

Refinery analytical techniques optimize unit performance

Use these laboratory tests to identify contaminants and improve operations

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Refinery process engineers need to consider benefits of laboratory analytical techniques when evaluating unit performance. Laboratory analytical techniques can improve refinery unit operations by relating test results and plant occurrences. Properly using lab tests can help identify process unit improvements. Lab separation techniques can pinpoint causes of stream contaminants. Entrained and volatile metals can be identified and appropriate operational changes made.

Refinery heavy-oil laboratory analytical techniques use both old and new technologies. Knowing how to use available laboratory analytical techniques within their limitations are critical to obtain correct refinery optimization decisions. Better refinery stream distillation and contaminant data ultimately improves the accuracy of various refinery decision-making tools.

These laboratory analytical techniques are covered:

- High-temperature simulated distillation (HTSD)^{1, 2}
- True boiling point (TBP) distillation—ASTM D2892
- Vacuum distillation—ASTM D5236
- Continuous-flash vaporizers
- Wiped-film evaporators
- Inductively coupled plasma atomic-emission spectroscopy (ICP-AES)^{3, 4}
 - Conradson—ASTM D189/Microcarbon residue—ASTM D4530
 - Asphaltene IP-143, ASTM D3279, ASTM D4124.

Analysis of atmospheric crude, vacuum crude and delayed coker units highlight these laboratory techniques to identify potential yield and product quality benefits. Physical distillation or wiped-film evaporation in conjunction with HTSD, ICP-AES, microcarbon residue and

Table 1. HCGO product vanadium

Boiling range, °F	Vanadium, ppmw	
	BCF 22 ¹	Blend ²
950 to 975	2.0	0.5
975 to 1,000	3.3	0.6
1,000 to 1,025	5.9	0.8
1,025 to 1,050	15.0	1.2
1,050 to 1,075	17.3	1.8
1,075 to 1,100	22.0	5.0
1,100+	45.0	41.0

Notes

¹ Venezuelan crude blend, primarily BCF 22

² Blend of heavy crudes

asphaltene data will better characterize a feedstock as well as determine the source of contaminants. Economics are refinery specific, therefore, these examples focus on applying laboratory techniques as opposed to discussing specifics of unit improvement. These are discussed qualitatively.

APPLYING LABORATORY TECHNIQUES

Refinery engineers must ultimately use lab data to make operational decisions to improve product yields and product quality. Refiners are always interested in the value of incremental product and feedstock laboratory analytical data is useful in gaining insight into necessary unit design or operation changes. **Example:** a delayed coker wash section. Lower-efficiency wash zones such as spray chamber or gravity settling in the column's bottom may, in fact, not be economic for some units.⁴ Incremental yield with low wash-zone efficiency allows increased liquid volume yield. However, the increased product contaminants may not allow the yield to be economically justified. Knowing the heavy coker gas oil (HCGO) contaminant distribution allows overall benefits of increased liquid volume yield to be assessed.

Conversion unit feedstock contaminants affect unit yields and catalyst life. Determining the contaminant

source can be done through judicious use of available lab techniques including chromatographic simulated distillation, physical distillation and various contaminant analysis techniques. Once the contaminant source is identified, modified unit operation or design changes can be made.

For instance, knowing that a vacuum unit will operate reliably over a four- to five-year run length is more important than maximizing vacuum gas oil (VGO) yield for a short period of time. Asphaltene compounds are nondistillable. Thus, asphaltenes in vaporized oil can only occur by mechanical entrainment into the vapor from the flash zone. The quantity of asphaltenes in the overflow stream can be used to estimate entrainment. HTSD analysis of the "overflow" stream and vacuum residue, in conjunction with asphaltene analysis, will indicate if the unit has enough wash oil. Inadequate wash oil to the vacuum column's wash section results in coking. This increases column pressure drop and VGO contaminants. Thus, yield and product quality decrease.

Lab analyses can improve results from rigorous computer simulations of heavy-oil main fractionators. Computer modeling is now commonplace in refining. Detailed feedstock contaminant data such as vanadium or microcarbon residue can be used to produce better unit designs. Knowing the contaminants in a crude vacuum unit as a function of boiling range allows the incremental gas oil yield and incremental contaminants to be calculated. Many process flowsheet simulators will extrapolate or interpolate distillation or contaminant input data to produce a TBP or a specific property curve as a function of vol% distilled. Accuracy of interpolated data is tied to the analysis methods, number of data points and inherent limitation of the lab test. However, without good lab data, conclusions drawn from the models' output may be wrong.

Table 1 shows a comparison of vanadium distributions for two HCGO products.⁴ This provides a good indication where most of the metals in these feedstocks come from. Distillation curves associated with the sample streams in Table 1 indicate how much of a given boiling range material is in the sample. Contaminants for a boiling range give insight into a potential solution to the problem. The problem may be high metals or microcarbon residue in HCGO from the coker. The quantity of 1,100+°F material in the HCGO product indicates the amount of entrainment from the coke drum. High coke drum and column superficial vapor velocity prevents settling of nondistillable material, therefore, a high-efficiency wash section may be required. If the feedstock metals are low, then entrainment may not present a problem.

Atmospheric crude, vacuum crude, lube vacuum, visbreaker vacuum, hydrocracker vacuum and delayed coker units are where these tests have been used alone or together to determine operational or capital investment directions. These tests can be used on atmospheric gas oil (AGO), atmospheric residue, heavy vacuum gas oil (HVGO) and delayed coker gas oil streams.

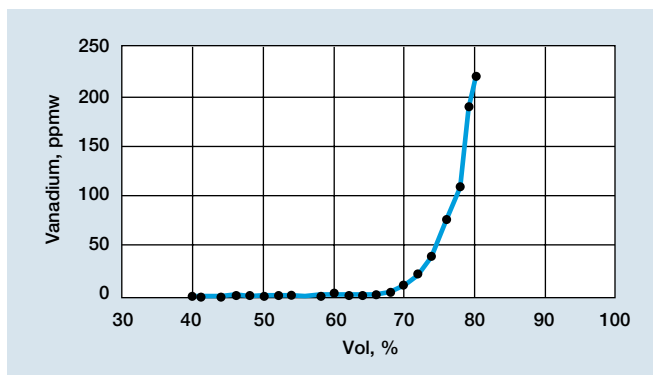


Fig. 1. Vanadium distribution of a medium-heavy crude.

LABORATORY AND REFINERY DISTILLATION

In a refinery, distillation is the primary means of product separation. The lab distillation unit can emulate the actual plant. However, the refinery unit has some non-ideality that is not reflected in a lab-scale device. Nonetheless, laboratory distillation is important when troubleshooting or making modifications in unit designs.

Unit revamps too often misuse crude assay data for feedstock characterization. These assays may be old or temperature limitations may not properly characterize oils in the range necessary for proposed unit modifications. If the project improvement is to increase the vacuum unit cutpoint, say from 1,025°F to 1,100°F, then the assay data will be of little value. TBP curve extrapolation and generating contaminant data from too large distillate cuts will be of little use. In fact, the data can be misleading.

For example, crude oil quality is getting worse. Refiners that can economically process the heaviest crude must determine the most economic balance between crude vacuum unit cutpoint and delayed coker charge rate. Determining an economic optimum is a complex function of feedstock costs, product values and the refinery processing scheme. However, better feedstock distillation and contaminant data allows refinery decision-makers to better optimize individual unit operations. Producing a higher-cutpoint HVGO may not be optimum with some crude oils.³

Optimizing vacuum distillate production and delayed coker charge rate requires well-defined incremental distillate vs. % distilled data. VGO contaminants must be assessed because the technology exists to reach VGO cutpoints above 1,130°F, even for heavy crudes. However, contaminant nonlinearity may make this vacuum column operation uneconomic for high-contaminant crude oils. Significant volumes of Venezuelan and Maya crude oils, which have very high vanadium levels, are processed in the U.S.

In the lab, reducing a sample's boiling range by separating the stream into smaller cuts improves subsequent analysis by more sophisticated techniques like HTSD. Understanding contaminant distribution also allows incremental properties to be established for accurate design work. With an ongoing push for optimum product recovery as opposed to running maximum feedrate, knowing more about the feedstock allows more accurate decision-making.

Fig. 1 shows the vanadium distribution for a medium-gravity crude oil. It is highly nonlinear. This curve was prepared by fractionating the crude oil into discrete cuts by several methods including ASTM D5236 and continuous flash vaporization of the whole crude TBP 900+°F boiling range material. Vanadium in individual cuts was determined by inductively-coupled plasma atomic-emission spectroscopy (ICP-AES). This data can be used to optimally define vacuum unit and delayed coker operations. Combinations of these analytical techniques can be used to perform these unit improvement studies:

1. Vacuum distillate recovery

2. VGO contaminants
 - a. Product contaminants
 - b. Contaminant source
3. Feedstock contaminant distribution
4. Product contaminant distribution.

Crude vacuum. These columns produce heavy distillate for downstream processing in an FCC or hydrotreater. Optimizing HVGO production requires an understanding of the feedstock distillation curve's slope and incremental gas oil contaminants in the region where it is yielded. Table 2 shows how the TBP distillation curve slope changes for West Texas Intermediate (WTI) crude oil based on an HTSD analysis.¹

On light, low-contaminant feedstocks like WTI, gas oil contaminant cutpoint limitations may depend on the economics of an incremental barrel of gas oil. Contaminants generally do not present a problem for downstream units when processing WTI, North Sea and many West African light paraffinic crudes. However, increasing vacuum unit HVGO yield to the limit of current technology may not be economic. On many crudes, the quantity of volatile metals and microcarbon residues results in severe downstream catalyst poisoning.^{3,4} Understanding contaminant distribution and potential HVGO product quality is important. Analytical techniques can be used to measure HVGO yields and quality at different cutpoints and to determine feedstock contaminant distributions for predictive design work.

Vacuum columns process feedstocks that must be analyzed under vacuum. This limits the tests that can be performed as well as their accuracy. Available tests to determine the distillation curve can be categorized as column, chromatographic and short-path distillations. Column distillation tests use phase equilibria including spinning-band distillation, ASTM D5236 batch distillation and continuous-flash vaporization.⁵

Spinning-band distillations make very sharp cuts. However, the atmospheric equivalent boiling point (AEBP)⁶ of the highest-boiling-range distillate is approximately 900°F. Batch distillations produce distillates with maximum cutpoints of approximately 1,040°F to 1,060°F. Continuous-flash vaporizers produce cutpoints up to 1,225°F, depending on feedstock stability. With the exception of the spinning-band distillation, there is considerable overlap between the cuts with all the vacuum distillations applicable to vacuum unit performance. Additionally, correcting the vacuum distillation to atmospheric pressure introduces errors.

The short-path distillation separation principle is kinetic. A laboratory short-path distillation (DISTACT)⁶ produces cutpoints up to 1,300°F. However, it is a nonequilibrium device. As with lab vacuum distillations, DISTACT results in overlaps between the cuts and, subsequently, some inaccuracy in producing the contaminant distribution curve. Analyzing each cut with a HTSD allows the contaminant curve to be corrected for overlaps.

DISTACT and continuous-flash vaporizers can produce cutpoints higher than refinery vacuum columns. Depending on the definition of cutpoint and the particular column operation, a commercial vacuum column has a maximum cutpoint potential of 1,150°F to 1,175°F on highly paraffinic feedstocks. Some claim 1,200°F cutpoints, but we have never seen this. A continuous-flash vaporizer operates at 0.5 mmHg and has a flash-zone

Table 2. TBP distillation slope

Boiling range, °F	Slope, °F per %
1,050 to 1,075	30.5
1,075 to 1,100	34.8
1,100 to 1,125	41.9
1,125 to 1,150	64.0

temperature of 700°F. This equates to an 800°F flash-zone temperature at 10 mmHg absolute pressure. Although refinery furnaces can reach these temperatures, it probably will not operate for very long due to tube coking. Peak coil temperatures for a furnace occur upstream of the furnace outlet thermocouples. A vacuum column flash-zone temperature of 800°F equates to approximately a 830°F furnace outlet temperature.

The first lab step is to cut the feedstock stream into discretely smaller cuts. These individual cuts can then be analyzed for contaminants. Microcarbon residues and metals poison downstream unit catalysts. Controlling contaminants requires an understanding of their distribution. Vacuum column bottoms are commonly fed to a delayed coker. Raising the HVGO TBP cutpoint increases VGO contaminants. Understanding the contaminant distribution allows the design engineer to determine the most economic unit design. This is a balance between HVGO yield, HVGO quality, capital investment and operating cost. This is true for any type of vacuum unit design.⁷

Delayed coker. These units thermally crack vacuum residue for maximum liquid yield at an acceptable quality. The heaviest fractionator sidecut is HCGO. Analytical techniques are used to determine proper wash-section operation and design. HCGO contaminants are a function of feedstock properties, processing severity and main fractionator wash-zone efficiency. Delayed cokers that produce HCGO for hydrocracker feed operate with very high recycle rates and 10 to 15 fractionation trays in the wash section. HCGO can contain entrainment and volatile contaminants from the coke drum. Essentially all entrainment and some volatile contaminants can be removed through wash-section modifications.⁸

HCGO analysis will indicate the contaminant source. Fractionating the stream into discrete cuts and analyzing for contaminants helps define existing unit performance and identify areas of improvement.

There are trade-offs in most refinery unit operating decisions. Increasing coker liquid volume yield will decrease HCGO product quality. Low system pressure and minimum recycle rates increase liquid yields, but the HCGO has a higher final boiling point. This material contains more microcarbons and volatile metals.

Atmospheric crude. Most of these units produce an atmospheric gas oil (AGO) product for a hydrocracker or FCC feed. Many units produce AGO with an ASTM D1500 color of 8+. This material is black and is caused by entrained residue. Although the black color clearly indicates residue, its quantity may vary. If the Conradson carbon, microcarbon or metals are high, then the stream

contains a high level of entrainment. AGO products containing nickel plus vanadium of 30 ppmw have been reported, which is extreme. A more typical value for a black AGO product may be total metals of 3 to 5 ppmw.

Atmospheric crude column temperatures and pressures prevent any appreciable quantity of feedstock components boiling above 1,000°F from vaporizing in the flash zone. In some cases, the AGO product ASTM D1160 endpoint is beyond the tests' limits. This means there is entrained material present. Comparing atmospheric residue product metals with the last 5 vol% of the AGO metals is a good indicator of the AGO entrainment level. Except on a few very high metal crude oils, there are no volatile metals present in AGO product. On a properly designed unit, AGO product metals will be at the ICP-AES detector limitation.

Fractionating AGO by ASTM D-5236 into two cuts containing the first 95 vol% and final 5 vol% will indicate the entrainment level. Analyzing the second cut by HTSD and metals by ICP-AES helps quantify this entrainment. Laboratory analytical data can help prove that AGO metals is caused by entrainment. Reducing atmospheric residue entrainment by 50 bpd on a unit processing a medium-heavy Venezuelan crude can reduce metals in the AGO product by 40%.⁴

LABORATORY ANALYTICAL TECHNIQUES

Most engineers deal only with the routine refinery laboratory analytical techniques like ASTM D86 or ASTM D1160. In recent years, refinery labs are beginning to use HTSD or ASTM D2887. However, lack of operator training and poor quality-control requirements can cause the data to be unreliable. At elevated vanadium levels, ICP-AES must be used because of detector accuracy limitations. Microcarbon residue is beginning to replace Conradson carbon. Results from the two tests are reportedly equal, however, the microcarbon test repeatability is better. As with all lab tests, the data is only as good as the operators and quality-control system. Finding an outside lab that specializes in column distillations, chromatographic simulated distillation and contaminant analysis to confirm in-house data is prudent. Bad data results in bad decisions.

Laboratory analytical test limitations must be considered when using data from various tests. A common refinery laboratory quality-control vacuum distillation test is ASTM D1160. Temperature readings on all laboratory vacuum distillations must be corrected to atmospheric pressure to produce an AEBP. Vacuum to atmospheric equivalent boiling range temperature conversions must be corrected for the cut's UOP-K value. Many labs assume a UOP-K value of 12. So the correction to atmospheric pressure will be wrong unless the material actually has a UOP-K value of 12.0. Some thermally cracked streams, such as the heaviest boiling range of the delayed coker drum effluent, have a UOP-K value of 10.8.

High-temperature simulated distillation.^{1,2} Hydrocarbon characterization by HTSD is a relatively new method that extends the ASTM D2887 determination of the boiling range distribution of hydrocarbons to a final boiling point of 1,400°F. By using recent advances in capillary GC column and stationary-phase technologies, together with programmed temperature vaporization or on-column injection technologies, adequate separation

from C₅ to C₁₂₀ normal paraffins allows the characterization of petroleum products from about 97°F to 1,380°F.

HTSD improves accuracy and precision of TBP distillation curves. The range of applications for HTSD include crude oil characterization, reduced crudes, FCC feeds, products, slurries, hydrotreater feed and products, VGO and vacuum residues.

As previously mentioned, HTSD is basically an extension of ASTM D2887 (IP-4060) for boiling range distribution of hydrocarbons by gas chromatography (GC). By proper choice of GC conditions and equipment, separation from C₅ to C₁₂₀ n-paraffins is routinely done to calibrate GC elution time to AEBP of paraffins (as described in API project 44).

Eluting heavy materials up to the equivalent of C₁₂₀ at or below the maximum-allowed column temperature requires a careful choice of chromatographic conditions. The most important is stationary-phase thickness. Typical films used in HTSD GCs vary from 0.05 to 0.15 microns. The resulting phase ratio (column volume vs. stationary phase volume) commonly exceeds 1,000°F for a 0.53 mm ID capillary column. This high phase ratio permits elution of materials from the column up to 500°F to 600°F below their AEBP. For instance, the elution of C₁₁₀ (BP 1,351°F) occurs at about 800°F column temperature.

A consequence of the conditions necessary for HTSD is a limited column concentration capacity due to a small stationary phase. This requires appropriate dilution of the standards and samples (usually in carbon disulfide). Careful operator evaluation of system performance due to loss of stationary phase at high temperatures (resulting in loss of film thickness and sample capacity) and the unavoidable buildup from residue-containing samples of nonvolatile material such as metals, asphaltenes, etc., in the injector and column is a condition for accurate HTSD data.

Little or no evidence of cracking is normally seen in HTSD because of the highly inert conditions of high-purity fused-silica GC columns, gentle injection techniques and short time at maximum temperature.

A blank GC run using solvent only should be recorded in the data system due to column breakdown (bleed) during the final portion of an HTSD analysis and the need to dilute the sample to approximately 1% to 2%. The solvent blank is then subtracted from all subsequent runs. This accomplishes two important goals: **1)** It removes the solvent signal (which could detract from accurate light-ends determination); **2)** Column bleed is compensated for. An assumption during this process is that solvent blank and column bleed profiles are constant during the calibration and sample analysis. It is the HTSD operator's duty to verify this criteria for statistically meaningful results.

The final step in the HTSD calibration is analyzing a reference oil that has been physically distilled by ASTM D2892 (TBP). This material is used to calibrate the system as an external standard for all sample recovery calculations. In addition, HTSD analysis results are compared to the physical weight distribution data from the TBP. Statistical error of the difference between HTSD data vs. actual boiling point data is then recorded.

ASTM D2892.⁹ This distillation method is a major tool for evaluating distillation yield curves of crude oils

and crude products for refinery design, operation and forecasting. The method, commonly referred to as a true boiling point (TBP) or 15/5 distillation, involves a batch distillation of the sample (1 to 30 liters) at prescribed conditions of boilup rate, reflux ratio and still pressure. Fractionation is accomplished with a 14 to 18 theoretical plate Oldershaw (perforated plate) column or a packed column of sufficient height to give an equivalent efficiency.

Still pressure can be varied from atmospheric to a reduced pressure of 2 to 100 mmHg abs. During the vacuum portion of the distillation, observed overhead vapor temperatures are corrected to atmospheric equivalent temperature (AET) using a nomograph or vapor pressure/temperature equation.¹⁰ Correction for UOP K-factor deviations from 12 are optional. Temperature and pressure drops associated with the column, combined with a pot temperature maximum of 590°F, limits the overhead distillate to about a 750°F AET. The still head/reflux splitter and its associated receiver permit recovery of distillate fractions from any portion of the distillation curve.

ASTM D5236.¹¹ The distillation of heavy hydrocarbon mixtures (vacuum potstill method) was developed to extend the distillation curve above the limits of ASTM D2892 (about 730°F AET) and to generate more distillate than ASTM D1160 (200 cm³ charge maximum). The method involves batch distillation of 1 to 16 liters in one of four appropriately sized stills using a low-efficiency (open) column fitted with one or two entrainment separators. Reflux control is not used in these stills. Rather, the take-off rate is controlled by adjusting the boilup rate.

Still pressure is limited to 0.1 to 50 mmHg abs. Overhead vapor temperatures are corrected to AETs using the same nomograph or vapor pressure/temperature equation as ASTM D2892. The useable upper limit of the distillate is about 1,050°F AET if the charge is relatively heat stable. Distillate fractions can be recovered from any portion of the distillation curve for further analysis.

Continuous-flash vaporizers. Using continuous-flash vaporizers to characterize crude oil and products dates back to the early 1920s. Advantages over batch distillation methods in lube oil and asphalt evaluations are still valid today. That is, short residence time of the charge oil at high temperature. This translates into higher cut points (>1,200+°F AET) and more representative distillates and residue at higher cutpoints. Distillate cuts up to 1,200+°F allows characterization of deep-cut vacuum tower feeds and products at or above their expected cutpoint without significant residue fraction cracking.

Design and operation of a continuous-flash vaporizer system is very similar to the flash zone of a typical vacuum column. Feed is pumped by a precision gear pump through a coil-tube heater into a small flash vessel. Residue flows out the bottom through a vapor trap and into a weighed receiver. The flash vessel and feed preheater tube are contained in a forced-air oven capable of close temperature control. Internal flash-zone temperature and pressure are monitored and controlled throughout the run. The cutpoint is determined from the pressure and temperature using Maxwell and Bonnell equation with K-factor correction. Since a single cut point is generated from each run, multiple runs are

required to define a flash curve or to generate a series of contiguous distillates for further analysis.

Wiped-film evaporators. Applying small laboratory wiped-film evaporator units (<1 ft²) to heavy-oil characterization offers the same advantages as continuous-flash evaporators (short residence time at high temperature). Another advantage is a short vapor path (< 1 in.) from point of vaporization to point of condensation, giving a negligible pressure drop. Operation of small wiped-film units is similar to flash evaporators in that feed is continuously pumped or gravity fed to the inlet. Oil is spread evenly around the inside surface of the heat exchange area by rotating wipers. The thin film of oil is heated and flash evaporated as it flows down the continuously-wiped heat exchanger. A vapor condenser is usually placed in the center of the wiper assembly so the wipers operate in an annular space between the condenser cold finger and the shell's heated inner surface. Bottoms collect in a trough below the heated surface then flow to the receiver. Condensed vapors flow down the condenser surface and collect in a separate receiver.

Heat-exchange surface temperature and system pressure are monitored and controlled during the run. The cutpoint is determined from the pressure and temperature using the Maxwell and Bonnell equation with K-factor correction. Again, since a single cutpoint is generated from each run, multiple runs are required to define a flash curve or to generate a series of contiguous distillates for further analysis.

ICP-AES. Analysis of trace metals in petroleum distillates by inductively-coupled plasma atomic-emission spectrometer (ICP-AES) enables more consistent low-detection limits. Additionally, the high throughput of these units keeps the cost down. Instrument operation involves aspirating the sample solution into a high-temperature argon plasma torch where it is dissolved. Trace metals are excited to produce their characteristic emission wavelengths. The plasma emission is monitored by a computer-controlled monochromator and photodetector system that isolates and measures the intensity of selected wavelengths for each element of interest.

Some instruments can simultaneously monitor multiple wavelengths and deliver multi-element results in seconds while other instruments sequentially scan through the selected wavelengths. Calibration is done by aspirating standards under the same conditions. Furthermore, background correction requirements and the presence of interfering wavelengths can be determined by visual inspection of the displayed spectra. Analysis of petroleum samples can be accomplished by two procedures. First, the sample can be wet ashed. This ash is dissolved in aqueous acid for introduction into the instrument. When using this sample-preparation procedure, the instrument is calibrated with aqueous standards. Second, the sample may be diluted in a low-viscosity solvent and aspirated directly into the torch. When using this approach, the instrument is calibrated with organometallic standards diluted in the same solvent.

ASTM D189 Conradson carbon residue. ASTM D4530 microcarbon residue. These procedures determine the carbon residue left after evaporation and pyro-

ysis of an oil sample under prescribed conditions. It is a rough indicator of an oil's relative coke-forming tendency or contamination of a lighter distillate fraction with a heavier distillate fraction or residue. The difference in the two methods involves how the sample is heated and the degree of control exerted on the sample temperature/time cycle.

In the original method, ASTM D189,¹² the sample is evaporated and pyrolyzed over a gas burner with temperature estimated by visual observation of the crucible's surface color. This can lead to judgment errors relating to actual sample temperature. This contributes to poor lab-to-lab reproducibility observed with this method (about 17% relative at 10% carbon residue).

The microcarbon method, ASTM D4530,¹³ uses a feedback control ramping temperature controller and electrically fired furnace with controlled nitrogen purging. The system uses smaller samples and allows multiple samples to be run simultaneously. This allows duplicate analysis and control samples to be included in each batch, giving better lab-to-lab reproducibility (about 12% relative at carbon residue).

Asphaltenes. These can be measured by several methods including IP-143,¹⁴ ASTM D3279¹⁵ and ASTM D4124.¹⁶ Main parameters to consider in any asphaltene analysis is solvent selection, solvent to sample ratio and specificity for asphaltenes.¹⁷ Solvents range from pentanes to heptanes and include mixtures of their carbon numbers. The lower the solvent carbon number, the higher the yield of insolubles. The standard definition of asphaltenes is generally based on the use of n-heptane as precipitation solvent.

The solvent to sample ratio also affects yield of insolubles. This increases with higher ratios. Typically, ratios in the range of 25:1 to 100:1 (vol:vol) are used to mitigate the solubility effect.

The specificity of any method to asphaltenes can be affected by the presence of additives, wax, catalyst fines, coke, scale, rust and other particulates. Procedures that do not include a filtering step can give high results due to the inclusion of these nonasphaltene particulates. Wax particles can be excluded by heated solvent extraction of the asphaltene filter cake. Comparison of asphaltene data from any two procedures (listed above or in-house methods) must be done considering these parameters.

CASE STUDIES

These present practical uses of analytical techniques in refinery heavy oil distillation unit operation and revamp design. Proper use of the laboratory techniques can pinpoint potential unit improvements.

Crude vacuum column. These columns that process high-metals feedstocks and operate at high HVGO product cutpoints require an awareness of the highly linear metals distribution. A well-documented case,³ where downstream catalyst poisoning problems were discovered after a deepcut revamp, shows the importance of good contaminants knowledge and the potential impact of high metals. Fractionating a vacuum column feedstock requires that the IBP 900°F portion be separated by spinning band or ASTM D5236.

Table 3. HTSD of adjacent continuous flash cuts

Wt%	1,000 to 1,025 °F		Wt%	1,025 to 1,050 °F	
	cut temp.			cut temp.	
70	1,022		IBP	529	
80	1,042		5	777	
90	1,069		10	867	
95	1,092		20	963	
FBP	1,152		30	990	

Table 4. Stream analysis, asphaltenes

	Overflash	Vacuum residue
Sp. gr.	0.9881	1.009
Asphaltenes, ppmw	4.8	5.9
Sodium, ppmw	16.0	16.0

The 900+°F cut must be separated by a continuous-flash vaporizer or wiped-film evaporator. These are required for cutpoints in excess of about 1,075°F. Neither are ASTM standard tests. In our example, the crude oil feed is fractionated by both an ASTM D5236 and a continuous-flash vaporizer.

It is imperative that the test limitations be understood to make correct decisions with analytical data. Generating a metals-distribution curve has some inherent inaccuracies. Metals distribution in the 1,000°F to 1,150°F range is very nonlinear. Therefore, the sample should be separated into 25°F increments. The curve generated by these methods is conservative.

These separation methods are essentially one-stage flashes, therefore, there is overlap between cuts. Evaluating individual cuts by HTSD gives a good indication of the degree of overlap. Table 3 shows HTSD 70%, 80%, 90%, 95% and FBP values of the 1,000°F to 1,025°F cut compared to the IBP, 5%, 10%, 20% and 30% points of the 1,025°F to 1,050°F cut. Lab data must be used properly and understanding the test limitations is essential.

The metals distribution curve generated by these lab tests can be input to a rigorous distillation model. The model can be used to evaluate various vacuum column unit designs as well as HVGO quality at different cutpoints. Small changes in cutpoint can yield significant changes in HVGO metals. However, overlap between cuts causes some inaccuracy when directly using the data.

Product metals estimates are higher than the actual lab test for the same cutpoint. For instance, if the HVGO has a 850°F to 1,050°F cutpoint and the product from a given feedstock is analyzed, it will show lower metals by 10% to 15% than predicted by the model. This is due to overlap between the cuts. However, the generated curve is reflective of relative changes that occur in a commercial unit.

Another example of using contaminants is the ASTM D3279/D4124/IP-143 asphaltene analysis to estimate residue entrainment in the wash section of a crude or lube vacuum column. Asphaltenes are nonvolatile. Hence, the only way they can reach the wash section is by mechanical entrainment. Vacuum column transfer lines and flash-zone designs affect the quantity of entrainment in rising vapor.

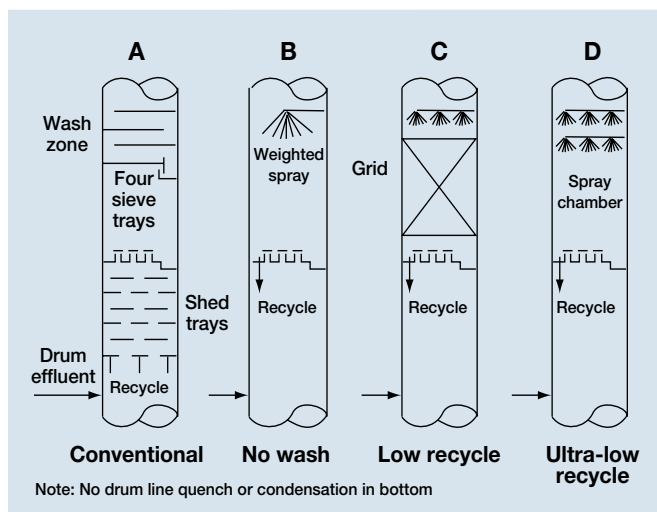


Fig. 2. Different delayed coker wash-zone designs.

Many deepcut vacuum columns have repeated severe wash-section coking. Liquid withdrawn from the overflash collector is mistakenly considered overflash. Liquid on all vacuum column collector trays contains entrainment and true overflash. True overflash is distillable material at flash-zone conditions and contains no asphaltenes.

Asphaltene data from a deepcut vacuum column operating on North Sea crudes is in Table 4. This column was revamped by replacing a low-efficiency wash section with a high-efficiency design. The wash bed coked in less than six months. Asphaltene data shows that a large percentage of the measured "overflash" on this unit is actually entrainment. Roughly 85% of liquid withdrawn from the collector tray below the wash section on this unit was entrainment, not overflash. If this is assumed to be all true overflash, then the wash bed packing will not have enough liquid to prevent coking. In some cases, this error has resulted in coke formation within three months of startup. Asphaltene analysis can be used to determine a proper wash rate. Sodium and microcarbon residue can also be used as entrainment indicators.

Delayed coker. Different wash-zone designs are shown in Fig. 2. A column designed with no wash section is the least efficient.¹⁸ It produces the highest liquid yield but the lowest quality product. HCGO quality is a function of several variables including wash-section efficiency and unit recycle. No wash section produces the lowest unit recycle.

Fig. 3 shows the HCGO product TBP distillation and vanadium content from a unit operating with no wash section. The stream was analyzed by ASTM D5236, continuous-flash vaporizers and HTSD. The vanadium content was determined by ICP-AES. Residue from the continuous-flash vaporizer was analyzed by HTSD.

Several interesting qualitative conclusions can be drawn from the data. A significant quantity of HCGO product is entrained from the drum. Approximately 4 vol% of HCGO is very heavy. Some of this material may be distillable. The HTSD shows that some of the sample boils above the maximum HTSD temperature limit. Approximately 40% of the bulk stream metals are concentrated in the last 4 vol% of the HCGO product.

The conclusion is that the HCGO product from this unit

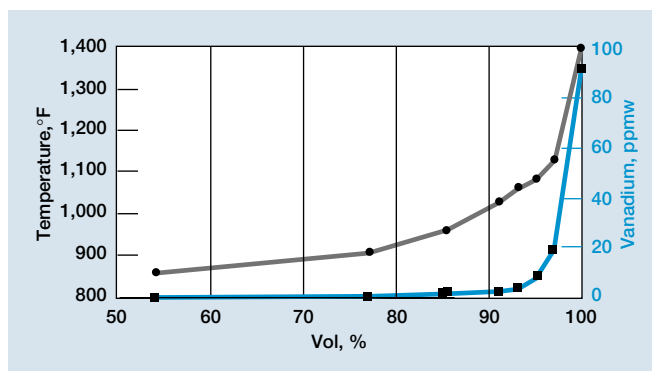


Fig. 3. HCGO TBP and vanadium distribution.

Table 5. AGO product D1160 distillation

Vol %	Temperature, °F
80	756
90	845
95	972
96	1,075

contains a significant quantity of entrained material from the coke drum or the column's bottom. Although maximum liquid volume yield is a general goal of delayed coker operation, it may not be an economic operation for some units. The issue of whether the wash-section operation and design should be modified is refinery specific. However, lab analytical techniques indicate that entrainment is occurring and unit improvements may be possible.

Atmospheric crude. Columns producing AGO for downstream conversion must minimize contaminants.¹⁹ A refinery processing crude with moderate metals was producing a black AGO. Table 5 shows the AGO's D-1160, which contained 7 ppmw nickel plus vanadium.

The AGO was fractionated by ASTM D5236. The first 95 vol% was discarded. The last 5 vol% was analyzed by HTSD and also for metals content by ICP-AES. It essentially contained 100% of the metals—close to 100 ppm. The HTSD showed an endpoint higher than the test's maximum. This unit had significant entrainment.

The unit was revamped to reduce entrainment. The AGO went from an ASTM D1500 color of 8+ diluted to less than 2.5. After the revamp, the AGO product D1160 endpoint was less than 1,025°F. The AGO metals content was less than the detectable limit for nickel and vanadium.

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⁹ ASTM D-2892 standard method for the distillation of crude petroleum (15 theoretical plate column).

¹⁰ Maxwell and Bonnell, *Ind. Eng. Chem.*, Vol 49, 1957.

¹¹ ASTM D-5236 standard method for distillation of heavy hydrocarbon mixtures (vacuum potstill method).

¹² ASTM D-189-91 test method for Conradson carbon residue of petroleum products.

¹³ ASTM D-4530-93 test method for carbon residue (micro method).

¹⁴ IP-143/90 determination of asphaltenes (heptane insolubles).

¹⁵ ASTM D3279-90 test methods for n-heptane insolubles.

¹⁶ ASTM D4124-91 test method for separation of asphalt into four generic fractions.

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¹⁹ Golden, S. W., and M. Binkley, "Crude tower modification stabilizes operations," *Oil and Gas Journal*, July 30, 1984, pp. 197-204.



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