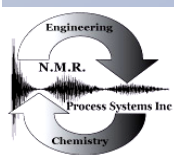


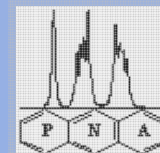
"Counting Carbons for Tighter Control: Combining GC and NMR to Improve Distillate Manufacturing"

Paul J. Giammatteo*, John C. Edwards and George Winter



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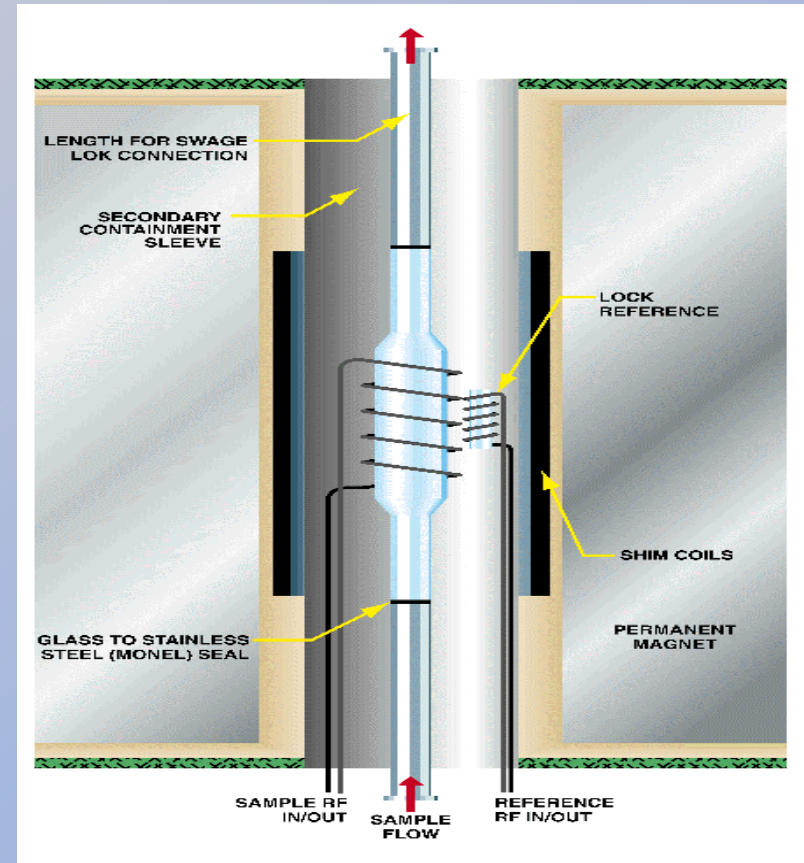
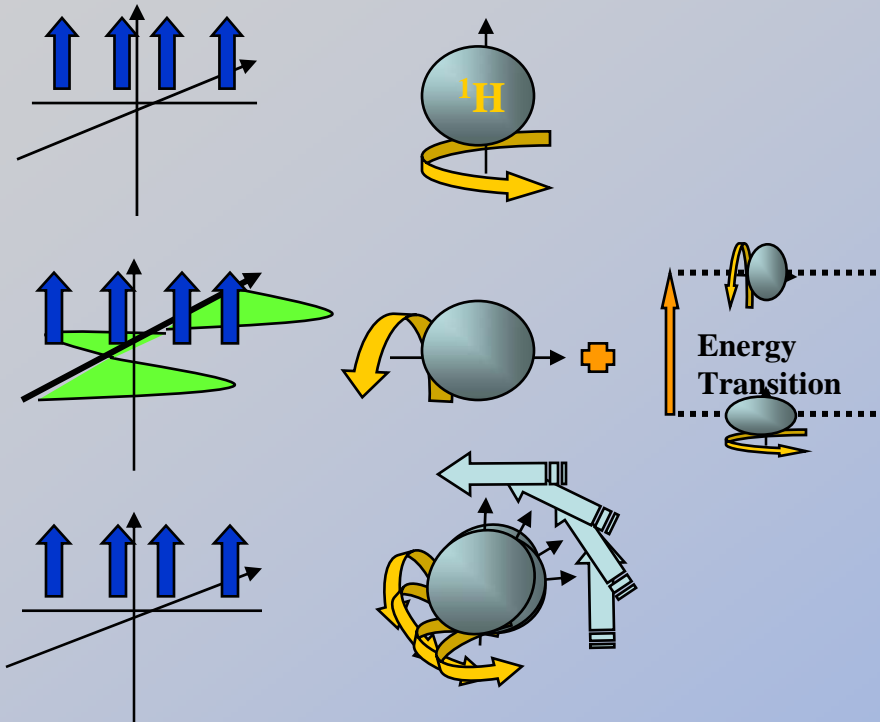
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Basic Principle of Operation

- In Practice

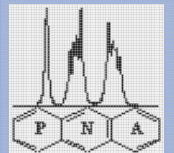
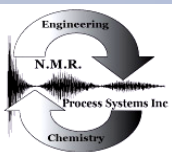
- In Theory



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All Diesels: (Data date range 1999 to present)

Atmospheric Crude Straight Run

Vacuum Crude Straight Run

Coker Diesel

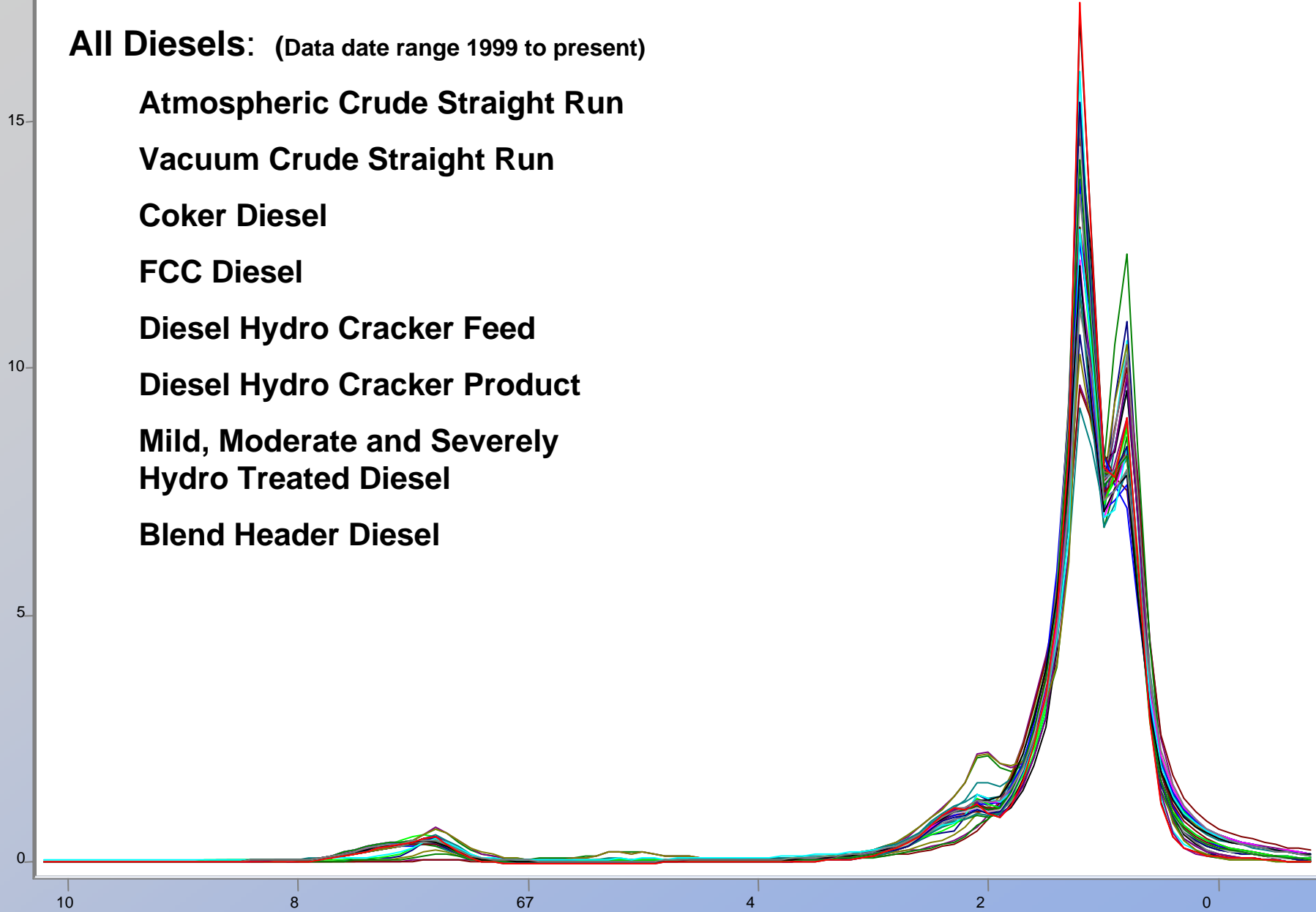
FCC Diesel

Diesel Hydro Cracker Feed

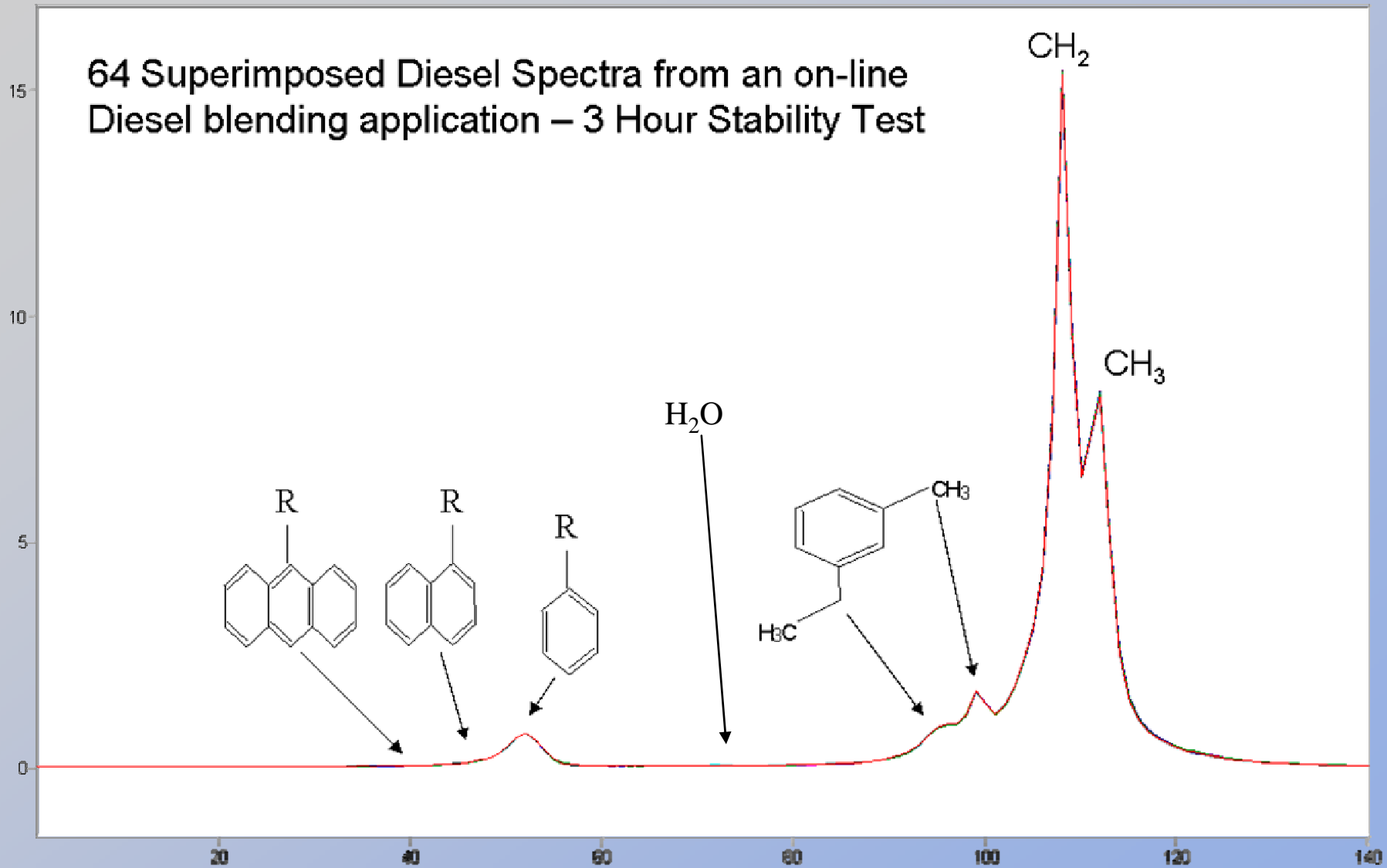
Diesel Hydro Cracker Product

**Mild, Moderate and Severely
Hydro Treated Diesel**

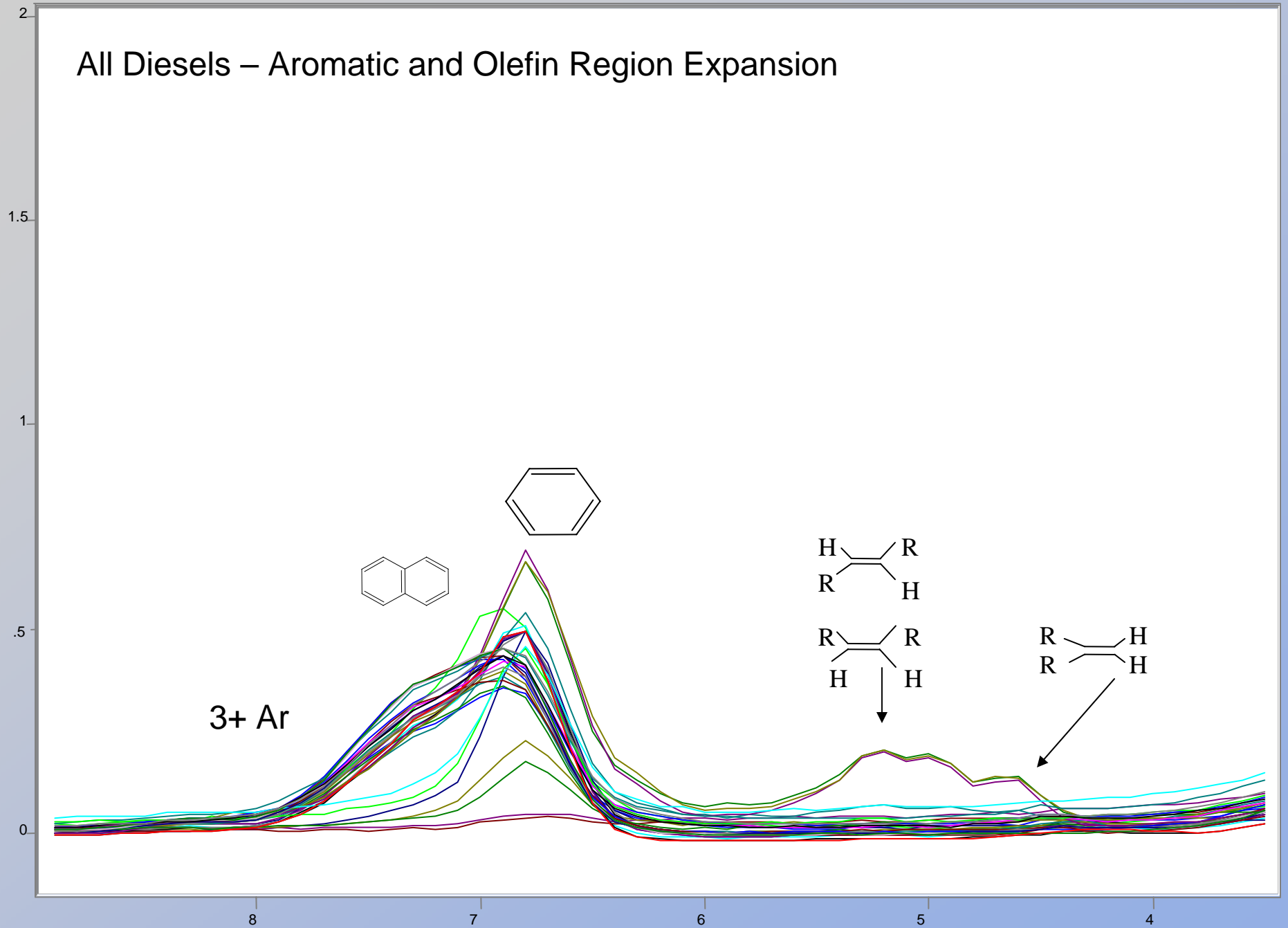
Blend Header Diesel



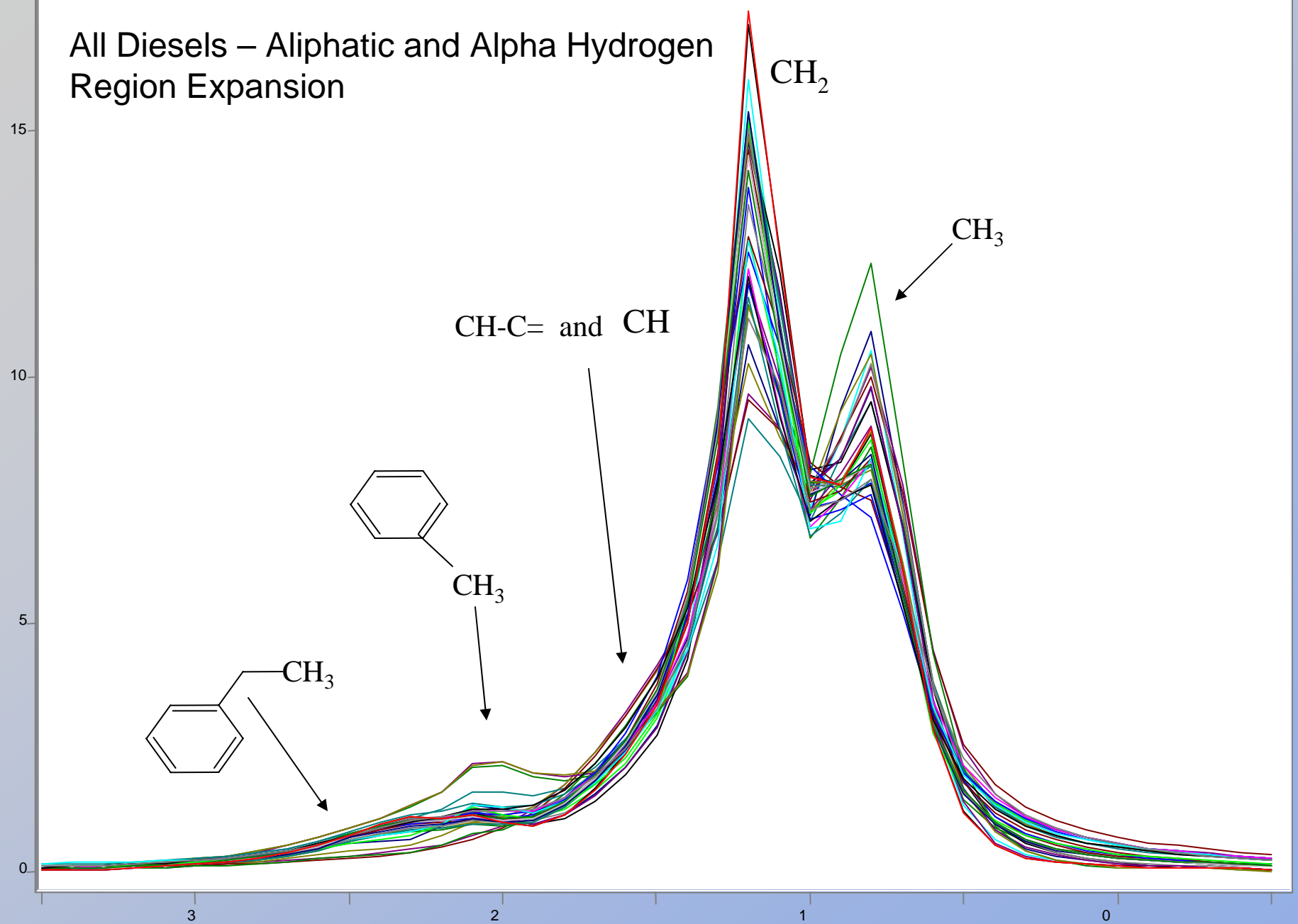
64 Superimposed Diesel Spectra from an on-line Diesel blending application – 3 Hour Stability Test



All Diesels – Aromatic and Olefin Region Expansion



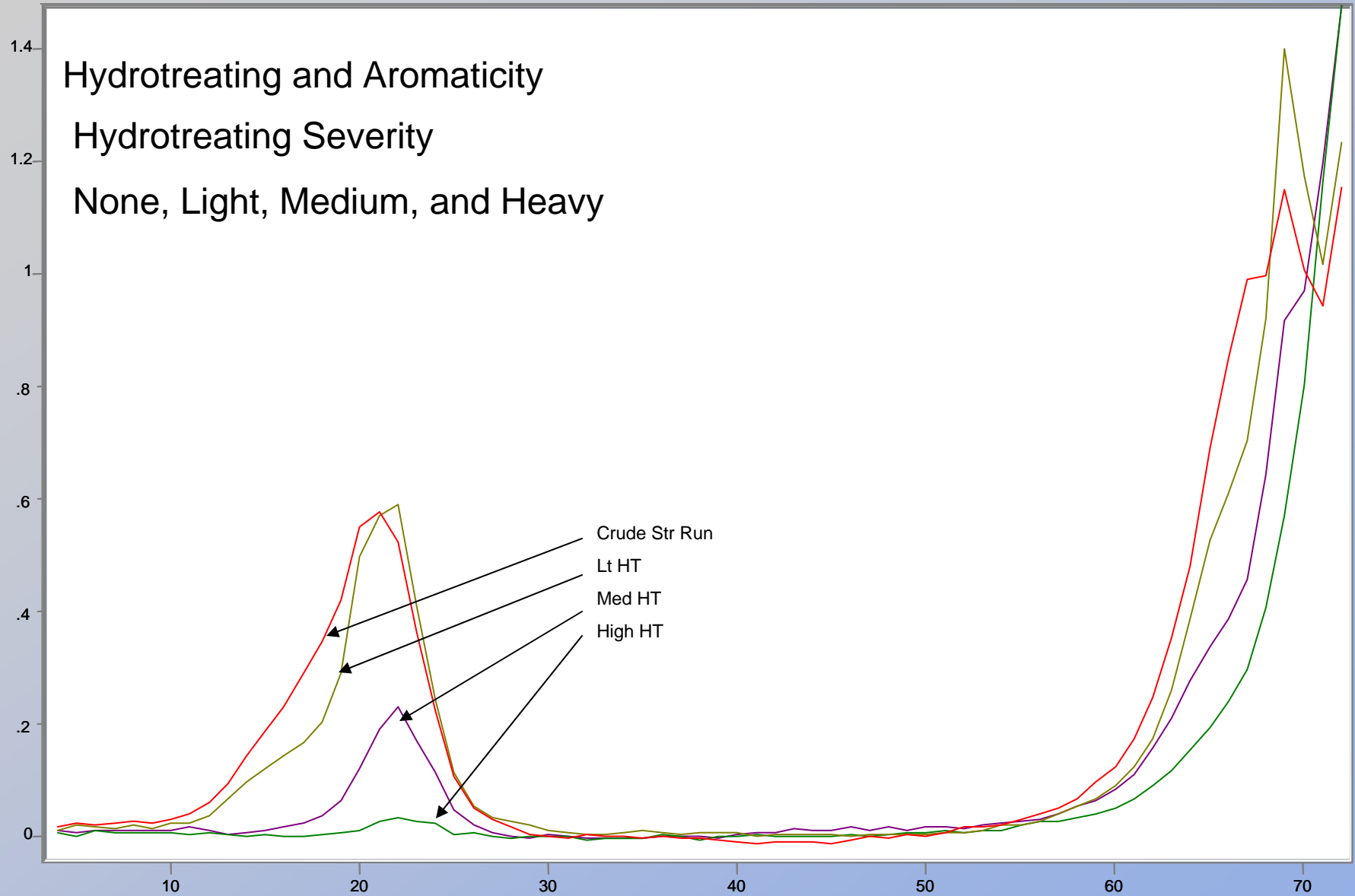
All Diesels – Aliphatic and Alpha Hydrogen Region Expansion



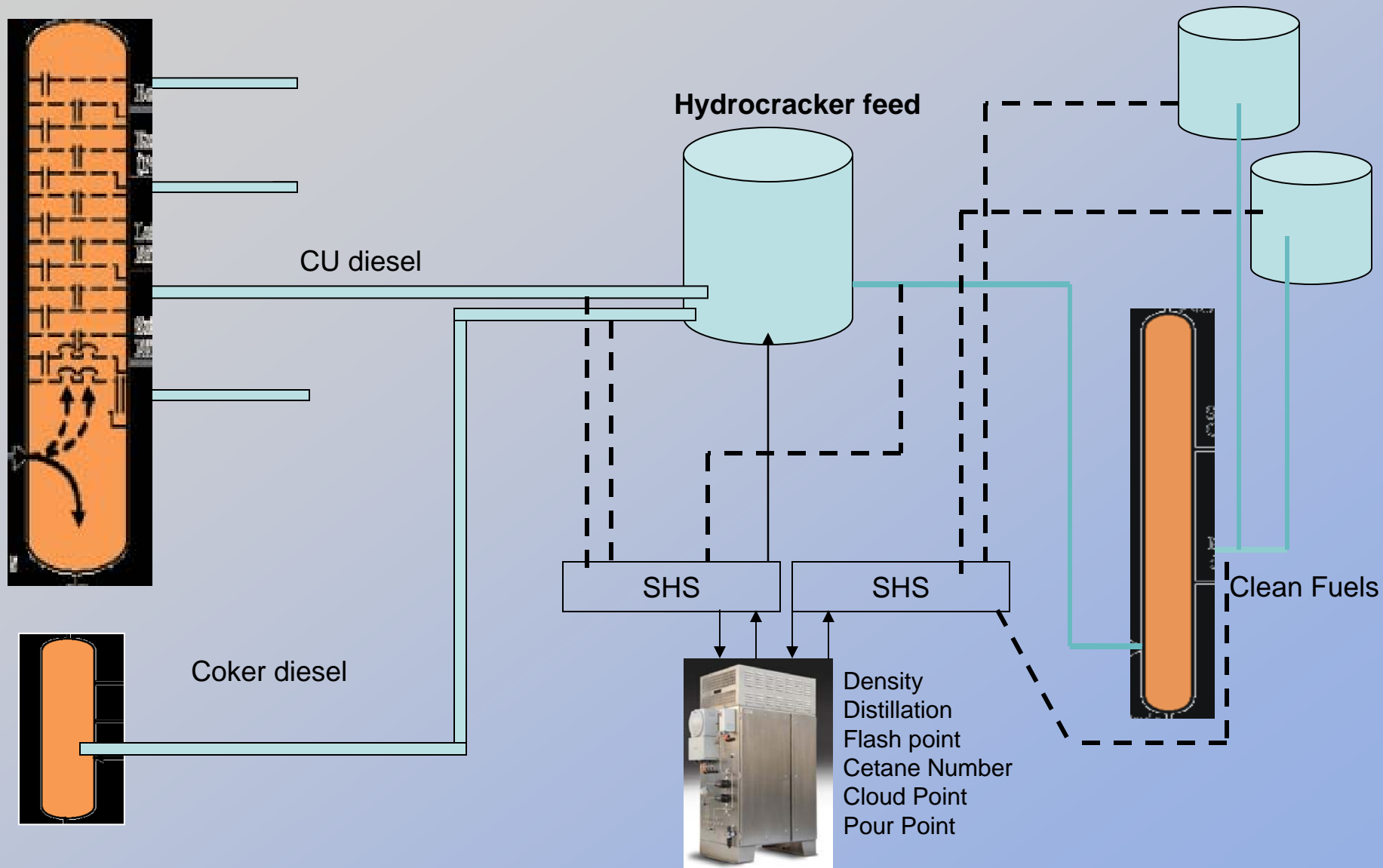
Hydrotreating and Aromaticity

Hydrotreating Severity

None, Light, Medium, and Heavy



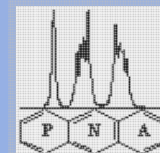
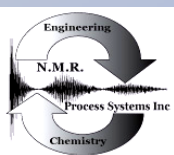


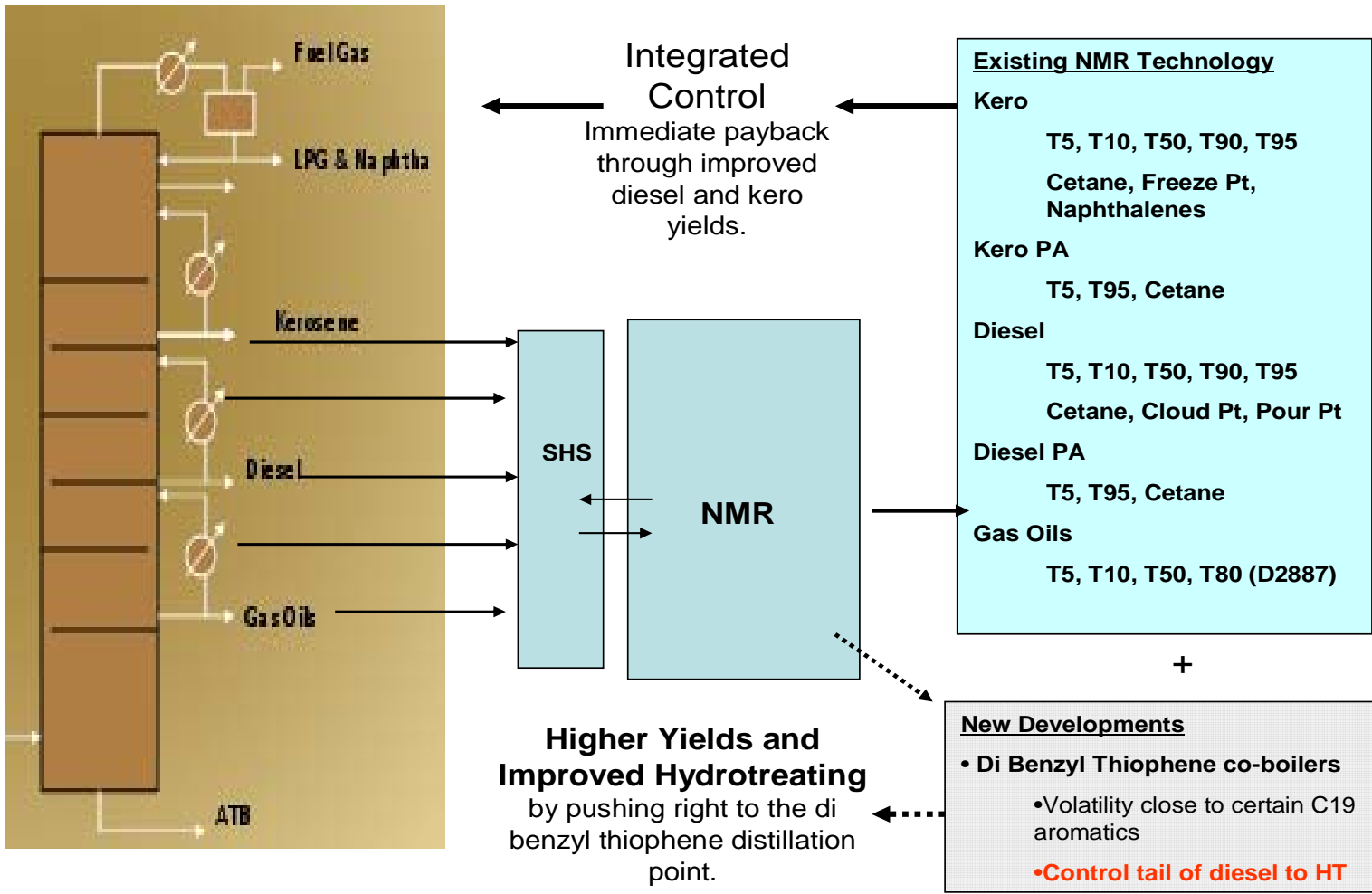


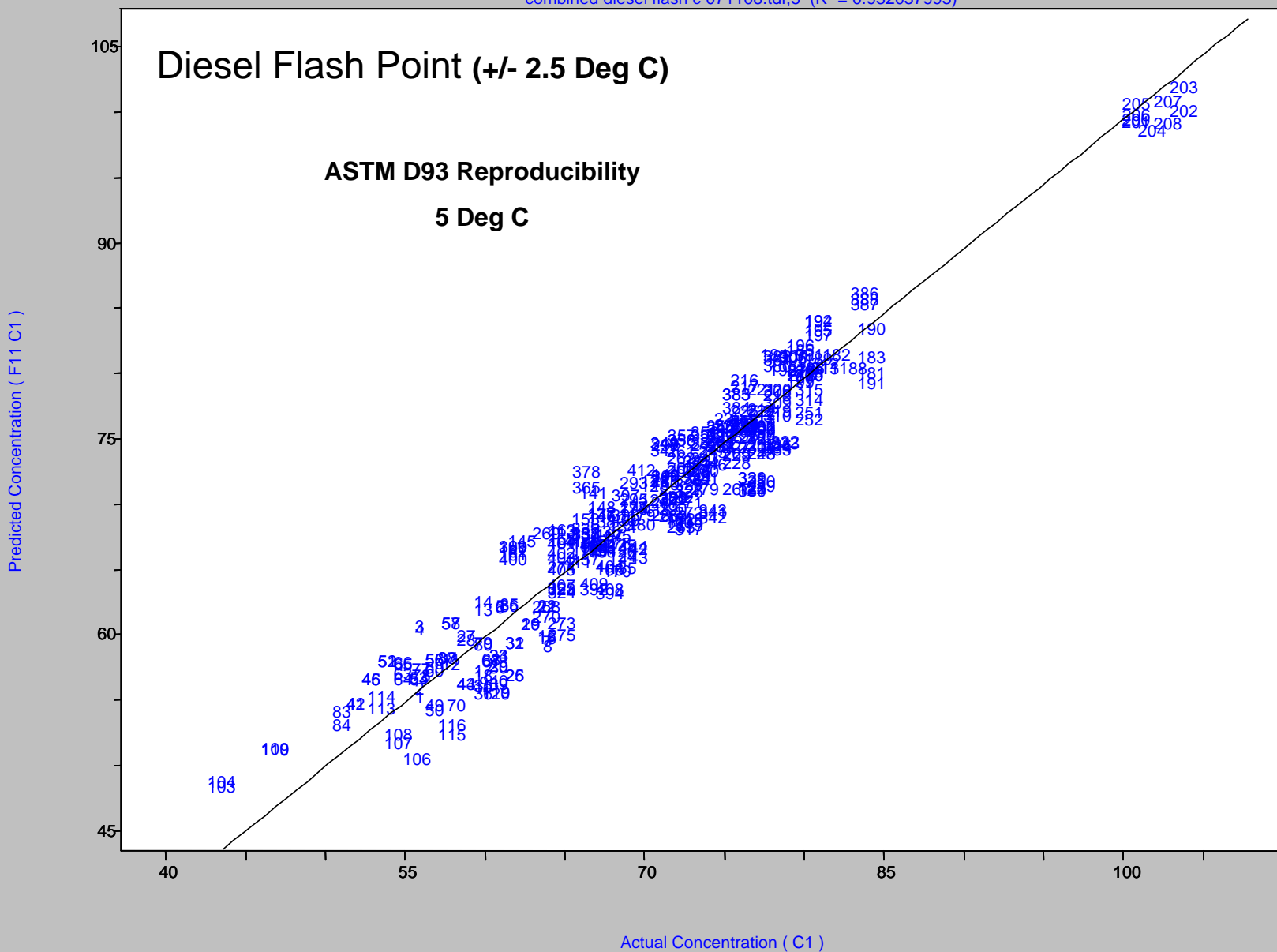
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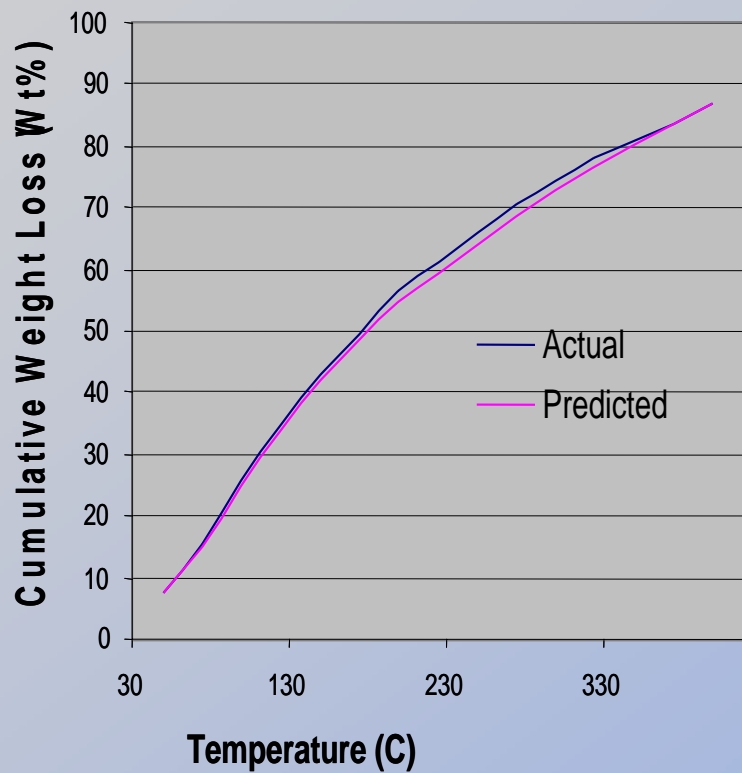




Full True Boiling Point (5 days) v. NMR Predicted TBP (2 minutes)

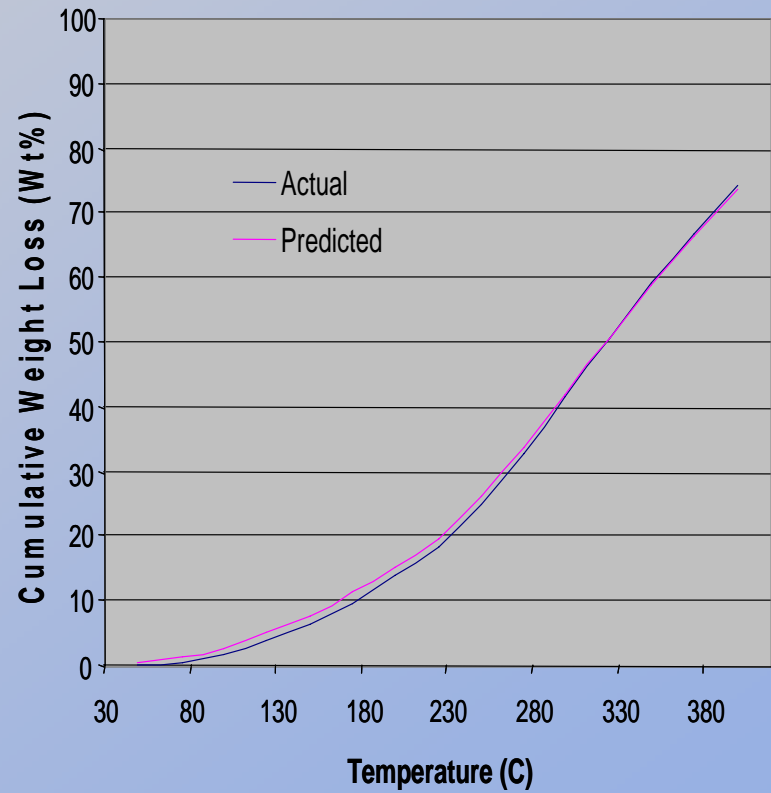
Marib Light Crude TBP Curves

(Actual and NMR Predicted)



Dulang Crude TBP Curves

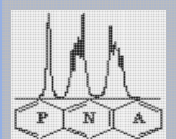
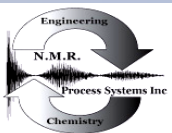
(Actual and NMR Predicted)



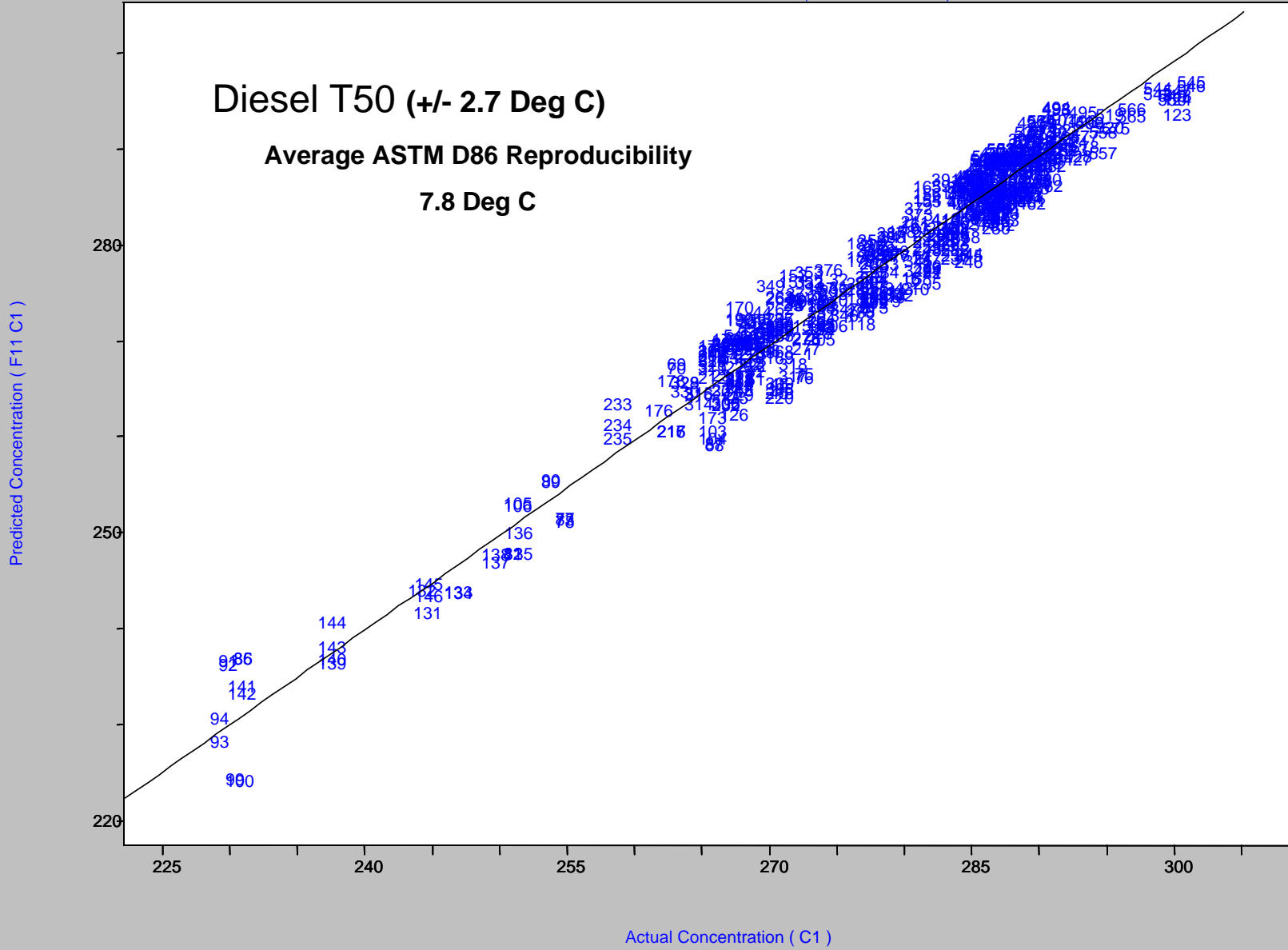
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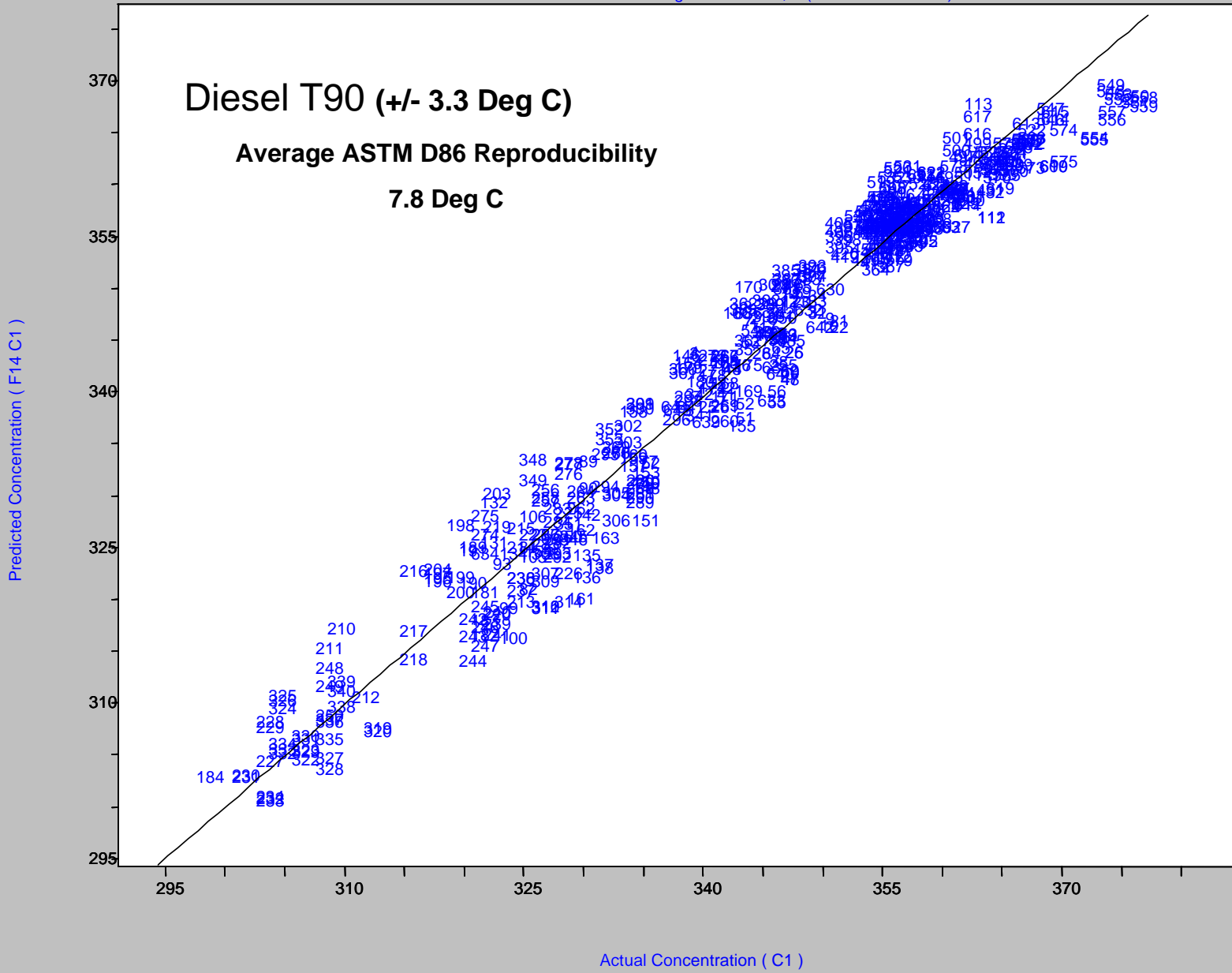
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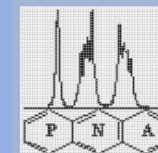
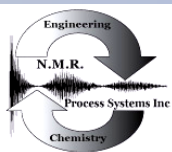
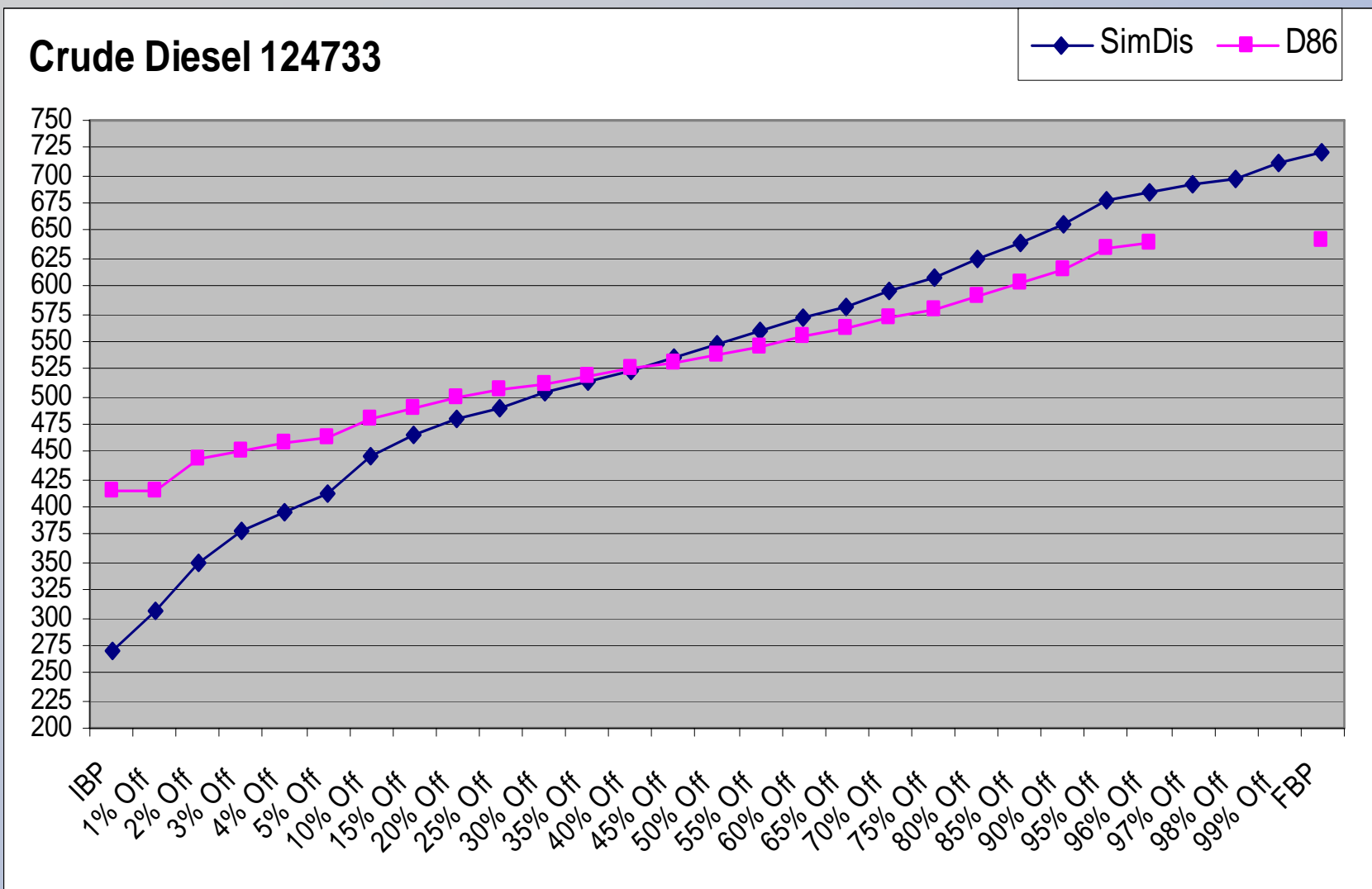
combined diesel t50 071108.tdf,4 (R² = 0.956120284)



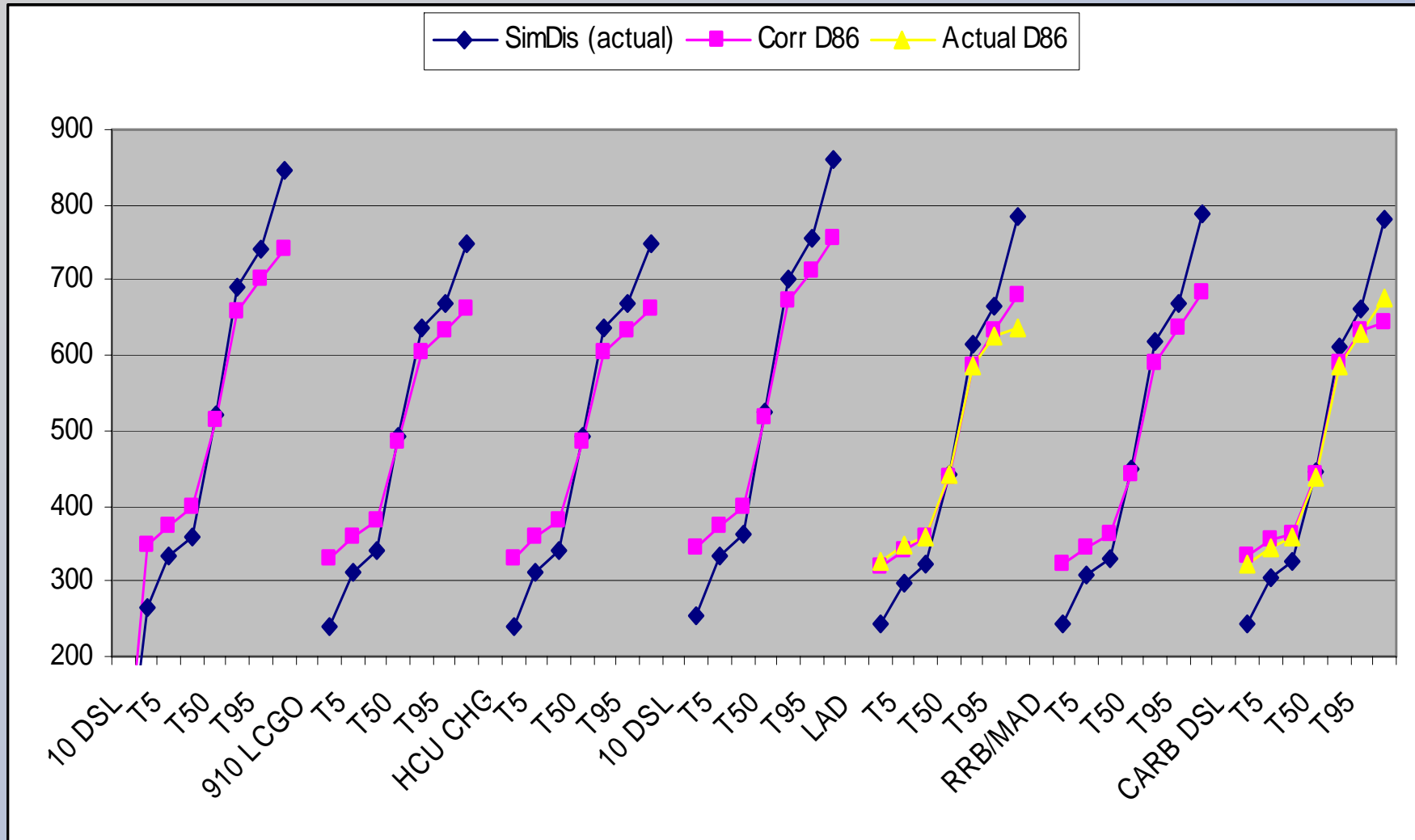
combined diesel t90 deg c 071108.tdf,6 (R² = 0.961256362)



Simulated Distillation and ASTM D86 Distillation are actually short cut approximations of True Boiling Point.

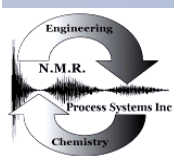
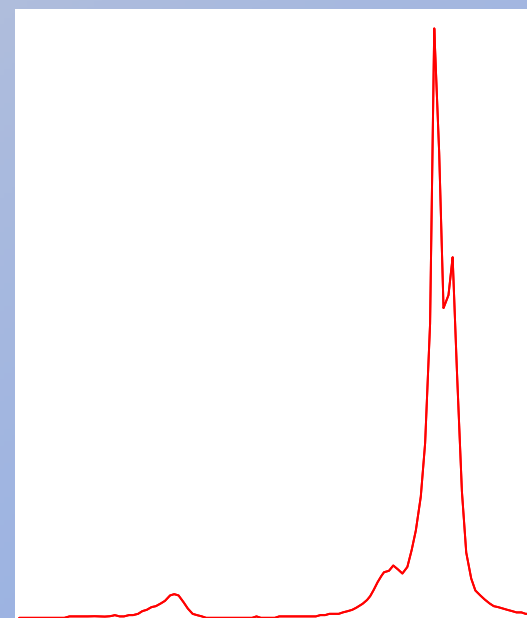
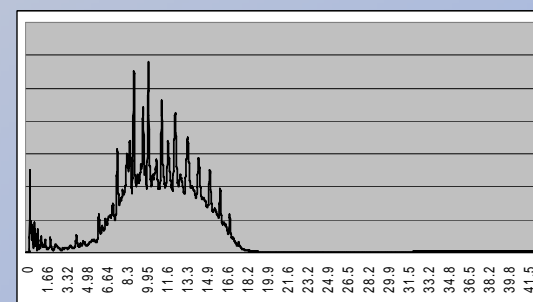


Numerous factors (especially aromatics) are responsible for deviations between distillation methods.



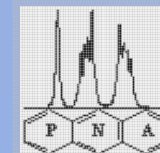
Diesel Simulated Distillation Carbon Number and NMR Analyses

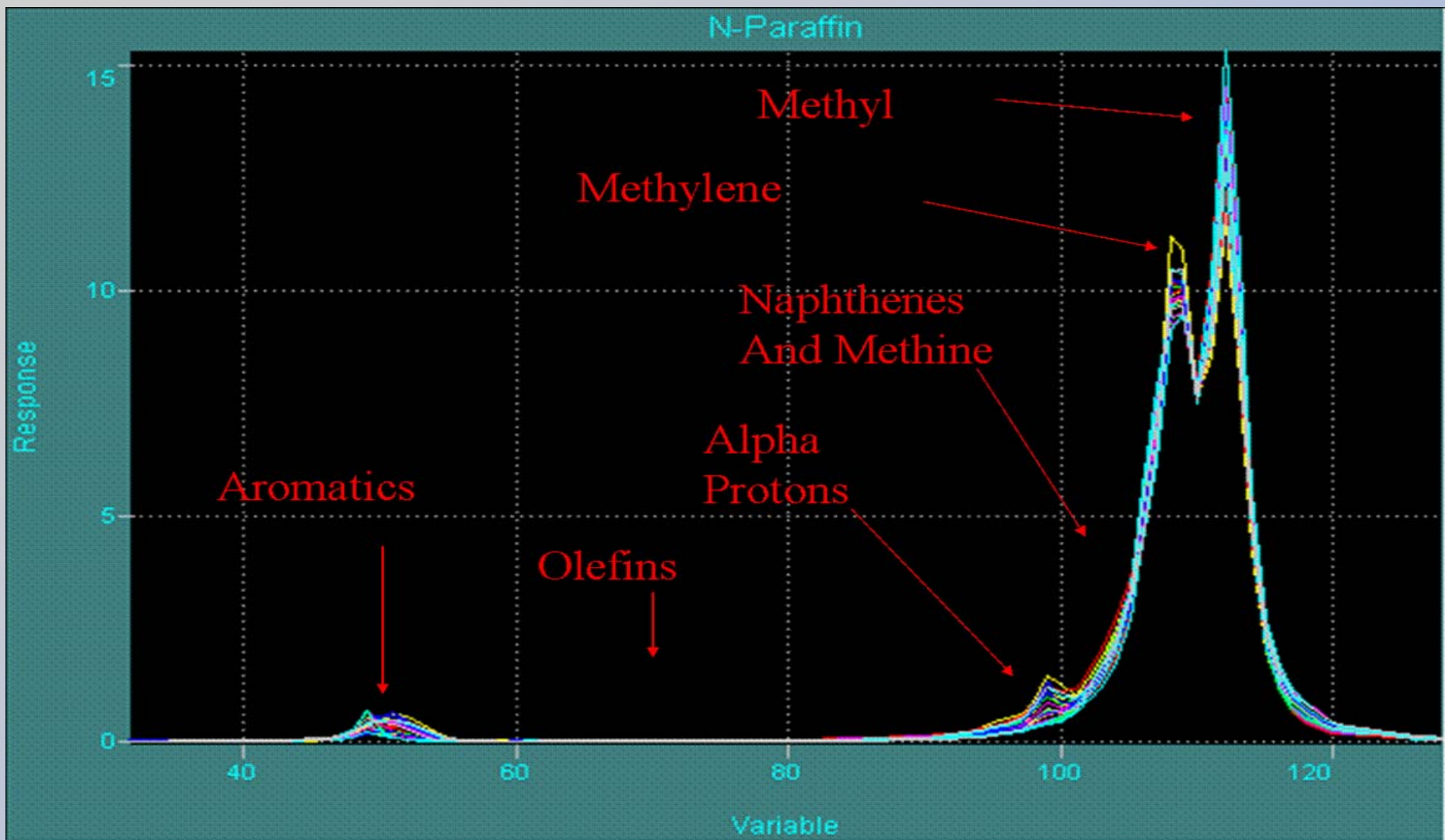
- Simulated Distillation GC of diesels is typically accurate and repeatable from T5 through T80.
- Delving into the actual chromatographic data files allows point by point access to the chromatogram from which we extract the carbon number distribution data for NMR modeling.
- Carbon Number Calibration Standards are used to determine the specific carbon number range in the chromatogram.
- As expected different diesels have both different chromatograms and NMR spectra.
- ASTM D2887 (SimDis) Run time: 40 – 50 minutes.
- NMR Run Time: 2 minutes.



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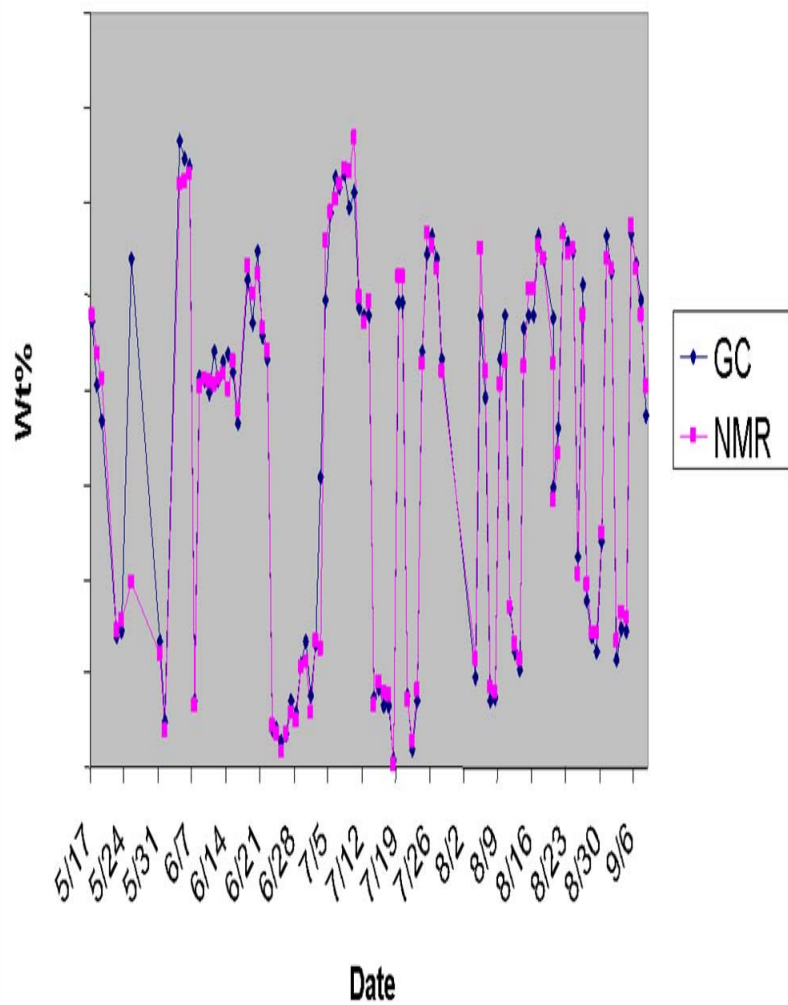
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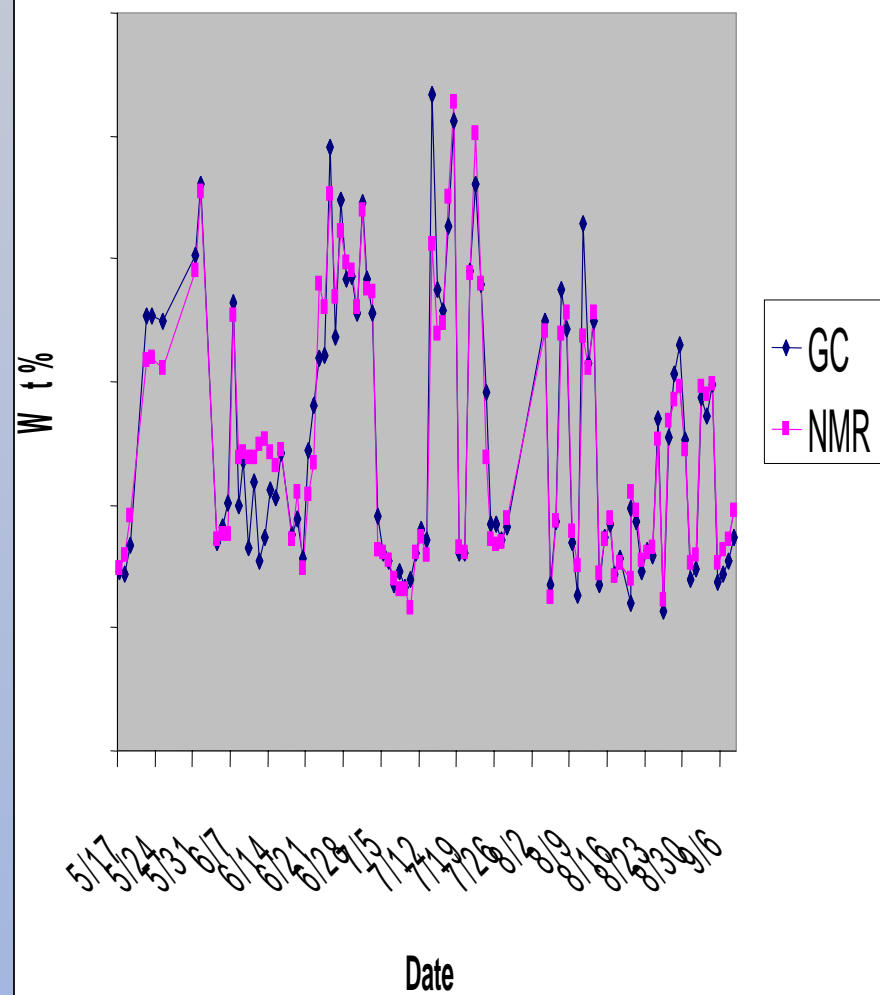


Spectral Variability Observed in Naphtha Samples

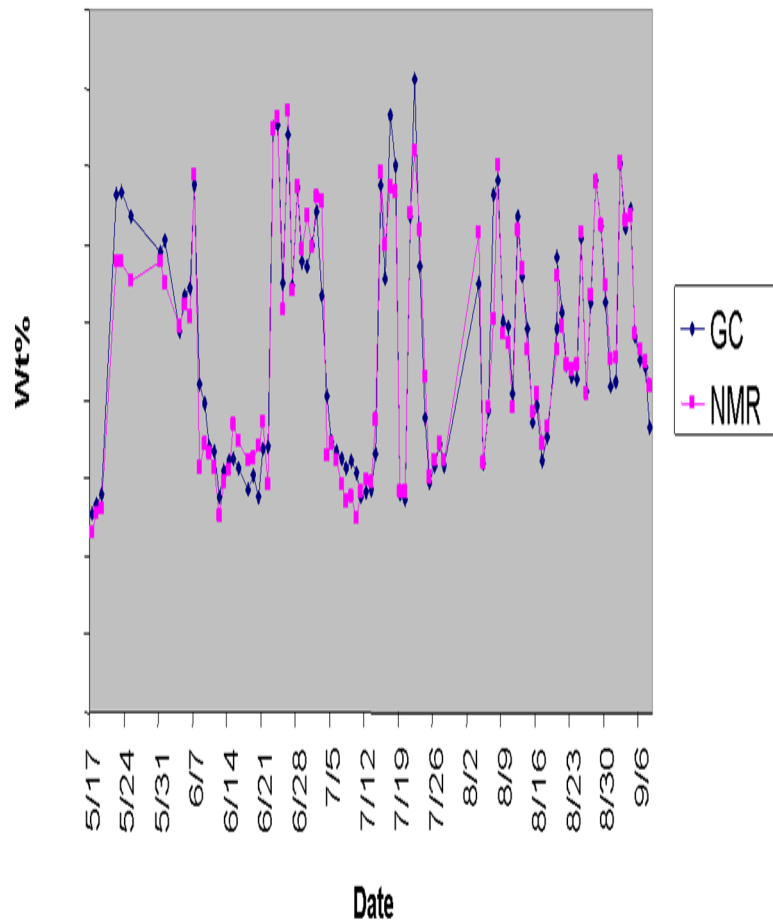
Xylenes



Cyclopentane

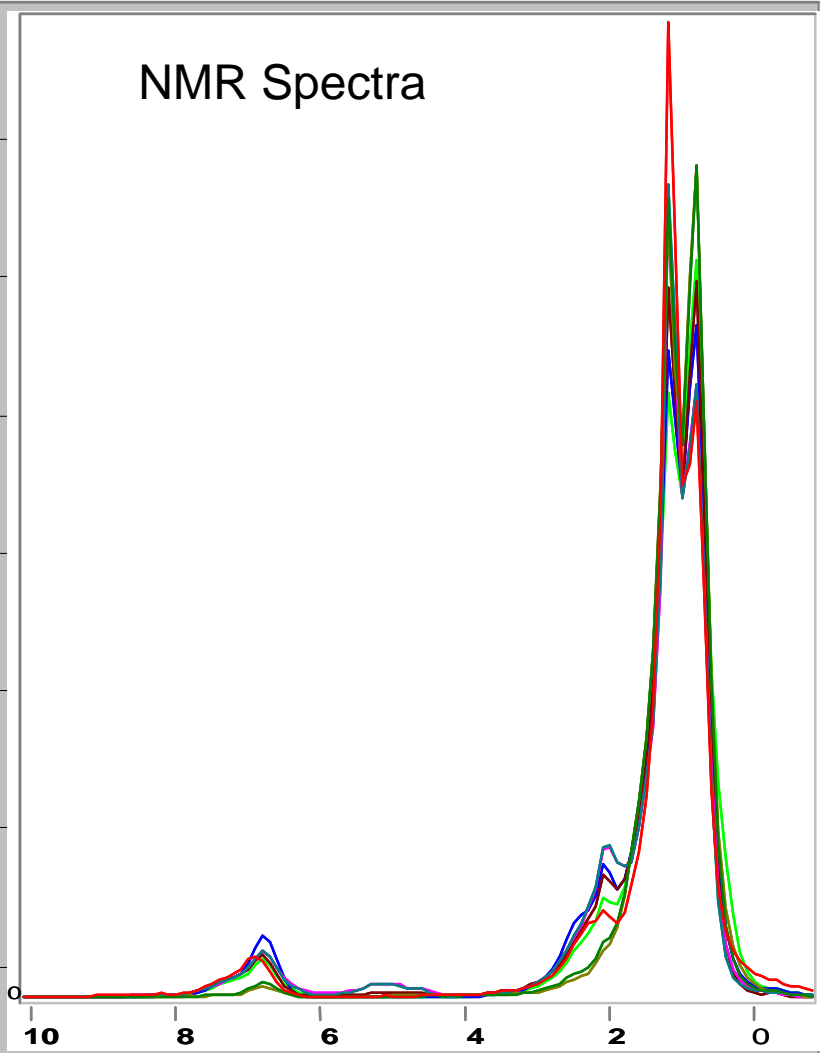
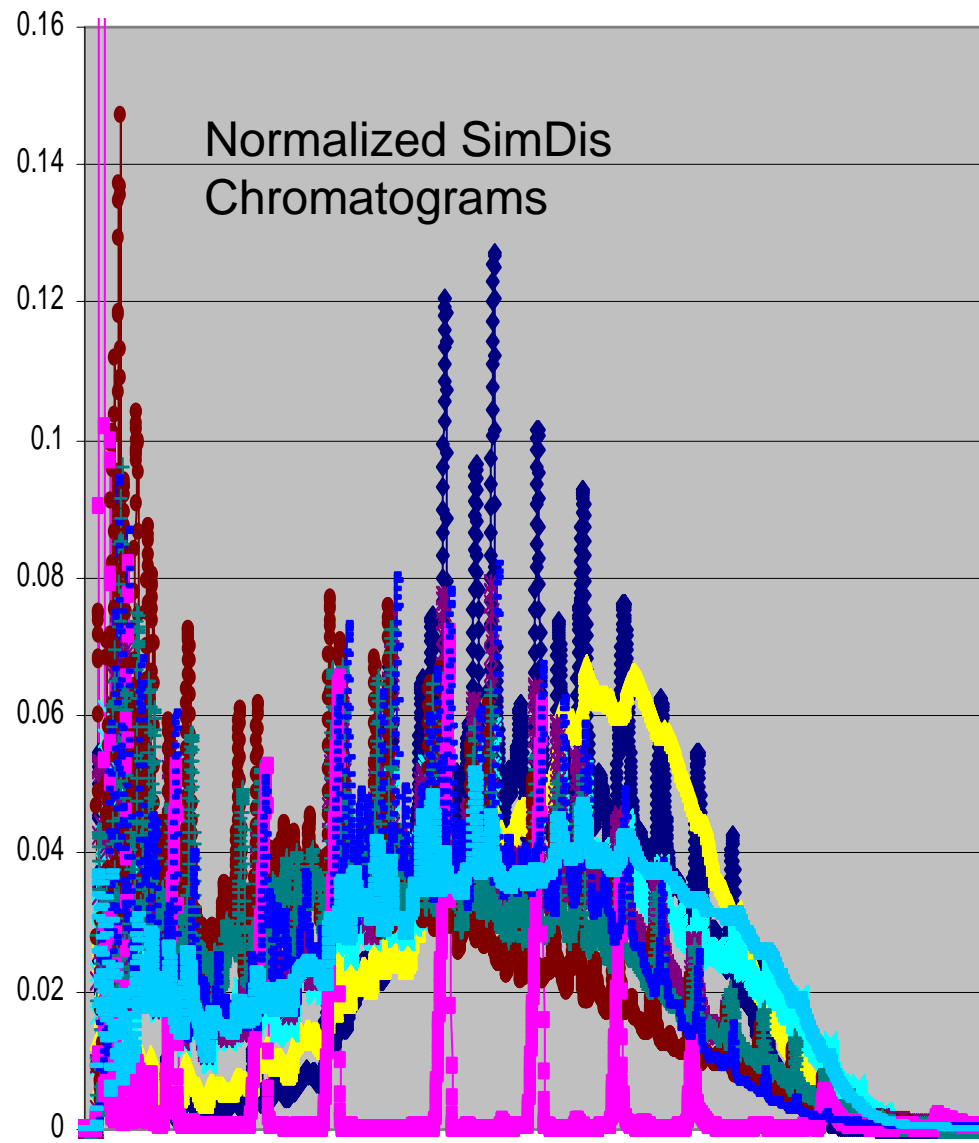


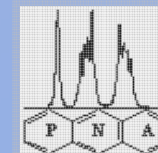
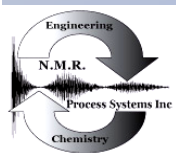
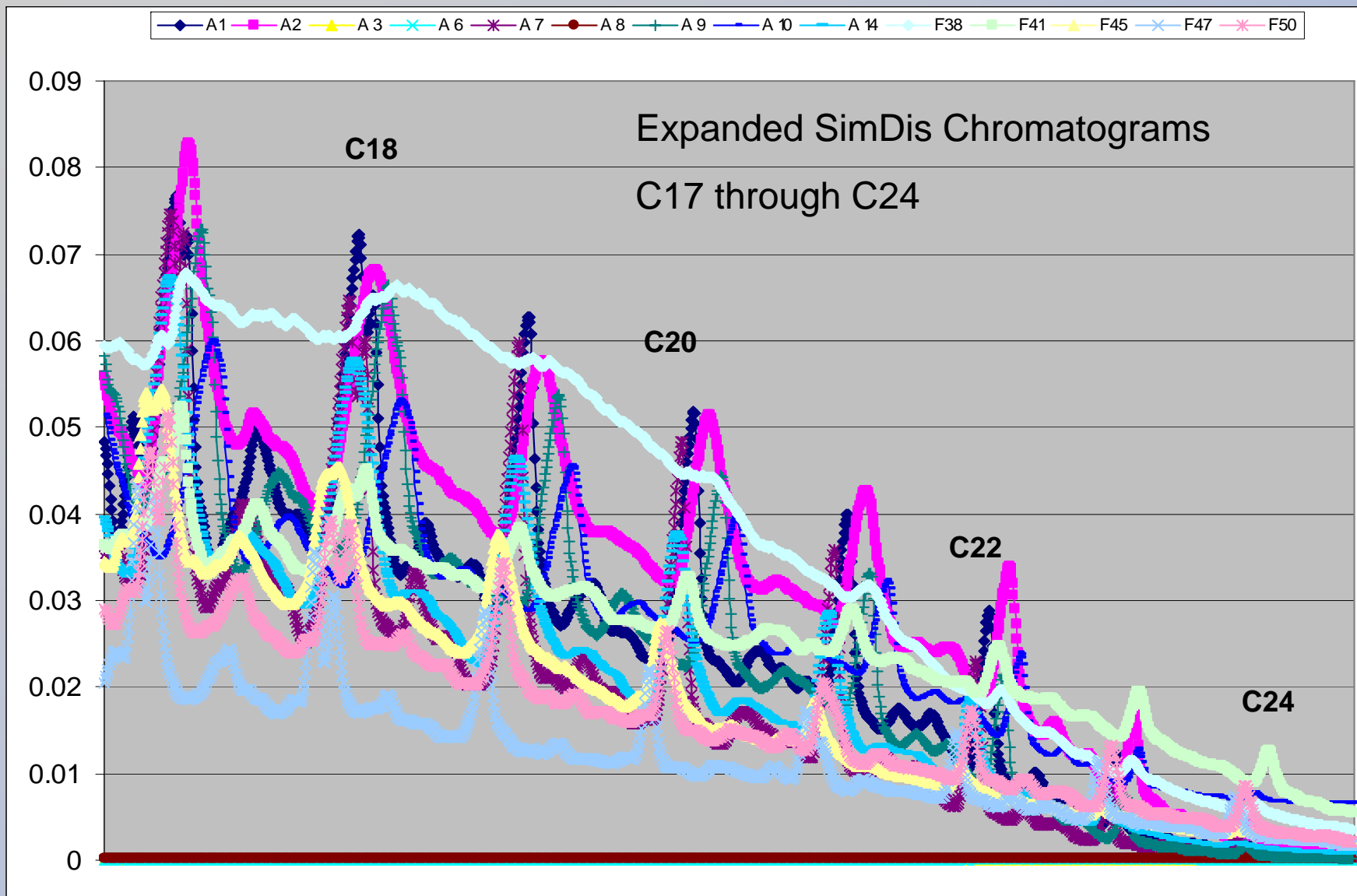
Iso-C5 Paraffin

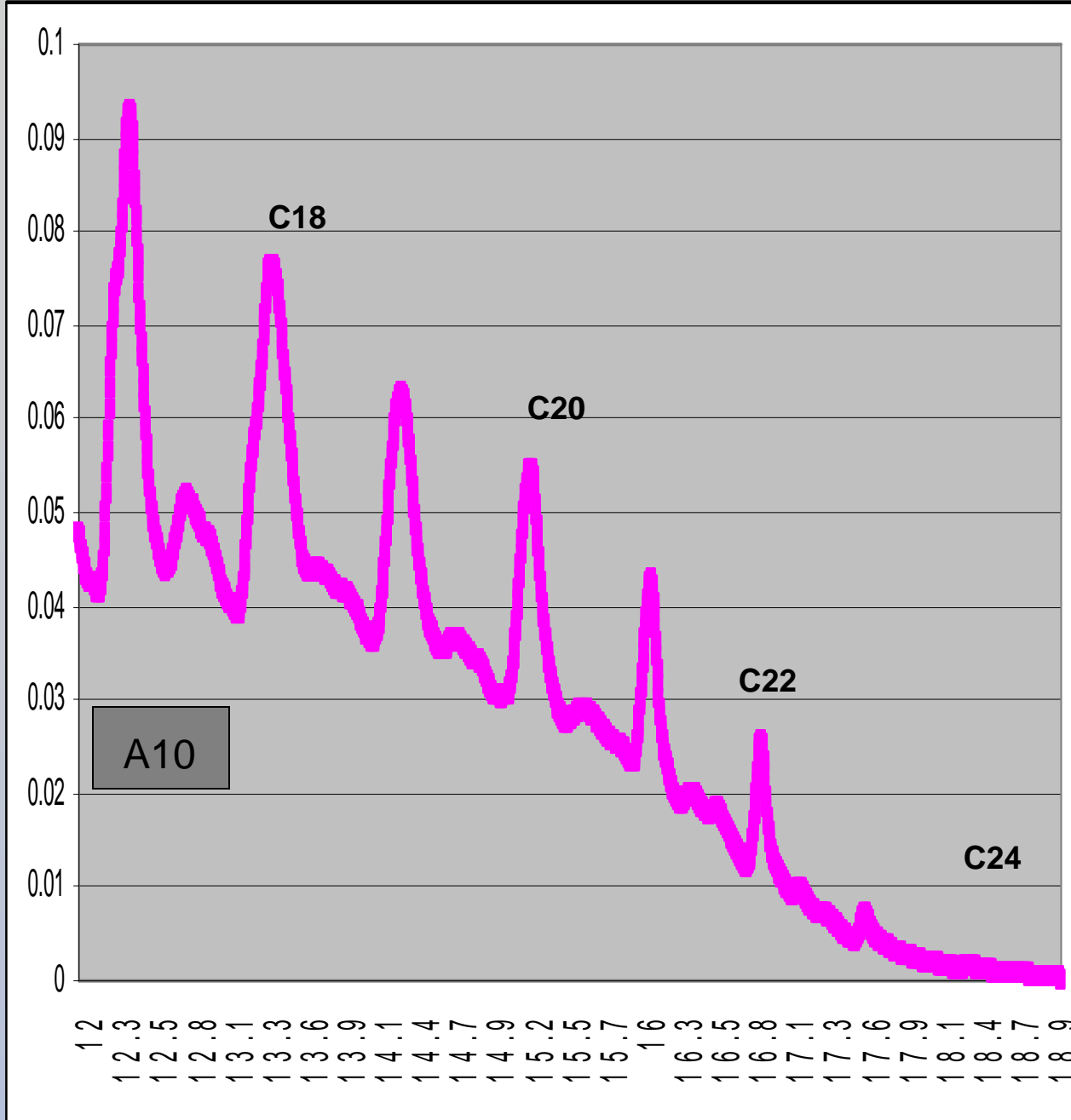


Parameter	R	Std Dev	Mean Dev
n-c4	0.9340	0.52	0.067
n-c5	0.9761	0.73	-0.004
n-c6	0.9616	0.73	-0.093
n-c7	0.9840	0.33	-0.032
n-c8	0.9882	0.29	-0.008
n-c9	0.9918	0.18	-0.003
n-c10	0.9716	0.13	0.022
Total n-paraffin	0.9840	0.81	0.013
I-c4	0.8765	0.07	0.001
I-c5	0.9834	0.76	0.043
i-C6	0.9865	0.59	-0.050
i-C7	0.9119	0.46	-0.015
i-C8	0.9800	0.42	-0.035
i-C9	0.9905	0.26	0.010
i-C10	0.9866	0.24	0.013
i-C11	0.9613	0.08	-0.007
Total I-paraffin	0.9617	0.81	-0.011
cyclopentane	0.9821	0.14	-0.004
me-cyclopentane	0.9937	0.23	-0.018
Cyclohexane	0.9940	0.26	0.034
Methylcyclohexane	0.9872	0.29	0.001
Other C7-Nap	0.9025	0.32	-0.052
c8-Nap	0.9713	0.36	0.002
c9-Nap	0.9892	0.28	0.026
c10-Nap	0.8950	0.06	-0.001
Total Naphthenes	0.9794	0.83	0.019
Benzene	0.9950	0.10	0.006
Toluene	0.9920	0.17	0.007
Ethylbenzene	0.9902	0.04	0.002
Xylenes	0.9951	0.14	0.003
C9 - Arom	0.9875	0.16	0.006
C10-arom	0.9586	0.07	0.001
Total Aromatics	0.9967	0.31	0.022

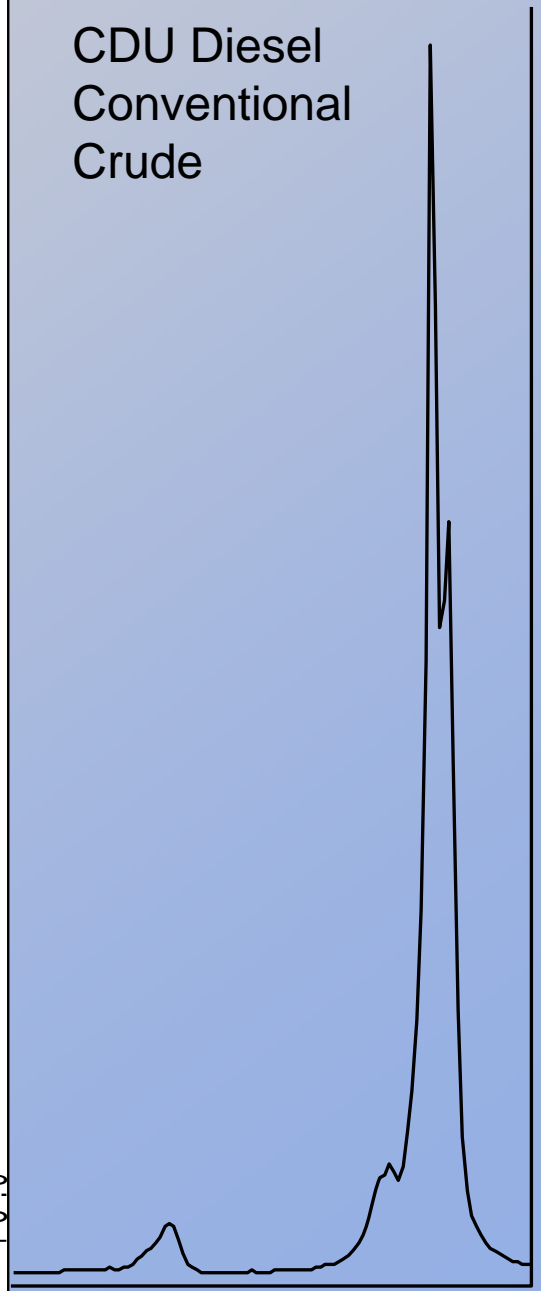
◆ A10 ▲ F38 ✕ F41 * F45 ● F47 + F50 ■ CalStd — F43 — F35

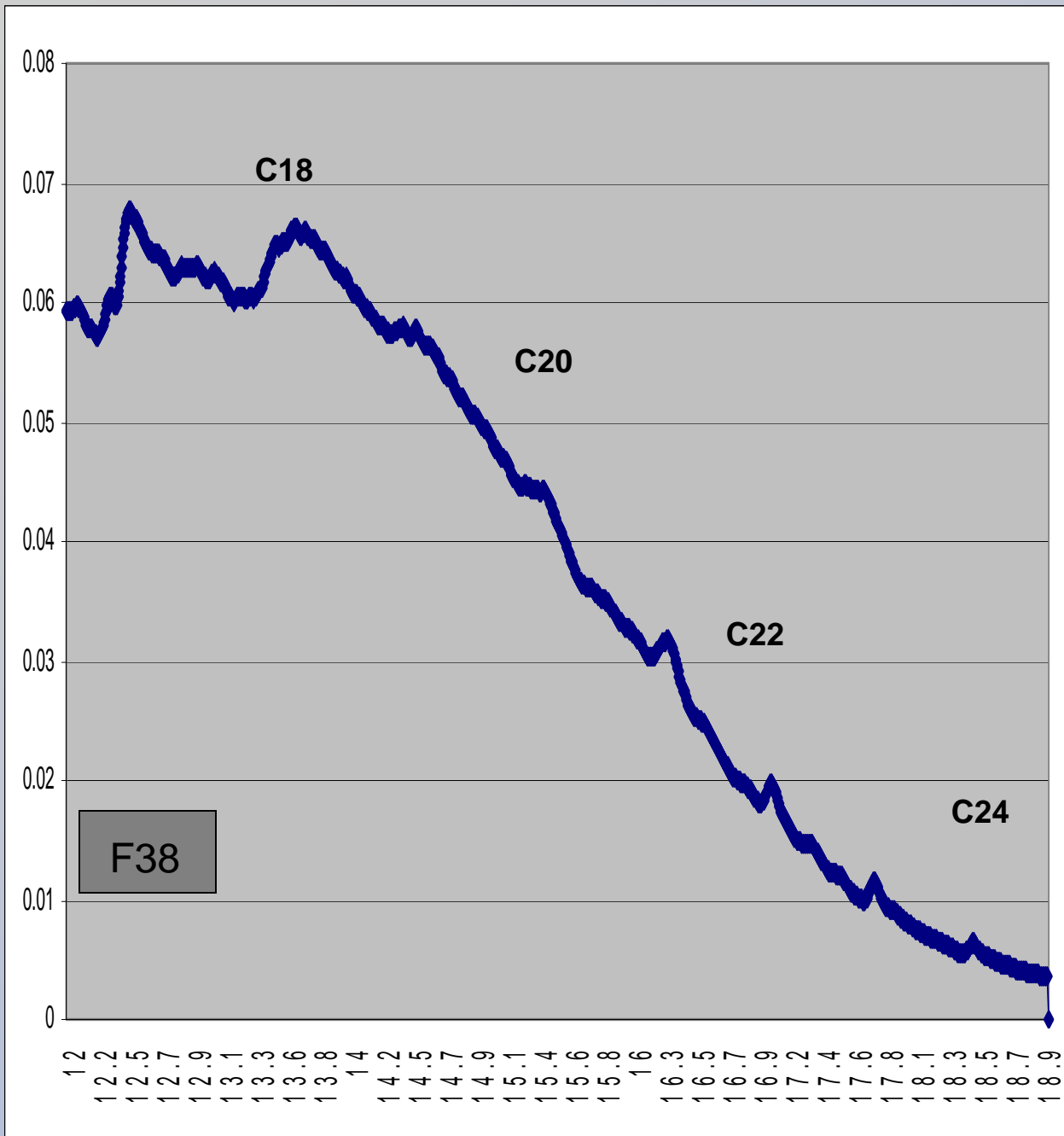




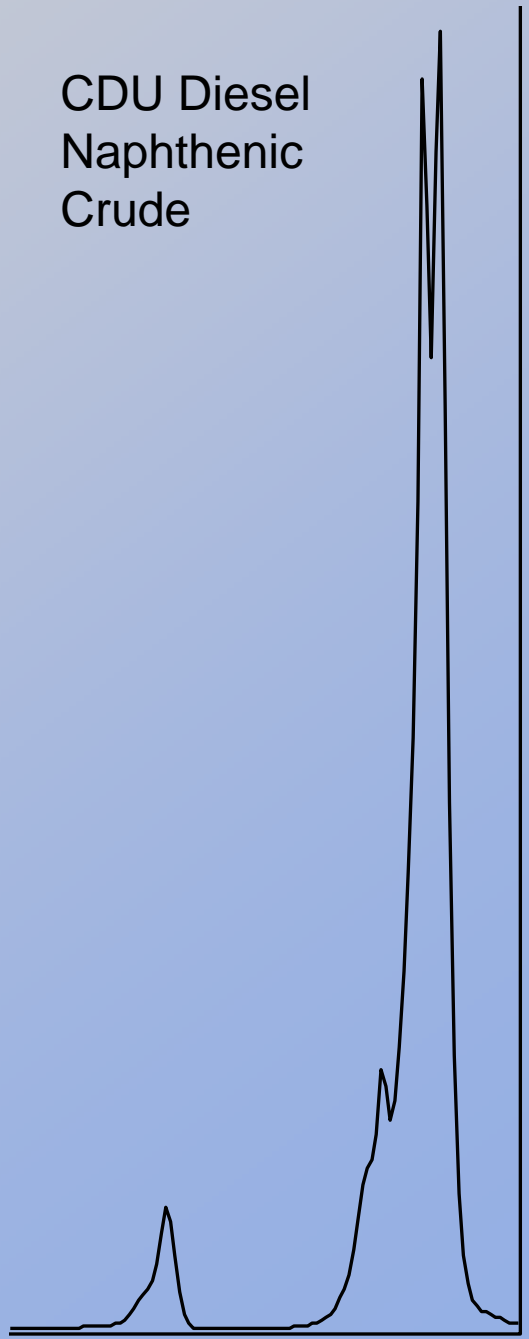


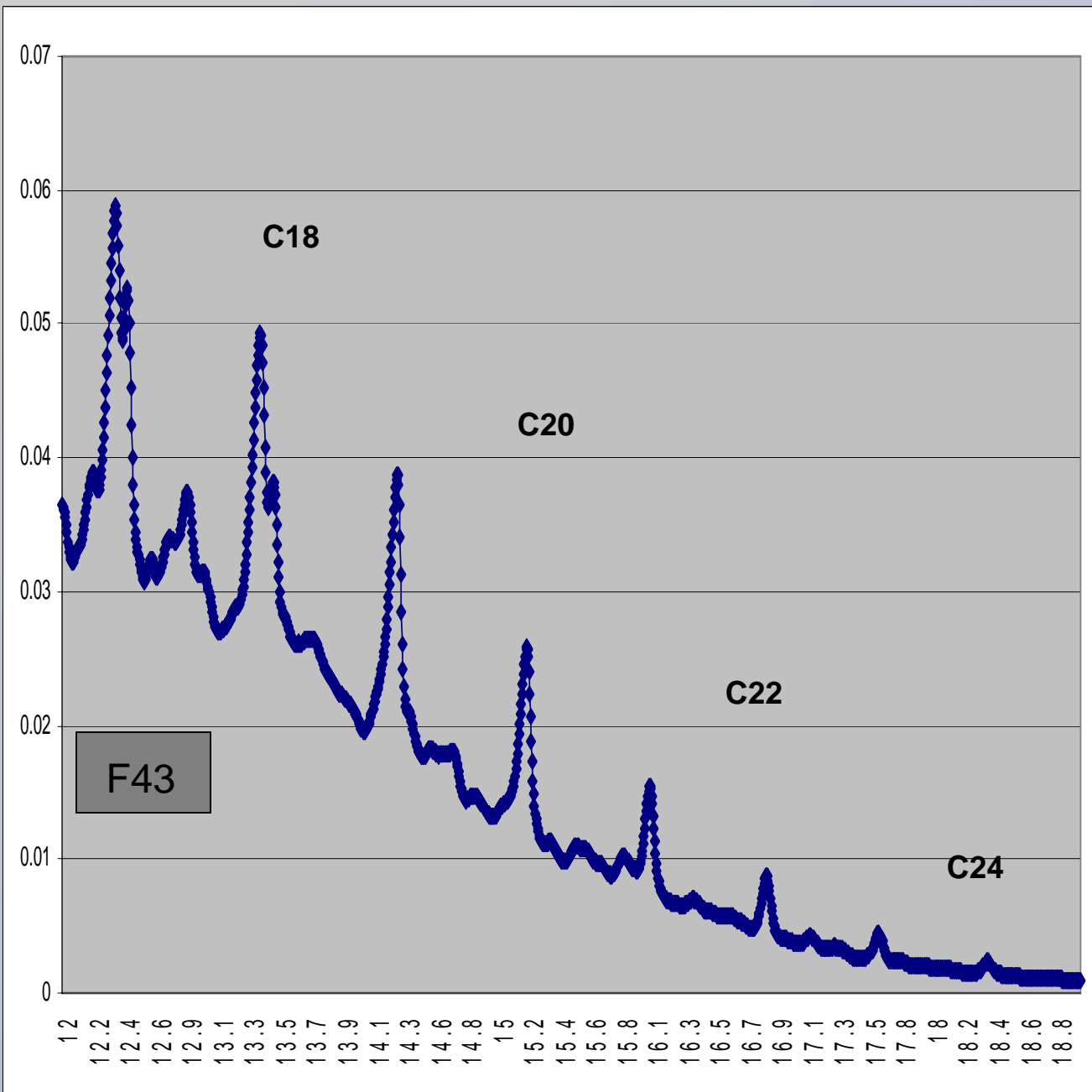
CDU Diesel
 Conventional
 Crude



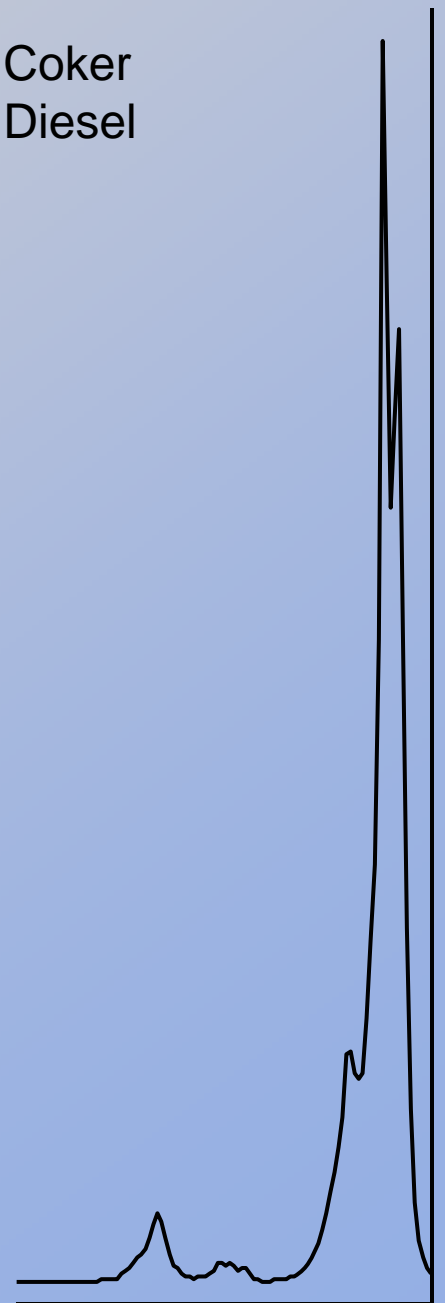


CDU Diesel
Naphthenic
Crude

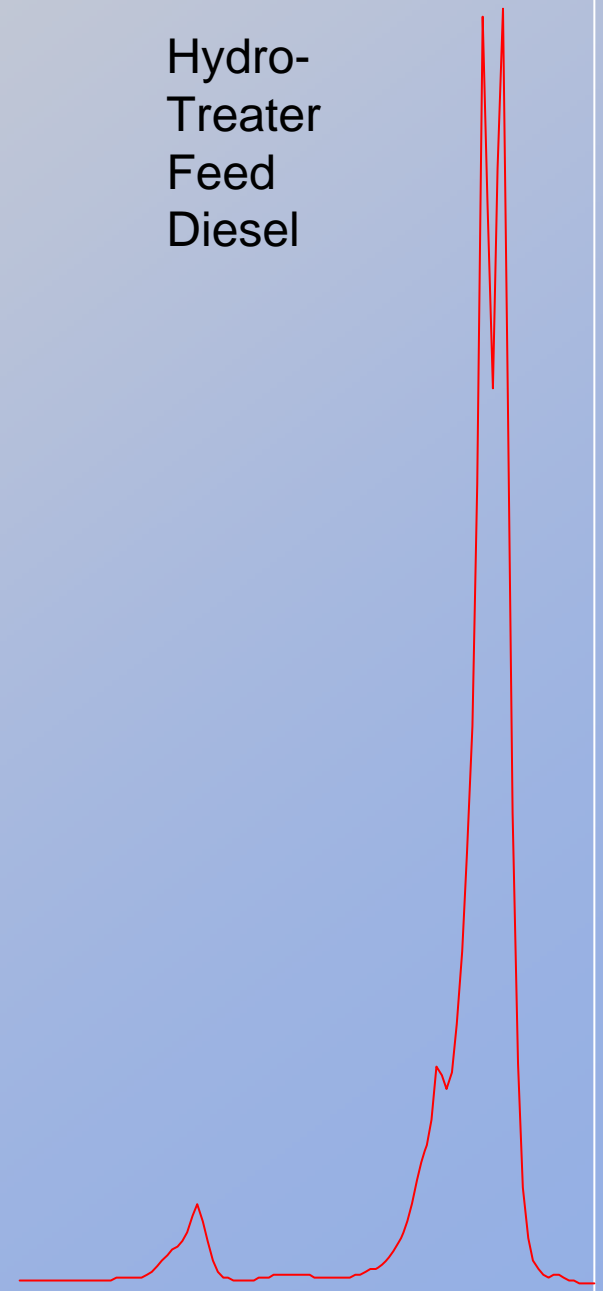
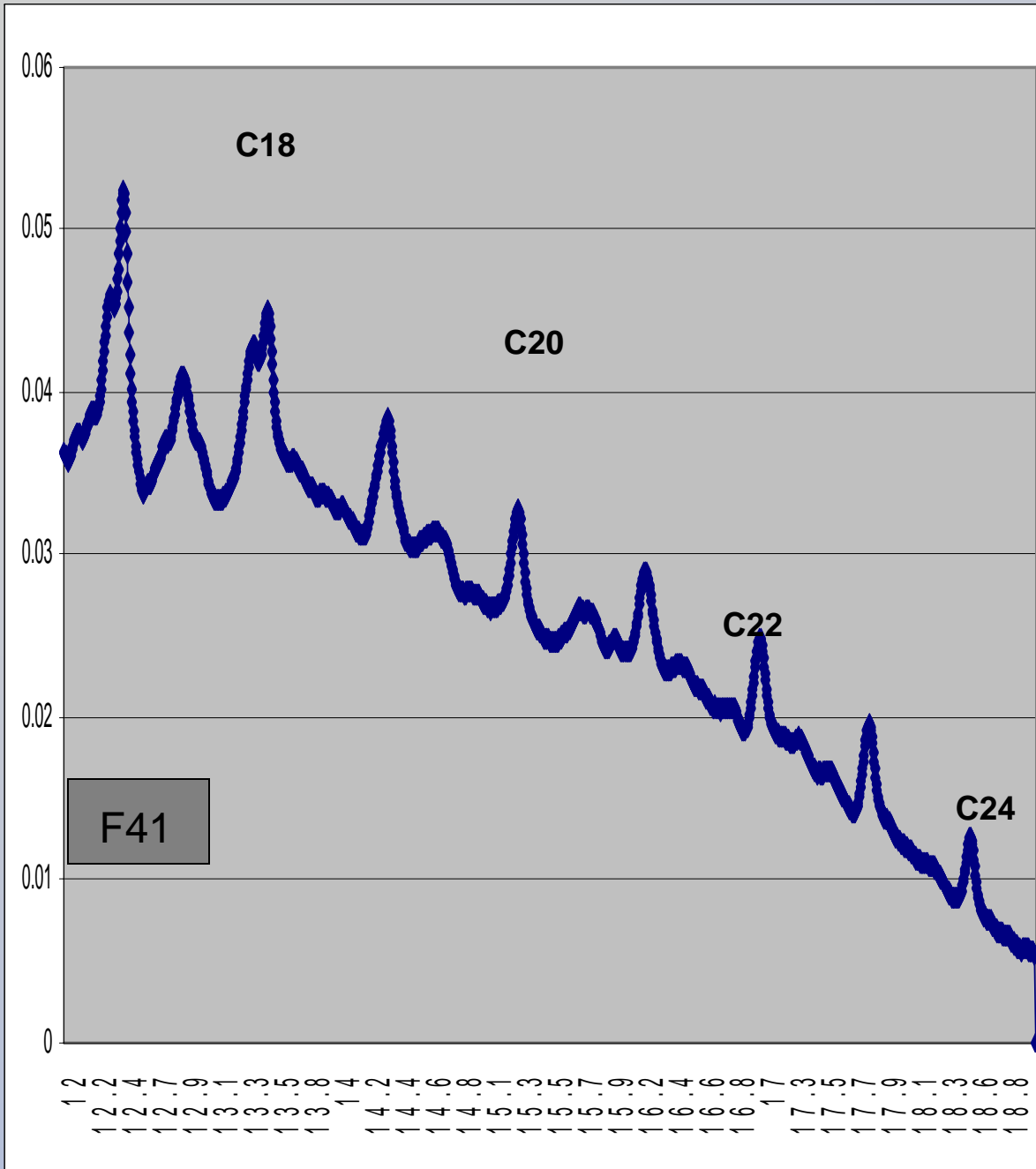


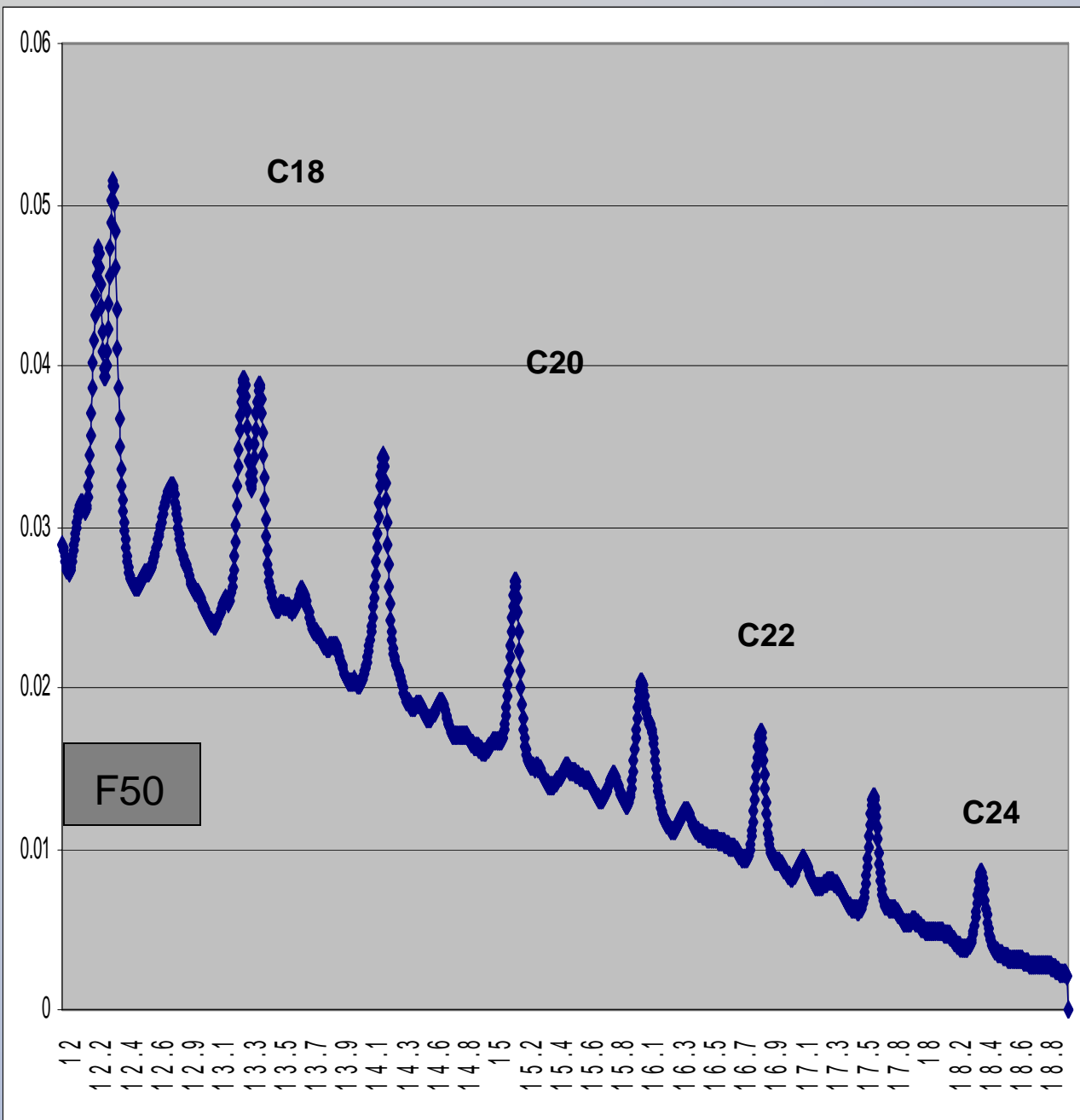


Coker
Diesel

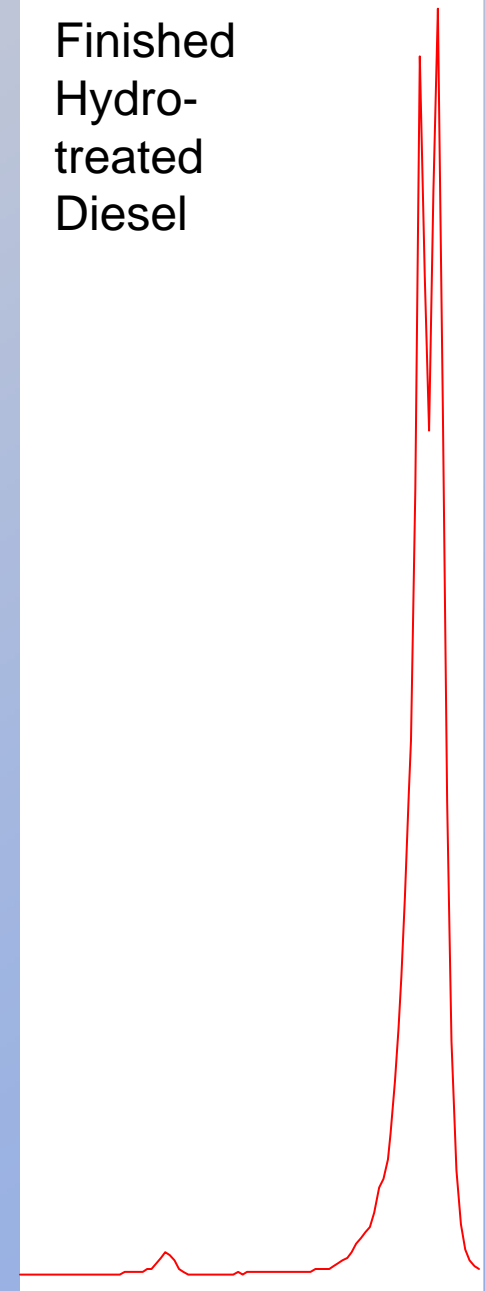


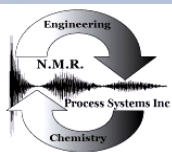
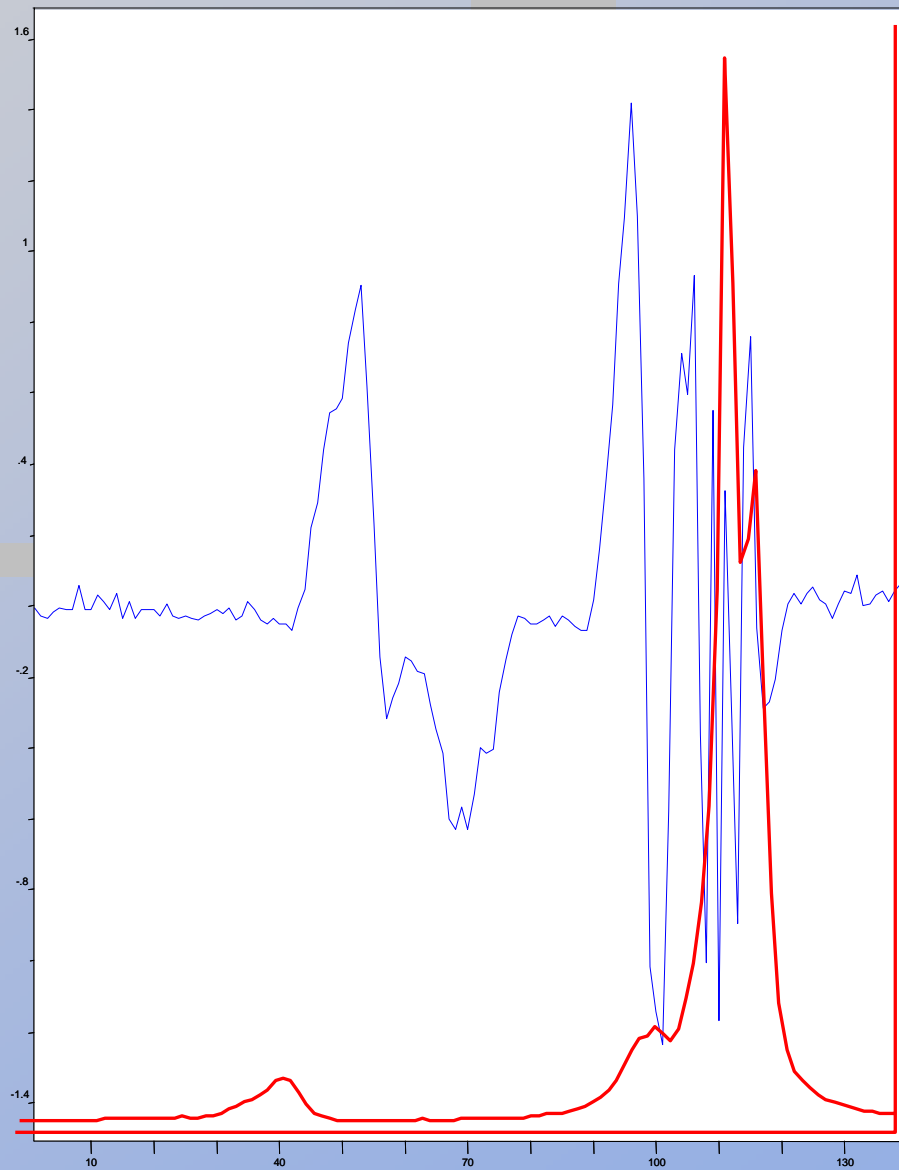
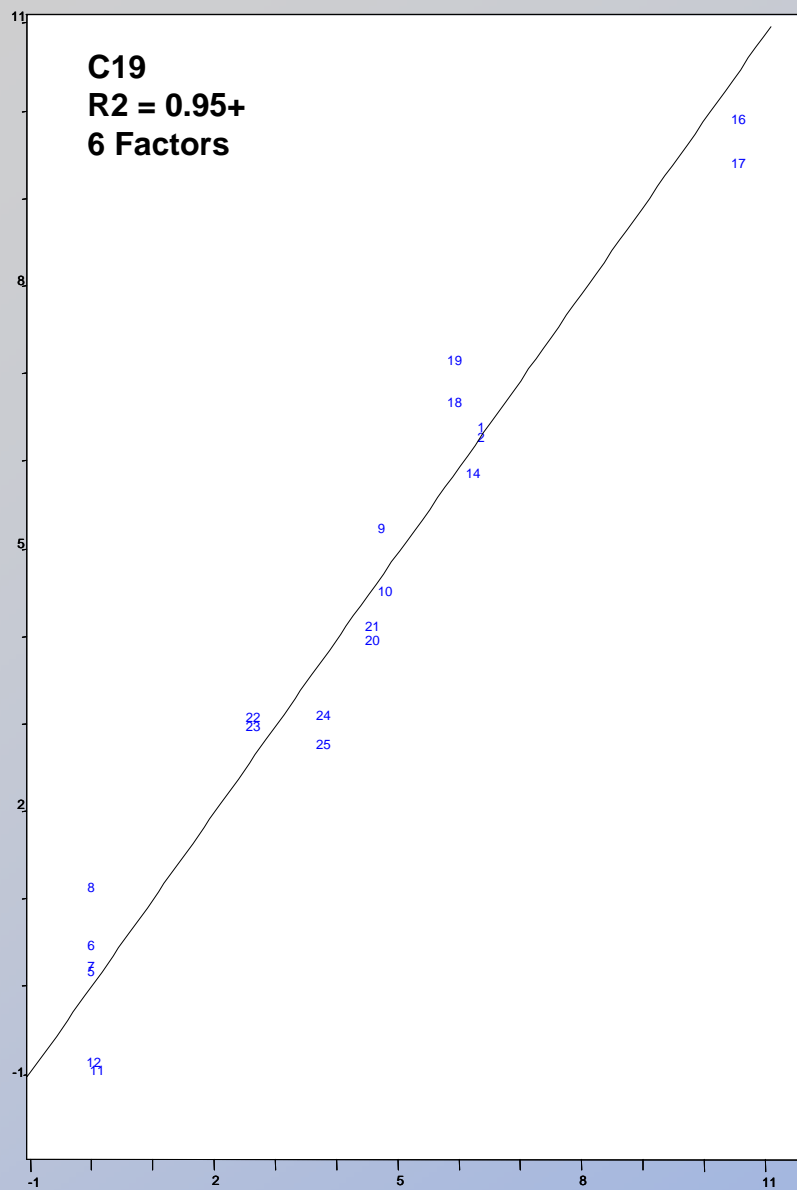
Hydro-Treater
Feed
Diesel





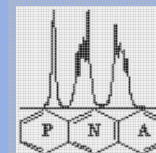
Finished
Hydro-
treated
Diesel

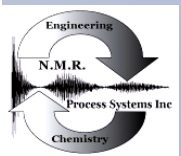
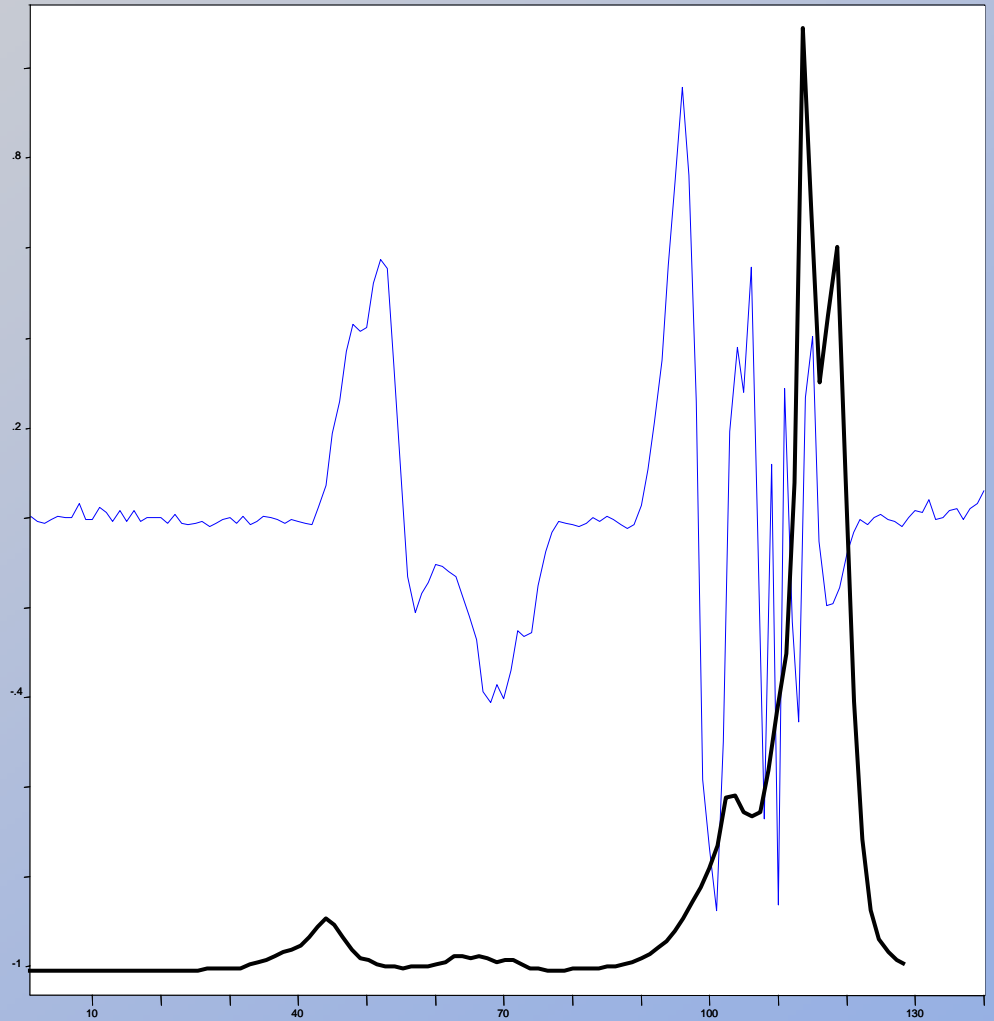
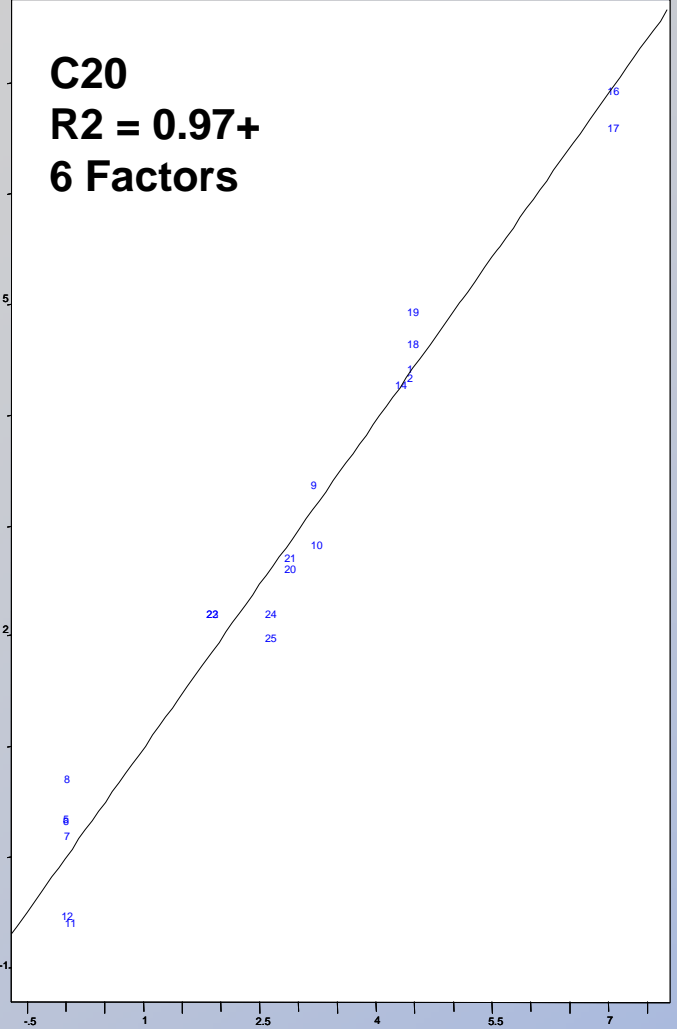




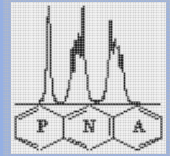
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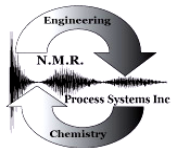
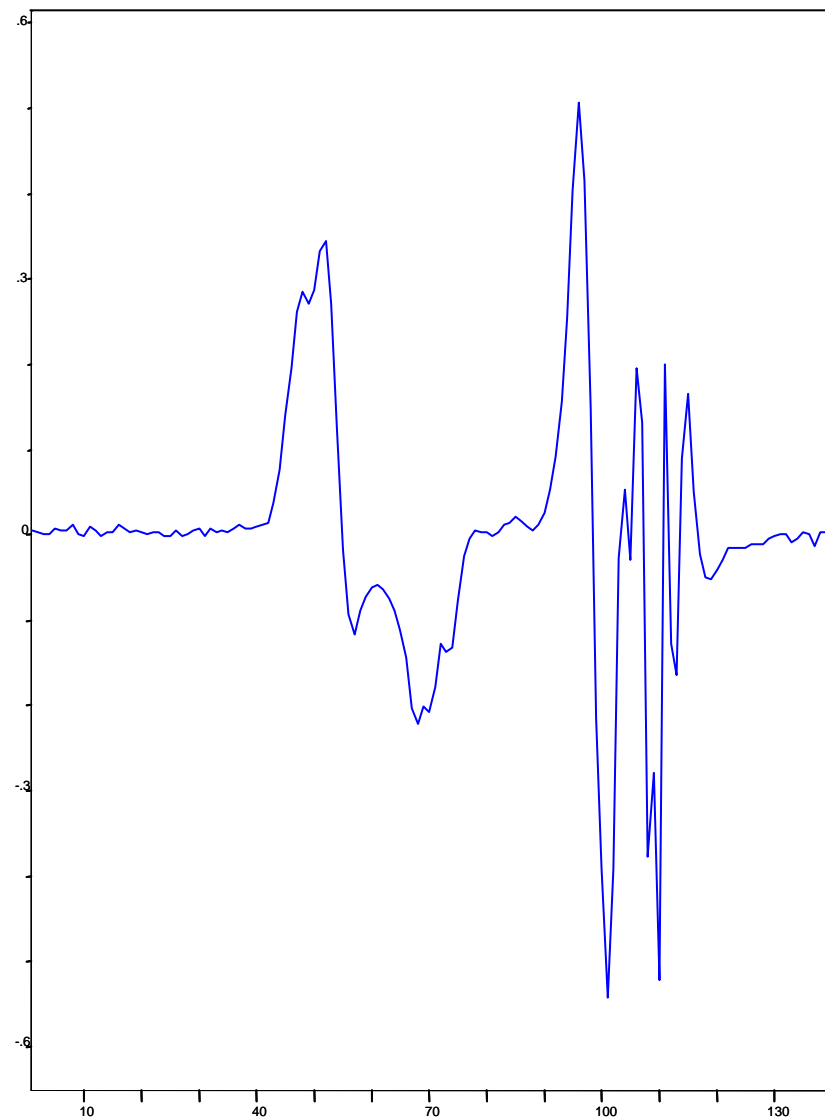
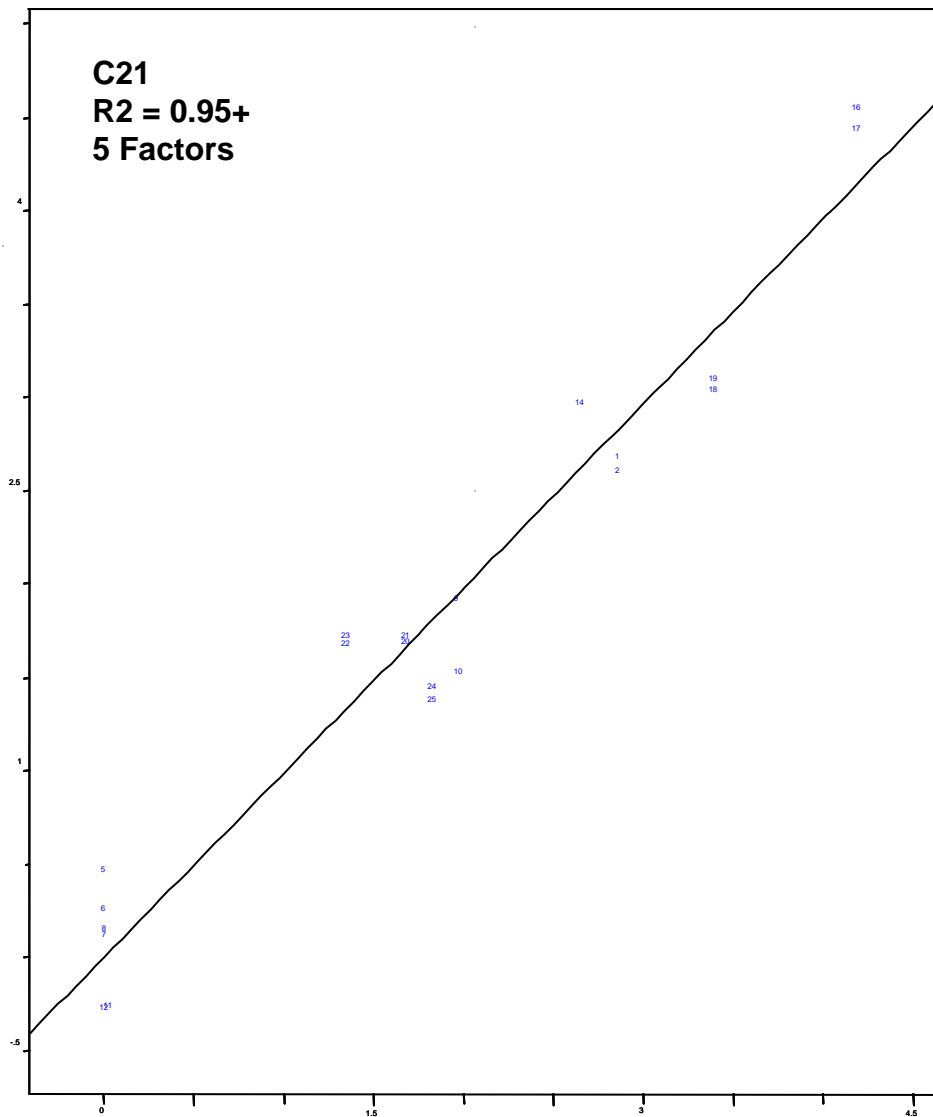




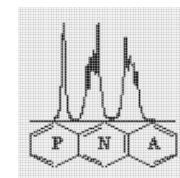
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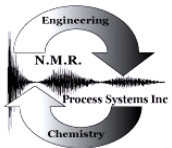
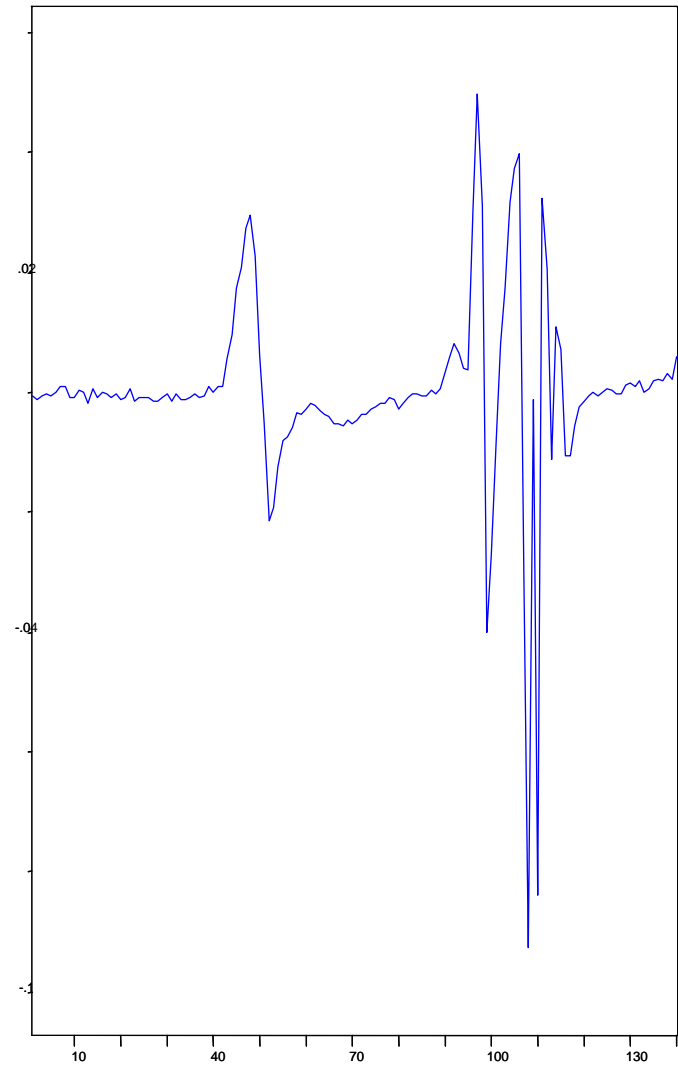
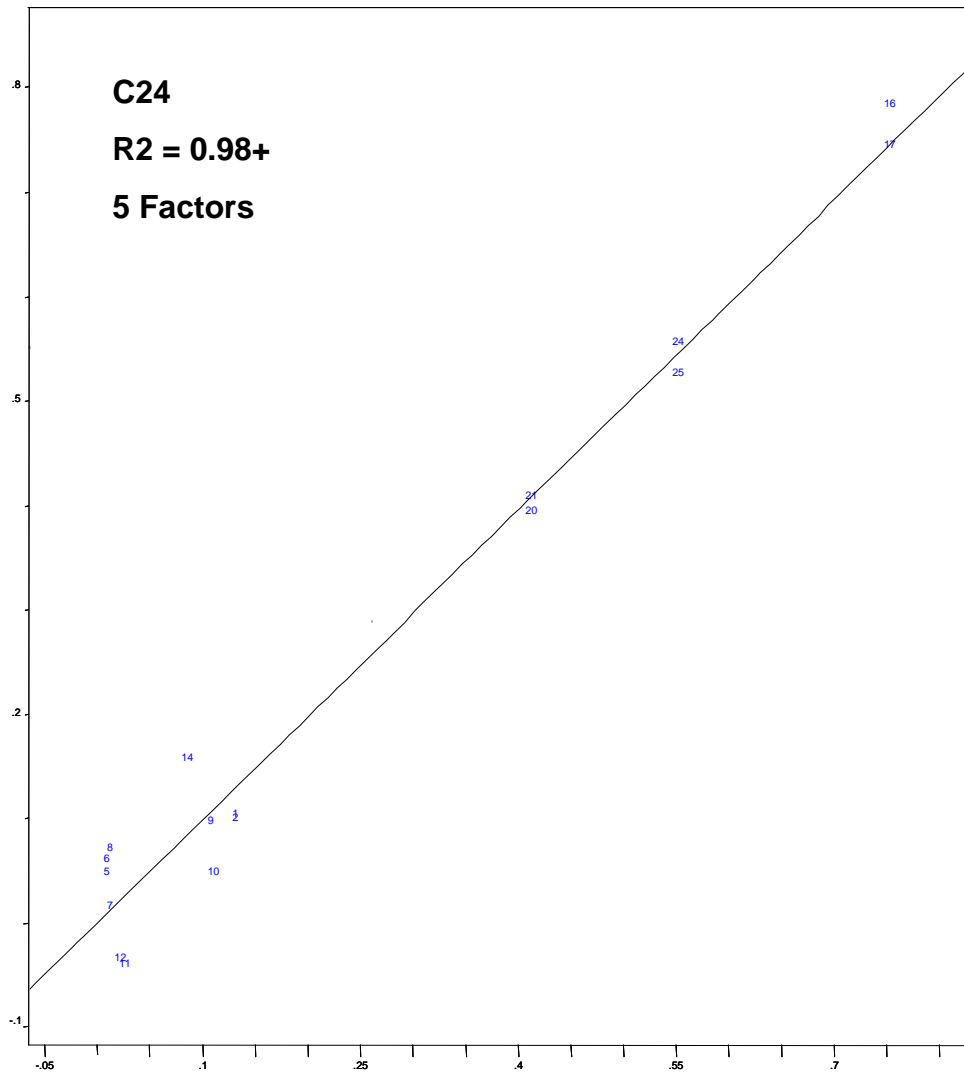
diesel simdis c21 102208.tbl.4 (R² = 0.954273416)



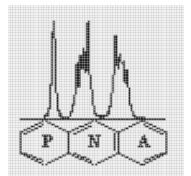
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diesel simdis c24 102208.tdf.4 (R² = 0.977496922)



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Existing NMR Technology

Kero

T5, T10, T50, T90, T95

Cetane, Freeze Pt,
Naphthalenes

Kero PA

T5, T95, Cetane

Diesel

T5, T10, T50, T90, T95

Cetane, Cloud Pt, Pour
Pt

Diesel PA

T5, T95, Cetane

Gas Oils

T5, T10, T50, T80
(D2887)

plus

New Developments

Di Benzyl Thiophene co-boilers

•Volatility close to certain C19
aromatics

•Control tail of diesel to HT

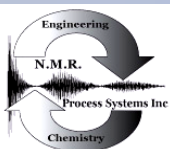
HOW?

There are several strategies that can be implemented:

1. NMR predicted TBP measurements of diesel and kero. As shown by our work in predicting full TBP curves on crude, this would be a very accurate approach to pushing the thiophene limit.
2. NMR predicted carbon number and aromatic ring distribution. These can be done using ASTM mass spec primary measurements (i.e. D2425), detailed hydrocarbon analyses correlation to isoboilers, or via carbon-13 NMR determined aromatics, naphthenes, and paraffin values.

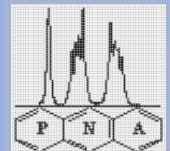
SPECTRO-MOLECULAR CONTROL TO ENHANCE DIESEL RECOVERY

On-line NMR based analytical and process control strategy for enhanced diesel recovery at the crude distillation unit. This solution maximizes clean diesel recovery by enabling closer cut point control in the mid-section of the CDU thereby reducing dibenzyl thiophene breakthrough downstream to the Hydrotreater.



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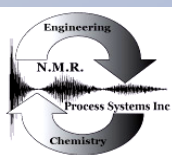


Questions?

NMR Process Systems, Inc.

NMR Process Systems, Inc. is a joint venture company between Process NMR Associates, LLC (Danbury CT), and TTC Labs Inc. (Fond du Lac WI). NPS markets, installs and supports process NMR and other technology solutions for control and optimization in the refining, petrochemical, pharmaceutical and food industries.

NPS is now advancing new concepts in process analysis by offering integrated analytical solutions into its product slate. Integrated NMR, NIR and other analyzer solutions offer strategic reliability, sampling, and control benefits to the end user.



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