Oxygen speciation in coal-derived liquids and bio-oil upgrading products

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[1] H. C. Andersen

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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 and upgraded bio-oils definitely appear among the new generation substitutes. To assist conversion reactions, it is essential to gain a deeper insight of these products compositions, in particular to characterize oxygenated species.

***

A state of the art of analytical tools deployed for the analysis of oxygenated species contained in direct coal liquefaction products highlights the complexity of these matrices. Among the different analytical techniques investigated in the literature (gas and liquid chromatography, mass spectrometry or NMR spectroscopy), comprehensive two-dimensional gas chromatography offers bright perspectives.

Therefore, the first step of this Ph.D. was to characterize a direct coal liquefaction atmospheric gas oil (AGO) using **GC×GC-FID and GC×GC-ToF/MS.** Ten column combinations were examined and one of them was selected (SolGel-WAX × DB-1). This particular reverse orthogonality system involving a highly polar column in the first dimension and a non-polar one in the second enabled the characterization of many oxygenates and hydrocarbons in one single run. In fact, 2D contour plots obtained in these conditions exhibits good resolution and high space occupation which was estimated using an innovative equation. GC×GC-ToF/MS allowed the characterization of more than fifty oxygenated molecular structures in the coal-derived middle distillate. They mainly consist in phenolic compounds with different alkyl chains, benzofurans, naphthols, and indanols. Experiments also revealed the presence of diols and naphthalenons which has never been demonstrated so far.

Then the spotlight of chapter 3 was on a direct coal liquefaction naphtha and, as this product is less complex, GC and GC-GC systems were firstly explored. A few oxygenated species contained in a direct coal liquefaction naphtha could be identified by **GC-ToF/MS**. The limitations consisting essentially on the presence of coelutions between oxygenates and hydrocarbons could be overcome by using **GC-GC-FID**. Nevertheless, there were too many oxygenated species and achieving such a high number of cuts tended to the use of a comprehensive technique. Therefore, **GC×GC** was finally considered and thanks to the column set selected in chapter 2, more than a hundred oxygenated compounds belonging to

five main families were identified: alcohols, phenols, ketones, carboxylic acids, and furans. To accentuate the second dimension separation, a novel polar × midpolar column set (SolGel-WAX × Rtx-200) enabled a selective separation of phenols and alcohols which were quantified using a definite methodology involving experimental response factors determination.

Hence, for both fractions (naphtha and gas oil), a quantification of phenols and alcohols was achieved using the advanced column set. To complement GC×GC results, other techniques were then investigated: **FT-ICR/MS, ^{31}P NMR, and UV-visible spectroscopy**. This transversal approach leads to a global vision of four oxygenated chemical families present in a coal derived naphtha and atmospheric gas oil. In fact, FT-ICR/MS enabled to confirm the presence of phenols and highlighted carboxylic acids which were then quantified by ^{31}P NMR. To finish, UV-visible spectroscopy led to the proportion of ketones among all oxygenated compounds present in both samples.

***

The second part of the manuscript focused on biomass fast pyrolysis which is considered as a promising technique to produce renewable liquid for the transportation field. However, bio-oils are mainly oxygenated (45-50%w/w O on woody biomass) and contain almost no hydrocarbons. Therefore, a two-stage upgrading is applied to obtain a liquid with lower oxygen content. Therefore, after the first stage, a partially upgraded bio-oil (PUB) is obtained (>10 %w/w O) and characterization of oxygenated compounds in this product is essential to assist conversion reactions.

By investigating different **GC×GC** conditions, a reverse orthogonality column combination which is adapted to oxygen speciation in a partially upgraded bio-oil was selected. Mass spectrometry data enabled the identification of more than 40 analytes of interest. Moreover, quantification was possible by creating blobs associated to the identified molecules and their corresponding response factors. In addition, 41 oxygenates belonging to eight chemical families were quantified: ketones, furans, alcohols, phenols, carboxylic acids, guaiacols, anisols, and esters. Each family content was expressed in terms of elemental oxygen so that the contribution of each family in the global oxygen elemental content can be evaluated.

These results lead to a better understanding of these upgraded bio-oils and represent a springboard towards conversion processes enhancement. However reversed combination

allows the separation of phenolics but do not offer enough intra-family resolution. Therefore, to reach a better insight on phenolic compounds, supercritical fluid chromatography was hyphenated to GC×GC. The ethylpyridine column is very selective towards the OH functional groups and allows an online pre separation of aromatic-OH compounds which can be analysed by GC×GC without coelutions with hydrocarbon aromatics. Consequently, a breakthrough molecular characterization of phenols and naphthols can be obtained. These results are necessary to understand reaction mechanisms during bio-oils upgrading and optimize conversion conditions.

***

Characterization of biomass and coal oils leads to a common conclusion concerning GC×GC: **Reverse orthogonality** is much more adapted to oxygen speciation in such matrices. Therefore, further considerations on reversed systems were discussed. Firstly, the general notion of orthogonality combining retention mechanisms independence and 2D space occupation was decoupled. Indeed, a reverse orthogonality system can offer a good separation and a great space occupation. It was also illustrated that orthogonality is intimately linked to the sample properties and cannot be considered as a *sine qua none* condition to achieve a good separation. To evaluate the pertinence of a separation conditions, it is necessary to deal with a more general notion of dimensionality taking into account the specificity of the sample of interest.

To finish, the analysis of a coal derived middle distillate by GC×GC using two different columns combinations involving the same second dimension stationary phase highlights the **influence of the first dimension on the second dimension**. In fact, combined to two different primary stationary phases, the use of the same second dimension involves two different families' elution orders. This can be explained by volatility difference of the focused analytes which involves a separation by boiling point in the second dimension for the polar × mid-polar combination.

RESUME

De par la hausse du prix du pétrole et l'émergence économique de certains pays, le développement de technologies et de systèmes énergétiques durables pour le secteur des transports devient une priorité, ceci afin de diminuer la dépendance au pétrole de nos sociétés et de réduire la pollution de notre environnement. Parmi les solutions étudiées, les carburants alternatifs et les biocarburants offrent de solides perspectives d'avenir.

Les produits issus de la **liquéfaction directe du charbon** représentent potentiellement de bons candidats pour la production de carburants alternatifs. Leur composition chimique est assez différente des produits pétroliers et s'apparente plutôt aux fractions issues du craquage catalytique et à celles provenant de la cokéfaction de résidus sous vide. Ces effluents ont d'importantes teneurs en hydrocarbures, mais ont surtout la particularité d'avoir une relativement forte teneur en oxygène (0,5-5% m/m) et en azote.

La valorisation de la **biomasse lignocellulose** sous forme de biocarburants dits de seconde génération tient aussi une place importante dans les travaux de recherche et développement actuels menés par IFPEN. Cette biomasse est constituée de bois, de pailles, de résidus forestiers et agricoles et d'autres ressources lignocellulosiques. La liquéfaction de cette ressource renouvelable est une voie thermochimique qui pourrait présenter un intérêt dans la conversion de biomasse lignocellulose en biocarburants. En particulier, la pyrolyse rapide permet de produire des liquides complexes dont le potentiel en tant que carburants est à l'étude.

Dans l'optique d'un raffinage, il s'avère important d'acquérir une connaissance plus étendue de ces deux types de matrices et en particulier d'élucider la composition chimique des oxygénés présents en relativement forte concentration avant hydrodéoxygénation. L'objectif de cette thèse est donc de développer des systèmes analytiques résolutifs permettant de séparer les molécules oxygénées présentes dans des matrices complexes et en mélange dans des hydrocarbures, en vue d'une caractérisation des liquéfiats de charbon et des huiles de biomasse upgradées.

***

Dans un premier temps, les produits issus de la liquéfaction directe du charbon seront à l'étude. La littérature montre que ces produits sont essentiellement composés d'hydrocarbures (paraffines, naphtènes, aromatiques), mais aussi d'espèces oxygénées présentes à des hautes teneurs (0,5-5%m/m) et appartenant essentiellement à la famille des furanes et des phénols. De nombreuses lacunes apparaissent pour l'analyse de ces matrices : haute limite de quantification de l'oxygène élémentaire (0,1%m/m), faible résolution et capacité de pics en chromatographie, méthodes souvent lourdes à mettre en place (extractions liquide-liquide et dérivations en amont), et manque d'information sur les composés présents dans ces matrices. Pour pallier ces problèmes, la chromatographie en phase gazeuse bidimensionnelle a été sélectionnée comme technique de cœur et deux distillats (naphta et gazole) ont été étudiés.

En ce qui concerne la coupe gazole (200-350°C), une optimisation de méthode mise en place en GC×GC a permis de sélectionner sur un large panel de colonnes chromatographiques des conditions permettant de répondre à notre problématique de séparation des oxygénés. Ainsi, plusieurs coélutions entre hydrocarbures et oxygénés ont été levées et l'identification de quatre familles chimiques a été permise par GC×GC-ToF/MS : phénols, alcools, cétones, et dibenzofuranes. Cependant, certaines coélutions subsistent encore, notamment entre furanes et aromatiques.

La caractérisation de la coupe naphta (PI-200°C) par GC-ToF/MS met en évidence de nombreuses coélutions entre oxygénés et hydrocarbures et ne permet que l'identification d'une dizaine de composés oxygénés. Afin de lever ce verrou technique, les espèces coéluées ont été séparées sur une seconde dimension plus polaire (GC-GC) en gagnant ainsi en résolution. Le montage dit en *heart-cutting* fait cependant apparaitre de nombreuses limitations : absence de modulation, nombre de coupes trop important, et méthode lourde à mettre en œuvre. Un couplage *comprehensive* (GC×GC) a permis de pallier ces problèmes et permet l'identification de phénols, cétones, acides carboxyliques, furanes, et alcools. Cette étude apporte de nombreux éléments de réponse par rapport à la littérature peu abondante pour ce type de matrice.

Par la suite, une quantification a été réalisée par GC×GC-FID pour les deux coupes en tenant compte des différents coefficients de réponse des composés oxygénés préalablement calculés pour plus de 20 composés modèles appartenant aux cinq familles chimiques identifiées. Une quantification globale par familles chimiques a été réalisée, suivie d'une

quantification individuelle de tous les alcools (linéaires, cycliques et aromatiques). La quantité correspondante en oxygène élémentaire a alors pu être évaluée. Selon ces données, les phénols constituent 86%m/m et 64%m/m de l'oxygène élémentaire présent respectivement dans les coupes gazole et naphta.

La chromatographie en phase gazeuse bidimensionnelle ne permet cependant pas d'atteindre un détail quantitatif sur trois familles chimiques : les cétones, les furanes, et les acides carboxyliques. Cette approche a donc été complétée par une démarche analytique multi-technique faisant intervenir la spectrométrie de masse très haute résolution ainsi que les spectroscopies RMN et UV-visible. La FT-ICR/MS par ionisation en electrospray négatif a permis de confirmer la présence des composés phénoliques (de C_6H_6O à $C_{11}H_{16}O$) et mis en évidence la présence probable d'acides carboxyliques (de $C_6H_{14}O_2$ à $C_{31}H_{64}O_2$). La quantification de ces acides carboxyliques, ainsi que des alcools, et phénols dans les produits ex-charbon a été accessible par RNM ^{31}P après phosphitilation de leurs protons labiles. Une analyse par spectrophotométrie UV-visible a par la suite permis d'obtenir la teneur en carbonyles dans ces effluents et de compléter le bilan d'oxygène. Au total, plus de 70%m/m de l'oxygène présent dans la coupe naphta de liquéfiat de charbon de référence a été quantifié par cette approche. Ce chiffre s'élève à 90% m/m dans la coupe gazole.

***

Par la suite, les huiles de pyrolyse de biomasse upgradées ont fait l'objet de nombreux travaux en GC×GC et en SFC-GC×GC. Leur teneur en oxygène est de l'ordre de 10-20%m/m (sur base humide) et la caractérisation des espèces oxygénées est indispensable à la mise au point des procédés de conversion.

Une première étape d'optimisation des conditions de chromatographie en phase gazeuse bidimensionnelle a été nécessaire. L'utilisation de plusieurs combinaisons de colonnes a conduit à la sélection d'un montage inverse adapté à la caractérisation des espèces oxygénées polaires (acides carboxyliques, alcools, phénols, méthoxyphénols et benzènediols). L'identification d'autres espèces de type furanes, esters, et cétones a été permise par déconvolution de spectre. Une quantification par GC×GC-FID a été possible grâce à une démarche similaire à celle employée pour la caractérisation des liquéfiats de charbon. Au total plus de 40 espèces oxygénées appartenant huit familles chimiques ont été

quantifiées : phénols, alcools, cétones, furanes, acides carboxyliques, guaiacols, anisoles, et esters. Chaque teneur a été exprimée en oxygène élémentaire de façon à évaluer la contribution des familles sur l'oxygène élémentaire total. Ce bilan ne tient pas compte des espèces oxygénées coéluées avec les hydrocarbures : cétones, furanes et esters.

La méthode dévelopée en GC×GC apporte une meilleure compréhension des huiles de biomasse upgradées mais reste cependant limitée du fait de la faible résolution intrafamille des composés phénoliques (phénols, naphtols, methoxyphénols, et benzènediols) inhérente aux montages inverses. Afin de gagner encore en résolution, une troisième dimension de séparation faisant appel à la chromatographie en fluide supercritique a été introduite. La colonne SFC greffée Ethylpyridine a été employée en amont de la GC×GC pour séparer ces espèces peu résolues et les injecter vers un jeu de colonnes orthogonal permettant de les séparer sans coélution avec les hydrocarbures. Il en résulte une quantification inédite des phénols et des naphtols par nombre d'atome de carbone dans la fraction phénolique. Ces recherches sont à approfondir pour avoir un détail sur les méthoxyphénols et benzènediols. De plus, la fraction non-phénolique est bien simplifiée et son analyse nécéssite de nouveaux développements.

***

Les résultats obtenus dans le cadre des précédents travaux permettent d'affirmer que les montages inverses sont les plus adaptés à la séparation des composés oxygénés en matrice hydrocarbure. Les deux derniers chapitres présentent une discussion sur ces montages inverses qui permettent d'obtenir des chromatogrammes structurés, des séparations interfamilles résolutives, et une occupation de l'espace 2D quasi maximale.

Le premier chapitre démontre qu'un couplage "inverse" entre une colonne polaire (PEG) en première dimension et une colonne semi-polaire en seconde dimension (trifluoropropylmethyl polysiloxane) permet d'identifier et de quantifier sélectivement les alcools linéaires, cycliques et aromatiques dans une matrice complexe. Ce montage à priori peu orthogonal met pourtant en jeu deux mécanismes de rétention différents. Ces derniers sont en revanche dépendants car les deux séparations sur chacune des dimensions ont en commun la volatilité. L'apport relatif de ce couplage de type polaire × semi-polaire par rapport à un montage conventionnel est présenté, et son intérêt pour la spéciation des

composés oxygénés dans différents produits issus de la liquéfaction du charbon est souligné. Il apparait donc clairement à travers ces deux exemples que la notion d'orthogonalité est intimement liée aux propriétés des composants à séparer et ne constitue pas en soi, une condition *sine qua non* pour la réussite d'une séparation. Il est donc nécessaire de revenir sur une notion plus générale d'occupation de l'espace qui s'avère plus adaptée pour juger de la pertinence d'une séparation.

Dans un dernier chapitre il est montré qu'une même colonne en seconde dimension (Rtx-200) donne lieu à deux séparations totalement différentes. Dans le cas où une colonne MTX-1 apolaire est placée en première dimension l'ordre d'élution en seconde dimension est Paraffines < Naphtènes < Aromatiques < Polaires. En revanche, dans le cas où une Solgelwax polaire est placée en première dimension, l'ordre d'élution est inversé : Polaires < Aromatiques < Naphtènes < Polaires. Pour expliquer ce phénomène, il est montré que le premier montage orthogonal implique une séparation par point d'ébullition en première dimension. Ainsi, le phénol est focalisé à une période de modulation proche de celle du tetraméthylbenzène et de la paraffine nC10. Ces composés ayant la même volatilité sont séparés par polarité en seconde dimension. En revanche, une colonne polaire en première dimension implique une élution pendant une période de modulation du phénol proche de celle du biphényl (C12) et de la paraffine nC20. La seconde séparation étant très courte et les composés ayant des volatilités très différentes, la sélectivité de la colonne a cette fois peu d'influence sur la seconde séparation et la volatilité régit la seconde séparation.

ABBREVIATIONS

AED: Atomic Emission Detector

AGO: Atmospheric Gas Oil

ASTM: American Society for Testing Materials

DCL: Direct Coal Liquefaction

GC: Gas Chromatography

GC×GC: Comprehensive two-dimensional gas chromatography

GC-GC: Heart-cutting two-dimensional gas chromatography

GO: Gas Oil

ECD: Electron Capture Detection

EIMS: Electron Impact Mass Spectrometry

ETBE: Ethyl-Tert-Butyl-Ether

FAME: Fatty Acid Methyl Ester

FBP: Final Boiling Point

FCC: Fluid Catalytic Cracking

FID: Flame Ionization Detector

FIMS: Field Ionisation Mass Spectrometry

FT: Fischer Tropsch

FT-ICR/MS: Fourier Transform – Ion Cyclotron Resonance / Mass Spectrometry

FT-IR: Fourier Transform InfraRed

HDT: Hydrotreatment

HPLC: High Performance Liquid Chromatography

IBP: Initial Boiling Point

IR: Infrared

LC: Liquid Chromatography

MS: Mass spectrometry

MTBE: Methyl-Tert-Butyl-Ether

NCD: Nitrogen Chimiluminescence Detection

NP: Normal Phase

NMR: Nucleon Magnetic Resonance

NPD: Nitrogen Phosphorus Detection

O-FID: Oxygen specific Flame Ionization Detection

PAC: Poly-Aromatic Cyclic

PAH: Poly Aromatic Hydrocarbon

PDMS: Poly DiMethyl Siloxane

PEG: Poly Ethylene Glycol

PONA: Paraffins, Olefins, Naphthenes, Aromatics

PUB: Partially Upgraded Bio-Oil

Py-GC: Pyrolysis-Gas Chromatography

RP: Reverse Phase

SAR: Saturates, Aromatics, Resins

SCD: Sulphur Chimiluminescence Detector

SEC: Size Exclusion Chromatography

SFC: Supercritical Fluid Chromatography

SFC-GC×GC: Supercritical Fluid Chromatography- Two dimensional gas chromatography

THF: TetraHydroFuran

TIC: Total Ion Chromatogram

ToF: Time of Flight

UV: Ultraviolet

VGO: Vacuum Gas Oil

INTRODUCTION

In order to alleviate the transport sector's reliance on oil, diversifying the liquid fuel supplies for the transportation field is of the upmost importance and many alternatives are promising. Recently, coal-derived liquids and bio-oils have sparked great interest as the new generation substitutes. However these liquids have high oxygen contents and characterizing oxygenated compounds is crucial to monitor reaction mechanisms and optimize conversion condition.

***

Before processing, coal-derived liquids properties and compositions are far from petroleum oils and upgrading must be applied to this product. In fact, they consist mainly of aromatic hydrocarbons, cyclic alkanes (naphthenes), linear alkanes and heteroatomic compounds (especially oxygenated species). To consider their refining, it is crucial to study their chemical and physical properties. Apart from the hydrocarbons, the requirements in terms of molecular characterization improvement concern oxygenated compounds which belong to different chemical families and are present in relatively high concentrations before hydrodeoxygenation (HDO).

Biomass-derived fuels can address the concerns of depleting fossil fuel reserves but also the concerns of carbon dioxide emissions. Fast pyrolysis is considered as a promising technique, but the derived bio-oils cannot be directly processed with petroleum feedstock and are far from fuel specifications. In fact, they are mainly oxygenated (45-50%w/w O on wet basis) and contain almost no hydrocarbons. Upgrading needs therefore to be applied to obtain products with lower oxygen content and characterization of oxygenates in these products is crucial to assist conversion reactions.

The composition of oxygenated compounds in these two matrices must be unravelled to envisage further processing. Therefore, the objective of the Ph.D. is to develop powerful analytical systems to characterize oxygenated compound in coal and biomass oils. The concerns of the two liquids are different. Coal-derived liquids consist mostly in hydrocarbons with relatively low oxygen content (0.1-5% w/w O), whereas partially upgraded bio-oils (PUB) are more oxygenated (>10%w/w O) and extremely complex as they contain a large variety of oxygenated chemical families in a hydrocarbon matrix. It was therefore decided to split the work into two parts and to focus on matrices of increasing chemical complexity.

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Consequently, the **first part** of the manuscript focuses on **coal-derived liquids** which can be distillated like petroleum products. A state of the art of coal-derived liquids analysis will firstly be presented to highlight the analytical limitations for characterizing these distillates. Then, two chapters focusing respectively on the atmospheric gas oil and the naphtha cuts will present the different developments achieved using one-dimensional gas chromatography (GC), heart-cutting two-dimensional gas chromatography (GC-GC) and comprehensive two-dimensional gas chromatography (GC×GC). Then, the focal point of the fourth chapter is the complementarities between GC×GC and three other analytical tools: High resolution mass spectrometry (FT-ICR/MS), ^{31}P NMR and UV-visible spectroscopy. This first part provides a detail level in terms of oxygen speciation in coal-derived liquids which was never reached so far.

The **second part** of the manuscript deals with **partially upgraded bio-oils** which are much more oxygenated. Once again, a state of the art of upgraded bio-oils characterization (chapter 5) will highlight technological locks. Then, GC×GC optimization for oxygen speciation in partially upgraded bio-oils will be presented in chapter 6. As this technique does not offer enough resolution, a third dimension of separation involving supercritical fluid chromatography was integrated online prior GC×GC analysis (chapter 7).

Throughout the two previous parts many columns combinations were investigated and it always appeared that non-conventional GC×GC conditions systems involving reverse column combinations provided the best solution to the oxygen speciation issue. Therefore the **third part** is a discussion on stationary phase combinations whose spotlight is **orthogonality**. The dual notion of this term is demonstrated in chapter 8 and advantages of reversed combinations are highlighted and explained. The reversal of elution order in a single second dimension by changing the first column nature is then evidenced in a last chapter. This third part relies on the use of chromatograms obtained through coal and biomass oils analysis.

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Figure 1-1 illustrates the whole PhD scope and numbers refer to the different chapters and appendixes of the dissertation. Each of the nine chapters of this dissertation was published in scientific reviews or at least submitted. The advantage of such a presentation is that each chapter

stands alone and the reader does not have to refer to any previous chapter to find the information. However, my apologies for the recurrence which may happen in the manuscript especially in the material and methods sections.

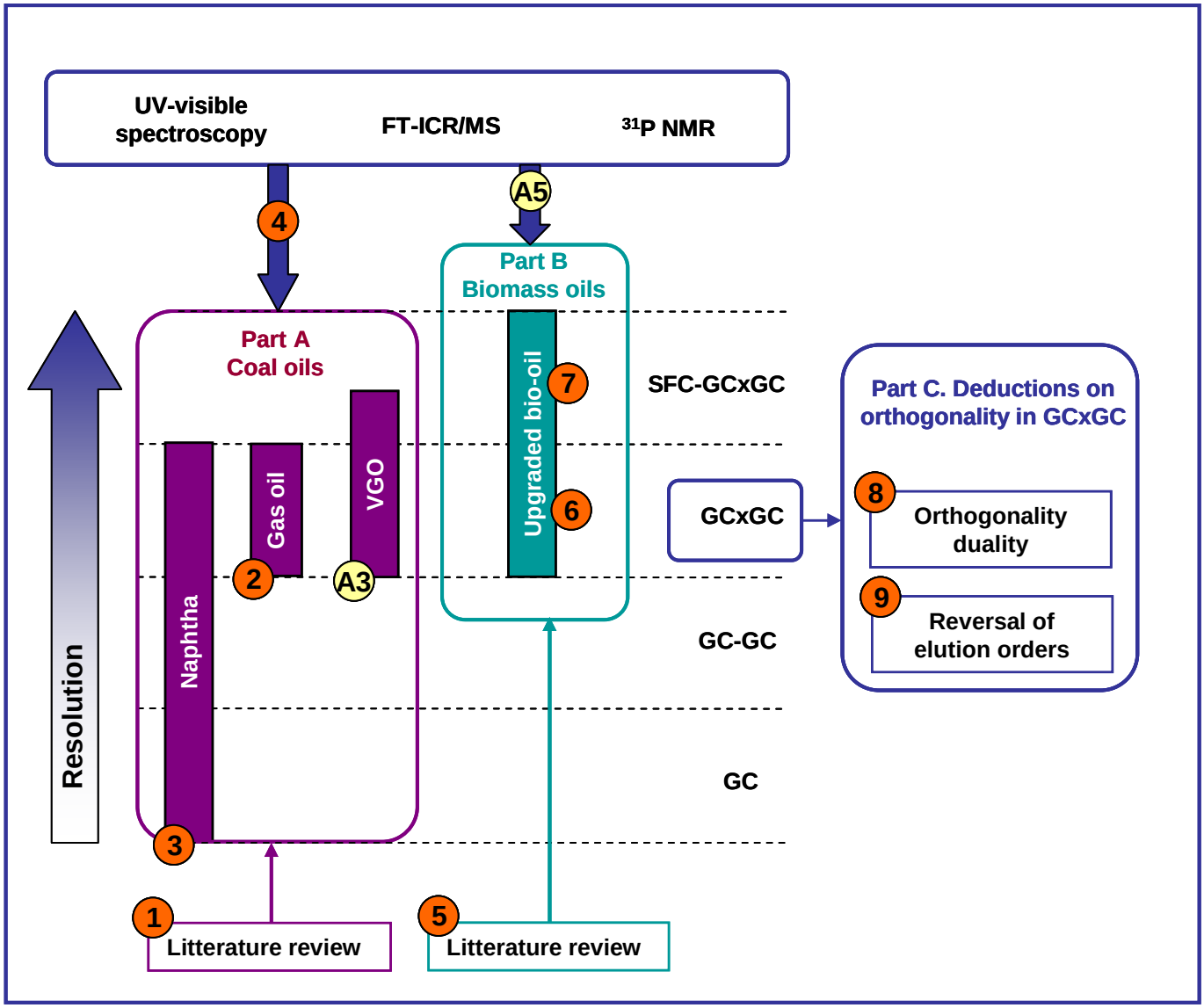
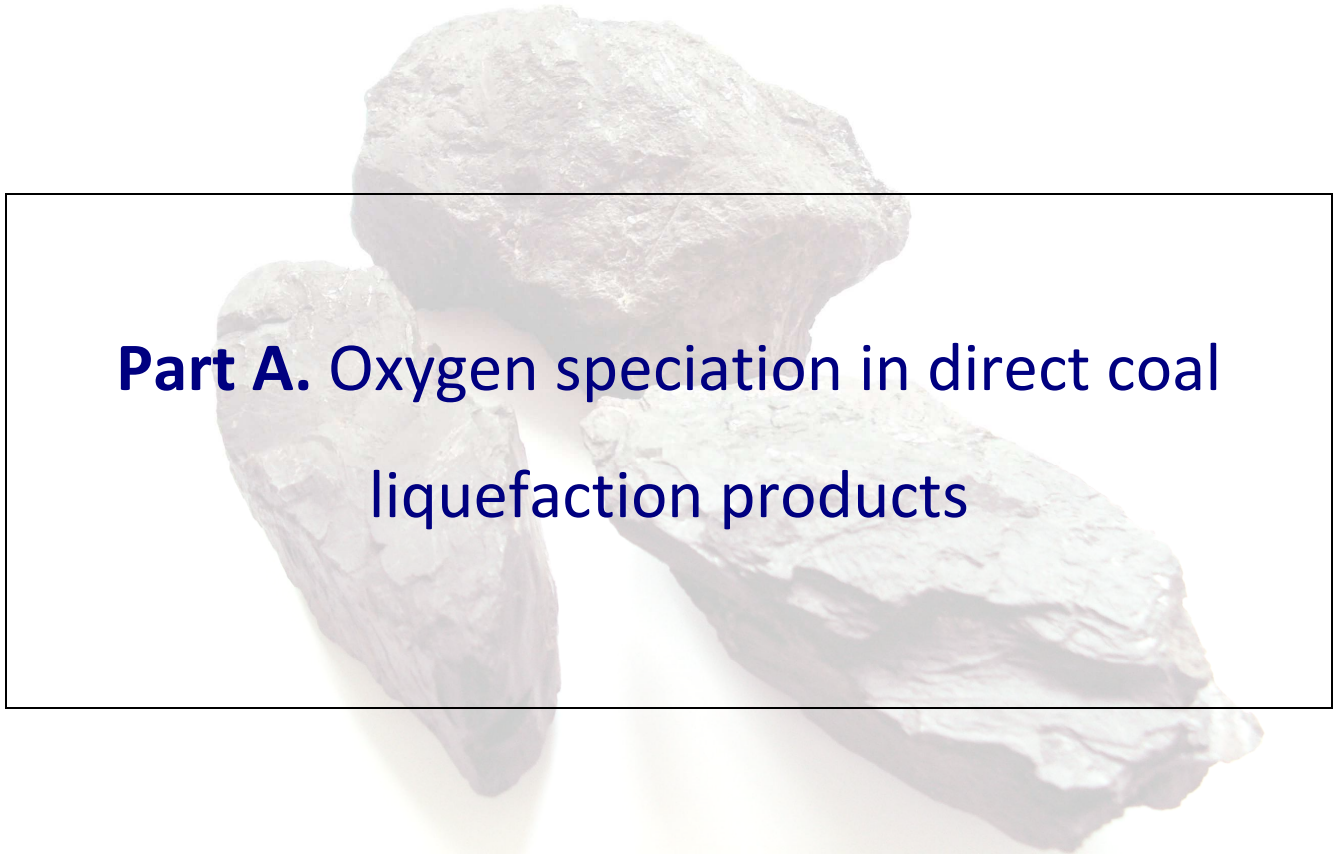


Figure 1-1. Global analytical approach developed in the PhD. Numbers with the orange and the yellow backgrounds refer respectively to the chapters and the appendices of the dissertation.



Part A. Oxygen speciation in direct coal liquefaction products

INTRODUCTION TO PART A: OXYGEN SPECIATION IN DIRECT COAL LIQUEFACTION PRODUCTS

As previously mentioned, it was decided in the single framework of this PhD that matrices would be investigated by increasing complexity. Therefore the first researches reported in part A were focused on oxygen speciation in direct coal liquefaction products. In fact a wider variety of oxygenated structures is present in these products which are also less oxygenated than partially upgraded bio-oils (0.5-5%w/w O for coal oils compared to >10%w/w for PUB).

This part is divided into four chapters. Chapter 1 presents a state of the art on these products. It aims to give a molecular cartography of oxygenated compounds present in such samples. Moreover it surveys the different analytical techniques investigated for their analysis. This literature survey leads to the conclusion that multi-dimensional chromatographic systems may offer interesting perspectives.

Then three chapters show the developments achieved on an industrial coal-derived liquid distilled at IFP Energies nouvelles into three cuts: a naphtha cut, an atmospheric gas oil cut and a vacuum gas oil cut. Researches on the vacuum gas oil cut are presented in appendix A3.

Chapter 2 shows first investigations on the AGO cut using comprehensive two-dimensional gas chromatography. It presents the evaluation of different column sets and the selection of a reversed combination which was particularly adapted to the oxygen speciation issue. Chapter 3 is focused on the naphtha cut which is less complex in terms of number of molecules. Therefore, instead of using directly very high-resolution techniques, investigations using GC/MS and GC-GC-FID were first achieved and for different reasons which will be detailed, GC×GC was finally selected.

Consequently, comprehensive two-dimensional gas chromatography enabled to unravel almost 150 compounds in the two fractions. However, this technique suffers from a lack of resolution as some species such as ketones, carboxylic acids and furans were still coeluted with other hydrocarbons. To overcome GC×GC limitations a multi-technical analytical approach applied to both cuts will be presented in chapter 4. This methodology involves the use of mass spectrometry, UV-visible spectroscopy and ^{31}P NMR. Thus a global quantification of oxygenated compounds could be expressed in elemental oxygen. These researches lead to a detailed characterization of oxygenated compounds in coal-derived products.

CHAPTER 1. Characterization of oxygenated species in coal liquefaction products: an overview [2]

FOREWORD

As mentioned in the introduction, identification and quantification of oxygen-containing compounds in coal-derived liquids is of considerable importance to understand their behaviours in further processing. However these species have not been characterized as fully as the predominant hydrocarbon components.

This first chapter surveys the analytical tools investigated for the separation, selective identification, and quantification of oxygenated compounds in coal oils. Although liquid and gas chromatography emerge as the most widespread techniques, many other spectroscopic techniques like FTIR (Fourier Transform Infrared), NMR, and mass spectrometry enabled to improve the understanding of these species. The state-of-the-art of preparative fractionation is also presented. Furthermore, the advantages and limitations of each technique are discussed and the potential contribution of multidimensional chromatographic systems to the analysis of complex matrices is highlighted.

[2] This chapter is based on an article published in Energy & Fuels, 2010 (24) p 5807-5816 by Omais *et al.*

1.1 Introduction

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 comes from two fundamental process schemes: direct coal liquefaction (DCL) based on research pioneered by Friedrich Bergius in the beginning of the twenties, and indirect liquefaction based on Fischer and Tropsch work [1, 2]. Coal upgrading into a synthetic fuel always emerged in particular geopolitical contexts. Indeed, during World War II, Germany faced crude restrictions imposed by the allies by launching an industrial production of coal liquids (DCL). A few years later, it is South Africa's turn to reply to crude embargo during the Apartheid by producing nearly 190,000 barrels of DCL a day in 2010. The 1st modern DCL unit is being started in Inner Mongolia in China by Shenhua, with a first DCL train producing 20 000 barrels per day of fuel, scheduled to be extended up to 60 000 barrels per day of fuel in the near future. Nowadays, petroleum decline and the rise of developing countries needs explain the special interest granted to coal-derived oils [3, 4]. Figure 1-1 shows the direct coal liquefaction conversion process used to transform coal into coal oil.

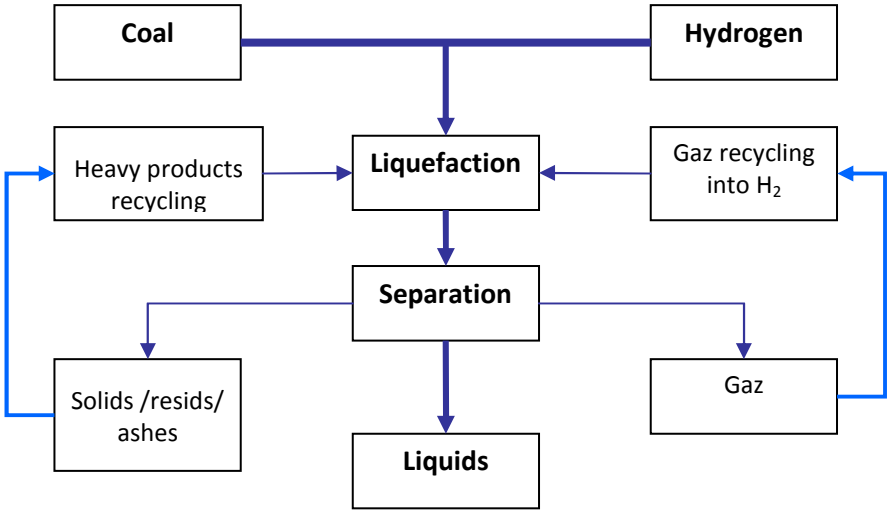


Figure 1-1. Direct coal liquefaction process

Before processing, DCL product characteristics are quite far from fuel specifications and upgrading must be applied to the gasoline and atmospheric gas oil cuts. In fact, they are mainly composed of naphthenes, polycondensed aromatic structures and heteroatomic compounds (Nitrogen and Oxygen) [1, 5-9]. To envisage their use as an alternative fuel, it is more than

necessary to study their chemical and physical properties. Except hydrocarbons, the needs in terms of molecular characterization enhancement concern oxygenated compounds which belong to many different chemical families and are present in high concentrations before hydrodeoxygenation (HDO). In order to find an adapted process scheme, a detailed characterization of oxygenates families must be carried out.

This chapter gives an overview of the analytical schemes developed in the literature focusing on the separation and selective detection of oxygenated compounds in DCLs. Liquid and gas chromatographies appear to be the most widespread solutions. However, several other techniques have been used in the literature such as FTIR, NMR, Mass spectrometry and the elucidation of the oxygenated matrix composition can be approached by achieving a retrospective of all these studies. Limitations of the previous techniques for the analysis of oxygenated compounds in Coal-derived liquids will be discussed throughout this chapter and the contribution of a multidimensional chromatographic system emphasized.

1.2 Properties of coal-derived liquids

The chemical composition of coal liquefaction products is very different from conventional oil fractions ones obtained by crude distillation. While classical petroleum fractions are usually rich in paraffinic compounds and in sulphur, coal products are mainly composed of aromatics, unsaturated species, and heteroatomic species (Nitrogen and Oxygen-containing molecules). Chemical properties of coal-derived liquids are also influenced by the origin and the maturity of the raw material. In fact, as geological processes apply pressure to biological derived material, it is successively transformed into lignite, sub-bituminous coal, bituminous coal, anthracite which finally turns into graphite. Thus, according to the type of coal used in the liquefaction process, the elemental compositions found in the literature are quite different. (Table 1-1)

Table 1-1. Elemental composition of different coal liquefaction products (AGO = Atmospheric Gas Oil, and VGO = Vacuum gas oil fraction)

Liquefaction process	*Cut*	*C (%w/w)*	*H (%w/w)*	*O (%w/w)*	*N (%w/w)*	*S (%w/w)*	Ref.
Direct Coal liquefaction	IBP-145°C	85.81	14.19	**0.43**	0.036	0.0047	[1]
Direct Coal liquefaction	145°C-220°C	88.03	12.07	**unknown**	0.098	0.0220	[1]
TH Coal NEDO liquefaction plant	AGO	86.88	9.71	**unknown**	0.82	unknown	[10]
Direct Coal	AGO	88.86	10.13	**unknown**	0.166	0.0445	[1]

liquefaction							
SRC-II[1] liquefaction of Powhatan Mine bituminous coal	238-482°C	89.5	7.7	**2.3**	1.1	0.4	[11]
HTI[2] Coal Process by SCCT[3] (China)	AGO	87.6	12.7	**unknown**	0.14	0.10	[12]
Hydrotreated two-stage liquefaction by NBCL[4] (Japan)	AGO	84.5	10.6	**0.47**	4.6	0.1	[13]
SRC-II[1] liquefaction of Powhatan Mine (Toluene fraction)	VGO	83.9-88.2	5.0-6.4	**4.4-6.5**	unknown	unknown	[14]
Direct Coal liquefaction	350°C +	90.08	8.04	**1.60**	0.447	0.12	[1]
SRC-II[1] liquefaction of Powhatan Mine (Pentane fraction)	VGO	82.2-90.3	6.6-7.4	**2.0-5.4**	unknown	unknown	[14]
Crude oil	Whole oil	84-87	11-14	**0.1-0.5**	0.1-1.5	0.04-6	[15]

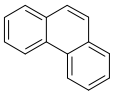
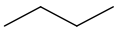
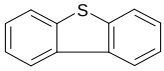
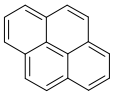
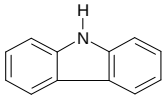
[1] Solvent Refined Coal
[2] Hydrocarbons Technology Inc
[3] Shenhua Clean Coal Technology Development
[4] Nippon Brown Coal Liquefaction

It is difficult to clearly conclude about the elemental composition of products described in Table 1-1 since different raw materials and different liquefaction processes including hydrotreatment step are used. Nevertheless, it clearly appears that globally, oxygen content is lower than those of products derived from the conversion of lignocellulosic biomass. Moreover coal liquefaction products exhibit lower H contents when compared to conventional petroleum distillation cuts.

When compared to physical properties of any processed crude oils, the key characteristics of these coal-derived distillates, before any subsequent hydrotreating or hydrocracking step, have very high densities (0.8-1) and poor combustion properties: low smoke point (10-15 mm) and low cetane number (20-30). This essentially results from the extremely low paraffin content and the high content of poly-naphthenic and naphtheno-aromatic structures [1].

Gates *et al.* [14] also improved the knowledge of coal oils by determining the relative concentrations of the functional groups. This structural characterization uses elemental analysis and NMR data and was applied on a heavy distillate into 9 fractions. The content of each functional group in the whole heavy distillate is given in Table 1-2.

Table 1-2. Functional groups in SRC-II heavy distillates functional groups concentrations (A) bound directly to an aromatic ring; (C_α) bound to a carbon α to an aromatic ring; (Cβ) bound directly to a carbon β or further from an aromatic ring[17]

Functional group	*Concentration (mol 100 g^{-1})*	*Functional group*	*Concentration (mol 100 g^{-1})*	*Functional group*	*Concentration (mol 100 g^{-1})*
	0.154	(A) 	0.104	(A) —OH	0.062
	0.273	(A) 	0.047	(A) 	0.005
	0.073	(A) 	0.155	(A) 	0.019
	0.036	(A)	0.014	(A) 	0.016
(A) —CH_3	0.108	(A) 	0.041	(A) —NH_2	0.013
(C_α) —CH_3	0.058	(A) 	0.039	(A) 	0.021
(C_β) —CH_3	0.128	(A) 	0.035	(A) 	0.002

1.3 Characterization by One-dimensional Gas Chromatography

Gas Chromatography has been widely used for the characterization of coal-derived products. O-FID is probably the first detector one thinks about for oxygen speciation. This detector was created to enable the selective identification of oxygen-containing species in hydrocarbon matrices. It appeared in 1980 and only a few articles mention its use. Most of these papers concern the ASTM D5599 which enables to quantify O-species at concentrations up to 0.1%w/w. The detector is composed of two microreactors and a Flame Ionization Detector installed in series. With this configuration, the oxygenated compounds eluted from the column enter the first reactor (cracking reactor with Pt/Rh catalyst) where they are selectively converted into CO. The methanizer installed downstream then converts this into methane. CH_4 is finally detected by the Flame Ionization Detector.

This detection device involves two main limitations as it is not compatible with products containing water and the presence of sulphur (>10ppm) poisons the catalyst. Hence, even if this detection is appealing for oxygen speciation it is understandable that it was never applied to coal-derived matrices. Therefore Atomic Emission Detection and Mass spectrometry are much more widespread and a review of different applications of gas chromatography coupled to these detectors is summarized in Table 1-3.

Table 1-3. A review of GC conditions for the analysis of Coal derived products

GC column	*Dimensions*	*Detection*	*Analytes*	*Reference*
SPB 1	30mx0.32mmx0.25µm	SCD	Sulphur species	[1]
SPB 1	30mx0.32mmx0.25µm	NCD	Nitrogen species	
BPX-5	25mx30mmx0.22µm	AED	O-PAC	[16]
HP-5	30mx0.25mmx1µm	AED	S-O-PAC	[17]
HP Ultra 2	25mx0.2mmx0.33µm	MS	S-O-PAC	
HP-1MS	30mx0.32mx0.1µm	AED	Phenols and dibenzofurans	[10]
DB-1	60mxnrxnr	MS	Phenols and indanols	[18]
Carbowax-20M OV-101	n.d.	MS	Phenols and indanols	[19]
HP-1	25mx0.32mmx0.17µm	FID and MS	Alkylphenols	[20]
Restek-XTI 5	30mx0.25mmx0.25µm	MS	O-PACs	[21]
OV-101	20mx0.25mmxnr	MS	Acid and phenols	[22]
Superow-20M	30mx0.20mmx0.10µm	MS	Phenols	[23]
Restek-XTI 5	n.d.	MS	Oxygenated compounds	[24]
HP-1MS	30mx0.32mmx0.1µm	AED	Oxygenated compounds	[25]
SE-54	25m x 0.25mmxnr	MS	Acidic Oxygenated compounds	[26]
Methyl Silicone 5% Phenyl	25mx0.32mmx0.17µm	MS	Coal maceral concentrates	[27]
BPX-5	25mx0.32mmx0.5µm	AED (also FPD and NPD)	Heteroatomic species	[28]
Carbowax 20M	25mxnrxnr	FID/TIC	Phenols	[29]

1.3.1 Selective characterization of oxygenates in coal-derived liquids by GC-AED

A few papers mention the coupling between Gas Chromatography and Atomic Emission Detector (AED) for the analysis of coal-derived products. This device is a multielement detector that can be used to measure up to 23 different elements. GC-AED played an important role in the detection of nitrogen and sulphur species in hydrocarbon matrices [30-32]. Thus, it enabled the identification of benzothiophenes, dibenzothiophenes, indols, and carbazoles in coal–derived liquids. Applications to oxygenated compounds have not been as widespread and concern mainly the petroleum field. However, Murti *et al.* in 2002, and in 2005 used this selective tool to analyze

kerosene-gas oil cuts respectively derived from the liquefaction of a sub-bituminous coal and South Banko coal [10, 25]. They highlighted the presence of many oxygenated compounds: alkylated phenols, benzofurans, naphthols and dibenzofurans [10, 25] (Figure 1-2).

Quantification could also be established for O-species which represent 3.7% of the fraction compared to 677ppm for S-species, 8400ppm for N-species, and 84.97%w/w for hydrocarbons. Among detected oxygenated compounds, phenols content is 51.16%w/w, compared to 33.07 %w/w for benzofurans, and 8.23 %w/w for dibenzofurans. Only 5.12% of oxygenated compounds are unknown which involves that phenols and benzofurans are the most predominant oxygen containing compounds. Bartle *et al.* also demonstrated in 2009 the potential of GC-AED for the analysis of oxygen-containing polycyclic aromatic compounds in coal-derived liquids [25]. Figure 1-3 shows the identified oxygenated species in an oil obtained from Samca coal treatment at 400 °C with a process-derived hydrogen donor solvent. It emphasizes the presence of dibenzofuran and its alkylated derivatives. Quantification was performed using a parent of benzonaphthofuran as an external standard. Oxygenated Poly Aromatic Cyclic (O-PACs) represent 0.03–0.3% in the tars, and 0.2– 0.1% in the neutral Poly Aromatic Cyclic (PAC) fraction of the pentane soluble product. Besides, in a recent study, this technique allowed the identification of phenyl-dibenzofuran, benzobisbenzofurans, triphenyleno[1,12-bcd]furan and 6-Oxa-12thia-indenol[1,2-b] fluorene [17] in coal tars, pitches and related materials. Other types of detectors are however preferred because AED device has a weak robustness and its sensibility to oxygen is not as appropriate as the one for carbon, hydrogen and sulphur. In fact, Gurka *et al.* studied detection limits for heteroatomic species i.e. hydrogen, nitrogen, oxygen, chlorine, and sulphur detection limit ranges are 0.17−3.0, 1.0−5.0, 0.65−11, 0.07−3.0, and 0.023−0.028 ng, respectively. This indicates that the order of increasing sensitivity to molecular structure is O < N < H < Cl < S.

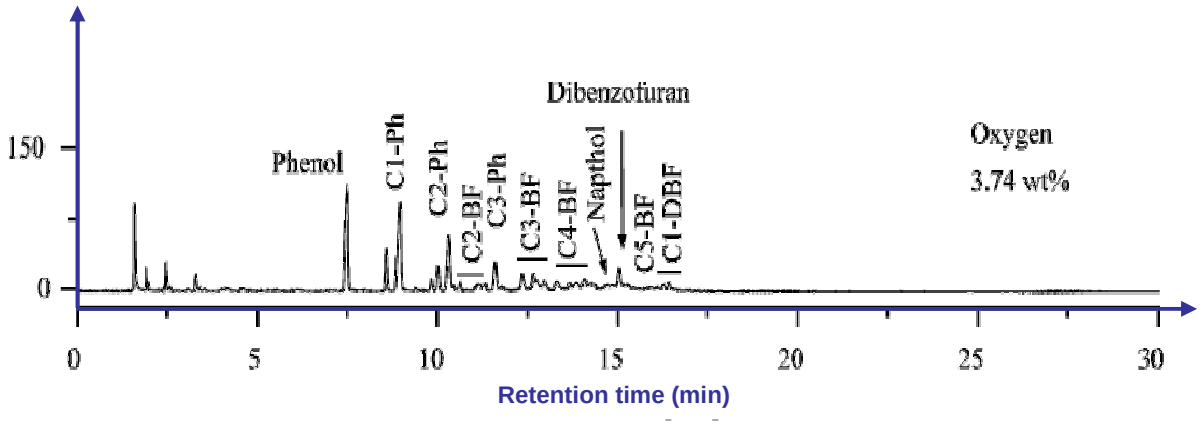


Figure 1-2. Oxygen (171nm) specific GC-AED chromatogram of South Banko Coal Liquid ; Ph, phenol; BF, benzofuran; DBF, dibenzofuran [25].

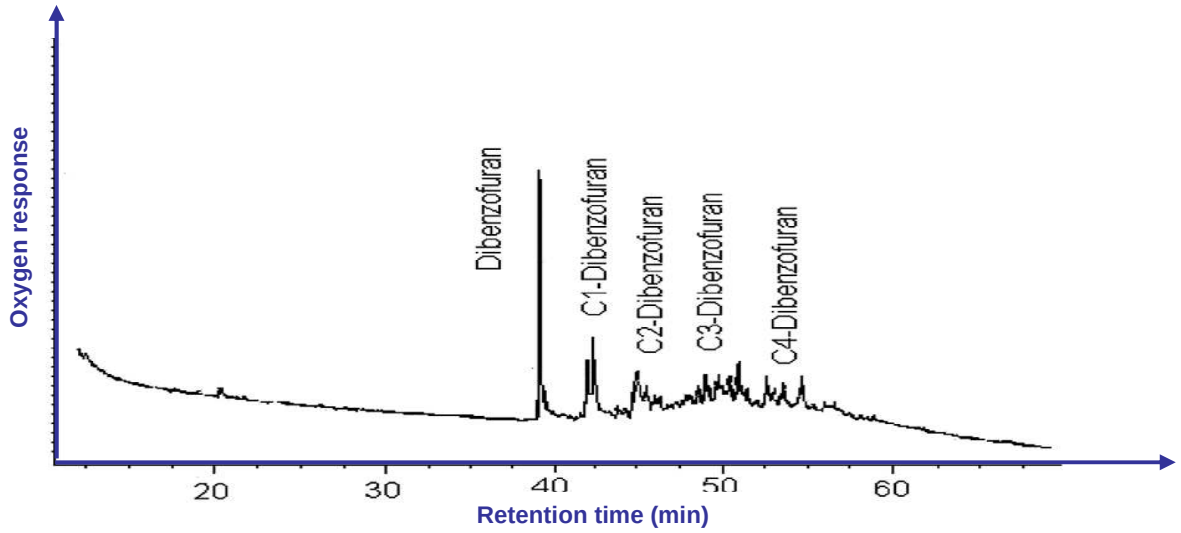


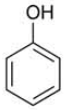
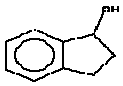
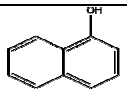
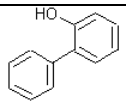
Figure 1-3. Oxygen (777 nm) specific GC-AED chromatogram of the oil derived from a Spanish coal [16]

1.3.2 Applications of GC-MS to characterize oxygenates in coal liquids

Furthermore, mass spectrometry detection was used to identify and quantify phenolic compounds in 175-425°C fractions of coal-derived distillates. In order to concentrate this fraction, a solvent extraction was used by Pauls *et al.* [18]. It consists on isolating an acidic concentrate by extraction with sodium hydroxide and in neutralizing the solution by acid addition. This strategy was also used in 1984 by Uchino *et al.* in order to separate the basic fraction and the acidic fraction from the hydrocarbon matrix [33]. In a phenol-containing fraction that Pauls *et al.* managed to separate, four types of ring structures with different short alkylated chains were characterized by GC-MS: phenols, indanols, naphthols, and biphenylols (Table 1-4). The recovery of phenol in the

fraction of interest is only 42% whereas recovery of the other compounds up to C3 is 70%. The quantification of these species is given in Table 1-4 for the atmospheric flash distillates of Illinois N ° 6 coal-derived oil obtained by a two stage liquefaction process. Another study using GC-MS also demonstrates that the phenols are essentially monocyclic and that methyl groups are the main substituents in an Irati shale Oil AGO cut [26]. It was found that phenols represent 4 w/%w/w using GC/MS. This product is however quite different from the matrix of interest.

Table 1-4. Quantification of phenolic species (including indanols) by GC/MS in a phenolic fraction of a two stage coal liquefaction product (normalized % at alkyl carbon number) [18]

	Structure	***C0***	***C1***	***C2***	***C3***	***C4***	***C5***	***C6***
Phenols		1.7	11.2	21.7	21.9	13.4	2.2	0.2
Indanols		2.3	6.3	4.4	1.3			
Naphthols				1.7	1.1	0.3		
Biphenylol		0.2		0.8				

As phenolic compounds are the most abundant oxygenated species in coal products, many authors focused on their identification by GC-MS. With non-polar phases, separations demonstrated important peak tailing that can be overcome by converting phenols into methyl [34], acetyl [35] or trimethylsilyl [36] derivatives as reviewed by Charlesworth *et al.* [37]. After isolation of the phenolic fraction of a SRC-II middle distillate, the use of a Superox-20M column enabled White and Norman to identify 29 compounds via chromatography with authentic standards and matching mass spectra [23]. In 1976, another study showed the advantages of using a tris- (2,4-xylenyl) phosphate stationary phase for the separation phenol alkyl-derivatives [38]. In fact nearly 40 phenolic compounds were identified in a coal tar (Table 1-5). Many other works reveal the presence of similar species [19, 22, 39, 40].

Table 1-5. Phenolic compoundscontained in coal tar and identified by GC/MS using tris- (2,4-xylenyl) open-tubular phosphate stationary phase [38]

Compounds identified Nabivach et al.		
phenol	3,4,5-trimethylphenol	2,4-diethylphenol
2-methylphenol	2-ethylphenol	2,5-diethylphenol
3-methylphenol	3-ethylphenol	2,3,5,6-tetramethyl-phenol
4-methylphenol	4-ethylphenol	2,4,5-tetramethylphenol
2,3-dimethylphenol	2-n-propylphenol	2,3,4,6-tetramethylphenol
2,4-dimethylphenol	3-n-propylphenol	2-sec-butylphenol
2,5-dimethylphenol	4-n-propylphenol	2-isopropyl-6-methylphenol
2,6-dimethylphenol	2-ethyl-4-methylphenol	2-isopropylphenol
3,5-dimethylphenol	2-ethyl-5-methylphenol	4-isopropyl-phenol
3,4-dimethylphenol	3-ethyl-6-methylphenol	3-isopropylphenol
2,3,4-trimethylphenol	4-ethyl-2-methylphenol	4-isobutylphenol
2,3,5-trimethylphenol	4-ethyl-3-methylphenol	2-methyl-4-n-propylphenol
2,3,6-trimethylphenol	5-ethyl-3-methylphenol	5-methyl-4-indanol
2,4,6-trimethylphenol	6-ethyl-2-methylphenol	4-indanol

Furthermore GC-MS was used to compare the composition of coal macerals liquefaction extracts. Macerals are to coal what minerals are to rock. These organic substances exhibit particular chemical and physical properties. Coal petrographers separate the macerals into three groups: liptinite, vitrinite, and inertinite [41]. Brodzki *et al.* carried out a very interesting study about the molecular composition of liquids derived from concentrates of each of these groups [27]. While many researches highlight hydrocarbons analysis in macerals using Py-GC-MS which enables the characterization of non-volatiles and intractable macromolecular complexes [8, 42], Brodzski et al focused on dibenzofuran and its alkylated derivatives and showed that they are present in higher content in fractions derived from inertinite than in liptinite or vitrinite extracts. Phenols are also identified in the three fractions but appear to be much less abundant in the inertinite extract. These findings lead to a better understanding of the liquefaction scheme.

To conclude, GC has considerably improved the knowledge of oxygenated compounds in direct coal liquefaction products. However, there remain some limitations considering the complexity of the matrices of interest and the relatively low peak capacity of the technique. Therefore, two-dimensional gas chromatography has extensively been used.

1.4 Applications of Two-dimensional Gas Chromatography to unravel oxygenated structures in DCL

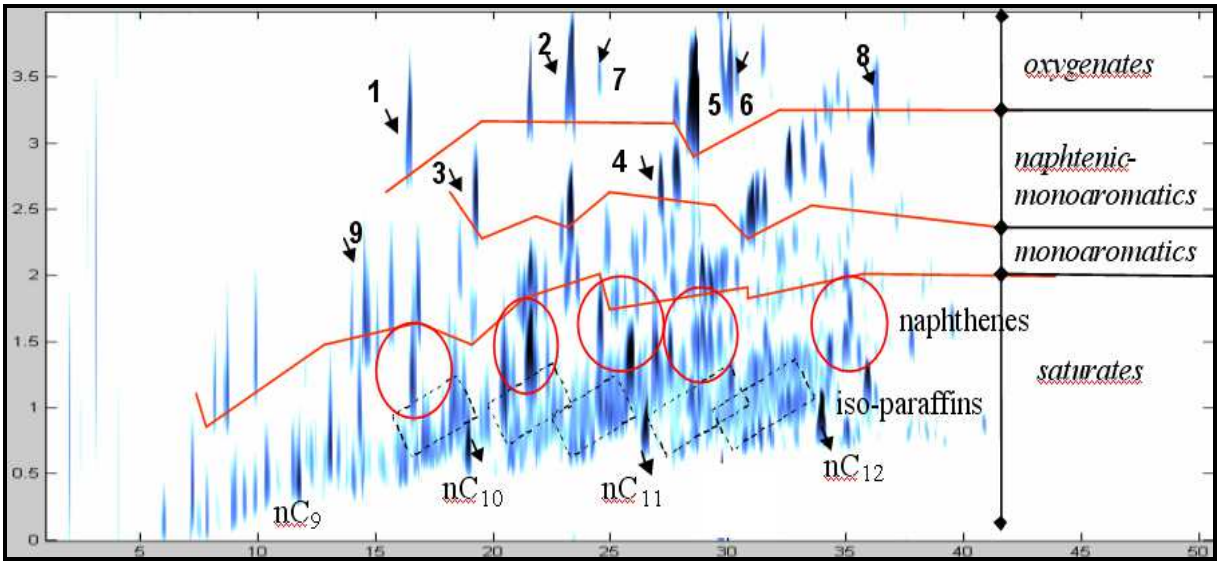
One-dimensional gas chromatography rests on only one separation criterion and is not sufficient if the vapour pressures of many analytes of a mixture are too close [43]. Separation of coeluted species requires the integration of another separation criterion. Hyphenated to a mass spectrometer or flame ionization detector or a specific detector of oxygen, two-dimensional gas chromatography can offer outstanding separations and appears as a very useful tool for the analysis of complex mixtures such as coal-derived products. Even if a few studies used this technique to characterize coal-derived products [44-46], as far as we know, by 2010, only one paper gives information about oxygenated compounds by GC×GC [1].

In fact, Bertoncini *et al.* focused on Direct Coal Liquefaction distillates and carried out two different analyses of oxygenated species by GC×GC-ToF/MS: one applied to the kerosene cut and the other to the atmospheric gas oil cut [1]. For quantification purposes, FID detection was also used. Modulation was carried out using by a thermal nitrogen modulator with a frequency of 50 Hz. Results as well as chromatographic conditions are displayed in Figure 1-4 concerning the kerosene cut. In a nutshell, the analysis of the kerosene cut gives structured chromatograms. As illustrated, elution zones of saturates, mono-aromatics, naphtheno-aromatics and oxygenates are delimited. These works are very successful in the separation of oxygenated compounds from the hydrocarbon matrix. As far as the analysis of the AGO cut is concerned, it enables the identification of 250 oxygenated molecular structures belonging mainly to the two families mentioned before i.e. phenols and benzofurans. These species are however not completely separated from the paraffins, naphthenes and aromatics. The column set on stake was PONA (10mx0.2mmx0.5µm) x BPX-50 (0.8x0.1mmx0.1µm). Moreover, a quantification of hydrocarbons with a classification by group type was carried out for naphtha, kerosene, and AGO cuts. However, quantitative information about oxygenated compounds is given only for the naphtha cut using a one-dimensional PIONA analysis.

Additionally, another study used GC×GC ToF/MS to characterize hydrocracking products. It was lead by Hamilton *et al.* in 2007 [44] and showed a comparative study between GC-MS and GC×GC-ToF/MS. Although one-dimensional results enabled the identification of more than a hundred compounds, the combination of two polarities clearly performs a separation between alkanes and aromatics, but no specific oxygenates zone was highlighted. The combination of HP-5 and DB-17 columns enabled the identification of many hydrocarbons with a good resolution. The use of the selective m/z ratio option allowed the identification of single ion m/z specific families. Apart from aromatic and paraffinic structures, this work highlights the presence of benzonaphtofuran (Figure 1-5). Many hydrogen donors structural isomers were also detected in the recycle solvent. Nevertheless, the maximal reachable mass of 210 units does not give access to heavier molecules highlighted by SEC analyses.

To conclude the use of new coupled techniques such as GC×GC would be of great interest to unravel oxygenated structures contained in these types of matrices. In fact GC×GC overcomes the limits of classical GC in terms of resolution and peak capacity. Recent advances also show the possibility to use an atomic emission detector (AED) coupled to a GC×GC device to improve the understanding of petroleum matrices.

Figure 1-4. GC×GC-FID of a direct coal liquefaction kerosene cut (1:benzofuran, 2: phenol, 3:indane, 4:tetraline, 5,6: diMePhenol, 7:2MeBenzofuran, 8:2,3 diMeBenzofuran) Conditions: PONA (10mx0.2mmx0.5µm) x BPX-50 (0.8x0.1mmx0.1µm) [1]



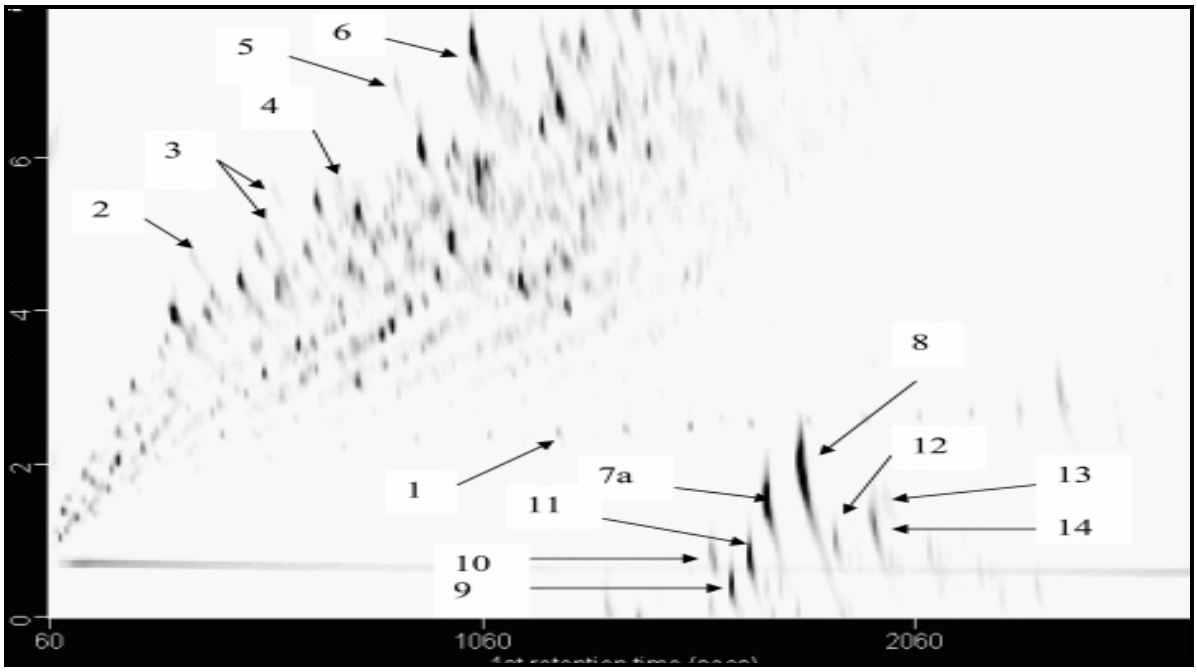


Figure 1-5. Total ion chromatogram obtained by GC/MS analysis of the hydrocracking products obtained with a combination of HP-5 and DB-17 columns: 1, *n*-alkane; 2, naphthalene; 3, methyl naphthalenes; 4, C2 alkyl naphthalenes; 5, acenaphthene; 6, C2 alkyl diphenyls; 7a, dihydropyrene; 8, pyrene; 9, 6H-fluoranthene; 10, 4H-fluoranthene; 11, 6H-fluoranthene; 12, isomer of pyrene and benzonaphthofuran; 13, benzofluorene isomer; et 14, benzofluorene isomer. [44]

1.5 Characterization by Liquid Chromatography

Liquid chromatography may be preparative or analytical. In the first case, its purpose is to separate the analytes from a matrix for further use. Coupled with various detectors, analytical liquid chromatography leads to structural information of the analytes.

1.5.1 Preparative Liquid Chromatography

Preparative Liquid Chromatography is broadly used in the petroleum field where it is referred as SESC (Sequential Elution Solvent Chromatography) [47]. In the petroleum industry a particular case of SESC called SARA (Saturates, Aromatics, Resin, Asphaltenes) is often used to unravel hydrocarbons composition and is mainly applied to vacuum distillates and residual cuts [48-50]. The intent of this analysis is double: on the one hand it gives quantitative information about each of these four classes, on the other hand it results in fractions that can be further subjected to other analytical tools [51].

According to Farcasiu *et al.* [47], SARA can definitely not be applied successfully on coal oils firstly, because some species can irreversibly be adsorbed on the substrates. Thus, other solvents are used for the fractionation of DCLs and enable the separation of oxygenated analytes from the hydrocarbon matrix. Many researchers used SESC to obtain simpler fractions [52] or to isolate target compounds such as phenols and indanols [20, 52]. A detail of the different solvents used in the literature for the fractionation of coal liquefaction products is shown in Table 1-6.

Table 1-6. Solvents used in the literature for the fractionation of DCLs using ion-exchange resins stationary phases. Stressed boxes correspond to fractions having the highest oxygenates content and figures in brackets corresponds to solvents ratios.

Solvent 1	*Solvent 2*	*Solvent 3*	*Solvent 4*	*Solvent 5*	*Solvent 6*	*Solvent 7*	*REF*
Hexane	Hexane-Benzene (8:1)	Benzene-Ether (4:1)	Benzene-Methanol (1:1)	/	/	/	[19, 52]
Hexane	Benzene-Hexane	Benzene-Hexane	Benzene-Acetone-CH_2Cl_2 (3:4:3)	Acetone-THF (1:4)	Methanol	/	[24, 29, 53-55]
Hexane	Toluene	Methanol	/	/	/	/	[56]
Petroleum ether	Petroleum-Ether-Toluene	Toluene	Chloroform	Methanol	/	/	[57]
Hexane	Hexane-Benzene	Chloroform	Chloroform-Et_2O	Et_2O-EtOH	Methanol	Chloroform +EtOH	[11, 47]
Heptane	Benzene-Heptane	Benzene-Heptane	THF-1%EtOH	THF-5%EtOH	THF-10%Water	/	[58]

Seshadri *et al* used Farcasiu's procedure to characterize two DCL distillates. These were obtained from the Ft. Lewis facility (Tacoma, Washington). Eighteen fractions stemmed from a middle distillate (193-288°C) and a heavy distillate (288-482°C) were analyzed. SESC enabled this separation by using nine solvents of increasing polarity. NMR, IR and elemental analysis show that oxygenates are concentrated in three particular fractions containing essentially phenols, indanols, furans, cresols, xylenols, and benzofurans (Table 1-7). The yield ratio of this procedure was high considering that only 0.9 %w/w of the initial product is lost.

Table 1-7. Species identified by NMR and IR in each fraction obtained by SESC and derived from a DCL middle distillate [11]

Fraction and yield	*Middle distillate (O: 3.2%)*	*Heavy distillate (O: 1.42%)*
Fraction 1 (50,6%w/w of the cut)	naphthalenes, alkylnaphthalenes, alkybenzenes, tetralines, indanes, alkanes **(O=0.3%w/w)**	fluorene, acenaphthene **(O= 0.5%w/w)**
Fraction 2 (3.1%w/w of the cut)	diphenyl ethers, biphenyls, diphenyl disulfide **(O=5.8%w/w)**	fluorene, acenaphtene, phenantrenes, aromatic hydrocarbons **(O= 0.3%w/w)**
Fraction 3 (8.7%w/w of the cut)	phenols, indoles, furans, benzofurans, et alkylated benzofurans **(O=9.3%w/w)**	phenolic, pyrolic nitrile, carbazoles **(O= 3.7%w/w)**
Fraction 4 (23.7%w/w of the cut)	phenolics: butphenol (17%), cresols (32%), xylenol (30%), EtPhenol (13%) **(O=10.6%w/w)**	hydroxypyridines, hydroxypquinoline, naphtols, 9-phenantrol **(O= 5.5%w/w)**
Fraction 5 (2.4%w/w of the cut)	phenolic, nitrogen compounds, Hydroxy Nitrogen compounds **(O=80.7%w/w)**	unknown **(O=4.4%w/w)**

Caramao et al, 2004 also used a preparative scale liquid chromatography and carried out an identification and quantification of phenolic compounds in coal tar from Brazil. The stationary phase was Amberlyst A-27(TM) ion-exchange resin and the fractions acquired were classified into acidic and non-acidic. GC-MS was then used to analyse the acidic fraction where nearly twenty-five phenols were identified and nine of them quantified.

To conclude, Sequential Elution by Solvent Chromatography can offer a great simplification of these complex matrices. The separation of a fraction containing most of oxygenates is very attractive, and the use of this technique to isolate an acidic fraction is also a good way to separate phenols. However, SESC involves information loss, and lower yield ratios. Moreover, this procedure is sample-consuming and takes more than 6 hours to be carried out. Consequently this preparative technique must be avoided if the sample and the separation technique allow it. Nevertheless, in some cases where the matrices are highly complex this preparative step remains unavoidable.

1.5.2 High Performance Liquid Chromatography

Normal (NP) and Reversed Phase (RP) High Performance Liquid Chromatography (HPLC) have been widely used to analyze Poly Cyclic-Aromatic hydrocarbons (PAHs) in coal-derived liquids or fossil-fuel. Usually, silica particles with chemically linked surface groups are used as column packing [9, 59]. The use of small particle sizes enhances the separation efficiency and the many

possible interactions between the stationary and the mobile phases result in structure-selective separations [60].

Oxygenated Poly-Aromatic Hydrocarbons OPAHs have also been investigated on coal tar creosote. This product is an oily, water-insoluble mixture from coal tar components. Meyer and co-workers separated an acidic fraction by SPE (Solid Phase Extraction) using a strong acidic exchange material. This fraction was analyzed by NP HPLC-DAD (Diodes Array Detector). The team validated a method for 22 hetero-PAHs and revealed the presence of benzo and benzonaphto-furans [17].

RP HPLC has also been used to separate and identify phenolic compounds in coal oils. Erdmann *et al.*, applied this technique to two Illinois No. 6 coal-derived liquids in 1996 and completed the analysis by an NMR study (see next paragraph) [61]. These works resulted in a better knowledge of phenolic compounds in coal oils and quantitative data are mentioned. In fact, phenols content was estimated by using response factors calculated from the chromatograms for standard solution of individual phenols. When many phenols were attributed to one single peak, an average of the different response factors was calculated. Aside from oxygenated species usually identified, thymol and carvacrol were detected by UV. The pros and the cons of a UV detection compared to a fluorescence detection for the identification of phenols in DCLs are elsewhere discussed by Ogan and coworkers [62]. This study demonstrates that fluorescence detection for phenolic compounds gives better sensitivity and selectivity than UV at 274 or 254 nm with 2-12 times better signal-to-noise. This is verified in Figure 1-6 which shows results obtained with each of the detectors and reveals the presence of phenols and cresols. 3,4-xylenol (eluted at 27min in the UV chromatogram) was also detected by UV but not by fluorescence, whereas 3,4,5-trimethylphenol was identified in both chromatograms (eluted at 37 min). A simple qualitative look at the chromatograms shows that more compounds are detected using UV detection.

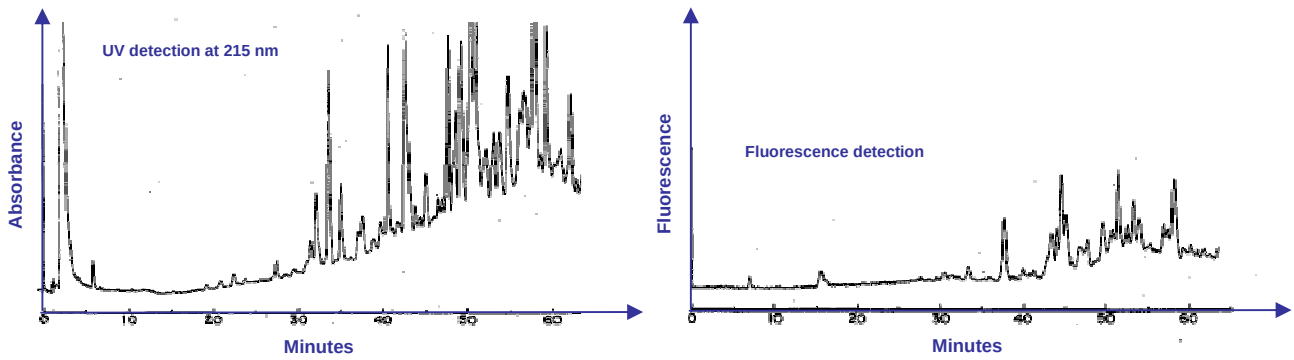


Figure 1-6. Reversed-phase chromatograms DCL product: UV detection at 215 nm was used for the left chromatogram and fluorescence detection (Ex = 274 nm, Em = 298 nm) for the right chromatogram [64].

Furthermore aluminium oxide activity was tested to separate phenols in coal oils and solids [63, 64]. Silver *et al.* studied the benefits of this phase compared to silica gel for the separation of phenols [63, 65]. They showed that most phenolic compounds strip on aluminium oxide chromatoplates, and that they are decomposed in the aluminium oxide column. Subsequently this technique was judged as unhelpful by the team. A summary of all HPLC analysis applied to Coal-derived materials is displayed on Table 1-8.

Table 1-8. A review of HPLC applications on Coal-derived oils

Column	***Mobile phase***	***Detection***	***Analytes***	***Ref***
Hypersil ODS (RP)	Acetonitril, Methanol, THF	Multiple wavelenght UV detector (215 and 274 nm)	Phenolic compounds	[61]
Zorbax SIL (RP)	Acetonitrile-water	UV (215 and 274nm) and fluorescence	Phenols, Xylenols	[62]
µ- Bondapak C18	HexaneToluene (96:4) Chloroform Chloroform: Ether (90:1)	UV (276 to 345 nm)and fluorescence	Phenols and alkylated derivatives	[65]
µ- Bondapak C18 (RP)	Methanol:water 65:35	UV (254 nm)	Alkylphenols	[66]
µ- Bondapak NH2 (NP)	Heptane-isoprpyl alcohol 99:1	UV (254 nm)	Alkylphenols	[66]
µ- Bondapak CN (RP)	n-Heptane	UV (254 nm)	Alkylphenols	[66]
µ- Porasil (NP)	Heptane-chloroform 90:10	UV (254 nm)	Alkylphenols	[66]
µ- Bondapak CN (RP)	Methanol:Water 50:50	UV (254 nm)	Alkylphenols	[66]
Zorbax NH2	n-Hexane, Chloroform	FIMS and EIMS	Hydrocarbons and polar compounds	[33]
Nucleosil 100-5 C18-HD	Trifluoroacetic acid and methanol mixtures	DAD (Diode Array Detection)	O-PAH	[67]

1.6 Selective analysis of phenols and alcohols by NMR spectroscopy

^{1}H, ^{13}C, and ^{31}P NMR have been extensively used these last two decades for the analysis of coal-derived products. These techniques can be helpful for qualitative as well as for quantification purposes on chemical functional groups. Many researches contributed to the progress made in coal-derived liquids hydrocarbons characterization by ^{1}H and ^{13}C NMR [11, 47, 56, 68-78]. As far as oxygenated compounds are concerned, only a few works mention the use of these techniques [11]. Nevertheless, a series of articles published by Verkade and co-workers focus on the specific characterisation of labile H functionalities in coal materials, in particular on speciation and quantification of phenolic compounds contained in CLs. This goal is achieved by derivatizing selectively phenolic compounds by using phosphorus-containing reagents and by analyzing the products by ^{31}P NMR [47, 61, 75-84]. This analysis is not time-consuming (105 minutes without derivation), amenable for a large range of solvents, and very selective towards the OH functional group. In fact polyalkylated phenols, carboxylic acids, alcohols, amines and thiols can be selectively identified. This technique is particularly interesting considering that by direct analysis, the use of ^{17}O nuclei involves noisy spectra, although certain absorption areas were well-separated [85]. Detection of these nuclei is difficult because of their low natural abundance, quadrupolar nature, and low receptivity.

Among all different tested reagents (Figure 1-7), the potential of molecules **1** [79-81] and **2** [80, 81, 86] has been highlighted. From now on, recent studies favour reagent **2** [61, 84].

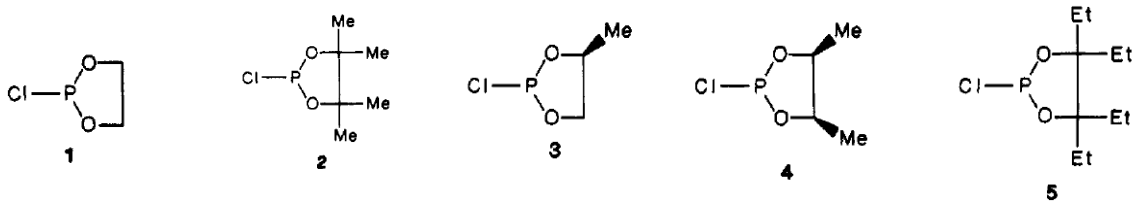


Figure 1-7. Different reagents used for the analysis of phenolic compounds in coal-derived products

Results obtained by using this method have been compared to RP HPLC spectra. With the exception of a few components, analyses are consistent. The total concentration of phenolic compounds has also been determined but it should be kept in mind that the phenol derivation ratio is 95%. Another comparison has been done in an earlier article and showed good agreement between ^{31}P NMR and FTIR [84].

To conclude ^{31}P NMR preceded by a derivation step enables selective analysis of phenols mixtures in hydrocarbon matrices such as direct coal derived liquids despite their relatively low concentration and the presence of free radicals which cause interferences. Moreover, this technique is very interesting because it is adapted to most types of solvents except those containing labile protons functional groups.

1.7 Characterization of oxygenated compounds by FT-ICR/MS

Compared to other mass spectrometry techniques, Fourier Transform Ion Cyclotron Resonance Mass Spectrometry (FT-ICR/MS) offers a 10–100 times higher mass resolving power [87]. This technique has allowed pursued characterization of petroleum crude oil, in particular the identification of heteroatom-containing elements. This application field also referred as "Petroleomics" by Marshall *et al.*, 2004 has recently been extended to coal liquefaction products [88]. In 2003, the first analysis of coal oil by ESI (ElectroSpray Ionosation) -FT-ICR/MS allowed full compositional characterization of two pyridine extracts derived from Illinois No. 6 and Pocahontas No. 3 coals [89]. This technique is strongly dependant on the ionization method. The Electrospray Ionization makes the ionization of polar heteroatom species selective and the detection of oxygenated species possible. Subsequently, thousands of different molecules were identified and sorted into compound classes (number of various heteroatoms), type (double bonds and rings) and alkylation degree. A suitable graphical tool for managing all this information is in the form of a Kendrick mass defect vs. Kendrick mass (Figure 1-8). One year later, the same author focused on acidic species in Illinois No.6 Direct Coal Liquid. This product was fractioned into an hexane-soluble (*hs*) and an hexane-insoluble (*hi*) fraction and each of these fractions was compared to the pyridine extract [88]. 5,000 compounds were identified in *hs* (coal acids with relatively low aromaticity), 10,000 in the *hi* (acidic asphaltenes with relatively high aromaticity) and 10,000 in the pyridine extract. To come to an end Wu *et. al* made use of the same technique to compare the composition of a heavy fraction (residue) and a lighter fraction (Still OverHead) [90]. This study showed that the resid fraction contains much more compounds than the liquid one what can be illustrated by the two Kendrick diagrams (Figure 1-9). Furthermore, the heavy distillate had a higher aromatic content and a wider methyl group distribution.

Ponthus *et al.* focused on applications of FT-ICR/MS to coal-derived liquids. Oxygen containing compounds were analyzed with ESI- (Negative ElectroSpray Ionisation) and ASAP-

(Negative Atmospheric Solids Analysis Probe). Negative ionisation was used because it facilitates the identification of acidic heteroatomic species. Using ESI – ions distribution range from m/z=180 to m/z=680 (Figure 1-10). The mass spectrum is complex: millions of ions were detected and the Kendrick diagram shows numerous families. ASAP – mass spectra is similar to the one obtained by ESI – but contains less compounds. It favours the identification of acidic heteroatomic compounds (diluted with a 0.01% ratio in a Toluene/Methanol mixture). High intensities ions distribution ranges from m/z=160 to m/z=420.

This study gave breakthrough results as it enabled the identification of hundreds of oxygenates. Other ionization modes led chemical formulas of many nitrogenates, naphthenes and polyaromatics: ESI +, ASAP+, APPI- and APPI + (negative and positive Atmospheric Pressure PhotoIonization).

To conclude, this analytical technique has the advantage to ionize only basic species to produce positive ions or acid species to produce negative ions. Thus, hydrocarbons, thiophenes, and other neutral species are inaccessible whereas the presence of polar heteroatomic compounds is emphasized. Coupled with a chromatographic system, FT-ICR/MS[91] can lead to outstanding results and the potential of this technique should be seen as a perspective for unravelling the composition of these matrices. However this technique is not quantitative considering the complexity of the matrix.

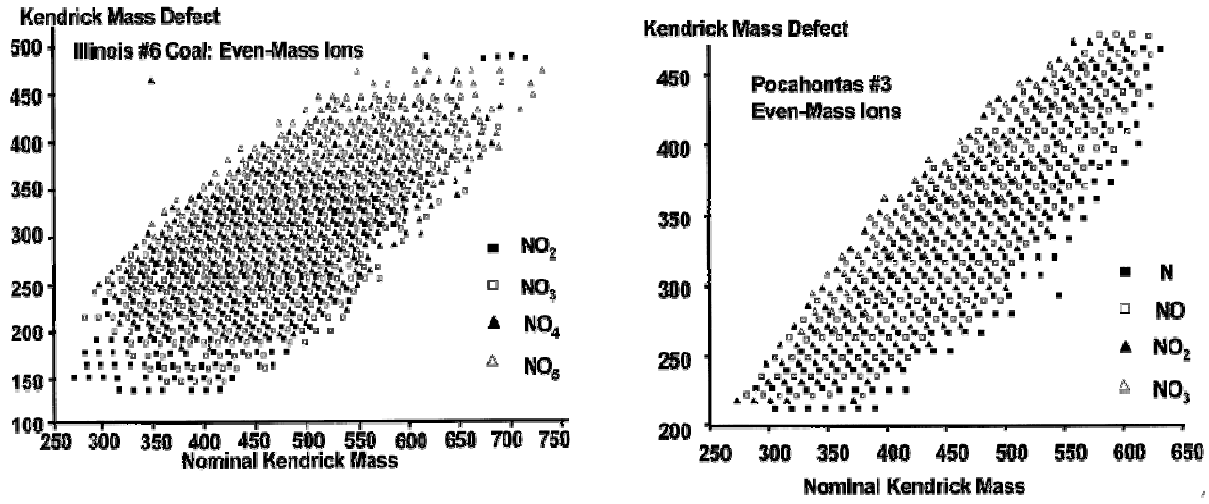


Figure 1-8. Kendrick diagrams of ESI-FT-ICR/MS spectra for even-mass ions (Pocahontas #3 on the right and Illinois #6 on the left) [92]

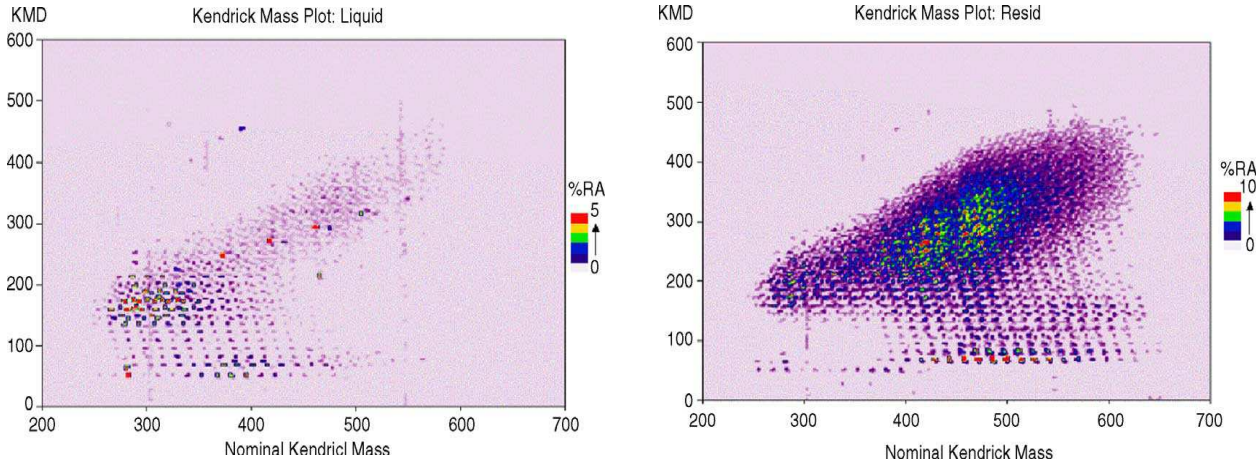


Figure 1-9. Kendrick diagrams of ESI-FT-ICR/MS spectra (Resid on the right and SOH on the left) [90]

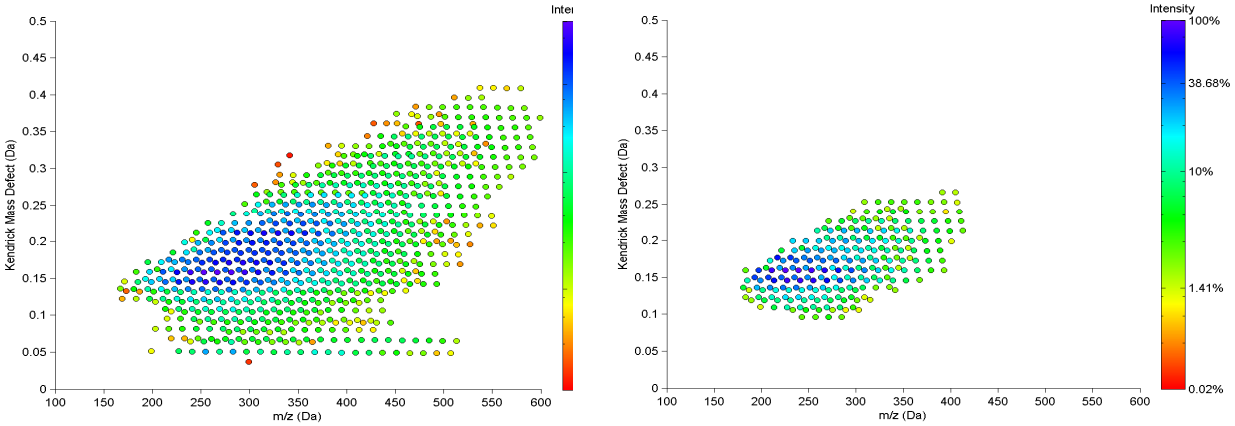


Figure 1-10. Kendrick diagrams obtained by FT-ICR/MS with ESI - (left) and ASAP - (right) 96

1.8 Conclusion

Many analytical strategies improved the knowledge of oxygenated compounds in coal-derived products (Table 1-9). Two classes of oxygen-containing species are emphasized in researches: phenols and furans. Even if pursued techniques enabled to approach the compositions of these two families, many gaps remain and quantifications are quite often inexistent. Strategies involving sample preparations or multi-coupled systems have been deployed to respond to the matrix complexity, but the separation of oxygenates from hydrocarbons remains a hard task. A panel of sophisticated techniques must be considered to unravel the oxygenated structures. Among these techniques, multidimensional chromatographic techniques and FT-ICR/MS proved to be very effective for similar matrices and offers bright perspectives. The state-of-art of all researches aiming to identify and quantify oxygenates in these matrices is a springboard leading to many experimental slopes.

Two-dimensional gas chromatography seems judicious for the characterization of a coal-derived middle distillate as it offers high selectivity, peak capacity and as a consequence high resolution. It has been used for hydrocarbons characterization but should be investigated to answer oxygen speciation issue. For lighter distillate GC/MS or GC-GC may be sufficient. Concerning FT-ICR/MS, it is interesting as it enables to support the characterization that can be obtained by chromatographic methods. To finish, ^{31}P NMR studies are of great interest for the characterization of species containing hydroxyl groups.

Table 1-9. Synthesis of applications of analytical tools to unravel the oxygenated compounds present in coal liquefaction products

O-species in CLs	*GC*	*LC*	*NMR ^{31}P*	*FT-ICR/MS*
Phenols	**X**	**X**	**X**	**X**
Furans	**X**	**X**		
Other O-species	**X**			**X**

CHAPTER 2. Investigating GC×GC to optimize the separation of oxygenated compounds in a Direct Coal Liquefaction middle distillate [3]

FOREWORD

The state-of-the-art presented in chapter 1 shows that coal-derived liquid characteristics are very different from those of petroleum fuel. They are indeed mainly composed of naphthenes, aromatics, naphtheno-aromatic structures, and heteroatomic compounds (Nitrogen and Oxygen), with a low paraffin content. Identification and quantification of oxygen-containing species in coal-derived liquids is of considerable importance to understand their behaviours 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.

As concluded in the previous chapter, comprehensive two-dimensional gas chromatography high resolution offers bright perspectives for oxygen speciation in coal-derived middle distillates. It has been investigated in this chapter to provide enhanced molecular characterization of these complex samples. Several different configurations involving innovative columns configurations were tested. Each of them was optimized by testing different columns 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 (PEG SolGel-WAX x PDMS DB-1) enabled an outstanding separation of paraffins, naphthenes, monoaromatics, diaromatics and targeted O-compounds in a direct coal liquefaction middle distillate. It was therefore subjected to further experiments using a time-of-flight mass spectrometer to validate the identification and unravel more than fifty oxygenated molecular structures. Group-type quantification was also established for four columns arrangements and gives the distribution of paraffins, naphthenes and aromatics. It can be concluded from this study that a reversed column combination involving a highly polar column in the first dimension was the most adapted one.

[3] This chapter is based on an article published in Journal of Chromatography A, 2011 (218) p 3233-3240 by Omais *et al.*

2.1 Introduction

The need to diversify energy sources in the transportation field has sparked great interest in direct coal liquefaction products. Before processing, these liquids properties and compositions are far from fuel specifications and upgrading must be applied to the gasoline and atmospheric gas oil cuts. In fact, they consist mainly of aromatic hydrocarbons, cyclic alkanes (naphthenes), and heteroatomic compounds especially oxygenated species [1, 5-8]. To consider their co-refining with petroleum cuts, it is crucial to study their chemical and physical properties. Apart from the hydrocarbons, the requirements in terms of molecular characterization improvement concern oxygenated compounds which belong to many different chemical families and are present in relatively high concentrations before hydrodeoxygenation (HDO).

Chapter 1 showed that gas chromatography has been broadly used for the characterization of coal oils [93]. GC-AED has been of great interest to reach a selective identification of oxygenates in these unconventional charges [10, 16, 17, 25, 30, 32, 94]. A mass spectrometer was also used as a detector to come up to this problematic [18, 22, 26, 27, 41]. 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 [53, 55, 56, 61] as well as ^{31}P NMR which permitted a selective identification of compounds containing a OH functional group (especially phenols) [61, 79-81, 86, 95]. Phenols can also be isolated by liquid chromatography [96, 97].

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 [98, 99]. GC x GC has been broadly used for the analysis of hydrocarbons in petroleum middle distillates using FID and ToF/MS detectors [99], and in lignin combustion gases using ToF/MS detection [44]. For this purpose, a non-polar x 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 detector.

Despite the fact that its application on coal oils never concerned O-species, many other 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 [2, 100]; biodiesels containing methylic fatty esters [101-103], and modified petroleum containing alcohols [104, 105].

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 is found for oxygenated species characterization. There is however important past chromatography research that accounts for the polar components in coal liquids middle distillates.

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

2.2 Experimental

2.2.1 Samples

2.2.1.1 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 11 oxygenates were mixed into a standard mixture SM (Table 2-1).

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: 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, naphthol, 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 solubilized in ethyl acetate and SM consist of 1/6 of A, 1/6 of P, 1/6 of O and 1/2 of ethyl acetate.

Table 2-1. Compounds contained in the test sample

N°	*Compounds*	*N°*	*Compounds*	*N°*	*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**	Benzofuran
9	nC22	**21**	Biphenyl	**33**	Dibenzofuran
10	nC24	**22**	Phenanthrene	**34**	Naphtol
11	nC25	**23**	Ethylanthracene	**35**	Fluorenol
12	nC26	**24**	Fluorene		

2.2.1.2 Real sample: Direct-Coal liquefaction product

The coal-derived oil used was provided by IFP New energy. It consists on 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).

2.2.2 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 (0.3µL) 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 normal and reversed column configurations. All of them are referred in Table 2-2 as well as investigated modulation periods.

Table 2-2. Experimental conditions

^{1}D column	***Dimensions***	***^{2}D column dimension***	***Dimensions***	***Modulation periods (s)***
Solgelwax	(30mx0.25mmx0.25µm)	DB-1	(1.1mx0.1mmx0.1µm)	10, 12, 15, and 20
Solgelwax	(30mx0.25mmx0.25µm)	DB-5	(1.1mx0.1mmx0.1µm)	12, and 15
SLB IL-100	(30mx0.25mmx0.2µm)	DB-1	(1.0mx0.1mmx0.1µm)	12 and 20
BPX-90	(30mx0.25mmx0.25µm)	DB-1	(0.8mx0.1mmx0.1µm)	12, and 15
DB-17	(30mx0.25mmx0.25µm)	DB-1	(1.0mx0.1mmx0.1µm)	12
DB-17	(30mx0.25mmx0.25µm)	Solgelwax	(1.0mx0.1mmx0.1µm)	12
DB-1	(30mx0.32mmx0.1µm)	Solgelwax	(1.0mx0.1mmx0.1µm)	10
DB-1	(30mx0.32mmx0.1µm)	SLB IL-100	(1.0mx0.25mmx0.2µm)	10 and 20
PONA	(30mx0.2mmx0.5µm)	Solgelwax	(1.0mx0.1mmx0.1µm)	12

2.2.3 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 70ev and a multiplate voltage of -1450V was used.

2.2.4 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 time's 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.

2.2.5 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 [106], the peak distortion by the means of the 2D asymmetry formulae [107], and space occupation will be represented thanks to orthogonality formulas [108-110].

2.2.5.1 2D resolution

A common method developed by Giddings *et al.* [106] 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 ^{1}Rs and ^{2}Rs as respectively the resolution in the first and second dimension can be written down (Equation 2-1):

$$Rs_{2D} = \sqrt{{}^1Rs^2 + {}^2Rs^2} \qquad \textbf{Equation 2-1}$$

In a developed form Rs_{2D} can be expressed as in Equation 2-2 [106], 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.

$$Rs_{2D} = \sqrt{\frac{2(\Delta^1 tr)^2}{({}^1\omega_A + {}^1\omega_B)^2} + \frac{2(\Delta^2 tr)^2}{({}^2\omega_A + {}^2\omega_B)^2}} \qquad \textbf{Equation 2-2}$$

For more transparency these values are illustrated in Figure 2-1.

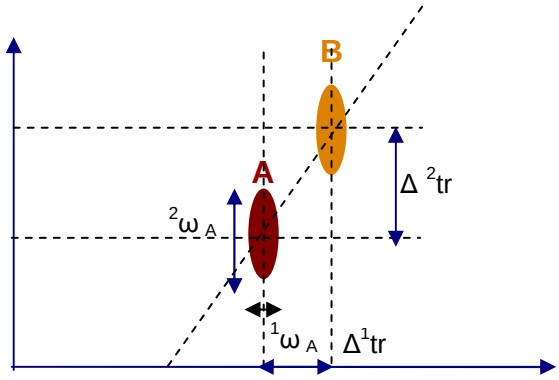


Figure 2-1. Scheme showing variables referred in the two-dimensional peak resolution formulae

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 work, to approach the propensity 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).

2.2.5.2 2D space occupation

Throughout this chapter, 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 in a reversed mode, the term "space occupation" will rather be used. Chapter 8 provides a discussion on these terms.

The first graphical expression consists on 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 [108].

A unique new concept of chromatographic space occupation is introduced in this chapter. It consists in determining the space occupations in the first and second dimensions through two dimensionless numbers ^{1}SO and ^{2}SO. These two variables are defined in equations 2-3 and 2-4 where $^{1}tr_n$ and $^{2}tr_n$ are the retention times of the last compound eluted respectively in the first and second dimensions, $^{1}tr_1$ and $^{2}tr_1$ 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:

$$^{1}SO = \frac{(^{1}\mathrm{tr_n} - ^{1}\mathrm{tr_1})}{\mathrm{T_{analysis}}} \qquad \textbf{Equation 2-3}$$

$$^{2}SO = \frac{(^{2}\mathrm{tr_n} - ^{2}\mathrm{tr_1})}{P_{Mod}} \qquad \textbf{Equation 2-4}$$

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

$$SO_{2D} = \sqrt{\frac{(^{1}\mathrm{tr_n} - ^{1}\mathrm{tr_1})^{2}}{2\mathrm{T_{analysis}}^{2}} + \frac{(^{2}\mathrm{tr_n} - ^{2}\mathrm{tr_1})^{2}}{2P_{Mod}^{2}}} \qquad \textbf{Equation 2-5}$$

2.3 Results and discussion

2.3.1 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, normal and reversed configurations will be exposed.

2.3.1.1 Non-polar × Polar configurations

Two orthogonal columns configurations have first been investigated. The first one consisted in coupling DB-1 (15mx0.32mmx0.1µm) column with an ionic liquid column SLB-IL 100 (1mx0.25mmx0.2µm). 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 seconds a clear separation has not been reachable.

Thus, a more conventional configuration has been tested. It consisted in coupling a PONA (30mx0.2mmx0.5µm) with a Solgelwax (0.8mx0.1mmx0.1µm). This configuration using conditions presented in part 2 led to a good separation. In fact hydrocarbons have been separated and different group types have been identified using the test mixture presented in part 2. As shown in Figure 2-2, paraffins, naphthenes, mono, di, and tri-aromatics have been separated. The elution zones are consistent with those generally obtained in petroleum samples [99]. 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 columns 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.

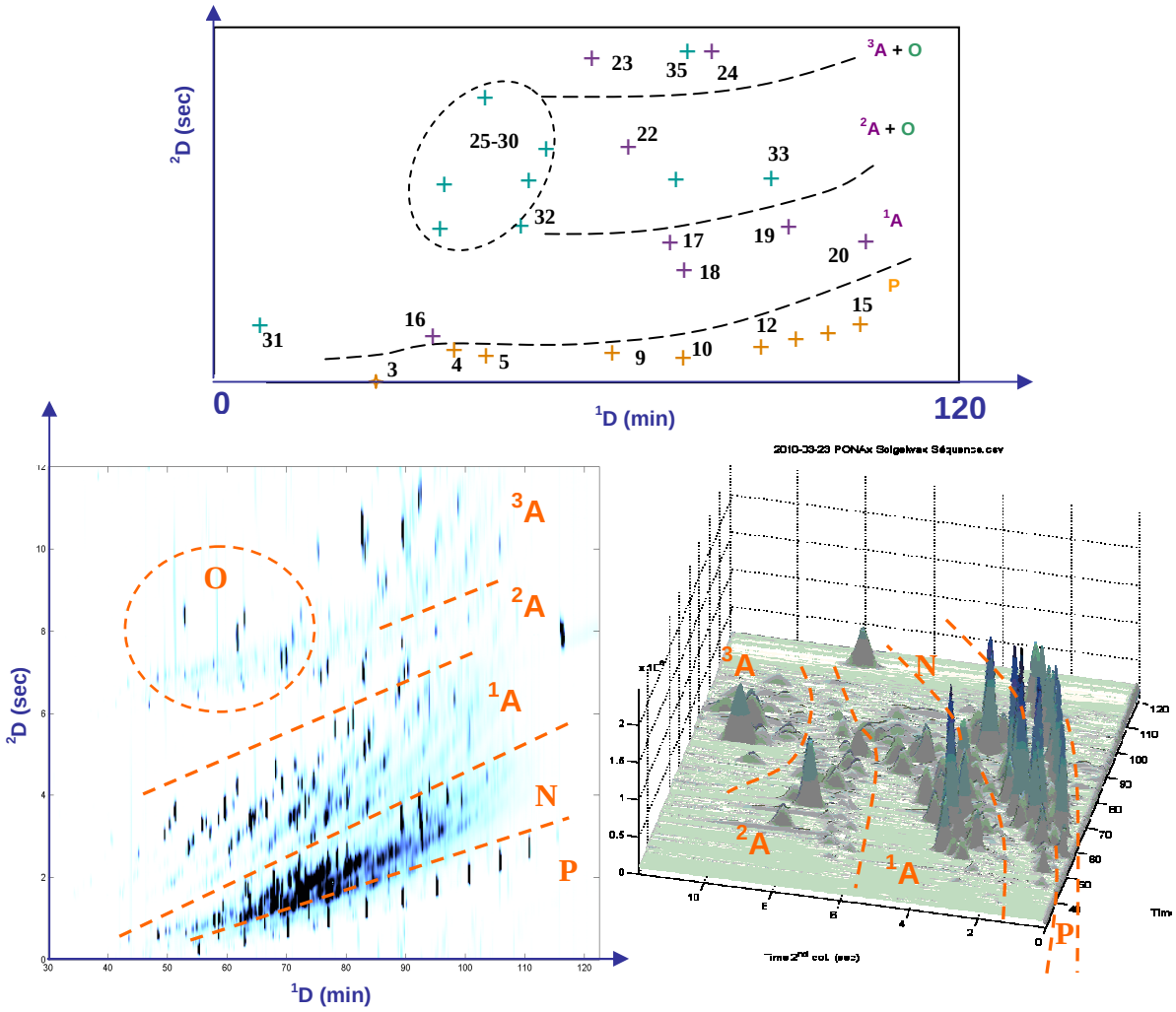


Figure 2-2. 2D contour plot of SM, numbers refer to table 2 (top); 2D contour plot (left), and 3D contour plot (right) of a direct coal liquefaction middle distillate using orthogonal conditions: PONA (30x0.2x0.5) x Solgelwax (0.8x0.1x0.1) with a scale ranging from 30 to 126. P

2.3.1.2 Polar × non-polar configurations

Four reversed configurations have then been investigated. This columns configuration has the advantage to extend the occupation space [111]. It has been used to unravel many oxygenated structures in biodiesels [103] or in Fischer-Tropsch products [100]. An ionic liquid column SLB-IL 100 (30mx0.2mmx0.2µm) has been set up in the first dimension coupled with a DB-1 (1mx0.1mx0.1µm). 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 (30mx0.25mmx0.25µm) coupled with a DB-1 (1.5mx0.1mmx0.1µm). Operating conditions are described in part 2. The 2D contour plot has a very high interfamily resolution and paraffins are well separated (Figure 2-3). However no distinction is possible between mono, and di-aromatics and oxygenated species elute in the same zone as hydrocarbons. A more polar first dimension is thus necessary to improve the separation.

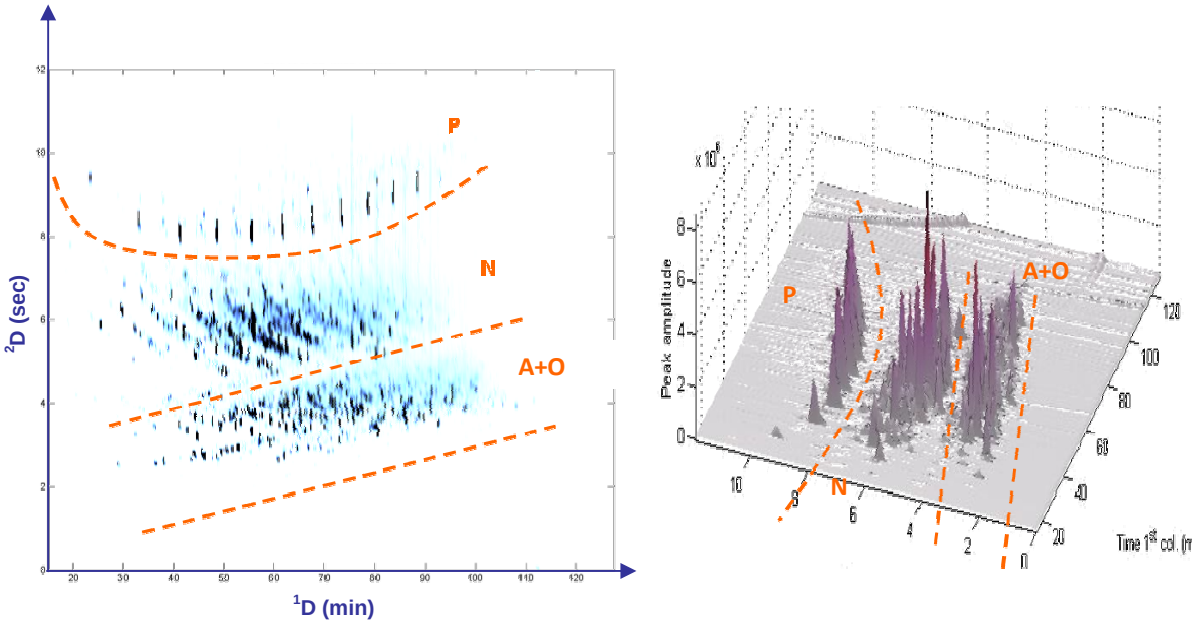


Figure 2-3. 2D contour plot (left), and 3D contour plot (right) of a direct coal liquefaction middle distillate (200-350°C) using reversed conditions: DB-17 (30x0.25x0.25) x DB-1 (1.5x0.1x0.1) with a scale ranging from 15 to 126 min. P: Paraffins; N: Naphthenes; A+O: Aromatics + Oxygenates

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 (Figure 2-4, Figure 2-5, and Figure 2-6). In fact Solgelwax (30mx0.25mmx0.25µm) coupled with a DB-1 (1mx0.1mmx0.1µm) 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 dimension 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.

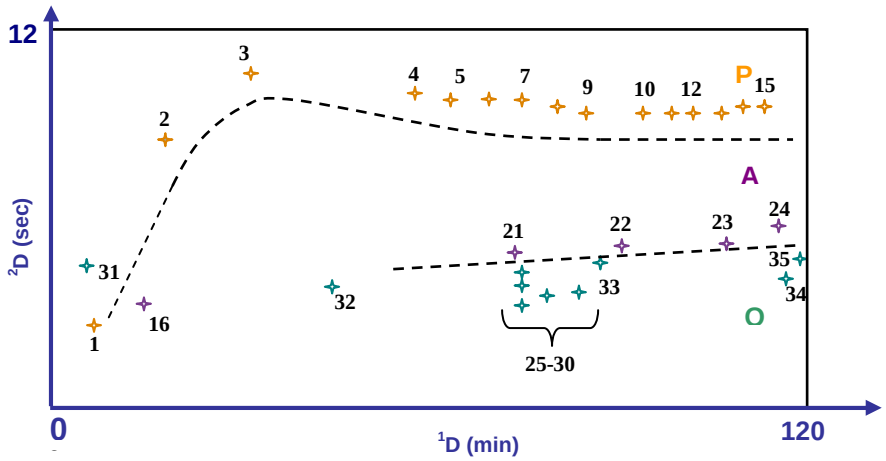


Figure 2-4. 2D contour plot of SM, numbers refer to table 2. Conditions Solgelwax x DB-1

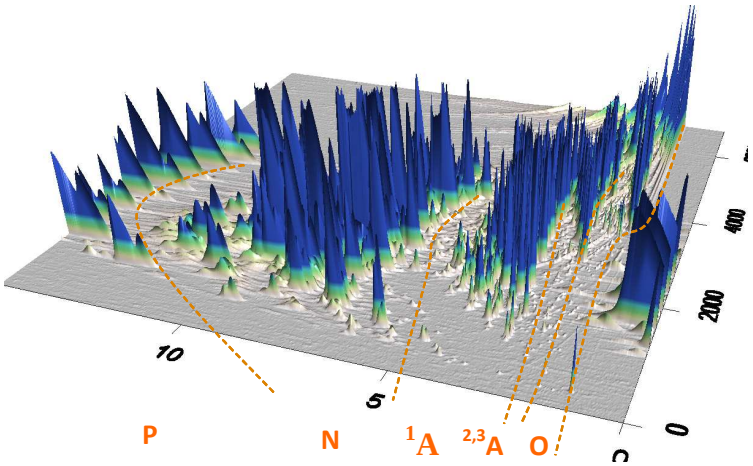


Figure 2-5. 3D plot of a coal-derived middle distillate using GC×GC. Configuration: Solgelwax x DB-1. P: Paraffins; N: Naphthenes; ^{1}A: Mono-aromatics; ^{2}A: Di-Aromatics, ^{3}A: Tri-aromatics, O: Oxygenated compounds

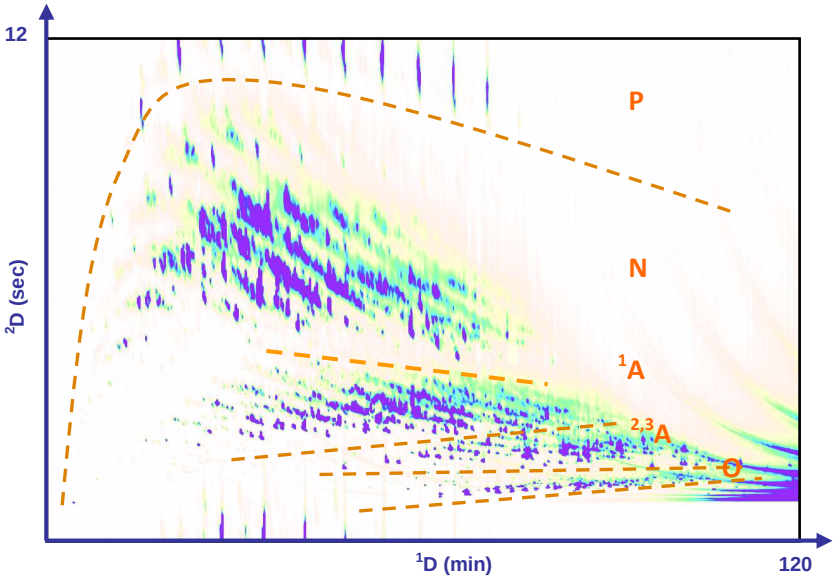


Figure 2-6. 2D contour plot of a coal-derived liquid using GC×GC. Configuration: Solgelwax x DB-1. P: Paraffins; N: Naphthenes; ^{1}A: Mono-aromatics; ^{2}A: Di-Aromatics, ^{3}A: Tri-aromatics, O: Oxygenated compounds

2.3.2 Selection of the most adapted configuration

2.3.2.1 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 Figure 2-7. They show that n-paraffins separation is resolutive for the four cases. However, to separate dibenzofuran and fluorene, DB-17 x Solgelwax and DB-1 x DB-17 configurations are not adapted. As far as 2D space occupation is concerned, both Ryan criterion and our equation show that PONA x Solgelwax and Solgelwax x DB-1 are the most interesting configurations (Figure 2-8). Results obtained using equation 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 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 are 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 our 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.

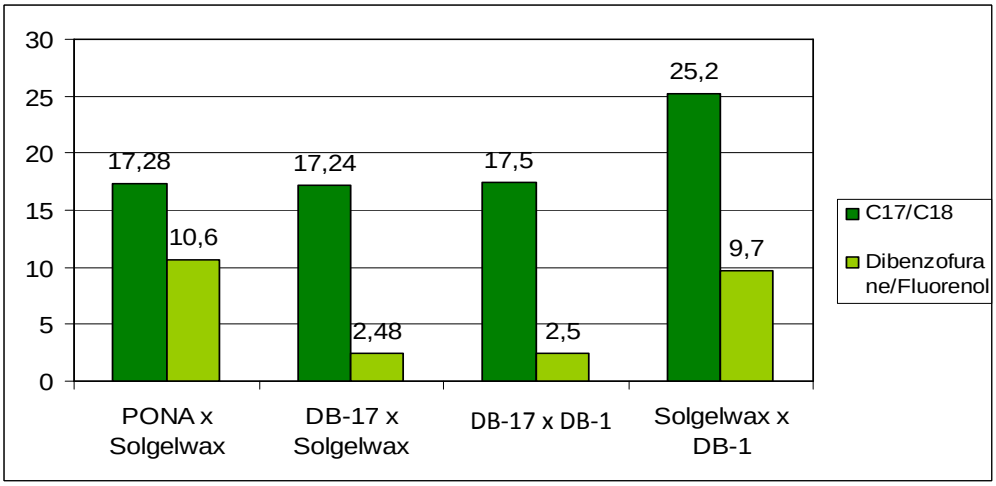


Figure 2-7. Resolutions between two paraffins and between fluorene and dibenzofuran for four columns configurations: PONA x Solgelwax, DB-17 x Solgelwax, DB-17 x DB-1, Solgelwax x DB-1

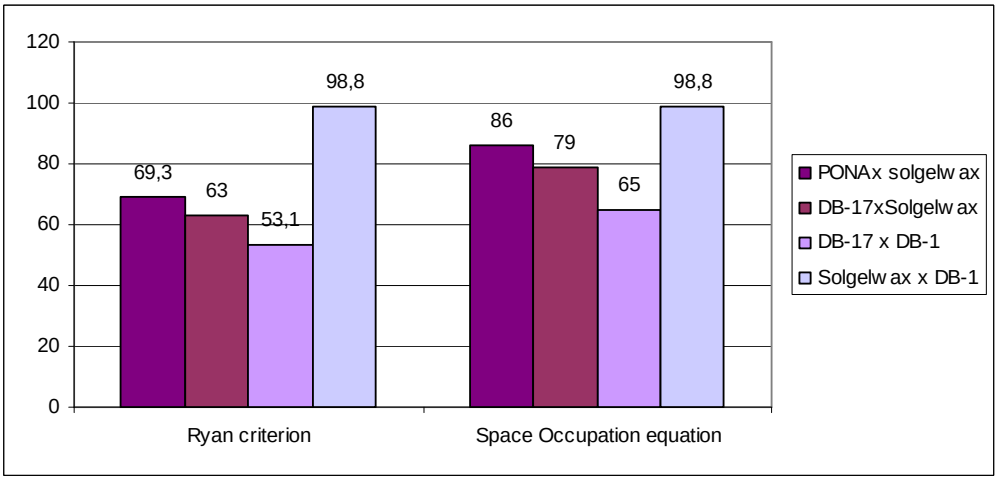


Figure 2-8. 2D space occupation using Ryan criterion and the 2D space occupation formula for four columns configurations: PONA x Solgelwax, DB-17 x Solgelwax, DB-17 x DB-1, Solgelwax x DB-1

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 dibenzofuran and fluorenol. The values are reported in Table 2-3. DB-17 x Solgelwax and DB-17 x DB-1 configurations have low selection criteria whereas PONA x Solgelwax and Solgelwax x DB-1 ones are more than four times higher. In definitive Solgelwax x DB-1 configuration was selected as it shows the best product between space occupation and resolution.

Table 2-3. Selection criteria for each columns configuration

Columns configurations	***Selection criteria***
PONA x Solgelwax	823.1
DB-17 x Solgelwax	176.1
DB-17 x DB-1	147.5
Solgelwax x DB-1	985.4

2.3.2.2 Semi-quantification

As some of the configurations do not allow the separation of oxygenates from aromatics, a general family semi-quantification has been established (Figure 2-9). 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 and aromatics and naphtheno-aromatics are also of high concentration. Concerning paraffins, they are of low content comparing to petroleum atmospheric 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 (See chapters 3 and 4).

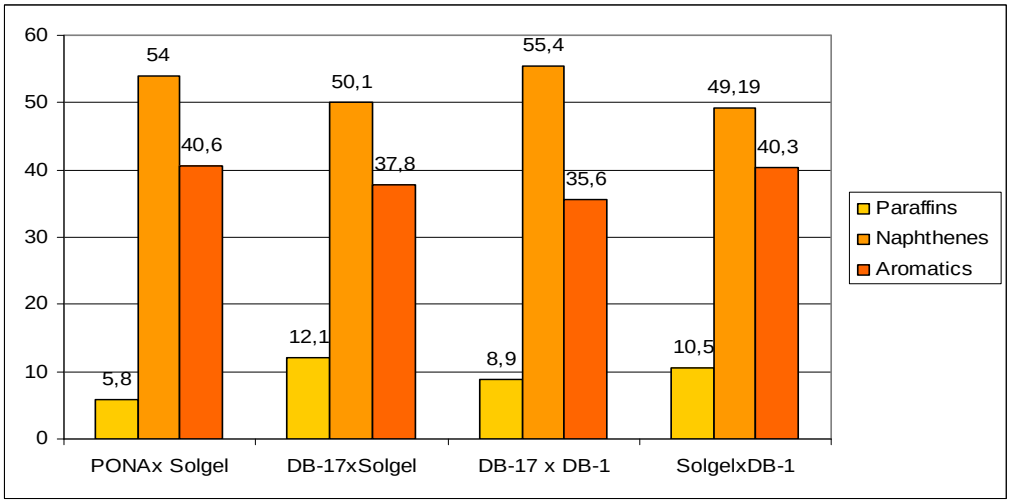


Figure 2-9. Group type quantification in a coal-derived product for four column configurations: PONA x Solgelwax, DB-17 x Solgelwax, DB-17 x DB-1, Solgelwax x DB-1

2.3.3 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 x DB-1) and a Time-of-flight Mass Spectrometer (Figure 2-10). 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 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 2-4) 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 [16-18] and GC-MS [1] while other compounds belonging to ketones (naphthalenons, furanone) and alcohols (benzenediols resorcinol) has been identified for the first time in these matrices. Nitrogenated compounds can also be found in oxygenates area but this does not compromise their identification.

The selected column set is adapted to oxygen speciation in such matrices but also gives access to nitrogenates and hydrocarbons 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 rings (pyrene). As far as nitrogenates are concerned, they mainly consist in anilines, quinolines, indoles, and nitriles.

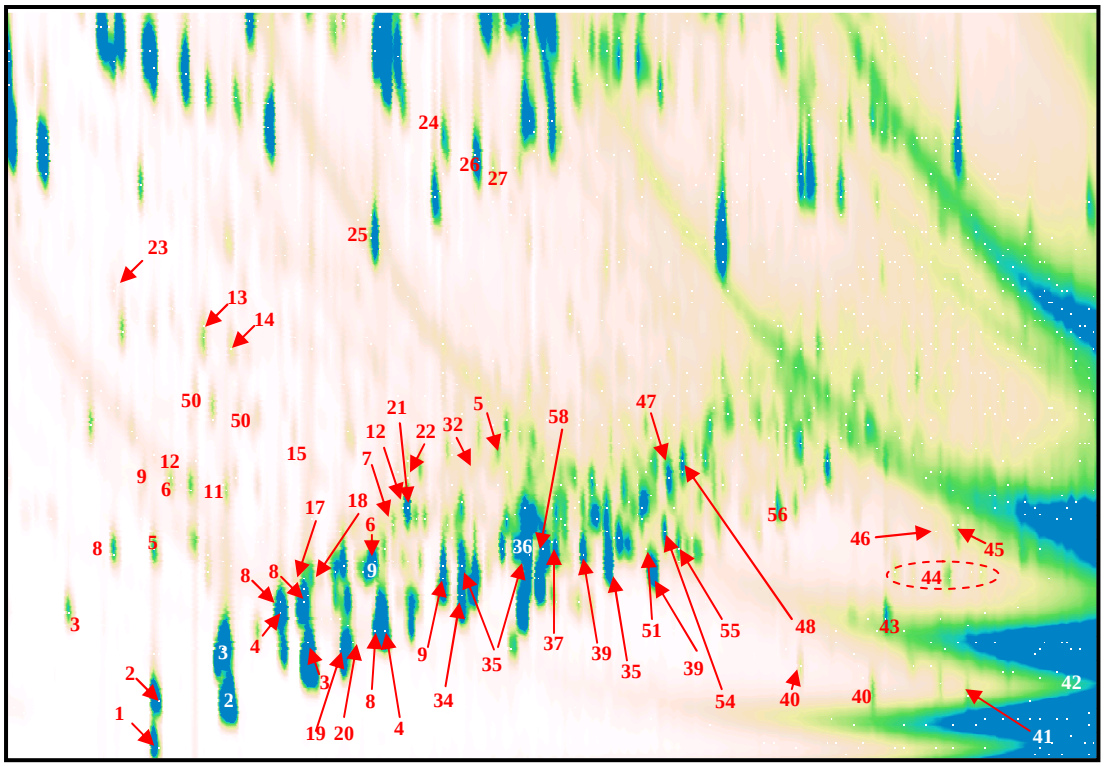


Figure 2-10. 2D contour plot obtained from coal liquid analysis. numbers refer to table 2-4. Conditions: Solgelwax × DB-1

Table 2-4. Oxygenated molecular structures identified by GC×GC-ToF/MS

N°	***Phenolic compounds***	*N°*	***Ketones***
1	Phenol	10	Methylfuranon
2	Cresol	12	Indenone,
3	Dimethylphenol	13	Heptenone
4	Propylphenol	24	Trimethylnaphthalenone
5	Trimethylphenol	31	Dimethylbenzofuranon
6	Propylmethylphenol	38	Dimethylbenzofuranon
7	Propylethylphenol	46	Ethylmethylene-indanone
8	Methylethylphenol	54	Dimethylbenzofuranone
9	Diethylephenol	55	Hydroxy,dihydronaphthalenon
11	Dimethylethylphenol	15	Naphthalenonedihydro
14	Tertbutylmethylphenol		
16	butylphenol		***Alcohols***
17	(Methylpropyl)phenol	39	Naphthalenol-tetrahydro
18	Thymol	40	Dimethylbenzenediol
20	(Methylethyl)phenol	41	Methylbenzenediol
21	Methylindanol	42	Resorcinol
22	Allylmethylphenol	43	Naphthalenol
29	Methylphenylphenol	44	Methylnaphthalenol
32	(Methylethyl)phenol		
34	Allylphenol		***Other oxygenates***
35	Methylindanol	19	O and S compound
36	Ethylbutylphenol	50	Oxygenate
37	Pentylphenol	51	Ethylvinylanisol
45	Dimethylnaphthol	52	O and N compound
47	Cyclohexylphenol	27	xantene
53	Methylinden-ol,dihydro	28	Lilial
56	Phenylphenol	30	Methoxynaphthalene
	Dibenzofurans		
25	Dibenzofuran		
26	Methyldibenzofuran		
57	Tetramethyl,dihydrobenzofuran		

2.4 Conclusion

Both results obtained using GC×GC-FID and GC×GC-ToF/MS enabled to unravel molecular structures of oxygenated compounds in a coal-derived middle distillate. 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 reversed configuration involving a highly polar column in the first dimension and a non-polar one in the second enables the identification 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 and a proper quantification is therefore hardly reachable. 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. Another solution would be to look for new GC×GC column combinations. Limitations of GC×GC can also be overcome by using a multi-technical analytical approach.

CHAPTER 3. Using gas chromatography to characterize a direct coal liquefaction naphtha [4]

FOREWORD

Speciation of oxygen in direct coal liquefaction naphthas is also important considering their significant roles in coal conversion reactions. This study attempts to characterize them as fully as possible using gas chromatographic systems. The investigated cut (IBP-200°C) is in principle not as complex as the atmospheric gas oil cut. In fact, it contains lighter compounds and consequently less isomers and less molecules. GC and GC-GC were therefore firstly examined. GC-MS was allowed the identification of a few ketones, alcohols, and phenols. This conventional analysis was complemented by the application of GC-GC-FID aiming to overcome the coelutions highlighted when using one-dimensional gas chromatography. Nevertheless, as there were too many oxygenated species, achieving such a high number of cuts tended to use a comprehensive technique. Therefore, GC×GC was finally considered and thanks to the column set selected in chapter 2, more than a hundred oxygenated compounds belonging to five main families were identified: alcohols, phenols, ketones, acids, and furans. To accentuate the second dimension separation, a novel polar × midpolar column set enabled a selective separation of phenols and alcohols which were quantified using a specific methodology.

Average response factors of each of these families were determined by GC×GC-FID using calibration curves and vary from 1 (hydrocarbons) to 2.50 (carboxylic acids). Thanks to the novel column set involving a trifluoropropyl stationary phase, alcohols and phenols which represent around 14% w/w of the sample were fully identified. A detailed quantification of these species was carried out for the first time in such products. It was concluded that 90% of the alcohols are aromatic (phenols), 5% are naphthenic and 5% are aliphatic. A quantification of hydrocarbon families was also achieved and shows that the matrix is mostly naphthenic (56%w/w), but also contains aromatics (22%w/w) and paraffins (8%w/w).

[4] This chapter is based on an article published in Journal of Chromatography A, 2011 (1226) p 61-70 by Omais *et al.*

3.1 Introduction

Since the production of crude oil may not meet the increasing demand in the next future, coal liquefaction products have gained interest as one of the possible substitutes of petroleum in the transportation field. These are derived from two liquefaction processes aiming to maximize the H/C ratio of coal: direct coal liquefaction (DCL) and indirect coal liquefaction (Fischer and Tropsch synthesis). In this chapter the focus is on DCL products which are complex matrices consisting in paraffins, naphthenes, aromatics, and heteroatomic compounds [1, 44].

Many researches have been led to unravel the predominant hydrocarbon structures in DCL samples, and studies concerning heteroelements such as nitrogen and oxygen-containing compounds are scarcer [112]. Nevertheless, it is essential to characterize these structures in order to understand their roles and behaviours during their processing. Moreover these species pose pollution problems because they are carcinogenic and mutagenic. This work focuses on the speciation of oxygenated compounds in the naphtha cut of a direct coal liquefaction sample. This cut consists in the lighter fraction obtained by distillation of the crude oil and its boiling points range from 30 to 200°C.

A literature survey shows that oxygenates contained in such samples mainly consist in phenols and furans. Many analytical tools have already been deployed to identify these structures and applications of gas chromatography has considerably improved the understanding of these unconventional matrices using a mass spectrometer [18, 22, 26, 27, 41] or an atomic emission detector [10, 16, 17, 25, 30, 32, 94].

GC has evolved over the last three decades and offers higher and higher performances. In fact, to get around the lack of separation given by one-dimensional gas chromatography for complex matrices, a heart-cutting multidimensional gas chromatography system (GC-GC) has emerged [113]. This hyphenated technique consists in transferring fractions of the primary separation dimension to a secondary column for further analysis. It has been broadly used for the analysis of oxygenates at trace levels in petroleum products [98], allergens in cosmetic products [114] or to separate enantiomers in the agricultural field [115]. Nevertheless, to our knowledge, none of its applications concerns coal oils.

Comprehensive gas chromatography (GC×GC) is also a two-dimensional approach in which the whole sample is subjected to a separation in the second dimension. This system allows advanced separation and increased sensitivity [98]. Many applications of this technique have

already been achieved to unravel oxygenated structures in complex matrices: acids, alcohols and esters in Fischer-Tropsch products [2, 100, 116], FAMEs in biodiesel [101-103], or alcohols in petroleum [104].

In this study, GC-MS was first used to identify oxygenates in a coal-derived naphtha cut. Granted ten oxygenates have been characterized, still there remains a lack of information due to many coelutions with the predominant hydrocarbons. This first step was therefore complemented by a GC-GC analysis aiming to separate targeted oxygenated compounds by overcoming these coelutions. As a third step, comprehensive two-dimensional gas chromatography was used to fully characterize the oxygenated species. Different columns sets were investigated to identify ketones, alcohols, phenols, and furans. A unique column set also enabled a breakthrough characterization of linear and cyclic alcohols in this matrix. Therefore, response factors of these species were calculated using calibration curves and a detailed characterization was obtained. This chapter shows the advantages and drawbacks of each of these three gas chromatography techniques to characterize oxygenates in a coal-derived light distillate and highlights the advances in terms of oxygenates characterization allowed by GC×GC.

3.2 Experimental

3.2.1 Materials

3.2.1.1 Test mixtures

Two model mixtures were prepared. The first one (MM1) was used to test the GC-GC system. It was established using ethyl acetate supplied by VWR (France) as a solvent (purity >99.0%). The latter contained eleven compounds representative of a coal derived naphtha and belonging to five families: normal paraffins, naphthenes, aromatics, furans, and phenols (Table 3-1). The content of these chemicals ranged from 500 to 1500 µg. g^{-1}.

Table 3-1. Compounds contained in the model mixture 1 (MM1)

N°	*Compound*	*%w/w*	*N°*	*Compound*	*%w/w*
1	Hexane	8	**7**	Toluene	13
2	Heptane	9	**8**	Xylene	12
3	Octane	8	**9**	Furan	9
4	Cyclohexane	8	**10**	Phenol	5
5	Methylcyclohexane	8	**11**	Cresol	11
6	Methylcyclopentane	8			

The second model mixture MM2 was used to calculate response factors of many oxygenated structures such as furans, ketones, alcohols, phenols, and carboxylic acids (Table 3-2). It also enabled the identification of elution zones in GC×GC. The solvent was ethyl acetate and the 22 investigated species content was around 1% w/w. This solution was diluted to obtain different concentrations: 40, 80, 160, 400, 600, 800, and 1000 $\mu g.g^{-1}$.

Table 3-2. Compounds contained in the model mixture 2 (MM2)

Family	*Compound*	*Content ($\mu g.g^{-1}$)*	*Family*	*Compound*	*Content ($\mu g.g^{-1}$)*
Phenols	Phenol	9824.6 ± 0.2	**Alcohols**	3-pentanol	9834.1 ± 0.2
	m-cresol	9511.7 ± 0.2		3-heptanol	10222.9 ± 0.2
	Ethyl phenol	10270.4 ± 0.2		3-Nonanol	10099.7 ± 0.2
	Dimethyl phenol	9236.7 ± 0.2	**Ketones**	Acetone	12868.8 ± 0.2
	Trimethyl phénol	10659.2 ± 0.2		2-pentanone	9103.9 ± 0.2
	2-tertbutyl-6-Methylphenol	9189.3 ± 0.2		4-heptanone	8961.6 ± 0.2
	2-Naphthol	10185.0 ± 0.2	**Carboxylic acids**	Formic acid	11882.5 ± 0.2
Furans	Furan	9900.5 ± 0.2		Propionic acid	8790.9 ± 0.2
	Benzofuran	9208.2 ± 0.2		Butanoic acid	13077.4 ± 0.2
	Dibenzofuran	10858.3 ± 0.2		Decanoic acid	10431.6 ± 0.2
Alcohols	1-propanol	9103.9 ± 0.2		Palmitic acid	8866.8 ± 0.2

3.2.1.2 Coal derived naphtha cut

The investigated coal-derived oil was provided by IFP Energies nouvelles and obtained by direct coal liquefaction. Its boiling points range from 30 to 200°C. CHONS results show that this naphtha fraction has a high oxygen content (2.89 % w/w O), a relatively high Nitrogen content (957ppm w/w N), and a sulphur content of 324 ppm w/w S.

3.2.2 GC-ToF/MS setup

GC-ToF/MS was performed with a Thermo Tempus Gas Chromatograph. A method dedicated to the analysis of gasolines was carried out: The column was a 50 meters PONA (Agilent Technologies) with an internal diameter of 0. 20 mm and a film thickness of 0.5µm. The oven temperature varies from 35°C to 114°C at 1. 1°C/min and then from 114°C to 280°C at 1. 7°C/min. Helium (99. 99% Air Liquide, France) was used as a carrier gas with a constant pressure of 105 kPa. The injection was achieved at 250°C with a 1:200 split ratio and an injection volume of 0. 5µL. Data was acquired thanks to Excalibur software (Thermo) and the mass spectra were compared to a database combining NIST and Wiley data.

3.2.3 GC-GC-FID setup

The chromatograph used in this study is an Agilent Technologies 7890 equipped with two flame ionization detectors (100Hz), a 7683 series auto sampler, and Chemstation software. This GC system was equipped with a Dean Switching system (model G2855B, Agilent Technologies, Burwood, Australia) to enable multiple heart-cuts of the effluent coming from the first dimension column. The role of the Dean Switching device is to transfer fractions coming from the first dimension either to the front detector or to the second dimension. Two columns sets were investigated: HP-5 (30mx0. 32mmx0. 25µm) x GS-Oxyplot (10mx0. 52mmx0. 5µm) and PONA (50mx0. 20mmx0. 5µm) x Solgelwax (9mx0. 25mmx0. 25µm). An uncoated restrictor (2. 4mx0. 18mm) was placed between the first column and the front detector to compensate for the pressure drops in the second dimension (Figure 3-1). The carrier gas was Helium with an inlet pressure of 13.16 psi and a split ratio of 1:100. The primary, secondary and restrictor flows were respectively equal to 0.15, 2.0, and 2.0 mL/min.

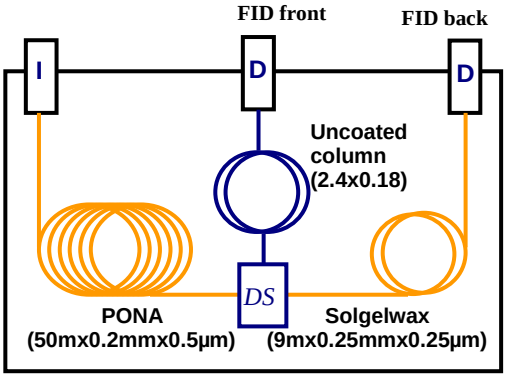


Figure 3-1. GC-GC-FID configuration for the analysis of the coal–derived naphta. DS: Dean Switching device, I: Injector, D: Detector.

3.2.4 GC×GC-FID

Experiments were performed using a Trace GC (Thermo, Italy). The injection was carried out with a split injector (Thermo) at 320°C and the split ratio was 1:100 (0. 3µL). A Flame Ionization Detector system set at 380°C was used to carry out the detection. H2, air, and helium makeup were set respectively at 35, 450, and 25 mL/min. Helium (99. 99% Air Liquide, France) was used as a carrier gas. Modulation was carried out using a double jet CO2 system which was not cold enough to trap the first eluted compounds (10 first minutes). A detail of these experimental conditions is shown in Table 3-3. This table shows that there were two investigated columns sets. The first one Solgelwax x DB-1 showed good results for the separation of oxygenated compounds in an atmospheric gas oil cut in the previous chapter. The second one involving a trifluoropropyle stationary phase as a second dimension was selected as it has a particular selectivity towards hydroxyle groups contained in phenols and alcohols. As the retention power of this phase is very low, a short modulation period was selected.

Table 3-3. Experimental GC×GC-FID conditions

	Set A	***Set B***
First dimension	Solgelwax (30mx0.25mmx0.25µm)	Solgelwax (30mx0.25mmx0.25µm)
Second dimension	DB-1 (1mx0.1mmx0.1µm)	Rtx-200 (1.5mx0.1mmx0.1µm)
Modulation period	20 s	7 s
Oven conditions	30°C to 200°C with a 2°C/min rate	30°C to 250°C with a 2°C/min rate
Front inlet	23 psig	23psig
Split ratio	1:100	1:100

The raw data of FID signals were exported as a csv file after their acquisition by Polycard software (Thermo). GC×GC contour plots with retention time's axis, as well as 1D and 3D-plots are displayed by a home-made software called 2DChrom version 2.2.6. Quantification is carried out by creating blobs and using the peak integration option. A blob is a contour delimiting a 2D peak, and for each blob created it was checked that the whole 1D peak was integrated. This software finds peaks automatically and fits blobs giving access to a reproducible and accurate integration. An external calibration (sum of the areas equal to 100) was used, and the areas are calculated with the associated response factor. To finish, intensity of peaks is displayed with a colour gradient varying from light blue to dark blue.

3.2.5 GC×GC-ToF/MS

For the identification of oxygenated compounds, a LECO Pegasus IV (LECO, St. Joseph, MI, USA) GC×GC-ToF/MS system was used. The chromatograph was a HP 6890 (Agilent Technologies, Massy, France) which was equipped with a split injector. The GC×GC-FID conditions are those described in the previous paragraph (Table 3-3). The modulation was performed by a liquid Nitrogen cooled gas jet cryogenic modulator which enabled to modulate all the compounds including the most volatile ones. The acquisition frequency was set at 100 Hz in a mass range of 75-500 amu and the resolution is 1000. Electron Impact was achieved at 70ev and a multiplate voltage of -1450V was used.

As far as ToF/MS data treatment is concerned, it was carried out by the ChromaTOF software of the Pegasus 4D platform which also allowed peak finding. Compounds could be identified by comparing the acquired spectra with the NIST database (National Institute of Standards and Technology, version 2002). Peak intensities are displayed with a colour gradient varying from yellow to purple for the first investigated conditions and from black to light yellow for the second.

3.3 Results and discussion

This part shows the results obtained for a coal-derived naphtha using many chromatographic systems. Conventional GC-ToF/MS results and the improvements using GC-GC-FID are highlighted. Finally, two different GC×GC configurations complement the two previous techniques and quantification is accessible via response factors calculations.

3.3.1 Speciation of oxygenated compounds by GC-ToF/MS

This part of the study consists in unravelling oxygenates in the naphtha cut using GC-ToF/MS, with a particular attention paid to the targeted oxygenated compounds (in particular phenols, alkylphenols, methoxyphenols and dibenzofuran) using specific ions detection. This identification must be considered with care because it is based on a comparison with reference spectra: many isomers can have the same spectrum and some of the oxygenates are not referenced in the library. Moreover the GC-ToF/MS analysis was achieved with a resolution of 1000. This is the ratio between the resolving power and the mass. However, resolution does not allow to confirm the presence of some compounds neither to separate their isobar ion peak. Concerning the mass accuracy, the chemical formula was determined using an integer mass.

Table 3-4 points up oxygenated compounds identified in the coal derived gasoline cut, and the corresponding chromatogram is shown in Figure 3-2. Alcohols, phenols, benzofurans, and ketones have been detected. Some characteristic ions are an evidence of the presence of an oxygenated structure. However, their coelution with hydrocarbons does not allow a proper identification because the spectra are overlaid. It is important to highlight that no dibenzofurans and methoxyphenols were detected. Moreover, after an elution time of 24 minutes, most of oxygenates are coeluted with hydrocarbons what makes the molecules identification tricky and inevitably skews the quantification. Therefore, no quantification accomplished. These results show the difficulty to characterize oxygenated species in such matrices which are predominantly composed of hydrocarbon structures. Two solutions can be envisaged to access to a precise characterization. The first one would be to extract selectively oxygenates from the matrix by liquid chromatography (LC), solid phase extraction (SPE), or liquid-liquid extractions. The second which will further be described consists in using high resolution multi-dimensional systems. Consequently, to gain resolution, GC-GC has been investigated.

Table 3-4. Oxygenated compounds identified by GC-ToF/MS in a coal-derived naphtha cut

Tr (min)	*Oxygenated Compounds*	*Tr (min)*	*Oxygenated Compounds*
6.29	Acetone	50.6	Oxygenate
6.24	Propanol	57.15	Phenol
9.51	2-Butanone	68.27	Methyl phenol + $C_{10}H_{20}$
10.19	Butanol	71.44	Methylphenol + hydrocarbon
13.61	Methyl butanone	78.79	Oxygenate + Hydrocarbon
15.94	$C_5H_{10}O$	80.71	Oxygenate
17.60	Oxygenate	82.49	Oxygenate + Hydrocarbon
27.73	Hexanone + Hydrocarbon (C_8H_{18})	84.64-85.6	Oxygenate + Hydrocarbon
34.06	$C_6H_{10}O + C_8H_{16}$	96.16	Oxygenate + Hydrocarbon
36.2	Oxygenate		

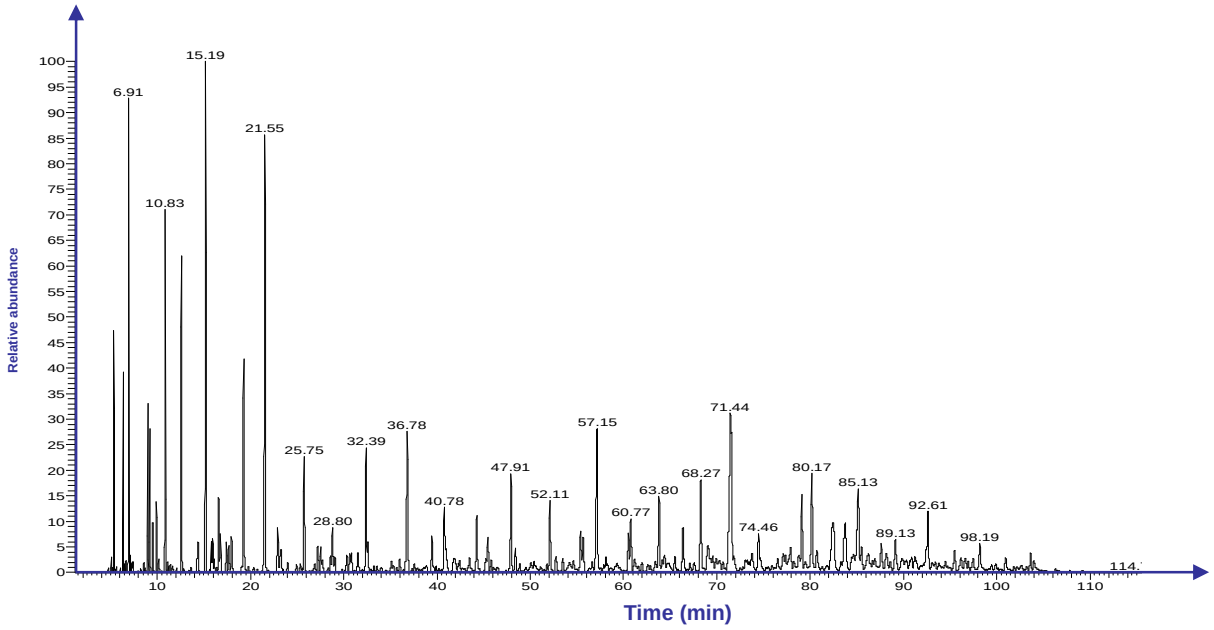


Figure 3-2. GC-ToF/MS chromatogram of the coal-derived naphtha cut

3.3.2 Towards a detailed characterization of oxygenates by GC-GC-FID

Capillary flow technology was successfully employed for the implementation of multi-dimensional gas chromatography to improve separation resolution, selectivity, and peak capacity for the measurement of compounds of interest. GC-GC-FID was therefore used to enhance the

separation which was carried out using GC-ToF/MS. The GC-GC system could not allow the identification of these unknown species as no mass detector was hyphenated.

3.3.2.1 Analysis of the test mixtures

First of all, the Dean switching device has been tested using a test mixture (Table 3-2). It was essential to ensure that the transferred zones in the first dimension were accurate and clearly defined, and that the areas of the targeted compounds were conserved from the first to the second dimension. The first investigated column set consisted on a HP-5 (30mx0. 32mmx0. 25µm) in the first dimension and a GS-Oxyplot (10mx0. 52mmx0. 5µm) as the second dimension. In fact GS-oxyplot shows a high selectivity towards oxygenated compounds. The oven temperature was firstly programmed from 30°C to 100°C what was far sufficient to elute the eleven model compounds.

Figure 3-3.A shows the signal detected by the Front FID. No cuts have been carried out for this first injection. The species elute distinctively with no coelutions. In a second run, the two phenolic compounds were transferred into the second dimension: Figure 3-3.B shows the front FID signal and one can notice that the two peaks corresponding to phenol and cresol are not present anymore. Figure 3-3.C shows the back FID signal after a second separation of the heart cut with the GS-Oxyplot. These chromatograms demonstrate the effectiveness of the Dean Switch. Even if the peaks obtained in the second dimension are distorted, they nearly have the same areas than the ones in the first separation (Table 3-5). This peak tailing due to the high affinity between the Oxyplot column and the phenolic compounds can be problematical for more complex matrices. The slight area difference can be explained by the integration bias owing to the bad peak shape in the second dimension, and the system seams to be reliable as no leak occurs during the transfer. The overlay of front signals corresponding to the coal-derived naphtha and the test mixture show that the eleven compounds of the test mixture are present in the naphtha sample.

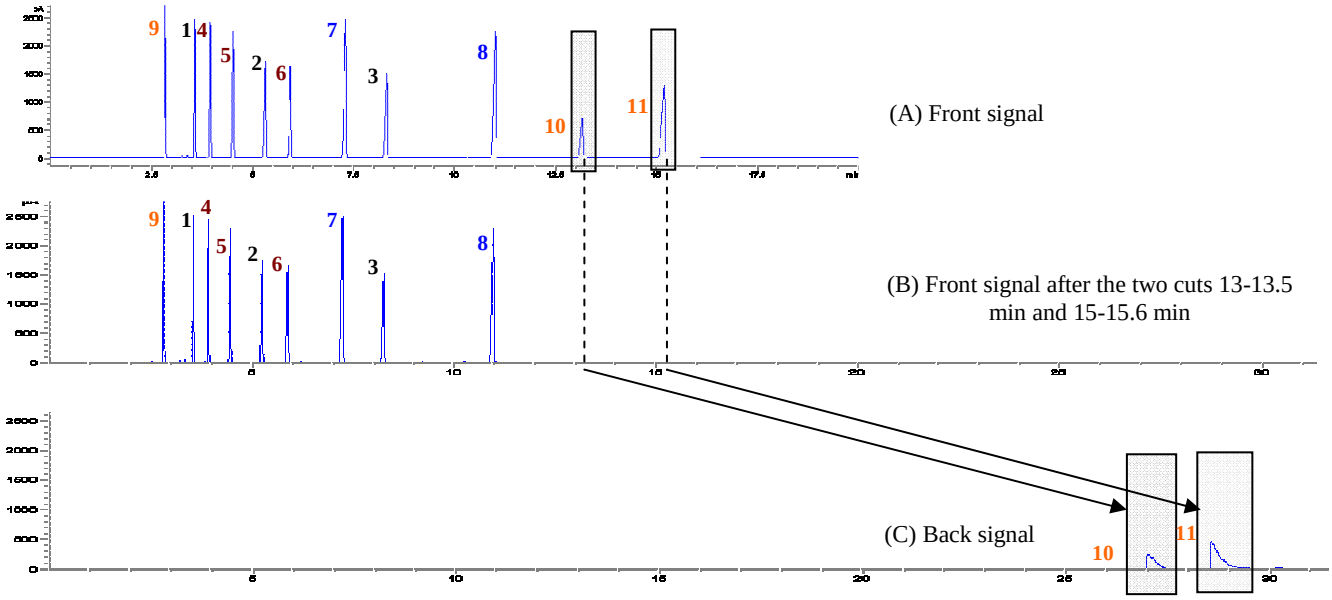


Figure 3-3. Dean switching device validation in the test mixture (numbers refer to Table 2-2)

Table 3-5. Conservation of the peak area from the first to the second dimension of separation

	^{1}D area	*^{2}D area*	*Difference (%)*
Phenol	2789.7	2832.3	1.5%
Cresol	6380.7	6376.7	0.06%

3.3.2.2 GC-GC on a coal derived light distillate

It has previously been concluded that the fractions coming from the first dimension are totally transferred into the second dimension via the Dean Switch. The conditions used for the GC-ToF/MS analysis were reproduced in the first dimension and the coeluted species were recognized in the GC-FID chromatogram despite a slight shift. A Solgelwax column (9mx0. 25mmx0. 25µm) was placed in the second dimension. Solgelwax was used because it is highly polar and demonstrated a good efficiency for the separation between oxygenated compounds and hydrocarbons [103].

Four cuts were carried out. These corresponds to the unknown oxygenates pointed out by the GC-ToF/MS analysis at tr_1 = 15. 94 min, tr_2 = 27. 73 min, tr_3 = 34. 06 min, and tr_4 = 36. 2 min. Among these cuts, two were successful (Figure 3-4). The others show a gain in terms of resolution but should be enhanced by placing a longer column in the second dimension.

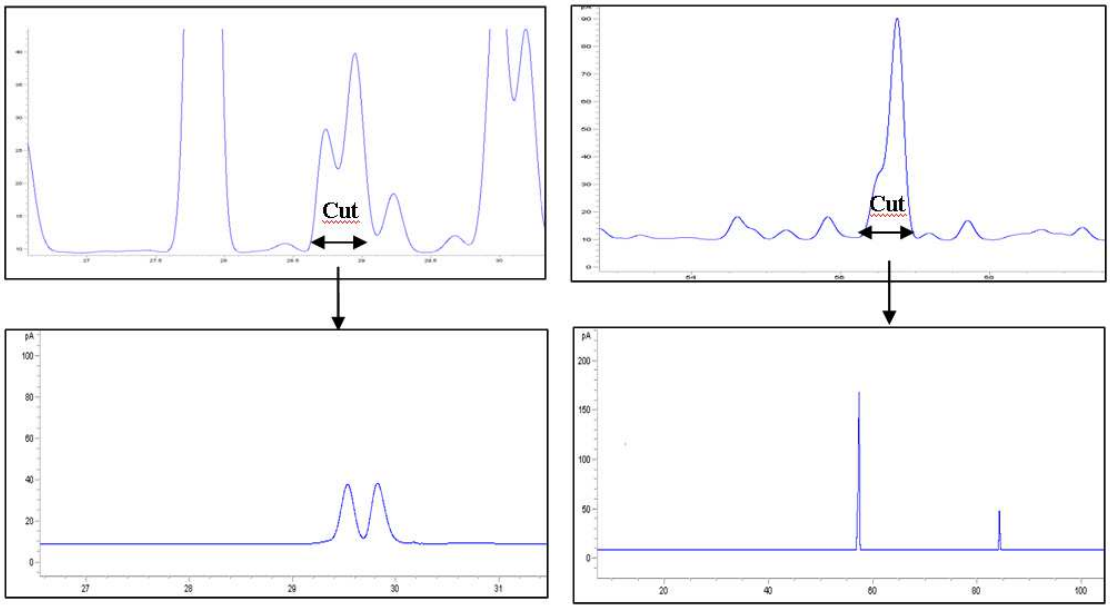


Figure 3-4. GC-GC-FID signals for a coal derived naphta . Top: Front detector signal with no cuts, Bottom: Back detector after the cut

These results are encouraging but far from our expectations. In fact, all cuts must be carried out independently as no modulator enable to simulate a second injection by refocusing the analytes. Thus, when too many cuts are done in a single run, coelutions can appear in the Back FID. Although the FID detector gives an evidence of the performances of GC-GC, it does not allow any proper identification and no information in terms of molecular structures can complement the GC-ToF/MS analysis. The back detector signal of the first cut exposed in Figure 3-4shows that the second dimension separation needs to be enhanced. Moreover, to overcome all the coelutions, a high number of cuts must be established and in this case, the system tends to a comprehensive GC×GC. It can be concluded that GC-GC was not the optimal solution with regard to the particular aim of the study which is to screen the entire mixture. For this purpose, a comprehensive technique is more convenient.

3.3.3 Speciation of oxygenated compounds using GC×GC

3.3.3.1 Separation and identification of oxygenated species using GC×GC-ToF

Two configurations were tested in this study. The first one described in the previous chapter enabled the identification of five families [112]. The second one which is unique allowed a precise characterization of alcohols and phenols. Chemical families elution zones were confirmed using model mixture 2 (MM2).

- Combination A: Solgelwax x DB-1

Previous researches on GC×GC analysis of a coal-derived middle distillate [112] showed hat among 8 columns configuration, the use of a Solgelwax (30mx0. 25mmx0. 25µm) as a first dimension and a DB-1 (1mx0. 1mmx0. 1µm) as a second dimension offered a good separation of oxygenates (in particular phenols) from the hydrocarbons. Thus, this column set was investigated and chromatographic conditions were adapted to the naphtha cut. The 2D chromatogram is displayed in Figure 3-5. It shows a separation between paraffins, naphthenes, aromatics, and in a tinier extent of oxygen and nitrogen compounds. Naphthenes and aromatics are totally separated. As far as phenolic compounds are concerned, their separation from the hydrocarbon matrix is good, and most of them can clearly be identified. They mainly consist in alkylated phenols and indanols.

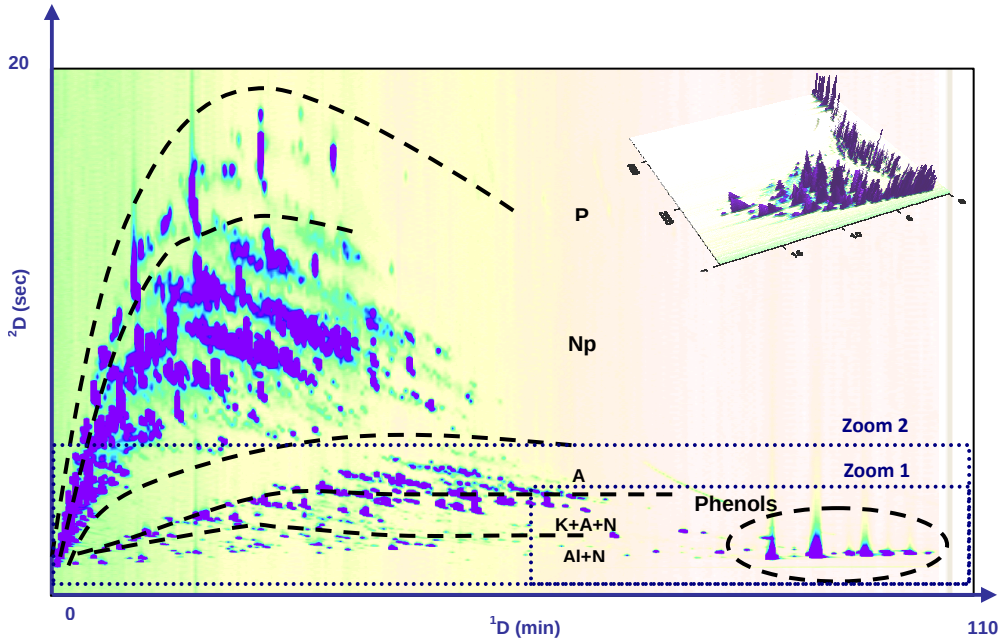


Figure 3-5. 2D contour plot of a direct coal liquefaction naphtha with the 3D representation on the top-right corner. P= Paraffins, Np=Naphthenes, A=Aromatics, K=Ketones, Al= Alcohols, N=Nitrogen-containing compounds. Column set: solgelwax x DB-1. Zooms 1 and 2 refer to respectively to Figures 3-6 and 3-7.

However there remain a many coelutions between phenols and nitrogen-containing compounds which mainly consist on nitriles, quinoline, indoles, and anilines with different alkylation degrees (Figure 3-6). On the left bottom of the plot, ketones and alcohols can also be identified. However, ketones coelute with aromatics and alcohols elute in the same area as some nitrogen compounds. Their identification is still allowed by the ToF/MS detector. A zoom of the targeted oxygenated zone is displayed on Figure 3-7 and numbers refer to Table 3-6 which also highlights the presence of furans and carboxylic acids. In total, 109 oxygenated compounds were identified and the families they belong to are consistent with the literature. To our knowledge, carboxylic acids and ketones are for the first time revealed in these products.

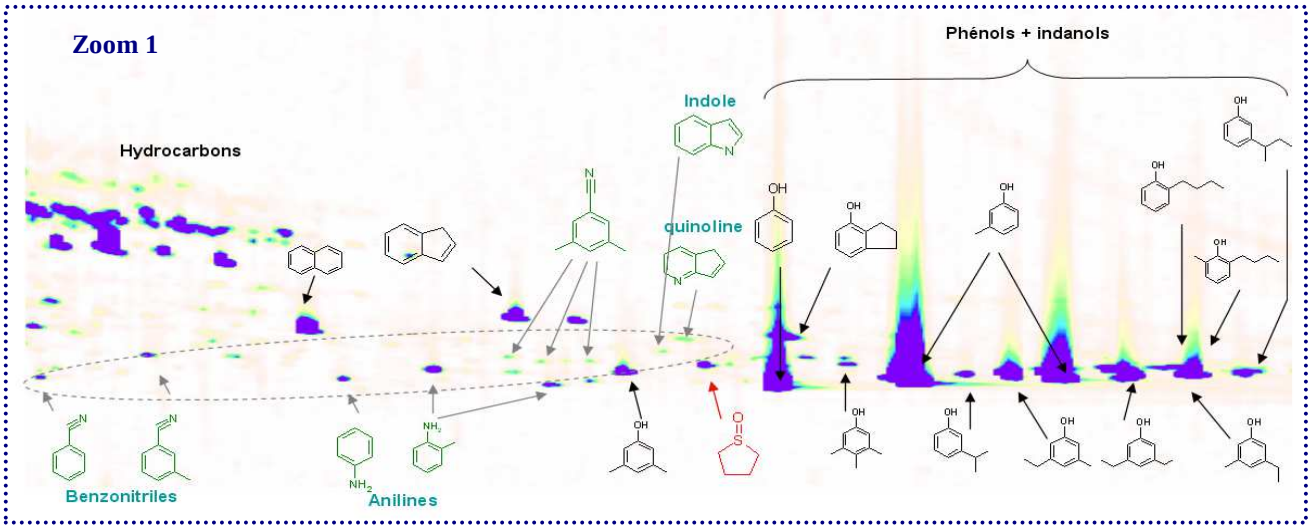


Figure 3-6. Zoom 1 on the GC×GC-ToF/MS chromatogram of a coal derived naphtha showing the coelutions between phenols and nitrogen-containing compounds. Column set: solgelwax x DB-1.

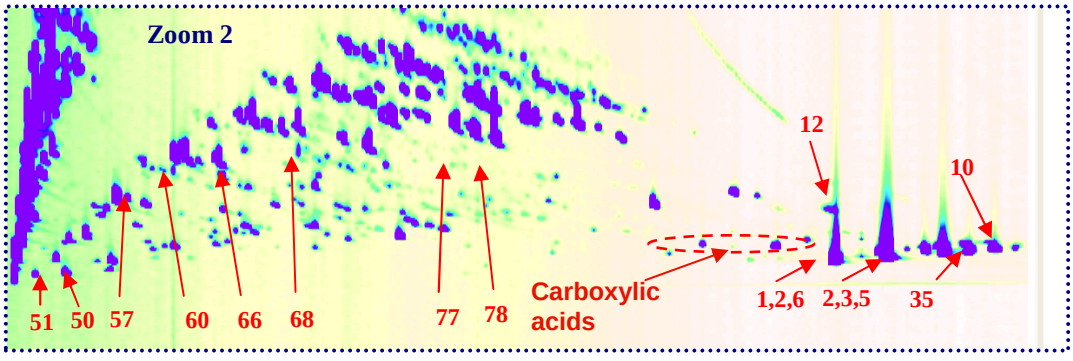


Figure 3-7. Zoom 2 on the oxygenated compounds elution zone on the GC×GC-ToF/MS chromatogram of a coal derived naphtha. Column set: Solgelwax x DB-1.

To conclude, this separation leads to an advanced characterization of oxygenates in coal-derived naphthas and a breakthrough characterization of phenols. As there remain some coelutions, in particular between ketones, alcohols, aromatics and nitrogen compounds, no quantification could be achieved. Thus, a slightly more polar second dimension (DB-5) was tried to enhance the separation, but no significant difference was obtained. To overcome this problem, an online or offline pre-separation aiming to trap aromatics and nitrogen compounds can be envisaged.

Table 3-6. Identified soxygenated species using the Solgelwax x DB-1 column set

N°	Identified compounds	N°	Identified compounds
Phenols		**Furans**	
1	Phenol	**16**	Dimethylbenzofuran
2	Cresol	**24**	Cyclopentenylfuran
3	Ethylphenol	**58**	Methyltetrahydrofuran
4	Ethylmethylphenol	**59**	Dimethylfuran
5	Dimethylphenol	**63**	Ethylmethylfuran
6	Trimethylphenol	**64**	Trimethylfuran
7	Propylphenol	**102**	Benzofuran
8	Methylpropylphenol	**103**	Methylbenzofuran
9	Butylphenol	**104**	Dimethylbenzofuran
10	(Methylpropyl)-phenol	**Ketones**	
11	(Methylethyl)-phenol	**28**	(methylphenyl)-ethanone
12	Indenol dihydro	**29**	Methylhexanol
13	Butylated hydroxytoluene	**51**	Acetone
23	Allyl-methylphenol	**50**	Butanone
25	Ethyldimethylphenol	**55**	Methylisobutyl-ketone
26	Methylindenol dihydro	**56**	Methypentanone
33	Methyl-(Methylethyl)phenol	**57**	Hexanone
35	Diethylphenol	**60**	Methylhexanone
38	(Dimethylpropylphenol	**61**	Dimethylcyclopentanone
Alcohols		**62**	Ethylpentanone
27	Nonenol	**65**	Heptanone
28	Naphtalenol tetrahydro	**66**	Trimethylcyclopentanone
52	Isopropylalcohol	**67**	Methylheptanone
53-54	Pentenol	**68**	Dimethylcyclohexanone
79	Propanol	**69**	Ethanone, cyclohexyl
80	Methylpentanediol	**70**	Ethylcyclohexanone
82	Butanol	**71**	Octanone
83	Pentanol	**72**	Dimethylhexanone
84	Methyl-pentanol	**73**	Ethylpentanone
85	Pentanol	**74**	Dimethylheptanone
86	Methylcyclopentanol	**75**	Nonanone
87	Methylhexanol	**76**	Methylethylcyclohexanone
88	Dimethylcyclopentanol	**77**	Butylcyclopentanone
89-90	Heptanol	**78**	Propylcyclohexanone
91	Methylbutanol	**95**	Cyclopentanone
92	Pentanol	**96**	Methylcyclopentanone
93	Methylpentanol	**103**	Dimethylcyclopentanone
94,97	Hexanol	**104**	Heptanone
98	Cyclohexanol	**105**	Octanone
99	Methylcyclohexanol	**Carboxylic acids**	
100	Octanol	**30**	Heptanoic acid
101	Dimethylcyclohexanol	**31**	Hexanoic acid phenylester
116	Cyclohexenol	**32**	Acetylbutyric acid
117	Ethylcyclohexanol	**120**	Hexanoic acid
		121	Methylhexanoic acid

- Combination B: Solgelwax x Rtx-200

Rtx-200 columns developed by Restek are intermediate in polarity and are coated with a trifluoropropyl methyl stationary phase. The unique selectivity resulting from the interaction of the trifluoropropyl methyl polysiloxane stationary phase with the electronegative centres was investigated to obtain a better separation of alcohols and ketones. Therefore an innovative combination of a Solgelwax (30mx0. 25mmx0. 25µm) and Rtx-200 (1. 5mx0. 1mmx0. 1µm) was investigated. As this new stationary phase is less retentive, a modulation period of 7 seconds was selected. The resulting chromatogram is displayed in Figure 3-8. It shows a good separation between paraffins, naphthenes, aromatics, and phenols. However, there is no distinction between ketones and aromatics. Appendix A shows how ketones were separated and characterized using a preparative step.

On the other hand, alcohols are totally separated from the rest of the matrix as displayed in Figure 3-9. In fact a zoom of this specific zone shows an ordered classification of alcohols according to their carbon atom number. The alkylation degree varies from three to six for linear alcohols and from five to eight for cyclic alcohols. Concerning phenols, their alkylation degree varies from six (phenol) to eleven. Generally, the heavier the molecule is, the higher the number of isomers will be. This column set has a double interest as it enables the separation of alcohols from a hydrocarbon matrix but it also classifies them into three groups: linear alcohols, cyclic alcohols, and phenols. Finally, identification of phenols is consistent with the results obtained using conditions A. Thanks to the high separation power of this combination, a quantification can this time be envisaged.

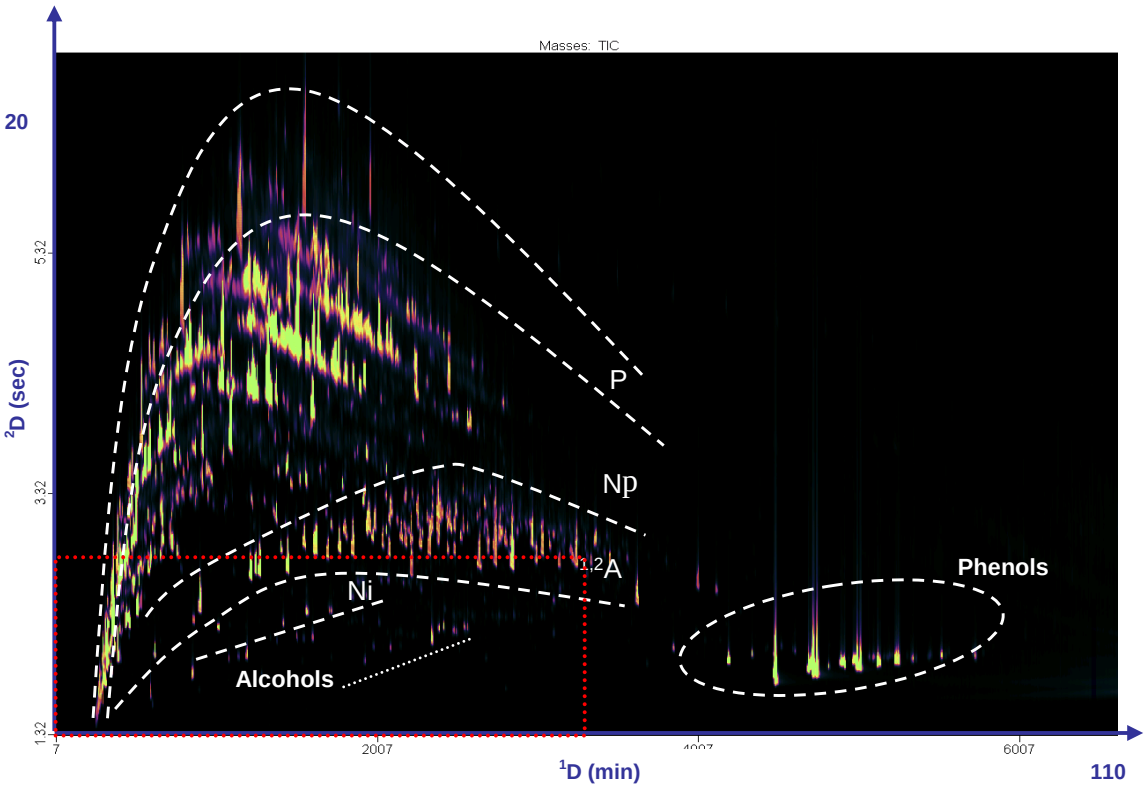


Figure 3-8. 2D contour plot of the coal derived naphtha using Solgelwax x Rtx-200 columns set. P= Paraffins, Np=Naphthenes, A=Aromatics, N=Nitrogen compounds.

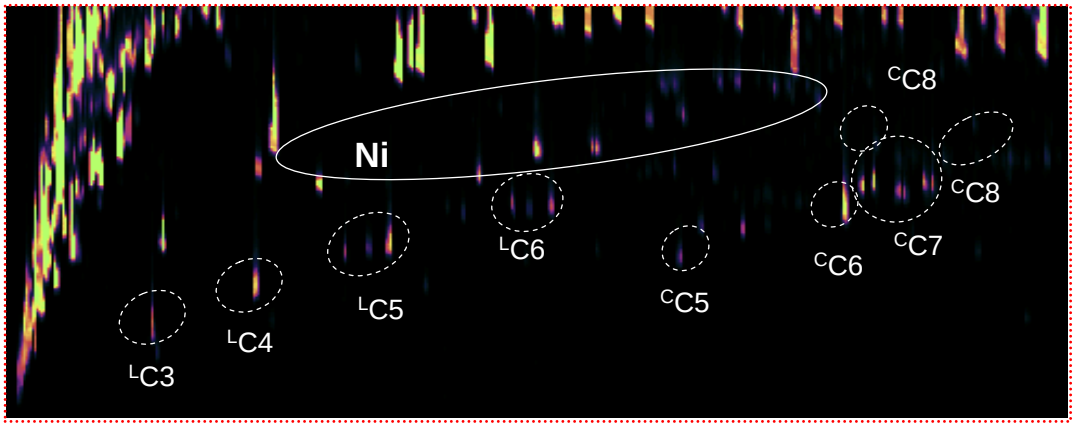


Figure 3-9. Alcohols separation in a coal derived light distillate using Solgelwax x Rtx-200 ^{L}Ci= linear alcohol with i carbon atoms, ^{C}Ci= cyclic alcohol with i carbon atoms, Ni: Nitrogen-containing compounds.

- <u>Identification using Nist database</u>

To validate the identification of a compound, both spectra comparison and model mixture 2 injections were used. Identification of oxygenated compounds was achieved using ion fragmentation spectra. Generally, molecules identification is validated for a similarity higher than 800 but only if the chromatographic retention times are in agreement with those expected. Concerning isomers, they cannot be identified properly but can be guessed considering the

interactions between alcohols and the stationary phase. In fact, the higher the steric hindrance of OH functional group is, the shorter the retention time of the compound will be.

3.3.3.2 Quantification using GC×GC-FID

The solutions derived from the dilution of the model mixture MM2 (Table 3-2) enabled the plotting of calibration curves by using GC×GC-FID. These are linear from 600µg.g^{-1} to 40µg.g^{-1}. Thus, response factors were calculated for each of the 22 compounds and by normalization with dibenzofuran. Then averages were calculated for each family as shown in Table 3-7.

Table 3-7. Response factors averages of five chemical families

	Response factors averages
Furans	1,00
Phenols	1,25
Alcohols	1,50
Ketones	1,75
Carboxylic acids	2,50

As previously mentioned, GC×GC analysis enabled to reach a total separation of linear, cyclic, and aromatic alcohols. In order to carry out a quantification of these species, a GC×GC system coupled with a Flame Ionization Detector was implemented using combination B. Thus it was possible to access to a global alcohols content of this naphtha cut with a distinction between the three classes using the previously calculated response factors. The global alcohol content of this cut is 14% w/w. It was concluded that 90% of the alcohols are aromatic, 5% w/w are linear, and 5% w/w are cyclic. A detailed quantification of these species is given in Figure 3-10. When injecting the sample five times, the coefficient of variation is always below 20% what shows that the method gives similar results from one injection to another. All errors are represented in Figure 3-10. As no coelutions appear for combination B, as response factors are taken into consideration and as results show low variation from one analysis to another, it can be concluded that this quantification has a great precision. This consists in the first quantification established so far in the literature for a coal derived naphtha cut. However many researches were achieved on the atmospheric gas oil cut and also show that the predominant oxygenated compounds are phenols [10, 18].

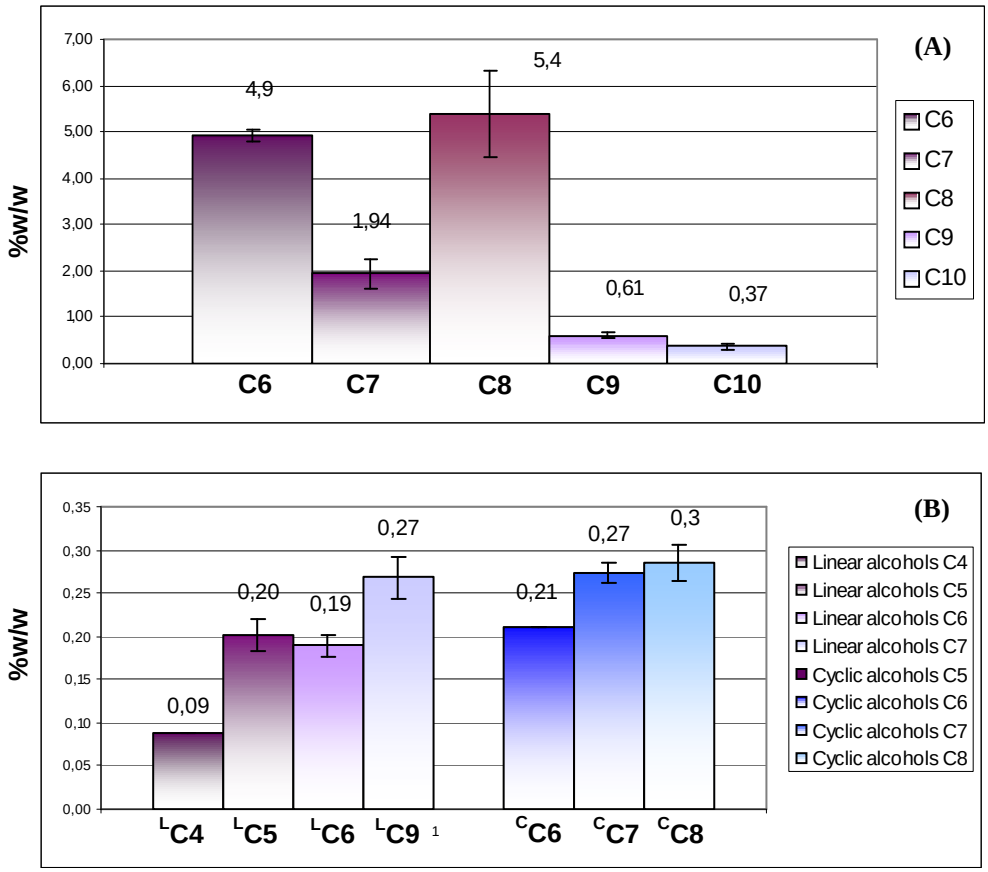


Figure 3-10. Detailed quantification of phenols (A) and other alcohols (B) using response factors by carbon atom number of the molecules

A quantification of hydrocarbons was also established and leads to the proportions of paraffins, naphthenes and aromatics in the sample (Table 3-8). However, the separation between paraffins and naphthenes is not very resolutive in the beginning of the analysis. Thus, the quantification results must be taken as estimation. Moreover, test mixtures show that some of the oxygenated compounds identified with the solgelwax x DB-1 columns set (furans and ketones) elute in the aromatic area. Therefore, not only aromatics are integrated and their content is overestimated.

Table 3-8. Hydrocarbons quantification in the coal-derived naphtha using GC×GC-FID (Solgelwax x Rtx-200)

Hydrocarbon family	*Content in the sample (%w/w)*
Paraffins	8
Naphthenes	56
Aromatics and naphtheno-aromatics	22

3.3.4 Comparison of the three techniques

It is clear that comprehensive two dimensional gas chromatography offers the highest performances in terms of selectivity and peak capacity and consequently in terms of resolution. For the analysis of a few targeted compounds, GC-GC enables to reach a higher resolution than GC×GC as a longer column can be used as a second dimension. However, this technique cannot be applied to the investigated sample as there are more than a hundred of targeted analytes. Thus, to reach a characterization of all oxygenated compounds, the number of cuts would be so important that it would almost be equivalent to use a comprehensive system. Moreover, its hyphenation to a FID detector did not allow any identification and as this technique was finally not selected, the hyphenation with a mass spectrometer was not established.

Concerning GC-ToF/MS analysis, although one-dimensional gas chromatography is insufficient to unravel such matrices, the use of the detection ion monitoring can lead to the identification of many compounds. In addition, more than a hundred compounds could be identified by GC×GC-ToF/MS while only ten compounds were identified by GC-ToF/MS.

For quantitative analysis the use of response factors makes the FID detector very adapted as it is linear for all hydrocarbons. However, the same analysis must be achieved with a mass spectrometer to identify the peaks of interest. Therefore, the dual analysis by GC×GC-ToF/MS and GC×GC-FID enables both identification and quantification of oxygenated compounds. Concerning one-dimensional gas chromatography, there are two many coelutions to envisage any quantification.

3.4 Conclusion

This study shows the improvement in terms of oxygenates characterization using more and more sophisticated gas chromatographic techniques. A few oxygenated species contained in a direct coal liquefaction naphtha could be identified by GC-ToF/MS. The limitations consisting essentially on the presence of coelutions between oxygenates and hydrocarbons can be overcome by using a heart-cutting system. Nevertheless this advanced technique which is ideal for targeted compounds identification is not sufficient in the case of such complex matrices and comprehensive techniques must be deployed. In fact, thanks to two columns sets, more than a hundred oxygenates were identified using GC×GC-ToF/MS. These belong to five main families: alcohols, phenols, ketones, acids, and furans. Phenols and alcohols were fully quantified by using response factors of the FID detection. Such a detailed characterization of O-compounds in a coal derived naphtha has never been reached so far and is essential to convert them into a fuel which fits engines requirements.

Concerning perspectives, this method should be adapted to the middle distillate in order to reach a similar characterization of alcohols and phenols. Even if most of ketones, furans and acids were identified, they do not elute in a specific zone. Thus GC×GC should also be complemented by other analytical tools. Both of these two perspectives will be achieved in the next chapter which presents a multi-technical analytical approach common to the coal-derived naphtha and AGO.

CHAPTER 4. A novel analytical approach for oxygen speciation in coal-derived liquids [5]

FOREWORD

GC×GC increased the separation power as described in chapters 2 and 3, but coelutions still occurred between ketones, furans, carboxylic acids and hydrocarbons. The originality of this chapter is based on the development of a complementary analytical approach to overcome GC×GC limitations and describe the composition of the two coal-derived distillates as completely as possible.

Two-dimensional gas chromatography (GC×GC), high resolution mass spectrometry (FT-ICR/MS), nuclear magnetic resonance (NMR), and UV-visible spectroscopy were applied to these two matrices. Quantification of alcohols and phenols by carbon atom number is also allowed by GC×GC-FID using the latter method. It shows that the carbon atom number varies from 6 to 11 for phenols and from 4 to 9 for alcohols. Similarly, carboxylic acids distribution by alkylation degree can be obtained by combining FT-ICR/MS and NMR results.

Among 2.89 %w/w of elemental oxygen present in the naphtha cut, 1.78%w/w O corresponds to phenols, 0.08%w/w O to alcohols and 0.21%w/w O to ketones. Concerning carboxylic acids, they are negligible (<0.01%w/w). Thus, a total of 2.07%w/w O is quantified what represents 72% of the oxygenated compounds contained in the naphtha cut. Similarly, in the atmospheric gas oil cut, among the 0.80 %w/w of elemental oxygen, 0.62%w/w O are attributed to phenols, 0.07%w/w O to alcohols, and 0.015%w/w O to ketones. Benzo and dibenzo-furans may represent the species which have not been quantified. This unique multi-technical approach offers a detail level which was never reached so far in terms of oxygenated compounds characterization for such products.

[5] This chapter is based on an article which was published in Fuel, 2012 *in press* by Omais *et al.*

4.1 Introduction

Considering the global energetic context, diversifying the liquid fuel supplies for the transportation field is of the upmost importance and many alternatives are promising. Coal-derived products surely appear among the new generation substitutes and come from two fundamental process schemes: direct coal liquefaction (DCL) based on research pioneered by Friedrich Bergius, and indirect liquefaction based on Fischer and Tropsch work after gasification [117].

DCL products characteristics are quite far from fuel specifications; thus, upgrading must be applied to the naphtha and atmospheric gas oil cuts. In fact, compared to petroleum products, these cuts contain less linear alkanes (paraffins), and much more cyclic alkanes (naphthenes); aromatic and naphtheno-aromatic structures are also present in relatively high concentrations [118]. Concerning heteroatomic species, nitrogen and oxygen-containing compounds are predominant compared to sulphur-containing species (<0.1%w/w S).

To envisage the use of coal-derived liquids as alternative fuels to petroleum products, it is necessary to have a deeper insight on their chemical and physical properties. Except hydrocarbons, the needs in terms of molecular characterization enhancement concern oxygenated compounds. These species belonging to different chemical families, are present in relatively high concentrations (0.5-3%w/w O) compared to usual fuels, and have not been characterized as fully as the predominant hydrocarbon components. The literature survey presented in chapter 1 shows that many analytical strategies were used to improve the knowledge of oxygenated compounds in coal-derived products [118]. These are focussed on two classes of oxygen-containing species: phenols [18] and furans [10, 16, 94]. Even if pursued techniques enabled to approach the compositions of these two families, many gaps remain and quantification is quite often non-existent. Strategies involving sample preparation or multi-coupled systems have been deployed to respond to the matrix complexity, but the separation of all oxygenates from hydrocarbons remains a hard task. The two previous chapters show that comprehensive two-dimensional gas chromatography (GC×GC) is very efficient for the characterization of phenols and alcohols; this technique allows the improvement of selectivity and peak capacity compared to one-dimensional gas chromatography. Besides, ESI (-) FT-ICR/MS (Negative Electrospray Ionisation - Fourier Transform Ion Cyclotron Resonance Mass Spectrometry) enables to deeply improve the knowledge of acidic O-compounds in coal derived vacuum gas oils [88, 89, 119]. Moreover, a series of articles published by Verkade and co-workers shows that it is possible to characterize labile H functionalities by ^{31}P NMR after

derivation of targeted compounds using phosphorous-containing reagents [79, 80, 86, 95, 120] in coal materials: phenols, aliphatic alcohols and carboxylic acids. Finally, to evaluate the carbonyl content, a standard spectrophotometric method is also available in the literature (ASTM E411) [121]. However, this technique was never applied to coal oils as no work has demonstrated the presence of carbonyl groups so far.

It appears that none of these techniques permits the characterization of all oxygenated compounds in one single analysis. However, the complementarity of these four analytical tools should be investigated to describe as completely as possible the oxygenates distribution in coal-derived liquids. Therefore, the objective of the present work is to use the combination of comprehensive two dimensional gas chromatography, high resolution mass spectrometry, ^{31}P NMR and UV-visible spectroscopy to enhance the knowledge of oxygenated species in coal derived liquids. Qualitative and quantitative data resulting from this work will be discussed in order to confront results obtained by the different techniques. Thanks to this approach, a global quantification of oxygenated species present in two coal-derived distillates is accessible and can be useful for hydroprocessing studies aiming to produce alternative fuels.

4.2 Materials and methods

4.2.1 Samples

The reference sample is obtained from a pilot. It was obtained by two-stage direct liquefaction of a sub-bituminous coal in the presence of a catalyst, with an H-donor solvent (VGO fraction) at high temperature (440-460°C) and high pressure (150-180 bars). Two distillates produced from this liquid were used: a naphtha cut (IBP-200°C), and an atmospheric gas oil cut (200-350°C). These fractions were provided by IFP Energies nouvelles and simulated distillation shows that the 5%-95% boiling points of the fractions are [36-222°C] and [232-344°C] respectively for the naphtha and the AGO cut. Elemental compositions of each cut are displayed on Table 4-1. The hydrogen content is determined by NMR (ASTM D4808), the carbon content is determined by combustion (ASTM D5291), the nitrogen content is measured by chemiluminescence (ASTM D4629), the sulfur content is provided by X-ray fluorescence (ASTM D2622), and the oxygen content by pyrolysis followed by

infrared detection (internal method). The density of the samples (NF EN ISO 12185) is 0.8224g/cm^3 for the naphtha cut and 0.9330g/cm^3 for the AGO cut.

Table 4-1. Elemental composition of the two coal-derived distillates

	Naphtha cut	*AGO cut*
C %w/w	84.3	87.5
H %w/w	12.6	11.4
O %w/w	2.89	0.8
N %w/w	0.09	0.2
S %w/w	0.03	0.007

4.2.2 Gas chromatography analysis

A LECO Pegasus IV (LECO, St. Joseph, MI, USA) GC×GC-ToF/MS and a Trace GC×GC-FID (Thermo, Italy) were used respectively to identify and quantify oxygenated compounds in the two distillation fractions. GC×GC-ToF/MS experiments were achieved with a HP 6890 chromatograph which was equipped with a split injector. For both chromatographs (GC×GC-FID (Themo, Italy) and GC×GC-ToF/MS (Agilent and LECO)), the injection (0.3µL) was carried out at 250°C for the naphtha cut and 320°C for the AGO cut with a split ratio equal to 1:100. Oven temperature was programmed from 30°C to 250°C for the naphtha and from 50°C to 280°C for the AGO, both at 2°C/min. A Solgelwax column (Poly ethylene glycol 30m×0.25mm×0.25µm) was used in the first dimension and coupled either to a DB-1 column (Polydimethyl siloxane 1m×0.1mm×0.1µm) or to a Rtx-200 column (Trifluoropropyl 1m×0.1mm×0.1µm) with modulation periods respectively equal to 12 and 7 seconds (to cope with the retention difference between the two second dimensions).

Detection was established with a flame ionization detector (FID) for quantification and with a time-of-flight mass spectrometer (ToF/MS) for identification purpose. The FID system was set at 380°C. H_2, air, and He makeup were set respectively at 35, 450, and 25mL/min. Concerning the ToF/MS analysis, it was performed with an acquisition frequency set at 100 Hz in a mass range of m/z 75-500. Electron ionization was achieved at 70eV and a multiplate voltage of -1450V was applied.

4.2.3 Mass spectrometry analysis

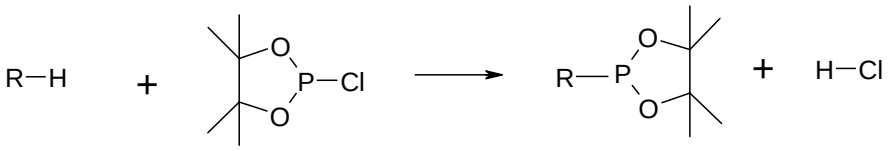
FT-ICR/MS (Fourier Transform Ion Cyclotron Mass Spectrometry) analyses were achieved using a Thermo Scientific LTQ FT Ultra (Bremen, Germany). It is composed of a linear ion trap and an ion cyclotron resonance cell located in a 7T superconducting magnet. The coal derived atmospheric gas oil was diluted in methanol with a 1:1000 ratio prior to injection by syringe infusion pump at a flow rate of 5µL/min. Methanol was the solvent used for the transfer of the fraction into the ESI source. It was ionized by electrospray in the negative mode (ESI -) which enables the ionization of polar acidic species.

Mass spectra were acquired with 64 microscans which were co-added prior to the Fourier Transform to reduce electronic noise and improve the signal-to-noise ratio of the resulting mass spectra. A resolution of 100,000 at m/z= 400 (Full Weight Height Medium) and a mass range set at m/z 50-750 were used. External mass calibration was achieved with a CalMix Proteomass mixture provided by Supelco (Bellefonte, PA, United States).

Data were acquired with Xcalibur software (Thermo Fisher Scientific, Bremen, Germany). The generated database only contains peaks with a signal-to-noise ratio higher than six times the standard deviation of the baseline noise. The mass spectra and Kendrick diagrams were built thanks to homemade software which enables to calculate and assign an elemental formula to each peak.

4.2.4 ^{31}P Nuclear Magnetic Resonance analysis

^{31}P NMR spectra were obtained on a Brucker Avance 600 spectrometer with a BBI 5 probe operating at 600 MHz. Samples were derivatized using 2-chloro-4,4,5,5-tetramethyl-1,3,2-dioxaphospholane provided by Sigma-Aldrich (Saint Quentin Fallavier, France) in a 5mm NMR tube. For a classic experiment, around 35mg of the coal derived samples (naphtha and atmospheric gas oil) was introduced in the tube with 100µL of pyridine, 100µL of an internal standard, 100µL of the derivatizing agent, and 400µL of $CDCl_3$. The internal standard is a mixture of 0.80g of cyclohexanol with 100mL pyridine. The analysis is carried out at least one hour later at room temperature. The derivatization reaction is shown in Equation 4-1.

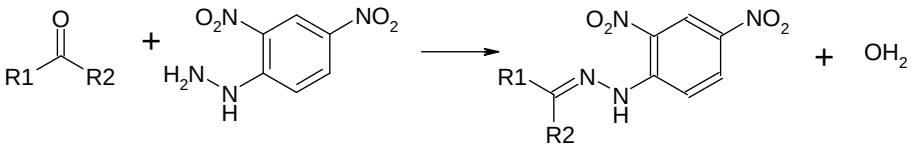


(Equation 4-1)

4.2.5 UV-visible spectroscopy analysis

The apparatus used in this study is a CARY-1E spectrometer (Varian, Les Ulis). The method consists in determining the total carbonyl content in petroleum samples and refers to ASTM E 411 standard method. The carbonyl number is determined by UV-spectroscopy. A calibration curve is used to deduce the carbonyl content (in mg/L) from the measured absorbance. This calibration is established using 4-ethylacetophenone diluted in toluene.

A known volume of sample reacts with an acidic solution of 2,4-dinitrophenylhydrazine to form a phenylhydrazone as follows:



(Equation 4-2)

Then, potassium hydroxide is added to convert the yellow phenylhydrazone into a red compound presumably due to a quinoidal ion. The absorbance of the red color at 480 nm, which is a function of the carbonyl concentration must be measured photometrically shortly after sample preparation as it is not stable. The carbonyl content is determined using a calibration curve (equation 3).

$$C = \frac{d}{V} \times \left(\frac{A - b}{a} \right)$$ **(Equation 4- 3)**

C: concentration of carbonyl in (mg/L)

d: dilution factor

V: volume of the introduced aliquot (L)

A: absorbance of the sample solution

b: intercept of the calibration curve

a: slope of the calibration curve

4.3 Results and discussion

4.3.1 Methodology

As shown in Figure 4-1, the first step of the multitechnical analytical approach involved comprehensive two dimensional gas chromatography which offers higher resolution than GC. As stated in two previous chapters, the Solgelwax × DB-1 combination enables the determination of more than a hundreds of oxygenated compounds belonging to five chemical families by GC×GC-ToF/MS: alcohols, phenols, carboxylic acids, ketones and furans. Then, the Solgelwax x Rtx-200 columns combination allowed the quantification of alcohols and phenols thanks to the selectivity of the trifluoropropyle stationary phase and the use of determined response factors of the FID detector.

To confirm and complement these results, high resolution mass spectrometry FT-ICR/MS was used in a negative mode electrospray. It is concluded that some phenols which were not detected using GC×GC should be present in the atmospheric gas oil cut. Moreover, the analysis highlights a carboxylic acids family which could not be identified by the previous technique.

Therefore, ^{31}P NMR after phosphytilation was applied to both fractions to confirm the content of phenols and determine the carboxylic acids content. There remained two chemical families which were coeluted with hydrocarbons in GC×GC and could not be quantified: furans and ketones. Thus, UV-visible spectroscopy was used to determine the ketones content. To finish, by assuming that no other oxygenated family is present, furanic content was determined by difference.

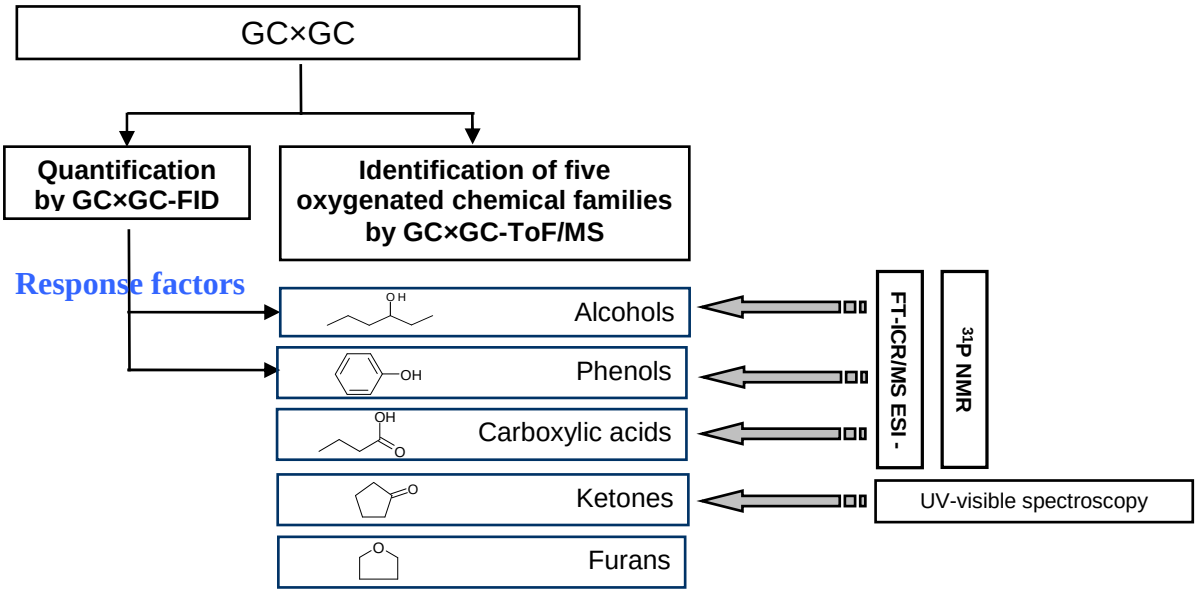


Figure 4-1. Methodology implemented for the characterization of oxygenated compounds in the naphtha and the atmospheric gas oil cuts.

4.3.2 Detailed quantification of alcohols and phenols by GC×GC

As reported in previous works[112], the combination of a Solgelwax (Poly ethylene glycol) and a DB-1 (Polydimethyl siloxane) columns reveals the presence of five oxygenated chemical families in coal-derived liquids: aliphatic alcohols, phenols, carboxylic acids, ketones, and furans. However no quantification of these species was accessible because there remained too many coelutions with the predominant hydrocarbon compounds.

Thus, an Rtx-200 (trifluoropropyl methyl) column was used in the second dimension. A selective separation of phenols and alcohols was obtained due to the unique selectivity resulting from the interaction of the stationary phase with the electronegative centers. A modulation period of 7 seconds could be selected because this stationary phase is less retentive than the DB-1. The resulting chromatograms obtained for the naphtha and the atmospheric gas oil cuts are displayed in Figure 4-2. For both cuts, paraffins, naphthenes, aromatics, alcohols and phenols are well separated. However, no distinction between ketones, furans and aromatics is possible.

As phenols and aliphatic alcohols are well separated, it is possible to quantify them in the two distillates. For this purpose, GC×GC-FID was used and average response factors of the FID detector were determined for each family taking into account 7 phenols and 4 alcohols. The quantification of all species belonging to these two families by carbon atom number is shown in Table 4-2.

Concerning the naphtha cut, phenolic compounds are predominant with a high content of phenol and xylenol (respectively 32.3%w/w and 43.3%w/w of the total phenolic content). Alcohols are essentially aliphatic with an alkylation degree varying from 4 to 8. Both alcohols and phenols represent an elemental oxygen content equal to 1.86%w/w which represents 64%w/w of the total elemental oxygen content of the sample measured by a pyrolysis-infrared detection. The elemental oxygen content determined by GC×GC can be calculated thanks to equation (4).

$$O_{Elemental}^{GCxGC} = \sum \frac{C_i * nM_O}{M_i} \qquad \text{(Equation 4-4)}$$

Where $O_{Elemental}^{GCxGC}$ is the elemental oxygen content calculated by GC×GC, C_i is the concentration of compound i, M_i its molecular mass, n its number of oxygen atoms, and M_O the oxygen molecular mass (M_O =16 g.mol^{-1}).

Concerning the atmospheric gas oil cut, no aliphatic alcohols are detected; phenolic compounds represent 78% of the global elemental oxygen content measured by pyrolysis-infrared detection. However, almost 50% of the phenols were not identified because of the lack of resolution and the bleeding of the stationary phase. As demonstrated in the literature, phenols alkylation degrees vary from C6 to C10 with a Gaussian distribution [18, 112]. It should be mentioned that indanols and tetrahydro naphthalenols are also identified and quantified as phenols. The two cuts were injected five times each to calculate precisions which are compiled in Table 4-2. The quantification limits were also calculated and are below 50µg.g^{-1}. Concerning furans and ketones, they are co-eluted with hydrocarbons and their quantification must be determined by other techniques.

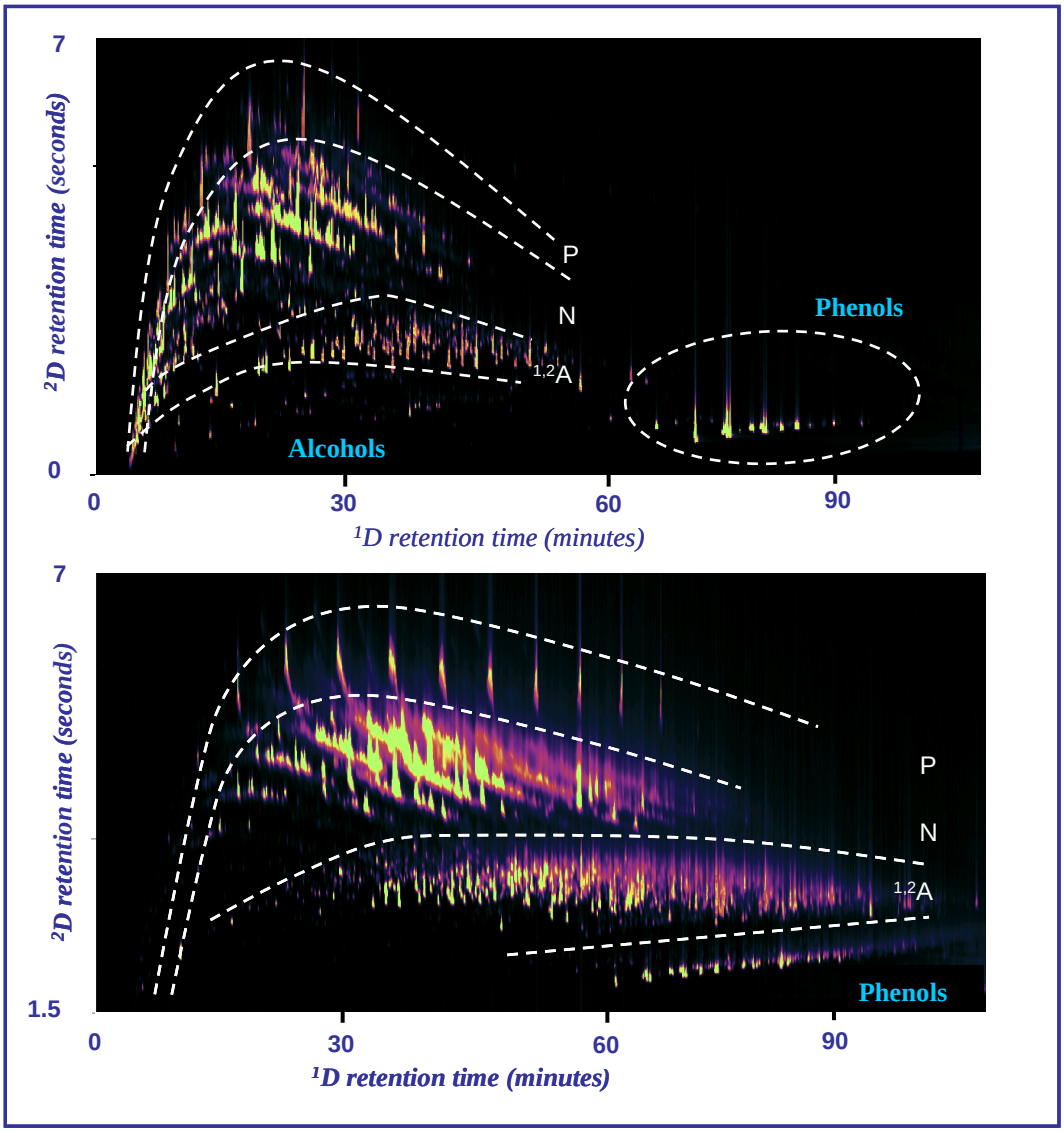


Figure 4-2. GC×GC-ToF/MS chromatograms of the naphtha cut presented in chapter 3 (Top) and the atmospheric gas oil cut (Bottom). Columns set: Solgelwax × Rtx-200. P: Paraffins, N: Naphthenes, ^{i}A: Aromatics with i rings.

Table 4-2. Quantification of alcohols and phenols in the two coal derived distillates using GC×GC. LoQ stands for Limit of Quantification

	Naphtha (%w/w)	*AGO (%w/w)*
Phenols C6	4.9 ± 0.13	0.1± 0.02
Phenols C7	1.9 ± 0.31	0.3 ± 0.06
Phenols C8	5.4 ± 0.93	0.7 ± 0.05
Phenols C9	0.6 ± 0.07	1 ± 0.1
Phenols C10	0.4 ± 0.06	0.3 ± 0.07
Phenols C11	<LoQ	<LoQ
Phenols (unknown)	<LoQ	3.1 ± 0.3
Total Phenols	**13.2 ± 1.5**	**5.5 ± 0.3**
Alcohol C4	0.03± 0.01	<LoQ
Alcohol C5	0.07 ± 0.02	<LoQ
Alcohol C6	0.2 ± 0.01	<LoQ
Alcohol C7	0.2 ± 0.03	<LoQ
Alcohol C8	0.08 ± 0.02	<LoQ
Alcohol C9	0	<LoQ
Total alcohols	**0.58 ± 0.08**	**<LoQ**

4.3.3 Identification of phenols and carboxylic acids by FT-ICR/MS in the coal derived AGO

FT-ICR/MS analysis enables the selective and non-quantitative identification of acidic polar compounds by ESI (-) [88-89]. Data treatment is achieved with a home-made software called Kendrick Inside. The mass spectrum shown in Figure 4-3.A representing the molecular mass distribution from 100 to 600 Da is centered on about 300 Da. The Kendrick diagram gives a classification of heteroatomic acid compounds by alkylation degree in the x-axis and the RDBE (Ring Double Bond Equivalent) in the y-axis. The resulting profile which is typical of a coal-derived liquid is presented in Figure 4-3.B. Each spot on this diagram corresponds to one raw formula and six of them seem to correspond to the phenols (red square in Figure 4-3.B). These are plotted individually in Figure 4-4 which shows that the characterization is consistent with GC×GC results except that a phenol containing eleven carbon atoms is revealed. Two reasons may explain that this compound was not identified by GC×GC: the low content of the molecule or the coelution of this molecule with other hydrocarbons. The hypothetical presence of carboxylic acids is also highlighted by this technique and was not evidenced by GC×GC because of the high limit of quantification for such species without any prior derivatization step. In accordance with Wu et al works [88], response of these compounds using ESI (-) is very intense as they are acidic. Figure 4-5 shows the Kendrick diagram of this family and the molecular structure that can be associated to some series of compounds. However, the raw formulae may correspond to other compounds such as polyalcohols

even if their presence would be surprising considering the literature [93]. Palmitic acid (C16) and stearic acid (C18) spots are more intense than the others what can be explained by a contamination of the coal-derived liquid by the user. In fact, the limit of detection of these species by FT-ICR/MS is below 10-7 %w/w.

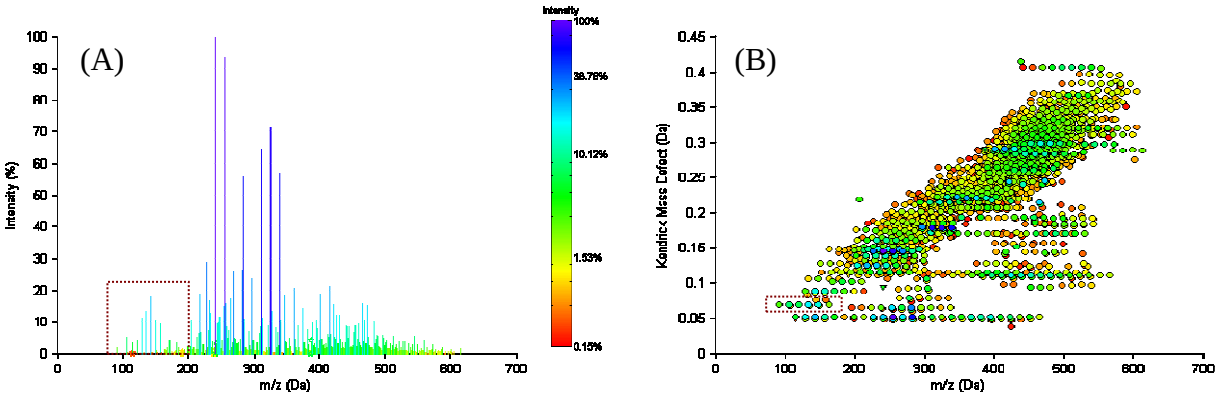


Figure 4-3. Mass spectrum (A) and Kendrick diagram (B) obtained by FT-ICR/MS ESI (-) for the coal derived AGO

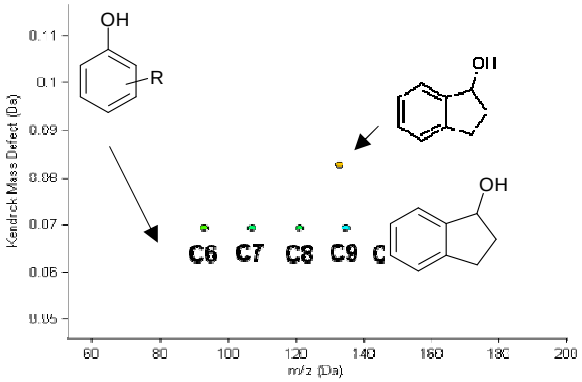


Figure 4-4. Kendrick diagram of the coal-derived AGO showing phenolic compounds spots.

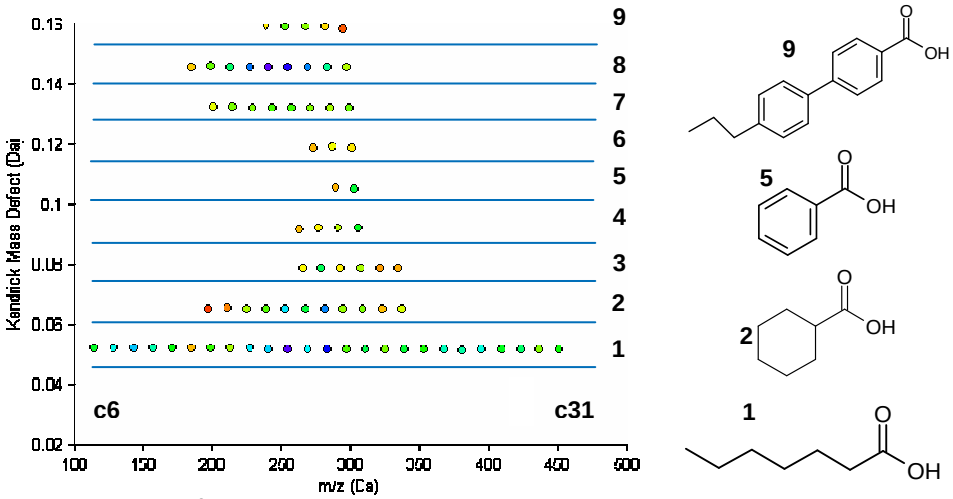


Figure 4-5. Kendrick diagram of the coal-derived AGO showing O2 spots. Numbers correspond to Ring Double Bond Equivalents and structures represent hypothetic corresponding carboxylic acids.

4.3.4 Global quantification of alcohols, phenols and carboxylic acids by ^{31}P NMR

In recent years there has been substantial success in utilizing reagents such as 2-chloro-4,4,5,5-tetramethyl-1,3,2-dioxaphospholane (TMDP) as ^{31}P NMR spectroscopic tags for speciating and quantifying total alcohols, phenols and carboxylic acids [80-83, 86, 95, 120]. In this work, the technique was applied to the two coal-derived distillates and the corresponding spectra are shown in Figure 4-6. The assignment of a family to the different zones was achieved according to the literature [80]. Alcohols are located between 150.3 and 140.3ppm, phenols between 140.3 and 136.5ppm, and carboxylic acids between 136.5 and 134.5ppm. Two other signals were also obtained at 175.5 and 132.7ppm. They correspond respectively to the derivatizing agent in excess and its hydrolysis product. The peak located at 145.6ppm corresponds to cyclohexanol which is used as an internal standard. Concerning the 134.5-126ppm zone, the signal has been attributed to amines even if their chemical shifts range from 130.5 to 152ppm [80]. In fact, these species are suspected to be present as raw formulas of anilines were evidenced by FT-ICR/MS in the positive electrospray ionization mode. This technique also highlights other raw formulas which might correspond to quinolines and indoles. To reach a molecular insight on nitrogen-species, GC×GC-NCD was applied to the atmospheric gas oil fraction and the mass distribution of nitrogen species shows that anilines are minor species among the 0.2%w/w of nitrogen elemental content as they represent less than 3%w/w of the nitrogen species, whereas quinoleines represent more than 60%w/w of the nitrogen species. These results will not be presented in the present dissertation as the focus is on oxygen speciation. However, they show that errors due to the chemical shifts of derivatized amines should be negligible using NMR.

From these NMR spectra, the concentration of each hydroxyl functional group was calculated on the basis of the hydroxyl content of the internal standard and its integrated peak area (Table 4-3). Results trend is consistent with GC×GC as it shows that phenols are the predominant oxygenated compounds in both distillates. The results are expressed in OH%w/w which stands for the hydroxyle w/w content of the family in the whole sample. Phenolic OH represents 2.19 OH%w/w of the naphtha cut and 0.612 OH%w/w of the atmospheric gas oil cut. To finish, less than 0.017%w/w of carboxylic acids OH are quantified in these products using ^{31}P NMR. It is not surprising that these species did not respond in GC×GC as gas chromatography is not very adapted to the analysis of these compounds because of strong peak tailing if no prior derivatization step is achieved.

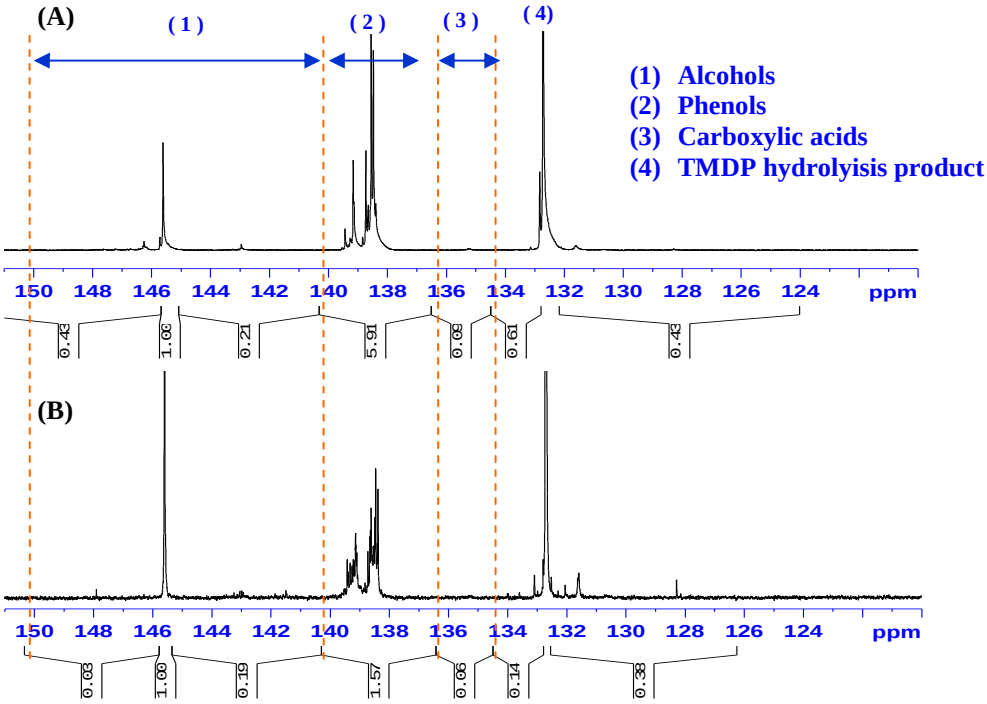


Figure 4-6. Quantitative ^{31}P NMR spectra of the naphtha cut (A) and the AGO cut (B) after phosphytilation

Table 4-3. Alcoholic OH, phenolic OH and carboxylic acids OH quantification by ^{31}P NMR

	Alcoholic OH (OH%w/w)	*Phenolic OH (OH%w/w)*	*Carboxylic acids OH (OH%w/w)*
Naphtha cut	0.24	2.19	0.034
AGO cut	0.085	0.612	0.017

4.3.5 Global quantification of ketones by UV-visible spectroscopy

Experiments by UV-visible spectroscopy were carried out twice and the resulting carbonyl number was averaged from two values (Table 4-4). From the density of each fraction, it is possible to calculate the carbonyl (C=O) content in mg per kilogram. Assuming that there are no aldehydes [112], the elemental oxygen present in ketones (%$O_{ketones}$ w/w) can be determined. According to these experiments, ketones which were never reported in the literature so far, represent 7.1%w/w of the elemental oxygen content (determined by pyrolysis-infrared detection) in the naphtha cut and 1.8%w/w in the atmospheric gas oil cut.

Table 4-4. Elemental content of ketones by UV-visible spectroscopy

	Carbonyl number (mg/L)	*$\%O_{ketones}$ w/w*	*$\%\ O_{ketones}/O_{elemental}$ w/w*
Naphtha cut	2983	0.21 ± 0.01	7.11
AGO cut	239	0.02 ± 0.001	1.8 1

4.3.6 Final quantitative assessment

The objective of this step was to correlate the results obtained by the different techniques. For this purpose, it was decided that all contents had to be expressed in elemental oxygen. Carboxylic acids were detected in such low quantities by ^{31}P NMR that it will be assumed they do not impact the global quantification. Concerning ketones content, it is already expressed in the form of elemental oxygen content. It was also shown in part 3.1 that phenols and alcohols contents can be expressed in that form.

As shown in Figure 4-7, the multitechnical analytical approach shows that among the 2.89%w/w±0.2 of oxygen present in the naphtha cut, 1.78%w/w O corresponds to phenols, 0.08%w/w O to alcohols and 0.21%w/w O to ketones. Concerning carboxylic acids, they are negligible. Thus, a total of 2.07%w/w O is quantified what represents 72% of the total oxygen content of the naphtha cut. Similarly, in the AGO cut, among the 0.80%w/w ±0.1 of elemental oxygen, 0.62%w/w O corresponds to phenols, 0.07%w/w O to alcohols, and 0.015%w/w O to ketones. Thus, 0.7%w/w O is quantified in the middle distillate what represents 87% of the total oxygen content. Assuming that furans are the only other oxygenated compounds, their content may be assessed by difference. However, this value should be considered with precautions.

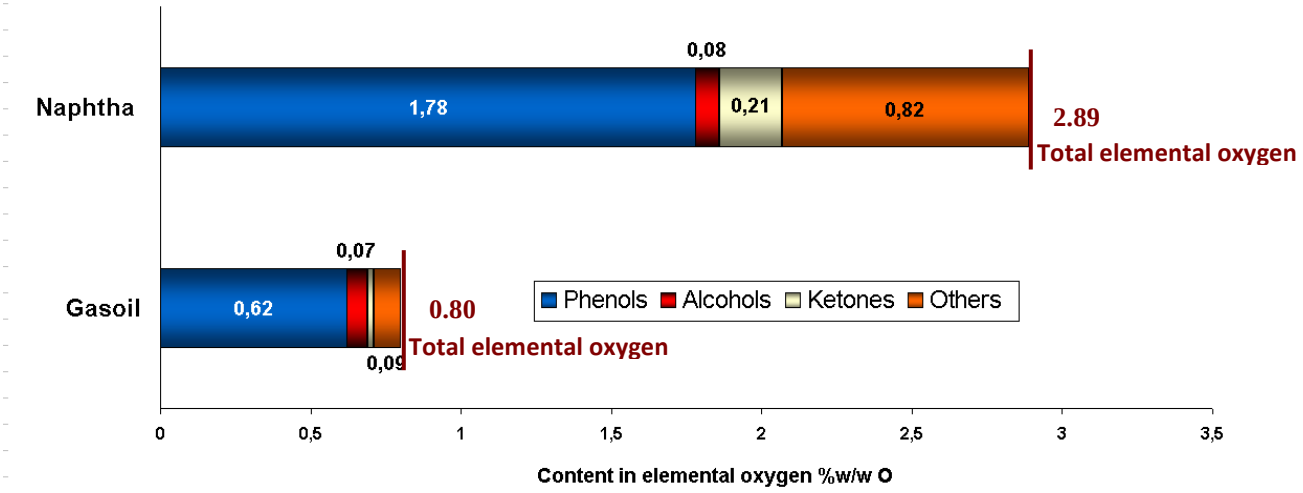


Figure 4-7. Final quantitative assessment for naphtha and AGO cuts obtained from coal-derived liquids.

4.4 Conclusion

The combination of GC×GC, FT-ICR/MS, ^{31}P NMR, and UV-visible spectroscopy techniques leads to a global vision of four oxygenated chemical families present in a coal derived naphtha and atmospheric gas oil. In fact, a detailed molecular characterization of phenols and alcohols was achieved by GC×GC thanks to an original columns combination. Then, FT-ICR/MS enabled to confirm the presence of phenols and identify carboxylic acids which were then quantified by ^{31}P NMR. To finish, UV-visible spectroscopy led to the proportion of ketones among all oxygenated compounds present in both samples. Phenols are the predominant compounds as they represent more than 60%w/w of the oxygenated compounds for both fractions. Ketones which were never highlighted so far in the literature represent 7.1 and 1.8%w/w of the oxygen content present respectively in the naphtha and the AGO cuts. Even if carboxylic acids exhibit an intense response in FT-ICR/MS (ESI-) they are present at low contents in both matrices.

The complementarity of high resolution analytical tools offers a detail level in terms of oxygenated compounds characterization which was never reached so far. A larger vision of the composition of these matrices which is as quantitative as possible can be attained. This information is crucial to evaluate the potential of these liquids as a substitute for fuel and envisage their processing. Furans are supposed to be present in relatively high concentrations according to the literature and pose problems for hydroconversion. Hence, to help process designers and make this analytical approach comprehensive, it is necessary to find a way to quantify this family and check if they do represent the part of uncharacterized oxygenates. For this purpose multidimensional chromatographic systems are developed. However, using GC×GC, it is very hard to separate furanic compounds such as benzo- or dibenzofurans from aromatics. To overcome this resolution problem, a pre separation should be considered.

CONCLUSION OF PART A

The state of the art presented in chapter 1 showed the limitations on coal-derived liquids characterization: lack of resolution using one-dimensional systems, use of preparative steps, lack of quantitative studies and also a focus mainly on phenols. Compared to past studies, the approaches presented in chapters 2, 3 and 4 gives a cartography of most of oxygenated compounds contained in direct coal liquefaction products. Two GC×GC methods dedicated to a coal-derived naphtha and a coal-derived AGO lead to a detailed quantification of alcohols and phenols. These methods are based on a screening of many column combinations and a selection of the most adapted one by specific criteria. Moreover, the quantification is extremely precise as it takes into account the specific response factors of the different oxygenated species.

As the previous analysis does not allow the characterization of carboxylic acids, furans and ketones, complementary techniques were used: FT-ICR/MS enabled to confirm the presence of phenols and identify carboxylic acids which were then quantified by ^{31}P NMR and UV-visible spectroscopy led to the proportion of ketones among all oxygenated compounds present in both samples.

Results show that phenols are the predominant compounds as they represent more than 60%w/w of the oxygen content for both fractions. Ketones which were never highlighted so far in the literature represent 7.1 and 1.8%w/w of the oxygen content present respectively in the naphtha and the AGO cuts. Even if carboxylic acids exhibit an intense response in FT-ICR/MS (ESI-) they are present at low contents in both matrices.

In addition, using a normalization by Py-IR oxygen content, almost 90%w/w of the oxygen content of the atmospheric gas oil cut were characterized, and more than 70%w/w of the naphtha was quantified. The uncharacterized species might correspond to furans for which no technique allowed the characterization. Further investigations on these species are in progress at IFPEN and are based on the use of a derivatization step specific to the lone pairs of electrons contained in furanic species.

This studies are focused on reference samples and for further applications to different coal oils with different origins, the reader should refer to Appendix A2. Moreover, these studies showed results on the naphtha and atmospheric gas oil cuts. Concerning the Vacuum Gas Oil cut, the reader should refer to Appendix A3 showing a comprehensive study of the fraction.

Part B. Oxygen speciation in bio-oil upgrading products

INTRODUCTION TO PART B: OXYGEN SPECIATION IN PARTIALLY UPGRADED BIO-OILS

The previous chapter shows investigations on direct coal liquefaction products. Compared to these previous matrices, partially upgraded bio-oils (PUB) studied in our work are much more oxygenated (10-20%w/w O instead of 0.5-5%w/w O). No distillation was applied to the investigated upgraded PUB. Concerning the oxygenated structures contained in such products, they are much more diversified than those contained in direct-coal liquefaction products.

This part is divided in three chapters. The first step of the approach was to present a state of the art of these products in chapter 5. This literature survey shows that PUBs are extremely complex as they contain a large variety of oxygenated chemical families in a hydrocarbon matrix.

Orthogonal GC×GC conditions generally used for petroleum fractions characterization do not allow the separation of phenolics from aromatic hydrocarbons as these two families involve similar interactions with the second dimension stationary phase (π-π interactions). Chapter 6 shows how a reversed configuration was selected as the most adapted one and allowed the molecular description of carboxylic acids, alcohols, some ketones and furans. Concerning phenols and methoxyphenols, they are separated from hydrocarbons but with an insufficient intra-family resolution.

Therefore, to separate phenolic compounds from hydrocarbons prior to GC×GC analysis, SFC was hyphenated to a GC×GC system in normal configuration (Chapter 7). In fact, ethylpyridine column is very selective towards OH functional groups and allows a pre separation of aromatic-OH compounds which can be analyzed offline or online by GC×GC without coelutions with hydrocarbon aromatics. Consequently, a breakthrough detailed characterization of phenols and naphthols could be obtained.

CHAPTER 5. Characterization of oxygenated compounds in upgraded bio-oils: a critical review [6]

FOREWORD

Biomass fast pyrolysis is considered as a promising technique to produce renewable liquid for the transportation field. However, bio-oils are mainly oxygenated (45-50%m/m O on wet basis) and contain almost no hydrocarbons. Upgrading leads to a liquid with lower oxygen content and characterization of oxygenated compounds in these products is essential to assist conversion reactions.

Many analytical tools were used in the literature to characterize as fully as possible biomass flash pyrolysis upgraded products. Spectroscopic methods such as NMR and FT-IR give information on different oxygenated functional groups whereas gas and liquid chromatography allow a molecular characterization. Recently two-dimensional gas chromatography has also provided a detailed quantification of oxygenated compounds in upgraded bio-oils.

This literature survey gives an overview of oxygenated compounds which can be encountered in biomass flash pyrolysis upgraded products. It has demonstrated a large variety of molecular compositions owing to different catalysts, different resources as well as different process routes. Phenols which are often refractory to hydrotreatment are present in most of upgraded bio-oils at relatively high contents. Some studies highlight esters formation by catalytic and thermal esterification. Concerning carbonyls, they are also present at high concentrations, in particular cyclopentanones, benzaldehydes and cyclohexanones. Other compounds such as syringols, eugenol, benzofurans and anisols are reported in the literature.

This critical review highlights the advantages and drawbacks of different analytical tools and addresses guidelines for comprehensive analyses of upgraded bio-oils. Among the different techniques, multi-dimensional chromatographic systems such as GC×GC and SFC-GC×GC offer bright perspectives, but as no technique is self-sufficient, a multitechnical analytical approach would be interesting as a complement.

[6] This chapter is based on an article submitted in Anal. Chem. in July 2012 by Omais *et al.*

5.1 Introduction

Since the production of crude oil may not meet the increasing demand in the next future, biomass flash pyrolysis oils have sparked great interest as one of the possible substitutes of petroleum in the transportation field [122-124]. This feasible route is a widespread for the production of biomass [124-126].

Fast pyrolysis consists in a thermochemical decomposition of a resource by heating at high temperatures (450-500°C), in a short period of time and in the absence of oxygen [129]. In the present case, the resource is lignocellulosic biomass (wood, hardwood, straw...) which is mainly composed of three macromolecules families which are intimately linked: cellulose [130-131], hemicellulose [132] and lignin [133]. These three families have different properties and reactivities involving different decomposition pathways during pyrolysis. Therefore, degradation products are extremely diversified in terms of chemical structures, molecular masses, and polarities. These products also combine with each other to form other sub-products by radical reactions. The resulting matrix is therefore much oxygenated (30-60%w/w O on wet basis [135-136, 138]) and complex in terms of functional groups diversity.

The molecular description of flash pyrolysis oils has been approached by different analytical tools. Gas chromatography is a solution which is hampered by the large diversity of oxygenated chemical families: ketones, furans, sugars, carboxylic acids, phenols, guaicols, syringols, anisols, esters, alcohols, naphthols, and catechols [137-139]. In addition, sugars are heat-sensitive and are therefore not adapted to GC without any prior derivatization step. Therefore HPLC was used [142-143] and evidenced four main compounds: levoglucosane, glucose, xylose, and cellobiose. Complex oligomeric structures are also present in the pyrolytic lignin fraction and were investigated, in particular by Meier et al. by different techniques: elemental analysis, infrared spectroscopy, and Py-GC/MS [130-131, 143-144]. Propositions of polymers structures were provided by this team [145] by a comprehensive multi-technical analytical approach.

Considering the matrix complexity as well as its thermal and chemical instability, biomass fast pyrolysis oils are far from conventional fuel specifications and cannot be directly processed with petroleum feedstocks. Upgrading consisting mainly on cracking and/or hydrotreating [146] is therefore applied over different catalysts [147] to obtain liquids with lower oxygen content (1-30%w/w O on wet basis). A literature survey shows that the number of publications dealing with

upgraded bio-oils has drastically increased from 2001 to 2011 (Figure 5-1). To assist conversion reactions, it is at that time crucial to gain insight into the composition of these products especially on oxygenated compounds. Characterization of crude bio-oils has been extensively described in the literature compared to upgraded bio-oils. Although both matrices contain a large diversity of oxygenated compounds, the technical problems at stake for the analysis of these two products are different. Raw bio-oils are complex as they contain high molecular weight oligomeric species, heat-sensitive sugars, carboxylic acids, extremely volatile molecules (methanol, formic acid), and as they can hardly be distilled, whereas upgraded bio-oils composition is hard to unravel because they consist on a blend between diversified oxygenates and hydrocarbons.

This article aims to describe as completely as possible analytical studies achieved on upgraded bio-oils and addresses a list of oxygenated compounds which can be found in these matrices. Analytical tools described in the literature will be developed: one-dimensional gas chromatography, two-dimensional gas chromatography, liquid chromatography and NMR and FT-IR spectroscopy. The advantages and drawbacks of each technique will be discussed and perspectives on the "right" way to analyse such matrices will be developed. This state of the art is of considerable importance to assist biomass conversion processes as it gives an exhaustive list of compounds which might be present in such matrices, but is also crucial in the analytical field as it opens bright perspectives on the analysis of complex mixtures.

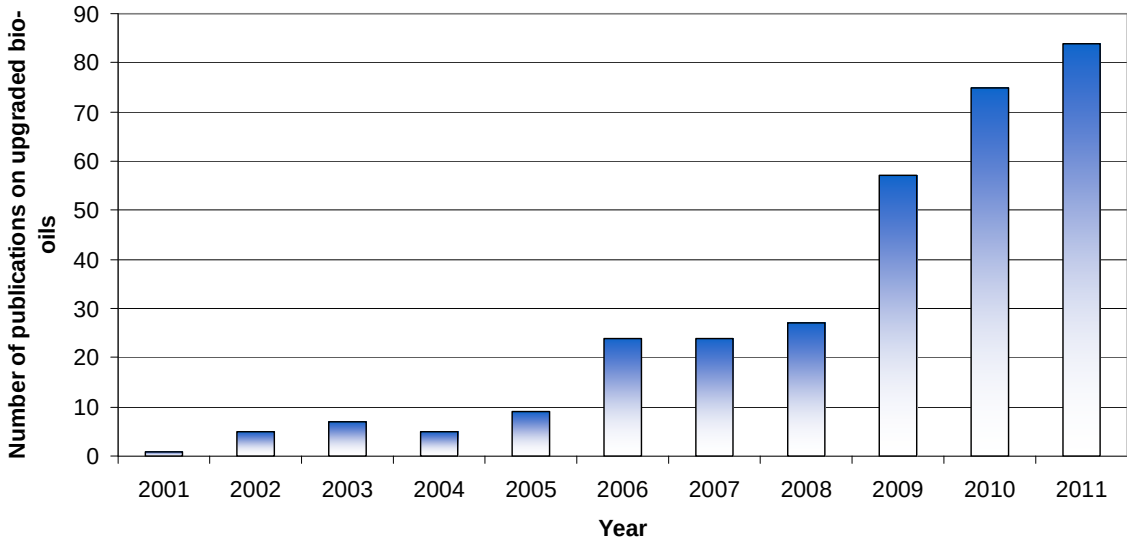


Figure 5-1. Evolution of the number of publications on biomass flash pyrolysis upgrading products from 2001 to 2011. This distribution is based on the number of results when typing "*bio* oil* upgrad" as the topic in Thomson Reuters website** http://portal.isiknowledge.com

5.2 Generalities on upgraded bio-oils

5.2.1 Properties

The chemical composition of upgraded bio-oils is also very different from conventional oil derived from petroleum. While classical petroleum fractions have a very low oxygen content, upgraded bio-oils oxygen content is much higher (Table 5-1).

Treated bio-oils are not compatible with conventional fuels due to their high oxygen content, high solid content, relatively high viscosity and chemical instability. Chemical properties of biomass-derived liquids are clearly influenced by the origin of the resource. In fact, different biomasses have different proportions of cellulose, hemicellulose and lignin involving different pyrolysis products. Secondly, upgraded bio-oils properties depend on the type of treatment applied to the resource (catalytic pyrolysis, deoxy-liquefaction, hydrotreatment (HDT)) and on upgrading conditions (pressure, temperature, catalyst...). Therefore, elemental compositions found in the literature are quite different (Table 5-1). Elemental analyses reported in the literature shows that the H/C ratio of petroleum products is much higher than biomass derived liquids. Moreover bio-oil oxygen content is much lower after upgrading.

Table 5-1. Elemental composition (CHONS) and water content determined by Karl-Fischer titration of different bio-oils from the literature

Reference	***Zhang et al. [153]***	***Zhang et al. [154]***	***Li et al. [155]***	***Guo et al. [148]***	***Williams et al. [156]***	***Xu et al. [157]***
Conversion route	Catalytic HDT	Catalytic HDT	Deoxy-liquefaction	Deoxy-liquefaction	Catalytic pyrolysis	Catalytic HDT
Feed	Biomass pyrolysis oil	Pine pyrolysis oil + solvents	Soybean stalk	Sunflower shells	Woods mix	Pine sawdust pyrolysis oil
Boiling points	Whole upgraded oil	Whole upgraded oil	101-450°C	Whole upgraded oil	Whole oil	Whole upgraded oil
C (%w/w)	87.7	60.9-61.1	80.1	82.2	59.9-79.0	25.0
H (%w/w)	8.9	10.0-10.8	12.7	13.6	1.5-7.8	6.9
O (%w/w)	**3.0**	**28.2-29.1**	**6.5**	**2.9**	**13.3-33.0**	**67.7**
N (%w/w)	0.4	0.0-0.2	0.7	1.3	0.3-0.8	0.39
Water (%w/w)	Unknown	6.5-7.4	Unknown	Unknown	24.0-35.7	58.7

5.2.2 Chemical functional groups

13C and 1H NMR spectroscopies have been widely investigated for the characterization of crude bio-oils in particular complex oligomeric structures present in the pyrolytic lignin [143-144, 188]. These two techniques were investigated to obtain information about the amounts of various organic groups in different upgrading products. Junming et al. [189] evidenced by 1H NMR that a large number of protons was aliphatic H adjacent to oxygen (Figure 5-3). Moreover protons of aliphatics (0.4-1.8 ppm) and aldehydes (8-9 ppm) are present at a high content (respectively 40%w/w and 11.3%w/w). Wildschut et al. analysed upgraded oils (over Ru/C and Pd/C catalysts) by the same technique. Only one article presents 13C NMR analysis of upgraded bio-oils [161]. It shows that most of carbons are aliphatic or aromatic, but also highlights the presence of carbonyl, carboxyl, phenolic, and ether carbons.

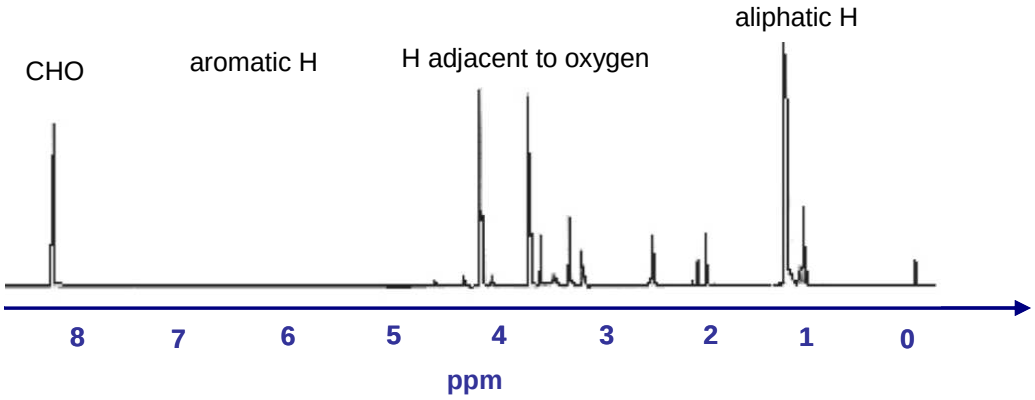


Figure 5-2. ^{1}H NMR spectra of an upgraded bio-oil [189]

The use of 17O nuclei NMR is absent in the literature because spectra are very noisy [85]. Detection of these nuclei is difficult because of their low natural abundance, quadrupolar nature, and low receptivity. To overcome this problem 31P NMR after phosphilitation of the sample labile protons has sparked great interest for the analysis of oxygenates in coal-derived products as described in chapter 4. As previously mentioned, a series of articles published by Verkade and co-workers focus on quantification of phenolic compounds contained in coal liquids. This analysis which lasts 105 min (without derivation) is amenable for a large range of solvents, and very selective toward the OH, NH and SH functional groups. This quantitative method would be

interesting for application to upgraded bio-oils as the groups of phenols, carboxylic acids and alcohols can be selectively quantified [79-86].

Besides FT-IR provides information on structural groups present in upgraded bio-oils. Vitolo et al. [190] have applied this technique to study two oils obtained by upgrading of a flash pyrolysis oil over two HZSM-5 zeolites differing on their silica-alumina ratio at 450°C. IR spectra evidenced the aromatization of the crude oil by the absorbance bands in four regions: 3100-3000cm-1 (aromatic C-H stretching vibration), 1600-1450cm-1 (C=C stretching vibration), 1300-1000cm-1 (in plane bending vibration of the Ar-H) and 900-650cm-1 (out-of-plane bending vibration of the Ar-H). Oxygenated organic groups are also evidenced by five regions: 3545-3400cm-1 (bands of the free and associated O-H stretching vibration, 1246 and 668 cm-1 OH group in and out-of plane bendings, 1066cm-1 (C-O stretching vibration), and 1721cm-1 (C=O stretching vibration). These different absorbance regions were used by another team [189] to highlight the presence of phenols, water and alcohols (3500-3200cm-1 region) as well as the existence of esters which corroborates their catalytic esterification theory. As an example, Figure 5-3 published by Vitolo *et al.* [190] reports the compositional change of the upgraded bio-oils along time with a fresh HZSM-5/50 catalyst.

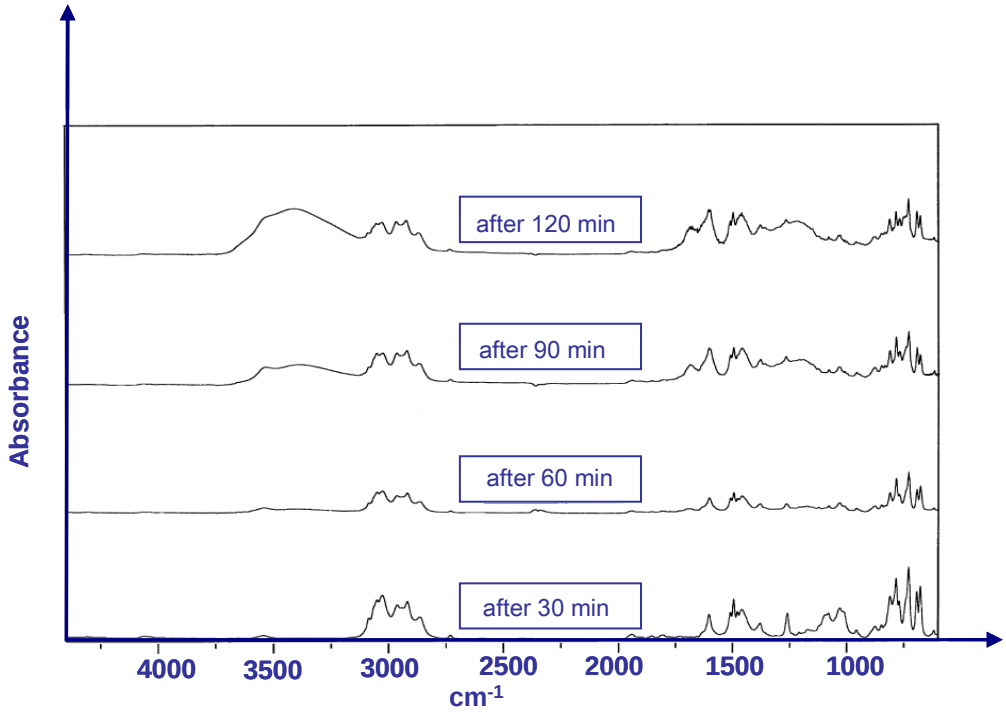


Figure 5-3. FT-IR spectrum of an upgraded bio-oil along residence time [190]

In conclusion, spectroscopic methods enable a fast overview of the different chemical oxygenated functional groups present in these oils. They can be sufficient to evaluate the potential of conversion routes but must be complemented by chromatographic techniques to reach a molecular characterization. Dosy NMR was never applied to such products and would be interesting as demonstrated in recent works [168].

5.3 Characterization by one-dimensional gas chromatography

Our literature survey shows that gas chromatography is by far the most investigated analytical technique for the characterization of upgraded bio-oils. Indeed, since 2001, 70% of the articles dealing with the characterization of upgraded bio-oils use this technique. In general, among the different detectors which can be coupled to gas chromatography, Flame Ionization Detectors (FID) and quadrupole Mass Spectrometers (qMS) are the most widespread. The advantages of the FID (i.e. robustness, universality and linear response to hydrocarbons) have been demonstrated through the analysis of petroleum products whose standard retention times are well described [159-160]. However, as upgraded bio-oils have emerged, their molecular composition is unknown and the first logical step for their characterization is the use of an informative detector. That is why mass spectrometry represents 95% of the detectors used in the literature for the characterization of such matrices. This value is based on the survey of 21 articles published from 2001 to 2011. Moreover the O-FID (see part 1.3) was never used for such products as it sensitive towards water which is often present in upgraded bio-oils.

Recently, GC/MS was investigated by Christensen et al. [161] for the analysis of light cut (IBP-71°C), naphtha (71-182°C), kerosene (182-260°C), and atmospheric gas oil cuts (260-338°C) of three hydrotreated bio-oils with different oxygen contents (8.2, 4.9, and 0.4%w/w O). In the three fractions derived from the upgraded bio-oil with an 8.2%w/w O oxygen content, many oxygenated chemical families were tentatively identified: carboxylic acids, alcohols, esters, furans, ketones, and phenols. Predominant O-species highlighted by this study are phenols which represent 30-40%w/w of the kerosene fraction. Christensen et al. results also show that the heavier the fraction is, the harder the identification becomes, as the number of unidentified species increase from 15%w/w in the light fraction to more than 70%w/w in the atmospheric gas oil fraction and hampers the Nist/Wiley database comparison. In fact, molecules contained in the atmospheric gas oil cuts are

present in many isomeric forms what creates coelutions. This study is nonetheless interesting as the analysis is made on distillation fractions and the totality of the fractions can be eluted. However, no information of the vacuum gas oil cut is provided and quantitative results must be interpreted with care as the detector response is not linear and internal standards are necessary to reach a precise quantification by GC/MS.

GC/MS is also a powerful tool which has been widely applied to catalytic pyrolysis products obtained with different catalysts. Lu et al. [162] have studied different effects of twelve catalysts on many families present in pyrolytic products: phenols, methoxyphenols, dimethoxyphenols, levoglucosane, furans, carbonyls, acids, and hydrocarbons. Despite the fact that results are non-quantitative, the relative proportions of each chemical family can be approached by using peaks area normalization. Thus, the transformation of pyrolysis products obtained with each catalyst can be evaluated. The same strategy was conducted by Fisk et al. [163] who studied the influence of a series of Pt supported catalysts. They showed that Pt/Al2O3 had a high activity affording an upgraded product rich in alkylbenzene and cyclohexanes, but also in phenolic compounds which are by far the predominant O-compounds (in particular phenol, cresols, and xylenols) (Figure 5-4). Benzofurans are also refractory to HDO and were quantified with no response factors by Williams et al. [164]. These species are difficult to characterize by 1D-GC as they generally elute with aromatics. In fact benzofurans are similar to naphtheno-aromatics hydrocarbon species in terms of polarity as they develop the same π-π interactions (see chapter 2).

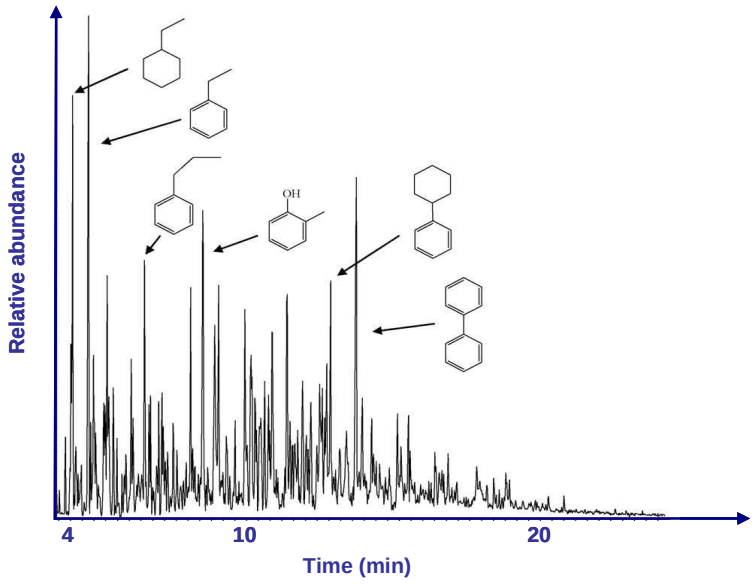


Figure 5-4. GC/MS chromatograms of an upgraded bio-oil produced over solid Pt/Al_2O_3 catalyst [163] Conditions: 30m RTX-5 column. [20-500 Da]

In another study, Xu et al. [165] compare GC/MS chromatograms of a bio-oil obtained by fast pyrolysis of pine sawdust (40.1%w/w O on wet basis) and its hydrotreatment product (39.2%w/w O) over MoNi/γ-Al2O3 catalyst. They conclude from the chromatograms that both hydrotreatment and esterification had happened during the upgrading process. Moreover, once again, predominant O-species in the upgraded bio-oil were phenolics and derivatives as they are the most refractory to hydrotreatment. The previous works can be complemented by Zhang et al. [154] who studied upgrading reactions of biomass pyrolysis oil using 1-octene and 1-butanol over sulfonic acid resin catalysts. GC/MS results were very interesting as they showed that during upgrading, alcohols react with carboxylic acids and carbonyls to form esters and acetals respectively. Moreover, O- and C-alkylations of phenolics were evidenced under these upgrading conditions. The identified species belong virtually to the same families as those highlighted by Christensen et al. [161]. However under Zhang et al. [154] upgrading conditions, acetals were created and sugars (levoglucosane), surprisingly, were still present in the final product. A few years before, this team had also studied the influence of solid acid 40SiO2/TiO2-SO42- and solid base 30K2CO3/AlO3-NaOH catalysts on upgrading products composition [149]. Most of identified compounds were phenols and their derivatives with methyl, methoxy, aldehydes, ketones, and propenyl groups substituted. Moreover the area of esters increased by 20-fold over the solid acid catalyst and by 13-fold over the solid base catalyst. However, resolution of these chromatograms was very poor as many coelutions occurred and only qualitative results could be deducted.

Guo et al. [148] and Li et al. [155] investigated GC/MS not to study the influence of the catalyst, but the influence of final conversion temperature. In the two cases, samples were “biopetroleum” obtained by deoxy-liquefaction. In the first case, the “biopetroleum” (2.92%w/w O) was obtained from sunflower shells. Four final conversion temperatures were studied (350°C, 400°C, 450°C, and 500°C). For each temperature, GC/MS chromatograms were obtained and revealed the presence of alkanes (C7-C19) and derivatives of benzene and phenol. Once again, it is shown that high temperatures are helpful to reduce the oxygen content, but that the oxygen in phenolic hydroxyl group was difficult to remove.

In the second case Li et al. [155] results focused on a “biopetroleum” obtained from soybean stalk (6.51%w/w O). GC/MS chromatograms showed that the deoxy-liquefaction product was mainly composed of aromatics, phenols, alkanes and "some kind of polar compounds". As shown in Figure 5-5, long-chain alkanes and phenols were dominant (respectively 49%w/w and 14%w/w)

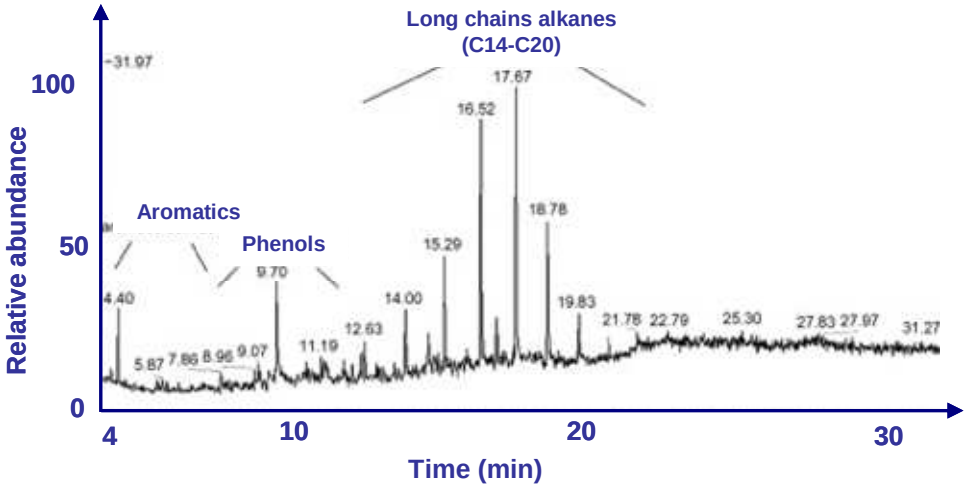


Figure 5-5. GC/MS chromatogram of a "biopetroleum" [155]

Finally, Bertero et al. [158] made a thoughtful use of GC/MS to study the influence of the resource on the composition of the bio-oil and on its upgrading product. Therefore, three residual sources were investigated (pine wood, mesquite wood and wheat shell). It is shown that in the treated liquid, concentration of furans increased slightly while the one of carboxylic acids increased substantially. Thermal treatment also decreased the content of phenols (reduction from 7% in pine bio-oil to 25% in mesquite bio-oil). Globally, the content of low molecular mass phenols (phenol, methylphenol) increased while content of heavier phenols (eugenols, syringols...) decreased. It is deplorable that the authors could not distinguish alkylphenols and methoxyphenols in this study as these species have different reactivities towards hydrotreatment.

All these GC/MS analyses give access to a deeper but limited insight into upgraded bio-oils by using different chromatographic stationary phases and oven conditions. A summary of the most widespread stationary phases is reported in Table 5-2 as many classical polarities were investigated offering different resolution levels. The investigation of ionic liquid columns may be interesting for such products. Their use was essentially focused on the separation between fatty methyl esters and hydrocarbons in biodiesel blends.

Many gaps remain from these studies. In fact, results are often claimed to be quantitative whereas mass spectrometry response is clearly not quantitative. Therefore, two options can be considered to solve this problem: the first one would be to use an internal standard for each injection [166], the second would be to use of an FID detector and identify peaks by retention times matching [167].

Moreover, quantifications were established without calculating any response factors of different species. In fact, it is known that compounds do not have the same response according to their chemical structure [160] and model compounds should be injected at different concentrations to evaluate and correct the response discrepancies. In addition, most of the past researches do not check the yield of elution: for this purpose a simulated distillation is very desirable [168].

Articles reported in this literature survey often give a detailed characterization of crude bio-oils. However, it is clear that only a part of the oil is eluted as it was demonstrated that only 40%w/w of a flash pyrolysis oil can be analysed by GC [150]. Besides, compounds present in such products are highly reactive and reactions are susceptible to occur in the chromatograph inlet which is generally at high temperatures (>200°C). Considering this, it is not very thoughtful to compare GC data between a crude oil and its upgraded product.

The last problem that emerges from these past studies is the lack of resolution between different molecules: the overlay of mass spectra of two coeluted peaks is matched with standard Nist database spectra leading to wrong identification in some cases. Coelutions also can also be responsible for quantitative bias. Therefore, chromatographic systems with more resolution should be investigated and multidimensional systems are a great solution. Heart-cutting GC-GC [169-171] is not very adapted to these matrices as the number of cuts would be too important. Comprehensive two-dimensional gas chromatography (GC×GC) seems to be a better answer for such complex matrices as shown in a few works.

Table 5-2.Review on different investigated stationary phases in the literature for GC analyses of upgraded bio-oils

Columns	***Stationary phase***	***Dimensions***	***References***
DB-5MS	95% Dimethyl arylenesiloxane, 5% Diphenyl	30m×0.25mm×0.1µm	Xu *et al.* [165]
Rtx-1701	86% PDMS 14% cyanopropylphenyl	60m×0.25mm×0.25µm	Christensen *et al.* [161]
TR-35MS	65% Dimethyl arylenesiloxane, 35% Phenyl	30m×0.25mm×0.25µm	Lu *et al.* [162]
DB-5	95% PDMS, 5% Diphenyl	25m×0.3mm	Paul *et al.* [156]
SGE-BP-1	100% PDMS	30m×*unk*mm×0.25µm	Strezov *et al.* [172]
Varian 24cb	50% PDMS, 50% Phenyl	30m×0.25mm×0.25µm	Chen *et al.* [173]
HP-1	100% PDMS	30m×0.25mm×0.25µm	Bertero *et al.* [158]
DB-5MS	95% Dimethyl arylenesiloxane, 5% Diphenyl	30m×0.25mm×0.1µm	Xu *et al.* [157]
VF-1701	86% PDMS 14% cyanopropylphenyl	60m×0.25mm×0.25µm	Tessini *et al.* [174]
Rtx-5	95% PDMS, 5% Diphenyl	30m	Fisk *et al.* [163]
Rtx-11	Crossbond 1, 100% PDMS	30m×0.32mm	Moskolczi *et al.* [175]
DB-5 MS	95% Dimethyl arylenesiloxane, 5% Diphenyl	30m×0.25mm×0.25µm	Zhang *et al.* [149]
HP-101	95% PDMS, 5% Diphenyl	30m×0.32mm×0.25µm	Zhou *et al.* [176]

5.4 Characterization by two-dimensional gas chromatography

The previous technique is based on only one separation criterion and is not sufficient if the vapor pressures of many analytes of a mixture are too close. Separation of coeluted species requires the integration of another separation criterion. Hyphenated to a mass spectrometer, a flame ionization detector or a specific detector, two-dimensional gas chromatography can offer outstanding separations and appears as a very useful tool for the analysis of complex mixtures such as upgraded bio-oils. However, only a few articles deal with the use of this technique for the analysis of different bio-oils [177-180]. This part will focus on three articles published by Marsman et al. [181-182] and by Wildschut et al. [183] in 2007, 2008 and 2009.

A beech wood flash pyrolysis oil was produced by BTG from a rotate cone pyrolysis technology [182]. The crude oil was then hydrodeoxygenated in the presence of hydrogen and of solid catalysts (Ru/carbon and NiMo/alumina). The upgraded products have an elemental oxygen content ranging from 10 to 15%w/w O. A 72 compound model mixture was injected in a classical orthogonal configuration [Sol-gel PDMS (30m×0.25mm×0.25µm) × OV-1701 (1.5m×0.1mm×0.1m)] which had already demonstrated a great space occupation and resolution between hydrocarbons for petroleum products analysis. New chemical families' elution zones were highlighted by GC×GC-FID allowing the classification of ten areas corresponding to ten chemical families: A-acids, B-aldehydes and ketones, C-alkylbenzenes, D-hydrocarbons, E-phenones, F-guaiacols and syringols, G-alcohols, H-furans, I-phenolics, and J-sugars. The 2D contour plot of the HDO oil obtained over Ru/carbon catalyst is presented in Figure 5-6. Globally, hydrotreated bio-oils contain less oxygenated compounds that the crude bio-oil. Moreover, GC×GC analysis shows that acids and sugars contents considerably decreased during hydrodeoxygenation, whereas alkylbenzenes, hydrocarbons and alcohols contents increased. Guaiacols and syringols concentrations significantly dropped off after upgrading.

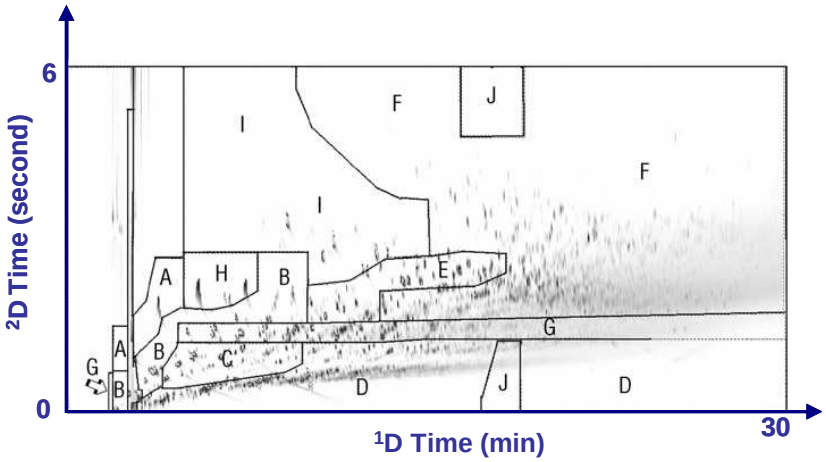


Figure 5-6. 2D contour plot of the HDO oil obtained over Ru/carbon catalyst. A-acids, B-aldehydes and ketones, C-alkylbenzenes, D-hydrocarbons, E-phenones, F-guaiacols and syringols, G-alcohols, H-furans, I-phenolics, and J-sugars [182] Sol-gel PDMS (30m×0.25mm×0.25µm) × OV-1701 (1.5m×0.1mm×0.1m)

In 2008, Marsman et al. [181] investigated another beech wood flash pyrolysis oil and its upgrading product. Hydrodeoxygenation step was this time achieved under a 25MPa hydrogen pressure at 300°C and over a two solid catalysts (Pd/C and Pt/C). Non-polar fractions of hydrotreated liquids were investigated by GC×GC-ToF/MS after elimination of the aqueous phase (35%w/w on the crude oil). A slightly more polar stationary phase was used in the first dimension (VF-5MS) and the resulting chromatogram is shown in Figure 5-7. This separation highlights different zones but delimitations seem unclear as many coelutions appear. Therefore, higher resolution techniques are needed. A quantification of crude and upgraded bio-oils is presented in Figure 5-8 and is based on total relative peak area. It shows that upgrading decreases oxygenated compounds content and increases hydrocarbons concentrations.

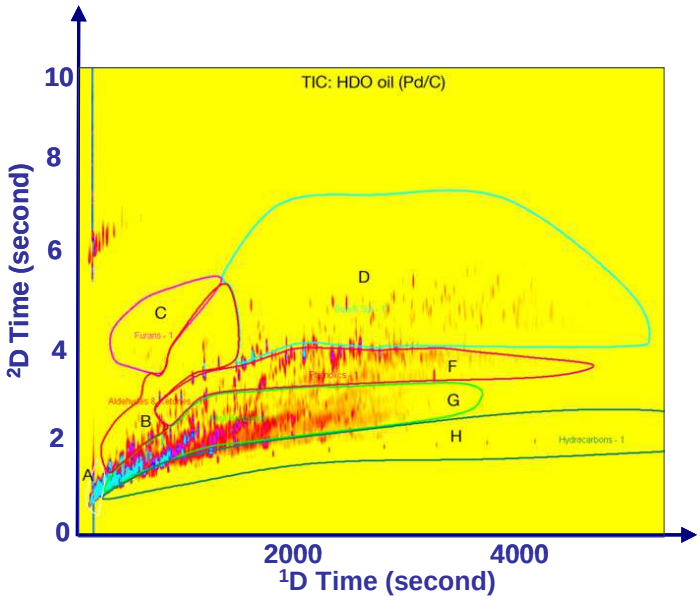


Figure 5-7. 2D contour plot of the HDO oil obtained over Pd/carbon catalyst. A-acids, B-aldehydes and ketones, C-furans, D-guaiacols and syringols, E: sugars, F-phenolics, G-alkylbenzenes, H-hydrocarbons and I-unknown [181] VF-5MS (30m×0.25mm×0.25µm) × VF-17MS (2m×0.1mm×0.2µm)

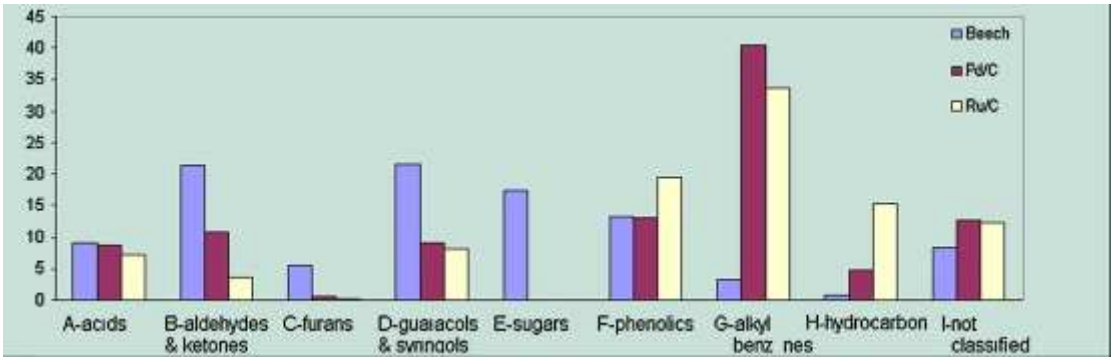


Figure 5-8. Quantification of the oils based on total relative peak area

Finally, Wildschut *et al.* used GC×GC to gain insight into the molecular composition of HDO oil produced at 350°C and 20 MPa using a Ru/C catalyst (23%w/w O). Many zones corresponding to different families were defined in the 2D-contour plot (Figure 5-9): alkanes, alkylbenzenes, alcohols, phenolics, guaiacols and acetophenones. However it seems that coelutions between oxygenates and aromatic hydrocarbons are still present for this orthogonal configuration. Among the different semi-quantified species, phenols (C6 to C10) are predominant compounds (3.8%w/w of the sample). For such products, the analytical challenge is to separate oxygenates from hydrocarbons.

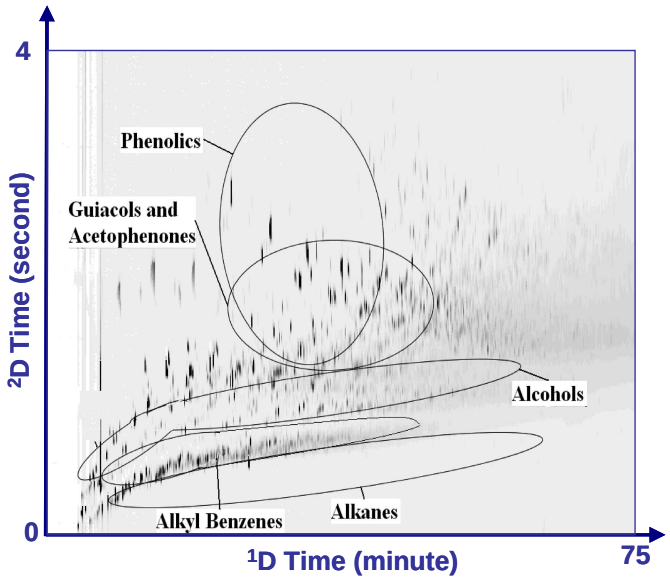


Figure 5-9. 2D contour plot of the HDO oil obtained over Ru/C catalyst [183]

Sol-gel PDMS (30m×0.25mm×0.25µm) × OV-1701 (1.48m×0.1mm×0.1m)

These different GC×GC applications show a great cartography of the different chemical families which can be found in bio-oils upgrading products. Even if more resolution is obtained using a second dimension of separation, coelutions still occur and hamper accurate identification and quantification. This lack of resolution can be overcome by investigating other columns combinations. In fact only normal orthogonality conditions were investigated (Table 5-3).

Table 5-3. Investigated GC×GC conditions for the analysis of upgraded bio-oils

1D column	*1D dimension*	*2Dcolumn*	*2D dimension*	*Modulation period*	*Ref*
Sol-gel PDMS	30m×0.25mm×0.25µm	OV-1701	1.5m×0.1mm×0.1µm	6 s	Marsman, 2007
VF-5MS	30m×0.25mm×0.25µm	VF-17MS	2m×0.1mm×0.2µm	10 s	Marsman, 2008
Sol-gel PDMS	30m×0.25mm×0.25µm	OV-1701	1.48m×0.1mm×0.1µm	4 s	Windt, 2009

However, reverse-orthogonality combinations recently proved to be efficient for the separation between hydrocarbons and polar compounds: by combining a more polar column in the first dimension than in the second dimension, oxygenated species were unravelled for Fischer

Tropsch products containing acids, alcohols, and esters [184]; biodiesels containing methylic fatty esters [45], and coal-derived liquids [195-196].

If even other GC×GC configurations are limited for the analysis of such products, a third dimension of separation can be integrated online. Among the different choices, liquid chromatography (LC) and supercritical fluid chromatography (SFC) merit attention. LC-GC hyphenation pioneered by Majors et al. [185] was deeply investigated by Mondello et al.. This hyphenation is interesting as it combines efficiency and sensitivity of GC to selectivity of LC. However solutes state difference involves a complicated interface. Therefore, priority is given to SFC-GC×GC hyphenation which is easier to implement and very powerful for the characterization of highly complex matrices such as petroleum vacuum gas oils or coal oils [203].

5.5 Discussion

Many analytical tools were used in the literature to characterize as fully as possible biomass flash pyrolysis upgrading products. Spectroscopic methods such as NMR and FT-IR give information on different oxygenated functional groups whereas gas and liquid chromatography allow a molecular characterization. Recently two-dimensional gas chromatography has also provided a detailed quantification of oxygenated compounds in upgraded bio-oils. Table 5-4 presents the advantages and drawbacks of each technique. The column usage is a ratio of the number of recorded publication of each of the fives techniques and the total number of recorded publications.

Table 5-4. Advantages and drawbacks of analytical techniques for oxygen speciation in upgraded bio-oils

Technique	*Advantages for oxygen speciation*	*Drawbacks for oxygen speciation*	*Usage %*
NMR	-Information on different functional groups	- No detailed molecular information - Noisy ^{17}O nuclei NMR response	5%
FT-IR	-Fast to operate -Information on different functional groups	- No detailed molecular information	24%
1D-GC	-Detailed molecular analysis	- Resolution not sufficient for such complex matrices : coelutions -Necessity to calculate response factors for accurate quantification -Time-consuming analyses -Elution limitations	50%
GC×GC	-Detailed molecular analysis -Separation along two criteria : more resolution -More possibilities in terms of stationary phases	-Detailed molecular analysis -Time-consuming analyses -Necessity to calculate response factors for accurate quantification -Elution limitations	7%
LC	-Detailed molecular analysis -Elution of heavier compounds	-Not enough resolution compared to GC -Solvent-consuming	14%

This literature survey gives an overview of oxygenated compounds which can be encountered in biomass flash pyrolysis upgrading products (Table 5-5). Different catalysts as well as different process routes lead to a large variety of molecular compositions. Phenols which are refractory to hydrotreatment are present in most of upgraded bio-oils at relatively high contents. Some studies highlight esters formation by catalytic and thermal esterification. Concerning carbonyls, they are also present at high concentrations, in particular cyclopentanones benzaldehydes and cyclohexanones. Other compounds such as syringols, eugenol, and anisols are reported in the literature but not in the review table as no quantification was provided.

Table 5-5. Composition of upgraded bio-oils reported in the literature. Results are at best semi-quantitative. Ci = i carbon atoms in the whole molecule

Compound	*Content (%)*	*Compound*	*Content (%)*
Phenols		**Carboxylic acids**	
Phenol	0.17-1.30	Acid C1	n.d.
O,m,p-cresols	0.24-1.10	Acid C2	0.01-6.14
Phenols C8	0.10-1.60	Acid C3	0.03-2.29
Phenols C9	0.01-1.05	Acids C4	0.08-3.21
Phenols C10	0.35-0.60	Acids C5	0.29-2.37
Alcohols		Acids C6	0.08-1.71
Alcohol C2	4.68	**Aldehydes**	
Alcohols C3	0.05-0.14	Aldehyde C1	0-0.02
Alcohols C4	0.00	Aldehyde C2	0-0.06
Alcohols C6	0.19-0.76	Aldehydes C3	0-1.14
Alcohols C7	0.2-0.3	Aldehydes C4	0-0.07
Alcohols C8	0.03-0.49	Aldehydes C5	0.02-1.1
Ketones		Aldehydes C6	n.d.
Ketone C3	0-0.04	Aldehydes C7	0-0.77
Ketones C4	0.02-0.06	Aldehydes C8	0-1.2
Ketones C5	0.09-1.26	Aldehydes C9	0-0.91
Ketones C6	0.02-1.31	**Benzofurans**	
Ketones C7	0.07-1.00	Benzofurans C8	0.14
Ketones C8	0.8-1.0	Benzofuran C9	0.13
Ketones C9	0.03	**Esters**	
Guaiacols		Esters C6	3.65
Guaiacol C7	0.65	Esters C7	11.34
Guaiacols C8	0.71	Esters C8	1.89
Guaiacols C9		Esters C9	0.44
Guaiacols C10	0.02-0.03	Esters C10	0.13
Furans		Esters C11	0.37
Furan C5	0.07-0.4	Esters C12	1.07
Furan C6	.01-0.02	Esters C13	0.46
Benzenediols			
Benzenediols C6	0.01-0.02		

5.6 Conclusion

Considering the complexity of these matrices in terms of oxygenated compounds, but also the large variety of hydrocarbons present in the solution the use of two-dimensional gas chromatography would be recommend. Optimisation of GC×GC conditions must be performed to gain resolution between oxygenates and hydrocarbons; reversed-type column configurations offer bright perspectives. If two dimensions of separation are still insufficient to overcome all coelutions, a third dimension of separation involving supercritical fluid chromatography (SFC) can be hyphenated to GC×GC. Nevertheless, to reach a precise quantification, the use of FID detection and a correction with response factors is recommended. These response factors as well as the use of SFC-GC×GC–FID were never reported in the literature for such products and offer bright perspectives. In definitive, more resolution and an insight into detectors response are necessary to reach for a detailed characterization; but as no technique is self-sufficient, a multitechnical analytical approach would be interesting to complement this three-dimensional chromatographic analysis.

CHAPTER 6. Oxygen speciation in partially upgraded bio-oils by comprehensive two-dimensional gas chromatography [7]

FOREWORD

The previous chapter showed that even if gas chromatography is a useful technique to characterize upgraded bio-oils, these matrices are so complex that higher resolution techniques should be investigated. For this purpose, comprehensive two-dimensional gas chromatography (GC×GC) was investigated. Oxygen speciation in such matrices is hampered by the large diversity of oxygenated families and the complexity of the hydrocarbon matrix. Moreover, response factors must be taken into account for oxygenates quantification as the Flame Ionization Detector (FID) response varies when a molecule contains heteroatoms.

To take up this analytical challenge, a thorough optimization approach was developed. In fact, four GC×GC column sets were investigated to separate oxygenated compounds from the hydrocarbon matrix. Both model mixtures and the partially upgraded biomass flash pyrolysis oil (PUBs) were analyzed using GC×GC-FID to reach a suitable chromatographic separation. The advantages and drawbacks of each column combination for oxygen speciation in PUBs are highlighted in this study.

Among the four sets, a polar × semi-polar column combination (SolGel-WAX × Rtx-200) was selected and enabled the identification by GC×GC-ToF/MS of more than 40 compounds belonging to eight chemical families: ketones, furans, esters, carboxylic acids, alcohols, phenols, guaicols and anisols. For quantification purpose, the GC×GC-FID chromatogram was divided into more than 60 blobs corresponding to the previously identified analytes and hydrocarbons zones. A database associating each blob to a molecule and its specific response factor (determined by standards injection at different concentrations) was created. A detailed molecular quantification by GC×GC-FID was therefore accessible after integration of the corrected normalized areas.

This paper aims to present a detail level in terms of oxygenated compounds characterization in upgraded bio-oils which was never reached so far to our knowledge. It is based on an original column set selection and an extremely accurate quantification procedure.

[7] This chapter was submitted in Analyst the 7th of May, 2012 by Omais *et al.*

6.1 Introduction

Since the production of crude oil may not meet the increasing demand in the next future, biomass flash pyrolysis oils have sparked great interest as one of the possible substitutes of petroleum in the transportation field. However, these products cannot be directly processed with petroleum feedstocks and are far from fuel specifications. In fact, they are mainly oxygenated (45-50%w/w O on wet basis) and contain almost no hydrocarbons. Upgrading is therefore applied to obtain a product with lower oxygen content and characterization of oxygenates in these products is crucial to assist conversion reactions.

Many analytical tools were used in the literature to characterize as fully as possible biomass flash pyrolysis upgraded products. Spectroscopic methods such as NMR [161, 187] and FT-IR [148, 155, 172, 173, 175, 176, 190-192] give information on different oxygenated functional groups whereas gas chromatography [148, 149, 153-156, 158, 161-163, 165, 172-176, 193, 194] and liquid chromatography [156, 161, 174, 191, 192] allow a molecular characterization. Recently two-dimensional gas chromatography has also provided a detailed quantification of oxygenated compounds in upgraded bio-oils [178, 181, 182].

Literature has demonstrated a large variety of molecular compositions owing to different catalysts, different biomass feedstocks as well as different process routes. Phenols which are refractory to hydrotreatment are present in most of upgraded bio-oils at relatively high contents (>3%w/w) [183]. Some studies highlight esters formation by catalytic and thermal esterification [161]. Concerning carbonyls, they are also present at high concentrations, in particular cyclopentanones, benzaldehydes and cyclohexanones [161, 174]. Other compounds such as syringols, eugenol, and anisols are reported in the literature [178].

Considering the complexity of these matrices in terms of oxygenated compounds, but also the large variety of hydrocarbons present in the solution two-dimensional gas chromatography will investigated.

Marsmann *et al.* investigated biomass-derived hydrodeoxygenated oils by GC×GC [178, 181, 182]. This was the only application of GC×GC on such products to our knowledge. The 2D contour plots were divided into ten zones corresponding to carboxylic acids, carbonyl compounds, alkylbenzenes, hydrocarbons, phenones, guaiacols and syringols, alcohols, furans, phenols and sugars. Even if they are only semi-quantitative (no response factors were determined), these

results provide an improved overview of the various chemical compounds present in upgraded bio-oils.

GC×GC also allows oxygenates analysis in many other hydrocarbon matrices. In fact oxygenated species were unravelled for Fischer Tropsch products containing acids, alcohols, and esters [2, 100]; biodiesels containing methylic fatty esters [101-103], modified petroleum containing alcohols [104, 105], and coal-derived liquids (part A). However, coelutions resulting from the matrix complexity often appear, and a fastidious response factors calculation must be achieved for quantitative purpose.

This paper gives a detailed quantitative characterization of oxygenated compounds present in a partially upgraded bio-oil. A GC×GC optimization procedure is described and leads to the selection of an optimal column combination for oxygen speciation in this kind of products. Four column sets were investigated to separate oxygenated compounds from the hydrocarbon matrix and the selected optimal reverse orthogonality configuration enabled the identification of eight oxygenated chemical families. A precise and detailed quantification of separated species (carboxylic acids, alcohols, phenols, ketones, and methoxyphenols) was established by using response factors adapted from previous works on coal liquefaction products.

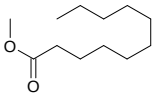
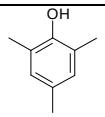
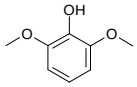
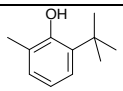
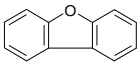
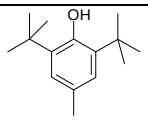
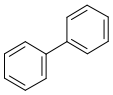
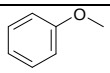
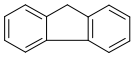
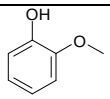
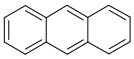
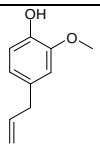
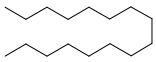
6.2 Experimental

6.2.1 Samples

6.2.1.1 Test mixture

The solvent used for the elaboration of test samples was ethyl acetate and was supplied by VWR. This solvent allows a good solubilization of both hydrocarbons and oxygenated compounds. Chemicals were provided by different suppliers: Sigma-Aldrich, Merck, Alpha Aesar, TCI, and Fluka. To evaluate the separation between oxygenated compounds and hydrocarbons, many standards were used. Previous works on coal derived products [112] showed that major oxygenated aromatic species are subjected to potential coelutions with hydrocarbon aromatics using conventional normal configurations. Therefore, the investigated model mixture MM (Table 6-1) contains hydrocarbon aromatics and other aromatics with different oxygenated functionalities which can be found in such products at concentrations ranging between 0.8 and 1.2%w/w. Coelutions between ketones, furans and naphthenic compounds are not studied by model mixtures.

Table 6-1. Model mixture (MM) investigated in this study

N°	*Compound*	*Structure*	*N°*	*Compound*	*Structure*
1	Ethyl decanoate		**9**	Catechol	
2	Trimethylphenol		**10**	Syringol	
3	6-tertbut-o-cresol		**11**	Dibenzofuran	
4	2,6-ditertbutyl-Methylephenol		**12**	Tetramethyl benzene	
5	Naphtol		**13**	Biphenyl	
6	Anisol		**14**	Fluorene	
7	Guaiacol		**15**	Phenanthrene	
8	Eugenol		**16**	nC16	

6.2.1.2 Partially Upgraded bio-oil

The investigated sample is a flash pyrolysis oil which was partially dehydroxygenated and was supplied by IFP Energies nouvelles. The upgrading process is presented in Figure 6-1 and consists in a hydrotreating of the pyrolysis oil. No distillation was applied to the liquid which has boiling points ranging from 30°C to 630°C according to the simulated distillation analysis (ASTM D2887). The hydrogen content is determined by NMR (ASTM D4808), the carbon content is determined by combustion (ASTM D5291), the nitrogen content is measured by chemiluminescence (ASTM D4629) and the oxygen content by pyrolysis followed by infrared detection (internal method). All values are summarized in .

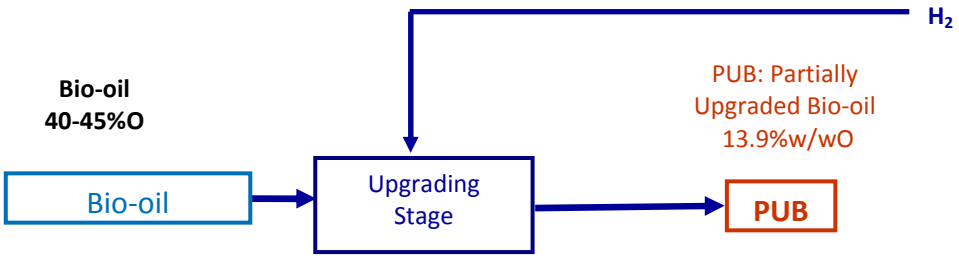


Figure 6-1. Schematic of the partially upgraded bio-oil production adapted from Dynamotive presentation

Table 6-2. Elemental composition of the upgraded bio-oil (on wet basis)

Element	*Content %w/w*
C	75.7
H	10.1
O	13.93
N	0.135
S	<0.1

6.2.2 GC×GC-FID setup

For optimization and quantification purposes, experiments were achieved with a Trace GC (Thermo, Italy). The injection was carried out using a split injector (Thermo) at 320°C (0.3µL) with a split ratio equal to 1:100. Detection was established with a flame ionization detector (FID) system set at 320°C. H_2, air, and He makeup were set respectively at 35, 400, and 25 mL/min. Helium (99.99% Air Liquid, France) was used as a carrier gas. Oven temperature was programmed from 30°C to the maximum operating temperature allowed by the columns (Solgelwax: 300°C, BPX-50: 340°C, DB-5: 325°C, RTX-200: 340°C, PONA: 325°C, MXT-1: 430°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 was used for all the columns configurations for comparison purposes. A constant pressure set at 27 Psi was used and the modulation period was set to cope with the differences of activity coefficients of each investigated column (Table 6-3). Modulation was performed using a dual CO_2 jets cryogenic modulator.

6.2.3 GC×GC-ToF/MS

For identification purposes, a LECO Pegasus IV (LECO, St. Joseph, MI, USA) GC×GC-ToF/MS system was used. Experiments were achieved 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. The acquisition frequency of the detector was set at 100 Hz in a mass range of 45-750 amu. Electron Ionization was carried out at 70ev and a multiplate voltage of -1450V was used. Concerning the modulation, it was performed by a liquid nitrogen cooled gas jet cryogenic modulator.

6.2.4 Capillary columns

Many dimensions of capilary GC columns were tested in the study involving orthogonal and non-orthogonal conditions. All of them are referred in Table 6-3 as well as investigated modulation periods. Columns dimensions and modulation periods were adapted to reach good space coverage of the analytes in the 2D space.

Table 6-3. Column sets investigated in this study

Ref	*1D column*	*1D Dimensions*	*2D column*	*2D Dimensions*	*Modulation period (s)*
(A)	PONA	20m×0,2mm×0,5µm	BPX-50	1,3m×0,1mm×0,1µm	10
(B)	MTX-1	17.5m×0,18mm×0,4µm	RTX-200	1,2m×0,1mm×0,1µm	10
(C)	Solgelwax	30m×0,25mm×0,25µm	DB-5	1,2m×0,1mm×0,1µm	15
(D)	Solgelwax	30m×0,25mm×0,25µm	RTX-200	1m×0,1mm×0,1µm	7

6.2.5 Data handling

When acquired by Polycard software (Thermo), the raw data of FID signals were exported as a csv file using a home-made software called 2DChrom® (IFP Energies nouvelles). This software allows the creation of GC×GC contour plots with retention time 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 allowed to reach a quantification and a report could be generated. Peaks intensity was displayed with a colour gradient varying from light blue to dark blue. To finish, this software helped 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 allowed peak finding. Identification of compounds was achieved by comparing the acquired spectra with the NIST database (National Institute of Standards and Technology, Gaithersburg, MD, USA version 2002). Peak intensities were displayed with a color gradient varying from pale green to blue.

6.3 Results and discussion

6.3.1 Investigating different column sets for oxygen speciation by GC×GC-FID

The first step of the study consisted in selecting the most adapted column combination. Therefore, the model mixture (MM) and the partially upgraded biomass flash pyrolysis oil were analyzed under the four conditions described in Table 6-3. The analysis of the model mixture was necessary to identify families' elution zones in the processed sample chromatogram.

Set (A) is the most widespread type of column combination in GC×GC as it involves a non-polar first dimension coupled to a mid-polar second dimension. This configuration is often used for the analysis of petroleum atmospheric gas oils [98] and the elution zones of hydrocarbons are clearly identified in the literature. As a result, this column set was firstly investigated to evaluate the matrix complexity. Figure 6-2-A shows that characteristic oxygenated compounds derived from biomass oils upgrading coeluted with aromatic hydrocarbons. The 2D contour plot of the PUB (6-1.B) is consistent with chromatogram of standards: one-, two- and three- rings hydrocarbon aromatics are coeluted with aromatic oxygenated compounds (phenols, benzenediols, methoxyphenols, dibenzofuran). In fact, π-π interactions in the second dimension are common to heteroatomic and hydrocarbon aromatics. Consequently, this column set is not selective towards oxygenated compounds in such matrices. As previously mentioned, the large diversity of expected chemical families hampers the analysis. Nevertheless, it can be concluded that normal and iso-paraffins as well as naphthenes and aromatics are formed by the biomass flash pyrolysis oil upgrading. Moreover, the zone ranging from 0 to 20 minutes corresponding to light molecules is highly concentrated. This result gives a first notion of the sample complexity in terms of number of components and boiling points and this is particularly evidenced in the 3D contour plot (Figure 6-2-C).

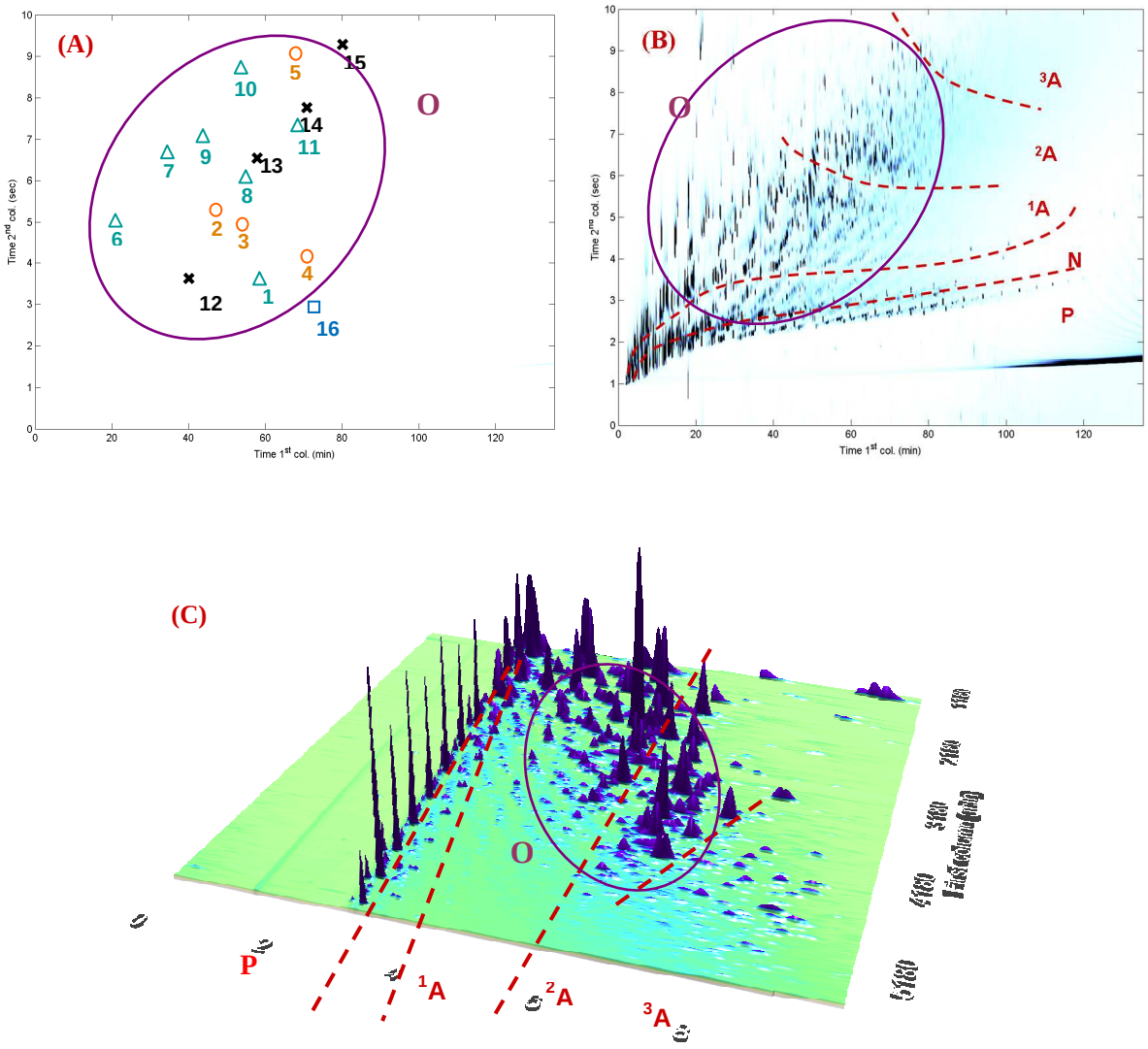


Figure 6-2. 2D chromatogram of the model mixture (A), 2D chromatogram of the PUB (B), and 3D chromatogram of the PUB (C) starting at ^{1}t=20min – PONA × BPX-50

O: Oxygenated compounds, P: paraffins, N: naphthens, ^{i}A: aromatics with i rings
□: n-C16 paraffin, ▲: oxygenated compound with methoxy groups, o: phenols, × : aromatics

To adapt the conventional column set to the oxygenated biomass-derived matrix, another stationary phase which showed good selectivity towards oxygenates [195] is selected in the second dimension. In fact, trifluropropyle stationary phase (RTX-200) which is also a mid-polar column involving electronegative centres was investigated as a second dimension. As expected, oxygenated aromatics are more retained in the second dimension than aromatic hydrocarbons (Figure 6-3-A) and a virtual zone dedicated to O-compounds appears. This is confirmed by real sample injection (Figure 6-3-B). The zone which might correspond to oxygenated compounds is circled. However, coelutions between O-compounds and hydrocarbons cannot be avoided from ^{1}tr= 45 min. The 2D contour plot exhibits good peaks shapes even if peak tailing appears for the first eluting

compounds which have very low boiling points (supposedly acetic acid and propanol) and are not fully trapped by the modulator cold jets. It is therefore worthwhile to use a mass spectrometry detection to identify all separated O-compounds and this will be studied in further works.

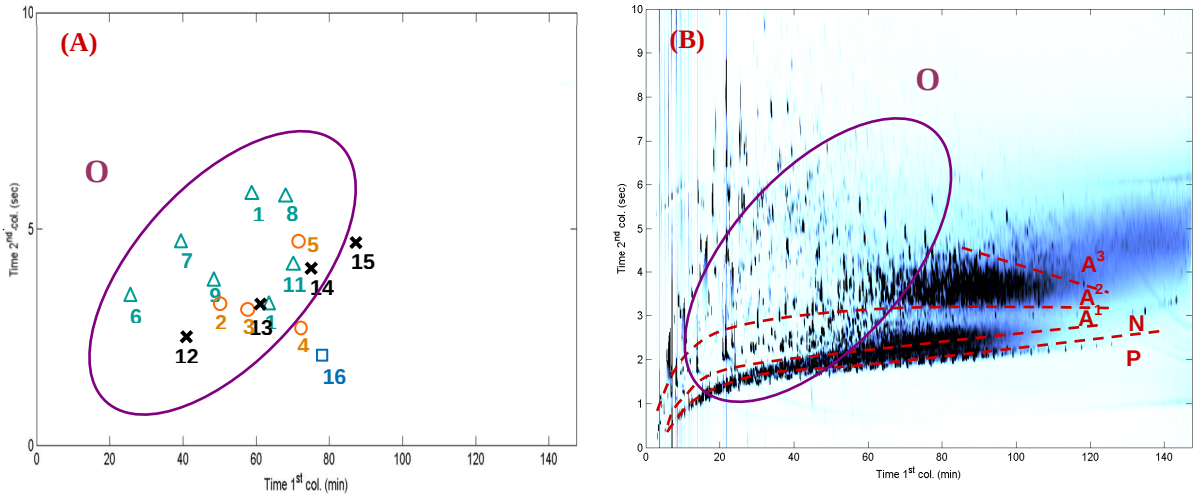


Figure 6-3. 2D chromatogram of the model mixture (A) and the PUB (B) – MXT-1 × RTX-200

O: Oxygenated compounds, P: paraffins, N: naphthens, $A^{i:}$ aromatics with i rings
□: n-C16 paraffin, ▲: oxygenated compound with methoxy groups, o: phenols, × : aromatics

Set (C) involving a polar Polyethylene glycol first dimension coupled to a 5% phenyl PDMS stationary phase is in reversed orthogonality configuration. Compounds are separated by polarity and boiling points in the first dimension and each fraction eluting from the first dimension contains species that differ so much in terms of boiling points, that volatility plays a key role in the second isothermal separation [196]. Figure 6-4 shows that no resolution is evidenced concerning oxygenated compounds. In fact, zone A contains oxygenated and hydrocarbon aromatics, but also other polar compounds. However, this set is optimal to separate saturated and unsaturated non-aromatic molecules as paraffins and naphthens are totally separated from the matrix.

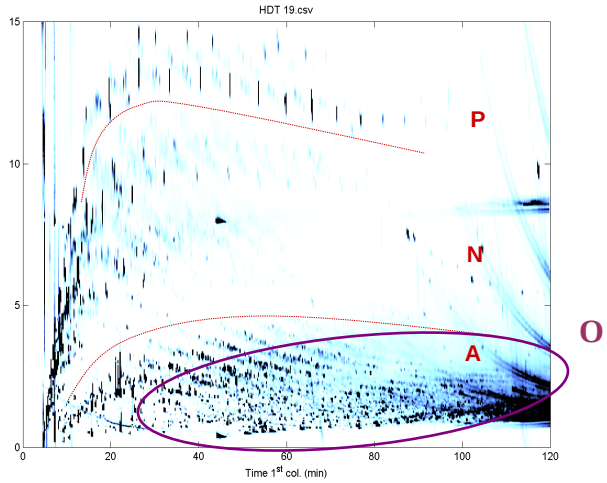


Figure 6-4. 2D chromatogram of the partially upgraded bio-oil – Solgelwax × DB-5

O: Oxygenated compounds, P: paraffins, N: naphthens, A^{i} aromatics

Finally, the analysis of MM using set (D) shows that all oxygenated compounds under study are located under the hydrocarbon aromatic zone except the ethyl caprate (N°1) (Figure 6-5-A). Consequently, this column combination seems adapted to oxygen speciation in partially upgraded bio-oils. The analysis of the "real" sample shows that even if coelutions remain (Zone circled in green in Figure 6-5-B), a zone is dedicated to oxygenated compounds which creates H bonds with the PEG stationary phase (zone circled in purple in Figure 6-5-B). However, the weak thermal resistance of the PEG stationary phase is evidenced by the large bleeding at high oven temperatures.

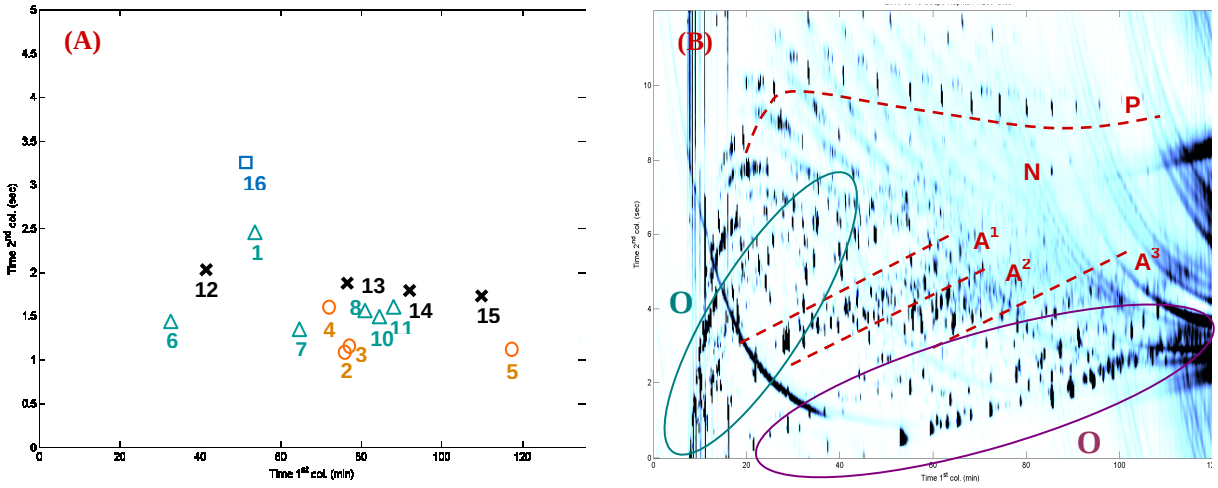


Figure 6-5. 2D chromatogram of the model mixture (A) and the PUB (B) – Solgelwax × RTX-200

O: Oxygenated compounds, P: paraffins, N: naphthens, A^{i} aromatics with i rings
□: n-C16 paraffin, ▲: oxygenated compound with methoxy groups, o: phenols, × : aromatics

The advantages and drawbacks of each column combination are compiled in Table 6-4.

Table 6-4. Column sets investigated in this study

Ref	*Column set*	*Advantages*	*Drawbacks*
A	PONA × BPX-50	– Global vision of the matrix – Great 2D space occupation	– Coelutions between hydrocarbons and O-compounds
B	MXT-1 × RTX-200	– Many O-compounds are separated	– Coelutions appear at ^{1}t=45 min
C	Solgelwax × DB-5	– Great separation between aliphatics and aromatics	– Coelutions between hydrocarbons aromatics and O-aromatics – Bleeding of the PEG stationary phase
D	Solgelwax × RTX-200	– Great 2D space occupation – Zone dedicated to O-compounds	– Bleeding of the PEG stationary phase

6.3.2 Identification by GC×GC-ToF/MS

In order to validate the elution zones of the families evidenced by the injection of model mixture MM, comprehensive two dimensional gas chromatography coupled to a time-of-flight mass spectrometry was used. The analysis was performed with set (D) as the Solgelwax × RTX-200 combination showed the highest resolution of oxygenated compounds. The GC×GC-ToF/MS chromatogram is consistent with the one obtained by GC×GC-FID. However, the modulation performed by liquid nitrogen cooled gas jet, the variation of columns lengths and the vacuum created inside the mass spectrometry detector had a slight influence on the separation. High quality mass spectra were obtained, which made possible accurate library matching. Many families were identified by this analysis: carboxylic acids, alcohols, furans, ketones, phenols, guaiacols, syringols, trimethoxyphenols, anisols, and benzenediols. Among the different families, a molecular composition is accessible for species having an elution time below 100 min. Figure 6-6 shows the different identified peaks and the numbers refer to Table 6-5. All 41 oxygenated analytes have similarities with NIST library spectra higher than 700 (a similarity of 999 represents a perfect match with the library): 24% of them have a similarity between 700 and 800, 27% of them between 800 and 900, and 49% of them superior to 900. To confirm the identification provided by the software, it was therefore crucial to use standards and confirm families elution zones using gas chromatography. Therefore, a model mixture containing alcohols (pentanol, heptanol, and nonanol), furans (furan benzofuran, dibenzofuran) and ketones (Acetone, 2-pentanone and 4-heptanone) was injected; the elution zones were totally consistent with the software identification.

Concerning phenols, methoxyphenols, anisols, and benzenediols, the identification was confirmed by the zone highlighted by the analysis of MM. Hence, identification of species presented in the table is accurate thanks to the dual use of gas chromatography and mass spectrometry considerations. However, many coelutions remain in the aromatics zone and there are still many unknown species.

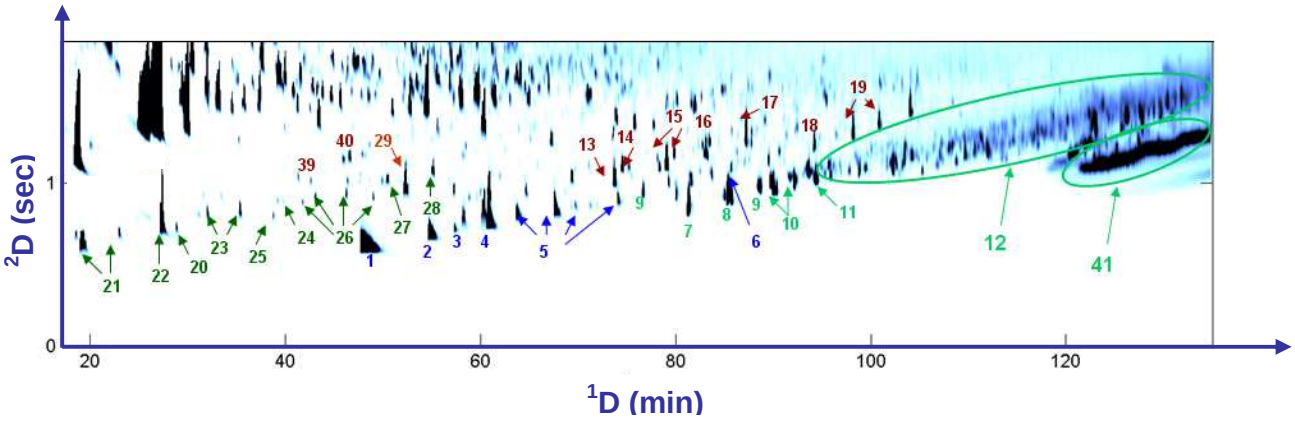


Figure 6-6. Zoom of the 2D chromatogram of the PUB – Solgelwax × RTX-200 and identification of different peaks (see table 6-5)

Three oxygenated families were identified by GC×GC-ToF/MS but not separated from hydrocarbons: furans, esters and ketones. No work on model mixtures was established to enhance their separation. The result is that they are coeluted with naphthenes. Even if no quantification of all species present in this family is possible, it is possible to reach a selective identification using specific ions. As furans are very stable, fragments are formed preferably in the carbon aliphatic chains, and some of these species can be selectively displayed in fragmentograms at m/z = 68, 82 and 96.

Concerning ketones, they were difficult to identify because they also coelute with naphthenic compounds. Therefore, spectral deconvolution was applied to properly identify these species. Mac-Lafferty fragments R-(HO)C + =CH2 which are characteristic of aliphatic ketones were observed for m/z 58. Figure 6-7 shows the m/z=58 2D-fragmentograms with all aliphatic ketones.

Table 6-5. Detailed characterization of oxygenated compounds in the partially upgraded bio-oil.

N°	Compounds	Raw formula	Reverse / Similarity	Response factors	Content (dry basis) % w/w	Content (dry basis) % O w/w
Carboxylic acids						
1	Carboxylic acid C^2	$C_2H_4O_2$	986/986	3.32[a]	2.117	1.129
2	Carboxylic acid C^3	$C_3H_6O_2$	939/939	2.73[a]	0.640	0.277
3	Carboxylic acid C^4	$C_4H_8O_2$	945/945	2.43[a]	0.172	0.063
4	Carboxylic acid C^5	$C_5H_{10}O_2$	924/864	2.26[b]	1.246	0.391
5	Carboxylic acid C^6	$C_6H_{12}O_2$	775/775	2.14[b]	0.792	0.219
6	Carboxylic acid C^8	$C_8H_{16}O_2$	864/773	1.99[a]	0.044	0.011
Total					**5.011**	**2.089**
Phenols						
7	Phenol C^6	C_6H_6O	928/928	1.24[a]	0.531	0.090
8	Phenol C^7	C_7H_8O	916/916	1.24[a]	0.563	0.083
9	Phenol C^8	$C_8H_{10}O$	955/955	1.24[a]	0.163	0.021
10	Phenol C^9	$C_9H_{12}O$	914/914	1.24[a]	0.441	0.052
11	Phenol C^{10}	$C_{10}H_{14}O$	892/870	1.22[a]	0.352	0.038
12	Phenols Unknown			1.24[a]	10.111	0.909
Total					**12.160**	**1.193**
Methoxyphenols						
13	Methoxyphenol C^7	$C_7H_8O_2$	904/904	1.63[a]	0.264	0.068
14	Methoxyphenol C^8	$C_8H_{10}O_2$	863/863	1.56[b]	0.135	0.031
15	Methoxyphenol C^9	$C_9H_{12}O_2$	927/768	1.49[b]	0.361	0.076
16	Methoxyphenol C^{10}	$C_{10}H_{14}O_2$	757/757	1.42[a]	0.251	0.048
17	Methoxyphenol C^{11}	$C_{11}H_{16}O_2$	865/748	1.35[b]	0.366	0.065
18	Dimethoxyphenol C^8	$C_8H_{10}O_3$	955/955	1.87[a]	0.186	0.058
19	Trimethoxyphenol C^{10}	$C_{10}H_{14}O_4$	786/762	2.01[c]	0.388	0.094
Total					**1.952**	**0.441**
Alcohols						
20	Methoxyethanol	$C_3H_8O_2$	973/973	2.10[c]	0.033	0.014
21	Propanol	C_3H_8O	909/899	2.10[a]	0.351	0.094
22	Butanol	$C_4H_{10}O$	979/979	1.76[b]	0.979	0.212
23	Pentanol	$C_5H_{12}O$	913/913	1.42[a]	0.078	0.014
24	Hexanol	$C_6H_{14}O$	920/920	1.38[b]	0.031	0.005
25	Cyclic alcohol C^5	$C_5H_{10}O$	956/956	1.42[b]	0.035	0.007
26	Cyclic alcohol C^6	$C_6H_{12}O$	907/907	1.38[b]	0.062	0.010
27	Cyclic alcohol C^7	$C_7H_{14}O$	805/805	1.34[b]	0.035	0.005
28	Cyclic alcohol C^8	$C_8H_{16}O$	904/904	1.33[b]	0.058	0.007
Total					**1.662**	**0.367**
Furans						
29	Benzofuran	C_8H_6O	833/822	1.13[a]	0.163	0.022
31	Furan C^5	C_5H_6O	963/879	4.6[a]	0.436	0.085
32	Furan C^6	C_6H_8O	819/737	4.3[b]	0.299	0.050
33	Furan C^7	$C_7H_{10}O$	794/768	4.0[b]	0.052	0.008
Total					**0.949**	**0.164**
Ketones						
34	Butanone	C_4H_8O	854/821	2.01[a]	0.564	0.125
35	Pentanone	$C_5H_{10}O$	938/915	1.82[a]	0.953	0.177
36	Hexanone	$C_6H_{12}O$	947/905	1.64[a]	1.102	0.176
37	Heptanone	$C_7H_{14}O$	945/801	1.46[a]	0.079	0.011
38	Octanone	$C_8H_{16}O$	906/863	1.25[a]	0.051	0.006

Total					**3.220**	**0.496**
Anisols						
39	Anisol C[7]	C_7H_8O	862/782	1.48[a]	0.074	0.011
40	Anisol C[8]	$C_8H_{10}O$	964/962	1.40[b]	1.180	0.155
					1.254	**0.166**
Benzenediols						
41	Benzenediols			1.64[a]	**5.808**	**1.347**
Water (Karl Fischer titration)					**2.0**	**1.8**
Total content by GC×GC (wet basis)					**34.016**	**8.061**

[a]: determined by standard molecule calibration
[b]: determined by standard molecule calibration extrapolation
c: determined using Kaiser's formulae [31]

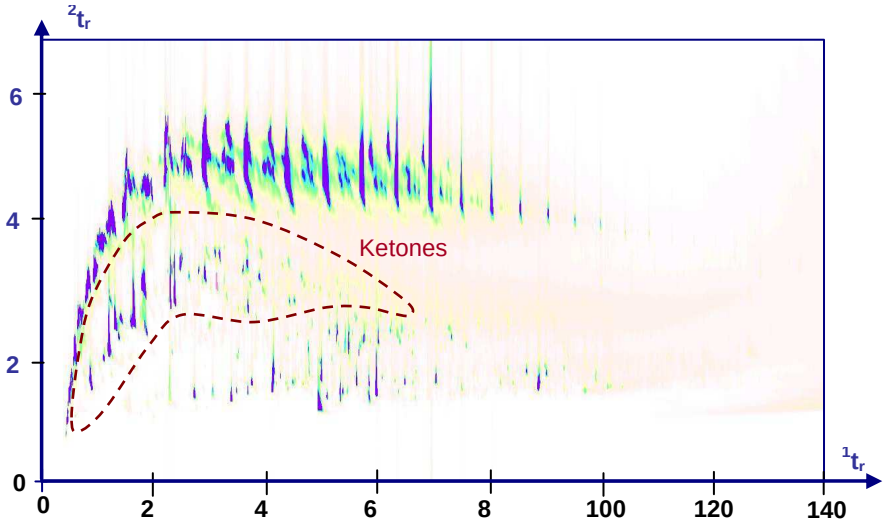


Figure 6-7. m/z=58 2D fragmentogram of the PUB – Solgelwax × RTX-200. Ketones are highlighted in red

6.3.3 Quantification by GC×GC-FID

The last three columns of Table 6-5 concern the quantification by GC×GC-FID. The FID detector was used due to its robustness, and its large linear range. Besides, the virtually linear dependence of its response on the number of carbon atoms in a hydrocarbon molecule is a main advantage. However for heteroatomic species, especially oxygenated compounds, the response is not linear; therefore response factors must be determined.

Response factors of many species were determined in this work what enabled precise quantification of these latter. In fact, a dozen of molecules where injected five times at 6 different concentrations ranging from 50 to 1000 ppm (30 analyses for each response factor) and an average value was deduced. If the response factor of an analyte was not experimentally determined, it was approached mathematically by a regression. For example, the response factor of 1-propanol and 3-pentanol was determined experimentally, and the one of butanol was deduced from the two

previous values. For trimethoxyphenols and methoxyethanol, no response factors were determined in this study. Therefore Kaiser formula approximation was used [160] showed in Equation 6-1 where RF is the response factor of a molecule, n_C the carbon atom number, and MM the molecular mass of the molecule. All response factors are explicitly shown in Table 6-5 with an indication on the way the value was obtained.

$$RF = 0.921 \times \frac{12 \times n_C}{MM} \qquad \text{(Equation 6-1)}$$

To evaluate the accuracy of Kaiser formula, a parity diagram was established representing in the x-axis calculated response factors and the y-axis experimental response factors of 21 oxygenated species (Figure 6-8). This diagram shows obvious discrepancies between the experimental and the theoretical approaches. Furan response factor seems aberrant and can be explained be the high volatility of this compound which does not allow a precise measurement. Concerning carboxylic acids, their peak tailing in GC may explain the underestimation of the Kaiser formula's response factor.

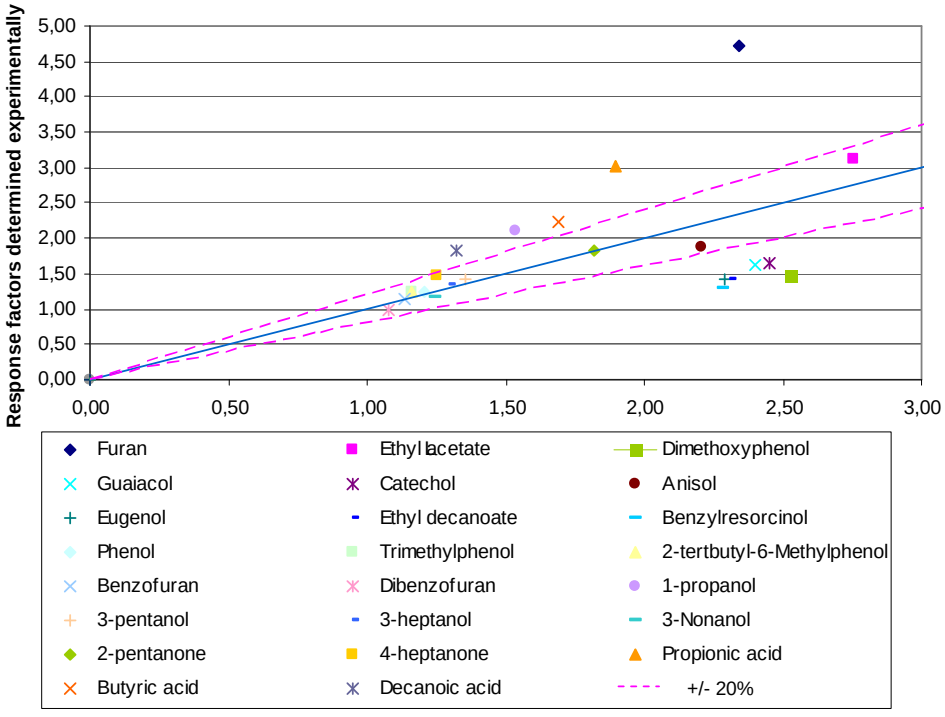


Figure 6-8. Parity diagram: Response factors determined experimentally and by Kaiser formula

For quantitative purpose, the GC×GC-FID chromatogram was divided into more than 60 blobs corresponding to the previously identified analytes, hydrocarbons and unknown zones. A database associating each blob to a molecule and its specific response factor was created. A

detailed molecular quantification by GC×GC-FID was carried out after integration of the corrected normalized areas. Five injections of the "real" sample also enabled the evaluation of the repeatability. Among the 41 compounds, quantification of contents for33 compounds had a relative error bellow 10%, and 8 compounds had a relative error ranging between 10 and 20%.

A classification and quantification of each analyte was then established and as the raw formula of molecules is known, the equivalent elemental oxygen content that each family represents is accessible. Therefore two types of results can be given. The first detailed molecular one is shown in column 6 of Table 6-5.

The second one which is interesting for a final assessment of oxygen content gives the family quantification in terms of elemental oxygen content compiled in the last column of Table 6-5. In fact, the objective of the study is oxygen speciation in the partially upgraded bio-oil. As the global elemental oxygen content of the sample was determined by pyrolysis followed by infrared detection (13.93%w/w O on wet basis), the contribution that each family represents in the global elemental content can be evaluated in %w/w O. Figure 6-9 represents the family quantification established in oxygen elemental content. Water was quantified using Karl Fischer titration.

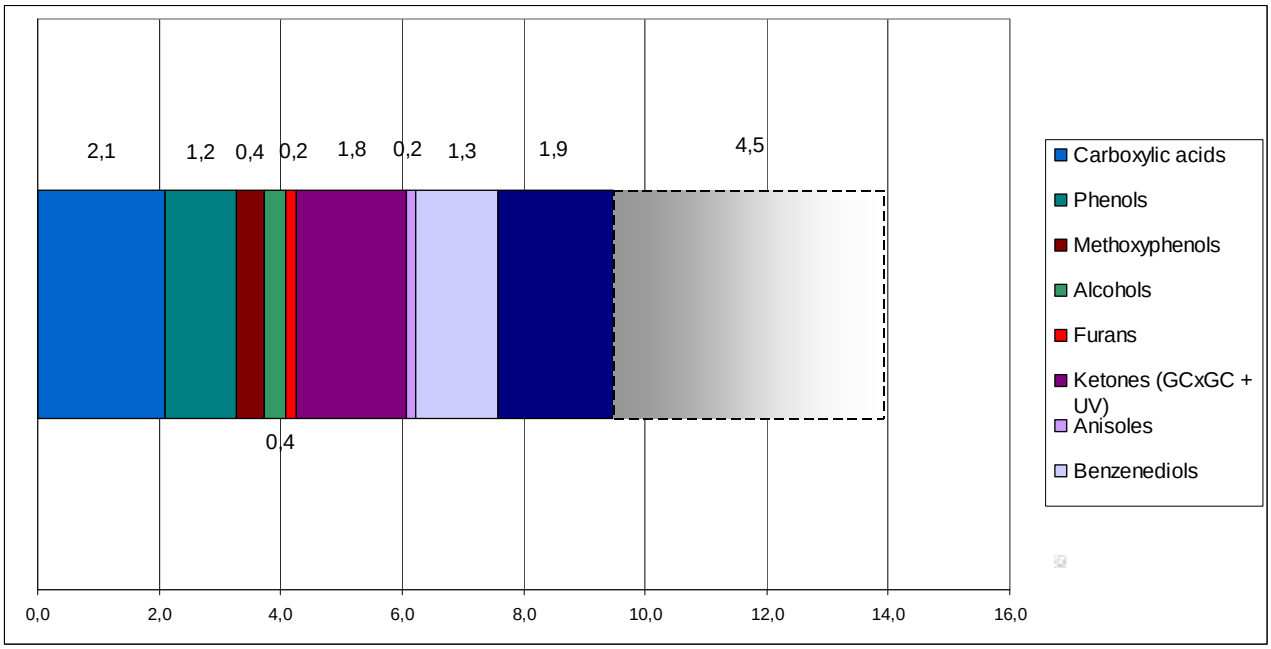


Figure 6-9. Quantification of oxygenated compounds by GC×GC expressed in elemental oxygen content (%w/w O) in the partially upgraded bio-oils

Results show that carboxylic acids are the species which contribute the most to the total oxygen content. Moreover, phenolic compounds, benzenediols and methoxyphenols are present in relative high concentrations. In total 9.7%w/w O of the oxygen content was quantified and the

unknown species (4.5%w/w O) were coeluted with aromatic and naphthenic hydrocarbons. It should be precised that the ketones content represented in Figure 6-9 is determined by UV-visible spectroscopy. By this technique, it is possible that polyfunctional groups containing other oxygenated functions such as –OH or -O-CH_3 were quantified. Therefore the total carbonyl content expressed in elemental oxygen is under-estimated.

6.4 Conclusion

By investigating different GC×GC conditions, a column combination which is adapted to oxygen speciation in a partially upgraded bio-oil was selected. Mass spectrometry data enabled the identification of more than 40 analytes of interest. Moreover quantification was possible by creating blobs associated to the identified molecules and their corresponding response factors. In addition, 41 oxygenated compounds belonging to eight chemical families were quantified: ketones, furans, alcohols, phenols, furans, carboxylic acids, guaiacols and anisols. Each family content was expressed in terms of elemental oxygen so that the contribution of each family in the global oxygen elemental content can be evaluated.

These results lead to a better understanding of these PUBs and represent a springboard towards conversion processes enhancement. The method was applied to many different samples as shown in Appendix A4. However, as many coelution remains in the aromatics zone, unknown O-species content is nearly 40%w/w O. Therefore, a separation with higher resolution or dimensionality must be achieved, and SFC-GC×GC offers bright perspectives.

CHAPTER 7. Characterization of phenolic compounds in partially upgraded bio-oils by SFC-GC×GC [8]

FOREWORD

On the one hand, normal GC×GC configurations (Non-polar × polar) generally used for petroleum fractions characterization do not allow the separation of phenolics from aromatic hydrocarbons as these two families involve similar interactions with the second dimension stationary phase which is generally phenyl PDMS (π-π interactions). On the other hand, the reversed configuration described in the previous chapter (polar × midpolar) allows the separation of phenolics but does not offer enough intra-family resolution.

Therefore, to separate phenolic compounds (which stand for phenols, methoxyphenols, benzenediols and naphthols) from hydrocarbons prior GC×GC analysis, supercritical fluid chromatography (SFC) was hyphenated to a GC×GC system in normal configuration. In fact, SFC-ethylpyridine column is very selective towards OH functional groups and allows a pre separation of aromatic-OH compounds which can be analyzed offline or online by GC×GC without coelutions with hydrocarbon aromatics. Consequently, a breakthrough detailed characterization of phenols and naphthols could be obtained. Phenols distribution is a Gaussian centered on $C_8H_{10}O$ and varies from C_6H_6O to $C_{17}H_{28}O$ whereas naphthols distribution varies from $C_{10}H_8O$ to $C_{17}H_{22}O$ and is centered on $C_{13}H_{14}O$. These results are necessary to understand reaction mechanisms during bio-oils upgrading and optimize conversion conditions.

[8] This chapter is based on two articles: one published in LC.GC Europe 2011 (24) p. 352-365 by Omais *et al.* and a second one submitted in Anal. Chem. in July 2012 by Omais *et al.*

7.1 Introduction

Considering the present energetic framework, diversifying fuel sources has become essential to meet the growing world demand sustainably. Biomass has sparked great interest as one of the possible substitutes of petroleum in the transportation field. Among the many pathways for converting biomass into biofuels, fast pyrolysis is a possible route. Biomass fast pyrolysis oils are obtained by rapidly heating biomass at around 500°C in the absence of oxygen. However, these products are far from fuel specifications and cannot be directly processed with petroleum feedstocks. In fact, they contain almost no hydrocarbons and consist mainly on oxygenated compounds (45-50%m/m O on wet basis).

Upgrading is therefore applied to obtain a product with lower oxygen and, as demonstrated in chapter 5, one of the bottlenecks in optimizing the catalytic upgrading of bio-oils is the lack of molecular information. Therefore, it is essential to characterize oxygenates in these products to understand and improve conversion reaction mechanisms.

To aid in this effort many analytical tools were deployed in the literature. Whereas spectroscopic methods such as NMR [161, 187] and FT-IR [148, 155, 172, 173, 175, 176, 190-192] gave information on different oxygenated functional groups, liquid chromatography[156, 161, 174, 191, 192] and one-dimensional gas chromatography[148, 149, 153-156, 158, 161-163, 165, 172-176, 193, 194] allowed a molecular characterization. In fact, a wide range of chemical families were identified: phenols, guaiacols, syringols, anisols, benzenediols, alcohols, furans, esters, and carbonyl compounds. However 1D-GC does not provide enough resolution for such complex matrices as coelutions with hydrocarbons are unavoidable.

Considering this, two-dimensional gas chromatography which offers a large increase in peak capacity was explored, in particular by Marsmann *et al.* who investigated biomass-derived hydrodeoxygenated oils by GC×GC [178, 181, 182]. The 2D contour plots were divided into ten zones corresponding to carboxylic acids, carbonyl compounds, alkylbenzenes, hydrocarbons, phenones, guaiacols + syringols, alcohols, furans, phenols and sugars. Even if they are only semi-quantitative (no response factors were determined), these results provided an overview of the various chemical compounds present in the investigated PUB. In this study, GC×GC separations are achieved using a first non-polar dimension combined to a polar second dimension. Thus, the first dimension stationary phase separates compounds by increasing boiling point, and the second one by polarity. In the previous chapter, reversed configurations (polar × mid-polar) were investigated

[197] and resulted in advanced separation between polar oxygenated compounds (alcohols, phenols, carboxylic acids, guaiacols) and hydrocarbons. Molecular-level quantification could therefore be reached for many species, but the method suffers from a lack of intra family resolution in particular for phenolic molecules (phenols, naphthols, benzenediols, and methoxyphenols).

To conclude, non-polar × mid-polar configurations exhibit good phenolics intra family resolution but suffers from coelutions, while reverse configurations proved high efficiency in separating phenolics from hydrocarbons but lead to low intra family resolution. The present paper presents researches aiming to overcome GC×GC limitations by gaining more resolution. In fact, a phenolic fraction was separated from the matrix (in particular from aromatic hydrocarbons) and analyzed online by GC×GC to benefit from the great intrafamily resolution without being limited by coelutions.

For online hyphenation purpose, a Supercritical Fluid Chromatography (SFC) dimension with CO_2 as a mobile phase appears more compatible to a gas phase dimension than a Liquid Chromatography (LC) dimension. In fact, SFC provides higher selectivity and can be carried out faster than LC separations [198]. The hyphenation of SFC with GC has been already demonstrated by the decompression of the supercritical fluid via a restrictor inserted into the GC inlet [199]. This simple interface was used in different multi-dimensional systems such as SFC-GC [200], SFC×GC [201, 202] and recently SFC-GC×GC [203].

In this chapter, SFC-GC×GC was implemented to separate the phenolic fraction by a selective ethylpyridine stationary phase, and transfer it online to a GC×GC system. Results show a breakthrough separation of phenols and naphthols which can henceforward be quantified at a molecular level. This detail level in terms of phenolic compounds characterization in such complex matrices was never reached so far.

7.2 Materials and methods

7.2.1 Samples

7.2.1.1 Dehydroxygenated biomass flash pyrolysis oil

The investigated sample is a fast pyrolysis oil which was partially dehydroxygenated and provided by IFP Energies nouvelles as shown in the previous chapter (Figure 6-1). No distillation was applied to the liquid which has boiling points ranging from 30°C to 630°C according to the simulated distillation analysis (ASTM D2887). The hydrogen content is determined by NMR (ASTM D4808), the carbon content is determined by combustion (ASTM D5291), the nitrogen content is measured by chemiluminescence (ASTM D4629), the sulphur content is provided by X-ray fluorescence (ASTM D2622), the oxygen content by pyrolysis followed by infrared detection (internal method), and the water content by Karl-Fischer titration. All values are summarized in Table 7-1.

The previous chapter investigating this sample showed that among the total elemental oxygen (13.93%w/w O on wet basis), 3.1%w/w O consists in phenolic compounds (phenols, naphthols, benzenediols and methoxyphenols). These species which will be called Ar-OH throughout the paper were separated by GC×GC but it was hard to reach a carbon atom distribution because of the lack of intra-family resolution.

Table 7-1. Elemental composition of the PUB (on wet basis)

	Content %w/w
C	75.7
H	10.1
O	13.93
N	0.135
S	<0.1
Water	2.0

7.2.1.2 Model mixtures

- MM1: This model mixture was prepared in the framework of oxygen speciation in coal-derived liquids. In order to evaluate the potential of different columns to separate targeted species,

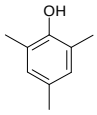
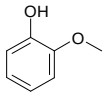
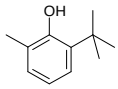
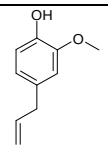
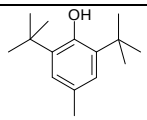
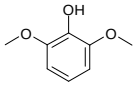
a model mixture (MM1) was prepared. Six families were selected because they were identified in previous work on coal-derived liquids: paraffins, naphthenes, aromatics, furans, phenols, and nitrogen-containing compounds. For each family a low and a high molecular mass compounds were selected (Table 7-2). 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.

Table 7-2. Model mixture MM1 composition

Family	***Compounds***	***Content %w/w***
Paraffins	nC8	0.95
	nC22	1.04
Naphthenes	Cyclohexane	1.09
	Fluorene	1.16
Aromatics	EtBenzene	1.28
	Pyrene	1.16
Furans	Benzofuran	1.35
	Dibenzofuran	0.96
Phenols	Cresol	1.32
	Naphthol	0.92
Nitrogenated compounds	DiMe-Indole	0.91
	Et-Carbazole	1.10
	Et-Aniline	1.12
	Et-Pyridine	1.28

- MM2: To complement MM1, a second model mixture (MM2) containing Ar-OH compounds was prepared to evaluate their elution zones in SFC-FID chromatograms and in GC×GC chromatograms. MM2 was composed of three phenolic compounds, two guaiacols, a naphthol and a catechol. These were dissolved in ethyl acetate with a content ranging from 0.8%w/w to 1.3%w/w. These targeted species were investigated as they were evidenced in chapter 6. Table 7-3 gives details on MM2 composition.

Table 7-3. Composition of the investigated model mixture (MM2)

Compound	*Raw formula*	*Structure*	*Molecular mass (g/mol)*	*Compound*	*Raw formula*	*Structure*	*Molecular mass (g/mol)*
Trimethyl-phenol	$C_9H_{12}O$		136	Guaiacol	$C_7H_8O_2$		124
6-tertbut-o-cresol	$C_{11}H_{16}O$		164	Eugenol	$C_{10}H_{12}O_2$		164
2,6-ditertbut-Methyl-phenol	$C_{15}H_{24}O$		220	Syringol	$C_8H_{10}O_3$		154
Naphtol	$C_{10}H_8O$		144	Catechol	$C_6H_6O_1$		110

7.2.2 SFC-FID

Samples injection in the SFC system was achieved using a 100 µL loop and carbon dioxide (Alphagaz CO_2 SFC grade) was used as the mobile phase. It was delivered at a constant flow rate of 2 mL/min by a pump PU-2080-CO_2 (Jasco, Bouguenais, France). A pressure regulator BP-2080 (Jasco, Bouguenais, France) was used to regulate the backpressure at 15 Mpa.

An in-house modified gas chromatograph (GC6890, Agilent, France) was used as the SFC oven and the SFC column were connected to a flame ionization detector. For this purpose, the total supercritical flow rate was split (about 1:100) by an inert restrictor (ID: 10µm, OD: 360µm, Postnova analytics) via a stainless steel cross union ZT1C (1/16'', 0.25mm, VICI). The FID was set at 350°C, with a H_2 flow, air flow and makeup respectively equal to 40, 450, and 45mL/min. Two two-positions switching valves were managed via a pneumatic controller (6 ports AC6W, VICI, Schenkon, Switzerland): valve V1 controled the injection, and valve V2 controled the front/backflush of the sample (Figure 7-1).

All tubular connections were in stainless steel (1/16 × 0.13 mm, 0.005', Interchrom, Montluçon, France) and valves were placed in regulated head chambers located at the top of the

GC chromatograph. The SFC system was controlled by independent Chemstation software (Agilent, Massy, France). The system is schematized in Figure 7-1.

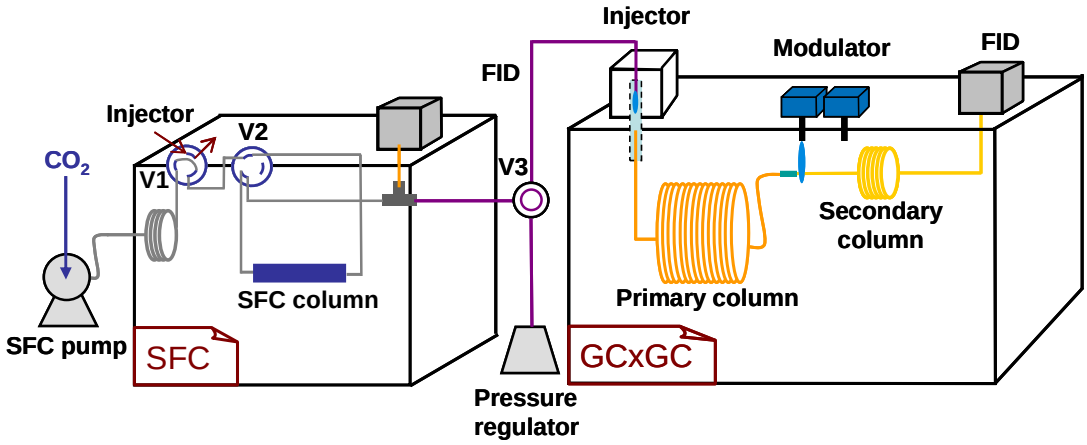


Figure 7-1. SFC-GC×GC system scheme

7.2.3 Online GC×GC-FID

The GC×GC system consisted of an in-house modified 6890 chromatograph (Agilent, Massy, France) equipped with dual stage carbon dioxide jets. It was equipped with a splitless inlet and a FID. H_2 and air flow rates were respectively 35 and 400 mL/min. Helium (99.99%) was used as the carrier gas at constant adapted pressure.

Components were cryofocused in the head of the first dimension at -30°C during the transfer of SFC fractions into the GC×GC system. Then, the oven was controlled to return to the initial temperature (30°C) at 20°C/min and the analytical ramp was programmed at 2°C/min up to 300°C (Figure 7-2).

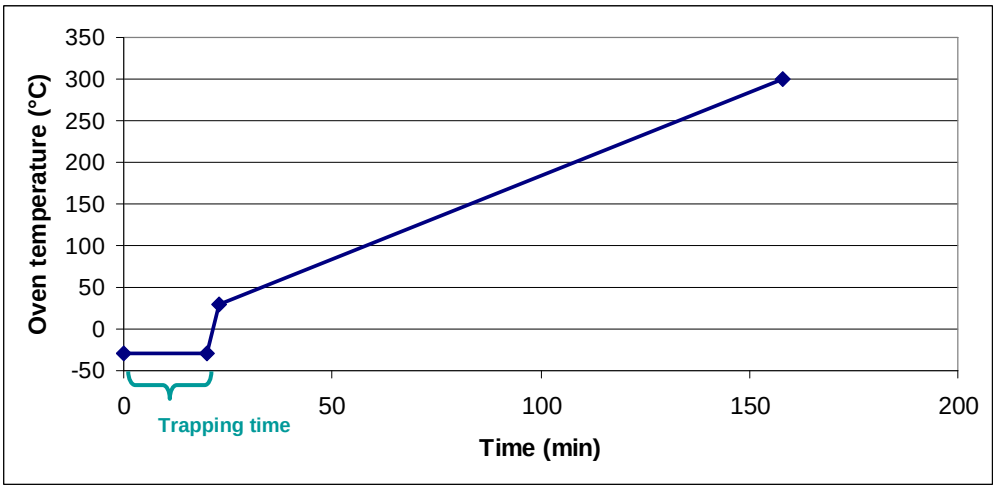


Figure 7-2. Oven temperature program

The data processing of 2D-GC contour plots was performed by 2DChrom® (IFP Energies nouvelles) after raw data transfer as CSV-files. The control of the GC×GC dimension, of the interface valve and of the data acquisition was performed using another independent Chemstation software (Agilent, Massy, France). The 2D modulation was controlled by a house-built controller, set at 14 seconds and carried out on the second column.

7.2.4 Offline GC×GC-FID and GC×GC-ToF/MS

Before the offline analysis by GC×GC, Ar-OH and non-Ar-OH supercritical fractions were collected at atmospheric pressure. To minimize pollution between fractions, the pressure regulator in which fractions were collected was rinsed with 5 mL of acetone and cleaned. Fractions were then dissolved in CS_2. The non-phenolic one (Non-AR-OH) was uncolored whereas the phenolic fraction (AR-OH) was light brown.

These fractions were analyzed using a HP 6890 chromatograph which was equipped with a split inlet (Agilent Technologies), a Flame Ionisation Detector (FID) and a Time of Flight Mass Spectrometry (ToF/MS) detector (LECO Pegasus IV, St. Joseph, MI, USA).

The injection was carried out at 320°C (0.3µL) with a split ratio equal to 1:10 to cope with samples low concentrations and a constant pressure set at 27 Psi. The flame ionization detector system was set at 320°C. H_2, air, and He makeup were set respectively at 35, 400, and 25 mL/min. Helium (99.99% Air Liquid, France) was used as a carrier gas. Oven temperature was programmed from 30°C to 300°C with a ramp of 2°C/min which was selected because it corresponds approximately to the inverse columns dead time. Concerning the modulation, it was performed by a liquid Nitrogen cooled gas jet cryogenic modulator and the modulation period was set at 10 seconds.

For identification purposes, ToF/MS detection was used. The acquisition frequency of the detector was set at 100 Hz in a mass range of 45-750 amu. Electron Ionization was carried out at 70eV and a multiplate voltage of -1450V was used.

7.2.5 SFC fractions transfer into the GC×GC system

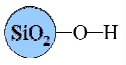
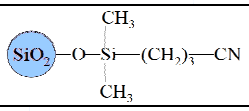
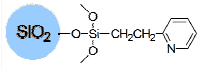
As described by Levy *et al.* [199] the transfer of SFC fractions to GC×GC was achieved by decompression of the supercritical fluid via a restrictor inserted into the GC inlet. Oven temperature was maintained at -30°C and the restrictor flow rate was approximately equal to 10 mL/min during transfer. Supercritical mobile phase is depressurized inside the restrictor and compounds were trapped on the first centimetres of the cold primary GC×GC column. After 20 minutes, once the transfer was achieved, the purge valve of the injector was opened to drain the residual CO2 out of the system and the oven returns to the initial temperature (30°C).

To monitor supercritical effluents transfer, valve 3 (see Figure 7-1) was introduced in a high capacity oven supplied by Interchrom (Montluçon, France) where the same temperature as the SFC separation was applied. Thus, any change in the physical state of the supercritical effluents can be avoided.

7.2.6 Stationary phases

In order to separate phenolic compounds, polar stationary phases were investigated. These SFC columns are compiled in Table 7-4.

Table 7-4. Model mixture representative of the coal derived middle distillate.

Name	*Structure*	*Dimensions*	*Provider*
Silica		5µm, 30x250mm	Sepax
Cyano		5µm, 30x250mm	Sepax
Ethyl-Pyridine		5µm, 30x250mm	Sepax

SFC-Pyridine stationary phase (5µm, 30x250mm) built by Sepax (Jasco, Bouguenais, France) was used for supercritical fluid chromatography pre-separation. The uniform, spherical SFC-Pyridine particles have a nominal surface area of 300 m^2/g with a controlled pore size of 120Å. Typical applications for SFC-Pyridine are the separations of both polar and non-polar compounds, such as pharmaceuticals, carbohydrates, amino acids, nucleotides, and organic acids. As far as GC×GC column set is concerned, it is composed of a PONA supplied by Agilent (20m×0.200mm×50µm) and a BPX-50 supplied by SGE (1.3m×0.10mm×0.10µm).

7.3 Results and discussion

7.3.1 SFC separation

7.3.1.1 SFC stationary phase selection

The objective of this part is to select among three stationary phases the most appropriate one to separate phenolic compounds from the rest of the matrix (hydrocarbons). As the same selectivity can happen with N- and O-compounds, and our sample contains N-compounds, it was judicious to investigate the retention of this heteroatomic class. These three phases were selected according to their interactions with phenolic compounds. In fact hydroxyl groups can form H-bonds with the various lone pairs of the stationary phases (Figure 7-3).

Thus, silica phase is very retentive towards phenolic compounds because it implies a double H-bond as described in Figure 7-4-A. Moreover, this phase interactions with the aromatic group is non-negligible. Concerning the Pyridine stationary phase, it involves O-H···N hydrogen bond which is stronger than the O-H···O one (29kJ/mol against 21kJ/mol). Besides, this phase is composed of three Si-O groups implying both two lone pairs of electrons which will form additional H-bonds with the labile proton. Π-π interactions between the two aromatic groups can also be formed. For all these reasons, the pyridine stationary phase will be very retentive towards phenols and stands as a solution to separate them from the hydrocarbon matrix. Cyano stationary phase was also studied because it implies H-bonds with phenols as it possesses one lone pair on the nitrogen atom and two others on the oxygen one.

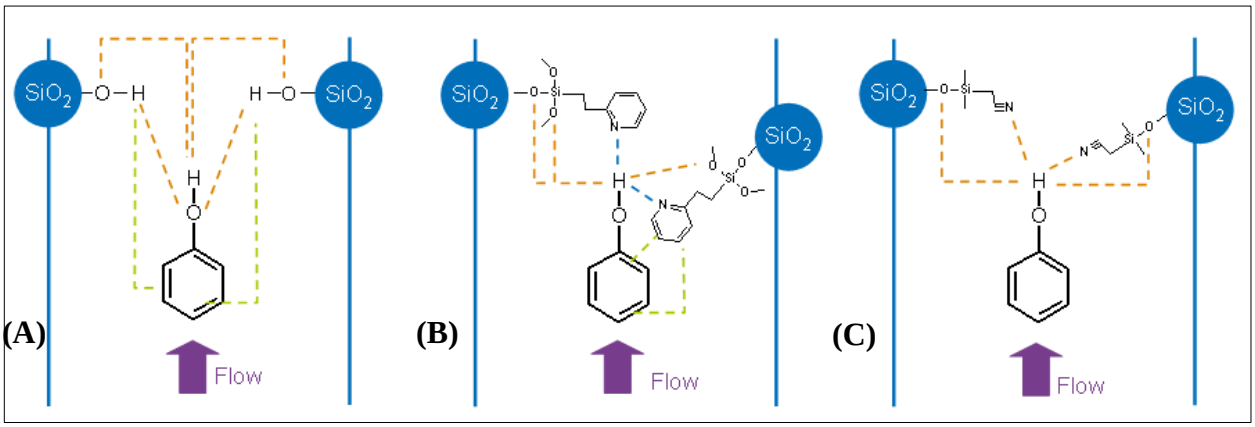


Figure 7-3. Interactions between phenols and stationary phases

In a nutshell, pyridine phase implies four strong H-bonds with phenols, while silica and cyano phases involve respectively three and two H-bonds with these targeted species. In order to gauge phenols separations with these three phases, cresol and naphthol were injected in the SFC-FID system. The elution times of these species are reported in Figure 7-4. Hydrocarbons and N-compounds were also injected to evaluate their elution times. As expected, hydrocarbons directly elute from the column as no strong hydrogen bonds are formed with these phases. N-compounds are also strongly retained by all these columns especially for the Silica one which can form H-bonds with aniline, pyridine, carbazoles and indoles.

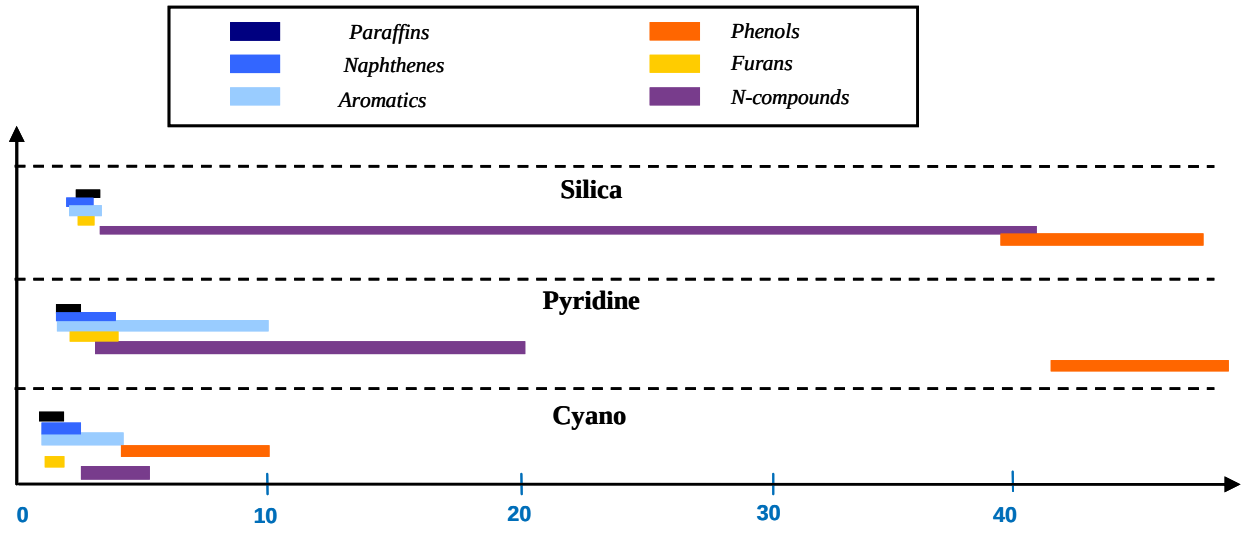


Figure 7-4. Elution zones of different chemical families based on the analysis of MM1 by SFC-FID

7.3.1.2 Test of SFC-Pyridine stationary phase on a reference sample

Considering the elution zones of all chemical families, pyridine stationary phase was selected to separate phenols. A reference sample (coal-derived middle distillated described in chapter 2) was investigated. Considering the previous separation of phenolic compounds, SFC was coupled to GCxGC in order to obtain a detailed characterization. Previous works in GCxGC showed that the stationary phases combination Polyethylene glycol x Polydimethyl siloxane leads to a specific elution zone corresponding to phenolic compounds as shown in Figure 7-5-A. When combined to the Pyridine SFC dimension, the GCxGC leads to a chromatogram where only this specific zone appears (Figure 7-5-B). This highlights the separation of phenolic compounds by the first SFC dimension. Moreover, the SFC separation is so selective in this case, that a one-dimensional GC should be sufficient to access to a detailed characterization of phenols.

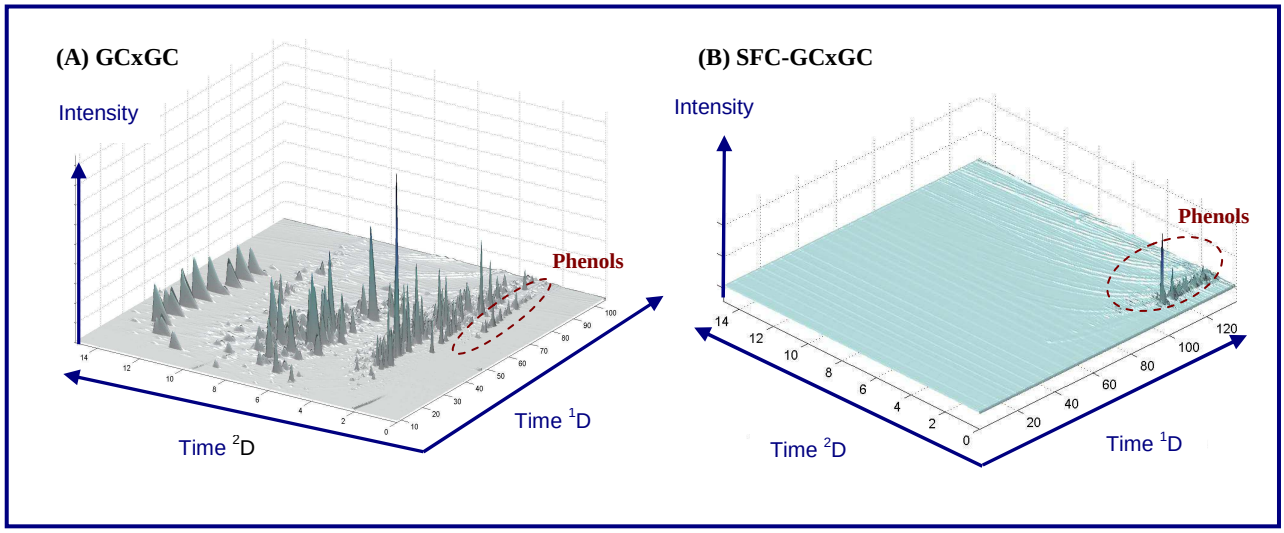


Figure 7-5. 3D chromatograms of a coal-derived middle distillate by GCxGC-FID (Solgelwax x DB-1). (A): without a SFC pre-separation, (B) with a SFC pre-separation (SFC-Ethylpyridine stationary phase) [202]

7.3.1.3 SFC-Pyridine stationary phase

The SFC-ethylpyridine stationary phase was considered in this study as it enables the separation of aromatic compounds with one or many –OH functional groups (Ar-OH): phenols, benzenediols, naphthols, methoxyphenols. Previous works [203] show that most of non-aromatic hydrocarbons elute very quickly from the SFC column. Only heavy three-ring and four-ring aromatics elute after 7 minutes but are supposed to be present in relatively low content in the sample according to the previous chapter. Concerning phenol, naphthol, guaiacol, syringol, eugenol and catechol, the injection of MM2 shows that they are all eluted after 7 minutes. It was therefore, decided to use this column to separate non-phenolics which elute before 7 minutes from phenolics by backflushing supercritical effluent at this precise time. The selectivity of the SFC stationary phase is based on strong H-bond interactions between ethylpyridine and hydroxyl groups. Such selectivity can hardly be reached using LC or GC stationary phases as this pyridine stationary phase was investigated only for supercritical fluid chromatography purpose to our knowledge. Compared to alkanes, aromatic hydrocarbons are eluted much later what is due to dipole-dipole interactions.

To make sure that all analytes are backflushed, to enable a fast pre-separation and to focus the backflushed fraction in a wide period of time, the pressure regulator was set at 35 MPa from 7 to 20 minutes during the backflush. This operation increases the eluent strenght of carbon dioxide. Backflushed compounds were transferred online in the GC×GC system by valve 3 or collected at the pressure regulator for further analyses.

Figure 7-6 shows the SFC-FID chromatogram of the investigated partially upgraded bio-oil. It exhibits a first non-phenolic broad peak from 3.3 to 8.6 minutes. Then, the backflushed Ar-OH fraction appears between 14.1 and 20 minutes. To reach a detailed characterization of the Ar-OH fraction, online and offline GC×GC was achieved. For online GC×GC analysis, valve 3 is opened at 7 minutes and the backflushed fraction was transferred in the GC×GC system and cryofocused at -30°C at the head of the first GC dimension. For collection purpose (offline mode), a vial was placed at the backpressure regulator and a low but sufficient volume of the backflushed phenolic fraction was recovered and stored at 4°C as explained in part 2.4. The normalized relative areas are respectively 79% w/w and 21% w/w for the non-Ar-OH and the Ar-OH fractions. These values cannot be considered as contents because no response factors are taken into account.

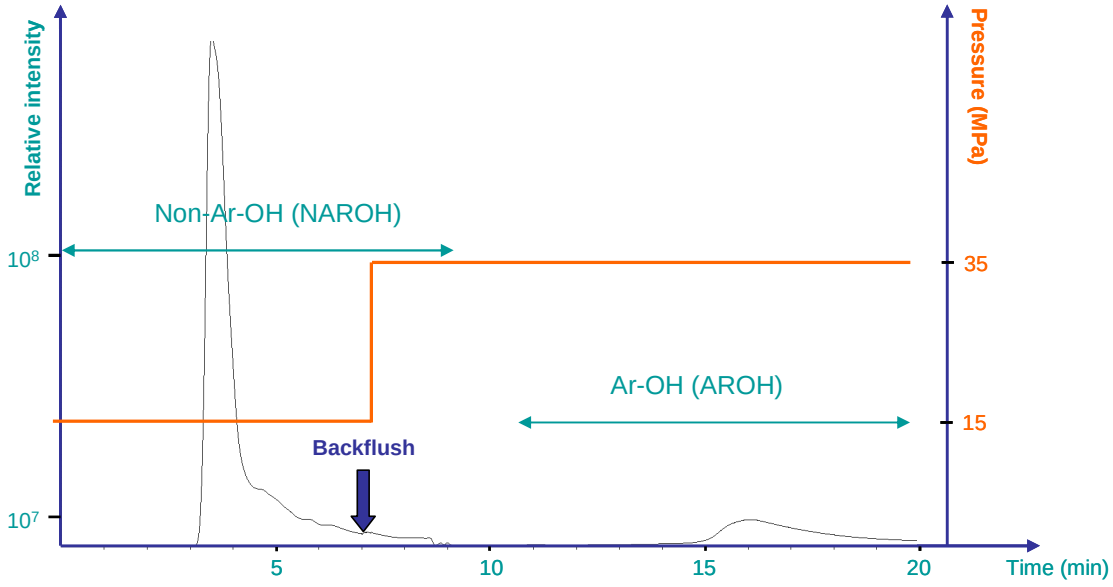
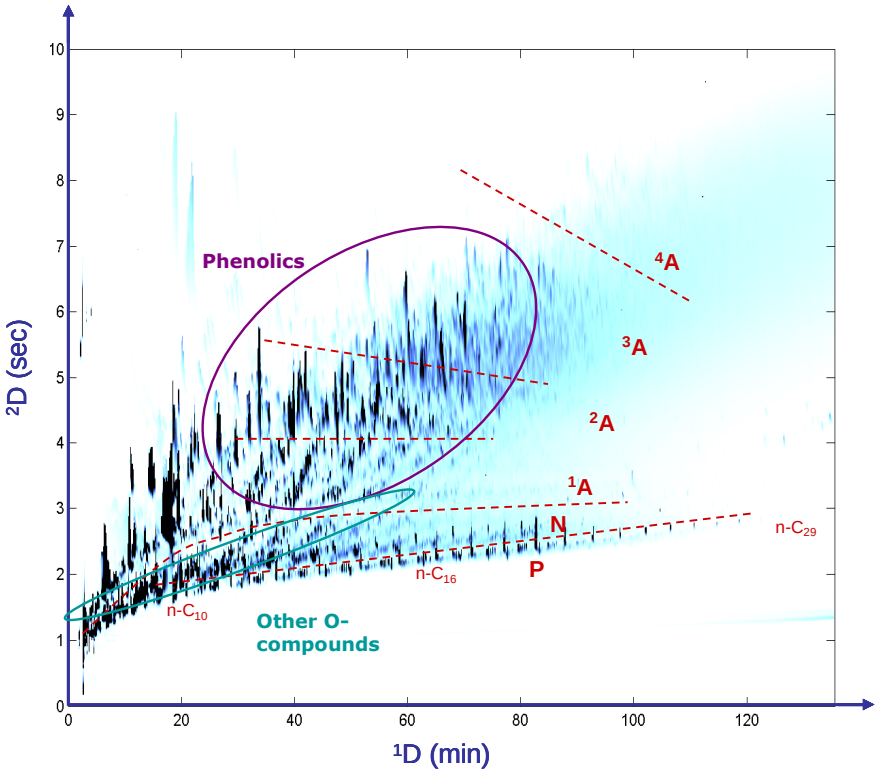


Figure 7-6. SFC-FID chromatogram of the PUB using SFC-EThyle pyridine phase

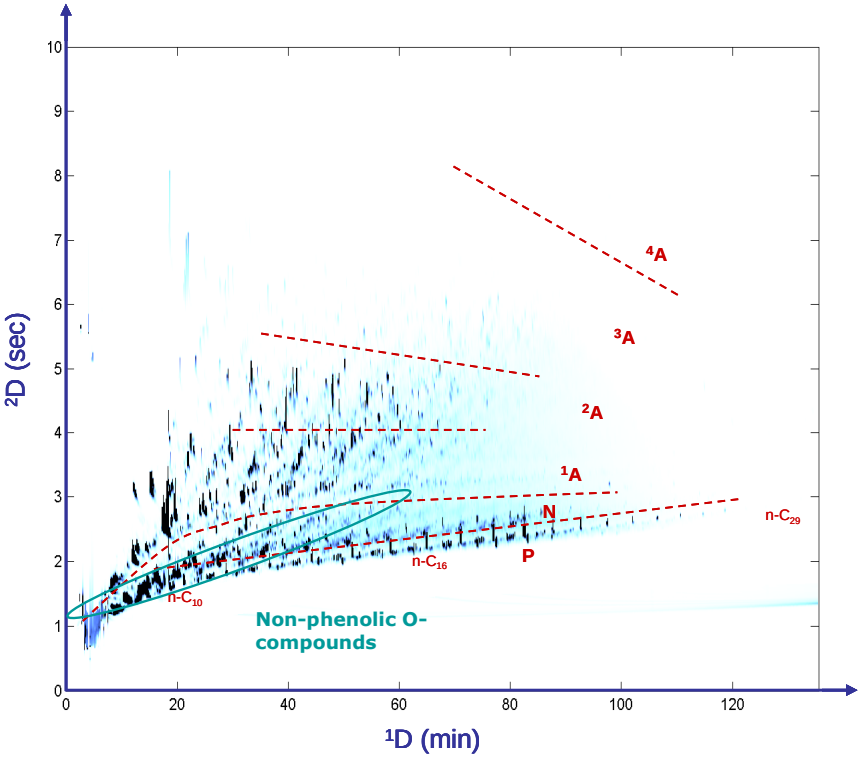
7.3.2 Offline GC×GC analysis of SFC fractions

Firstly, the whole PUB was analyzed by GC×GC using the column set described in section 2.6. The 2D contour plot is shown in Figure 7-7-A. This column set, usually implemented for petroleum AGO analysis shows that for the investigated PUB, many coelutions appear between hydrocarbon aromatics and phenolics.

The non-AR-OH fraction 2D contour plot is more structured and highlights hydrocarbon compounds (Figure 7-7-B). Other oxygenated compounds such as ketones, furans and alcohols are also present but coelute with naphthenic compounds. A deeper insight on this fraction must be obtained and is still an analytical challenge today.



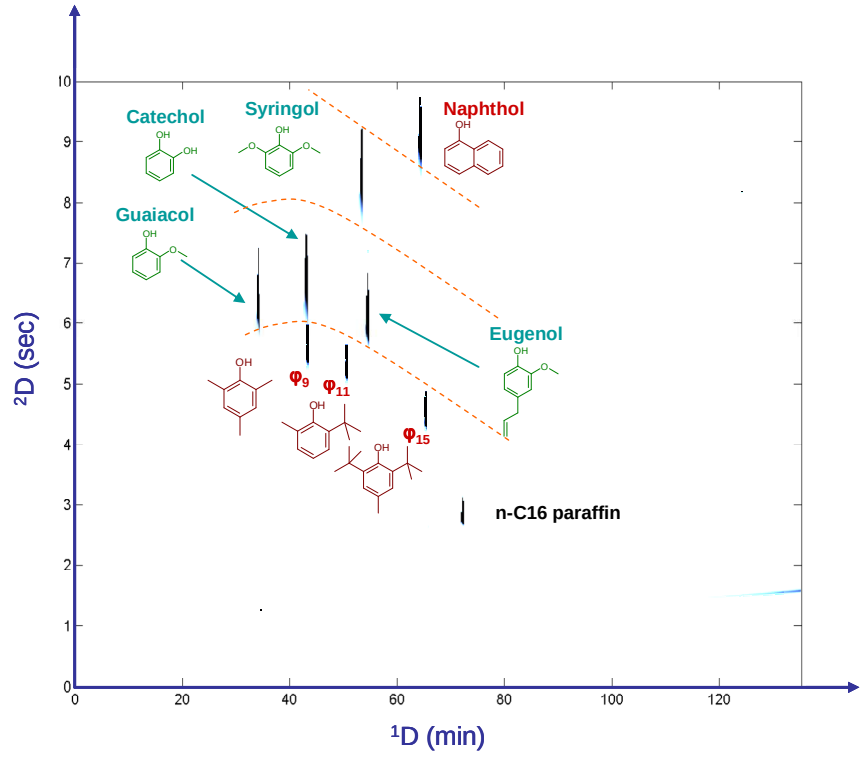
(A)



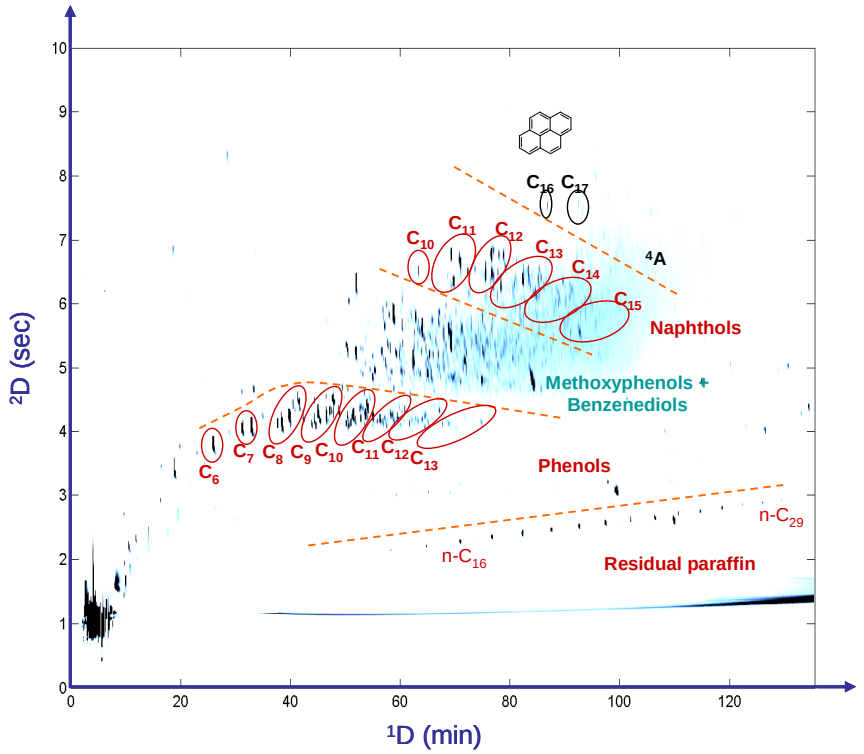
(B)

Figure 7-7. GC×GC-FID chromatogram of PUB (A) and its non-AR-OH fraction obtained by SFC (B). P: paraffins, N: naphthens, iA: aromatics with i rings PONA (20m×0.2mm×0.50µm)×BPX-50 (1.3m×0.1mm×0.1µm)

As mentioned in the experimental section, the injection of MM model mixture (Figure 7-8-A) and the use of offline GC×GC-ToF/MS enabled the identification of compounds contained in AR-OH. Four main elution zones are emphasized in Figure 7-8-B: phenols, methoxyphenols and benzenediols, naphthols, heavy aromatic hydrocarbons and residual paraffins. The phenol zone exhibits a very high resolution between different species. Compounds are well-organized according to their structure. In fact clusters can be defined to gather alkylated phenols families versus their number of carbon atom in the alkyl chain(s). For example, cluster corresponding to C9-phenol is likely to contain trimethylphenols, propylphenols, or ethylmethylphenols. A precise and detailed distribution by carbon atom number is henceforth reachable. The second zone offers less resolution as it includes guaiacols, syringols and catechols. Finally, as naphthols are much more retained than the other species, a zone corresponding exclusively to this family is observed and clusters can also be easily defined. For quantitative purpose, it is however meaningful to use online coupling between SFC and GC×GC.



(A)



(B)

Figure 7-8. GC×GC-FID chromatogram of MM (A) and the Ar-OH fraction obtained by SFC (B). PONA (20m×0.2mm×0.50µm)×BPX-50 (1.3m×0.1mm×0.1µm)

7.3.3 Online SFC-GC×GC analysis

Online SFC-GC×GC was implemented to achieve the analysis in one single run and avoid contamination from one recovered fraction to another during the collection step. This system should provide more accurate results as supercritical effluents are directly transferred into the GC×GC inlet. The SFC-GC×GC chromatogram obtained online (Figure 7-9) is similar to the GC×GC chromatogram of the recovered fraction (Figure 7-8) and confirms the efficiency of the interface as shown previously. GC×GC conditions have however slightly changed and the modulation was achieved by dual-stage CO_2 jets instead of liquid Nitrogen cooled gas jet. Therefore peaks broadening can be observed in the second dimension.

Blobs were then created to quantify phenols and naphthols by clusters. As the FID response varies with the presence of heteroatoms in the molecule, response factors of these targeted species were calculated in the previous chapter. It was demonstrated that response factors of phenols and naphthols vary from 1.2 to 1.3 according to their carbon atom number. Concerning zone 21, an average response factor equal to 1.6 was used (according to chapter 6). A database associating each blob to a molecule and its specific response factor was created. A detailed molecular quantification by GC×GC-FID was carried out after integration of the corrected normalized areas. There are not enough identification details in zone 21 to allow a molecular description of methoxyphenols and benzenediols.

Results show that two Gaussian distributions can be obtained for the two targeted families (Figure 7-10). Phenols distribution is centred on an alkylation degree of 2, whereas naphthols distribution is centred on alkylation degree of 3. Compared to previous works [181] using a normal GC×GC combination, no coelution with aromatic hydrocarbons occurs and response factors are taken into account what increases the quantification precision. Moreover, compared to reversed configuration analysis, there is much more intrafamily resolution. However, it is not possible to reach an absolute quantification taking into account the whole sample without making approximation on average response factors for each of the two SFC fractions. These advanced results are of major importance to have a deeper insight on conversion routes of these liquids into alternative fuels.

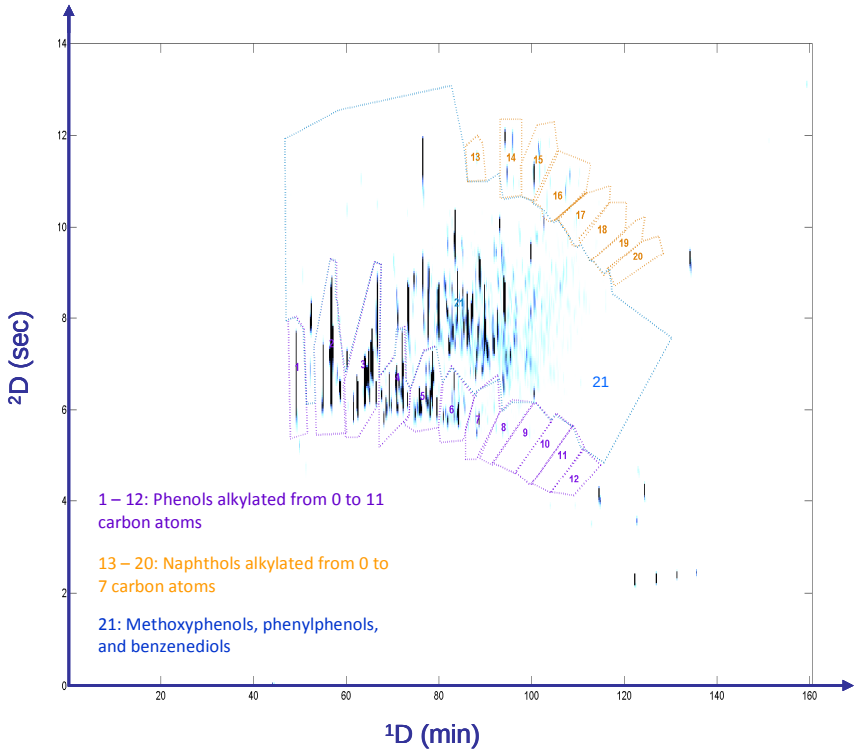


Figure 7-9. Online SFC-GC×GC-FID chromatogram of the AR-OH fraction. SFC-Pyridine-PONA (20m×0.2mm×0.50µm) × BPX-50 (1.3m×0.1mm×0.1µm)

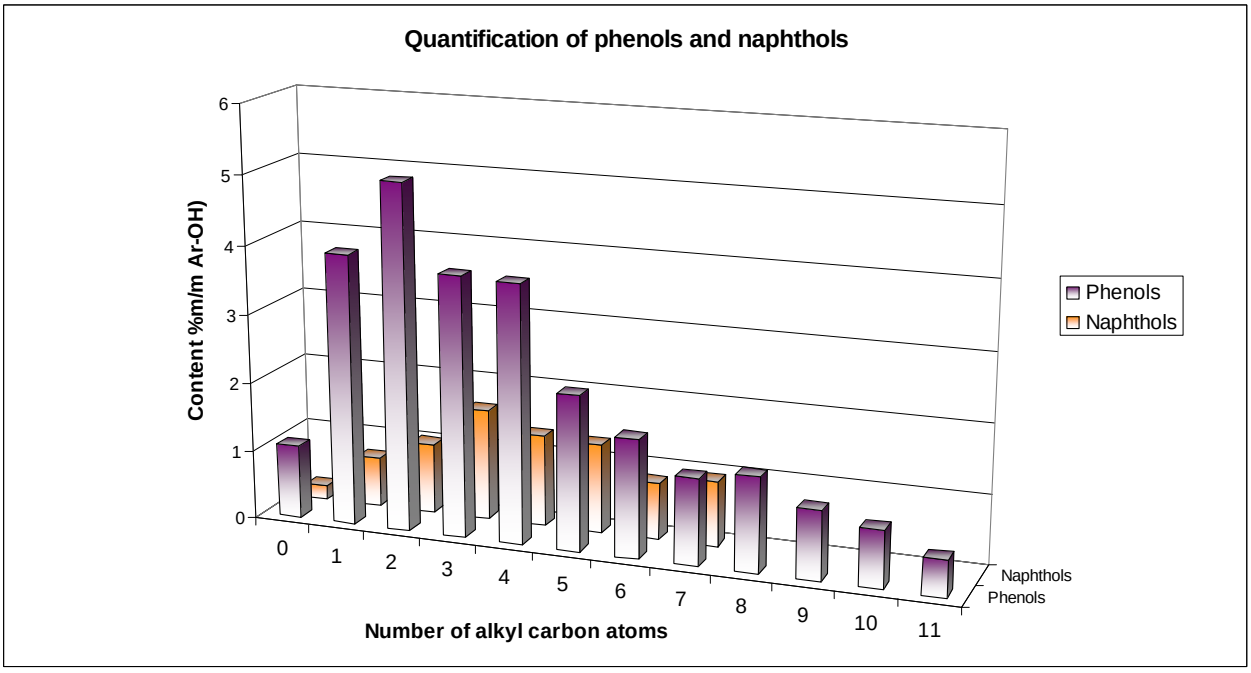


Figure 7-10.Quantification of phenols and naphthols in the Ar-OH fraction of the investigated PUB using online SFC-GC×GC.

7.4 Conclusion

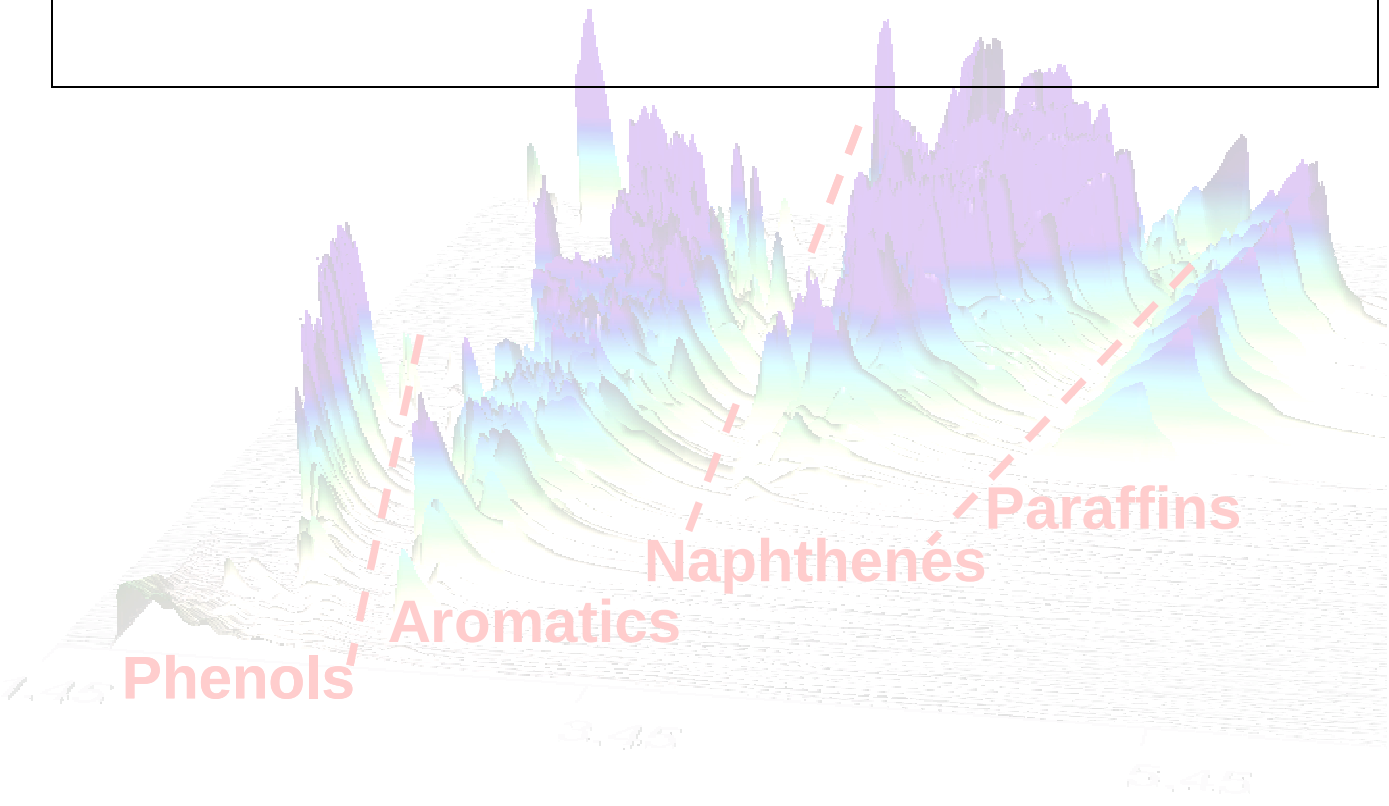
A better insight on phenolic compounds was reached *via* the SFC hyphenation to GC×GC. The ethylpyridine column used in this work is very selective towards the aromatics containing one or more -OH functional group and allows their online pre separation. These species can then be analysed by GC×GC without coelutions with hydrocarbon aromatics. Consequently, a breakthrough detailed characterization of phenols and naphthols was obtained. These results will be useful to monitor reaction mechanisms during bio-oils upgrading and optimize conversion conditions.

Nevertheless, further investigations must be completed to provide a better insight on methoxyphenols and benzenediols. Moreover, the non-phenolic fraction should be characterized to evaluate hydrocarbon conversion products as well as other non-phenolic oxygenated compounds such as ketones, furans, and esters contents. This step is a real analytical challenge which can be taken up by using other SFC columns selectivities and new high resolution mass spectrometry systems.

CONCLUSION TO PART B.

This part led to a better understanding of partially upgraded bio-oils composed of hydrocarbons and a wide range of chemical families. Two analytical methods were developed. The first one using GC×GC reversed configuration enables a quantification of all carboxylic acids, and alcohols. Some furans, phenols and ketones were also quantified. Phenolics content can be determined at a non-molecular level as, even if separated from the rest of the matrix, these species coelute with each other. A better insight on phenolic compounds therefore reached *via* the SFC hyphenation to GC×GC. Using H-bond interactions of the Ethyl pyridine SFC stationary phase, these species can be separated in a fraction and analysed on-and off-line by GC×GC without coelutions with hydrocarbon aromatics. Consequently, a breakthrough detailed characterization of phenols and naphthols was obtained. These results will be useful to monitor reaction mechanisms during bio-oils upgrading and optimize conversion conditions. However developments are still in progress to a detail on methoxyphenols and benzenediols also present in the phenolic fraction.

Part C. Deductions on orthogonality in GC×GC



INTRODUCTION TO PART C: DEDUCTIONS ON ORTHOGONALITY IN GC×GC

Researches presented on Parts A and B exposed the analytic achievements on coal and biomass-derived matrices. By investigating different GC×GC conditions in these two previous parts, reversed configurations which could be considered as less orthogonal than normal configurations always showed the best separations of oxygenated compounds. Therefore, a discussion on these reversed systems is introduced in part C.

Firstly, the notion of orthogonality which implies space occupation is discussed in chapter 8. This discussion is based both on retention mechanisms dependence of the two dimensions and on 2D space occupation equations. Then, the reversal of elution order by changing the first stationary phase nature is discussed in chapter 9. This chapter shows why reversed configurations are often more adapted for polar compounds analysis and discusses the advantages and the drawbacks of these "unconventional" configurations.

CHAPTER 8. Considerations on orthogonality duality in comprehensive two-dimensional gas chromatography [9]

FOREWORD

The term "orthogonal" in comprehensive two-dimensional gas chromatography has a double sided meaning as it stands for a separation resulting from the combination of two independent retention mechanisms [106] but also for a 2D separation where the components are evenly distributed over the entire 2D space.

It is shown in the present chapter that a reversed GC×GC system associating a polar stationary phase in the first dimension (Polyethylene glycol) to a non-polar one in the second dimension (Polydimethyl siloxane) leads to a structured chromatogram, a high peak capacity, and a great 2D space occupation. This idea is demonstrated through the characterization of oxygenated compounds in a coal-derived middle distillate investigated in part A. Results show a clear separation between oxygenated species and hydrocarbons which are classified into linear alkanes, cyclic alkanes, and aromatics.

As shown in previous chapters an unconventional configuration combining a polar polyethylene glycol first dimension and a trifluoropropyl methyl stationary phase in the second dimension enabled a unique identification and quantification of linear, cyclic, and aromatic alcohols. This configuration which could be considered as poorly orthogonal still involves two different retention mechanisms: polarity and boiling point in the first dimension, boiling point and electronic interactions in the second dimension. It is selective towards electronegative poles of alcohols and phenols.

The contributions of these two configurations compared to a conventional orthogonal system as well as their roles for oxygenated compounds speciation are highlighted. This contribution is measured through three 2D space occupation factors. It appears through these two examples that orthogonality is intimately linked to analytes properties and a general concept of dimensionality must be considered.

[9] This chapter is based on an article published in Analytical Chemistry, 2011 (19) p 7550-7554 by Omais *et al.*

8.1 Introduction

Orthogonality in comprehensive two-dimensional gas chromatography separations is a topic of "active discussion" according to Watson *et al.*[205]. To be orthogonal, a GC×GC system must be a combination of two stationary phases involving two independent separation mechanisms [106]. In other terms, retention times in each dimension should be able to be treated as statistically independent [206]. Usually, a first non-polar dimension is combined to a polar second dimension. Thus, the first dimension stationary phase separates compounds by increasing boiling point, and the second one by polarity considering the short separation time in the second dimension. In view of this configuration, the system can be considered as orthogonal because compounds are separated by two different retention mechanisms. In opposition, when a GC×GC system associates a polar stationary phase in the first dimension to a non-polar one in the second dimension, components are separated both by polarity and boiling points in the two dimensions. Therefore, it is often said that the system is not or poorly orthogonal, even if the polar first dimension only indicates what types of intermolecular interactions were involved between the analytes and the stationary phase.

Graphically, orthogonality defines in which extent the peaks occupy the 2D separation space [207]. According to Ryan *et al.* [108], it measures the "magnitude of two-dimensional separation space that is utilized".

However, many separations in GC×GC involving a "poorly orthogonal" columns set (Polar × non-polar) greatly occupies the 2D space especially for petroleum products [208], Fischer-Tropsch products [100, 116] and biodiesel blends [216]. Adahchour *et al.* [208] shows that the BP21 × BPX-35 combination that they define as "non-orthogonal" gives a good separation between alkanes and aromatics. Concerning Adam *et al.*, the same type of combination (Solgelwax x DB-1) is used to separate FAMEs in biodiesel blends. van der Westhuizen *et al.*[116] refer this approach as a "reverse polarity mode" (DB-Wax x TRB-5) and differentiate cyclic olefins, dienes, and cyclic dienes in Fischer Tropsch products. All these studies lead to high space coverages. Consequently the notion of orthogonality appears as a dual concept dealing with theoretical considerations on retention mechanisms independence, and experimental concepts on space occupation. The aim of this study is to show the inconsistence between these two definitions and to decouple the concept of orthogonality and the one of 2D space occupation.

Different methods to evaluate orthogonality will first be described. These approaches will then be used to evaluate the space occupation of four separations. Materials and methods will then be described before discussing the duality in the orthogonality description. These investigations are oriented towards the separation of phenolic compounds in a coal-derived middle distillate which have been targeted in Part A.

8.2 Theory

To select the optimal conditions in an analytical method optimization, it is useful to evaluate "orthogonality" or 2D space peaks coverage. Many criterions exist to quantify this variable.

Graphical approaches consist in determining the occupation ratio of components. For this purpose Gilar *et al.* suggest to use the degree of surface coverage with peaks [110]. This approach consists in dividing the 2D space into rectangular bins and in evaluating the number of occupied bins. The corresponding equation is cited as equation 8-1 below where P_{max} is the sum of all bins (total peak capacity) and Σbins is the number of bins containing data points.

$$O = \frac{\sum bins - \sqrt{P_{\max}}}{0.63 P_{\max}} \qquad \text{Equation 8-1}$$

Limitations of this theory have been discussed by Watson *et al.*[1] In fact, for a given percentage, O is constant for large P but deviates drastically for smaller P. The more bins there are, the more relevant the value will be. Figure 8-1-A illustrates an example of 2D space meshing. It shows that among 36 bins, 9 are occupied by at least one peak.

Ryan *et al.* investigate the orthogonality of separations through the combination of many stationary phases with different properties. They use the available separation space of the analytes corresponding to peaks eluting between the holdup time (t_0, lower trace) and the most retained compounds (t_{max}, upper trace) in the second dimension (Figure 8-1-B).

Another graphical concept of chromatographic space occupation determines the space occupations in the first and second dimensions through two dimensionless numbers ^1SO and ^2SO [112] (equations 1 and 2). These two variables are defined in equations 8-2 and 8-3 where $^1tr_1$ and $^2tr_1$ are the retention times of the first compound eluted respectively in the first and second dimensions, ^1tr_n and ^2tr_n are the retention times of the last compound eluted respectively in the

first and second dimensions, $T_{analysis}$ corresponds to the total running time, and P_{Mod} is the modulation period (Figure 8-1-C):

$$^{1}SO = \frac{(^{1}\mathrm{tr_n} - ^{1}\mathrm{tr_1})}{\mathrm{T_{analysis}}} \qquad \textbf{Equation 8-2}$$

$$^{2}SO = \frac{(^{2}\mathrm{tr_n} - ^{2}\mathrm{tr_1})}{P_{Mod}} \qquad \textbf{Equation 8-3}$$

Thus, one can estimate the 2D space occupation SO_{2D} as the Euclidian norm of these two values (Equation 3).

$$SO_{2D} = \sqrt{\frac{(^{1}\mathrm{tr_n} - ^{1}\mathrm{tr_1})^2}{2\mathrm{T_{analysis}}^2} + \frac{(^{2}\mathrm{tr_n} - ^{2}\mathrm{tr_1})^2}{2P_{Mod}^{\ 2}}} \qquad \textbf{Equation 8-4}$$

Liu *et al.* combined a statistical and geometrical approach to calculate the β angle of dispersion of chromatographic peaks along the two dimensions[109]. This angle can be determined by a matricidal calculation taking into account retention times. Its value determines the correlation between the two dimensions: 0 for a maximal correlation and 90° for no correlation (Figure 8-1D).

Another approach developed by Slonecker *et al.* [209] consists in quantifying similarity which is a measure of dimension saturation. Thus, high informational similarities describe mobile phase, stationary phase, and solute intermolecular interactions that involve the crowing of solutes. This value varies from 0 (for a totally unsaturated dimension) to 1 (for a saturated dimension). Cordero *et al.* [210] evaluated separations orthogonality using this criterion as well as Gilar *et al.*, Liu *et al.*, Ryan *et al.*, and Slonecker *et al.* approaches. It was concluded in this study that the best GC×GC chromatogram was obtained for a non-polar x polar combination. Depending on the investigated test mixture, different values were obtained what clearly showed the dependence between orthogonality and the nature of analytes of interest.

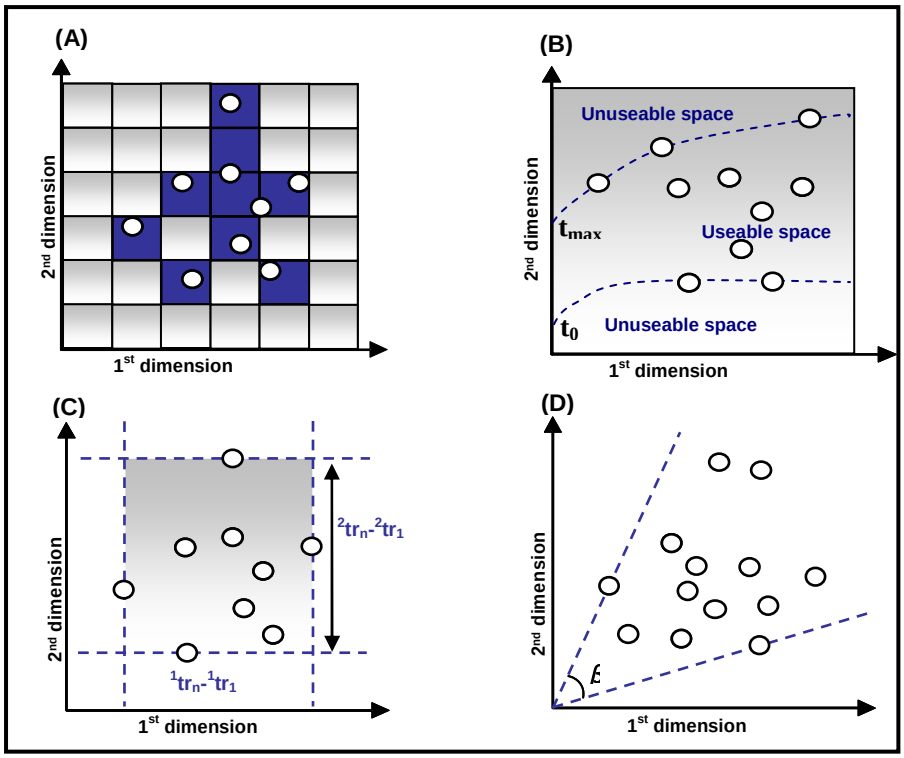


Figure 8-1. Representation of (A) Gilar *et al.* method, (B) Ryan *et al.* method, (C) Omais *et al.* method, (D) Liu *et al.* method.

Among all these approaches, three have been selected to determine separations orthogonality in this study: Gilar *et al.*, Ryan *et al.* and Omais *et al.* methods. In our cases, all x-axis vary from 0 to 120 minutes and the y-axis was automatically normalized by a home-made software to generate chromatograms with similar height-over-length ratios (h/w=0.8). To determine the orthogonality according to Gilar *et al.*, Equation 1 was applied and 196 bins were used. Concerning Ryan *et al.* criterion, a home-made software generates normalized areas manually. Concerning Omais *et al.* equation, each dimension coverage (^{1}SO and ^{2}SO) is normalized by definition.

8.3 Experimental section

8.3.1 Samples

The sample of interest is a coal-derived oil which was provided by IFP Energies nouvelles and which stands as a possible substitute for petroleum. It consisted on 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 X-Fluorescence 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).

8.3.2 GC×GC systems

8.3.2.1 GC×GC-FID

A Trace GC (Thermo, Italy) was used to achieve the experiments. The injection was carried out using a split injector (Thermo) at 320°C (0.3µL) with a split ratio of 1:100. Detection was carried out 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 30°C to the maximum operating temperature allowed by the column set (Solgelwax: 280°C, DB-1: 325°C, DB-17: 280°C, Rtx-200: 250°C, PONA: 325°C) at 2°C/min. Column sets will be discussed in the next paragraph.

8.3.2.2 Investigated columns

Four columns sets involving normal and poorly reversed conditions were tested in the present study. All column combinations are compiled in Table 8-1 as well as modulation periods. The first dimension is (30mx0.25mmx0.25µm) and the second (0.5-1.5mx0.1mmx0.1µm). One of them (A) is supposed to be highly orthogonal as it combines a non-polar first dimension with a polar second dimension. (B) and (C) are supposed to be less orthogonal, and (D) combines a polar first dimension to an electronegative stationary phase.

Table 8-1. Experimental conditions

	^{1}D column	*^{2}D column*	*Modulation*
(A)	PONA	BPX-50	8 s
(B)	DB-17	DB-1	15s
(C)	Solgelwax	DB-1	12s
(D)	Solgelwax	Rtx-200	7s

8.3.2.3 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 time's axis, as well as 1D and 3D-plots. Intensity of peaks is displayed with a color gradient varying from light blue to dark blue.

8.4 Results and discussion

Different retention mechanisms

To simplify the study, three retention mechanisms are involved in this chapter. The conventional PONA and DB-1 coated with a polydimethyl siloxane stationary phase enable a separation by **volatility** of compounds when placed in the first dimension with a temperature program. BPX-50 and DB-17 (50% Phenyl Polysilphenylene-siloxane) as well as Solgelwax (Polyethylene glycol or PEG) separate compounds by **polarity**. However, even if different polarity scales are generally used, this scaling poses problems as it does not consider the specific analyte-stationary phase interactions. Phenyl groups of a mid-polar stationary phase develop π-π interactions with aromatic compounds which are not as strong as H-bonds developed by the lone pairs of oxygen atoms present in the PEG stationary phases. Moreover PEG phase creates very strong H-bond with hydroxyl groups of phenolic compounds. To finish, Rtx-200 is coated with a trifluoropropyl methyl stationary phase. The unique selectivity resulting from the interaction of the fluorine with the electronegative centers offer a separation by **electronic interactions**. Hence, polarity is not sufficient to describe these compounds-phase interactions. As an example, aromatic and phenolic compounds present in the investigated sample should interact differently because the OH groups possess lone pairs. Depending on columns combinations (Table 8-1) normal and reversed systems are formed and the 2D space occupations are calculated for each of them.

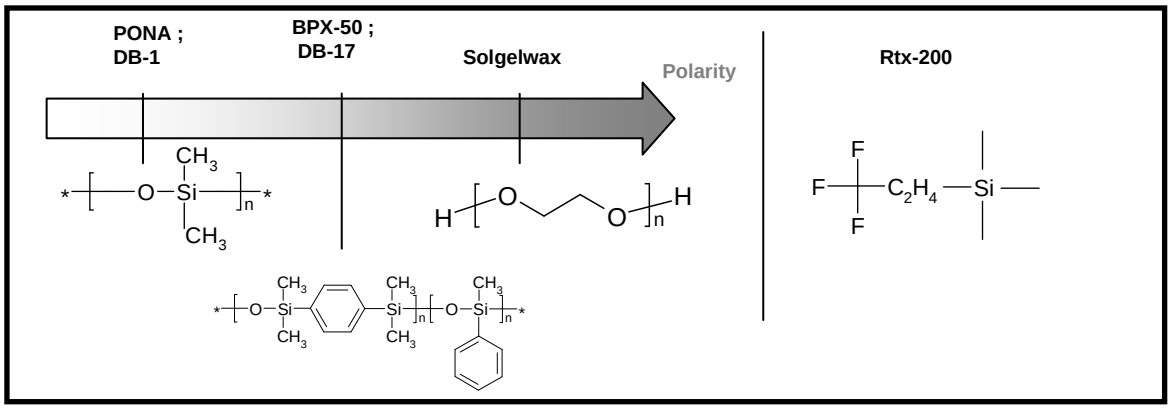


Figure 8-2. Investigated stationary phases

Group-type separation

A direct coal liquefaction middle distillate is analyzed with the four columns combinations displayed on Table 8-1. This liquid is mostly composed of paraffins (alkanes), naphthenes (cyclic alkanes), aromatics, and phenols. Figure 8-3-A shows that separation between these different families is not clearly accessible by combination (A) and that phenolic compounds are coeluted with aromatics. The reversed combination (B) does not offer a separation of phenolic compounds either but shows a clear distinction between the three families (paraffins, naphthenes and aromatics) as shown in Figure 8-3-B Set (C) combining a high polarity stationary phase in the first dimension and a non-polar column in the second dimension shows a good separation between, paraffins, naphthenes and aromatics but also gives a intra family classification of aromatics according to the number of aromatic rings (Figure 8-3-C). Concerning phenols they elute with other polar heteroatomic species at the bottom of the chromatogram. Combination (D) gives access to hydrocarbon separations but also shows a tremendous selectivity towards phenolic compounds which are totally separated from the rest of the matrix (Figure 8-3-D). To conclude in terms of chemical family separations, combinations (C) and (D) have a real interest especially for the characterization of oxygenated compounds.

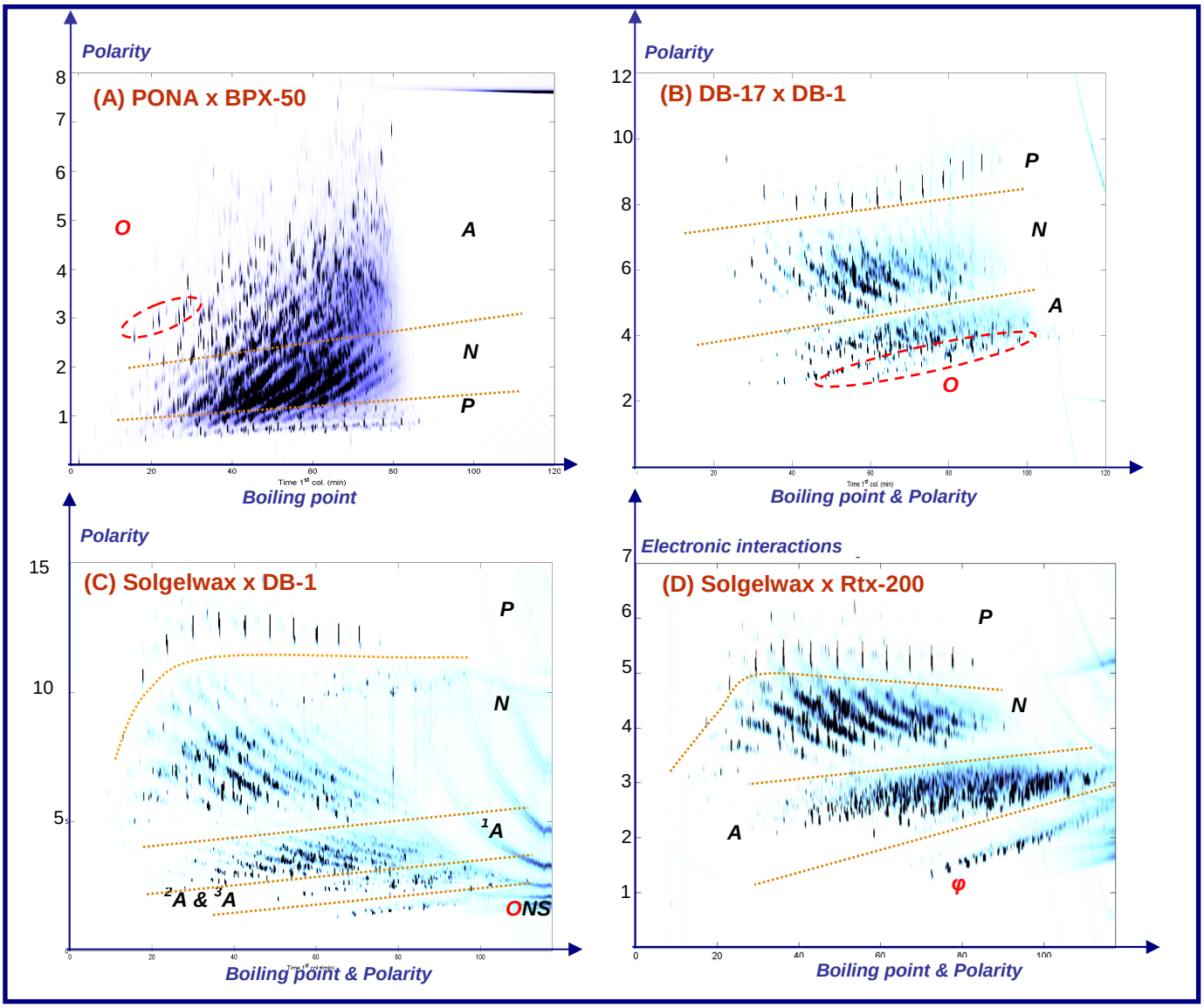


Figure 8-3. 2D chromatograms of direct coal liquefaction product using (A) PONA X BPX-50, (B) Solgelwax x Rtx-200, (C) Solgelwax x DB-1, (D) DB-17 x DB-1 columns combinations. P stands for paraffins, N for naphthenes, A for aromatics (^{1}A for mono-aromatics, ^{2}A for diaromatics, ^{3}A for triaromatics), ONS for oxygen-, sulphur-, and nitrogen-containing species, and ϕ for phenols.

Orthogonality and 2D space coverage

The only true orthogonal combination is set (A) involving two different retention mechanisms (boiling point in the first dimension and polarity in the second dimension). Sets (B) and (C) are poorly orthogonal according to Giddings theory because they involve a common polarity retention mechanism in the first and second dimensions. Concerning set (D), it is over-dimensioned: compounds are separated by boiling points and polarity in the first dimension and by electronic interactions and volatility in the second dimension (see next chapter). Despite the fact that this system can be qualified as orthogonal considering the mechanisms independence, two

retention mechanisms are involved in the first dimension. This GC_{polar} x $GC_{semipolar}$ system also shows that polarity is not sufficient to describe interactions.

Three methods for determining orthogonality have then been applied to the four chromatograms: Gilar *et al.[110],* Ryan *et al.[108]*, and Omais *et al.[112]* methods (Figure 8-4). Gilar *et al.* method shows the lowest values for the four combinations because a low number of bins were taken into account. Concerning Omais *et al.* criterion described in chapter 2, it shows that combination (A) is the second most adapted in terms of space coverage what is contradictory with the other criteria which ranks combination (D) as second. This can be explained by the fact that this formula consists in the Euclidian norm between the space occupations of each dimension, whereas Ryan criterion is a graphical method giving the occupied area. In fact, if compounds occupy 100% of the first dimension but are in a x-axis parallel line i.e. no occupation in the second dimension, space occupation using Ryan *et al.* criterion will be almost zero whereas Omais *et al.* criterion will provide a value close to 0.50 ($^{1}SO=1$ and $^{2}SO=0$). This bias does not appear for the other criteria. A drawback of both approaches is that the useable space depends on the last eluting compounds more than the overall space coverage. Nevertheless, they are adapted for such matrices which contain so many isomers that there are only a few empty spaces between the first and last eluted compound. An alternative for a more accurate measure of orthogonality should involve the investigated columns parameters instead of retention data of analytes.

Anyways, all values obtained by the different methods are maximal for set (C) which can be considered as the most orthogonal system in terms of 2D space occupation. However, this set is poorly orthogonal according to Giddings definition because it involves a polar stationary phase in the first dimension. It appears clearly in this example that retention mechanisms independence is not a sine qua none condition to obtain a great 2D space occupation and that these two notions combined into a general concept of orthogonality must be decoupled. It is clear that a two-dimensional separation combining two independent retention mechanisms has a greater chance to offer good peaks coverage in the 2D plan but this is not a necessary condition. Moreover saying that polarity is a common retention mechanism of two dimensions can be incorrect considering that according to the analytes functional groups different interactions may appear for a GC_{polar}×$GC_{semipolar}$ combination.

This is the case of set (D). This combination is interesting in terms of separation and peaks coverage because the sample contains phenols which are well separated from the rest of the matrix by a mechanism described in chapter 9. This phase also shows low retention towards all

compounds. In fact, even with a column length equal to 1 meter in the second dimension, a modulation period of 7 seconds was selected. Thus the space occupation is very closely linked to the nature of the sample as demonstrated by Cordero *et al[210].*

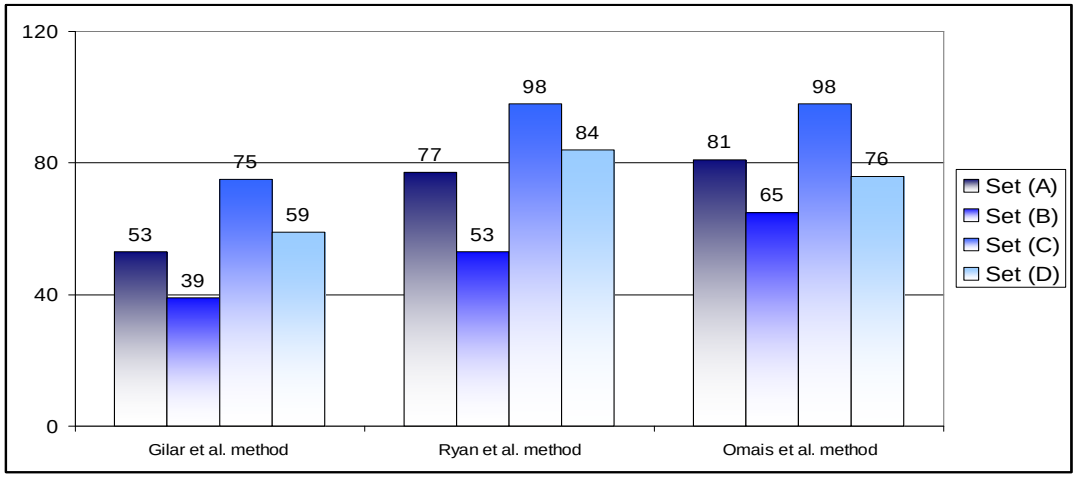


Figure 8-4. Orthogonality of the four combinations using Gilar *et al.*, Ryan *et al.*, and Omais *et al.* methods. Gilar *et al.* method was exploited using 196 bins

To finish, although the numbers present in Figure 8-4 are different, the same basic patterns seem to hold for the orthogonality determination indicating that none of the methods does a better (or worse) job of predicting the orthogonality of the separation. In fact, the objective of these methods is to link data distribution pattern in the 2D space and orthogonality of the system.

8.5 Conclusion

This chapter shows through the example of the characterization of a coal-derived middle distillate, that the general notion of orthogonality combining retention mechanisms independence and 2D space occupation must be decoupled. Indeed, a system with two dependant retention mechanisms can offer a good separation and a great space occupation. These results also show that orthogonality is intimately linked to the sample properties and cannot be considered as a sine qua none condition to achieve a good separation. To evaluate the pertinence of a separation conditions, it is necessary to deal with a more general notion of dimensionality taking into account the specificity of the sample of interest. Therefore as suggested by the use of combination (D), the selection of the most adapted chromatographic conditions should include properties of stationary phases seeking independent phase-analyte interaction. To simplify the approach two variables can be considered: one characteristic of the compound, and the other of the chromatographic conditions (stationary phases included). Even if columns are classified by polarity, the specific interaction with different analytes should be taken into consideration.

This chapter should be fleshed out by the use of additional sample types and a wider range of analytes with the chosen column set. These researches are indeed based on one only coal-derived sample and to generalize these conclusions, different samples from many other domains must be taken into consideration: petroleum industry, environment...

CHAPTER 9. Reversal of elution order in a single second dimension by changing the first columns nature in comprehensive two-dimensional gas chromatography [10]

FOREWORD

Chapter 8 discussed the non-correlation between orthogonality and 2D space occupation. The present chapter offers a deeper insight on polar × semi-polar configurations. In fact it evidences how one single stationary phase can involve two different elution orders for linear alkanes, cyclic alkanes, aromatics and phenols using comprehensive two-dimensional gas chromatography. For this purpose, a coal-derived middle distillate was injected in nonpolar × semipolar and polar × semipolar configurations implying the same second dimension stationary phase (Trifluoropropyl). Results show that even if the same column is utilized as a second dimension, the group-type elution order is reversed from one combination to the other.

This can be explained as follows: for the polar×semipolar combination, each fraction eluting from the first dimension contains species that differ so much in terms of boiling points, that volatility plays a key role in the second isothermal separation. This is exemplified by the separation of a phenol and demonstrated using the proportional relationship between retention times, vapor pressures and activity coefficients. Moreover, van't Hoff plots (plots of ln k vs. 1/T) demonstrated the influence of the elution temperature from the first dimension on the second dimension separation.

Therefore, available choice of stationary phase's combinations is much higher considering that one single column leads to very different retentions for similar compounds. Finally, this can explain why a reverse orthogonality approach is usually proficient for the separation of polar compounds.

[10] This chapter is based on an article published in Journal of Chromatography A, 2012 *in press* by Omais *et al.*

9.1 Introduction

The choice of stationary phases is usually governed by the orthogonality principle according to which two independent separation mechanisms must be used in each dimension [106]. In fact, according to Schoenmakers *et al.*, retention times in each dimension should be able to be treated as statistically independent [206]. That is why generally, a first non-polar dimension is combined to a (semi-)polar second dimension especially for group-type analysis in petroleum samples [213-215]. Hence, compounds are separated by increasing boiling point in the first dimension and by specific interactions in the second dimension considering the fast isothermal separation [108,110,205]. The system can then be considered as orthogonal because analytes are separated by two different retention mechanisms. In opposition, when a GC×GC system associates a polar stationary phase in the first dimension, components are separated both by polarity and boiling points, and the orthogonality principle is disregarded.

Therefore most of the columns combinations involves a non-polar first dimension coupled to a (semi)-polar second dimension [111]. The polar × nonpolar combination which was not very widespread in the begining of 2000 is now sparking great interest for the analysis of polar compounds such as FAMEs in biodiesel blends [216,45], alcohols in Fischer-Tropsch products [100], or heteroatomic compounds in hydrocarbon matrices [112, 116, 167, 184, 203]. Usually, for this type of analysis, a polyethylene glycol is coupled to a non-polar column (Polydimethyl siloxane).

Previous works on coal and biomass-derived liquids has also shown that polar × semi-polar combinations can lead to structured chromatograms and group-type separation. In fact, it was demonstrated that a polyethylene glycol first dimension coupled to a trifluoropropyl second dimension enabled the separation of alcohols from hydrocarbons. The resulting high resolving power as well as the high 2D space coverage was highlighted for this combination. While conventional nonpolar × polar mechanisms are well described in the literature, there are only a few articles dealing with polar×semipolar combinations.

In fact, many articles focused their study on the inversion of the two dimensions and show the differences between a "normal" and a "reverse-type separation". That is the case of Adahchour *et al.* who highlight a reversed elution order of the paraffins, mono-aromatics and di-aromatics in a petroleum product [208]. In this case, two combinations were investigated DB-1×BP20 and

BP21×BPX-35. Vendeuvre *et al.* also analyzed a atmospheric gas oil using PONA×BPX-50 and BPX-50×DB-1 combinations. The same elution zone inversion was stated.

As the structure of a chromatogram is inverted from a normal to a reverse configuration, one can then have interrogations about the behaviour of a same secondary dimension coupled to different primary dimensions. The idea that the first and secondary columns play an important role in the retention order along the second dimension was already demonstrated since the inception of GC×GC. In fact this is one of the repeated themes of John Phillips' papers throughout the 90s [212] according to who "Strong interaction with the first column stationary phase decreases retention in the second dimension". The influence of the primary stationary phase on secondary retention has also been addressed in numerous papers that model GC×GC retention and compare results to experimental values [217-219]. In fact, Seeley *et al.* used solvation parameter model to generate comprehensive two-dimensional gas chromatography retention diagrams for 54 solutes on four different stationary phase combinations [219].

These different ideas are exemplified through the novel approach adopted in this paper. In fact, instead of inverting the two dimensions, two columns sets (normal and reversed) involving the same mid-polar second dimension were investigated. The first dimension is in one case a non-polar stationary (polydimethyl siloxane) and in the second case a highly polar phase (polyethylene glycol). Therefore, two chromatograms can be obtained: a normal configuration (nonpolar × semipolar), and a reverse configuration (polar × semi-polar). The present article explores the dependence of the two dimensions and leads to a guidance of columns sets selection. The sample of reference is a coal-derived middle distillate which offers a large diversity of chemical families: linear alkanes, cyclic alkanes, mono-, di-, and tri-aromatics, and phenolic compounds as demonstrated in part A.

9.2 Experimental section

9.2.1 Samples

9.2.1.1 Coal liquefaction middle distillate

The sample of interest is an industrial coal-derived middle distillate provided by IFP Energies nouvelles. It was obtained by direct liquefaction of a sub-bituminous coal in the presence of a catalyst, with an H-donor solvent and at high pressure

The investigated sample 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 X-ray fluorescence 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).

Part A on this sample showed that it consists mainly of a hydrocarbon matrix containing phenolic compounds with a carbon atom number varying from 6 to 11. The molecular detailed composition of the sample is given in Table 9-1. This sample was selected as a reference in this study because it represents a large range of volatility and polarity.

Table 9-1. Group-type quantification of the coal-derived middle distillate

Family	***Content % w/w***
Linear alkanes	24 $^{+}/_{-}$ 4
Cyclic alkanes	33 $^{+}/_{-}$ 3
Aromatics	37 $^{+}/_{-}$ 3.2
Phenols	5.2$^{+}/_{-}$ 0.7

9.2.1.2 Model mixture for van't Hoff plots (VHM)

To evaluate the difference of retention between linear alkanes, aromatics and phenols, a five compounds model mixture (VHM) was prepared. Phenol, n-C10 paraffin, tertbutylbenzene, biphenyl and n-C20 paraffin at concentrations ranging from 0.5 to 1.5 % w/w were solubilized in carbon disulphide. The choice of these compounds will be detailed throughout the chapter.

9.2.1.3 Model mixture for identification of families (SM)

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 prepared:

samples P composed of 15 n-paraffins, A composed of 9 aromatic hydrocarbons, and O composed of 8 phenolic compounds were mixed into a standard mixture SM.

Sample P contained 15 n-paraffins (from C7 to C29) at concentrations varying from 0.6%w/w to 1.3%w/w. Sample A includes aromatic and naphtheno-aromatic compounds: toluene, trimethylbenzene, isobutylbenzene, triisobutylbenzene, tetraisobutylbenzene, biphenyl, phenanthrene, ethylanthracene, and fluorene with concentrations ranging from 1 to 2.6%w/w. O was constituted by phenol, 4-Ethylphenol, 2,4-dimethylphenol, 2,4,6-trimethylphenol, p-cresol, m-cresol, ditertbutylmethylphenol, 6-tert-butylcresol, furan, and fluorenol at contents ranging from 0.9%w/w to 2.98%w/w. These choices were oriented by a literature survey giving the most accurate vision of a coal oil composition. All these compounds were solubilised in ethyl acetate and SM consist 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 9-2.

Table 9-2. Compounds contained in the test sample

Compounds			
Paraffins		**Aromatics**	**Phenolics**
nC7	nC24	Toluene	Phenol
nC11	nC25	Trimethylbenzene	Ethylphenol
nC13	nC26	Isobutylbenzene	Dimethylphenol
nC17	nC27	Triisobutylbenzene	Trimethylphenol
nC18	nC28	Tetraisobutylbenzene	P-cresol
nC19	nC29	Biphenyl	M-cresol
nC20		Phenanthrene	Naphthol
nC21		Ethylanthracene	Fluorenol
nC22		Fluorene	

9.2.2 GC×GC systems

9.2.2.1 GC×GC-FID conditions

A Trace GC (Thermo, Italy) was used to achieve the experiments. The injection was carried out using a split inlet (Thermo) at 320°C (0.3µL) with a split ratio of 1:100. Flame ionization detector (FID) system carried out 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 program is shown in Table 9-3. The temperature rate used for both combinations is 2°C/min as it corresponds to the inverse of the dead time of the columns. A constant pressure set at 23 Psi was used and the modulation period was usually set at 5 and 7 s to cope with the differences of retention power of the two investigated sets.

Table 9-3. Experimental conditions

^{1}D	*Dimension ^{1}D*	*^{2}D*	*Dimension ^{2}D*	*Oven temperature*	*Modulation*
MTX-1	(17.5mx0.18µmx0.48µm)	RTX-200	(1.5mx0.1mmx0.1µm)	30-300°C	5 s
Solgelwax	(30mx0.25µmx0.25µm)	RTX-200	(1mx0.1mmx0.1µm)	50-280°C	7 s

9.2.2.2 Data handling

Raw data of FID signals were acquired by Polycard software (Thermo) and exported as a csv file. A home-made software called 2DChrom was used to display GC×GC contour plots with retention times axis, as well as 1D and 3D-plots from exported data. Intensity of peaks was displayed with a color gradient varying from black to light blue.

9.2.3 GC-FID conditions

All 1D experiments were conducted on a Trace GC (Thermo, Italy) equipped with split/splitless injector. A constant pressure of helium (99.99% Air Liquide, France) close to 10 Mpa was used as the carrier gas with a 1:50 split ratio. GC-FID experiments were performed to study the selectivity of the secondary stationary phase with compounds contained in VHM at 90, 120, 180, 200 and 230°C. Oven temperature was kept constant at five temperatures during 30 minutes. The FID conditions are the same as those detailed in paragraph 2.2.1. Methanol was injected to evaluate the dead time of the column,

9.3 Results and discussion

9.3.1 One column, two elution orders.

Two chromatograms are presented in Figure 9-1: The first one combines a dimethyl polysiloxane stationary phase (MTX-1) with a trifluoropropyl stationary phase (RTX-200). This combination leads to a separation between paraffins, naphthenics and aromatics. Concerning phenolics, they elute in the aromatics zone. The second chromatogram (B) combining a poly ethylene glycol stationary phase (Solgelwax) with an RTX-200 shows a different separation as naphthenics and aromatics are separated from each other and a phenolic zone appears. This configuration leads to a better group-type separation even if the aromatics are not separated according to their ring numbers and the elution zones are packed tighter together. This can be related to what has already been shown in the literature [208], and is not the focus of the present chapter.

In fact, unexpectedly, it can be noticed that even if the same secondary column is used in the two cases, the elution order is reversed. In fact, it is in the first case paraffins< naphthenes< aromatics and phenols while it is in the second case phenols< aromatics< naphthenes< paraffins. This inversion was stated when inverting the two dimensions (for instance Rtx-5 x Stabilwax versus Stabilwax x Rtx-5) [184] but never with the same second dimension. This illustration of the influence of the first dimension on the second dimension separation will be detailed on the next sections.

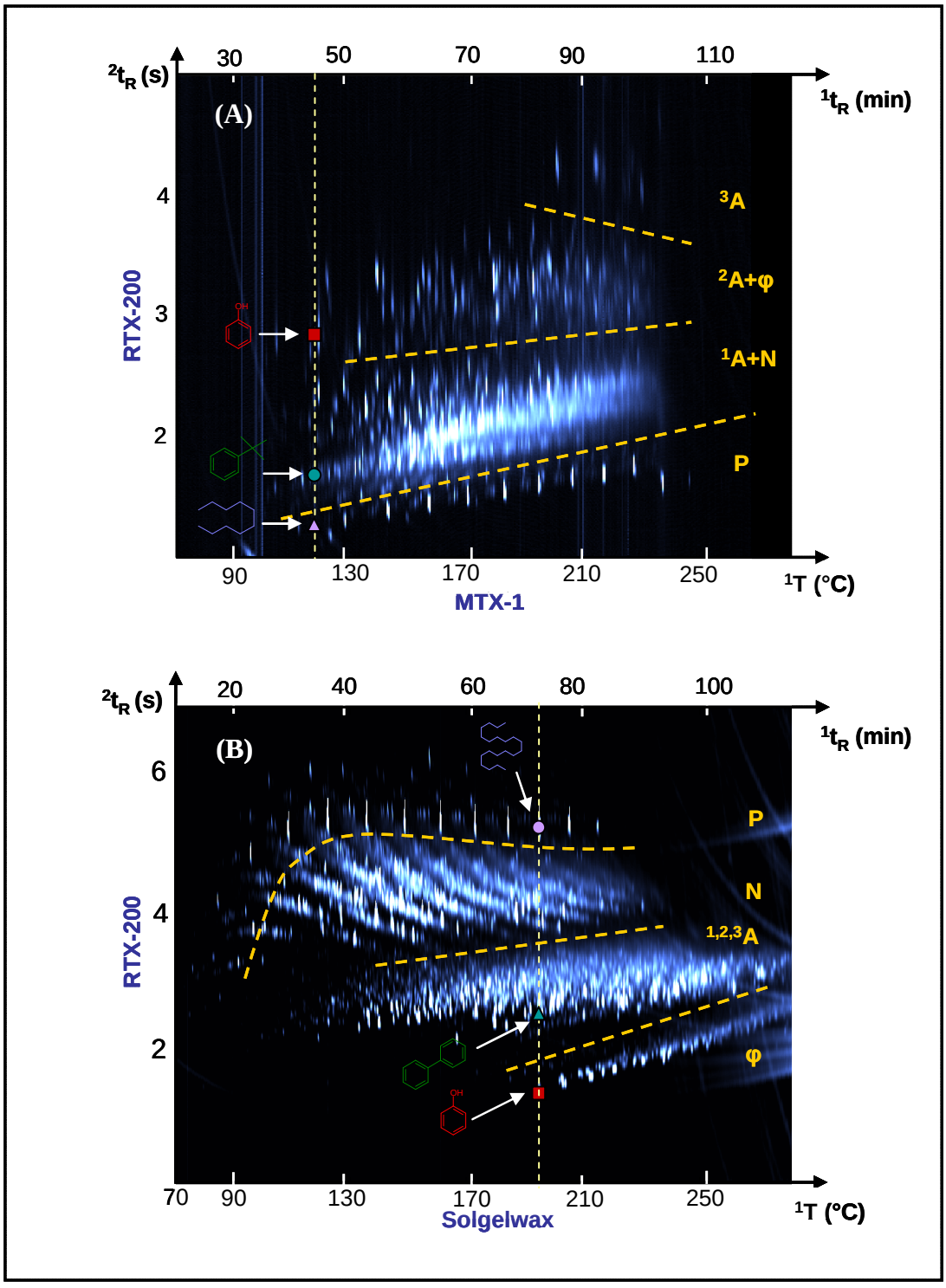


Figure 9-1. GC×GC chromatograms of a coal derived middle distillate using (A) MTX-1 x RTX-200 and (B) Solgelwax × RTX-200. (P: paraffins, N: naphthenes, ^{i}A: aromatic with i rings, ϕ: phenols)

9.3.2 Influence of the first dimension on the second separation

To answer this question, let us consider the orthogonal separation conditions involving a nonpolar polydimethyl siloxane stationary phase in the first dimension. The only parameter which governs the first separation is volatility. Therefore, analytes with the same volatility are separated in the second dimension according to their activity coefficient under isothermal conditions. In our example, using normal orthogonality conditions, a phenol (BP=181°C) elute approximately at the same ^{1}D retention time as decane (BP=174°C) and tertbutylbenzene (BP=169°C) at an oven temperature nearly equal to 120°C. Therefore, their separation is only governed by specific interactions with the trifluoropropyl stationary phase and the elution order is shown in Figure 9-2. The reversed orthogonality system (Solgelwax×Rtx-200) implies a very polar first dimension. Therefore, the first separation depends on a mix between specific interactions and volatility. For instance, compared to the first case, a phenol (BP=181°C) elutes much later in the first dimension, with other analytes like biphenyl (BP=255°C) and eicosane (BP= 344°C) when the oven is at a much higher temperature (approximately 195°C). The eluting fraction contains species that differ so much in terms of boiling points that volatility plays a key role in the second isothermal separation explaining the elution order shown in Figure 9-3.

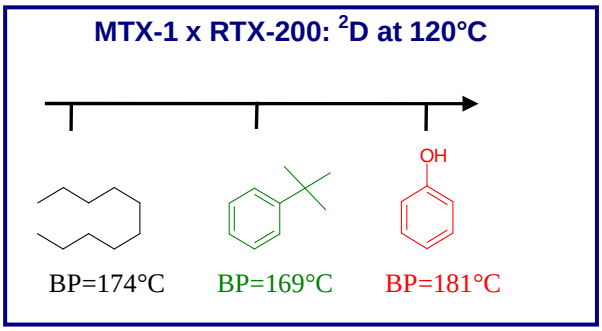


Figure 9-2. Elution order in the second dimension of C10 n paraffin, tertbutylebenzene and phenol using MTX-1 × RTX-200 combination.

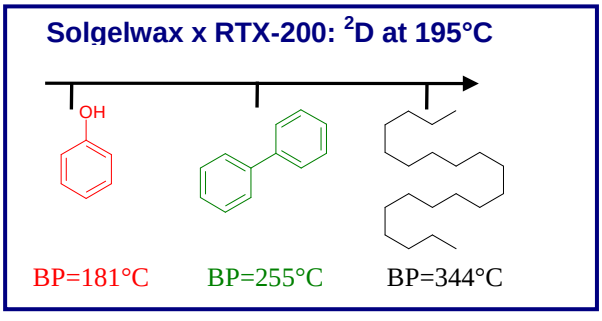


Figure 9-3. Elution order in the second dimension of C20 n-paraffin, biphenyl and phenol using Solgelwax × RTX-200 combinations.

9.3.3 van't Hoff plots

A van't Hoff plot gives thermodynamic information for investigated compounds, in particular information about compound specific retention with a particular stationary phase at different temperatures [220-222].

The enthalpy of interaction of compounds with a stationary phase can be evaluated using the van't Hoff equation (Eq. (0)) [223] where k is the retention factor, ΔH is the enthalpy, R is the ideal gas constant, T is the temperature, ΔS is the entropy and φ is the phase ratio.

$$\ln(k) = \frac{\Delta H}{RT} + \frac{\Delta S}{R} + \ln(\phi) \qquad (0)$$

The specific retention of a compound on the stationary phase at a given temperature is related to the van't Hoff curve y-intercept. If the distance between the lines for two compounds is large, then the isothermal separation is selective. The van't Hoff plot presented in the Figure 9-4 shows that for a 3.50 meters RTX-200 column, at 120°C, the elution order is n-C10 paraffin < tertbutylbenzene < phenol. This confirms the assumptions of the previous paragraph. Similarly, at 200°C, the elution order is phenol < biphenyl< n-C20 paraffin. This illustrates the reversal of family elution order due to the nature of the focused analytes eluting from the first dimension.

Moreover, the van't Hoff plot clearly exhibits the gain in terms of selectivity between phenols and hydrocarbons. In fact it is interesting to focus on the circled values of the plot. For the orthogonal system (MXT-1×RTX-200), phenol elute from the first non-polar column with tertbutylbenzene and n-C10 paraffin at 120°C (right circled zone). In a reversed orthogonality separation, phenol elute with biphenyl and n-C20 at 195°C and the selectivity between phenol and heavy hydrocarbons shown in the left circled zone is much higher. This illustrates why in previous works [112, 195], reversed configurations showed better results for polar compounds.

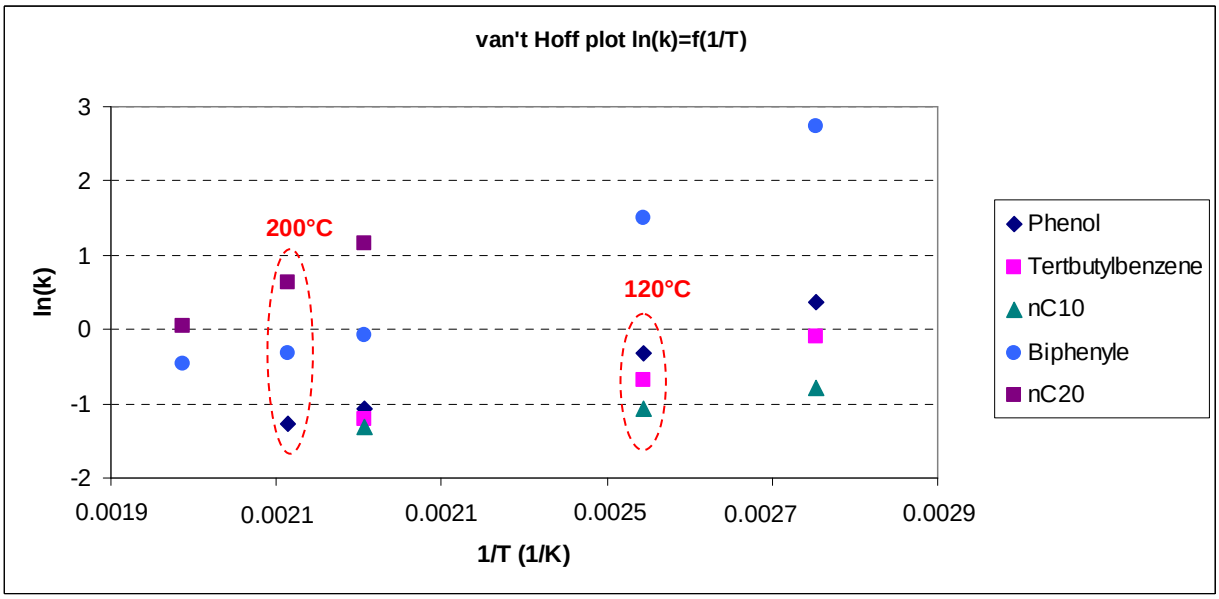


Figure 9-4. van't Hoff plot (ln(k) = f(1/T)) for phenol, tertbutylbenzene, biphenyle, n-10 and n-C20 paraffins (P=10MPa).

9.3.4 Equations of the problem

To equate the problem, let us remind that retention in gas chromatography is inversely proportional to $p_i°\gamma_i^{\infty}$, with $p_i°$ the pure component vapour pressure and ${}^{SP}\gamma i^{\infty}$ the activity coefficient of the component in the stationary phase SP at infinite dilution (each peak of the chromatogram represent in average 100µg.g^{-1}). Considering the temperature program this relation must be considered at a certain temperature T_n and at a certain time n. Therefore the relationship between t and $p_i°\gamma_i^{\infty}$, can be written as:

$$t_i \alpha \frac{1}{p_i^0(T_n)\gamma_i^{\infty}(T_n)} \quad (1)$$

For the normal combination (MTX-1 x RTX-200), it can be assessed that the activity coefficient at infinite dilution is the same for all analytes. Therefore, three coeluted species present in a same modulation period will have equal p_i^0. For example at a temperature T_N:

$$p^0_{phénol}(T_N) \approx p^0_{tertbutylebenzene}(T_N) \approx p^0_{C10}(T_N) \quad (2)$$

It was also demonstrated in paragraph 3.3. that in the second semipolar column

$$^{RTX-200}\gamma^{\infty}_{phenol}(T_N) \leq {}^{RTX-200}\gamma^{\infty}_{tertbutylbenzene}(T_N) \leq {}^{RTX-200}\gamma^{\infty}_{C10}(T_N) \quad (3)$$

Therefore in the first dimension (MTX-1):

$$t^1_{phenol} \approx t^1_{tertbutylbenzene} \approx t^1_{C10} \quad (4)$$

and in the second dimension (RTX-200):

$$\boxed{t^2_{N,phenol} > t^2_{N,tertbutylbenzene} > t^2_{N,C10}} \quad (5)$$

For the polar × semipolar configuration (Solgelwax x Rtx-200), as in a highly polar first dimension $^{Solgelwax}\gamma^{\infty}_{phenol}(T_n) < ^{Solgelwax}\gamma^{\infty}_{tertbutylbenzene}(T_n) < ^{Solgelwax}\gamma^{\infty}_{C10}(T_n)$, (6)

phenol will elute much later from the first dimension at a temperature $T_M > T_N$:

$$t^1_{phenol} > t^1_{tertbutylbenzene} > t^1_{C10} \quad (7)$$

At T_M, phenol is trapped in a fraction which contains a heavier paraffin and a heavier aromatic so that

$$p^0_{phenol}(T_M) \times ^{Solgelwax}\gamma^{\infty}_{phenol}(T_M) \approx p^0_{aromatic}(T_M) \times ^{Solgelwax}\gamma^{\infty}_{aromatic}(T_M) \approx p^0_{paraffin}(T_M) \times ^{Solgelwax}\gamma^{\infty}_{paraffin}(T_M) \quad (8)$$

Experiments show that biphenyl and C20 n-paraffin satisfy this equation:

$$p^0_{phenol}(T_M) \times ^{Solgelwax}\gamma^{\infty}_{phenol}(T_M) \approx p^0_{biphenyl}(T_M) \times ^{Solgelwax}\gamma^{\infty}_{biphenyl}(T_M) \approx p^0_{C20n-paraffin}(T_M) \times ^{Solgelwax}\gamma^{\infty}_{C20n-paraffin}(T_M) \quad (9)$$

In this case, at T_M, the difference of vapour pressure of the three focused analytes is very important. Consequently, as demonstrated in paragraph 3.3, in the second less polar dimension, activity coefficients are negligible so that:

$$p^0_{phenol}(T_M) \times ^{RTX-200}\gamma^{\infty}_{phenol}(T_M) > p^0_{biphenyl}(T_M) \times ^{RTX-200}\gamma^{\infty}_{biphenyl}(T_M) > p^0_{n-C20}(T_M) \times ^{RTX-200}\gamma^{\infty}_{n-C20}(T_M) \quad (10)$$

Therefore in the first dimension (Solgelwax):

$$t^1_{phenol} = t^1_{biphenyl} = t^1_{C20n-paraffin} \quad (11)$$

and in the second dimension (RTX-200):

$$\boxed{t^2_{M,phenol} < t^2_{M,biphenyl} < t^2_{M,n-C20}} \quad (12)$$

Equations (5) and (12) exemplify how the same second dimension stationary phase can lead to two different family elution orders and corroborate the fact that a GC×GC separation is intimately linked to the nature of the analytes.

9.3.5 Guidance on columns sets selection

These results are the perfect example of Phillips *et al.* idea according to which both first and secondary columns play an important role in the retention order along the second dimension. In fact this idea was evocated in the title of one of their paper "Comprehensive two-dimensional gas chromatography: a hyphenated method with strong coupling between the two dimensions" [212]. Specific interactions of the first dimension govern the composition of the focused fraction as well as the constant temperature of the second dimension separation.

A common assessment for group type separation but also for targeted species analysis is to exclude a second dimension stationary phase when it does not show a good separation at a constant temperature. This methodology becomes nonsense for reverse orthogonality systems. In fact, this same excluded column can lead to a great separation if the appropriate first dimension is selected. For example, RTX-200 seems to be useless for phenols characterization when coupled to a MTX-1, but enables their separation when coupled to a Solgelwax. Consequently, the number of existing stationary phases combinations is much higher than what one could expect.

It is also often claimed in the literature that the reverse orthogonal approach is more suitable for polar compounds separation [224]. The present work clearly exemplifies this theory. In fact, this configuration enables polar compounds to be trapped in an eluting fraction which contains less volatile compounds at a high oven temperature. Therefore they elute without delay from the second short dimension and are shifted from the rest of the matrix. Moreover, high-polarity species are less retained in the secondary dimension for reverse orthogonality configurations what involves better peak shapes and exclude wrapping around to occur.

9.4 Conclusion

The analysis of a coal derived middle distillate by GC×GC using two different columns combinations involving the same second dimension stationary phase highlights the influence of the first dimension on the second dimension. In fact, combined to two different primary stationary phases, the use of the same second dimension involves two different families' elution orders. This can be explained by volatility difference of the focused analytes which involves a separation by boiling point in the second dimension for Solgelwax × RTX-200 combination.

This statement has many consequences. Firstly, it illustrates the "strong coupling" between the two dimensions. Secondly, the available choice of stationary phases combinations is much higher considering that one single column can lead to different elution orders. Moreover, this explains why a reverse orthogonality approach is usually proficient for the separation of polar compounds. Finally, when classing the GC×GC systems, one often refers to stationary phases to the detriment of the temperature which is an obvious orthogonality factor that is often forgotten.

GENERAL CONCLUSION

A state of the art of analytical tools deployed for the analysis of oxygenated species contained in direct coal liquefaction products highlights the complexity of these matrices. Many locks are revealed in this review: high elemental oxygen quantification limit (0.1%w/w O), low resolution and peak capacity using one-dimensional gas chromatography, time-consumming separation steps (liquid-liquid extractions, derivatizations), and lack of information on the different species which compose these products. To overcome these limitations, comprehensive two-dimensional gas chromatography was selected as the main technique and two distillates were investigated: an atmospheric gas oil cut and a naphtha cut.

Therefore, the first step of this Ph.D. was to characterize a direct coal liquefaction gas oil cut using **GC×GC-FID and GC×GC-ToF/MS.** Ten column combinations were examined and one of them (SolGel-WAX × DB-1) was selected. This particular reverse orthogonality system involving a highly polar column in the first dimension and a non-polar one in the second enabled the characterization of many oxygenates 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. GC×GC-ToF/MS allowed the characterization of more than fifty oxygenated molecular structures in the coal-derived middle distillate. They mainly consist in phenolic compounds with different alkyl chains, benzofurans, naphthols, and indanols. Experiments also revealed the presence of diols and naphthalenons which has never been demonstrated so far.

Then the spotlight of chapter 3 was on a direct coal liquefaction naphtha and, as this product is less complex, GC and GC-GC systems were firstly explored. A few oxygenated species contained in a direct coal liquefaction naphtha could be identified by **GC-ToF/MS**. The limitations consisting essentially on the presence of coelutions between oxygenates and hydrocarbons could be overcome by using **GC-GC-FID**. Nevertheless, there are too many oxygenated species and achieving a high number of cuts tends to the use of a comprehensive technique. Therefore, **GC×GC** was finally considered and thanks to the column set selected in chapter 2, more than a hundred oxygenated compounds belonging to five main families were identified: alcohols, phenols, ketones, carboxylic acids, and furans. To accentuate the second dimension separation, a novel polar × midpolar column set enabled a selective separation of phenols and alcohols which were quantified using a definite methodology involving experimental response factors determination for 20 compounds belonging to the 5 chemical families.

Hence, for both cuts (naphtha and atmospheric gas oil), a quantification of phenols and alcohols was achieved using the advanced column set. To complement GC×GC results, other techniques were then investigated: **FT-ICR/MS, ^{31}P NMR, and UV-visible spectroscopy**. This transversal approach leads to a global vision of four oxygenated chemical families present in a coal derived naphtha and atmospheric gas oil. In fact, FT-ICR/MS enabled to confirm the presence of phenols and highlighted carboxylic acids which were then quantified by ^{31}P NMR. To finish, UV-visible spectroscopy led to the proportion of ketones among all oxygenated compounds present in both samples. Furans remain unseparated from the other compounds and developments involving NMR spectroscopy are currently in progress. Finally, this first part leads to the quantification of 90%w/w of the oxygen content in the AGO cut and 70%w/w in the naphtha cut. However, furans are still unseparated and further development using NMR spectroscopy are in progress at IFPEN. Moreover, the vacuum gas oil cut (VGO) of the direct coal liquefaction product is chemically very complex and characterization of oxygenated compounds in this matrix remains a real challenge. Appendix A3 shows first encouraging results but to complement these first achievements more sophtisticated techniques should be investigated.

***

The second part of the manuscript is focused on biomass fast pyrolysis which is considered as a promising technique to produce renewable liquid for the transportation field. However, bio-oils are mainly oxygenated (45-50%w/w O on woody biomass) and contain almost no hydrocarbons. Therefore, upgrading is applied to obtain a liquid with lower oxygen content (10-20%w/w O) and characterization of oxygenated compounds in these products is essential to assist conversion reactions.

By investigating different **GC×GC** conditions, a reverse orthogonality column combination which is adapted to oxygen speciation in a partially upgraded bio-oil was selected. Mass spectrometry data enabled the identification of more than 40 analytes of interest. Moreover, quantification was possible by creating blobs associated to the identified molecules and their corresponding response factors. In addition, 41 oxygenates belonging to eight chemical families were quantified in oxygen content: ketones (1.8 %w/w O), furans (1.8 %w/w O), alcohols (0.4 %w/w O), phenols (1.2 %w/w O), furans (0.2 %w/w O), carboxylic acids (2.1 %w/w O), guaiacols (0.4 %w/w O), benzenediols (1.3%w/w O) and anisols (0.2 %w/w O). Each family content was expressed in terms of elemental oxygen so that the contribution of each family in the global oxygen elemental content can be evaluated.

These results lead to a better understanding of these partially upgraded bio-oils and represent a springboard towards conversion processes enhancement. However reverse orthogonality stationary phases allow the separation of phenolics but do not offer enough intra-family resolution. Therefore, to reach a better insight on phenolic compounds, supercritical fluid chromatography was hyphenated to GC×GC (**SFC-GC×GC**). The ethylpyridine column is very selective towards the OH functional group and allows an online pre separation of aromatic-OH compounds which can be analysed by GC×GC without coelutions with hydrocarbon aromatics. Consequently, a breakthrough molecular characterization of phenols and naphthols can be obtained in the phenolic fraction. However, further developments must be achieved to characterize the oxygenated species of the non-phenolic fraction.

***

Characterization of biomass and coal oils leads to a common conclusion concerning GC×GC: **Reverse orthogonality** is much more adapted to oxygen speciation in such matrices. Therefore, further considerations on reversed systems were discussed. Firstly, the general notion of orthogonality combining retention mechanisms independence and 2D space occupation was decoupled. Indeed, a reverse orthogonality system can offer a good separation and a great space occupation. It was also illustrated that orthogonality is intimately linked to the sample properties and cannot be considered as a sine qua none condition to achieve a good separation. To evaluate the pertinence of a separation conditions, it is necessary to deal with a more general notion of dimensionality defined by Giddings and taking into account the specificity of the sample of interest.

Last of all, the analysis of a coal derived middle distillate by GC×GC using two different columns combinations involving the same second dimension stationary phase highlights the **influence of the first dimension on the second dimension**. In fact, combined to two different primary stationary phases, the use of the same second dimension involves two different families' elution orders. This was explained by volatility difference of the focused analytes which involves a separation by boiling point in the second dimension for the polar × mid-polar combination.

***

These researches led to many analytical methods to characterize oxygenated compounds in alternative fuels. The issue of oxygenated compounds separation from hydrocarbons was treated at different levels as the issues involved by the two investigated products were different. In general, GC×GC reversed configuration was proved to be the reference tool to characterize them but remains limited. To overcome GC×GC limitations, the use of SFC-GC×GC provides breakthrough

separations and enables to characterize very complex matrices such as upgraded bio-oils at a molecular level. This three-dimensional tool is sparking great interest in the petrochemical field and more and more applications have recently emerged. These developments will contribute to an enhancement of the two potential fuels conversion into proper energy for the transportation field.

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