Investigating comprehensive two-dimensional gas chromatography conditions to optimize the separation of oxygenated compounds in a direct coal liquefaction middle distillate

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ABSTRACT

Considering the global energetic context, diversifying fuels is of growing importance and many new alternatives are promising. Coal liquefaction products definitely appear among the new generation substitutes. These product's characteristics are very far from fuel specifications as they are mainly composed of naphthenes, aromatics, polycondensed naphthenic and aromatic structures and heteroatomic compounds (nitrogen and oxygen), with a very low paraffin content. Identification and quantification of oxygen-containing species in coal-derived liquids are of considerable importance to understand their behaviors in further processing. However, these species have not been characterized as fully as the predominant hydrocarbon components. Literature shows that these compounds consist mainly in alkylated phenolic and furanic structures. Therefore, comprehensive two-dimensional gas chromatography has been investigated to provide enhanced molecular characterization of these complex samples. Several different configurations involving innovative column configurations were tested. Each of them was optimized by testing different column lengths, modulation periods, and oven conditions. A comparison of the contribution of each column configuration was carried out regarding four main criteria: individual separation of oxygenates, group type separation, resolution, and space occupation. One of them enabled an outstanding separation of paraffins, naphthenes, monoaromatics, diaromatics and targeted O-compounds in a direct coal liquefaction product. It was therefore subjected to further experimentations using a time-of-flight mass spectrometer to validate the identification and unravel more than fifty oxygenated molecular structures. A group-type quantification was also established for four column arrangements and gives the distribution of paraffins, naphthenes and aromatics. It can be concluded from this study that a non-orthogonal arrangement involving a highly polar column in the first dimension was the most adapted one.

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1. Introduction

The need to diversify energy sources in the transportation field has sparked great interest in direct coal liquefaction products. Before processing, these liquid properties and compositions are far from fuel specifications and upgrading must be applied to the gasoline and atmospheric gasoil cuts. In fact, they consist mainly of aromatic hydrocarbons (polycondensed), insaturates (naphthenes), and heteroatomic compounds especially oxygenated species [1–5]. To consider their co-refining with petroleum cuts, it is crucial to study their chemical and physical properties. The requirements in terms of molecular characterization improvement concern hydrocarbons as well as oxygenated compounds which belong to many different chemical families and are present in relatively high concentrations before hydrodeoxygenation (HDO).

Gas chromatography has been broadly used for the characterization of coal oils [6]. GC-AED has been of great interest to reach a selective identification of oxygenates in these unconventional charges [7–13]. A mass spectrometer was also used as a detector to come up to this problematic [14–18]. Two classes of oxygenated compounds are emphasized in these researches: phenols and furans. For preparative or analytical purposes, liquid chromatography allowed the identification of many species belonging to these two families [19–22] as well as ^{31}P NMR which permitted a selective identification of compounds containing a OH functional

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group (especially phenols) [20,23–27]. Phenols can also be isolated by ion-exchange chromatography [28] or by open tubular liquid chromatography [29].

Multidimensional gas chromatography has never been at stake to surmount this challenge. Yet, this powerful tool allows the analysis of complex samples and offers a high peak capacity by combining two different stationary phases with different separation mechanisms [30,31]. Many applications to oxygenated species in complex hydrocarbon matrixes showed the benefits of this technique in terms of peak capacity and sensitivity. In fact oxygenated species were unravelled for Fischer Tropsch products containing acids, alcohols, and esters [32,33]; biodiesels containing methylic fatty esters [34–36], and modified petroleum containing alcohols [37,38].

Moreover, GC × GC has been broadly used for the analysis of hydrocarbons in petroleum middle distillates using FID and ToF/MS detectors [31], and in lignin combustion gases using ToF/MS detection [39]. For this purpose, a non-polar × polar column configuration is generally used and enables the separation of the different hydrocarbon families. Concerning heteroatomic compounds in oil samples, they consist in S-containing and N-containing compounds. These molecules are identified respectively using a SCD and NCD.

The need to use multicoupled systems and to integrate a pre-separation can be explained by the complexity of these samples. Even if GC × GC has been used to characterize the predominant hydrocarbon compounds, no applications of this hyphenated system are found for oxygenated species characterization. There is however important past chromatography research that accounts for the polar components in coal liquids middle distillates.

This paper presents the strategy to develop a method dedicated to these feedstocks. On the one hand, the selection of the most adapted column configuration will be described (Solgelwax × DB-1). On the other hand, a semi-quantitative study will be shown and discussed for the selected configuration.

2. Experimental

2.1. Samples

2.1.1. Test mixtures

The solvent used for the elaboration of test samples was ethyl acetate and was supplied by VWR. Chemicals were provided by different suppliers: Sigma–Aldrich, Merck, Alpha Aesar, TCI, and Fluka. Different family mixtures and a global mixture including all families have been established. In fact, sample P composed of 16 n-paraffins, A composed of 9 aromatics, and O composed of 13 oxygenates were mixed into a standard mixture SM.

Sample P contains 15 n-paraffins (from C7 to C29) at concentrations varying from 0.6% (w/w) to 1.3% (w/w). Sample A includes aromatics and naphteno-aromatiques: toluene, trimethylbenzene, isobutylbenzene, triisobutylbenzene, tetraisobutylbenzene, biphenyl, phenanthrene, ethylanthracene, and fluorene with concentrations ranging from 1 to 2.6% (w/w). To finish, O was constituted by phenol, 4-ethylphenol, 2,4-dimethylphenol, 2,4,6-trimethylphenol, p-cresol, m-cresol, ditertbutylmethylphenol, 6-tert-butylcresol, furan, benzofuran, dibenzofuran, naphtol, and fluorenol at contents ranging from 0.9% (w/w) to 2.98% (w/w). These choices were oriented by a literature survey that had been established to give the most accurate vision of a coal oil composition [15–28]. All these compounds were solubilised in ethyl acetate and SM consists of 1/6 of A, 1/6 of P, 1/6 of O and 1/2 of ethyl acetate. These data are summarized in Table 1.

Table 1
Compounds contained in the test sample.

No.	Compounds	No.	Compounds	No.	Compounds
1	nC7	13	nC27	25	Phenol
2	nC11	14	nC28	26	Ethylphenol
3	nC13	15	nC29	27	Dimethylphenol
4	nC17	16	Toluene	28	Trimethylphenol
5	nC18	17	Trimethylbenzene	29	P-cresol
6	nC19	18	Isobutylbenzene	30	M-cresol
7	nC20	19	Triisobutylbenzene	31	Furan
8	nC21	20	Tetraisobutylbenzene	32	Benzofurane
9	nC22	21	Biphenyl	33	Dibenzofurane
10	nC24	22	Phenanthrene	34	Naphtol
11	nC25	23	Ethylanthracene	35	Fluorenol
12	nC26	24	Fluorene		

2.1.2. Real sample: direct-coal liquefaction product

The coal-derived oil used was provided by IFP New Energy. It consists of a middle distillate (boiling points range = 200–350 °C) of a coal oil produced by direct liquefaction. The sample used in this study has a hydrogen content of 11.4% (w/w) (by NMR), N content equal to 0.24% (w/w) (measured using NF07058), S content provided by FX of 0.0072% (w/w), and an oxygen content equal to 0.80% (w/w). The refractive index and density of the sample are respectively 1.5129 (ASTM D1747) and 0.9330 g/cm^3 (NF EN ISO 12185).

2.2. GC × GC-FID setup

For optimization and quantification purposes, experiments were achieved with a Trace GC (Thermo, Italy). In fact, hydrocarbons FID response depends only on the mass of carbon in a molecule. Thus quantification of hydrocarbons can be performed even if no individual standards are available.

The injection was carried out using a split injector (Thermo) at 320 °C (0.3 μL) with a split ratio varying from 1:40 to 1:100 depending on the injected sample. Detection was established with a flame ionization detector (FID) system set at 380 °C. H$_2$, air, and He makeup were set respectively at 35, 450, and 25 mL/min. Helium (99.99% Air Liquid, France) was used as a carrier gas. Oven temperature was programmed from 50 °C (0.5 min) to the maximum temperature (2 min) allowed by the columns (Solgelwax: 280 °C, DB-1: 325 °C, DB-17: 280 °C, PONA: 325 °C, SLB IL-100: 230 °C). During the whole analysis a ramp of 2 °C/min was selected because it corresponds approximately to the inverse of the dead time of the columns. The same temperature programming which allows the elution of all the compounds was used for all the columns configurations for comparison purposes. A constant pressure set at 100 kPa was used and the modulation period was usually set at 12 s and variations of this value will be specified throughout the article to cope with the differences of retention power of each investigated column. Many dimensions were tested in the study involving orthogonal and non-orthogonal conditions. All of them are referred in Table 2 as well as investigated modulation periods.

2.3. GC × GC-ToF/MS

In order to identify targeted compounds, a LECO Pegasus IV (LECO, St. Joseph, MI, USA) GC × GC-ToF/MS system was used. Experiments were carried out using a HP 6890 chromatograph which was equipped with a split injector (Agilent Technologies). Operating conditions were the same as those described in the previous paragraph. Concerning the modulation, it was performed by a liquid nitrogen cooled gas jet cryogenic modulator. The acquisition frequency was set at 100 Hz in a mass range of 75–500 amu. Electron impact was achieved at 70 eV and a multiplate voltage of −1450 V was used.

Table 2
Experimental conditions.

[1]D column	Dimensions	[2]D column dimension	Dimensions	Modulation
Solgelwax	(30 m × 0.25 mm × 0.25 μm)	DB-1	(1.1 m × 0.1 mm × 0.1 μm)	10, 12, 15, and 20 s
Solgelwax	(30 m × 0.25 mm × 0.25 μm)	DB-5	(1.1 m × 0.1 mm × 0.1 μm)	12 and 15 s
SLB IL-100	(30 m × 0.25 mm × 0.2 μm)	DB-1	(1.0 m × 0.1 mm × 0.1 μm)	12 and 20 s
BPX-90	(30 m × 0.25 mm × 0.25 μm)	DB-1	(0.8 m × 0.1 mm × 0.1 μm)	12 and 15 s
DB-17	(30 m × 0.25 mm × 0.25 μm)	DB-1	(1.0 m × 0.1 mm × 0.1 μm)	12 s
DB-17	(30 m × 0.25 mm × 0.25 μm)	Solgelwax	(1.0 m × 0.1 mm × 0.1 μm)	12 s
DB-1	(30 m × 0.32 mm × 0.1 μm)	Solgelwax	(1.0 m × 0.1 mm × 0.1 μm)	10 s
DB-1	(30 m × 0.32 mm × 0.1 μm)	SLB IL-100	(1.0 m × 0.25 mm × 0.2 μm)	10 and 20 s
PONA	(30 m × 0.2 mm × 0.5 μm)	Solgelwax	(1.0 m × 0.1 mm × 0.1 μm)	12 s

2.4. Data handling

When acquired by Polycard software (Thermo), the raw data of FID signals are exported as a csv file. A home-made software called 2DChrom displays GC × GC contour plots with retention times axis, as well as 1D and 3D-plots. A defined area called "blob" can be created by the user to circle each 2D peak. Blob creation and peak integration also allow to reach a quantification and a report can be generated. Intensity of peaks is displayed with a colour gradient varying from light blue to dark blue. To finish, this software helps reaching a reproducible and accurate integration by finding peaks automatically and fitting blobs.

Concerning ToF/MS data treatment, it was performed by the ChromaTOF software of the Pegasus 4D platform. This interface also allows peak finding. Identification of compounds is achieved by comparing the acquired spectra with the NIST database (National Institute of Standards and Technology, Gaithersburg, MD, USA version 2002). Peak intensities are displayed with a colour gradient varying from pale green to blue.

2.5. Two-dimensional decisive factors

The exploitation of data must be achieved by using theoretical variables which can illustrate by means of figures the potential of a separation. The resolution will be expressed by using Giddings formulae [40], the peak distortion by the means of the 2D asymmetry formulae [41], and space occupation will be represented thanks to orthogonality formulas [42–44].

2.5.1. 2D resolution

A common method developed by Giddings [40] for determining the resolution between two compounds in a 2D contour plot consists in defining it as the Euclidian norm of the resolutions calculated for each dimension. Thus, considering ^1Rs and ^2Rs as respectively the resolution in the first and second dimension can be written down (Eq. (1)):

$$Rs_{2D} = \sqrt{^1Rs^2 + {}^2Rs^2} \tag{1}$$

In a developed form Rs_{2D} can be expressed as in Eq. (2) [40], where $^2\omega_A$ and $^1\omega_A$ are respectively the peak widths of compound A in the second and first dimension, $^2\omega_B$ and $^1\omega_B$ are respectively the peak widths of compound B in the second and first dimension, and where Δ^2tr and Δ^1tr are the differences of retention times between the apexes of A and B respectively along the second and the first dimensions. For more transparency these values are illustrated in Fig. 1.

$$Rs_{2D} = \sqrt{\frac{2(\Delta^1tr)^2}{(^1\omega_A + {}^1\omega_B)^2} + \frac{2(\Delta^2tr)^2}{(^2\omega_A + {}^2\omega_B)^2}} \tag{2}$$

To calculate $^1\omega$, it appears judicious to consider it as the product of the number of modulations separating these two peaks and the modulation period. In this paper, to approach the propensity
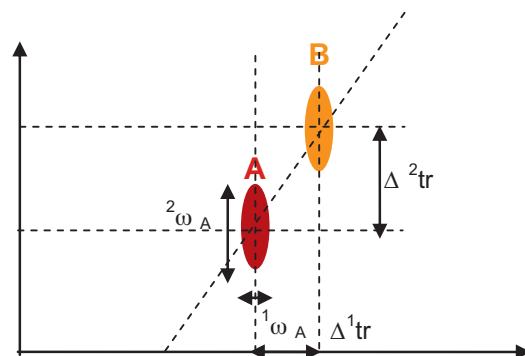

Fig. 1. Scheme showing variables referred in the two-dimensional peak resolution formulae.

of a column configuration to separate oxygenates from hydrocarbons, the resolution between fluorene and dibenzofuran will be estimated. These two molecules were selected because their only difference consists in one atom in the central ring (carbon for fluorene and oxygen for dibenzofuran). An intrafamily resolution will also be calculated for two paraffins (nC17 and nC18).

2.5.2. 2D space occupation

Throughout this paper, occupation of the 2D space will be expressed thanks to two criteria. However as these values reflect the separation orthogonality and some of our configurations are not orthogonal, the term "space occupation" will rather be used.

The first graphical expression consists of the ratio between the area of the separation plane and the area occupied by the analytes without considering the space of the free-area caused by the columns dead time [42].

A unique new concept of chromatographic space occupation is introduced in this paper. It consists in determining the space occupations in the first and second dimensions through two dimensionless numbers ^1SO and ^2SO. These two variables are defined in Eqs. (3) and (4) where ^1tr_n and ^2tr_n are the retention times of the last compound eluted respectively in the first and second dimensions, $^1tr_1$ and $^2tr_1$ are the retention times of the first compound eluted respectively in the first and second dimensions, $T_{analysis}$ corresponds to the total running time, and P_{Mod} is modulation period:

$$^1SO = \frac{(^1tr_n - {}^1tr_1)}{T_{analysis}} \tag{3}$$

$$^2SO = \frac{(^2tr_n - {}^2tr_1)}{P_{Mod}} \tag{4}$$

Thus, one can estimate the 2D space occupation SO2D as the Euclidian norm of these two values (Eq. (5)).

$$SO_{2D} = \sqrt{\frac{(^1tr_n - {}^1tr_1)^2}{2T_{analysis}{}^2} + \frac{(^2tr_n - {}^2tr_1)^2}{2P_{Mod}{}^2}} \tag{5}$$
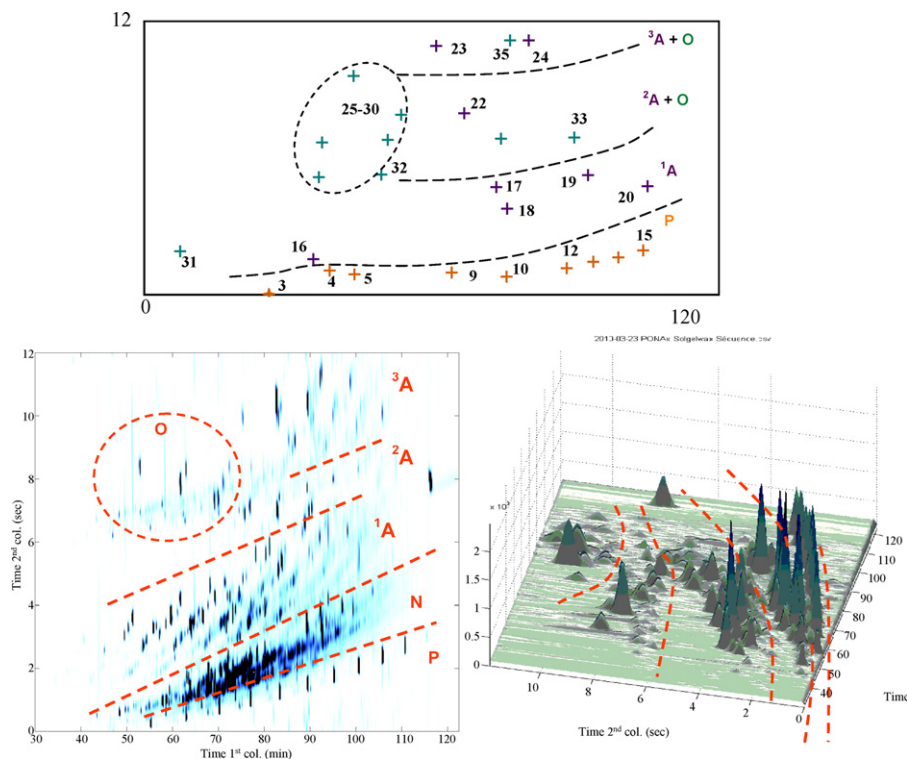
Fig. 2. 2D contour plot of SM, numbers refer to Table 1 (top); 2D contour plot (left), and 3D contour plot (right) of a direct coal liquefaction product using orthogonal conditions: PONA (30 × 0.2 × 0.5) × Solgelwax (0.8 × 0.1 × 0.1) with a scale ranging from 30 to 126 min. P: paraffins; N: naphthenes; [1]A: mono-aromatics; [2]A: di-aromatics, [3]A: tri-aromatics; and O: oxygenated suspected elution zone.

3. Results and discussion

3.1. Investigated configurations

As previously mentioned, the objective of this study is to characterize oxygenates in a coal-derived product by using comprehensive two-dimensional gas chromatography. For this purpose many dimensions have been investigated and optimization for each arrangement was achieved. In this study, orthogonal and non-orthogonal configurations will be exposed.

3.1.1. Orthogonal separations

Two orthogonal column configurations have first been investigated. The first one consisted in coupling DB-1 (15 m × 0.32 mm ×

0.1 μm) column with a ionic liquid column SLB-IL 100 (1 m × 0.25 mm × 0.2 μm). As the second dimension stationary phase has a great affinity with highly polar compounds like aromatics and phenols, it was almost impossible to obtain a separation without wrap-around effect. This phenomenon was also due to the large diameter of the second dimension column, and even with a high modulation period of 20 s a clear separation has not been reachable.

Thus, a more conventional configuration has been tested. It consisted in coupling a PONA (30 m × 0.2 mm × 0.5 μm) with a Solgelwax (0.8 m × 0.1 mm × 0.1 μm). This configuration using conditions presented in part 2 led to a good separation. In fact hydrocarbons have been separated and different group types have
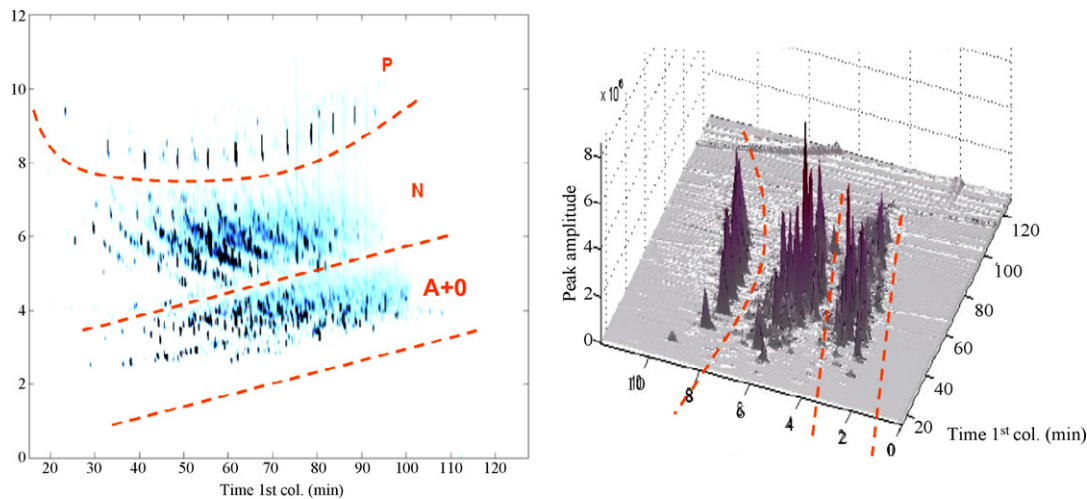

Fig. 3. 2D contour plot (left), and 3D contour plot (right) of a direct coal liquefaction product using non-orthogonal conditions: DB-17 (30 × 0.25 × 0.25) × DB-1 (1.5 × 0.1 × 0.1) with a scale ranging from 15 to 126 min. P: paraffins; N: naphthenes; and A + O: aromatics and oxygenates.
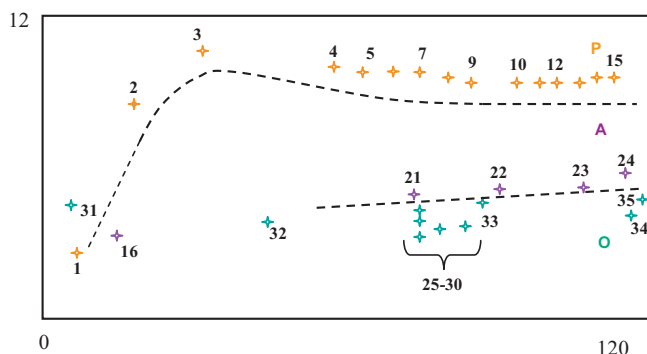
Fig. 4. 2D contour plot of SM, numbers refer to Table 1. Conditions Solgelwax × DB-1.

been identified using the test mixture presented in part 2. As shown in Fig. 2, paraffins, naphthenes, mono, di, and tri-aromatics have been separated. The elution zones are consistent with those generally obtained in petroleum samples [31]. As far as oxygenates are concerned, phenols are suspected to elute in the circled zone. In fact the injection of sample O highlighted the elution of phenols in this dedicated area. Hypothetically this column arrangement permits the characterization of hydrocarbons and oxygenates in one single run and appears as an appealing solution to unravel the sample molecular composition. However oxygenates still elute with the other aromatic compounds.

3.1.2. Non-orthogonal separations

Four non-orthogonal configurations have then been investigated. This column configuration has the advantage to extend the occupation space [45]. It has been used to unravel many oxygenated structures in biodiesels [36] or in Fischer–Tropsch products [32]. An ionic liquid column SLB-IL 100 (30 m × 0.2 mm × 0.2 μm) has been set up in the first dimension coupled with a DB-1 (1 m × 0.1 m × 0.1 μm). The injection of oxygenated model molecules showed that only ditertbutylmethylphenol and 6-tert-butylcresol could be eluted and other oxygenates like phenol, benzofuran, or cresols were trapped in the column. The extremely high polarity of this column is consequently not adapted to oxygen-containing compounds. The two eluable species had in common a high steric hindrance of the functional group –OH which involves less interaction with the stationary phase. This phase was therefore neglected and replaced by a DB-17 (30 m × 0.25 mm × 0.25 μm) coupled with a DB-1 (1.5 m × 0.1 mm × 0.1 μm). Operating conditions are described in part 2. The 2D contour plot has a very high interfamily resolution and paraffins are well separated (Fig. 3). However no distinction is possible between mono, and di-aromatics and oxygenated species elute in the same zone as
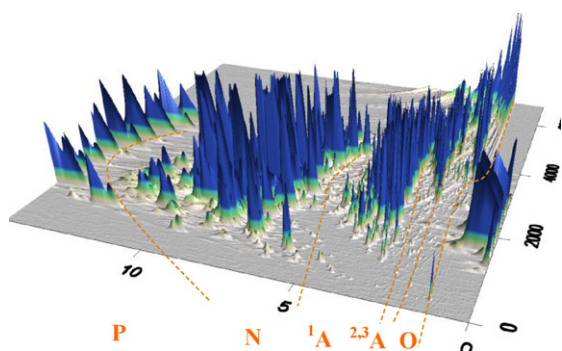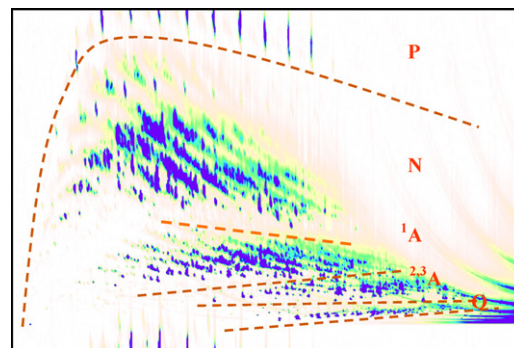

Fig. 6. 2D contour plot of a coal-derived liquid using GC × GC. Configuration: Solgelwax × DB-1. P: paraffins; N: naphthenes; [1]A: mono-aromatics; [2]A: di-aromatics; and [3]A: tri-aromatics.

hydrocarbons. A more polar first dimension is thus necessary to improve the separation.

Among the many non-orthogonal tested configurations, one stands out from the other as it enables to fully separate oxygenates from hydrocarbons and also offers a good separation between mono and di-aromatics (Figs. 4–6). In fact Solgelwax (30 m × 0.25 mm × 0.25 μm) coupled with a DB-1 (1 m × 0.1 mm × 0.1 μm) is of great interest. This configuration deserved further experiments in particular a precise identification of targeted species using GC × GC-ToF/MS (see next paragraph). In fact, in the first the stationary phase has a great affinity with oxygenated compounds, in particular phenols. The model mixture 2D chromatogram shows that aromatics and phenols are clearly separated. This is confirmed by the 2D chromatogram of the real sample.

3.2. Selection of the most adapted configuration

3.2.1. Resolution and space occupation

To evaluate the performances of each arrangement, resolution between dibenzofuran and fluorene was calculated as well as the one between two n-paraffins. Space occupation was also calculated using the formula detailed in the previous paragraph and Ryan criterion. Resolution results are summarized in Fig. 7. They show that n-paraffins separation is resolutive for the four cases. However, to separate dibenzofuran and fluorene, DB-17 × Solgelwax and DB-1 × DB-17 configurations are not adapted. As far as 2D space occupation is concerned, both Ryan criterion and our equation show that PONA × Solgelwax and Solgelwax × DB-1 are the most interesting configurations (Fig. 8). Results obtained using Eq. (5) are in good agreement with those deduced from Ryan graphical method. However this formula consists in the Euclidian norm between the space occupation of each dimension, whereas Ryan criterion is a graphical method giving the occupied area. Thus, if the
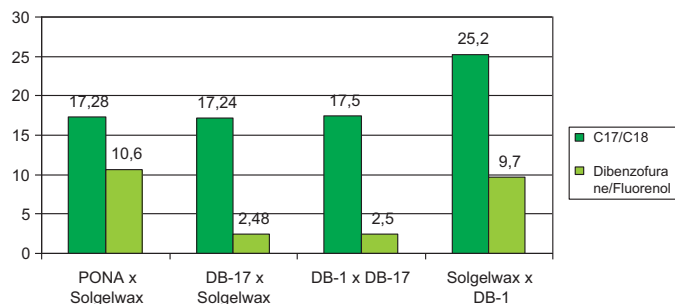

Fig. 5. 3D plot of a coal-derived liquid using GC × GC. Configuration: Solgelwax × DB-1. P: paraffins; N: naphthenes; [1]A: mono-aromatics; [2]A: di-aromatics; and [3]A: tri-aromatics.

Fig. 7. Resolutions between two paraffins and between fluorene and dibenzofuran for four column configurations: PONA × Solgelwax, DB-17 × Solgelwax, DB-1 × DB-17, and Solgelwax × DB-1.

Table 3
Selection criteria for four column configurations: PONA × Solgelwax, DB-17 × Solgelwax, DB-1 × DB-17, Solgelwax × DB-1.

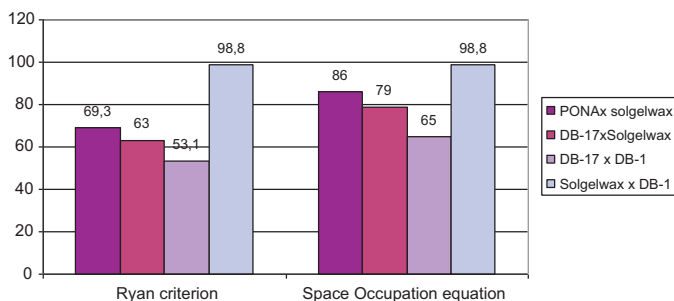| Column configurations	Selection criteria
PONA × Solgelwax	823.1
DB-17 × Solgelwax	176.1
DB-1 × DB-17	147.5
Solgelwax × DB-1	985.4

Fig. 8. 2D space occupation using Ryan criterion and the 2D space occupation formula for four column configurations: PONA × Solgelwax, DB-17 × Solgelwax, DB-1 × DB-17, and Solgelwax × DB-1.

first dimension occupation is null and the second maximal, then the space occupation using our criteria will be 0.50 whereas Ryan criterion will give a value close to zero. Moreover if there is only two well-separated peaks in each dimension of the chromatogram then Ryan criterion will give a bad space occupation and the equation developed in this work a good one. Thus, results can be compared only for a product which contains a large number of molecules. In this case where the matrix is quite complex, this novel concept of space occupation offers accurate results but would be limited in the case of a model mixture which does not contain enough molecules.

To conclude, a quantitative measure called selection criterion taking into account the resolution and the 2D space occupation was calculated and systematically applied to each configuration. An average 2D space occupation was calculated between the two values (Ryan criterion and 2D space occupation equation) and multiplied with the resolution between dibenzofurane and fluorenol. The values are reported in Table 3. DB-17 × Solgelwax and DB-1 × DB-17 configurations have low selection criteria whereas PONA × Solgelwax and Solgelwax × DB-1 ones are more than four times higher. In definitive Solgelwax × DB-1 configuration was selected as it shows the best product between space occupation and resolution.
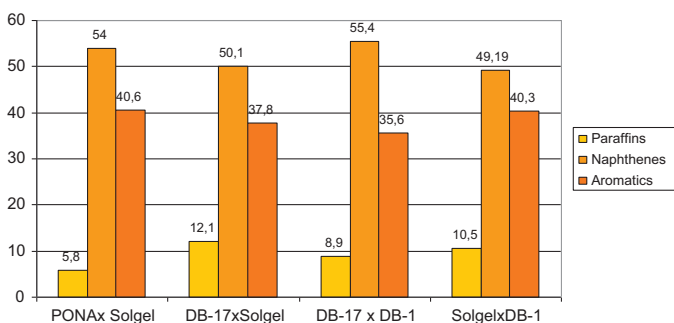

Fig. 9. Group type quantification in a coal-derived product for four column configurations: PONA × Solgelwax, DB-17 × Solgelwax, DB-1 × DB-17, and Solgelwax × DB-1.

Table 4
Oxygenated molecular structures identified by GC × GC-ToF/MS.

No.	Phenolic compounds
1	Phenol
2	Cresol
3	Dimethylphenol
4	Propylphenol
5	Trimethylphenol
6	Propylmethylphenol
7	Propylethylphenol
8	Methylethylphenol
9	Diethylephenol
11	Dimethylethylphenol
14	Tertbutylmethylphenol
16	Butylphenol
17	(Methylpropyl)phenol
18	Thymol
20	(Methylethyl)phenol
21	Methylindanol
22	Allylmethylphenol
29	Methylphenylphenol
32	(Methylethyl)phenol
34	Allylphenol
35	Methylindanol
36	Ethylbutylphenol
37	Pentylphenol
45	Dimethylnaphthol
47	Cyclohexylphenol
53	Methylinden-ol,dihydro
56	Phenylphenol

No.	Dibenzofuranes
25	Dibenzofurane
26	Methyldibenzofurane
57	Tetramethyl,dihydrobenzofurane

No.	Ketones
10	Methylfuranon
12	Indenone
13	Heptenone
24	Trimethylnaphthalenone
31	Dimethylbenzofuranon
38	Dimethylbenzofuranon
46	Ethylmethylene-indanone
54	Dimethylbenzofuranone
55	Hydroxy, dihydronaphthalenon
15	Naphthalenonedihydro

No.	Alcohols
39	Naphthalenol-tetrahydro
40	Dimethylbenzenediol
41	Methylbenzenediol
42	Resorcinol
43	Naphthalenol
44	Methylnaphthalenol

No.	Other oxygenates
19	O and S compound
50	Oxygenate
51	Ethylvinylanisole
52	O and N compound
27	Xantene
28	Lilial
30	Methoxynaphthalene

3.2.2. Semi-quantification

As some of the configurations do not allow the separation of oxygenates from aromatics, a general family semi-quantification has been established (Fig. 9). Although results obtained are not accurate considering that no response factors have been used, it allows a global vision of families distribution. Oxygenated compounds are thus underestimated because their response factors are superior to 1. Results obtained by each column arrangement are in agreement. Basically, naphthenes are present in majority in this sample
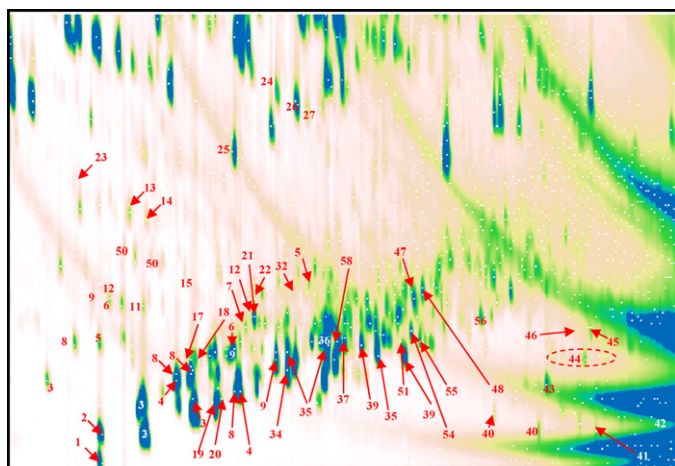
Fig. 10. 2D contour plot obtained from coal liquid analysis. Numbers refer to Table 4. Conditions: Solgelwax × DB-1

and aromatics and naphtheno-aromatics are also of high concentration. Concerning paraffins, they are of low content comparing to petroleum gas oil. These results must be complemented by further investigations aiming to apply an average response factor for each family and reach a more precise quantification.

3.3. GC × GC-ToF/MS analysis of the selected configuration

To confirm identification data obtained from model mixtures analysis the sample was injected using optimal chromatographic conditions previously described (Solgelwax × DB-1) and a time-of-flight mass spectrometer (Fig. 10). This technique allowed the identification of oxygenated compounds and confirmed the expectations deduced from model mixtures previously detected with a flame ionization detector. However, modulation performed by a liquid nitrogen cooled gas jet cryogenic modulator and the vacuum created inside the detector may have a slight influence on the separation. Targeted oxygenated compounds were clearly identified at the bottom of the chromatogram and are well separated from the hydrocarbon matrix. The 57 identified molecular structures (Table 4) mainly belong to six families: phenolic compounds, naphthols, indanols, naphthalenons, diols, and benzofurans. Spectra deconvolution was also applied in order to identify oxygenates and led to a good selectivity although it does not have a real meaning considering that the selected m/z ratio (121) is not common to all oxygenates.

These results are in total agreement with other studies involving GC-AED [9,13,14] and GC–MS [1] while other compounds belonging to ketones (naphthalenons, furanone) and alcohols (benzenediols resocinol) have been identified for the first time in these kind of matrices. Nitrogenated compounds can also be found in oxygenates area but this does not compromise their identification.

This non-orthogonal system is adapted to oxygen speciation in such matrices but also gives access to nitrogenates and hydrocarbon identification in one single run. Although distinction between two position isomers cannot be properly established, it can be approached with steric hindrance considerations. In fact, in the case of phenolic compounds which are predominant, the more the functional group –OH is surrounded by alkyl groups the earlier it elutes in the first dimension, because interactions with the stationary phase are inhibited. Concerning non-oxygenated compounds, these results reveal the presence of n-paraffins from C11 to C24, of naphthenes with up to five rings, many naphthenoaromatics, and aromatics with up to four ring (pyrene). As far as nitrogenates are

concerned, they mainly consist in anilines, quinolines, indoles, and nitriles.

4. Conclusion

Correlation between results obtained using GC × GC-FID and GC × GC-ToF/MS enabled to unravel molecular structures of oxygenated compounds in coal-derived materials. It shows that oxygenated structures mainly consist in phenolic compounds, benzofurans, naphthols, and indanols. It also revealed the presence of diols and naphthalenons which has never been demonstrated so far. Compared to more conventional configurations, a non-orthogonal system involving a highly polar column in the first dimension and a nonpolar one in the second enables the characterization of oxygenates but also nitrogenates and hydrocarbons in one single run. In fact, 2D contour plots obtained in these conditions exhibit good resolution and high space occupation which was estimated using an innovative equation. Nevertheless, nitrogenates elute in the same zone as oxygenates. A separation involving SFC, LC or GC can be of great interest upstream from the GC × GC system in order to trap these compounds and exalt oxygenates. This stage would lead to a generic method for unraveling O-compounds in hydrocarbon matrices contained in coal-derived materials and could be extended to similar products. These results lead to a better understanding of these matrices and represent a springboard towards conversion processes enhancement.

References

[1] F. Bertoncini, ACS National Meeting Book of Abstracts, vol. 232, 2006, p. 1.
[2] T.J. Morgan, A. George, P. Alvarez, M. Millan, A.A. Herod, R. Kandiyoti, Energy Fuels 22 (2008) 3275.
[3] V.L. Cebolla, L. Membrado, M. Matt, E.M. Galvez, M.P. Domingo, Anal. Adv. Hydrocarbon Res. (2003) 95.
[4] M.A. Ali, A. Hassan, Petroleum Sci. Technol. 20 (2002) 751.
[5] T. Jorjorian, Org. Geochem. 17 (1991) 711.
[6] B. Omais, M. Courtiade, N. Charon, D. Thiébaut, A. Quignard, Energy Fuels 24 (2010) 5807–5816.
[7] S.D.S. Murti, K.H. Choi, K. Sakanishi, Fuel 84 (2005) 135.
[8] S.D.S. Murti, K. Sakanishi, O. Okuma, Y. Korai, I. Mochida, Fuel 81 (2002) 2241.
[9] K.D. Bartle, S.R. Hall, K. Holden, S.C. Mitchell, A.B. Ross, Fuel 88 (2009) 348.
[10] G. Becker, Anal. Chim. Acta 376 (1998) 265.
[11] C. Ostman, J. Chromatogr. B: Anal. Technol. Biomed. Life Sci. 826 (1998) 57.
[12] I. Mochida, Fuel 84 (2005) 135.
[13] R. Meyer zu Reckendorf, Chromatographia 52 (2000) 67.
[14] R.E. Pauls, M.E. Bambacht, C. Bradley, S.E. Scheppele, D.C. Cronauer, Energy Fuels 4 (1990) 236.
[15] J.N. Cardoso, Ind. Eng. Chem. Res. 31 (1992) 1045.
[16] M. Novotny, Fuel 60 (1981) 213.
[17] J. Misiak, Int. J. Coal Geol. 68 (2006) 117.
[18] D. Brodzki, Fuel 74 (1995) 407.
[19] H. Lin, D. Zang, Energy Sources Part A: Recovery Utilization Environ. Effects 31 (2009) 118.
[20] K. Erdmann, T. Mohan, J.G. Verkade, Energy Fuels 10 (1996) 378.
[21] L. Mauro, J. Microcolumn Sep. 12 (2000) 292.
[22] E.A.F. Gobato, J. High Resolut. Chromatogr.: HRC 17 (1994) 237.
[23] T. Mohan, J.G. Verkade, Energy Fuels 7 (1993) 222.
[24] A.E. Wroblewski, R. Markuszewski, J.G. Verkade, Abstr. Pap. Am. Chem. S 194 (1987), 60-FUEL.
[25] A.E. Wroblewski, C. Lensink, R. Markuszewski, J.G. Verkade, Energy Fuels 2 (1988) 765.
[26] C. Lensink, J.G. Verkade, Energy Fuels 4 (1990) 197.
[27] A.E. Wroblewski, C. Lensink, J.G. Verkade, Energy Fuels 5 (1991) 491.
[28] M. Diaz, R. Moliner, J.V. Ibarra, J. Chromatogr. 607 (1992) 353.
[29] M.P. Maskarinec, J.D. Vargo, M.J. Sepaniak, J. Chromatogr. 261 (1983) 245.
[30] F. Bertoncini, C. Vendeuvre, D. Thiebaut, Oil Gas Sci. Technol.-Revue de l Institut Francais du Petrole 60 (2005) 937.
[31] M. Adahchour, J. Beens, U.A.T. Brinkman, J. Chromatogr. A 1186 (2008) 67.
[32] M.J. Janse van Vuuren, Catal. Commun. 10 (2009) 1674.
[33] F. Bertoncini, M.C. Marion, N. Brodusch, S. Esnault, Oil Gas Sci. Technol.-Revue de l Institut Francais du Petrole 64 (2009) 79.
[34] J.D. McCurry, J. Chromatogr. Sci. 45 (2007) 650.
[35] W. Tiyapongpattana, P. Wilairat, P.J. Marriott, J. Sep. Sci. 31 (2008) 2640.
[36] F. Adam, F. Bertoncini, V. Coupard, N. Charon, D. Thiebaut, D. Espinat, M.C. Hennion, J. Chromatogr. A 1186 (2008) 236.
[37] M. van Deursen, J. Chromatogr. B: Anal. Technol. Biomed. Life Sci. 878 (2000) 205.

[38] R.B. Gaines, J. High Resolut. Chromatogr.: HRC 22 (1999) 251.
[39] J.F. Hamilton, A.C. Lewis, M. Millan, K.D. Bartle, A.A. Herod, R. Kandiyoti, Energy Fuels 21 (2007) 286.
[40] J.C. Giddings, J. High Resolut. Chromatogr. (now called J. Sep. Sci.) 10 (1987) 319.
[41] T. Dutriez, M. Courtiade, D. Thiebaut, H. Dulot, F. Bertoncini, J. Vial, M.C. Hennion, J. Chromatogr. A 1216 (2009) 2905.
[42] D. Ryan, P. Morrison, P. Marriott, J. Chromatogr. A 1071 (2005) 47.
[43] Z. Liu, D.G. Patterson, Anal. Chem. 67 (1995) 3840.
[44] M. Gilar, Anal. Chem. 77 (2005).
[45] J.M.D. Dimandja, G.C. Clouden, I. Colon, J.F. Focant, W.V. Cabey, R.C. Parry, J. Chromatogr. A 1019 (2003) 261.