Industrial Applications of Offline and Online Comprehensive Gas Chromatography

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Comprehensive GC, or GCxGC, is used regularly at Dow Benelux BV, where both offline and online approaches are being utilised in research and development and in routine applications. This technical article describes the offline GCxGC analysis of hydrocarbon streams with comparison of the accuracy and precision to the detailed hydrocarbon analysis (DHA). Also discussed in this article is how a seven parallel reactor setup was coupled to online GCxGC for the evaluation and optimisation of catalyst formulations.

Introduction

The spectrum for hydrocarbon streams is extensive, ranging from light streams of two to four carbon numbers (C2-C4) up to heavy streams, which can extend to C15 and higher carbon numbers. Accurate determination of the hydrocarbon composition of such streams is essential to maximise operating margins; however, analysis of each hydrocarbon stream has different method requirements (Figure 1).

For the lighter hydrocarbon streams, a one-dimensional gas chromatographic (1D GC) method is sufficient, where the PIONA or DHA methods are typically utilised. The PIONA, or Paraffin (P), Isoparaffin (I), Olefin (O), Naphthene (N), Aromatic (A) analyser, quantifies each compound class as weight percent in the sample [1]. The DHA method, or Detailed Hydrocarbon Analysis, not only provides the quantification of the compound classes as weight percentage in the sample, but also provides quantitative information for the individual components [2]. Having such detailed information is extremely important as the input data for modelling operating margins.

For heavier hydrocarbon streams, the level of compositional complexity increases. Consequently, a 1D GC method is not sufficient to separate all components from one another, and as such, two-dimensional GC is required [3]. By utilising comprehensive GC (GCxGC), separation based on carbon number and group type can be achieved, affording the same level of detail as the
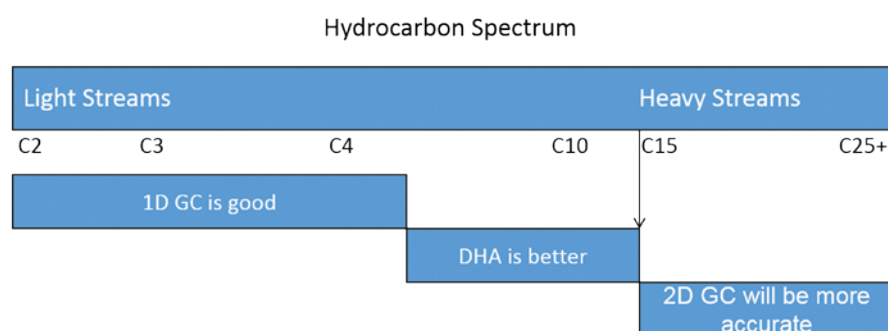

Figure 1: Spectrum of hydrocarbon streams.

DHA, but for heavier hydrocarbon streams. However, there are many considerations for the successful implementation of GCxGC, including column selection, detector selection, and modulator, to name a few.

There are two approaches for column selection in GCxGC; a normal column set or a reversed column set can be utilised [4]. With a normal column set, a non-polar stationary phase is selected for the first dimension separation, and a polar stationary phase is utilised for the second dimension. For the reversed column set, a polar stationary phase is installed for the first dimension separation, while a non-polar stationary phase is used in the second dimension. No matter which column set is selected, the first dimension column will be longer than the second dimension and operated at a slow temperature gradient (1-5°C) with typical total run times between 45-120 min, while the separation on the second dimension column will be typically between 3-10 sec [5]. This,

in turn, requires extremely fast detection after the second dimension column, limiting detector options to those capable of operating at 100 Hz. To transfer the sample from the first column to the second, a modulator is utilised. Flow and thermal modulators are commercially available, and they both serve the same purpose; to collect the fractions eluting from the first dimension column, re-inject the fractions on to the second dimension column, and trap eluents from the first column during the launch of the preceding fraction onto the second column [6].

Typically, GCxGC is utilised as an offline analytical technique (i.e. not in process); however, Dow has coupled an analytical GCxGC instrument to a seven parallel reactor setup for the online analysis of complex reaction mixtures generated by catalysis research and development. This article will detail how both offline and online GCxGC are utilised for quantification of hydrocarbon compositions.
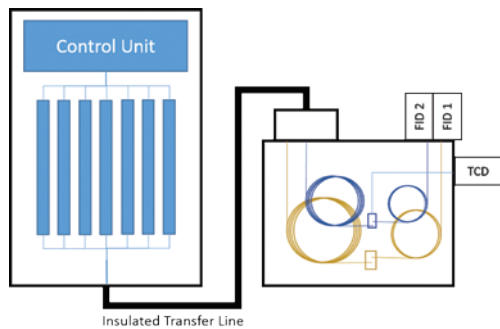
Experimental
Offline GCxGC

Offline GCxGC was performed using a reversed column set; the 1D column was a DB-17 (10 m x 0.100 mm x 0.20 µm), and the 2D column was a DB-1 (5 m x 0.250 mm x 0.12 µm). Both columns were purchased from Agilent. An Agilent flow modulated GCxGC instrument was utilized for these experiments. Injection was performed using the split/splitless inlet of the GC at 0.1 µL SPLIT 1:500 at 280°C. The injection volume and split ratio were optimised such that the samples were injected without the need for sample preparation/ dilution. Hydrogen was used as the carrier gas for both the first and second dimension separations. The first dimension was operated at 0.2 mL/min (ramped pressure), while the second dimension was operated at 25 mL/min (constant flow). Both the first and second dimension columns were exposed to the same oven program: 30°C (3 min) –2°C/min –200°C (5 min). A forward flow modulator was installed between the first and second dimension columns with a modulation time of 7 sec. The signal from the flame ionisation detector (FID) was collected at 100 Hz and recorded the signal obtained from the eluent exiting the second dimension column. GC Image Software (v 2.4 and 2.7) purchased from JSB Nederland was used to process the offline GCxGC data.

Parallel Reactor

The seven parallel reactor setup was applied for catalyst performance evaluations in a range of chemistries that can feed both liquids and gasses and can operate at pressures up to 100 bar and temperatures up to 700°C (Figure 2). The reactors with their heating blocks were all separately insulated and located in a heated box (typical at 150°C). Gasses were fed to the reactors through the process stream via individual mass flow controllers (for each gas and each reactor). Helium was used as an internal standard. The exits of the individual reactors were connected to knock-out pots to condense heavy products, while the gaseous outlet flows of the reactors were connected to a sample selection valve to allow for on-line analysis by using GC.

Online GCxGC

Online GCxGC was performed using similar conditions to the offline configuration stated above. Differences between the two systems was limited to the sample introduction. The injector was modified in-house to allow selective injection onto the front and back inlets of the GC from the selected parallel reactor using fixed loops. A heat traced transfer line was used to connect the selected reactor to the GC. The GCxGC separation focusing on hydrocarbons C7 through C30 was performed using the back inlet, while a different column combination for Heart-cut GC-GC was installed on the front inlet for permanent gasses and hydrocarbons from C2 through C10. To accomplish this, an Agilent CP-Porabond-Q column (30 m x 0.32 mm x 5 µm) was connected to a Deans Switch (also from Agilent), which either directed flow to a second FID (hydrocarbons from C2-C10) or performed a heart-cut to an Agilent CP-Molsieve 5A column (15 m x 0.32 mm x 10 µm) connected to a thermal conductivity detector (TCD) for evaluation of the permanent gasses. Agilent OpenLab CDS, EZChrom Edition (version A.04.04),

and GC Project (v 2.4) were used for data interpretation. A schematic of the setup is given in Figure 2.

Results and Discussion
Offline GCxGC

For quantification of the hydrocarbon content from hydrocarbon streams, method development began on an offline GCxGC instrument. While both normal and reversed column sets were evaluated, it was determined that a reversed column set afforded better separation of the different hydrocarbon groupings (i.e. PIONA). The modulation time and temperature program were optimised in order to obtain the best group type separation in the second dimension. The GCxGC plot obtained from FID detection of a hydrocarbon stream analysed using the optimised offline conditions is shown in Figure 3.

To confirm that the GCxGC method provided the same accuracy and precision as the DHA, a comparison study was performed where the same hydrocarbon stream was analysed by both techniques. Five injections per day over three days were made. In order to compare data from two different instruments, total abundance normalisation was performed on the data, which eliminated detector bias. Only compounds that were fully resolved in both the GCxGC and DHA data were chosen for comparison; additionally, elution time (e.g. early, middle, and late eluting), signal intensity (e.g. low, middle, and high signal intensity), and compound class (e.g. paraffin/
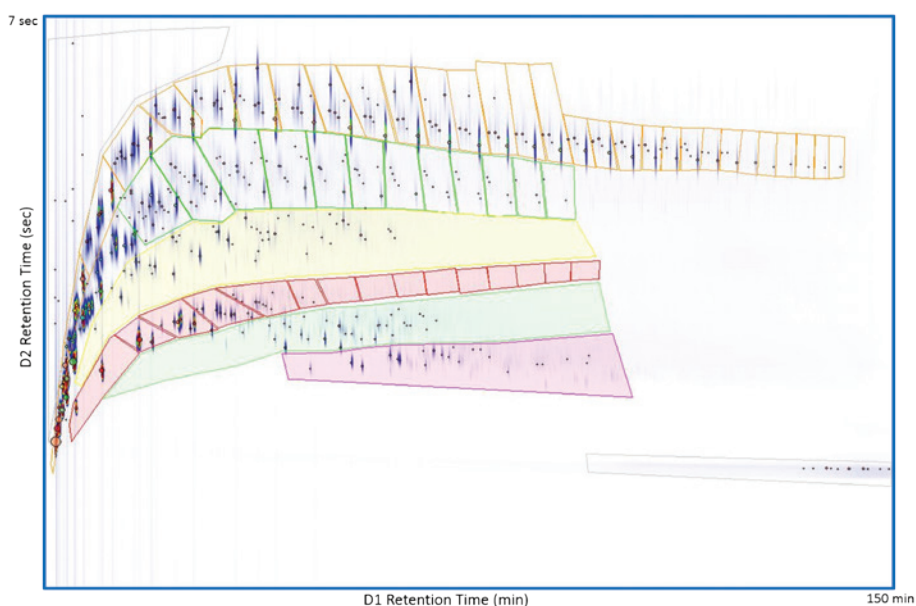

Figure 3: Offline GCxGC plot of a hydrocarbon stream using a reversed column set; full separation conditions are given in the experimental. The bands are identified from top to bottom: Paraffin + Iso-paraffin, Olefin, Naphthene, Mono-aromatic, Di-aromatic, Tri-aromatic. The two grey bands correspond to column bleed and are excluded from integration.

Reproducibility After Total Abundance Normalization
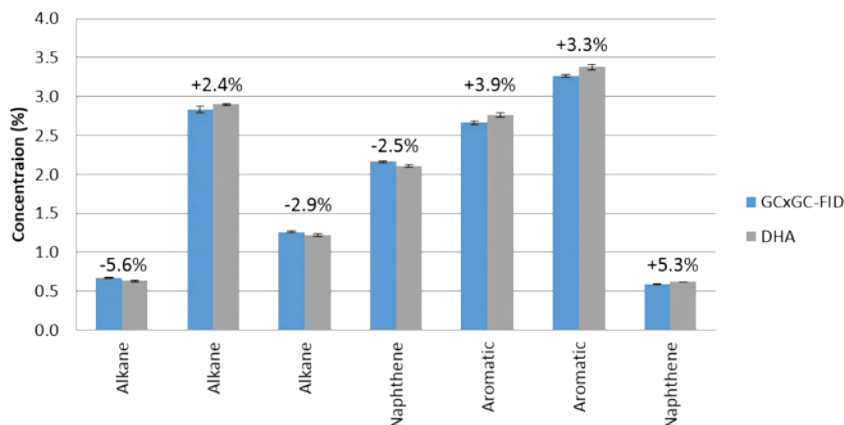

Figure 4: Bar plot of the comparison of the GCxGC and DHA results from five injections a day over three days of a hydrocarbon stream. The bar plots indicate the concentration of various compounds calculated after total abundance normalisation. The error bars indicate the spread of all injections over the three days (RSD < 3.5%), and the percentages above the bars indicate the absolute difference between the two techniques.

iso-paraffin, and aromatic) were considered. Figure 4 shows the concentration of the selected compounds calculated after total abundance normalisation. The error bars indicate the spread of all injections over the three days, which was determined to be less than 3.5% RSD. The values above the bars indicate the absolute difference between the GCxGC and DHA results; as can be seen, the absolute difference was less than 6%, indicating good agreement between the two sets of data.

Online GCxGC

In process development, evaluation and optimisation of catalyst formulations is an important undertaking. In a typical approach, catalyst descriptors (based on synthesis and characterisation data) are coupled to catalyst performance data (based on experimental testing). Testing is usually performed in fixed-bed reactors, from which the reactor effluent composition is monitored as a function of process conditions at various moments in time. Such data are crucial to monitor the conversion level of the feed, the selectivities to products and the stability of performance as a function of conditions, and time on stream. For many reactions, this becomes complicated when reaction products are diverse (isomers, different groups and types, etc.), which does not allow the application of traditional 1D GC. For specific chemistries such as syngas to olefins (typically 15-25% heavy by-products) and syngas to liquid hydrocarbons (typically > 85 liquid products

with long hydrocarbon chains), Dow has developed on-line GCxGC in order to analyse reaction products at short intervals during operation.

One of the requirements for an online system is that it is stable. In order to determine this, a reference standard is measured regularly, which must fall between the upper and lower control limits. The current system requirements have the upper and lower control limits set at a significance level of 0.03, or a confidence level of 97%. The long term reference monitoring data is shown in Figure 5, and as can be seen, the system has been operating with stability for over three years. However, it should be noted that there is a gap in reference data for much of 2015, which is explained by the fact that the previously collected reference data were overwritten when new reference

data were collected. This has been modified such that the old reference data are no longer overwritten.

The successful application of an online approach requires full automation of the analysis from the sampling to the analysis and reporting of the results. For the online application of GCxGC in catalysis laboratories in Dow, the full automation for the analysis was provided by the in-house customised commercial reactor control system, which controlled the sampling via sequentially selecting reaction streams for an individual reactor at a time and triggering analysis start as well as position tagging and time stamping of samples. The GC analysis, integration of results and reporting automation were made possible by configuring the commercial control and analysis software packages mentioned in the experimental section. The automation in further processing and storing of the results to a database system was enabled by in-house written macros.

From each reactor in the instrument setup, three sets of data were collected, one-dimensional TCD data, one-dimensional FID data, and two-dimensional FID data. The macros for data automation described above converted the three sets of data collected from each individual reactor at a given time into a bar plot (Figure 6). The colour coding of the bar plot corresponds to the different hydrocarbon groups (PIONA), and allows for a visual comparison of the data collected from all of the reactors over the study duration.

Examples of chemistries explored by Dow in this unit include syngas and CO_2 to alcohols [7], syngas to light hydrocarbons [8, 9], syngas to olefins [10], and syngas to synthetic liquids [unpublished data].
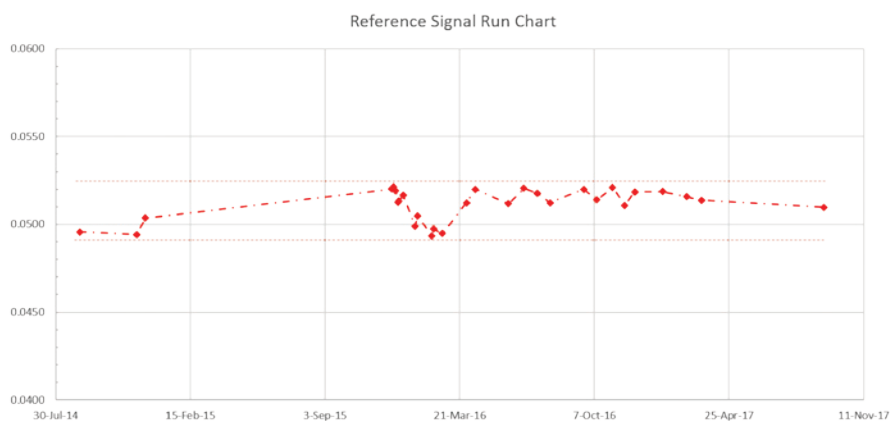

Figure 5: Run chart of the reference signal obtained from the reference standard (arbitrary units) collected from the online GCxGC system including upper and lower control limits.
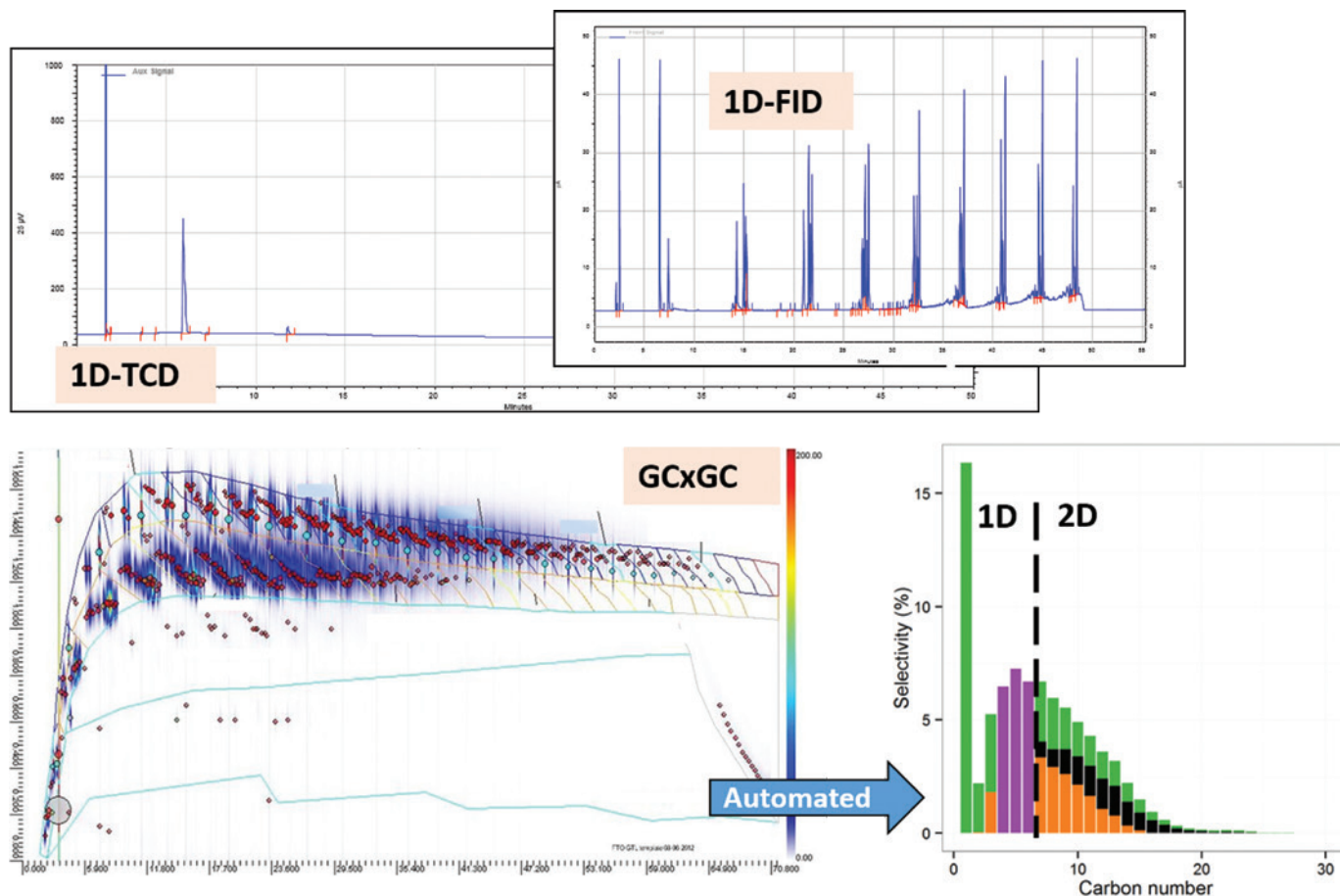
Figure 6: Overview of the data collected from one reactor of the online system, including the one-dimensional TCD plot, the one-dimensional FID plot, the GCxGC plot, and the automation step to convert the three sets of data into a colour-coded bar plot.

Conclusions

In conclusion, an example of offline GCxGC was given with the analysis of a hydrocarbon stream, which provided both group type information as well as quantification of the hydrocarbon composition. A comparison was made between the GCxGC and DHA analysis of the same sample, which showed that GCxGC has the same level of accuracy and precision as the DHA method. In addition to offline GCxGC, an example of catalysts screening using a seven parallel reactor setup coupled to online GCxGC was discussed, including the automation of the data processing.

Acknowledgements

References

1. J. Curvers, P.Van Der Sluys, J. Chromatogr. Sci., 26 (1988) 267.

2. S.T. Teng, A.D. Williams, K. Urdal, J. Sep. Sci., 17 (1994) 469.

3. J. Beens, J. Blomberg, P.J. Schoenmakers, J. High Resol. Chromatogr., 23 (2000) 182.

4. M. Adahchour, J. Beens, U.A.T. Brinkman, J. Chromatogr. A, 1186 (2008) 67.

5. J. Dalluge, R.J.J. Vreuls, J. Beens, U.A.T. Brinkman, J. Sep. Sci., 25 (2002) 201.

6. E.M. Kristenson, P. Korytar, C. Danielsson, M. Kallio, M. Brandt, J. Makela, R.J.J. Vreuls, J. Beens, U.A.T. Brinkman, J. Chromatogr. A, 1019 (2003) 65.

7. D.L.S. Nieskens, D. Ferrari, R. Kolonko, Catal. Commun., 14 (2001) 111.

8. A. Kirilin, J.F.D. Wilde, V. Santos, A. Chojecki, K. Scieranka, A. Malek, Ind. Eng. Chem. Res., 56 (2017) 13392.

9. D.L.S. Nieskens, A. Sandikci, P.E. Groenendijk, M.F. Wielemaker, A. Malek, Ind. Eng. Chem. Res., 56 (2017) 2722.

10. H.T. Galvis, J.H. Bitter, C.B. Khare, M. Ruitenbeek, A.I.C. Dugulan, K.P. De Jong, Science, 335 (2012) 6070.