

# Petroleum Refinery I

[2022]

## An introduction to crude oil and its processing

- The composition and characteristics of crude oil
- The crude oil assay
- Other basic definitions and correlations
- Predicting product qualities
- Basic processes
- The processes common to most energy refineries
- Processes not so common to energy refineries
- The non-energy refineries

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.
- 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.

# The true boiling point curve

 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.



#### The ASTM distillation curve

• This type of distillation curve is used to 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.

# 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

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

# 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 <u>closed cup containing the oil, heating and stirring equipment</u>, and a special adjustable flame.
- The type of apparatus used for middle distillate and fuel oils is called the <u>Pensky Marten</u> (PM), while the apparatus used in the case of Kerosene and lighter distillates is called the <u>Abel</u>. 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. <u>The higher this resistance</u> 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.

## 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.

### 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<sub>2</sub>).
- The temperature at which the oil becomes hazy or cloudy is taken as its <u>cloud point</u>.
- 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.

### Basic Definitions and Correlations

- 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.



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

# Mid boiling point components

- 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 component and continue until the whole curve is divided into these mid boiling point components.



### Good, Connel et al Method:

- Good, Connel et al accumulated data to relate the ASTM end point to a TBP cut point the light and middle distillate range of crude.
- Their correlation are shown in the figure 1 beside :
- Thrift derived a probable shape of ASTM data. As shown in figure 2 beside:
- The probability graph that he developed is given as Figure 2. 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.



A End Points Vs TBP Cut Point for fractions starting at 200°F TBP or Lower B End Points Vs TBP Cut Point for fractions starting at 300 C End Points Vs TBP Cut Point for fractions starting at 400 D End Points Vs TBP Cut Point for fractions starting at 500

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 Correlation between TBP and ASTM end points.



ASTM distillation probability curves.

# 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.
- 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.

### Mid-volume percentage 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.



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# Laboratory Testing of Crude Oils

# True Boiling Point (TBP) Curve

- The composition of any crude oil sample is approximated by a true boiling point (TBP) curve.
- The method for determining this is a batch distillation operation using a large number of stages, usually > 60, and high reflux to distillate ratio (> 5).

Test name	Reference	Main applicability
ASTM (atmosphere)	ASTM D 86	Petroleum fractions or products, including gasoline turbine fuels, napthas, kerosines, gas oils, distillate fuel oils, and solvents that do not tend to decompose when vaporized at 760 mm Hg
ASTM [vacuum often 10 torr ASTM D 1160 (1.3 kPa)]		Heavy petroleum fractions or products that tend to decompose in the ASTM D86 but can be partially or completely vaporized at a maximum liquid temperature of 750 °F (400 °C) at pressures down to 1 torr (0.13 kPa)
TBP [atmospheric or 10 torr (1.3 kPa)]	Nelson*, ASTM D 2892	Crude oil and petroleum fractions
Simulated TBP (gas chromatography)	ASTM D 2887	Crude oil and petroleum fractions
EFV (atmospheric, superatmospheric, or subatmospheric)	Nelson†	Crude oil and petroleum fractions

## ASTM D86 Distillation

D86 distillation uses a simple Engler flask containing a calibrated thermometer to measure the temperature of the vapor at the inlet to the condensing tube. An inclined brass condenser in a cooling brass is attached, to remove all distilled vapors; no liquid reflux is returned to the flask. The condenser tube is cooled in an ice water bath to maintain the condensing temperature between 32 and 40 °F (0–4.5 °C). The light components that boil at temperatures lower than the condensing temperature are lost from the distilled product.

#### Procedure

100 ml of sample is distilled and the vapor temperature against volume recovered is recorded. The initial boiling point (IBP) is defined as the temperature at which the first drop of liquid leaves the condenser tube. The final boiling point (FBP) or "end point" is the highest temperature recorded during the text. The total volume of the distillate is recorded as the recovery. Any liquid left in the still after the end point temperature is recorded is cooled and measured as the residue. The difference between 100 ml (initial sample volume) and the sum of the recovery and the residue is referred to as the loss. Repeated tests give ±6 °F for the initial boiling and end points. Intermediate distillation points are reproducible within 2 ml of distillate which corresponds to 6-7 °F. Figure beside shows a modern TBP apparatus.



Snapshot of liquid volume (%) vs. Temperature (oC) of TBP and ASTM D86 plots of distillation blend (Courtesy of Honeywell UniSim software, Honeywell (R) and UniSim (R) are registered trademarks of Honeywell International Inc.).



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### **Boiling Points**

- Figure beside illustrates the interconversion between <u>ASTM D –86</u> distillation 10% to 90% slope and <u>the</u> <u>different boiling points</u> used to characterize fractions of crude oil.
- This is done to determine the properties such as the
  - volumetric average boiling (VABP) point,
  - weight average boiling point (WABP),
  - molal average boiling point (MABP),
  - mean average boiling point (MeABP)
  - and cubic average boiling point (CABP).
    On the basis of ASTM D-86 distillation data, the VABP is :

 $VABP = (t_{10} + t_{30} + t_{50} + t_{70} + t_{90})/5$ 

where the subscripts 10, 30, 50, 70 and 90 refer to the volume per cent recovered during the distillation.



Characterizing Boiling Points of Petroleum Fractions (From API Technical Data Book). Used by permission, Gas Processing Suppliers Association Book Data, 12th ed., v.1 and 2. (2004).

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- To locate the curve for the distillation VABP in the appropriate set for the type of boiling point desired.
- For a known 10–90% slope, to read a correction for the VABP from the selected VABP curve.





### Problem

Determine the mean average boiling point (MeABP) and the molecular weight for a 56.8 °API petroleum fraction with the following ASTM distillation data.

% Over	Temperature, °F
IBP	100
5	130
10	153
20	191
30	217
40	244
50	280
60	319
70	384
80	464
90	592
EP	640

(Source: Engineering Data Book: Gas Processors Suppliers Association, Tulsa, Oklahoma, 12<sup>th</sup> ed., 2004)

#### Solution

IBP = initial boilingEP = end pointSlope (592-153)/80 = 5.49VABP =  $(153 + 217 + 280 + 384 + 592)/5 = 325 \ ^{\circ}F$ From Figure 3.6, Read down from a slope of 5.49 onthe x-axis to the interpolated curve closest to 325 \ ^{\circ}F

in the set drawn with the dashed lines (MeABP). Read across to obtain a correction value of -54 on the ordinate. MeABP = 325-54 = 271 °F. At °API = 56.8, the molecular weight is 198 from



Dr.Omar Al-Kubaisi Correlations between MeABP. SpGr and Mol. Wt

#### Conversion Between ASTM and TBP Distillation

The True Boiling Point distillation determination of petroleum crudes can often be time consuming and tedious as compared to the ASTM method. Therefore, a correlation between ASTM and TBP distillation is employed that achieves the separation of TBP with little effort of the ASTM distillation

 $\text{TBP} = a \big(\text{ASTM D86}\big)^b$ 

 where a and b are constants varying with percent of liquid sample distilled as shown in Table 3.10. TBP is true boiling point temperatures at 0, 10, 30, 50, 70, 90 and 95 volume percent distilled, in degrees Rankine (°R).

Volume% distilled	a	Ь
0	0.9167	1.0019
10	0.5277	1.0900
30	0.7429	1.0425
50	0.8920	1.0176
70	0.9490	1.0110
90	0.9490	1.0110
95	0.8008	1.0355

Watson's Characterization Factor:

The MeAPB is used in the determination of Watson characterization factor as expressed by:

$$K = \frac{\left(\text{MeABP}\right)^{1/3}}{\text{SpGr}}$$

where MeAPB is in degrees Rankin(°R).

#### Example

A petroleum cut has the following ASTM data

Volume% distilled	0	10	30	50	70	90	95
Temperature °C	36.5	54	77	101.5	131	171	186.5

Convert these data to TPB data using the API method. Plot the result and compare. If the API gravity of this fraction is 62, Calculate the Watson's characterization factor.

1- VAPB  
$$VABP = (t_{10} + t_{30} + t_{50} + t_{70} + t_{90})/5$$

- VAPB= 224.2 °F (106.9 °C)
- Slope  $Slope = \frac{(t_{90} t_{10})}{(90 10)}$ 
  - Slope =2.6325
- MeAPB= VAPB-In∆
- In∆

$$\ln \Delta = -0.94402 - 0.00865 (VABP - 32)^{0.6667} + 2.9979 (Slope)^{0.333}$$

	Index	Volume%			Temp D86	Temp D86	TBP	TBP	TBP
	number, i	distilled	a	b	°C	°F	°R	°F	°C (Eq 3.8)
	1	0	0.9167	1.0019	36.5	97.7	517.4	57.4	14.1
	2	10	0.5277	1.09	54	129.2	552	92	33.3
	3	30	0.7429	1.0425	77	170.6	616.1	156.1	68.9
	4	50	0.892	1.0176	101.5	214.7	674.9	214.9	101.6
	5	70	0.8705	1.0226	131	267.8	735.3	275.3	135.2
	6	90	0.949	1.011	171	339.8	816.9	356.9	180.5
	7	95	0.8008	1.0355	186.5	367.7	841.4	381.4	194.1

MEABP = VABP = 224.4–18.3 = 206.1 °F (96.8 °C)

°API = 62 Specific gravity = 141.5/(62+131.5) = 0.731Watson characterization factor from Equation is:







# Process Descriptions of Refinery Processes

# Process Descriptions of Refinery Processes

#### Introduction

Refinery and Distillation Processes

Process Description of the Crude Distillation Unit

Crude Oil Desalting

# The purpose of refinery is :

Separate the crude oil into different "fractions" or saleable components.

Shift the original component ratio and properties to meet the customer's demand and

Remove the impurities detrimental to product quality.

# Types of refinery processing

Skimming of Topping Processing

**Cracking Processing** 

#### Lubricating Oil Processing

### Skimming or Topping Processing (Figure a):

This occurs by simple atmospheric pressure distillation; the crude oil is separated into gasoline, kerosene and fuel oil, or reduced crude oil, and sometimes reformer charge stock, jet fuel or gas oil. Topping is often practiced on all types of crude oil.



### Cracking Processing (Figure b)

This refers to a combined operation of

topping and thermal cracking; in most

refinery facilities, the gas oil is catalytically

cracked. No lubricating oils are produced in

this type of operation, and catalytic cracking

yields smaller residual fuel oil.



### Lubricating-oil Processing (Figure c):

This process involves topping with the manufacture of lubricants from the residue of the crude oils. Paraffin-base crude oils are generally processed for lubricants, while mixed-base oils are often processed by solvent extraction in Figure c. Naphthalene oils are processed for lubricants only under the most favorable condition.




# Important Points about the Processing

- Characteristics provide the methods of processing that are employed for the different base of oils and the products that are manufactured.
  - Paraffin-base oils are particularly adaptable for the manufacture of lubricating oils.
- Lubricating oils are produced from mixed-base oils, but acid and solvent treatment is usually necessary.
- Vacuum distillation or precipitation of asphalt by liquid propane is suited to the processing of mixed and naphthalene-base oils because most of the asphalt or tarry material may be left behind as a residue, and the cleaned lubricating-oil stocks can be treated more cheaply than asphalt-bearing stocks.
- Naphthalene-base oils produce good asphalt and are usually in large quantities to justify their manufacture.
- The gasoline from naphthalene crude oils is usually antiknock and may be sold directly as premium-grade motor fuel.

illustrates the boiling range of refinery products of Texas mixed-base crude oil at 31.7°API,



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Flow diagram of a refinery facility for light oils (mainly gasoline, kerosene and distillates).

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Figure shows a process flow diagram of a refinery unit, involving three main processes as separation, conversion, and treating

## **Process Description**

Figure show a process flow diagram of a complex refinery unit involving further processing as crude product handling and auxiliary facilities. Here, the feed is Arabian light crude oil from tank farm, which is processed in the crude distillation unit. The first physical separation process produces distillate streams of Liquefied petroleum gas (LPG), naphtha, kerosene, light gas oil, heavy gas oil and long residue.



# Functions of some units

#### The hydrodesulfurizer units

• Remove the sulfur components contained in the naphtha, kerosene and heavy gas oil.

#### The high-vacuum unit (HVU)

• processes long residue, which comes from the mild-vacuum columns of the crude distillers.

#### hydrocracker unit (HCU)

• The main product is a waxy distillate comes from (HVU) which is used as feed to the hydrocracker unit (HCU). The unit also produces short residue and black wash oil to be used as feed-to the visbreaker unit (VBU).

#### The visbreaker unit(VBU)

• The visbreaker unit processes the short residue from the HVU, alternatively, long residue from the crude distillers. The resulting products are naphtha and gas oil, and the visbroken residue goes for blending either with kerosene or gas oil to be used as fuel oil.

## Steps of Hydrocracking

The first section of hydrocracking unit consists of a hydrocracker and fractionating unit, sour gas and LPG treating units such as aqueous di-isopropanolamine (ADIP).

The ADIP treating system consists of:

- ADIP Gas Absorption Systems
- LPG ADIP Extraction Systems
- ADIP Regeneration Section



# First Section of Hydrocracking

• The hydrocracker takes a heavy waxy distillate feed from the high-vacuum unit (HVU) and converts it in the reactors by using a catalyst under highly exothermic reaction to LPG and light gases, naphtha, and kerosene and gas oil.

• The separation of the final products is achieved in the fractionating unit. Naphtha is sent to storage as platformer feed, while the kerosene is sent to storage together with the kerosene from the hydrodesulfurization unit of the crude distillation unit (CDU).

• Hydrocracker gas oil is also sent to storage with the gas oil from the hydrodesulfurization unit of the CDU. The LPG (gas and liquid) is treated in the ADIP unit before being pumped to LPG unit

## Second Section of Hydrocracking

The second section consists of:

- hydrogen manufacturing unit (HMU),
- LPG unit,
- sour water strippers,
- regeneration units,
- sulfur recovery units (SRU).

•The HMU takes in natural gas (NG) as feed and converts it to produce high-purity hydrogen gas, which is then fed to the hydrocracker unit and other various units in the refinery that use hydrogen as feed in their processes.

•The LPG unit receives gas and liquid; the light gas is used as fuel for the refinery furnaces and the liquid is separated into two final products: LPG is pumped to another facility, and butane is added to chemical feed naphtha for KVP correction

Sour water strippers collect water from all the other refinery units and remove the sour gases from it, which are mainly dissolved hydrogen sulfide (H2S) and ammonia (NH3).
The cleaned up water is then pumped to utilities facility of the refinery for further treatment before being pumped for irrigation. The sour gas is fed to the sulfur recovery unit (SRU) where it is burnt in a series of furnaces, leaving the residual hot liquid sulfur that is then pumped to a gas plant facility.

hydrogen manufacturing unit (HMU),

LPG Unit

Sour water

strippers

## Table summarizes the various processes in a typical refinery

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Separation	Crude oil desalting/dewatering
	Atmospheric distillation
	Vacuum distillation
	Light ends recovery.
Conversion	Thermal cracking-coking, visbreaking
	Catalytic cracking
	Hydrocracking
	Steam cracking
	Catalytic reforming
	Isomerization
	Alkylation and polymerization.
Treating	Hydrodesulfurization
	Hydrotreating
	Extraction
	Bitumen blowing
	Lube oil manufacture (large or specialist
	refineries only).
Crude and product handling	Unloading
	Storage
	Blending
	Loading.
Auxiliary facilities	Boiling/process heaters
	Hydrogen production
	Sulfur recovery and production
	Cooling towers
	Compressor engines
	Power generation
	Blow down system
	Wastewater treatment
	Flares.



# Process Descriptions of Refinery Processes

## Process Description of the Crude Distillation Unit

Lecture 4

# Process Description of the Crude Distillation Unit

- Crude oil distillation columns are in various sizes and the capacities for processing the feed range from 5,000 to 10,000 barrels per day (700 to 1,400 metric tons per day) to 400,000 barrels per day (56,000 metric tons per day).
- The first stage in the processing of crude oil is referred to as crude distillation units (CDUs), crude topping units (CTUs), topping units, atmospheric crude distillation units, atmospheric pipe-stills, etc.

# Typical refinery products.

Name/abbreviation	Major uses
Crude oil (Arab light)	To obtain various products, e.g., Liquefied Petroleum Gas (LPG), naphtha, gasoline, kerosene, diesel, fuel oil, tar and sulfur.
Natural gas (NG)	To produce hydrogen and various petrochemicals, e.g., methanol (CH <sub>3</sub> OH), ethylene (C <sub>2</sub> H <sub>4</sub> ), ammonia (NH <sub>3</sub> ), etc. As a heating source in boilers and furnaces. To drive gas turbines.
Liquefied Petroleum Gas (LPG)	Domestic use: for cooking and heating. Industrial use: to produce petrochemicals, intermediates and for blending in gasoline.
Chemical Feed Naphtha (CFN)	As feed to various petrochemicals and plastic industries (as an alternative to natural gas).
Motor Gasoline Component Naphtha (MGC)	Fuel for vehicles. For the manufacture of aviation gasoline, aromatics (e.g., Benzene $C_6H_6$ , Toluene $C_7H_8$ ), Xylene ( $C_8H_{10}$ ), i.e. BTX).
Dual Purpose Kerosene, illuminating kerosene, Jet Fuels (DPK, KERO, JET A1)	Domestic use-cooking, illuminating, heating, Jet aviation fuel, manufacturing detergents, paint thinner, carbon black, etc.
Auto Diesel Oil (ADO)/Gas oil (GO)	As a heating oil in cold countries, fuel for trucks, trains power generators.
Heavy Fuel Oil (HFO)	Fuel for ships, power generators, boilers and furnaces.
Sulfur (solid)	For the manufacture of fertilizers, match sticks, explosives, sulfuric acid (H <sub>2</sub> SO <sub>4</sub> ) and pharmaceuticals.
Benzene ( $C_6H_6$ ) pure aromatic compound.	For the manufacture of petrochemicals, e.g., styrene, pesticides, dye intermediates, detergents, resins, solvents.

## **CDU** Steps

- The CDU is accomplished in multi-draw columns (strippers) for which all the heat is supplied to the feed.
- The products are condensed and withdrawn as side products, as the hot vapor portion of the feed are contacted with colder liquid reflux flowing down the column.
- The reflux is provided at the top of the flask by pumping some of the condensed liquid back to the top tray (Figure beside).
- The reflux is also provided at intermediate locations in the column with pump around cooling circuits.
- The hot liquid portions of the crude oil feed are stripped with steam to remove dissolved light hydrocarbons before leaving the bottom of the column



# Crude Oil Desalting

- Crude oil carries with it some brine in the form of very fine water droplets emulsified in the crude.
- The salt content of the crude measured in pounds per thousand barrels (PTB) can be as high as 2000.
- Desalting of crude oil is an important part of the refinery operation as the salt content should be minimized to 5.7 and 14.3 kg/1000 m3 (i.e., 2 and 5 PTB).

# What are the impacts of poor desalting?

• Poor desalting of the crude could adversely impact on the following:

Corrosion of overhead equipment.

Salt deposits inside the tubes of furnaces and tube bundles of heat exchangers. This causes fouling of the exchanger and thereby reducing the heat transfer efficiency.

Salts are carried with the products and can poison the catalyst in the catalytic cracking unit.

## Types of Salts in Crude Oil

- Salts in the crude oil are mostly in the form of dissolved salts in fine water droplets emulsified in the crude.
- This is referred to as water-in-oil emulsion, where the continuous phase is the oil, and the dispersed phase is the water.
- The water droplets are relatively tiny such that they cannot settle by gravity.
- These fine droplets have on their surfaces the big asphaltene molecules with the fine solid particles coming from sediments, sand or corrosion products.
- The presence of these molecules on the surface of the droplets acts as a protector that prevents the droplets from uniting with each other in what is referred to coalescence.
- Furthermore, the salts can be in the form of crystals that are suspended in the crude. Removing the salts requires that they must be ionized in the water. Therefore, wash water is added to the crude to enhance the desalting process

HCl dissolves in the overhead system water producing hydrochloric acid, which is extremely corrosive

#### magnesium chloride (MgCl2)

#### calcium chloride (CaCl2)

sodium chloride (NaCl) with sodium chloride being the abundant type.

These chlorides except NaCl hydrolyze at high temperatures to hydrogen chloride (HCl):

 $CaCl_2 + 2H_2O \rightarrow Ca(OH)_2 + 2HCl$ 

 $MgCl_2 + 2H_2O \rightarrow Mg(OH)_2 + 2HCl$ 



# Process Descriptions of Refinery Processes

## **Process Description of the Desalting Process**

Lecture 5

## **Desalting Process**

The desalting process is accomplished through the following steps:

### Water washing:

- Water is mixed with the incoming crude oil through a mixing valve.
  - The water dissolves salt crystals, and the mixing distributes the salts into the water, uniformly producing fine droplets.
  - Demulsifying agents are added to break the emulsion by removing the asphaltenes from the surface of the droplets

## Heating:

• The crude oil temperature should be in the range of 120–130 °F (48.9–54.4 °C) since the water-oil separation is affected by the viscosity and density of the oil.

#### Coalescence:

The water droplets are so fine in diameter in the range of 1–10 µm that they do not settle by gravity. Coalescence produces larger drops that can be settled by gravity.

## Coalescence

- This is accomplished through electrostatic electric fields between two electrodes.
  - The electric field ionizes the water droplets and orients them so that they are attracted to each other.
  - Agitation is also produced and assists in coalescence. The force of attraction between the water droplets is given by:

 $F = KE^2 d^2 \left(\frac{d}{s}\right)^4$ 

where

- K = a constant
- E = Electric field
- d = drop diameter
- s = the distance between drops centers.

## Settling:

According to Stake's law, the settling rate of the water droplets after coalescence is:



where

 $\rho$  = density  $\mu$  = viscosity d = droplet diameter k = a constant

- The crude oil is injected with five to six liquid volume percent water at a temperature 200–300 °F (93– 149 °C).
- Both the ratio of water to oil and the operating conditions are functions of the specific gravity of the crude oil, and typical operating conditions.
- The salts are dissolved in the wash water; oil and water phases are separated in a settling vessel either
- by adding chemicals to aid in breaking up the emulsion or
- by the application of an electrostatic field to coalesce the droplets of salt water.
  - Either an AC or DC field may be applied at potentials of 16,000–35,000 V. In the desalter, the salts (e.g., magnesium chlorides) selectively migrate to the aqueous phase which forms a brine solution at the bottom of the desalter while the crude oil that floats above forms a separate stream. Efficiencies up to 90–95% water removal are achieved in a single stage and up to 99% in a two-stage desalting process.



Two-stage desalter.



The application of an electrostatic field to coalesce the droplets of salt water.

- Either an AC or DC field may be applied at potentials of 16,000– 35,000 V. In the desalter, the salts (e.g., magnesium chlorides) selectively migrate to the aqueous phase which forms a brine solution at the bottom of the desalter while the crude oil that floats above forms a separate stream. Efficiencies up to 90–95% water removal are achieved in a single stage and up to 99% in a two-stage desalting process.
- A high-voltage field referred to as the "secondary field" of about 1000V/cm is applied between these two electrodes. Both the ionization of the water droplets and coalescence takes place, and the design achieves ~90% salt removal.

## Chemical Demo



## Electrostatic Settler



# How to achieve the successful desalting process?

**Residence** Time **Pressure Drop Polymer Injection** Water quality

# Residence Time

- The higher the residence time in a desalter, the better the oil/water separation.
- This variable can be only controlled with the vessel size, operating level in the size or the feed rate. Since the vessel size cannot be increased in size or reduce the feed rate, <u>a small increase in operating</u> level may significantly improve the quality of the brine.

# Pressure drop

- This variable can be optimized, which is across the desalter mix valve.
- The higher the pressure drop, the better the mixing and thus the improved removal of salts.
  - However, too high a pressure drop can result in the formation of emulsion layers that are difficult to break.
  - The optimal pressure drop depends on the types of crudes; thus it is important to perform test runs at dedicated periods to ensure that correct operation is achieved.(Why?)

# Polymer injection:

- Polymers tend to assist in solids separation and emulsion breaking; therefore, correct solution is applied for the system.
- Polymer types can effectively enhance the separation process for the crudes that are used.
- Both the injection type and location are important as the longer a chemical interacts with the crude, the better its separation.
- Polymer injection may be considered for solids separation at the crude tank with another injection for breaking emulsions at the desalter.

# Water quality:

- The quality of water employed for desalting is an essential requirement.
- Some refinery facilities utilize stripped sour water as a source for the desalter and contaminants in this waste stream may affect its performance. Therefore, <u>monitoring the quality of water is essential</u> <u>so as not to pose problems in the desalter (Why?).</u>

# What does the desalter process provide to the refineries?

• The desalter provides a very critical service for the refinery, and thus requires careful monitoring and regular optimization



# Process Descriptions of Refinery Processes

Reflux arrangement

Lecture 6

## **Desalting Process**

The desalting process is accomplished through the following steps:

### Water washing:

- Water is mixed with the incoming crude oil through a mixing valve.
  - The water dissolves salt crystals, and the mixing distributes the salts into the water, uniformly producing fine droplets.
  - Demulsifying agents are added to break the emulsion by removing the asphaltenes from the surface of the droplets

## Heating:

• The crude oil temperature should be in the range of 120–130 °F (48.9–54.4 °C) since the water-oil separation is affected by the viscosity and density of the oil.

#### Coalescence:

The water droplets are so fine in diameter in the range of 1–10 µm that they do not settle by gravity. Coalescence produces larger drops that can be settled by gravity.
#### Coalescence

- This is accomplished through electrostatic electric fields between two electrodes.
  - The electric field ionizes the water droplets and orients them so that they are attracted to each other.
  - Agitation is also produced and assists in coalescence. The force of attraction between the water droplets is given by:

 $F = KE^2 d^2 \left(\frac{d}{s}\right)^4$ 

where

- K = a constant
- E = Electric field
- d = drop diameter
- s = the distance between drops centers.

#### Settling:

According to Stake's law, the settling rate of the water droplets after coalescence is:



where

 $\rho$  = density  $\mu$  = viscosity d = droplet diameter k = a constant

- The crude oil is injected with five to six liquid volume percent water at a temperature 200–300 °F (93– 149 °C).
- Both the ratio of water to oil and the operating conditions are functions of the specific gravity of the crude oil, and typical operating conditions.
- The salts are dissolved in the wash water; oil and water phases are separated in a settling vessel either
- by adding chemicals to aid in breaking up the emulsion or
- by the application of an electrostatic field to coalesce the droplets of salt water.
  - Either an AC or DC field may be applied at potentials of 16,000–35,000 V. In the desalter, the salts (e.g., magnesium chlorides) selectively migrate to the aqueous phase which forms a brine solution at the bottom of the desalter while the crude oil that floats above forms a separate stream. Efficiencies up to 90–95% water removal are achieved in a single stage and up to 99% in a two-stage desalting process.



Two-stage desalter.



The application of an electrostatic field to coalesce the droplets of salt water.

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- A high-voltage field referred to as the "secondary field" of about 1000V/cm is applied between these two electrodes. Both the ionization of the water droplets and coalescence takes place, and the design achieves ~90% salt removal.

#### Chemical Demo



#### Electrostatic Settler



# How to achieve the successful desalting process?

**Residence** Time **Pressure Drop Polymer Injection** Water quality

### Residence Time

- The higher the residence time in a desalter, the better the oil/water separation.
- This variable can be only controlled with the vessel size, operating level in the size or the feed rate. Since the vessel size cannot be increased in size or reduce the feed rate, <u>a small increase in operating</u> level may significantly improve the quality of the brine.

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# What does the desalter process provide to the refineries?

• The desalter provides a very critical service for the refinery, and thus requires careful monitoring and regular optimization

## The reflux arrangements:

Top tray Reflux

#### Pump back reflux

#### Pump around Reflux



## Process Descriptions of Refinery Processes

Reflux arrangement

Lecture 6

#### Top tray reflux.

This reflux takes place at the top of the tray, and the reflux is cooled and returned to the tower.

In some towers/columns, no reflux is provided to any other plate.

Operating the tower only with top reflux has some disadvantages.(Why?)

The heat input to the column is through heated crude at the bottom, and removal is from the top. This creates a large traffic vapor that requires a larger tower diameter. The recovery of heat is less efficient, but the unit is simple in design and operation (Figure1 beside).



Figure 1

#### Pump back reflux

- The reflux is provided at regular intervals as this helps every plate to act as a true fractionator.
- The vapor load on the tower is fairly uniform and requires a smaller column size.
- The rejected heat at the reflux locations can be effectively utilized.
- Since the tower temperature increases downwards, the reflux location can be placed where the temperature is sufficient for transferring heat to another stream.
- Many refineries employ this arrangement as the towers provide excellent service. (Figure beside).



#### Pump around reflux

- In this arrangement, the reflux from a lower plate is taken, cooled and fed into the column at a higher level by 2 to 3 plates.
- This creates a local problem of mixing uneven compositions of reflux, and liquids present on the tray.
  - This can be overcome by treating all the plates in this zone as a single plate, which results in an increase in the height and the number of plates of the column (Figure beside).



# What are the functions of pumparound cooling?

- To remove latent heat from the hot flash zone vapors and help condense the side products.
- To improve the efficiency of the crude preheat train by allowing heat recovery at higher temperature levels than the overhead condenser, thus reducing the required crude furnace duty.
- To reduce the vapor flow rate through the column; this reduces the required size of the column.

## How does these reflux arrangement work?

- The maximum boiling point of the liquid side products is controlled on the main column by their draw rates. For example, to increase the maximum boiling point of the kerosene product as shown in Figure 1,
- it is necessary to decrease the flow of the diesel product (which has a higher boiling range) and to increase the flow of the kerosene product.
- This adjustment allows heavier components to travel up the column to the kerosene draw tray, thereby increasing the maximum boiling point of the kerosene product. There may also be a decrease in the lightest portion of the diesel product because of this adjustment.

#### Pumparound Heat removal

• There are two possible ways to remove the heat from distillation column:

Top Tower Reflux (External Reflux)

Circulating Reflux (Internal Reflux)

### The circulating/internal reflux

- The circulating/internal reflux stream is referred to as the pumparound that aids to remove heat from a tower. Figure d shows a pumparound or internal reflux.
- The hot liquid at 550 °F is drawn from tray 11, which is referred to as the pumparound draw tray. The liquid pumparound is cooled to 450 °F and returned to the tower at a higher elevation onto tray 10. Figure d shows that the cold 450 °F pumparound return liquid enters the downcomer from tray 9. Tray 10 is called the pumparound <u>return tray.</u>



(**d**)

Further explanation :-



(**d**)

Calculation i-  
Specific heat of the pump around liquid = 0.65 
$$\frac{BTW}{Ib-T}$$
 (hot side)  
 $Q = (W \ Q \ DT)_{tube} = (2000)(0.65)(550 - 450) = /30,000 \ Btue/h$   
Liquid shell (cold side) of the pump around heat exchanger:-  
Specific heat = 0.55  $\frac{BTW}{Ib}$ . F  
 $W = \frac{Q}{Cp \ DT} = \frac{130,000}{(3-55)(350-250)} = 2,364 \ Ib/h$ 



## The reflux arrangements in atmospheric crude distillation unit (CDU)

Part 2

## Another Purpose of the Pumaround

• Another purpose of the pumparound is to suppress top-tray flooding. For example, if tray 1 or 2 floods, the following would occur:



What is the indication of flooding in the distillation column? How it is corrected?

• If the reflux rate is increased to reduce the tower-top temperature, the top temperature will increase further rather than decrease. This is an indication of top-tray flooding. This is corrected by increasing the pumparound duty.

## Tower Pressure Drop and Flooding

- A characteristic of process equipment is such that the best operation is attained at neither a very high nor a very low loading.
- The intermediate equipment load that results in the most efficient operation is known as the best efficiency point.
- For distillation trays, the incipient flood point corresponds to the best efficiency point.

### Flooding and Entertainment Demonstration



## Correlation to find Efficiency

 Correlations have been carried out to determine the best efficiency point for valves and sieve trays and are determined by:

$$\Delta P = K \frac{(NT)(TS)(SpGr)}{28}$$

where

 $\Delta P$  = pressure drop across a tray section, psi NT = the number of trays

TS = tray spacing, in.

SpGr = specific gravity of clear liquid at flowing temperatures.

- K = 0.18 to 0.25: Tray operation is close to its best efficiency point.
- K = 0.35 to 0.40: Tray is suffering from entrainment–increase in reflux rate, noticeably reduces tray efficiency.
- $K = \ge 0.5$ : Tray is in fully developed flood-opening a vent on the overhead vapor line will blow out liquid with the vapor.
- K = 0.10 to 0.12: Tray deck is suffering from low tray efficiency, due to tray deck leaking.
- K = 0.00: The liquid level on the tray is zero, and quite likely the trays are lying on the bottom of the column.



## Thermal Cracking Processes

Lecture 8

## Thermal Cracking Processes

- Thermal cracking is the cracking of short and long chain residues under severe thermal conditions.
- The liquid products from processes are highly olefinic, aromatic and have high-sulfur content.
  - They require hydrogen treatment to improve their properties.
- Coking is the process of carbon removal from the heavy residues in producing lighter components that are lower in sulfur as most of the sulfur is retained in the coke.
- The thermal treatment of hydrocarbons involves a free-radical mechanism where reactions take place in the initiation step.
- The reactions in the final step result in the formation of heavy fractions and coke.

## Classes of Thermal Cracking Processes

#### Mild cracking (Visbreaking)

• The mild cracking involves sufficient heating to crack the residue just enough to lower its viscosity and to produce some light products.

#### Delayed coking

 Delayed coking requires moderate thermal cracking to convert the residue into lighter products, leaving coke behind.

#### Sever thermal Cracking

- The third process requires severe thermal cracking in which part of the coke is burned and used to heat the feed in the cracking reactor, as in fluid coking.
- In another part of the process, steam is used to crack most of the coke (flexicoking).

# The conditions for industrial thermal cracking processes:

#### Visbreaking

- Mild heating (471-493
   °C) at (3.4-14bar)
- Reduced viscosity of fuel oil.
- Low conversion at 221 oC
- Heated oil or soaking drum

#### **Delayed coking**

- Moderate heating (482-516 °C); 6.2 bar
- Soak drums (452-482oC)
- Residence time until they are full of coke
- Coke is removed hydraulically
- Coke Yield ~ 30% wt.

#### Fluid coking and flexicoking

- Sever heating (482-566 °C)at 0.7 bar.
- Fluidized bed with steam
- Higher yields of light ends
- Less coke yield (20% for fluid coking and 2% for flexi-coking)
## Vacuum distillation

- The vacuum distillation unit (VDU) follows the atmospheric or the crude distillation unit (CDU) in refineries.
- The bottom of the atmospheric distillation is known as the reduced crude or topped crude.
- The reduced crude bottoms from the atmospheric tower provide the feed to the vacuum column where the second stage of distillation takes place.

## Cracking does not occur in a vacuum column

 Cracking does not occur in a vacuum column because the column has a large diameter and is operated at very low pressure, and subsequently boiling takes place at a low temperature.

# Types of vacuum distillation columns

#### wet type

- The wet type unit uses steam to reduce the partial pressure of oil in the flash zone of the column to the required level
- The wet type unit requires a huge quantity of steam, which is dependent on the amount of vacuum

#### dry type

- The dry type unit depends solely on the effectiveness of the vacuum inside the column to vaporize the heavy oil
- The dry vacuum type has a higher flash zone temperature than the wet vacuum unit for the same service, and as it provides a boot cooling circuit to keep the column boot from coking and becoming plugged. The boot cooler subcools the liquid from the flash zone and prevents coking.

# Wet and dry vacuum units



# What is the both unit have? How it works?

- The both unit have a wash grid above the flash zone, the feed to the column enters the flash zone at very high velocity, and high amount of heavy liquid entertained in the flash zone vapor.
- The heavy gas oil that is returned to the column over the wash grid washes down the entrained liquids.



# hermal Cracking Processes

Lecture 10

## Pressure Drop

- The pressure drop that occurs between the barometric condenser and the vaporizer section of the column is essential, as the purpose of vacuum operation is to produce a low effective pressure at the vaporizer, and thus the vacuum must not be lost by excessive friction loss through the vapor line, condensers and column plates.
- Avoiding a few millimeters (mm) of pressure drop from the barometric to the vaporizer can save many pounds of process steam as the saving in the quantity of steam is important.

## Vacuum Distillation Operation

• The operation of vacuum column is similar to that of crude oil distillation (atmospheric) column with refluxes, side strippers, pumparounds, steam injection, etc., except that the operation is under vacuum conditions. Figure beside shows a schematic of high-vacuum distillation column for processing long residue to waxy distillate and short residue, respectively.



# Steps of fractionation in the vacuum distillation

- This process has more internal reflux, and the side products are drawn to meet specified viscosities and other related properties that are important for lubricating oils.
- Not all topped crude oil is suitable for the production of lubricating oils. For asphalt type crude oils, the vacuum column bottoms product is used to make the road asphalt.
- For other types of crude oils, the material is charged to a coking process, where it is cracked to petroleum coke and low-grade gas oils.
- The gas oils from the coking process must usually be treated to remove sulfur and nitrogen before they are suitable for charge to cracking units

## **Process Description**

- What are the causes of losses of products and equipment fouling in the atmospheric pressure distillation?
  - Highest temperature is required in the equipment, and thermal cracking would occur-heavier fractions of crude oil will cracked.
- Why heavier fraction is fractioned under vacuum condition?
  - Distillation is carried out with an absolute pressure in the tower flash zone area of 25-45 mm Hg.
- What we can do to enhance the vaporization in the distillation column?
  - To enhance vaporization, the pressure is lowered even further to 10 mm Hg.
  - Addition of steam increases the furnace tube velocity and reduces the coke formation as well as decreasing the total hydrocarbon partial pressure in the vacuum tower.

#### Enters at the lower part of the column

• 3-5 % vapors are produced

Feed Entry

between the High –Vacuut gas oil(HVGO) draw-off tray and the flash zone.

#### Products

- The distillate is low vacuum gas oil(LVGO)
- Medium vacuum
- gas oil (MVGO)
- High vacuum gas-oil (HVGO)
  The two cuts of MVGO and HVGO are essential to extract heat

- Columns equipped with packing for fractionation, heat exchange
  - Vacuum equippedwith...

### in the colur, n, which is important for creating the a low vacuum in

low section of

Dr.Omar Al-Kubaisi

#### Vacuum Creation

 Created by a series of steam jet ejectors that use `100 psi (6.9 bar) steam.



Thermal Cracking Processes Steam Jet Ejectors

Lecture 11

# **Steam Jet Ejector**

• The ejector gas load consists of two sources:

air in-leakage uncondensed gas

• The amount of air sucked into the system is independent of throughput.

• The uncondensed gas that results from thermal cracking of the vacuum column charge in the preheat furnace is proportional to the load on the ejector interstage condensers and hence the feed rate.



## Explain the Steam Jet Ejectors Operation

- The convergent-divergent steam jet is rather like a two-stage compressor with no moving parts [4]. The figure in the previous slide shows a simplified steam jet ejector, where high-pressure motive steam enters through a steam nozzle.
- As the steam flows through this nozzle, its velocity greatly increases as it flows to the condenser. The condenser condenses the steam at a low temperature and low pressure. The steam accelerates toward the cold surface of the tubes in the condenser, where its large volume will disappear as the steam turns to water. The motive steam accelerates to such a great velocity that it can exceed the speed of sound (i.e., sonic velocity). This high increase in velocity of the steam represents a tremendous increase in kinetic energy of the steam. The source of this kinetic energy is the pressure of the steam.
- As the high-velocity steam enters the mixing chamber (Figure), it produces an extremely low pressure. The gas flows from the jet suction nozzle and into the low pressure mixing chamber. The rest of the jet is used to boost the gas from the mixing chamber up to the higher pressure in the condenser, which is carried out in two compression steps: converging and diverging.



# Demonstration for the Steam Jet Ejectors



# Steam Jet Ejector

# What will happen if an ejector is not overloaded at a normal gas rate?

• If an ejector is not overloaded at a normal gas rate, reducing the gas load will not result in the greatly improved vacuum. The ejector is simply oversized at the lower charge rate and wastes steam without obtaining any appreciable benefit in lower vacuum tower pressure.

# For what purpose steam jet ejectors are employed?

• Steam jet ejectors are employed to recompress low pressure steam to a higher-pressure steam. They are sometimes used to compress low pressure hydrocarbon vapors to higher-pressure hydrocarbon gas.

#### Vacuum Distillation Unit – Production of Waxy Distillate

- Vacuum distillation units have a system to create the vacuum that uses either <u>ejectors or a combination of</u> <u>ejectors and liquid ring pumps.</u>
- <u>Ejectors</u> recompress the gases through a nozzle where vapors from the column are sucked into the venturi section of the nozzle by a stream of medium- or low-pressure steam.
- The vapor phase at the ejector exit is *partially condensed in* an exchanger with cooling water.
- The liquid phase flows to the overhead drum. The vapor phase goes from the condenser to another ejector-condenser stage.



## Vacuum Distillation Unit –Production of Waxy Distillate

- Liquid ring pumps are similar to rotor gas compressors. One pump can replace two or three stages of ejectors in dry or wet type vacuum distillation.
- They do not use steam and can therefore reduce hydrocarbon-rich aqueous condensates in a system using ejectors.
- Systems with ejectors are flexible and easy to operate.
- The higher investments required by liquid ring pumps are offset by steam consumption and lower installation costs.





# Thermal Cracking Processes Coking

Lecture 12

# Coking

- Coking is a thermal cracking process as the operation is often considered to be the last stage in the refining since the heaviest fraction (pitch or tar) is converted into very useful products. Coking is a process by which the vacuum residue obtained from vacuum column is processed to making carbon electrodes.
- The process of coking is rather complex involving batch and continuous operations <u>as it produces solid, liquid</u> and gaseous products.







# **Delayed** Coking

- Objective
  - The process objective is to convert low-value residue to valuable products such as naphtha, diesel and coker gas oil
- Where this process occur?
  - This process occurs in a large vessel at a slow pace (delayed), and it is the most important process among the various coking methods (the precursor to delayed coking is the two-coil cracking process).
- Capabilities
  - It is capable of cracking all types of feed materials, including solvent extracts. Thermo-cracking increases the hydrogen/ carbon ratio by carbon rejection in a semi-batch process.
- Feed Condition
  - The feed to the delayed coker can be any undesirable heavy stream that contains high metal content. This could be from a vacuum residue, a fluid catalytic cracking slurry and visbreaking tar (residues).
  - The products from the coker are unsaturated gas (C1 C4), olefins C C and iC<sub>4</sub>. The olefins are very desirable feedstocks to the petrochemical industry. Isobutane (iC4) and olefins are sent to the alkylation units, and the C<sub>3</sub>/C<sub>4</sub> gases are sent to the LPG plant.
  - The coker unit is the only unit in the refinery that produces coke. The highly aromatic naphtha does not require reforming and is sent to the gasoline pool. Light coker gas oil is hydrotreated and sent to the kerosene pool. Heavy coker gas oil is sent to the FCC for further cracking.





# Delayed Coking Process Steps

- In delayed coking process, heating is carried out in the furnace to initiate cracking, and the chemical reactions are completed in huge and tall coke drums.
- Several coke drums in series are operated in a cyclic manner. While one drum is being filled, the other drums are in the process of coking and decoking. By orderly rotating of the drums, the process can be termed continuous, and a minimum of two drums are essential even for small capacity plants.
- Superheated feed in a large coke drum is flashed where the coke remains, and vapors leave the top and returns to the distillation column.
- The heavy oils and light oils are recycled in different ratios to maximize the yield of either coke or distillates as per the requirement. The off-line coke drum is drilled, and the petroleum coke is removed via hydro-jetting.

# Replacing for the Large drums in one of the refinery...



https://youtu.be/6KUDX1gLIF8

# The expected yield of coke

The expected yield of coke may be ~ 30% for reduced crudes or 80% for tars and pitches. Coke from these
units contains volatile matter up to 8–15%, and the bulk density of the coke obtained may be around 9 kg
per liter.

CDE (Conradson Decarbonizing Efficiency) of the plant may be reaching up to 99.8% [5]. The conditions and parameters in delayed coking are given:

Heavy oil, discharge temperature, °C	470-520
Coking temperature, °C	450-470
Pressure in coke drums, atm.	5-6
Drum diameter, m.	4-5
Drum height, m.	14-20
Thickness of drum walls, mm	~40

# What are the licensors that provide the technologies for the coking method?

- The following licensors have provided the technologies for the delayed coking method:
  - ABB Lummus Global
  - Conoco Philips
  - Exxon Mobile Research
  - Foster Wheeler/UOP LLG

# What are the delayed coking unit operations consist of?



# What are the product of delayed coking unit?



### Figure shows the schematic of the delayed coking process.





# Thermal Cracking Processes Coking

**Other Types of Coking** 

Lecture 13

# **Fluid Coking**

- The vacuum residue is converted to valuable products as naphtha, diesel and coker gas oil.
- Fluid catalytic crackers use catalysts to aid cracking and here cracking and coking are catalyzed by coke particles.



Typical yields and dispositions of delayed and fluid coking processes.

Product	Yield, wt% of feed	Disposition
Light ends	12.5-20	LPG
Naphtha	10-15	Naphtha hydrotreating
Light Coker Gas Oil	18-24	Distillate hydrotreating
Heavy Coker Gas Oil	30-40	Fluid catalytic cracking
Petroleum Coke	20-35	Sponge-carbon anodes; Needle-graphite electrodes Any coke-power generation

- -

# The process involves:

- Preheating the residue feed,
- Scrubbing the coke particles and providing primary condensing of reactor vapors by introducing the feed to the scrubber.
- The residue is atomized into a fluid coke bed, and thermocracking occurs on the particle surface.
- Coke particles leaving the reactor are steam stripped to remove remaining liquid hydrocarbons.
- Coke particles produced in the same unit assume more or less spherical shape and act as heat carriers while travelling from the burner (regenerator) to the reactor; and coke carriers in reverse travel.
- Some portion of steam stripped coke is burnt, and the remaining coke is taken out.
- The hot coke particles are in a state of fluidization caused by incoming vapors. Therefore, the effective continuous circulation of coke particles is unavoidable.
- Sub stoichiometric air is introduced to the burner to burn some of the coke and provide the necessary heat for the reactor, and the reactor vapors leave the scrubber and flow to the fractionator.

### Process flow diagram of fluidic coking unit.



## **Flexi-Coking**

- The feed consists of heavy residue and is fed into a scrubber fractionator reactor where thermal cracking occurs.
- Steam is admitted from the bottom, and the coke fines circulate through the heater where further coke formation takes place and then passes onto a gasifier where it encounters a stream of air and steam.
- Coke is withdrawn between the heater and the gasifier.
- The process heat is supplied by circulating hot coke between the heater and the reactor.
- Coke reacts with air and steam in the gasifier to produce heat and low Btu gas that can be used as fuel in furnaces and boilers.
- About 97% of the coke generated is consumed during the process as a small amount of coke is withdrawn from the heater and fine system which can be disposed in cement kilns or used in metals recovery.
- Partial gasification and oxygen-enrichment can be used to provide additional process flexibility.
- The primary advantage of the flexi coking (Figure beside) over fluid coking is that most of the heating value of the coke product is made available as low-sulfur fuel gas, which can be burned without an SO<sub>2</sub> removal system on the resulting stack gas, whereas the system would be required if coke that contains 3–8 wt% sulfur is burned directly in a boiler.

Process flow diagram of flexi-coking.


The yields for a typical Middle East vacuum residue (~25 wt%,Concarbon, ~5 wt% sulfur) are:

	Recycle	Once-through
Light ends, wt%	11.8	10.4
Naphtha (C <sub>5</sub> , 350 °F), wt%	11.5	9.5
Distillate (350–650 °F), wt%	14.5	13.1
Heavy gas oil (650 °F $_{+}$ ), wt%	32.1	39.7
Low Btu gas, MBtu/bbl	1.2	1.1
C <sub>5+</sub> Liquids, wt%	58.1	62.3

#### **Contact Coking**

- In contact coking, coke circulates between the reactor and the heater.
- A part of the coke is always necessary for supplying thermal energy, and the remaining portion is separated in the disengager. This method gives great flexibility in operation and control.

· · · · · · · · · · · · · · · · ·				
	Delayed coking	Fluid coking	Flexi coking	Contact coking
Gravity °API	15	15	18.9	18.8
Conradson Carbon Residue	9	9	11.7	11.7
Sulfur	1.2	1.2	0.6	0.6
Products				
C <sub>3</sub> and lighter fractions%	6	5	7.5	14.9
Coke%	22	11	13.0	20.0
CDE%	99.8	91.2	99.3	99.3

Note: CDE = Conradson Decarbonizing Efficiency.



## Thermal Cracking Processes Coking

**Coke Drums** 

Lecture 14

#### **Coke Drums**

- Vacuum residue from <u>VDU</u> is preheated in preheat exchangers against heavy coker gas oil <u>HCGO</u> and heavy coker gas oil pumparound and passes through the fractionator boot where it is heated by mixing with the heavy fractions, and the resulting heater charge enters the coker heater coil at a high velocity.
- Steam is introduced into the coil which prevents coke deposition in the coil.
- The hot and partially vaporized mixture enters the coke drum. The coke drum is charged with the hot mixture to <u>1/2 to 2/3</u> of the height of the drum.



# How does the hot-mix level measured in the coke drums?

• The level of the hot-mix in drums is measured and controlled by a cathode-ray monitoring device.

## What is the time required to charge the drum? What will happen after the after the charging is complete?

The charging of a coke drum may require a period of 4–5 hrs. Once the charging is complete, the drum is isolated from the stream. Effluents of the coke heater are then switched to the second drum.

## What is the time required for the coking?

 Coking is a slow process, and it usually takes a period of 10–16 hrs. The time of charging coke drums must balance the time of coking and decoking operations.

## Explain the process of coking?

- The feed is mixed with the stripped liquid (internal recycle) at the bottom of the coker fractionator. This recycled stream is heavier than the heavy coker gas oil and condenses in the wash section of the column.
- The mixture is referred to as the heater charge. The introduction of relatively cool coker feed into the fractionator bottom reduces the tendency of coke formation in the column bottoms.
- Fractionator bottoms liquid level is maintained by regulating the flow rate of coker feed from the coker feed drum.
- A side stream of fractionator bottom liquid is continuously circulated through the fractionator bottoms strainers by the fractionator bottoms recirculating pump to remove the coke fines.



#### Process continues...

- The coker heater charge is pumped by the coking heater charge pump, as <u>the primary function of the</u> <u>coker heater is rapidly to heat the feed to the required reaction temperature while avoiding premature</u> <u>coke formation in the heater tubes.</u>
- This steam is used for stripping light coker gas oil (LCGO) and heavy coker gas oil (HCGO).
- The coker heater combustion air is also preheated against flue gas in the convection section to increase efficiency.
- The coker heater is fired with fuel oil or fuel gas or combination of both fuels.
- A heater fuel gas drum separates any condensable liquids in the fuel gas before they reach the coker heater.

## Some important points about the coke drums

- What is benefit of using two-heater configuration in the coke drum?
  - A two-heater configuration would allow offline decoking of one furnace without having to shut down the entire unit.
- The coke drum feed leaves the heater at ~ 1040 °F (506 °C) and 4.0 kg/cm2. The coke drum inlet switch valve diverts the hot coker feed to the bottom of the filling or coking mode coke drum.
- In the coke drum, the hot feed cracks to form coke and cracked products. Each coke drum is filled in a 24-hour period.
- Why we need to use an antifoam chemical into the coke drums?
  - An antifoam chemical is injected into the coke drum to prevent foam going into the coker fractionator.
- How we can prevent the coke formation in the coke drums?
  - The cracked product leaves the top of the coke drum at 842 °F (450 °C) and 1.05 kg/cm<sup>2</sup>, which is quenched to 799 °F (426 °C) or less with heavy coker gas oil to stop the cracking and polymerization reactions, and thus to prevent coke formation in the vapor line to the coker fractionator.

### Fractionator column

- The fractionator column of 24 trays and a spray zone divided into two major sections by the heavy coker gas oil (HCGO) draw pan.
- The quenched coke drum effluent vapor flows upwards through the spray chamber, with some degree of cooling accomplished by contact with HCGO wash liquid.
- The heavy recycled liquid is condensed and collected on the wash section chimney and flows to the bottom sump to combine with fresh coker feed.
- The product vapor flows to the upper section of the column through the vapor risers in the heavy coker gas oil draw-off pan.
- This vapor consists of the products and steam. Heat removal and fractionation are accomplished in the upper section of the fractionator



#### Heavy Coker Gas Oil (HCGO) Production

- HCGO draws are taken from the same draw tray and used for quenching, pumparound and HCGO stripper feed.
- The HCGO quench, HCGO wash and HCGO pumparound are pumped by common pumps.
- The heat in the pumparound is also used to produce steam.
- The HCGO product draw from the coker fractionator flows under level control by gravity to the stripper. It is steam-stripped in the stripper, and vapors are returned to the fractionator.
- The stripped HCGO product is pumped by the HCGO product pumps to heat the fresh feed, which is then utilized in generating steam in the medium pressure (MP) steam generator.
- Finally, the HCGO product stream is cooled to 176 °F (80 °C) in the HCGO product air cooler and is routed as cold HCGO product to the refinery fuels blending section.

#### Light Coker Gas Oil (LCGO) Production

- LCGO is withdrawn from the chimney tray below tray 15 of the coker fractionator, and flows by gravity under level control to the light coker gas oil stripper.
- Medium pressure superheated steam is used for stripping LCGO product, which is then successively cooled to 104 °F (40 °C) and flows to the coalescers and salt driers and finally to storage and blending.



## Thermal Cracking Processes Coking

**Yield Correlations for Flexi-coking** 

Lecture 15

## Yield Correlation for flexi-coking

- The yield correlations for flexi-coking are based on the <u>Conradson carbon content</u> of the vacuum residue (CCR, wt%), its °API gravity and sulfur content (Sf).
- Correlations based on data compiled by *Maples* are expressed in weight percent yields as:

Gas wt% = 0.171943 × CCR wt% + 5.206667

Gasoline wt% = -0.115234 × CCR wt% + 18.594587

Coke wt% = 1.037233 × CCR wt% + 1.875742

Gas oil wt% = 100 – Gas wt% – Gasoline wt% – Coke wt%

#### **Gas composition:**

- C<sub>4</sub> wt% = -0.028627 × CCR wt% + 3.200754
- C<sup>-</sup><sub>2</sub>wt% = 0.647791 × [Gas wt%–C<sub>4</sub> wt%] + 0.456001
  - $C_3$  wt% = Gas wt% C4 wt%  $C_2^-$  wt%

#### **Sulfur distribution in products:**

- S wt% in Gasoline =  $0.193461 S_f$
- S wt% in Gas oil = 0.91482 S<sub>f</sub> + 0.16921
- S wt% in Coke =  $1.399667 S_f + 0.18691$
- S in Gas = S in Feed S in Gasoline S in Gas oil– S in Coke

#### Gravity of flexi-coker feed and gas oil

- Feed  $API_f = 0.5 \times CCR \text{ wt\%} + 0.932644$
- Gas oil API =  $1.264942 \times API_f + 0.506675 \times CCR wt\% 0.79976$

A vacuum residue of Conradson carbon residue (wt% CCR= 15) is fed into a delayed coker at a rate of 350,000 lb/h of API = 8.5 and a sulfur content of 3.0 wt%. Determine the amount of yield (lb/h) and their sulfur content. Calculate the yields of liquid products in BDP.