Handbook of Petroleum Processing

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Chapter 1

An introduction to crude oil and its processing

D.S.J. Jones

The wheel, without doubt, was man's greatest invention. However until the late 18th century and early 19th century the motivation and use of the wheel was limited either by muscle power, man or animal, or by energy naturally occurring from water flow and wind. The invention of the steam engine provided, for the first time, a motive power independent of muscle or the natural elements. This ignited the industrial revolution of the 19th century, with its feverish hunt for fossil fuels to generate the steam. It also initiated the development of the mass production of steel and other commodities.

Late in the 19th century came the invention of the internal combustion engine with its requirement for energy derived from crude oil. This, one can say, sparked the second industrial revolution, with the establishment of the industrial scene of today and its continuing development. The petroleum products from the crude oil used initially for the energy required by the internal combustion engine, have mushroomed to become the basis and source of some of our chemical, and pharmaceutical products.

The development of the crude oil refining industry and the internal combustion engine have influenced each other during the 20th century. Other factors have also contributed to accelerate the development of both. The major ones of these are the increasing awareness of environmental contamination, and the increasing demand for faster travel which led to the development of the aircraft industry with its need for higher quality petroleum fuels. The purpose of this introductory chapter is to describe and define some of the basic measures and parameters used in the petroleum refining industry. These set the stage for the detail examination of the industry as a whole and which are provided in subsequent chapters of this encyclopedia.

The composition and characteristics of crude oil

Crude oil is a mixture of literally hundreds of hydrocarbon compounds ranging in size from the smallest, methane, with only one carbon atom, to large compounds

containing 300 and more carbon atoms. A major portion of these compounds are paraffins or isomers of paraffins. A typical example is butane shown below:

Н Н Н Н H-C- $-\dot{C}$ $-\dot{C}$ -H Normal butane (denoted as nC4) Н Н Н Н Н Η· C Н Н Isobutane (denoted as iC4) C - H Н н Н Н

Most of the remaining hydrocarbon compounds are either cyclic paraffins called naphthenes or deeply dehydrogenated cyclic compounds as in the aromatic family of hydrocarbons. Examples of these are shown below:



Only the simplest of these homologues can be isolated to some degree of purity on a commercial scale. Generally, in refining processes, isolation of relatively pure

products is restricted to those compounds lighter than C7's. The majority of hydrocarbon compounds present in crude oil have been isolated however, but under delicate laboratory conditions. In refining processes the products are identified by groups of these hydrocarbons boiling between selective temperature ranges. Thus, for example a naphtha product would be labeled as a 90°C to 140°C cut.

Not all compounds contained in crude oil are hydrocarbons. There are present also as impurities, small quantities of sulfur, nitrogen and metals. By far the most important and the most common of these impurities is sulfur. This is present in the form of hydrogen sulfide and organic compounds of sulfur. These organic compounds are present through the whole boiling range of the hydrocarbons in the crude. They are similar in structure to the hydrocarbon families themselves, but with the addition of one or more sulfur atoms. The simplest of these is ethyl mercaptan which has a molecular structure as follows:

$$H H H H H C - C - SH Ethyl Mercaptan H H H H H$$

The higher carbon number ranges of these sulfur compounds are thiophenes which are found mostly in the heavy residuum range and disulfides found in the middle distillate range of the crude. The sulfur from these heavier sulfur products can only be removed by converting the sulfur to H_2S in a hydrotreating process operating under severe conditions of temperature and pressure and over a suitable catalyst. The lighter sulfur compounds are usually removed as mercaptans by extraction with caustic soda or other suitable proprietary solvents.

Organic chloride compounds are also present in crude oil. These are not removed as such but metallic protection is applied against corrosion by HCl in the primary distillation processes. This protection is in the form of monel lining in the sections of the process most vulnerable to chloride attack. Injection of ammonia is also applied to neutralize the HCl in these sections of the equipment.

The most common metal impurities found in crude oils are nickel, vanadium, and sodium. These are not very volatile and are found in the residuum or fuel oil products of the crude oil. These are not removed as metals from the crude and normally they are only a nuisance if they affect further processing of the oil or if they are a deterrent to the saleability of the fuel product. For example, the metals cause severe deterioration in catalyst life of most catalytic processes. In the quality of saleable fuel oil products high concentrations of nickel and vanadium are unacceptable in fuel oils used in the production of certain steels. The metals can be removed with the glutinous portion of the fuel oil product called asphaltenes. The most common process used to accomplish this is the extraction of the asphaltenes from the residue oils using propane as solvent.

Nitrogen, the remaining impurity is usually found as dissolved gas in the crude or as amines or other nitrogen compounds in the heavier fractions. It is a problem only with certain processes in naphtha product range (such as catalytic reforming). It is removed with the sulfur compounds in this range by hydrotreating the feed to these processes.

Although the major families or homologues of hydrocarbons found in all crude oils as described earlier are the paraffins, cyclic paraffins and aromatics, there is a fourth group. These are the unsaturated or olefinic hydrocarbons. They are not naturally present in any great quantity in most crude oils, but are often produced in significant quantities during the processing of the crude oil to refined products. This occurs in those processes which subject the oil to high temperature for a relatively long period of time. Under these conditions the saturated hydrocarbon molecules break down permanently losing one or more of the four atoms attached to the quadrivalent carbon. The resulting hydrocarbon molecule is unstable and readily combines with itself (forming double bond links) or with similar molecules to form polymers. An example of such an unsaturated compound is as follows:

$$\begin{array}{c|c} H & H \\ | & | \\ H - C = C - H & \text{Ethylene} \end{array}$$

Note the double bond in this compound linking the two carbon atoms.

Although all crude oils contain the composition described above, rarely are there two crude oils with the same characteristics. This is so because every crude oil from whatever geographical source contains different quantities of the various compounds that make up its composition. Crude oils produced in Nigeria for example would be high in cyclic paraffin content and have a relatively low specific gravity. Crude drilled in some of the fields in Venezuela on the other hand would have a very high gravity and a low content of material boiling below 350°C. The following table summarizes some of the crude oils from various locations (Table 1.1).

Worthy of note in the above table is the difference in the character of the various crudes that enables refiners to improve their operation by selecting the best crude or crudes that meet their product marketing requirements. For example, where a refining product slate demands a high quantity of 'no lead' gasoline and a modest outlet for fuel oils then a crude oil feed such as Hassi Messaoud would be a prime choice. Its selection provides a high naphtha yield with a high naphthene content as catalytic reforming feedstock. Fuel oil in this case also is less than 50% of the barrel. The Iranian light crude would also be a contender but for the undesirably high metal content of the fuel oil (Residuum).

In the case of a good middle of the road crude, Kuwait or the Arabian crude oils offer a reasonably balanced product slate with good middle distillate quality and yields.

IdDIE 1.1. CIIAL	acteristics of	source crude (UIIS IFUII VAL	ious world-wide	locations						
	Arabian light	Arabian heavy	Iranian light	Iranian heavy (Gach Saran)	Iraq (Kirkuk)	Kuwait	Algerian (Hassi Messaoud)	Libyan (Brega)	Nigerian (Bonny medium)	North Sea (Ekofisk)	South American (Bachequero)
% vol. boiling below 350°C	54.0	46.5	55.0	53.0	61.1	49.0	75.2	64.0	54.5	61.2	30.0
gravity, API sulfur. wt%	33.4 1.8	28.2 2.84	33.5 1.4	30.8 1.6	35.9 1.95	31.2 2.5	44.7 0.13	40.4 0.21	26.0 0.23	36.3 0.21	16.8 2.4
PONA of heavy nap	ohtha, vol%										
cut, °C	100 - 150	100 - 150	149–204	149–204	100 - 150	100 - 150	95-175	100 - 150	100 - 150	100 - 200	93-177
paraffins	69.5	70.3	54.0	50	69.0	67.9	56.5	53.0	27.5	56.5	27.6
olefins	I	I	I	Ι	265 ppm	I	I	20 ppm	1.5	I	I
naphthenes	18.2	21.4	30.0	35	21.0	22.1	32.9	39.3	57.0	29.5	58.5
aromatics	12.3	8.3	16.0	15	9.8	10.0	10.6	7.7	14.0	14.0	13.9
Metals in residuum											
residuum temp. °C vanadium,	>565	>565	>538	>538	>370	>370	>350	>570	>535	>350	>350
wt ppm nickel,	94	171	188	404	58	59	ŝ	24	L	1.95	437
wt ppm	22	53	70	138	<3	18	<5	32	52	5.04	75
		1									

Table 1.1. Characteristics of some crude oils from various world-wide locations

The Bachequero pour point is 16°C.

For bitumen manufacture and lube oil manufacture the South American crude oils are formidable competitors. Both major crudes from this area, Bachequero, the heavier crude and Tia Juana, the lighter, are highly acidic (Naphthenic acids) which enhance bitumen and lube oil qualities. There is a problem with these crude oils however as naphthenic acid is very corrosive in atmospheric distillation columns, particularly in the middle distillate sections. Normal distillation units may require relining of sections of the tower with 410 stainless steel if extended processing of these crude oils is envisaged.

Refiners often mix selective crude oils to optimize a product slate that has been programmed for the refinery. This exercise requires careful examination of the various crude assays (data compilation) and modeling the refinery operation to set the crude oil mix and its operating parameters.

The crude oil assay

The crude oil assay is a compilation of laboratory and pilot plant data that define the properties of the specific crude oil. At a minimum the assay should contain a distillation curve for the crude and a specific gravity curve. Most assays however contain data on pour point (flowing criteria), sulfur content, viscosity, and many other properties. The assay is usually prepared by the company selling the crude oil, it is used extensively by refiners in their plant operation, development of product schedules, and examination of future processing ventures. Engineering companies use the assay data in preparing the process design of petroleum plants they are bidding on or, having been awarded the project, they are now building.

In order to utilize the crude oil assay it is necessary to understand the data it provides and the significance of some of the laboratory tests that are used in its compilation. Some of these are summarized below, and are further described and discussed in other chapters of the Handbook.

The true boiling point curve

This is a plot of the boiling points of almost pure components, contained in the crude oil or fractions of the crude oil. In earlier times this curve was produced in the laboratory using complex batch distillation apparatus of a hundred or more equilibrium stages and a very high reflux ratio. Nowadays this curve is produced by mass spectrometry techniques much quicker and more accurately than by batch distillation. A typical true boiling point curve (TBP) is shown in Figure 1.10.

The ASTM distillation curve

While the TBP curve is not produced on a routine basis the ASTM distillation curves are. Rarely however is an ASTM curve conducted on the whole crude. This type

6

of distillation curve is used however on a routine basis for plant and product quality control. This test is carried out on crude oil fractions using a simple apparatus designed to boil the test liquid and to condense the vapors as they are produced. Vapor temperatures are noted as the distillation proceeds and are plotted against the distillate recovered. Because only one equilibrium stage is used and no reflux is returned, the separation of components is poor. Thus, the initial boiling point (IBP) for ASTM is higher than the corresponding TBP point and the final boiling point (FBP) of the ASTM is lower than that for the TBP curve. There is a correlation between the ASTM and the TBP curve, and this is dealt with later in this chapter.

API gravity

This is an expression of the density of an oil. Unless stated otherwise the API gravity refers to density at 60° F (15.6°C). Its relationship with specific gravity is given by the expression

$$API^{\circ} = \frac{141.5}{\text{sp.gr.}} - 131.5$$

Flash points

The flash point of an oil is the temperature at which the vapor above the oil will momentarily flash or explode. This temperature is determined by laboratory testing using an apparatus consisting of a closed cup containing the oil, heating and stirring equipment, and a special adjustable flame. The type of apparatus used for middle distillate and fuel oils is called the Pensky Marten (PM), while the apparatus used in the case of Kerosene and lighter distillates is called the Abel. Reference to these tests are given later in this Handbook, and full details of the tests methods and procedures are given in ASTM Standards Part 7, Petroleum products and Lubricants. There are many empirical methods for determining flash points from the ASTM distillation curve. One such correlation is given by the expression

Flash point
$$^{\circ}F = 0.77$$
 (ASTM 5% $^{\circ}F - 150^{\circ}F$)

Octane numbers

Octane numbers are a measure of a gasoline's resistance to knock or detonation in a cylinder of a gasoline engine. The higher this resistance is the higher will be the efficiency of the fuel to produce work. A relationship exists between the antiknock characteristic of the gasoline (octane number) and the compression ratio of the engine in which it is to be used. The higher the octane rating of the fuel then the higher the compression ratio of engine in which it can be used.

By definition, an octane number is that percentage of isooctane in a blend of isooctane and normal heptane that exactly matches the knock behavior of the gasoline. Thus, a 90 octane gasoline matches the knock characteristic of a blend containing 90% isooctane and 10% *n*-heptane. The knock characteristics are determined in the laboratory using

a standard single cylinder test engine equipped with a super sensitive knock meter. The reference fuel (isooctane blend) is run and compared with a second run using the gasoline sample. Details of this method are given in the ASTM standards, Part 7 Petroleum products and Lubricants.

Two octane numbers are usually determined. The first is the research octane number (ON res or RON) and the second is the motor octane number (ON mm or MON). The same basic equipment is used to determine both octane numbers, but the engine speed for the motor method is much higher than that used to determine the research number. The actual octane number obtained in a commercial vehicle would be somewhere between these two. The significance of these two octane numbers is to evaluate the sensitivity of the gasoline to the severity of operating conditions in the engine. The research octane number is usually higher than the motor number, the difference between them is termed the 'sensitivity of the gasoline.'

Viscosity

The viscosity of an oil is a measure of its resistance to internal flow and is an indication of its lubricating qualities. In the oil industry it is usual to quote viscosities either in centistokes (which is the unit for kinematic viscosity), seconds Saybolt universal, seconds Saybolt furol, or seconds Redwood. These units have been correlated and such correlations can be found in most data books. In the laboratory, test data on viscosities is usually determined at temperatures of 100° F, 130° F, or 210° F. In the case of fuel oils temperatures of 122° F and 210° F are used.

Cloud and pour points

Cloud and Pour Points are tests that indicate the relative coagulation of wax in the oil. They do not measure the actual wax content of the oil. In these tests, the oil is reduced in temperature under strict control using an ice bath initially and then a frozen brine bath, and finally a bath of dry ice (solid CO_2). The temperature at which the oil becomes hazy or cloudy is taken as its cloud point. The temperature at which the oil ceases to flow altogether is its pour point.

Sulfur content

This is self explanatory and is usually quoted as %wt for the total sulfur in the oil.

Assays change in the data they provide as the oils from the various fields change with age. Some of these changes may be quite significant and users usually request updated data for definitive work, such as process design or evaluation. The larger producers of the crude oil provide laboratory test services on an 'on going' basis for these users.

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The next few sections of this chapter illustrate how the assay data and basic petroleum refining processes are used to develop a process configuration for an oil refining complex.

Other basic definitions and correlations

As described earlier the composition of crude oil and its fractions are not expressed in terms of pure components, but as 'cuts' expressed between a range of boiling points. These 'cuts' are further defined by splitting them into smaller sections and treating those sections as though they were pure components. As such, each of these components will have precise properties such as specific gravity, viscosity, mole weight, pour point, etc. These components are referred to as pseudo components and are defined in terms of their mid boiling point.

Before describing in detail the determination of pseudo components and their application in the prediction of the properties of crude oil fractions it is necessary to define some of the terms used in the crude oil analysis. These are as follows:

Cut point

A cut point is defined as that temperature on the whole crude TBP curve that represents the limits (upper and lower) of a fraction to be produced. Consider the curve shown in Figure 1.1 of a typical crude oil TBP curve.



Figure 1.1. Cut points and end points.

A fraction with an upper cut point of 100° F produces a yield of 20% volume of the whole crude as that fraction. The next adjacent fraction has a lower cut point of 100° F and an upper one of 200° F this represents a yield of 30-20% = 10% volume on crude

End points

While the cut point is an ideal temperature used to define the yield of a fraction, the end points are the actual terminal temperatures of a fraction produced commercially. No process has the capability to separate perfectly the components of one fraction from adjacent ones. When two fractions are separated in a commercial process some of the lighter components remain in the adjacent lighter fraction. Likewise some of the heavier components in the fraction find their way into the adjacent heavier fraction. Thus, the actual IBP of the fraction will be lower than the initial cut point, and its FBP will be higher than the corresponding final cut point. This is also shown in Figure 1.1.

Mid boiling point components

In compiling the assay narrow boiling fractions are distilled from the crude, and are analyzed to determine their properties. These are then plotted against the mid boiling point of these fractions to produce a smooth correlation curve. To apply these curves for a particular calculation it is necessary to divide the TBP curve of the crude, or fractions of the crude, into mid boiling point components. To do this, consider Figure 1.2. For the first component take an arbitrary temperature point A. Draw a horizontal line through this from the 0% volume. Extend the line until the area between the line and the curve on both sides of the temperature point A are equal. The length of the horizontal line measures the yield of component A having a mid boiling point A °F. Repeat for the next adjacent components.

Mid volume percentage point components

Sometimes the assay has been so constructed as to correlate the crude oil properties against components on a mid volume percentage basis. In using such data as this the TBP curve is divided into mid volume point components. This is easier than the mid boiling point concept and requires only that the curve be divided into a number of volumetric sections. The mid volume figure for each of these sections is merely the arithmetic mean of the volume range of each component.

Using these definitions the determination of the product properties can proceed using the distillation curves for the products, the pseudo component concept, and the assay data. This is given in the following items:

Predicting TBP and ASTM curves from assay data

The properties of products can be predicted by constructing mid boiling point components from a TBP curve and assigning the properties to each of these components.

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Figure 1.2. Example of mid boiling points.

These assigned properties are obtained either from the assay data, known components of similar boiling points, or established relationships such as gravity, molecular weights, and boiling points. However, before these mid boiling points (pseudo) components can be developed it is necessary to know the shape of the product TBP curve. The following is a method by which this can be achieved. Good, Connel et al. (1) accumulated data to relate the ASTM end point to a TBP cut point over the light and middle distillate range of crude. Their correlation curves are given in Figure 1.3, and are self explanatory. Thrift (2) derived a probable shape of ASTM data. The probability graph that he developed is given as Figure 1.4. The product ASTM curve from a well designed unit would be a straight line from 0 %vol to 100 %vol on this graph. Using these two graphs it is possible now to predict the ASTM distillation curve of a product knowing only its TBP cut range.



E & F ASTM End Points Vs TBP Cut Point 300 ml STD col & 5 ft Packed Towers.

G 90% vol temp Vs 90% vol TBP cut (All Fractions).

Figure 1.3. Correlation between TBP and ASTM end points.

An example of this calculation is given below:

It is required to predict the ASTM distillation curve for Kerosene, cut between $387^{\circ}F$ and $432^{\circ}F$ cut points on Kuwait crude.



Figure 1.4. ASTM distillation probability curves.

Solution:

Yield on crude = 3.9% vol Cut range = 27.3-31.2% vol on crude. 90%Vol of cut = 30.81 which is = $430^{\circ}F$ From Figure 1.3, curve B ASTM end point = $432 - 13^{\circ}F = 419^{\circ}F$ From Figure 1.3, curve G ASTM 90% point = $430 - 24^{\circ}F = 406^{\circ}F$

These two points are plotted in Figure 1.4 and a straight line drawn through them to define the probable ASTM distillation of the cut. This is plotted linearly in Figure 1.5



Figure 1.5. Comparison between calculated ASTM curve and lab data.

and can be seen to compare well with laboratory results of the actual product from a crude distillation unit.

Developing the TBP curve and the EFV curve from the ASTM distillation curve

Using a product ASTM distillation curve developed as shown above the TBP curve is developed as follows.

Converting the product ASTM distillation to TBP

Most crude distillation units take a full range naphtha cut as the overhead product. This cut contains all the light ends, ethane through pentanes, in the crude and of course the heavier naphtha cut. All the light ends are in solution, therefore it is not possible to prepare a meaningful ASTM distillation on this material directly. Two routes can be adopted in this case, the first is to take naphtha samples of the heavy naphtha and debutanized light naphtha from downstream units. Alternatively the sample can be subject to light end analysis in the lab such as using POD apparatus (Podbielniak) and carrying out an ASTM distillation on the stabilized sample. It is the second route that is chosen for this case.

There are two well-proven methods for this conversion. The first is by Edmister (3) and given in his book *Applied Thermodynamics* and the second by Maxwell (4) in his book *Data Book on Hydrocarbons*. The correlation curves from both these sources



Figure 1.6. ASTM-TBP correlation-Edmister method.

are given as Figures 1.6 and 1.7. In this exercise Edmister's method and correlation will be used.

The ASTM distillation is tabulated as the temperature for IBP, 10%, 20% through to the FBP. IBP is the Initial Boiling Point (equivalent to 0% over) and the FBP is the Final Boiling Point (equivalent to 100% vol over). The multiples of 10% reflect the volume distilled and the temperature at which each increment is distilled. Using Figure 1.6 the 50% vol TBP point (in degrees Fahrenheit) is calculated from the 50% vol point of the ASTM distillation.





^{**} $\Delta t'$ is the deparature of the actual flash and distillation curves from their respective reference lines. While the individual ($\Delta t'$)'s may be either plus or minus, the ratio is always poistive.

Figure 1.7. EFV-TBP correlation-Maxwell method.

	ASTM (Lab Data)		TBP (from Figure 1.6)	
	°F	$\Delta^\circ F$	$\Delta^{\circ}F$	°F
IBP	424	29	61	361
10 %vol	453	31	52	423
30 %vol	484	18	52	475
50 %vol	502			507
70 %vol	504	2	31	538
90 %vol	536	32	41	579
FBP	570	34	40	619

Table 1.2. Converting ASTM to TBP distillation

Figure 1.6 is then used to determine the TBP temperature difference from the ASTM temperature difference for the 0-10% vol, 10-30% vol, 30-50% vol, 50-70% vol, 70-90% vol, and 90-100% vol. Moving from the established 50\% vol TBP figure and using the temperature differences given by Figure 1.6 the TBP temperatures at 0, 10, 30, 50, 70, 90, and 100\% vol are obtained (Table 1.2).

Developing the equilibrium flash vaporization curve

The Maxwell curves given as Figure 1.7 are used to develop the equilibrium flash vaporization curve (EFV) from the TBP. The EFV curve gives the temperature at which a required volume of distillate will be vaporized. This distillate vapor is always in equilibrium with its liquid residue. The development of the EFV curve is always at atmospheric pressure. Other temperature and pressure related conditions may be determined using the vapor pressure curves or constructing a phase diagram.

The TBP reference line (DRL) is first drawn by a straight line through the 10% vol point and the 70% vol point on the TBP curve. The slope of this line is determined as temperature difference per volume percent. This data are then used to determine the 50% volume temperature of a flash reference line (FRL). The curve in Figure 1.7 relating Δt_{50} (DRL–FRL) to DRL slope is used for this. Finally, the curve on Figure 1.7 relating the ratio of temperature differences between the FRL and flash curve (EFV) from that for the TBP to DRL is applied to each percent volume. From this the atmospheric EFV curve is drawn.

A sample calculation for the compilation of the EFV curve follows. Note the TBP curve is used to define product yields while the EFV curve is used to define temperature/pressure conditions in distillation. This example uses the TBP curve developed above as a starting point (Table 1.3).

The resulting TBP curves and EFV curves are shown in Figure 1.8.