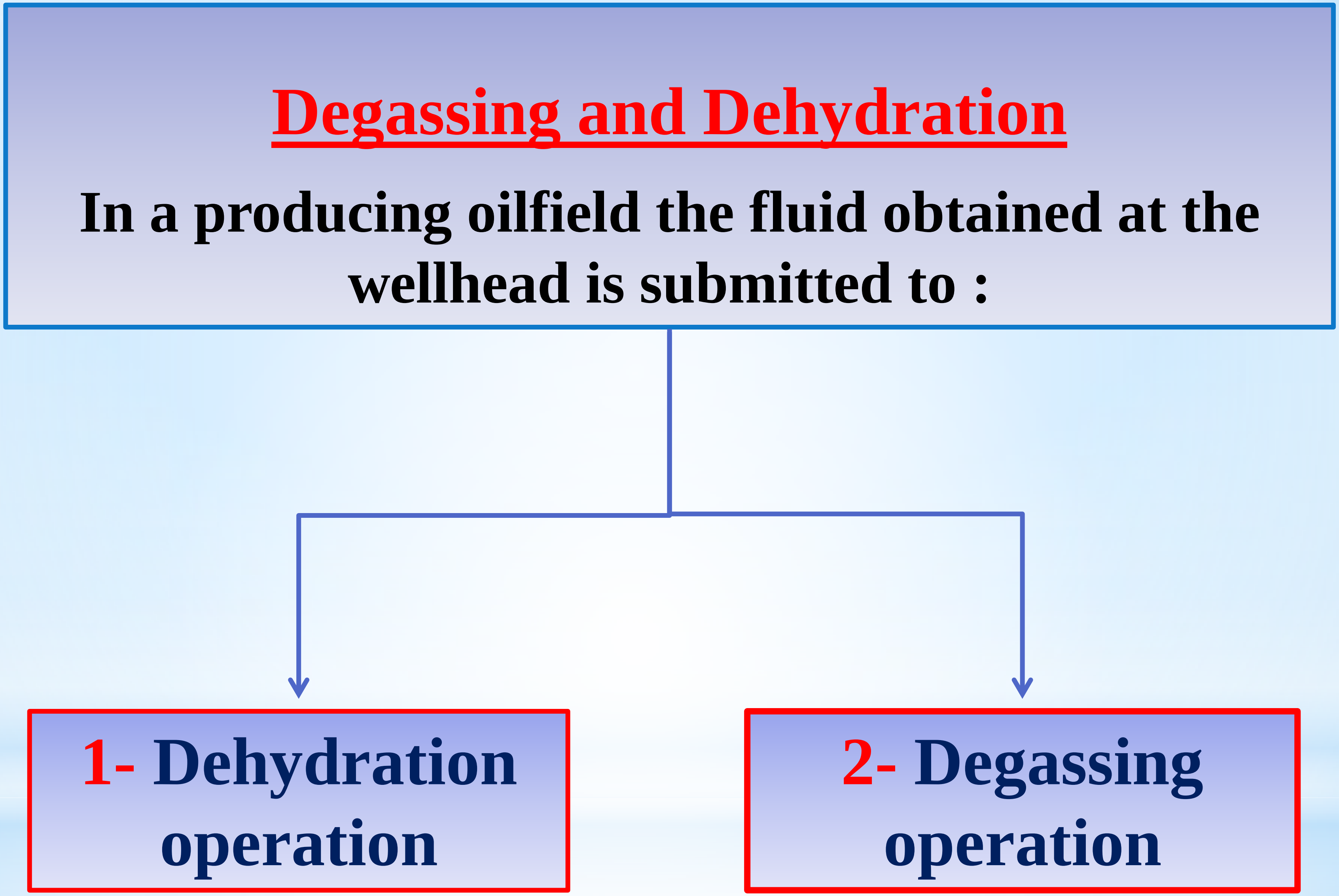
Fourth Year - Chemical Process Eng. Branch
Petroleum Refinery Eng. Lectures
By
Dr. Adnan A. Abdul Razak

Degassing and Dehydratio

Degassing and Dehydration

In a producing oilfield the fluid obtained at the wellhead is submitted to :



1- Dehydration operation

2- Degassing operation

Degassing and Dehydration

1- Degassing: -

At the high pressure existing at the bottom of the producing well, crude oil contains great quantities of dissolved gases. When crude oil is brought to the surface, it is at a much lower pressure. Consequently, the gases that were dissolved in it at the higher pressure tend to come out from the liquid.

Two-Phase Gas–Oil Separation

High-pressure crude oils containing large amount of free and dissolved gas flow from the wellhead into the flow line, which routes the mixture to the GOSP. (This is usually done by admitting the well fluid into a gas–oil separator plant (GOSP) through which the pressure of the gas–oil mixture is successively reduced to atmospheric pressure in a few stages). In the separator, crude oil separates out, settles, and collects in the lower part of the vessel.

Degassing and Dehydration

Gas goes out the top of the separators to a gas collection system, a vapor recovery unit (VRU), or a gas flow line. Crude oil, on the other hand, goes out the bottom and is routed to other stages of separation, if necessary, and then to the stock tank (Fig. 1).

Degassing and Dehydration

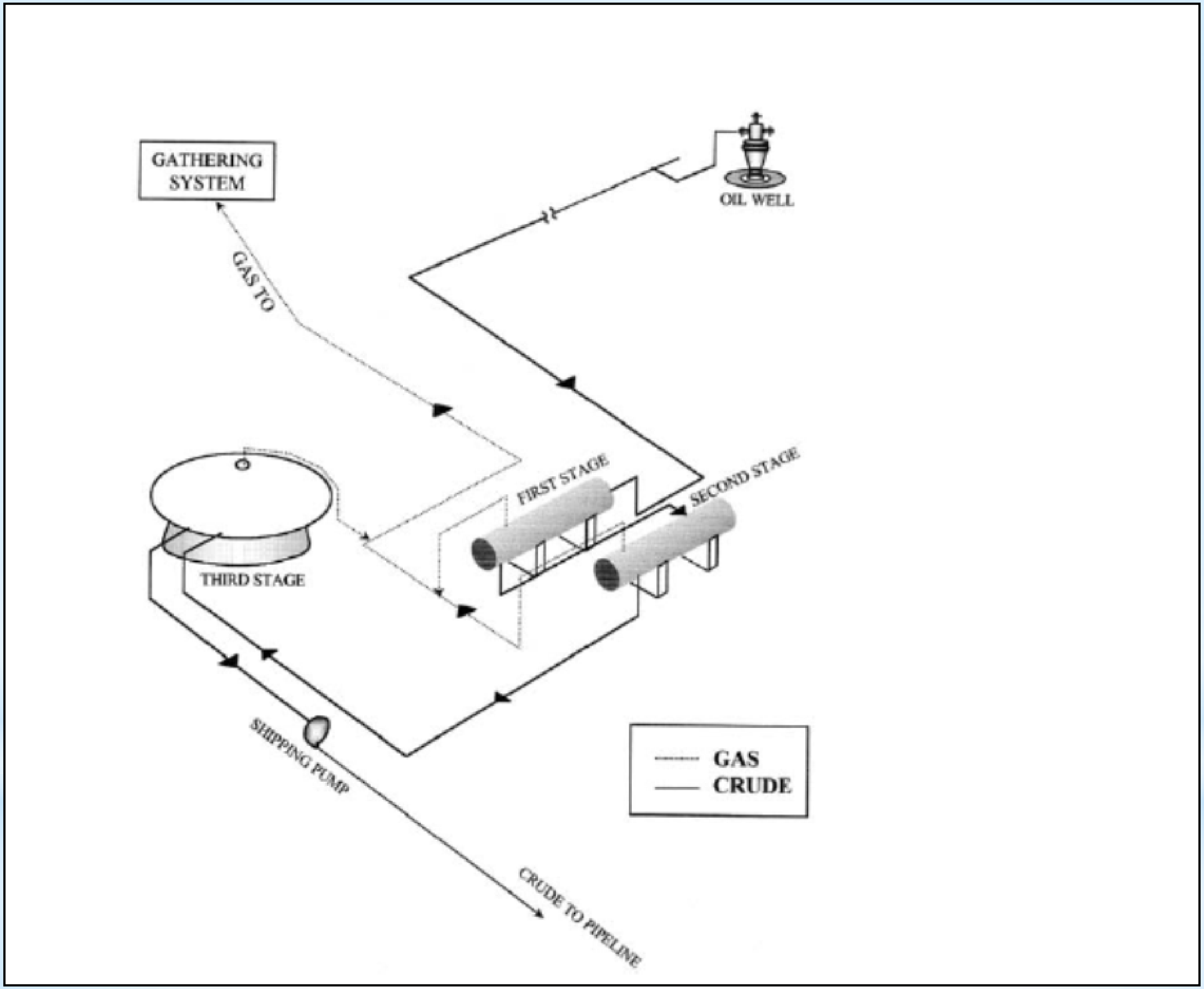


Figure 1 Flow of crude oil from oil well through GOSP.

Degassing and Dehydration

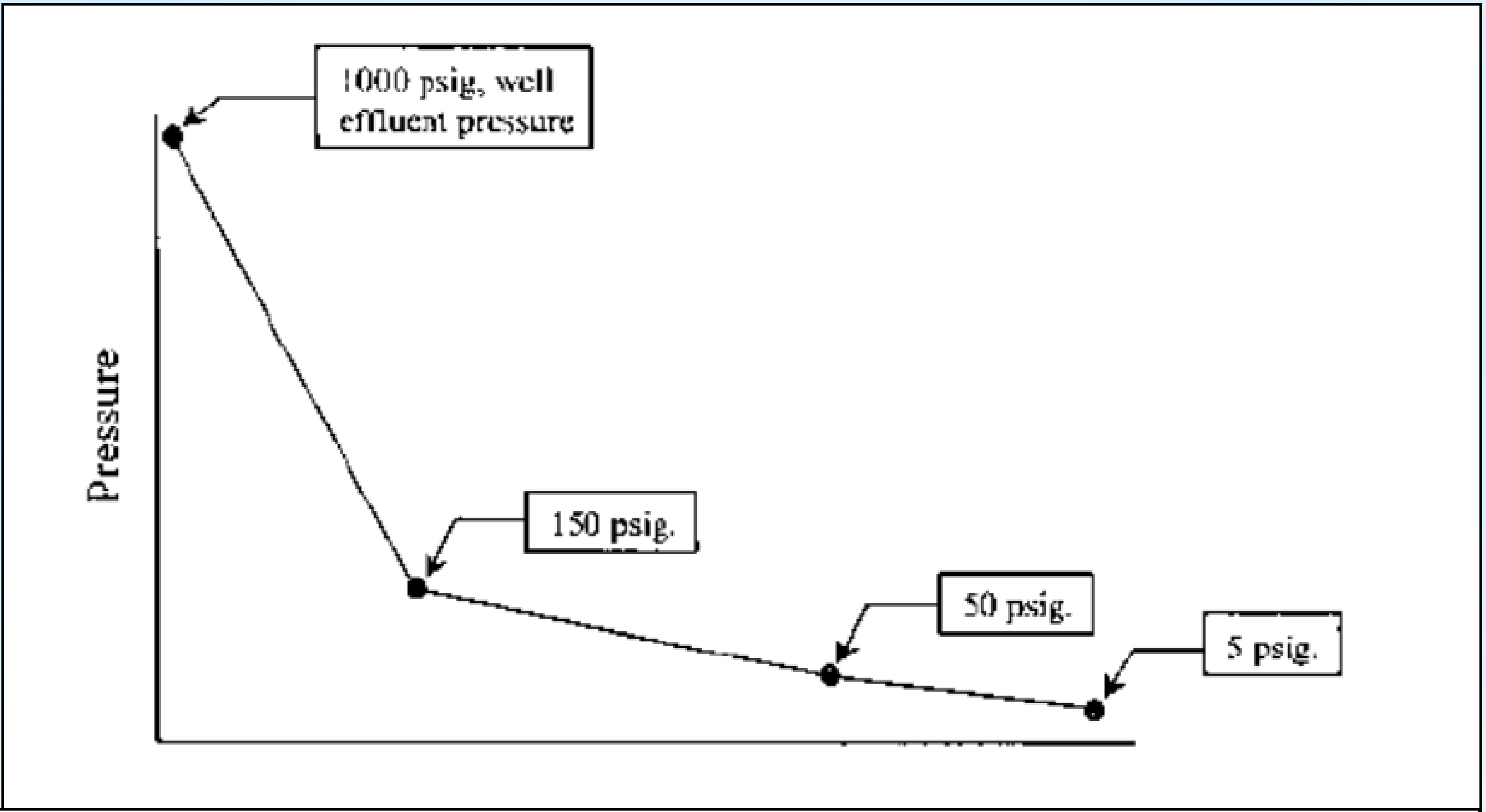
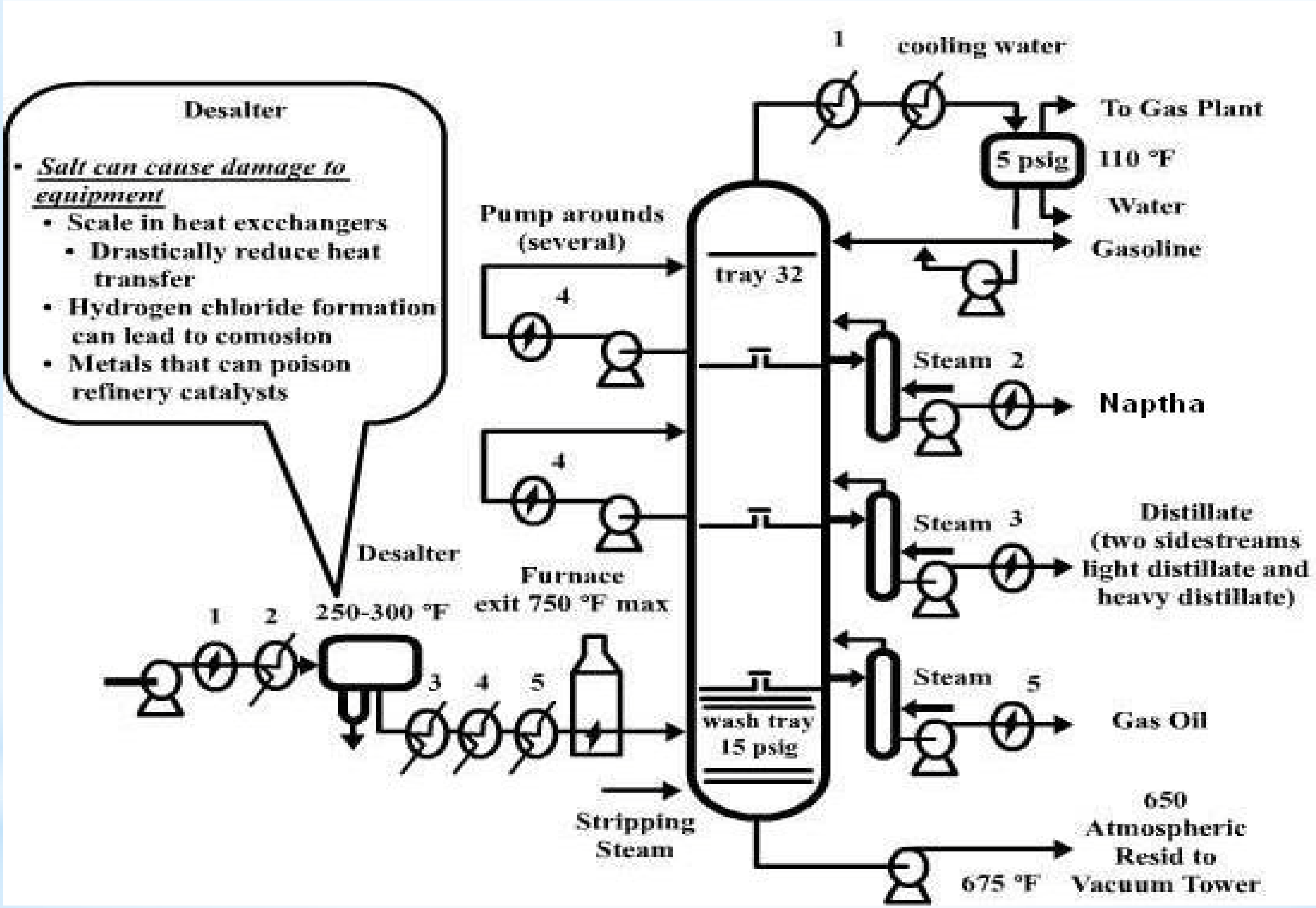


Figure 2 : Pressure-drop profile for a typical GOSP in the Middle East.

- Volatile components either sent to consumer centers as ***natural gas or used to repressurize*** the oilfield.
- The stripped liquid components are marketed as ***stabilized natural gasoline.***

CRUDE OIL (DESALTING)

- The fluid produced at the wellhead consists usually gas, oil, free water, and emulsified water (water–oil emulsion).
- The gas remove by degassing process
- First step in the refining process is to remove salt and solids to reduce corrosion, plugging, and fouling of equipment and to prevent poisoning of the catalysts in processing units.
- contaminants must be removed by desalting (dehydration).
- If the salt content of the crude is greater than 10 lb/1000 bbl (expressed as NaCl), the crude requires desalting to minimize fouling and corrosion caused by salt deposition on heat transfer surfaces and acids formed by decomposition of chloride salts.(<1000 lb/bbl).



Desalter

- *Salt can cause damage to equipment*
  - Scale in heat excchangers
    - Drastically reduce heat transfer
  - Hydrogen chloride formation can lead to comosion
  - Metals that can poison refinery catalysts

Typical Configuration Atmospheric Column w/o Preflash

Degassing and Dehydration

The basic principles for the treating process are as follows:

1. **Removal of free water.**
2. **Resolution of Emulsified Oil.**

Degassing and Dehydration

1. Removal of free water:-

Free water is simply defined as that water produced with crude oil and will settle out of the oil phase if given little time.

There are several good reasons for separating the free water first:

3. Minimization of corrosion because free water comes into direct contact with the metal surface, whereas emulsified water does not.

2. Reduction of heat input when heating the emulsion (water takes about twice as much heat as oil).

1. Reduction of the size of flow pipes and treating equipment.

Degassing and Dehydration

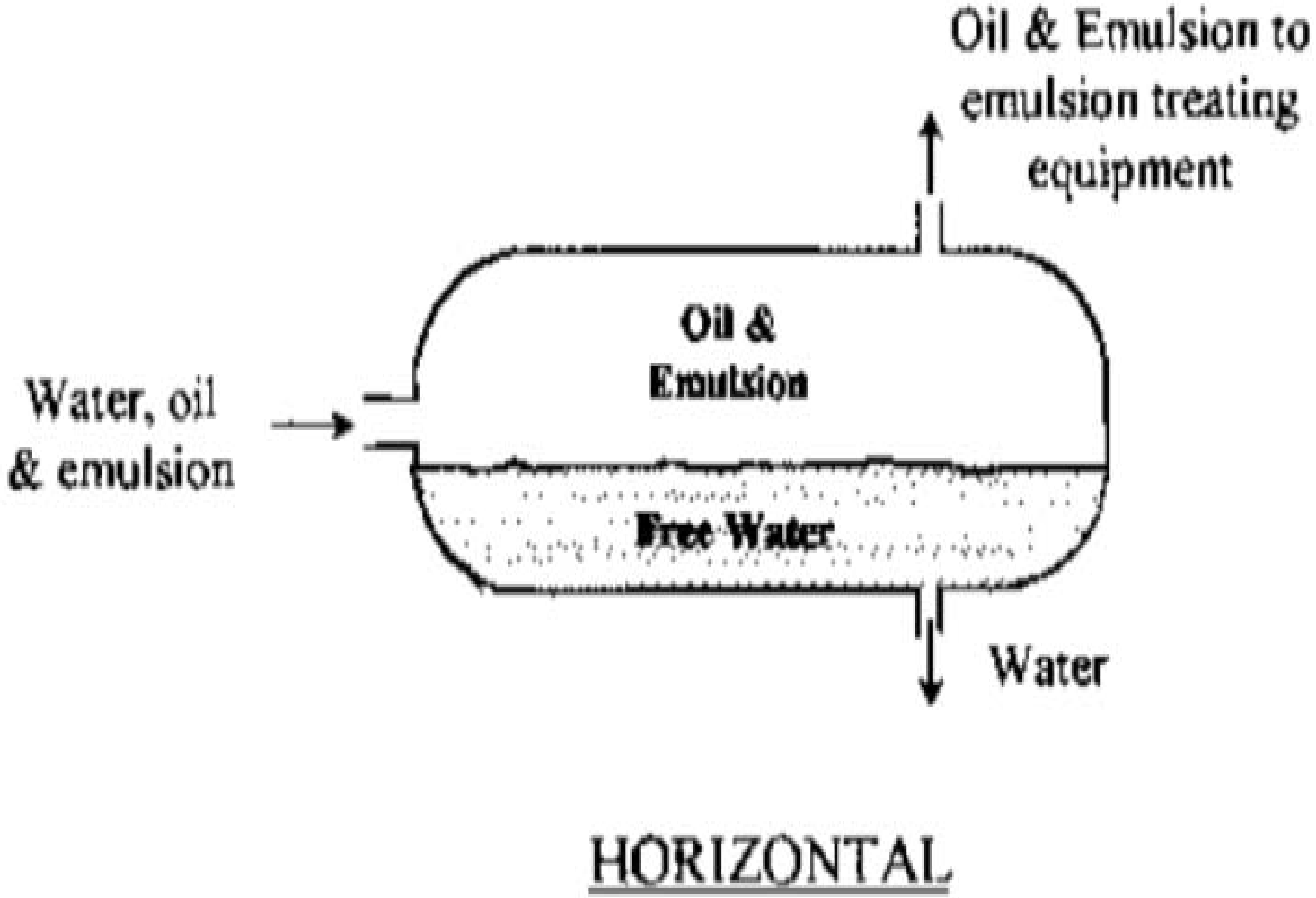
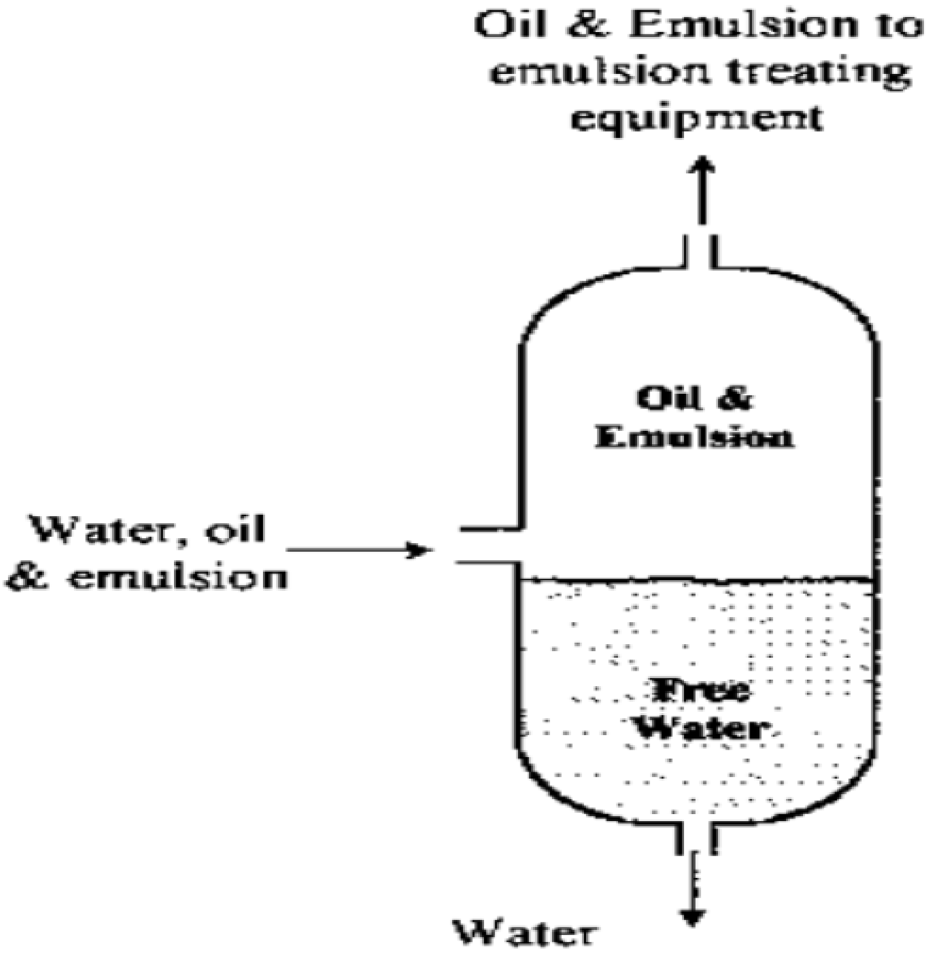


Figure 8 Two-phase free-water knockouts.

Degassing and Dehydration



VERTICAL

2. Resolution of Emulsified Oil:

Oil emulsions are mixtures of oil and water. In general, an emulsion can be defined as a mixture of two immiscible liquids, one of which is dispersed as droplets in the other (the continuous phase), and is stabilized by an emulsifying agent.

Degassing and Dehydration

In the oil field, crude oil and water are encountered as the two immiscible phases together. They normally form water-in-oil emulsion (W/O emulsion), in which water is dispersed as fine droplets in the bulk of oil. This is identified as type C in Figure 2.

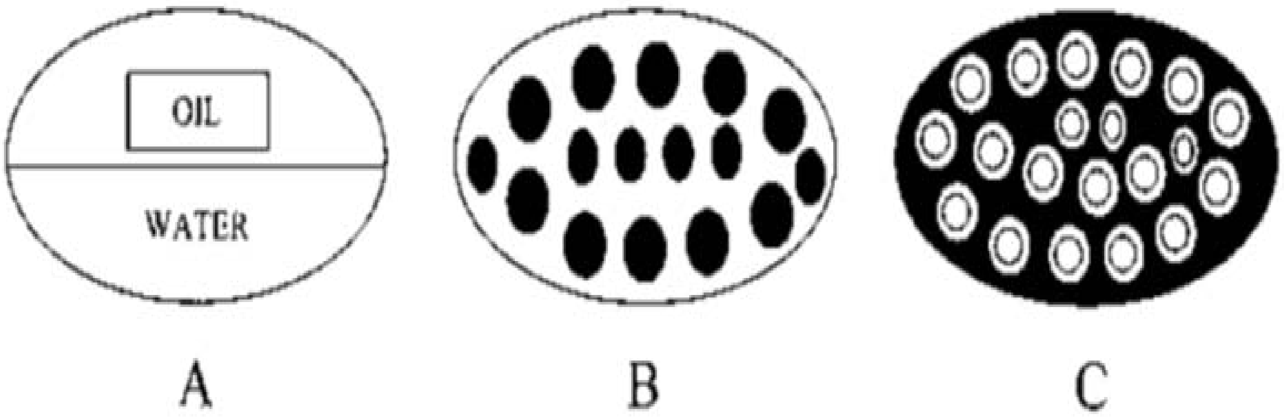


Figure 2 Schematic representation of (A) a non-dispersed system, (B) an O/W emulsion, and (C) a W/O emulsion.

Degassing and Dehydration

For two liquids to form a stable emulsion, three conditions must exist:

1. The two liquids must be immiscible.
2. There must be sufficient energy of agitation to disperse one phase into the other.
3. There must be the presence of an emulsifying agent.

Degassing and Dehydration

Some of the common emulsifiers are as follows:

1. Asphaltic materials
2. Resinous substances
3. Oil-soluble organic acids
4. Finely dispersed solid materials such as sand, carbon, calcium, silica, iron, zinc, aluminum sulfate, iron sulfide, and so on.

Crude possessing emulsifying

To increase the coalescence of water drops. (Soda ash, sodium hydroxide, salt of fatty acids petroleum sulfonates which assist coalescence of water droplets).

Resolution of Emulsified Oil consists of three consecutive steps:

A. Breaking the emulsion:

- Using chemicals followed by settling can break some emulsions.
- Other emulsions require heating and allowing the water to settle out of the bulk of oil.
- More difficult (tight) emulsions require, however, both chemicals and heat, followed by coalescence and gravitational settling.
- Basically, a dehydration process that utilizes any or a combination of two or more of the treatment aids mentioned earlier (heating, adding chemicals) is used to resolve water-oil emulsions.

B. Coalescence: This involves the combination of water particles that became free after breaking the emulsion, forming larger drops.

C. Gravitational settling and separation of water drops:

The larger water droplets resulting from the coalescence step will settle out of the oil by gravity and be collected and removed.

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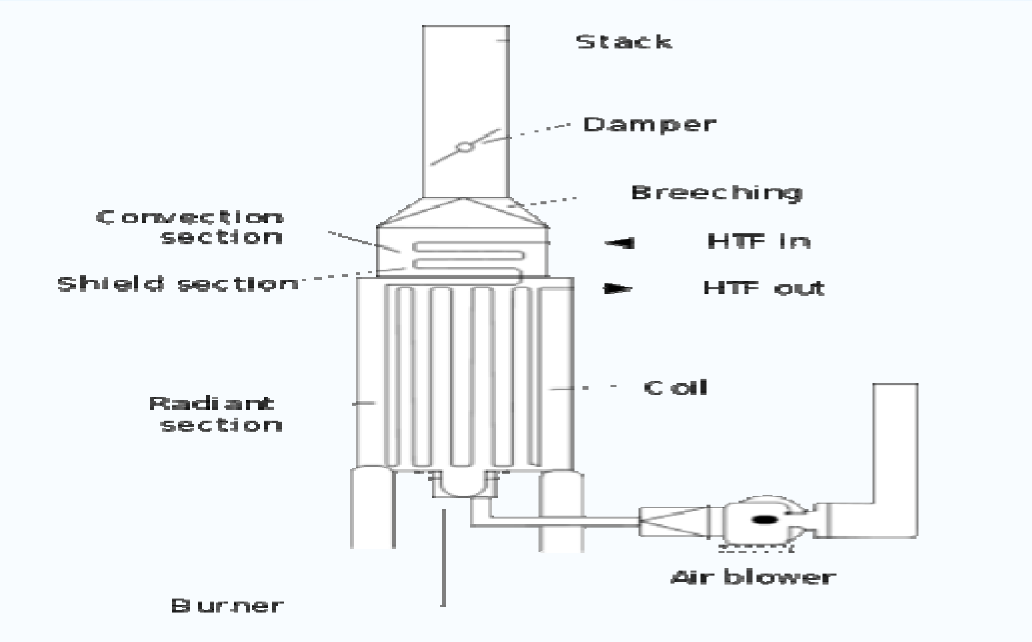
Heating of Crude Oil

1.Introduction:

- Furnaces are used throughout the industry to provide the heat, using the combustion of fuels.
- These fuels are solid, liquid or gaseous.
- Furnaces consist essentially of an insulated, refractory lined chamber containing tubes.
- Tubes carry the process fluid to be heated, and sizes are device for burning the fuel in air to generate hot gases. A great variety of geometries and sizes are used.
- However, all furnaces have in common the general feature of heat transfer from hot gas source to a cold sink.

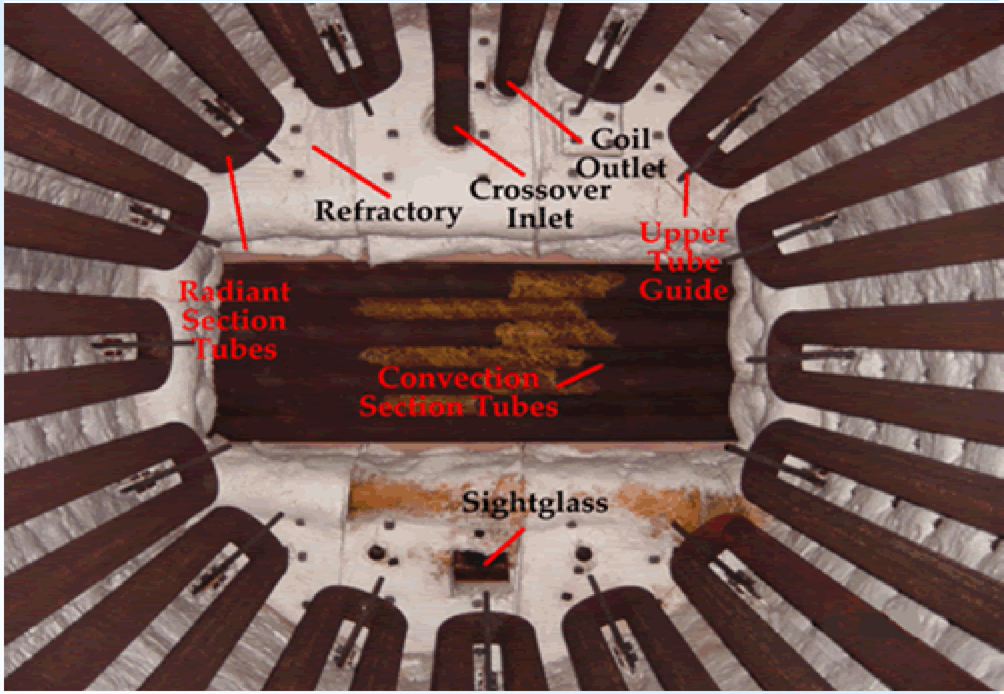
- **2.Types of furnaces used in process plant**
- An industrial furnace or direct fired heater, Fig.(1), is an equipment used to provide heat for a process or can serve as reactor which provides heats of reaction.
- Furnace designs vary as to its function, heating duty, type of

  fuel and method of introducing combustion air. However, most process furnaces have some common features.

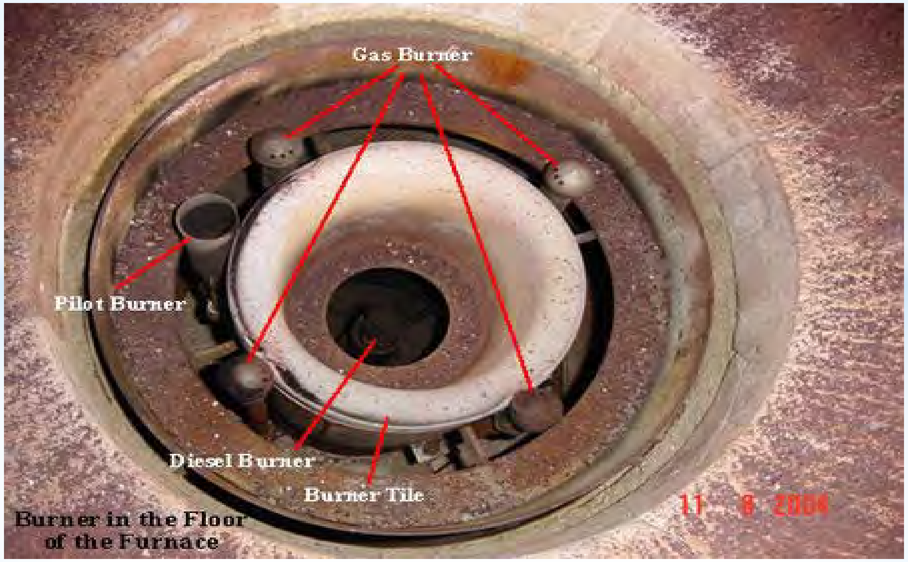


- Fuel flows into the burner and is burnt with air provided from an air blower.
- There can be more than one burner in a particular furnace which can be arranged in cells which heat a particular set of tubes.
- The flames heat up the tubes, which in turn heat the fluid inside in the first part of the furnace known as the radiant section or firebox.
- In this chamber where combustion takes place, the heat is transferred mainly by radiation to tubes around the fire in the chamber.
- The heating fluid passes through the tubes and is thus heated to the desired temperature.
- The gases from the combustion are known as flue gas.
- After the flue gas leaves the firebox, most furnace designs include a convection section where more heat is recovered before venting to the atmosphere through the flue gas stack.

Middle of radiant section



Convection section



Furnace burner

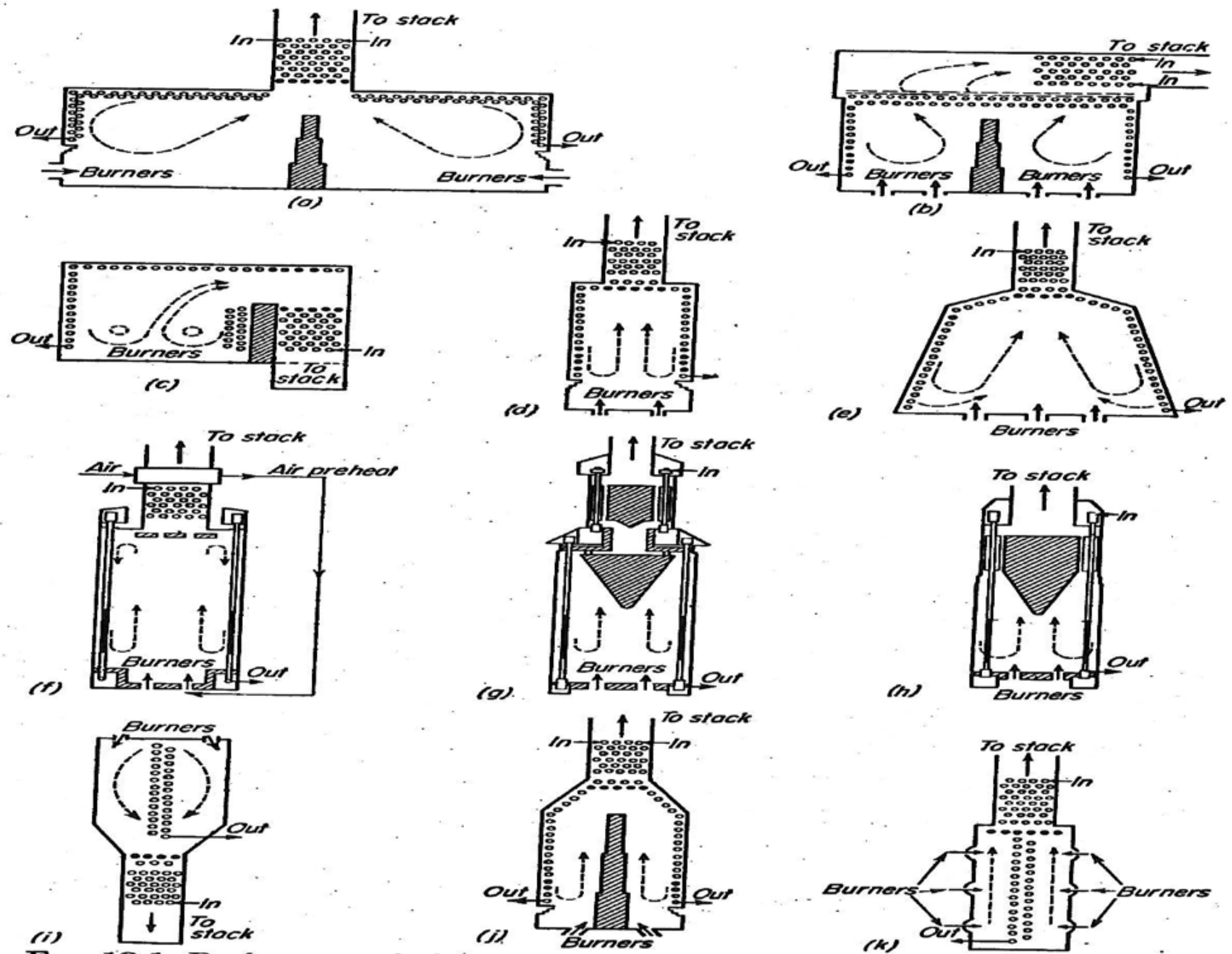
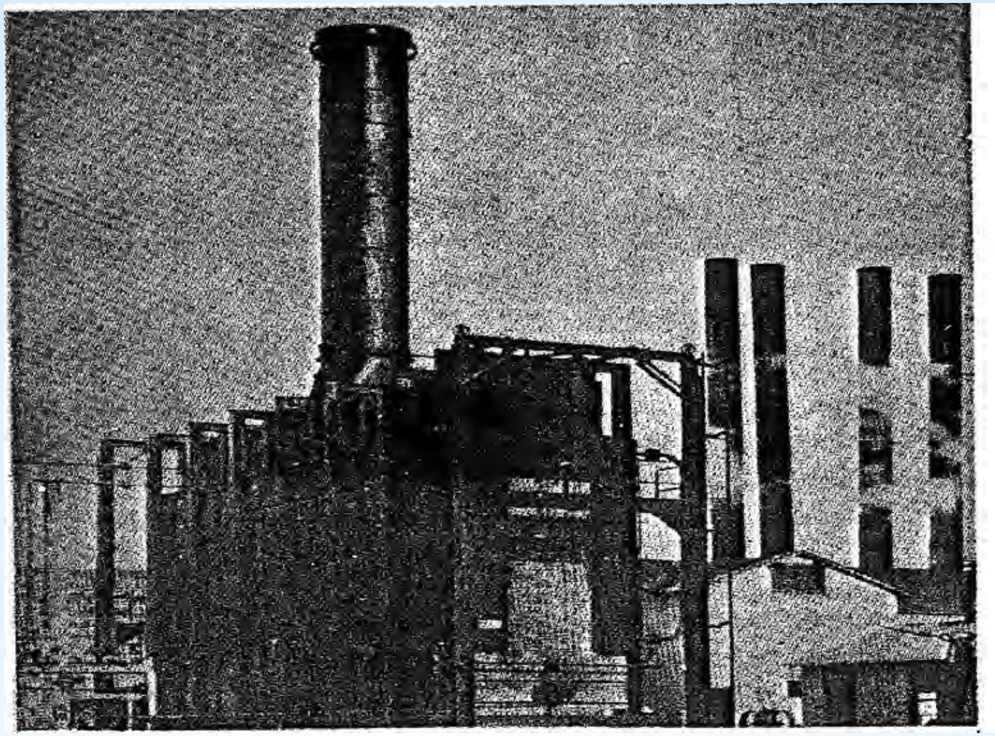


FIG. 18-1. Basic types of pipestill heaters (see text for meaning of letters).



Pipe Still Heater

Pipe heaters can be categorized into three types:

- 1) Box/ Rectangular.
- 2) Cylindrical.
- 3) Radiant Wall

All these furnaces have got separate radiation section and convection section. The most universal classification is based on direction of tubes as well as shape of furnace and mode of application of heat.

Heating of Crude Oil

In most of the furnaces, the direction of tubes is horizontal as in all box type heaters and vertical in cylindrical stills. Radiant walls also use horizontal tubes; however tubes can be placed vertically also.

The radiant section design is based on ***Stefan's law of radiation***:

$$Q_r = bAT^4 = bA(T_G{}^4 - T_B{}^4)$$

A: area of radiating surface, ft^2

b : $1.72x10^9$ Btu/ ^oF ft^2 hr. at black bod conditions.

T: absolute temperature of the surface,^oF

Heating of Crude Oil

For a satisfactory design, the following schedule of heat distribution may be employed:

Type of heat	Percent
Convection heat transfer	**30-50%**
Radiant heat transfer	**45-60%**
Losses (Furnace)	**5%**
Stack losses	**12%**

Design of a furnace radiation section is based on ***Hottle, Wilson method*** and radiant heat absorption is given as:-

$$R = \frac{1}{1 + \frac{G\sqrt{Q/\alpha A_{cp}}}{S}} x100$$

R= % heat absorbed in radiant section.

Q = Total heat developed by flame

G= Air /fuel ratio (wt. basis).

α = Factor to convert actual exposed surface to cold surface:

0.986 for ***two*** rows at spacing 2 OD.

0.88 for ***one*** rows at spacing 2 OD.

If

Q in Kj / hr	S=14200	Area in m^2
Q in Btu/hr	S=4200	Area in ft^2
Q in Kcal/hr	S=6930	Area in m^2

Heating of Crude Oil

$$A_{cp} = LN\frac{C}{12}$$

A_{cp} = area of furnace wall that has tube mounted on it (ft^2).

$\alpha\, A_{cp}$ = equivalent cold plane surface (ft^2)

L= length.

C= Center to center spacing.

N= Number of tube per row.

$$A = LnN\frac{D}{12}$$

A= Projected area

D= Tube diameter (in)

Heating of Crude Oil

n= no. of rows

$$A = nA_{cp}\frac{D}{C}$$

$$A_{cp} = \frac{A}{n}\frac{C}{D}$$

RQ = Aq

q= rate of heat absorption per square foot of projected tube area

$$Q = \frac{Aq}{R} = \frac{nA_{cp}(D/C)q}{R}$$

Heating of Crude Oil

$$R = \frac{1}{1 + \frac{G\sqrt{\frac{q}{R}\frac{n}{\alpha}\frac{D}{C}}}{S}} x100$$

$$q(\frac{D}{C}\frac{n}{\alpha}) = \frac{(1-R)^2}{R}(\frac{S}{G})^2$$

For a most commercial case D/C= 0.5 , n=2

$$1.014xq^{'} = \frac{(1-R)^2}{R}(\frac{S}{G})^2$$

$$q = 1.014x\frac{C}{D}x\frac{a}{n}q^{'}$$

Heating of Crude Oil

Example:-

A petroleum stock at a rate of 1200 bbl/hr. of sp. gr. 0.8524 is passed through a train of heat exchangers and is allowed to enter directly the radiant section of box type heater at 220 °C . The heater is designed to burn 3500 kgs per hour of refinery off gases as fuel.

The net heating value of fuel is 47.46×10^3 Kj per kg.

The radiant section contains 150 sq. meters of projected area of one row of tubes (10.5 cm, 12 m long and spaced at 2 OD).

>> Find the outlet temperature of the petroleum stock?

Where,

$\alpha = 0.88$

Air fuel ratio= 25

Average Specific heat of stock=2.268 Kj/Kg °C.

Heating of Crude Oil

Solution

Total heat liberated (Q) = m $_{fuel}$ * NHV

= $47.46*10^3 * 3500 = 1.66*10^8$ Kj/hr.

Projected area of one tube (L * D) = 12 * 0.105

No. of tubes = 150 / (12 * 0.105) = 120 tubes

$\alpha A_{cp} = 0.88 * 120 * 0.105 * 2 * 12 = 266$ Sq. m.

Heat absorption %(R) $= \dfrac{1}{1+\dfrac{G\sqrt{Q/\alpha A_{cp}}}{S}} x100$

Heating of Crude Oil

$$= \frac{1}{1 + \dfrac{25 * \sqrt{\dfrac{1.66 * 10^{8}}{266}}}{14200}} = 44\%$$

Outlet temperature of the stock:-

$$Q = m\,Cp\,\Delta t$$

$$0.44*1.66*10^{8} = 1200 * 200 * 0.8524* 2.268 * \Delta t$$

❖ $\Delta t = 157\ ^{o}C$

So the outlet temperature is equal to 157 + 220 = 377 ^{o} C

Heading of Crude Oil

Example

A pipe still uses 7110 lb/hr of a cracked gas (Net Heating Value (NHV) 20560 Btu/lb). The radiant section contains 1500 sq ft of projected area, and the tube (5 in. outside diameter) are spaced at a center-to-center distance of 10 in. there is only one row of radiant tubes, and they are 40 ft long. The ratio of air to fuel is (21 - 30 percent excess air).

a) What percentage of the heat liberation is absorbed in the radiant section?

b) How many Btu are absorbed per hour through each square foot of projected area?

Heating of Crude Oil

Solution

Total heat liberated(Q)= m_{fuel} * NHV

= 7110 * 20560

=146000000 Btu/hr

$$A = LnN\frac{D}{12}$$

$$A = 1500$$

N = number of tubes $= \dfrac{1500}{40*5/12}$ = 90

$$A_{cp} = LN\frac{C}{12}$$ = 40 * 90 *10 / 12 = 3000

αA_{cp}= 0.88 * 3000 = 2640 sq ft

Heating of Crude Oil

$$\text{Heat absorption \%(R)} = \frac{1}{1+\dfrac{G*\sqrt{Q/\alpha A_{cp}}}{S}} x100$$

$$= \frac{1}{1+\dfrac{21*\sqrt{\dfrac{1.46x10^{6}}{2640}}}{4200}} = 45.8\%$$

Heat absorption in radiant section = 0.458 *146 *10^6

= 66900000 Btu/hr

Heat absorbed / sq ft projected area = q = 66900000/1500

= 44500 Btu/hr.ft^2

Heating of Crude Oil

H.W (1)

A furnace is to be designed for a heat duty of 30 x 10^6 Btu/hr and efficiency of 75%.

The furnace is fired with gaseous fuel at a rate of 17 lb air/lb fuel (NHV = 17000 Btu/lb).

The tube are arranged in two rows and are of 5 in OD., 40 ft length and 2x OD.

Spacing, heat rate of 35000 Btu/hr of projected area is recommended.

calculate:

1) % heat absorbed in radiation section (R %).
2) Heat absorbed in the convection section.
   (State any assumptions used).
3) The number of tubes in the radiation section.

Solution

a)

$$q(\frac{D}{C}\frac{n}{\alpha}) = \frac{(1-R)^2}{R}(\frac{S}{G})^2$$

$$35000(\frac{5}{10}\frac{2}{0.986}) = \frac{(1-R)^2}{R}(\frac{4200}{17})^2$$

$0.581 = (1-R)^2$

R= 47.55%

Heat absorbed in radiation zone = R x Q= 0.4755X 40×10^6 = 19020000 Btu

b)

q x A = R x Q

35000 x A= 19020000

A= 543.42 ft^2

A= L n N D/12

N= 543.42 x12/(40x2x5)

N= 16

C)

% Heat absorbed in the convection section= 100%- (Heat absorbed in radiation zone+ Losses (Furnace)+ Stack losses)

% Heat absorbed in the convection section= 100%- (47.55+ 5+12)%

%Heat absorbed in the convection section =32.45%

Heat absorbed in the convection section=0 .3275 X 40×10^6 = 13.1×10^6 Btu

Heating of Crude Oil

H.W (2)

7000 lb/hr of cracked gas of 20560 Btu/lb NHV is used as a fuel in a furnace.

The radiant section absorbed 44500 Btu/hr ft^2 of projected area. The tubes are 5 in. OD. , 10 in. spacing, and 20 ft long. They arranged in two rows. The air to fuel ratio is 21- 0. Calculate :

1) the number of tubes in the radiation section.
2) the amount of heat absorbed in this section.

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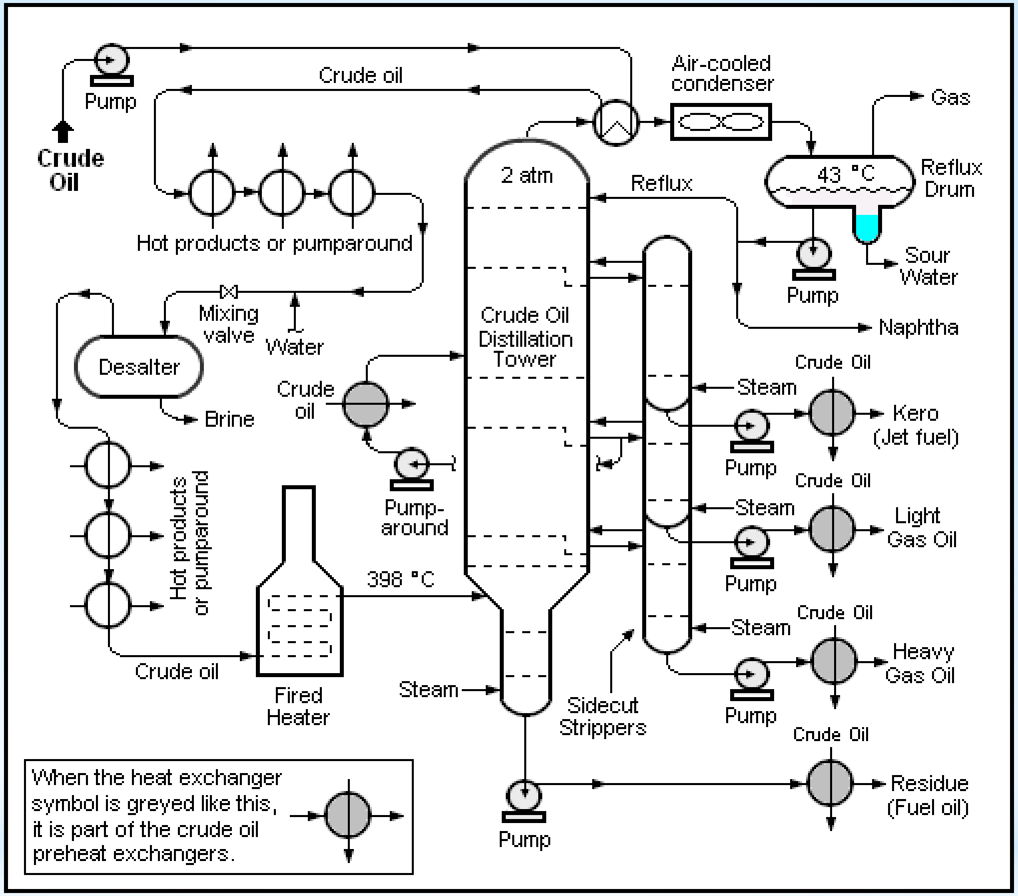
Crude Distillation



When the heat exchanger symbol is greyed like this, it is part of the crude oil preheat exchangers.

Atmospheric Topping Unit

After desalting, the crude oil is pumped through a series of heat exchanger and its temperature raised to about 550^o F (288^o C) by heat exchange with product and reflux streams.

It is then further heated to about 750^o F (399^o C) in a furnace (i.e. direct fired heater or "pipe still") and charged to flash zone of atmospheric fractionators.

The furnace discharge temperature is sufficiently high to cause vaporization of all products with drawn above the flash zone + about 20% of the bottom product.

The 20% "over flash" allows some fractionation to occur on the trays just above the flashing zone by providing internal reflux in excess of side stream withdrawals.

Atmospheric Topping Unit

In many petroleum distillations, steam is admitted to the space in which vaporization occurs, the steam reduce the partial pressure in the vapor by Dalton's law, the boiling point of a material may be reduced in only two ways:

1) the pressure may be reduced.
2) or some inert gas such as steam may be introduced.

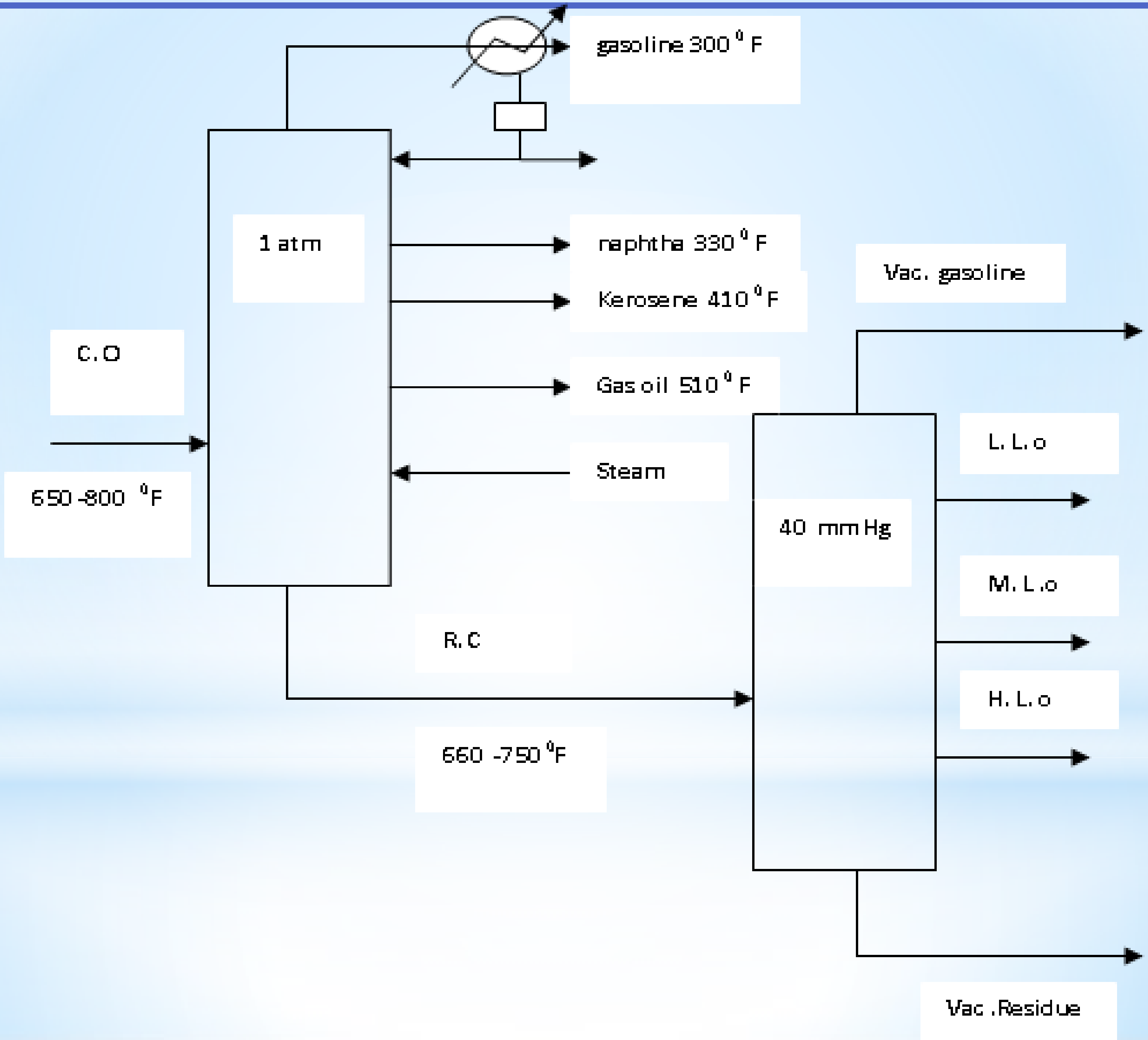
The distillation causes the fractions to separate in increasing order of boiling point. The top product being highly volatile has to be condensed in a reflux condenser. Some portion of the condensed fraction goes back as reflux.

All other fractions form the side draw products of distillation column. There fractions are usually classified as heavy naphtha, kerosene, gas oil.

Atmospheric Topping Unit

Bottom product of atmospheric column is now again routed through a furnace to reach a temperature of 350 to 400^{o}C and is allowed to flash in a vacuum column, vacuum gas oil, heavy diesel, lubrications oil cuts / pressure distillates shall be the side cuts.

Atmospheric Topping Unit



gasoline 300 °F

1 atm

naphtha 330 °F

Kerosene 410 °F

Vac. gasoline

C.O

Gas oil 510 °F

L. L.o

Steam

650-800 °F

40 mm Hg

M. L.o

R. C

H. L.o

660 -750 °F

Vac .Residue

Heat and Material Balances

1) The vapor liquid feed enters the tower at a high temperature, and the product are withdrawn at lower temperature , hence heat must be removed, and it is referred as
" reflux heat ".

2) The most satisfactory temperature datum is the **vaporizer temperature** because this temperature can be accurately estimated and is the temperature about which the entire design of tower, and pipe still hinges.

3) By using this datum plane , the heat balance consists simply of the **sensible heat** required to:

a) Cool each product from vaporizer temperature to its withdrawal temperature.

b) Condense the products that are withdrawal as liquid.

Example (1) :

Heat Balance of a Fractionating Tower

A heat balance of the simple tower system shown in Fig. below will be computed to determine the amount of heat that must be removed to keep the tower in thermal balance.

The capacity is 1200bbl per day (2100 gal per hour of a 12.1 to 12.2 Characterization Factor crude oil.

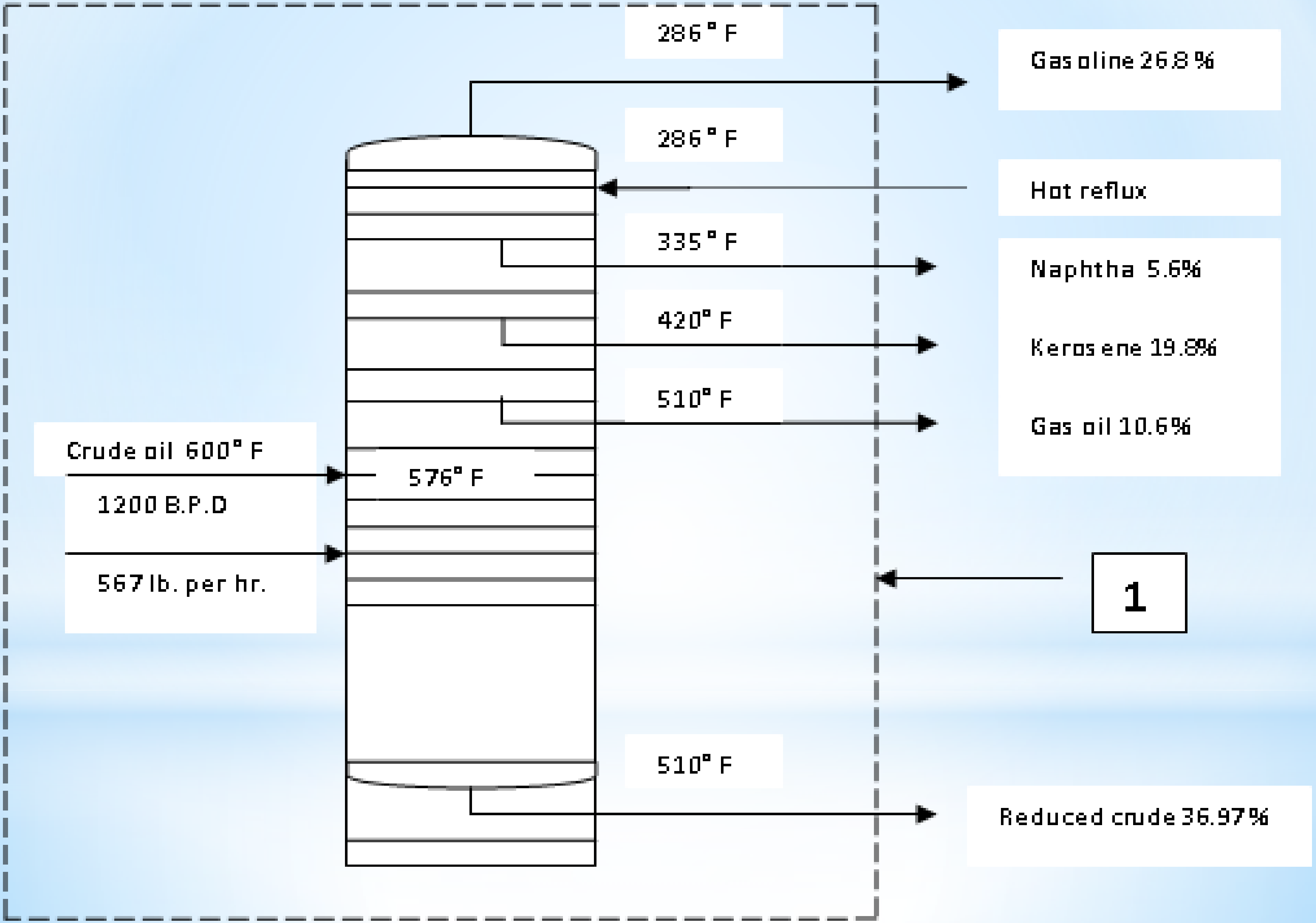
At 576 ^{o} F the gasoline, naphtha, kerosene, and gas oil are vapor and the reduced crude oil is a liquid.

A sufficient quantity of heat must removed from the vapors to cool them as vapors to the temperature at which they are withdrawn from the tower and to condense the naphtha, kerosene, and gas oil at their withdrawal temperature.

Atmospheric Topping Unit

	Volume %	API	Lb/gal	Gal/hr	Lb/hr	50 % bp	Mol. wt	Latent heat
Gasoline	26.8	62.8	6.06	563	3415	260	110	**120**
Naphtha	5.63	52.8	6.39	118	754	370	155	**113**
Kerosene	19.8	45.6	6.65	416	2765	460	185	**100**
Gas oil	10.6	39.4	6.89	222	1530	585	240	**90**
Reduced crude	36.97	31.2	7.24	776	5610			
Loss	0.2				96			
Crude	**100.00**	**43.0**	**6.75**	**2100**	**14170**			

Atmospheric Topping Unit



Atmospheric Topping Unit

Solution : Energy Balance Basis =1hr

Sensible heat **Btu**

Gasoline (vapor) 3415 * (576 - 286) * 0.56 = 589000

Naphtha (vapor) 754 * (576 - 335) * 0.55 = 106000

Kerosene(vapor) 2765 * (576 - 420) * 0.57 = 261000

Gas oil (vapor) 1530 * (576 - 510) * 0.59 = 63000

Reduced crude (liquid) 5610 * (576 - 510) * 0.72 = 276000

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1295000

Steam (vapor) 567 * (535 - 286) * 0.5 = 70600

\----------------

1365600

Atmospheric Topping Unit

Latent heat		**Btu**
Gasoline	(withdraw as vapor)	
Naphtha	754x113 =	85100
Kerosene	2765x100=	276500
Gas oil	1530x90=	138000

Total heat to be removed		1865200

Atmospheric Topping Unit

Kinds of Reflux :

- 1) Cold Reflux
- 2) Hot Reflux
- 2) Circulating Reflux

1) Cold Reflux :

Is defined as reflux that is supplied at some temperature below the temperature at the top of the tower. Each pound of this reflux removes a quantity of heat equal to the its latent heat and the sensible heat required to raise it temperature from the storage tank temperature to the temperature at the top of the tower

$$Q = m\lambda + mC_{pL}\Delta T$$

2) Hot Reflux:-

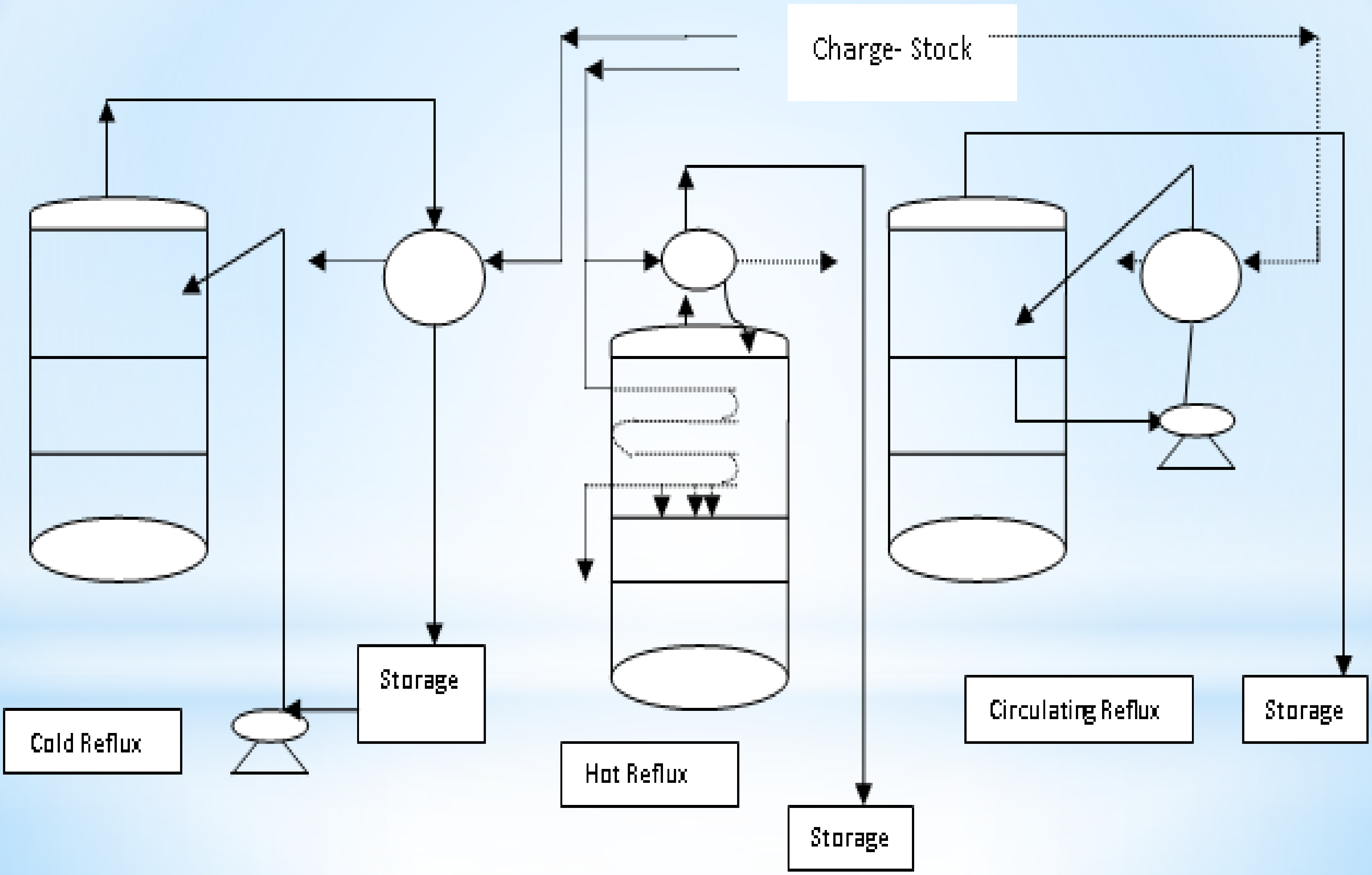
Admitted to the tower at the same temperature . Reflux or over flow from plate to plate in the tower is essentially hot reflux because it is always substantially at its boiling point. Hot reflux capable of removing only the latent heat because no difference in temperature is involved

$$Q = m\lambda$$

3) Circulating Reflux : It is not vaporized. It is only able to remove the sensible heat that is represented by its change in temperature as it circulate. This reflux is withdrawn from the tower as a liquid at a high temperature as a liquid and is returned to the tower after having been cooled.

$$Q = mC_{pL}\Delta T$$

Atmospheric Topping Unit



Example (2) : (Quantity of Reflux)

A tower fractionating system is such that 1865200 Btu/hr of reflux heat must be removed.

Example (1) illustrates the method of determining the reflux heat.

How many pounds of (1) hot (2) cold, and (3) circulating reflux are required?

Solution

Hot reflux:

λ (Gasoline) =123 Btu/lb

lb of hot reflux = 1865200/120 = 15500 lb/hr

mole hot reflux = 15500/110 = 141

mole gasoline = 3415/110 = 31

moles vapor = 141 + 31 = 172

moles steam = 567/18 = 31.5

total moles at the top of the tower = 172 + 31.5 = 203.5

total pressure at the top of the tower = 780 mm Hg
the partial pressure in the gas phase is (172/203.5) * 780
= 660 mmHg (according to Daltons law $P_i = y_i P_T$)

The dew point of 100% gasoline on EFV curve = 296 °F
(at 760 mm Hg)
>> At 660 mm Hg the temperature is calculated according to
Claussius – Clapeyron Eq.

$$\ln \frac{p}{p_o} = \frac{\lambda}{R}\left(\frac{1}{T_o} - \frac{1}{T}\right)$$

$R = 1.987$ Btu/lbmole.°R

$$\ln \frac{660}{760} = \frac{120x110}{1.987}\left(\frac{1}{296+460} - \frac{1}{T}\right)$$

Atmospheric Topping Unit

T=284 °F

The actual top temperature when using hot reflux = 286 °F

Cold reflux :

Assume storage tank at 80°F

$$\text{Lb cold reflux} = \frac{1865200}{120 + (286 - 80) * 0.58} = 7950$$

Moles cold reflux	= 7950/110 = 72.3
Mole gasoline	31
Moles vapor	103.3
Moles steam	31.5
Total moles	134.8

$$p = \frac{103.3}{134.8} * 780 = 600 \text{ mm Hg}$$

The equilibrium temperature of 296°F corrected to 600 mmHg= 275 °F

Atmospheric Topping Unit

Circulating reflux :

Assuming the reflux is cooled from 286 to 200 ^{o} F.

Mole gasoline	31
Mole steam	31.5
Total moles	62.5

$$\text{Partial pressure} = \frac{31}{62.5} * 780 = 387 \ \text{mmHg}$$

Correction 296 to 387 mm pressure gives 253 ^{o} F

$$\text{Lb circulating reflux} = \frac{1865200}{(286-200)*0.605} = 35849$$

Moles reflux = 10403/110 = 94.6

Side-Draw Temperature:

1) The method of calculating side-draw temperature is much the same as the calculation of the top temperature except that complications arise because of the presence of the low boiling materials that pass the draw plate.

2) Making heat balance upon the drawn plate.

3) In practice, steam and vapor of lighter products are usually present, and hence the effect of these vapors on the final condensation temperature must be estimated. The lighter vapors extended from materials boiling at almost the same temperature as the side-draw product to materials that are substantially **fixed gases**.

Atmospheric Topping Unit

4) Those vapor materials which are far above their boiling point behave as fixed gases and lower condensation point by **Dalton's law of partial pressures**, just as steam does, but those vapor materials which are at or near their boiling point are not effective in reducing the partial pressure.

5) Arbitrarily, **the vapors materials that will be condensed at the second or higher draw plate above the plate under consideration may be considered to act as fixed gases.**

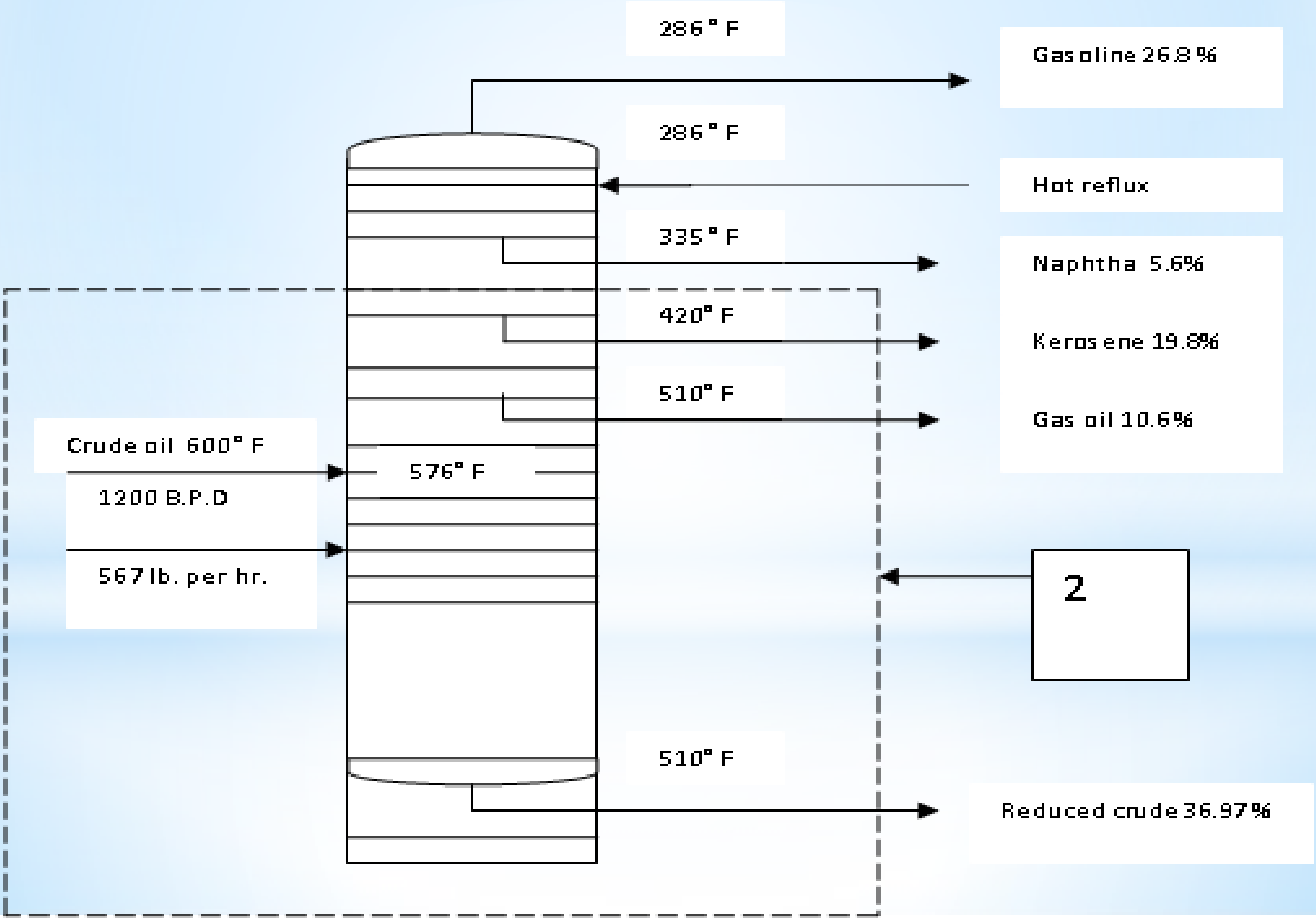
6) Also, **the vapor constituting the materials that is withdrawn from the draw plate above the one under consideration are assumed to have no effect at all on the partial pressure.**

7) thus in a tower producing, **gasoline, naphtha, kerosene, and gas oil , at the kerosene draw plate the gasoline vapor would be considered as a fixed gas , whereas naphtha vapor would assumed to have no effect on the condensation point.**

Atmospheric Topping Unit

Example (3) : (Calculation of Side Temperature)

This example is a continuation of examples (1) and (2). The temperature of the kerosene plate will be computed.(actual temperature = 420°F)



Solution :

Heat balance on kerosene plate, quantity of reflux and reflux (or vapor reflux) must be determined.

Cool gasoline (vapor) = 3415 * (576 – 420) * 0.58 = 327000
Cool naphtha (vapor) = 754 * (576 – 420) * 0.57 = 71000
Cool kerosene(vapor) = 2765 * (576 – 420) * 0.57 = 260000
Cool gas oil (vapor) = 1530 * (576 – 510) * 0.58 = 62000
Reduced crude (liquid) = 5610 * (576 – 510) * 0.72 = 276000

996000

Cool steam = 567 * (535 – 420) * 0.5 = 44000
Condense kerosene = 2765 * 100 = 276500
Condense gas oil = 1530 * 90 = 138000

Reflux heat at kerosene plate 1454000

Atmospheric Topping Unit

Moles internal reflux = $\dfrac{Q_T}{(\lambda x M_W)_K} = \dfrac{1454500}{185x100} = 78.6$

Moles fixed gases

Steam	31.5
Gasoline	31
Naphtha no effect	-------
	62.5

Total moles vapor = 62.5 + 78.6 = 141.1

Assume tower pressure at kerosene plate = 950 mmHg

$$P_i = P_T * y_I$$

Partial pressure $= \dfrac{78.6}{141.1} * 950 = 530 \text{ mmHg}$

$$\ln \frac{p}{p_o} = \frac{\lambda}{R}\left(\frac{1}{T_o} - \frac{1}{T}\right)$$

Atmospheric Topping Unit

$$\ln\frac{530}{760}=\frac{100*185}{1.987}\left(\frac{1}{445+460}-\frac{1}{T}\right)$$

T= 414°F

T actual = 420°F

H.W:

Repeat the example above, recalculate the temperature of the naphtha plate, assume a tower pressure of 810 mmHg?

H.W :

A) Calculate the amount of Hot, Cold and circulating reflux if the storage temperature is 100ºF and $Cp_v = 0.6$ and $Cp_l = 0.7$ Btu/lb.ºF

B) Check the top tower temperature if hot reflux is used. The dew point of gasoline is 296 º F and the pressure at the top plate is 780 mm Hg.

Fraction	Lb\hr	M.w.	λ	Temperature º F
Gasoline	33500	101	120	**310**
Kerosene	11800	185	108	**410**
Gas oil	32200	270	95	**510**
R.C	43500	-	-	**510**
Steam	600	18	-	**530**
C.O.	**121000**	**-**	-	**576**

Calculation of The Diameter of Distillation Column.

Example (4): See examples 1, 2 and 3 the quantities and conditions will be taken from these examples.

Solution:

Density of vapor at top of column (the reflux in the column is always hot reflux)

Mole gasoline	31
Mole hot reflux	141
Mole steam	31.5

Total moles	203.5

P=780 mm Hg

T=286 ° F

$$\text{Volume of vapors} = \frac{nRT}{P} = \frac{203.5 * 379 * (286 + 460) x 760}{780 * 520} = 107600\ ft^3$$

Atmospheric Topping Unit

Mass of vapor =

mass of gasoline + mass of hot reflux + mass of steam

= 3415 + 15500 + 567 = 19482 lb/hr

ρ_V =19482 / 107600 = 0.181 lb/ft^3

Assume density of liquid ρ_l = 42.7 lb/ft^3

$$\frac{w}{a} = K\sqrt{\rho_v(\rho_l - \rho_v)}$$

Assume K= 735, K is constant dependent primarily on the tray spacing.

$$\frac{w}{a} = 2040\frac{lb}{hrxft^2}$$

$$A = \frac{mass}{massvelocity} = \frac{19482}{2040} = 9.55\,ft^2$$

Atmospheric Topping Unit

$$D = \sqrt{\frac{4A}{\pi}} = \sqrt{\frac{4x9.55}{\pi}} = 3.5\,ft^{3}$$

To check the vapor velocity at top (3.5 ft/sec)

$$u = \frac{v}{A} = \frac{107600}{9.55*3600} = 3.13\,ft/\sec \;,\; u \text{ is ok}$$

H.W:

120000 Lb/hr of 34°API crude oil at 650°F is fed to an atmospheric distillation unit. Steam at a rate of 600 lb/hr and 850°F is used.

The fraction obtained were 34000 lb/hr gasoline (MW=110, λ=120) at 310 °F; 12000 lb/hr kerosene (MW=185, λ=108) at 420 ° F; 30000 lb/hr gas oil (MW=270, λ=95) at 510 °F .

The residue is withdrawn at 510°F. **Assume** C_{PL}= 0.7 ,C_{PV}= 0.6 Btu/lb.°F.

a) Check the top tower temperature if the dew point of gasoline is 296 ° F and the pressure at the top plate is 780 mm Hg.

b) Calculate the diameter of the tower if K=735 and ρ_l= 42.7 lb/ft^3.

H.W

1000 BPD of 32 ° API crude oil at 650 ° F is fed to an atmospheric distillation unit. Steam at a rate of 600 lb/hr and 530 ° F is used. The fractions obtained were 3500 lb/hr gasoline (MW=110, λ=120) at 310 ° F; 3000 lb/hr kerosene (MW=185, λ=100) at 420 ° F; 1500 lb/hr gas oil (MW=240, λ=90) at 510 ° F. The residue is withdrawn at 510 ° F. Assume CPL=0.7, CPV=0.6 Btu/lb ° F. and the vaporizion temperature=576^0F .

Given: 1 BPD = 42gal , ρ_{water}= 8.324 lb/gal

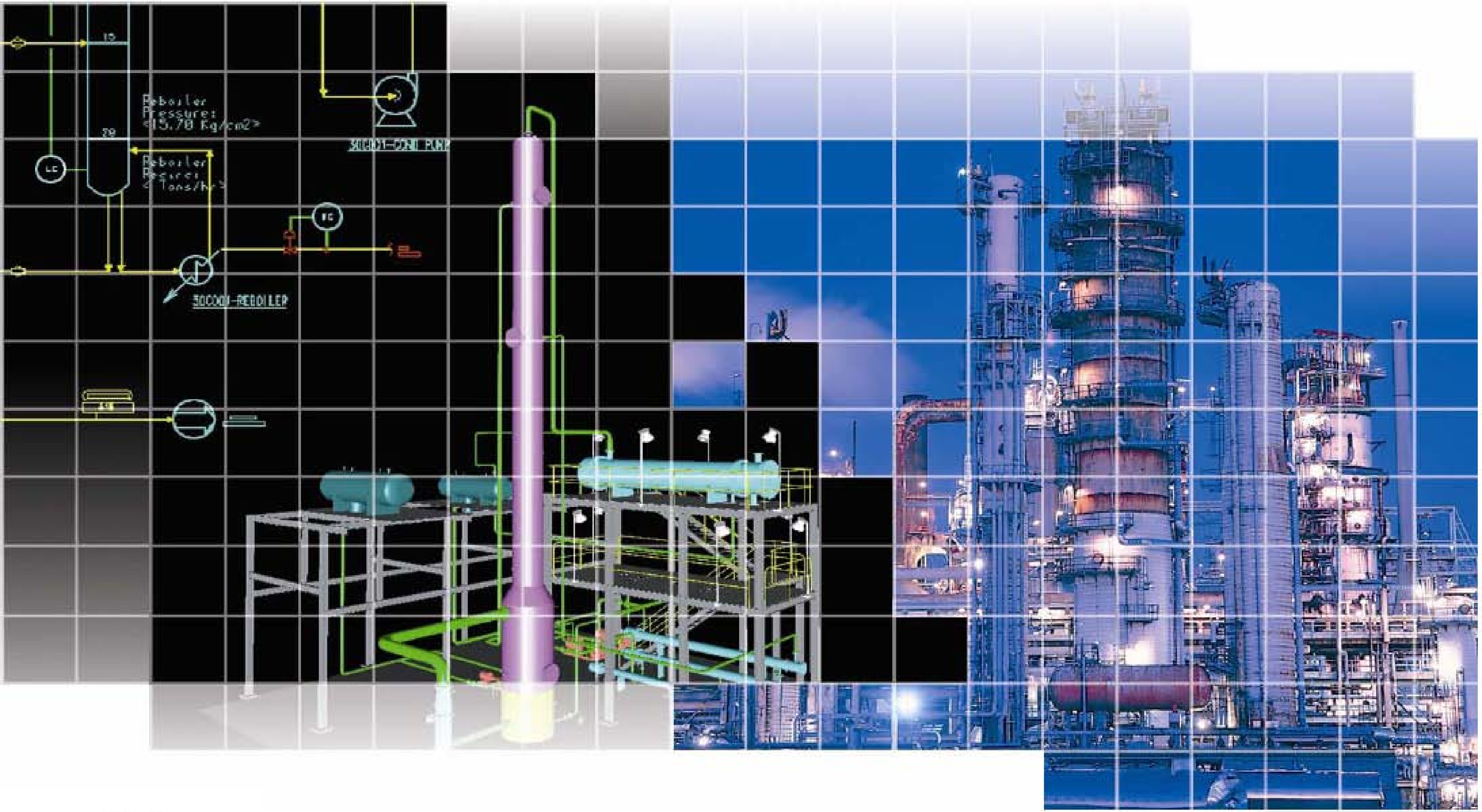
Check the gas oil plate temperature if the dew point and bubble point of gas oil are 600 ° F and 580 ° F respectively and the pressure at the withdrawn plate is 990 mm Hg.

Fourth Year – Chemical Process Eng. Branch

Petroleum Refinery Eng. Lectures

By

Dr. Adnan A. Abdul Razak



Lect./7

Conversion Processes

A) Thermal cracking

Thermal cracking:

- Is defined as the thermal decomposition, under pressure, of large HC molecules to form smaller molecules. Lighter, more valuable HC may be obtained from such relatively low value stocks as heavy gas oils (boiling up to 540 °C (1005 °F)) and residues.
- These processes are considered as upgrading processes for vacuum residue.

Requirements of Thermal cracking:

- Residual fractions (bottom of barrel) are the least valuable streams of a refinery.
- Nearly 30-40 % of the typical C.O in Iraq contains 370 $^{+}$ ^{0}C fractions.
- Worldwide limited reserve of sweet crude oil.
- Disposal problems due to stringent environmental regulations.
- Decreasing demand of fuel oil.
- Gradually increasing demand of middle distillates.

Advantages of Thermal cracking:

- It is simple and cost effective process. However rapid uncontrolled thermal cracking produces undesirable products like gas and coke.
- Limitation of catalytic cracking for resid processing :

1. In resid feed stock presence of high molecular weight compounds like resins, asphaltenes and metals it unsuitable for catalytic cracking, FCC can process resid feed only to certain limit.
2. Metal and sulfur compounds in resid feedstock as catalyst poison.

Coking:

- Coking are severe thermal cracking operations, most commonly used carbon rejection process that upgrades residues to a wide range of lighter H.C gases and distillates through thermal cracking.
- The byproduct of coking process is petroleum coke.
- The goal of coker operation is to maximize the yield of clean distillates and minimize the yield of coke.

Feed stock of coking process:

- Wide variety of feed stocks (can have considerable metals (nickel &vanadium) , sulfur, resin and asphaltens.
- Most contaminants exit with coke.
- Typical feed is vacuum resid.

The main produts:

- Off-gas → from which LPG is recovered.
- Naphtha → may be used as gasoline blending agent although its O.N = 65-80 RON.
- Gasoil → may be catalytic cracking
- Coke → the main uses of petroleum coke:

1. Fuel
2. Manufacture of anode for electrolytic cell reduction of alumina
3. Direct use as chemical carbon source for manufacture of elemental phosphorus, calcium carbide, and silicon carbide.
4. Manufacture of electrodes for use in electric furnace production of elemental phosphorus, titanium dioxide, calacium carbide, and silicon carbide.
5. Manufacture of graphite.

The major coking processes:

1) Delayed Coking

- ☐ Semi-continuous process.
- ☐ Feed :atm. Residue, cracked tar, and heavy cycle oil
- ☐ Feed heated and transferred to large soaking (or coking drum).
- ☐ Long residence time need to allow the cracking reactions to complete.

1. Moderate heating : 482-516 ºC (900-960) º F
2. Soak drum : 452-482 ºC (845-900) º F
3. Residence time : until they are fill of coke.
4. Coke is removed hydraulically
5. Coke yield= 30 %

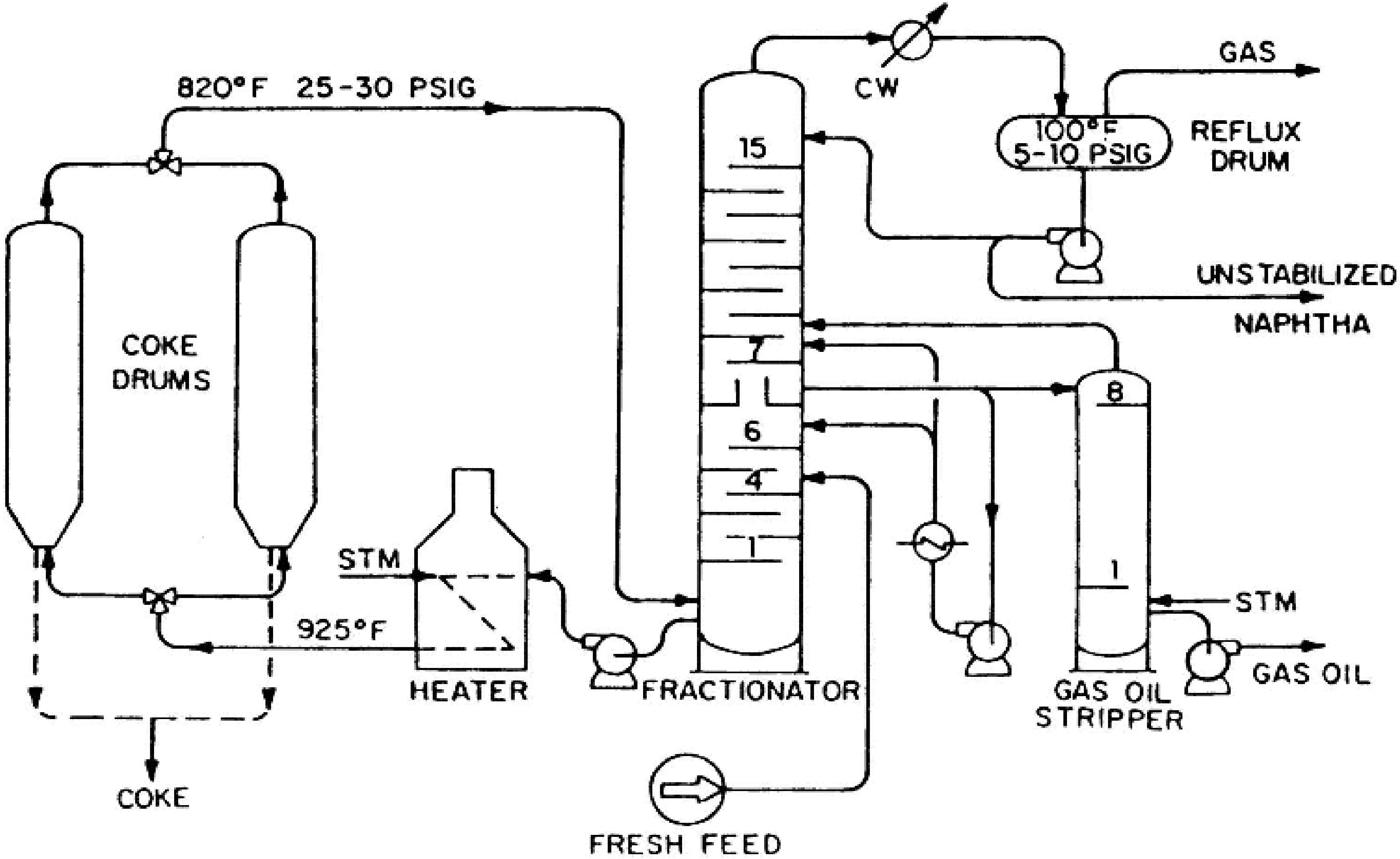


Fig 1: Delayed coking unit

2) Fluid Coking or flexicoking

- A continuous process which uses the fluidized- solids technique to convert residues to more valuable products.
- The residue is coked by being sprayed into a fluidized bed of hot, fine coke particles.
- The use of a fluid bed permits the coking reaction to be conducted at higher temperature and shorter contact times than those in delayed coking: Fluidized bed with steam.
- Severe heating 482- 566 °C (900–1050) ° F at 10 psig.
- Higher yields of light ends.
- Less coke yields (20 % for fluid coking and 2 % for flexicoking)

Coke & liquid yields may be estimated by simple equations:

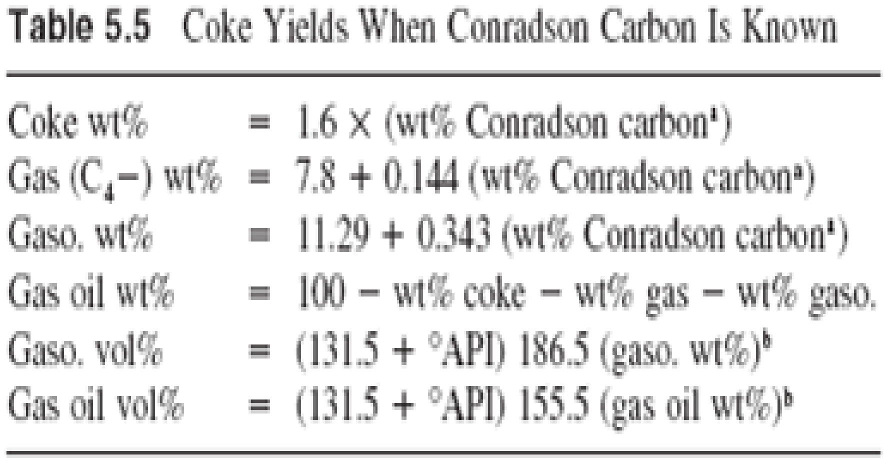


Table 5.5 Coke Yields When Conradson Carbon Is Known

Coke wt% = 1.6 × (wt% Conradson carbon[a])
Gas (C_4-) wt% = 7.8 + 0.144 (wt% Conradson carbon[a])
Gaso. wt% = 11.29 + 0.343 (wt% Conradson carbon[a])
Gas oil wt% = 100 − wt% coke − wt% gas − wt% gaso.
Gaso. vol% = (131.5 + °API) 186.5 (gaso. wt%)[b]
Gas oil vol% = (131.5 + °API) 155.5 (gas oil wt%)[b]

30% S

30% S (H_2S)

5% S

35% S

Example (1) : Develop preliminary estimate of product yields on the processing of 1000^+ Rc of 23760 BPD capacity. Conrad son carbon = 19%, 2.3% S, API = 10.7.

Solution :

Feed	BPD	API	(lb/bbl) lb/ hr (348.56)	lb/ hr	wt% S	lb/hr
1000^+ RC	23700	10.7	14.52	345080	2.3	7940

Products	**wt%**	**lb/ hr**	**lb/ hr S**
Coke wt %	30.4	104900	2382
Gas (C4 –) wt%	10.5	36230	2382
Gasoline wt%	17.8	61450	397
Gas oil wt%	41.3	142500	2779
	-----	---------	--------
	100	345080	7940

Visbreaking:

- Visbreaking is a relatively mild thermal cracking operation mainly used to reduce the viscosities and pour points of vacuum tower bottoms to meet the requirements of fuel oil
- reduce the amount of cutting stock required to dilute the residue to meet the specifications.
- It is also used to increase catalyst cracker feed stocks and gasoline yields.

Visbreaking:

The principal reactions which occur during the visbreaking operation are :

1) Cracking of the side- chains attached to cyclo-paraffin and aromatic rings.

2) Cracking of resins to light HC (primarily olefins) and compounds which convert to asphaltenes.

3) At temperature above 900 °F some cracking of naphthene rings.

Visbreaking:

There are two types of visbreaker operation

1) Coil or furnace cracker

Uses high furnace outlet temperature (885-930 ºF), and reaction time from 1-3 minutes. The feed is heated in a furnace or coil and quenched as it exits the furnace with gas oil or tower bottoms to slop the cracking reaction.

2) Soaker

The feed leaves the furnace at (800- 820) ºF and pass through a soaking drum which provides an additional reaction time, before it is quenched.

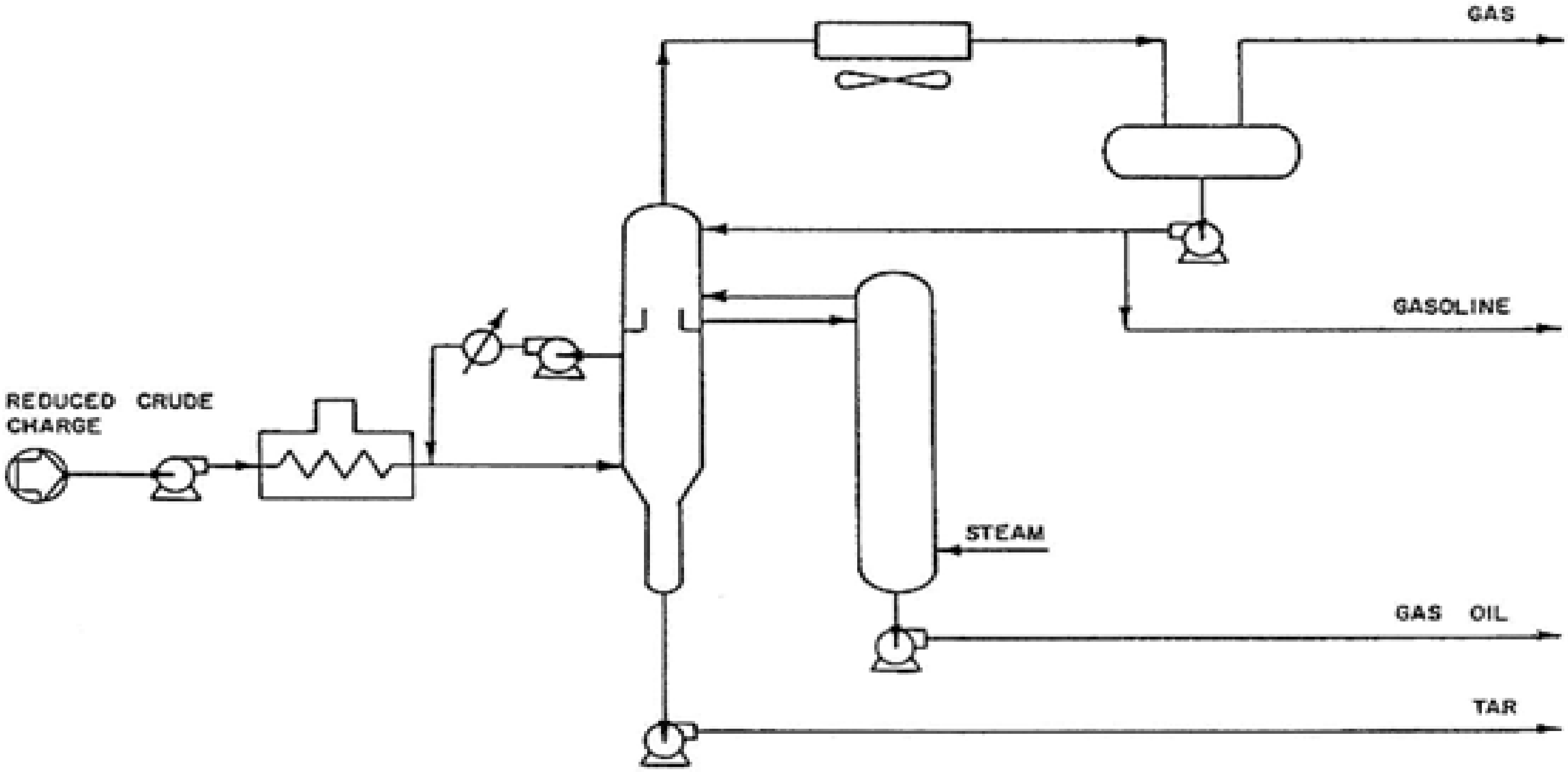


Fig 2 : Coil visbreaker

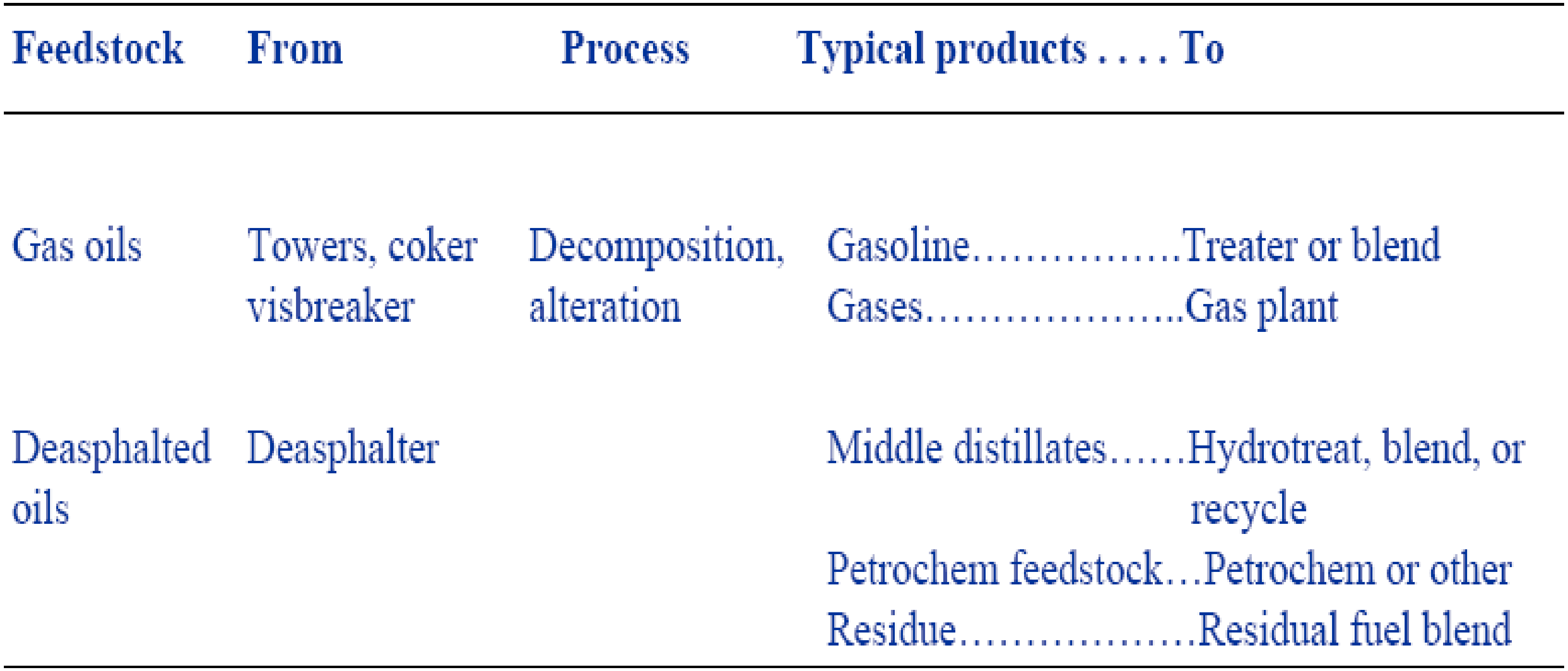
B) Catalytic cracking

- Catalytic cracking is the most important and widely used refinery process for converting heavy oils into more valuable gasoline and lighter products.
- Catalytic cracking breaks complex hydrocarbons into simpler molecules in order to increase the quality and quantity of lighter, more desirable products and decrease the amount of residuals.
- This process rearranges the molecular structure of hydrocarbon compounds to convert heavy hydrocarbon feedstock into lighter fractions such as kerosene, gasoline, LPG, heating oil, and petrochemical feedstock.
- Catalytic cracking is similar to thermal cracking except that catalysts facilitate the conversion of the heavier molecules into lighter products.
- Use of a catalyst (a material that assists a chemical reaction but does not take part in it) in the cracking reaction increases the yield of improved-quality products under much less severe operating conditions than in thermal cracking.

There are three basic functions in the catalytic cracking process:

1. Reaction: Feedstock reacts with catalyst and cracks into different hydrocarbons;
2. Regeneration: Catalyst is reactivated by burning off coke; and
3. Fractionation: Cracked hydrocarbon stream is separated into various products.

Catalytic Cracking



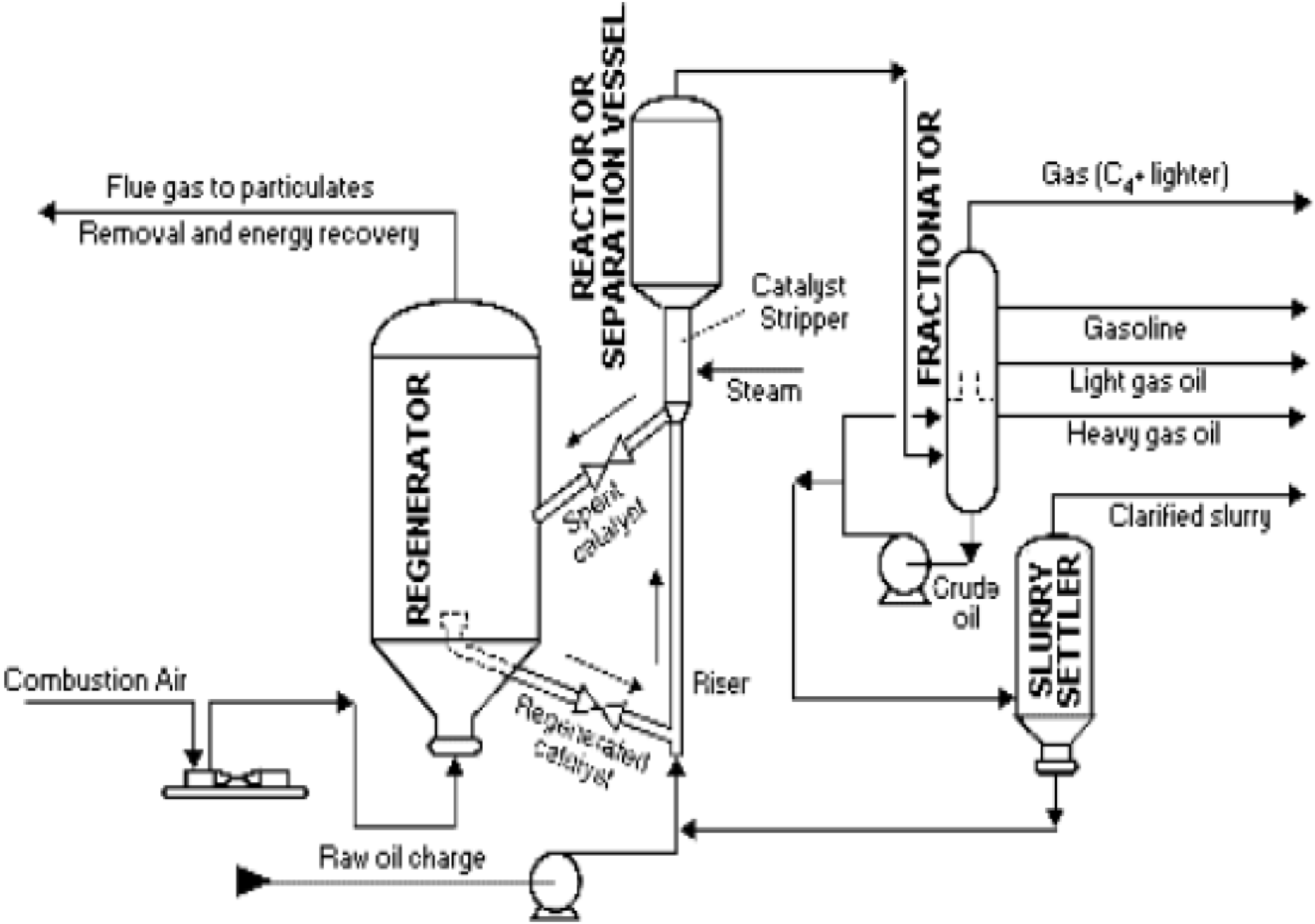
Feedstock	From	Process	Typical products . . . . To
Gas oils	Towers, coker visbreaker	Decomposition, alteration	Gasoline……………Treater or blend Gases………………..Gas plant
Deasphalted oils	Deasphalter		Middle distillates……Hydrotreat, blend, or recycle Petrochem feedstock…Petrochem or other Residue………………Residual fuel blend

Fluid Catalytic Cracking (FCC)

- The most common process is FCC, in which the oil is cracked in the presence of a finely divided catalyst which is maintained in an aerated or fluidized state by the oil vapors.
- The fluid cracker consists of a catalyst section and a fractionating section that operate together as an integrated processing unit.
- The catalyst section contains the reactor and regenerator, which, with the standpipe and riser, forms the catalyst circulation unit.
- The fluid catalyst is continuously circulated between the reactor and the regenerator using air, oil vapors, and steam as the conveying media.
- A typical FCC process involves mixing a preheated hydrocarbon charge with hot, regenerated catalyst as it enters the riser leading to the reactor.

- The charge is combined with a recycle stream within the riser, vaporized, and raised to reactor temperature (900°-1,000° F) by the hot catalyst.
- As the mixture travels up the riser, the charge is cracked at 10-30 psi. In the more modern FCC units, all cracking takes place in the riser.
- The "reactor" no longer functions as a reactor; it merely serves as a holding vessel for the cyclones.
- This cracking continues until the oil vapors are separated from the catalyst in the reactor cyclones.
- The resultant product stream (cracked product) is then charged to a fractionating column where it is separated into fractions, and some of the heavy oil is recycled to the riser.
- Spent catalyst is regenerated to get rid of coke that collects on the catalyst during the process.
- Spent catalyst flows through the catalyst stripper to the regenerator, where most of the coke deposits burn off at the bottom where preheated air and spent catalyst are mixed.
- Fresh catalyst is added and worn-out catalyst removed to optimize the cracking process.

Fluid Catalytic Cracking



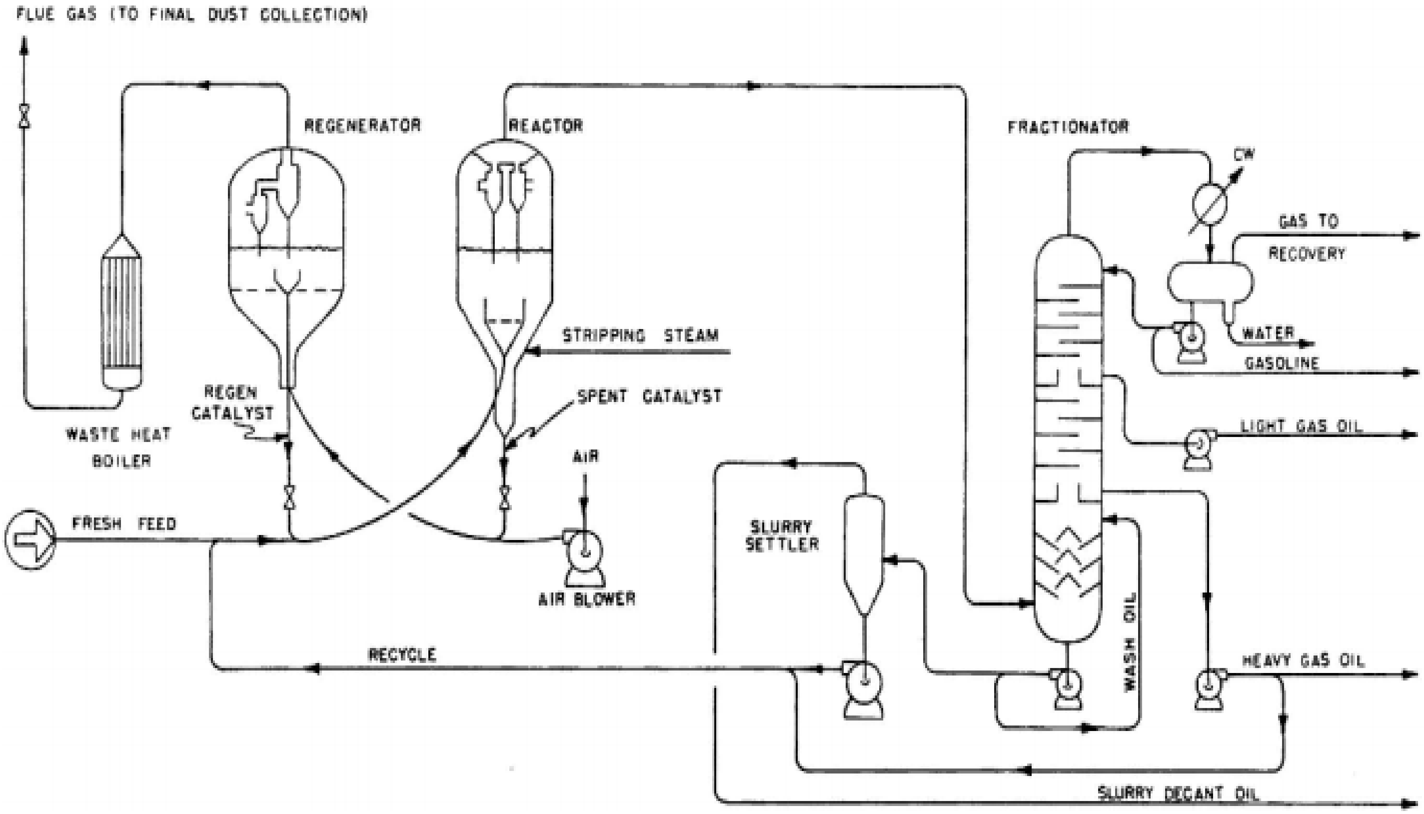


Figure 6.3 FCC unit, Model III.

Moving-Bed Catalytic Cracking

- The moving-bed catalytic cracking process is similar to the FCC process.
- The catalyst is in the form of pellets that are moved continuously to the top of the unit by conveyor or pneumatic lift tubes to a storage hopper, then flow downward by gravity through the reactor, and finally to a regenerator.
- The regenerator and hopper are isolated from the reactor by steam seals.
- The cracked product is separated into recycle gas, oil, clarified oil , distillate, naphtha, and wet gas.

Catalyst

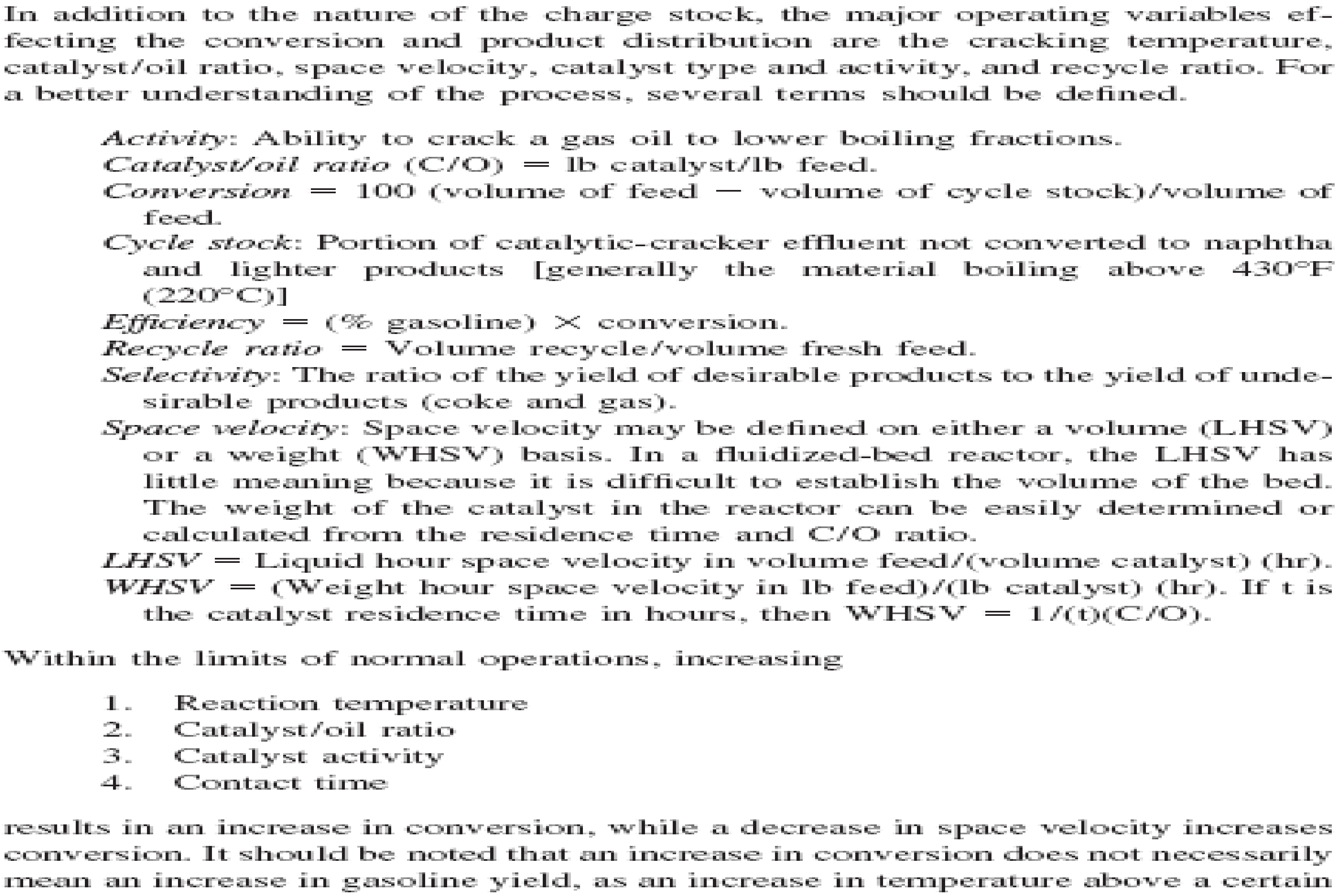
- Both systems use basically similar catalysts but produced in a different form, in the shape of beds for moving bed and fine powder for fluidized bed.

1. Acid treated clays ground to a powder
2. Synthetic silica- alumina catalysts of higher activity (amorphous)
3. Crystalline synthetic silica – alumina catalyst called zealots or molecular sieves.

The advantages of zealots over the natural and synthesis amorphous catalyst are

1) Higher activity.
2) Higher gasoline yields at a given conversion.
3) Production of gasoline containing a larger % of paraffinic and aromatic HC.
4) Lower coke yield.
5) Increased iso-butane production.
6) Ability to go for higher conversion per pass without over cracking.

PROCESS VARIABLES



In addition to the nature of the charge stock, the major operating variables effecting the conversion and product distribution are the cracking temperature, catalyst/oil ratio, space velocity, catalyst type and activity, and recycle ratio. For a better understanding of the process, several terms should be defined.

Activity: Ability to crack a gas oil to lower boiling fractions.
Catalyst/oil ratio (C/O) = lb catalyst/lb feed.
Conversion = 100 (volume of feed − volume of cycle stock)/volume of feed.
Cycle stock: Portion of catalytic-cracker effluent not converted to naphtha and lighter products [generally the material boiling above 430°F (220°C)]
Efficiency = (% gasoline) × conversion.
Recycle ratio = Volume recycle/volume fresh feed.
Selectivity: The ratio of the yield of desirable products to the yield of undesirable products (coke and gas).
Space velocity: Space velocity may be defined on either a volume (LHSV) or a weight (WHSV) basis. In a fluidized-bed reactor, the LHSV has little meaning because it is difficult to establish the volume of the bed. The weight of the catalyst in the reactor can be easily determined or calculated from the residence time and C/O ratio.
LHSV = Liquid hour space velocity in volume feed/(volume catalyst) (hr).
WHSV = (Weight hour space velocity in lb feed)/(lb catalyst) (hr). If t is the catalyst residence time in hours, then WHSV = 1/(t)(C/O).

Within the limits of normal operations, increasing

1. Reaction temperature
2. Catalyst/oil ratio
3. Catalyst activity
4. Contact time

results in an increase in conversion, while a decrease in space velocity increases conversion. It should be noted that an increase in conversion does not necessarily mean an increase in gasoline yield, as an increase in temperature above a certain

Comparison between thermal and catalytic cracking

Catalytic cracking is differences with respect Thermal Cracking

- uses a catalyst
- lower temperature
- lower pressure
- more flexible
- different reaction mechanisms : ionic vs. free radical
- High thermal efficiency
- Good integration of cracking and regeneration

- High yields of gasoline and other distillates
- Low gas yields
- High product selectivity
- Low n-alkane yields
- High octane number
- Chain-branching and high yield of C4 olefins
- High yields of aromatics