Faculty of Chemical Engineering and Technology
University of Zagreb

Petroleum Refining and Petrochemical Processes

Crude oil: main properties

Ante Jukić

ajukic@fkit.hr

CRUDE OIL ASSAY

INTRODUCTION

A crude oil assay is essentially the chemical evaluation of crude oil feedstocks by petroleum testing laboratories. Each crude oil type has unique molecular, chemical characteristics.
No crude oil type is identical and there are crucial differences in crude oil quality.

The results of crude oil assay testing provide extensive detailed hydrocarbon analysis data for refiners, oil traders and producers.
Assay data help refineries determine if a crude oil feedstock is compatible for a particular petroleum refinery or if the crude oil could cause yield, quality, production, environmental and other problems.

The assay can be an inspection assay or comprehensive assay.
Testing can include crude oil characterization of whole crude oils and the various boiling range fractions produced from physical or simulated distillation by various procedures.
Information obtained from the petroleum assay is used for detailed refinery engineering and client marketing purposes. Feedstock assay data are an important tool in the refining process.

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.

PPROPERTY MEASUREMENTS / CRUDE INSPECTIONS

1. API Gravity / Density

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** (nowdays, also by digital density meters) 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. 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 <u>extremely low levels</u> 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.

3. Pour Point

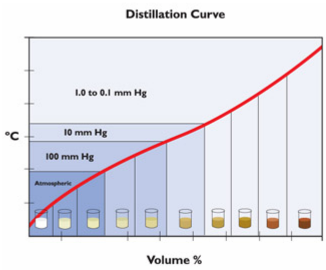
The pour point of a sample is defined as **the temperature normally 3 degrees above the point a sample no longer moves when inverted**. The pour point of a liquid is the lowest temperature at which it becomes semi solid and loses its flow characteristics. In crude oil a high pour point is generally associated with a high paraffin content, typically found in crude deriving from a larger proportion of plant material. 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.

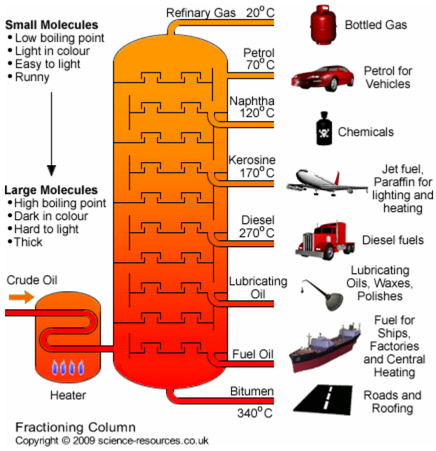
4. Whole Crude Simulated Distillation

This method normally is performed by ASTM D5307. 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.

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 <u>collection of distillation fractions that can be utilized for testing</u>.
While each of the distillations techniques have been standardized by ASTM, <u>cut schemes tend to mimic Refinery product classifications</u> 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.





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.

Table: 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+

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 Hi-vac 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 canattain.

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

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 Hi-vac 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.

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.

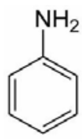
10. Physical Property Test

10.1 API Gravity

This is the most common measurement performed on petroleum products; density is expressed in terms of API gravity.
This measurement determines the weight of a crude oil per unit volume at 60 °F, normally measured by the Hydrometer method ASTM D 287.

10.2 Aniline Point

This point is defined as the lowest temperature at which aniline is soluble in a specified amount of sample.
This measure is used to determine the solvency of the hydrocarbons Typically paraffinic hydrocarbons have higher aniline points than aromatic hydrocarbons. This method is usually performed under the guidelines of ASTM D 611.
Aniline point can be used to determine the quality of ignition in diesel cuts.



10.3 Cloud Point

This is defined as the temperature at which a haze appears in a sample which is attributed to the **formation of wax crystals**.
Cloud point data is used to determine the tendency of small orifices to plug in cold operating temperatures, normally measured on middle distillate cuts. This property can 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.

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.

10. Physical Property Test

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 ICPCES*.
X-ray fluorescence can be a viable technique depending on the concentration.

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.

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.

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.

10. Physical Property Test

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.

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 P-N-A molecules in oil fractions.

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.

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.

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.

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.

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 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.

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.

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.

11 Asphalt Properties

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.

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.

The Prediction of Crude Assay Properties

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 providetimely information for rapid decision making.

The Prediction of Crude Assay Properties

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.

Analytical approaches for the prediction of the properties of crude oils:

- Predictions from Measurement of Selected Whole Crude Oil Properties
- Predictions from NMR Measurements
- Predictions from Chromatographic Data
- Predictions from GC/MS Measurements
- Predictions from NIR Data
- Property Determination from First Principles
  (molecular-based model - greatly depend on the availability of detailed molecular information)