



ELSEVIER

Journal of Chromatography A, 750 (1996) 97–104

JOURNAL OF  
CHROMATOGRAPHY A

# Coupled simulated distillation–mass spectrometry for the evaluation of hydroconverted petroleum residues

R. Bacaud\*, L. Rouleau

*Institut de Recherches sur la Catalyse, C.N.R.S., 2 Avenue Albert Einstein, 69626 Villeurbanne, France*

## Abstract

The coupling of simulated distillation by gas chromatography with mass spectrometry has been applied to the characterization of the products obtained by hydroconversion of a deasphalted vacuum residue, performed either in thermal, non-catalytic conditions, or in the presence of various dispersed catalysts. Applying spectra deconvolution techniques, the relative contribution of four saturated and four aromatic classes of hydrocarbons to the spectra is obtained and simulated distillation–mass spectrometry coupling provides the distribution of these classes of compounds along the distillation profile of the products. The impact of catalysts upon the distribution of the considered classes of hydrocarbons has been evidenced. It consists in a reduction of aromatics and an increase of saturates. This analytical data can be rationalized and correlated with hydrogen distribution during hydroconversion, indicating that the role of catalysts does not consist in a simple hydrogenation of aromatics but in a complete redistribution of hydrogen. Coupled simulated distillation–mass spectrometry appears to be a valuable tool for a fast analytical characterization of complex hydroconversion products, without the need for previous separation steps.

*Keywords:* Simulated distillation; Petroleum; Process analysis; Catalysis

## 1. Introduction

Heavy feeds derived from the development of non-conventional oilfields are progressively introduced in refining processes. They contain high levels of asphalt which concentrate in distillation residues; as a result, a straight vacuum distillation of these feeds produces a large percentage of low-value by-products. The market for heating fuels, which is the main outlet of non-distillable residues, is being progressively reduced for ambient considerations and, in parallel, the demand for distillate and light products like transport fuels is increasing. This conflictive evolution of supply and demand implies that petroleum residues must be converted and that

processes for this transformation have to be developed.

Since residues are hydrogen deficient, conversion processes will aim at increasing their hydrogen content. In this respect, processes can be classified according to the pathway selected for improving hydrogen-to-carbon ratio. Two broad categories appear: those performing an improvement of H/C through carbon rejection (coking or deasphalting), and at the opposite, those increasing the hydrogen content of the feed (hydrocracking). Obviously, the latter performs a better valorisation of the fossil carbonaceous matter contained in residues than coking does. Hydrocracking involves a complex set of reaction pathways whose ultimate goal is to cause a decrease of the mean molecular mass of the feed, and may also involve a reduction of hetero-atoms

\*Corresponding author.

content. The control of such reactions relies essentially upon an adequate balance between the depth of conversion and the cost of hydrogen incorporation [1]. In order to achieve a proper control of process conditions, an adequate and fast responding technique for products evaluation is necessary. Analytical procedures for characterizing processed products rely upon a compromise between extensive, time consuming determinations and the necessity for a rapid response. They must provide information concerning the yield of distillate, which is the desired product, and its properties. Simulated distillation by gas chromatography (Simdist) is able to provide the first information. As described in ASTM method D2887, Simdist is based upon the use of packed columns [2]. The multiple drawbacks of this technology induced the introduction of capillary-based methods, which produce more precise results than ASTM method D2887 [3]. Capillary columns are presently applicable to a wide range of boiling points, since stationary phases withstanding temperature up to 440°C allow the elution of hydrocarbons containing up to 120 carbon atoms [4]. The yield of any given fraction of products can be deduced from Simdist data.

Low-resolution mass spectrometry has long been applied to the analysis of distillates by direct introduction of pre-vaporized samples. The resulting spectra can be deconvoluted and it is possible to extract the respective contribution of saturates and aromatics, as described in the quantitative method developed for the determination of 4 saturated hydrocarbons types and 12 aromatic types in samples boiling between 100 and 600°C [5,6]. We propose, in the present work, the coupling of a simulated distillation GC column with a low-resolution quadrupole mass spectrometer for a fast determination of distillation profiles and distribution of hydrocarbons types as a function of boiling point in raw hydrotreated samples.

## 2. Experimental

### 2.1. Hydroconversion

The feed for hydroconversion experiments was a butane-deasphalted oil (DAO) obtained from a

510°C vacuum residue. Its analytical characteristics were: H/C atomic ratio=1.64; S=0.85 mass%; specific gravity=1.058 g cm<sup>-3</sup>.

Hydroconversion was performed either in thermal conditions (without catalyst), or in the presence of catalysts. The catalysts of this study were used as dispersed, disposable solids. Three different kind of solids have been used: a nickel-carbon plasma-prepared catalyst [7], molybdenum naphtenate and alumina-supported Ni-Mo catalyst (Shell 424). The catalyst-to-feed ratio was 450 ppm, expressed as metal (Ni or Mo+Ni).

Hydroconversion experiments were carried out in a 250 cm<sup>3</sup> autoclave equipped with a magnetically driven impeller (Autoclave Burton Corblin, Paris, France), a cooling coil and a pressure transducer. Hot DAO (100 g) was poured into the autoclave at 373 K. This temperature is required owing to the high viscosity of the charge at a lower temperature. The desired amount of catalyst was added. After the autoclave had been purged and cooled, hydrogen at a pressure of 14 MPa was introduced and the pressure was accurately measured. The temperature was then raised to 373 K and kept at this value for 10 min in order to start mixing and to enable the speed of the impeller to stabilize at 600 rpm. Afterwards, the heating program was started. The reaction temperature (713 K) was maintained for 1 h.

During a run, pressure and temperature were continuously monitored. After the desired residence time, the reactor was cooled down and the final pressure was measured. Gases were recovered by heating the autoclave at 373 K in order to strip the liquid products; a trap maintained at 273 K and positioned at the output of the reactor condensed volatile products (mainly C<sub>5</sub> to C<sub>7</sub> hydrocarbons). This liquid fraction was collected together with the total liquid content of the autoclave. The volume of recovered gases was metered and analyzed by gas chromatography in order to establish a material balance of hydrogen consumption. The distribution of hydrogen utilization, between gas production and liquid incorporation, was defined as:

Total H=consumption of gaseous hydrogen  
(mmol of H<sub>2</sub>/100 g feed)

Gas H=hydrogen consumed for gases formation

Liquid H=Total H-Gas H

## 2.2. Simulated distillation

A sample of the liquid products was diluted with carbon disulfide at the concentration of 0.4% (w/w). 1  $\mu$ l of this solution was injected into a HT5 column (6 m $\times$ 0.53 mm) equipped with a 1.25 m precolumn. The gas chromatograph (HP 5890), equipped with on-column injector and flame ionization detector, was programmed from 303 to 673 K at 10 K min<sup>-1</sup>. The temperature of the injector was maintained at 3 K above the column temperature.

### 2.2.1. Calibration of retention time scale

Retention time ( $t_R$ ) can be converted to a scale of equivalent number of carbon atoms,  $x$ , contained in a series of linear paraffins which are eluted in a given range of  $t_R$ . Low  $x$  values (C<sub>12</sub> to C<sub>40</sub>) were calibrated with pure paraffins. A mixture of linear, even polyethylene (Polywax 655, Luzzato and Figlio, Paris, France) was used as calibration standard in the range C<sub>24</sub> to C<sub>100</sub>. The resulting chromatogram is presented in Fig. 1.

### 2.2.2. Quantitation

The detector signal was integrated every 0.1 min. On completion of the temperature program, the signal corresponding to a blank run performed in the same conditions was subtracted. If the sample was totally eluted during the analysis, the total area of the detector signal was normalized to 100% and the amount of material eluted in a given range of temperature was simply deduced from its contribution to the total area. In this procedure, it is assumed that the molar response of the detector is constant over the whole elution range of the sample, i.e. that the mean molecular structure of the eluted compounds is constant. When solutions of unconverted DAO were analyzed, elution was limited to 92% of the injected material; in that case, an internal standard (dodecane) was added to the sample.

## 2.3. Coupled simulated distillation–mass spectroscopy

Analysis were performed with a Shimadzu QP1000 GC–MS system. A sample of the total liquid products was diluted with carbon disulfide at the concentration of 5% (w/w). 0.5  $\mu$ l of this

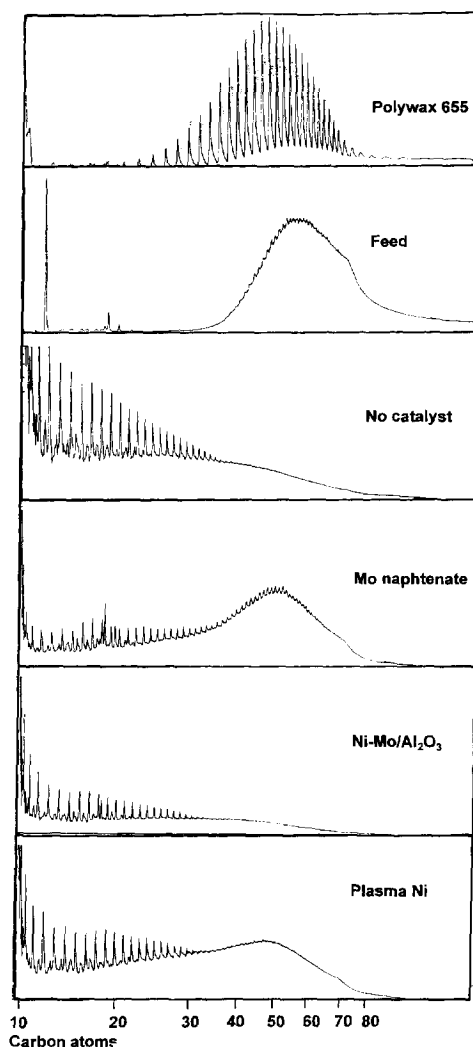


Fig. 1. Simulated distillation chromatograms.

solution was injected by direct on-column injection, into a HT5 column (4 m $\times$ 0.32 mm). The initial temperature was kept at 313 K for 1 min, then programmed up to 623 K at 15 K min<sup>-1</sup>. The final temperature was maintained for 5 min. The coupling of the GC column and the ion source of the spectrometer consisted of a glass jet-separator heated at 623 K. The source was maintained at 623 K. Mass spectra, obtained in the electron impact mode at 70 eV, were acquired in the range 40–600 u every 5 s. Blank spectra were obtained through the same acquisition protocol, after injection of pure solvent in

the gas chromatograph, applying the same temperature program.

### 2.3.1. Methodology of mass spectra data reduction

The total ion current curve of a hydroconverted sample is presented in Fig. 2. It must be noticed that, owing to the limited source temperature, the heating program of the column was stopped at a lower temperature than during quantitative Simdist with flame ionization detection. Consequently, elution was limited to fractions containing up to 36 carbon atoms. Applying the calibration of  $t_R$  scale obtained with pure paraffins, the  $x$ -axis was divided into sections of carbon atoms numbers. In a given range (for instance  $C_{16}$ – $C_{18}$ ), spectra were summed and averaged. Thus a mean spectrum corresponding to a given range of carbon atoms number was obtained. The same procedure was applied to blank spectra (obtained with pure solvent), and finally the corresponding blank spectrum was subtracted from the sample spectrum for correction of column bleeding.

The procedure for spectra processing follows the model developed by Robinson and Cook [5]. It consists in extracting the saturates spectrum and aromatics spectrum from the global data. Cross contributions of each hydrocarbon family to the spectrum of the other one are eliminated by the procedure described in [6]. After the contribution of

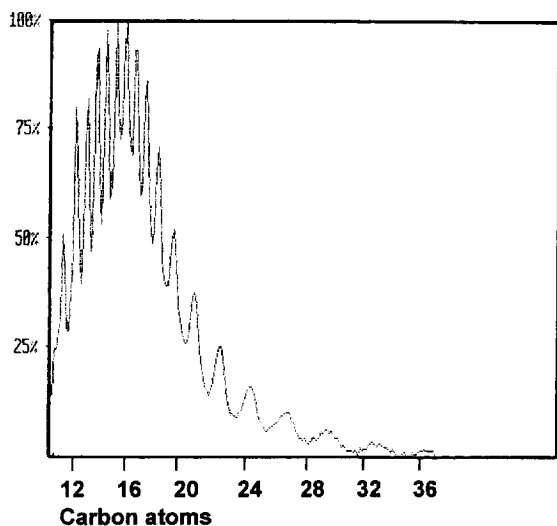


Fig. 2. Total ion current obtained by coupling simulated distillation column to mass spectrometry.

Table 1

Classes of aromatics and saturated hydrocarbons evaluated by processing of mass spectral data

Saturates	Aromatics
Paraffins	Monoaromatics
Cycloparaffins	Naphtenoaromatics
Bicycloparaffins	Dinaphtenoaromatics
Tricycloparaffins	Naphthalenes
(include heavier cycloparaffins)	Acenaphthenes
	Fluorenes, Phenanthrenes

each hydrocarbon type to the total ionization has been calculated, the volume percent of the four classes of saturated and six classes of aromatic hydrocarbons are obtained by normalization to 100%. Table 1 gives the list of the corresponding hydrocarbon families.

Possible interferences in saturates spectra concern the presence of olefins. Interferences in aromatic spectrum are caused by sulfur compounds. Owing to the low olefins content in the converted products, (less than 500 ppm olefinic hydrogen) and the low sulfur content of the feed, these interferences could be neglected. Since the contribution of the last three classes of aromatic compounds (acenaphthenes, fluorenes and phenanthrenes) was less than 1% of the total products, the corresponding values were not reported.

### 3. Results

Raw data from quantitative simulated distillation (Fig. 1) illustrate the fact that catalysts have a clear impact upon conversion of the considered feed. Particularly, it can be noticed that the simulated distillation chromatogram of the products obtained in the presence of molybdenum naphthenate exhibits some high-boiling-point fractions. In contrast, the products obtained in non-catalytic conversion elute essentially in lower range of boiling point. Other catalysts display intermediate patterns. Cumulative Simdist curves presented in Fig. 3 indicate that the yield of low-boiling-point products is effectively limited when hydroconversion is performed in the presence of catalysts.

The main interest in adapting the analytical MS protocol to simulated distillation consists in the

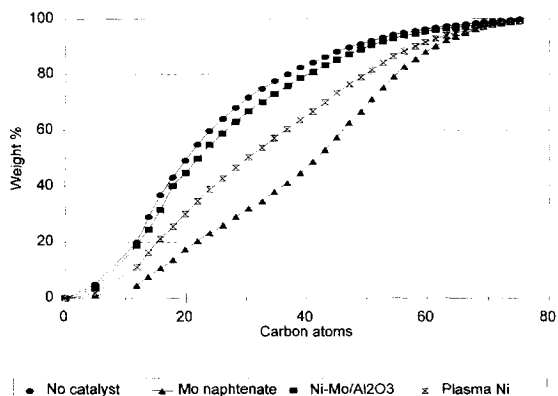


Fig. 3. Cumulated simulated distillation curves of hydroconverted samples.

possibility of deriving the quantitative distribution of hydrocarbons types as a function of the boiling point (or equivalent number of carbon atoms) of distilled fractions. Fig. 4 illustrates this raw information: as the number of carbon atoms increases, the contribution of paraffins declines and is compensated by a corresponding increase of condensed cycloparaffins. The total content of saturated hydrocarbons increases slightly, along with carbon atom number. Correspondingly, aromatic structures are more abundant in low-molecular-mass fractions, monoaromatics being the essential entities, and the total aromatics concentration declines as the carbon atom number of distillate fractions increases. It could be expected that this distribution pattern is affected by the presence of a catalyst. Fig. 5 compares the distribution of monoaromatics, respectively, obtained in

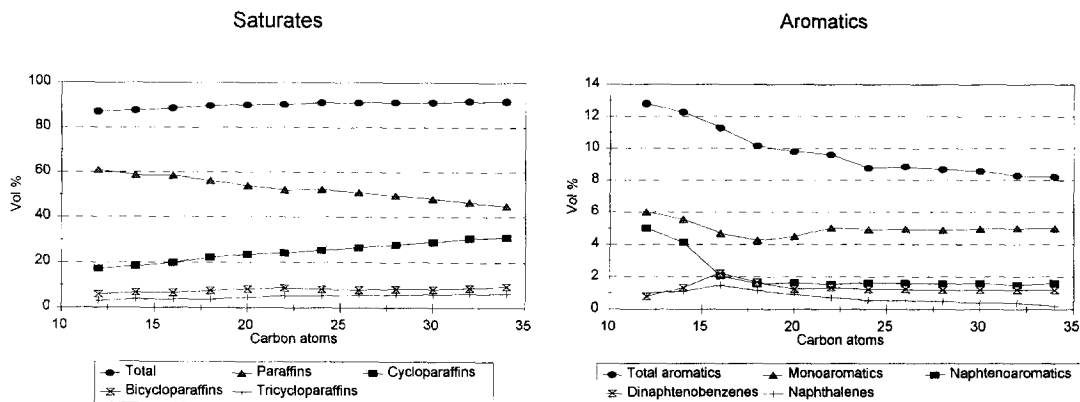


Fig. 4. Distribution of saturates and aromatics as a function of carbon atom number of eluted fractions.

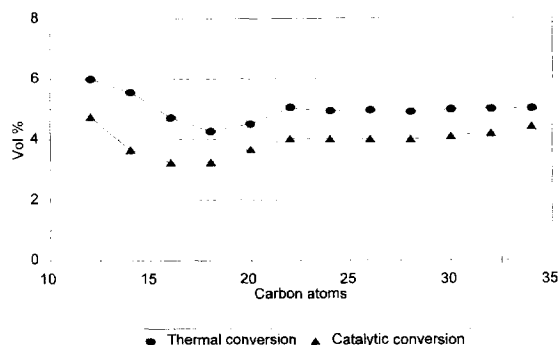


Fig. 5. Comparison of monoaromatics distribution obtained in thermal and catalytic conversion.

thermal conversion and in the presence of molybdenum naphtenate (which is the most active among the hydrogenation catalysts of this study). It appears that the curves follow a parallel evolution. Hence, the presence of this catalyst reduces the content of monoaromatics in the whole range of distillable fractions.

Despite this apparent similarity in products distribution, the amount of each distilled fraction must be taken into account in an attempt to quantify the integrated concentration of each product family in the range of carbon atom numbers involved in GC-MS acquisition (from 12 to 34 carbon atoms). It must be stressed that this range concerns the lighter fractions of hydroconverted products, the amount of which being strongly influenced by the nature of catalyst as evidenced by the cumulative Simdist curves in Fig. 3. In order to obtain the cumulative

distribution of hydrocarbon types measured by GC–MS, the concentration of each hydrocarbon family in each fraction was multiplied by the relative amount of the corresponding fraction, then summed and normalized over the range  $C_{12}$  to  $C_{34}$ . The resulting distributions, normalized to 100%, are presented in Fig. 6. Any one of the considered catalysts causes a decrease of all aromatic classes and a corresponding increase of total saturates. A possible interpretation would be the transformation of aromatic entities in the corresponding saturated species through catalytic hydrogenation. For example, monoaromatics would be converted into cycloparaffins. Such an assumption implies that a correlation exists between the concentration of both classes of compounds. The existence of correlations between the considered classes of compounds is illustrated by Fig. 7. It appears that the concentrations of monoaromatics and cycloparaffins are effectively correlated (regression coefficient,  $R = -0.97$ ). Therefore, a process involving a conversion of aromatics into cycloparaffins could effectively contribute to the decline of aromaticity. However, the slope of the linear correlation between the concentration of monoaromatics and cycloparaffins is different from unity. Furthermore, a plot of the variation of the concentration of the different classes of saturated compounds against the total contribution of saturates, indicates that the only classes whose concentrations are positively correlated with the total saturates content are paraffins and monocycloparaffins; other saturated species are negatively correlated.

In contrast, the concentrations of the different aromatic classes correlate with total aromaticity.

These results indicate that the influence of catalysts upon the respective distribution of saturates and aromatics does not consist of a mere catalytic hydrogenation of aromatic species and that hydrogen transfer reactions are probably more complex. Thus, an examination of analytical parameters of hydroconverted products, in relation with hydrogen balance, might provide some insight into the mechanism of hydrogen distribution during catalytic hydroconversion. As illustrated by Fig. 8, the total hydrogen consumption is only slightly or not affected by the presence of the catalysts used in this study. However, the distribution of hydrogen utilization between gas production and incorporation in the liquid products is extremely different, indicating that thermal, non-catalytic conversion produces extensive hydrocracking and generates large amounts of gases and light distillate. These reactions are hydrogen consuming and, although the global balance of the reaction indicates a consumption of hydrogen, the quantities of this reactant involved in transformations concerning the liquid products are negative. Thus, thermal conversion generates products which are hydrogen deficient—more aromatic—as compared to the feed. In contrast, the values of this parameter observed in catalytic conversion are positive, indicating an incorporation of hydrogen in the liquid products.

A plot of aromatics against hydrogen incorpora-

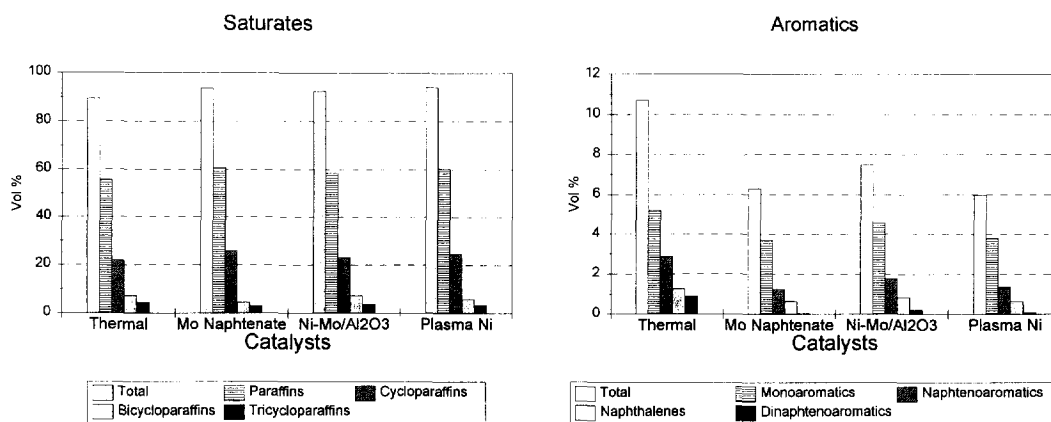


Fig. 6. Distribution of saturate and aromatics classes obtained in the presence of various catalysts.

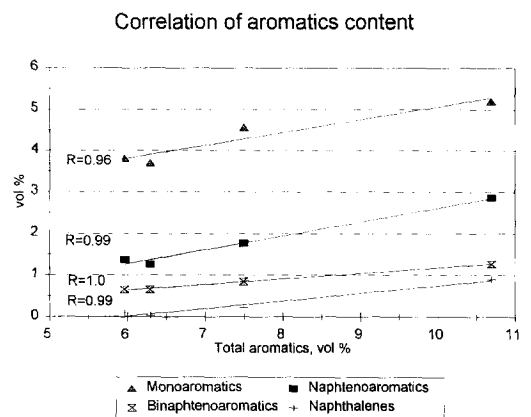
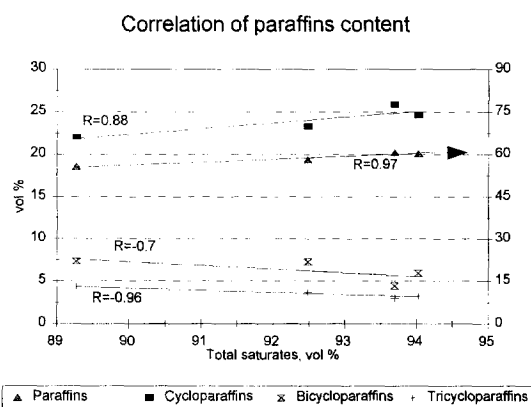
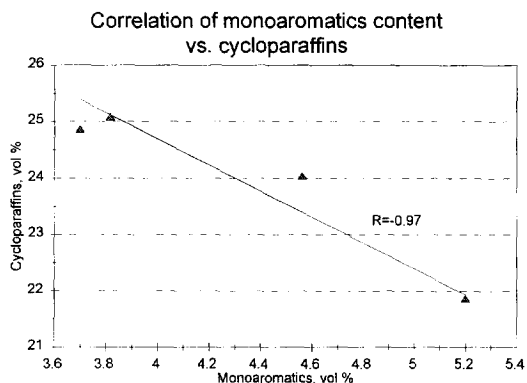


Fig. 7. Correlations between the concentrations of aromatics and saturates classes.

tion reveals a linear relationship (Fig. 9). In thermal conversion, hydrogen depletion of the liquid products is associated with a corresponding decrease of saturates, i.e. an increase in total aromaticity. The resulting products are more aromatic and hydrogen

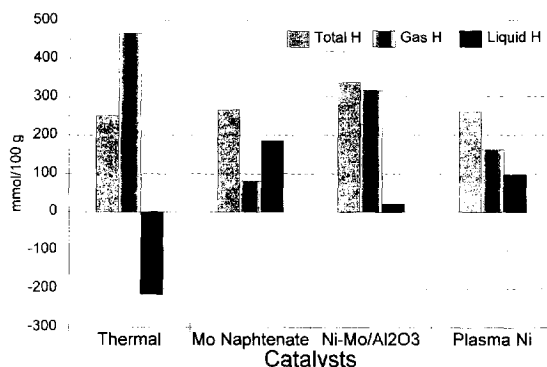


Fig. 8. Hydrogen balance observed in hydroconversion.

deficient, as compared to the feed. A fraction of this hydrogen deficiency of the liquid products is utilized for the production of gases, as evidenced by the material balance in Fig. 8.

In the light of the preceding data, the mechanism of hydroconversion and the role of catalysts can be rationalized. The initial stage of hydroconversion consists of a thermal initiation step producing radical species through C-C or C-heteroatoms bond cleavage. Once generated, these radicals can follow various evolution pathways:

- condensation, forming heavier entities by recombination;
- propagation inducing multiple bond cleavages and producing light distillate and gases;
- stabilization by hydrogen atoms.

This latter way can be favoured, provided the rate of production of activated hydrogen is larger than the

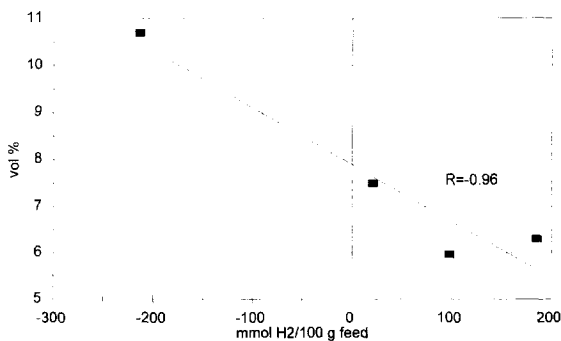


Fig. 9. Correlation of total aromatics vs. hydrogen incorporation.

rate of radicals formation. Such a situation prevails in the presence of hydrogenation catalysts which provide a source of activated hydrogen. As a consequence, the alternative stabilization routes are limited, as is illustrated by the observed decrease of light distillate and gas formation.

#### 4. Conclusion

Hydroconversion of a deasphalted vacuum residue has been performed either in thermal, non-catalytic conditions, or in the presence of various dispersed catalysts. The coupling of Simdist with MS has been applied to the characterization of the converted products, without previous fractionation. Applying spectra deconvolution techniques, the relative contribution of four saturated and four aromatic classes of hydrocarbons to the spectra is obtained. Hence, Simdist–MS coupling provides the distribution of these classes of compounds along the distillation profile of the products.

As the number of carbon atoms of the eluting fractions increases, the relative contribution of saturates increases, at the expense of aromatics. The presence of catalysts during hydroconversion does not modify this trend. However, if the relative amounts of eluted fractions are taken into account and the total concentration of the different classes of hydrocarbons is integrated along the eluting fraction analyzed by Simdist–MS, the impact of catalysts is

evidenced. It consists in a reduction of aromatics and an increase of saturates. This analytical data can be rationalized and correlated with hydrogen distribution during hydroconversion. The reduction of aromatics observed in the presence of catalysts correlates with the amount of hydrogen incorporated in the products. These correlations indicate that the role of catalysts does not consist of a simple hydrogenation of aromatics but in a complete redistribution of hydrogen. Finally, the contribution of coupled Simdist–MS to the analytical characterization of complex hydroconversion products, without the need for previous separation steps, indicates that this relatively simple technique is a valuable tool for a fast evaluation and control of conversion processes.

#### References

- [1] L. Rouleau, R. Bacaud, M. Breysse, *Prepr. Am. Chem. Soc., Div. Petrol. Chem.*, 39 (1994) 403–407.
- [2] A.W. Drews, *Manual on Hydrocarbon Analysis*, 4th ed., American Society for Testing of Materials, Philadelphia, 1989, ASTM D2887.
- [3] D.S. Workman, F. Noel, M.R. Watt, *J. Chromatogr. Sci.*, 31 (1993) 95–99.
- [4] J. de Zeeuw, *Chrompack news*, 17 (1990) 3.
- [5] C.J. Robinson, G.L. Cook, *Anal. Chem.*, 41 (1969) 548–1554.
- [6] C.J. Robinson, *Anal. Chem.*, 43 (1971) 1425–1434.
- [7] L. Rouleau, R. Bacaud, M. Breysse, J. Dufour, *Appl. Catal. A: General*, 104 (1993) 137–147.