

<p><b>KLM Technology Group</b></p> <p>Practical Engineering Guidelines for Processing Plant Solutions</p>	<div style="border: 1px solid black; padding: 5px; display: inline-block;">  </div> <p><b>ENGINEERING SOLUTIONS</b></p> <p><a href="http://www.klmtechgroup.com">www.klmtechgroup.com</a></p>	<p>Page : 1 of 81</p> <hr/> <p>Rev: 01</p> <hr/> <p>Rev 01 Jan 2017</p>
<p>KLM Technology Group P. O. Box 281 Bandar Johor Bahru, 80000 Johor Bahru, Johor, West Malaysia</p>	<p><b>Kolmetz Handbook Of Process Equipment Design</b></p> <p><b>Introduction to Crude Oil Refining</b></p> <p><b>(ENGINEERING DESIGN GUIDELINES)</b></p>	<p>Co Author Rev 01 Yulis</p> <hr/> <p>Author / Editor: Karl Kolmetz</p>

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## INTRODUCTION

### Scope

The complexity of modern refinery operations are difficult to people that are not involved with the industry. This introduction to refining is aimed to cover the technical issues into a business perspective. The explanation begins with the history of crude petroleum oil and where it generated, how people first get crude petroleum oil traditionally, how it generally shifted into two major part : (1) *Upstream Process* and (2) *Downstream Process* and how it was developed through centuries to become a modern plant in many places around the world.

### History

Crude oils or “nature petroleum” occurs as an accumulations in the subsurface of the earth. Petroleum compositions are so various based on its physical condition :

- 1) *Natural Gas*, composed from hydrocarbon-rich gases.
- 2) *Liquid Oil*, composed by liquid phase petroleum (crude oil).
- 3) *Tar and Bitumen*, formed mostly from high-molecular weight solids.

Petroleum was generated from insoluble organic material in source rocks. A biogenic origin for carbonaceous in petroleum is universally accepted. The process including organic matter which incorporated into sediments are deposited, shallow generation of biogenic methane, conversion of organic matter into petroleum-like materials according several influences (Temperature, Pressure), migration materials from the source rock through permeable carrier beds to the reservoir, then final compositional changes of petroleum caused by temperature, microorganism activities, and water washing. (Figure 1).

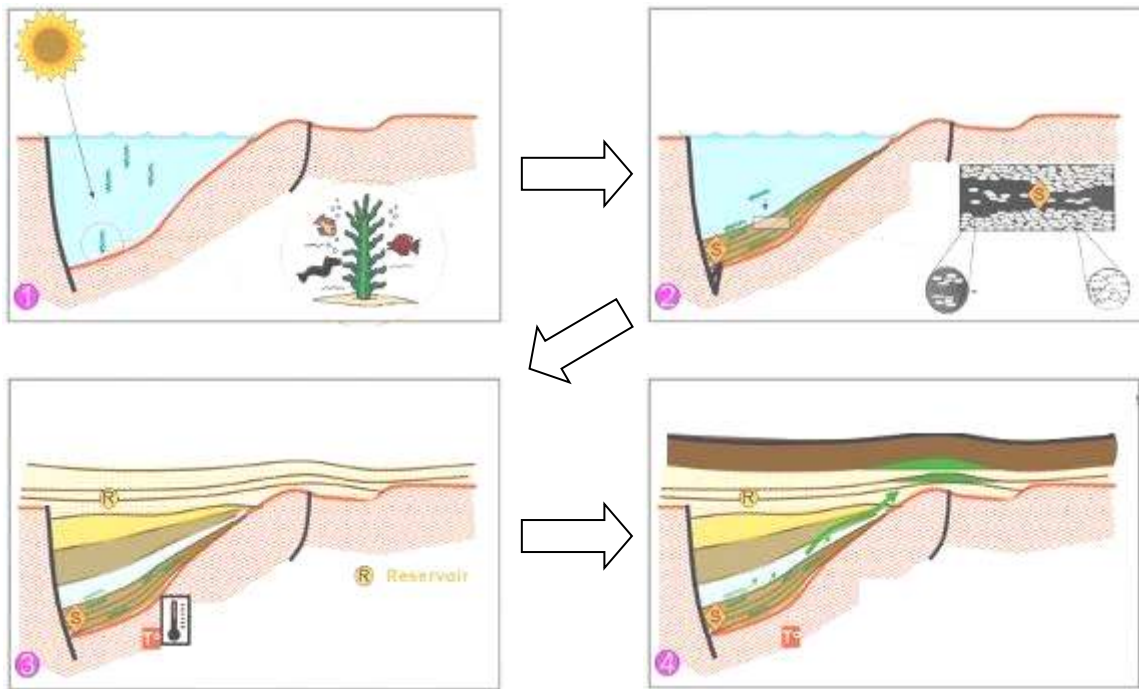


Figure 1. Petroleum generation.

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Selected Producers, 1973–2015

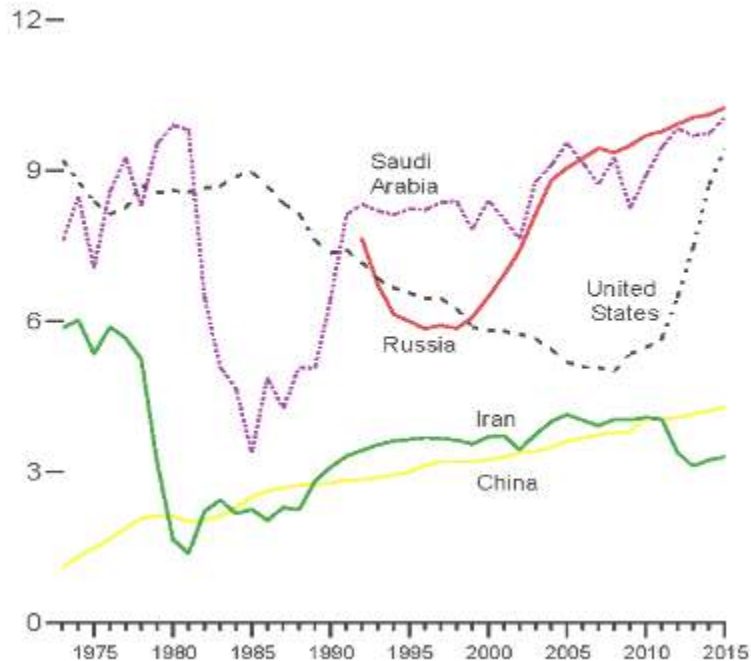


Figure 2. Top oil producers.

### *Upstream Process*

After crude oil is generated, people take an advantage of it by processing the crude oil from earth's subsurface above the soil. One of the most important operations of upstream is drilling.

Drilling costs range from several thousand to several millions dollars for each well depending on the nature of the well itself. The length of drilling time could be only for few days to more than a year. As approximation, about 6 to 8% of the total drilling costs arises directly from the drilling fluid and additives. On 1994, total worldwide sales was estimated to be  $\$1.2 \times 10^9$ . And half of it were spent by U.S. Drilling fluids could be categorized as :

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- 1) *Gas-Based Muds*, mostly used for hard-rock drilling which consists from compressed dry air and natural gas to water-based mist and foams. No additives needed for gas drilling operations whilst aqueous additives were injected to generate mists and foams. Gas-based fluids are not recirculated and materials are added continuously to reservoir.
- 2) *Water-Based Muds*, filled by 85% of water-based systems. The fluids depend on the composition of water phase, viscosity builders and also rheological control agents.
- 3) *Oil-Based Muds*, oil-based drilling fluids consists mostly of diesel and mineral oil as a continuous phase. Low or havng no content of water. Employed for high angle wells where good lubricity is necessary.
- 4) *Synthetic-Based Muds*, has been introduced to counteract the high costs with disposal of drill cuttings generated when oil-based muds are used. A substitute liquids operates as a pseudo-oil inside reservoir to help fluids pumped out of earth surface.

Most of drilling required an additives to run operation smoothly. The price of drilling fluids additives is vary depend to company and location. Table 1 valued an example price of drilling fluid additives which typically used for North Sea region consumption around late 1990's.



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Table 1. Prices of Additives

Additive	Function	Estimated Price (\$/tonnes)
<b>Barite,</b>	Increase density	140
<b>Hematite</b>		155
<b>Attapugite,</b>	Increase viscosity	300
<b>Bentonite,</b>		165
<b>Hydroxylethylcellulose,</b>		11,500
<b>Xanthan Gum</b>		23,000
<b>Causticized,</b>	Reduce viscosity	1,200
<b>Chrome-</b>		1,150
<b>lignosulfonate,</b>		1,500
<b>Lignosulfonate (Chrome-free),</b>		510
<b>Pyrophosphate Lignite,</b>	Filtrate rate reduction	11,000
<b>Carboxymethyl cellulose,</b>		1,300
<b>Corn starch,</b>		3,000
<b>Modified starch</b>	Viscosity stabilization	13,000 (powder)
<b>Polyacrylamide</b>		7,100 (liquid)
<b>Lime,</b>	Alkalinity control	220
<b>Potassium hydroxide,</b>		2,200
<b>Sodium hydroxide</b>		1,050
<b>Cellulose fiber,</b>	Lost circulation control	1,500
<b>Mica,</b>		590
<b>Walnut shells</b>		750

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As crude oil wells operates by time, the pressure inside reservoir is also reducing time after time. Such an addition recovery system is urgently required to keep crude oil produce with the same rate. A better technology to pumped out drilled crude oil named as Enhanced Oil Recovery (EOR). In 1994, EOR has been contributed about 3.2% of oil production ( $1.9 \times 10^6$  barrel/day). In U.S, approximately 10% of total production (709,000 barrel/day) at that time gained from EOR method. As the year goes by and oil production more dependent to existing fields, EOR has raise an interest in many places around the world. Oil recovery mechanisms using EOR system could summarized into two major stages :

- 1) Increasing volumetric sweep efficiency.
- 2) Increasing oil displacement efficiency.

Indeed, poor reservoir volumetric sweep efficiency becomes one of the greatest obstacle to increasing oil recovery. Both of these stage commonly used substitute fluids such as miscible gas (CO<sub>2</sub>, natural gas), immiscible gas (Nitrogen) or Water to increase the efficiency of EOR method.

### *Downstream Process*

Downstream process of crude oil is next after the drilled-fluids approached earth's surface in order to chemically modify them for making the daily products and making them ready to consume. Downstream process including :

- 1) *Refinery Process*, aiming the recovery of usable fraction from crude oil either using physical and chemical modification to get the first derivatives petroleum products.
- 2) *Petrochemical Process*, aiming further modification of the first derivative petroleum products to become intermediate chemical compounds or daily basis products.

Historically, it was believed about two thousand years ago, Arabian scientists developed methods what people named : "Distillation" which later introduced into Europe through Spain. In China (approximately third century), petroleum accidentally occured when drilling for salt. Marco Polo in 1271 – 1273 has been reported a 'commercial' petroleum industry built in Baku region (currently Northern Iran).

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Mixture of compounds boiling at different temperatures that can be separated into various different fractions which sometimes overlapped called "Crude Petroleum". Table 2 showed classification of crude petroleum in order of its boiling point.

Table 2. Fractions of Petroleum

Fraction	Boiling Point (°C)
Light naphtha	-1 – 150
Gasoline	-1 – 180
Heavy naphtha	150 – 205
Kerosene, Stove oil	205 – 290
Light gas oil	260 – 315
Heavy gas oil	315 – 425
Lubricants	> 400
Residuum	> 600

Crude petroleum utilization had been recorded at least 500 years. Mesopotamian (currently Iraq) documents explained products that came from nonvolatile derivatives (approximately derives from asphalt compounds) which used as an adhesive for jewelry or construction purposes. The document also showed the use of bitumeous compound as medicines.

A refinery could be group as manufacturing plants that vary in number due to the variety of products produced. Refinery plant shall be flexible and able to change its operations if needed. Universally, a refinery plant obey three basic process concepts following :

- 1) *Carbon rejection*, in order to reduce the number of carbon compound such as coking processes.
- 2) *Hydrogen addition*, in order to extend the number of hydrogen compound like hydroprocesses.
- 3) *Catalysis*, in order to rearrange and manipulate compounds to become different structure without changing the number of carbon and hydrogen element.

Crude petroleum consisted not only liquid phase materials but also gas phase. The gas streams produced during petroleum refinery obtained many noxious elements which could affected the use of gas for further purposes such as fuel and petrochemical feedstocks.

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Therefore, gas purification processes are necessarily required. Purifying process for gas constituents divided into three classes :

- 1) *Removal of Gaseous Impurities.*
- 2) *Removal of Particulate Impurities.*
- 3) *Cleaning.*

Gas purification performed such a complex treating due to many variables involved. Several considerations shall be determined which generally followed the rules of :

- 1) Kind of contaminants and its concentrations within processed gas.
- 2) How much desired contaminant to be removed.
- 3) Selectivity of acid gas removal required.
- 4) Physical influence such as : Pressure, Volume, and Composition of processed gas.
- 5) Carbon dioxide to Hydrogen Sulfide ratio.
- 6) Sulphur recovery desired for economical purposes.

Both of petroleum and natural gas could be based material for petrochemical products. In general, petrochemicals separated into three different groups, following :

- 1) *Aliphatics*, a straight-chained carbon hydrocarbon compounds.
- 2) *Cycloaliphatics*, a rounded-chained carbon hydrocarbon compounds, including aromatics classes.
- 3) *Inorganics*, which contained inorganic elements like sulphur (S) and nitrogen (N).

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## Design Consideration

### Units

#### *Petroleum Units*

Crude oils usually counts by unit called : “barrel” (acronym : ‘bbl’) which equals to 42 U.S Gallons, 5.61 ft<sup>3</sup>, 0.159 m<sup>3</sup> or 158.8 L. When one fields have proven recoverable oil more than 100 x 10<sup>6</sup> bbl of 500 x 10<sup>6</sup> bbl of preserved oil, this called the ‘Giants’. Density of crude oils is important units to be count with. Oil density could be texted in such an appropriate way, the most common unit which had been used is degrees API (°API) or API gravity. API stands for American Petroleum Institute. The following relationship between API gravity and density is :

$$^{\circ}API = \left( \frac{141.5}{\text{specific gravity at } 60^{\circ}F} \right) - 131.5$$

Water having an API gravity of 10 whilst oils counted between 10 and 60 °API. Generally crude oils values in the range of 35 – 40 °API.

There are several other term which related to physical propoerties of crude oils involving :

- 1) Viscosity.
- 2) Refractive Index.
- 3) Pour Point.
- 4) Flash Point.

Viscosity defined as the readiness of a fluid to flow when it is acted upon by an external force. Meanwhile, absolute viscosity describes as a measure of fluid for its resistance to internal deformation or shear. Centipoise (cP) or centistokes (cSt) often used as viscosity units, but centipoise is more popular.

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Conversion from centistoke to centipoise equated as :

$$cSt = \frac{cP}{\text{specific gravity}}$$

Where :

cSt : centistoke.

cP : centipoise.

Specific gravity is a density referenced to water at 60°F.

Viscosity of liquid is very dependent and varies with the slightest temperature changes. Another unit that often used is the watson number. The Watson number is a unit which characterized of chemical components from crude oil or its fraction, followed by an equation of :

$$K = \frac{(T_B)^{1/3}}{sp\ gr}$$

Where :

$T_B$  : Absolute boiling point (Rankine, °R = 9/5\*K)

$Sp\ gr$  : Specific gravity compare to water at 60°F (15.6°C)

The boiling point of crude oil taken from an average at five temperatures point where 10, 30, 50, 70, and 90% material vaporized. A highly paraffinic crude oil usually has watson number of 13, whereas naphthenic crude oil has watson number about 10.5. The term determined under defined conditions which explained in details by ASTM (American Society for Testing and Materials).

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### *Natural Gas*

Production of Natural Gas (NG, Nat-Gas) usually determined in cubic feet or cubic meters which :

$$1000 \text{ ft}^3 = 1 \text{ Mcf} = 28.3 \text{ m}^3$$

When a gas field reserves 1 Tcf or more than  $28.3 \times 10^{12} \text{ m}^3$  the field calls a 'Giant' one. Natural Gas classified into two types :

- 1) *Dry Gas* (dominantly consist of methane,  $\text{CH}_4$ ).
- 2) *Wet Gas* (if it consists more than 4 L/100  $\text{m}^3$  of natural gas liquids or more than 0.3 gal/1000  $\text{ft}^3$ ).
- 3) *Sour Gas* (when reserve gas contained high concentrations of Hydrogen Sulfide,  $\text{H}_2\text{S}$ , and volatile sulfur which has bad odor).
- 4) *Sweet Gas* (when reserve gas contained Sulphur compounds but odorless).

To convert natural gas units and petroleum units, people often normalized it based upon an equivalent heating capacity, which :

$$\frac{6000 \text{ ft}^3}{1 \text{ bbl}} = 1 \text{ boe}$$

Note that *boe* stands for barrel oil equivalent.

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## Composition

Crude oil was refined as a preservation of common products like: Fuel, Gas, Raw Material for Petrochemical etc. As its named, “hydrocarbon” of crude oil built from two main atoms : Carbon (C) and Hydrogen (H). Crude oil consists of wide range of hydrocarbons. From Straight chain to branched, ring compounds and also complex compounds incorporated with other components such as Nitrogen, Oxygen, and Sulphur (NOS). Classification of hydrocarbon within crude oil could be simplified into :

- 1) *Paraffins*, mostly consists of normal alkanes compound, straight-chained, range from 1 to >100 number of carbon atoms.
- 2) *Aromatics*, minority found yet also important for final products, composed by ring molecules of hydrocarbon from single to multiring compounds, Benzene, Toluene, and Xylene (BTEX) are such an examples of aromatics.

The most dominant process of oil refinery is distillation. Most of petroleum products exhibited by simple distillation. Material which too weight to be distilled form an “asphalt” or “asphaltenes”. “Naphtha” is a distilled product (distillate) that consists of hydrocarbon mixture which having boiling point lower than 260°C (in some occasion up to 350°C). Figure 3 and Table 3 aimed the generalization distillation range for products obtained during crude oil refining.

Table 3. Oil Refinery Products

Product	Temperature range, °C	Carbon number range
<b>Gasoline</b>	30 – 210	5 – 12
<b>Naphtha</b>	100 – 200	8 – 12
<b>Kerosene, Fuel jet</b>	150 – 250	11 – 13
<b>Diesel, Fuel oils</b>	160 – 400	13 – 17
<b>Heavy fuel oils</b>	315 – 540	20 – 45
<b>Atmospheric residue</b>	≥ 450	30+
<b>Vacuum residue</b>	≥ 615	60+



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On atomic scale, Hydrogen to Carbon (H/C) ratio of petroleum range from 1.5 – 2.0. The range of elemental composition of crude oil may be given as represented in Table 4.

Table 4. Elemental Composition

<b>Element</b>	<b>Composition range (%wt)</b>
<b>Carbon</b>	84 – 87
<b>Hydrogen</b>	11 – 14
<b>Sulphur</b>	< 0.1 – 8
<b>Oxygen</b>	< 0.1 – 1.8
<b>Nitrogen</b>	< 0.1 – 1.6

Vanadium and Nickel occasionally occurred as a trace amount up to 1000 ppm. Crude oil with low sulphur contain is more favorable rather than high concentration of sulphur. Corrosion stimulated by sulphur element was the main reason.

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## DEFINITION

**Absolute viscosity** – A measurement of fluid for its resistance to internal deformation or shear.

**Carbon rejection** – A process in order to reduce the number of carbon elements within hydrocarbon compounds.

**Catalysis** – A process in which to rearrange and manipulate compounds to become different structure without changing the number of carbon and hydrogen elements.

**Downstream process** – A part of crude oil processing after petroleum reached earth's surface in order to chemically modified and making them daily products.

**Hydrogen addition** – A process in which to extend the number of hydrogen elements within hydrocarbon molecules.

**Inorganics** – A space in which composed not only hydrocarbon elements but also inorganic elements like sulphur (S) and nitrogen (N).

**Liquid Oil** – A mixture substance composed by liquid phase petroleum (crude oil).

**Natural Gas** - A mixture substance composed from hydrocarbon-rich gases.

**Petrochemical process** – A process in which purposes of further modification of first derivative petroleum products to intermediate chemical compounds or daily basis products.

**Production** – A branch of crude oil petroleum processing in which bringing crude oils to earth's surface.

**Refinery process** – A process which aiming the recovery of usable fraction from crude oil either using physical and chemical modification to get the first derivatives petroleum products.

**Tar and Bitumen** – A mixture substance formed mostly from high-molecular weight solids.

**Upstream process** – A process to bringing up crude petroleum oils flew out from earth's subsurface to above the soil.

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## NOMENCLATURE

A	: The size of units which cost is known (m <sup>3</sup> )
ACF	: Annual Cash Flow (\$/year)
API	: American Petroleum Institute
ASTM	: American Society for Testing and Materials
B	: The size of units for which a cost is required (m <sup>3</sup> )
bbl	: Barrel (42 US Gallons)
boe	: Barrel oil equivalent
BTEX	: Benzene, Toluene, and Xylene
C	: Crude oil cost (\$/metric ton)
c	: Crude requirement (metric ton)
C <sub>A</sub>	: Actual cost of unit A (\$)
C <sub>B</sub>	: Cost of unit B (\$)
cP	: Centipoise
cS	: Centistroke
DFI	: Depreciable Fixed Investment (\$)
EOR	: Enhanced Oil Recovery
F	: Residual fuel oil price (\$/metric ton)
f	: Incremental residual fuel oil production (metric ton)
FI	: Base Fixed Investment (\$)
I <sub>A</sub>	: Index value of an old cost
I <sub>B</sub>	: Current Index value
K	: The Watson number
Mcf	: Metric cubic feet (1000 ft <sup>3</sup> )
n	: An exponent value (typically 0.6)
NG	: Nat-Gas, Natural Gas
P	: Product Break-Even-Value (BEV, \$/metric ton)
P	: Average annual profit (\$)
POT	: Pay Out Time (year)
ROI	: Return on Investment
sg	: Specific Gravity
T <sub>B</sub>	: Absolute boiling point (Rankine)
V	: Incremental variable costs (\$/metric ton)
WC	: Working Capital (\$)
°API	: Degree API