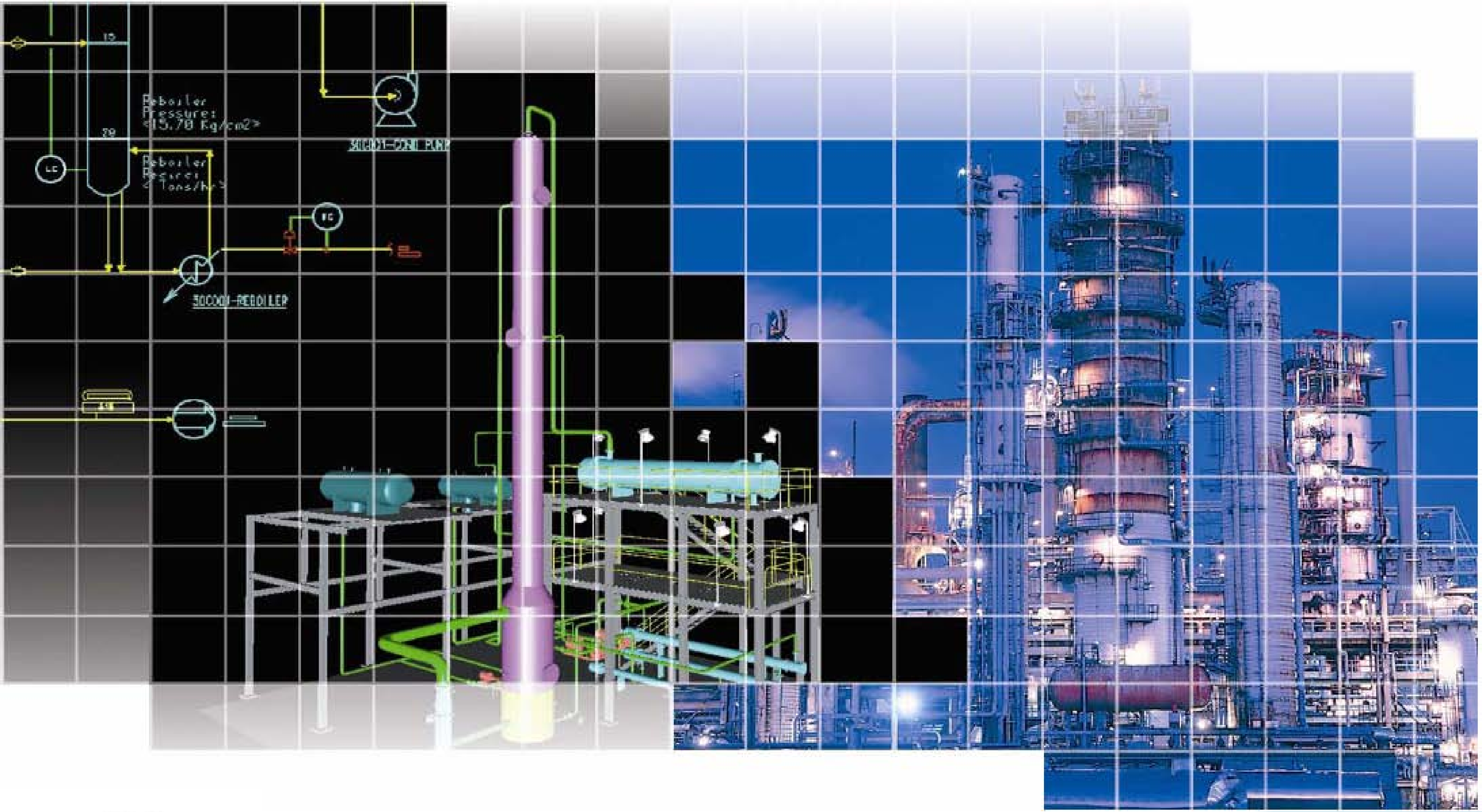
Fourth Year – Chemical Process Eng. Branch
Petroleum Refinery Eng. Lectures
By
Dr. Adnan A. Abdul Razak

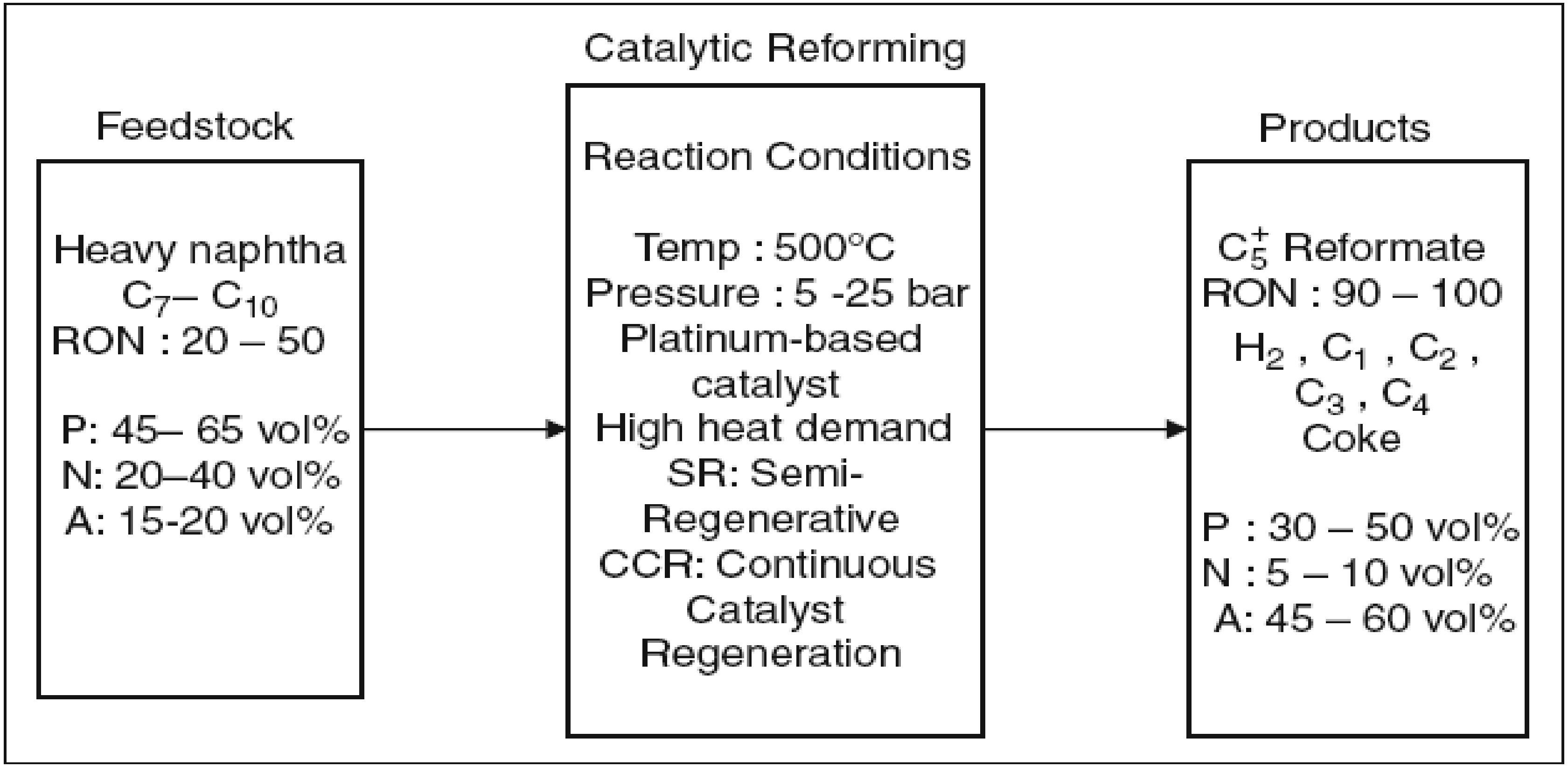


Lect./8
Upgrading Naphtha

A) Catalytic Reforming

Catalytic Reforming

- Catalytic reforming is the process of transforming C7-C10 hydrocarbons with low octane numbers to aromatics and iso-paraffins which have high octane numbers. It is a highly endothermic process requiring large amounts of energy.
- Depending on the properties of the naphtha feedstock (as measured by the paraffin, olefin, naphthene, and aromatic content) and catalysts used, reformates can be produced with very high concentrations of toluene, benzene, xylene, and other aromatics useful in gasoline blending and petrochemical processing.
- Hydrogen, a significant by-product, is separated from the reformate for recycling and use in other processes.
- A catalytic reformer comprises a reactor section and a product recovery section.



Catalytic Reforming

Feedstock

Heavy naphtha
$C_7 - C_{10}$
RON : 20 – 50

P: 45– 65 vol%
N: 20–40 vol%
A: 15-20 vol%

Reaction Conditions

Temp : 500°C
Pressure : 5 -25 bar
Platinum-based catalyst
High heat demand
SR: Semi-Regenerative
CCR: Continuous Catalyst Regeneration

Products

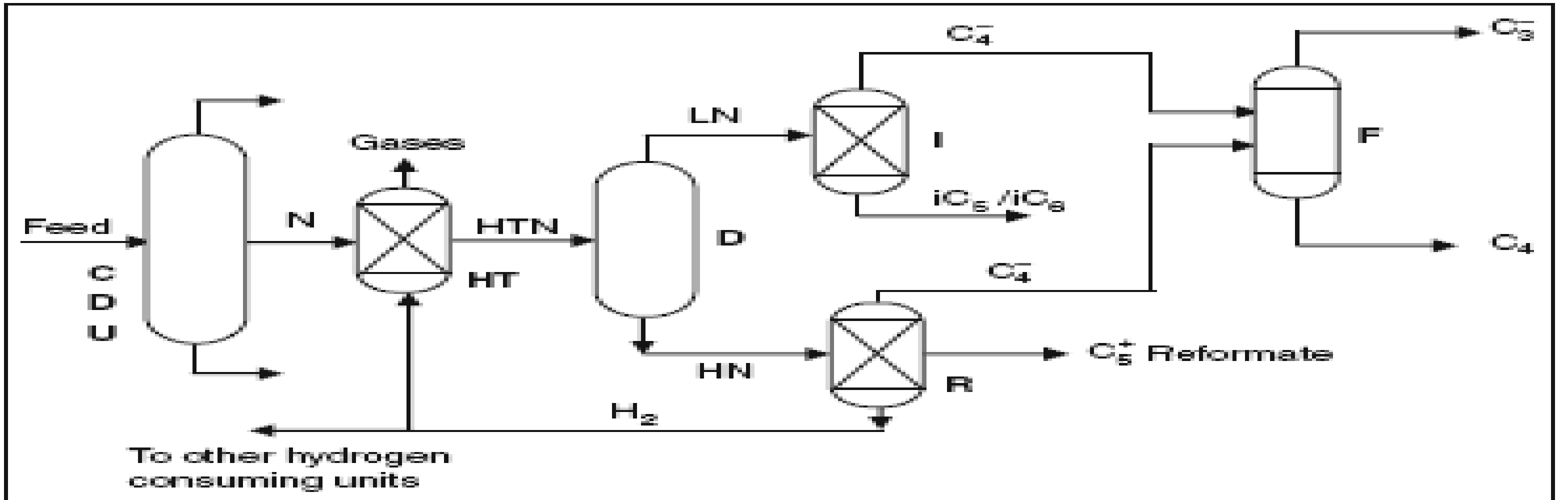
C_5^+ Reformate
RON : 90 – 100
H_2 , C_1 , C_2 , C_3 , C_4
Coke

P : 30 – 50 vol%
N : 5 – 10 vol%
A: 45 – 60 vol%

Figure 5.1 Catalytic reforming process

Role of Reformer in the Refinery and Feed Preparation

- ❑The catalytic reformer is one of the major units for gasoline production in refineries. It an produce 37 wt% of the total gasoline pool. Other units such as the fluid catalytic cracker (FCC), the methyl ter-butyl ether (MTBE) production unit, alkylation unit and isomerization unit, also contribute to this pool.
- ❑The straight run naphtha from the crude distillation unit is hydrotreated to remove sulphur, nitrogen and oxygen which can all deactivate the reforming catalyst.
- ❑The hydrotreated naphtha (HTN) is fractionated into light naphtha (LN), which is mainly C5-C6, and heavy naphtha (HN) which is mainly C7-C10 hydrocarbons.
- ❑Light naphtha (LN) is isomerized in the isomerization unit (I). Light naphtha can be cracked if introduced to the reformer.
- ❑The role of the heavy naphtha (HN) reformer in the refinery is shown in Figure 5.2.
- ❑ Hydrogen, produced in the reformer can be recycled to the naphtha hydrotreater, and the rest is sent to other units demanding hydrogen.



CDU	Crude distillation unit
D	Distillation
F	Flash
I	Isomerization
HN	Heavy Naphtha
HT	Hydrotreater
HTN	Hydro Treated Naphtha
LN	Light Naphtha
N	Naphtha
R	Reformer

Figure 5.2 Role of reformer in the refinery

Reforming Reactions

(PONA) **{Paraffin, Olefin,** Naphthene, **Aromatic}**

1) **P** → isomerizes to some extent converted to **N**, and **N** subsequently converted to **aromatics**.

2) **O** → saturated to form **P** which then react as in (1) **{hydro-cracking}**.

3) **N** → converted to **aromatics. {dehydrogenation}.**

4) A→ **unchanged.**

Process Technology

- There are several commercial processes available for reforming.

1. Semi-regenerative Fixed Bed Process :The name semi-regenerative comes from regeneration of the catalyst in the fixed bed reactors after shut down by burning off the carbon formed on the catalyst surface. *(Low capital cost)*.
2. Continuous Regenerative (moving bed) CCR Platforming :Catalyst can be regenerated continuously and maintained at a high activity . *(Higher capital cost)*.
3. Cyclic :compromise between the two extremes having a swing reactor for regeneration.

Catalyst

All of the reforming catalyst contains ***platinum supported on a silica alumina base***.

In most cases ***rhenium is combined with platinum*** to form a more stable catalyst which permits operation at lower pressure.

Platinum serve as a catalytic site for hydrogenation and dehydrogenation reactions.

Chlorinated alumina provides an acids site for isomerization and hydro- cracking reactions and cyclization.

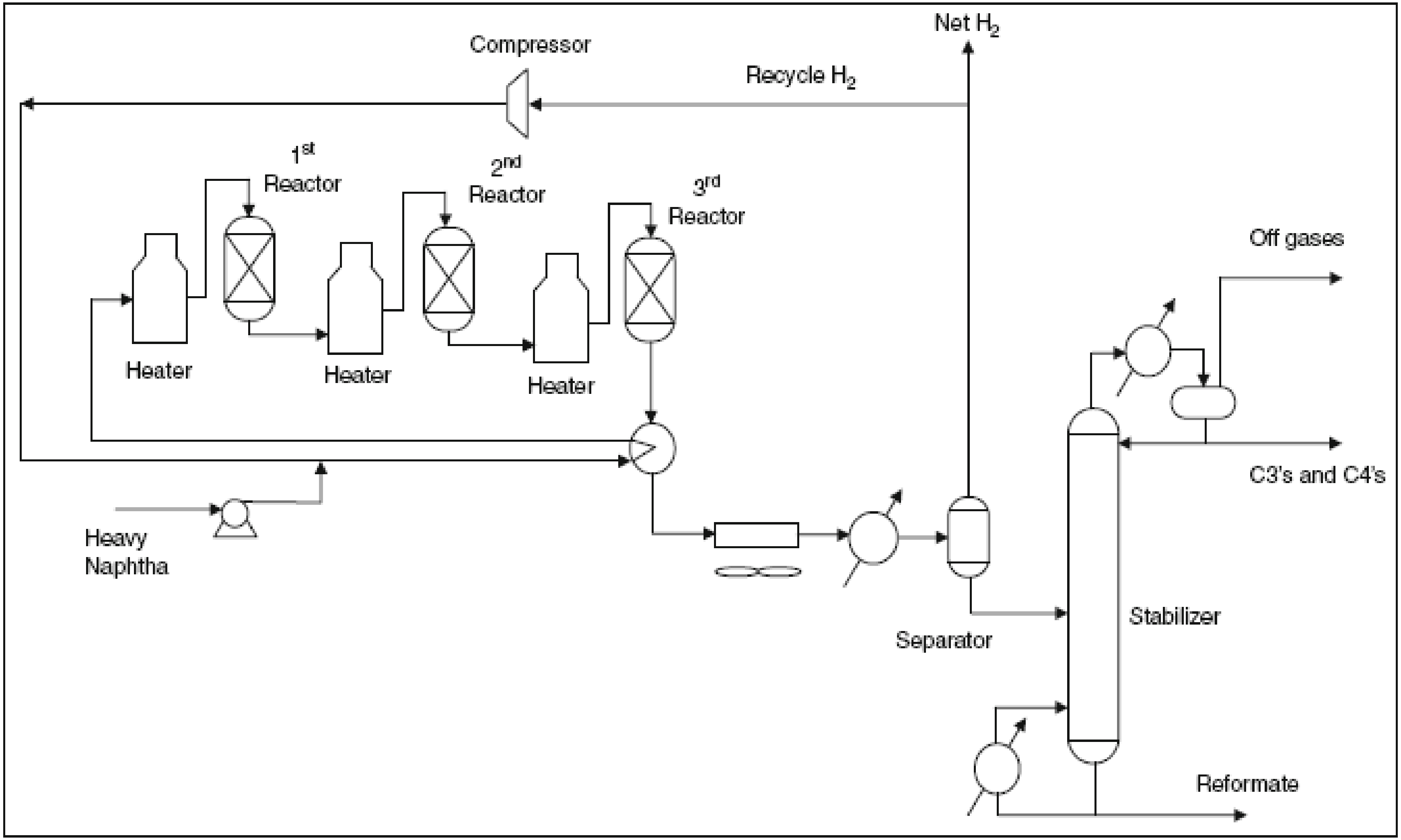
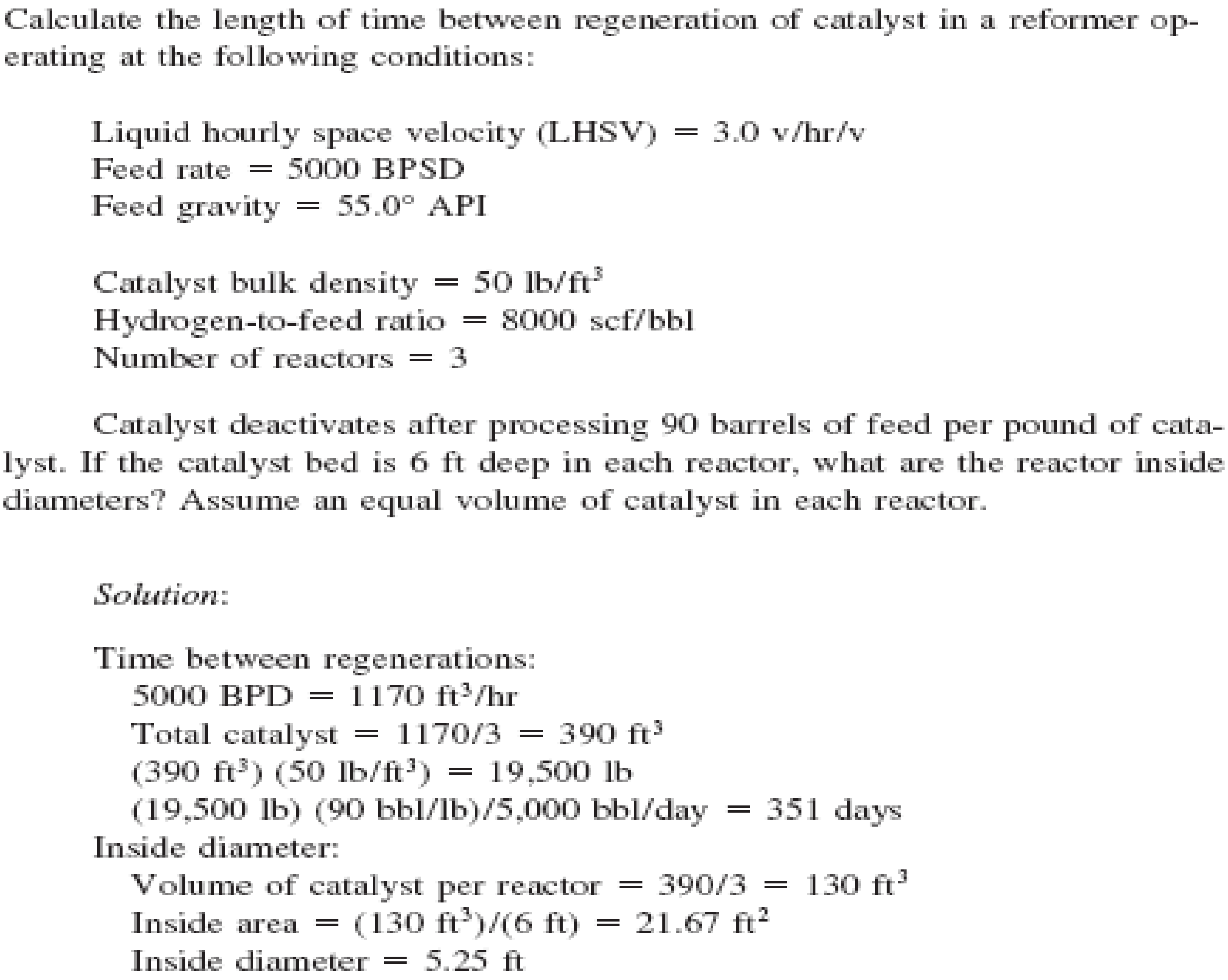


Figure 5.5 Semi-regenerative (SR) fixed bed reforming process

Example (2)



Calculate the length of time between regeneration of catalyst in a reformer operating at the following conditions:

Liquid hourly space velocity (LHSV) = 3.0 v/hr/v
Feed rate = 5000 BPSD
Feed gravity = 55.0° API

Catalyst bulk density = 50 lb/ft^3
Hydrogen-to-feed ratio = 8000 scf/bbl
Number of reactors = 3

Catalyst deactivates after processing 90 barrels of feed per pound of catalyst. If the catalyst bed is 6 ft deep in each reactor, what are the reactor inside diameters? Assume an equal volume of catalyst in each reactor.

Solution:

Time between regenerations:
5000 BPD = 1170 ft^3/hr
Total catalyst = 1170/3 = 390 ft^3
(390 ft^3) (50 lb/ft^3) = 19,500 lb
(19,500 lb) (90 bbl/lb)/5,000 bbl/day = 351 days
Inside diameter:
Volume of catalyst per reactor = 390/3 = 130 ft^3
Inside area = (130 ft^3)/(6 ft) = 21.67 ft^2
Inside diameter = 5.25 ft

Example (3)

On processing 1200 ton / day of 27 API catalyst crackers feed stock at a temperature of 450 °C, pressure =1050 mm Hg the following products were obtained:

Products	wt %	API	Mw
Gases	15	--	32
C_5^+ gasoline	55	63	110
TCGO	26	5	260
Coke	4	--	12

Given that: WHSV = 0.7 hr^{-1}, Linear velocity of vapor (U) = 0.3 m/s,

$\rho_{catalyst}$ = 420 Kg /m^3

Calculate: a) diameter of the cracker, b) weight of catalyst needed, c) conversion, and d) efficiency.

Solution :

$$m_{feed} = \frac{1200 \text{ ton/day} * 1000 \text{ Kg/ton}}{24 \text{ hr/day}} = 50000 \text{ Kg /hr}$$

$m_{gases} = 0.15 * 50000 / 3600 = 2.08$ Kg/s

$m_{C5^+ gasoline} = 0.55 * 50000/ 3600 = 7.64$ Kg/s

$m_{TCGO} = 0.26 * 50000/ 3600 = 3.61$ Kg/s

Total moles of vapor = $(2.08/ 32) + (7.64/ 110) + (3.61/ 260)$

n = 0.1479 Kg mole / s

$$R = \frac{22.4\ (m^3/\ kg\ mole)\ *\ 760\ mm\ Hg}{1\ Kg\ mole\ *\ 273} = 62.359$$

$$V = \frac{n\ R\ T}{P} = \frac{0.1479 * 62.359 * (450+273)}{1050} = 6.35\ m^3/s$$

$$A = \frac{\Pi}{4} D^2 = \frac{V}{U} = \frac{6.35\ m^3/s}{0.3\ m/s} = 21.17\ m^2$$

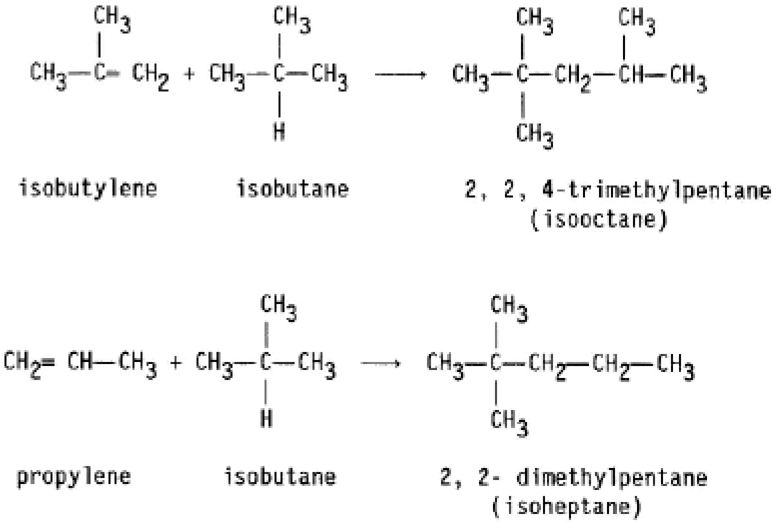
$m_{catalyst} = 50000/0.7 = 71428\ Kg$

$V_{catalyst} = m/\ \rho = 170\ m^3$

$$H = \frac{4 * 170}{3.14 * (5.19)^2} = 8\ m$$

B) Alkylation

- Alkylation combines low-molecular-weight olefins (primarily a mixture of propylene and butylene) with isobutane in the presence of a catalyst, either sulfuric acid or hydrofluoric acid.



- The product is called alkylate and is composed of a mixture of high octane, branched-chain paraffinic hydrocarbons.
- Alkylate is a premium blending stock because it has exceptional antiknock properties and is clean burning.
- The octane number of the alkylate depends mainly upon the kind of olefins used and upon operating conditions.

C) Isomerization

- Isomerization is the process in which light straight chain paraffins of low RON (C6, C5 and C4) are transformed with proper catalyst into branched chains with the same carbon number and high octane numbers.
- The hydrotreated naphtha (HTN) is fractionated into heavy naphtha between 90–190 C (190–380 F) which is used as a feed to the reforming unit. Light naphtha C5 – 80 C (C5 – 180 F) is used as a feed to the isomerization unit.
- Isomerization Reactions:

Isomerization is a reversible and slightly exothermic reaction:

$$\text{n-paraffin} \rightleftharpoons \text{i-paraffin}$$

- The isomerization reactions are slightly exothermic and the reactor works in the equilibrium mode. There is no change in the number of moles and thus the reaction is not affected by pressure change. Better conversions are achieved at lower temperature
- The conversion to iso-paraffin is not complete since the reaction is equilibrium conversion limited. It does not depend on pressure, but it can be increased by lowering the temperature. However operating at low temperatures will decrease the reaction rate. For this reason a very active catalyst must be used.

Isomerization Catalysts

- There are two types of isomerization catalysts:

1. The standard Pt/chlorinated alumina with high chlorine content, which is considered quite active,
2. and the Pt/zeolite catalyst.

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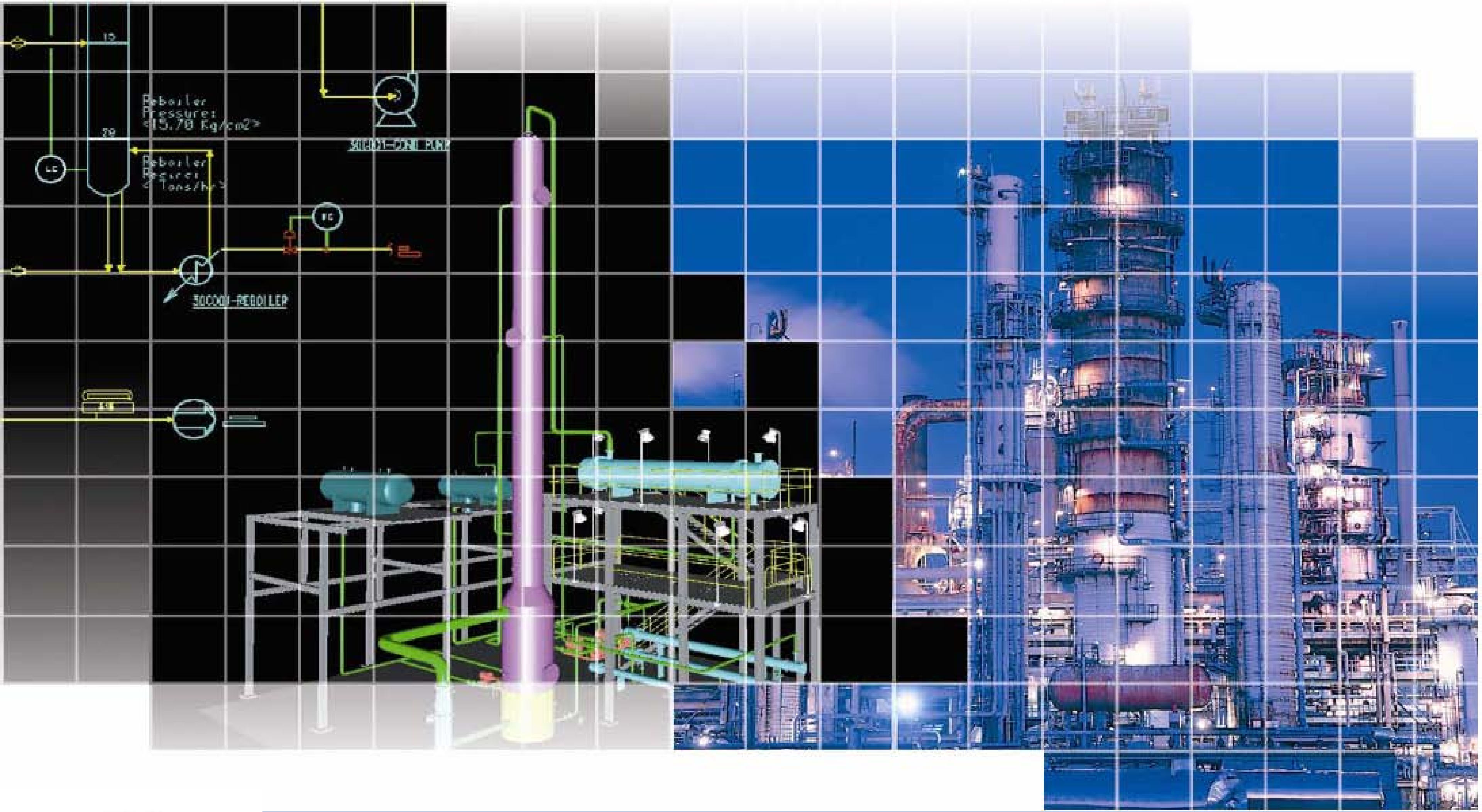


الجامعة التكنولوجية

Lect./9

Product Blending

Product Blending

❖ Blending purpose is to allocate the available blending components in such a way to meet product demands and specification at the least cost. We now review how the properties of mixtures are estimated based on the properties of the components.

Octane Blending:

True octane numbers do not blend linearly. It is therefore necessary to use especial “blending” octane numbers to obtain linear expressions. The blending is performed on a volumetric average basis.

The formula used for calculation is:

$$B_t ON_t = \sum_{i=1}^{n} (B_i ON_i) \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad 1$$

where

B_t = total amount of blended gasoline , *bbl*

ON_t = desired octane of blend

B_i = bbl of component i

ON_i = blending octane number of component i.

contributing to product t and blending octane numbers, respectively. The practice has been to use the following expression for the "blending" octane number:

$$ON_i = (MON_i + RON_i)/2 \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad 2$$

where MON and RON are the motor and research octane numbers, respectively. Note that the true octane number is the one obtained using a CFR test engine. For example, consider a 30% isomerate and 70% reformate blend. Isomerate has the following octane values: MON=81.1, RON=83.0, whereas reformat has the following octane numbers: MON=86.9 and RON=98.5. When blended in the proportion given above, the blended pool has ON=89.505.

Pool Octane : is the average octane of the total gasoline production of the refinery, if the regular, mid- premium, and super- premium gasolines are blended together.

Posted Octane numbers (PON): are the arithmetic average of the motor octane number (MON) and research octane number (RON).

Reid vapor pressure:

The desired RVP of a gasoline is obtained by blending n-butane with C_5 (380 °F) with C_5 (193 °F) naphtha. The amount of n-butane required to give the needed RVP is calculated by:

$$M_t (RVP)_t = \sum_{i=1}^{n} M_i (RVP)_i \quad \text{.....................................} \quad 3$$

Where:

M_t = total moles blended product

$(RVP)_t$ = specification RVP for product, psi

M_i = moles of component i

$(RVP)_i$ = RVP of component i, psi or kPa

The desired RVP for a blended gasoline is obtained by adding n-butane to reach the desired value.

Example (1): calculate the amount of n-butane to be added to following base stock to achieve an RVP of 10 psi(n- butane: MW=58, RVP=52).

Base stock	BPD	Lb/hr	MW	RVP (psi)
LSR gasoline	4000	39320	86	11.1
Reformate	6000	69900	115	2.8
Alkylate	3000	30690	104	4.6
FCC gasoline	8000	87520	108	4.4
Total	21000			5.38

Solution:

Base stock	BPD	Lb/hr	MW	mol/hr	mol%	RVP	PVP
LSR gasoline	4000	39320	86	457	21	11.1	2.32
Reformate	6000	69900	115	617	28.4	2.8	0.80
Alkylate	3000	30690	104	295	13.4	4.6	0.62
FCC gasoline	8000	87520	108	810	37.2	4.4	1.64
Total	21000			2179	100		

Butane requirement : (use Eq. (3))

$(2179)(5.38) + M(52) = (2179 + M)(10)$

$11732 + 52M = 21790 + 10M$

$M = 240$ moles n-butane required.

The above method requires obtaining the molecular weight of each of the streams involved, which could be a problem sometimes, although there are good ways of estimating such molecular weights. To makes matter simpler, one can use the method developed at Chevron. In this method “Vapor blending indices” (VPBI), which work well. The RVP of a blend is then calculated using the following volume averaging formula:

$$(RVP)_{blend} = \sum V_i (RVP)_i \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad 4$$

In the case where the volume of the butane to be blended for a given RVP is desired :

$$A(VPBI)_a + B(VPBI)_b + C(VPBI)_c + - - - - + W(VPBI)_w = (Y+W)(VPBI)_m \quad \ldots\ldots\ldots\ldots \quad 5$$

where

A= bbl of component a, etc

W= bbl of n- butane (w)

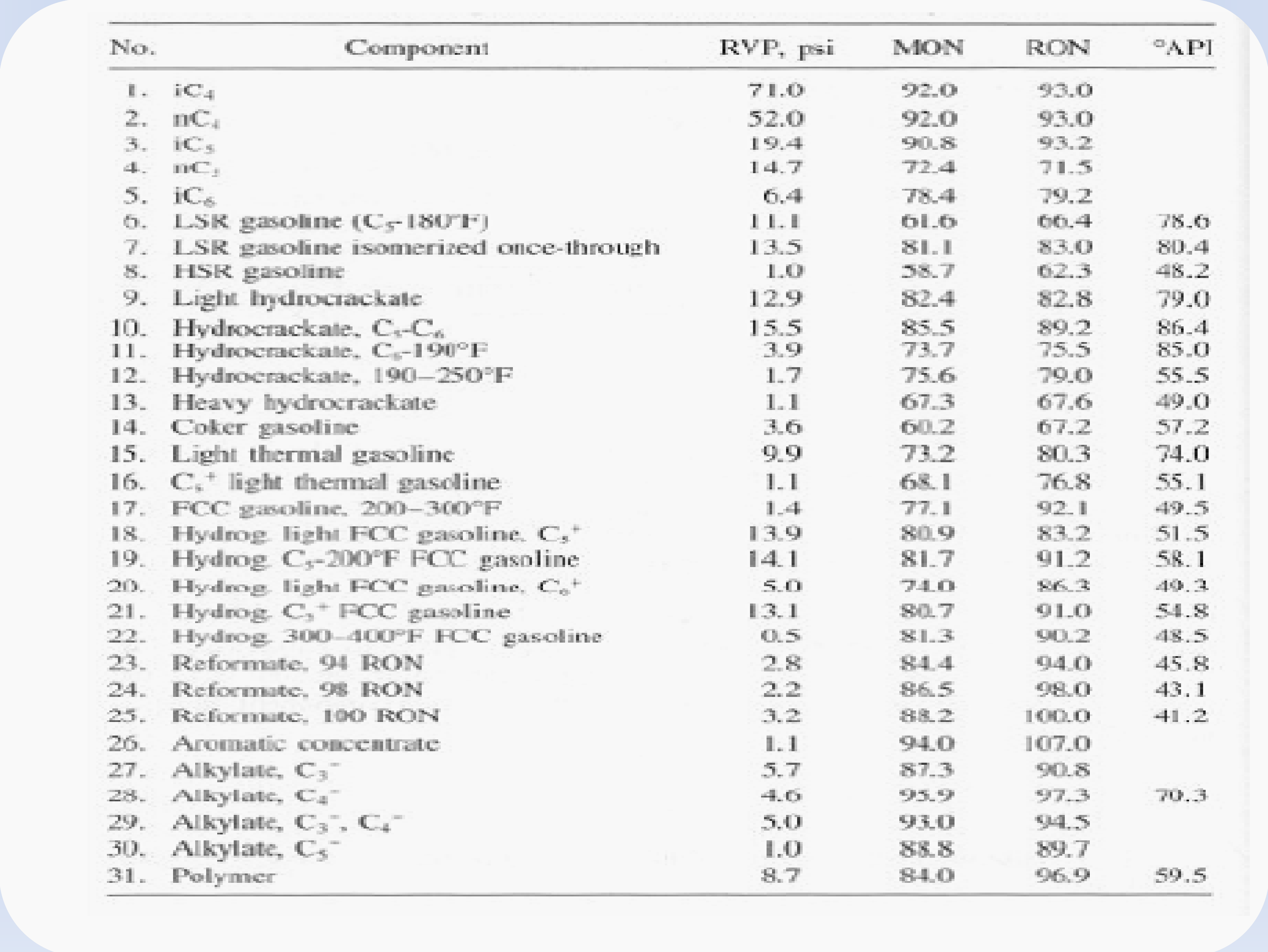
Y= A+B+C+ ----------- (all component except n- butane)

$(VPBI)_m$ = VPBI corresponding to the desired RVP of the mixture

w= subscript indicating n- butane.

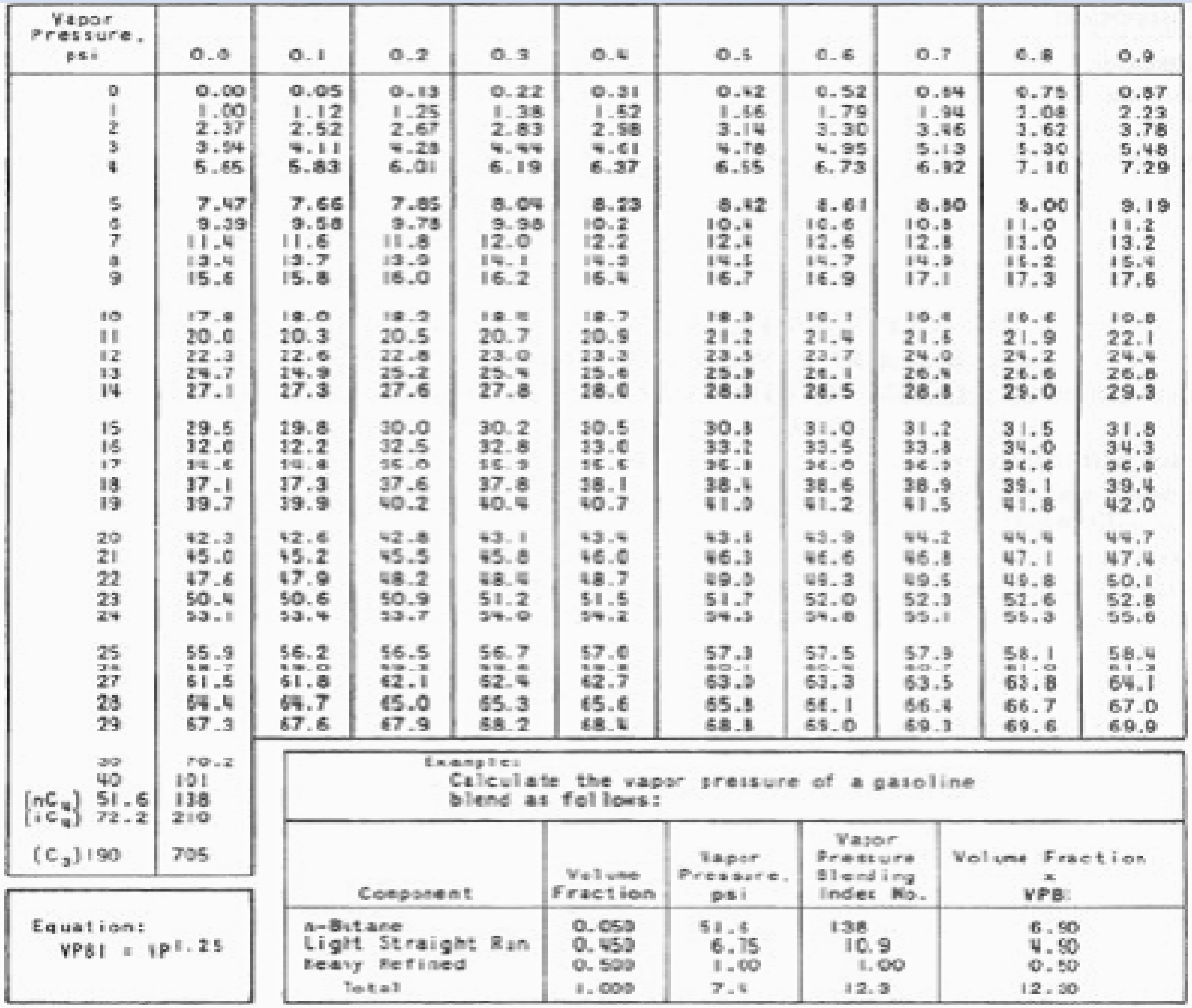
Table 11-1 and 11-2 show the blending component values for different blending streams and the blending indexes as a function of RVP values.

Table 11-1: Blending Component values (Gary and Handwerk, 2001)



No.	Component	RVP, psi	MON	RON	°API
1.	iC_4	71.0	92.0	93.0	
2.	nC_4	52.0	92.0	93.0	
3.	iC_5	19.4	90.8	93.2	
4.	nC_5	14.7	72.4	71.5	
5.	iC_6	6.4	78.4	79.2	
6.	LSR gasoline (C_5-180°F)	11.1	61.6	66.4	78.6
7.	LSR gasoline isomerized once-through	13.5	81.1	83.0	80.4
8.	HSR gasoline	1.0	58.7	62.3	48.2
9.	Light hydrocrackate	12.9	82.4	82.8	79.0
10.	Hydrocrackate, C_5-C_6	15.5	85.5	89.2	86.4
11.	Hydrocrackate, C_6-190°F	3.9	73.7	75.5	85.0
12.	Hydrocrackate, 190–250°F	1.7	75.6	79.0	55.5
13.	Heavy hydrocrackate	1.1	67.3	67.6	49.0
14.	Coker gasoline	3.6	60.2	67.2	57.2
15.	Light thermal gasoline	9.9	73.2	80.3	74.0
16.	C_6^+ light thermal gasoline	1.1	68.1	76.8	55.1
17.	FCC gasoline, 200–300°F	1.4	77.1	92.1	49.5
18.	Hydrog. light FCC gasoline, C_5^+	13.9	80.9	83.2	51.5
19.	Hydrog. C_5-200°F FCC gasoline	14.1	81.7	91.2	58.1
20.	Hydrog. light FCC gasoline, C_6^+	5.0	74.0	86.3	49.3
21.	Hydrog. C_5^+ FCC gasoline	13.1	80.7	91.0	54.8
22.	Hydrog. 300–400°F FCC gasoline	0.5	81.3	90.2	48.5
23.	Reformate, 94 RON	2.8	84.4	94.0	45.8
24.	Reformate, 98 RON	2.2	86.5	98.0	43.1
25.	Reformate, 100 RON	3.2	88.2	100.0	41.2
26.	Aromatic concentrate	1.1	94.0	107.0	
27.	Alkylate, $C_3^=$	5.7	87.3	90.8	
28.	Alkylate, $C_4^=$	4.6	95.9	97.3	70.3
29.	Alkylate, $C_3^=$, $C_4^=$	5.0	93.0	94.5	
30.	Alkylate, $C_5^=$	1.0	88.8	89.7	
31.	Polymer	8.7	84.0	96.9	59.5

Table 11-2: Blending Component values (Gary and Handwerk, 2001)



Vapor Pressure, psi	0.0	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9
0	0.00	0.05	0.13	0.22	0.31	0.42	0.52	0.64	0.75	0.87
1	1.00	1.12	1.25	1.38	1.52	1.66	1.79	1.94	2.08	2.23
2	2.37	2.52	2.67	2.83	2.98	3.14	3.30	3.46	3.62	3.78
3	3.94	4.11	4.28	4.44	4.61	4.78	4.95	5.13	5.30	5.48
4	5.65	5.83	6.01	6.19	6.37	6.55	6.73	6.92	7.10	7.29
5	7.47	7.66	7.85	8.04	8.23	8.42	8.61	8.80	9.00	9.19
6	9.39	9.58	9.78	9.98	10.2	10.4	10.6	10.8	11.0	11.2
7	11.4	11.6	11.8	12.0	12.2	12.4	12.6	12.8	13.0	13.2
8	13.4	13.7	13.9	14.1	14.3	14.5	14.7	14.9	15.2	15.4
9	15.6	15.8	16.0	16.2	16.4	16.7	16.9	17.1	17.3	17.6
10	17.8	18.0	18.3	18.5	18.7	18.9	19.1	19.4	19.6	19.8
11	20.0	20.3	20.5	20.7	20.9	21.2	21.4	21.6	21.9	22.1
12	22.3	22.6	22.8	23.0	23.3	23.5	23.7	24.0	24.2	24.4
13	24.7	24.9	25.2	25.4	25.6	25.9	26.1	26.4	26.6	26.8
14	27.1	27.3	27.6	27.8	28.0	28.3	28.5	28.8	29.0	29.3
15	29.5	19.8	30.0	30.2	30.5	30.8	31.0	31.2	31.5	31.8
16	32.0	32.2	32.5	32.8	33.0	33.2	33.5	33.8	34.0	34.3
17	34.6	34.8	35.0	35.3	35.6	35.8	36.0	36.3	36.6	36.8
18	37.1	37.3	37.6	37.8	38.1	38.4	38.6	38.9	39.1	39.4
19	39.7	39.9	40.2	40.4	40.7	41.0	41.2	41.5	41.8	42.0
20	42.3	42.6	42.8	43.1	43.4	43.6	43.9	44.2	44.4	44.7
21	45.0	45.2	45.5	45.8	46.0	46.3	46.6	46.8	47.1	47.4
22	47.6	47.9	48.2	48.4	48.7	49.0	49.3	49.5	49.8	50.1
23	50.4	50.6	50.9	51.2	51.5	51.7	52.0	52.3	52.6	52.8
24	53.1	53.4	53.7	54.0	54.2	54.5	54.8	55.1	55.3	55.6
25	55.9	56.2	56.5	56.7	57.0	57.3	57.5	57.9	58.1	58.4
26	58.7	59.0	59.3	59.6	59.8	60.1	60.4	60.7	61.0	61.3
27	61.5	61.8	62.1	62.4	62.7	63.0	63.3	63.5	63.8	64.1
28	64.4	64.7	65.0	65.3	65.6	65.8	66.1	66.4	66.7	67.0
29	67.3	67.6	67.9	68.2	68.4	68.8	69.0	69.3	69.6	69.9
30	70.2									
40	101									
[nC_4] 51.6	138									
[iC_4] 72.2	210									
(C_3) 190	705									

Equation:

$$VPBI = VP^{1.25}$$

Example:

Calculate the vapor pressure of a gasoline blend as follows:

Component	Volume Fraction	Vapor Pressure, psi	Vapor Pressure Blending Index No.	Volume Fraction x VPBI
n-Butane	0.050	51.6	138	6.90
Light Straight Run	0.450	6.75	10.9	4.90
Heavy Refined	0.500	1.00	1.00	0.50
Total	1.000	7.4	12.3	12.30

Example (2): Repeat Example (1) use vapor blending indices (VPBI) method.

Component	BPCD	RVP	VPBI	Vol x VPBI
n-Butane	W	51.6	138	138 W
LSR gasoline	4000	11.1	20.3	81200
Reformat	6000	2.8	3.62	21720
Alkylate	3000	4.6	6.73	20190
FCC gasoline	8000	4.4	6.37	50960
Total	21000 + W			174070 + 138 W

Given : VPBI of n- butane =138

For 10 psi RVP, $(\mathrm{VPBI})_m = 17.8$

Solution

$17.8\ (21000 + W) = 174070 + 138\ W$

$(138-17.8)\ W = 373800-174070$

W= 1660 bbl n-butane required

Total 10 psi RVP gasoline =21000 + 1660 = 22660 BPCD

Although this differs slightly from the result in Example (1)

<u>Example (3):</u> Consider the following gasoline blending streams are available from the various units. It is desired to produce a 50-50 split of premium and regular gasoline having 91 and 87 posted octane numbers respectively, with both having an RVP= to 10.2 psi . calculate the quantity of n- butane required to give the desired vapor pressure.

Component	Volume	MON	RON	VPBI
Isomerate	5735	81.1	83	25.9
Reformat	14749	86.9	98.5	2.7
FCC gasoline	20117	76.8	92.3	6.4
Light hydrocrackate	814	82.4	82.8	24.4
Alkylate	4117	95.9	97.3	6.7
Polymer	2071	84	96.9	14.9
Total	47603			

Given : VPBI of n- butane =138

For 10.2 psi RVP, $(VPBI)_m$ = 18.2

<u>Solution</u>

Starting with the given flow for all of the above streams and calculating the amount of n-butane to add to fix the RVP.

Component	Vol.	RVP	VPBI	Vol (VPBI)
n- butane	W	51.6	138	138 W
Isomerate	5735	13.5	25.9	148395
Reformate	14749	2.2	2.7	39517
FCC gasoline	20117	4.4	6.4	128199
Light hydrocrackate	814	12.9	24.4	19895
Alkylate	4117	4.6	6.7	27732
Polymer	2071	8.7	14.9	30950
Total	47603 +W			394688+138W

18.2 (47603 + W)= 394688 + 138 W

W = 3937 bbl n- butane

The total volume of 10.2 psi RVP premium gasoline = 47603 + 3937 = 51540 BPCD

Octane calculations for pool Gasoline

Component	Volume	Vol. fract.	MON	∑ MON	RON	∑ RON
n- butane	3937	0.077	92.0	7.05	93.0	7.12
Isomerate	5735	0.111	81.1	9.02	83.0	9.23
Reformate	14749	0.286	86.9	24.85	98.5	28.18
FCC gasoline	20117	0.390	76.8	29.97	92.3	36.02
Light hydrocrackate	814	0.016	82.4	1.30	82.8	1.31
Alkylate	4117	0.080	95.9	7.66	97.3	7.77
Polymer	2071	0.040	84.0	3.38	96.9	3.89
Total	51540	1.000		83.23		95.53

Pool octane [(∑ MON + ∑ RON) / 2)] = 88.38 PON
This is not acceptable, as the octane requirement for pool gasoline is 89 PON.
There are several ways of correcting this. Among the possibilities are :
Increase severity of reforming to produce a 98.8 to 100 RON clear reformate.
Use an octane blending agent, such as MTBE (methyl tertiary butyl ether) and ETBE (ethyl tertiary butyl ether).

Recalculating pool gasoline RVP and PON after adding sufficient MTBE to increase the PON to 89.0 gives the following .

Component	Vol.	RVP	VPBI	Vol (VPBI)
n- butane	W	51.6	138	138 W
Isomerate	5735	13.5	25.9	148395
Reformate	14749	2.2	2.7	39517
FCC gasoline	20117	4.4	6.4	128199
Light hydrocrackate	814	12.9	24.4	19895
Alkylate	4117	4.6	6.7	27732
Polymer	2071	8.7	14.9	30950
MTBE	1593	9.0	15.6	24832
Total	49195 +W			419520+138W

49195 +W=18.2 (419520+138W)
119.8W=895349-419520=475829
W=3984 bbl
Total pool 10.2 RVP, 89.0 PON gasoline= 53179 BPCD

Other properties:

Several other properties of blend pools (viscosities, aniline point, pour points, flash points) can be estimated using a technique similar to that of the Chevron Method for RVP, that is:

$$P_t = \sum_{i=1}^{n} (v_i P_i) \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad 6$$

where v_i is the volume fraction of blending stream *i* as above, and P_t as well as P_i are the "blending" properties of the product and the blending streams, respectively. The blending properties are, of course, compiled in tables much in the same way as in the case of RVP. These additional properties are important for Diesel blending. Finally, properties like sulfur or nitrogen content are monitored and blended linearly with percentages.

Home work (1) :

Using the value from the following table, calculate the number of barrels of n-butane that have to be added to a mixture of 1250 barrels of HSR gasoline, 750 barrels of LSR gasoline, and 620 barrels of C_5 FCC gasoline to produce a 9.0 psi Reid vapor pressure . What are the research and motor octane number of the blend?

Component	Volume	MON	RON	RVP	VPBI
HSR gasoline	1250	58.7	62.3	1.0	1.0
LSR gasoline	750	61.6	66.40	11.1	20.3
C_5 FCC gasoline	620	77.1	92.1	4.4	6.4

Given : VPBI of n- butane =138 , MON=92.0 , RON=93

For 8 psi RVP, $(VPBI)_m$ = 13.4

Home work (2) :

Calculate the octane number of the final blend and amount of n- butane needed for producing a 9.5 psi RVP gasoline from 5100 BPSD of LSR gasoline, 3000 BPSD light hydrocrackate,4250 BPSD alkylate, 10280 BPSD heavy hydrocrackate, 14500 BPSD C_5 FCC gasoline,14200 BPSD of 96 RON reformat, and 2500 BPSD of polymer gasoline.

Component	Volume	MON	RON	RVP	VPBI
LSR gasoline	5100	61.6	66.4	11.1	20.3
light hydrocrackate	3000	82.4	82.8	12.9	24.4
alkylate	4250	95.9	97.3	4.6	6.7
heavy hydrocrackate	10280	67.3	67.6	1.1	1.24
C_5 FCC gasoline	14500	77.1	92.1	4.4	6.4
Reformate RON 96	14500	86.5	98.0	2.2	2.7
Polymer	2500	84	96.9	8.7	14.9

Given : VPBI of n- butane =138

For 9.5 psi RVP, $(\text{VPBI})_m$ = 17.6

Home work (3) : A regular gasoline is to be blended using the components listed in the table below. The target (ON) specification is 90. Using the information provided, determine the volume of Reformate required meeting the blending specification.

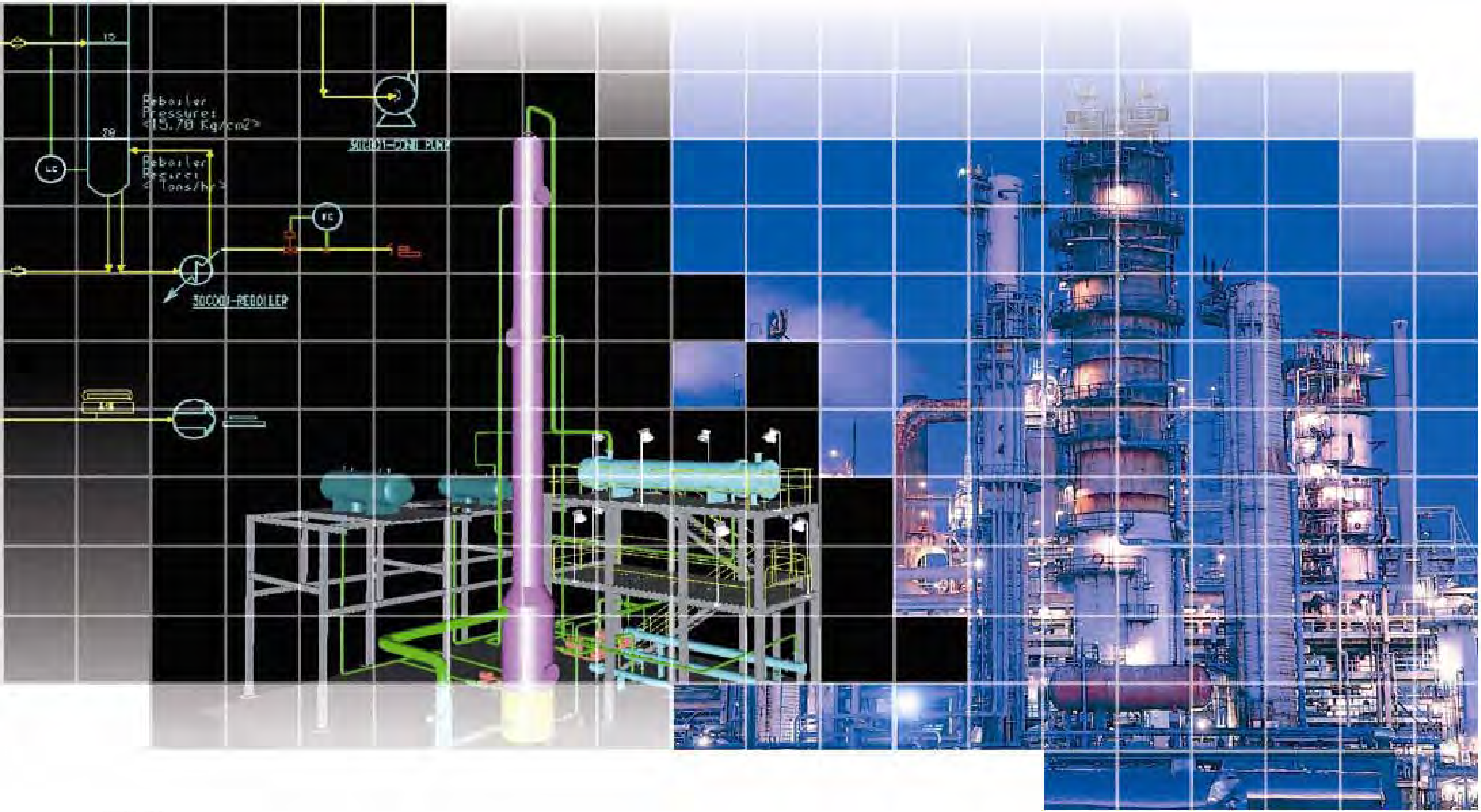
Component	Volume (barrels)	RON	MON
Hydrocracate	3000	82.8	82.4
Alkylate	1000	89.7	89
Reformate	-------	98	91
Straight run naphtha	1000	79	78

Fourth Year - Chemical Process Eng. Branch

Petroleum Refinery Eng. Lectures

By

Dr. Adnan A. Abdul Razak



Lect./10

Supporting Processes

Supporting Processes

- Not directly involved in the processing of petroleum based fuels Processes

» Hydrogen production & purification
» Acid gas treating
» Sulfur recovery
» Gas processing units
» Water treatment

Hydrogen Production & Purification

- Many refineries produce sufficient quantities of hydrogen for hydro treating from their naphtha-fed platinum catalyst reforming operations.
- however, require more hydrogen than is produced by their catalytic reforming units
- This supplemental hydrogen requirement can be Provided by one of two processes:

1. Steam reforming of light ends such as methane (natural gas), ethane, or propane
2. Partial oxidation of heavy hydrocarbons such as fuel oil

Steam reforming

Steam reforming for hydrogen production is accomplished in four steps:

1. *Reforming*. This involves the catalytic reaction of methane with steam at temperatures in the range of 1400 to 1500°F (760–816°C), according to the following equation:

$CH_4 + H_2O \rightarrow CO + 3H_2$ (1)

This reaction is endothermic and is carried out by passing the gas through catalyst-filled tubes in a furnace. The catalyst usually is in the form of hollow cylindrical rings ranging up to 3/4 inch in diameter. It consists of 25 to 40% nickel oxide deposited on a low-silica refractory base.

2. *Shift conversion*. More steam is added to convert the CO from step 1 to an equivalent amount of hydrogen by the following reaction:

$CO + H_2O \rightarrow CO_2 + H_2$ (2)

This is an exothermic reaction and is conducted in a fixed-bed catalytic reactor at about 650°F (343°C). Multiple catalyst beds in one reactor with external cooling between beds are commonly employed to prevent the temperature from getting too high. The catalyst used is a mixture of chromium and iron oxide.

3. *Gas purification*. The third step is removal of carbon dioxide by absorption in a circulating amine or hot potassium carbonate solution. Several other treating solutions are in use. The treating solution contacts the hydrogen and carbon dioxide gas in an absorber containing about 24 trays, or the equivalent amount of packing. Carbon dioxide is absorbed in the solution, which is then sent to a still for regeneration.

4. *Methanation*. In this step, the remaining small quantities of carbon monoxide and carbon dioxide are converted to methane by the following reactions:

$$CO + 3H_2 \rightarrow CH_4 + H_2O$$

$$CO_2 + 4H_2 \rightarrow CH_4 + 2H_2O \qquad (3)$$

This step is also conducted in a fixed-bed catalytic reactor at temperatures of about 700 to 800°F (427°C). Both reactions are exothermic and, if the feed concentration of CO and CO_2 is more than 3%, it is necessary to recycle some of the cooled exit gas to dissipate the heat of reaction. The catalyst contains 10 to 20% nickel on a refractory base.

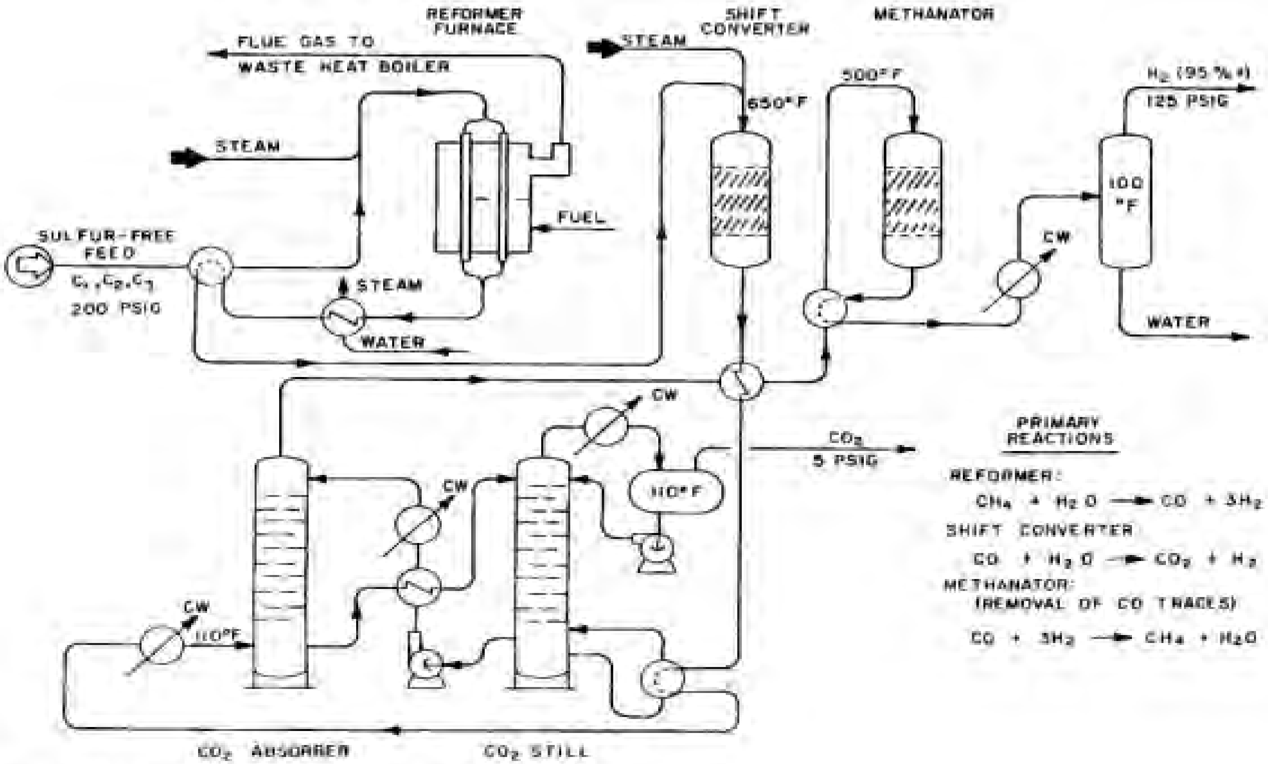


Figure 13.1 Hydrogen production by steam reforming.

Partial oxidation of fuel oils

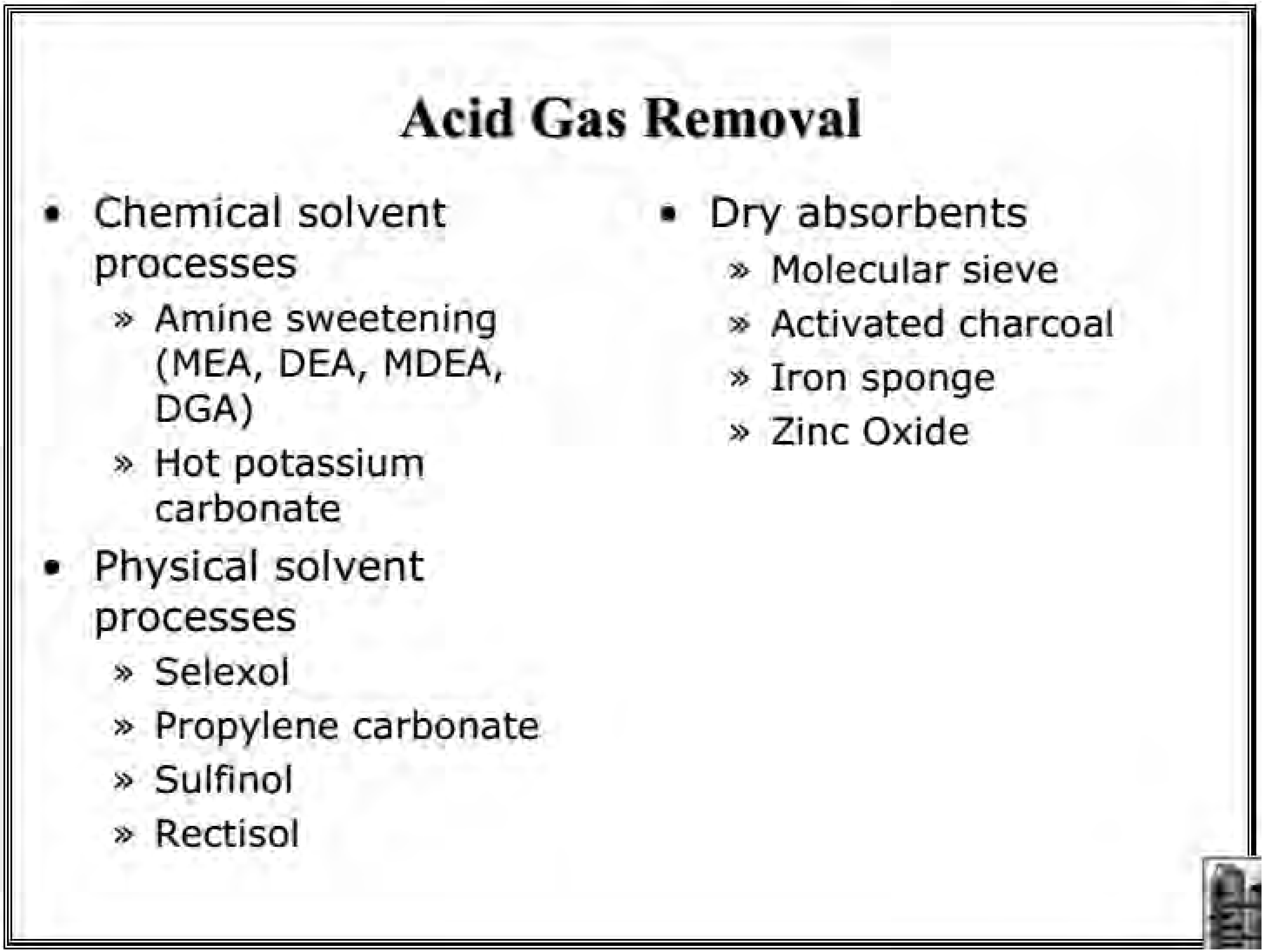
- Partial oxidation of fuel oils is accomplished by burning the fuel at high pressures (800 to 1300 psig) with an amount of pure oxygen which is limited to that required to convert the fuel oil to carbon monoxide and hydrogen.
- Enough water (steam) is added to shift the carbon monoxide to hydrogen in a catalytic shift conversion step.
- The resulting carbon dioxide is removed by absorption in hot potassium carbonate or other solvents.
- Ideally the partial oxidation reactions are as follows:

$$2C_nH_m + nO_2 \rightarrow 2nCO + mH_2$$

$$2nCO + 2nH_2O \rightarrow 2nCO_2 + 2nH_2$$

ACID GAS REMOVAL

- Gases from various operations in a refinery processing sour crudes contain hydrogen sulfide and occasionally carbonyl sulfide.
- Some hydrogen sulfide in refinery gases is formed as a result of conversion of sulfur compounds in processes such as hydrotreating, cracking, and coking. Recent air pollution regulations, however, require that most of the hydrogen sulfide be removed from refinery fuel gas and converted to elemental sulfur.
- In addition to hydrogen sulfide many crudes contain some dissolved carbon
dioxide which through distillation finds its way into the refinery fuel gas.
- These components—hydrogen sulfide and carbon dioxide—are generally termed acid gases.
- They are removed simultaneously from the fuel gas by a number of different processes, some of which are:



Acid Gas Removal

- Chemical solvent processes
  - Amine sweetening (MEA, DEA, MDEA, DGA)
  - Hot potassium carbonate
- Physical solvent processes
  - Selexol
  - Propylene carbonate
  - Sulfinol
  - Rectisol
- Dry absorbents
  - Molecular sieve
  - Activated charcoal
  - Iron sponge
  - Zinc Oxide

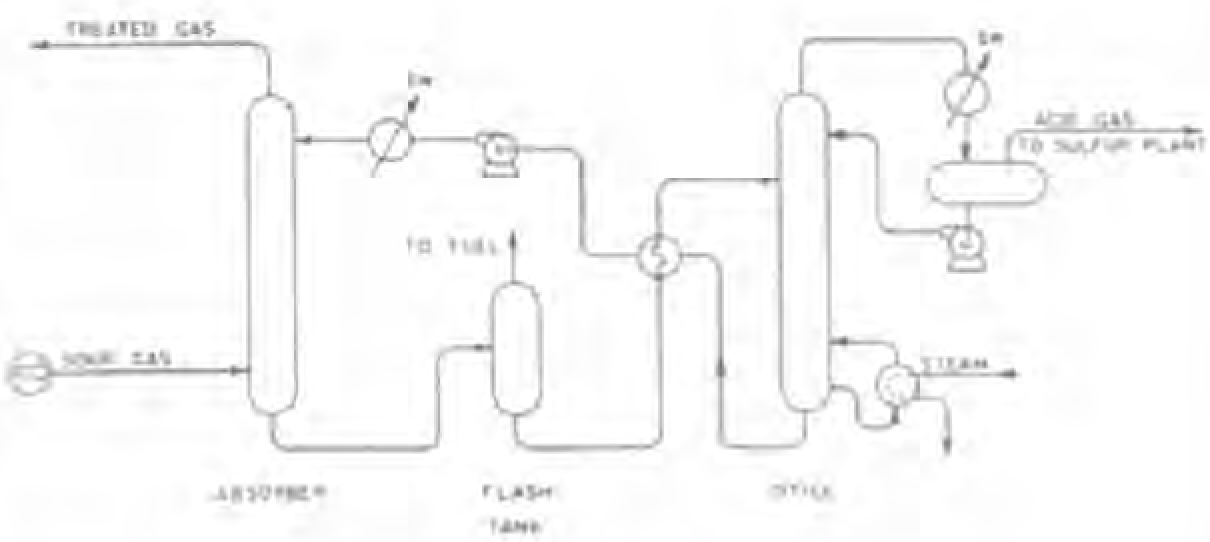
Amine Treating Unit

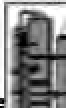
- **Hydrogen sulphide and carbon dioxide readily combine with aqueous solutions of certain alkanol amines at temperatures usually close to ambient ,**
- **and may be driven off from the fat solutions by heating to about 100 ºC .**
- **The reaction with hydrogen sulphide is :**

- $2\ RNH_2 + H_2S \rightleftarrows (RNH_3)_2S$
- Amine (mono- di and tri ethanol amines and methyl di ethanol amine)

- The conventional equipment , comprising a bubble- cup tower together with a bubble cup tower for regeneration.
- The treating temperature is 5 to 10 ^oC above the dew point of the gas to ensure that no hydrocarbons liquid condenses out of the plant.
- This process is the most widely used method for the regenerative removal of H_2S from both gases and liquids.
- Its use is not only in refineries but also for oilfield treatment of natural gases and LPG.
- The choice of the proper amine and solution depends on the composition of the gas to be treated and the final purity desired.

Amine Treating Unit





Sulphur Recovery

- Acid gas streams from hydrodesulphurization containing H_2S are sent to sulphur recovery unit (Claus unit).
- Furthermore, sulphur removal is carried out by tail gas clean up schemes.
- The purpose of removing the sulphur is to reduce the sulphur dioxide (SO_2) emissions in order to meet environmental guidelines.

Claus Process

- The Claus process is the most significant elemental sulphur recovery process from gaseous hydrogen sulphide.
- Gases with an H_2S content of over 25% are suitable for the recovery of sulphur in the Claus process.
- Hydrogen sulphide produced, for example, in the hydrodesulphurization of refinery products is converted to sulphur in Claus plants .
- The main reaction is

$$2H_2S + O_2 \longrightarrow 2S + 2H_2O$$

- The Claus technology can be divided into two process stages : thermal and catalytic.
- In the thermal stage, hydrogen sulphide partially oxidized at temperatures above 850 0C (1562 F) in the combustion chamber.
- This causes elemental sulphur to precipitate in the downstream process gas cooler.

If more oxygen is added, the following reaction occurs:

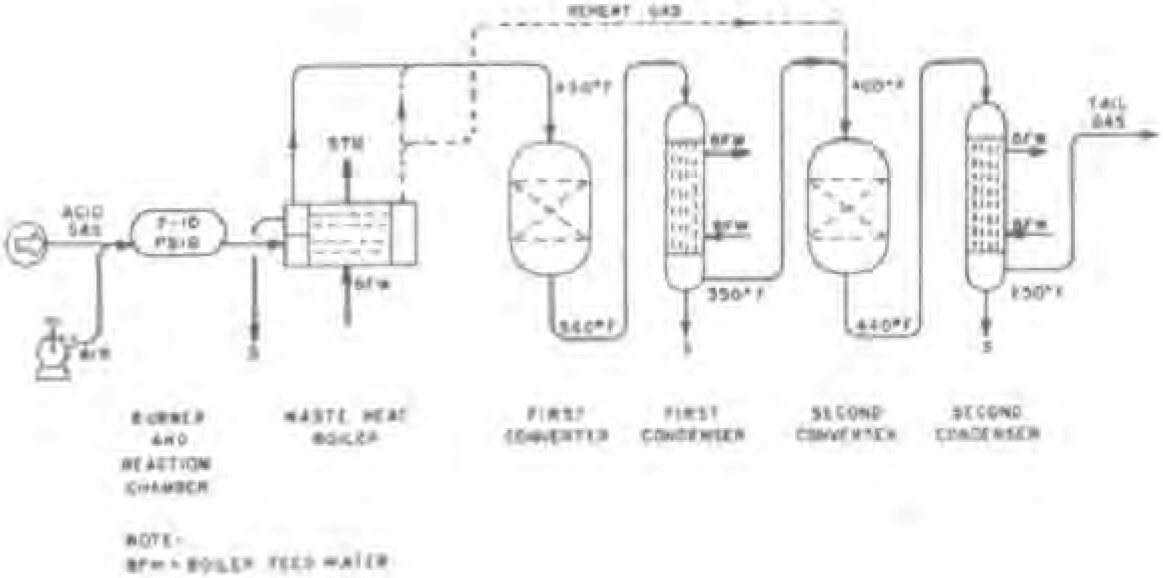
$$2H_2S + 3O_2 \longrightarrow 2SO_2 + 2H_2O$$

- This gas contains 20–30% of the sulphur content in the feed stream. Activated

alumina or titanium dioxide is used. The H_2S reacts with the SO_2 and results in gaseous, elemental sulphur. This is called the Claus reaction:

$$2H_2S + SO_2 \longrightarrow 3S + 2H_2O$$

Modified Clause Process



GAS PROCESSING UNIT

Gaseous Fuels

The Importance of Gaseous Fuel

- Generally very clean burning. Little soot.
- Easy to burn - No grinding or atomisation. Excellent mixing
- No problems with erosion or corrosion
- No ash
- The gas is easy to clean. E.g. if sulphur is present, it may be easily removed prior to combustion.
- Simplest combustion plant of all - Burners
- Problems with distribution and storage
- Explosion risk - very volatile.
- Relatively costly. Offset by cheaper and more efficient plant.

Classification of Gaseous Fuels

(A) Fuels naturally found in nature:

Natural gas

Methane from coal mines

(B) Fuel gases made from solid fuel

Gases derived from Coal

Gases derived from waste and Biomass

From other industrial processes (Blast furnace gas)

(C) Gases made from petroleum

Liquefied Petroleum gas (LPG) Refinery gases

Gases from oil gasification

(D) Gases from some fermentation process

Natural Gas

Natural gas is a gaseous fossil fuel consisting primarily of methane but including significant quantities of ethane, butane, propane, carbon dioxide, nitrogen, helium and hydrogen sulfide.

It is found in oil fields and natural gas fields, and in coal beds. When methane-rich gases are produced by the anaerobic decay of non-fossil organic material, these are referred to as biogas.

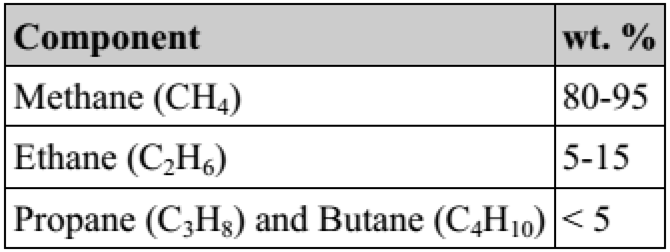
Natural gas is often informally referred to as simply **gas**, especially when compared to other energy sources such as electricity.

Before natural gas can be used as a fuel, it must undergo extensive processing to remove almost all materials other than methane.

The by-products of that processing include ethane, propane, butanes, pentanes and higher molecular weight hydrocarbons, elemental sulfur, and sometimes helium and nitrogen.

Chemical composition

- The primary component of natural gas is **methane** ($CH4$), the shortest and lightest hydrocarbon molecule.
- It also contains heavier gaseous hydrocarbons such as ethane ($C2H6$), propane ($C3H8$) and butane ($C4H10$). as well as other sulphur containing gases, in varying amounts.
- Nitrogen, helium, carbon dioxide and trace amounts of hydrogen sulfide, water and odorants can also be present.
- Mercury is also present in small amounts in natural gas extracted from some fields.
- The exact composition of natural gas varies between gas fields.
- Organosulfur compounds and hydrogen sulfide are common contaminants which must be removed prior to most uses.
- Gas with a significant amount of sulfur impurities, such as hydrogen sulfide, is termed sour gas; gas with sulfur or carbon dioxide impurities is acid gas.



Component	**wt. %**
Methane (CH_4)	80-95
Ethane (C_2H_6)	5-15
Propane (C_3H_8) and Butane (C_4H_{10})	< 5

Natural gas processing plant

There are a great many ways in which to configure the various unit processes used in the processing of raw natural gas.

The block flow diagram , Fig. (3), is a generalized, typical configuration for the processing of raw natural gas from non-associated gas wells.

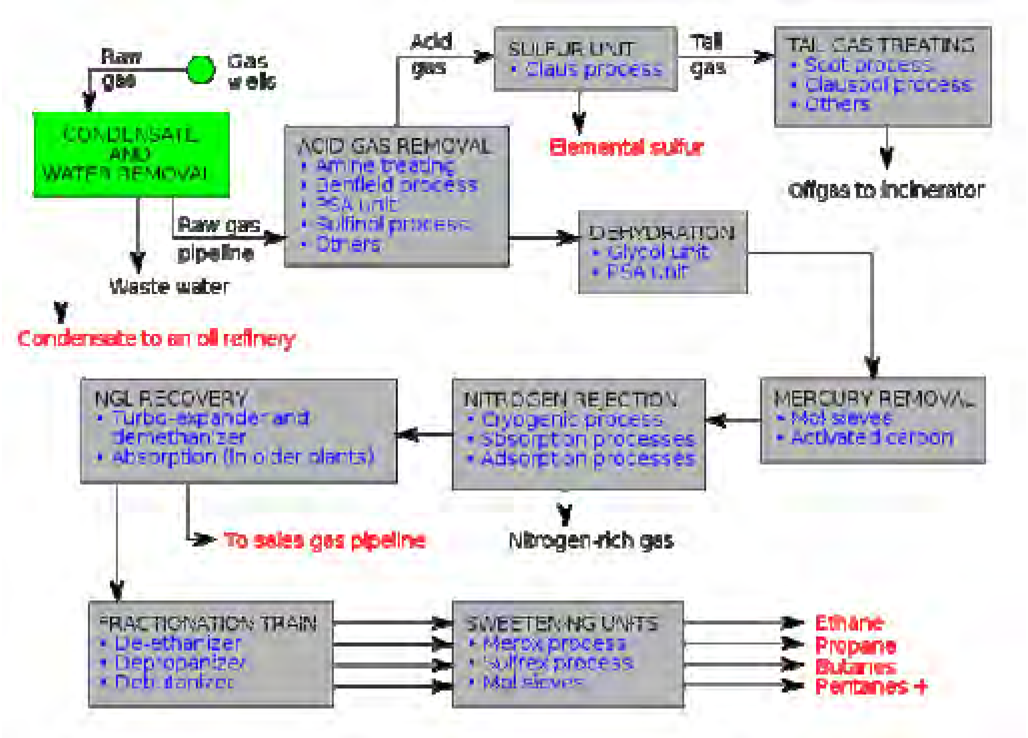


Figure 3: Natural gas processing plant

It shows how raw natural gas is processed into sales gas pipelined to the end user markets.

It also shows how processing of the raw natural gas yields these byproducts:

- Natural gas condensate
- Sulfur
- Ethane
- Natural gas liquids (NGL): propane, butanes and C5+ (which is the commonly used term for pentanes plus higher molecular weight hydrocarbons) .

1- Raw natural gas is commonly collected from a group of adjacent wells and is first processed at that collection point for removal of free liquid water and natural gas condensate. The condensate is usually then transported to an oil refinery and the water is disposed of as wastewater.

2- The raw gas is then pipelined to a gas processing plant where the initial purification is usually the removal of acid gases (hydrogen sulfide and carbon dioxide). There a many processes that are available for that purpose as shown in the flow diagram, but amine treating is the most widely used process.

3- The acid gases removed by amine treating are then routed into a sulfur recovery unit which converts the hydrogen sulfide in the acid gas into elemental sulfur. There are a number of processes available for that conversion, but the Claus process is by far the one usually selected. The residual gas from the Claus process is commonly called **tail gas** and that gas is then processed in a tail gas treating unit (TGTU) to recover and recycle residual sulfur-containing compounds back into the Claus unit.

4- The next step in the gas processing plant is to remove water vapor from the gas using the either regenerable absorption in liquid triethylene glycol (TEG) or a Pressure Swing Adsorption (PSA) unit which is regenerable adsorption using a solid adsorbent. Another newer process using membranes may also be considered.

5- Mercury is then removed by using adsorption processes (as shown in the flow diagram) such as activated carbon or regenerable molecular sieves.

6- Nitrogen is next removed and rejected using one of the three processes indicated on the flow diagram:

7- The next step is to recover of the natural gas liquids (NGL) for which most large, modern gas processing plants use another cryogenic low temperature distillation process involving expansion of the gas through aturbo-expander followed by distillation in a demethanizing fractionating column. Some gas processing plants use lean oil absorption process rather than the cryogenic turbo-expander process.

8- The residue gas from the NGL recovery section is the final, purified sales gas which is pipelined to the end-user markets.

9- The recovered NGL stream is processes through a fractionation train consisting of three distillation towers in series: a dethanizer, adepropanizer and and a debutanizer. The overhead product from the deethanizer is ethane and the bottoms are fed to the depropanizer. The overhead product from the depropanizer is propane and the bottoms are fed to the debutanizer. The overhead product from the debutanizer is a

mixture of normal and iso-butane, and the bottoms product is a C5+ mixture.