

On-line chromatographic analyser for determining the composition and octane number of reforming process effluents

J. P. DURAND*, Y. BOSCHER and M. DORBON

Institut Français du Pétrole, B.P. 311, 92506 Rueil-Malmaison (France)

ABSTRACT

An on-line analyser for reforming process effluents was developed from a commercial chromatograph and a computer. A temperature-programmed capillary column is used with software to make a detailed analysis (by automatic identification on the chromatogram) and to determine different physical properties (specific gravity, molecular weight, research and motor octane numbers, etc.).

INTRODUCTION

The growth in the demand for unleaded gasoline is a new challenge for refiners to produce high-octane gasoline during the next decade. In consequence, optimization of refining processes and development of new analysers are required. The on-line determination of octane number has become an important technique for refiners. The Cooperative Fuel Research engine is not well suited for on-line applications because it requires constant maintenance and frequent standardization, and consumes 0.5 l per test.

Numerous methods based on capillary gas chromatographic (GC) columns have been described during the last 20 years for determining different physical properties, especially the octane number, from detailed analysis²⁻⁴. Recently, several reports of octane-number determinations by spectroscopic techniques, such as nuclear magnetic resonance⁵ and infrared spectroscopy⁶ have appeared. Although these techniques have the advantage of being much faster than GC, they do not give a complete analyse of gasoline and their use in process control has not yet been developed or is difficult. GC is widely used in process control, but the development of an automatic analyser depends on the automatic identification of complex chromatograms (more than 200 peaks for gasoline chromatograms). With advances in the reliability of chromatographs and in GC data systems, this automatic identification has become feasible. A method using temperature-programmed retention indices has been described⁷, with *n*-alkanes as reference peaks. These retention indices are reproducible by different chromatographs and commercial columns having the same characteristics

if the retention times of *n*-alkanes are within $\pm 5\%$ of those used for setting up the reference table of retention times.

This paper describes an automatic on-line GC analyser for determining the composition and octane number of reforming process effluents.

EXPERIMENTAL

The instrumentation consists of a Hewlett-Packard (Palo Alto, CA, U.S.A.) apparatus package and software developed in our research institute.

Equipment and chromatographic conditions

The GC analyses were performed with a Hewlett-Packard HP 5890 gas chromatograph equipped with a flame ionization detector and with liquid valve injection by a split injector. Different effluents were selected by multi-port valves.

A fused-silica capillary column (50 m \times 0.2 mm I.D.) cross-linked with a 0.52- μ m film of OV-1 methylsilicone was used. The column oven temperature was increased from 40 to 200°C at 2°C/min with a final isothermal time of 20 min. The helium carrier gas flow-rate was set at 1.2 ml/min. The detector and injector temperature were held at 250°C. The splitting ratio was 1:170 and the sample size was 0.5 μ l. The time between two analyses was 2 h.

Data integration was carried out using an HP 3392 A integrator and data handling using an HP 1000 computer (A 400 series).

Software package

The software was a Fortran program developed in our institute. It allows the analyser to run automatically while controlling different components, selecting effluents, calibrating, identifying and quantifying components and determining physical properties.

Control of the analyser. The analyser is computer controlled. At the outset the software checks to see if the chromatograph and integrator are ready. Then it selects an effluent with a purge period and, at the same time, it starts the injection, chromatograph and integrator. At the end of the analysis it transfers the data from the integrator to the computer.

Calibration. Calibration is carried out with a mixture of C₅–C₁₈ *n*-alkanes. The software automatically identifies the reference peaks and creates a reference table of the retention times of *n*-alkanes, in which an identification zone is defined for each. This reference table is updated with the calibration mixture when the retention time of *n*-alkanes is between 60 and 100% of the identification zone.

Identification and calculation. *n*-Alkanes are identified from the reference table. Then, for each peak, an index I_{ip} is calculated, defined as

$$I_{ip} = \frac{t_{R,i} - t_{R,n}}{t_{R,n+1} - t_{R,n}}$$

where t is the retention time of compound i , eluted between *n*-alkanes with n and $n+1$ carbon atoms. The I_{ip} values calculated are compared with the reference index file. For each compound this file contains the index for the analytical conditions listed above

together with an identification window. The compounds are classified into five hydrocarbon groups: *n*-alkanes, isoalkanes, naphthenes, alkenes and aromatics.

Physical properties are determined by weight percentage analysis. For non-additive properties, coefficients are calculated by correlation with the properties measured for a batch of samples.

RESULTS AND DISCUSSION

Detailed analysis

More than 200 peaks were identified in gasoline up to C₁₀ for saturates and C₁₆ for aromatics (at a low level after C₁₂). Table I gives the final report on the aromatic group. The report also gives the distribution by carbon number and hydrocarbon group and the weight percentage of carbon-hydrogen. The results were compared with the PNA method [where P (paraffins) = alkanes, N = naphthenes and A = aromatics]⁸ for about 100 samples. The difference between the methods was less than 2% for the aromatic group.

Determination of physical properties

The specific gravity at 15°C and the molecular weight are calculated from the properties of pure components. For octane numbers the chromatogram is condensed into 45 groups according to the hydrocarbon group and carbon number of each compound. The coefficient for each group was adjusted to fit with the research octane number (RON) and motor octane number (MON) determined experimentally with the CFR engine; 150 samples of reformates selected for their different compositions by hydrocarbon groups were used for RON correlation. The octane number ranges of

TABLE I
FINAL REPORT ON THE AROMATIC GROUP

% (w/w)	Component	% (w/w)	Component
4.92	Benzene	0.12	1-Methyl-4- <i>n</i> -propylbenzene
22.56	Toluene	0.29	1,3-Dimethyl-5-ethylbenzene
5.47	Ethylbenzene	0.05	1-Methyl-2- <i>n</i> -propylbenzene
13.53	<i>m</i> -Xylene	0.17	1,4-Dimethyl-2-ethylbenzene
3.71	<i>p</i> -Xylene	0.16	1,3-Dimethyl-4-ethylbenzene
7.19	<i>o</i> -Xylene	0.29	1,2-Dimethyl-4-ethylbenzene +
0.26	Isopropylbenzene		1,3-Dimethyl-2-ethylbenzene
0.93	<i>n</i> -Propylbenzene	0.02	C ₁₀ aromatic
3.76	1-Methyl-3-ethylbenzene	0.06	1,2-Dimethyl-3-ethylbenzene
1.64	1-Methyl-4-ethylbenzene	0.22	1,2,4,5-Tetramethylbenzene
1.75	1,3,5-Trimethylbenzene	0.30	1,2,3,5-Tetramethylbenzene
1.41	1-Methyl-2-ethylbenzene	0.05	5-Methylindan
5.46	1,2,4-Trimethylbenzene	0.01	C ₁₁ aromatic
1.09	1,2,3-Trimethylbenzene +	0.01	Methylindene
	1-Methyl-4-isopropylbenzene	0.06	4-Methylindan
0.23	Indan	0.09	C ₁₁ aromatic +
0.02	Indene + 1 methyl-2-isopropylbenzene		1,2,3,4-tetramethylbenzene
0.09	1,3-Diethylbenzene	0.24	Naphthalene
0.17	1-Methyl-3- <i>n</i> -propylbenzene	0.01	C ₁₁ aromatic

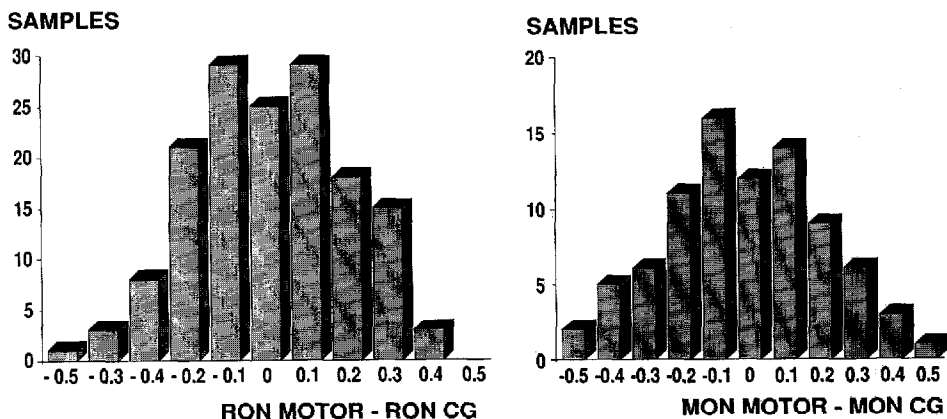


Fig. 1. Distribution of the samples versus the difference between the measured and determined research and motor octane numbers for determining the correlation.

these samples are 88–107 for RON and 78–95 for MON. Fig. 1 shows the distribution of the samples versus the difference between the measured and determined octane numbers.

Test of the analyser

The analyser was tested for 2 years on reforming and aromizing effluents with on-line and off-line configurations. The same capillary column was used, and calibration was done once per month. The difference between the measured and determined RON and MON was the same as for the correlation determination.

Intervention by the operator was required only for sample injection, *i.e.*, selection of different effluents (by modifying a sequence) or mixture calibration. Some chromatographic problems such as leaks or level of the baseline are given in the final report as a warning.

CONCLUSION

The development of an automatic capillary GC analyser has become feasible with advances in the reliability of chromatographs using a GC data system, and chromatographic data handling permits the direct determination of different physical properties. An automatic on-line capillary GC analyser was developed for determining the composition and octane number of reforming process effluents. With one analysis every 2 h, this analyser can control and optimize the operating conditions of a plant. However, the use of such an analyser on-line in a refinery requires the analyser to be explosion-proof. Such an operation is the next step of development. The best way for the analyser to be made explosion-proof is to locate the chromatograph, the integrator and the computer in a small pressurized shelter. The equipping of the shelter is now in progress, and an on-line test of the reforming unit of a refinery will take place in the near future.

REFERENCES

- 1 I. P. Karlin, S. A. Leont'eva, E. P. Semkin, V. A. Kvasova, V. N. Galyashin and N. M. K. Urz'min, *Zh. Anal. Khim.*, 39 (1984) 75.
- 2 G. I. Jenkins, N. G. Mc Taggart and B. L. H. Watkin, in C. L. A. Harbourn and R. Stock (Editors), *Gas Chromatography 1968*, Institute of Petroleum, London, 1969, p. 185.
- 3 R. P. Walsh and J. V. Mortimer, *Hydrocarbon Process.*, 50 (1971) 153.
- 4 P. CV. Anderson, J. M. Sharkey and R. P. Walsh, *J. Inst. Petrol.*, 58 (1972) 83.
- 5 J. Mühl, V. Srica and M. Jednacak, *Fuel*, 68 (1989) 201.
- 6 J. J. Kelly, C. H. Barlow, M. Jinoye and J. B. Callis, *Anal. Chem.*, 61 (1989) 313.
- 7 J. P. Durand, Y. Boscher, N. Petroff and M. Berthelin, *J. Chromatogr.*, 395 (1987) 229.
- 8 H. Boer, P. van Arkelp and W. J. Boersma, *Chromatographia*, 17 (1980) 500.