# Managing microdistillation

## Understanding the benefits of ASTM D7345 test method

In the past, refiners enjoyed a constant supply of the same crude with little variation. As such, refineries were designed for stable feed.

Yet today's heavy competition drives refiners to operate with razor-thin margins. As a result, they often buy low-cost, heavy crude that are made up of various hydrocarbons and vary in quality

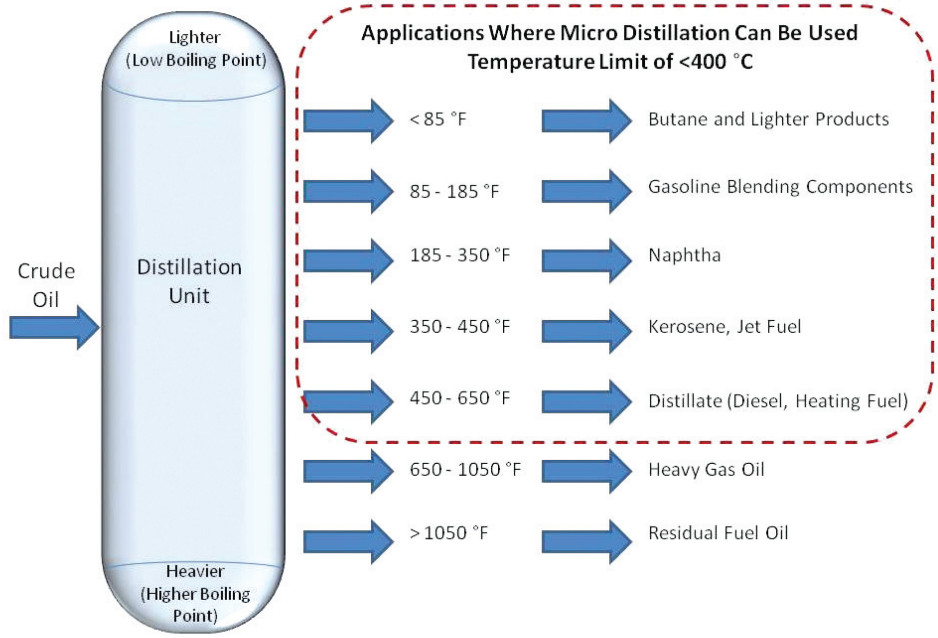
To separate a liquid feed mixture into its components, refineries use a distillation process that involves heating a liquid mixture to the point of boiling, whereby the components separate through evaporation and condensation.

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 impact the safety and performance of end products, particularly with fuels and solvents. The boiling range gives information on the composition, properties and behavior of the fuel during storage and use.

While ASTM D86 has historically been the benchmark test method to determine the boiling range of a petroleum product — through a simple batch distillation — ASTM D7345 offers an alternate distillation method.

The microdistillation process, as described in ASTM D7345, provides faster results using small sample volume, and eliminates much of the operator time and subjectivity in comparison to test method D86. This microdistillation method also can demonstrate temperature limitations up to 400 C (752 F).




**A microdistillation method demonstrates temperature limitations at 400 C (752 F). *Illustration courtesy PAC.***

### Typical challenges

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 vapour pressure; initial, intermediate and final boiling points; sulfur content, colour, stability, aromatics content, olefin content and octane measurements for several different portions of the blend; and other local government and market requirements.

### Comparing test methods

The D7345 test method for microdistillation determines the distillation characteristics of petroleum products with boiling ranges from 20 to 400 C at atmospheric pressure using automatic microdistillation apparatuses. It is applicable to products such as light and middle distillates, as well as engine fuels containing up to 10 per cent ethanol and up to 20 per cent biodiesel blends.

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.

### The effective solution

Because microdistillation determines the distillation characteristics of petroleum products with boiling points between 20 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 per cent ethanol, aviation gasolines, aviation turbine fuels, regular and low-sulfur diesel fuels, biodiesel blends (up to 20 per cent biodiesel), special petroleum spirits, naphtha, white spirits, kerosene, burner fuels, and marine fuels.

Other hydrocarbons such as organic solvents or oxygenated compounds that have narrow boiling ranges are also good choices for microdistillation.

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 vapour variations while monitoring the pressure inside a special micro-distillation flask as the sample gradually distills under atmospheric temperature. During the distillation cycle, the measured vapour 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 will change for refineries, simulation technologies are not practical for measuring within the process due to the time needed to adjust correlations. An online micro-distillation analyzer distills small amounts of the actual product, so it doesn't rely on product specific calculations, and is the best method to detect product contamination.

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 faster.

## Typical 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 downgrade the end product. Since refinery optimization objectives change daily, refiners need the ability to optimize cutpoint in consideration of these changing variables.

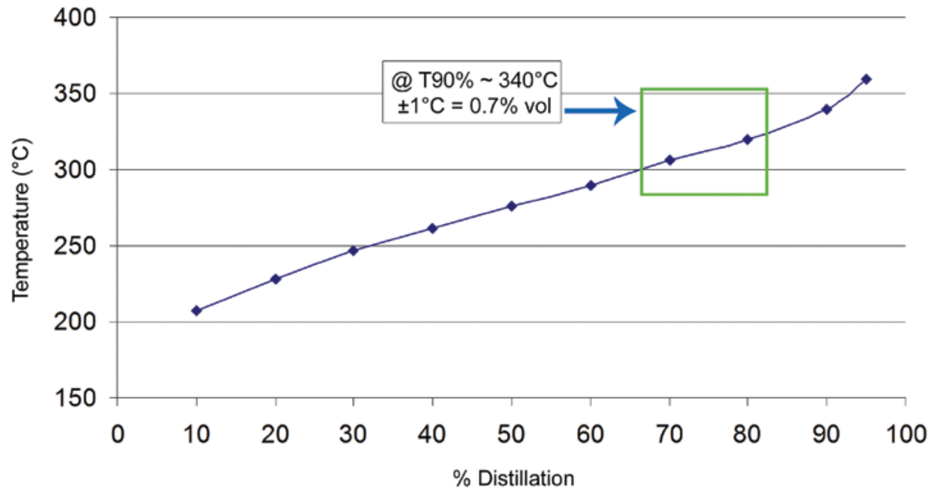
Microdistillation is ideal for optimizing naphtha, gasoline, diesel and jet fuel distillation cutpoints. Refiners can maximize high-value components throughput by using real, online distillation, rather than a simulation.

**Benefits:** 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.

Since the crude quality can change, refiners cannot run on temperature alone; they also need boiling point measurements. 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 cheaper product.

Consider a situation where increasing T90% by 1 C results in 0.5 to one per cent additional diesel production; depending on production capacity, this can impact up to $1 Million US of incremental profits.

**Cetane Index:** This determines the ignition quality of diesel fuel. It is ideal for monitoring




**With HDT diesel capacity at 22,000 barrels per day (bpd), a 1 C optimization impact increases volume by 0.7 per cent, which is 152 bpd. Residual fuel to ULSD upgrade is $29 US per barrel, which increases profitability by $1.1M. *Illustration courtesy PAC.***

product quality and the operation of middle distillate hydrotreaters.

The Cetane Index correlation uses a four-variable equation of 10, 50 and 90 per cent 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:** 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 create 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. Refiners use less-than-ideal blending equations for ASTM distillation, which can 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 (i.e.,, 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; and
- T50% and T90% are the heavier components, which represent the ability to vaporize and combust once the motor is warmed up.

**Benefits:** 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.

## Results

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. It also 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 right analyzer can provide complete distillation and density results within 10 minutes that correlate to ASTM D86 and ASTM D7345 test methods and their analogs. Such an analyzer can determine 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.

*For more information, visit PAC's website at www.paclp.com*