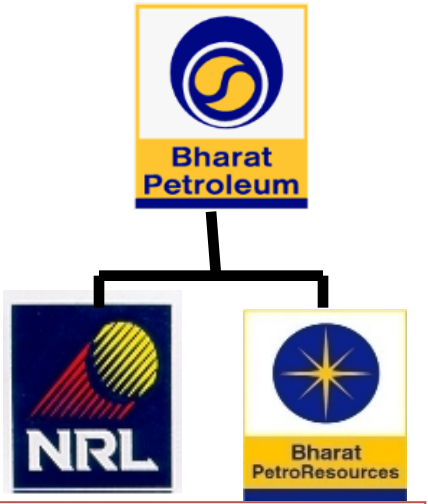
Thermal, Spectral, oxidation stability and anti- oxidation behavior on selected Petroleum Group I & II Base oils

Dr. RAJENDIRAN ADIMOOLAM

Presentation Overview

- Overview of BPCL
- Group II base oils
  - ✓ Base oil description
  - ✓ Physiochemical study
  - ✓ Oxidation stability evaluation
  - ✓ Structural composition analysis study (NMR)
  - ✓ (before & after heating)
  - ✓ Kinematic viscosity with various temperature
  - ✓ Vacuum distillation
- Conclusion

BPCL group



Major JVs (12Nos)
Bharat Oman Refineries Ltd
Petronet LNG Ltd
Indraprastha Gas Ltd
Central UP Gas Ltd
Maharashtra Natural Gas Ltd
Sabarmati Gas Ltd
Petronet CCK Ltd
Delhi Aviation Fuel facility Pvt Ltd
Matrix Bharat Marine Services Pte Ltd.
Bharat Star Services Ltd
Bharat Renewable Energy

Refining

- 13.41 MMTPA in Mumbai (Bharat Petroleum)
- 10.71 MMTPA in Kochi (Bharat Petroleum)
- 6.4 MMTPA in Bina (BHARAT OMAN REFINERIES LIMITED)
- 3 MMTPA in Numaligarh 61.65 % holding (NRL)

BPCL's group share in overall refining capacity in India 14.57 % (out of 230 MMTPA)

Group share in Marketing 22.9 %

BPCL :Performance highlights (2015-16)

Sl.no	Marketing network	Quantity
1	Retail outlets	13439
2	Installations	13
3	Depots	118
4	Aviation service stations	40
5	LPG Distributorship	4494
6	LPG Bottling plants	50
7	LPG customers(in millions)	50.6
8	Market sales, MMT	36.53
9	Total Manpower	12623
10	Total sales, (profit)crores	2,17,806(7432)







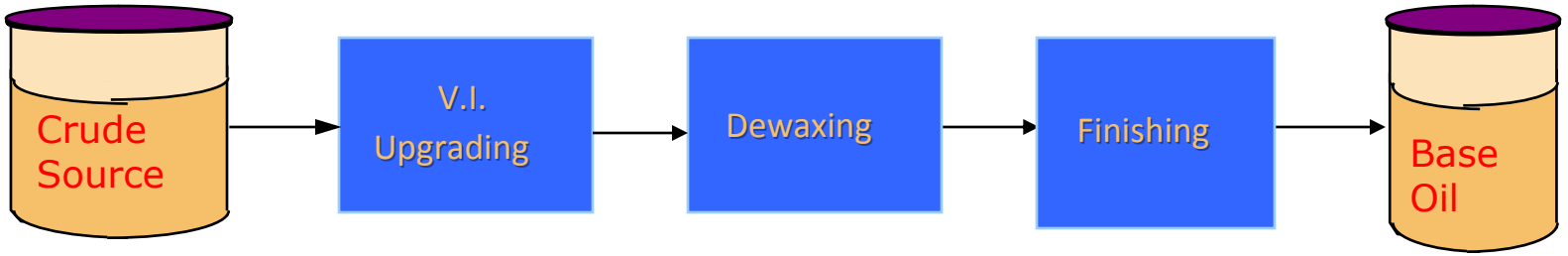
Presentation Overview

- Overview of BPCL
- Group II base oils
  - ✓ Base oil description
  - ✓ Physiochemical study
  - ✓ Oxidation stability study
  - ✓ Structural composition analysis study (NMR)
  - ✓ (before & after heating)
  - ✓ Kinematic viscosity with various temperature
  - ✓ Vacuum distillation
- Conclusion

Base oil description

- **M1,M2,H1&H2** **are Group II base oils**
- M1 & M2 are manufactured in hydro cracking with iso-dewaxing and hydro- finishing technology
- **H1 & H2** **are manufactured in solvent extraction with catalytic iso-dewaxing technology**

Technology differs…



Conventional	Solvent Refining	Solvent Dewaxing	Clay Treating/ Low Pressure Hydrotreating
Hybrid	Solvent Refining	Catalytic Dewaxing	Hydrofinishing (With Base Metal Catalyst)
Hydroprocessing	Iso-cracking	Isodewaxing (IDW)	Hydrofinishing (HDF) (With Noble Metal Catalyst)

MAK® makes it possible.

Presentation Overview

- Overview of BPCL
- Group II base oils
  - ✓ Base oil description
  - ✓ Physiochemical study
  - ✓ Oxidation stability study
  - ✓ Structural composition analysis study (NMR)
  - ✓ (before & after heating)
  - ✓ Kinematic viscosity with various temperature
  - ✓ Vacuum distillation
- Conclusion

Oxidation stability, Noack data

Tests	M1(150)	M2(500)	H1(150)	H2(500)
Batch no	TK1207/July 2010	TK1206/Mar 2010	82015T0908	82050T0106
Density@15°C,g/ml	0.8401	0.8525	0.8521	0.8644
KV@40°C	31.0	90.2	32.56	88.00
KV@100°C	5.483	10.80	5.398	10.76
VI	119	108	105	106
Pour Point,°C	Minus 12	Minus 12	Minus 15	Minus15
Flash Point,°C	220	230	215	230
Sulphur, ppm	16	19	79	36
Nitrogen, ppm	Traces	Traces	Traces	Traces
Aniline Point, °C	116	124	111	114
Refractive Index @20,°C	1.467	1.474	1.473	1.481
Composition, %				
Ca	-	-	-	-
Cp	87.73	83.89	76.56	76.23
Cn	12.27	16.11	23.43	23.76
ACL	14.57	14.52	14.83	15.58
KV@100°C, cSt (Fresh Oil)	5.483	10.80	5.398	10.76
KV@100°C, cSt (After heating the oil @200°C for 2 hrs.)	5.565	10.93	5.489	10.98
% Increase over fresh oil viscosity and after heating	1.49	1.20	1.69	2.04
RPVOT, minutes	41	42	57	42
RPVOT,minutes(with 0.2% DBPC	285	284	204	216
PDSC	4.46	3.68	5.06	3.30
Noack evaporation	7.07	1.23	13.5	2.30
HFRR,mm	369.5	282.5	369.5	329.0

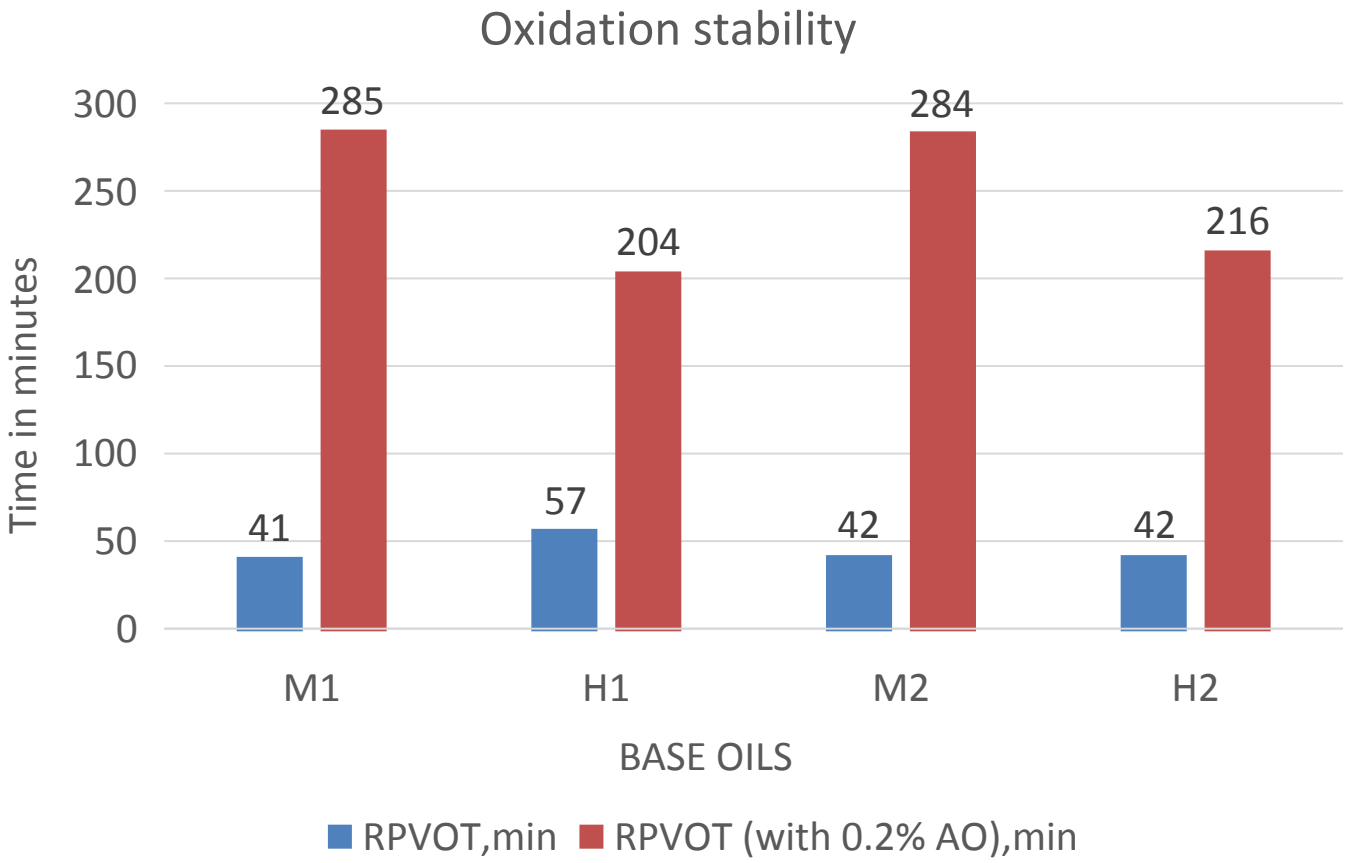
Presentation Overview

- Overview of BPCL
- Group II base oils
  - ✓ Base oil description
  - ✓ Physiochemical study
  - ✓ Oxidation stability study
  - ✓ Structural composition analysis study (NMR)
  - ✓ (before & after heating)
  - ✓ Kinematic viscosity with various temperature
  - ✓ Vacuum distillation
- Conclusion

Relationship between base oil structure and thermo-oxidative properties

Tests	M1	H1	M2	H2
RPVOT, min	41	57	42	42
RPVOT, min (with 0.2% antioxidant)	285	204	284	216
BI	35	46	35	42
Sulfur, ppm	16	79	19	36

Oxidation stability



M1 is better than H1 similarly M2 is better than H2

Presentation Overview

- Overview of BPCL
- Group II base oils
  - ✓ Base oil description
  - ✓ Physiochemical study
  - ✓ Oxidation stability study
  - ✓ Structural composition analysis study (NMR)
  - ✓ (before & after heating)
  - ✓ Kinematic viscosity with various temperature
  - ✓ Vacuum distillation
- Conclusion

Table of Alkanes

Alkanes	Formula	Boiling Point° C / 760mm Hg	Density @ 20 ° C
Undecane	$C_{11}H_{24}$	196	0.740
Dodecane	$C_{12}H_{26}$	216	0.749
Tridecane	$C_{13}H_{28}$	236	0.756
Tetradecane	$C_{14}H_{30}$	255	0.760
Pentadecane	$C_{15}H_{32}$	270	0.769
Hexadecane	$C_{16}H_{34}$	287	0.773
Heptadecane	$C_{17}H_{36}$	302	0.778
Octadecane	$C_{18}H_{38}$	317	0.777
Pristane	$C_{19}H_{40}$	343	0.783
Icosane	$C_{20}H_{42}$	343	Solid

NMR Spectra : Equipment

- Quantitative ^{1}H and ^{13}C NMR spectra of all samples were recorded.

- Brucker AV III 500 MHz NMR spectrometer

  - Chemical shifts were measured in TMS as an internal standard

  - ^{13}C NMR was measured:
    50% (W/W) sample solution was in Deuterated chloroform solvent containing in 0.1% M Cr (AC)3 as relaxing agent.

Use of NMR Spectra

- Carbon 13 NMR is an important analytical technique which is use to identify chemical structure of organic compounds.

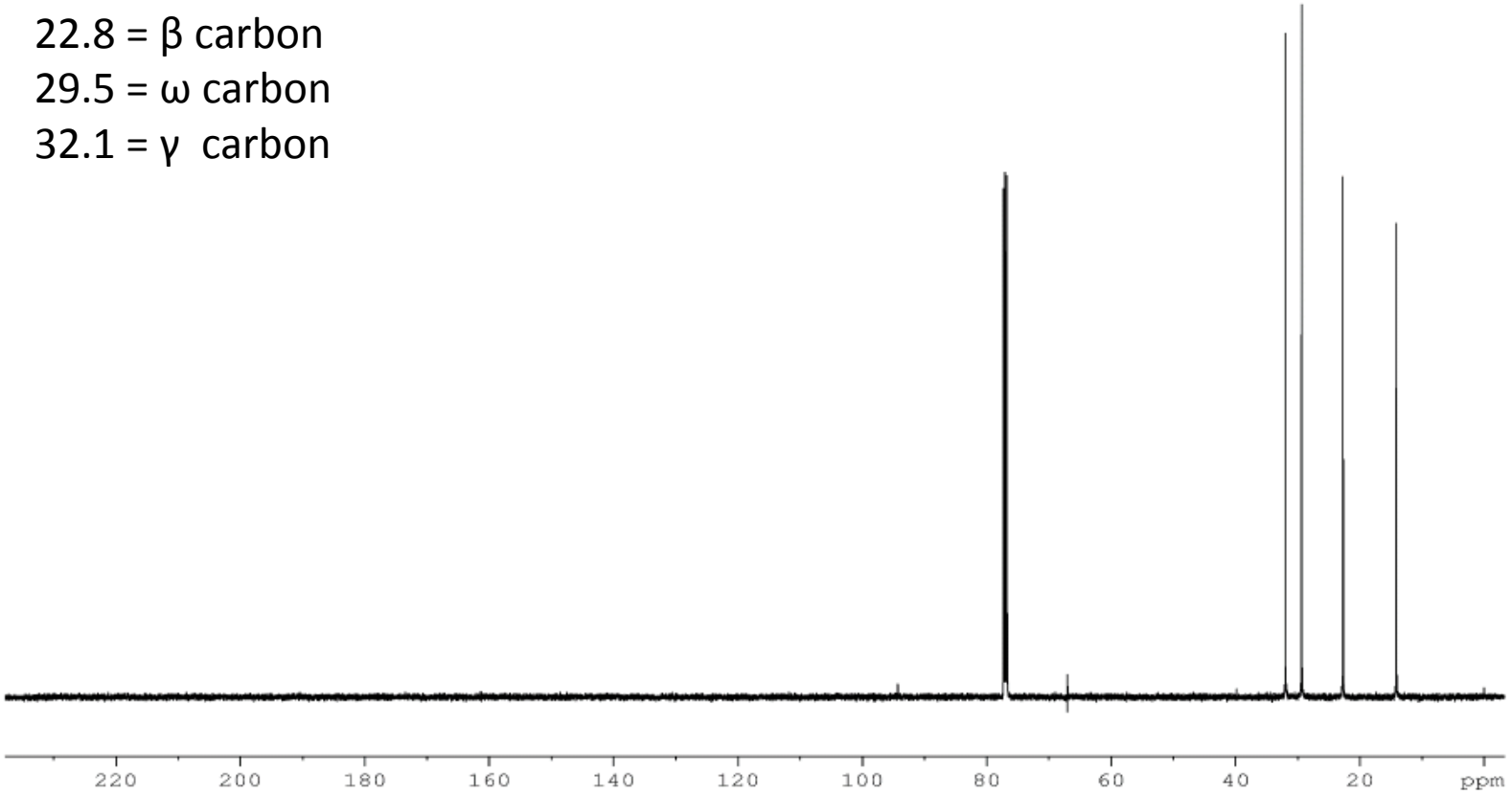
✓Carbon 13 NMR provides two key factors about an organic compound.

- How the carbon backbone of the compound is arranged
- Presence of functional groups .

- The NMR spectrum of one of the Alkane is ……

NMR Spectra of alkane: n-octane

14.1 = α carbon
22.8 = β carbon
29.5 = ω carbon
32.1 = γ carbon

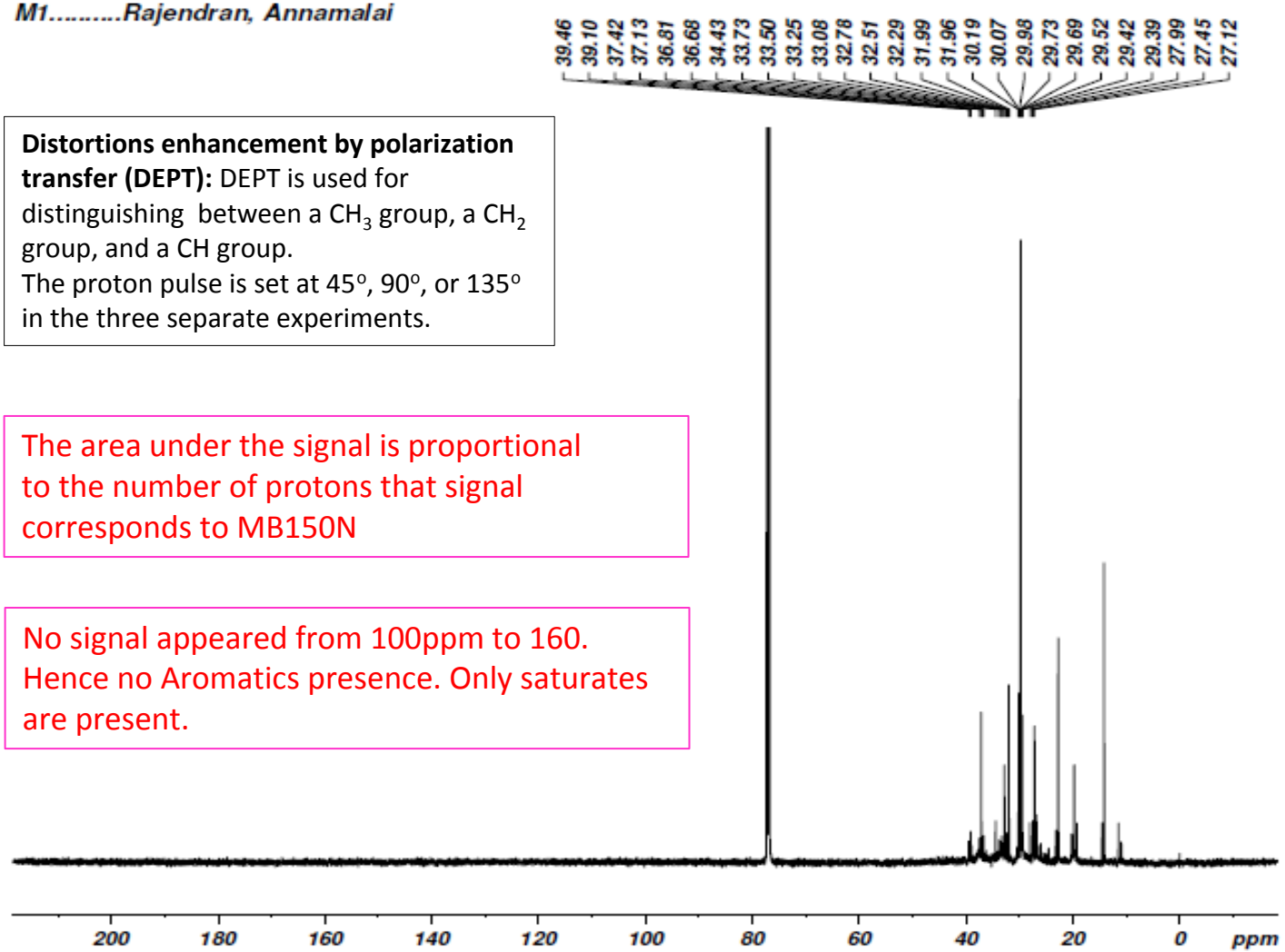


Average structural parameters of base oils

Sl. No.	Parameter	NMR region / peak positions
1	Saturated carbons (C_s)	5-60 ppm
2	Naphthenic carbons (C_n)	Hump in region, 24-60 ppm
3	Paraffinic carbons (C_p)	C_s-C_n
4	n-Paraffinic α-carbon ($C_{np\alpha}$)	14.1 ppm
5	n-Paraffinic β-carbon ($C_{np\beta}$)	22.7 ppm
6	n-Paraffinic γ-carbon ($C_{np\gamma}$)	32.0 ppm
7	n-Paraffinic δ ($C_{np\delta}$) or higher carbon (C_{npn})	29.4 and 29.9 ppm
8	Normal paraffins (C_{np})	$C_{np\alpha} + C_{np\beta} + C_{np\gamma} + C_{np\delta}$
9	Isoparaffins (C_{ip})	$C_p – C_{np}$
10	Aromatic carbons (C_a)	100-160 ppm
11	Average chain length (ACL)	$2 \times C_{np}/C_{np\alpha}$

^{13}C NMR spectra - M1

M1.....Rajendran, Annamalai



Distortions enhancement by polarization transfer (DEPT): DEPT is used for distinguishing between a CH_3 group, a CH_2 group, and a CH group.
The proton pulse is set at 45°, 90°, or 135° in the three separate experiments.

The area under the signal is proportional to the number of protons that signal corresponds to MB150N

No signal appeared from 100ppm to 160. Hence no Aromatics presence. Only saturates are present.

```
Current Data Parameters
NAME                  Aug27-2010
EXPNO                         27
PROCNO                         1

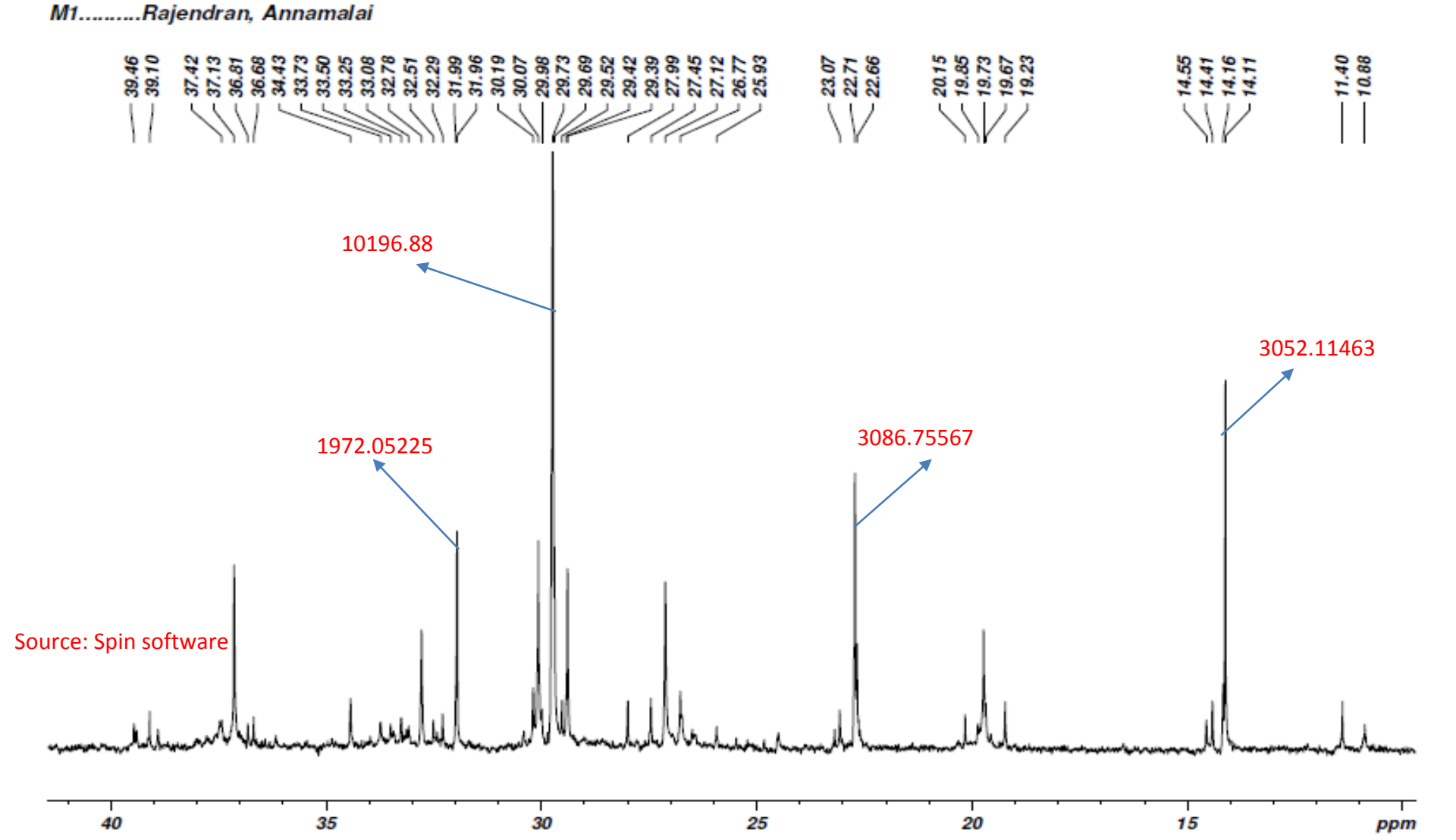
F2 - Acquisition Parameters
Date_                   20100828
Time                        4.03
INSTRUM                    spect
PROBHD     5 mm PABBO BB-
PULPROG                  zgig30
TD                        32768
SOLVENT                   CDCl3
NS                         1024
DS                            4
SWH                   29761.904 Hz
FIDRES                 0.908261 Hz
AQ                     0.5505524 sec
RG                          203
DW                       16.800 usec
DE                        6.50 usec
TE                       300.2 K
D1                    2.00000000 sec
D11                   0.03000000 sec
TD0                            1

======== CHANNEL f1 ========
NUC1                         13C
P1                          7.80 usec
PL1                         0.00 dB
PL1W                 70.83519745 W
SFO1                125.7703643 MHz

======== CHANNEL f2 ========
CPDPRG2                  waltz16
NUC2                         1H
PCPD2                      80.00 usec
PL2                         0.00 dB
PL12                       17.50 dB
PL2W                23.53637505 W
PL12W                0.41854253 W
SFO2                500.1320005 MHz

F2 - Processing parameters
SI                        32768
SF                  125.7577890 MHz
WDW                          EM
SSB                           0
LB                         1.00 Hz
GB                            0
PC                         1.40
```

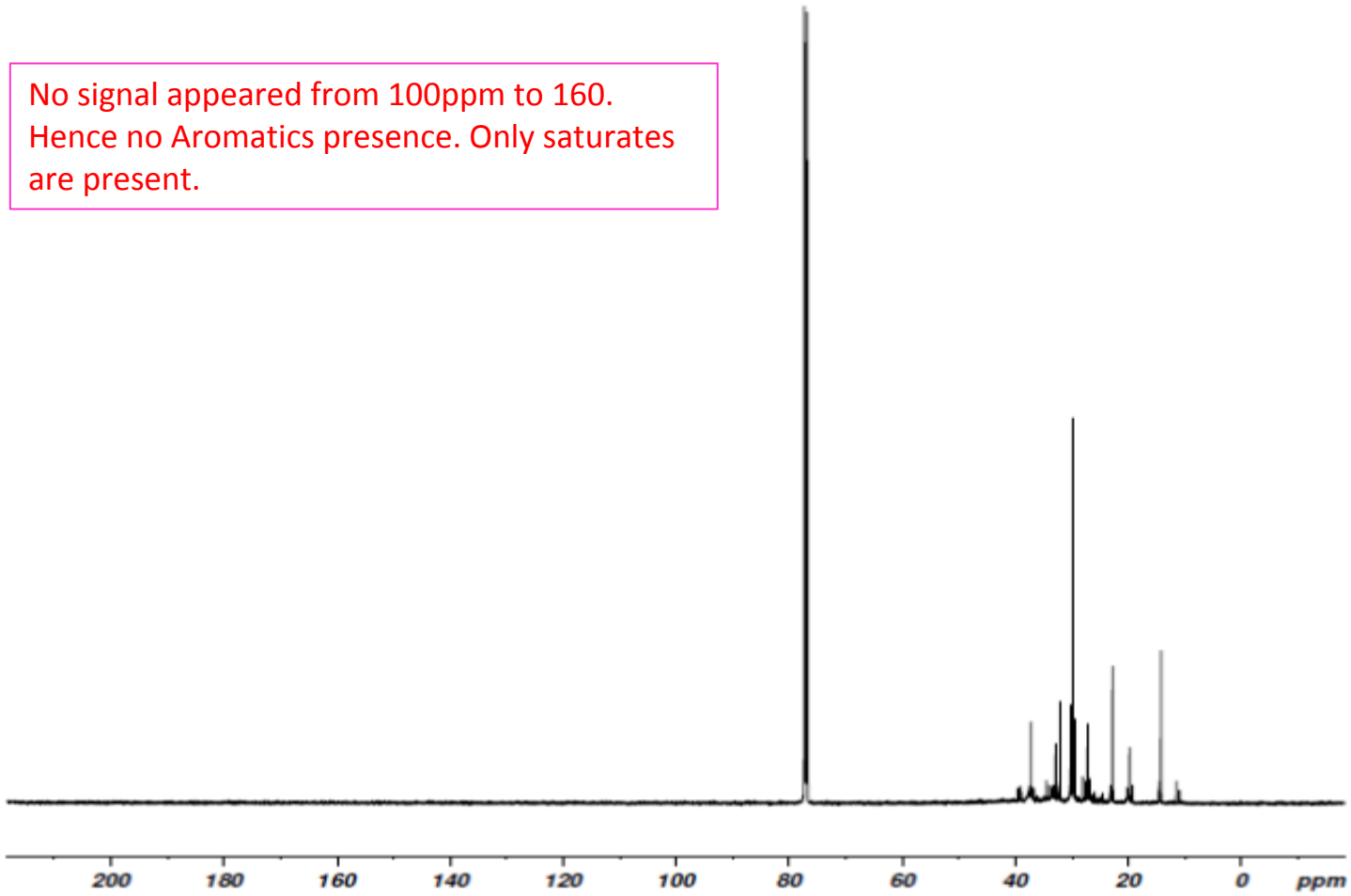
C^{13} NMR Spectra – M1



C^{13}NMR Spectra – M1 after heating 200 Deg C

M1...Rajendiran

No signal appeared from 100ppm to 160.
Hence no Aromatics presence. Only saturates are present.




```
Current Data Parameters
NAME                  Jan27-2011
EXPNO                          8
PROCNO                         1

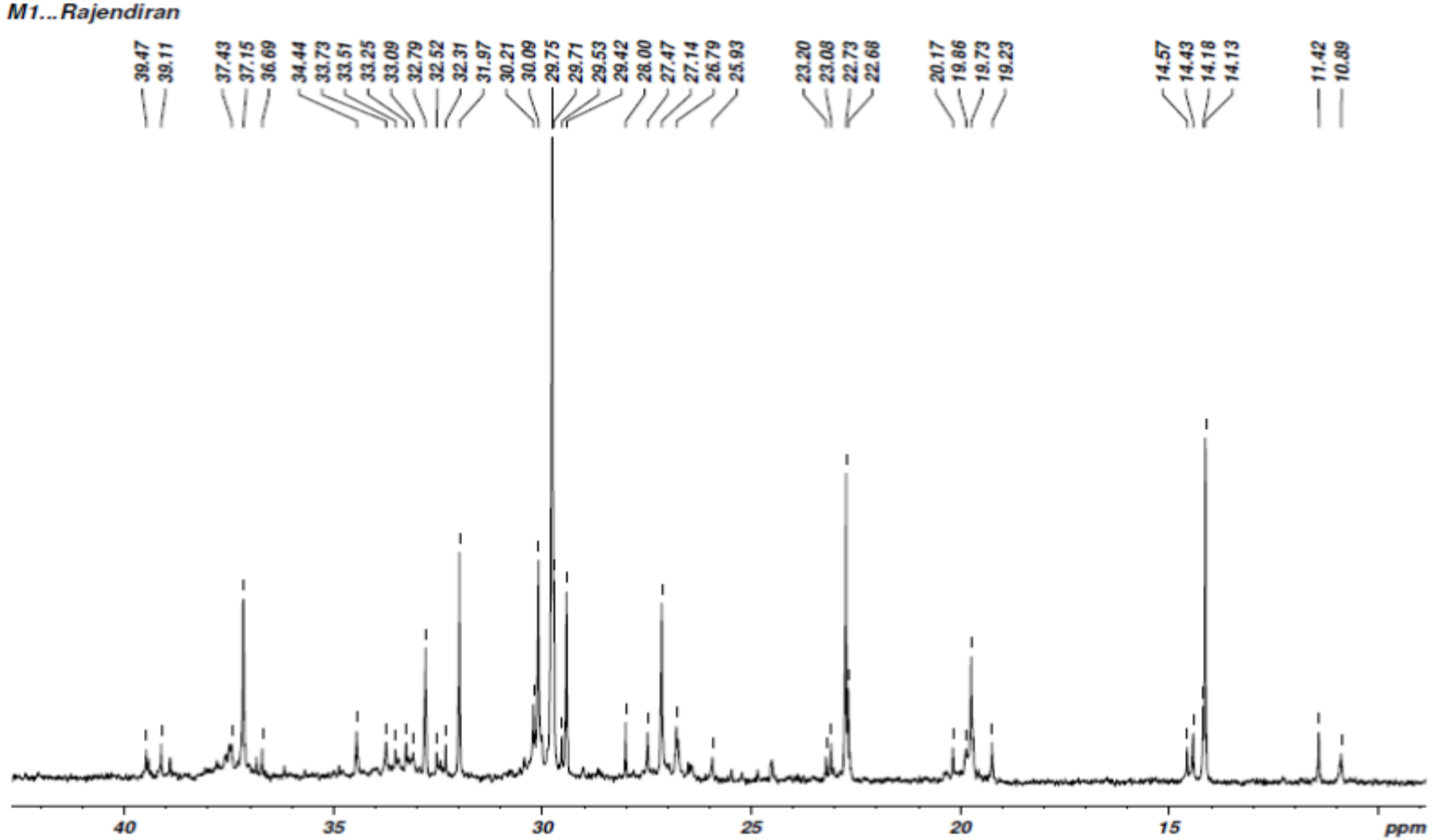
F2 - Acquisition Parameters
Date_                   20110127
Time                       19.48
INSTRUM                    spect
PROBHD     5 mm PABBO BB-
PULPROG                  zgig30
TD                        32768
SOLVENT                   CDCl3
NS                         1024
DS                            4
SWH                   29761.904 Hz
FIDRES                0.908261 Hz
AQ                    0.5505524 sec
RG                          203
DW                       16.800 usec
DE                        6.50 usec
TE                       298.3 K
D1                    2.00000000 sec
D11                   0.03000000 sec
TD0                            1

====== CHANNEL f1 ======
NUC1                         13C
P1                          7.80 usec
PL1                         0.00 dB
PL1W                 70.83519745 W
SFO1                125.7703643 MHz

====== CHANNEL f2 ======
CPDPRG2                  waltz16
NUC2                          1H
PCPD2                      80.00 usec
PL2                         0.00 dB
PL12                       17.50 dB
PL2W                23.53637505 W
PL12W                0.41854253 W
SFO2                500.1320005 MHz

F2 - Processing parameters
SI                        32768
SF                  125.7577890 MHz
WDW                          EM
SSB                           0
LB                         1.00 Hz
GB                            0
PC                         1.40
```

C^{13}NMR Spectra – M1 after heating 200 DegC

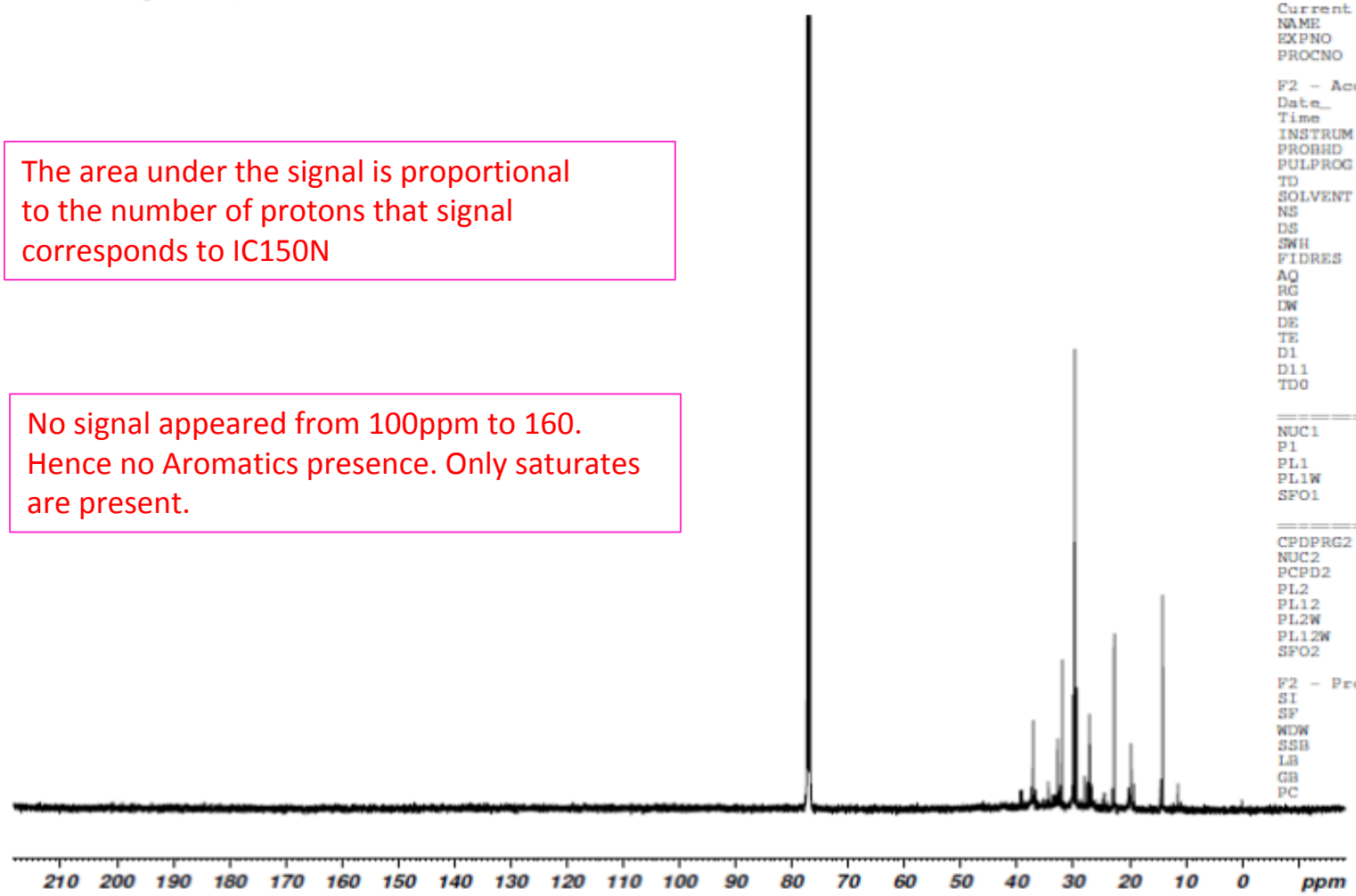


C^{13}NMR Spectra – H1

H1.....Rajendran, Annamalai

The area under the signal is proportional to the number of protons that signal corresponds to IC150N

No signal appeared from 100ppm to 160. Hence no Aromatics presence. Only saturates are present.




```
Current Data Parameters
NAME                  Aug27-2010
EXPNO                         29
PROCNO                         1

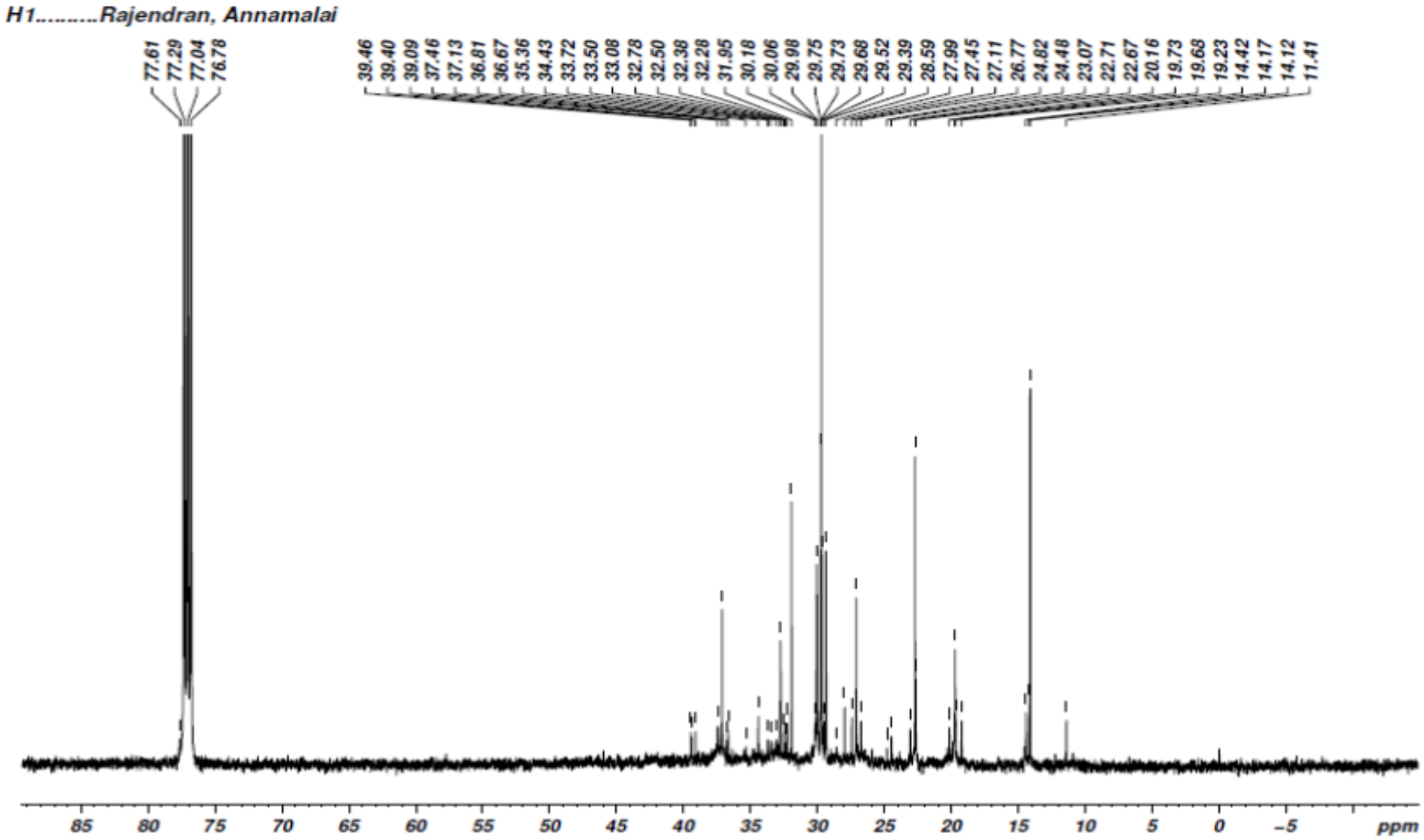
F2 - Acquisition Parameters
Date_                   20100828
Time                        5.41
INSTRUM                    spect
PROBHD     5 mm PABBO BB-
PULPROG                  zgig30
TD                        32768
SOLVENT                    CDC13
NS                          1024
DS                             4
SWH                    29761.904 Hz
FIDRES                 0.908261 Hz
AQ                     0.5505524 sec
RG                           203
DW                        16.800 use
DE                         6.50 use
TE                        300.2 K
D1                     2.00000000 sec
D11                    0.03000000 sec
TD0                            1

======== CHANNEL f1 ========
NUC1                         13C
P1                          7.80 use
PL1                         0.00 dB
PL1W                70.83519745 W
SFO1               125.7703643 MHz

======== CHANNEL f2 ========
CPDPRG2                  waltz16
NUC2                         1H
PCPD2                      80.00 use
PL2                         0.00 dB
PL12                       17.50 dB
PL2W                23.53637505 W
PL12W                0.41854253 W
SFO2               500.1320005 MHz

F2 - Processing parameters
SI                        32768
SF                 125.7577890 MHz
WDW                          EM
SSB                           0
LB                         1.00 Hz
GB                            0
PC                         1.00
```

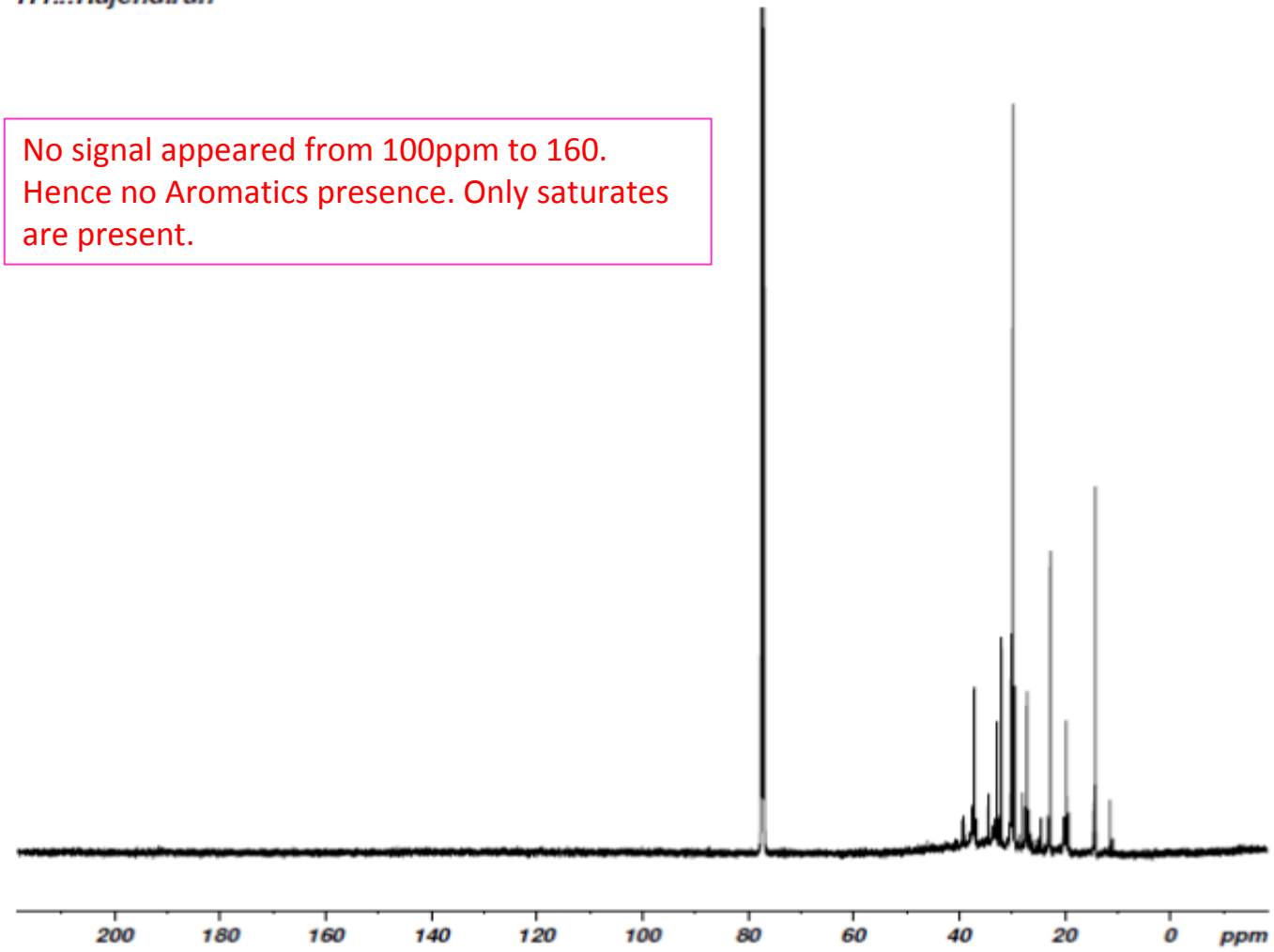
C^{13}NMR Spectra – H1



C^{13}NMR Spectra – H1 after heating 200 DegC

H1...Rajendiran

No signal appeared from 100ppm to 160. Hence no Aromatics presence. Only saturates are present.




```
Current Data Parameters
NAME                  Jan27-2011
EXPNO                          2
PROCNO                         1

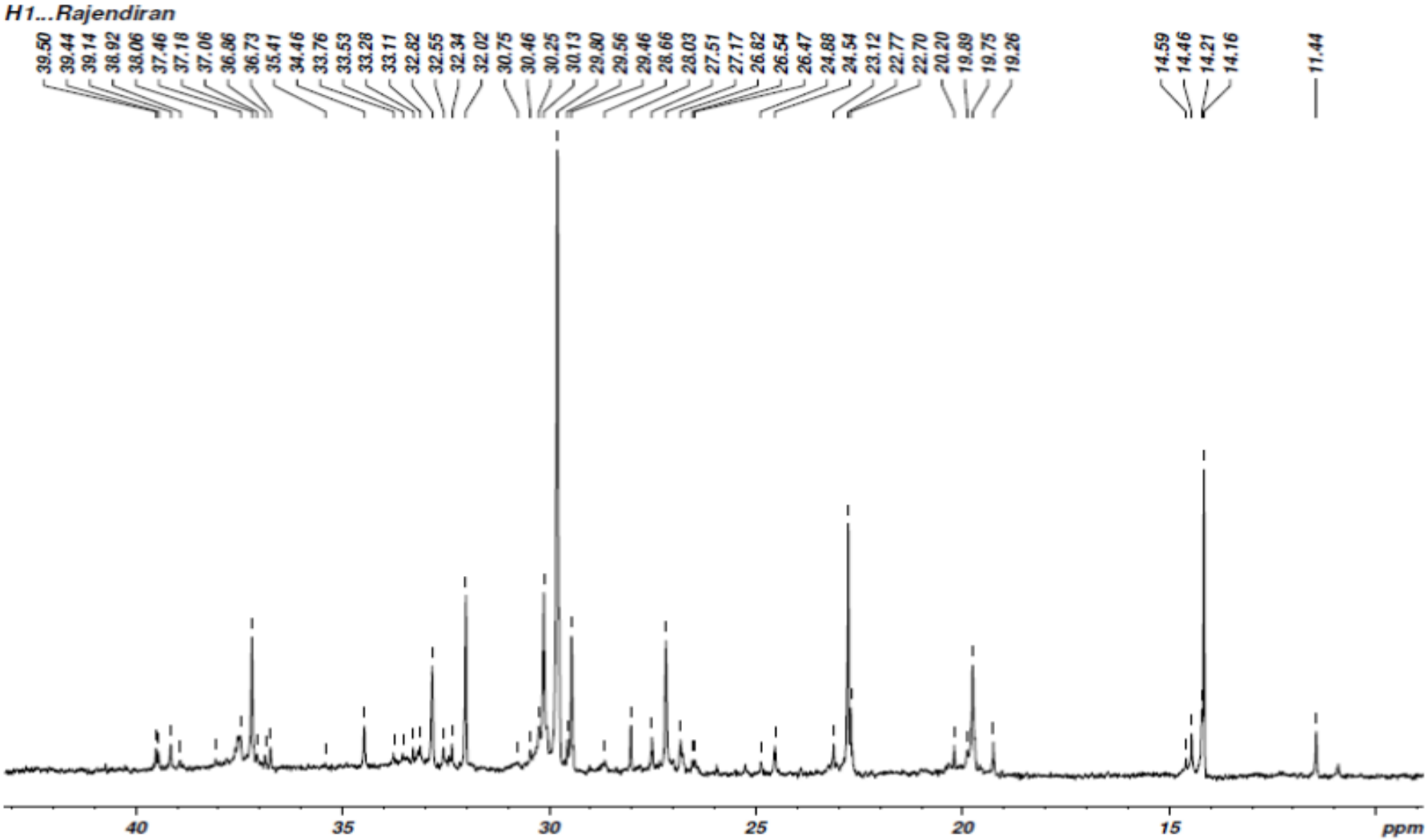
F2 - Acquisition Parameters
Date_                   20110127
Time                       15.27
INSTRUM                     spect
PROBHD    5 mm PABBO BB-
PULPROG                  zgig30
TD                        32768
SOLVENT                   CDCl3
NS                          965
DS                            4
SWH                   29761.904 Hz
FIDRES                0.908261 Hz
AQ                    0.5505524 sec
RG                          203
DW                       16.800 usec
DE                        6.50 usec
TE                       298.4 K
D1                    2.00000000 sec
D11                   0.03000000 sec
TD0                            1

====== CHANNEL f1 ======
NUC1                         13C
P1                        7.80 usec
PL1                       0.00 dB
PL1W                 70.83519745 W
SFO1                125.7703643 MHz

====== CHANNEL f2 ======
CPDPRG2                  waltz16
NUC2                         1H
PCPD2                    80.00 usec
PL2                       0.00 dB
PL12                     17.50 dB
PL2W                23.53637505 W
PL12W                0.41854253 W
SFO2                500.1320005 MHz

F2 - Processing parameters
SI                        32768
SF                  125.7577890 MHz
WDW                          EM
SSB                           0
LB                        1.00 Hz
GB                            0
PC                        1.40
```

C^{13}NMR Spectra – H1 after heating 200 Deg C



NMR derived average structural parameters of M1, M2, H1 and H2

Tests	M1	H1	M2	H2
C_s (5-60 ppm)	≈99-100	≈99-100	≈99-100	≈99-100
C_n	12.27	23.43	16.11	23.76
C_a	Nil	Nil	Nil	Nil
C_p	87.73	76.56	83.89	76.23
α-Carbon (14.1 ppm)	2.9657	2.9096	2.2861	2.6649
β-Carbon (22.7 ppm)	3.0559	3.2630	2.4167	3.2537
γ-Carbon (32.0 ppm)	1.9562	2.1147	1.3157	1.8045
δ-Carbon (29.4 and 29.9 ppm)	13.6280	13.2919	10.5770	13.0300
C_{np} (α+β+γ+δ)	21.6059	21.5793	16.5955	20.7531
Isoparaffin (C_p-C_{np})	66.12	54.98	67.30	55.48
Viscosity index (VI)	119	105	108	106
Average chain length (ACL)	14.57	14.83	14.52	15.58
Using ^{1}H NMR				
$-CH_3$	6	6	7	5
$-CH_2$ and CH	16	13	20	12
Branchiness index	35	46	35	42

Comparative NMR derived average structural parameters of M1

At room temperature		After heating up to 200°C	
Using ^{13}C NMR			
C_s (5-60 ppm)	99-100	C_s	99-100
C_n	12.27	C_n	18.9242
C_p	87.73	C_p	81.0758
α-Carbon (14.1)	2.965747	α-Carbon	3.1969
β-Carbon (22.7)	3.055902	β-Carbon	3.2332
γ-Carbon (32.0)	1.956242	γ-Carbon	2.0656
δ-Carbon (29.4 and 29.9)	13.62799	δ-Carbon	10.6805
CPN = α + β + γ + δ = 21.60588	21.60588	CPN = α + β + γ + δ = 19.1762	19.1762
Isoparaffin = C_p–CPN = 87.73–21.60588	66.12489	Isoparaffin = C_p–CPN = 81.0758-19.1762	61.8996
Average chain length= 2×CPN/CPN_α = 2×21.6059/2.96575 = 14.57028	14.57	Average chain length= 2×CPN/CPN_α = 2×19.1762/3.1969 = 11.9968	11.9968
Using ^{1}H NMR			
$-CH_3$ = 6 (6.30)	6	$-CH_3$ = 1 (1.00)	1
$-CH_2$ and CH = 16 (15.87) 14.13 + 0.74 + 1.00 = 15.87	16	$-CH_2$ and CH = 2.5 (2.45) 0.22 + 1.95 + 0.28 = 2.45	2.45
Branchiness index = 100×6/16 = 37.5	35	Branchiness index = 100×1/2.45 = 40 Note: Naphthenes got changed	40

Comparative NMR derived average structural parameters of M2

At room temperature		After heating up to 200°C	
Using ^{13}C NMR			
C_s	99-100	C_s	99-100
C_n	16.10	C_n	25.78
C_p	83.89	C_p	74.21
α-Carbon	2.286091	α-Carbon	4.1158
β-Carbon	2.416747	β-Carbon	3.9519
γ-Carbon	1.315718	γ-Carbon	1.7926
δ-Carbon	10.57696	δ-Carbon	17.9923
CPN = α + β + γ + δ = 16.59551	16.59551	CPN = α + β + γ + δ = 27.85259	27.8526
Isoparaffin = C_p–CPN = 83.89–16.59	67.3016	Isoparaffin = C_p–CPN = 74.21-27.8526	46.3631
Average chain length= 2×CPN/CPN_α = 2×16.59551/2.286091 = 14.518	14.518	Average chain length= 2×CPN/CPN_α = 2×27.852/4.1157 = 13.5346	13.5346
Using ^{1}H NMR			
$-CH_3$ = 7 (7.28)	7	$-CH_3$ = (1.00)	1
$-CH_2$ and CH = (20.24) 18.05 + 1.19 + 1.00 = 20.24	20	$-CH_2$ and CH = (2.85) 0.39 + 2.13 + 0.33 = 2.85	2.85
Branchiness index = 100×7/20 = 35	35	Branchiness index = 100×1/2.85 = 35.09 Note: No change even heating up to 200°C	35.09

Comparative NMR derived average structural parameters of H1

At room temperature		After heating up to 200°C	
Using ^{13}C NMR			
C_s (5-60 ppm)	99-100	C_s	99-100
C_n	23.43	C_n	14.6631
C_p	76.56	C_p	85.3368
α-Carbon (14.1)	2.9096	α-Carbon	3.76619
β-Carbon (22.7)	3.26304	β-Carbon	4.35757
γ-Carbon (32.0)	2.11471	γ-Carbon	2.75387
δ-Carbon (29.4 and 29.9)	13.2918	δ-Carbon	14.9307
CPN = α + β + γ + δ = 21.5793	21.5793	CPN = α + β + γ + δ = 27.85259	25.8083
Isoparaffin = C_p–CPN = 76.56-21.5793	54.98	Isoparaffin = C_p–CPN = 74.21-27.8526	59.5284
Average chain length= 2×CPN/$CPN_α$ = 2×21.5793/2.9096 = 14.833	14.83	Average chain length= 2×CPN/$CPN_α$ = 2×27.852/4.1157 = 13.5346	13.71
Using ^{1}H NMR			
$–CH_3$ = 6 (5.85)	6	$–CH_3$ = 1 (1.00)	1
$–CH_2$ and CH = 13 (12.53) 10.72 + 0.91 + 1.00 = 12.53	13	$–CH_2$ and CH = 2.0 (2.33) 1.93 + 0.40 = 2.33	2.33
Branchiness index = 100×6/13 = 46.0	46	Branchiness index = 100×1/2.33 = 40 Note: Naphthenes got changed.	40

Comparative NMR derived average structural parameters of H2

At room temperature		After heating up to 200°C	
Using ^{13}C NMR			
C_s (5-60 ppm)	99-100	C_s	99-100
C_n	23.76	C_n	21.4466
C_p	76.23	C_p	78.5533
α-Carbon (14.1)	2.6648	α-Carbon	2.3776
β-Carbon (22.7)	3.2537	β-Carbon	2.9605
γ-Carbon (32.0)	1.8044	γ-Carbon	1.6147
δ-Carbon (29.4 and 29.9)	13.0299	δ-Carbon	10.7874
CPN = α + β + γ + δ = 20.753	20.753	CPN = α + β + γ + δ = 17.740	17.740
Isoparaffin = C_p–CPN = 76.23-20.753	55.48	Isoparaffin = C_p–CPN = 78.5533-17.740	60.8129
Average chain length= 2×CPN/CPN_α = 2×20.753/2.6648 = 15.575	15.575	Average chain length= 2×CPN/CPN_α = 2×17.74/2.3776 = 14.922	14.92
Using ^{1}H NMR			
$-CH_3$ = 5 (4.87)	5	$-CH_3$ = 17 (17.02)	17
$-CH_2$ and CH = 12 (11.97) 10.292 + 0.68 + 1.00 = 11.97	12	$-CH_2$ and CH = 43.0 (43.10) 36.36 + 6.74 = 43.10	43
Branchiness index = 100×5/12 = 41.67	42	Branchiness index = 100×17/43 = 39.53 Note: Naphthenes got changed.	39.5

Relationship of kinematic viscosity with temperature

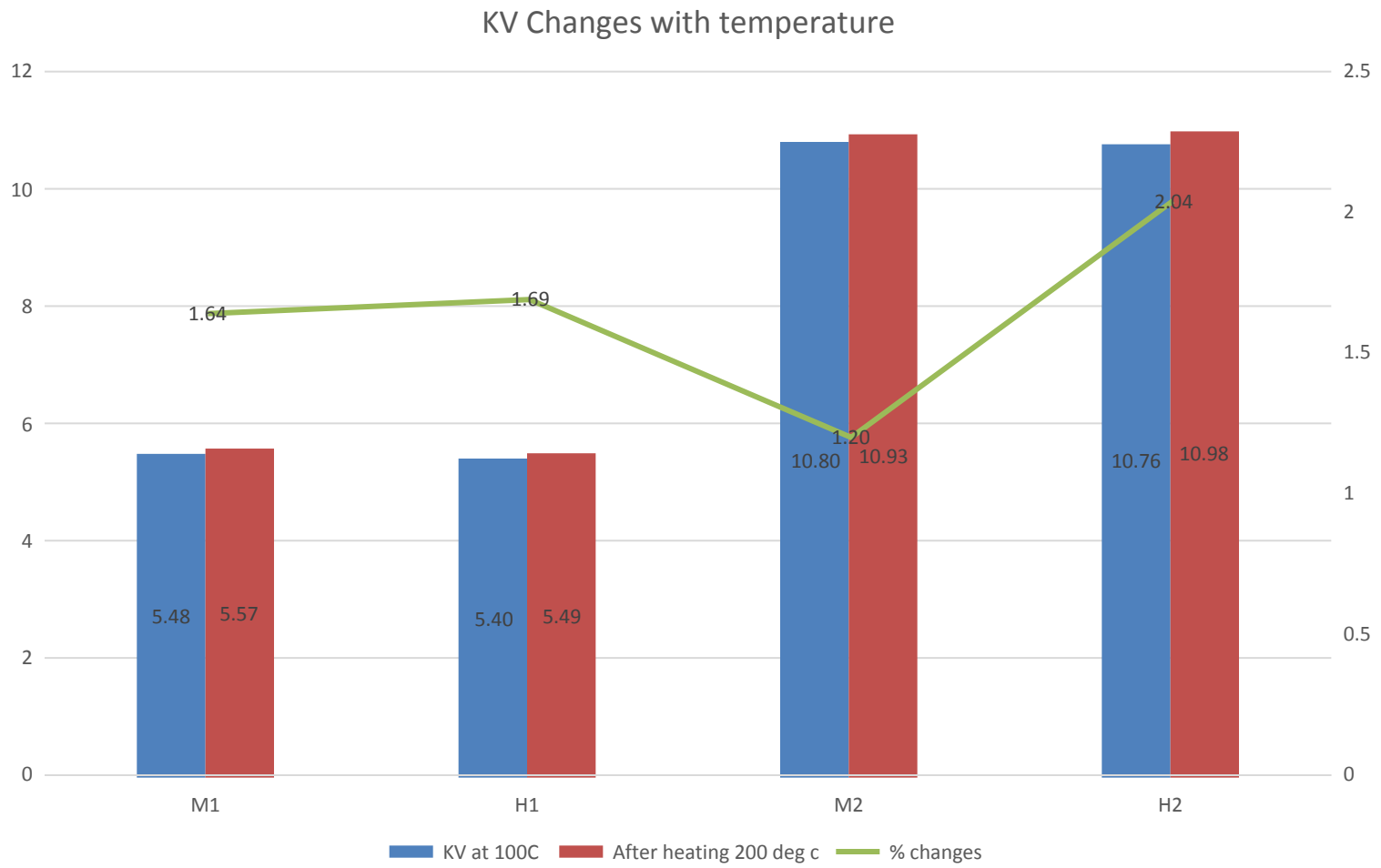
Tests	M1	H1	M2	H2
KV@40°C, cSt	31.0	32.56	90.2	88.01
KV@50°C, cSt	21.10	21.56	56.12	55.00
KV@60°C, cSt	15.00	15.31	37.0	36.45
KV@70°C, cSt	11.07	11.35	25.68	25.40
KV@80°C, cSt	8.60	8.50	18.56	18.45
KV@100°C, cSt	5.483	5.40	10.8	10.76
% Decrease from 40 to 100°C	82.32	83.42	88.02	87.77
Viscosity index (VI)	119	105	108	106
KV@100°C (after heating at 200°C for 2 h)	5.57	5.49	10.93	10.98
% increase	1.49	1.69	1.20	2.04

% Increase of M1 is lesser than H1 similarly M2 is lesser than H2

Kinematic viscosity values with various temperatures

Samples	KV @100 Deg C	After heating 200 Deg C	Difference	% changes
M1	5.48	5.57	0.11	1.64
H1	5.40	5.49	0.09	1.69
M2	10.80	10.93	0.13	1.20
H2	10.76	10.98	0.22	2.04

Kinematic viscosity values with various temperatures



Distillation range with Noack evaporation

Tests	M1	H1	M2	H2
Noack evaporation, %wt	7.07	13.5	1.23	2.30
Distillation range (IBP to 5%), °C	23	49	25	31

Vacuum distillation results of M1, M2, H1 and H2 samples (°C)

Range	M1	H1	M2	H2
IBP	387	324	442	402
5	410	373	467	433
10	414	375	473	435
20	424	383	478	438
30	427	389	484	441
40	430	394	492	444
50	434	399	494	445
60	436	401	499	448
70	438	404	509	450
80	443	407	515	451
90	451	410	523	453
95	460	412	530	454
99	466	414	535	456
Range IBP-5%	23	49	25	31

Conclusion of Group II base oils

- A decrease in average chain length among the paraffinic oils increases the viscosity index (VI).
- Lower naphthenic (Cn) carbon content increases the oxidation stability.
- Increase in iso-paraffinic (Cip) carbon content increases the thermal stability.
- Addition of antioxidant remarkably enhances the oxidation stability of the base oils.
- Viscosity index value of the base oils are more influenced by the paraffinic carbon content rather than the iso-paraffinic carbons.
- Hydro-processing technology is better than hybrid technology for manufacturing Group II base oils.

MAK LUBRICANTS

Thank You for your time



Bharat Petroleum

energising lives

www.bharatpetroleum.in

MAK® makes it possible.