ELSEVIER

Catalysis Today 43 (1998) 171–186

CATALYSIS TODAY

Evaluation of hydroconverted residues. Rationalization of analytical data through hydrogen transfer balance

Robert Bacaud[a,*], Loïc Rouleau[a], Vicente L. Cebolla[b], Luis Membrado[b], Jesús Vela[b]

[a] *Institut de Recherches sur la Catalyse, CNRS, 2 Avenue Albert Einstein, 69626 Villeurbanne Cedex, France*
[b] *Departamento de Procesos Químicos, Instituto de Carboquímica, CSIC, Calle Poeta Luciano Gracia, 5, 50015 Zaragoza, Spain*

Abstract

Analytical evaluation of petroleum based materials and processed feeds is a complex task relying on a compromise between tedious in-depth characterizations and fast responding tools for process control. In the present paper, a large number of hydroprocessed vacuum residues, obtained either under catalytic or thermal conditions, have been submitted to the following analytical techniques: Simulated distillation, coupled Simdist/MS, UV spectroscopy, ^{13}C NMR, quantitative thin-layer chromatography/FID, vapor phase osmometry. A confrontation of analytical data in the light of correlations with hydrogen transfer evaluation is proposed, which accounts for observed variations in aromatic content. Conradson carbon residue largely influences the results obtained with some of the examined techniques. Apparent discrepancies are rationalized and a strategy for a comprehensive analytical evaluation of hydroprocessed feeds is proposed. © 1998 Elsevier Science B.V. All rights reserved.

Keywords: Aromatic hydrocarbons; Hydrogen transfer; Hydroconversion; Residue; Simulated distillation; UV spectrometry; NMR; Thin-layer chromatography; Conradson carbon residue

---

1. Introduction

Heavy feeds derived from the exploitation of non-conventional oilfields are progressively being introduced in refining processes. They contain high levels of asphalt which concentrates in the distillation residues; as a result, a straight vacuum distillation of these feeds produces large amounts of low value by-products. The market for heating fuel, which is the main outlet for non-distillable residues, is being gradually reduced for ambient considerations, and, in parallel, the demand for distillate and light products such as 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.

As the 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 (H/C). Two broad categories appear: those performing an improvement of H/C through carbon rejection (coking or deasphalting), and oppositely, those adding hydrogen to the feed (hydrocracking). Obviously, hydrocracking makes better use of the inherent fossil carbonaceous matter contained in resi-

---

*Corresponding author. Tel.: +33 472 44 5339; fax: +33 472 445399; e-mail: bacaud@catalyse.univ-lyon1.fr

PII S0920-5861(98)00147-3

dues than does coking. Hydrocracking involves a complex set of reaction pathways which ultimately leads to a decrease of the mean molecular weight of the feed, and may also involve a reduction of heteroatoms content. The economics of such reactions relies essentially upon an adequate balance between the depth of conversion and the cost of hydrogen incorporation which can be substantial [1]. In order to achieve a proper control of process conditions, a reliable and convenient technique for product evaluation is necessary. Analytical procedures for characterizing processed products rely on a compromise between extensive, but time-consuming determinations and the necessity for a rapid response. They must provide information concerning the yield of distillate, which is the desired product, as well as its quality, which must meet commercial specifications.

2. Criteria for selecting analytical techniques

Analytical techniques to be used for the characterization of heavy oils and derived products must be fast, (i.e. applicable without previous fractionation), repeatable and quantitative to provide information for control of the refinery. They must also provide information regarding conversion and distribution of chemical families, alternatively referred to as hydrocarbon group type analysis (HGTA). A rigorous analysis of complex mixtures typically involves at least one chromatographic separation step during sample preparation, which is followed by consecutive characterization of the fractions. These fractionation steps are lengthy and tedious, and one of the goals of this work was to select analytical tools that provide valuable information without the need for such previous sample treatments. Some spectroscopic techniques may provide HGTA data without any previous separation. This is the case of ultra-violet spectroscopy (UV) or ^{13}C nuclear magnetic resonance (NMR). However, the former relies upon dubious hypotheses for solving multi-component analysis, whereas the latter provides only limited information about hydrocarbon groups.

Repeatability of analytical techniques is generally considered as a criterion for protocol selection, along with reliable quantitation. It must be pointed out that, in the absence of detailed information concerning individual constituents of complex mixtures, quantitation is connected to internal consistency. Effectively, the definition of the considered hydrocarbon groups is often ambiguous; for example, if aromatic and saturated hydrocarbons are distinguished by a given analytical method, the distribution of hydroaromatic species between these two classes will depend on the chosen protocol. Thus, internal consistency does not implies the exactness of data, and comparisons to additional analytical techniques must be made in order to assess the meaningfulness of one particular technique.

Another kind of difficulty arises from tentative comparisons of data obtained with distinct tools. It comes from the fact that the results provided by distinct analytical techniques are expressed in distinct units: some are expressed on a weight basis, others on a molar basis. Direct comparison of the results are meaningless, since unit conversion relies upon some external hypothesis concerning the composition of the analyte. Thus, although analytical data are interrelated, the correlation between two distinct techniques relies upon a third external data or upon some hypothesis concerning the molecular structure.

The techniques presented hereafter were selected because the methodologies previously developed are sufficiently established as to provide rapid and reliable quantitative results. A justification of the choice and a description of the state-of-the-art concerning heavy oils characterization are briefly presented in this work.

2.1. *Simulated distillation by gas chromatography (Simdist)*

With regard to the techniques which provide information concerning process conversion, simdist is probably the most useful one for its ease and rapidity. When performed with capillary columns withstanding temperature up to 440°C, this technique allows the elution of hydrocarbons containing up to 120 carbon atoms. The yield of any considered distillable fraction can be deduced from simdist data. Consequently, it can be considered as a convenient tool for process monitoring.

Additional information concerning conversion severity and the mechanism of conversion is obtainable through mathematical modeling. A proposed model of simdist distributions [2,3] relies upon the assumption that the boiling points of processed feeds and products are conveniently described by a normal (Gaussian) distribution function. Experimental simdist data, derived from hydroconverted residues, are modeled as the sum of the contributions of three distinct populations: a light component issued from extensive hydrocracking, an intermediate fraction generated through single-bond cleavage, and a heavy one possessing the characteristic parameters of the feed. The derived model parameters are correlated with conversion and may be related to hydrogen transfer, but they do not provide any information concerning products quality.

2.2. *Simulated distillation–mass spectrometry*

The coupling of simdist with mass spectrometry provides additional information concerning HGTA. Low-resolution mass spectrometry has long been applied to the quantitative analysis of complex volatile hydrocarbons mixtures. The determination of paraffins, cycloparaffins and aromatic families by direct introduction of volatile samples in the ionization source is efficient and fast [4,5]. The coupling of simulated distillation by gas chromatography with mass spectrometry confers an additional dimension to this method, since the distribution of hydrocarbons families is obtained as a function of boiling point [6].

2.3. *TLC–FID*

Information on HGTA is usually obtained through chromatographic techniques which allow a separation and quantitation of the groups, after an adequate calibration procedure. High performance liquid chromatography (HPLC) has not been considered in the present work due to possible irreversible adsorption of heavy and/or polar compounds on the columns and, hence, incomplete elution. The coupling of thin-layer chromatographic separation methods with quantitative flame ionization detection (TLC–FID) is more appropriate for these products since it permits the analysis of whole samples without previous fractionation. The possibility of quantifying the uneluted heavy and polar products, as well as increasing the speed of the analyses must also be considered [7]. Hydrocarbon groups are classified according to elution sequences with selected solvent systems, a practice which allows the determination of saturates, alkylaromatic, aromatics and polar compounds. As with other chromatographic methods, quantitative results are based on absolute calibration, which requires a previous preparative chromatographic step in order to obtain external standards. However, a rapid internal calibration procedure has been developed [8].

2.4. *UV spectrometry*

The distribution and content of aromatic hydrocarbon is easily obtainable by this popular and fast technique whose experimental background is well established [9]. The exploitation of UV absorption spectra is based upon multi-component analysis, which in turn relies upon the additive contribution of each component to the total absorbance at selected wavelengths. Since there does not exist a clear relationship between the molecular structure of a given compound and absorbance, many interferences may affect quantitative analysis.

A correction for some identified interfering classes of compounds is possible in the calculation matrix. This is the case for heterocyclic compounds and pyrenes. But other spectral interferences are more subtle and may be overlooked by commonly practiced analytical methods. For instance, the interference caused by benzofluoranthenes is structure dependent: *g, h*, and *i* isomers interfere, while *j* isomer does not. As a consequence of variable interferences, UV spectroscopy may be considered as a fast, comparative method for a continuous monitoring of samples whose composition varies within restricted limits.

The results presented in the present work were obtained with samples generated from a unique feed which was converted under varying conditions of severity. Since sample histories were comparable, it may be assumed that they did not undergo any qualitative changes. However, caution must be exerted when large variations in samples history and composition are expected.

2.5. *^{13}C NMR*

This technique allows the quantitative determination of aromatic and aliphatic carbon atoms in the

Table 1
Comparison of some analytical techniques applicable to the characterization of hydroconverted residues

Method	Apply to	Hydrocarbon families	Results expressed as
Simdist	distillate	no distinction	wt%
UV	whole sample	aromatics	mol/unit weight
^{13}C NMR	whole sample	aromatic, aliphatic	% carbon
TLC–FID	whole sample	saturate, aromatic, polar, asphaltenes	wt%
Simdist–MS	distillate	saturate, aromatic	vol%

absence of olefinic and phenolic compounds. Detection limit is ca. 0.5 wt% aromatic carbon. This is an absolute method which does not require standards of known aromatic carbon content and it is applicable to a wide range of sample compositions. However, NMR provides an atom-based composition of the sample. It does not measure the content of aromatic compounds because aliphatic signal arise from both paraffins and aliphatic substituents in aromatic compounds.

2.6. *Objective of the present work*

Our laboratories have been concerned with catalytic hydroconversion of heavy oils. A thorough evaluation of catalytic activity, including hydrogen mass balance and analytical characterization of hydroconverted products using the above referred techniques has been performed with samples generated under widely different conversion levels. The distinct features of considered techniques are compared in Table 1. As was mentioned earlier in a preceding paragraph, the results obtained by application of the analytical techniques are expressed in different, non-correlated units which are either atom-based, mole-based or weight-based. Furthermore, each one of these techniques concerns a variable fraction of the sample. For instance, simdist characterizes the distillable fraction, while in contrast, TLC–FID is applied to the whole sample.

In the present paper, we present an attempt to rationalize analytical data under the light of an external parameter. Hydrogen consumption was chosen because it is directly related with process conditions, it reflects product properties and can be measured with a convenient accuracy; this parameter was used as a base for the confrontation of analytical data resulting from the above-mentioned techniques and for the rationalization of the observed results

3. Experimental

3.1. *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 (obtained by elemental analysis); S=0.85 wt%; specific gravity=1.058 g cm^{-3}.

Hydroconversion was performed either in thermal conditions (without catalyst), or in the presence of a catalyst. The catalysts of this study were Ni or Mo-based plasma-prepared solids [10], molybdenum naphtenate, and alumina-supported Ni–Mo. They were introduced in the feed as dispersed, disposable solids, at low catalyst-to-feed ratio (<800 ppm expressed as metal).

Hydroconversion experiments were carried out in a 250 cm^3 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 maintained 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 each 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_5 to C_7 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:

H_{Total}=consumption of gaseous hydrogen (mmol H_2/100 g feed);
H_{Gas}=hydrogen consumed for gases formation;
$H_{Liquid}=H_{Total}-H_{Gas}$.

From the material balance of eluted material, the yield of 510°C$^-$ distillate was determined and defined as *conversion* according to the following expression:

Conversion=(wt% 510^- in products−wt% 510^- in feed)/wt% 510^+ in feed.

3.2. Simulated distillation

A sample of the liquid products was diluted with carbon disulfide at the concentration of 0.4% by weight. One µl of this solution was injected into a HT5 column (obtained from Scientific Glass Engineering, 6 m×0.53 mm,) equipped with a 1.25 m precolumn. The gas chromatograph (Hewlett–Packard 5890), equipped with on-column injector and flame ionization detector, was programmed from 303 to 673 K at 10 K min^{-1}. The temperature of the injector was maintained at 3 K above the column temperature. Retention time scale can be converted to a scale of equivalent number of carbon atoms, x, contained in a series of linear alkanes which are eluted in a given range of R.T. Low x values (C_{12} to C_{40}) 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_{24}–C_{100}. 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 mass response of the detector is constant throughout 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; incomplete elution was corrected by addition of an internal standard (dodecane) to the sample.

3.3. Coupled simulated distillation–mass spectroscopy

Analyses 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% by weight. A volume of 0.5 µl of this solution was injected by direct on-column injection, into a HT5 column (4 m×0.32 mm). The initial temperature was kept at 313 K for 1 min, then programmed up to 623 K at 15 K min^{-1}. 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 E.I. mode at 70 eV, were acquired in the range 40–600 amu 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. Elution was limited to fractions containing up to 36 carbon atoms. Applying the calibration of R.T. scale obtained with pure paraffins, the RT axis was divided into sections of carbon atoms numbers. An averaged 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 [4]. 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 by Robinson [5]. After the contribution of each hydrocarbon type to the total ionization has been calculated, the volume percent of the four classes of saturated and six

Table 2
Classes of aromatics and saturated hydrocarbons evaluated by processing of mass spectral data

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

classes of aromatic hydrocarbons are obtained by normalization to 100%. Table 2 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, (<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 <1% of the total products, their contribution was not reported.

3.4. TLC–FID

A Iatroscan Mark 5 (Iatron Labs., Japan) apparatus was used for the chromatographic separation and quantification of DAO and hydroconversion products. The separations were carried out on chromarods S-III (silica gel 5mm, pore diameter 60 A). In a typical experiment, a set of 10 chromarods are preassembled in a frame, and, after application of the sample and subsequent development with solvents, they were passed at a constant speed through the H_2 flame of an FID for quantification of peaks.

Samples were dissolved in CH_2Cl_2 (10 mg ml^{-1}). Volumes between 0.5 and 2 μl were typically applied on the chromarods. The hydrogen and air flows were 160 and 2100 ml min^{-1}, respectively. The duration of the scan was 30 s. Other parameters which influence the procedure, such as the temperature of drying of chromarods and their stabilization were also controlled [8].

The following development sequence of eluents was chosen: (1) *n*-hexane (38 min), (2) toluene (3 min), and (3) CH_2Cl_2/methanol, 95/5 v/v (30 s). The peaks separated were attributed, according to FTIR spectra, to: saturates (retention time, r.t.= 0.1 min), alkylaromatics (r.t.=0.19 min), aromatics (r.t.=0.37 min), polars (r.t.=0.43 min), and uneluted compounds (r.t.=0.47 min). This last peak is generally considered as asphaltenes in petroleum literature when using similar sequences of development [11].

Table 3
Hydrocarbon groups determined by TLC–FID

Hydrocarbon group	Eluent	RT (min)	Repeatability (±wt.%)
Saturates	*n*-hexane	0.1	0.5
Alkylaromatic	*n*-hexane	0.19–0.26	0.6
Aromatic	toluene	0.37	1.1
Polar	CH_2Cl_2/methanol, 95/5 v/v	0.43	0.3
Uneluted		0.47	0.2

The conditions of elution and the identified classes of compounds are presented in Table 3. FID response is known to depend on the chemical nature of the separated peaks in TLC–FID. Quantitation was performed through a rapid, internal calibration procedure described by Cebolla et al. [8], as an alternative to absolute calibration. Repeatability of the developed method was better than admitted in ASTM D2007. Mass range interval for 95% confidence level are reported in Table 3. Two considerations about the attribution of chemical nature to the separated peaks must be taken into account, according to their FTIR spectra [12]: (1) the fraction referred to as alkylaromatic is composed of saturates and a small concentration of aromatic entities, and (2) the fraction referred to as polar also presents a strong aromatic character and a small concentration of carbonyl groups.

3.5. Vapor pressure osmometry

Determination of number-average molecular weight of DAO and its derived catalytic hydroconversion products were carried out using a Knauer vapor pressure osmometer. Calibration was performed using benzil ($C_{14}H_{10}O_2$) in the range 4×10^{-3}–1.2×10^{-1} molal (the regression coefficient was 0.999). Measurements were performed in $CHCl_3$ at 298 K (six determinations per sample) and extrapolated to infinite dilution.

Table 4
Aromatic hydrocarbons families determined by UV spectrometry

Aromatic families	Wavelength (nm)
Benzenes	196–201
Naphthalenes	226–234
Phenanthrenes	251–259
Chrysenes	261–269
Tetraphenes and benzophenanthrenes	281–289
Ramsbottom carbon	340

3.6. UV spectrometry

The spectra of isooctane solutions of DAO or hydroconverted products were obtained in the range 195–300 nm. The determined aromatic hydrocarbons families and the corresponding considered wavelength ranges are listed in Table 4.

Quantitative determination of each hydrocarbon class is obtained applying a calibration matrix generated from comparative standard samples. A correction for interferences arising from benzothiophenes and pyrenes is applied to the absorbance measurements. Other recognized interfering classes of compounds are fluorenes and biphenyls, whose absorption cannot be corrected for in the calculation matrix.

3.7. ^{13}C NMR

Spectra of 40 w% solutions in $CDCl_3$ 99.8% purity (plus tetramethyl piperidine oxide as a relaxing agent) were obtained with a Varian Unity 300 MHz spectrometer, the probe size was 5 mm. Spectral integration was performed in the range from -10 to 70 ppm for aliphatic carbons and in the range 100–170 ppm for aromatic carbons. Tetramethylsilane was used as a chemical shift reference.

4. Results and discussion

4.1. Evaluation of hydrogen incorporation from simdist data

The hydrogen mass balance performed during hydroconversion experiments does not allow a distinction between hydrogen consumption involved in hydrocracking reactions and saturation of double bonds. Insight concerning hydrogen distribution is provided by the GC analysis of the gas phase produced during hydroconversion, which gives access to the amount of hydrogen involved in the production of gases (C_5^-). This calculation was performed assuming that C_1 to C_4 products were generated from the initial feed whose elemental composition is known. The remaining quantity, designated as H_{Liq}, effectively reflects hydrogen involved in modifications of the liquid phase. It includes two distinct classes of hydrogen consumption: one is related with hydrogenolysis reactions which cause a decrease of the mean molecular weight of the products through consecutive bond cleavage; the other one consists in the hydrogenation of unsaturated species.

An evaluation of hydrogenolysis contribution can be obtained by a mathematical modeling of simdist data, assuming that the distillation curves of processed feeds and products are conveniently described by a normal (Gaussian) distribution function. Experimental data, derived from hydroconverted residues, are consistent with the model that simdist curves are the sum of the contribution of three distinct Gaussian populations, resulting from a consecutive bond cleavage mechanism [3] schematically described as:

Feed → Fraction 3 → Fraction 2 → Fraction 1

The feed and the generated fractions are characterized by three parameters: the center of distribution (X), the width of distribution (W) and the relative amplitude (A), which are calculated through curve-fitting techniques. The amount of hydrogen involved in each step can be determined, considering that the mean number of bond ruptures involved in the production of a fraction possessing a mean number of carbon atoms X_i through bond cleavage of a X_{i+1} fraction is:

$$\frac{X_{i+1}}{X_i} - 1 \tag{1}$$

The number of 'moles' of the corresponding entities in 100 g of feed is obtained from the mean formula $CH_{1.66}$, corresponding to the elemental composition of the feed:

$$\frac{100}{13.66X_i} \tag{2}$$

Taking into account the relative amount of fraction i (A_i), with respect to the feed, the number of moles hydrogen involved in this transformation is:

$$\mathrm{H}_i = \left(\frac{X_{i+1}}{X_i} - 1\right)\frac{A_i}{13.66X_i} \tag{3}$$

expressed as moles of H_2 for 100 g feed, for one step generating a fraction i from a fraction i+1. Due to the variations of H/C ratio in the distinct fractions, this expression is not rigorous; the results are marginally affected by this approximation. This calculated amount of hydrogen is subtracted from the previously determined H_{Liquid}, yielding a net hydrogen incorporation, H_{Inc}, which reflects the actual variation of hydrogen content in the products (presumably corresponding to variations in aromaticity).

The hydrogenation of unsaturated species during hydroconversion of residues is either favored by hydrogen donors or by the presence of a catalyst. Thus the value of H_{Inc} must be correlated with catalyst addition, as is effectively observed in Fig. 1, which illustrates the variation of H_{Inc} vs. catalyst loading. Positive values of H_{Inc} are only attainable in the presence of high catalyst concentration. It can also be observed that using high catalyst concentration limits the production of distillate, expressed as conversion in Fig. 2; in that sense, the presence of a catalyst has a counterproductive effect, but product quality must also be considered.

Once the mean number of carbon atoms and the relative amplitudes of each component in the proposed consecutive scheme are calculated, a mean molecular weight can be obtained, combining elemental analysis for carbon, hydrogen and the calculated mean number of carbon atoms. This calculation was performed for a large number of hydroconverted products and a plot of this calculated mean molecular weight vs. conversion indicates a good correlation. (Fig. 3).

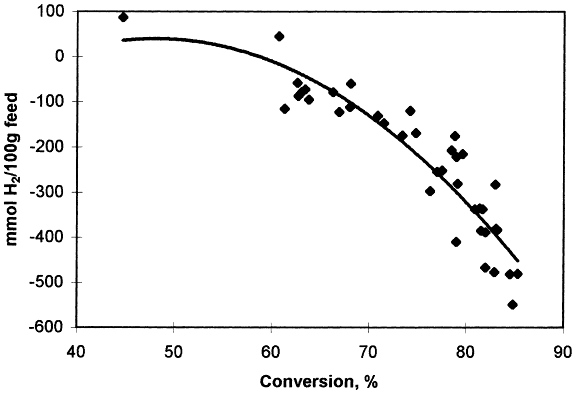


Fig. 2. Variation of incorporated hydrogen as a function of conversion of DAO. Experimental conditions are the same as in Fig. 1.

In order to assess the validity of the preceding calculations, some of the obtained molecular weights were compared with VPO data. The corresponding data points are shown in the graph (Fig. 3) and some discrepancies are apparent. Considering that simdist only concerns the distillable fraction, whereas VPO is applied to the whole products, the observed inconsistency must correlate with the non-eluted fraction of

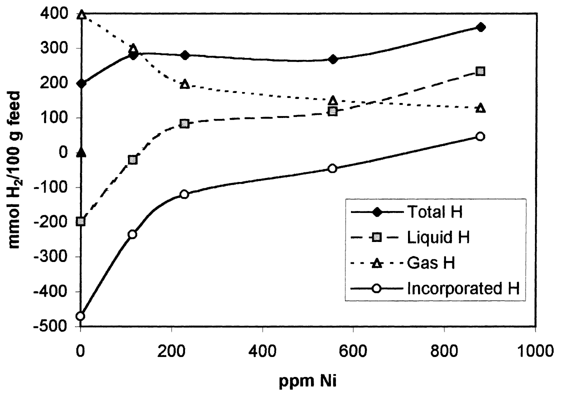


Fig. 1. Amount of transferred hydrogen as a function of catalyst loading during hydroconversion of DAO, 713 K, 14 MPa hydrogen (cold).

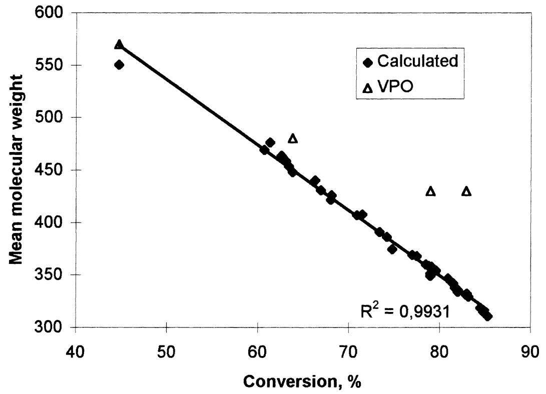


Fig. 3. Correlation of mean molecular weight as calculated by simdist, with conversion.

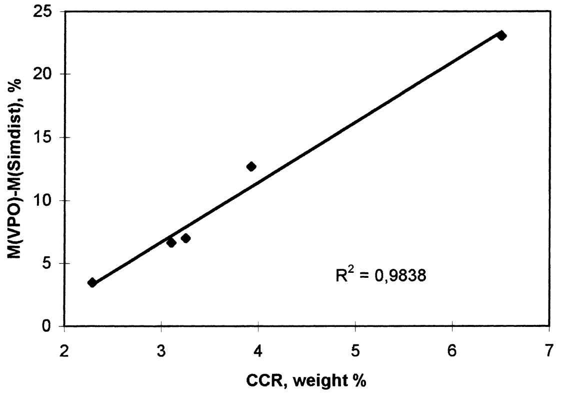


Fig. 4. Correlation of Conradson carbon content with the relative difference between VPO and simdist mean molecular weight.

the samples, mainly represented by Conradson carbon residue (CCR), which is not sensitive to simdist determination. A plot of the relative difference between VPO and simdist calculated mean molecular weight, as functions of CCR content effectively indicates a linear relation (Fig. 4). Consequently, a distinction must be made between those analytical techniques which consider the whole products and those determinations which are only concerned with the distillable portion.

4.2. *Evaluation of hydrogen involved in the formation of aromatic*

As outlined in the Section 3, hydroconversion products are hydrogen deficient as compared to the initial feed. The corresponding deficiency is likely to originate from variations in the content of unsaturated products (olefinic or aromatic species). ^{1}H NMR indicates that the content of olefinic hydrogen is systematically <100 ppm and that no significant variation is induced by hydrotreatment. Therefore, aromatic hydrocarbons are the only significant contributing species in hydrogen transfer reactions and consequently, the amount of incorporated hydrogen must fit analytical aromatic data. Two methods yield indications concerning the content of aromatic species:

- UV spectroscopy gives access to the molar content of aromatic hydrocarbons, classified according to ring condensation.
- ^{13}C NMR supplies the aromatic carbon atoms content. Thus, the two types of data can be combined and related through hydrogen incorporation.

4.2.1. *UV spectrometry*

In order to relate hydrogen transfer and UV data, two approaches concerning stoichiometric processes have been taken.

4.2.1.1. Dehydrogenation It is assumed that a given class of aromatic compounds is generated from the feed (of mean composition $CH_{1.66}$) through a stoichiometric process consisting in a dehydrogenation described by Eq. (4):

$$nCH_{1.66} \rightarrow C_nH_{2n-x} + (x-(2-1.66)n)/2H_2 \qquad (4)$$

The stoichiometric coefficients, C, corresponding to the distinct classes of aromatic hydrocarbons are presented in Table 5.

The coefficient for CCR is unknown since the composition for this class of products is not determined. A tentative value can be deduced, assuming that the difference between the calculated amount of hydrogen involved in the formation of the preceding identified aromatic species and the total incorporated hydrogen is attributable to CCR. The resulting calculated value is:

$$x\mathrm{CCR} = 90 \pm 30$$

The uncertainty is very large, but the magnitude order of this stoichiometric coefficient indicates that CCR consists of highly condensed aromatic species.

4.2.1.2. Linear regression Another approach consists in determining a mean stoichiometric coefficient by a linear regression of the graph of total aromatic as a

Table 5
Calculated stoichiometric coefficients of reaction (4) for aromatic families determined by UV spectrometry

Aromatic	Formula	Stoichiometric coefficient, C
Monoaromatic	C_nH_{2n-6}	1.95
Diaromatic	C_nH_{2n-12}	4.25
Triaromatic	C_nH_{2n-18}	6.65
Chrysenes	C_nH_{2n-22}	8.85
Tetraphenes	C_nH_{2n-22}	8.85

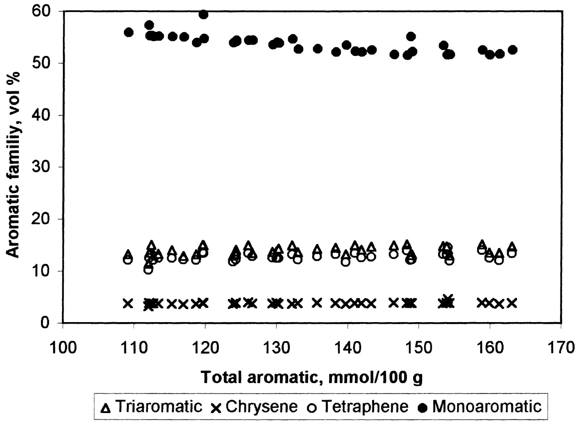


Fig. 5. Variation of individual aromatic families as a function of total aromatic content determined by Simdist–MS.

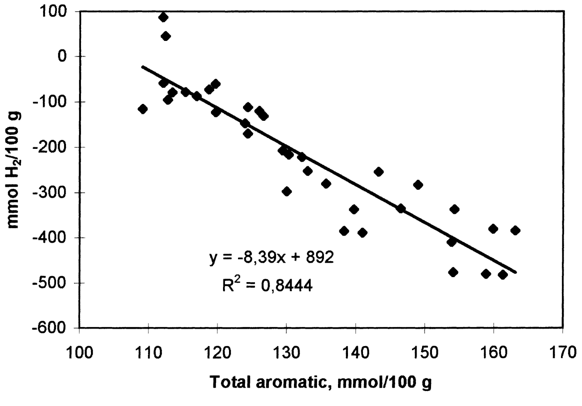


Fig. 6. Correlation of incorporated hydrogen with total aromatic, determined by UV spectroscopy.

function of incorporated hydrogen. In order to produce valid data, the distribution of aromatic families must be constant at variable conversion. This is effectively the case, as illustrated in Fig. 5. The equation resulting from a linear regression of data plotted in Fig. 6 is:

$$H_{\mathrm{Inc}} = 892 - 8.39\ \mathrm{Arom} \qquad (5)$$

with H_{Inc} and Arom (sum of aromatic species obtained from UV spectroscopy) expressed in mmoles. This mean stoichiometric coefficient is indicative of the mean number of moles of hydrogen involved in the formation of 1 mol of aromatic entity from the initial feed which possesses a mean composition $CH_{1.66}$. A tentative stoichiometric equation describing the formation of aromatic species would be:

$$n\mathrm{CH}_{1.66} \rightarrow \mathrm{C}_n\mathrm{H}_{1.66n-16.8} + 8.39\ \mathrm{H}_2 \qquad (6)$$

The general formula of aromatics can be expressed as: C_nH_{2n-z}. Although a determination of n and z is impossible, some trends in z and n values can be inferred considering that:

$$n(2 - 1.66) = z - 16.78 \qquad (7)$$

Realistic values for z (i.e. corresponding to mono- or polyaromatic structures) are only possible if n>10. It means that aromatic species generated by a dehydrogenation process from the initial feed contain more than 10 carbon atoms as a mean value.

A comparison of both methods of calculation can be performed, deducing the stoichiometric coefficient for CCR formation from a linear addition of the contributions of each aromatic family, expressing that the sum of the pondered stoichiometric coefficients must be equal to the mean coefficient of Eq. (5). The deduced value for CCR is:

$$x\mathrm{CCR} = 130$$

This result is effectively comparable to the preceding calculated value. This large value must concern highly condensed aromatic species possessing a number of carbon atoms exceeding 100 and it cannot be related with any proposed structure. However, it must be remembered that species possessing up to 120 carbon atoms are eluted in simdist chromatographic process; thus, it is not surprising that molecular entities responsible for CCR contain numerous carbon atoms.

4.3. ^{13}C NMR

In contrast with UV spectroscopic data, ^{13}C NMR data is expressed as a percentage of aromatic vs. total carbon atoms. In order to establish the basis for a comparison, the corresponding values must be converted in a common molecular based unit. Given the mean molecular weight (M) and the elemental formula (n carbon atoms), the atomic% of aromatic carbon (C_{aro} NMR) can be converted in carbon atom/100 g product:

$$C_{\mathrm{aro}}\mathrm{NMR\ atom/100\,g\ product} = 100n\,(C_{\mathrm{aro}}\mathrm{NMR})/M \qquad (8)$$

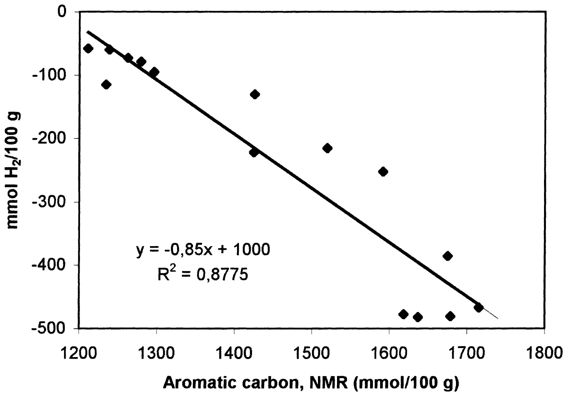


Fig. 7. Correlation of incorporated hydrogen with aromatic carbon determined by ^{13}C NMR.

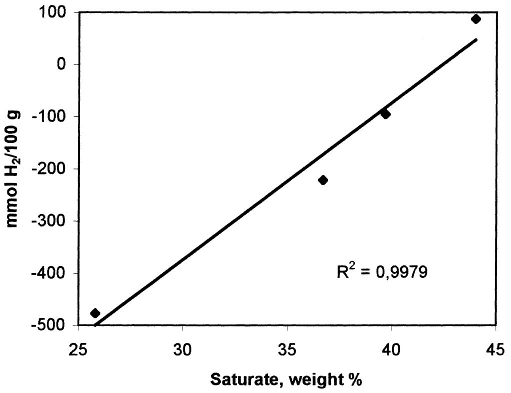


Fig. 8. Variation of H_{liq} as a function of saturates determined by TLC–FID.

A stoichiometric coefficient for the number of atoms of hydrogen involved in the formation of one aromatic carbon atom can be deduced from the slope of the plot of H_{Inc} vs. C_{aro} (Fig. 7). A linear regression yields the relation:

$$H_{Inc} = 1000 - 0.85\ C_{aro} \tag{9}$$

indicating that 0.85 mol hydrogen are involved in the formation of 1 mol aromatic carbon. The ratio of this stoichiometric coefficient to the calculated value deduced from UV spectroscopy in Eq. (5), is:

$$\text{Stoichio UV/Stoichio NMR} = 10 \tag{10}$$

This value indicates that generated aromatic species would contain a mean number of 10 carbon atoms. This is consistent with the tentative stoichiometric Eq. (6) deduced from UV spectrometry data.

4.4. *Hydrogen transfer derived from hydrocarbon group type analysis methods*

4.4.1. *TLC–FID*

The definition of hydrocarbon group resulting from this chromatographic method relies upon adsorption/elution properties on silica gel. Spectroscopic evidence contributes to the classification of the separated species which are: saturated, alkylaromatic, aromatic, and polar. On silica gel, separation phenomena are related to both polarity and molecular weight. Polarity is a confusing and relative term: the polar fraction of a deasphalted oil does not necessarily implies the occurrence of heteroatomic compounds in such a fraction. In the absence of heterocompounds, and for a given molecular weight, hydrogenated species (naphthenes) may possess a higher polarity – and hence elute later – than the corresponding aromatic hydrocarbon.

Attempts to correlate the resulting classification with hydrogen consumption data have been performed. A plot of saturates content as a function of H_{Liq} produces a linear positive correlation (Fig. 8). Since this data for hydrogen incorporation includes the consumption associated with hydrogenolysis reactions, this trends indicates that the corresponding decrease of the mean molecular weight produces an increase in the total saturates population. Other correlations concerning aromatic groups are not easily deduced. Effectively, the distinction between the identified hydrocarbon groups is not absolute and overlapping zones contribute to some uncertainty concerning the identity of eluted material. However, grouping some related families produces pertinent correlations. This is the case, for example, when the sum of aromatic and polar compounds is considered and plotted as a function of H_{Inc} (Fig. 9). Correspondingly, uneluted material is directly correlated with CCR as determined by UV spectrometry (Fig. 10). However, the slope of the correlation cannot be expressed in a molar unit and no structural information concerning hydrogen transfer can be deduced.

Despite the fact that stoichiometric data is not obtainable from TLC–FID, another type of mechanistic information can be inferred if the impact of various classes of catalysts upon products distribution is considered. The quantitative hydrocarbon groups

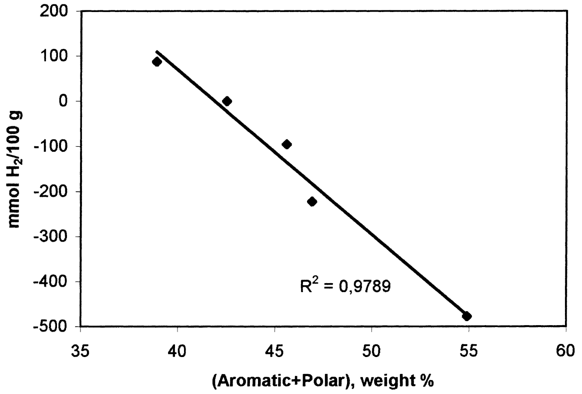


Fig. 9. Variation of incorporated hydrogen as a function of the sum (saturates+aromatic) as determined by TLC–FID.

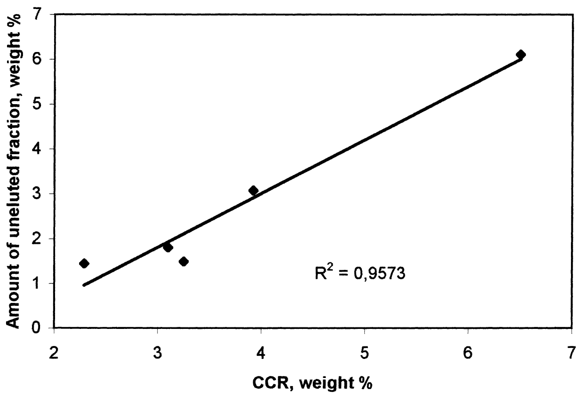


Fig. 10. Variation of the amount of uneluted fraction (TLC–FID) as a function of Conradson carbon residue (UV).

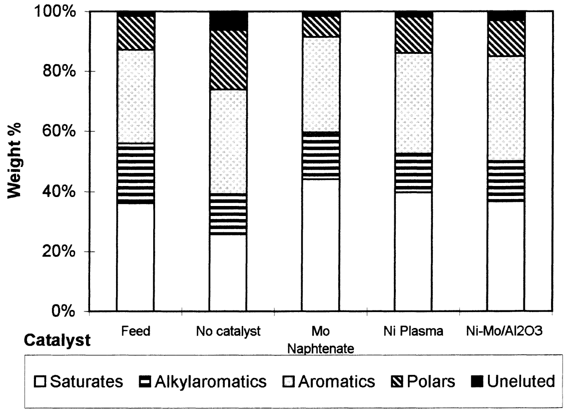


Fig. 11. Hydrocarbons group type analysis (TLC–FID) of hydroconverted samples obtained in the presence of various catalysts.

type analysis respectively obtained in the absence and in the presence of various catalysts is presented in Fig. 11. A significant difference was evident between catalytic and non-catalytic experiments. Thermal conversion causes a decrease of saturates and a corresponding increase of polar and uneluted fractions. The aromatic fraction is slightly increased, while the alkylaromatic fraction decreased. Given that the polar and the uneluted fractions also have an aromatic character, the total aromaticity of the feed (expressed as 100%−saturates %) is increased by thermal conversion. In this context, a decline of alkylaromatic can be interpreted as a reduction of the number and length of the alkyl substituents of aromatic entities.

When hydroconversion is performed in the presence of any of the considered catalysts, a considerable modification of this analytical pattern is observed. In contrast with thermal conversion which generates uneluted and polar compounds at the expense of the saturate portion contained in the feed, catalytic conversion more or less preserves the distribution of fractions of the feed. Some distinctions concerning the respective action of the considered catalysts are evident: the tendency of decreasing the polar and uneluted fractions and to increase the contribution of saturates follows the order: molybdenum naphthenate>Ni plasma>Ni–Mo/Al_2O_3. This classification coincides with the observed catalytic activity for hydrogenation reactions [3].

4.4.2. *Simdist–MS*

In contrast with the preceding analytical techniques, this coupled method is only concerned with distillable material. Furthermore, the considered range of elution is more restricted than conventional simdist with FID detection.

The main interest in adapting the analytical M.S. protocol to simulated distillation consists in deriving the quantitative distribution of hydrocarbons types as a function of boiling point range (or equivalent number of carbon atoms) of distillated fractions. Fig. 12 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 with carbon atom number. Correspondingly, aromatic structures are more abundant in low molecular weight fractions,

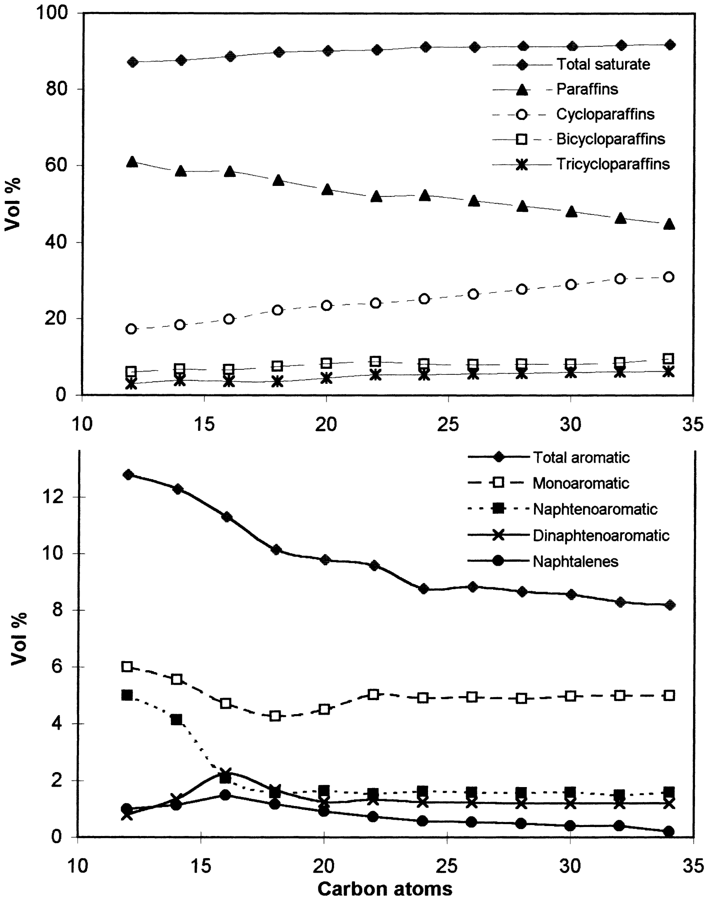


Fig. 12. Distribution of saturate and aromatic hydrocarbons (Simdist–MS) as a function of carbon atom number.

monoaromatics being the most common entities, and the total aromatics concentration declines as the carbon atom number of the distillate fractions increases.

Despite this apparent similarity in product distribution, the amount of each distilled fraction must be taken into account in order to quantify the integrated concentration of each product family in the range of carbon atom numbers involved in GC–MS acquisition (C_{12} to C_{34}). It must be stressed that this range concerns the lighter fractions of hydroconverted products. 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 from C_{12} to C_{34}. This determined amount of total aromatics effectively correlates with H_{Inc} (Fig. 13). This correlation has a limited information value since no molar relation can be inferred.

The resulting distributions, normalized to 100%, are presented in Fig. 14. Each 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 to 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 confirmed in Fig. 15. It appears that the concentrations of monoaromatics and cycloparaffins correlate well (regression coefficient, R=0.97). Therefore, a process involving a conversion of aromatics

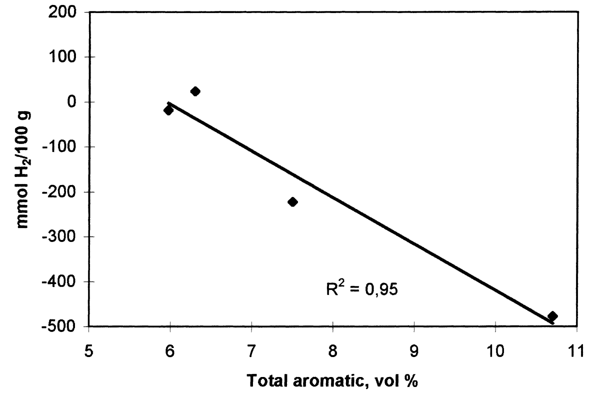


Fig. 13. Correlation of incorporated hydrogen with total aromatic (Simdist–MS).

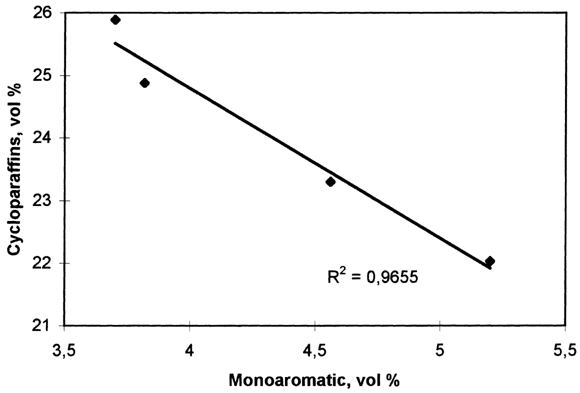


Fig. 15. Correlation of monoaromatics vs. cycloparaffins (Simdist–MS).

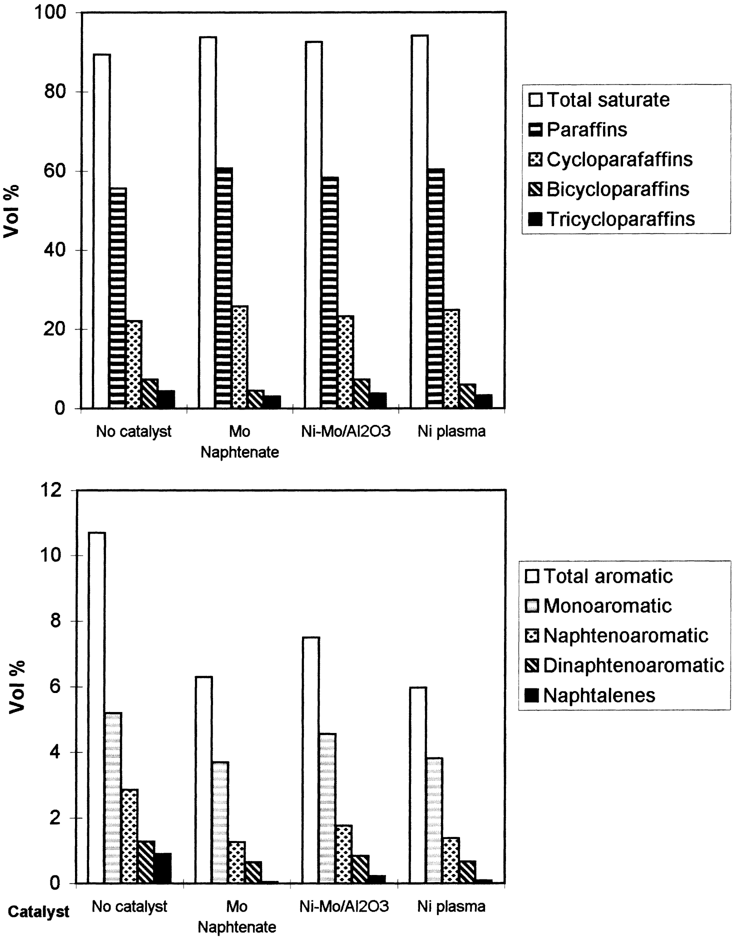


Fig. 14. Hydrocarbons group type analysis (Simdist–MS) of hydroconverted samples obtained in the presence of various catalysts.

Table 6
Amount of distillable material as determined by Simdist–MS

Sample	% distillate
No catalyst	77
Ni–Mo supported catalyst	72
Ni plasma catalyst	56
Mo naphtenate	37

into cycloparaffins would effectively contribute to the decline of aromaticity. However, the slope of the linear correlation between the concentration of monoaromatics and cycloparaffins is less than unity.

These results indicate that the influence of catalysts upon the respective distribution of saturates and aromatics does not consist in a mere catalytic hydrogenation of aromatic species and that hydrogen transfer reactions are probably more complex.

A tentative comparison of Simdist–MS and TLC–FID data in Figs. 11 and 15 reveals a large discrepancy concerning aromatic content. It must be considered that TLC concerns the whole sample and includes non-distillable fractions. In contrast, Simdist–MS data exclusively reflects the composition of distillate. Furthermore, the aromatic fraction in TLC–FID includes some contribution of hydroaromatic species. The apparent inconsistency between these analytical methods simply illustrates the fact that the samples effectively considered by the respective techniques are quantitatively different. This is evidenced by data collected in Table 6, which indicates the amount of distillable material considered by Simdist–MS in several samples. It must be noticed that conversion of the feed to distillate is decreased in the presence of catalysts. This effect varies accordingly to the hydrogenation activity of the considered catalysts: molybdenum naphthenate>Ni plasma>Ni–Mo/Al_2O_3 and is correlated with an improved utilization of hydrogen in transfer reactions as was evidenced by Rouleau et al. [1].

5. Conclusion

The multiplicity of analytical techniques for the evaluation of products resulting from hydroconversion of residues reflects the difficulty in defining a unique protocol. Anyone of the considered techniques gives access to a limited information. The limits either concern the considered portion of the sample (distillable fraction or whole sample) or the basis for results expression (atomic-, molar- or weight-based).

Applying selected techniques to the characterization of products obtained through hydroconversion of a residue, we attempted to correlate analytical data with hydrogen consumption, considered as an external, non-protocol-dependent parameter.

The objective of hydroconversion processes is to optimize distillate production, hence, analytical methods dedicated to the quantitative evaluation of this fraction are the most informative. Simulated distillation is relatively fast, it does not require time-consuming sample preparation and the information it produces is largely independent from sample composition. Additionally, a simple modeling of simdist data yields more information related with conversion depth and hydrogen utilization, which in turn reflects distillate properties.

The determination of aromatic hydrocarbon families by UV spectrometry applies to the whole sample. It relies upon correlations assuming the additivity of the contribution of individual components to the total absorbance. Despite possible interferences, the distribution of aromatic families obtained by this technique are consistent with hydrogen material balance, assuming that aromatic are formed through dehydrogenation of the feed. The calculated stoichiometric coefficients for this reaction are in agreement with hydrogen transfer. Furthermore, an hypothetical stoichiometric coeffiecient for the formation of CCR can be calculated; its value indicates that CCR has a major impact upon the amount of transferred hydrogen.

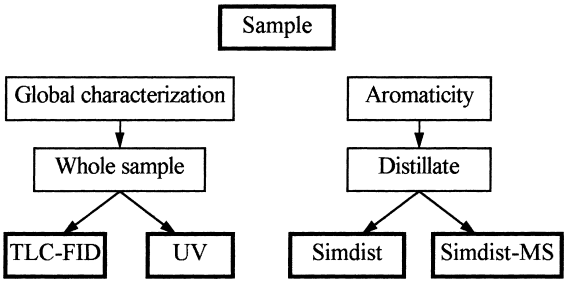
Information concerning aromaticity, as obtained from ^{13}C NMR data, is consistent with the preceding calculation. NMR provides atom based results concerning the whole sample. But the lack of any information about the molecular structure limits the interest of this technique.

HGTA methods are convenient for obtaining the distribution of hydrocarbon families in complex samples. TLC–FID is fast and it applies to the whole sample without prior preparation. The identified groups separated by elution with various solvents may overlap. The separation process based on polarity leads to some ambiguity in the attribution of eluted compounds to some class of hydrocarbon. The sum of aromatic and polar compounds as obtained by

TLC–FID correlates with hydrogen transfer balance, but no stoichiometric information can be derived.

Simdist–MS is concerned with the distillable portion of the analyzed material. It gives access to the distribution of hydrocarbon families as a function of boiling point. The content of aromatic hydrocarbons obtained by this technique effectively correlates with hydrogen transfer data. However, a comparison of aromatic hydrocarbons content, respectively, derived from Simdist–MS and from TLC–FID indicates that the fraction of sample effectively considered by the techniques are different and that the results are largely influenced by the presence of CCR, which is the most aromatic fraction and causes apparent discrepancies between analytical methods.

Finally, a tentative strategy for the evaluation of complex hydrocarbon samples would consist of the following Scheme 1:



Scheme 1.

Acknowledgements

V.L. Cebolla, L. Membrado and J. Vela acknowledge the financial support of Spanish DGICYT (Project PB93-0100) and European Steel and Coal Community (Project 7220-EC/765).

References

[1] L. Rouleau, R. Bacaud, M. Breysse, Preprints, A.C.S., Div. of Petrol Chem., 39(3), 1994, p. 403.
[2] R. Bacaud, L. Rouleau, B. Bacaud, Energy and Fuels 10 (1996) 915.
[3] R. Bacaud, L. Rouleau, B. Bacaud, Energy and Fuels 10 (1996) 1171.
[4] C. J Robinson, G. L Cook, Anal. Chem. 41 (1969) 1548.
[5] C.J. Robinson, Anal. Chem. 43 (1971) 1425.
[6] R. Bacaud, L. Rouleau, J. Chromatogr. A 750 (1996) 97.
[7] M. Ranny, Thin-Layer Chromatography with Flame Ionization Detection, D. Reidel Publishing Company, Dordrecht, 1987.
[8] V.L. Cebolla, L. Membrado, J. Vela, R. Bacaud, L. Rouleau, Energy and Fuels 9 (1995) 901.
[9] R.A. Burdett, L.W. Taylor, L.C. Jones, Molecular Spectroscopy, Rept. Conf., Inst. Petroleum, London, 1954, pp. 30–41.
[10] L. Rouleau, R. Bacaud, M. Breysse, J. Dufour, Appl. Catal. A: General 104 (1993) 137.
[11] B. Fixari, S. Peureux, J. Elmouchnino, P. Le Perchec, M. Vrinat, F. Morel, Energy and Fuels 8 (1994) 588.
[12] J. Vela, V.L. Cebolla, L. Membrado, J.M. Andrés, J. Chromatogr. Sci. 33 (1995) 417.