Enabling FCC Optimisation with Process MRA ^{13}-C Feed analysis

- **Legacy Measurement**
  - The higher the RI the more aromatics and the less crackable the feed.
  - With dark and viscous fluids both analine point & RI have their limitations
- **Online Real-time13-C Analysis**
  - **1,2,3 & 6** Step change in Aromatics correctly followed by RI.**1 & 3, 2 & 6** Same source.
  - **3 & 4** Similar Density, 4 has lower TBP
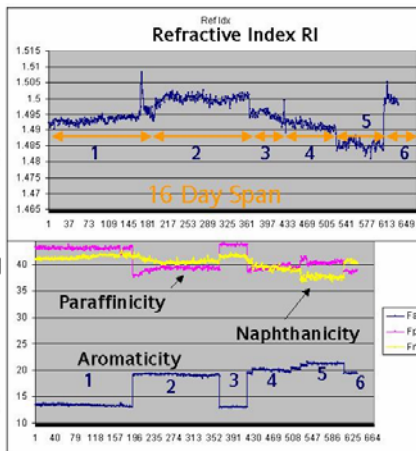 - **5** Lowest Density & TBP, this ties in with Aromaticity evidence. Eg: Light coker stocks are Very Aromatic

Fig 1:Feed Characterisation

Why is feed measurement important?

Many Refiners live in a dynamic environment, where Crude selections and inventory are changed on a regular basis. In addition over time it is expected that there will be a move towards heavier and less sweet Crude Oil purchases.

Improving the bottom of the barrel performance will become even more of an issue, not only to remain within more demanding environmental legislation, but to improve the financial bottom line. This has a direct impact on cat cracking feedstock analysis requirements. Understanding feed properties and knowing their impact on unit performance are essential.

Trouble-shooting, catalyst selection, unit optimisation and subsequent process evaluation all depend on the feedstock.

Sophisticated analytical techniques such as mass spectrometry or Super conducting ^{13}-C Nuclear Magnetic Resonance analysers are not found routinely in the Refinery laboratory. Simpler empirical correlations are often used to bridge this measurement gap. These can be prone to error since they are usually intended for olefins free feed. They cannot differentiate well between Paraffinic / Naphthenic molecules and they cannot segregate aromatic compounds that may also contain Paraffinic and Naphthenic structures.

Nevertheless, these correlations e.g. (Watson & UOP K-Factor or TOTAL Carbon Aromaticity method), have proved very practical tools for tracking unit performance and for troubleshooting.

Unit Optimisation.
The objective of optimisation can often be described as Increasing yields of most valuable products.
Maximise production rates, by co-ordinating several APC applications to push against the constraints set best for the FCCU, plus feedback analysis of main fractionation to reduce valuable product slippage to low value slurry. Due to Crude slate changes or feedstock imports, valuable feed quality information is lost (CLRTO is often forced off-line due to poor model convergence) until laboratory data can be collected to update the Feed quality properties. As a result of this many closed-loop Optimisation projects have failed to deliver the expected economic improvement or have subsequently been relegated to a supervisory role.

Based on developments at an Oil Major, Process MRA can bridge this measurement gap, bringing valuable information online as Fig1 demonstrates.

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Development Rationale

If you consider the published TOTAL method for Carbon Aromaticity

$$TOTAL (C_A) = -814.136 + (635.192\ RI_{(20)}) - (129.266\ X(SG)) + (0.013\ X\ (MW)) - (0.34\ X\ (S)) + \ln(v)$$

Where SG = Specific Gravity at 20^0c, RI = Refractive Index at 20^0c, MW = Molecular Weight, S = Sulphur wt% & v = Viscosity. There are a number of operational considerations.

It has been shown that RI measurement on dark and viscous fluids has its limitations. Using empirical methods there can be a 35% drop in aromatic content in using an RI of 1.5000 instead of 1.5105.
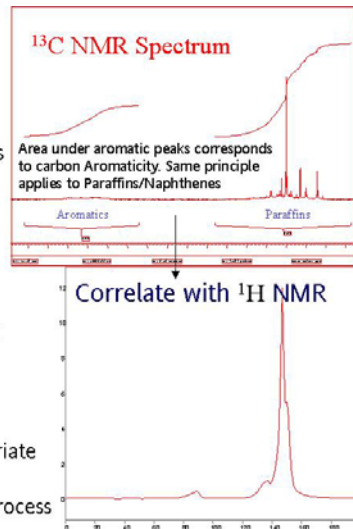
Mass spectrometry is an offline analytical method.

Each individual measurement has its own individual error.

Why not measure the Aromaticity, Paraffinicity and Naphthanicity directly?

This is not an option since a superconducting 300 Mhz NMR spectrometer is required.

However an Oil Major R&D project in 1994 identified the potential of correlating the offline measurement with recently released ^{1}H-NMR technology for online analytical applications.

In 1997 Invensys-Foxboro launched the technology with the technology developers (PNA) for process applications. The first application went online August 2002.

[13]C Online Method

- Offline conduct ^{13}C NMR Experiment
  - using Varian 300S Spectrometer
  - Experiment conducted using samples to PNA Laboratory
- Post Process using PNA Methodology
  - Aromaticity (Fa)
  - Paraffinicity (Fp)
  - Naphthanicity (Fn)
- Relate ^{13}C NMR to Online ^{1}H NMR using
  - Empirical Relationship where
  - $Fa = a + b(Ca) + c(Ca)^2$
  or
  - Chemometric method using Multivariate PLS
- Download calibrated model to Online Process MRA Analyser
- **Single Calibration Model for all Feed types**

^{13}C NMR Spectrum

Area under aromatic peaks corresponds to carbon Aromaticity. Same principle applies to Paraffins/Naphthenes

Aromatics   Paraffins

Correlate with ^{1}H NMR

The Process MRA System

The Process MRA System is based on magnetic resonance technology utilising high-resolution FT-NMR proton spectra in conjunction with partial least squares modelling techniques to obtain highly linear and robust predictive models. Modelling requirements are limited with single predictive models being used to predict across the entire variability range of each property.

How does it work? The technique, developed in the 1950's, reveals the hydrocarbon structure of the fluid being analysed without the need of temperature or chemical pre-conditioning. This is due to the fact that when a hydrogen proton is introduced into a homogeneous magnetic field, the random nature of their magnetic fields align, this magnetic moment is known as a vector. If the sample is then given a short duration radio frequency pulse (at its resonant frequency), the vectors will rotate by up to 90^0. Once the radio frequency pulse stops, the vectors relax back to the original state, depending on the proton location within the structure. If a Fourier Transform is performed, the structural information is revealed and can be modelled to quantify physical or chemical properties of interest

Process MRA Features

1) The only spectroscopic method that is linear.
2) Reproducibility of $C_A < 1$ wt%. Plus C_P & $C_N < 2$ wt%
3) Non invasive, solvents not require for routine measurement cell cleaning.
4) Samples circa 90^0c with 140-micron sample screening for valve seat protection.
5) ATEX II 2G EEx pdem[ib]T4
6) Can also measure Mono and Tri Aromatics, MCRT, TBP, Hydrogen, Sulphur etc
7) Single calibration model incorporating VGO, HVGO, Base Oil & Heavy Residue.
8) No local laboratory required for C_A calibration.
9) < 60 samples required for site calibration.(Typical)
10) Also measures product streams (Cycle Oil, Gasoline, ICCS etc)

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