Video Article

On-line Analysis of Nitrogen Containing Compounds in Complex Hydrocarbon Matrixes

Nenad D. Ristic[1], Marko R. Djokic[1], Kevin M. Van Geem[1], Guy B. Marin[1]

[1]Laboratory for Chemical Technology, Faculty of Engineering and Architecture, Ghent University

Correspondence to: Kevin M. Van Geem at kevin.vangeem@ugent.be

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Abstract

The shift to heavy crude oils and the use of alternative fossil resources such as shale oil are a challenge for the petrochemical industry. The composition of heavy crude oils and shale oils varies substantially depending on the origin of the mixture. In particular they contain an increased amount of nitrogen containing compounds compared to the conventionally used sweet crude oils. As nitrogen compounds have an influence on the operation of thermal processes occurring in coker units and steam crackers, and as some species are considered as environmentally hazardous, a detailed analysis of the reactions involving nitrogen containing compounds under pyrolysis conditions provides valuable information. Therefore a novel method has been developed and validated with a feedstock containing a high nitrogen content, *i.e.,* a shale oil. First, the feed was characterized offline by comprehensive two-dimensional gas chromatography (GC × GC) coupled with a nitrogen chemiluminescence detector (NCD). In a second step the on-line analysis method was developed and tested on a steam cracking pilot plant by feeding pyridine dissolved in heptane. The former being a representative compound for one of the most abundant classes of compounds present in shale oil. The composition of the reactor effluent was determined via an in-house developed automated sampling system followed by immediate injection of the sample on a GC × GC coupled with a time-of-flight mass spectrometer (TOF-MS), flame ionization detector (FID) and NCD. A novel method for quantitative analysis of nitrogen containing compounds using NCD and 2-chloropyridine as an internal standard has been developed and demonstrated.

Video Link

The video component of this article can be found at http://www.jove.com/video/54236/

Introduction

The reserves of light sweet crude oils are gradually diminishing, and hence, alternative fossil resources are being considered to be used in the energy and petrochemical industry. In addition, renewables such as bio-oils produced by fast pyrolysis of biomass are becoming a more attractive resources of bio-based fuels and chemicals. Nevertheless, heavy crude oil is a logical first choice because of the large proven reserves in Canada and Venezuela[1-3]. The latter are being recognized as the largest crude oil reserves in the world and their composition is similar to the composition of natural bitumen. Similar to bio-oils, heavy crude oils differ from light crude oils by their high viscosity at reservoir temperatures, high density (low API gravity), and significant contents of nitrogen, oxygen, and sulfur containing compounds[4,5]. Another promising alternative is shale oil, derived from oil shale. Oil shale is a fine-grained sedimentary rock containing kerogen, a mixture of organic chemical compounds with a molar mass as high as 1,000 Da[6]. Kerogen can contain organic oxygen, nitrogen, and sulfur in the hydrocarbon matrix; depending on the origin, age, and the extraction conditions. Global characterization methods have shown that the concentration of heteroatoms (S, O and N) in shale oil and heavy crude oils is typically substantially higher than the specifications set for the products used in for example the petrochemical industry[6]. It is well documented that nitrogen containing compounds present in heavy conventional crude oil and shale oil have a negative effect on the catalyst activity in hydrocracking, catalytic cracking and reforming processes[7]. Similarly, it has been reported that the presence of nitrogen containing compounds are a safety concern because they promote gum formation in the cold-box of a steam cracker[8].

These processing and safety challenges are a strong driver to improve the current methods for off-line and on-line characterization of nitrogen containing compounds in complex hydrocarbon matrices. Two-dimensional gas chromatography (GC × GC) coupled with a nitrogen chemiluminescence detector (NCD) is a superior characterization technique compared to one-dimensional gas chromatography (GC) for analyzing conventional diesels or liquefied coal samples[7]. Recently a method has been developed and applied to the offline characterization of nitrogen content in shale oil[6], the identification of extracted nitrogen compounds present in middle distillates[9], and the determination of the detailed composition of plastic waste pyrolysis oil[10].

It is thus clear that GC × GC analysis is a powerful offline processing technique for analyzing complex mixtures[11-17]. However, on-line application is more challenging due to the need for a reliable and non-discriminating sampling methodology. One of the first developed methodologies for comprehensive on-line characterization was demonstrated by analyzing steam cracking reactor effluents using a TOF-MS and a FID[18]. The optimization of the GC settings and an appropriate column combination enabled analysis of samples consisting of hydrocarbons ranging from methane up to polyaromatic hydrocarbons (PAHs)[18]. The present work takes this method to a new level by extending it to the identification and quantification of nitrogen compounds present in the complex hydrocarbon mixtures. Such a method is among others needed to improve fundamental understanding of the role these compounds play in several processes and applications. To the authors' best knowledge, information concerning kinetics of conversion processes of nitrogen containing compounds is scarce[19], partly due to the lack of an adequate method to identify and quantify nitrogen containing compounds in the reactor effluent. Establishing the methodology for offline and on-line analyses is thus a prerequisite before one can even attempt feedstock reconstruction[20-27] and kinetic modeling. One of the fields which would benefit from the accurate identification and quantification of nitrogen containing compounds is steam cracking or pyrolysis. Bio and heavy fossil feeds for steam cracking or pyrolysis reactors contain thousands of hydrocarbons and compounds that contain heteroatoms. Moreover, because of the complexity of the feed and the radical nature of the occurring chemistry, ten thousands of reactions can occur among the thousands free radical species[28], which makes the reactor effluent even more complex than the starting material.

In hydrocarbon mixtures nitrogen is mainly present in aromatic structures, *e.g.,* as pyridine or pyrrole; hence most experimental efforts have been dedicated to the decomposition of these structures. Hydrogen cyanide and ethyne were reported as major products for the thermal decomposition of pyridine studied in a temperature range of 1,148-1,323 K. Other products such as aromatics and nonvolatile tars were also detected in minor quantities[29]. The thermal decomposition of pyrrole was investigated in a broader temperature range of 1,050-1,450 K using shock wave experiments. The main products were 3-butenenitrile, *cis* and *trans* 2-butenenitrile, hydrogen cyanide, acetonitrile, 2-propenenitrile, propanenitrile, and propiolonitrile[30]. Additionally thermal decomposition shock tube experiments were performed for pyridine at elevated temperatures resulting in comparable product spectra[31,32]. Product yields in these studies have been determined by applying GC's equipped with a FID, a nitrogen-phosphorus detector (NPD)[31], a mass spectrometer (MS)[32] and a Fourier transform infrared (FTIR) spectrometer[32]. A similar methodology implementing the FID and the NPD was applied to analyze the shale oil pyrolysis products in a continuous flow reactor[8]. Using a cold trap at 273.15 K and GC-MS, Winkler *et al.* [33] showed that during pyridine pyrolysis heteroatom-containing aromatic compounds are formed. Zhang *et al.*[34] and Debono *et al.*[35] applied the method of Winkler *et al.* for studying the pyrolysis of organic waste. The nitrogen rich reaction products were analyzed on-line, using a GC coupled to a thermal conductivity detector (TCD)[34]. The collected tars were analyzed offline using GC-MS[34,35]. Simultaneous pyrolysis of toluene and pyridine showed a difference in soot formation tendency compared to pyridine pyrolysis, indicating the complex nature of the free-radical reactions[31,36].

One of the most comprehensive analytical methodologies was developed by Nathan and co-workers[37]. They used FTIR, nuclear magnetic resonance (NMR) and GC-MS for analyzing decomposition products of pyridine and diazine and electron paramagnetic resonance (EPR) spectroscopy for tracing free radical species. FTIR analysis can be a very effective approach for the identification of a large range of products, even PAHs[38-40], nevertheless quantification is extremely challenging. Calibration requires a full set of infrared spectra at different concentrations for each target species at a specific temperature and pressure[41]. Recent work of Hong *et al.* demonstrated the possibilities of using molecular-beam mass spectrometry (MBMS) and tunable synchrotron vacuum ultraviolet photoionization for determination of products and intermediates during pyrrole and pyridine decomposition[42,43]. This experimental method enables selective identification of isomeric intermediates and near-threshold detection of radicals without inflicting fragmentation of the analyzed species[44]. However, the uncertainty on the measured concentrations using MBMS analysis is also substantial.

In this work, first the offline comprehensive characterization results of the complex shale oil are reported. Next, the limitations of using an on-line GC × GC-TOF-MS/FID for the analysis of nitrogen compounds in a complex hydrocarbon matrix are discussed. Finally, the newly developed methodology for the on-line quantification of nitrogen containing compounds by GC × GC–NCD is demonstrated. The qualitative analysis of products was carried out using TOF-MS, while FID and NCD were used for quantification. The application of the NCD is a substantial improvement compared to using the FID because of its higher selectivity, lower detection limit and equimolar response.

Protocol

Caution: Please consult relevant material safety data sheets (MSDS) of all compounds before use. Appropriate safety practices are recommended. Solutions and samples should be prepared in the fume hood, while using personal protective equipment. Best practice implies use of safety glasses, protection laboratory gloves, lab coat, full length pants, and closed-toe shoes. The reactor should be properly sealed as several reactants and reaction products can be acutely toxic and carcinogenic.

1. Offline GC × GC–NCD Analysis

1. **Sample Preparation for offline GC × GC analysis**
    1. Select 2-chloropyridine as an internal standard. Make sure that the concentration of the internal standard in the prepared sample is within the range of the concentrations of nitrogen containing compounds present in the analyzed mixture. The concentration of the internal standard must be at least ten times higher than the detection limit of the NCD. Furthermore the concentration of the internal standard should not be more than two times higher than the concentration of the nitrogen compound with the highest concentration in the sample.
    2. Prepare and weigh two glass vials using an analytical balance.
    3. Add 20.498 mg of 2-chloropyridine to the first vial using an analytical balance.
    4. Tare the balance with the first vial and add 1024.287 mg of a shale oil sample. Gently mix the vial content.
    5. Transfer 23.369 mg of the prepared mixture into a second vial and add 435.195 mg of the original shale oil sample. The obtained concentration of the internal standard in the sample is approximately 1,000 ppmw.

2. **GC × GC–NCD analysis and operating conditions**
    1. Perform the analysis using a GC × GC equipped with a dual-stage cryogenic liquid CO_2 modulator[45].
        1. Connect the first dimension non-polar column (PONA, 50 m L × 0.25 mm I.D. × 0.5 µm d_f) directly to the second dimension mid-polar column (BPX-50, 2 m L × 0.25 mm I.D. × 0.25 µm d_f). Apply the GC × GC operating conditions optimized for detection of nitrogen containing compounds in shale oil, with the parameters presented in **Table 1**.

        2. Inject the sample using the auto sampler, with the settings stated in the Supplementary Table.
    2. For the NCD, set the flow rates at 5 and 11 ml min^{-1} for the H_2 and O_2 respectively, while keeping the burner temperature at 1,198 K. Use a data acquisition rate of 100 Hz. The detector settings are presented in **Table 1**.

3. **Reprocessing of results**
    1. Perform data acquisition using the data system for the NCD. Export the raw data to a .cdf file and import into an analytical software (*e.g.,* GCImage).
    2. Use the analytical software to construct the contour plot, to determine the retention times, and to perform peak fitting and blob integration according to the software protocols. Identify each blob as a compound of a specific nitrogen group with a specific carbon number.
    Note: Response signal of NCD is equimolar[6,46,47,48], hence the procedure for quantification of nitrogen containing compounds in the sample is straightforward.
    3. Calculate the concentration of detected compounds using the following equation:
    $$W_i = \frac{V_i}{V_{st}} \cdot W_{st} \cdot \frac{M_i}{N_i \cdot M_{st}}$$
    where V_i *and* V_{st} are the peak volumes of the nitrogen containing compound *i* and the internal standard respectively. W_{st} is the concentration of the internal standard compound, N_i is the number of nitrogen atoms in compound *i*, M_i and M_{st} are the molar masses of the nitrogen containing compounds and of the nitrogen internal standard respectively[6].

2. On-line Analysis

1. **Pilot plant steam cracking unit**
Note: The pilot plant steam cracker consists of three sections: the feed section, the furnace/reactor section and the analysis section. The unit is explained in detail elsewhere[18,49,50,51]. A schematic description of the setup can be found in the Supplementary Information.
    1. During the experiments, as heptane is fed using a computer controlled rotary pump by setting the flowrate using the Programmable Logical Controller (PLC), introduce pyridine to the reactor convection section by manually setting the speed of the piston pump. The diluent used depends on the purpose of the test and can be varied. Depending on the requirements of the experiment, use the gas controllers for helium and nitrogen dilution, and regulate the water feeding pump frequency for steam dilution.
    2. Prior to the reaction section of the furnace, evaporate and mix the feedstock in two separately heated zones kept at a temperature of 773 K.
    3. Impose a temperature profile to the Incoloy 800HT 12.4 m long and 9 mm internal diameter reactor by setting the temperatures in the five heated zones using the PLC. Different experiments with varying process conditions can be performed. Use the process conditions applied to perform method testing as outlined in **Table 2**.

2. **Analysis methodology**
    1. Use the refinery gas analyzer (RGA) equipped with three detectors working on parallel channels in order to detect as many compounds as possible. Two TCD's and a FID allow detection of CO, CO_2, H_2, and hydrocarbons up to four carbon atoms, using three different columns for separating the reaction products. The RGA setting are presented in **Table 3**.
    2. For the GC × GC set-ups, use a non-polar PONA (50 m L × 0.25 mm I.D. × 0.5 µm d_f) column in the first dimension and a mid-polar BPX-50 (2 m L × 0.15 mm I.D. × 0.15 µm d_f) column in the second dimension. Ensure that the temperature in the oven can be lowered to 233 K by addition of liquid nitrogen inside the GC oven. Use the GC × GC settings given in **Table 4** for the on-line analyses.
    3. Ensure that TOF-MS electron impact ionization is 70 eV, and detector voltage 1,700 V by setting these values in the software. Additionally set the acquisition frequency to 30 spectra/sec in a mass range of 15-400 amu in the same software.
    4. For the NCD, manually set flow rates at 5 and 11 ml min^{-1} for the H_2 and O_2 respectively, while keeping the burner temperature at 1,198 K. The data acquisition rate needs to be 100 Hz.
    5. For FID H_2, air and N_2 (make-up gas) flow rates are respectively 35, 350 and 35 ml min^{-1}. Ensure that the FID temperature is set at 573 K with a data acquisition rate of 100 Hz.
    6. Sample the pilot plant effluent on-line, *i.e.,* during pilot plant operation, and at high temperature (673 - 773 K). Use a valve-based sampling system, positioned in the sampling oven kept at 573 K, see **Figure 1**.
        1. Turn the pneumatic 6-port 2-way valve to the position shown in **Figure 1a** using the PLC, flush the sample loop for at least 2 min.
        2. Turn the pneumatic 6-port 2-way valve to the position shown in **Figure 1b** using the PLC, a gaseous sample from the sample loop is carried with helium and injected onto selected GC × GC. Keep the valve in the injection position for 20 sec. Turn the pneumatic 6-port 2-way valve back in the position shown in **Figure 1a**.

3. **Internal standard addition**
    1. Use 2-chloropyridine as an internal standard for the NCD analyses. The introduced amount of this compound depends on the purpose of the experiment (values illustrated in **Table 2**). To add 2-chloropyridine precisely and uniformly, dissolve the compound in n-hexane (values illustrated in **Table 2**) and gentle stir the mixture after preparation.
    2. Add the internal standard 2-chloropyridine continuously by pumping the prepared mixture through a capillary transfer line, which is centrally positioned in the product stream before the sampling system. For this purpose use a peristaltic pump and keep the flow rate stable (values indicated in **Table 2**).

4. **Data acquisition and quantification**
    1. Acquire the data obtained with TOF-MS, and use the results for product identification and establishing the retention times of the reaction products. Acquisition and reprocessing of data obtained from FID is similar to the procedure applied to reprocessing of results gathered using the NCD, as explained in section 1.3.2.

2. Recalculate the product yields using an internal standard[18]. Introduce a fixed amount of nitrogen (N_2) continuously to the product stream and use it as a reference compound as shown in **Figure 2**.
3. Combine the data obtained on the different instruments. Apply the calibration factors for each compound depending on the detector.
    1. Set the methane calibration factor to 1.
    2. Obtain response factors relative to methane for permanent gases detectable on RGA by calibration. Ensure that for all major compounds detected on the GC × GC the relative response factors are determined by calibration. For minor products use the FID calibration factors reported by Dietz[52]. If the response factors for a compound are not available, calculate values using the group contribution method developed by Dierickx *et al.*[53].
    3. Methane functions as a secondary internal standard, and its concentration is needed to determine the concentrations based on the peaks of the GC × GC–FID chromatogram. Therefore determine the methane mass flow rate using equation 2:

$$\dot{m}_{CH_4} = \frac{f_{CH_4}}{f_{N_2}} \cdot \frac{A_{CH_4}}{A_{N_2}} \cdot \dot{m}_{N_2}$$

Where, f_{CH4} and f_{N2} are the calibration factors of methane and nitrogen on TCD respectively. A_{CH4} and A_{N2} are peak areas obtained during analysis, while $\dot{m}_{N_2}$ is the nitrogen mass flow rate added to the effluent stream.

4. Carry out quantification of the nitrogen containing products by applying the procedure explained in section 1.3.3.

Representative Results

The chromatogram obtained using the offline GC × GC–NCD for characterization of nitrogen containing compounds in a shale oil sample is given in **Figure 3**. The following classes were identified: pyridines, anilines, quinolines, indoles, acridines, and carbazoles. Moreover, detailed quantification of the individual compounds was possible. The gathered data was used to determine the individual compound concentrations, and the obtained values are presented in **Table 5**. The analyzed sample contains 4.21 wt.% of nitrogen containing compounds mainly belonging to pyridine class. From a processing point of view this high nitrogen content is a concern when shale oil is considered to replace traditional steam cracking feedstocks where nitrogen containing compounds are typically only present in ppm levels.

On-line analysis of the reactor effluent during pyrolysis of a pyridine-heptane mixture at a coil outlet temperature (COT) of 1,073 K and a coil outlet pressure (COP) of 170 kPa, performed with GC × GC-TOF-MS (see **Figure 4a**), was used for identifying the reaction products and establishing the compound retention times for a specific set of GC × GC operating conditions. GC × GC–FID (see **Figure 4b**) analysis was used for determining the reactor effluent composition while using steam as a diluent. The obtained product concentrations, normalized to 100%, are given in **Table 6**. The identified products in these chromatograms show that the addition reactions of pyridine are favorable compared to pyridine decomposition. Hauser and Lifshitz[29,30] reported the formation of light nitriles in pyrolysis experiments of pyridine and pyrrole. Since these molecules were not detected in the present set of experiments and the nitrogen molar balances in the experiments closed, it can be concluded that pyridine is not decomposing to a great extent at the selected process conditions.

Testing of the on-line GC × GC–NCD method was performed in a separate experiment, at conditions that preclude pyridine decomposition, *i.e.*, a temperature of 823 K and a COP of 170 kPa. A pyridine concentration of 841.4 ppmw was added to the nitrogen and water flow, and after addition of the internal standard, the reactor effluent sample was injected on the GC × GC. Using the obtained detector response and known concentration of the internal standard, a concentration of 819 ppmw pyridine was measured. Hence, the relative error of the measurement was determined to be less than 3% (see **Figure 5**).

Finally a heptane steam cracking experiment under more severe conditions was conducted with a small amount of pyridine added to the n-heptane feed. The experiment was performed under typical steam cracking conditions, with a steam dilution of 0.5 kg/kg, a COT of 1,123 K and a COP of 170 kPa. **Figure 6** shows the resulting GC × GC–NCD and FID chromatograms. The compounds were identified based on retention times and data obtained from the TOF-MS. The following compounds were detected on the GC × GC–NCD chromatogram: acetonitrile, pyridine, 2-methylpyridine, 3-methylpyridine, 3-ethylpyridine, 3-ethenylpyridine, 3-methylbenzonitrile, and indole. Using their respective Kovats retention indices 2-butenenitrile and propanonitrile could be tentatively identified. The quantitative results are shown in **Table 7**. The mass flow rate of pyridine to the reactor was set to 1.2 mg/sec, *i.e.*, concentration of elemental nitrogen in the reaction mixture was 125.9 ppmw. After reprocessing of the acquired data, the nitrogen concentration in the reaction effluent was determined to be 124.5 ppmw, which corresponds to a nitrogen recovery of 98.5%.

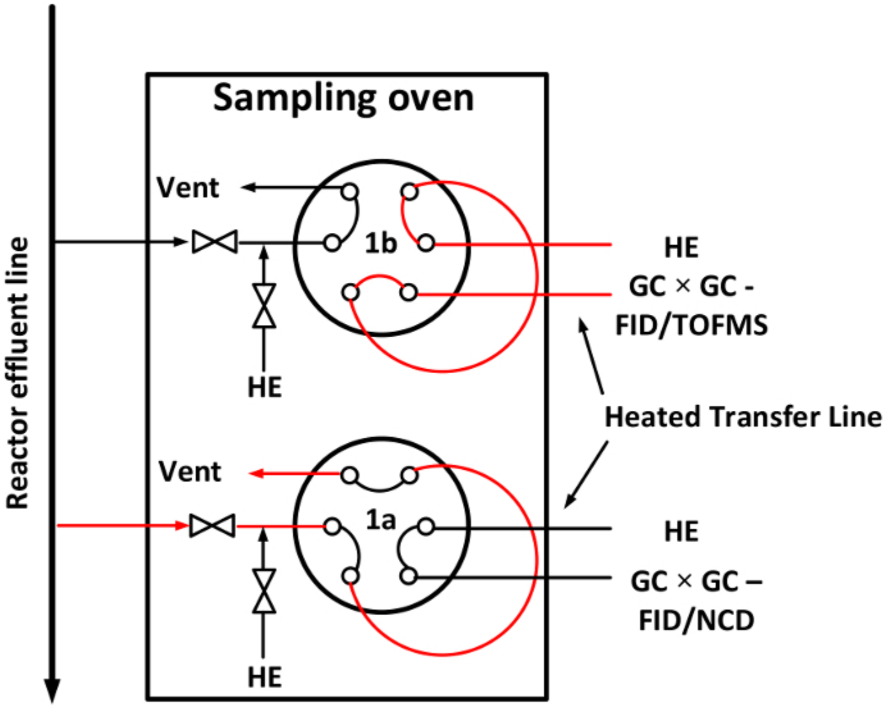

Figure 1. Detailed schematic representation of the GC × GC sampling oven and valves. Valve 1a is shown in the purging position, flushing the sample loop with effluent. Valve 1b is shown in injection position: carrier gas (helium) is rerouted to the sampling oven, where it is used to transport the effluent sample to the respective GC via a transfer line[18]. Please click here to view a larger version of this figure.

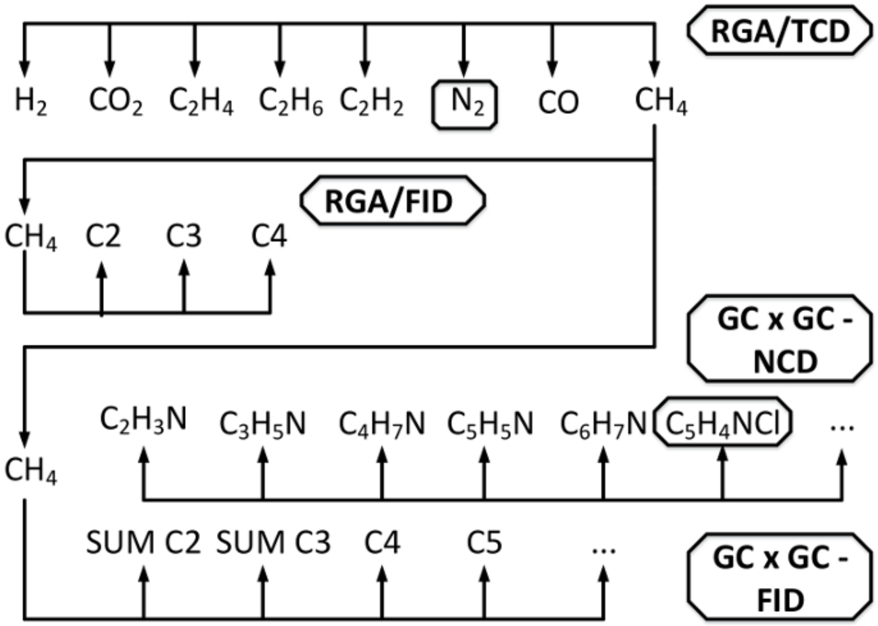

Figure 2. Schematic representation of the quantitative on-line effluent analysis method using a reference compound. The known amount of nitrogen added to the effluent stream is detected on the RGA/TCD and used to determine the concentration of methane which is a reference compound for reactor effluent analysis. Similarly a known amount of 2-chloropyridine is added to the effluent stream and used as internal standard for GC × GC–NCD analysis. Please click here to view a larger version of this figure.

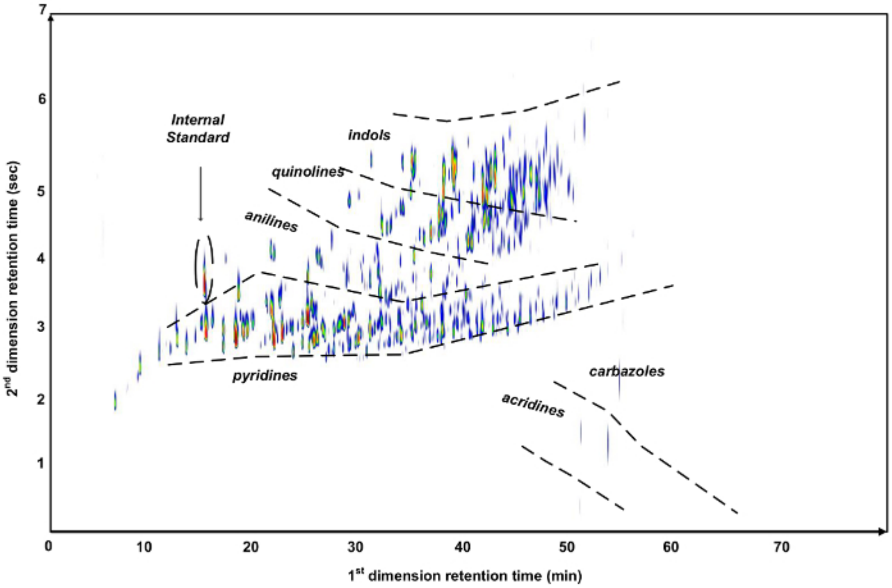

Figure 3. GC × GC–NCD chromatogram of the shale oil sample. The internal standard and separated nitrogen containing hydrocarbon group types, pyridines, anilines, quinolines, indoles, acridines, and carbazoles are illustrated. Please click here to view a larger version of this figure.

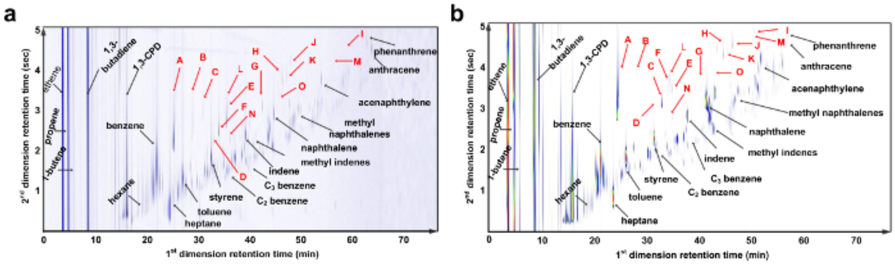

Figure 4. Analysis of the pyridine-heptane mixture pyrolysis products. (**a**) GC × GC - TOF-MS chromatogram, (**b**) GC × GC–FID chromatogram. The nitrogen containing products of the pyrolysis experiment performed at a COT of 1,073 K and a COP of 170 kPa are presented with capital letters (A: pyridine, B: 2-methylpyridine, C: 3-methylpyridine, D: 4-ethylpyridine, E: 3-ethenylpyridine, F: 4-ethenylpyridine, G: 2-methylbenzonitrile, H: quinoline, K: isoquinoline, I: 1-H-indole-7-methyl, J: indole, L: benzonitrile, M: 4-methylquinoline, N: 5-ethenyl-2-methylpyridine, O: 7-methylindolizine). Please click here to view a larger version of this figure.

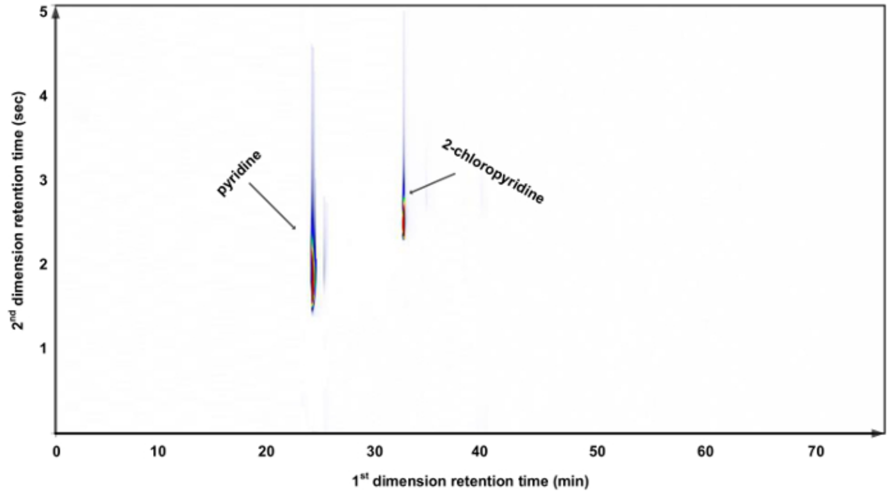

Figure 5. GC × GC–NCD on-line detection of pyridine in the reactor effluent stream under non-reactive conditions. The experiment is performed isothermally at 773 K and a COP of 170 kPa and used for the evaluation of the internal standard quantification method. Please click here to view a larger version of this figure.

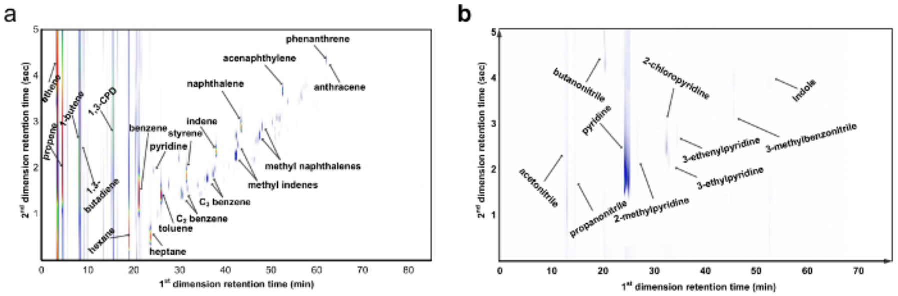

Figure 6. Product analysis during steam cracking of heptane with traces of pyridine. (**a**) GC × GC–FID chromatogram (**b**) GC × GC–NCD chromatogram. Detection of major steam cracking products with FID and minor nitrogen containing steam cracking products with NCD. The experiment is performed with steam dilution of 0.5 kg/kg, a COT of 1,123 K, and a COP of 170 kPa. Please click here to view a larger version of this figure.

Detector	**NCD**
Injector	573 K
Split flow	200 ml/min
Carrier gas	2.1 ml/min
Initial oven temperature	313 K
Heating rate	3 K/min
Final temperature	573 K
Modulation time	7 sec
Detector settings	
Temperature	1,198 K
Range	1
Acquisition rate	100 Hz

Table 1. Overview of the GC × GC conditions applied to offline shale oil characterization.

Detector	**Pyrolysis**	**Steam Cracking**	**Method Test**	**Steam Cracking**
Heptane flowrate, g/hr	2,480	2,880	98.89	4,000
Water flowrate, g/hr	/	1,440	2,000	2,000
Nitrogen flowrate, g/hr	/	/	4,000	/
Helium flowrate, g/hr	507	/	/	/
Pyridine flowrate, g/hr	25.1	29.1	5.21	4.33
2-Chloropyridine flowrate, g/hr	/	/	4.21	0.85
Hexane flowrate, g/hr	/	/	85.91	83.63
Coil outlet temperature (COT), K	1,073	1,073	823	1,123
Coil outlet pressure (COP), bar	1.7	1.7	1.7	1.7
Detector	TOF-MS	FID	NCD	NCD

Table 2. Applied experimental conditions.

RGA			
Channel	**Channel 1**	**Channel 2**	**Channel 3**
Injection	50 µl (gas), 353 K	150 µl (gas), 353 K	150 µl (gas), 353 K
Carrier gas	He	He	N_2
Pre-column	Fused Silica Capillary Precolumn (15 m × 0.53 mm × 3 µm)	Packed Porous Polymers Column (0.25 m × 3.175 mm)	Packed Porous Polymers Column (1 m × 3.175 mm)
Analytical	Alumina bond Column (25 m × 0.53 mm × 15 m)	Packed Porous Polymers Column (1 m × 3.175 mm, 1 m × 3.175 mm)	Carbon Molecular Sieve Column (2 m × 3.175 mm)
Oven	323→393 K (5 K/min)	353 K	353 K
Detector	FID, 473 K	TCD, 433 K	TCD, 433 K

Table 3. Pilot plant on-line analysis section - RGA settings.

Detector	FID	TOF-MS	NCD
Injector	573 K	573 K	573 K
Split flow	30 ml/min	30 ml/min	10 ml/min
Carrier gas	2.1 ml/min	2.6 ml/min	2.1 ml/min
Initial oven temperature	233 K	233 K	233 K
Heating rate ramp I	4 K/min	4 K/min	4 K/min
Temperature hold, min	4	4	4
Temperature ramp	313 K	313 K	313 K
Heating rate ramp II	5 K/min	5 K/min	5 K/min
Final temperature	573 K	573 K	573 K
Modulation time	5 sec	5 sec	5 sec
Detector			
Temperature	573 K	473 K	1,198 K
Range	10	n.a.	1
Acquisition rate	100 Hz	30 Hz	100 Hz

Table 4. Pilot plant on-line analysis section - GC × GC settings.

Carbon number	pyridines, wt.%	anilines, wt.%	quinolines, wt.%	indoles, wt.%	acridines, wt.%	carbazoles, wt.%
5	0.01	0.00	0.00	0.00	0.00	0.00
6	0.04	0.00	0.00	0.00	0.00	0.00
7	0.11	0.02	0.00	0.00	0.00	0.00
8	0.26	0.05	0.00	0.01	0.00	0.00
9	0.47	0.07	0.01	0.06	0.00	0.00
10	0.15	0.11	0.08	0.17	0.00	0.00
11	0.18	0.11	0.17	0.28	0.00	0.00
12	0.12	0.08	0.19	0.30	0.00	0.00
13	0.18	0.03	0.12	0.16	0.00	0.02
14	0.17	0.00	0.03	0.14	0.01	0.02
15	0.13	0.00	0.00	0.00	0.02	0.00
16	0.10	0.00	0.00	0.00	0.00	0.00
17	0.05	0.00	0.00	0.00	0.00	0.00
18	0.03	0.00	0.00	0.00	0.00	0.00
19	0.00	0.00	0.00	0.00	0.00	0.00
20	0.00	0.00	0.00	0.00	0.00	0.00
21	0.00	0.00	0.00	0.00	0.00	0.00
22	0.00	0.00	0.00	0.00	0.00	0.00
23	0.00	0.00	0.00	0.00	0.00	0.00
24	0.00	0.00	0.00	0.00	0.00	0.00
25	0.00	0.00	0.00	0.00	0.00	0.00
26	0.00	0.00	0.00	0.00	0.00	0.00
27	0.00	0.00	0.00	0.00	0.00	0.00
28	0.00	0.00	0.00	0.00	0.00	0.00
29	0.00	0.00	0.00	0.00	0.00	0.00
30	0.00	0.00	0.00	0.00	0.00	0.00
31	0.00	0.00	0.00	0.00	0.00	0.00
32	0.00	0.00	0.00	0.00	0.00	0.00
33	0.00	0.00	0.00	0.00	0.00	0.00
Total, wt.%	**1.98**	**0.46**	**0.59**	**1.10**	**0.04**	**0.04**

Table 5. Concentration of nitrogen containing compounds in the shale oil.

Table 6. Concentrations of the compounds in the reactor effluent during cracking of heptane with 1.0 wt.% of pyridine (steam dilution 0.5 kg/kg, COT 1,073 K, COP 170 kPa). Please click here to download this file.

Table 7. Concentrations of the compound in the reactor effluent during steam cracking of heptane with traces of pyridine (steam dilution 0.5 kg/kg, COT 1,123 K, COP 170 kPa). Please click here to download this file.

Discussion

The described experimental procedures enabled a successful comprehensive off-line and on-line identification and quantification of nitrogen containing compounds in the studied samples.

The separation of nitrogen containing compounds in shale oil was accomplished using GC × GC–NCD, as shown in **Figure 3**. Since the NCD cannot be used for identification, the retention times of the observed species need to be established in advance by carrying out analyses on the GC × GC coupled to TOF-MS, based on the detailed procedure of carrier gas flowrate optimization for each detection method[18,54]. Flow rate adaptation leads to similar retention times of compounds on chromatograms obtained using different detectors[18]. In addition to the established TOF-MS retention times, literature data and Kovats retention indices were used for a tentative identification of compounds. To enable precise quantification of individual compounds, the internal standard should be chosen in such a way that peak overlap with peaks from other compounds in the sample is avoided. The bidimensional resolution should be higher than 1.5[15]. Repeat measurements show that the NCD has

±3% uncertainty for concentrations higher than 100 ppmw. The uncertainty increases to ±10% as the concentration of the nitrogen containing compounds decreases to only a few ppmw[6].

In a second step the focus was switched to the on-line detection of nitrogen compounds in an abundant hydrocarbon matrix. Samples of the reactor effluent were taken at an elevated temperature preventing condensation of molecules with a molecular weight higher than 128 Da[18]. The combination of gas chromatography columns enables a separation of products based on differences in the compound volatility in the first dimension and based on differences in the specific polarity of compounds in the second dimension. Hence a truly comprehensive system is established. Nevertheless the most volatile compounds present in the reactor effluent cannot be trapped and refocused by the cryogenic CO_2 modulation. First the pyrolysis products of heptane with 1.0 wt.% of pyridine were analyzed using GC × GC-TOF-MS, enabling identification of the obtained products. Calibration of the MS detectors is shown to be strongly dependent on the tuning parameters[55], hence, using this type of detector for quantification is laborious and can give substantial uncertainty. Helium was chosen as the diluent for the tests, minimizing the background noise on the detector during analysis. In the complex reactor effluent nitrogen atoms are incorporated in several aromatic structures. Separation of these nitrogen containing compounds was possible in the second dimension column since their polarity is higher in comparison to the other obtained products, as shown in **Figure 4a**. Furthermore the developed experimental procedure was applied to product quantification using the FID, see **Figure 4b**. The presented experimental work illustrates that detailed product characterization is possible using this method. Moreover, the same procedure will be applied in follow-up studies of pyrolysis reactions of nitrogen containing compounds.

Quantification of the compounds masked by the hydrocarbon matrix is a challenge using only the FID, especially when the matrix becomes increasingly complex. Modulation of the peaks corresponding to compounds with a boiling point that is lower than 313 K is not possible using the CO_2 modulator. This implies that the peaks of the nitrogen containing compounds with a low boiling point overlap with the hydrocarbon matrix on the FID chromatogram. Consequently the application of the NCD can be considered as a substantial improvement. The experimentally determined minimum detection level of 1.5 pgN/sec obtained using a reference mixture[56] gives an indication that it is possible to trace even ppm and ppb concentrations of nitrogen containing compounds in the analyzed samples. Unlike the NPD detector, a NCD gives an equimolar response and it is not substantially affected by the matrix[57,58]. However, quantification of nitrogen containing compounds detected by the NCD requires introducing an internal standard to the reactor effluent. Therefore the method has been tested using 2-chloropyridine as the internal standard as this compound is not formed during pyrolysis and it does not overlap with nitrogen containing products on the NCD chromatogram (see **Figure 6**). The internal standard thus fulfills the criterion to have a peak bidimensional resolution that exceeds 1.5. The obtained relative experimental error — less than 3% obtained under nonreactive conditions — illustrates the accuracy and reliability of the method. The same procedure applied to quantification of nitrogen containing products in a steam cracking effluent resulted in a nitrogen recovery of 98.5% in the analysis. The application range of the method could be further broadened by enhancing the separation power using a differential flow modulator[59] for the GC × GC, enabling also a two dimensional separation of the most volatile products.

The described work demonstrates the accuracy, repeatability and reproducibility of the methodology for on-line quantification of nitrogen containing products in an abundant hydrocarbon matrix. The high separation power of the GC × GC combined with a sensitive selective detector significantly goes beyond the present state of the art, resulting in a more detailed product detection and quantification.

Disclosures

The authors have nothing to disclose.

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