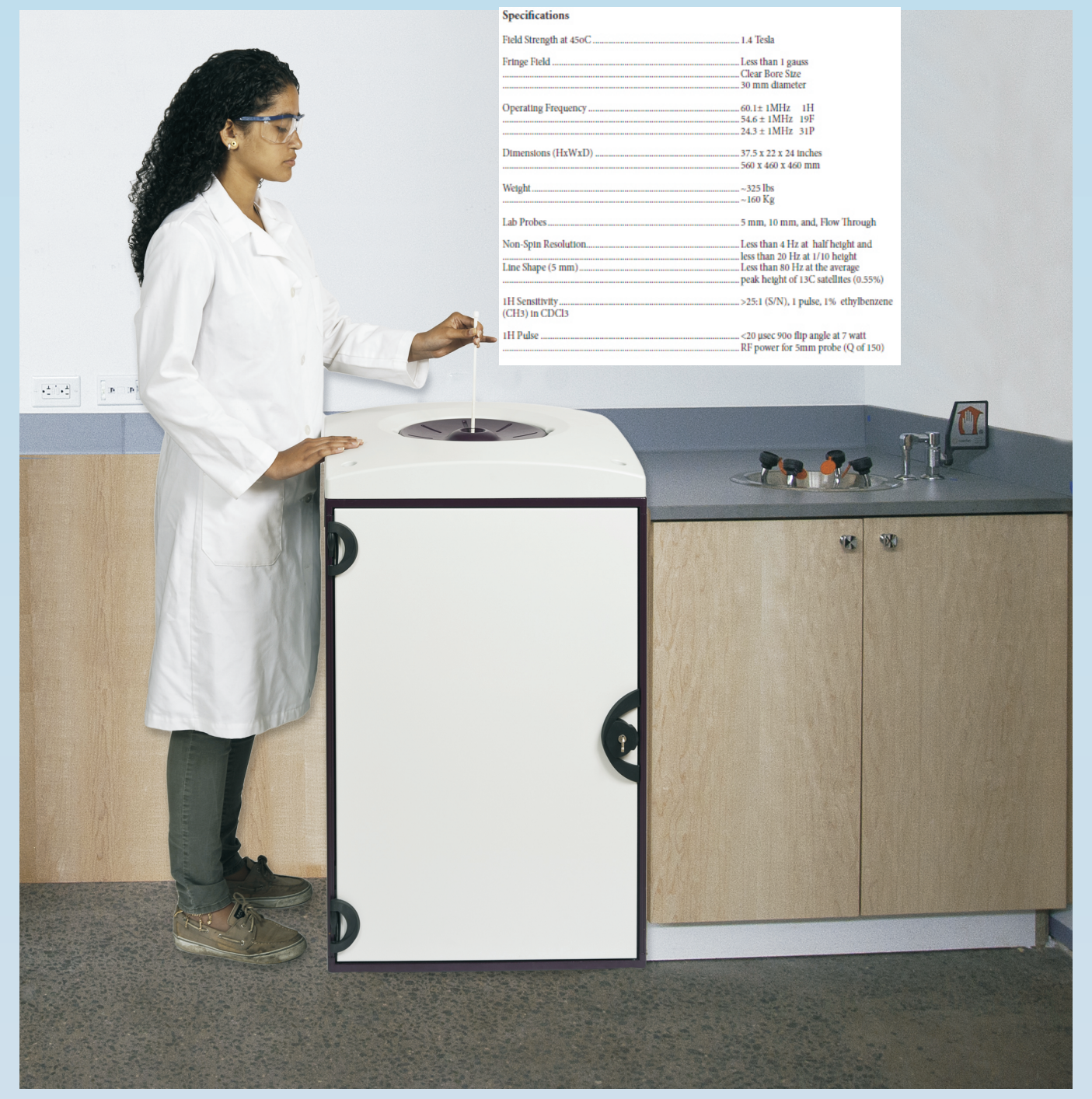
# New Developments in Compact High Resolution NMR Technologies: Multi-Nuclear Applications for Laboratory, At-Line, On-Line and Process Control

**Paul J. Giammatteo** and John C. Edwards, Process NMR Associates, LLC,
87A Sand Pit Road, Danbury, Connecticut 06810, and,
Tal Cohen, Aspect AI, 27 Hashaked Street, Industrial Area Hevel Modi'in,
PO Box 926, Shoham 60850, Israel

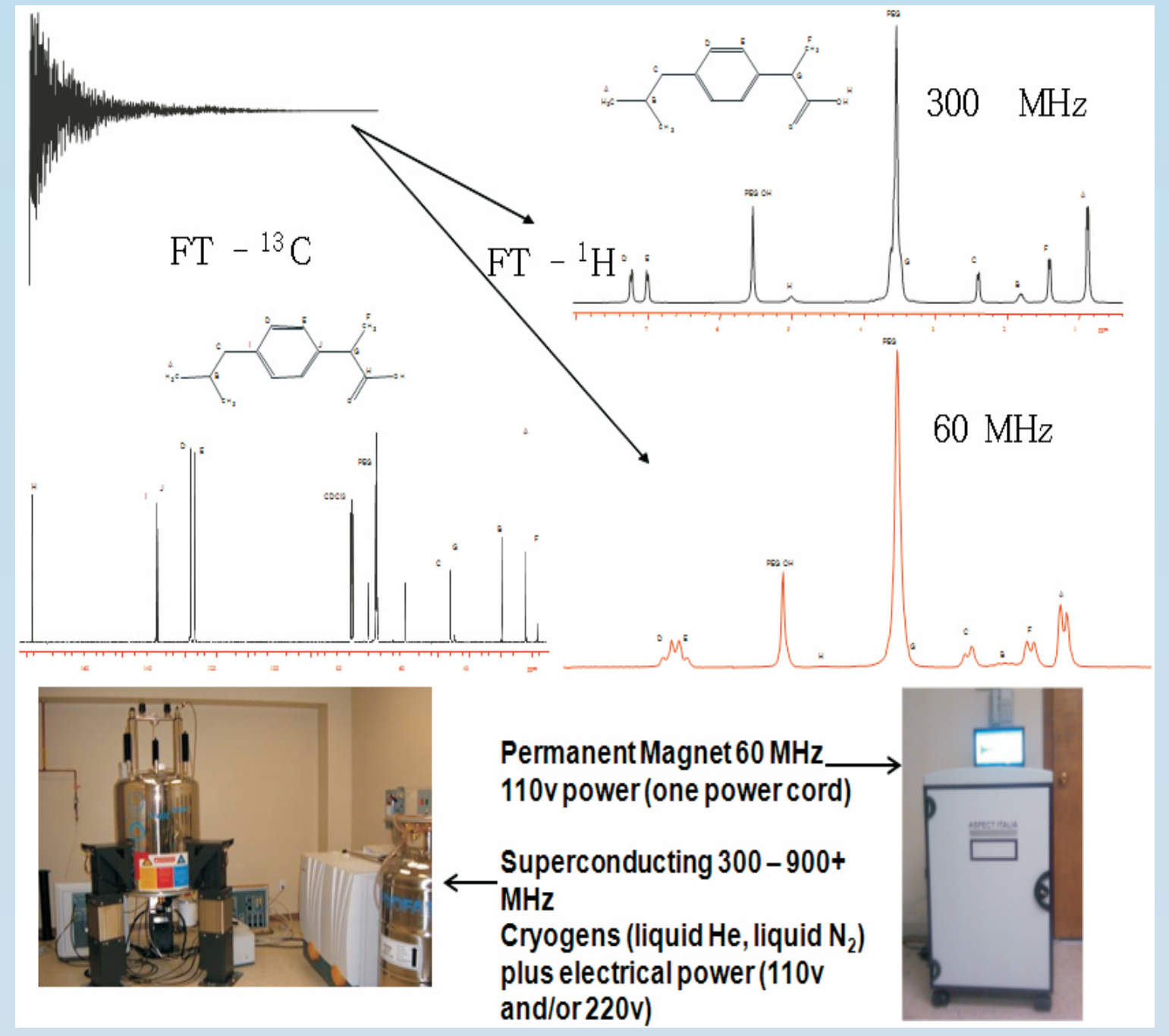
## ABSTRACT

On-line high resolution NMR analyses ranging from gasoline manufacturing to butter production, from control of polyethylene manufacturing to performing crude oil assays, and, for process control and product quality evaluations, have been on-going for almost two decades. This presentation introducse the next generation of compact high resolution NMR systems: The Aspect AI-60 high resolution FT-NMR. The Aspect AI-60's break-through technologies in permanent magnet, electronics, and, software expands the utility of multi-nuclear NMR analyses beyond traditional high field NMR analyses. Cryogen free and without the requirements for deuterated solvents the Aspect AI-60 enables fully automated NMR analysis capabilities in laboratory, at-line and on-line applications. The AI-60's design enables the use of a variety of sampling options from traditional 3mm, 5mm, and 10mm NMR tubes, to low volume (<5ml) continuous flow (2-20ml/min) cells for HPLC detection and/or reaction monitoring, to on-line process measurements. Examples of applications in continuous reaction monitoring, at-line phosphorus NMR reactor monitoring,



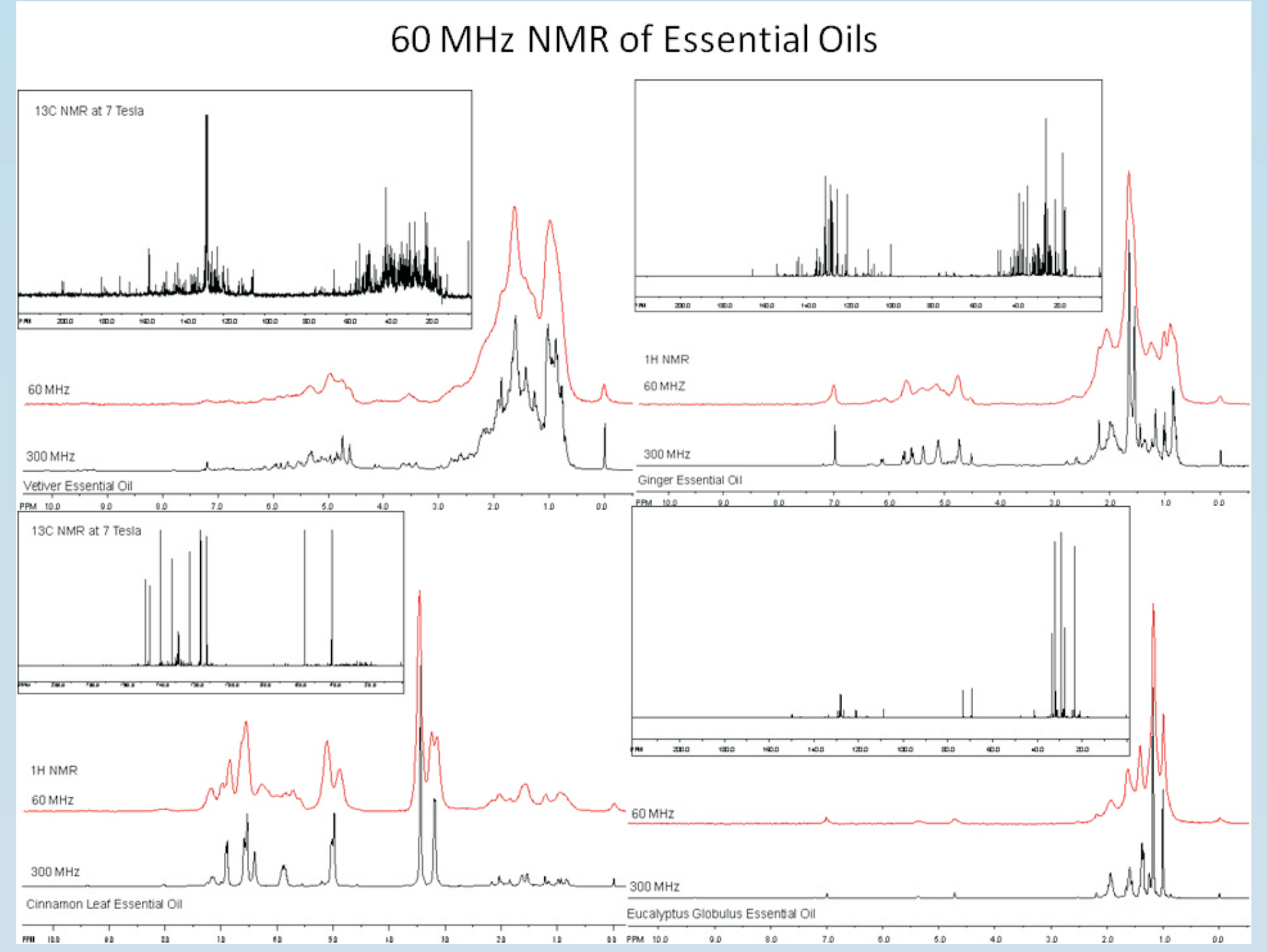
**Specifications**

| | |
|---|---|
| Field Strength at 45oC | 1.4 Tesla |
| Fringe Field | Less than 1 gauss<br>Clear Bore Size<br>30 mm diameter |
| Operating Frequency | 60.1± 1MHz 1H<br>54.6 ± 1MHz 19F<br>24.3 ± 1MHz 31P |
| Dimensions (HxWxD) | 37.5 x 22 x 24 inches<br>560 x 460 x 460 mm |
| Weight | ~325 lbs<br>~160 Kg |
| Lab Probes | 5 mm, 10 mm, and, Flow Through |
| Non-Spin Resolution | Less than 4 Hz at half height and<br>less than 20 Hz at 1/10 height |
| Line Shape (5 mm) | Less than 80 Hz at the average<br>peak height of 13C satellites (0.55%) |
| 1H Sensitivity (CH3) in CDCl3 | >25:1 (S/N), 1 pulse, 1% ethylbenzene |
| 1H Pulse | <20 µsec 90o flip angle at 7 watt<br>RF power for 5mm probe (Q of 150) |

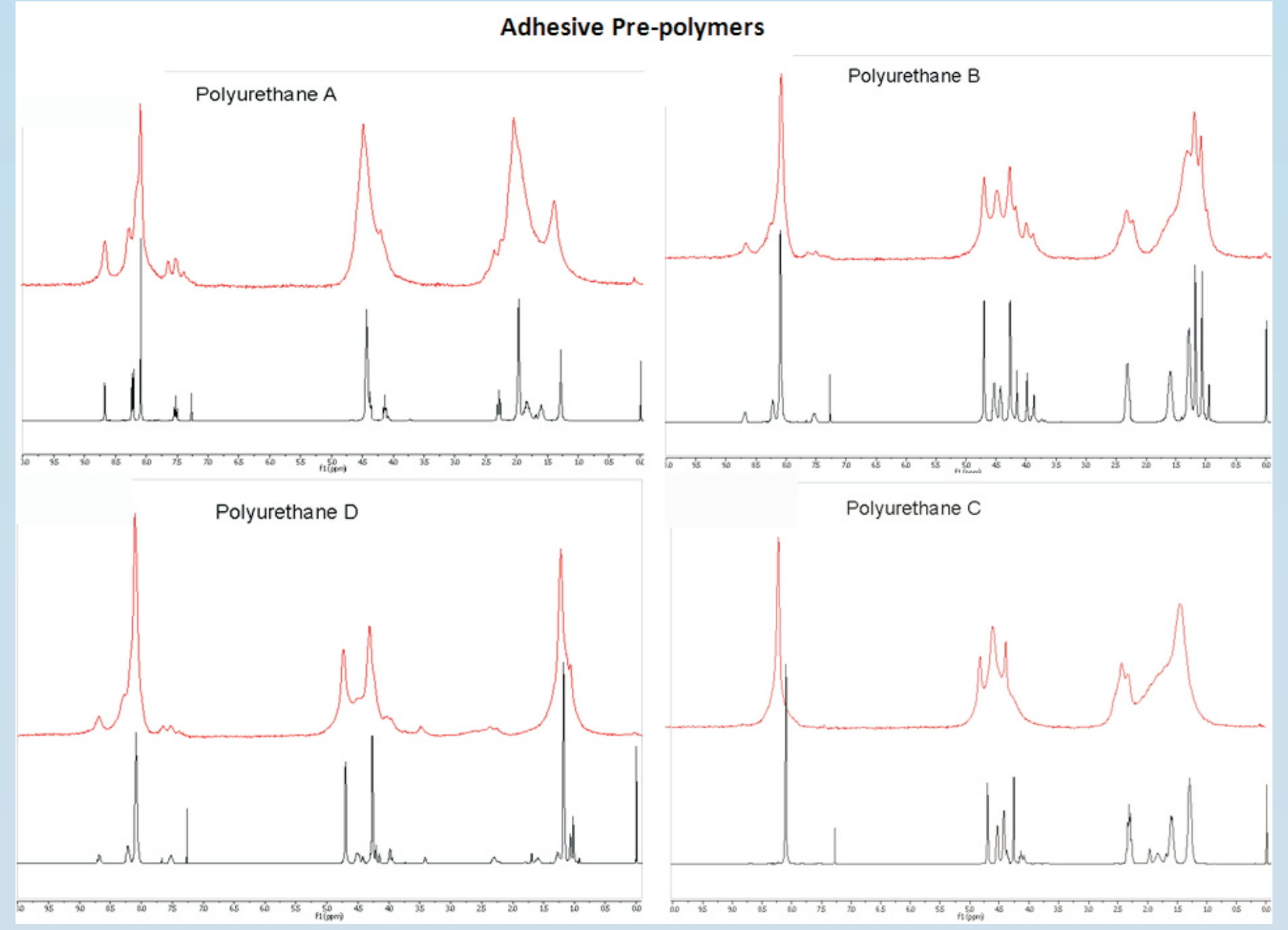


Permanent Magnet 60 MHz
110v power (one power cord)

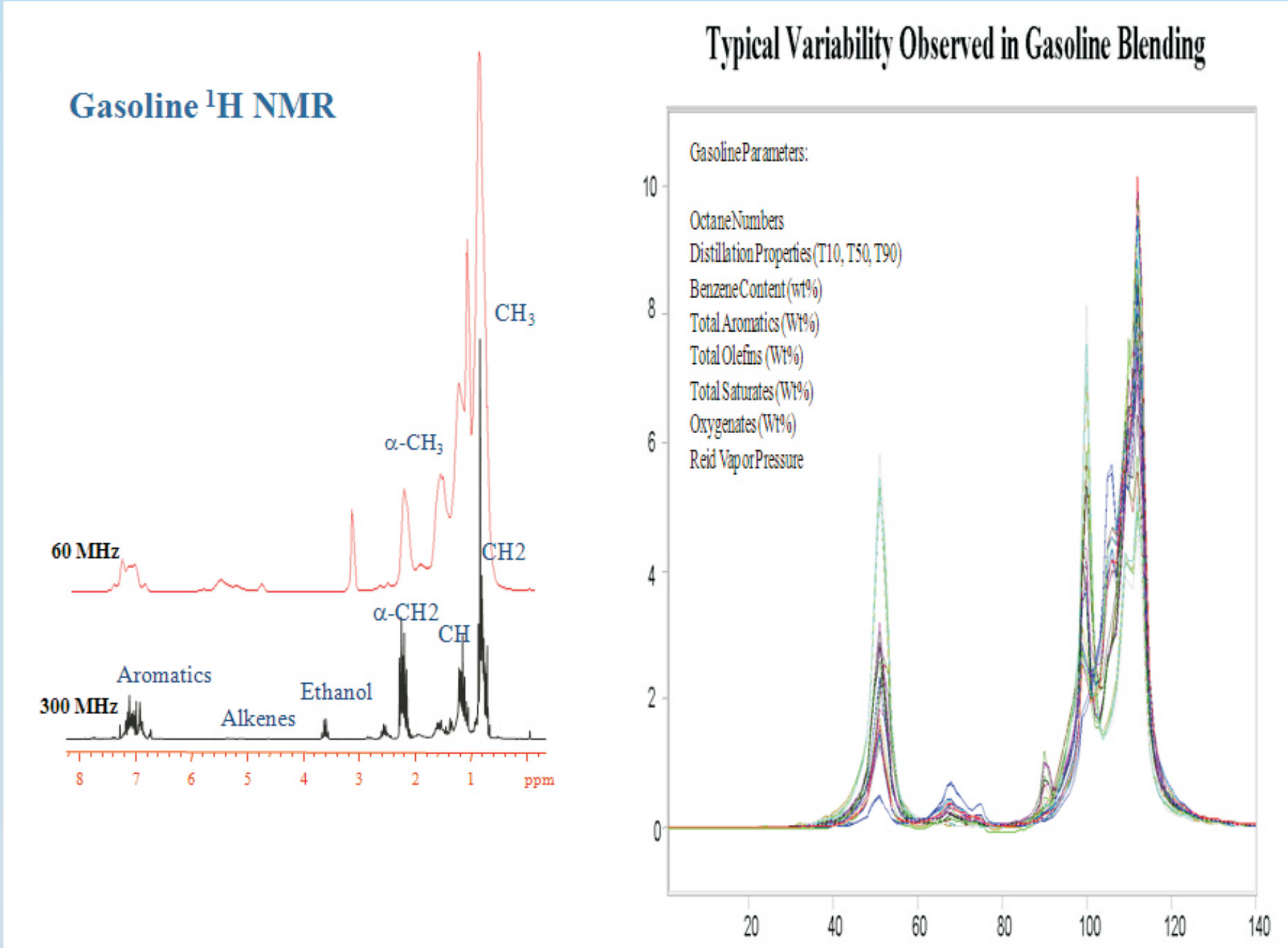
Superconducting 300 – 900+ MHz
Cryogens (liquid He, liquid $N_2$) plus electrical power (110v and/or 220v)



60 MHz NMR of Essential Oils

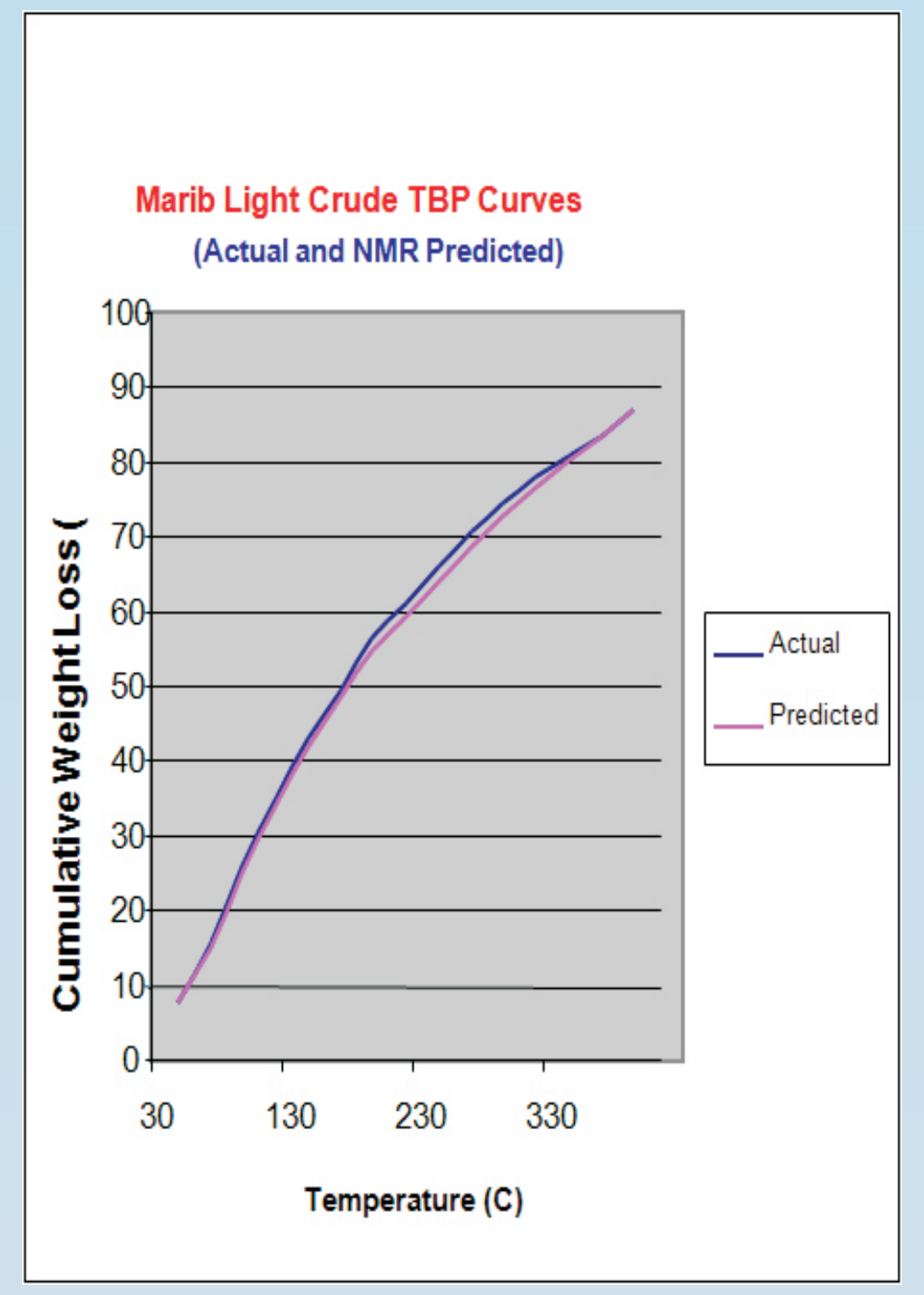


Adhesive Pre-polymers

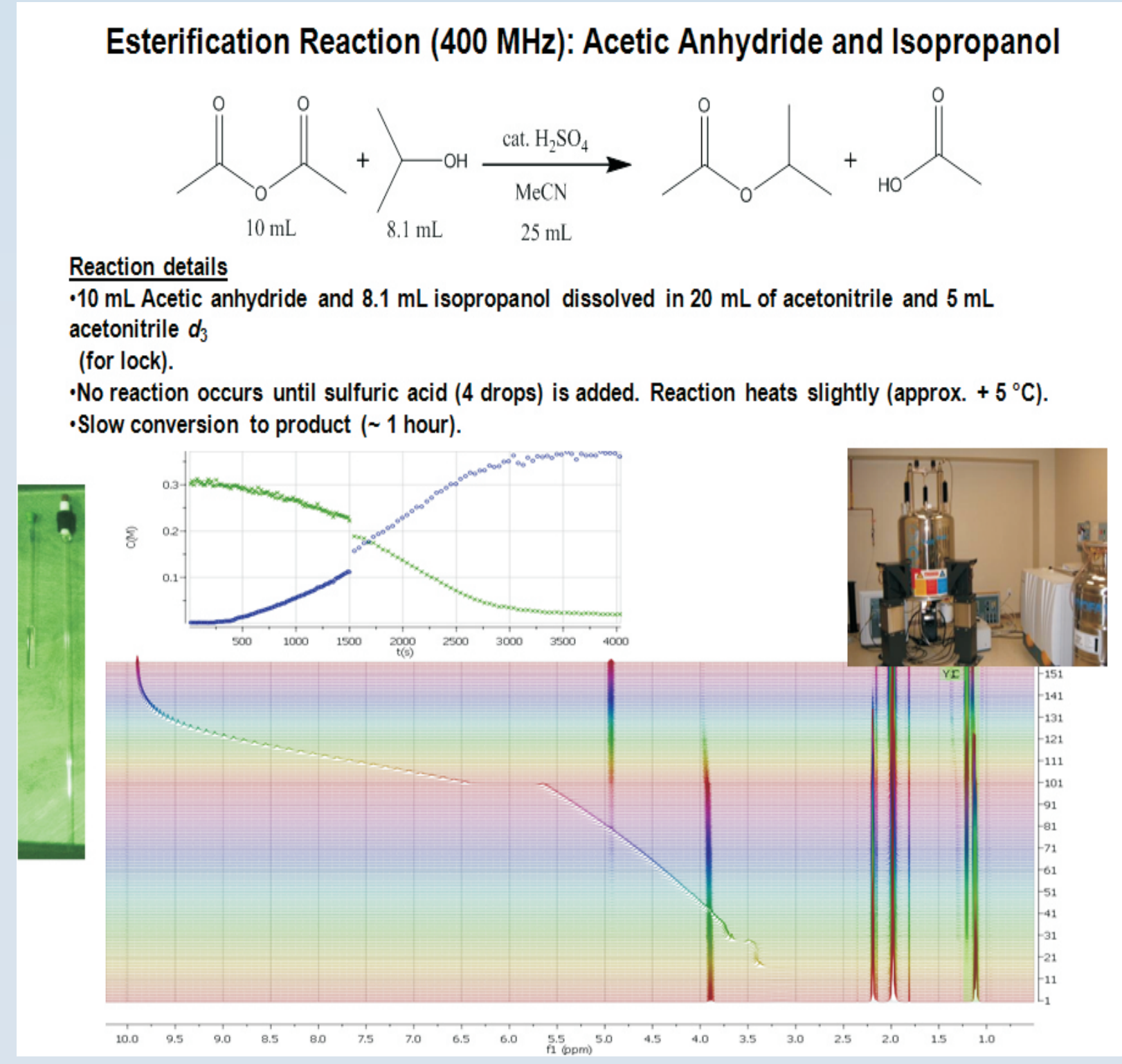


Gasoline $^{1}$H NMR

Typical Variability Observed in Gasoline Blending

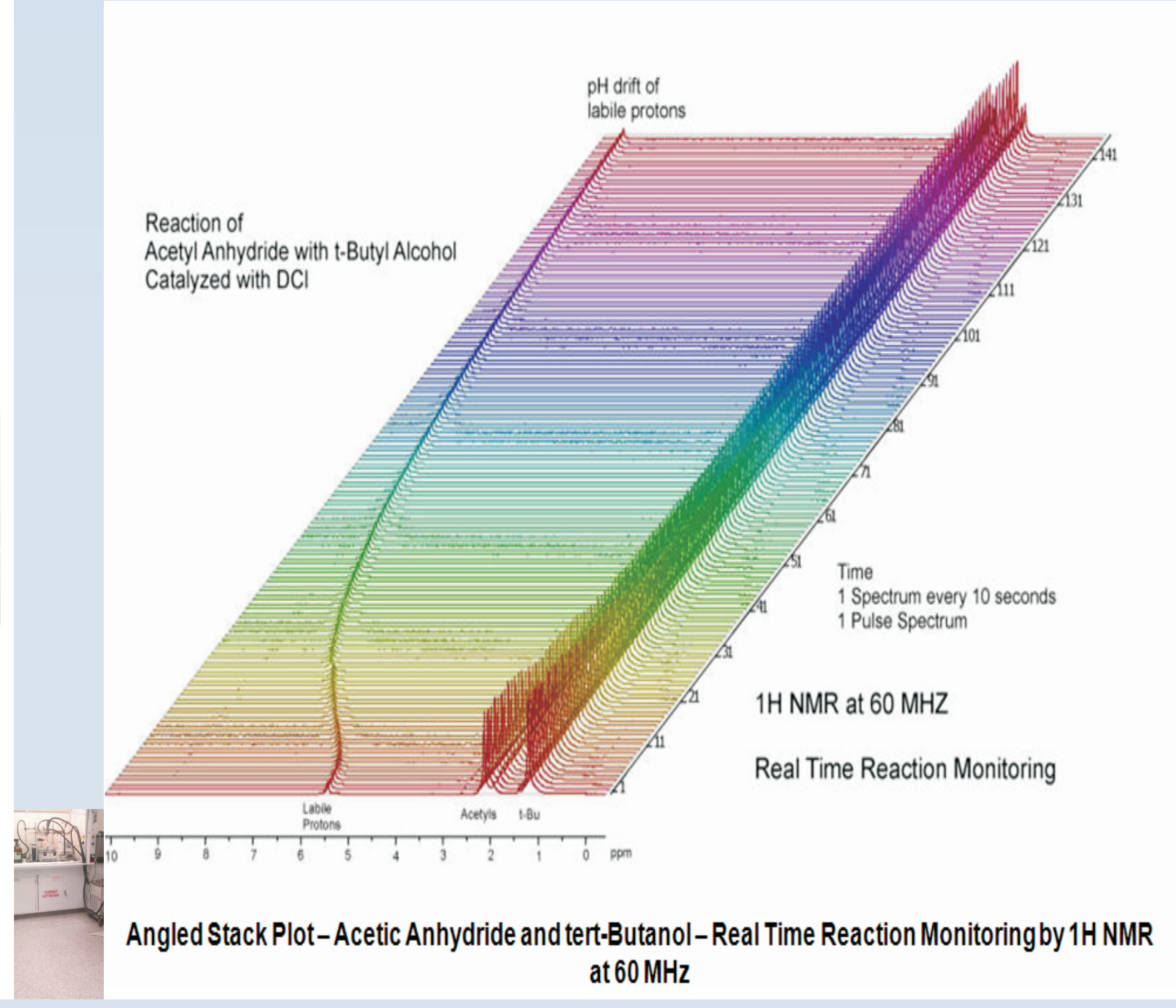


Marib Light Crude TBP Curves
(Actual and NMR Predicted)

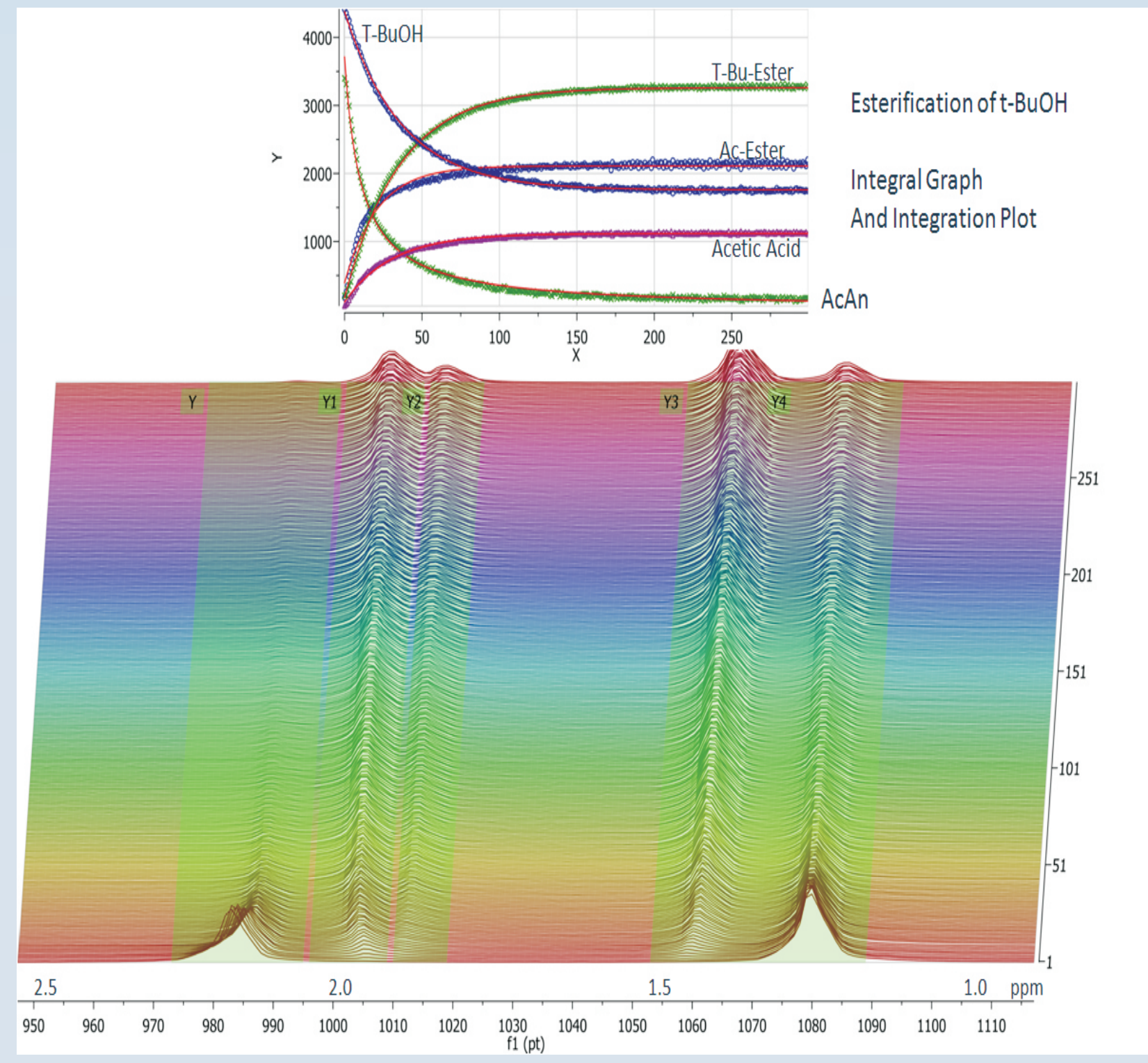


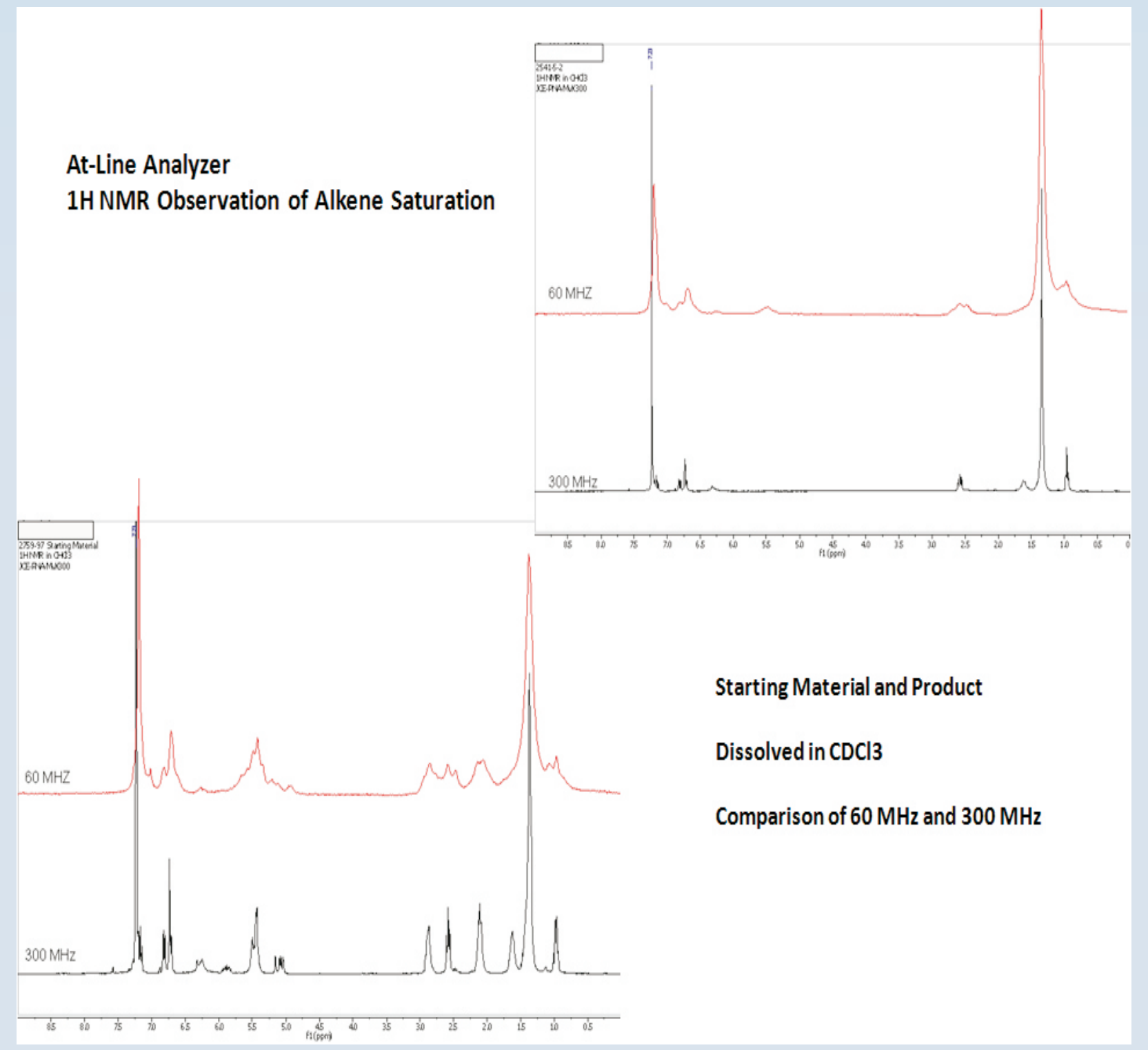
Esterification Reaction (400 MHz): Acetic Anhydride and Isopropanol

Reaction details
- 10 mL Acetic anhydride and 8.1 mL isopropanol dissolved in 20 mL of acetonitrile and 5 mL acetonitrile $d_3$ (for lock).
- No reaction occurs until sulfuric acid (4 drops) is added. Reaction heats slightly (approx. + 5 °C).
- Slow conversion to product (~ 1 hour).



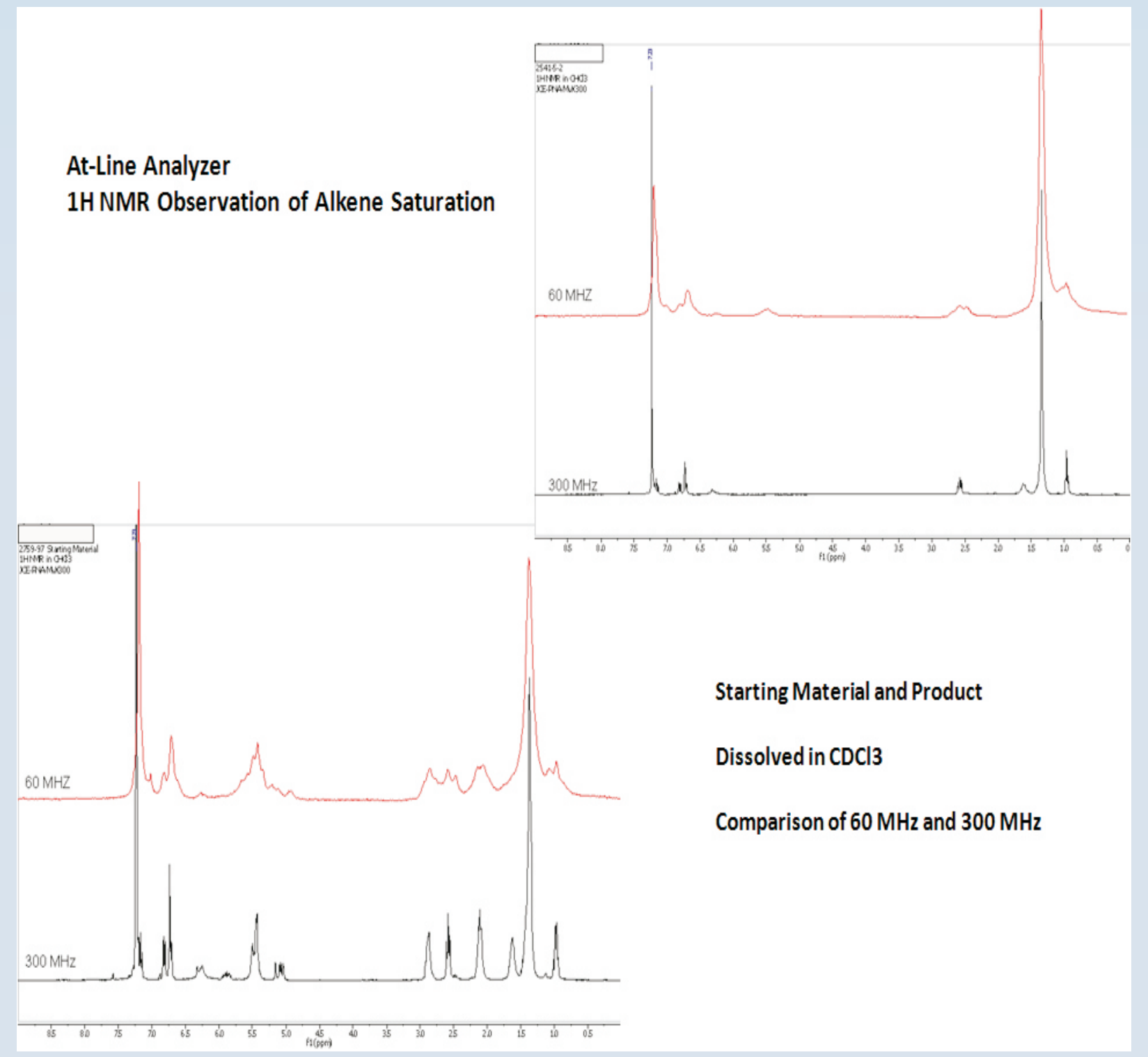
Angled Stack Plot – Acetic Anhydride and tert-Butanol – Real Time Reaction Monitoring by 1H NMR at 60 MHz





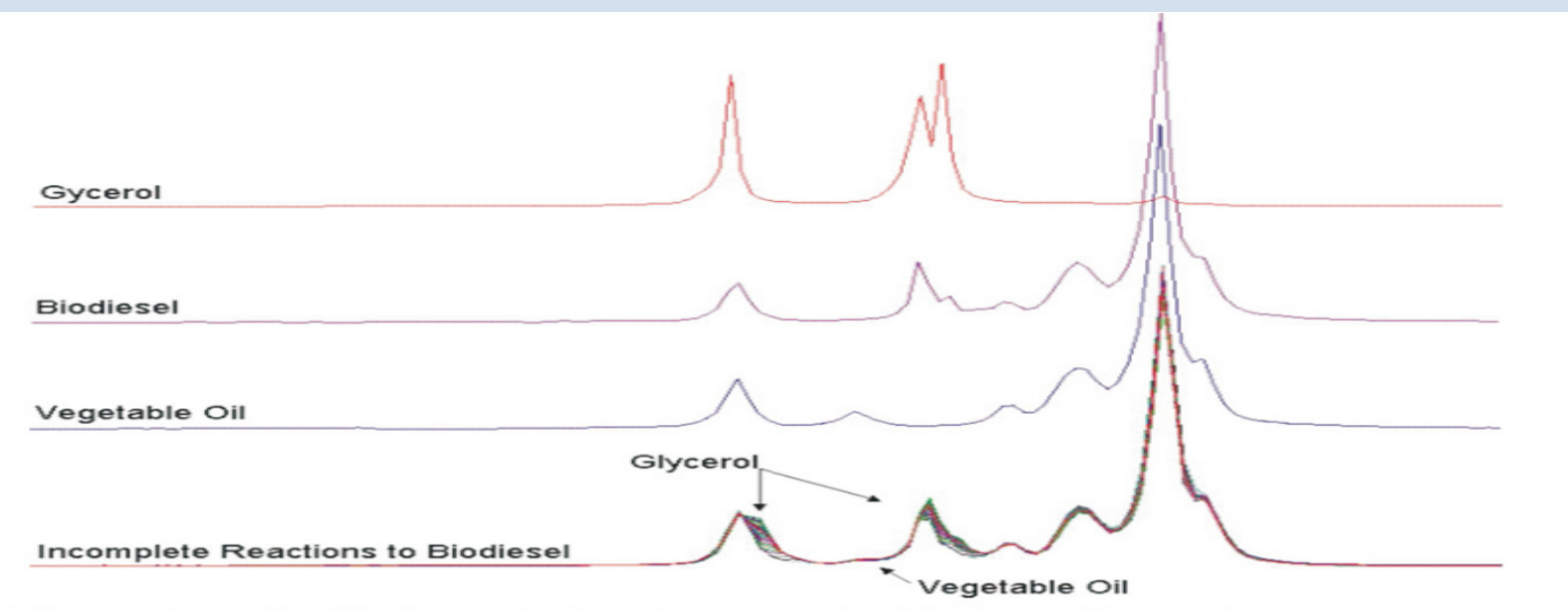
At-Line Analyzer
1H NMR Observation of Alkene Saturation

Starting Material and Product
Dissolved in CDCl3
Comparison of 60 MHz and 300 MHz

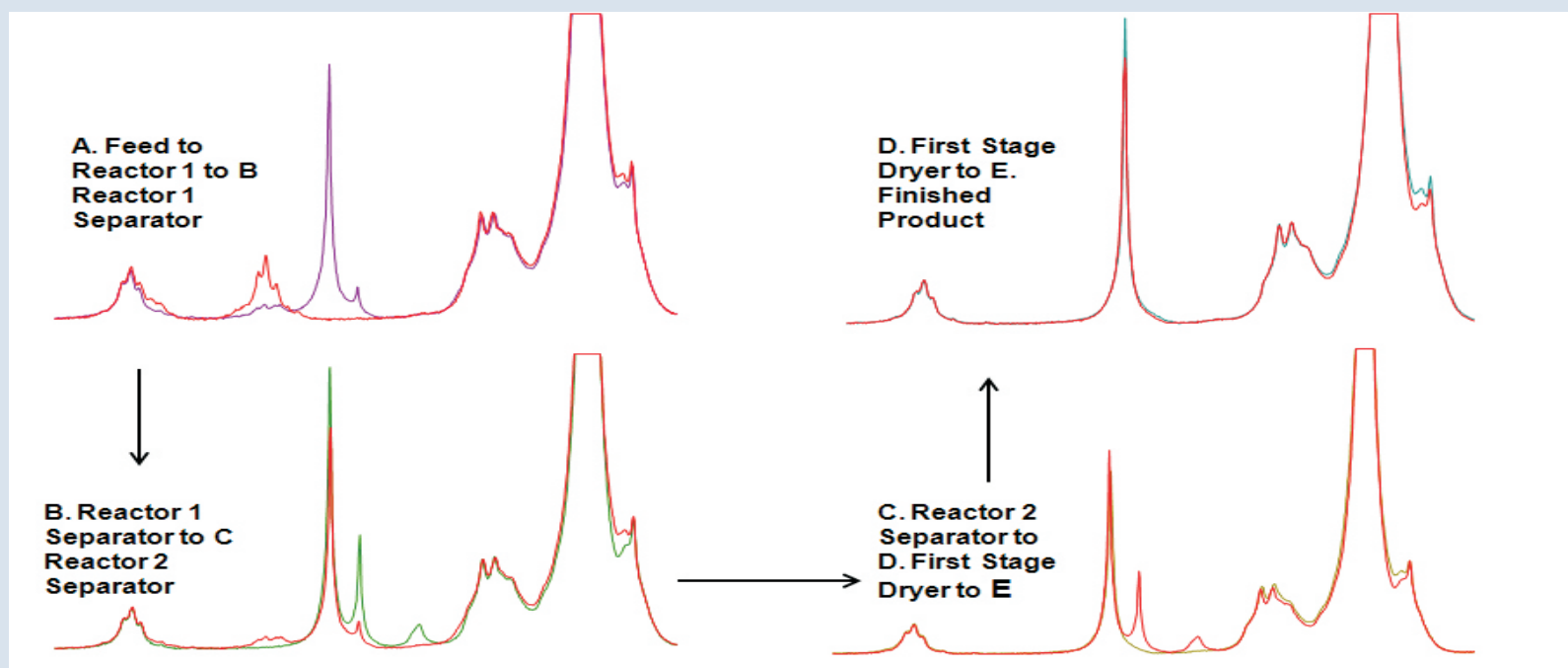


At-Line Analyzer
1H NMR Observation of Alkene Saturation

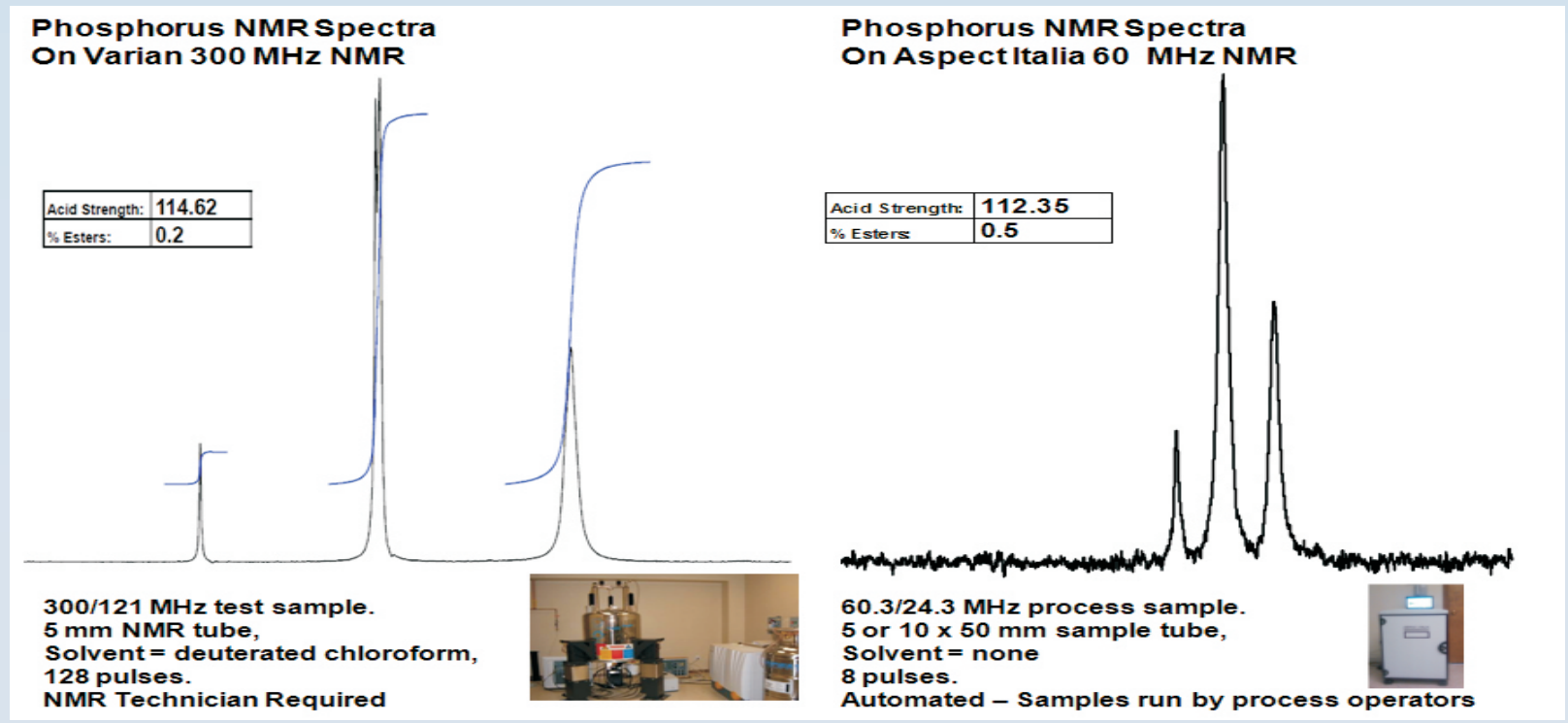
Starting Material and Product
Dissolved in CDCl3
Comparison of 60 MHz and 300 MHz



Glycerol content in the biodiesel or un-esterified vegetable oil can be determined easily from the spectrum. http://www.process-nmr.com/biodiesel.htm



60 MHz 1H spectra following biodiesel process: A. Feed to Reactor 1 Separator B. Reactor 1 Separator to Reactor 2 Separator C. Reactor 2 Separator to First Stage Dryer D. First Stage Dryer to Finished Product.



Phosphorus NMR Spectra
On Varian 300 MHz NMR

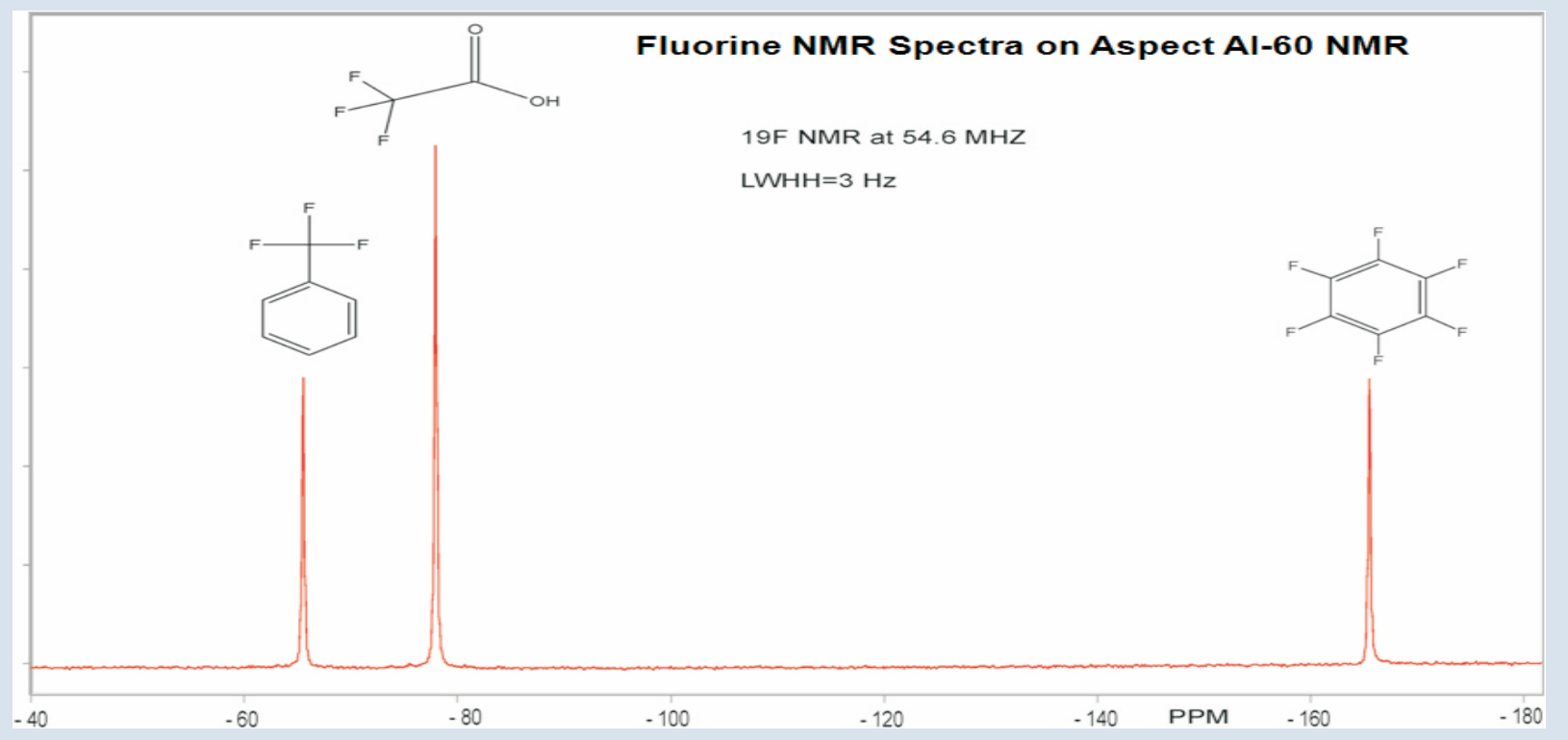
Phosphorus NMR Spectra
On Aspect Italia 60 MHz NMR

| | |
|---|---|
| Acid Strength: | 114.62 |
| % Esters: | 0.2 |

| | |
|---|---|
| Acid Strength: | 112.35 |
| % Esters: | 0.5 |

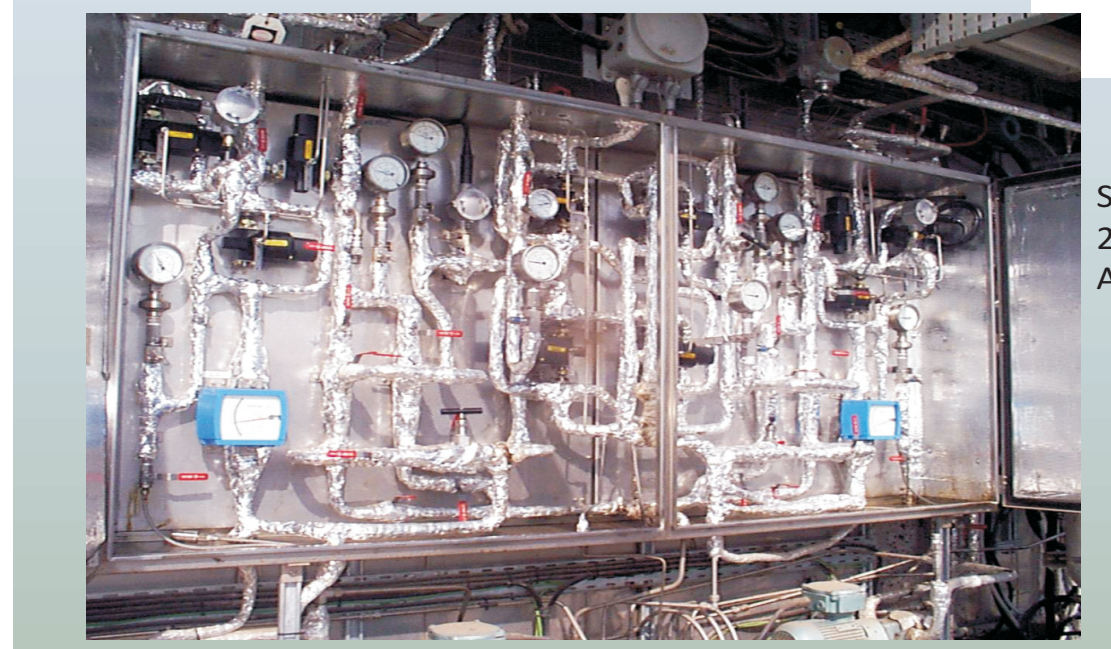
300/121 MHz test sample.
5 mm NMR tube,
Solvent = deuterated chloroform,
128 pulses.
NMR Technician Required

60.3/24.3 MHz process sample.
5 or 10 x 50 mm sample tube,
Solvent = none
8 pulses.
Automated – Samples run by process operators



Fluorine NMR Spectra on Aspect AI-60 NMR

2nd Generation NMR Analyzer
Qualion Ltd. 2003-2011

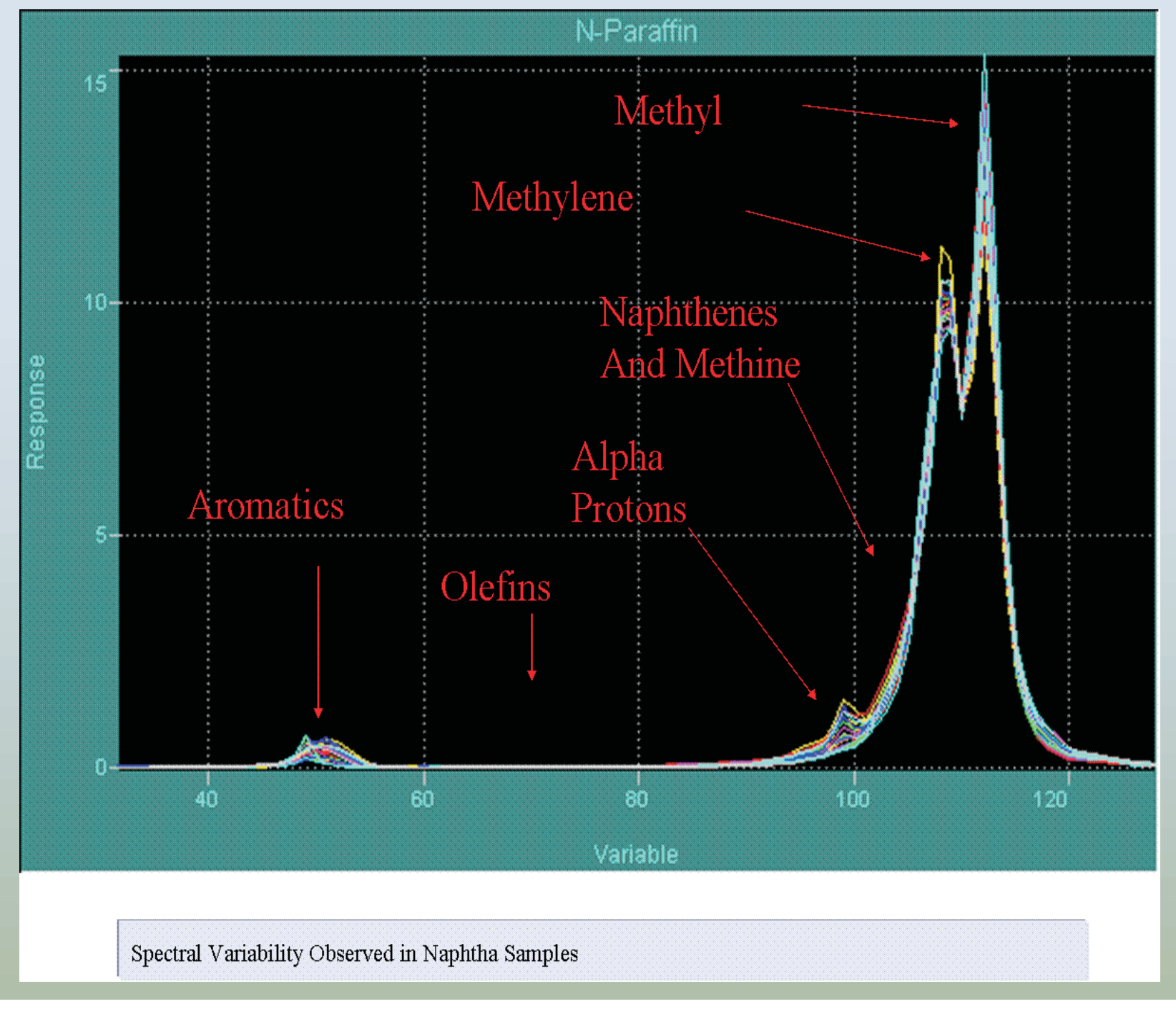


Sample system providing
2 conditioned streams to NMR Analyzer

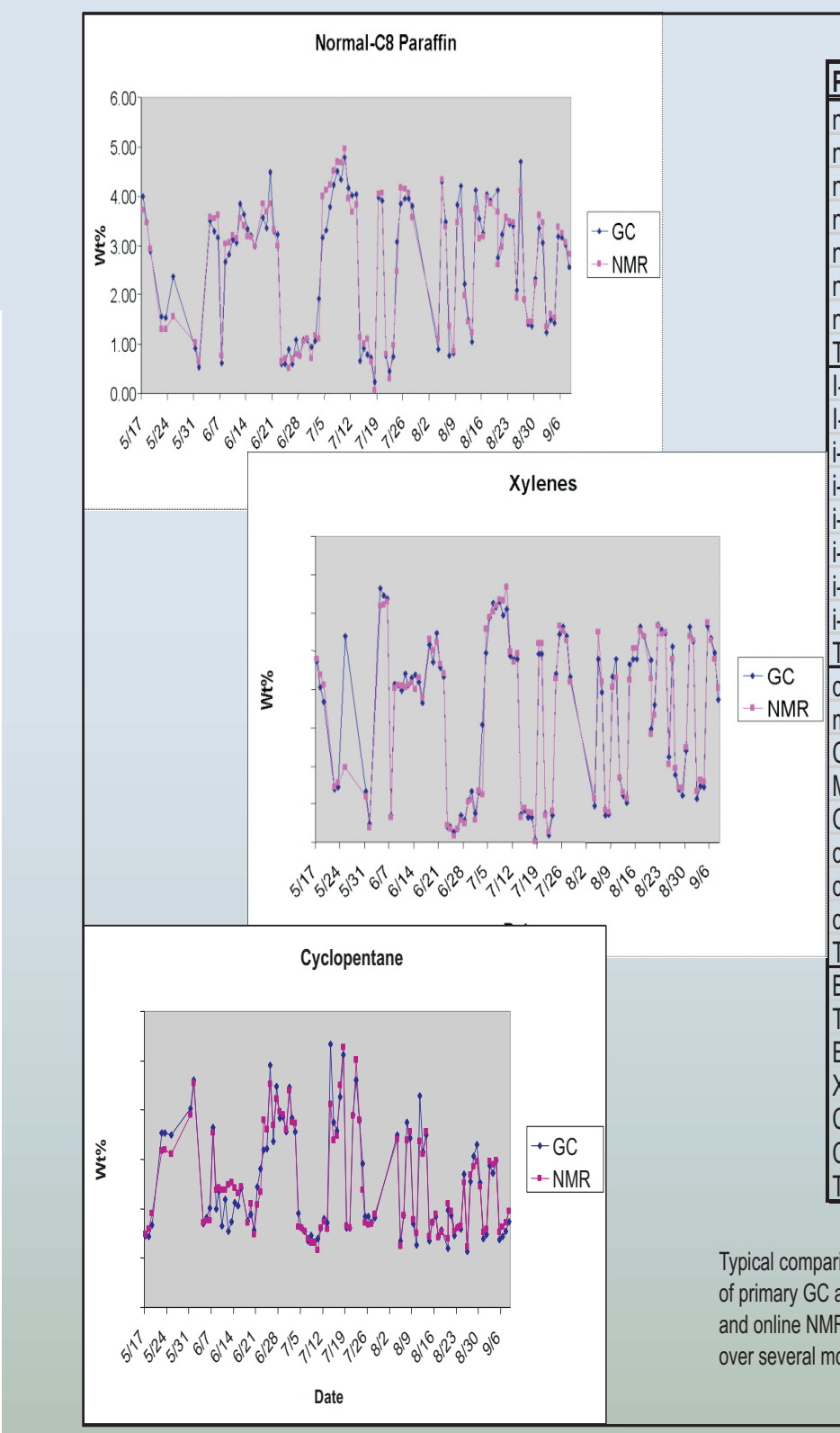
Typical NMR Analyzer Environment
Shelter House at Base of Vaccuum Tower

| Features | 3rd Generation | Advantages & Benefits |
|---|---|---|
| **Magnet**<br>Weight & Size<br>Field strength<br>Bore size<br>Mechanical | 170Kg; 40 x 40 x 45 cm<br>1.47 Tesla (60Mhz for H+)<br>30mm to 34mm<br>10 pieces | Improvement in the mechanical structure and enhances the overall magnet stability.<br>Better temperature insulation between magnet and the process probe. |
| **Process Probe** | Plain Ceramicpipe | Minimize heat transfer between samples and magnet. Better temperature insulation.<br>Increased reliability and robustness.<br>Higher Q (better SNR) |
| **Shim Coils** | 2 PC boards contain 40 copper coils, fit together as a SHIM cassette | Standardize location of the shim coils.<br>Additional thermal insulation.<br>Easy replacement of the SHIM cassette.<br>Elimination of cables & soldering. |
| **Hardware** | 3 Electronic units<br>Minimal wiring | Increased reliability.<br>Overall small foot-print. |
| **Software** | Windows XP or 7; | New algorithm for standard Models.<br>Fully automated process capacity.<br>Extensive remote diagnostic capabilities. |
| **Temperature Susceptibility**<br>Environment Fluctuations between streams | Must be within :±3°C<br>Should not exceed : ±10°C | Enables the analyzer to be applied to any stream, notwithstanding the temperature differences between them.<br>Simpler Sampling System. |

Example Application: Steam Cracking Optimization Installed at BASF, Ludwigshaven 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 Hydrocarbon PONA Analysis, Density
C4-C10 normal-paraffin, iso-paraffin, aromatics, naphthenes



Spectral Variability Observed in Naphtha Samples

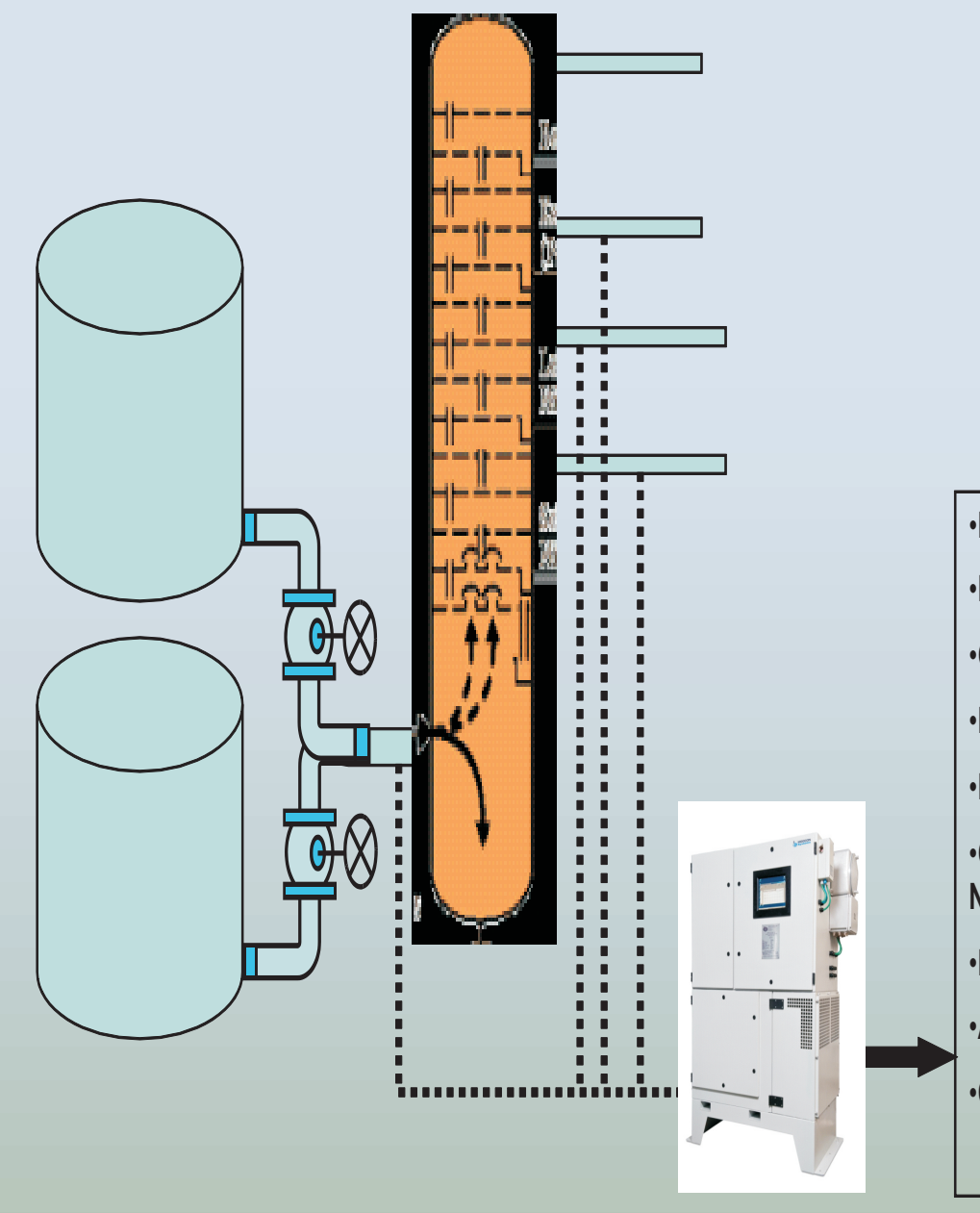


| Parameter | R | Std Dev | Mean Dev |
|---|---|---|---|
| n-c4 | 0.9340 | 0.52 | 0.067 |
| n-c5 | 0.9761 | 0.73 | -0.004 |
| n-c6 | 0.9616 | 0.73 | -0.093 |
| n-c7 | 0.9840 | 0.33 | -0.032 |
| n-c8 | 0.9882 | 0.29 | -0.008 |
| n-c9 | 0.9918 | 0.18 | -0.003 |
| n-c10 | 0.9716 | 0.13 | 0.022 |
| Total 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 |

Typical comparisons of primary GC analysis and online NMR prediction over several months

PLS Model Performance

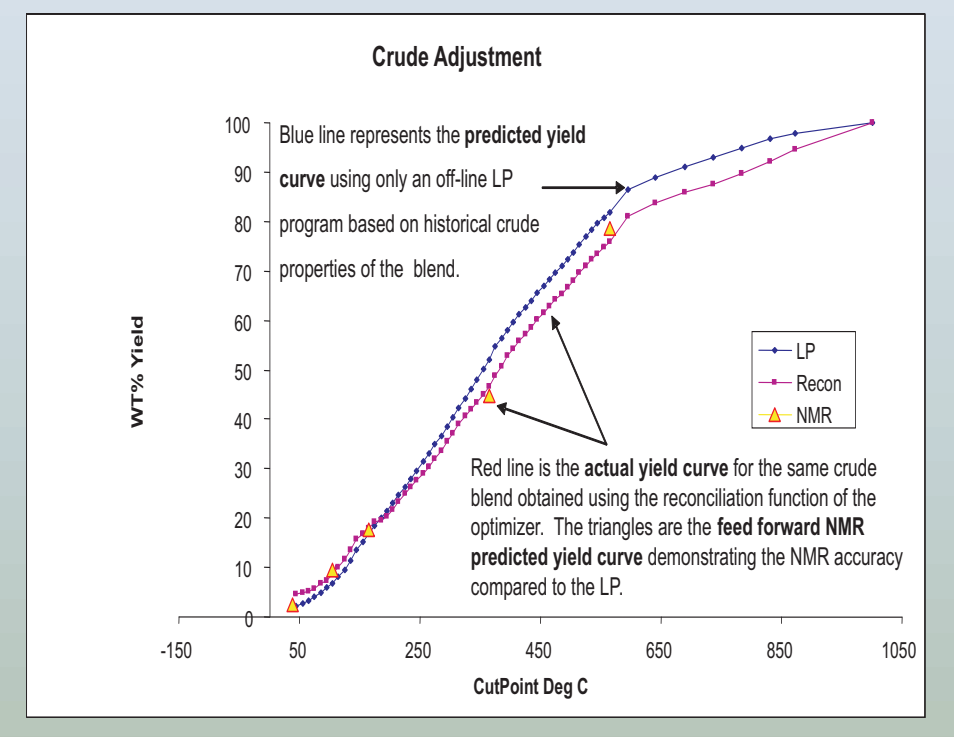
Crude Unit Overview



APC and Optimization

- Distillation (D86, Sim Dis, TBP)
- Flash Point
- Cloud Point
- Pour Point
- Freeze Point
- Chemistry (Fa, Fn, Fp, Naphthalene)
- PONA/PIONA
- API Gravity/Density
- Octane/Cetane

- On-Line Analysis:
  - Light to Heavy Crude
  - Accurately measured both Actual Crudes and Blends
  - Database of more than 110 Crudes in the Model
  - Does not require exact Crude and/or Blend for an accurate Measurement
- Universal Model
  - Reproducibility
  - Yield Curve < 2 %
  - Broad Range, API Gravity from >9 to 52 deg



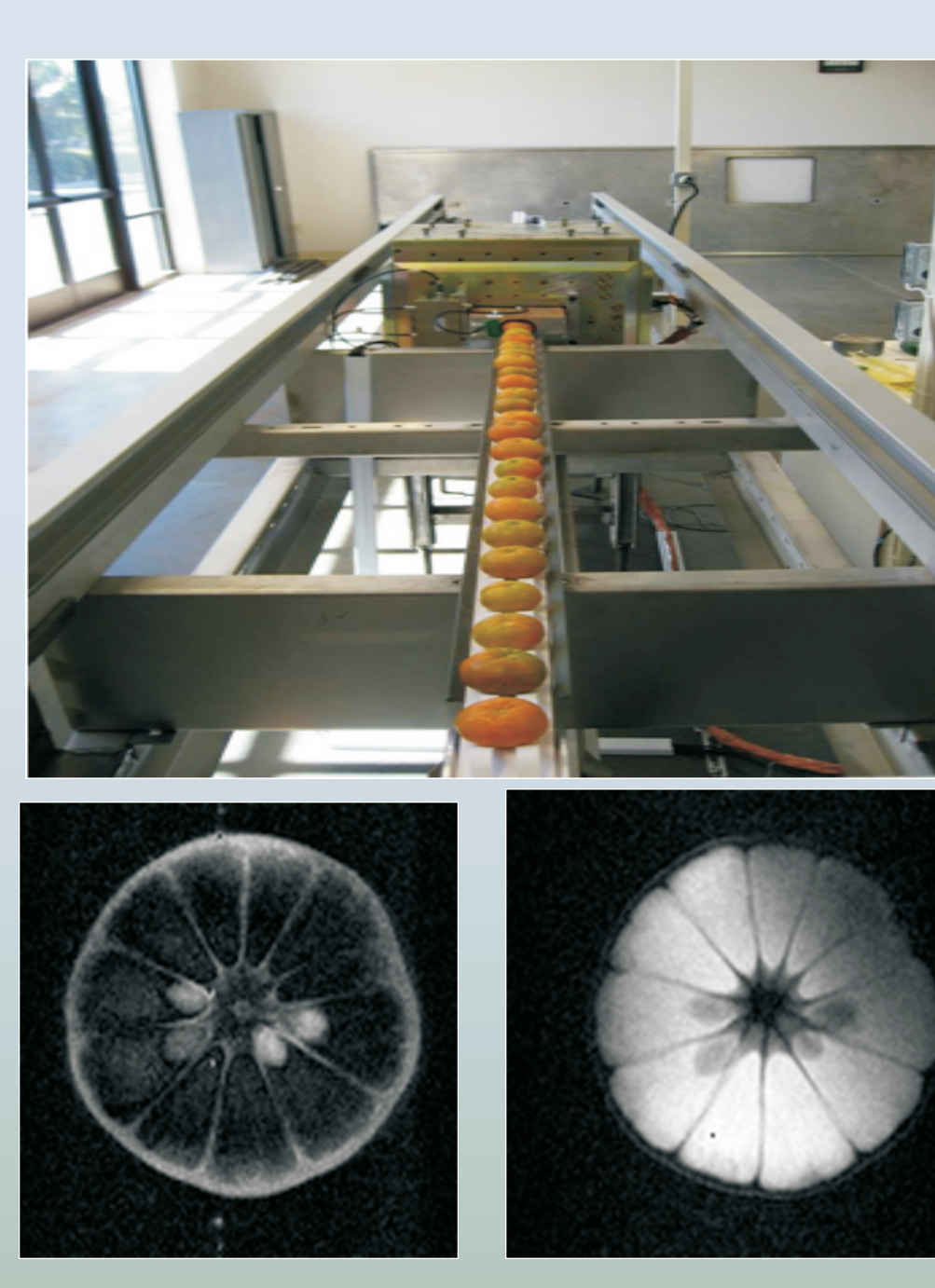
Crude Adjustment

Blue line represents the **predicted yield curve** using only an off-line LP program based on historical crude properties of the blend.

Red line is the **actual yield curve** for the same crude blend obtained using the reconciliation function of the optimizer. The triangles are the **feed forward NMR predicted yield curve** demonstrating the NMR accuracy compared to the LP.

Net Benefit of NMR + Optimization - $3 million/yr.

PDVSA-Curacao implemented their own Romeo Optimization project. The NMR feed forward predictions accurately measured the crude blend properties eventhough no individual crudes, crude blends, or, on-site lab measurements were used in the NMR crude property models



Seed Detection in "seedless" fruit

## SUMMARY

- No cryogens, no deuterated solvents.
- Small footprint
- Fume Hood
- Pilot Scale
- At-line or On-line
- 60 MHz 1H spectra have all the same spectral information as higher field systems. Spectral overlap/resolution can be "resolved" chemometrically if needed.
- Sensitivity is good at typical NMR detection limits (500-1000 ppm)
- Options for spectra:
- Single pulse
- Signal Averaging (last in/first out)
- Signal averaging (stop flow)

## ACKNOWLEDGMENTS

Uri Rapoport
Aspect Imaging, Shoham, Israel

Mark Zell and David Foley
Pfizer, Groton, Connecticut

Cosa Xentaur
Yaphank, New York
(Booth 4003)