Integrating Detailed Hydrocarbon Analysis Data with Simulated Distillation to Improve the Characterisation Of Crude Oils By Gas Chromatography

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Simulated distillation (SimDis) is one of the most important analyses done in petrochemical laboratories. Many refinery units are controlled based on the SimDis report. Therefore having an accurate SimDis GC (Gas Chromatography) analysis is critical for these laboratories.

The SimDis GC application utilises a non-polar column to separate analytes based on boiling point. Then special software matches the crude oil fractions in the chromatogram with boiling point information. There are multiple crude oil SimDis methods available, primarily differing based on the carbon range required.

One of the most widely used SimDis methods for crude oils is ASTM D7169. ASTM D7169 is a high temperature SimDis, for characterising crude oil up to nC_{100}. A common issues associated with this method is the interference by carbon disulfide between nC_5 and nC_6 in the chromatogram. The large carbon disulfide peak hides peaks in this range and affects the accuracy of the mass recovery of the SimDis curve below nC_6.

One approach to eliminate the effect of carbon disulfide on the SimDis curve is to use low boiling point data from DHA. DHA (Detailed Hydrocarbon Analysis) is another common petrochemical GC application. It can provide component details for the light hydrocarbons not captured with SimDis. This application report will present an improved DHA analysis to be combined with the SimDis. Significant improvements to the DHA analysis will be presented here: easy back flushing, fast set up, and a significantly faster run time. In addition to providing a variety of improvements the method presented here is also a solution to the carbon disulfide interference in the SimDis analysis. Finally a merging software will be used to combine DHA boiling point data with SimDis to replace the data up to nC_9 in the SimDis report producing a more accurate boiling point curve for crude oils.

Fast DHA Analysis

Figure 1: S-Swafer dimensions 20mm diameter x 3mm thick

The major problem faced in the chromatography of crude oil is that the bulk of the sample will be left in the column after the volatile components of interest have eluted. Prevention of the accumulation of heavy crude oil components in the chromatographic column is achieved with a combination of moderate-temperature injection, using a programmable injector (PSS) and a simple dual column backflush with an S-Swafer™. Enabling volatiles to enter the analytical column and eliminating non-volatile components through the injector split vent.

The Swafer technology is an innovative micro-channel flow switching device used to streamline the set up and operation of the back flush method methods (figure 1). In many cases the Swafer technology can be a replacement for older valve technology used in the switching or splitting of flows.

Another important change to the enhanced DHA methodology is the use of hydrogen as a carrier gas. Hydrogen gas enables higher linear velocities while maintaining chromatographic resolution. Higher linear velocities also result in significantly shorter retention times and overall time saving. This time savings can literally be half the time of what is typically expected (Example: traditional DHA run time is 160min, the fast DHA runtime is 75mins). In addition to providing fast run times hydrogen provides the additional advantages of easy bench top production and is significantly less expensive than helium.

Figure 2 shows a diagram of the S-Swafer system used in this analysis. This 2-column backflushing configuration enables the first column to be backflushed while the analytes are chromatographed on the second column. A restrictor tube is also connected to one of the S-Swafer outlets to enable the carrier gas flow rate to be increased.

The sample of crude oil is injected and chromatographed on the semi-polar precolumn. The volatile components elute into the analytical column. Once the volatile hydrocarbon compounds of interest are in the second column, the first column is backflushed to remove the residual heavier hydrocarbons from the GC system. While the backflushing is in progress, the volatile compounds are chromatographed on the high resolution
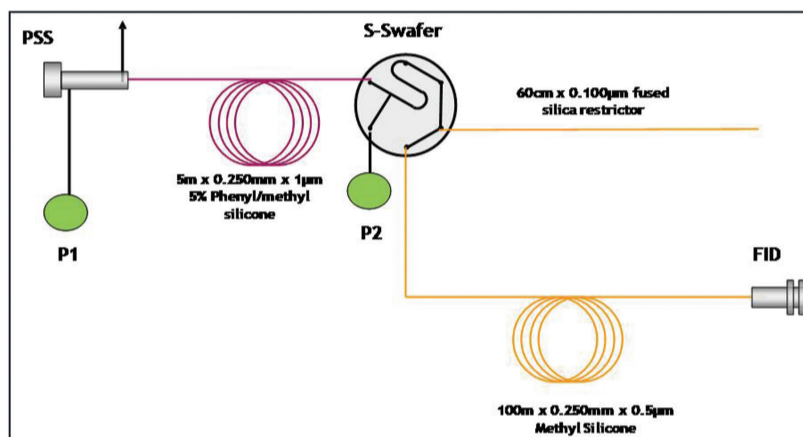

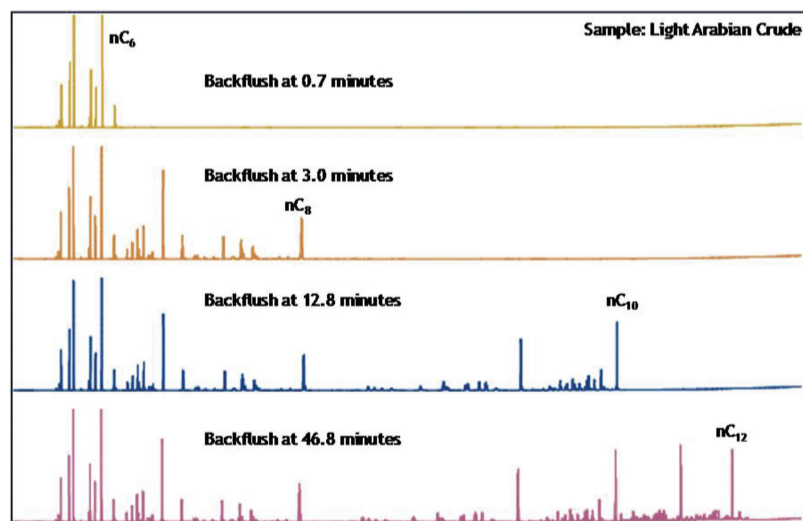*Figure 2: The S-Swafer system used for DHA of volatile components in crude oil*

Figure 3: DHA chromatograms showing the fast DHA analysis presented here and illustrating the effect of varied back flush times.

analytical column.

In order to eliminate unwanted material from entering the columns a 2-step injection procedure was followed. In the first step the PSS is set to a low temperature and the sample is injected. The second step occurs a short time later when the precolumn is backflushed and the injector is raised to a high temperature and the heavier components are vaporised and flushed out of the split vent. The precolumn backflushing prevents any of this material from entering the columns.

For this method, an injection temperature of 200°C was adopted. This gave good peak shape of the early eluting peaks and would leave the heavy crude oil components in the injector liner.
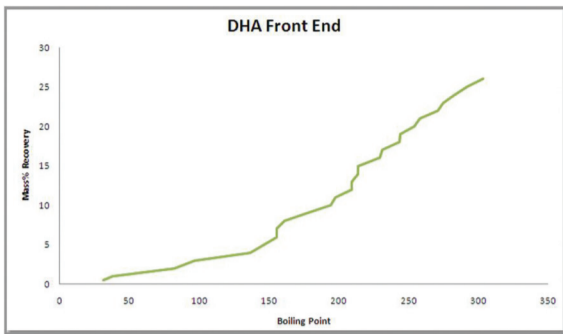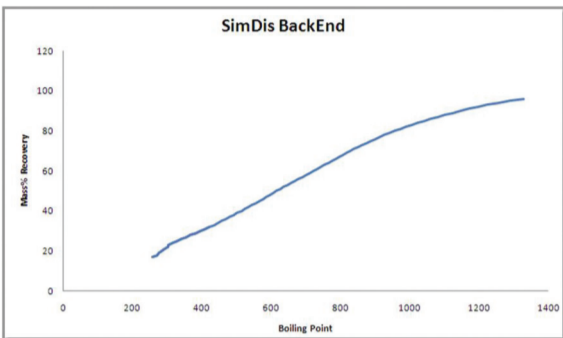
Figure 4: DHA boiling point curve from C2-C9

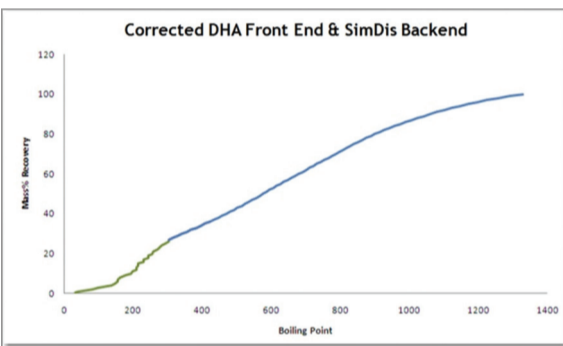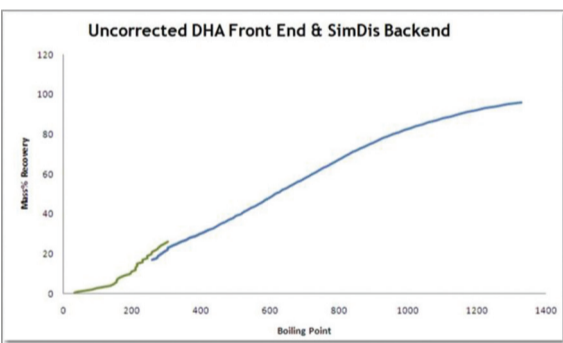*Figure 5: SimDis boiling point curve from C7-C100*

Figure 6: SimDis corrected boiling point curve from C2-C100

DHA Backflush Timing

While the reduced liner temperature will keep much of the heavy sample material out of the columns, some unwanted heavier hydrocarbons will still pass into the columns. Fortunately these are very easy to eliminate from the pre-column using a simple backflushing technique provided by the S-Swafer.

The pre-column backflushing is initiated by a timed event at the desired time that reduces the pressure inside the injector to 20.0 psig so that carrier gas flows backwards. The initial inlet pressure is set to 20.0 psig in the GC method to maintain the backflushing of the precolumn during oven cooling. A pre-run timed event sets the inlet pressure (P1) to a slightly higher pressure than the midpoint pressure (P2) so that forward flow is restored by the time the GC becomes ready to inject

the next sample.

The time at which backflushing is initiated during the run controls the volatility range of the hydrocarbons that are determined. In this particular application the back flush time is around 10mins or after the capture of the C_9 paraffins. Figure 3 demonstrates the final chromatography from the DHA analytical method described here, you can see that without any hard ware changes different hydrocarbon ranges can be easily analysed.

DHA Results

Following the analysis the data is process with the Dragon DHA software. The data is tabulated and correlated to boiling points. When plotted it creates a detailed boiling point distribution curve for the front end of the crude oil (Figure 4).

SimDis Results

Simulated Distillation (SimDis) methods designed for Crude Oil include hydrocarbons through C_{100} (or beyond) and the boiling point curve correlates the chromatographic analysis to true physical distillations. SimDis methods are generally faster, easier, and require less operator intervention than actual distillations; therefore, they are favored in more high production environments.

SimDis produces very accurate data in the C_7 - C_{100}, but the front end fraction can cause unreliable mass recoveries due to sample solvents and generally have poor resolution due to short, thin filmed columns, even with cryogenically cooled ovens. Typical results generated from a SimDis analysis are shown in figure 5.

MergeIT Results

The MergeIT calculator effectively merges the data of the DHA front end fraction and the SimDis back end fraction. The software allows many customisable features such as selectable cut-over component points, internal standards, precision calculations and reporting options.

Data from both DHA and SimDis are loaded into the merge program as comma separated value (.CSV) files and can be input from a variety of commercially available software packages.

The output of the merge replaces the mass recovery offset of the SimDis with the DHA data, and effectively gives a truer representation of the full boiling point

distribution curve from C1 to C100 (Figure 6). Output from MergeIT includes detailed spreadsheets with cutpoint data as well graphical depictions of the boiling point distribution curves (Figure 7).

Conclusion

This method uses a combination of GC techniques including the novel micro-channel Swafer technology to enable a very difficult analysis to be performed in a straightforward and rugged manner. There are many features in this application that users will find beneficial:

• Merging DHA analysis with the SimDis analysis provides more precise characterisation of crude oils, for an improved boiling point curve.

DHA System

• The unwanted heavier components of the crude oil sample matrix are eliminated by a combination of pre-column backflushing and reduced injection temperature with a PSS injector. This reduces time, prevents contamination of the columns and reduces thermal stress on the columns as now extended temperature programs are not needed.

• The range of hydrocarbons monitored by this system is easily adjusted through simple timed events to change the backflush point giving the user great flexibility over the scope of this method and reduce wasted time waiting for unwanted components to elute.

• Hydrogen is used as carrier gas to reduce analysis time and completely eliminate the consumption of expensive helium carrier gas.

• The polarity tuning of the pre-column is achieved by a simple adjustment to the pressure of the carrier gas at the inlet. This is simple to perform and is not irreversible like the traditional method of progressively shortening the length of the pre-column as in D6730.

DHA Light Ends - HTSimdis Merged Boiling Point Distribution

Samplename: PerkinElmer Test Crude Oil A

| DHA Datafile: | CrudeOil-A.csv |
| HTSD Datafile: | CrudeOil-A.csv |

| Observed Recovery: | 91.81 % | @ | 2421.9 deg F | DHA Results Normalization Factor: | 1 |
| Used Recovery: | 91.81 % | | | DHA Results CutOver At: | n-nonane 303.48001 °F |

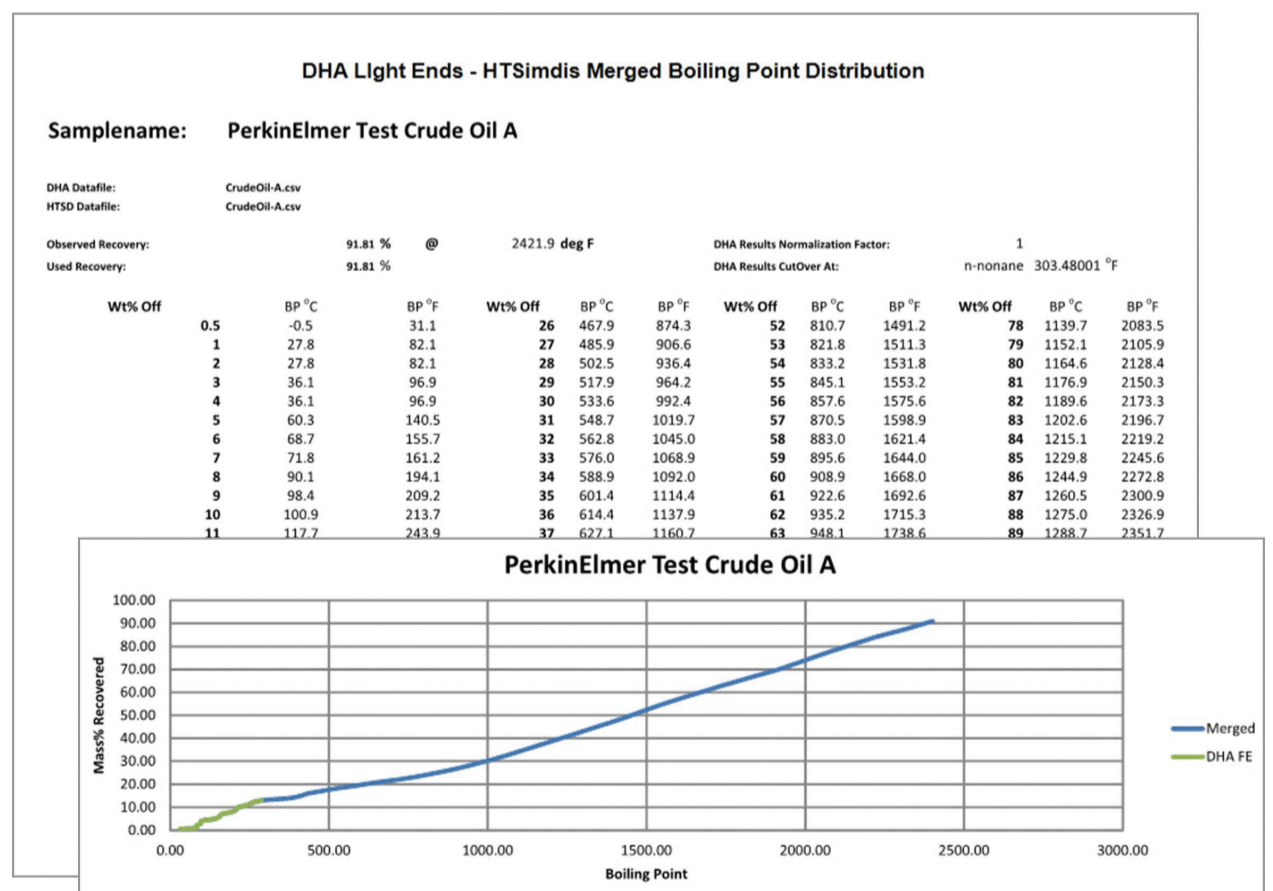| Wt% Off	BP °C	BP °F	Wt% Off	BP °C	BP °F	Wt% Off	BP °C	BP °F	Wt% Off	BP °C	BP °F
0.5	-0.5	31.1	26	467.9	874.3	52	810.7	1491.2	78	1139.7	2083.5
1	27.8	82.1	27	485.9	906.6	53	821.8	1511.3	79	1152.1	2105.9
2	27.8	82.1	28	502.5	936.4	54	833.2	1531.8	80	1164.6	2128.4
3	36.1	96.9	29	517.9	964.2	55	845.1	1553.2	81	1176.9	2150.3
4	36.1	96.9	30	533.6	992.4	56	857.6	1575.6	82	1189.6	2173.3
5	60.3	140.5	31	548.7	1019.7	57	870.5	1598.9	83	1202.6	2196.7
6	68.7	155.7	32	562.8	1045.0	58	883.0	1621.4	84	1215.1	2219.2
7	71.8	161.2	33	576.0	1068.9	59	895.6	1644.0	85	1229.8	2245.6
8	90.1	194.1	34	588.9	1092.0	60	908.9	1668.0	86	1244.9	2272.8
9	98.4	209.2	35	601.4	1114.4	61	922.6	1692.6	87	1260.5	2300.9
10	100.9	213.7	36	614.4	1137.9	62	935.2	1715.3	88	1275.0	2326.9
11	117.7	243.9	37	627.1	1160.7	63	948.1	1738.6	89	1288.7	2351.7

Figure 7: MergeIT Simulate Distillation Merging Software; Final SimDis Merged Report