NCUT
National Centre for Upgrading Technology
'a Canada–Alberta alliance for bitumen and heavy oil research'

NMR Fingerprinting

^{1}H and ^{13}C NMR Analyses

Background

Nuclear magnetic resonance (NMR) spectroscopy is an analytical technique that can quantitatively evaluate the carbon functional group composition (referred to as the NMR fingerprint) of complex mixtures such as heavy oil and bitumen. Unlike gas chromatographic techniques, NMR can be used to analyze whole crudes and total liquid products, including residue and asphaltenes. In some cases, even coke can be studied.

Potential applications of this technique include:

- Assessment of the quality of product generated using new process technologies
- Determination of the net chemistry occurring during processing
- Measurement of residual solvent contamination in oil after extraction

Methodology

Information from both quantitative ^{1}H and ^{13}C NMR spectra is used. The assignment of carbon types were chosen based the data obtained from two advanced NMR techniques. The first is called DEPT (Distortionless Enhanced Polarization Transfer). This is a 1-dimensional experiment that shows the number of protons attached to each carbon in a carbon spectrum (see Figure 1).

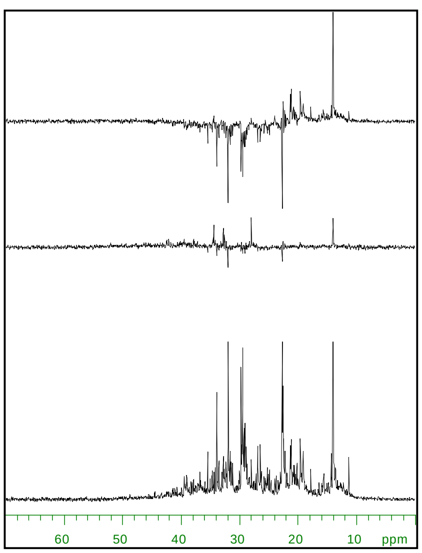

Figure 1 – The paraffinic regions of the DEPT spectra of a petroleum product.

The top spectrum shows CH_3 and CH resonances "up" and CH_2 resonances "down", the centre spectrum shows CH resonances only, and the bottom spectrum shows all protonated carbon species.

The second advanced technique used to assign spectra is HETCOR (Heteronuclear correlation). This is a 2-dimensional NMR experiment that allows the identification of the ^{1}H resonances of the protons attached to each protonated carbon. For an example, see Figure 2. The horizontal line through the spectrum (indicated by an arrow) separates methyl groups, above, and CH_2 and CH groups, below.

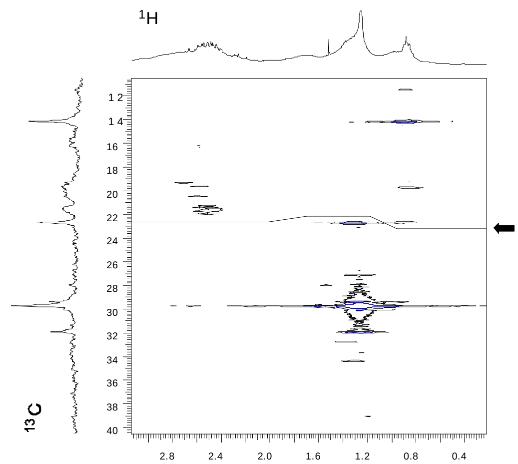

Figure 2 - Paraffinic region of HETCOR spectrum of petroleum vacuum residue.

Information Obtained

Integration of the ^{1}H and ^{13}C NMR spectra allows the quantification (mole %) of the carbon functional groups identified. The functional groups are markers for aromatic, cycloparaffinic or branched paraffinic, olefinic, and chain paraffinic compounds. As all carbon is observed, changes due to process chemistry results in changes in the relative quantities of the species. For example, if the oil is hydrotreated, there will be a decrease in the content of aromatic and olefinic species and an increase in the content of cycloparaffinic and paraffinic chain species.

1 Oil Patch Drive, Suite A202, Devon, Alberta, Canada T9G 1A8
Phone: (780) 987-8682 / Fax: (780) 987-5349
E-mail: ncut@nrcan.gc.ca / URL: www.ncut.com

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The functional group content information can also be used to calculate average structural characteristics including:

- Aromaticity (fraction of aromatic carbon in the sample)
- Paraffinic chain length
- Number of aromatic carbons per aromatic ring cluster (i.e. number = 10 for naphthalene)
- Hydrogen to carbon ratio

Possible Applications

Possible applications for the information obtained from NMR fingerprinting include:

- Product stability indicator – detection of olefinic carbon suggests that the petroleum product may have sludge formation with time
- Coke precursor generation – if a process results in increasing the number of carbons in aromatic clusters (increasing the average aromatic carbon cluster size), the impacts downstream will include the need for more hydrogen during hydroprocessing and possible incompatibilities (insolubility) of the product with paraffinic streams.
- Fundamental understanding of process chemistry – fingerprinting reveals the major chemical reactions occurring during the process such as hydrogenation, dehydrogenation, removal of polyaromatic species, and cracking of long paraffinic chains. As well, NMR can give further insight into the chemical changes such as showing whether dehydrogenation results in generation of polyaromatic species (coke precursors), or mono- aromatic species.

Staff

Heather Dettman obtained her Ph.D. from the University of Alberta in 1984. Before joining NCUT, she worked as the Manager of the NMR Facility at the University of Ottawa Chemistry Department. Her professional experience includes deuterium tracer studies of the fate of process hydrogen during primary and secondary hydroprocessing and quality assessments of diesel fuel, partially upgraded heavy crude, and coker naphtha and gas oil.

Contact:

Dr. Heather Dettman
Research Scientist, Adjunct Professor,
Chemical and Materials Engineering
University of Alberta
Phone: (780) 987-8629
Fax: (780) 987-5349
E-mail: hdettman@nrcan.gc.ca