Pulse, Acquire, Control: Ten Years of On-Line High Resolution NMR In Refining, Petrochemical, and Food Manufacturing

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1992 – 1995

Elbit-ATI develops first hi-resolution on-line NMR system operating at 53 MHz.

1995 – 1996

First 2 on-line systems installed: 1 on a refinery gas process, 1 on a refinery gas/liquid emulsion.

1997 – 1999

Systems move from prototypes to full installations. Operating frequency at 58 MHz.

Chemometric methodologies developed and applied on-line.

2000-2005

Worldwide installations in refining and petrochemical plants. Multiple stream systems installed. NMRs linked to advanced process control and optimization.

2005+

Food and Pharma are on the horizon.

A retrospective on the application of high-resolution FT-NMR to on-line analysis on the 10th anniversary of the first installation.

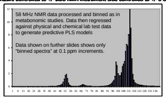
NMR Innovations Developed to Bring NMR On-Line
- Permanent magnet stability and design
- Shimming protocols
- Intrinsically Safe flow-through probe technology
- Novel locking mechanism
- Chemometric method development
- Post processing developments
  - Robust auto-phasing routines
  - Frequency domain averaging
  - Post-processing monitoring of each constituent spectrum for heavy stream analyses where sediment/rust may be present.

NMR Applied to Online Process Control

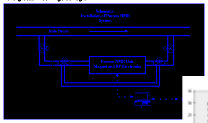
Advantages:
- Non-optical spectroscopy
- No spectral temperature dependence ****
- Minimal sampling requirements
- Spectral response to sample chemistry is linear
- Chemical regions of NMR spectra are orthogonal
- Entire volume is sampled by the RF experiment
- Water is in distinct region and can be digitally removed
- Detailed hydrocarbon information is readily observed
- Colored/black samples readily observed quantitatively
- Fundamental chemical information can be derived directly from the spectrum.

Disadvantages:
- Solids cannot be observed
- Individual molecular component sensitivity not observed directly
- Low sensitivity to impurities – Quantitative > 1000 ppm
- Sensitive to ferro-magnetics
- Sample viscosity causes resolution changes
- Non-hydrogen containing species are not observed

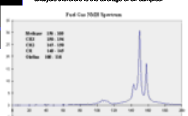
Certified NMR unit ready for placement in the field. Magnet side of enclosure temperature controlled to +/- 0.5C NMR instrument side controlled to +/- 5 C



NMR Fuel Gas Analysis at Texaco's Los Angeles Refinery: The unit was installed October, 1995, on the refinery's co-generation unit's fuel gas stream as a beta test to assess process NMR's performance, reliability, accuracy, support and maintenance requirements. Measuring BTU, specific gravity, methane content, hydrogen content, and, hydrocarbon content, the NMR compares favorably with the GC. Unlike the GC, process NMR does not require component speciation to determine, BTU and specific gravity. With respect to maintenance and reliability, the process NMR requires no column changes, minimal calibration and minimal manpower in either operating or maintaining the analyzer. The refinery is currently using 2 4-20 mA output signals from the process NMR, one for BTU and one for specific gravity, in their operations. Further, the analyzer has been registered with the Southern California Air Quality Monitoring District, an environmental agency responsible for monitoring and permitting air emission sources in the greater Los Angeles region.



A typical fuel gas spectrum is shown below. Typical stream conditions are 50 - 55 psia and 20 - 25 degrees C resulting in a total concentration of less than 6 micro moles of gas in the NMR probe. To improve sensitivity, the NMR averages 32 scans per analysis. However, before each scan, a new sample of gas is purged into the probe. Each analysis therefore is the average of 32 samples.



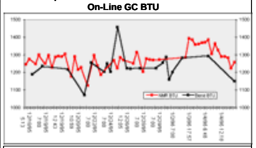
Currently, the refinery is performing a fuel gas analysis every half hour. Further, as required by its environmental permit, a methane spectrum is obtained daily, and the measured methane value is compared to the predicted methane value from the calibration curve at the pressures and temperatures obtained during the daily calibration run. Predicted verses measured methane values must be within +/- 2.5% for the NMR to be within daily calibration. Examples of the daily calibration and fuel gas analysis reports are also shown below.

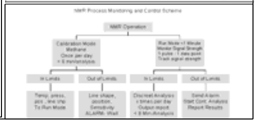
From Poster Session of the 36th ENC, 1996 – Boston, MA

Fuel Gas Analysis

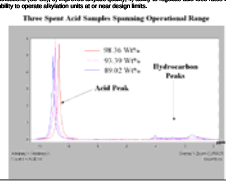
Run Report	
Sample No	a092096.3
Date	9/20/1996
Time	3:54 AM
Pressure in PSIA	50.6
Temperature in C	24
RMS	194
BTU/Cu. Ft.	1301
Specific Gravity	0.873
Vol% Methane	43.9
Vol% Hydrogen	17.7
Vol% C2 - C5+	25 with 11.7% Olefin
Vol% Non-Detected	13.4
CH4	2.0932
CH3	2.9747
CH2	1.7702
CH	2.2866
dCH2	0.4014
dCH	0.5336
H2	0.8464
sum noise	9.19
CH4 peak	158

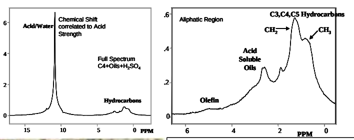
Comparison of NMR BTU vs. Bendix 9000 On-Line GC BTU



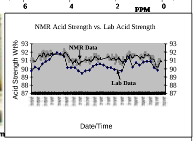


On-line Acid Strength Measurement and Sulfuric Acid Alkylation Process Control Using Process NMR - April 1998, Los Angeles Refinery. On-line NMR technology measures acid strength, acid/hydrocarbon emulsion quality, hydrocarbon to olefin ratios, and acid soluble oil content on the intact emulsion stream in the reaction zone of the alkylation process. By using a process line slip-stream from the reaction zone, non-invasive NMR analysis overcomes most of the limitations of other analyzer technologies. With no direct analyzer contact with the acid stream in the NMR, corrosion, response deterioration, wear, and/or contamination problems experienced by other acid strength measurement technologies do not interfere with NMR analyses. Longer on-stream analysis times, high accuracy, rapid measurement capabilities, and low instrument maintenance, make process NMR unique in acid alkylation control. Since the measurement is done at the reaction zone, NMR measures the intact acid/hydrocarbon emulsion, typically in well under two minutes. Acid strength determination by NMR does not require any emulsion breaking, and, along with acid strength, the same NMR analysis measures the emulsion quality, feed ratios, and acid soluble oil content. Utilizing these parameters, true process optimization and improved margins can be obtained through: 1) reduced acid consumption, 2)expanded utilization of hydrocarbon feed types and distributions (C3-C5), 3) improved alkylate quality, 4) ability to regulate acid feed rates with changing feed compositions 5) ability to operate alkylation units at or near design limits.

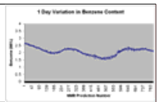


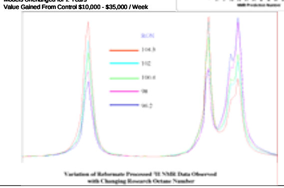


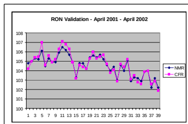
LA Refinery Alkylation Unit NMR and Sampling System

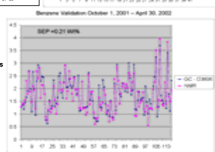


Closed Loop Reformer Control
(Reformers catalytically convert cyclic paraffins to high octane aromatics).
Installation: BP Refinery in U.K. – 1999
Reformer Capacity: 34,000 Barrels per Day
Control Strategy: Control on MON and Benzene Content
NMR Analysis: 2 Minute Analysis
NMR PLS Outputs: RON, MON, Benzene, Total Aromatics
Value Added: Maximize Benzene Content of Reformate
Feed Forward to Benzene Splitter and Gasoline Blending
Conservatively 4 cents per Barrel (Can Be Much More)
Performance: NMR Available 98%+ For Past 3 Years
Models Unchanged for 2 Years
Value Gained From Control $10,000 - $35,000 / Week









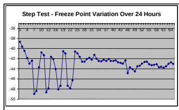
RON and MON are research octane number and motor octane number. Both values are generated a standardized CFR engine test that is very costly and requires expert technicians to perform the test. RON simulates highway driving while MON simulates local driving.

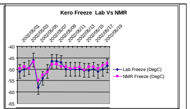
Benzene values used in the PLS modeling were derived from GC analysis (ASTM method D3606).

This application represented the first chemometric NMR analysis placed on-line.

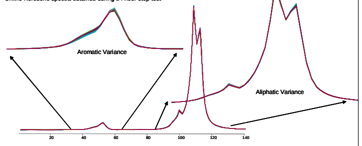
Application: Crude Distillation Unit Optimization and Control
PDVSA Refineria Isla, Curacao - 2000
Crude Unit Capacity: 180,000 Barrels per Day
Control Strategy: Control on Kerosene Freeze Point
Crude Tower Optimization
NMR Analysis: 15 Minute Cycle (5 minutes per stream inclusive 5-volume of flushing)
NMR Results into ROMEO CDU Optimization Package
NMR PLS Outputs: Naphtha – T10, T50, T90, EP
Kerosene – Freeze, Flash
Crude – API, Sulfur, TBP (38, 105, 165, 365, 565C)
Value Added: Kero - Approach Freeze Point Limit – Worth $600K/Year
CDU Optimization- Conservatively 4 cents per Barrel
Performance: NMR Available 98%

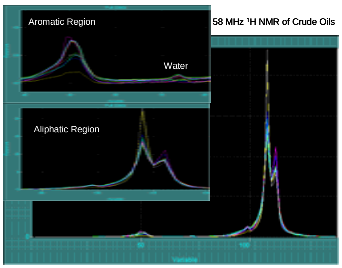
MRA Sample System
1) Crude oil brought into NMR at 55C (crude fast loop heater)
2) Kerosene and Naphtha also brought to NMR at 55C (sample heater With PID control at NMR SSC)
3) All Samples are routed to crude sample return and pass through CDU again
4) Double block-and-bleed and flushing protocol to prevent cross contamination of light ends with crude.

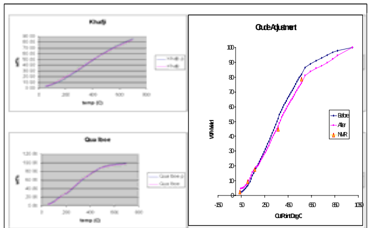




Online Kerosene spectra obtained during 24 hour step test

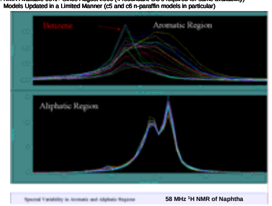






True Boiling Point (TBP) Curves of Crude Oil. Used as the basis for predicting the quality of a crude oil. Test takes over 2 days and often a purchase decision has been made and the crude processed by the refinery before a TBP test result can be obtained. Test costs $10K. ^{1}H NMR can predict a TBP curve in 2 minutes meeting a demand for spot analysis. The operational decisions based on NMR analysis as an assay tool run into the $10M range.

Application: Steam Cracking Optimization by ^{1}H NMR Analysis
Location: BASF Ludwigshaven - 2000
Cracker Facility Capacity: 600,000 Tonnes per Year
Control Strategy: Feed forward detailed hydrocarbon analysis (GC-PIONA) to SPYRO optimization package controls furnace temperatures to optimize cracking to ethylene or propylene
NMR Analysis: 3-4 Minute Cycle (Single Stream), 16 Minute Cycle (4 Feed Streams)
^{1}H NMR PLS Outputs: Naphtha – Detailed PIONA (c4-c10 n-paraffin, c4-c10 i-paraffin, c6-c10aromatics, c5-c10 naphthenes)
Value Added: Unit Optimization - $150K /year - 4 Units Now Being Optimized ($600K/year)
Performance: NMR Available 98%+ Since August 2000 (4 redundant GC's required for same availability)
Models Updated in a Limited Manner (c5 and c6 n-paraffin models in particular)



Spectral Variability in Aromatic and Aliphatic Regions   58 MHz ^{1}H NMR of Naphtha

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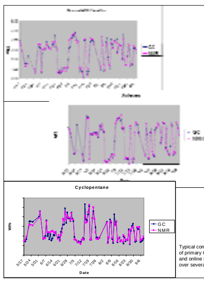
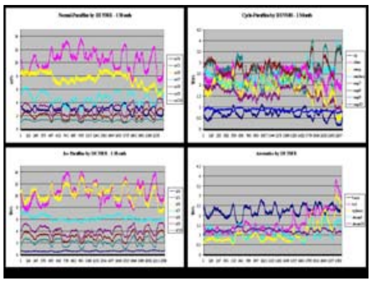
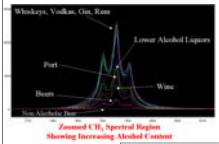


Parameter	R	Std Dev	Mean Dev
n-c4	0.9340	0.52	0.067
n-c5	0.9761	0.73	-0.004
n-c6	0.9616	0.73	-0.093
n-c7	0.9840	0.33	-0.032
n-c8	0.9882	0.29	-0.008
n-c9	0.9918	0.18	-0.003
n-c10	0.9716	0.13	0.022
Total n-paraffin	0.9840	0.81	0.013
I-c4	0.8765	0.07	0.001
I-c5	0.9834	0.76	0.043
i-C6	0.9865	0.59	-0.050
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

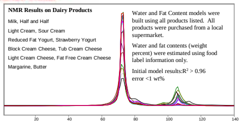
PLS Model Performance





Process NMR has been used effectively to obtain real time alcohol content. However a minimum of a 300 MHz supercon is required to obtain useful low intensity C1, C3, C4 alcohol and other ester/acid molecule information to be used for authentication applications by cluster analysis or principal component analysis.

Dairy processing is a natural fit for process NMR as the water and fat content are readily observed and models can be developed based on a water calibration in absolute intensity mode or PLS models can be utilized. PLS models can run into trouble if significant protein content is present such as in cream cheese. The issue is that the protein is simply not observed at 58 MHz and the total water and fat contents effectively float due to the variation of an unobserved component.



Future Directions of Process NMR Technology

PAT Initiative in the pharmaceutical industry – applications are being targeted in reaction monitoring as well as clean-in-place procedures where the NMR may be combined with other spectroscopic techniques to yield an analyzer that can properly analyze bulk chemistry (NMR) and final cleanliness of reaction vessels (higher sensitivity spectroscopy).

Food industry applications – the ideas that have been developed for the on-line application of NMR are applicable in food authentication as well as in food manufacturing and processing. The key to NMR instrumentation entering this area is the ability to develop robust automated NMR methodologies on a lower price-point instrument. These instruments could be bench top 60 MHz or on-line 60 MHz, as well as at-line 300 MHz instruments that can be developed at a cost that does not exclude NMR from process analytical or at-line testing for QC or process control. The current drive to 500 MHz+ NMR instrumentation will drive process analytical personnel to cheaper optical spectroscopies.

^{13}C NMR chemometric applications for key industry sectors may be a by product of producing lower cost 200/300 MHz instrumentation. An example of these applications is aromaticity measurement and "average molecule parameters" derived from ^{13}C NMR and used to control refinery and petrochemical processes on heavy petroleum products such as residues and vacuum gas oils.