AC Analytical Controls' Productivity Center combines full ASTM D86 alternative in a single GC

- Unique AC8612 model allows highly accurate analysis for gasoline and naphtha
- AC8634 listed as alternative method in various jet-fuel and diesel specifications
- High workload and fast turnaround time: 4-5 samples per hour
- Unattended use, high level of automation and lower cost per analysis
- Better health & safety

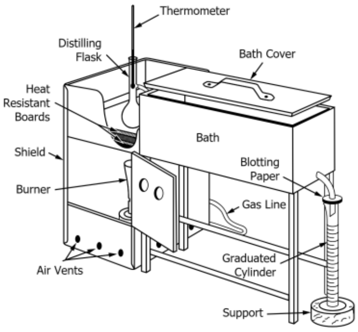
Keywords: Distillation, D86 & ISO 3405 alternative, Gasoline, Jet Fuel, and Diesel

Introduction:

Distillation is a method that separates a liquid mixture by boiling and subsequent condensation of the gas phase. Evidence of the use of distillation has been traced as far back as 800 BC in Asia. Today, it is the most widely used processing method in the hydrocarbon processing industry. In fact, it is one of the first processes that crude oil is subjected to, as it is being distilled in the atmospheric distillation unit. Even if it is not a main goal of the specific processing step in question, it is still frequently used as a post-treatment step of the process. If distillation is employed as an analytical technology, it describes the volatility properties of a material.

Distillation can be used as a quality-control tool for end products. For example, with gasoline, volatility requirements are imposed to ensure vehicle drivability in both hot and cold conditions. Distillation is then used to categorize the volatility class of the fuel. If there is too little light material present in the sample, the engine may not start at low temperatures. However, if there is too much light material in the gasoline, vapor lock may occur where the flow of gasoline in the fuel lines is obstructed by the formation of gas bubbles. Needless to say, refiners use distillation as an analytical technology in various streams in their refinery with the goal to monitor and optimize production processes. As such, various lab and process applications exist for distillation technology.

Methods



A frequently used distillation method in the HPI laboratories is physical distillation, per the methods:

ASTM D86: *"Standard Test Method for Distillation of Petroleum Products and Liquid Fuels at Atmospheric Pressure",*

ISO 3405: *"Petroleum and related products from natural or synthetic sources — Determination of distillation characteristics at atmospheric pressure".*

These test methods cover the atmospheric distillation to determine quantitatively the boiling range characteristics of products like gasoline, gasoline feedstocks, aviation fuels diesel (including biodiesel blends), and naphtha's, etc. The method was introduced in 1927, has been revised numerous times since then, and is still used as the referee method in various fuel specification methods.

Over the last decades, various alternative distillation methods have been developed, such as simulated distillation (also called SIMDIS or SimDist). The huge product portfolio of AC Analytical Controls includes numerous solutions to determine the boiling point distribution for the same sample scope of samples as described by ASTM D86 & ISO 3405. For more than 20 years, AC has offered two ASTM D86 / ISO 3405 alternatives, which have been recently combined in one system, called the Productivity Center. This analyzer is reporting D86 data based on two different principles, depending on the product group type as defined in the D86 method:

Table 1: ASTM D86 group type definitions

TABLE 1 Group Characteristics

	Group 1	Group 2	Group 3	Group 4
Sample characteristics				
Distillate type				
Vapor pressure at				
37.8°C, kPa	≥65.5	<65.5	<65.5	<65.5
100°F, psi	≥9.5	<9.5	<9.5	<9.5
(*Test* Methods D323, D4953, D5190, D5191, D5842, IP69 or IP394)				
Distillation, IBP °C			≤100	>100
°F			≤212	>212
EP °C	≤250	≤250	>250	>250
°F	≤482	≤482	>482	>482

Group 1 & 2: This application is called the AC8612. It calculates the boiling distribution of a product based on a DHA analysis and a Fugacity Film model. This model uses the sample composition, individual component characteristics, and various thermodynamic processes (and related formulas) to describe the evaporation and condensation processes as they take place in a traditional physical distillation process as described in the ASTM D86. The application considers the various requirements of this method, like time to IBP, start temperature, distillation rate, etc. Further details of the calculation are described in Appendix 1.

The result is like what D86 reports: IBP, distillation points (evaporated and recovered), FPB, loss, residue, recovery, etc.

The AC8612 application is not compliant to any standardization method. It can, however, be used for intermediate streams like a straight run naphtha, reformate, reformer feed, FCC naphtha, etc. However, regular motor gasolines and reformulated finished gasolines can be analyzed as well and fit perfectly in the model.

Group 3 & 4: This application is called the AC8634. It correlates mid-distillate Simdis results (mass percent off) to D86 boiling point distribution (volume percent off), based on mathematical equations. For details of the correlation, see Appendix 2. The correlation is described in both ASTM D2887 and ISO 3924, and currently valid for B7 samples, as well.

There are various fuel specification methods allowing reporting of correlated Simdis data, for which the AC8634 is a great tool:

Region	Product	Specification	Referee method	Alternative	AC8634
EU (ISO / EN)	Jet fuel	DEF STAN 91 091	D86	D2887 (D86 correlated)	√
EU (ISO / EN)	Diesel	EN 590	EN ISO 3405	EN ISO 3924 (D86 correlated)	√
US (ASTM)	Jet fuel	D1655 D7566 (synthetic)	D86	D2887 (D86 correlated)	√
US (ASTM)	Diesel	D975 D7467 (B6 – B20)	D86	EN ISO 3924 (D86 correlated)	√
US (ASTM)	Fuel oils	D396	D86	D2887 (D86 correlated)	√
US (ASTM)	Kerosene	D3699	D86	D2887 (D86 correlated)	√

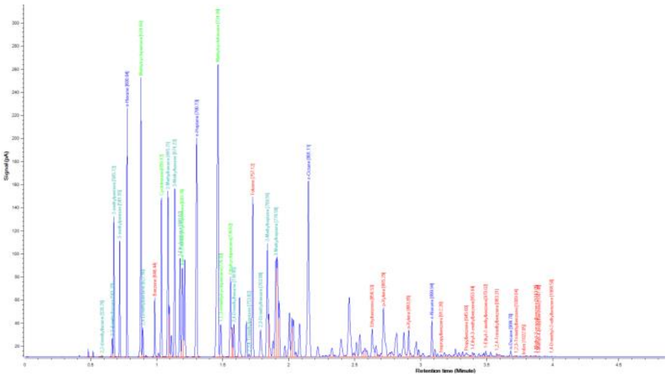
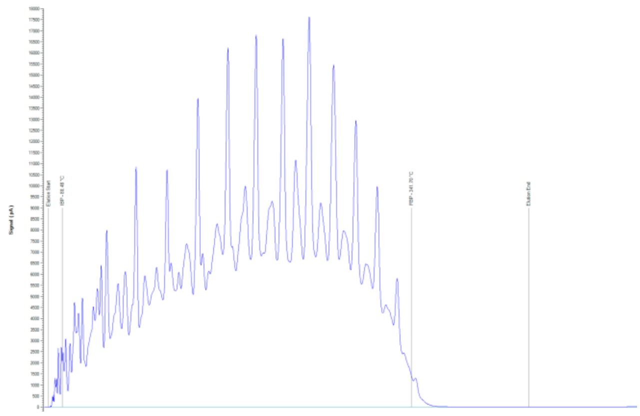
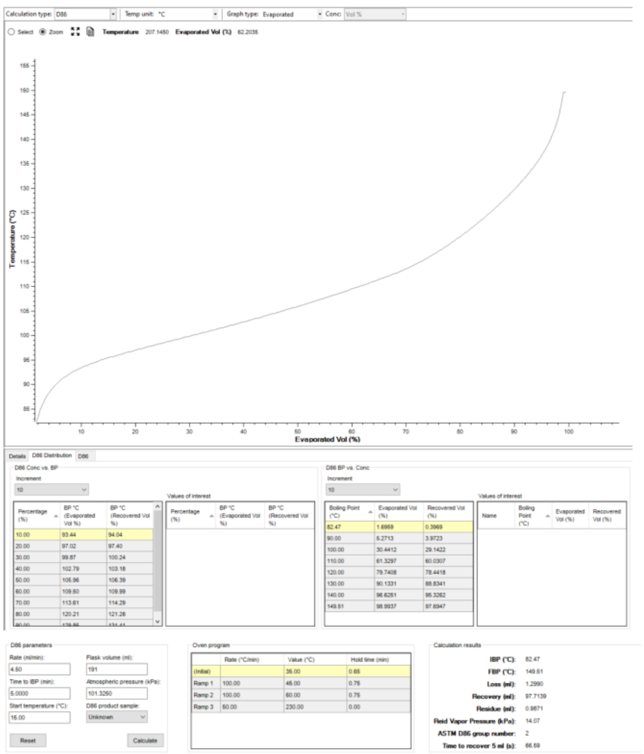
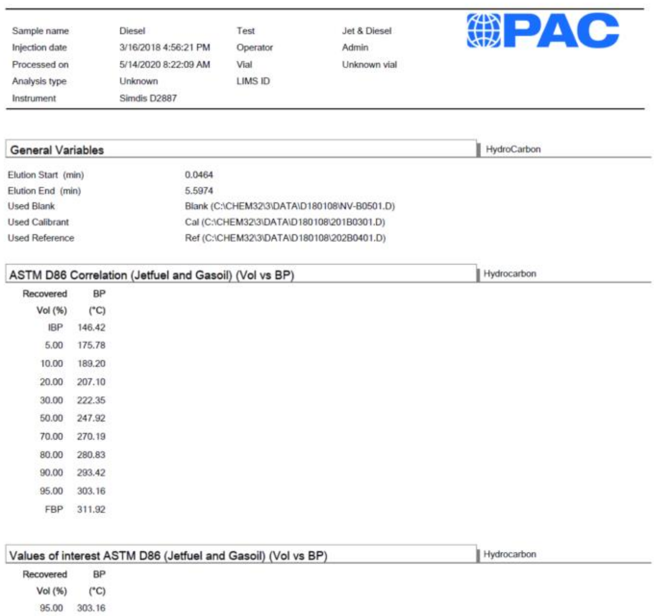
Hardware configuration

Historically these applications have been sold as separated systems. AC Analytical Controls has taken the introduction of the Agilent 8890 as an opportunity to combine both applications in one dual-channel analyzer, known as the Productivity Center.

With the new design that features both applications in one analyzer, a laboratory has the option to run both methods (in random order) in one sequence. This translates into increased lab capacity for distillation analysis by a factor of two or three. With the Productivity Center, it is possible to run at least 4-5 samples per hour, while a classic D86 analysis takes about half an hour. Another huge advantage is that the system runs the sequence of samples without user intervention (one cannot operate of both applications simultaneously, since the oven temperature program used is optimized for the applications and thus different).

The AC8634 is configured with the AC temperature programmable inlet (TPI), an inlet specially designed by AC Analytical Controls for Simdis analysis. It has proven industry-leading performance, confirmed by AC's performance monitoring program, where repeatability and reproducibility results at all levels outperform the method's accuracy. This translates into tighter control options.

With the Productivity Center setup for dual-channel application (AC8612 & AC8634 in one system), the AC8634 scope is limited to the scope of the ASTM D86 group 3 & 4 type of products (thus not the D2887 scope). Heavier samples (FBP >C36) cannot be analyzed due restrictions that oven temperature program may not exceed the MAOT (Maximum Allowable Oven Temperature) of the AC8612 column.

Channel 1: AC8612	**Channel 2: AC8634**
Autosampler	Autosampler
Split injection	TPI (direct injection)
	
Flame Ionization Detector (FID)	Flame Ionization Detector (FID)
	

Sample name	Diesel	Test	Jet & Diesel
Injection date	3/16/2018 4:56:21 PM	Operator	Admin
Processed on	5/14/2020 8:22:09 AM	Vial	Unknown vial
Analysis type	Unknown	LIMS ID	
Instrument	Simdis D2887		

General Variables — HydroCarbon

Elution Start (min)	0.0464
Elution End (min)	5.5974
Used Blank	Blank (C:\CHEM32\3\DATA\D180108\NV-B0501.D)
Used Calibrant	Cal (C:\CHEM32\3\DATA\D180108\201B0301.D)
Used Reference	Ref (C:\CHEM32\3\DATA\D180108\202B0401.D)

ASTM D86 Correlation (Jetfuel and Gasoil) (Vol vs BP) — Hydrocarbon

Recovered Vol (%)	BP (°C)
IBP	146.42
5.00	175.78
10.00	189.20
20.00	207.10
30.00	222.35
50.00	247.92
70.00	270.19
80.00	280.83
90.00	293.42
95.00	303.16
FBP	311.92

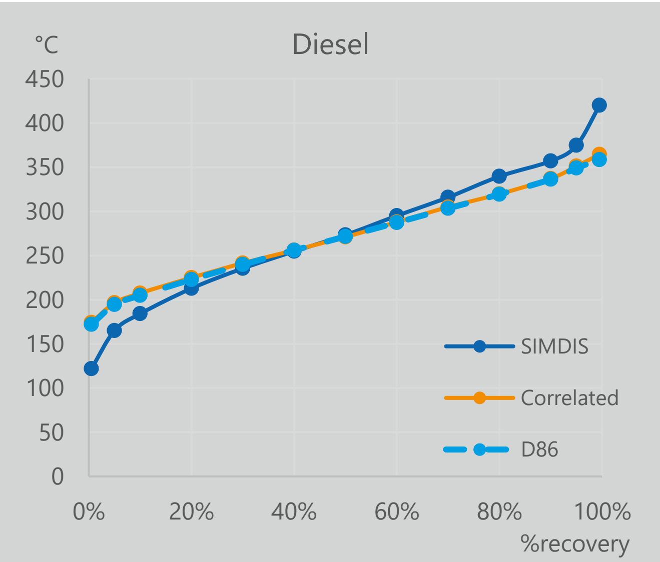
Values of interest ASTM D86 (Jetfuel and Gasoil) (Vol vs BP) — Hydrocarbon

Recovered Vol (%)	BP (°C)
95.00	303.16

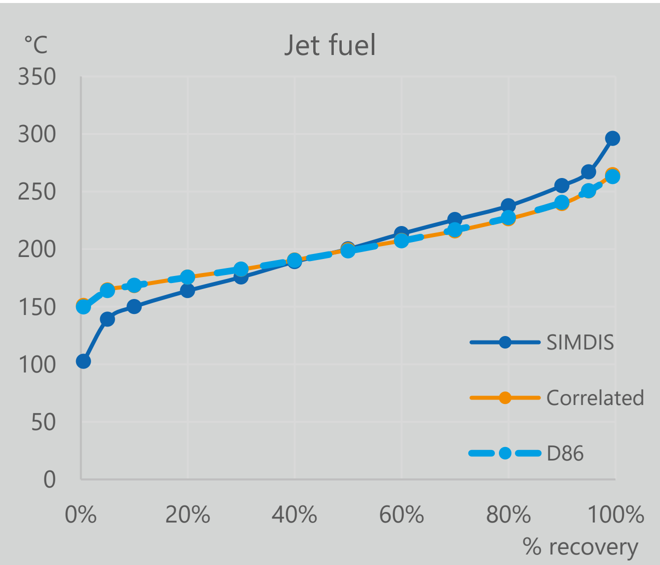
The PAC IRIS-based Simdis^{xlnc} & DHA^{xlnc} software includes the AC8612 calculations and AC8634 correlations and can be installed in a standalone as well as a client server environment. After starting the analysis in the chromatography data system, results are calculated automatically and automatic data transfer into LIMS is an option as well.

Results

Historical data from PTP programs show an excellent correlation of Simdis to D86 or ISO 3405. Below graphs and table shows some results.

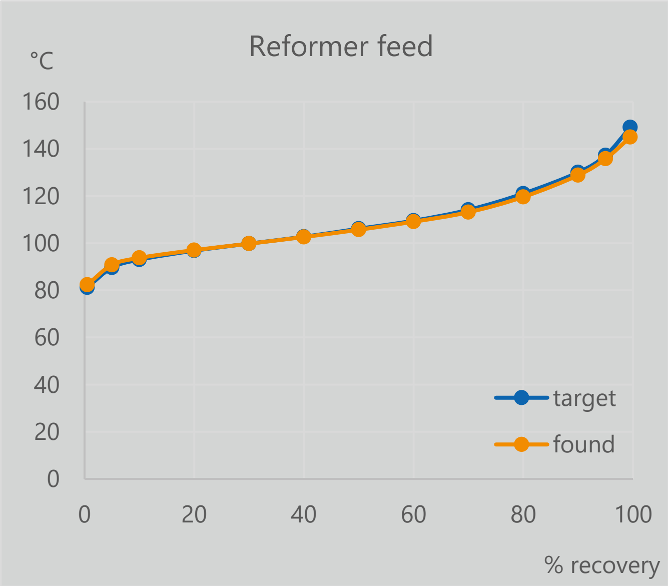


% evaporated	SIMDIS	Correlated	D86	delta
0.5%	115.35	169.10	164.70	-4.40
5.0%	159.99	187.10	184.30	-2.80
10.0%	173.85	195.40	191.80	-3.60
20.0%	196.52	209.50	205.80	-3.70
30.0%	216.91	224.40	220.60	-3.80
40.0%	236.52	239.20	237.10	-2.10
50.0%	256.12	255.40	254.70	-0.70
60.0%	287.72	273.80	273.10	-0.70
70.0%	303.05	293.40	292.80	-0.60
80.0%	331.42	312.90	313.40	0.50
90.0%	356.71	334.00	333.70	-0.30
95.0%	371.73	348.20	347.60	-0.60
99.5%	416.18	360.70	357.40	-3.30

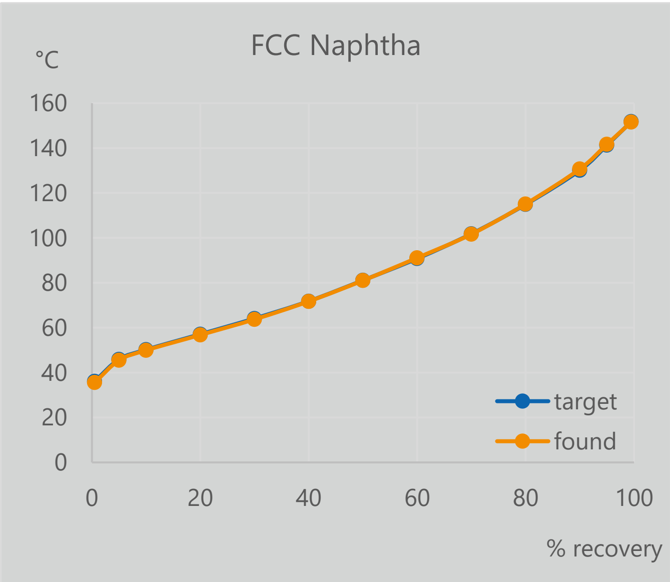


% evaporated	SIMDIS	Correlated	D86	delta
0.5%	102.40	151.0	149.7	-1.3
5.0%	138.99	164.4	163.9	-0.5
10.0%	150.02	168.1	168.4	0.3
20.0%	163.80	175.6	175.5	-0.1
30.0%	175.65	182.3	182.5	0.2
40.0%	188.98	190.4	190.1	-0.3
50.0%	200.11	199.3	198.3	-1.0
60.0%	213.4	207.3	207.1	-0.2
70.0%	225.54	215.7	216.7	1.0
80.0%	237.55	226.2	227.2	1.0
90.0%	255.04	239.4	240.4	1.0
95.0%	266.99	250.5	250.6	0.1
99.5%	295.99	264.5	262.8	-1.7

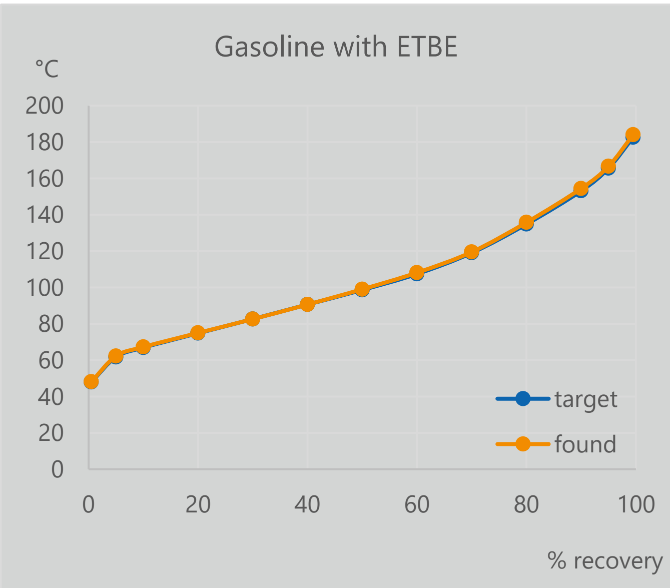
For the AC8612 a comparison check has been performed on some of the AC Reference samples. See tables and graphs below.



% evaporated	Temperature reading		Tolerance	deviation
	Target	Found		
0.5	81.2	82.33	4.3	1.13
5	89.6	90.78	2.1	1.18
10	93.0	93.74	2.3	0.74
20	96.8	97.02	2.0	0.22
30	99.8	99.77	2.0	-0.03
40	102.7	102.60	2.0	-0.10
50	106.1	105.68	2.2	-0.42
60	109.5	109.09	2.4	-0.41
70	114.1	113.13	2.6	-0.97
80	121.0	119.59	2.5	-1.41
90	130.0	128.80	2.2	-1.20
95	137.2	135.77	3.0	-1.43
99.5	149.1	144.94	5.3	-4.16



% evaporated	Temperature reading		Tolerance	deviation
	Target	Found		
0.5	36.1	35.59	3.6	-0.51
5	45.9	45.52	3.7	-0.38
10	50.2	49.97	2.8	-0.23
20	57.1	56.80	2.5	-0.30
30	64.1	63.74	2.2	-0.36
40	71.8	71.73	2.3	-0.07
50	81.1	81.03	2.4	-0.07
60	90.8	91.11	2.5	0.31
70	101.8	101.66	2.7	-0.14
80	114.9	115.09	2.5	0.19
90	130.1	130.68	2.2	0.58
95	141.3	141.67	4.2	0.37
99.5	151.8	151.60	4.5	-0.20



% evaporated	Temperature reading		Tolerance	deviation
	Target	Found		
0.5	47.9	48.11	4.3	0.21
5	61.7	62.20	4.3	0.50
10	66.9	67.23	3.9	0.33
20	74.8	74.98	3.8	0.18
30	82.6	82.57	4.3	-0.03
40	90.6	90.60	4.3	0.00
50	98.6	98.99	3.6	0.39
60	107.4	108.12	3.4	0.72
70	119.0	119.47	3.8	0.47
80	134.8	135.75	3.5	0.95
90	153.1	154.41	3.2	1.31
95	165.6	166.63	4.6	1.03
99.5	182.6	183.97	5.3	1.37

Conclusion

The AC Productivity Center is a great alternative for classic D86 analysis. It is a huge cost saver for modern laboratories who are tasked with delivering D86 distillation results in shortest possible time with the best possible accuracy:

- Unique AC8612 model allows highly accurate analysis for gasoline and naphtha
- AC8634 listed as alternative method in various jet-fuel and diesel specifications
- High workload and fast turnaround time: 4-5 samples per hour
- Unattended use, high level of automation and lower cost per analysis
- Better health & safety

Part number: AN-2020-C-001

Appendix 1: AC8612

Calculation of the boiling distribution for ASTM D86 group 0, 1 & 2 type of products, like gasoline, gasoline feedstocks, etc. This calculation is based on applying the Fugacity Film model of ASTM D86 distillation to results of an DHA analysis.

GC analysis → DHA identification & quantification → Fugacity Filmmodel calculation → D86 results for group 1 & 2 type of products

The heart of a D86 analyzer is the distillation flask (Figure 1). The boiling sample in the flask is in a turbulent state: the rising bubbles stir the liquid very well. Stirring is so rapid, that the concentration of one component is uniform in the bulk of either the liquid (L) phase or vapor (G) (horizontal red lines in Figure 2). Stirring is less rapid at the interphase between gas and liquid, due to surface tension. In a stagnant liquid film, a gradient is present (tilted red line in Figure 2) due to slow diffusion. The velocity of a molecule (*i*) through the liquid surface film depends on the pace of random walk diffusion (D_i^L) and film thickness δ.

Figure 1: D86 Distillation flask

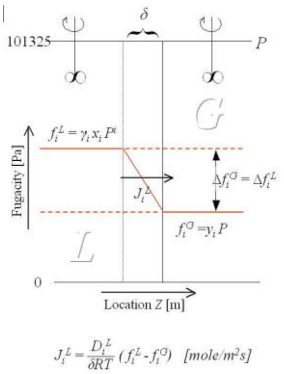


Figure 2: Fugacity-Film model of Evaporation

Fugacity stems from Latin *fugere*: fleeing or escaping. Fugacity is the tendency to escape from a phase compartment. Fugacity is the partial pressure of a component in a system under normal pressure. At equilibrium, liquid and vapor are equal ($f_i^L = f_i^G$) for all components in the system. Then, all fluxes in the system equal zero ($J_i^L = 0$). The driving force of evaporation is to achieve the equilibrium state (dotted red lines in Figure 2). Then, are equal at all points in the system. Evaporation takes place, if partial pressure is lower than the equilibrium pressure, or if the liquid fugacity is higher than the equilibrium fugacity (Figure 2).

The D86 distillation apparatus is an open system, operated at atmospheric pressure. The working pressure in the Fugacity-Film model of D86 is normal pressure (101325 Pa). The sample at the initial temperature is heated to arrive at the initial boiling point (IBP) within the time to IBP. During heating, unsaturated vapors escape from the open D86 system resulting in loss [ml], which is found from evaporation through the quiescent surface of the 100 ml sample in the D86 flask. After reaching the boiling point, a condensation front creep up the flask wall (reflux). The condensating saturated vapor rises up to the thermometer tip and the condenser. The first droplets condensate at the thermometer tip (Figure 1) and the cooler entrance. The residence time of droplets running down the cooler is ignored, and it is assumed that the distillation rate setpoint (4.5 ml/minute) can be maintained from the moment the first droplet is recovered into the 100 ml receiving cylinder.

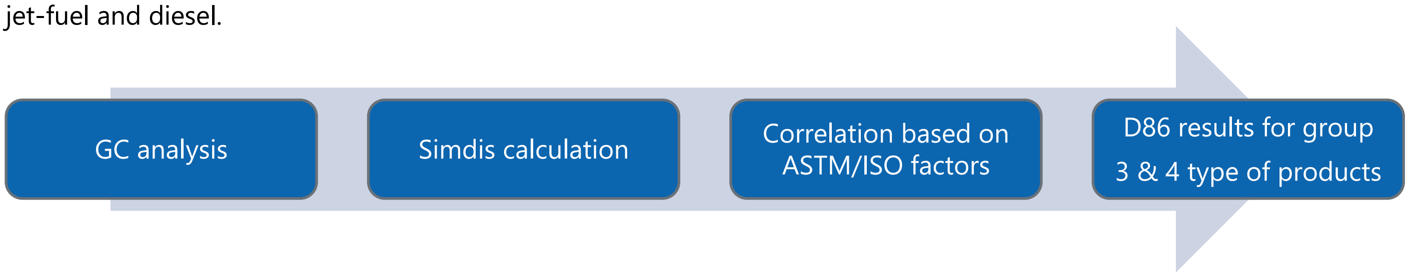
Table 3: Physical properties from DHA

Property	DHA	Unit
Molefraction (x_i)	Wt %	-
Pure liquid pressure (P^i)	Index and component	Pa
Activity coefficient (γ_i^L)	Wilson and x_i P^i	Pa

The dewpoints (DP) at the thermometer tip, the batch boiling point (BP), and the evaporated volume (Evaporated %) are plotted in Figure 3. At the final boiling point, the dry flask contains remaining vapor. The standardized D86 flask volume is 191±9 ml below the cooler entrance (Figure 1). The liquid residue [ml] is calculated with the ideal gas law, using the vapor composition, system pressure and temperature. The Fugacity-Film model of ASTM method D86 uses detailed hydrocarbon analysis input (Table 3).

Appendix 2: AC8634

Correlating mid-distillate SIMDIS data to D86/ISO3405, the scope covers ASTM D86 group 3 & 4 type of products, like jet-fuel and diesel.



The AC8634 application is based on the fast Simdis according to the ASTM D2887 or ISO3405 methods. These methods are based on the simulated distillation (SIMDIS) technology, whereby petroleum products are separated into boiling point fractions by the use of gas chromatography. The mass percentage of each fraction can be calculated such that a cumulative mass% boiling point distribution curve can be obtained. This is correlated with the cumulative volume % boiling point distribution of the ASTM D86 / ISO3405 application. ASTM originally created this correlation in a separate book called STP 577. The correlation was recreated by ASTM around 2004 using only jet fuels and gas oils. The correlation is based on data for 46 jet fuel samples and 39 gas oil (diesel) samples that were analyzed using the methods for ASTM D86 and ASTM D2887. This new correlation adequately predicts the D86 temperature from corresponding temperatures obtained from D2887 because spread in data used for the correlation.

For a given D86 temperature, only the closest D2887 temperatures could influence its value. The correlation for predicting D86 from D2887 data is, therefore, based on the following equation.

$$\mathbf{t_n = a_0 + a_1 T_{n-1} + a_2 T_n + a_3 T_{n+1}} \qquad (1)$$

Where:

t_n	Is the D86 temperature to be predicted for the nth cut-point.
T_n	Is the corresponding D2887 temperature
n	Corresponds to the cut point TBP, 10%, 20% etc.
T_{n-1} and T_{n+1}	Cut-point temperatures above and below T_n
a_0, a_1, a_2, a_3	Coefficients developed by the correlation

The table below shows the temperatures used to create equation (1) and the value of the constants a_i. The correlation uses temperatures in °C.

Variables used for Correlation based on D 2887-19a							
t_n °c	a_0	a_1	a_2	a_3	T_n °C		
IBP	25.35060	0.32216	0.71187	-0.04221	T_{ibp}	T_5	T_{10}
5%	18.82210	0.06602	0.15803	0.77898	T_{ibp}	T_5	T_{10}
10%	15.17260	0.20149	0.30606	0.48227	T_5	T_{10}	T_{20}
20%	12.2992	0.227681	0.291586	0.462078	T_{10}	T_{20}	T_{30}
30%	9.66687	0.365291	0.29752	0.305422	T_{20}	T_{30}	T_{50}
50%	5.41890	0.07763	0.68984	0.18302	T_{30}	T_{50}	T_{70}
70%	0.35246	0.16136	0.41511	0.37715	T_{50}	T_{70}	T_{80}
80%	-0.21536	0.25614	0.40925	0.27995	T_{70}	T_{80}	T_{90}
90%	0.09966	0.24335	0.32051	0.37357	T_{80}	T_{90}	T_{95}
95%	0.89880	-0.09790	1.03816	-0.00894	T_{90}	T_{95}	T_{fbp}
FBP	21.6311	-0.36378	1.06499	0.16901	T_{90}	T_{95}	T_{fbp}