



# A novel analytical approach for oxygen speciation in coal-derived liquids

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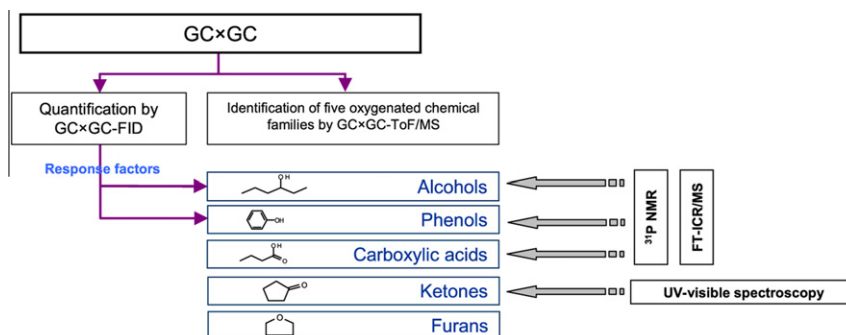
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## HIGHLIGHTS

- ▶ A detailed quantification of phenols, alcohols, acids, and ketones was established.
- ▶ 72% w/w of the oxygen content was quantified in a coal-derived naphtha.
- ▶ 88% w/w of the oxygen content was quantified in a coal-derived gasoil.
- ▶ Four analytical techniques were used: GC×GC, FT-ICR/MS, UV-visible, and NMR <sup>31</sup>P.

## GRAPHICAL ABSTRACT



## ARTICLE INFO

### Article history:

Received 10 January 2012

Received in revised form 18 April 2012

Accepted 26 April 2012

Available online 10 May 2012

### Keywords:

Coal oil  
UV-visible spectroscopy  
NMR Spectroscopy  
Gas chromatography  
Mass spectrometry

## ABSTRACT

Since the production of crude oil may not meet the increasing demand in the next future, coal liquefaction products have sparked great interest as one of the possible substitutes of petroleum in the transportation field. Speciation of oxygen in direct coal liquefaction products is essential considering the important role of oxygenated compounds in coal conversion reactions. This study attempts to characterize them as fully as possible. The originality of this approach is based on the development of complementary analytical tools to describe the composition of two coal-derived distillates: a naphtha cut and a gasoil cut.

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. This analytical scheme shows that 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 gasoil cut, among the 0.80%w/w O 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 dibenzofurans may represent the species which have not been quantified.

Quantification of alcohols and phenols by carbon atom number is also allowed by GC × GC-FID using response factors. 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. This unique multi-technical approach offers a detail level which was never reached so far in terms of oxygenated compounds characterization for such products. This information is crucial to evaluate the potential of these liquids as a substitute for fuel and envisage their upgrading.

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## 1. Introduction

Considering the global energetic context, diversifying the liquid fuel supplies for the transportation field is of the utmost

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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 [1].

DCL products characteristics are quite far from fuel specifications; thus, upgrading must be applied to the naphtha and atmospheric gasoil cuts. In fact, compared to petroleum products, these cuts contain less linear alkanes (paraffins), and much more cyclic alkanes (naphthenes); aromatic and naphtho-aromatic structures are also present in relatively high concentrations [2]. Concerning heteroatomic species, nitrogen and oxygen-containing compounds are predominant compared to sulfur-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. A literature survey shows that many analytical strategies were used to improve the knowledge of oxygenated compounds in coal-derived products [2]. These are focussed on two classes of oxygen-containing species: phenols [3] and furans [4–6]. 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. Recent works show that comprehensive two-dimensional gas chromatography (GC × GC) is very efficient for the characterization of phenols and alcohols [7–10]; this technique allows the improvement of selectivity and peak capacity compared to one-dimensional gas chromatography. Besides, ESI (–) FT-ICR/MS (Negative Electrospray Ionization – Fourier Transform Ion Cyclotron Resonance Mass Spectrometry) enables to deeply improve the knowledge of acidic O-compounds in coal-derived vacuum gas oils [11–13]. Moreover, a series of articles published by Verkade and co-workers shows that it is possible to characterize labile H functionalities by <sup>31</sup>P NMR after derivation of targeted compounds using phosphorous-containing reagents [14–18] 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) [19]. 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, <sup>31</sup>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.

**Table 1**

Elemental composition of the two coal-derived distillates.

	Naphtha cut	Gasoil 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

## 2. Materials and methods

### 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 a 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 a gasoil 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 gasoil cut. Elemental compositions of each cut are displayed in Table 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 0.8224 g/cm<sup>3</sup> for the naphtha cut and 0.9330 g/cm<sup>3</sup> for the gasoil cut.

### 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 (Thermo, Italy) and GC × GC–ToF/MS (Agilent and LECO)), the injection (0.3 μL) was carried out at 250 °C for the naphtha cut and 320 °C for the gasoil 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 gas oil, both at 2 °C/min. A Solgelwax column (Poly ethylene glycol 30 m × 0.25 mm × 0.25 μm) was used in the first dimension and coupled either to a DB-1 column (Polydimethyl siloxane 1 m × 0.1 mm × 0.1 μm) or to a Rtx-200 column (Trifluoropropyl 1 m × 0.1 mm × 0.1 μm) with modulation periods respectively equal to 12 and 7 s (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<sub>2</sub>, air, and He makeup were set respectively at 35, 450, and 25 mL/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 ionisation was achieved at 70 eV and a multiplate voltage of –1450 V was applied.

### 2.3. Mass spectrometry analysis

Fourier Transform Ion Cyclotron Mass Spectrometry (FT-ICR/MS) analyses were achieved using a Thermo Scientific LTQ FT Ultra (Bremen, Germany). It is composed of a linear ion trap and an ion

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