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Kolmetz Handbook Of Process Equipment Design

CRUDE OIL PROPERTIES

(ENGINEERING DESIGN GUIDELINES)

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INTRODUCTION

Scope

Petroleum exploration is largely concerned with the search for oil and gas, two of the chemically and physically diverse group of compounds termed the hydrocarbons. Physically, hydrocarbons change grades from gases, via liquids and plastic substances, to solids. The hydrocarbon gases include dry gas (methane) and the wet gases (ethane, propane, butane, etc.). Condensates are hydrocarbons that are gaseous in the subsurface, but condense to liquid when they are cooled at the surface. Liquid hydrocarbons are termed oil, crude oil, or just crude, to differentiate them from refined petroleum products[13].

Crude oil, liquid petroleum that is found accumulated in various porous rock formations in Earth's crust and is extracted for burning as fuel or for processing into chemical products. Crude oils are customarily characterized by the type of hydrocarbon compound that is most prevalent in them. They are paraffins, naphthenes, and aromatics.

Paraffins are the most common hydrocarbons in crude oil; certain liquid paraffins are the major constituents of gasoline (petrol) and are therefore highly valued. Naphthenes are an important part of all liquid refinery products, but they also form some of the heavy asphalt like residues of refinery processes. Whereas, aromatics generally constitute only a small percentage of most crudes. The most common aromatic in crude oil is benzene, a popular building block in the petrochemical industry[11]. Refinery crude base stocks usually consist of mixtures of two or more different crude oils.

Crude oils are complex mixtures containing many different hydrocarbon compounds that vary in appearance and composition from one oil field to another. Crude oils range in consistency from water to tar-like solids, and in color from clear to black. An average crude oil contains about 84% carbon, 14% hydrogen, 1%-3% sulfur, and less than 1% each of nitrogen, oxygen, metals, and salts[14].

In most refineries, this process is carried out in two stages. The oil is first heated to the maximum temperature allowable for the crude being processed and for the operation being practiced and then fed to a fractionating tower which operates at slightly above atmospheric pressure. It yields several distillate products and a bottoms product. This tower is usually called the atmospheric tower.

This module provides an overview one of crude oil properties. The knowledge of basic crude oil, the composition, pretreatment of crude oil before to be processed in refinery, crude assay, how to analyze crude oil and the products, and refineries. This module will help develop the basics of crude oil and the refineries.

This module is also completed crude assay for example and reference. It is available in appendix. These properties are important in design and operation of almost every piece of equipment in the petroleum industry. Crude oil characteristics plays important role in the product distribution, processing scheme and quality of product.

General Consideration

A. Basic of Crude Oil

Crude oil is a complex liquid mixture made up of a vast number of hydrocarbon compounds that consist mainly of carbon and hydrogen in differing proportions[2]. Refining adds value by converting crude oil (which in itself has little end use value) into a range of refined products, including transportation fuels. The primary economic objective in refining is to maximaze the value added in converting crude oil into finished products.

Petroleum refineries are large, capital intensive manufacturing facilities with extremely complex processing schemes. They convert crude oils and other input streams into dozens of refined (co-) products as shown in figure 1[14]:

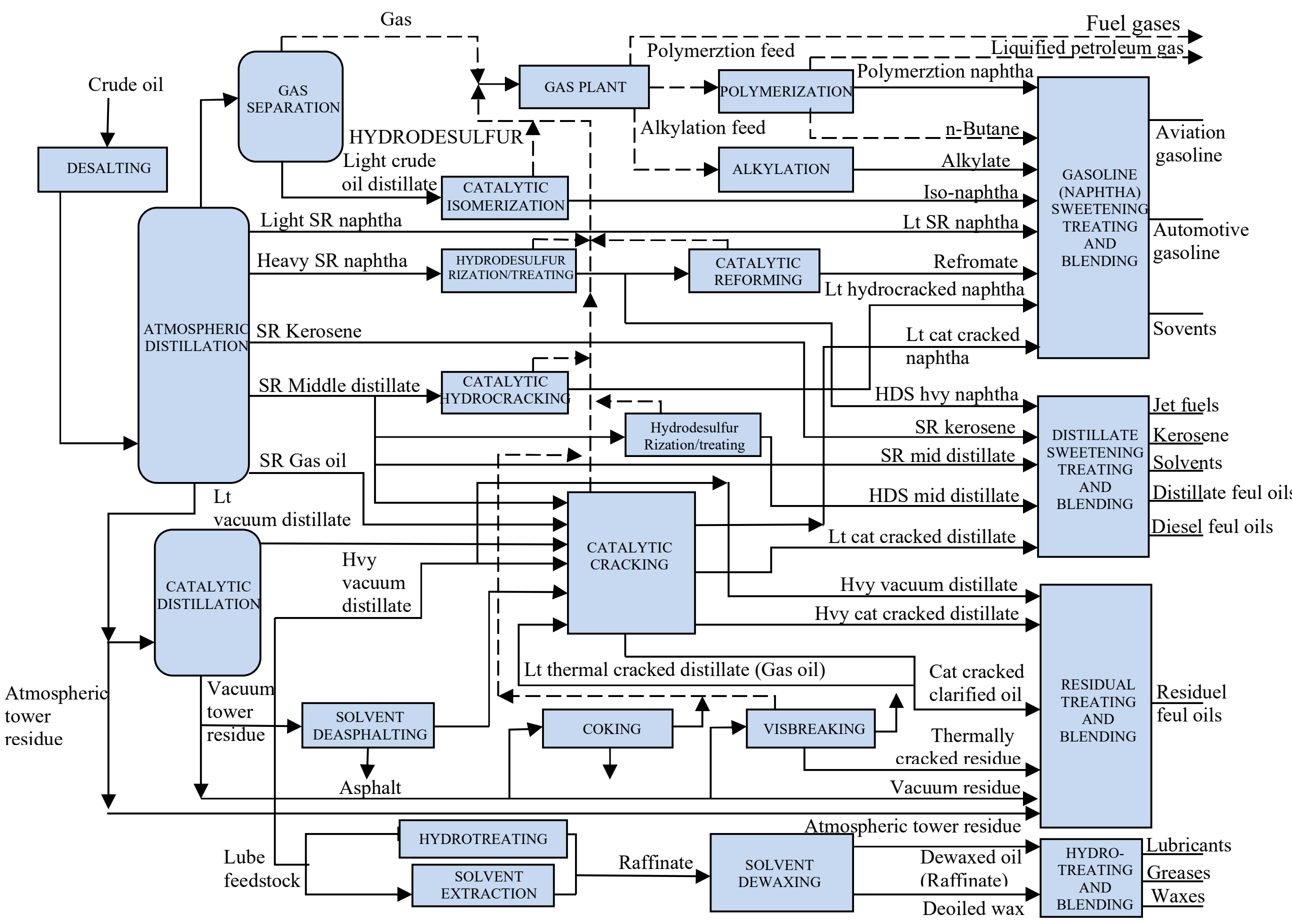


Figure 1 : refinery process

B. Origin of Hydrocarbons

It is generally agreed that crude petroleum oil was formed from decaying plants and vegetables and dead animals and converted to oil by the action of high pressure and high temperature under the earth surface, and by the action of the biological activities of micro-organisms. Organic materials of plant or animal origin accumulate in the lowest places, usually in the crevices, low-lying land, sea bed, coral reefs, etc., and are gradually buried under the surface of Earth. Thus, huge amounts of organic matter are trapped layer after layer in the earth crust and rock.

Rocks that bear these organic layers are called sedimentary rocks. Several kilometres below the earth surface, organic sediments are decayed biologically to a mass, known as kerogen, which has a very high mass of organic-to-inorganic ratio favourable for conversion to hydrocarbon.

The temperature of Earth increases with depth (geothermal gradient) at the rate of approximately 30°C per kilometre. Thus, at a depth of 4–5 km, called kitchen by geologists, temperatures of 120°C–150°C exist where kerogen is converted to hydrocarbon oil under very high pressure of rocks and soil. But this conversion takes millions of years (geological time period) to complete.

Methane is also formed thermogenically (i.e., thermal conversion of kerogen) along with biogenic methane already present before the formation of crude oil. Migration of oil with gas occurs within the rock layers by the pressure gradient from high to low pressure zones. The formation of crude (or crude deposit) oil has been found in the sedimentary porous rock layers trapped under the hard and impervious igneous rock layers. Crude oil and gas accumulate in the pores of the sedimentary rocky layer as shown in Figure 2.

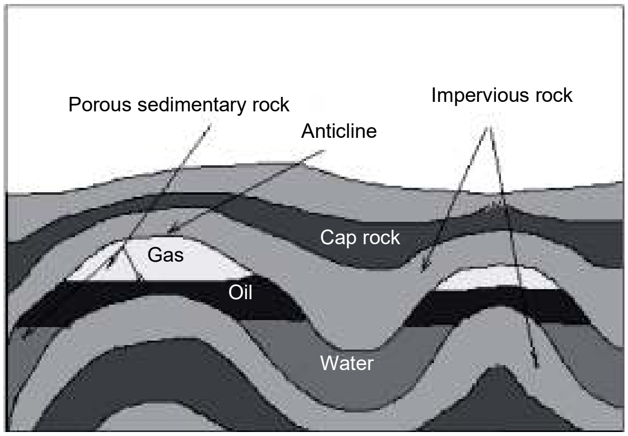


Figure 2 : oil and gas accumulate in the pores of the sedimentary rocky layer

C. Composition of Crude Oils

Overall properties of crude oils are dependent upon their chemical composition and structure. Not all compounds contained in crude oil are hydrocarbons. There are present also as impurities, small quantities of sulfur, nitrogen and metals. The composition of crude oil, on an elemental basis, falls within certain ranges regardless of its origin. Table 1 shows that carbon and hydrogen contents vary within narrow ranges.

Table 1: elemental composition of crude oils

Element	Composition (wt%)
Carbon	83.0 – 87.0
Hydrogen	10.0 – 14.0
Sulphur	0.05 – 6.0
Nitrogen	0.1 – 0.2
Oxygen	0.05 – 2.0
Ni	<120 ppm
V	< 1200 ppm

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 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.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[4].

In fact, there are three main classes of hydrocarbons. These are based on the type of carbon–carbon bonds present. These classes are[2]:

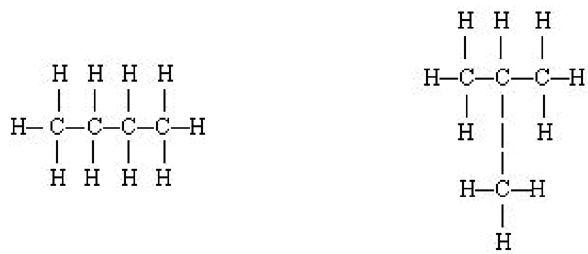
1. Saturated hydrocarbons contain only carbon–carbon single bonds. They are known as paraffins (or alkanes) if they are acyclic, or naphthenes (or cycloalkanes) if they are cyclic.
2. Unsaturated hydrocarbons contain carbon–carbon multiple bonds (double, triple or both). These are unsaturated because they contain fewer hydrogens per carbon than paraffins. Unsaturated hydrocarbons are known as olefins. Those that contain a carbon–carbon double bond are called alkenes, while those with carbon–carbon triple bond are alkyenes.
3. Aromatic hydrocarbons are special class of cyclic compounds related in structure to benzene.

The refining process also rearranges their structures and bonding patterns into different hydrocarbon molecules and compounds. Therefore, it is the type of hydrocarbon (paraffinic, naphthenic, or aromatic) rather than its specific chemical compounds that is significant in the refining process. The three principal groups or series of hydrocarbon compounds that occur naturally in crude oil can be described as follow :

a. Paraffins

The paraffinic series of hydrocarbon compounds found in crude oil have the general formula C_nH_{2n+2} and can be either straight chains (normal) of carbon atoms in lighter fractions of crude oil (gasses and paraffin waxes) or branched chains (isomers) in heavier fractions.

Examples of straight chain paraffin molecule (Butane) and branched paraffin molecule (Isobutane) with same chemical formula (C_4H_{10}) are given as follow :



a. Butane b. Isobutane

Figure 3 : example of paraffins

b. Aromatics

Aromatics are unsaturated ring-type (cyclic) compounds which react readily because they have carbon atoms that are deficient in hydrogen. All aromatics have at least one benzene ring as part of their molecular structure. The one-ring compounds are most abundant and are referred to collectively as BTEX (Benzene, Toluene, Ethyl Benzene, Xylene). Naphthalenes are fused double-ring aromatic compounds. The most complex aromatics, polynuclears (three or more fused aromatic rings) or polycyclic aromatic hydrocarbons (PAHs), are found in heavier fractions of crude oil.

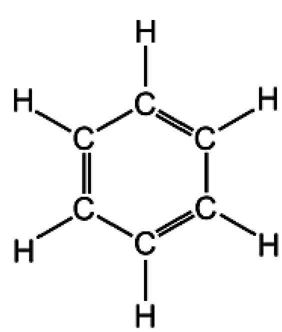


Figure 4 : example of aromatics; Benzene

c. Naphthenes

Naphthenes are saturated hydrocarbon groupings with the general formula C_nH_{2n}, arranged in the form of closed rings (cyclic) and found in all fractions of crude oil except the very lightest. Single-ring naphthenes (monocycloparaffins) with five and six carbon atoms predominate, with two-ring naphthenes (dicycloparaffins) found in the heavier ends of naphtha[14].

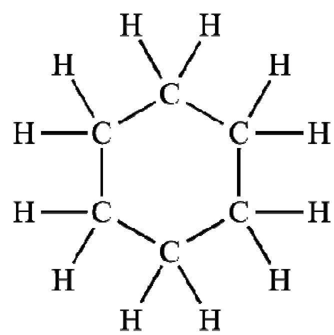


Figure 5 : example of naphthenes; Cyclohexane

The example of detailed crude oil composition is given in table 2.

Table 2 : example of detailed crude oil composition[10]

Paraffins	Naphthenes	Aromatics
All normal paraffins to $C_{10}H_{22}$	Cyclopentane	Benzene
Isobutane	Cyclohexane	Toluene
2-Methylbutane	Methylcyclopentane	Ethylbenzene

Table 2 Cont'd

Paraffins	Naphthenes	Aromatics
2,3-Dimethylbutane	1,1-Dimethylcyclopentane	Xylene
2-Methylpenthane	Methylcyclohexane	1,2,4-Trimethylbenzene
3-Methylpenthane	1,3-Dimethylcyclohexane	
2-Methylhexane	1,2,4-Trimethylcyclohexane	
3-Methylhexane		
2-Methylheptane		
2,6-Dimethylheptane		
2-Methyloctane		

The proportions of the various hydrocarbon classes, their carbon number distribution, and the concentration of hetero-elements in a given crude oil determine the yields and qualities of the refined products that a refinery can produce from that crude, and hence the economic value of the crude. Different crude oils require different refinery facilities and operations to maximize the value of the product slates that they yield[17].

In fact, 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 compound 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 3 : characteristics of some crude oils from various world-wide locations

Parameter	Arabian heavy	Kuwait	South America (Bachequero)
% vol. boiling below 350°C	46.5	49.0	30.0
gravity, API	28.2	31.2	16.8
sulfur, wt%	2.84	2.5	2.4
PONA of heavy naphtha, vol%			
cut, ◦C	100–150	100–150	93–177
paraffins	70.3	67.9	27.6
olefins	-	-	-
naphthenes	21.4	22.1	58.5
aromatics	8.3	10.0	13.9
Metals in residuum			
residuum temp. ◦C	>565	>370	>350
vanadium, wt ppm	171	59	437
nickel, wt ppm	53	18	75

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.

D. Types of Composition

Based on the nature of petroleum mixture, there are several ways to express the composition of a petroleum mixture. Some of the most important types of composition are given below :

- PONA (paraffins, olefins, naphthenes, and aromatics)
- PNA (paraffins, naphthenes, and aromatics)
- PIONA (paraffins, isoparaffins, olefins, naphthenes, and aromatics)
- SARA (saturates, aromatics, resins, and asphalthenes)
- Elemental analysis (C, H, S, N, O)

Since most petroleum fractions are free of olefins, the hydrocarbon types can be expressed in terms of only PINA and if paraffins and isoparaffins are combined a fraction is simply expressed in terms of PNA composition. This type of analysis is useful for light and narrow boiling range petroleum products such as distillates from atmospheric crude distillation units[6].

E. Types of Crude Oils

The petroleum industry often characterizes crude oils according to their geographical source. They are comprised to be light crude oils and heavy crude oils.

- Light crude oil

  Lighter crudes contain higher proportions of small molecules, which the refinery can process into gasoline, jet fuel, and diesel (for which demand is growing).

- Heavy crude oil

  Heavier crudes contain higher proportions of large molecules, which the refinery can either use in heavy industrial fuels, asphalt, and other heavy products (for which the markets are less dynamic and in some cases shrinking) or process into smaller molecules that can go into the transportation fuels products. Typical natural yields of light and heavy crude oils can be ilustrated in figure 6[17].

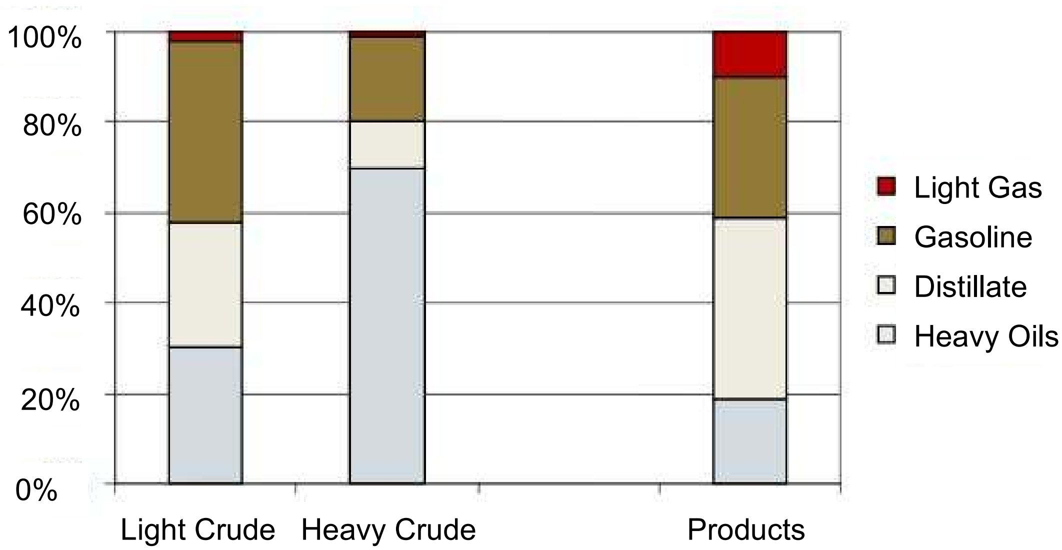


Figure 6 : typical natural yields of light and heavy crude oils

F. Pretreatment of Crude Oils

Crude oil comes from the ground, which contains variety of substances like gases, water, dirt (minerals) etc. Pretreatment of the crude oil is important if the crude oil is to be transported effectively and to be processed without causing fouling and corrosion in the subsequent operation starting from distillation, catalytic reforming and secondary conversion processes. Impurities in the crude oil are either oleophobic or oleophilic. They are described as follow :

1. Oleophobic Impurities

Oleophobic impurities include salt, mainly chloride & impurities of Na, K, Ca& Mg, sediments such as salt, sand, mud, iron oxide, iron sulphide etc. and water present as soluble emulsified and /or finely dispersed water.

2. Oleophilic Impurities

Oleophilic impurities are soluble and are sulphur compounds, organometallic compounds, Ni, V, Fe and As etc, naphthenic acids and nitrogen compounds. Pretreatment of the crude oil removes the oleophobic impurities.

Pretreatment takes place in two ways, those are field separation then crude desalting. They are described as follow.

a. Field Separation

Field separation is the first step to remove the gases, water and dirt that accompany crude oil coming from the ground and is located in the field near the site of the oil wells. The field separator is often no more than a large vessel, which gives a quieting zone to permit gravity separation of three phases: gases, crude oil and water (with entrained dirt). It is given as shown in figure 7.

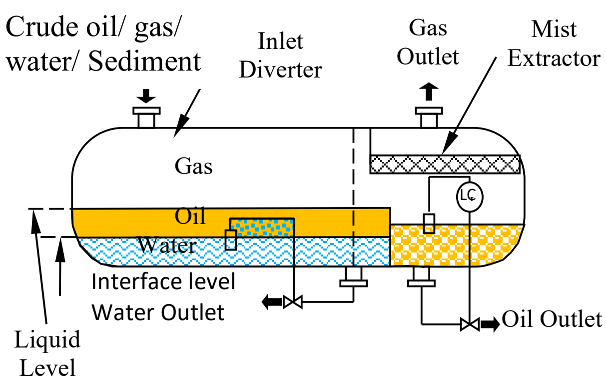


Figure 7 : field separator

b. Crude Desalting

It is a water washing operation performed at the refinery site to get additional crude oil clean up. Crude Oil Desalting consists of :

- Purifying process
- Remove salts, inorganic particles and residual water from crude oil
- Reduces corrosion and fouling

Desalting process is used for removal of the salts, like chlorides of calcium, magnesium and sodium and other impurities as these are corrosive in nature. The crude oil coming from field separator will continue to have some water/brine and dirt entrained with it.

Desalting process is two stage process. They are forming emulsion of crude and water and demulsification in which emulsion is broken by means of electric field and demulsifying chemicals. Desalting is carried out by emulsifying the crude oil and then separating the salt dissolved in water. Two phases water/oil is separated either by using chemicals to break down the emulsion or by passing high potential electric current. By injecting water the salts dissolved in the water and solution are separated from the crude by means of electrostatic separating in a large vessel[9].

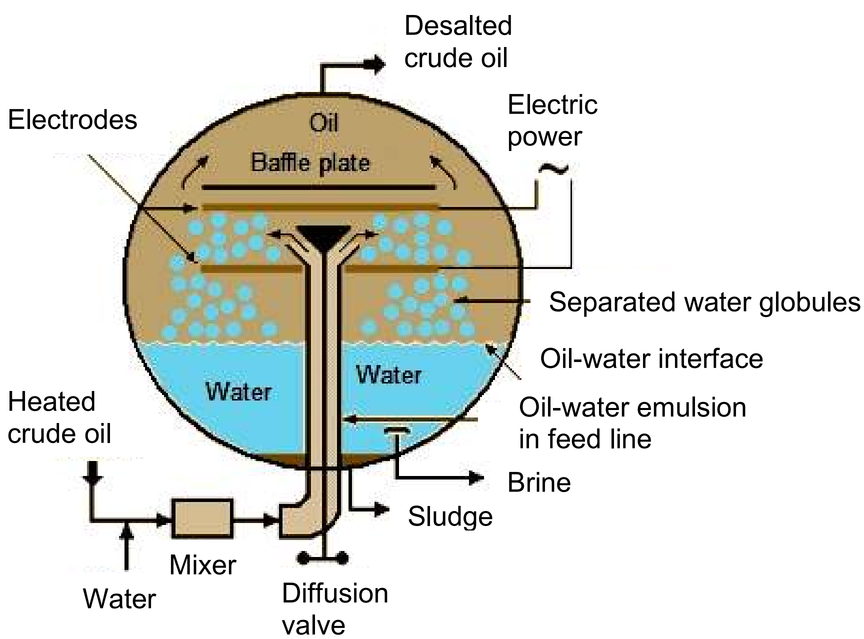


Figure 8: electrostatic crude oil desalter

G. Crude Assay

Crude oil assay is a compilation of laboratory and pilot plant data that define the properties of the specific crude oil[4]. Crude oil assay also indicates distribution quantity and quality of crude oil feedstock[3]. A complete crude assay will contain some or all of the following[8]:

1. Whole crude gravity, viscosity, sulfur content, pour point, etc.
2. TBP curve, mid-volume plot of gravity, viscosity, sulfur, etc.
3. Light-ends analysis up through C8, or C9.
4. Properties of fractions (naphtha, middle distillates, gas oils and residua)-yield as volume percent, gravity, sulfur, viscosity, octane number diesel index, flash and fire point, freeze point, smoke point, pour point, vapor pressure, etc.

5. Properties of lube distillates (only if the crude is suitable for the manufacture of lube base stocks).
6. Properties of asphalts (only if the residua have suitable characteristics for preparation of asphalts).
7. Detailed studies of fractions for various properties, e.g., octane number versus yield for naphtha or viscosity versus yield for lube stocks.
8. EFV curve run at atmospheric pressure and/or phase diagram, although this is rarely done.

Relatively simple crude oil assays are used to classify crude oils as paraffinic, naphthenic, aromatic, or mixed. One assay method (United States Bureau of Mines) is based on distillation, and another method (UOP "K" factor) is based on gravity and boiling points. More comprehensive crude assays determine the value of the crude (i.e., its yield and quality of useful products) and processing parameters.

Crude oils are usually grouped according to yield structure[14]. Crude oils that are light (higher degrees of API gravity, or lower density) and sweet (low sulfur content) are usually priced higher than heavy, sour crude oils. One of crude oil assay can be shown in table 4. Other data assay are given in appendix completely.

Table 4 : example of crude assay (whole crude data)[8]

Whole Crude Data		
Gravity Specific gravity	°API 60/60	31.6 0.8676
Sulfur Pour Point	Wt.% °F	1.08 -5
Water and sediment Salt Content, NaCl	Vol % Ptb	0.0 0.85
Reid Vapor Pressure H_2S (disolved) Neut. No. (D664)	psi ppm mg KOH/gm	4.9 0 0.11
Viscosities : Kinematic @ 70 °F 100 °F	 cs cs	 16.1 10.2
Saybolt Universal @ 70 °F 100 °F	sec sec	81.4 59.5
Light Hydrocarbons		
% on Crude	Wt.	Vol.
Methane Ethane Propane	 0.02 0.22	 0.04 0.37
Iso Butane Normal Butane	0.18 0.60	0.27 0.89
Iso Pentane Normal Pentane	0.56 0.82	0.77 1.13

DEFINITION

Alkylation - the process in which isobutane reacts with olefins such as butylene to produce a gasoline range alkylate.

Aniline point - the minimum temperature for complete miscibility of equal volumes of aniline and a test sample. This test is an indication of paraffinicity and the ignition quality of diesel.

API gravity - an arbitrary scale expressing the density of petroleum products.

Aromatics - unsaturated ring-type (cyclic) compounds which react readily because they have carbon atoms that are deficient in hydrogen.

ASTM distillation - standardized laboratory batch distillation for naphtha and middle distillate at atmospheric pressure.

Atmospheric tower - distillation unit operated at atmospheric pressure.

Catalytic cracking - the process of breaking up heavier hydrocarbon molecules into lighter hydrocarbon fractions by use of heat and catalysts.

Characterization factor - a systematic way of classifying a crude oil according to is paraffinic, naphthenic, intermediate or aromatic nature.

Cetane number - related to ignition quality and defined as the time period between the start of injection and start of combustion (ignition) of the fuel.

Cloud point - temperature at which a haze appears in a sample which is attributed to the formation of wax crystals.

Coke - a high carbon-content residue remaining from the destructive distillation of petroleum residue.

Crude assay - a procedure for determining the general distillation and quality characteristics of crude oil.

Cut point - temperature on the whole crude TBP curve that represents the limits (upper and lower) of a fraction to be produced (yield of a fraction).

Distillate - the products of distillation formed by condensing vapors.

End points - the actual terminal temperatures of a fraction produced commercially.

Flash point - the temperature at which the vapor above the oil will momentarily flash or explode.

Fluid catalytic cracking (FCC) - the main player for the production of gasoline. The catalyst in this case is a zeolite base for the cracking function.

Finishing - the purification of various product streams by processes such as desulfurization or acid treatment of petroleum fractions to remove impurities from the product or to stabilize it.

Fractionating tower - process unit that separates various fractions of petroleum by simple distillation, with the column tapped at various levels to separate and remove fractions according to their boiling ranges.

Freezing point - temperature at which the hydrocarbon liquid solidifies at atmospheric pressure.

Isomerization of light naphtha - the process in which low octane number hydrocarbons (C4, C5, C6) are transformed to a branched product with the same carbon number.

Lubricant - any material interposed between two surfaces that reduces the friction or wear between them.

Mid boiling point components - typically useful in compiling the assay narrow boiling fractions are distilled from the crude, and are analyzed to determine their properties by plotting against the mid boiling point of these fractions

Naphthenes - saturated hydrocarbon groupings with the general formula C_nH_{2n}, arranged in the form of closed rings (cyclic).

Partial pressure - the contribution of one component of a system to the total pressure of its vapor at a specified temperature and gross composition.

Pour point - the temperature at which the oil ceases to flow.

Octane number - a measure of a gasoline's resistance to knock or detonation in a cylinder of a gasoline engine.

Overflash - to provide additional heat (over and above that set by the product vaporization required) required by the process to generate the internal reflux required by the process.

Reflux - the portion of the distillate returned to the fractionating column to assist in attaining better separation into desired fractions.

Reid vapour pressure (RVP) - the vapour pressure determined in a volume of air four times the liquid volume at 37.8 ^oC (100 ^oF)

Separation - a physical process where compounds are separated by different techniques.

Smoke point - an indication of the smoking tendency of fuel. It is used for evaluating the ability of kerosene to burn without producing smoke.

Stripping - the removal (by steam-induced vaporization or flash evaporation) of the more volatile components from a cut or fraction.

Sulfur content - a measure of "sourness" & "sweetness" of crude passed onto products as much as regulations or market accepts.

Visbreaking - a mild thermal cracking process used to break the high viscosity and pour points of vacuum residue to the level which can be used in further downstream processes.

Viscosity - resistance to flow, usually measured at 100 ^oF.

NOMENCLATURE

AP = aniline point, ^oC
API = API gravity, (dimensionless)
K = characterization factor, (dimensionless)
K = average boiling point, K
MeABP = mean average boiling points, ^oR
P = pressure. psia
SG = specific gravity, (dimensionless)
T = temperature, ^oF
T_b = normal boiling point, K
VABP = volume average boiling point, ^oF

Greek letter
%A = percent aromatic content, %