Fuel 140 (2015) 398–406

Contents lists available at ScienceDirect

Fuel

journal homepage: www.elsevier.com/locate/fuel

Comprehensive compositional analysis of sulfur and nitrogen containing compounds in shale oil using GC × GC – FID/SCD/NCD/TOF-MS

Thomas Dijkmans, Marko R. Djokic, Kevin M. Van Geem *, Guy B. Marin

Ghent University, Laboratory for Chemical Technology, Technologiepark 914, 9052 Zwijnaarde, Belgium

HIGHLIGHTS

- Combination of the information of an FID, SCD, NCD and TOF-MS on a GC × GC.
- Analysis of sulfur and nitrogen containing hydrocarbon in a shale oil.
- Composition of a shale oil into 20 different compound classes and carbon number.
- 2-chloropyridine allows to quantify the nitrogen compounds without elemental analysis.

ARTICLE INFO

Article history:
Received 16 April 2014
Received in revised form 13 September 2014
Accepted 18 September 2014
Available online 1 October 2014

Keywords:
Shale oil
GC × GC – FID/NCD/SCD/TOF-MS
Sulfur containing hydrocarbons
Nitrogen containing hydrocarbons

ABSTRACT

The detailed composition of a shale oil was determined using a novel comprehensive 2D gas chromatographic (GC × GC) method, extending the method of Dijkmans et al. (2014). Four different detectors (flame ionization detector (FID), sulfur chemiluminescence detector (SCD), nitrogen chemiluminescence detector (NCD) and time of flight mass spectrometer (TOF-MS)) mounted on different GC × GC's were used. The use of two internal standards; 2-chloropyridine and 3-chlorothiophene; allowed quantification of the shale oil's composition by carbon number and by structural class. 20 different classes were detected in the shale oil: paraffins, isoparaffins, olefins/mononaphthenes, dinaphthenes, monoaromatics, naphthenoaromatics, diaromatics, naphthenodiaromatics, triaromatics, thiols/sulfides, benzothiophenes, naphtenobenzothiophenes, dibenzothiophenes, pyridines, anilines, quinolines, indoles, acridines, carbazoles and phenols. A significant amount of sulfur and nitrogen containing compounds, 2.2 wt% and 4.2 wt% respectively, were detected.

1. Introduction

In 2012 total worldwide energy demand was 5.51×10^{20} J [2] and is expected to grow to 7.06×10^{20} J by 2035 [3]. About 80% of this energy was provided by fossil fuels (crude oil, coal and natural gas) [4]. With only a limited amount of crude oil available and a decline in the discovery of conventional reservoirs [5] there is a need to investigate alternative energy resources. The most promising one on short notice is the vast resources of oil shale [6,7]. Oil shale is a fine-grained sedimentary rock containing kerogen, a mixture of organic chemical compounds with a molar mass as high as 1000 g mole^{-1} [4,8]. Kerogen mainly consists of carbon and hydrogen, but low amounts of organic oxygen, nitrogen, and sulfur compounds are also present. Oxygen, nitrogen and sulfur are associated with carbon atoms in various structural forms, which are the building blocks of the whole molecular structure of kerogen [9]. Extraction of oil and gas from oil shale is based on retorting or pyrolysis. Upon heating to approximately 500 °C without oxygen, the kerogen decomposes to yield shale oil, gas, and char, which remains in the shale residues. The produced shale oil is a mixture that is similar to petroleum containing thousands of hydrocarbon, oxygen-, sulfur- and nitrogen-containing organic compounds [10]. Those nitrogen and sulfur containing compounds have an adverse influence on the shale oils' potential exploitation as substitute transport fuels [11]. In addition combustion of nitrogen and sulfur containing compounds leads to the emission of NO_x and SO_x which are an important source of air pollution and acid rain [12,13]. As such the presence of these sulfur and nitrogen containing compounds lowers the quality of the produced shale oil, making it less attractive than sweet crude oil because of the additional upgrading processes that will be required before the shale oil can be used in a refinery [4]. Currently there is only limited information available about the composition of the produced shale oils [14–16], as research on oil shale pyrolysis is mainly focused on the investigation of the overall yields of shale oil, gas and cokes [17–20].

---

* Corresponding author. Tel.: +32 9 264 56 77.
E-mail address: Kevin.VanGeem@UGent.be (K.M. Van Geem).

http://dx.doi.org/10.1016/j.fuel.2014.09.055
0016-2361/

Recently additional insight has been obtained in the composition of shale oils such as sulfur speciation [21,22] and quantifying the oxygen containing compounds present in shale oil [23]. Geng et al. used a fractionation technique applicable for crude oil, coal liquids and shale oil samples, to divide the mixture into different acid, basic and neutral fractions, separating the oxygenates from the hydrocarbon matrix [23–27] and making their analysis possible with techniques such as GC–MS. Oxygenates reported to be present in shale oil are phenols, indanols, naphthols, phenylphenols, fluorenols, phenanthrenols, ketones and esters [23,24].

However, detailed compositional information of the produced shale oil and a proper methodology to determine a detailed composition of shale oil are essential for further improving the production process and to better assess required upgrading strategies. Several techniques to obtain more information about the detailed composition of shale oils have been developed and applied. One of the most used techniques is GC–MS [15,23,28–33]. A disadvantage of GC–MS is that in a fuel the complex hydrocarbon matrix fragmentation will interfere with other hetero-compounds of interest because the hydrocarbon content is several orders of magnitude larger [34]. Heart-cutting multidimensional gas chromatography is a first step forward [35] but comprehensive two-dimensional gas chromatography (GC × GC) is a lot more powerful. Another technique that has been used successfully to obtain information about the heteroatom content of shale oil is ESI FT-ICR MS [23,36,37]. The advantage of this technique is that it can identify the elemental composition, double bond equivalents, rings plus double bonds to carbon, and the carbon number, based on ultra-high-resolution and accurate mass measurements [38]. The disadvantages of FTICR-MS are the fact that it is not quantitative [39] and the formidable cost of the device which prohibits its widespread availability and routine use [40].

In the present work a new methodology to gain more insight into the detailed composition of shale oil is described and applied based on the combination of the results from different GC × GC chromatograms. GC × GC's are coupled with a flame ionization detector (FID), sulfur chemiluminescence detector (SCD), nitrogen chemiluminescence detector (NCD) and a time of flight mass spectrometer (TOF-MS). GC × GC – FID [41–47], GC × GC – SCD [48–52], GC × GC – NCD [53–55] and GC × GC – TOF-MS [43,46,47,53] have already been shown to be valuable techniques in the analysis of crude oil derived fractions. One of the main difficulties is combining the information obtained using these different detectors to allow detection and quantification of hydrocarbon compounds, sulfur containing compounds and nitrogen containing compounds inside the shale oil. In previous work [1] the combination of an FID with an SCD already proved a powerful combination to obtain the composition of atmospheric gas oils in terms of pure and sulfur containing hydrocarbons. In this article an NCD is also included. A quantitative separation in 20 different classes is obtained: paraffins, isoparaffins, olefins/mononaphthenes, dinaphthenes, monoaromatics, naphthenoaromatics, diaromatics, naphthenodiaromatics, triaromatics, thiols/sulfides, benzothiophenes, naphtenobenzothiophenes, dibenzothiophenes, pyridines, anilines, quinolines, indoles, acridines, carbazoles and phenols. A distribution based on carbon number is obtained for each individual group. The information derived from the chromatograms gives an unprecedented insight into the composition of shale oils.

2. Experimental

2.1. Samples and chemicals

Table 1
Measured elemental composition and initial (IBP) and final boiling point (FBP) of the shale oil (ASTM-D) and a reference crude oil sample. The elemental composition was measured by elemental analysis (EA) or based on the GC.

	Shale oil (EA and ASTM-D)	Shale oil (GC × GC)	Crude oil
C (wt%)	85.79 ± 0.4	85.3	84.0–87.5 [74]
H (wt%)	13.2 ± 0.05	13.8	12.5–16.0 [74]
S (wt%)	0.46 ± 0.05	0.47	0.01–4.2 [75]
N (wt%)	0.40 ± 0.01	0.38	0.0–0.5 [74]
O (wt%)	0.15 ± 0.01	0.12	0.5–1.2 [74]
IBP (K)	327	–	363–455 [76]
FBP (K)	751	–	460–670 [76]

Analytical gases (helium, oxygen, nitrogen, hydrogen and air) were provided at a minimum purity of 99.99% (Air Liquide, Belgium). 3-chlorothiophene was purchased from Sigma–Aldrich with a minimum purity of 98%. 2-chloropyridine, hexane, o-cresol, 2,3-dimethylphenol, 2,3,5-trimethylphenol and 4-isopropyl-3-methylphenol were also purchased from Sigma–Aldrich with a minimum purity of 99%. Dichloromethane was purchased from Chem-Lab at a minimum purity of 98% while acetone was purchased from Chem-Lab at a minimum purity of 99.5%. The shale oil sample was derived from oil shale from the Piceance Basin in Colorado, USA. The elemental composition of the shale oil was determined using a Flash EA2000 (Interscience, Belgium) equipped with a TCD. The elemental composition is based on three repeat analyses of the shale oil and can be found in Table 1.

2.2. Sample preparation

Four different samples of the shale oil sample were prepared for the separate analysis of the sample on GC × GC – FID, GC × GC – SCD, GC × GC – NCD and GC × GC – TOF-MS. An internal standard was added to the samples for the FID, NCD and SCD. The internal standards for each of the chromatograms were chosen in such a way that they were properly separated from all other peaks as will be illustrated further on. An additional pre-requisite is that for the NCD and SCD analysis nitrogen or sulfur also needs to be present in the internal standards. Therefore for the FID and the SCD analysis 3-chlorothiophene was chosen, while for the NCD analysis 2-chloropyridine was chosen. The amount of internal standard that is added is chosen in such a way that the internal standard would have a similar peak height as the components quantified by the internal standard. This resulted in 2 wt% of 3-chlorothiophene for the FID analysis, 400 ppm of 3-chlorothiophene for the SCD analysis and 1000 ppm of 2-chloropyridine for the NCD analysis. Different quantities of internal standard are needed because of the large difference in concentration between hydrocarbons (wt% level) and hetero-atom containing compounds (ppm level) in the shale oil.

To help with the identification of the nitrogen compounds (using TOF-MS) preparative chromatography was carried out. A solid phase extraction (SPE) according to Lissitsyna et al. [55] extracted the N-compounds and separated the shale oil into three fractions. This was done using 0.5 g silica SPE cartridges with a volume of 3 ml (Restek). The SPE column was activated using 6 ml of hexane prior to applying 2 ml of sample. The hydrocarbon matrix was eluted from the column using 9 ml of hexane while the nitrogen containing compounds stayed on the column. Afterwards the column was washed with two solvents providing two different nitrogen containing fractions. The first fraction was obtained by flushing with 9 ml of dichloromethane while the second fraction was obtained by flushing the column with 6 ml of acetone.

2.3. GC × GC – FID/SCD/NCD/TOF-MS analysis

All experiments were carried out using three Thermo Scientific TRACE GC × GC's (Interscience, Belgium). For modulation all devices