ASTM D86 DISTILLATION OF LIGHT HYDROCARBON SAMPLES – CAN IT BE REPLACED BY GAS CHROMATOGRAPHY TO DELIVER AN AUTOMATED, FASTER AND SAFER ANALYSIS? –

Distillation limits are included in petroleum product specifications in all aspects of the supply chain from the refinery to product specification and regulatory compliance. ASTM D86 (1) is the basic test method of determining the boiling range of a petroleum product by performing a simple batch distillation and has been in use for as long as the petroleum industry has existed. It is one of the oldest test methods under the jurisdiction of ASTM Committee D02. However, it does have some significant drawbacks for use in modern petroleum laboratories including:

Time consuming and potentially Hazardous ASTM D86 analytical distillation involves batch evaporation and thermometer droplet mass exchange.

- ASTM D86 requires at least a 100ml sample which may not always be available and in addition many laboratories are actively trying to reduce the quantity of highly flammable samples they process, analyse and store in the laboratory.
- ASTM D86 is labour intensive requiring constant operator monitoring and control of the distillation rate throughout to comply with the method.
- It has a relatively long cycle time, a full distillation cycle according to ASTM D86 requirements takes 29 to 39 minutes, but many laboratories and processes require faster response times.
- The manual handling, transfer and physical distillation of highly flammable samples in an open laboratory poses a significant safety risk.

As a result, many laboratories and suppliers have looked at faster and safer alternative routes to obtain comparable data to ASTM D86. Simulated Distillation (SIMDIS) of Petroleum products by gas chromatography has been widely accepted by the industry, but SIMDIS is not suited for light end hydrocarbon samples such as gasoline and naphtha.

In this article we look at an approach based on novel modelling software with detailed hydrocarbon analysis by fast gas chromatography to predict D86 results of light end hydrocarbon samples including gasolines, alkylates, isomerate, reformate, FCC and naphtha.

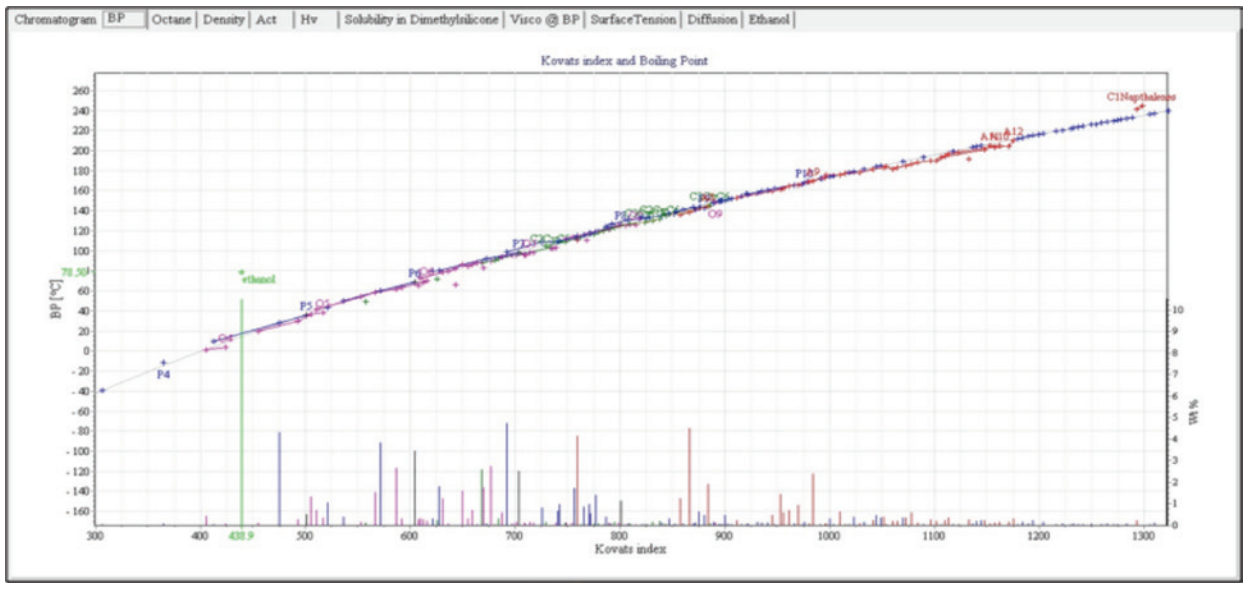
The Fugacity-Film Model for Predicting D86 Distillation of Gasolines and Napthas

The theoretical basis for the technology described in this article was first published by Walter Spieksma (2) who concluded that "D86 distillation of naphtha and gasoline can be predicted from gas chromatographic detailed hydrocarbon analysis by virtue of the fugacity-film model. The fugacity-film model is based on Fick's Law and Henry's Law. The StillPeaks DHA fugacity-film model of D86 distillation can predict experimentally determined boiling point ranges within several degrees Celsius."

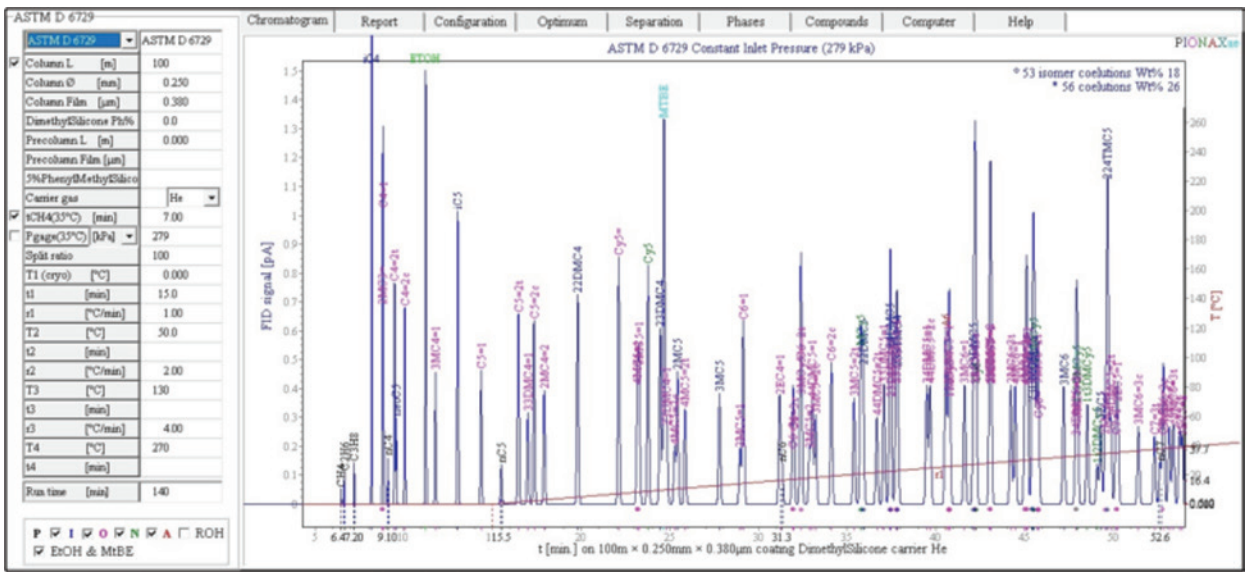
Repeatability and Reproducibility

In an inter-laboratory crosscheck five gasolines from ASTM were measured in duplicate by 10 labs using the 5.8 minute Fast GC DHA method and the results of the Stillpeaks software compared to the standard ASTM D86 method and the Repeatability of the StillPeaks DHAtoD86 calculated D86 cut points was 1°C.

The reproducibility of Stillpeaks DHAtoD86 is comparable to D86. The DHAtoD86 software contains several innovations in both the Detailed Hydrocarbon Analysis and in the D86 distillation calculation. The software solution can be applied to any temperature programmed GC method on a Phenyl-Methyl Silicone coated capillary column and with a couple of mouse



StillPeaks D86 Kovats Index plot versus Pure Liquid Boiling Point



StillPeaks Virtual GC method illustration for ASTM D 6729 of CH4 to 224TMP from Isothermal Kovats Index and Giddings PeakMove TPGC model

clicks the application can analyse runs of ASTM D6729, D6730, D6733 or the 5.8 minute Fast-DHA method. The StillPeaks DHA-report optimally connects to the D86-part of the application and automatically constructs D86 cut points for gasoline and blend feed samples. This software currently reads integration report data from Agilent's OpenLab and Scion Compass, and is potentially open for other GC platforms, avoiding any constraints with current instruments and software.

Detailed Hydrocarbon Analysis by Gas Chromatography

The advent of gas chromatography (GC) in the late 1950s and especially the subsequent development of high-resolution capillary columns and flame ionisation detectors revolutionised the detailed analysis of hydrocarbon samples. This allowed individual component resolution and quantification in samples, generating a report of retention times and area% of integrated peaks. This subsequently developed into Detailed Hydrocarbon Analysis (DHA), which converts a GC integration report (retention times and area%) into a DHA-report including retention index and weight% of the hydrocarbon compounds in the sample. The Detailed Hydrocarbon Analysis methods vary from 2.5 hours up to the fast 5.8 minute method.

As the DHA-report is the input for the fugacity-film model, the quality of the DHA-report severely impacts the D86 distillation calculation and therefore optimising the fast 5.8 minute GC-method for Detailed Hydrocarbon Analysis will improve results.

Temperature Programmed GC Kovats index data can be calculated from stable Isothermal Kovats index data based on Vapor Liquid Equilibria (VLE) and the Giddings Peak move model and Spieksma integrated this into the package to model the GC analysis (Virtual GC) in the StillPeaks DHA-software.

Virtual GC in Detailed Hydrocarbon Analysis

This Virtual GC module calculates the n-Paraffin times and generates a list of Temperature Programmed GC (TPGC) Kovats indices for peak identification. Virtual GC is a unique computed model of a dimethylsilicone coated capillary gas chromatographic column using typical GC-configuration input settings and a Kovats Isothermal index Database (KID). The configuration settings in Virtual GC should match the actual GC configuration for optimal DHA-results and the subsequent D86 distillation report.

StillPeaks DHA

The DHA software also contains pattern recognition, toluene deconvolution, a switch between constant inlet pressure and outlet flow and the flexibility to run samples using any predefined or custom temperature programmed GC method which employs Phenyl-Methyl Silicone wall coated capillary columns (containing up to 75% phenyl groups in the phase).

StillPeaks Detailed Hydrocarbon Analysis in combination with Virtual GC modelling employs a unique 3-step peak identification process:

- Peaks bigger than 2% are identified first,
- Pattern recognition with deconvolution of co-eluting peaks is then performed,
- Remaining peaks are identified by comparing the measured and calculated Temperature Programmed Kovats index data

As the temperature programmed GC Kovats index data is being calculated, the application also calculates the n-Alkanes based on the modelled temperature program, bleed and methane time which allows peak identification in samples when measured n-Alkanes are not present.

StillPeaks D86 calculation

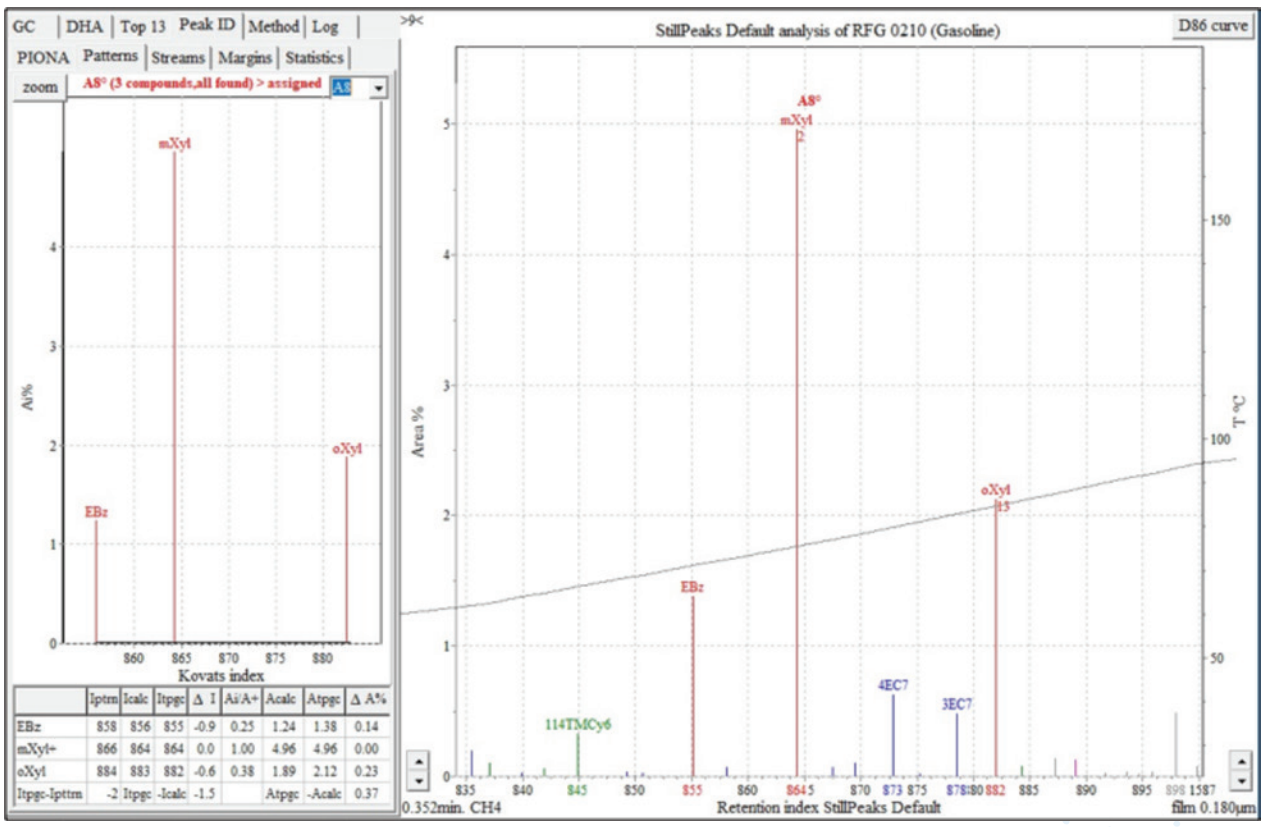
The D86-part of the software features Automatic Sample Type Assignment (ASTA) which identifies the sample type and assigns the correct settings for D86 cut points calculation based on the composition of the sample. Up to 15 Sample Types can be managed including common products such as Alkylate, Isomerate, Reformate, Light-, Medium-, Heavy Naphtha, Light-, Medium-, Heavy FCC, RBOB, Summer Gasoline and Winter Gasoline. In addition, up to 3 custom options can be manually entered such that the D86 settings of your 'typically' expected cut points can be predefined.

In addition, StillPeaks has added the variables 'Sample Temperature' and 'Heater Temperature' to model the physical ASTM standard D86 method in even more detail and also the options to vary barometric pressure, which impacts boiling points in general, and the possibility to adjust the thermometer Eo number as droplet size shifts the dewpoint curve.

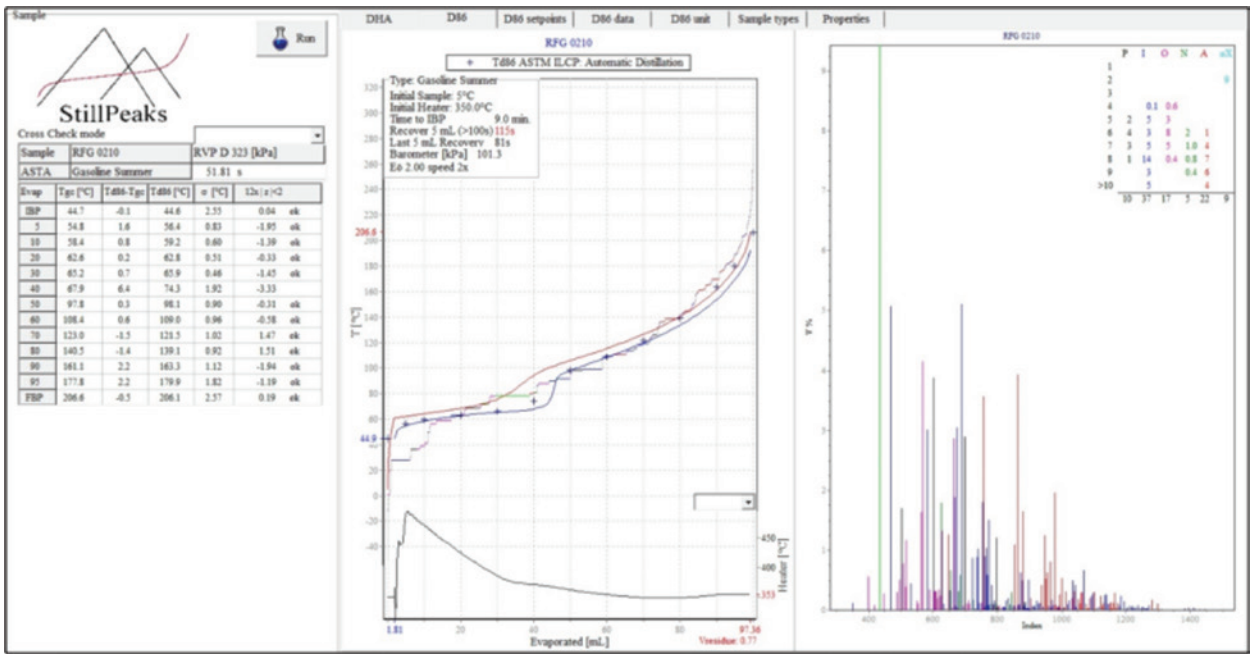
As a result, monitoring D86 result accuracy is easier than ever through one-to-one monitoring when D86 cut points are available or with the option to set 'Typical Offsets per Sample-Type' for one-to-many monitoring. It also includes the option to monitor against inter-laboratory crosscheck data with delta and z-scores presented.

DHA GC Method Development, Validation and Additional Capabilities by Virtual GC

The StillPeaks Virtual GC software also makes it a lot easier to compare the performance of any temperature programmed GC method thereby simplifying method development and validation of in-house methods. For example, comparing the 5.8 minute Fast DHA method with the 3 hour ASTM D6730 (3) with better separation, results in only a marginally better calculated D86 cut points. For most of Gasoline analysis the 5.8 minute Fast DHA method provides sufficient input for the calculation of acceptable D86 cut points. The software also has the capability to confirm that Isomerate and Alkylate blend feeds have no non-isomer co-elutions even on the 5.8 minute Fast-DHA method



StillPeaks DHA Peak Identification: Pattern recognition example for identifying C8-aromatics



StillPeaks Distillation Curve and Cut Points calculated from Fast GC Detailed Hydrocarbon Analysis of Gasoline with Ethanol

Summary and Conclusions

The combination of the 5.8 minute Fast-GC method and StillPeaks Detailed Hydrocarbon Analysis with the StillPeaks D86 application has shown to reliably predict D86 cut points of gasolines and light hydrocarbon blend feeds.

This approach significantly overcomes many of the drawbacks of the conventional D86 distillation method. Sample volumes can be dramatically reduced from hundreds of millilitres to tens of microlitres resulting in significant safety improvements and risk reduction from the handling, processing and storage of highly volatile samples in the laboratory. This also means the method is applicable to situations where sample volumes are limited such as in high throughput catalyst screening. The fast DHA method reduces sample analysis time by circa a factor of 5 resulting in faster result turnaround and higher throughput. In addition the analysis can be automated and run in batches, removing the need for constant operator monitoring and control and allowing analyses to be run unattended in the silent hours.

The StillPeaks DHAtoD86 application employs a combination of unique modelling techniques and established theory to construct D86 distillation cut points and physical properties of gasoline and blend feed samples. The applications can be employed with any GC is fully supported, quick to download and easy to install.

Future Developments

The unique approach of modelling GC performance combined with theoretical correlations to physical and performance characteristics could have many other future applications for a range of sample types and these are currently under development. The father of the DHAtoD86 application, Walter Spieksma, admits to being interested in all kinds of more environmentally friendly fuels and gasoline types based on the Fischer-Tropsch and other similar processes. If you would like to discuss possible future applications of this type of approach please contact StillPeaks directly by email (info@StillPeaks.com) or via their website StillPeaks.com (https://stillpeaks.com)

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