

Chapter 3

CRUDE ASSAY

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1. INTRODUCTION

The well-developed crude assay program is crucial to the success of an organization that deals with diverse crude slates. Purchasing decisions and ultimately processing capability all begin with having high quality assay data that reflect the needs of the organization. Most crude oils have a lot of variability in their compositions from one source to another. Also as a crude oil field ages property data will change. These needs are especially important if the organization wants to deal with spot market crude purchasing from various parts of the world.

Crude assay programs can be subdivided into various formats, one format being Whole Crude property measurements/inspections and the other being a full assay including distillations and inspection data. The quality of either program is dependent on the care and attention paid to crude sampling and storage. Care is needed in some geographic locations, in the sampling from the crude container, especially in hot climates. In this case, the container may need to be cooled prior to the measurement in order to insure that light ends are not lost. Conversely, in colder climates containers need to be brought up gradually to room temperatures. ASTM D 4057 and D 5854 methods provide information on the sampling/mixing of petroleum products.¹

2. PROPERTY MEASUREMENTS/CRUDE INSPECTIONS

2.1 API Gravity

This industry standard that is based on ASTM D287/1298, is the single most utilized crude property measurement for making crude purchases. It is quite common for measurements to range from values in the low teens (asphaltic crude) to those having values in the 50's (condensates). While this test normally is done by the hydrometer method and is simple to perform, it does have some crucial steps that need to be performed. The first step is to insure that the crude aliquot taken is representative. API is measured along with the temperature of the crude that is then converted to an API at 60 °F (the industry standard).

2.2 Sulfur Content

The sulfur content of crude oils is normally in the range of 0.1-5.0-wt %. Sulfur is normally measured utilizing an x-Ray technique such as the following two methods ASTM D4294 or D5291 using a technique known as X-Ray Fluorescence. The methods have large dynamic ranges and allow analysis to be completed in about 3-5 minutes. Samples having sulfur contents greater than 5.0 % are measured by methods such as D1552, a combustion technique. For extremely low levels an Ultraviolet fluorescence technique is employed (ASTM D5453). Again most of these methods are very robust, but can be influenced by not having a representative sample.

2.3 Pour Point

The pour point of a sample is defined as the temperature normally 3 degrees above the point a sample no longer moves when inverted. This value is of particular importance for crudes that are transported through pipelines from source to load ports.

Currently the method of choice for whole crudes is ASTM D5853 which handles crudes that have pour points greater than -36 °C. For crudes that have pour points lower than -36 °C ASTM D97 tends to be the method of choice.

2.4 Whole Crude Simulated Distillation

This method normally is performed by ASTM D5307.¹ This gas chromatography method is a quick and robust method for determining a true boiling point curve and predicting crude yields. This external standard method is done on 5 metre fused silica columns having thin film thickness allowing

the analysis to be completed within an hour. A true boiling point curve can be determined by plotting % off (cumulative yield) versus temperature. Comparing a full assay TBP curve to this data and then monitoring the crude over time is a valuable tool to determine whether or not a full assay may need to be done/updated.

2.5 Full Assay

Assay analyses of whole crudes are done by combining an atmospheric and vacuum distillation run. These two runs when combined will provide a TBP (True Boiling Point Curve). While these batch distillation methods are labor intensive, taking between three to five days, they allow the collection of distillation fractions that can be utilized for testing. While each of the distillations techniques have been standardized by ASTM, cut schemes tend to mimic Refinery product classifications and there is no standardization of the individual inspection formats. Each corporation tends to perform both physical and chemical testing that best meet the needs of their refining operations and product suites.

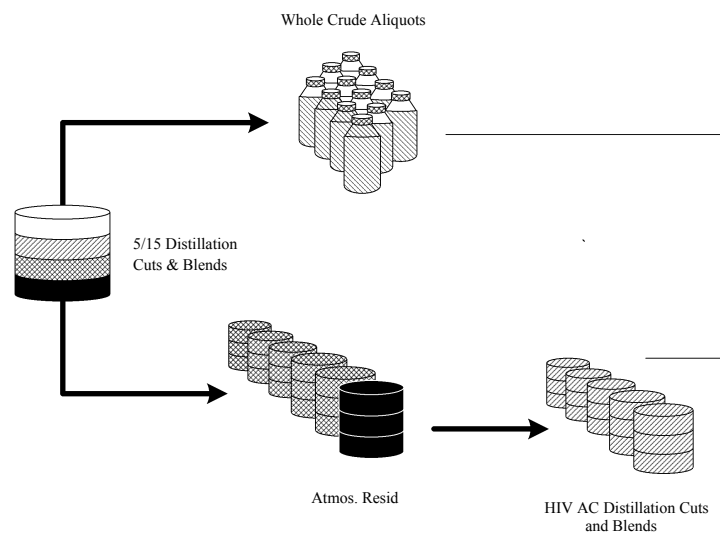


Figure 1. Crude Distillation

2.6 Physical Distillation - ASTM D 2892 Method

This technique is performed on a 15 theoretical plate fractionation column to obtain a true boiling point curve while maintaining an approximate 5:1 reflux ratio. The still pressure is reduced in order to prevent decomposition

due to high pot temperatures. This fractionation determines accurate boiling points (TBP) and agrees with the fractionation produced in the refinery.

These narrow fractions are sent for physical property measurements as well as chemical typing analysis. A typical cutting scheme is listed below.

Table 1. Temperature Ranges for Typical Distillation Cuts

Distillation Cut	Temperature Range in °C
Light Ends/Natural Gas	Trap
Light Gasoline	Trap-70
Light Naphtha	70-100
Medium Naphtha	100-150
Heavy Naphtha	150-190
Light Kerosene	190-235
Heavy Kerosene	235-265
Atmospheric Gas Oil	265-343
Atmospheric Resid	343+

2.7 ASTM D 5236 Method

The atmospheric resid taken from the D 2892 distillation run is charged into the vacuum potstill. The method produces distillation fractions in the gas oil and traditional lube oil range as well as producing a vacuum resid. While there is no industry standard cutting scheme for Hivac distillation runs, narrow cuts in the 25-50 degree intervals are common. The final cut temperature is normally done to 565°C, a temperature that most crudes can attain.

Care needs to be taken to identify the early stages of cracking. It is recommended that the last distillation cut be taken within one hour of the pot temperature reaching 310°C.

2.8 TBP Curves

The physical distillation data from the D 2892 and D 5236 distillation runs are used to create a True Boiling Point Curve (TBP). These two curves will have a disparity in the area corresponding to the overlap between the 15/5 and Hivac distillation runs. This artifact is due to the Hivac still not being at optimum conditions at the early stages of the run. Once a TBP curve has been created property measurements can then be curve fit.

2.9 Property Measurement/Assay Grid

At present there is not a standardize grid for physical property and chemical typing information. The grid inspection format is based on customer need as well affordability. Please refer to Figure 2 as an example of a typical grid.

be measured manually by utilizing ASTM D 2500, since many laboratories utilize similar equipment to perform pour points. With the development of new analytical equipment many laboratories are now utilizing phase technology and are performing ASTM D 5773 which is less labor intensive and more robust.

2.10.4 Freeze Point

The temperature at which crystal start to form in hydrocarbon liquids and then disappear when the liquid is heated is the freeze point. Normally performed by ASTM D2386, this method like cloud point is done by ASTM D 5972 by phase technology.

2.10.5 Metals

The metals concentration in crude can range from a few to several thousand ppm. Low values of certain elements such as nickel vanadium can severely affect catalyst activity. In the past metals were determined by Atomic Absorption, but now most metals are determined by Inductively Coupled Plasma Emission Spectroscopy ICPAES. X-ray fluorescence can be a viable technique depending on the concentration.

2.10.6 Mercaptan Sulfur

Mercaptan Sulfur species are undesirable in crude oils, and in some cases are toxic. These species are normally attributed to sour crudes. Analysis is normally based on UOP 163, a potentiometric titration method. A hydrocarbon sample is added to a solution of isopropyl alcohol containing a small amount of ammonium hydroxide. The solution is then titrated with a solution of silver nitrate.

2.10.7 Micro Carbon Residue

The carbon residue of a petroleum crude oil is proportional to the asphalt content, normally measured by Conradson Carbon ASTM D 189. In most cases the lower the carbon residue, the higher the value that can be placed on the crude oil.

2.10.8 Nitrogen

Nitrogen species in crude oils can cause catalyst poisoning. ASTM D 3228 or ASTM D 4629 normally determines nitrogen content. Either a syringe inlet or boat inlet analyzes distillate cuts by Oxidative Combustion and Chemiluminescence detection. Whole crude, atmospheric and vacuum

resids are analyzed by Kjeldahl methodology, a labor intensive method involving digestion/distillation and finishing up with a titration.

2.10.9 Pour Point

The lowest temperature at which a hydrocarbon fraction is observed to pour when cooled under prescribed conditions. The pour point of a sample is determined to be 3 degrees Celsius above the point at which a sample can be horizontally held and no movement occurs for five seconds. The most frequently utilized method for this test is ASTM D 97, which can be used for all assay fractions/ blends. For whole crudes that have pour points greater than -36°C, a new method has been developed (ASTM D 5853). Also for fractions that contain wax, a new method utilizing phase technology ASTM D 5949. Normally low pour points are due to low paraffin content and high aromatics.

2.10.10 Refractive Index

Refractive index is a ratio technique that takes the velocity of light in air at a specific wavelength and compares that to the velocity in the sample tested. Normally this is performed under the guidelines of ASTM D 1218. This test method can be performed at various temperatures. The refractive index can be used to estimate the distribution of PNA molecules in oil fractions.

2.10.11 Reid Vapor Pressure (RVP)

RVP is measurement of the volatility of a liquid hydrocarbon. Normally this is performed by ASTM D 323. This measurement is normally used to predict gasoline performance, normally expressed in pounds per square inch (psi). This is normally an inspection that is performed on Whole Crudes having relatively high API's.

2.10.12 Salt Content

The salt content is measured by ASTM D 3230 to determine the corrosiveness of a Crude oil. It is this conductivity method that measures a sample of crude oil dissolved in water and compares that to reference solutions of salt.

2.10.13 Smoke Point

Performed by ASTM D 1322, this test determines the maximum flame height in a lamp without smoke forming. Normally high values represent

clean burning fuels. In normally practice this test is performed on jet fuels and kerosene cuts.

2.10.14 Sulfur Content

The sulfur content of crude oils is normally in the range of 0.1-5.0-wt %. Sulfur is normally measured by an x-ray technique such as ASTM D 4294 or D 5291. These methods have large dynamic ranges and allow analysis to be completed in about 3-5 minutes. Samples having sulfur contents greater than 5.0 % are measured by methods such as ASTM D 1552, a combustion technique. For extremely low levels an ultraviolet fluorescence technique is employed (ASTM D 5453) Again most of these methods are very robust, but can be influenced by not having a representative sample. Crudes are determined to be sweet or sour based on the amount of dissolved hydrogen sulfide.

2.10.15 Total Acid Number

The industry standard for this test is based on ASTM D 664. Normally expressed as Neutralization Number, this test predicts the acidity of an oil/distillate fraction. The sample normally dissolved in Toluene/IPA/Water is titrated with potassium hydroxide and the results are expressed as mg KOH per gram of sample. Crude Oils having high acid numbers are purchased cautiously due to possible corrosion problems in the refineries. Crudes typically have TAN values form 0.05-6.0 mg KOH/gm of sample. While whole crudes are outside the scope of this titration method, it is the only recognized method in the industry.

2.10.16 Viscosity

Viscosity is a measurement of a fluid resistance to flow. Most measurements use the force of gravity to produce the flow through a small capillary tube called a viscometer; thus the measurement is known as kinematic viscosity having a unit of centistoke (cSt). The viscosity of a fluid is always reported with a temperature, since viscosity will vary inversely with temperature. Most viscosity measurements follow the guidelines of ASTM D445. Normally in an inspection grid the viscosity will be measured at three different temperatures and then plotted on semi-log graph paper. If all measurements are performed properly a straight line will result.

2.10.17 Water & Sediment

Sediment and water values in crude oils are critical parameters as to whether problems will occur in the processing in the refinery. In many cases, desalting equipment may be required in order to handle a given crude slate.

2.11 Asphalt Properties

2.11.1 Penetration

Penetration is a method for determining the consistency of semi-solid material normally performed by ASTM D 5. A sample of resid is weighed, cooled, and a needle is positioned above the surface and allowed to penetrate the sample. The penetration measure in millimeters is also based on the temperature of the sample.

2.11.2 Softening Point

Usually determined by ASTM D 36, softening point determines the temperature at which hard asphalts reach an arbitrary degree of softening.

3. THE PREDICTION OF CRUDE ASSAY PROPERTIES

3.1 Needs for Rapid and Accurate Prediction of Crude Assay Properties

Conventional crude assays provide accurate and detailed information about the physicochemical properties of crude oils across the boiling range. This information is used for critical purchasing and processing decisions. However, the determination of the crude oil properties is a lengthy, tedious, and costly process. Crude oils must be transported in large volumes (e.g., barrels) over significant geographic distances to analytical facilities capable of performing the required tests. Physical distillation must be conducted for the determination of the distillation yield profiles (weight and volume %) and is a prerequisite to the collection of narrow distillation cuts for further testing. The time period for crude oil transportation from the well to the analytical lab can range from several weeks to several months. Once in the lab, distillation can take 2-4 days for completion and complete testing of the various properties for each distillation cut may require 2 to 6 weeks. It is obvious, that despite the great accuracy and detailed information provided by conventional crude assay methodologies, newer analytical methodologies are required to provide timely information for rapid decision making.

The ideal crude oil assay should be able to provide on-line, instantaneous and detailed determination of all crude oil properties across the boiling range. Unfortunately, such a method is not yet available. However, several efforts have been made to that end. The most successful approach has been the prediction of the physicochemical properties of crude oils by correlating the data obtained by a rapid, surrogate method (usually spectroscopic) to the data

obtained by the conventional, lengthy crude assays. The testing time, degree of accuracy and extent of information greatly depend on the characteristics of the surrogate method. The following sections present some of the efforts associated with the development of analytical approaches for the prediction of the properties of crude oils.

3.2 Predictions from Measurement of Selected Whole Crude Oil Properties

Gaylor and Jones developed an early method for the rapid and comprehensive determination of crude oil properties without the need for distillation.² Information for all fractions through asphalt was obtained in two to three hours. The method relied on six measurements made on the whole crude oil: gravity, sulfur, nitrogen, pentane insolubles, condensed aromatics, and gas chromatography. Using multiple regression equations, it was possible to correlate the six properties of the whole crude oils to the properties of selected crude oil fractions. The method allowed for the rapid evaluation of important properties, such as: gravity of all fractions, smoke point and freezing point of kerosine, wax content and viscosity index of lubricating oils. Correlations were obtained for yields, paraffins, aromatics, gas oil, cracking stock, and asphalt quality properties. The 3-hour test allowed for the determination of a total of 59 parameters from the six measurements on the whole crude oil. The Gaylor and Jones approach is a relatively simple approach that can be readily implemented in most labs capable of performing the six tests on whole crude oils. The suitability of the approach to specific applications will depend on the accuracy required for reliable decision making.

3.3 Predictions from NMR Measurements

NMR is not an obvious analytical method suitable for the prediction of crude oil properties. However, it has been used for the estimation of the physical properties of petroleum reservoir fluids leading to the performance of phase equilibrium calculations (PVT properties). Using NMR data, it has been possible to solve the equation of state and to predict the changes in the relative volume versus pressure.³ Crude oil cuts were collected and separated into aromatic and (paraffin and naphthene) fractions. Group contribution methods were developed using several structural hypotheses to improve the efficiency of NMR data in the characterization of the petroleum fluids. The NMR data used in this study led to the successful prediction of PVT properties, in good agreement with the experimental data. The authors, however, concluded that despite the good predictions, NMR is a lengthy and expensive method with no particular advantage over other methods. Although

these conclusions are still valid, the methods and structural hypotheses developed by these authors may be useful in the future, when smaller and less costly NMR instruments become available.

3.4 Predictions from Chromatographic Data

Burg and co-workers developed a chromatographic approach for the prediction of the kinematic viscosity of crude oil.⁴ The ability to predict viscosity is very important as it has direct impact on the production and transportation of crude oils and their products. Prediction using compositional information can be problematic since the property can be modified by small amounts of molecules. In this study, the fractions boiling higher than 200 °C were used as stationary phases, and retention time measurements were made with 13 solutes at 50°C. Five parameters were determined relating the intermolecular interactions to kinematic viscosity. The interaction parameters are: a dispersive/cavity term (London forces), a dipolarity/polarizability term (Keesom and Debye forces), an acidic term, a basicity term, and a term for the tendency of crude oil to interact with polarizable solutes. The obvious advantage of this approach, in comparison to other approaches, is that the parameters have physical meaning and are directly linked to the molecular interactions. Crude oil viscosity was found to depend primarily on dipole-dipole and dipole-induced dipole interactions. Hydrogen bonds were not found to play a predominant role in the viscosity of the crude oils examined. Understanding of the different effects the five intermolecular parameters have on viscosity can lead to the development of novel approaches for the modification of the viscosity of crude oils and their products.

3.5 Predictions from GC/MS Measurements

A simple and rapid method was developed using gas chromatography-mass spectrometry (GC/MS) for the prediction of the properties of crude oils and their boiling fractions.⁵ The method creates a statistical correlation between the known properties of a training set of crude oils and their GC/MS data. The properties of unknown crude oils are thus predicted from the training set and the measured GC/MS data of the unknown crude oils. A major advantage of this method is that the simulated distillation information provided naturally by gas chromatography is coupled to detailed compositional information possible by the mass spectrometer. The method not only provides detailed information rapidly which can be used for the chemometric predictions of the crude oils properties across the boiling range, it can also provide molecular information for the determination of the properties of crude oils and their fractions from first principles. Most importantly, the molecules affecting specific crude oil properties can be determined by the method and the information can be used for the design of

products with desirable properties. The approach, although based on relatively simple low-resolution GC/MS instrumentation, it currently requires skilled operators and a laboratory environment for the performance of tests. Future developments in miniaturized, rugged and portable GC/MS systems are expected to significantly improve the practicality of the approach and provide routine molecular characterization in the field.

3.6 Predictions from NIR Data

Near infrared (NIR) spectroscopic methods have been developed to rapidly determine the properties of crude oils.⁶ The method is used to control the separation of components in crude oil downstream of a well head. Measurements are made at or before the pipeline between the analyzer and the separator. Optimization of the separation process is based on the NIR results. The method is also used to determine crude oil properties (e.g., content of naphtha, gas oil and/or fuel oil). Chemical, physical, physicochemical, optical and mechanical properties can be determined by the method at the same time, from the same oil sampling. The spectroscopic analysis is done in a standard cell maintained at a constant temperature. The analysis is performed in real time or near real time. The absorption of the oil is measured in the region 600-2700 nm. The properties of the oils are then determined by direct, indirect, or statistical correlations with a set of standard oils of known properties. The capability of the method for on line or at line measurements makes it highly suitable for automated control applications. The wavelengths used in the calculations are generally chosen by statistical means. Multiple linear regression, principle component regression, canonic regression and partial least squares statistical methods can be used for the correlations. Most interestingly, a preferred method is the direct comparison of the absorptions of the unknown crude oils with those of a set of standard crude oils of known properties. Unknown crude oils with the nearest absorption values at the same wavelengths to the standards have similar properties to the properties of the nearest standards. The advantage of the direct comparison of absorptions is that there is no need for development of rigorous statistical correlations between the measured NIR data and the known properties of crude oils. Accurate property determination is possible by the direct comparison method, provided that very similar crude oils are present in the database. The simplicity and practicality of the NIR method makes it the most suitable current approach for rapid, on-line prediction of the properties of crude oils. Real time decisions can be made using the method. The main disadvantage over the GC/MS method is the lack of specific information about the molecular makeup of the crude oils. This can be problematic for properties that can be affected by small amounts of molecules (e.g., additives).

NIR has been used for the determination of the total boiling point profiles and densities of crude oils.⁷ 110 crude oils were used for the development of

the correlations. The reproducibility limits of the approach are equivalent to those of the ASTM reference procedures. The correlation coefficients were better than 0.98. The success of the method clearly demonstrates the capabilities of NIR to provide rapid information on critical properties of crude oils.

3.7 Property Determination from First Principles

The optimization of the refinery performance for individual crude oil feedstocks requires the development of simulation and prediction models of the individual refinery processes. Such a model is Quann and Jaffe's Structure-Oriented Lumping.⁸ Individual hydrocarbon molecules are represented by this model, as vectors of incremental structural features that can describe the composition, reactions and properties of petroleum mixtures. The approach allows for the molecular modeling of all refinery processes.

The accuracy and utility of such molecular-based models greatly depend on the availability of detailed molecular information. Most importantly, for timely decision making, real time molecular characterization of petroleum feeds and products would be ideally required for continuous input to the models. Stand-alone NMR and NIR spectroscopic methods are limited due to their inability to identify individual molecules in complex mixtures. Mass spectrometry is more suitable for the characterization of complex petroleum mixtures and it has been extensively applied to that end.⁹ Increased molecular speciation can be obtained by coupling chromatographic means of separation to the spectroscopic detection methods. A multitude of hyphenated analytical methods has been developed for the acquisition of detailed molecular information of petroleum samples.¹⁰ At present, not a single analytical methodology can provide complete characterization of crude oils at the molecular level. Limitations range from the inability of the methods to separate overlapping components to the inability to introduce the heavy petroleum fractions into the analytical instruments. The most successful current approach involves tedious sample preparation procedures, followed by lengthy component separation steps, using advanced analytical instrumentation. Significant future advances in analytical instrumentation will be required for the ideal rapid and complete characterization of crude oils at the molecular level by a single comprehensive hyphenated technique.

4. REFERENCES

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