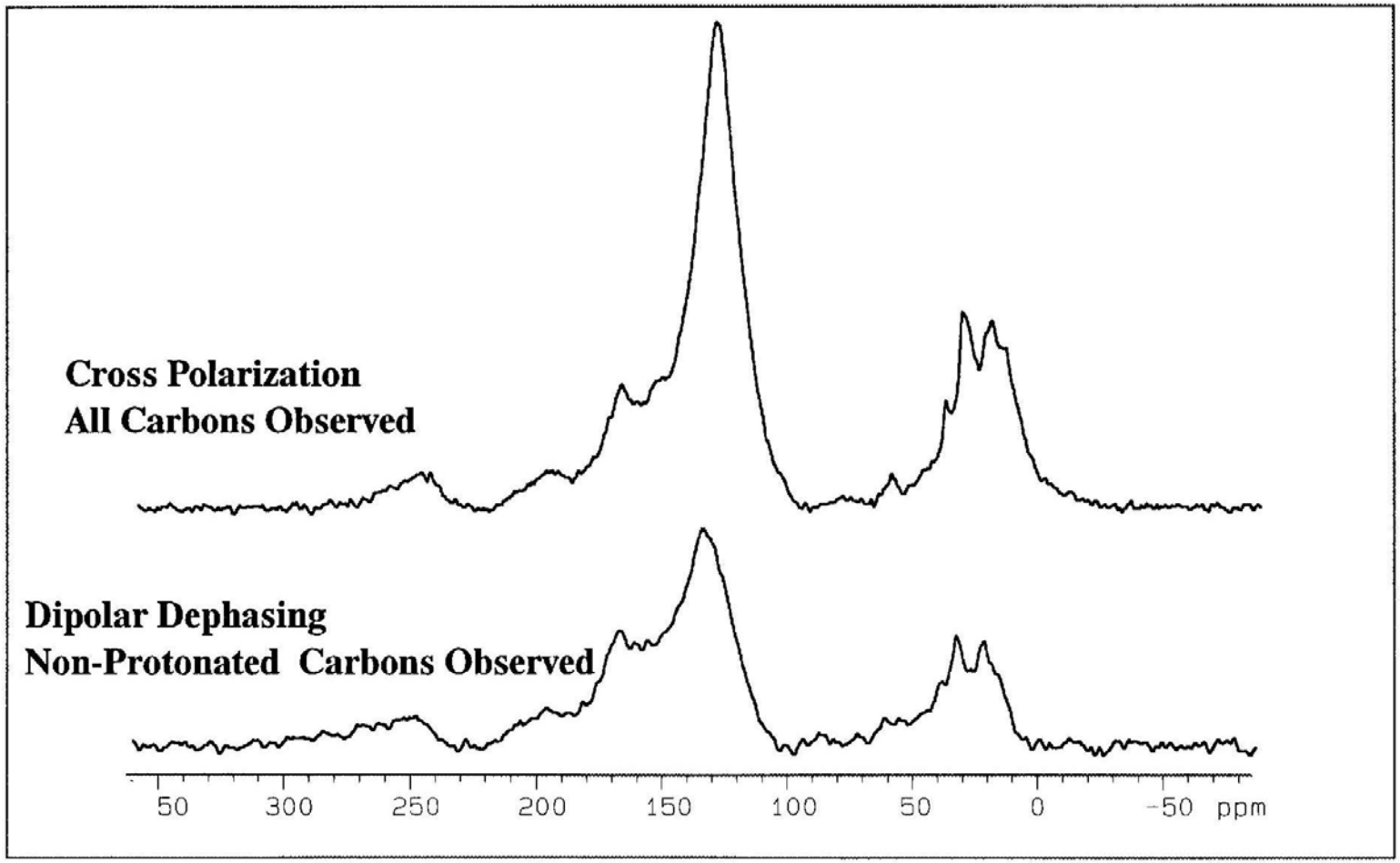
Develop a foundation for using NMR to study combustion chamber deposits (CCDs), Intake Valve Deposits (IVDs) and Crankcase Sludge and Varnish Deposits

- Identify the "average molecular" structure of the polymeric backbones of these deposits using 13C Cross-Polarization, Dipolar Dephasing and MAS techniques.
- Investigate differences in deposit structure based on engine location.
- Determine if CCDs produced in different engines, under different conditions are different in molecular structure.
- Verify similarities of automotive engine CCDs with coal, and bench test CCDs with asphaltene.
- Observe effects of fuel aromatic content on the molecular structure of CCDs produced.
- Use NMR to determine the effect of engine modifications, in established bench tests, on CCDs and IVDs

Regions of Carbon-13 NMR Spectrum Used in the Analysis



Comparison of Experiments Used to Determine Mole Fraction of Bridgehead Aromatic Carbon



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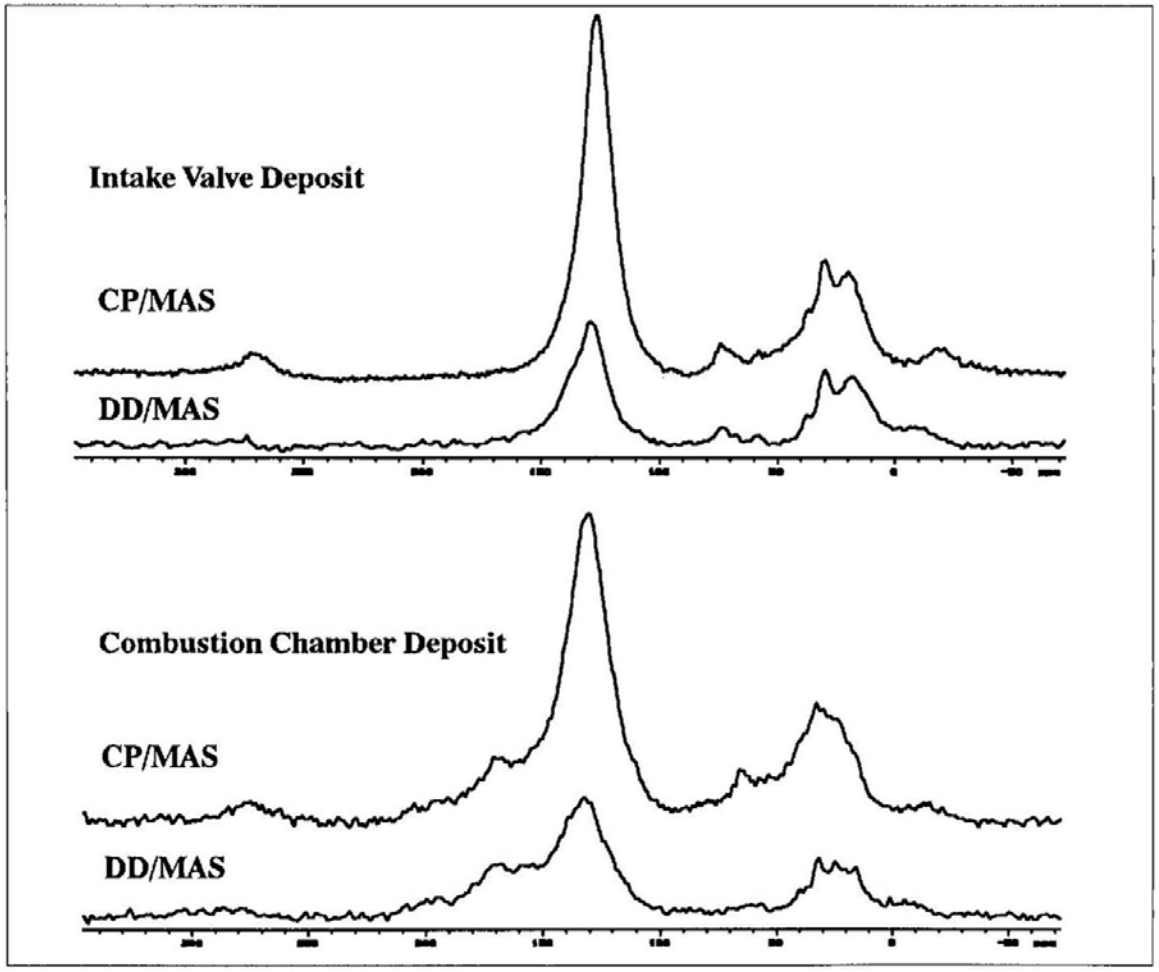
NMR Experiments and Conditions

Spectrometers Used : Varian Unity-300, Varian UnityPlus-200
Probes Used : Doty Scientific 7mm High-Speed CP/MAS Probe, and Doty Scientific 7mm Supersonic CP/MAS Probe



Cross Polarization

Contact time = 0.8 ms
relaxation delay = 1 s
pulse width = 4.5 us
acquisition time=20 ms
line broadening = 30 hz

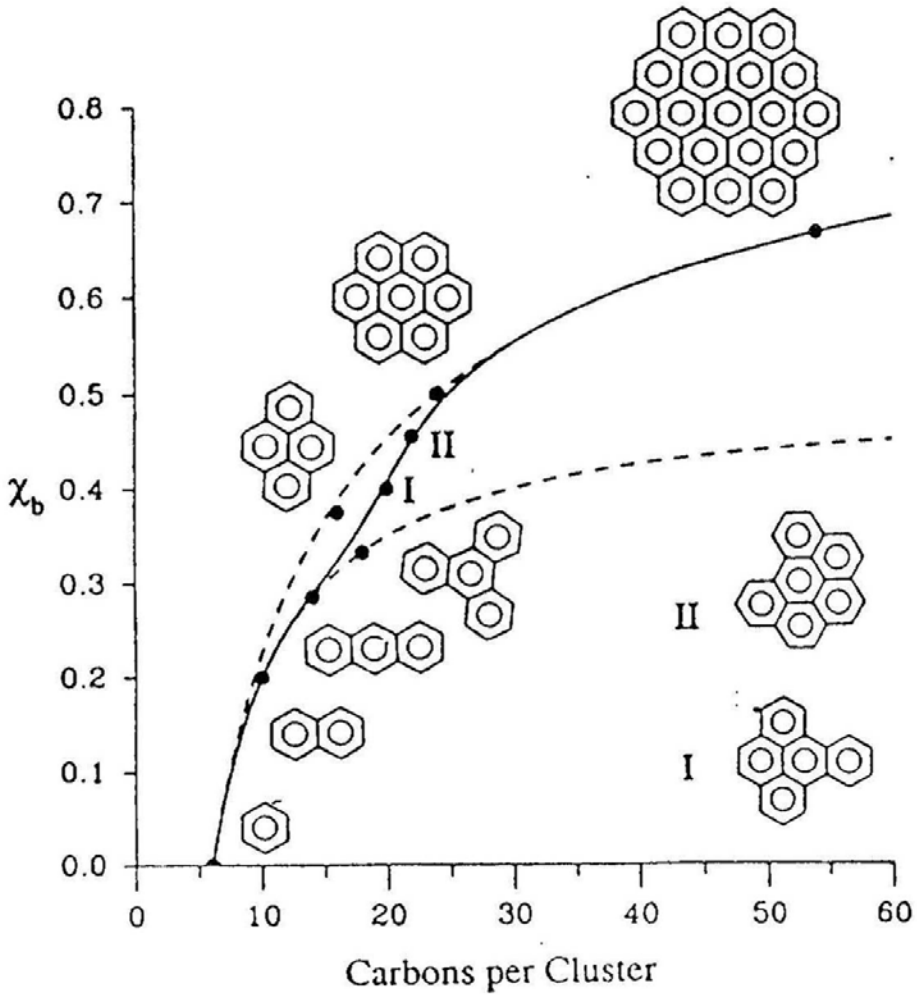
Dipolar Dephasing

All conditions same as above except, interrupted decoupling for 60 us

MAS rate =7 kHz on UP-200

MAS rate = 7.5 kHz on U-300

Mole Fraction of Bridgehead Aromatic Carbon Vs Carbons per Aromatic Cluster



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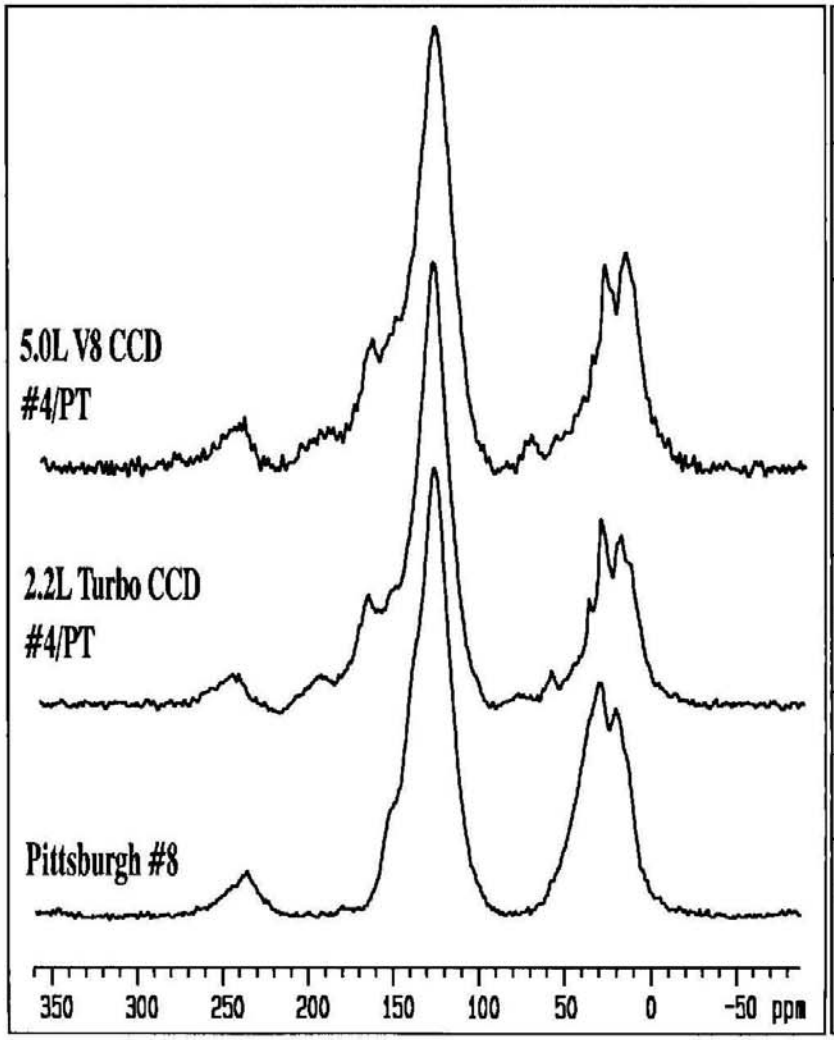
NMR Derived Structural & Molecular Parameters

Structural Parameter	Carbon Type Represented	Typical Values IVD	CCD
fa	aromatic/carboxylic/carbonyl	0.69	0.77
fa'	aromatic	0.68	0.61
faC	carboxylic/carbonyl	0.00	0.16
faH	protonated aromatic	0.46	0.22
faN	non-protonated aromatic	0.22	0.40
faP	phenolic	0.01	0.08
faS	alkyl-substituted aromatic	0.10	0.16
faB	bridgehead aromatic	0.11	0.16
fal	aliphatic	0.31	0.23
falH	methylene/methine	0.17	0.13
fal*	methyl	0.09	0.05
falO	alcohol/ether	0.05	0.05
faB/fa' = Xb		0.17	0.28

Molecular Parameter	Description		
C	Av. # of aromatic carbons per cluster	9	13
(S+1)	Av. # of attachments per cluster	1.4	4.8
Po	Av. fraction of Intact Bridges (Polymericity)	0.13	0.80
B.L.	Av. # of intact bridges & loops per cluster	0.18	3.8
S.C.	Av. # of terminal side chains per cluster	1.24	1.0
Phi-O	Av. # of phenolic groups per cluster	0.15	1.6
Phi-CO	Av. # of carboxyls per cluster	0.00	3.3
n'	Av. aliphatic chain length per attachment	2.92	1.0
Mw	Av. molecular weight per cluster	175	303

7 Comparison of CCD with High Volatile Bituminous Coal



Structural Parameter	Pittsburgh #8	2.2L Turbo	5.0L V8
Aromaticity	0.63	0.63	0.61
Carboxyls per cluster	0.53	2.81	3.26
Average chain length	1.84	0.97	0.96
Polymericity	0.72	0.75	0.8
Attachments per cluster	4.82	5.11	4.77
Carbons per aromatic cluster	16	13	13

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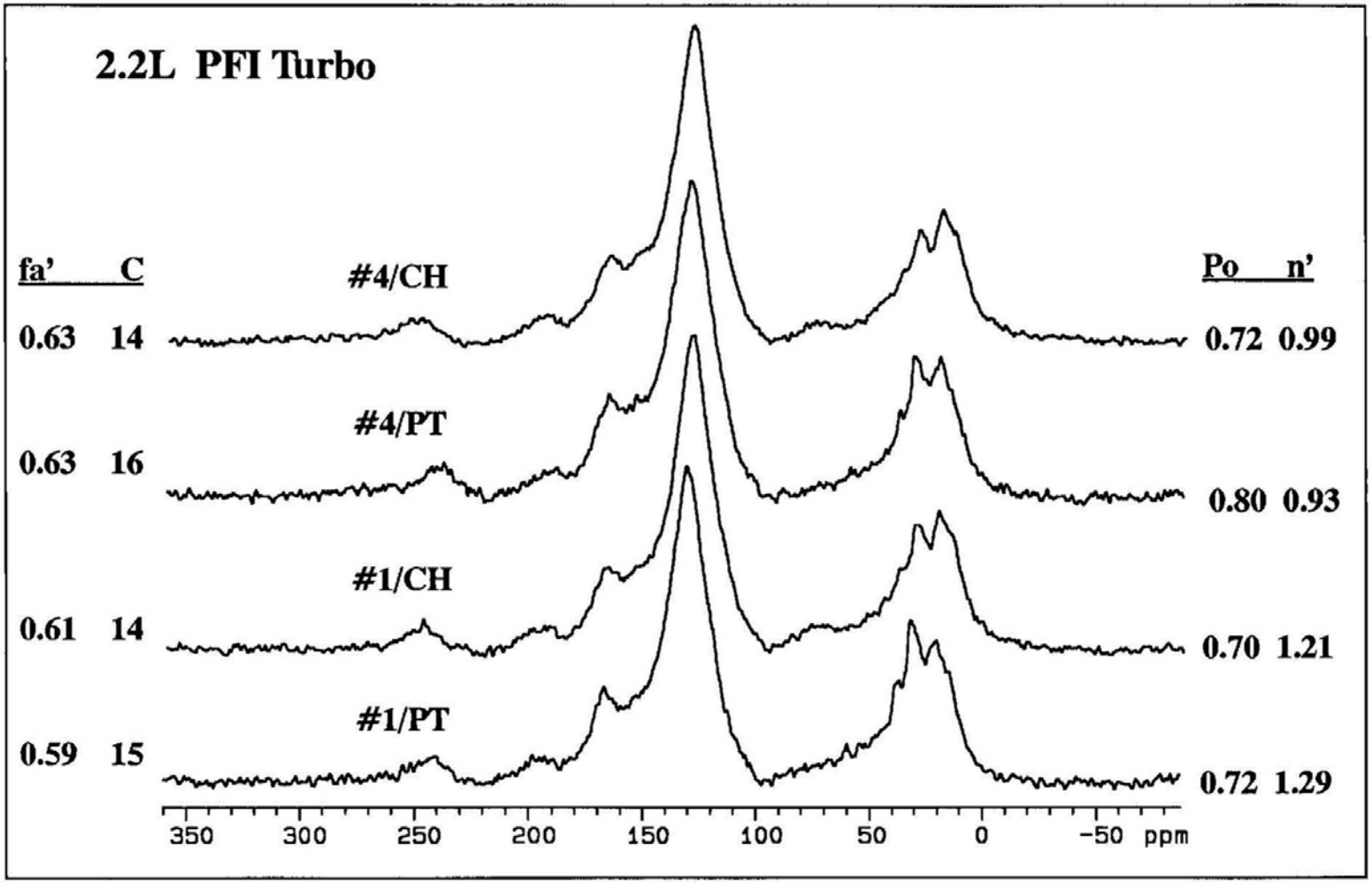
Cylinder-To-Cylinder Variation of CCD Structure



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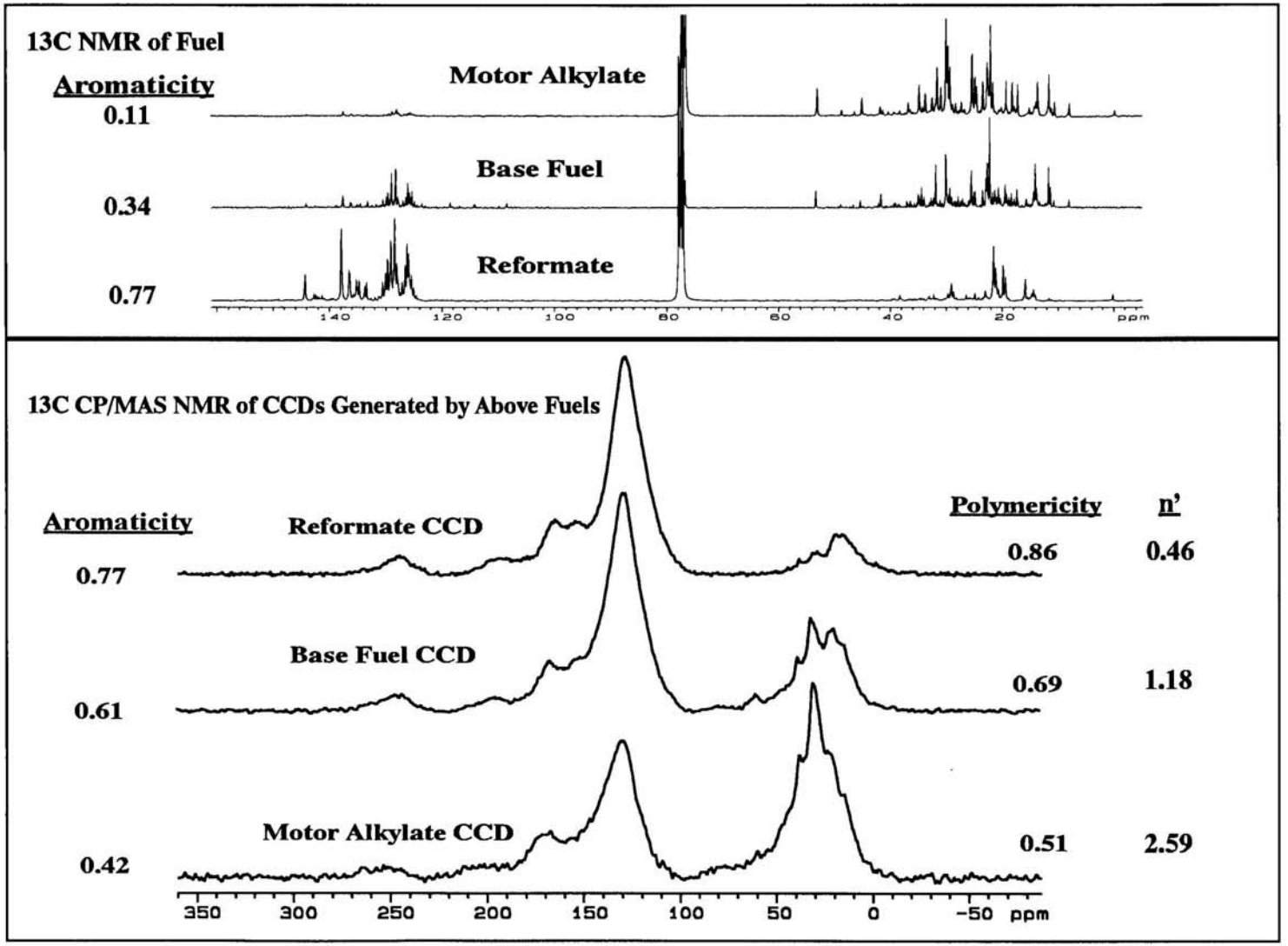
Effect of Fuel Composition on CCD Molecular Structure



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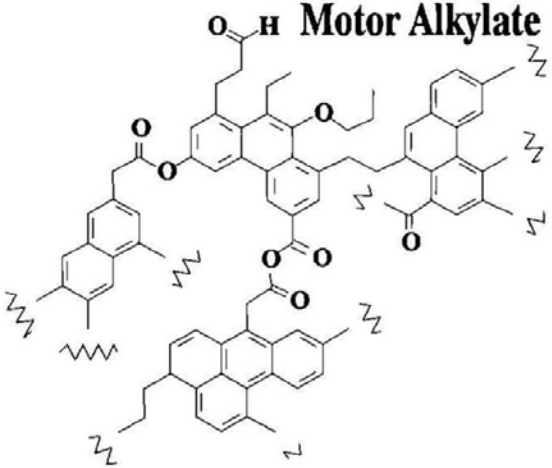
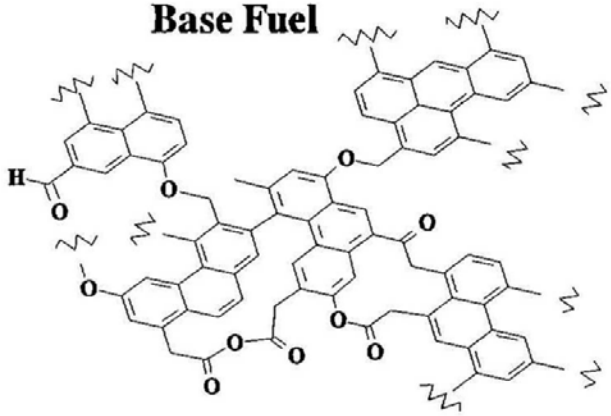
"Average Molecule" Representations of the CCDs Generated by Motor Alkylate, Base Fuel, and Reformate

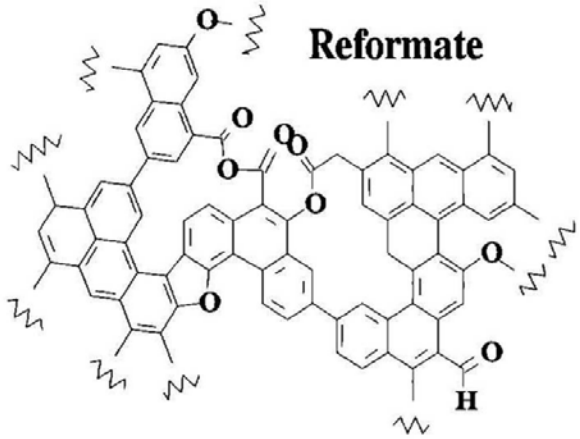
Motor Alkylate



Base Fuel



Reformate



Selected Parameters for 2.2L & 5.0L CCDs

		Aromaticity	Polymericity	Chain Length
Motor Alkylate	2.2L 5.0L	0.42 0.48	0.51 0.54	2.59 1.71
UBF	2.2L 5.0L	0.61 0.60	0.69 0.68	1.18 1.19
Reformate	2.2L 5.0L	0.77 0.79	0.86 0.91	0.46 0.29

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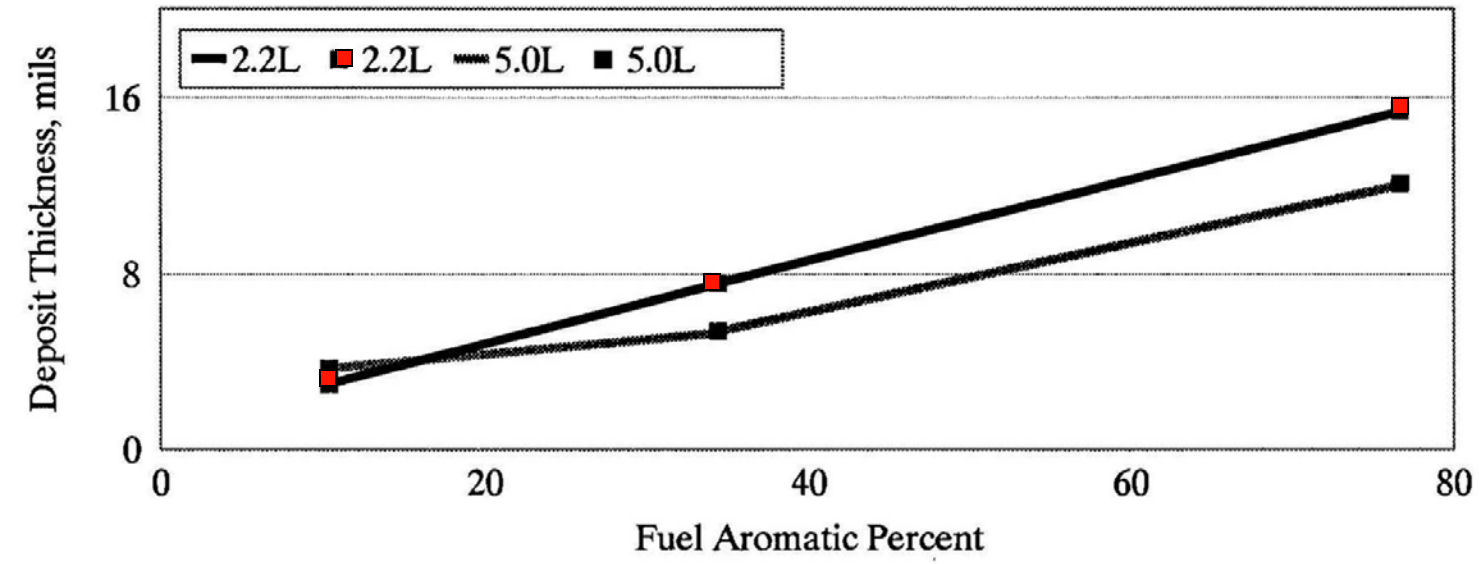
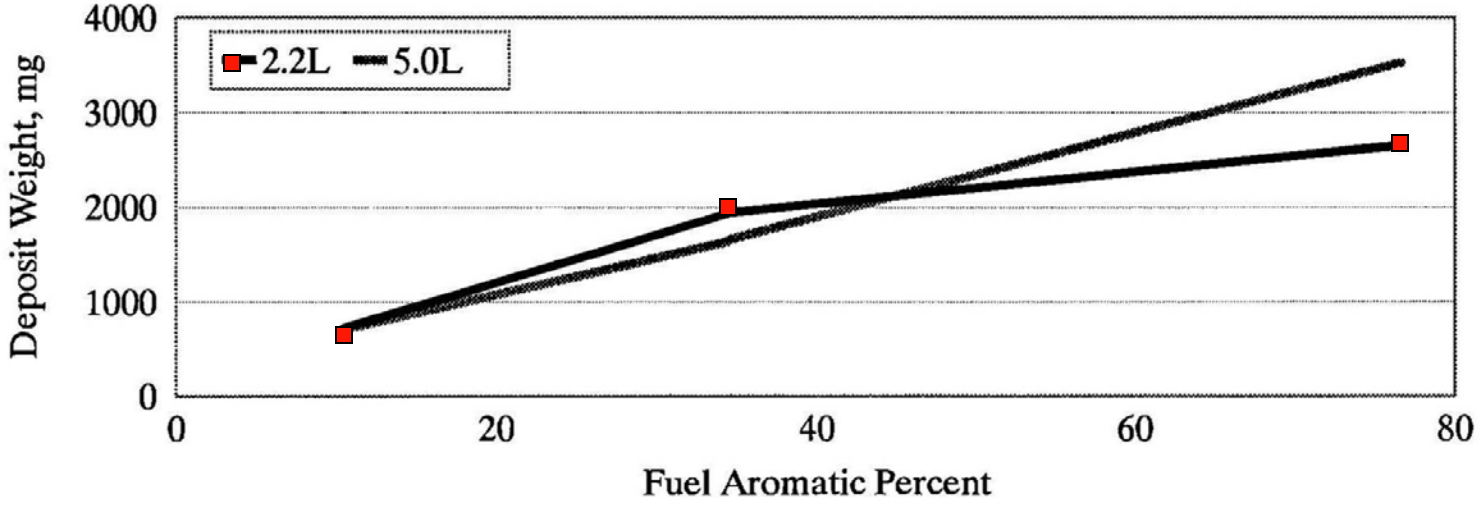
Engine Test Derived Parameters Versus Fuel Aromatic Content





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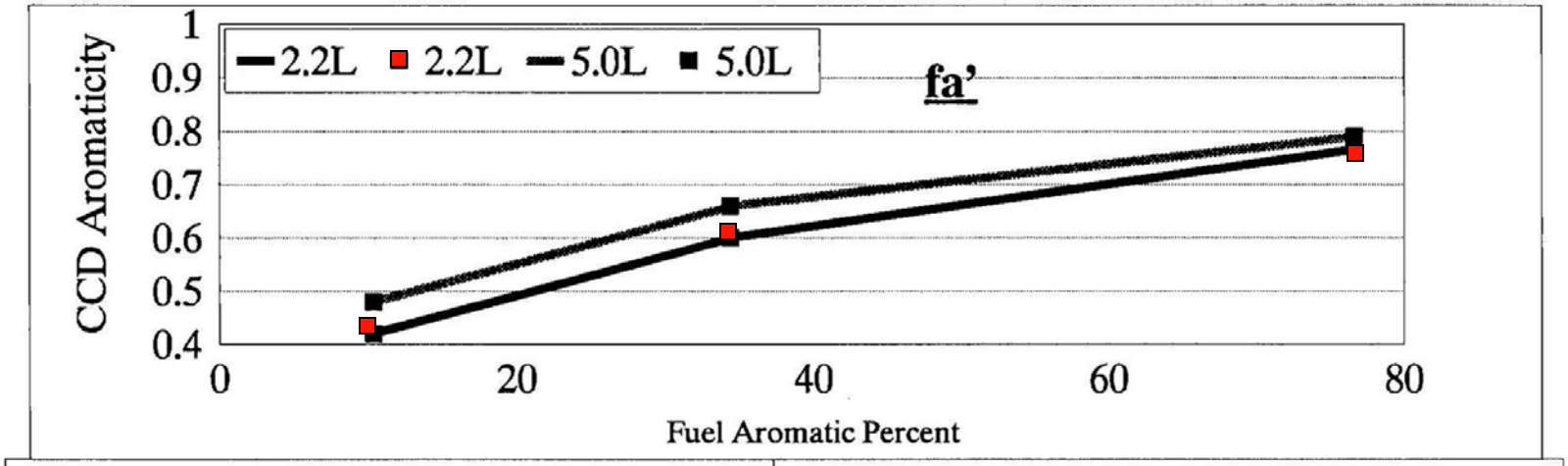
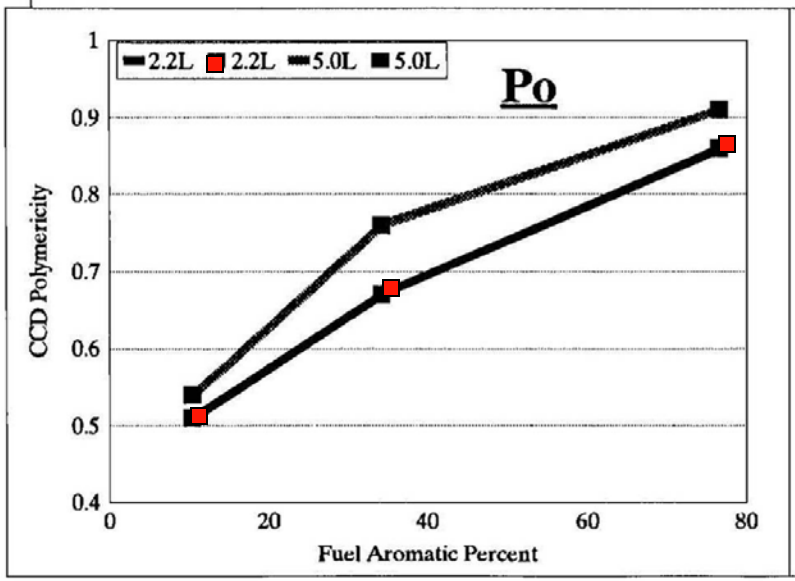
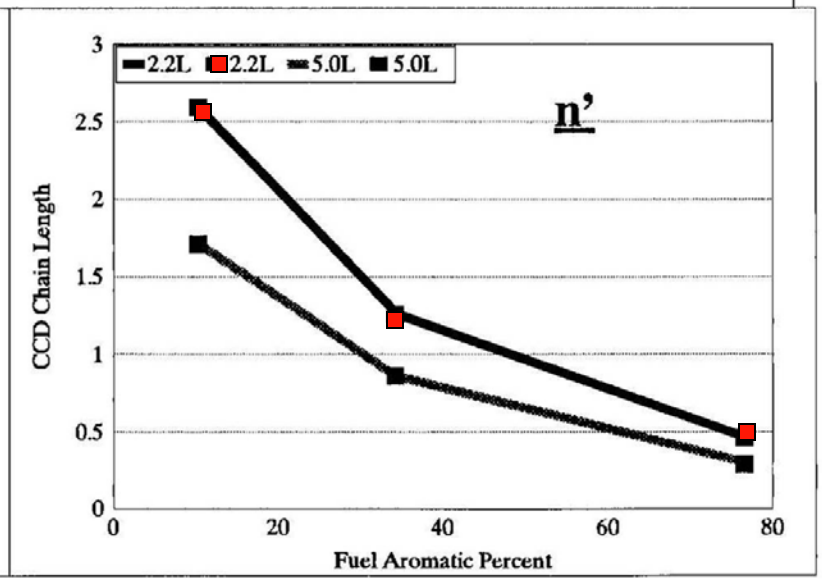
NMR Derived CCD Structural Parameters Versus Fuel Aromatic Content







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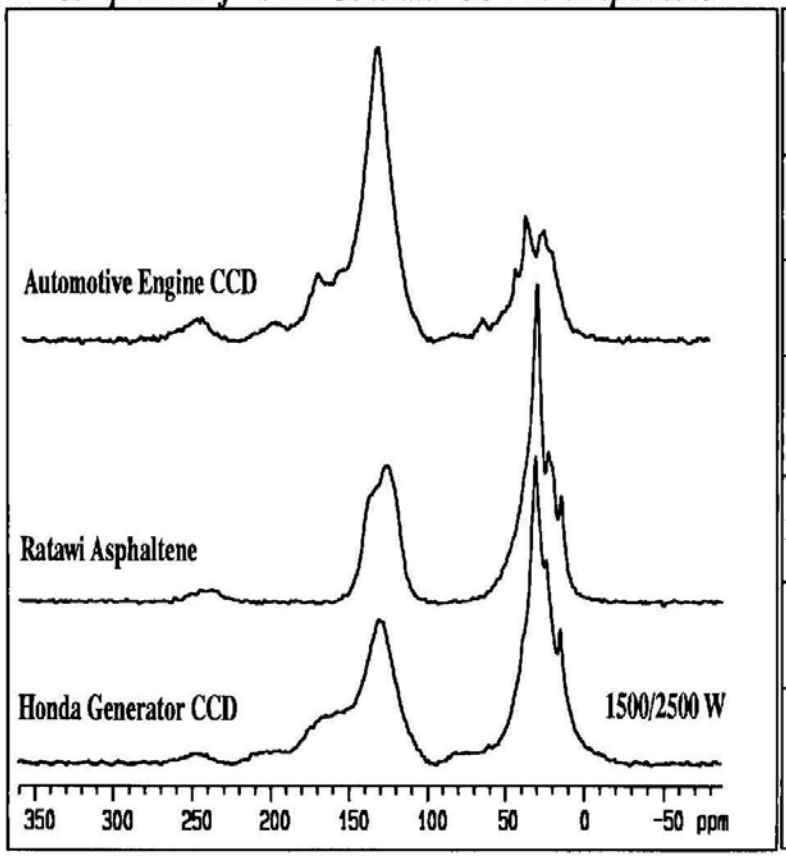
Honda Generator Test

Screening Test Used to Determine Candidate Additive Packages and Fuels for Automotive Engine Testing

80 hour test : 2 load conditions of 1500 and 2500 W, 2 hours at each condition, Lube=10W-40 SF

Comparison of Honda-Generator CCD with Asphaltene



Structural Parameter	Honda PT	Honda CH	2.2L Turbo PT	Ratawi Asphaltene
Aromaticity	0.46	0.43	0.63	0.42
Carboxyls per cluster	3.8	2.8	2.8	0
Average chain length	2.24	2.54	1	4.5
Polymericity	0.59	0.69	0.75	0.29
Attachments per cluster	7.28	5.19	5.11	5
carbons per aromatic cluster	17	12	13	16

Note large difference between automotive engine CCD and the Honda generator CCD

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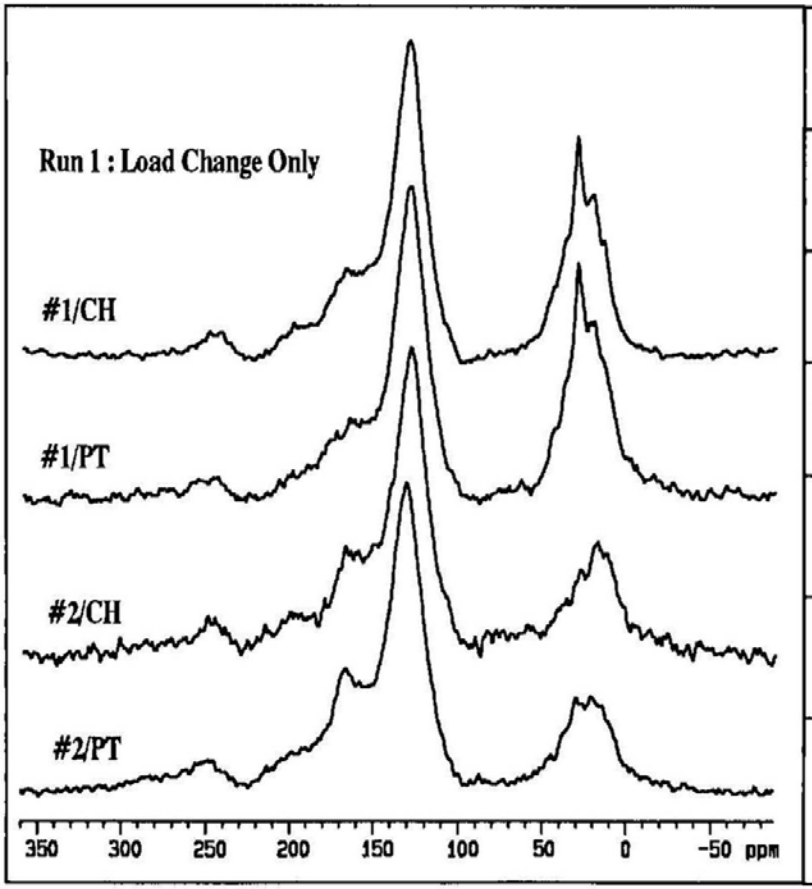
Modified Honda Generator Tests

Test Load Modified (to 2500/4000W) to Generate Deposits which More Closely Resemble Deposits Generated in Automotive Engines

80 Hour Tests : Load Condition Modified to Cycle Between 2500 and 4000 W
2 Hours at each Condition



Structural Parameter	PT/1	PT/2
Aromaticity	0.57	0.66
Carboxyls per cluster	1.9	4.1
Average chain length	1.4	0.5
Polymericity	0.65	0.86
Attachments per cluster	3.08	5.48
Aromatic carbons per cluster	9	13

Note: Large Structural Difference Observed Between the Two Cylinders

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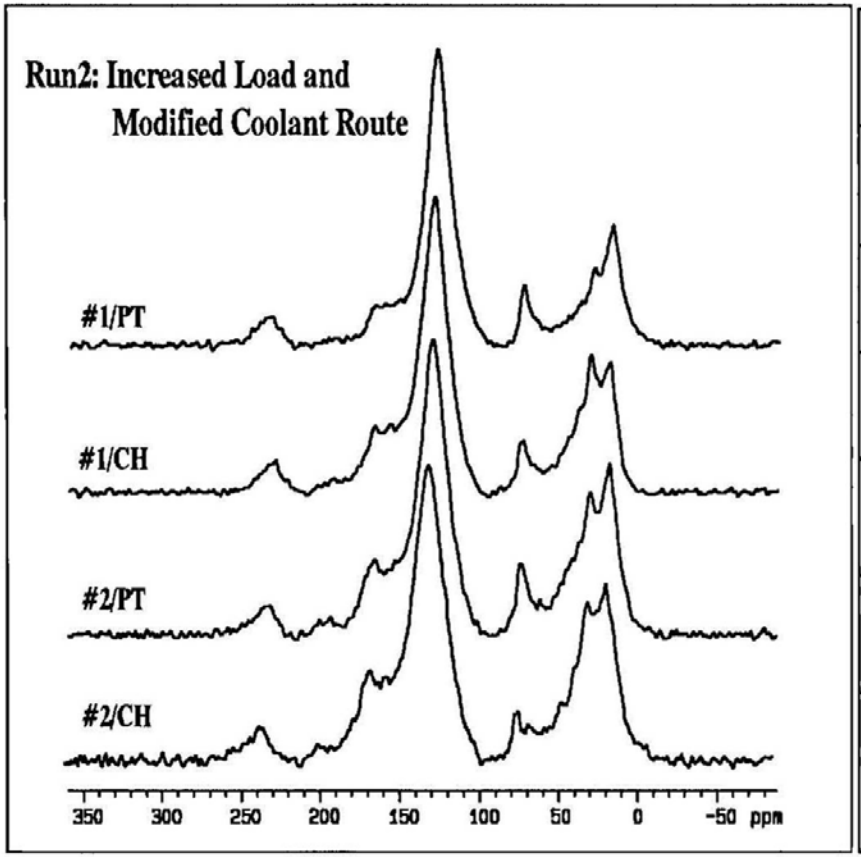
Honda Generator CCDs Produced at 2500/4000 W Conditions

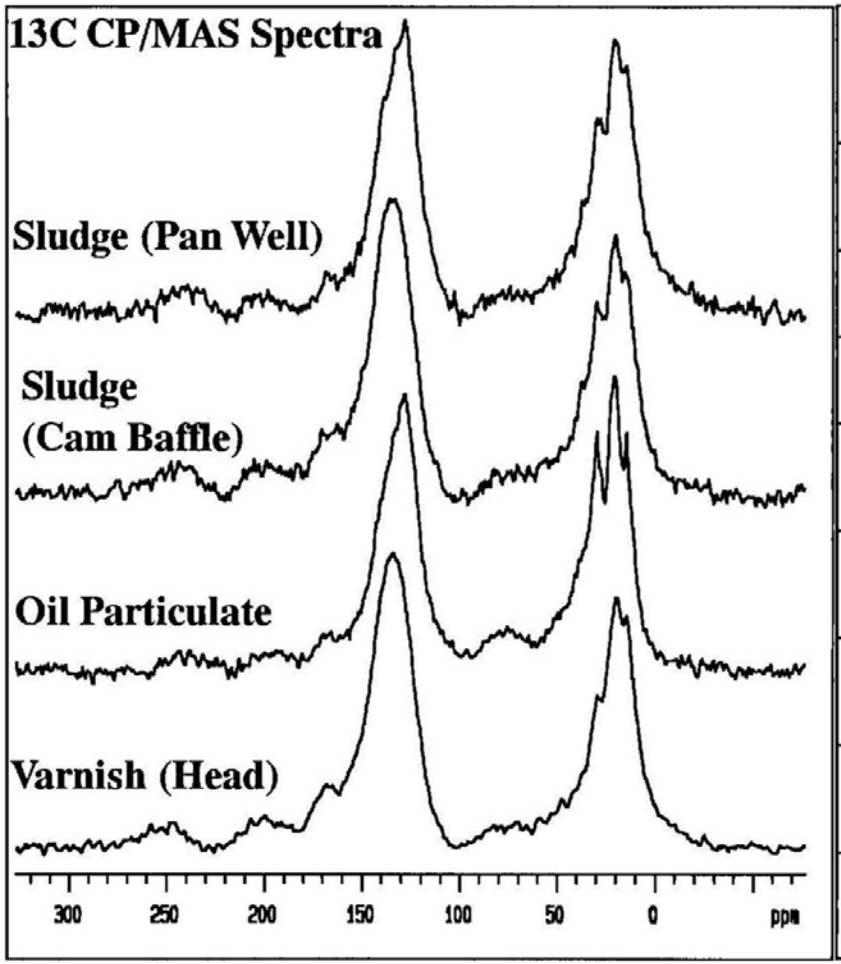
Test Further Modified to include a rerouting of the coolant in order to equilibrate heat differences between the 2 cylinders and produce similar deposits in the 2 cylinders



Structural Parameter	PT/1	PT/2
Aromaticity	0.56	0.59
Carboxyls per cluster	2	3.1
Average chain length	1.7	1.4
Polymericity	0.52	0.71
Attachments per cluster	5.94	6.65
Aromatic carbons per cluster	16	18

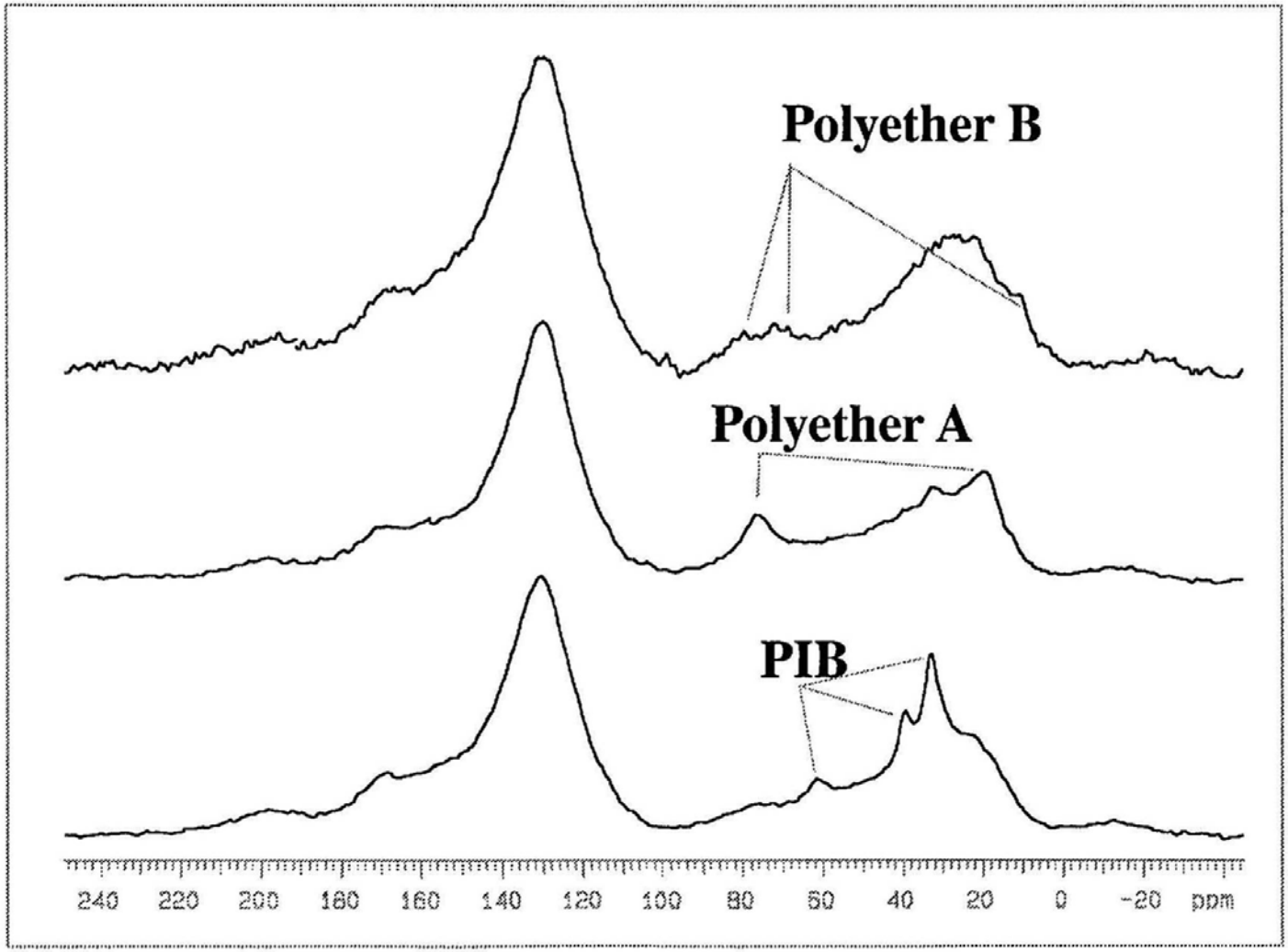
Crankcase Deposits : Sludge, Particulate and Varnish

Deposits were prepared by multiple hexane extractions and centrifugations to remove excess oil

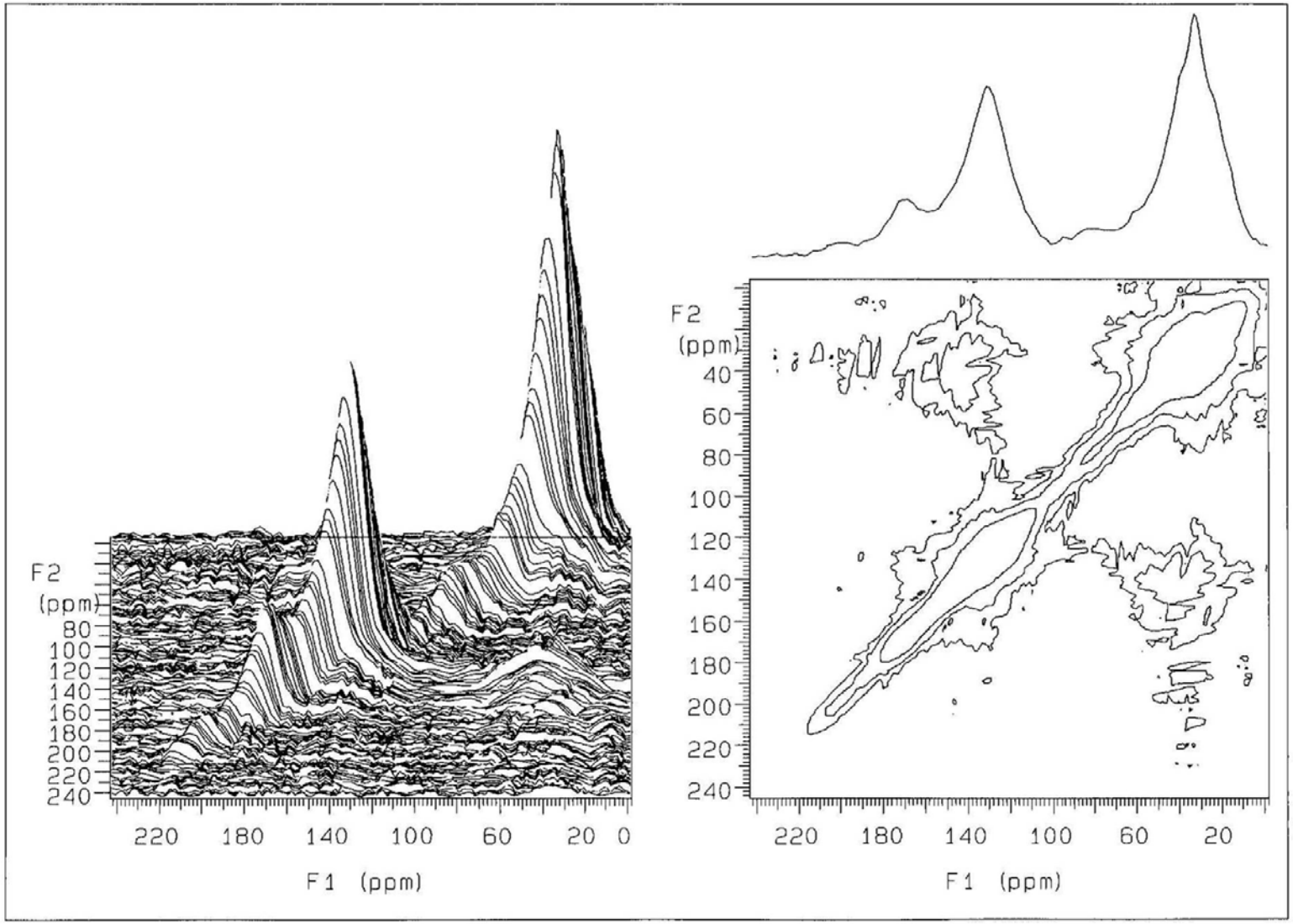


Parameter	Sludge (pan well)	Sludge (cam baffle)	Oil Particulate	Varnish (cam baffle
fa'	0.49	0.49	0.46	0.51
C	10	12	9	11
(S+1)	4.1	6.4	3.1	5.7
Po	0.14	0.44	0.1	0.42
Phi-O	0.8	1.5	0.6	1.3
Phi-CO	1.2	2.4	1.1	2.2
n'	2.2	1.6	3	1.5
Mw	289	346	276	309

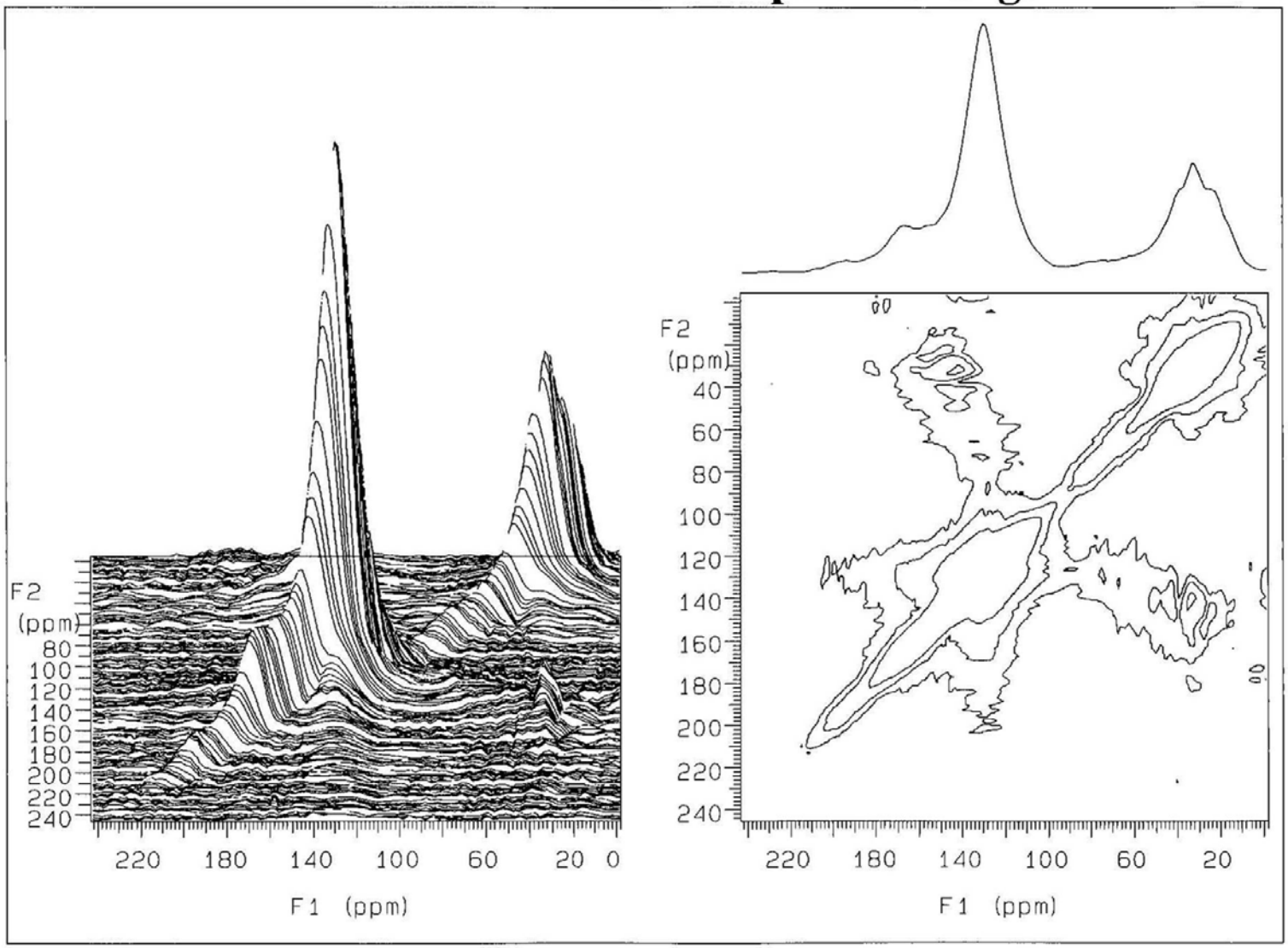
The Observation of Fuel Additives in CCDs



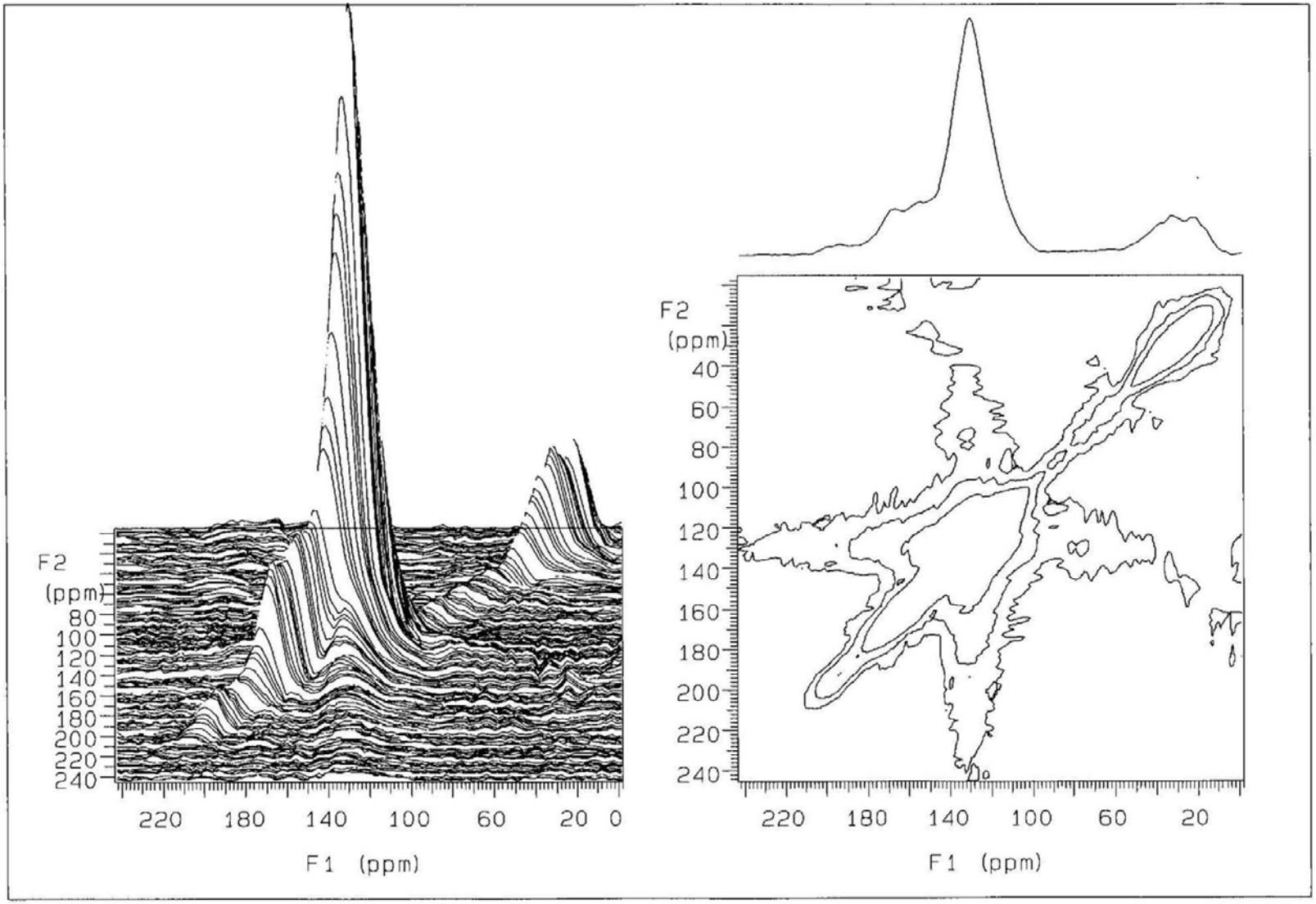
Motor Alkylate CCD - 13C 2D Spin-Exchange



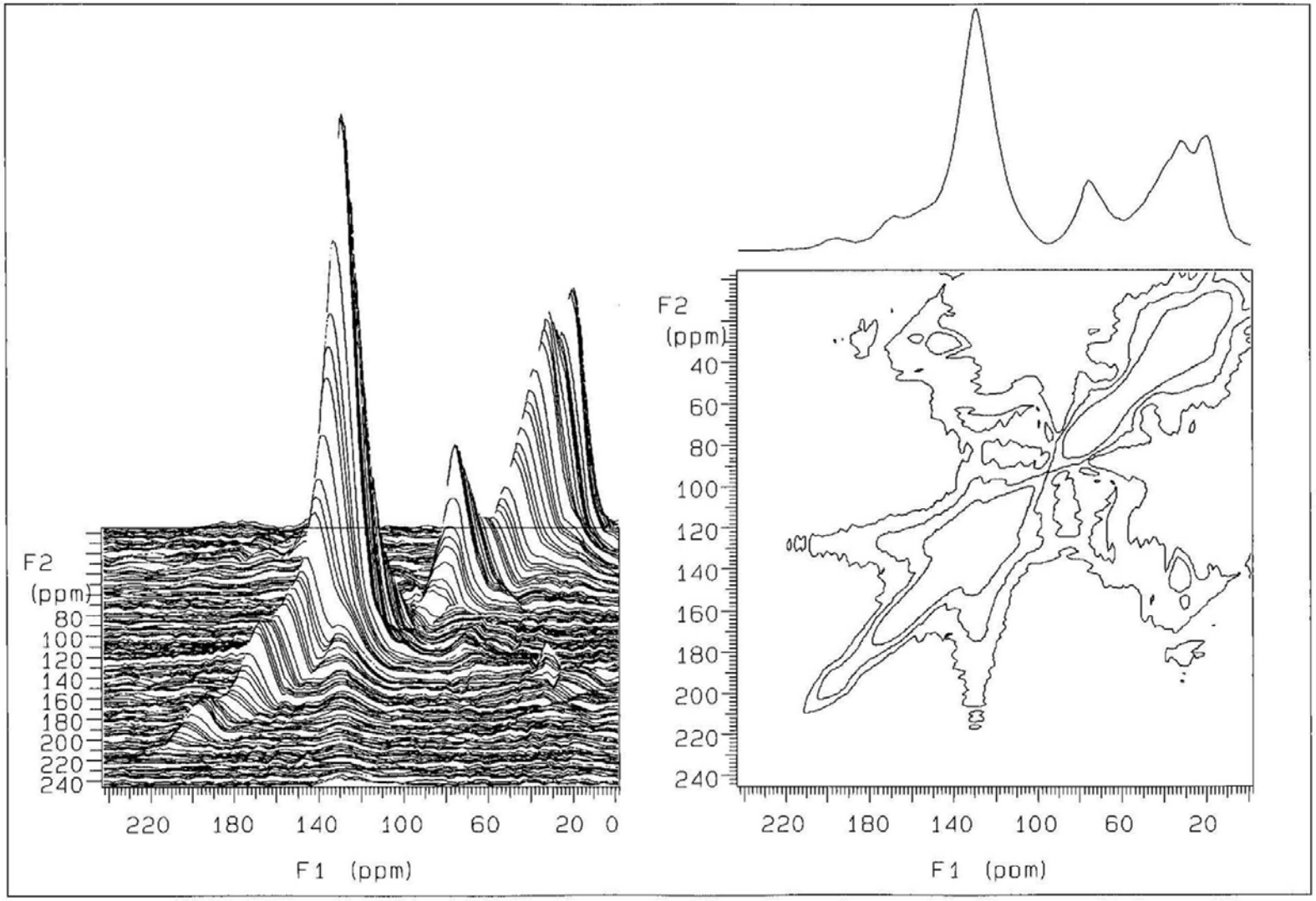
Base Fuel CCD - 13C 2D Spin-Exchange



Reformate CCD - 13C 2D Spin-Exchange



Base Fuel/Polyether Additive CCD - 13C 2D Spin-Exchange



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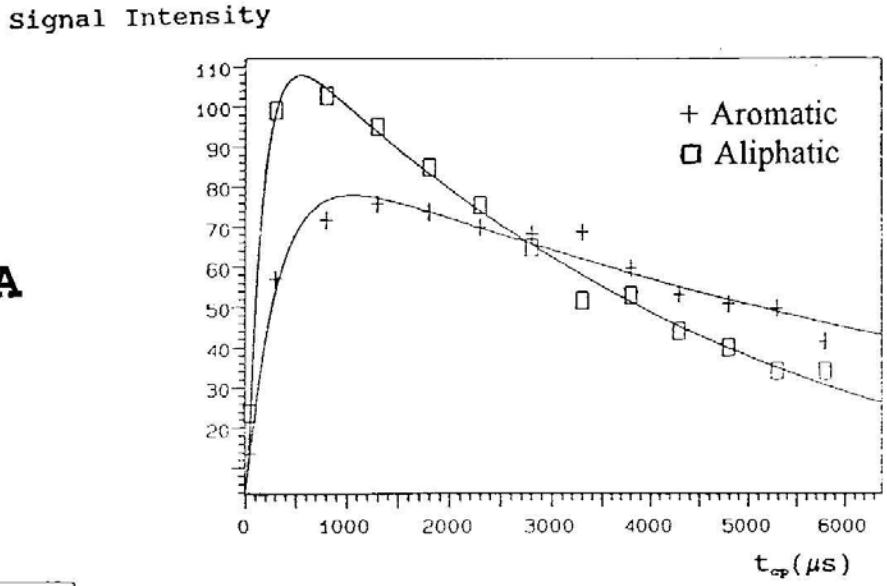
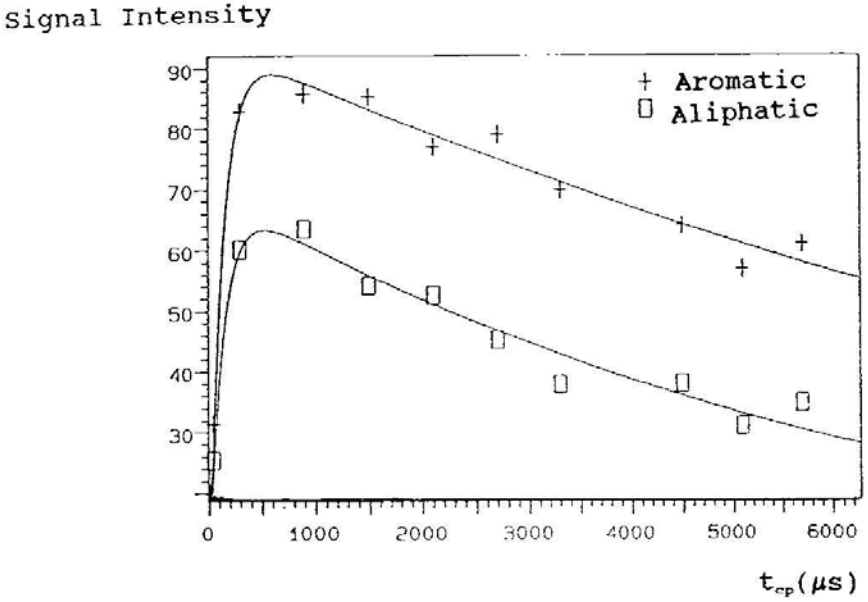

Signal Intensity
+ Aromatic
□ Aliphatic
110
100
90
80
70
60
50
40
30
20
0
1000
2000
3000
4000
5000
6000
$t_{cp}(\mu s)$

B


Signal Intensity
+ Aromatic
□ Aliphatic
90
80
70
60
50
40
30
0
1000
2000
3000
4000
5000
6000
$t_{cp}(\mu s)$

Proton Spin-Locked T1-Relaxation Parameters

Aromatic T1rho Data (ms)

Fuel	Alkylate	Base Fuel	Reformate	Base Fuel/Polyether
Mobile Component	5.7	5.8	6.6	2.9
Immobile Component	15.0	22.3	25.8	13.9

Aliphatic T1rho Data (ms)

Fuel	Alkylate	Base Fuel	Reformate	Base Fuel/Polyether
Mobile Component	2.1	6.0	8.6	3.9
Immobile Component	8.6	18.2	28.7	12.6

Conclusions

1 > Carbon-13 NMR yields reliable molecular structure information on CCD polymeric backbones.

2 > The Average building block of the polymer backbone is a 2-4 ring polynuclear aromatic, independent of engine test or fuel type.

3 > Large variations in molecular structure can be observed for:

i. different fuel types, and

ii. different combustion environments caused by engine variables such as heat, air/fuel ratio, load, etc.

4 > NMR analysis can be used to monitor the effects of bench test modifications.