Nuclear Magnetic Resonance Analysis On-line

Overview of the technology, benefits, solutions and applications to the Refinery
The NMR Technology

The analytical measurement principle
What is $^1$H NMR in general?

- Hydrogen Nuclear Magnetic Resonance

- Provides picture of the hydrocarbon structure. From this we determine physical and chemical information.

- It is non-invasive like MRI*, therefore all samples can be returned back to the process.

- Heavy opaque or dark materials easily analyzed.

- Technology developed from 1950’s

* Magnetic Resonance Imaging
What is $^1$H NMR Analysis?

- NMR = **Nuclear Magnetic Resonance**
- "Nuclear" because NMR looks at the nuclei of molecules (protons-neutrons)
- More specific at their "nuclear spin"
- Some nuclei have a "magnetic moment" due to that spin (behave like a small magnet)
- Most important nuclei are $^1$H, $^{13}$C, $^{19}$F and $^{31}$P
- $^1$H-NMR is looking at $^1$H-protons in molecules, excellent for hydrocarbon analysis
The Electromagnetic Spectrum

NMR spectroscopy uses radio-waves to interact with samples
$^1\text{H}$ Proton – Magnetic Moment ($M$)

Hydrogen Atom (Proton)

Proton is spinning

Magnetic moment ($M$) generated
Nuclear Spins and Magnetic Fields

With no magnetic field, magnetic moments $M$ are random oriented.

In strong magnetic field ($B_0$), magnetic moments $M$ align along $B_0$. 
Alignement and precessing of M

Magnetic Moments Align and Precess at a Frequency $w_0$

$w_0$ is proportional to size of $B_0$

e.g. $B_0 = 1.35$ Tesla $\rightarrow w_0 = 57$ MHz
Precessing spins can be described as a bulk magnetic moment $M_0^*$

$M_0^* = \text{Summation of individual magnetic moments of all protons in the sample}$
Re-align to second magnetic axis

RF pulse turned on for 4-20 microseconds generates a second magnetic field $B_1$

Magnetic field $B_1$ causes $M_0$ to move and re-align to second magnetic axis
Re-align to original magnetic axis

The protons relax and re-align to their original equilibrium position along Bo Axis

“Relaxation” of Mo generates a RF Current that is picked in the irradiation coil: A decay signal is generated called Free Induction Decay signal (FID)
Measurement in a NMR Process analyser

Magnet

Flow Pipe Probe

Top View

FLOW PROBE
LOCK REFERENCE
SECONDARY CONTAINMENT SLEEVE
SHIM COILS
MAGNET BORE

Technology and Quality

ISAB
QUALION
NMR ANALYZERS
Fast Fourier Transform - FFT

Time domain signal

Free Induction Decay (FID)

Frequency domain signal

NMR Spectrum

F.F.T.

\[ f(\omega) = \int_{-\infty}^{\infty} f(t) e^{-i\omega t} dt = \int_{-\infty}^{\infty} f(t) \left[ \cos(\omega t) - i \sin(\omega t) \right] dt \]
Chemical Shift in NMR spectra

- How does the NMR resolve the different protons in the spectra?
- Each proton in a different chemical environment (bond) “senses” a different magnetic field $B_X$ due to the shielding created by surrounding electrons
- More electrons = more shielding
Protons in different chemical environment

External applied field $B_0$

Actual field at protons
Difference in “sensed” magnetic field

Due to difference in “sensed” magnetic field, protons A and B precess at a different frequency $w_A$ and $w_B$.

$w_A$ and $w_B$ are proportional to size of $B_A$ and $B_B$.

The precessing frequency becomes the fingerprint of the chemical environment of the different protons.
From FID to results

Free Induction Decay (FID)

Time domain signal

Frequency domain signal

Fast Fourier transform

NMR Spectrum

Chemometric calibration models

Results
WHAT IS CHEMOMETRICS?

- “Chemometrics is the science of relating measurements made on a chemical system or process to the state of the system via application of mathematical or statistical methods”.

Definition by the International Chemometrics Society (ICS)

*Application and development of mathematical and statistical methods to extract information from chemical or process data*
Multivariate statistical analysis:

*is that branch of statistical analysis which is concerned with the simultaneous investigation of two or more variable characteristics which are measured over a set of objects.*
TYPES OF MULTIVARIATE DATA

- Sensory data
- Chemical data
- Spectral data
  - Near-infrared (NIR)
  - Excitation-emission matrix (EEM) fluorescence
  - Nuclear Magnetic Resonance (NMR)
MULTIVARIATE REGRESSION

- Near-infrared (NIR)
- Excitation-emission matrix (EEM) fluorescence
- Nuclear Magnetic Resonance (NMR)

Regression is a generic term for all methods attempting to fit a model to observed data, in order to quantify the relationship between two groups of variables. The fitted model may then be used either to merely describe the relationship between the two groups of variables, or to predict new values.
TBP of Crude predictions

\[ \text{TBP} @ 365^\circ C \text{ (Wt\%)} \]
\[ R^2 = 0.972 \]
\[ \text{SECV} = 1.8 \text{ Wt\%} \]
TBP of Crude predictions

TBP @ 565°C (Wt%)  
$R^2 = 0.975$  
SECV = 1.4 Wt%
NMR benefits

What advantages can the NMR spectrum offer?
The NMR key spectral advantages

- Linear response
- Orthogonality
- Signal Variance
- Structural info
The NMR key spectral advantages

**Linear response**

- Area under the peaks of all chemical components is linear proportional to the concentration of these components.
- Respons is equal accross the spectrum: equal amount of protons gives equal signal.
Linear response in gasoline NMR spectra

Superimposed $^1$H NMR spectra for samples spanning the entire MON range

- MON 78.3
- MON 82.7
- MON 85.0
- MON 88.9

Same variation across the spectrum
Linearity in gasoline NMR spectra

Fig 3: Empirical Olefins Quantification in Gasoline
The NMR key spectral advantages

Orthogonality

Different chemical types have their own distinct and unique region of chemical shift where peaks can be identified (no overlap)
All functional groups are clearly resolved and have unique and documented location.
The NMR key spectral advantages

Signal Variance

The NMR spectrum shows a high signal variance with respect to the chemical property changes.
NMR signal variance

Identical 90 sample Gasoil data-set

High \textit{Signal -Variance - to - Noise Ratio} provides high reliability in determining the precision and accuracy of the property predictions.
The NMR key spectral advantages

- **Relative** amplitude of the NMR signal is proportional to amount of nuclei in molecular structure

  - Signal split or *broadness of the features*: information on neighbouring nuclei in molecule
Benefits offered by NMR spectra

- Linear response
- Orthogonality
- Signal Variance
- Structure

Benefits:

- Simpler models and easy to maintain
- Extrapolation for “out-of-range” samples: robust
- Low running maintenance cost of model (cost of ownership)
- Fewer data points required to build model
Models – advantage of extrapolation

NMR spectral quality allows extrapolate outside the calibration set
Extrapolation outside calibration set

NMR PLS Model contains RON data in the range 94-104 octane
Process NMR applications
Applications: distinct NMR analyser features

Some distinct features have oriented NMR in certain application fields:

- Non-invasive analytical technology
  - Electronic, not optical

- Ability to analyse dark and opaque samples
  - High temperature/wide flow-through probe for highly viscous samples
  - Limited filtering of sample required

- Robust models due to highly resolved quality spectra, structural information
  - Limited calibration data: short time-to-profit
  - No moving parts inside – reduced maintenance
Key application: Crude feed & distillation
Why measure crude?

In the past...
- Little variation, constant supply of same crude
- Refineries were contracted for this stable feed
- Advance Control mainly on the CDU run-down products: feed-back control only

The market today...
- Increased competition & drive to maximise profits
  - Buying of low-cost crudes (heavier types)
  - Buying on spot markets
  - High variability in crude quality offered
- The refiner today must cope with this variation in order to ensure profitability
Effect of crude quality variation on CDU

- Cut point optimisation affected
- Product quality control risks
- Feed rate is not maximised
- Energy consumption not optimal
- Risk of violating the process equipments constraints

- Unit operating conditions are upset by changing feed composition
- Product slate is not maintained at optimum
- User incurs significant financial penalties
Traditional Crude CDU control

- laboratory TBP Analysis 2/day
- Crude-Assay Information
- Off-line planning model
- On-line model

CDU

- Residue

- Gas / LPG / Gasoline
- Light Naphtha
- Heavy Naphtha
- Kerosene
- Light Gas Oil
- Heavy Gas Oil

On-line Inferential feedback every 15 mins
Problem with Crude Assay data?

- The crude assay data may be old
- Every crude tank has a heel of mixed crudes received earlier
- Crude in a tank will settle
  - Compatibility
  - Solubility
  - Stratification
- A crude switch (normally 7 to 8 hours) results in an unknown blend of the old and new crude in the pipeline
CDU feed/distillation real time NMR data

Run down

- Octane (RON, MON)
- Specific Gravity @ 15°C
- Density
- RVP
- Naphthalene Content
- PIONA
- Viscosity
- Pour Point
- Cetane Index
- Flash point
- Cloud point
- Freeze point
- Distillation

Feed

- API Gravity
- TBP
- Sulfur Content
- Water
- TAN
- Aromaticity
- API Pred. Yields
The following table is a description of the data upon which the design of the NMR Analyser application is based. The stream to be measured (Topping feed) includes the parameters, the ranges to be measured, the acceptance criteria of the different parameters and Reference Method.

- Density API
- Sulphur % Wt
- Cuts TBP in % Wt

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Range Min</th>
<th>Range Max</th>
<th>Reference Method</th>
<th>Acceptance Criteria</th>
</tr>
</thead>
<tbody>
<tr>
<td>TBP atmospheric</td>
<td>NR</td>
<td>NR</td>
<td>ASTM D 2892</td>
<td>1.4 %wt</td>
</tr>
<tr>
<td>TBP vacuum</td>
<td>NR</td>
<td>NR</td>
<td>ASTM D 5236</td>
<td>1.7 %wt</td>
</tr>
<tr>
<td>Api density</td>
<td>33</td>
<td>27</td>
<td>ASTM D 1298</td>
<td>0.75</td>
</tr>
<tr>
<td></td>
<td>calculated</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Density</td>
<td>860</td>
<td>900</td>
<td>ASTM D 1298</td>
<td>0.01 x measured lab value (Kg/m³)</td>
</tr>
<tr>
<td>Sulphur % Wt</td>
<td>1.5</td>
<td>2.8</td>
<td>ASTM D 1552</td>
<td>Average 0.40%wt</td>
</tr>
</tbody>
</table>

NR: not relevant
<table>
<thead>
<tr>
<th>RANGE (°C)</th>
<th>Delta (NMR - Lab)</th>
<th>% Wt Lab</th>
<th>Prediction value</th>
</tr>
</thead>
<tbody>
<tr>
<td>IBP-71</td>
<td>-0,69</td>
<td>5,28</td>
<td>4,59</td>
</tr>
<tr>
<td>71-100</td>
<td>-0,53</td>
<td>2,91</td>
<td>2,38</td>
</tr>
<tr>
<td>100-125</td>
<td>-0,23</td>
<td>2,65</td>
<td>2,4</td>
</tr>
<tr>
<td>125-149</td>
<td>0,04</td>
<td>2,66</td>
<td>2,7</td>
</tr>
<tr>
<td>149-165</td>
<td>0,36</td>
<td>1,84</td>
<td>2,2</td>
</tr>
<tr>
<td>165-182</td>
<td>0,23</td>
<td>2,02</td>
<td>2,3</td>
</tr>
<tr>
<td>182-200</td>
<td>0,50</td>
<td>2,20</td>
<td>2,7</td>
</tr>
<tr>
<td>200-230</td>
<td>0,10</td>
<td>3,81</td>
<td>3,9</td>
</tr>
<tr>
<td>230-250</td>
<td>0,57</td>
<td>2,65</td>
<td>3,2</td>
</tr>
<tr>
<td>250-275</td>
<td>0,73</td>
<td>3,42</td>
<td>4,2</td>
</tr>
<tr>
<td>275-300</td>
<td>0,28</td>
<td>3,55</td>
<td>3,8</td>
</tr>
<tr>
<td>300-315</td>
<td>0,04</td>
<td>2,19</td>
<td>2,2</td>
</tr>
<tr>
<td>315-340</td>
<td>0,31</td>
<td>3,76</td>
<td>4,07</td>
</tr>
<tr>
<td>340-355</td>
<td>0,25</td>
<td>2,32</td>
<td>2,57</td>
</tr>
<tr>
<td>355-371</td>
<td>0,71</td>
<td>2,52</td>
<td>3,23</td>
</tr>
<tr>
<td>371-400</td>
<td>-1,70</td>
<td>4,71</td>
<td>3,01</td>
</tr>
<tr>
<td>400-525</td>
<td>4,63</td>
<td>22,27</td>
<td>26,91</td>
</tr>
<tr>
<td>525-560</td>
<td>-1,23</td>
<td>6,81</td>
<td>5,58</td>
</tr>
<tr>
<td>560+</td>
<td>-4,39</td>
<td>22,43</td>
<td>18,05</td>
</tr>
<tr>
<td>API</td>
<td>1,6</td>
<td>30,4</td>
<td>31,96</td>
</tr>
<tr>
<td>S % m/m</td>
<td>0,7</td>
<td>1,33</td>
<td>2,02</td>
</tr>
</tbody>
</table>
### COMPARISON LAB vs PREDICTED VALUES TBP TO TOPPING FEED
SAMPLE WITHDRAWN ON LINE 28.1.11 AT 12:31 PM

<table>
<thead>
<tr>
<th>RANGE (°C)</th>
<th>Delta (NMR - Lab)</th>
<th>% Wt Lab</th>
<th>Prediction value</th>
</tr>
</thead>
<tbody>
<tr>
<td>IBP-71</td>
<td>0,17</td>
<td>4,59</td>
<td>4,76</td>
</tr>
<tr>
<td>71-100</td>
<td>-0,92</td>
<td>3,28</td>
<td>2,36</td>
</tr>
<tr>
<td>100-125</td>
<td>-0,50</td>
<td>2,92</td>
<td>2,4</td>
</tr>
<tr>
<td>125-149</td>
<td>-0,57</td>
<td>2,89</td>
<td>2,3</td>
</tr>
<tr>
<td>149-165</td>
<td>0,27</td>
<td>1,97</td>
<td>2,2</td>
</tr>
<tr>
<td>165 - 182</td>
<td>-0,01</td>
<td>2,13</td>
<td>2,1</td>
</tr>
<tr>
<td>182 - 200</td>
<td>0,15</td>
<td>2,30</td>
<td>2,5</td>
</tr>
<tr>
<td>200 - 230</td>
<td>-0,11</td>
<td>3,94</td>
<td>3,8</td>
</tr>
<tr>
<td>230 - 250</td>
<td>0,43</td>
<td>2,70</td>
<td>3,1</td>
</tr>
<tr>
<td>250 - 275</td>
<td>0,46</td>
<td>3,45</td>
<td>3,9</td>
</tr>
<tr>
<td>275 - 300</td>
<td>-0,03</td>
<td>3,54</td>
<td>3,5</td>
</tr>
<tr>
<td>300 - 315</td>
<td>0,00</td>
<td>2,16</td>
<td>2,2</td>
</tr>
<tr>
<td>315 - 340</td>
<td>0,53</td>
<td>3,68</td>
<td>4,21</td>
</tr>
<tr>
<td>340 - 355</td>
<td>0,22</td>
<td>2,25</td>
<td>2,47</td>
</tr>
<tr>
<td>355 - 371</td>
<td>0,77</td>
<td>2,43</td>
<td>3,2</td>
</tr>
<tr>
<td>371 - 400</td>
<td>-1,44</td>
<td>4,50</td>
<td>3,06</td>
</tr>
<tr>
<td>400 - 525</td>
<td>5,96</td>
<td>20,75</td>
<td>26,71</td>
</tr>
<tr>
<td>525 - 560</td>
<td>-0,71</td>
<td>6,20</td>
<td>5,49</td>
</tr>
<tr>
<td>560+</td>
<td>-4,65</td>
<td>24,31</td>
<td>19,66</td>
</tr>
<tr>
<td>API</td>
<td>-0,3</td>
<td>28,68</td>
<td>28,38</td>
</tr>
<tr>
<td>S % m/m</td>
<td>0,5</td>
<td>1,72</td>
<td>2,23</td>
</tr>
</tbody>
</table>
**COMPARISON LAB vs PREDICTED VALUES TBP TO TOPPING FEED SAMPLE WITHDRAWN ON LINE 20.1.11 AT 2:49 PM**

<table>
<thead>
<tr>
<th>RANGE (°C)</th>
<th>Delta (NMR - Lab)</th>
<th>% Wt Lab</th>
<th>Prediction value</th>
</tr>
</thead>
<tbody>
<tr>
<td>IBP-71</td>
<td>0,23</td>
<td>4,88</td>
<td>5,11</td>
</tr>
<tr>
<td>71-100</td>
<td>-1,37</td>
<td>3,58</td>
<td>2,21</td>
</tr>
<tr>
<td>100-125</td>
<td>-0,82</td>
<td>3,15</td>
<td>2,3</td>
</tr>
<tr>
<td>125-149</td>
<td>-0,46</td>
<td>3,09</td>
<td>2,6</td>
</tr>
<tr>
<td>149-165</td>
<td>0,22</td>
<td>2,09</td>
<td>2,3</td>
</tr>
<tr>
<td>165 - 182</td>
<td>0,12</td>
<td>2,25</td>
<td>2,4</td>
</tr>
<tr>
<td>182 - 200</td>
<td>0,14</td>
<td>2,41</td>
<td>2,6</td>
</tr>
<tr>
<td>200 - 230</td>
<td>-0,14</td>
<td>4,09</td>
<td>4,0</td>
</tr>
<tr>
<td>230 - 250</td>
<td>0,59</td>
<td>2,78</td>
<td>3,4</td>
</tr>
<tr>
<td>250 - 275</td>
<td>0,28</td>
<td>3,53</td>
<td>3,8</td>
</tr>
<tr>
<td>275 - 300</td>
<td>0,21</td>
<td>3,59</td>
<td>3,8</td>
</tr>
<tr>
<td>300 - 315</td>
<td>0,01</td>
<td>2,18</td>
<td>2,2</td>
</tr>
<tr>
<td>315 - 340</td>
<td>0,69</td>
<td>3,69</td>
<td>4,38</td>
</tr>
<tr>
<td>340 - 355</td>
<td>0,30</td>
<td>2,24</td>
<td>2,54</td>
</tr>
<tr>
<td>355 - 371</td>
<td>0,88</td>
<td>2,42</td>
<td>3,3</td>
</tr>
<tr>
<td>371 - 400</td>
<td>-1,08</td>
<td>4,45</td>
<td>3,37</td>
</tr>
<tr>
<td>400 - 525</td>
<td>4,19</td>
<td>20,14</td>
<td>24,33</td>
</tr>
<tr>
<td>525 - 560</td>
<td>-0,50</td>
<td>5,92</td>
<td>5,42</td>
</tr>
<tr>
<td>560+</td>
<td>-3,37</td>
<td>23,52</td>
<td>20,15</td>
</tr>
<tr>
<td>API</td>
<td>2,2</td>
<td>29,99</td>
<td>31,81</td>
</tr>
<tr>
<td>S % m/m</td>
<td>0,4</td>
<td>1,73</td>
<td>2,09</td>
</tr>
</tbody>
</table>
Nuclear Magnetic Resonance Analysis On-line

Conclusion
The NMR Analyzer Advantage - Control

- Real time, accurate stream analysis
  - Reduction in response time from Lab allows tighter control
  - Multi-property analysis and increased information regarding stream matrix to allow better management decisions

- Avoid errors in stream analysis
  - Measurements are reliable and done online in real time
  - Eliminates data entry errors from Lab input
The NMR Analyzer advantage - analytical

- Simple sample conditioning required
  - No water removal
  - Coarse or limited filtering to protect valve seats
- Linear Spectral Response across broad range
  - Models can be extrapolated accurately
- Multi-property analysis replaces conventional analyzers and provide much faster results
- Minimal maintenance required
  - No moving parts in sensor
Thanks for Your attention !!!