The Advantage of Real Atmospheric Distillation Complying with the ASTM D7345 Test Method in the Distillation Process

Introduction / Background

In the past, refiners enjoyed a constant supply of the same crude with little variation. Due to this, refineries were designed for stable feed. Today's heavy competition drives refiners to operate with razor-thin margins. Therefore, they buy low-cost, heavy crude that has high variability in quality. They use crude oil feedstock that consists of a complex mixture of hydrocarbons. In order to separate a liquid feed mixture into its components, refineries use a distillation process that involves heating a liquid mixture to the point of boiling, where by the components separate through evaporation and condensation. During this process, different products boil off and are recovered at different temperatures, separating the feedstock into broad categories of its component hydrocarbons, such as kerosene, naphtha, and jet fuel.

The distillation characteristics, i.e., volatility, of hydrocarbons significantly impact the safety and performance of end-products, particularly with fuels and solvents. The boiling range gives information on the composition, the properties, and the behavior of the fuel during storage and use. Volatility is the major determinant of the tendency of a hydrocarbon mixture to produce potentially explosive vapors[1]. These characteristics are critically important for fuel products that affect starting, warm up, and tendency to vapor lock at high operating temperatures or high altitude or both. When fuels have high-boiling-point components, the degree of formation of solid combustion deposits can be significantly affected[2].

ASTM D86 is the historical test method to determine the boiling range of a petroleum product. It determines the boiling range by performing a simple batch distillation, and it has been in use as long as the petroleum industry has existed. ASTM recently published the ASTM D975-12, which includes an alternate distillation method, ASTM D7345. The process of microdistillation, as described in test method ASTM D7345, provides fast results using small sample volume, and eliminates much of the operator time and subjectivity in comparison to test method D86. This microdistillation method demonstrates temperature limitations at 400 °C, 752 ˚F (see Illustration 1).

This paper discusses the benefits of using a process application of the ASTM D7345 test method to provide real, online distillation analysis to prevent product giveaway and reprocessing, and to meet tight blending specifications at the most reasonable cost.

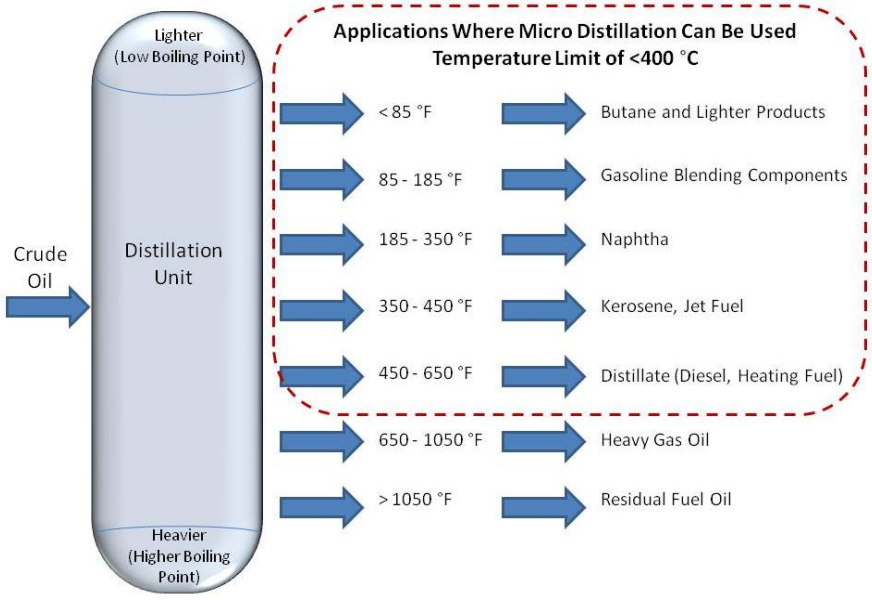

Illustration 1 - Crude Oil Distillation Unit & Products

[1] http://www.astm.org/Standards/D7345.htm, Significance and Use, paragraph 1
[2] http://www.astm.org/Standards/D7345.htm, Significance and Use, paragraph 2

Typical Challenges Faced by Refineries

Selecting the most cost-effective blend to produce gasoline and diesel products is a critical economic issue for refineries. Refineries may have up to 15 different hydrocarbon streams to use as blending stock, as well as 15 different quality specifications for each type of blend. These specifications may include vapor pressure; initial, intermediate and final boiling points; sulfur content, color, stability, aromatics content, olefin content, and octane measurements for several different portions of the blend, and other local government and market requirements.

While there are several ASTM methods that are designed to determine critical boiling point profiles for petroleum products, the ASTM D86 method is considered the referee method for certification of atmospheric distillation of light and middle distillate fuels with boiling points in the range of 20 °C to 400 °C. Other methods include ASTM D7345, ASTM D2887, and ASTM D3710. This paper focuses primarily on ASTM D7345. See Table 1 for method details.

ASTM Method	Technology/Description	Application
D3710-95 (2010)	Determination of Boiling Range Distribution of Gasoline and Gasoline Fractions by Gas Chromatography	• Gasoline and gasoline components with a final boiling point of 500 °F (260 °C) or lower.
D2887-08	Determination of Boiling Range Distribution of Petroleum Fractions by Gas Chromatography	• Petroleum products and fractions having a final boiling point of 538 °C (1000°F) or lower at atmospheric pressure. • Limited to samples having a boiling range greater than 55.5 °C (100 °F), and having a vapor pressure sufficiently low to permit sampling at ambient temperature.
D7345-08	Distillation of Petroleum Products at Atmospheric Pressure (Micro Distillation Method)	• Petroleum products with a boiling range between 20 °C to 400 °C at atmospheric pressure using an automatic micro distillation apparatus • Light and middle distillates, and engine fuels containing up to 10% ethanol, and up to 20% biodiesel blends.
D86-11b	Test Method for Distillation of Petroleum Products at Atmospheric Pressure	• Petroleum products with a boiling range between 20 to 400 °C at atmospheric pressure • Distillate fuels and ethanol fuel blends.

Table 1- Comparison of Test Methods

Comparing Test Methods: ASTM D7345 vs. ASTM D86

The ASTM D7345 test method for microdistillation is a procedure for determination of the distillation characteristics of petroleum products having boiling range between 20 °C to 400 °C at atmospheric pressure using an automatic microdistillation apparatus. It is applicable to such products as light and middle distillates, as well as engine fuels containing up to 10% ethanol and up to 20% biodiesel blends.

This paper asserts that physical distillation complying with ASTM D7345 is the most reliable principle to determine distillation of petroleum products for process applications, as well as terminals and pipelines. While staying tightly correlated to D86, D7345 performs a much faster analysis using a smaller sample. See Table 2 for specific aspects of each method.

Distillation ASTM D86	MicroDist D7345
Sample volume 100 ml	Sample volume 10 ml
Ceram plates	No ceram plates
PT 100's: 7C/7F and 8C/8F	Liquid T/C and vapor T/C
PT 100 position is critical	Detectors are fixed (quick connection)
Standard flask (non-restriction)	Flask capillary (.004 inches) (1.1 mm)
Condenser and receiver cooling – AC Compressor	Condenser air cooling – fan
Condenser cleaning after each distillation	No condenser cleaning necessary
Vapor losses	No vapor losses
Laboratory personnel expertise	Not mandatory
Sample group knowledge 1 – 4 by operator	Detects sample group automatically
Distillation is volume dependent 4 – 5 ml/min	Measure vapor and liquid temperatures, %distilled is calculated over the boiling point curve.
Speed of distillation approx 45 minutes	Speed of distillation less than 10 minutes
Boiling stones recommended	Boiling stones recommended
No pressure sensor	Pressure sensor is introduced

Table 2 - Comparison of ASTM D86 and ASTM D7345

Microdistillation is the Effective Solution

Because microdistillation determines the distillation characteristics of petroleum products with boiling points between 20 °C and 400 °C at atmospheric pressure, it is ideal for light and middle distillates, automotive spark-ignition engine fuels, automotive spark-ignition engine fuels containing up to 10% ethanol, aviation gasolines, aviation turbine fuels, regular and low-sulfur diesel fuels, biodiesel blends (up to 20% biodiesel), special petroleum spirits, naphtha, white spirits, kerosene, burner fuels, and marine fuels. Other hydrocarbons like organic solvents or oxygenated compounds that have narrow boiling ranges are also good choices for microdistillation[3].

Microdistillation determines the complete distillation curve using data from a single phase transition – evaporation. This method, which is based on thermodynamic dependencies, measures liquid and vapor variations while monitoring the pressure inside a special micro-distillation flask as the sample gradually distills under atmospheric temperature (see Illustration 2). During the distillation cycle, the measured vapor pressure characterizes the product flow rate through the hydrodynamic process in the capillary.

Microdistillation, in compliance with ASTM D7345, is characterized by its high sensitivity, repeatability, and fast results. The microdistillation process is true physical distillation, which means it is much better correlated to D86 than any simulated or modeled distillation curves. With simulation technologies, the measurements need product specific calculations based on sample matrices that are used to develop a correlation between the process measurement and lab measurement. A significant amount of data is used to generate these correlations. Since the source of crude changes often for a refinery, simulation technologies are not practical for measuring within the process due to the time needed to adjust correlations. An online micro distillation analyzer distills very small amounts of the actual product, so it doesn't rely on product specific calculations, and is the best method to detect product contamination.

[3] http://www.astm.org/Standards/D7345.htm

With fast results and small sample size, microdistillation is ideal for process control. It can also provide tight correlation between the process and refinery labs. Typically samples are sent to the lab so the quality of the product can be confirmed. Online analyzers following the D7345 Method can provide results in 10 minutes, which enables refiners to make changes to the process must faster.

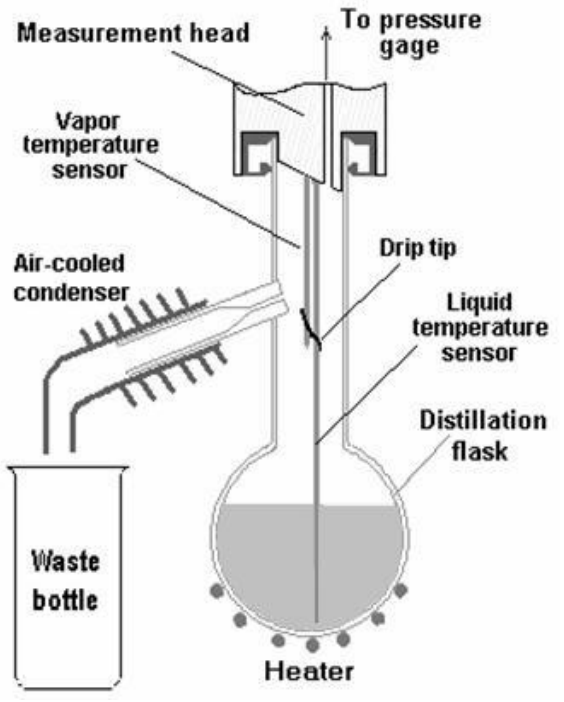

Illustration 2 – Schematic of Microdistillation flask

Microdistillation Applications and Results

Cutpoint Optimization

Cutpoints between overhead products and side-cuts can be controlled on the basis of temperature, but doing so can result in the downgrading of the more valuable product to the stream of lesser value. Since refinery optimization objectives change daily depending on the economic availability of feedstocks, quality of feedstocks, product markets and accessibility, product specifications, and seasonality impact on specifications and end-user demands, refiners need the ability to optimize cutpoint in consideration of these changing variables[4].

Microdistillation is ideal for optimizing naphtha, gasoline, diesel, and jet fuel distillation cutpoints. Refiners can maximize high-value components throughput by using real, online distillation, rather than a simulation.

Benefits of Cutpoint Optimization using Microdistillation

Refineries must manage the temperature of the distillation tower at different levels, so the products separate at the right level of the tower. The final boiling point of one product ends at the starting boiling point of the next. By monitoring the boiling point of the product, the refiner can get the maximum amount of high-value product. In case of jet fuel blending, if a lower value product like kerosene penetrates the stream, the boiling point measurements fall. The control system then adjusts the temperatures within the distillation tower to get the optimal separation.

Since the crude quality can change, refiners cannot run on temperature alone; boiling point measurements are also needed. With confidence in their measuring system and fast results (less than 10 minutes), refiners can use microdistillation data to move the temperature of the cutpoints closer to the target without waiting for laboratory measurements. Moving closer to the target helps refiners produce more of the expensive product and less of the

[4] Liptak, Bela, "Distillation Control and Optimization," *Control Engineering*, http://xa.yimg.com/kq/groups/18125250/1751783716/name/liptak_distillation_ebook.pdff, 2007

cheaper product. Increasing T90% by 1 °C may result in 0.5 to 1% additional Diesel production; depending on production capacity, this can impact up to $1 Million USD of incremental profits. In the case of chart 1, with HDT Diesel Capacity at 22,000 barrels per day (bpd), a 1 °C optimization impact increases volume by 0.7%, which is 152 bpd. Residual Fuel to ULSD upgrade is $29 USD per barrel, which increases profitability by $1.1M USD.

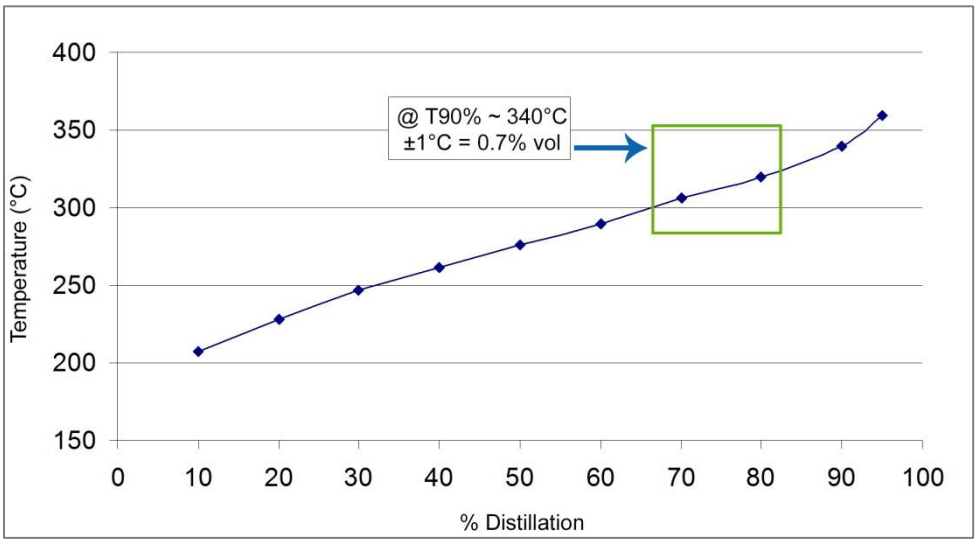

Chart 1 - Cutpoint Optimization

Cetane Index

The Cetane Index determines the ignition quality of diesel fuel. It is ideal for monitoring product quality and the operation of middle distillate hydrotreaters. The Cetane Index correlation uses a four-variable equation of 10%, 50%, and 90% recovery temperature and density. By monitoring the Cetane Index, refiners can determine how much cetane improver to add to the product.

Microdistillation, when combined with density analysis, provides a reliable Cetane Index calculation that is fully independent of blended components. It offers tight correlation to ASTM D86, D4737 and D976, and determines the density measurement of the same sample with a precision of +/- 0.2.

Benefits of Cetane Index Determination

Failure to meet a specified cetane index can lead to shipping delays, limited storage tank availability, and reduced profitability. Improving the accuracy of a refinery's cetane predictions can have a cost savings by optimizing the amount of cetane improver used in the product.

Driveability Index

Microdistillation provides reliable, repeatable data to determine optimal blending equations and increase profitability. It is widely acknowledged that refiners use less-than-ideal blending equations for ASTM distillation, which can significantly impact profitability of operations. One of the most significant variables that microdistillation can impact in the gasoline blending process is driveability index.

Driveability (or Distillation) Index (DI) is a function of distillation temperatures of gasoline and the oxygen content contributed by alcohols (e.g., ethanol). It is expressed by the formula:

DI = 1.5 x T10% + 3 x T50% + T90%

Where
T10% is the fuel's ability to vaporize and enable cold starting
T50% and T90% are the heavier components, which represent the ability to vaporize and combust once the motor is warmed up.

The American Automobile Manufacturer Association recommends DI = <1250.

Benefits of Driveability Index Determination

The T50, or DI, is constantly monitored to ensure the gasoline specifications are met. The specifications change seasonally. To meet specifications, refineries continuously adjust the recipe to increase or decrease the T50, Reid Vapor Pressure (RVP), octane, and other parameters. The components in the mix have different values, so it is a constant adjustment to meet the specifications at the minimum costs.

In the winter when it's cold, the refineries need to increase the RVP to make the gasoline more volatile so automobile engines work under colder temperatures. The cheapest component to increase RVP is butane. However, butane has a negative effect on the T50 specification. The refinery must optimize the blend in the winter to maximize the use of butane and still hit the specification. The cost differential between butane and the more expensive ingredient drives the economics. The more confidence a refinery has in the measurement, the closer they can be to the limit, and the more profitable it can be.

PAC MicroDist Online Analyzer

The PAC MicroDist is an online analyzer utilizing the microdistillation method described above. Its unique technology provides complete and accurate distillation and density analysis in a single instrument. With the density analysis, the MicroDist can calculate the Cetane Index for diesel fuel process streams and intermediate blends as well. It features a precision-equivalent or better correlation to ASTM D86 to deliver exceptional results for blended gasolines with oxygenates, diesel, and other light and mid distillate blends. It has an excellent repeatability factor of +/- 1.5 °C. A recent test in an operating refinery evaluated the MicroDist on its repeatability for the following distillation ranges: 5%, 10%, 85%, and 90%. The resulting test data shown in chart 2 displays that the MicroDist performed better than ASTM D7345 (see Appendix A for more details).

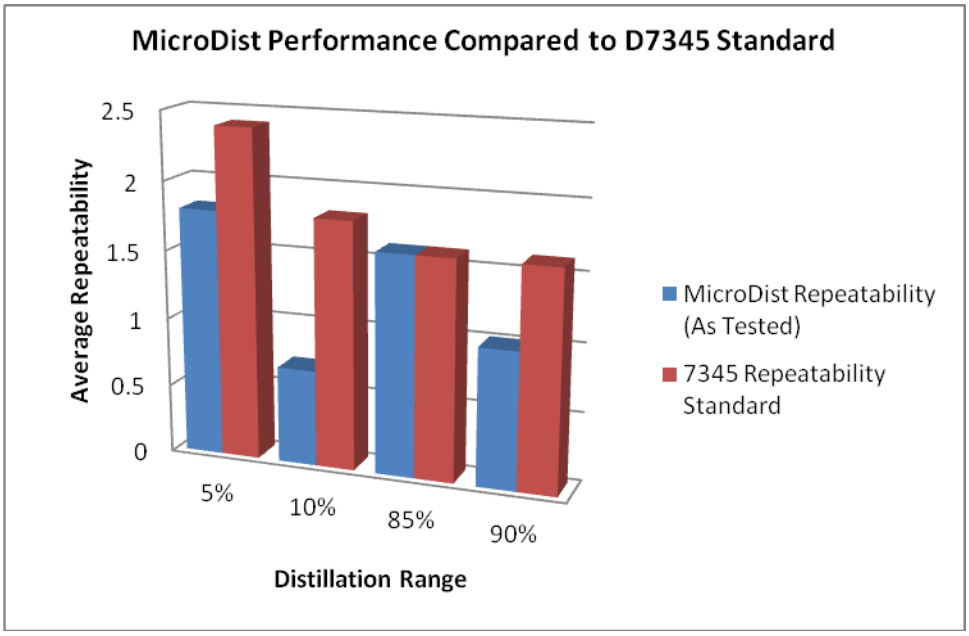

Chart 2 - MicroDist Performance Compared to D7345 Standard

The two major differentiators between the MicroDist and other online distillation analyzers is its fast response time and extremely high availability factor. It delivers reliable, repeatable results in 7-10 minutes, depending on the sample. It also features auto-flask regeneration that maximizes analyzer up-time and lowers maintenance costs. This translates into an available factor of >98%.

With a 10-minute cycle time, the MicroDist allows refiners to calculate cut points as fast as variables can change. This ensures minimal product giveaway and maximum profitability.

Results / Conclusion

ASTM recently published the ASTM D975-12, which included an alternate distillation method, ASTM D7345, “Distillation of Petroleum Products at Atmospheric Pressure (Micro Distillation Method)”. This alternate method achieves significant response time improvements and requires less sample compared to the conventional ASTM D86 method, which leads to tighter cutpoint optimization, less product giveaway, real distillation, and a very short cycle time.

The PAC MicroDist analyzer provides complete distillation and density results within 10 minutes that correlate to ASTM D86 and ASTM D7345 test methods and their analogs. It determines the boiling range characteristics of petroleum products, light distillates, and middle distillates on process streams, as well as the Cetane Index for diesel fuel process streams and intermediate blends. Since the measurements match those obtained by refinery quality control laboratories, the MicroDist is the preferred choice for refineries that are focused on optimization through precise and continuous adjustment of the process streams.

PAC-ProccessWP-0001-2013.1

Appendix A: Repeatability Test at an Operating Refinery

5%	
Repeatability Evaluation	
Result 1	162.1
Result 2	161.9
Result 3	162.9
Result 4	161.4
Result 5	162.9
Result 6	161.5
Average	162.1
Standard Deviation	0.7
Repeatability	1.8
Repeatability ASTM 7345	2.4
Repeatability Comparison	Accepted

10%	
Repeatability Evaluation	
Result 1	185.3
Result 2	185.5
Result 3	185.9
Result 4	185.8
Result 5	185.5
Result 6	185.3
Average	185.6
Standard Deviation	0.3

Repeatability	0.7
Repeatability ASTM 7345	1.8
Repeatability Comparison	Accepted

85%	
Repeatability Evaluation	
Result 1	359.4
Result 2	358.7
Result 3	359.6
Result 4	358.6
Result 5	359.7
Result 6	358.4
Average	359.1
Standard Deviation	0.6
Repeatability	1.6
Repeatability ASTM 7345	1.6
Repeatability Comparison	Accepted

90%	
Repeatability Evaluation	
Result 1	385.5
Result 2	385.7
Result 3	385.0
Result 4	384.9
Result 5	385.3

Result 6	385.7
Average	385.4
Standard Deviation	0.3
Repeatability	1.0
Repeatability ASTM 7345	1.6
Repeatability Comparison	Accepted