Pinpoint hydrocarbon types

New analytical method helps in processing clean fuels

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A fundamentally new method identifies components of hydrocarbon streams heavier than gasoline. It pinpoints structure and concentration. It's quick and cheap. The data now available will aid refinery and olefin plant operations, promote better fuels and save money. The nitric oxide ionization spectrometry evaluation (NOISE) has been called the first fundamentally new analysis method in 25 years which identifies hydrocarbons by quantity, and by carbon number (n) and hydrogen deficiency (Z). This information can be crucial in making clean fuels and in optimizing hydrotreater and refinery operation.

It is now being used to direct feedstocks to the most profitable process stream, set unit operating parameters and check results (Table 1). Exact composition of intermediate streams has never before been available without very rigorous and expensive analysis. No conventional method provides this knowledge. So processors have a new tool for optimizing.

Overview. The analysis consists of three advancements. It starts with a fundamentally new technique based on Townsend discharge nitric oxide chemical ionization. Next, specially built instruments apply the method to ordinary hydrocarbon streams. Finally, a special computer program manipulates the digital results to yield practical, usable information.

Nitric oxide ionization spectrometry evaluation works with petroleum distillates with a boiling range of 250°F to 950°F. It does not work with very light ends. Distillates below carbon number 6 or 7 usually are fairly simple. There are relatively few molecular permutations. And several alternate analysis methods do a fine job.

Gas chromatography first separates samples by boiling point. This segregates look-alike molecules and helps distinguish compounds within traditional reporting categories. In addition, gas chromatography separates sulfur-containing compounds from aromatics of the same molecular weight.

Boiling point fractions are then bombarded with "soft" NO^+ ions. Mass spectrometry identifies each component, and reports by carbon number and by degree of saturation. The instrument is a modified gas chromatograph/mass spectrometer[1] (GC/MS). Pure researchers have worked with similar devices for about 20 years. Instruments have been modified to automate thruput, handle samples across a broad boiling range and work specifically with hydrocarbons. The biggest modification was the implementation of Townsend discharge. It took several years and hundreds of runs to get the parameters just right to yield useful data on real-world problems.[2]

The analysis report represents another advance in practicality. Rather than list hundreds of substances, it organizes similar molecules into classes. Processors want to know the carbon chain lengths and the degree of saturation (or undersaturation). From this, they can develop answers on what to do with a specific stream or whether a specific process or catalyst is working adequately. NOISE report gives percentages by boiling range and by Z-number (for C_nH_{2n+Z}) where Z distinguishes between paraffins, cycloparaffins, mono-, di- and tri-aromatics. The latter represent a crucial step. Triton's technique helps refiners control aromatic content and meet changing product specifications. Streams that look alike to conventional analysis can be revealed as quite different with the new technique.

Table 1. About NOISE analysis

Applicable to:
Boiling point 250°F to 950°F
Carbon number C_6 through about C_{44}
Naphtha through light bunker
Intermediate streams
Crude oil
Identifies:
Normal and isoparaffins
Rings
Double bonds
Di- and tricyclic compounds
Complex multinuclear compounds
Sulfur-containing rings
Useful in:
Optimizing hydrotreater operations
Directing incoming streams
Determining severity needed to meet diesel specs
Optimizing catalysts
Identifying spills or unknowns
Making the most out of a new crude
Conserving hydrogen
Scheduling maintenance or evaluating unit performance
Better understanding complex reactions and processes

APPLICATIONS AND HISTORIES

Setting severity. Refinery operators use the ionization spectrometry analysis to set process severity for different streams. Checks after treating determine effectiveness. One company uses frequent analysis to characterize feed and product on CFH and FCC units for process and catalyst optimization. NOISE reports measure the depth of hydrotreating and help set working temperatures and pressures. This in turn optimizes production of naphtha, jet-A and diesel and maintains quality control.

Analysis of diesel fuels and fuel blends as well as ATFs have been carried out extensively. The results can predict cetane number with good precision on the basis of an extensive, proprietary, correlation effort. Analyses of hydrotreated, high-sulfur diesel fuels, which contain benzothiophenes and dibenzothiophenes suggest that these convert to alkylbenzenes and alkylbiphenyls under proper hydrotreating conditions.

We have analyzed hydrotreat-

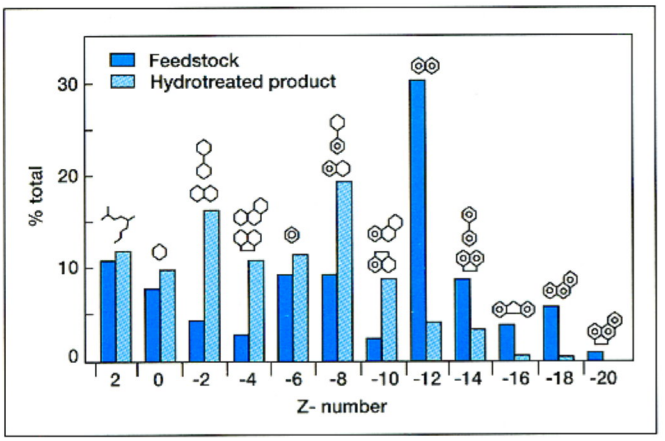

Fig. 1. Feed and product of a hydrotreater.

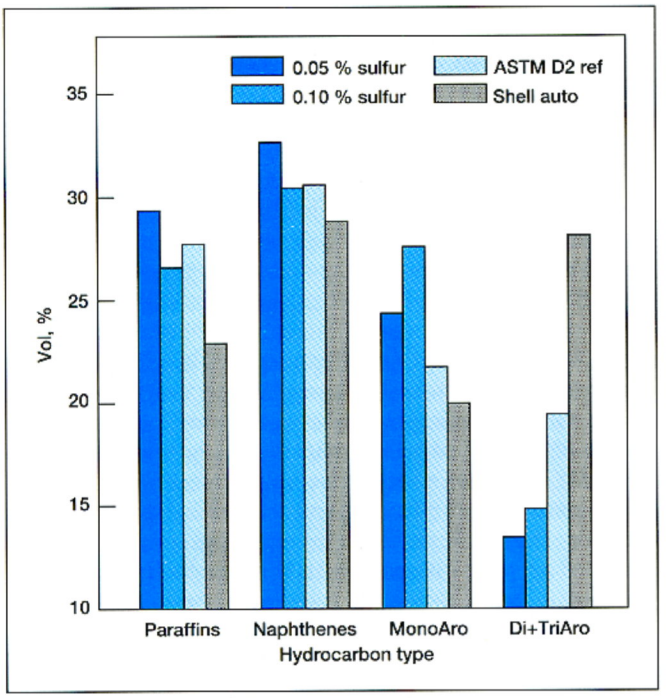

Fig. 2. Plot of NOISE analysis of four diesels.

ing/hydrocracking feed and product streams (Fig. 1) to study the effects of catalyst changes and process conditions. Fig. 1 shows Z number on the X-axis with typical structure above the bars. Note the dramatic change in hydrocarbon type, indicating the process effectiveness. Analysis of CCU feeds have also been made to establish the CC unit operating conditions and to predict yields. These jobs have enjoyed good in-plant success.

Directing streams. The new spectrometry technique also provides operators economic and logistical incentives for selecting olefin plant and reformer feeds. Without spectrometric analysis, the best use of a specific feed might not be known.

The mass spectrometer is an excellent comparator. It is particularly useful in "before and after" type studies. Analysis of crudes for hydrocarbon types by boiling range together with the determination of alkyl benzo- and dibenzothiophene types have been valuable in establishing how the crude may be best used as a feedstock. Several operators have evaluated crudes and distilled crudes using this GC/MS technique. Results give their potential as lubricating feedstocks based on their naphthene content. One client identifies biomarkers as an indication of the source of crudes.

Long-term evaluation project. NOISE analysis results are typically a one or two page report. Table 2 shows work on an experimental, low sulfur (0.1%) diesel fuel from Phillips. The concentrations reported in this analysis are tabulated by three boiling point regions. The report gives Z number both for the individual boiling point fractions and normalized for each fraction. The last column shows sample totals.

Phillips reported the ASTM D-1319 hydrocarbon type analysis by FIA for this sample. Comparison of these FIA with the NOISE GC/MS results shows good agreement.

Component	FIA	NOISE
Aromatics	36.8	37.7
Saturates	61.9	62.4
Olefins	1.3	N/A

Results are in percent by volume. The analysis did not determine olefins in this sample. Olefins present could be distributed, depending on their chemical structure, between the aromatic and saturates classification.

Replicate analyses of this sample by this GC/MS method

Table 2. Typical NOISE report

Triton Analytics Corp. GC/MS results by noise method

Sample name: reference diesel ex Phillips lot R-309 0.1% S GC/MS
Run #: LRI02908

Bp range* (°F):	lbp—450	450 to 615	615+	
Fraction, %	28.72	63.95	7.35	
C_NH_{2N+Z} Z number	**Concentration by Vol% (normalized by fraction)**			
+2	31.04	24.40	26.67	
+0	21.58	17.86	25.17	
−2	16.94	9.05	8.84	
−4	1.29	3.93	1.90	
−6	19.81	5.48	5.31	
−8	8.33	13.92	3.95	
−10	0.00	5.44	7.35	
−12	1.02	13.91	5.17	
−14	0.00	5.20	8.03	
−16	0.00	0.71	2.99	
−18	0.00	0.10	4.49	
−20	0.00	0.00	0.14	
−22	0.00	0.00	0.00	
−24	0.00	0.00	0.00	
−26	0.00	0.00	0.00	
−28	0.00	0.00	0.00	
Sum	100.00	100.00	100.00	
Z type	**Percent of total sample**			
+2	8.91	15.60	1.96	26.47 Paraffin
+0	6.20	11.42	1.85	19.47 Cyclopar
−2	4.86	5.79	0.65	11.30 "
−4	0.37	2.51	0.14	3.02 "
−6	5.69	3.50	0.39	9.58 Mono-arom
−8	2.39	8.90	0.29	11.58 "
−10	0.00	3.48	0.54	4.02 "
−12	0.29	8.90	0.38	9.57 Di-arom
−14	0.00	3.32	0.59	3.91 "
−16	0.00	0.45	0.22	0.67 "
−18	0.00	0.07	0.33	0.40 Tri-arom
−20	0.00	0.00	0.01	0.01 "
−22	0.00	0.00	0.00	0.00 "
−24	0.00	0.00	0.00	0.00 Tetra-arom
−26	0.00	0.00	0.00	0.00 "
−28	0.00	0.00	0.00	0.00 "
Sum	28.72	63.95	7.35	100.00

Remarks:
* BP ranges correspond to emergence times of N-paraffins, BR 1: NC_{12}^-, BR 2: NC_{13} to NC_{18}, and BR 3: NC_{19}^+

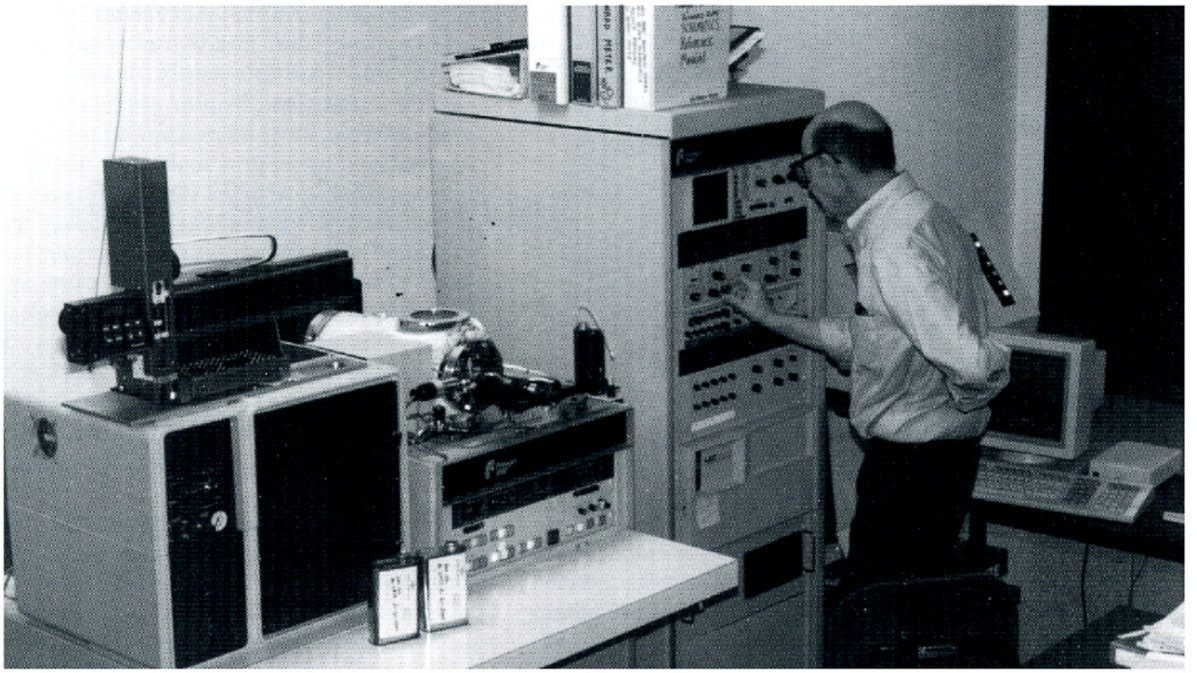

Fig. 3. Combination GC and MS first separates samples by boiling range, then determines molecular weights and saturations.

over a period of several months show for the saturates an average value of 61.7 vol% (± 1.6%), and for the aromatics, 38.3 vol% (± 1.6%). Results from the two entirely different methods of analysis show close concurrence.

We analyzed three other diesel fuels over a number of months for quality control. They show the same reproducibility. Two samples are reference fuels from Phillips (ASTM D-2 standard and a 0.05% sulfur). The other sample is an automotive diesel fuel, purchased at a service station (Fig. 2).

METHOD DETAILS

During the 1980s, there became available a new method of ionization of molecules. Chemical ionization uses a low molecular weight material. The charged species (reagent ion) serves to ionize the sample molecules. Energy levels distinguish chemical ionization (CI) from electron ionization (EI).

The resulting difference between the EI and CI mass spectra of various substances can be dramatic. CI can produce a simplified sample mass spectrum, often with enhanced sensitivity.

How NOISE works. The method uses GC followed by MS (Fig. 3) with a novel ionization method. NO^+ ions at relatively low energy replace ionization by the conventionally used electron impact mode. The combination of the separation power of the gas chromatographic techniques together with the unique ionization characteristics of nitric oxide provide unambiguous determination of certain hydrocarbon types.

A useful and much-used classification scheme for hydrocarbons is the equation C_nH_{2n+Z} where Z is defined as the hydrogen deficiency. For example, a paraffin of any C number has a Z number of + 2. An alkyl monoaromatic has a Z number of −6. Benzene, C_6H_6, the beginning of the alkyl monoaromatic series of compounds, is expressed as C_nH_{2n-6}. Mass spectrometric hydrocarbon type reports usually follow this format.

For example, the naphthalene, (Z = −12) and paraffin (Z = + 2) types of hydrocarbons, which have the same nominal mass, resolve on the basis of their characteristic ionization using NO^+ ion. The naphthalene types produce an M^+ ion. The paraffin types produce an $M-1^+$ ion under these conditions. We observe this effect for other saturated aromatic hydrocarbon overlaps in EI-type mass spectra. Benzothiophenes and dibenzothiophenes separate by gas chromatographic technique from the alkyl aromatic and alkyl naphthalenes respectively.

The NO^+ reagent ions react with the analyte hydrocarbons through the three reactions: hydride ion abstraction (reaction 1), charge exchange (reaction 2) or addition reaction (reaction 3). The specific reaction or combinations of reactions seem to depend primarily on the carbon skeleton and the C-C bond configuration of the hydrocarbon molecule, M, as well as the ionization potential of the molecule.

$$NO^+ + M \rightarrow (M-H)^+ + HNO \quad (1)$$

$$NO^+ + M \rightarrow M^+ + NO \quad (2)$$

$$NO^+ + M \rightarrow (MNO)^+ \quad (3)$$

Reaction 1 is most characteristic for saturated hydrocarbons. Reaction 2 predominates for aromatics with some minimal reaction 3 observed for the beginning members of each aromatic homologous series. Reaction 2 also occurs for the condensed polycyclic saturated hydrocarbons such as cholestane. Olefins show a mixed reaction depending on their structure for reactions 1, 2 and 3.

The most abundant reactions take place without cleaving carbon-carbon bonds in the parent molecule. The lower energy (compared to EI) allows structure to survive. Thus we can measure the original constituents directly rather than extrapolating from fragments.

Accuracy. Before offering the new method, we tested it with a wide variety of aggregates of hydrocarbon types, including model compounds and aromatic and saturate blends. The n-paraffin blends served to calibrate emergence times of the GC with temperature and recovery efficiency. For n-$C_{40}H_{82}$, bp at 977°F, recovery is 60+%. But we do not detect n-$C_{44}H_{90}$, bp at 1,018°F.

Reproducibility is surprisingly good. Analysis of diesel

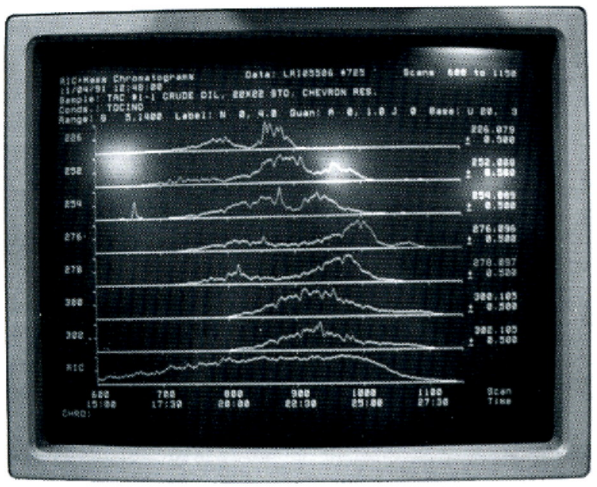

Fig. 4. NOISE gives real-time display. This screen establishes the presence of dibenzothiophenes at mass 226.

boiling range materials over a period of several months show a relative standard error of from 3% to 6% of the amount for those concentrations greater than 5% to 8% volume. Spiking experiments, using blends of model compounds, indicate that the accuracy and precision of the method are about the same, 3% to 7%. Comparison of the results with other methods of analysis, specifically C_{13} NMR, and UV also provide verification.

Analyzing and using data. Our GC/MS passes raw data to a computer. A set of simultaneous equations then apply to take into account the mass spectral characteristics for each class of compounds by the prespecified boiling ranges (Fig. 4). Results are expressed as liquid vol%. Estimates can be provided for the iso/normal paraffin distribution as well as certain of the aromatic thiophenic type sulfur compounds for some types of samples.

The new method provides the quantitative distribution of hydrocarbon types within specified boiling ranges. It can differentiate aromatic and saturated hydrocarbon compounds of the same nominal molecular weight as well as sulfur compounds from hydrocarbons of the same nominal molecular weight. The method can also provide an estimate of the normal/isoparaffin concentrations by either C number or boiling region.

Advantages over EI. With EI, most of the detected mass spectrum results from carbon-carbon bond fission. While one can guess the extent of fragmentation for any speculated type of hydrocarbon, nothing quantitative can be realized for the relative intensities of the observed ions. Under EI ionization, paraffin hydrocarbons of the general formula, C_nH_{2n+2}, the most abundant ions observed are ions of formula, C_nH_{2n+1}. This class is formed by the C-C bond fission.

For the analysis of gasoline range and higher boiling mixtures, any of the mass spectrometric methods of analysis have very little utility in determining individual compounds. However, for the analysis of very complex mixtures, type analysis has proven very useful. Type analysis determines component distribution by Z value, and, to a lesser degree of reliability, C number of these Z types. The utility of these type methods is that they provide a detailed and precise means of evaluating the mixture for value as a feedstock or effectiveness of a particular chemical or physical process.

Well established and tested mass spectrometric methods of type analysis apply to gasoline boiling range (<450°F) mixtures. Similar styles of mass spectrometric type analyses have been applied to kerosines and heavier fractions up to and including heavy lubricating oils. These methods provide a more approximate analysis than that determined for the gasoline boiling range. Mass spectral sensitivities used in these later methods were extrapolated from a very limited set of pure compounds and a limited number of separated hydrocarbon type aggregates.

For heavier materials, there are two kinds of hydrocarbon type analyses. The older method is the fragment peak method that estimates the distribution of substances by number of rings per molecule. It attempts to estimate the polyring molecules as condensed and noncondensed ring systems.

The other method, used with a high resolution mass spectrometer, is the parent peak method. This method depends on measurement of the intensities of what are believed to be the molecular ions in the sample. It applies appropriate sensitivity coefficients to determine a distribution of both N and Z of the mixture. The determination of Z number distribution is usually well-defined while the N distribution is, at best, an estimate. Various laboratories often use combinations of the fragment and parent peak methods combined in such ways as to suit their individual needs.

All the competing analytical methods, whether using a single focusing (low resolution), or a double focusing (high resolution) mass spectrometer, analyze the sample in the batch mode. Analysis time ranges from minutes to a few hours with the data reduction usually done in background. There is no means of fractionating the sample into specific boiling ranges except by prior separation into boiling point cuts from a distillation or some other sort of separation means.

LITERATURE CITED

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