University of Technology
Chemical Engineering Department
Oil and Gas Refinery Eng Branch
Fourth Class

PETROLEUM REFINING

Ass. Prof. Dr. Adel Sharif Hamadi

CE 544-R

Petroleum Refining

Refinery Engineering Branch

Units	6
Theoretical	2 hr/week
Tutorial	1 hr/week
Practical	3hr/week

1. **Introduction:**
   History and Development of Refining Processes Kinds of Refineries.
   (2 hrs)
2. **Chemical Composition of Petroleum:**
   (2 hrs)
3. **Physical and Thermodynamic Properties of Petroleum Oil :**
   (2 hrs)
4. **Evaluation of Oil Stocks:**
   (4 hrs)
5. **Introduction to Processing:**
   Stabilization, dehydration, tube still heaters
   (10 hrs)
6. **Fractionation of Petroleum:**
   Atmospheric and Vacuum Fractionation
   (2 hrs)
7. **Fractionation Towers**:
   Material and Energy Balances, Reflux Temperate Distribution in Fractionation Tower, Tower Diameter
   (8 hrs)
8. **Treating Processes:**
   Removal of Acid Gases, Sweetening Processes, Improvement in Performance and Storage Stability
   (8 hrs)
9. **Upgrading Processes**:
   Thermal Cracking, Cooking. Visbreaking, Catalytic Cracking, Hydrocracking, Catalytic Reforming, Alkylation, Isomerisation.
   (10 hrs)
10. **Product Blending**:
    Blending of Vapor Pressure, Octane Number, Viscosity, Flash Point, Aniline Point and Pour Point.
    (6 hrs)
11. **Manufacturing of Lubricating Oils:**
    (4 hrs)

TEXT BOOK:

1) Nelson, W. L. Petroleum Refinery Engineering, Tata McGraw Hill Publishing Company Limited, 1985.

REFERENCES:

1) James H. Gary & Glenn E. Handwerk "Petroleum Refining, Technology & Economics", 4th ed., Marcel Dekker, Inc., 2001
2) B.K. Bhaskara Rao, “Modern Petroleum Refining Processes” Edn. 3, Oxford & IBH Publishing Company Pvt. Ltd. New Delhi

History and Development of Refining

المقدمة

تزداد أهمية النفط الخام في العالم يوما بعد يوم وتتعد استعمالاته و تنبع أهمية النفط الخام الإستراتيجية من حقيقتين:

1. كونه مصدر للطاقة
2. كونه مادة خام أساسيه لفروع الصناعات الكيماوية والبتروكيمياوية المختلفة.

يحض النفط الخام بمكانه متميزة بين مصادر الطاقة المختلفة للأسباب التالية :

1. يحتوي على منتجات عديدة يمكن فصلها عن بعضها عن طريق التكرير وتمثل مصادر متنوعة في استعمال الوقود وإنتاج منتجات مساعده كزيوت التزييت والإسفلت والمذيبات البترولية كما تشكل بعض مشتقاته بعض مواد مهمة في الصناعات البتروكمياويه .
2. وجود الغاز الطبيعي مع النفط الخام تحت سطح الأرض.
3. سهوله نقله إلى مسافات بعيدة.
4. انخفاض كلفة أنتاجه ونقله وتكريره .

نبذه تاريخيه

- البترول مصطلح لاتيني قديم يأتي بمعنى زيت الصخر (Rock Oil) أو الزيت الصخري.
- وهو مشتق من كلمتين

بترا (Petr) وتعني الصخر (Rock)
(Oleum) وتعني الزيت

- يرجع استخدام الإنسان للبترول إلى عصور ما قبل التاريخ حيث استعمله السومريون و البابليون في وادي الرافدين و قد وجد أثار البترول في أماكن أخرى في العالم و في شرق البحر الأبيض المتوسط كالبحر الميت و كان يعرف ببحيرة الإسفلت و الذي يعود إليها مصطلح الإسفلت الشائع حاليا .
- يرجع اكتشاف البترول إلى وجود مستودعات بترولية قريبه من سطح الأرض والتي كانت تتحرر منها الآبخرة و تندلع فيها النيران التي كانت تدعى (النيران الازليه) وكانت تعبدها بعض المذاهب الزرادشتية .
- في عام 1859 م حفر دريك (Drake) أول بئر بحثا عن البترول في ولاية بنسلفانيا في الولايات المتحدة الأمريكية على عمق 21.11 متر ، ويوجد البترول بصوره عامه على أعماق مختلفة تتراوح بين 20 – 20 ألف متر .
- أول مصفى تم بناءه عام 1860 م في الولايات المتحدة الأمريكية بكلفه 15000 $
- المسجل تاريخيا أول عمليه تقطير للبترول جرت في روسيا عام 1735 م
- نظريات و فرضيات تكون البترول :

1. يعتقد البعض أن البترول قد تكون نتيجة تحلل المواد الحيوانية و النباتية بفعل البكتريا الاهوائيه و التقطير الاتلافي للبقايا الدهنيه من الحيوانات البرية ألمجهريه

2. البعض الأخر يعتقد أن أصل البترول يرجع إلى الميثان بفعل المواد المشعة أو من الكربيدات الثقيلة مثل كاربيد الحديد او المنغيز مع الماء و تكون مواد استلينيه ، التي تنتج بتأثير الحرارة العالية مزيج أو خليط من هيدروكاربونات متباينة التركيب و الخواص .

التقطيرالمستمر (Continuous Distillation)

- المصافي الاوليه كانت تستخدم نظام التقطير (على شكل وجبات Batch distillation)
- في بدايات عام 1860 م تم استخدام نظام التقطير المستمر، و قد استمر تطوير طرق الإنتاج المستمر وقد سجل بصوره واسعة استخدام وحدات الإنتاج المستمر عام 1912 م.
- حاليا و حدات الإنتاج المستخدمة جميعها تعمل بطريقه التقطير المستمر .

التكسير الحراري (Thermal Cracking)

- يقصد بالتكسير الحراري في مجال تكنولوجيه البترول استخدام الحرارة وحدها أو مع وجود عوامل مساعده معينه لتغير مكونات البترول و كسر الأواصر للحصول على مكونات جديدة لهل أوزان جزيئيه أوطأ من الخامات.
- أول تسجيل لعمليه التكسير الحراري عام 1861 م

التقطير ألتجزيئي (Fractionation)

هي عمليه فصل المزيج السائل إلى عدد من النواتج لها مدى غليان ضيق.

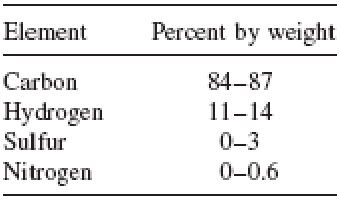
- في المصافي الأولية كانت عمليه الفصل تتم بعدد من عمليات التقطير المتعاقبة .
- لاحقا حدث تطوير في طريقه الإنتاج حيث استخدمت أبراج تقطير تعمل بعمليه التكثيف الجزئي (Partial Condensation) وفيها يتم استخدام المكثفات لتكثيف خليط البخار بدرجات حرارة مختلفة.

العمليات الكيماوية (Chemical Processing)

- عام 1927 م تم تطوير طريقه الهدرجة وهي عبارة عن عمليه تكسير حراري في ضغوط عاليه بوجود الهيدروجين .
- عام 1937 هودري استخدم العامل المساعد في هذه الطريقة (سيليكات الألمنيوم)

Chemical Composition of Petroleum

Petroleum is a mixture of hundreds of hydrocarbons of all type with water, salts, sulfur and nitrogen containing compounds and some metal complexes.
The elementary composition of crude oil usually falls within the following ranges.

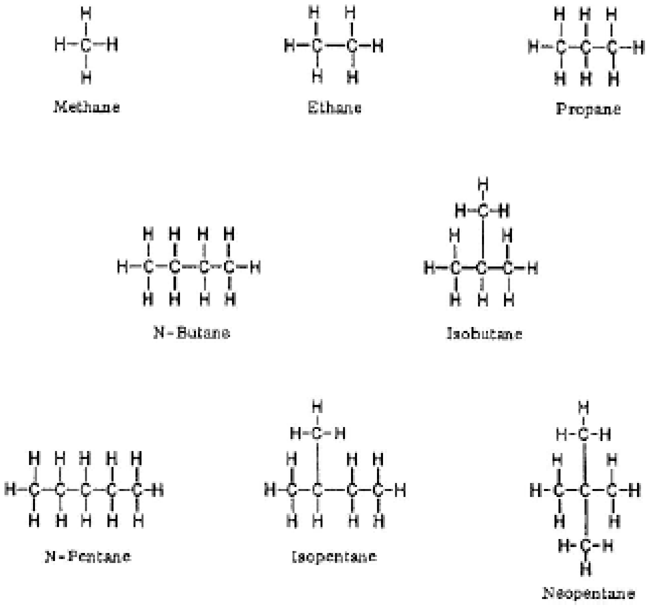


Element	Percent by weight
Carbon	84–87
Hydrogen	11–14
Sulfur	0–3
Nitrogen	0–0.6

The three different types of hydrocarbons that crude has are paraffins, aromatics, cyclo-alyphatic or naphthenes and olefins.

Paraffins

The paraffin series of hydrocarbons is characterized by the rule that the carbon atoms are connected by a single bond and the other bonds are saturated with hydrogen atoms. The general formula for paraffins is C_nH_{2n+2}. The simplest paraffin is methane, CH_4, followed by the homologous series of ethane, propane, normal and isobutane, normal, iso-, and neopentane, etc. (Fig. 1).



Figure(1) Paraffins in crude oil.

Saturated alkanes: (n-alkane and i-alkane)

- General formula C_nH_{2n+2}
- Boiling point and density increase with increasing # of C atoms.
- Branched alkanes (iso-alkanes) is very small in quantity
- Boiling point of straight chains > iso-alkanes with the same # of C

Naphthenes or cycloparaffins

Cycloparaffin hydrocarbons in which all of the available bonds of the carbon atoms are saturated with hydrogen are called naphthenes. Typical examples of these are cyclopentane, cyclohexane, etc. (Figure 2).

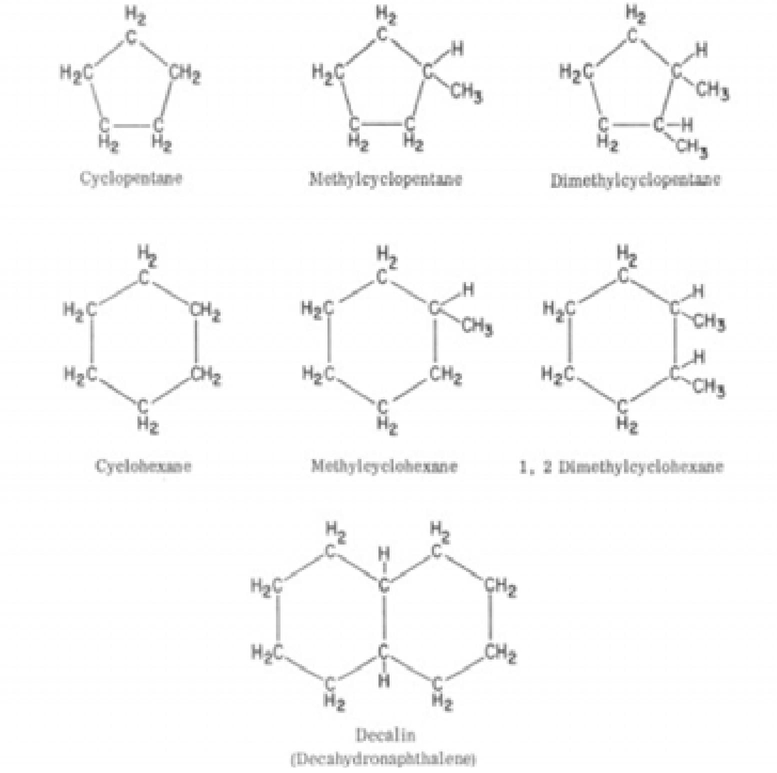

Cyclopentane
Methylcyclopentane
Dimethylcyclopentane
Cyclohexane
Methylcyclohexane
1, 2 Dimethylcyclohexane
Decalin
(Decahydronaphthalene)

Figure 2: Naphthene compounds

- General formula C_nH_{2n} for one ring compounds

Aromatics

The aromatic series of hydrocarbons is chemically and physically very different from the paraffins and cycloparaffins (naphthenes). Aromatic hydrocarbons contain a benzene ring which is unsaturated but very stable and frequently behaves as a saturated compound. Some typical aromatic compounds are shown in (Figure 3).

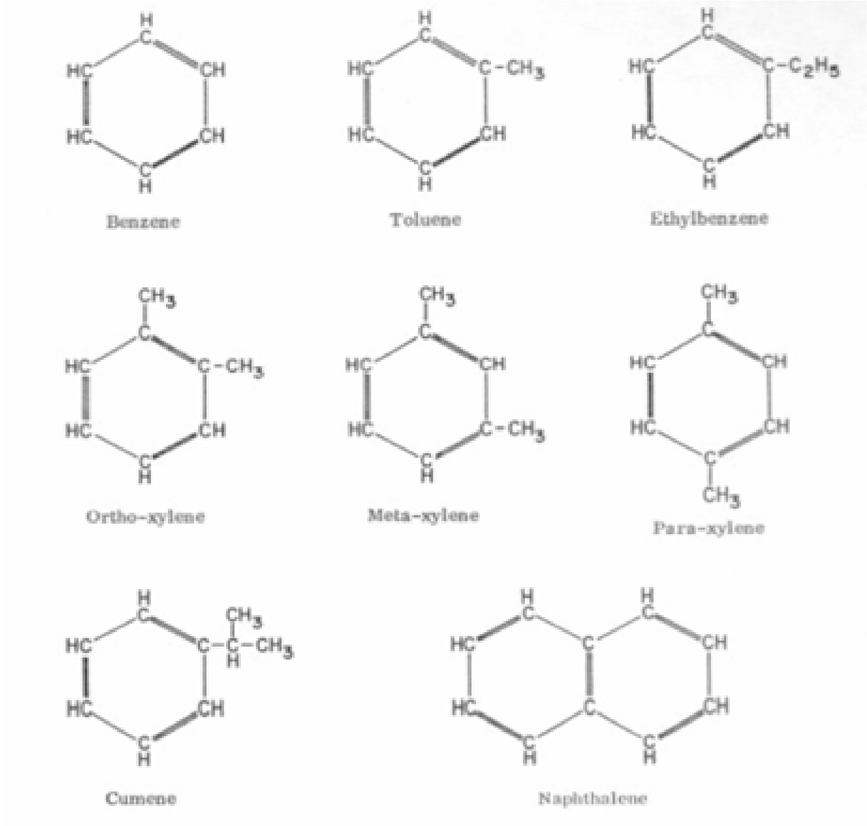
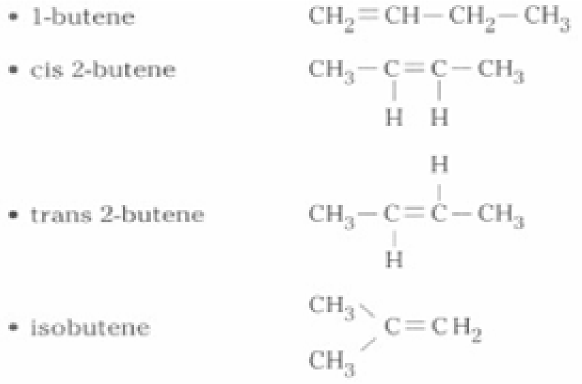


Figure 3: Aromatic compounds

Olefins

Olefins do not naturally occur in crude oils. However, they are formed during its processing. They are very similar to paraffins, but they exhibit double bonds, usually one per molecule (Figure 4), although some di-olefins (two double bonds in the same molecule, (Figure 5) can be found.



- 1-butene $CH_2{=}CH{-}CH_2{-}CH_3$
- cis 2-butene $CH_3{-}\underset{H}{C}{=}\underset{H}{C}{-}CH_3$
- trans 2-butene $CH_3{-}\underset{H}{C}{=}\overset{H}{C}{-}CH_3$
- isobutene $(CH_3)_2C{=}CH_2$

Figure 4: Olefin compounds

$CH_2{=}CH{-}CH{=}CH_2$ 1-3 butadiene

$CH_2{=}C(CH_3){-}CH{=}CH_2$ isoprene

Figure 5: Di-olefin compounds

Heteroatom compounds

- Sulfur compounds might be present in inorganic and organic forms. In crude oils sulfur concentration can range from 0.1 to more than 8 weight percent. Such as dibenzylthiophene (2 benzene rings separated by 1 S atom) – is most difficult to relase the Sulfur
- Oxygen compounds are responsible for petroleum acidity in particular.
  Carboxylic (OH-C=O bonded to a benzene ring)
  Phenolic (OH bonded to a benzene ring)
- Nitrogen compounds
  carbazole (2 benzene rings separated by 1 N atom) – neutral
  Quinoline (2 benzene rings with 1 N atom on 1 ring) - basic

Metal Compounds

- Porphyrins contain Ni, V, or Fe

Physical properties of feedstocks and products

^{o}API

^{o}API = (141.5/SG $_{15^oF}$) – 131.5 The purpose of this equation was to extend the range of the specific gravity scale. Crude oil SG changes, although small, may be important.
Crude Oils ^{o}API = 10 – 50

Higher ^{o}API, more paraffinic crude, higher yields of gasoline.
Lower ^{o}API, more aromatic crude, lower yields of gasoline.

Viscosity

Resistance to flow, usually measured @ 100^{o}F in centistokes (kinimatic viscosity)

Pour Point

Measured by ASTM D-97 – temperature at which oil ceases to flow. Diesel may contain waxes, smaller than candle wax, which could solidify in cold weather.

Flash Point

Temperature above which the oil will spontaneously combust. Fractions in vacuum tower are the least combustible. They are the heaviest.

Vapor Pressure

Measured by ASTM D-323. Also know as Reid vapor pressure (RVP). True vapor pressure is usually 5-9% > RVP

Carbon Residue

The solid residue (%wt) remaining after heating to coking temperatures (700-800^{o}C)
ASTM D-524 Ramsbottom Carbon
ASTM D-189 Conradson Carbon
CCR incr. then Asphaltene incr.

Salt Content

Measured by ASTM – 3230 (lb NaCl/1000 bbl)
Desalting is necessary because NaCl content > 10 lbs/1000 bbl leads to corrosion

Metals

Measured by EPA Method 3040 These include Ni, V, Ag, Hg, Na, and Ca. Metals can cause catalyst deactivation and corrosion.

Sediment and Water

Measured by ASTM D – 96 These inorganic particles can lead to operational problems.

Acidity

Measured by ASTM – 664

Sulfur

Measured by ASTM D – 129, 1552, 2622

Sour crudes > 0.5 wt% and sweet crudes < 0.5 wt%. Today it is difficult to find crudes below 1% sulfur.

TBP Distillation Data

Butanes and lighter	55-175 °F-
Light Gasoline	175-300 °F
Light naphtha	300-400 °F
Heavy naptha	400-500 °F
Kerosene	500-650 °F
Atmosphere Gas Oil	650-800 °F
Light Vacuum Gas Oil	800-1000 °F
Hvy. Vacuum Gas Oil	1000 °F
Vacuum Residue	> 1000 °F

Specifications and Environmental Regulations for Gasoline and Diesel

Gasoline-octane number

ON range	Gasoline type
87	Regular
88	Plus
93	Super

Octane # of straight run crude oil is 0 ~ 40

EPA regulations limiting benzene to 1%, aromatics to 10%, and sulfur to 30 ppm

Diesel-cetane nuber

The desirable range for the cetane number is between 40-50

EPA regulations limiting sulfur content to 50 ppm in diesel.

Evaluation of Crude Oil

Evaluation of crude oil is important for refiner because it gives the following types of information:

1. Base and general properties of the crude oil.
2. Presence of impurities such as sulfur, salt, and emulsions which cause general difficulties in processing.
3. Operating or design data. Primarily this necessitates curves of temperature and gravity vs. per cent distilled.
   a. Fractionating or true boiling point distillation curve.
   b. Equilibrium or flash-vaporization curve.
   c. API or specific gravity curve of each fraction distilled.
4. Curves of the properties of the fractions vs. percent distilled (mid per cent curves) or the average properties of a series of fractions vs. Percentage yield (yield curve) by which common realization of yields can by prepared. Among property curves are
   a. Viscosity of lubricating-oil fractions
   b. Octane number of gasoline fractions.
   c. Aniline point of solvents, kerosene, or diesel fractions.
   d. Percentage of asphaltic residues.
   e. Viscosity of distillation residues.
5. Finished products. Having established the general properties and yield by means of distillation and property curves and exploring the economy of the various break-ups of the crude oil.

Base of crude oil

1)Mallison classification according to residuum:(a material left behind after distillation of fractions.)

Residue > 50% paraffins	Paraffinc base
Residue < 20% paraffins	Asphaltic base
Residue 20-50% paraffins	Mixed base

2)The U.S. Bureau of Mines designated eight base of crude oil

Key Fraction	Boiling point	Pressure	API	Note
No. 1	482-527 ^{0}F	atm.	> 40 (Paraffinic Base) 33 <API >40 (Intermediate Base) API < 33 (Napthene Base)	
No. 2	527-572 ^{0}F 733-779 ^{0}F	(40-mm)Hg 1 atm	> 30 (Paraffinic Base) API < 22 (Napthene Base) 22<API<30 (Intermediate Base)	The presence of wax is noted by cloud point (if below 5^{0}F) it indicates little wax (Wax-free)

3) Specific Gravity and API Gravity:

Specific gravity and API (American Petroleum Institute) gravity are expressions of the density or weight of a unit volume of material.
The specific gravity is the ratio of the weight of a unit volume of oil to the weight of the same volume of water at a standard; both specific gravity and API gravity refer to these constants at 60 ^{0}F (16 ^{0}C).

$$API = \frac{141.5}{Sp.gr.} - 131.5$$

or

$$Sp.gr. = \frac{141.5}{API. + 131.5}$$

Corresponding values of API gravity (0 to 100)

4) Characterization Factor: (C.F), (K)

The most widely used index is characterization factor (Watson, Nelson and Murphy).
It was originally defined as:

$$K = \frac{\sqrt[3]{T_B}}{S}$$

In which:
TB is the average molal boiling point (R)
S: is the specific gravity at 60 ^{0}F
It has since related to viscosity, aniline, temperature, molecular weight, critical temperature, percentage of hydrocarbon etc.

K≥ 12.15 (Paraffinic Base)
K< 11.5 (Napthene Base)
K between 11.5-12.15 (Intermediate Base)

5) Correlation Index: (C.I)

Like (C.F) related to boiling point and gravity

$$C.I = \frac{48640}{T_B} + 473.7S - 456.8$$

TB is the average modal boiling point (K)
S: is the specific gravity at 60 ^{0}F
C.I for Parafine =0
C.I for Benzene =100
C.I =0-15 Parafine
C.I =15-50 either Naphtenes or mix (Parafine + Naphtenes)
C.I = above 50 Aromatic

6) Viscosity Index : (V.I)

A series of numbers ranging from 0-100 which indicate the rate of change of viscosity with temperature.
Paraffinic base C.O V.I =100
Naphthenic base C.O V.I = 40
Some Naphthenic base C.O V.I =0

The presence of impurities in the crude oil

1. Sulfur

Difficulties with oils that contain sulfur compounds arise in only three main ways: corrosion, odor and poor explosion characteristics of gasoline fuels.

a) Corrosion: corrosion by finished products presents little difficulty because most products are used at low temperatures. The main bulk of the corrosive sulfur compounds can by removed by treatment with alkalis or the sweetening treatments. In presence of air and moisture the sulfur gases produced during the burning of oil may cause corrosion, as in steel stacks, ducts, and engine exhaust pipes and mufflers.

Real difficulties arise when high sulfur oils are heated to temperature 300 ^{0}F or higher for copper, or 400 0F for steels.

b) Odor : Odor is most obnoxious with low boiling or gaseous sulfur compounds, as H_2S or SO_2 in flue gases, mercaptans up to even six carbons atoms (B.P. of about 400 ^{0}F), sulfides up to 8 carbons atoms (about 350 ^{0}F), and among disulfides only methyl disulfide (B.P. 243 ^{0}F) . This odor is not obnoxious in sweetened products except in certain extremely high- sulfur gasoline.

Percentage of S in crude oil ranges from nearly 0.1 for high API- gravity crude oils as high 5 percentage in a few very heavy crude oils.

Generally crude with greater than **0.5%** S require more extensive processing than those with lower sulfur content.

2. Salt

Salt carried into the plant in brine associated with crude oils is a major cause of the plugging of exchangers and coking of pipe still tubes.

If salt content expressed as NaCl , is greater than 10 lb/1000 bbl, it is generally necessary to desalt the crude before processing.

3.Carbon Residue :

The less the value of carbon residue the more valuable the crude.

4. Nitrogen Compounds:

The nitrogen compounds in petroleum are not of major importance, but they do tend to cause a reduction in the activity of the catalysts used in catalytic cracking and they may assist in the formation of so- called "gum" in distillated or diesel fuel oil.

Crude containing in amount above 0.25 % by weight require special processing to remove the nitrogen.

5. Hydrocarbons Gaseous

The amount of gaseous hydrocarbons dissolved in crude oil is almost totally a function of the degree of weathering that the oil has undergone or the pressure at which it is collected. The percentage of involved when the dissolved gases are lost cannot be stated with accuracy but it is about

$$\text{Liquid vol. \% loss} = \frac{\text{Reid V. P} - 1}{6}$$

If the gas have M.W= 40, the gas amount to about 16.1 ft^3 per 1% loss of liquid.

6. Metallic Content (Ni, V, Cu)

The metal content in crude oil can vary from a few ppm to more than 1000 ppm, disadvantages affect activities of catalyst, corrosion, deterioration of refractory furnace lining and stacks. Can be reduced by solvent extraction with C_3.

Analysis of Crude Petroleum

1) Distillation Curves : When a refining company evaluate its own crude oils to determine the most desirable processing sequence to obtain the required products, its own laboratories will provide data concerning the distillation and processing of the oil and its fractions. The first step in refinery is distillation in which the crude oil separated into fractions according to its boiling point.

There are at least four types of distillation curves or ways of relating vapor temperature and percentage vaporized

a) True-boiling-point (T.B.P): (Fractional, run only on crude oil, batch) .

Distillation characteristics of a crude are assessed performing a preliminary distillation called "True Boiling Point" analysis (TBP). This test enlightens the refiners with all possible information regarding the percentage quantum of fractions, base of crude oil and the possible difficulties beset during treatment operation etc.

True boiling point (TBP) and gravity-mid percent curves can be developed from U.S Bureau of mines crude petroleum analysis data sheet Fig. (1) which is reported in two portions: The first is the portion of the distillation at atmospheric pressure and up to 527 ^{0}F (275 ^{0}C) end point, the second at 40 mm Hg total pressure to 572 ^{0}F (300 ^{0}C) end point. The portion of distillation at reduced pressure is necessary to prevent excessive pot temperature which cracking of the crude oil. The distillation temperatures reported in the analysis be corrected to 760 mm Hg pressure. Generally, those reported in the atmospheric distillation section need to be corrected. The distillation temperature at 40 mm Hg can by converted to 760 mm Hg by use of chart Fig. (2) shows the relationships between boiling temperatures at 40 mm Hg and 760 mm Hg pressure. The gravity mid- percent curve is plotted on the same chart with TBP. The gravity should be plotted on the average volume percent of the fraction, as the gravity is the average of the gravities from the first to the last drops in the fractions. For narrow cuts, a straight line relationship can be assumed and the gravity used as that of the mid-percent of the fraction. Smooth curves are drawn for both TBP and gravity mid- percent curves. Fig. (3) illustrated these curves for the crude oil.

b) Equilibrium or Flash Vaporization (EFV). The feed material is heated as it flows continuously through a heating coil. As vapor is formed it kept cohesively with liquid at some temperature and a sudden release of pressure quickly flashes or separates the vapor from the mixture without any rectification. By successive flash evaporation like this the stock can be progressively distilled at different increasing temperatures. a curve of percentage vaporized vs. temperature may be plotted.

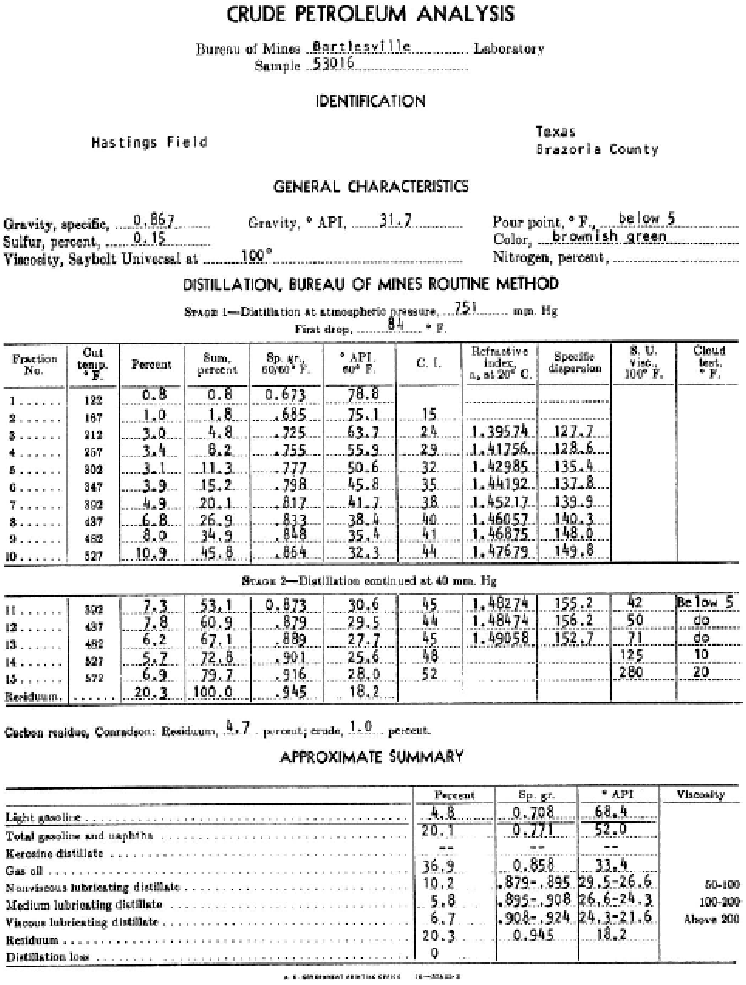
travels along in the tube with remaining liquid until separation is permitted in a vapor separator or vaporizer. By conducting the operation at a series of outlet temperature, a curve of percentage vaporized vs. temperature may be plotted.

c) ASTM or no fractionating distillation: (no fractional , run on fractions) .

It is supposed to be like EFV, a non fractionating distillation system, distinguishing itself as differential distillation. It is a simple distillation carried out with standard ASTM flasks 100,200,500 ml flasks. The data obtained is similar to TBP data

d) Hempel: (Semi fractional).

It is considered as a semi-fractionating type of distillation like Saybolt 's, Where TBP data is insufficient , this can be used.



CRUDE PETROLEUM ANALYSIS

Bureau of Mines Bartlesville Laboratory
Sample 53016

IDENTIFICATION

Hastings Field

Texas
Brazoria County

GENERAL CHARACTERISTICS

Gravity, specific, 0.867 Gravity, ° API, 31.7 Pour point, ° F., below 5
Sulfur, percent, 0.15 Color, brownish green
Viscosity, Saybolt Universal at 100° Nitrogen, percent,

DISTILLATION, BUREAU OF MINES ROUTINE METHOD

Stage 1—Distillation at atmospheric pressure, 751 mm. Hg
First drop, 84 ° F.

Fraction No.	Cut temp. ° F.	Percent	Sum, percent	Sp. gr., 60/60° F.	° API, 60° F.	C. I.	Refractive index, n_D at 20° C.	Specific dispersion	S. U. visc., 100° F.	Cloud test, ° F.
1	122	0.8	0.8	0.673	78.8					
2	167	1.0	1.8	.685	75.1	15				
3	212	3.0	4.8	.725	63.7	24	1.39574	127.7		
4	257	3.4	8.2	.755	55.9	29	1.41756	128.6		
5	302	3.1	11.3	.777	50.6	32	1.42985	135.4		
6	347	3.9	15.2	.798	45.8	35	1.44192	137.8		
7	392	4.9	20.1	.817	41.7	38	1.45217	139.9		
8	437	6.8	26.9	.833	38.4	40	1.46057	140.3		
9	482	8.0	34.9	.848	35.4	41	1.46875	148.0		
10	527	10.9	45.8	.864	32.3	44	1.47679	149.8		

Stage 2—Distillation continued at 40 mm. Hg

11	392	7.3	53.1	0.873	30.6	45	1.48274	155.2	42	Below 5
12	437	7.8	60.9	.879	29.5	44	1.48474	156.2	50	do
13	482	6.2	67.1	.889	27.7	45	1.49058	152.7	71	do
14	527	5.7	72.8	.901	25.6	48			125	10
15	572	6.9	79.7	.916	28.0	52			280	20
Residuum		20.3	100.0	.945	18.2					

Carbon residue, Conradson: Residuum, 4.7 percent; crude, 1.0 percent.

APPROXIMATE SUMMARY

	Percent	Sp. gr.	° API	Viscosity
Light gasoline	4.8	0.708	68.4	
Total gasoline and naphtha	20.1	0.771	52.0	
Kerosine distillate	--	--	--	
Gas oil	36.9	0.858	33.4	
Nonviscous lubricating distillate	10.2	.879-.895	29.5-26.6	50-100
Medium lubricating distillate	5.8	.895-.908	26.6-24.3	100-200
Viscous lubricating distillate	6.7	.908-.924	24.3-21.6	Above 200
Residuum	20.3	0.945	18.2	
Distillation loss	0			

Figure (1) U.S Bureau of Mines crude petroleum analysis (From Gary and Handwerk, 2001)

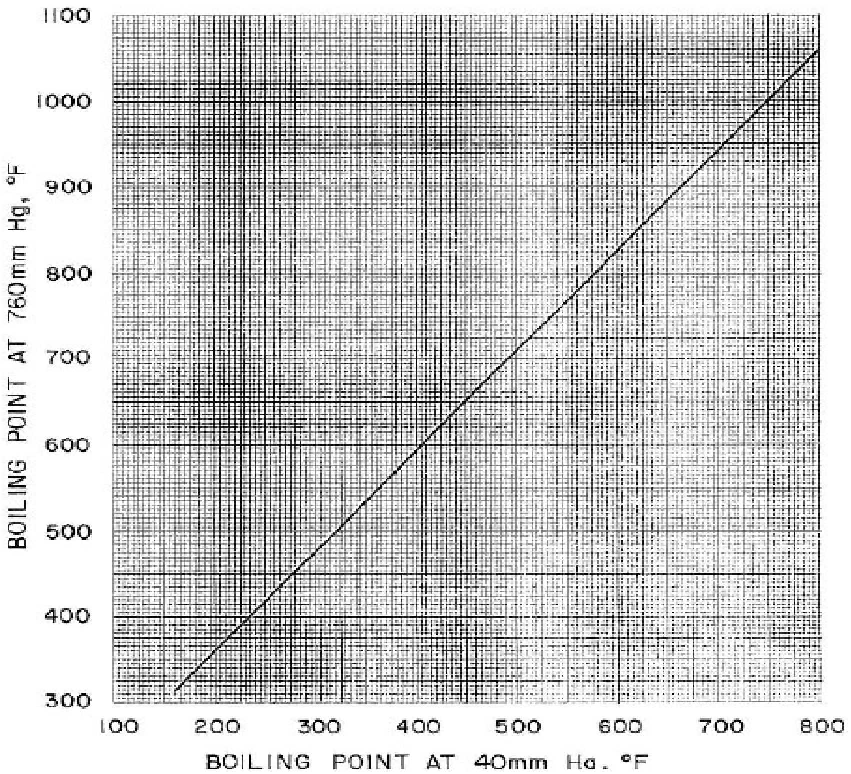


Figure (2) Boling point at 760 mmHg versus boiling point at 40mmHg (From Gary and Handwerk, 2001)

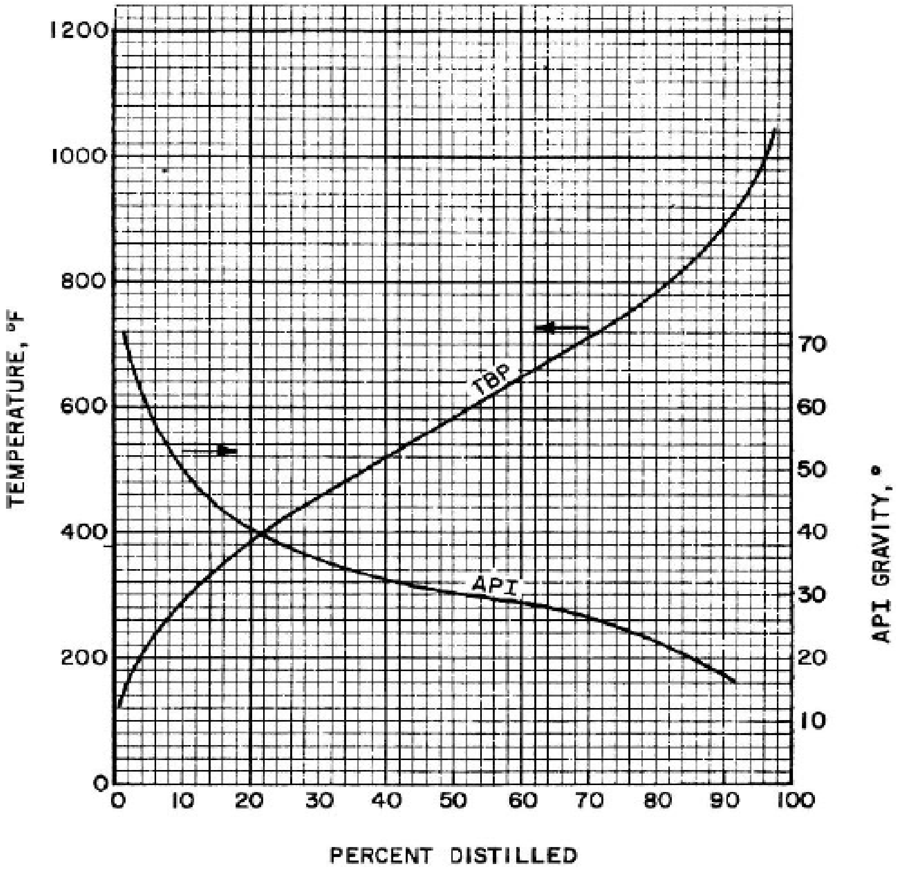


Figure (3): TBP and gravity- mid percent curves. Hasting Field, Texas crude: gravity 31.7 ^{o}API; sulfur, 0.15 wt%.(From Gary and Handwerk, 2001)

2) <u>Mid Percent Curves</u>:

The physical properties of an oil found to vary gradually throughout the range of compounds that constitute the oil. Distillation is a means of arranging of compounds these chemical compounds in order of their boiling points. The properties such as color, specific gravity, and viscosity are found to be different for each drop or fraction of the material distilled. The rate at which these properties change from drop to drop may plot as mid per cent curves.

In reality, <u>the specific gravity or viscosity</u> of a fraction is an average of the properties of the many drops that constitute the fraction. If each drop is equally different from the last drop and from the succeeding one, then the drop that distills at exactly half of the fraction has the same property as the average of all the drops. This would be the condition for a mid per cent that is a straight line, but they are substantially straight through any short range of percentage. For a short range of percentage the average property is equal to the property at the mid-point of the fraction. The arithmetical average of the properties of these small fractions is the property of the total or large fraction, or even the entire sample.

Integral- averaging by adding together the properties of a series of short fractions and dividing by number of fractions can not be used on properties that are not additive. Specific gravity (not API gravity) is an example of an additive property, e. g. 10 volumes of an oil of specific gravity 0.8 when mixed with an equal volume of 0.9 specific gravity oil yields a mixture that has a specific gravity 0.85.

Additive Properties	**Non additive Properties**
Boiling Point (T.B.P)	API Gravity
Vapor Pressure	Viscosity
Specific Gravity	Color
Aniline Point	Flash Point
Sulfur Content	
Hydrogen/Carbon ratio	

3) <u>Yield Curves</u>:

If a property is not additive, the property of various ranges of fractions can be determined experimentally by blending and plotting the property value as obtained as a function of yield or amount of blended material.

<u>Crude Suitable for Asphalt Manufacture</u>

If a crude oil residue (750 ^{0}**F mean average boiling point**) having a Watson **characterization factor < 11.8** and **gravity < 35 ^{0}API** , it is usually suitable for asphalt manufacture.

If however, the difference between the K values for the **750 ^{0}F** and **550 ^{0}F** fraction is grater than **0.15**, the residue may contain too much wax to meet most asphalt specification.

<u>Calculation of (K) (Characterization Factor) for The Whole Crude</u>

1. Calculate the TVABP using 20, 50, and 80 volume % TBP temperature.
2. Calculate the 10 to 70% slope of the whole curve.
3. Using a proper correction factor, convert TVABP to TMABP. (or some time given): (TMABP=TVABP-ΔT)
4. Constract a spg mid percent curve and evaluate the spg for the whole crude.
5. K is found as a function of TMABP and spg.

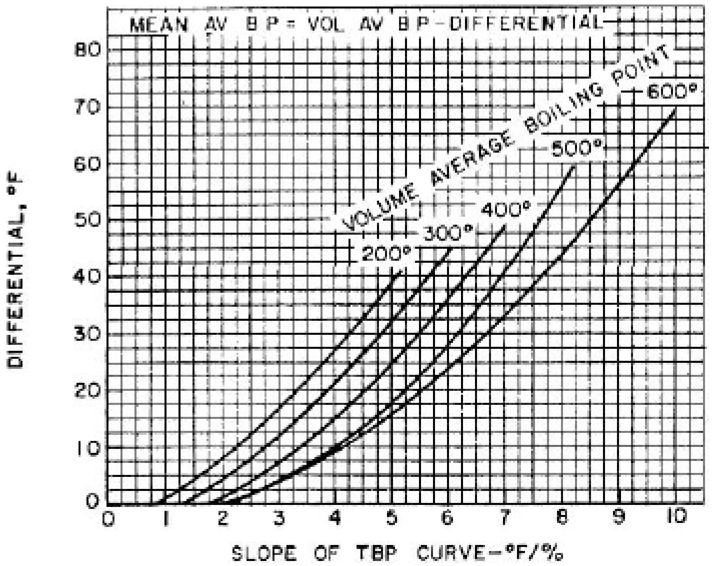


Figure (4): Mean average boiling point of petroleum fractions. (From Gary and Handwerk, 2001)

Estimation of EFV Distillation Curve

A- Estimation of the straight line EFV curve:

1. Estimate of t 50% of ASTM/ TBP using:
2. Estimate the 10 to 70% slope of ASTM/TBP using

$$Slope(ASTM/TBP) = \frac{t_{70} - t_{10}}{60}$$

3. Use Fig. (5) to convert slope (ASTM/TBP) to slope of EFV

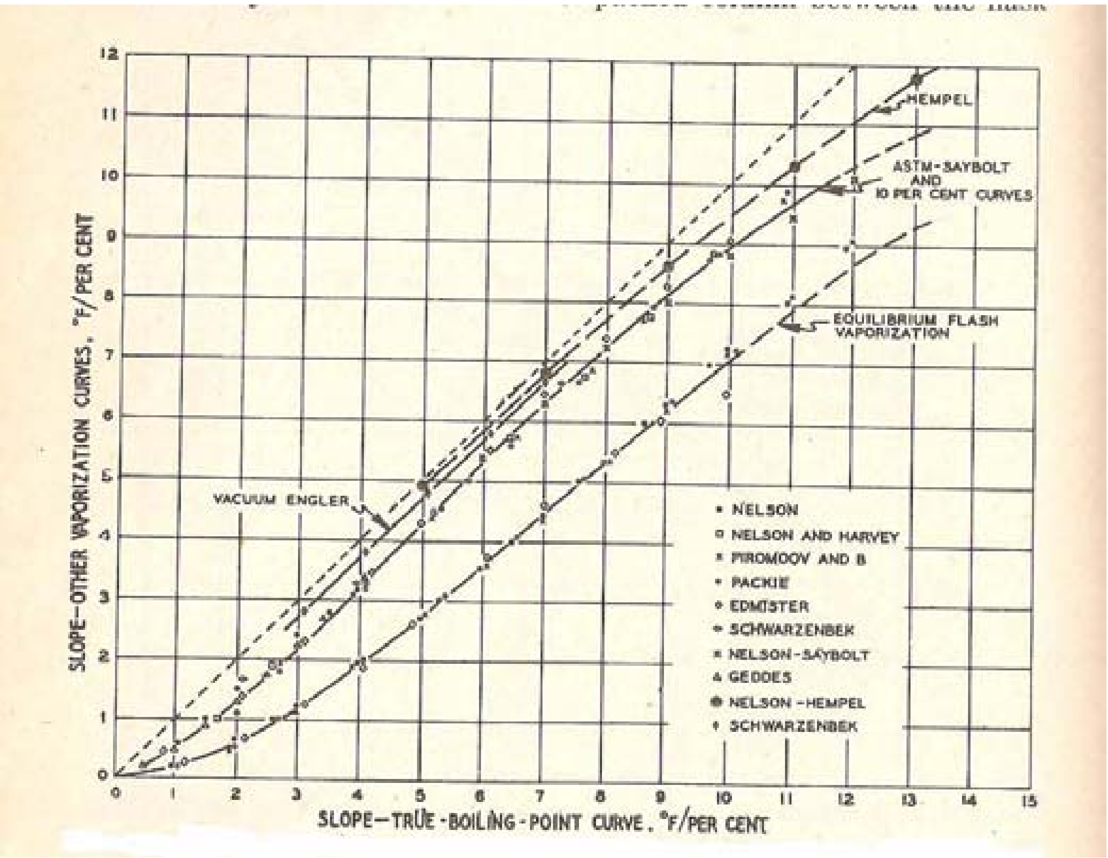


Fig (5): Relationships between the slopes (degrees/ per cent) of various distillation or vaporization curves. (From, Nelson, W. L, 1985)

4. Estimate t 50% of EFV from Fig. (6)

$t_{50\%} = t_{50\%} - \Delta T$

EFV EFV/TBP

5. Draw a straight line through $t_{50\%}$ EFV with slop of EFV.

6. t $_{0\%}$ (bubble point)=t $_{50\%}$ - slope*(50)

EFV EFV

7. t $_{100\%}$ (dew point)= t $_{50\%}$+slope*(50)

EFV EFV

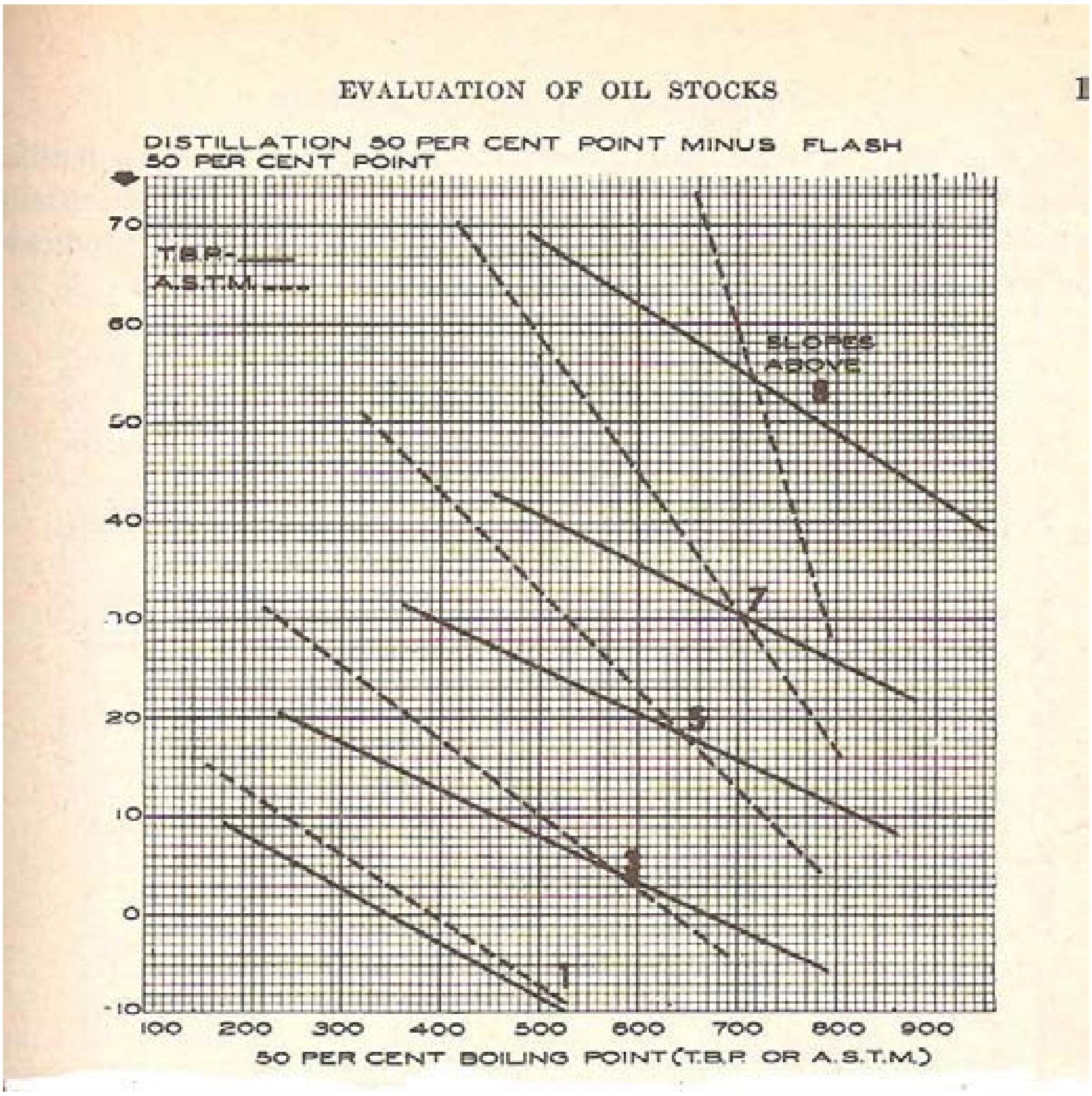


Fig (6): Relationship between distillation temperatures at 50 per cent vaporized and the flash (E. F.V.) temperatures at 50 per cent. (From, Nelson, W. L, 1985)

B. Estimation of EFV Curvature

1. Estimate $t_{50\%}$ (ASTM/TBP)

The proper 50% temperature is intermediate between the temperature on the distillation curve and the temperature on a straight line connecting the 10 and 70 percent points, and usually about halfway between.

2. Convert to $t_{50\%}$ EFV using Fig (6)
3. Estimate the (ASTM/TBP) 10-70 % slope
4. Estimate the EFV slope from Fig (5)
5. Estimate $t_{100\%}$ on flash curve = $t_{50\%}$ + slope *(50)
   $t_{0\%}$ on flash curve= $t_{50\%}$ - slope *(50)
6. Ratio of 10-70 slopes = R
7. Starting at the 10 % and compute the 5 %
   $t_{10\%} = t_{50\%} - 40*$ (slope)
   EFV
8. Slope of (ASTM/TBP) through 5-10 % = r
9. Slope of EFV through 5-10 % = r / R
10. Temperature at 5 % on EFV = $t_{10\%}$- slope * (5)

$$R=\frac{\text{Slope of dist. Curve (10 -70)}}{\text{Slope of flash. Curve (10 -70)}}=\frac{\text{Slope of dist. Curve through short range (r)}}{\text{Slope of EFV through short range}}$$

Average Boiling point

1) Volume Average Boiling Point (TVABP)

$$TVABP=\frac{t_{10\%}+t_{20\%}+-----------+t_{90\%}}{9}$$

If such data is not available then it may be defined as

$$TVABP=\frac{t_{30\%}+t_{50\%}+t_{70\%}}{3}$$

Where all % are in volumes

2) Weight Average Boiling Point (TWABP)

$$TWABP=\frac{t_{10\%}+t_{20\%}+-----------+t_{90\%}}{9}$$

Where % are based on weight

3) Molar Average Boiling Point (TMABP)

$$TWABP=\frac{t_{x1}+t_{x2}+t_{x3}}{x_1+x_2+x_3}$$

where x_1,x_2,x_3 are mole fractions

t_{x1}, t_{x2}, t_{x3} are corresponding boiling points.

All these boiling point are interconvertable.

Interconvertability of boiling points can be worked out by knowing the slope of distillation curve of a fraction. The method of finding out the slope for ASTM/TBP/EFV is the same

TBP slope is given as $\frac{t_{70}-t_{10}}{60}$ i.e. ${}^{0}t$/ percent; where

70% and 10% are volumetric boiling points on vaporization curve.

The conversion of TBP slope to ASTM or EFV slope can be done with Fig (5)

Example (1) :(Use of Gravity Mid percent Curve) (Nelson p/106)
Compute the spg of a 41.4 API (0.8183 spg) mixed base crude oil from the spg mid percent

Fraction No.	Range of %	spg	Fraction No.	Range of %	spg
1	0 - 5	0.6506	11	50-55	0.8280
2	5-10	0.6939	12	55-60	0.8388
3	10-15	0.7227	13	60-65	0.8498
4	15-20	0.7420	14	65-70	0.8602
5	20-25	0.7583	15	70-75	0.8713
6	25-30	0.7720	16	75-80	0.8827
7	30-35	0.7844	17	80-85	0.8939
8	35-40	0.7958	18	85-90	0.9065
9	40-45	0.8067	19	90-100	0.9340
10	45-50	0.8170			

$$\textbf{Spg of c.o} = \frac{\begin{array}{l}5(0.65+0.69+0.72+0.74+0.76+0.77+0.78+0.79+0.81+0.815+0.82+0.83+0.85\\+0.86+0.87+0.88+0.89+0.91)+10(0.93)\end{array}}{100}$$

Computed Sp.gr = 0, 8171, Actual Sp.gr = 0.8183 reasonable check (good for most engineer design work), See fig (7).

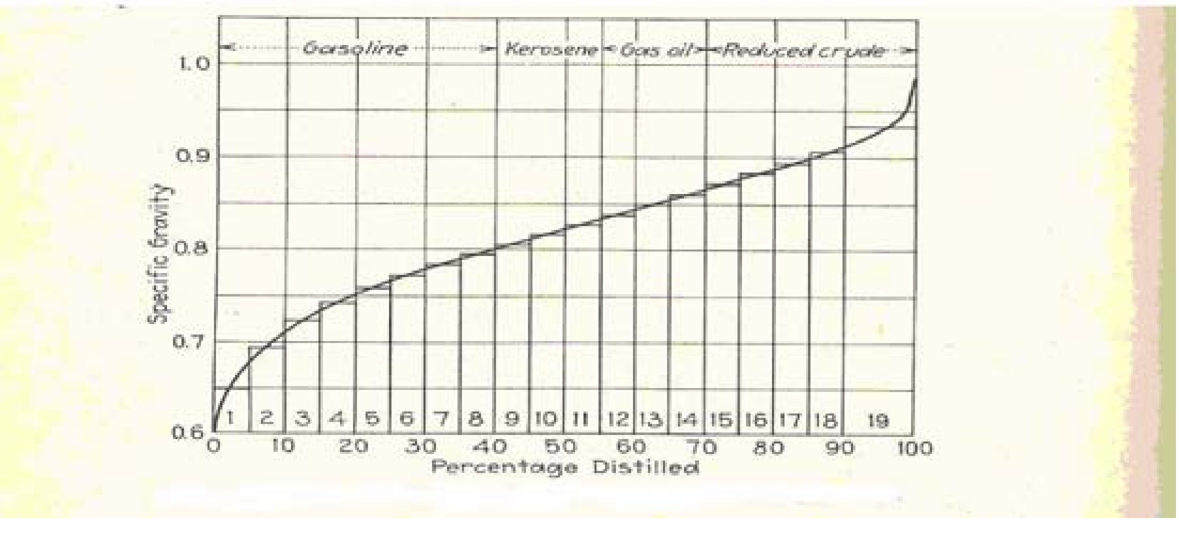


Fig (7): Gravity mid per cent curve. (From, Nelson, W. L, 1985)

Example (2): (Estimate of Flash Vaporization Curve) p/113 Nelson

1) The TBP curve of Fig (8) has a slope (degree/percent) between 10 and 70 percent point of;

$$\frac{t_{70}-t_{10}}{60}=\frac{775-210}{60}=9.4 \text{ Deg/percent}$$

2) According to Fig (5) the slope of EFV curve will be 6.5 Deg/percent.

3) From Fig (9), 50 % percent temperature of TBP curve =576 ^{0}F

4) From Fig (6), the50 % percent temperature of flash curve will be about 64 ^{0}F below of 5) percent temperature of the TBP curve

576- 64 =512 ^{0}F

6) A straight line flash curve can be drawn through 512 ^{0}F with slope of 6.5

Thus at zero percent the temperature=512-50*6.5=187 ^{0}F

At 100 percent the temperature =512+50*6.5= 837 ^{0}F

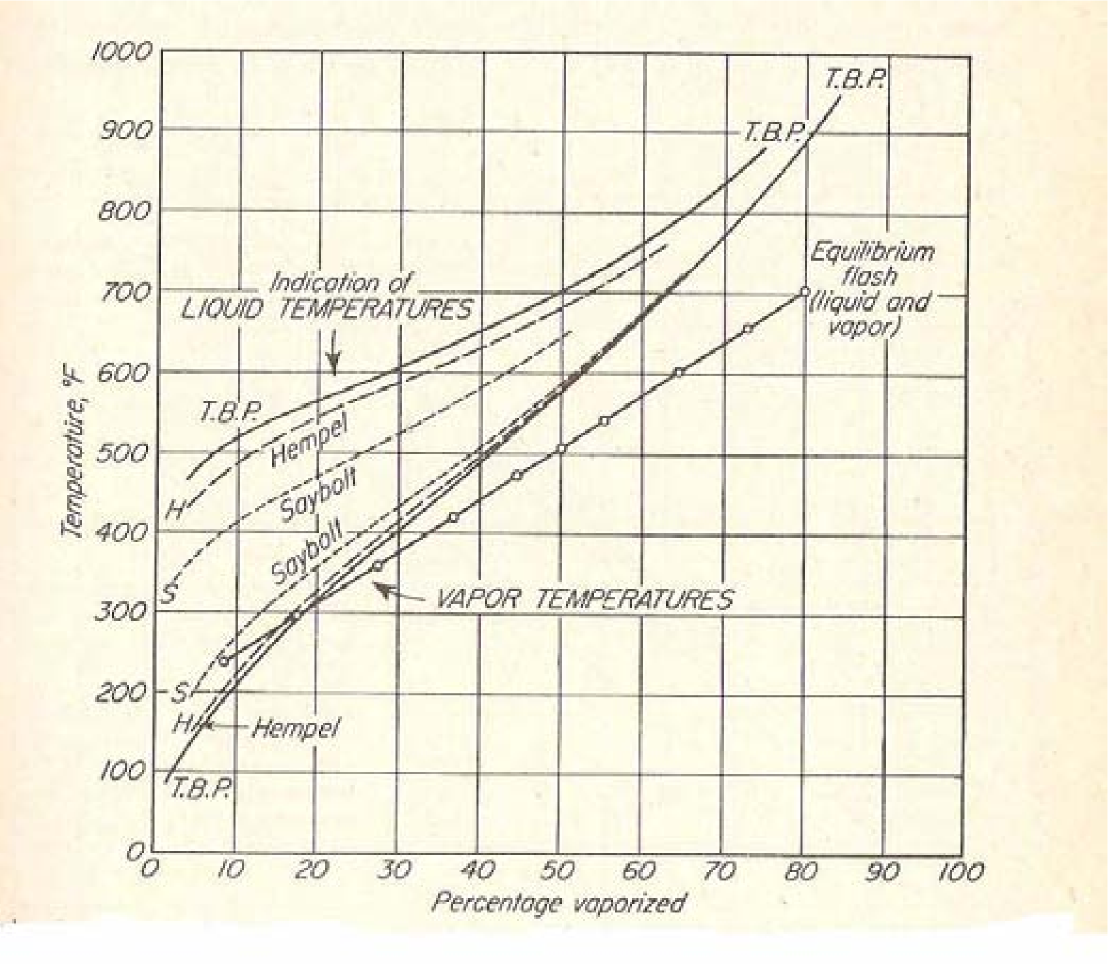


Fig (8) typical liquid and vapor temperature distillation of a 35 API crude oil (From, Nelson, W. L, 1985)

Example (3) :Curvature of Flash Vaporization Curve. (P/119) Nelson.

1) The slope of ASTM, 10-70 percent Fig (9)

$$\frac{430-170}{60} = 4.34$$

2) Slope of flash, 10-70 percent Fig (5) = 2.8

3) The 50 percent point on a straight line connecting 430 and 170 on the ASTM curve is (170+4.34*40) or (430-4.34*20) = 343 ^{0}F

where as it is about 365 on the ASTM curve Fig(9)

A compromise temperature halfway between ,i. e, 354 ^{0}F , is selected

4) 50% on flash curve Fig (6) (354, 2.8) =354-37=317 ^{0}F

100% on flash curve =317+50 *2.8=456 ^{0}F

0 % on flash curve =317-50 *2.8=176 ^{0}F

5) Computing curvature

$$\text{Ratio of 10-70 slope} = \frac{\text{Slope of Flash}}{\text{Slope of ASTM}} = \frac{2.8}{4.34} = 0.645$$

6) Starting at the 10 percent and computing the 5 percent point as an illustration

10 % on flash curve : 317-40*2.8=205 ^{0}F

7) Slope of ASTM curve between 5 and 10 % Fig (9)

$$\frac{170-125}{5} = 9.0$$

8) Slope of flash curve between 5 and 10 %

$$R = \frac{\text{Slope of dist. Curve(10 -70)}}{\text{Slope of flash. Curve(10 -70)}} = \frac{\text{Slope of dist. Curve through short range (r)}}{\text{Slope of EFV through short range}}$$

$$= \frac{4.34}{2.8} = \frac{9}{\text{Slope of flash through short range}}$$

Temperature at 5 % on flash curve = 205-5.8*5 = 176 ^{0}F

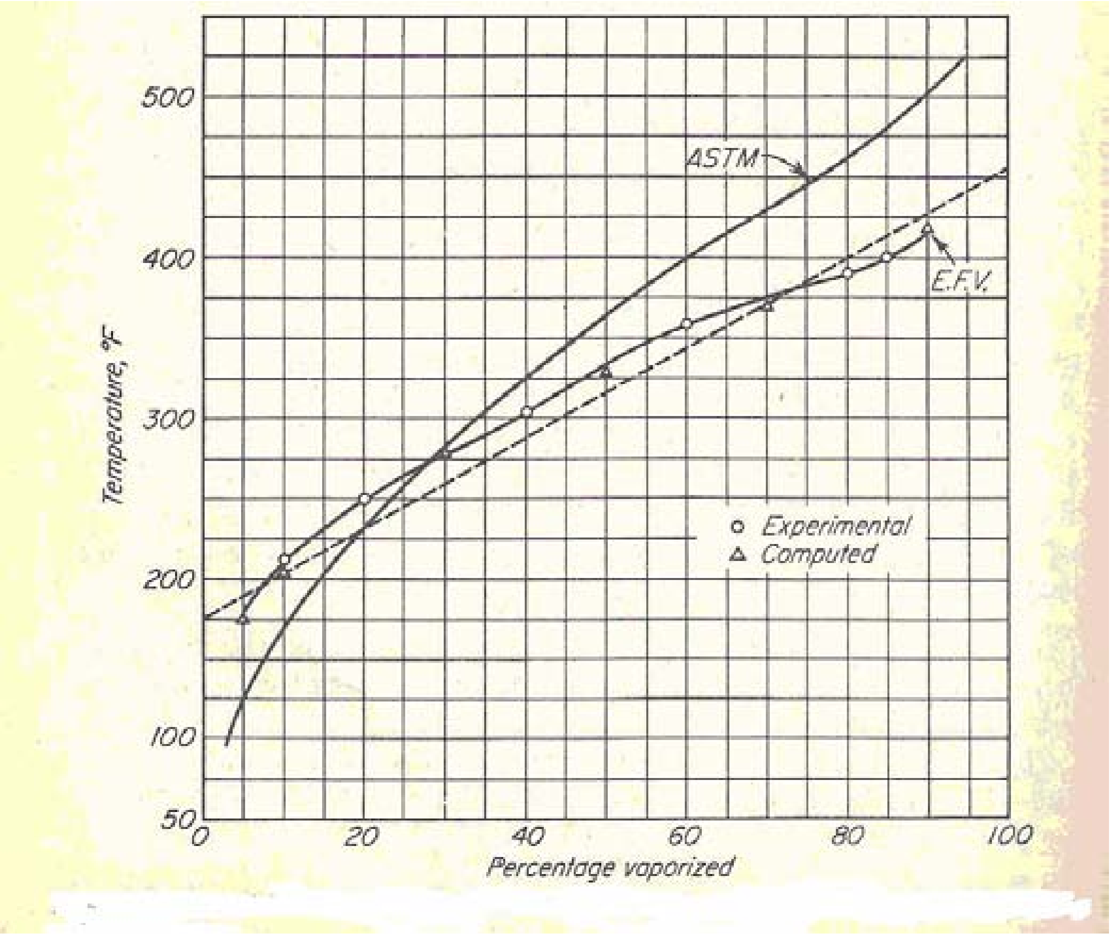
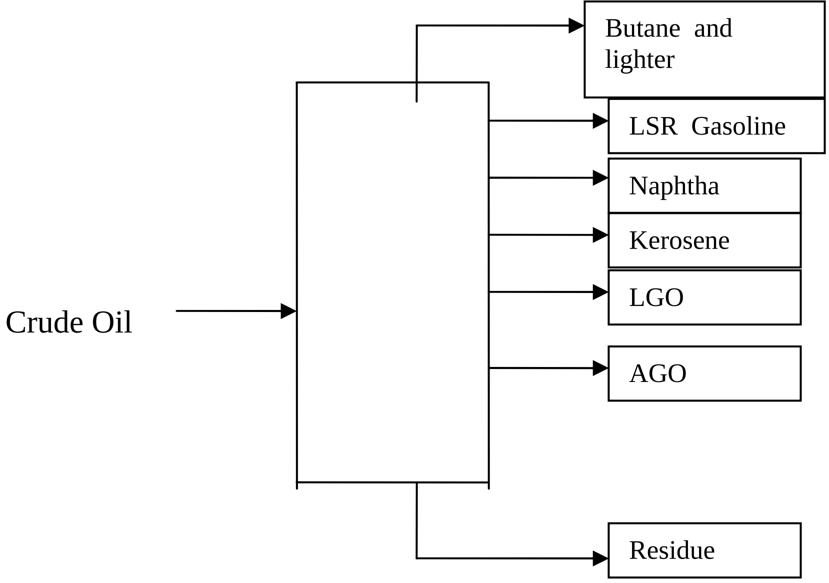


Fig (9): Curvature in the distillation curves of a pressure still distillate. (From, Nelson, W. L, 1985)

Distillation Fractions: All the components that boil between the two specified temperature which called the cut point



Fractions	**Cut points**	**Cut points**
C4 and ltr	< 32 ^{0}C	< 90 ^{0}F
Light Straight Run (LSR) Gasoline	32-105 ^{0}C	90-220 ^{0}F
Naphtha HSR Gas	105-150 ^{0}C	220-300 ^{0}F
Kerosene	150-282 ^{0}C	300-540 ^{0}F
Gas oil	282-425 ^{0}C	540-800 ^{0}F
Residue	425^{+} ^{0}C	800 $^{+}$ ^{0}F

Cut Point

Each fraction has an **IBP** and **EP** on **ASTM** curve because of un efficient fractionation the **IBP** of heavier fraction is interrelated with the **EP** of lighter fraction.

H.W (1): The ASTM data for a pressure distillation are as given. Estimate the EFV curve.

% volume dist.	ASTM (temp. ^{0}F)	% volume dist	ASTM (temp. ^{0}F)
5	125	50	365
10	175	55	380
15	200	60	400
20	230	65	420
25	255	70	425
30	280	75	450
35	300	80	460
40	325	85	480
45	350	90	500

H.W (2): Evaluate the crude oil whose ^{0}API= 35, MABP=600, sulfur%= 0.52%.

H.W (3): 4000 BPD of (35 ^{0} API) crude oil having the given TBP data is available.

TBP ^{0}F	% vol. Distilled	^{0}API	% Sulfur
85	1	110	-
180	13	63	-
385	30	49	0.1
510	50	38	0.3
620	63	23	0.5
750	73	20	0.8
1000	84	17	1.5
1000^{+}	100	11	2.3

a) Draw an assay curve.

b) Evaluate the given crude ; TMABP=TVABP- 120 (^{0} F)

c) Select TBP cut temperature for the products to be obtained from distilling this crude and estimate their yields.

H.W (4) : For the given crude oil ;

a) Evaluate the given oil.

b) Select TBP cut points for the products to be obtained from processing this crude in an atmospheric distillation unit and estimate the %yield for each cut.

% vol. Distilled	TBP (^{0} F)	API	% S
0	40	---	---
20	200	40	0.1
40	280	35	0.18
60	330	30	0.25
80	410	26	0.42
90	500	25	0.68

95	520	20	0.8

H.W (5) : For the given crude oil (31.7 0 API),sulfur percent 0.15 ;

a) Evaluate the given oil.

b) Select TBP cut points for the products to be obtained from processing this crude in an atmospheric distillation unit and estimate the %yield for each cut.

Stage 1- Distillation at atmospheric pressure 751 mm Hg

Fraction No.	Cut Temp. ^{0}F	Percent Distilled	Sum. Percent	Sp. gr. 60/60 ^{0}F	^{0} API 60 ^{0}F
1	122	0.8	0.8	0.673	78.8
2	167	1.0	1.8	0.685	75.1
3	212	3	4.8	0.725	63.7
4	257	3.4	8.2	0.755	55.9
5	302	3.1	11.3	0.777	50.6
6	347	3.9	15.2	0.798	45.8
7	392	4.9	20.1	0.817	41.7
8	437	6.8	26.9	0.833	38.4
9	482	8.0	34.9	0.848	35.4
10	527	10.9	45.8	0.864	32.3

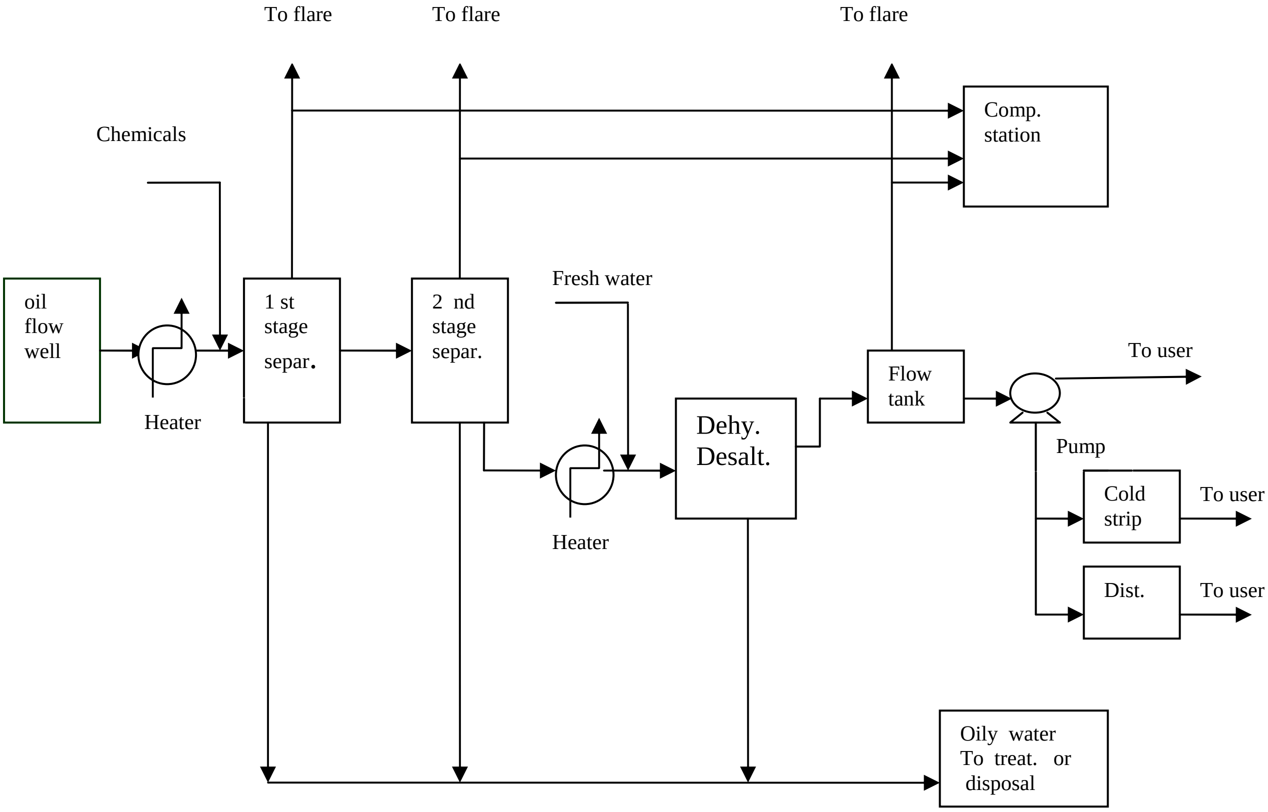
Stage 2- Distillation at atmospheric pressure 40 mm Hg

Fraction No.	Cut Temp. ^{0}F	Percent Distilled	Sum. Percent	Sp. gr. 60/60 0F	^{0} API 60 ^{0}F
11	392	7.3	53.1	0.873	30.6
12	437	7.8	60.9	0.879	29.5
13	482	6.2	67.1	0.889	27.7
14	527	5.7	72.8	0.901	25.6
15	572	6.9	79.7	0.916	22.94
16	-------	20.3	100.0	0.945	18.2

Degassing and Dehydration

In a producing oilfield the fluid obtained at the wellhead is submitted to ***degassing*** and ***dehydration*** operations . In the first operation the gases evolved by releasing the pressure of the fluid are recovered, stripped of the less volatile components, and 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 Degassing station (From Gary and Handwerk, 2001)

Dehydration and desalting of crude

The second operation aims to completely eliminate the water that appears in the fluid forming stable emulsions, and the removal of water-soluble inorganic salts associated with the water which, if left in the oil, would give rise to serious corrosion problems in the course of refining operation.

All crude contain moisture and salts to varying degrees. Water is likely to occur in emulsion form when the crude are naphthenic or sulfurous *(**No harm may be expected to the distillation column due to the presence of moisture , as there is always steam in distillation. However , crude has to be dehydrated to remove the salts**).*

Water being good solvent for these salts the removal is very much effective in the form of brine.

Of all of the existing salts, chlorides of calcium and magnesium distinguish themselves in playing an invincible role in overhead corrosion . *(**These salts in presence of steam at 150-200 ^{0}C easily hydrolyze generating hydrochloric vapors.***

These vapors cause corrosion to equipments). Any crude that contains more than 5 kgs of total salts expressed in terms of sodium chloride per thousand barrels may be regarded as ***salty crude***.

Dehydration of crude is practiced in two stages, first in the site and later in the refinery.

At the site (oil field) : salt is removed by 1) settling or by 2) adding chemicals or by 3) Combination of these two.

Crude possessing emulsifying characteristics are not responsive to settling method; these demand demulsifying agent to increase the coalescence of water drops. (Soda ash, sodium hydroxide, salt of fatty acids petroleum sulfonates which assist coalescence of water droplets).

A good amount of water should be available in crude for such treatment ; lack of water demands the fresh additions to about 20 % . After adding the chemicals and water to the desired extent the crude mixture is allowed to stand 75-80 ^{o}C at 15 kgs/cm^2 in huge tall tanks. Demulsifying chemicals , if necessary are added in very small amounts. Retention time is about 48 hours.

Coalescence

Water droplets will settle at a velocity proportional to the square of their diameter

$$V = c\frac{D^2(\rho_w - \rho_o)}{\mu}$$

Salt water is present in oil in the form of an emulsion, created by dispersion of water in droplet form, and held by emulsifying agents present in the oil.

These emulsifying agent are generally

Resin, asphalts, organic acids, and solids which are produced with the oil, and aid in the formation of a tough film around the droplet, thus isolating each separate water droplet from the other. The film which isolates the water droplets from the other must be broken before coalescence take place

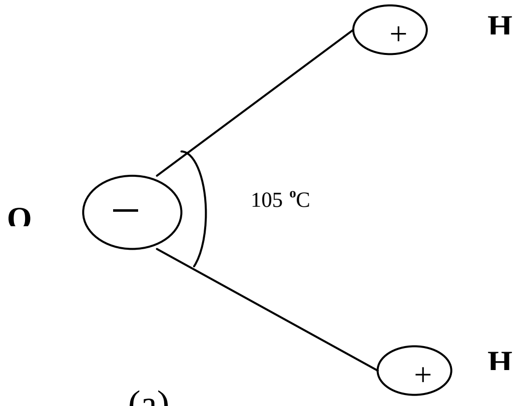
1)Chemical aids deemulsifiers
2)Heat

are used to displace this film from the water droplet. The proper use of heat is also an aid

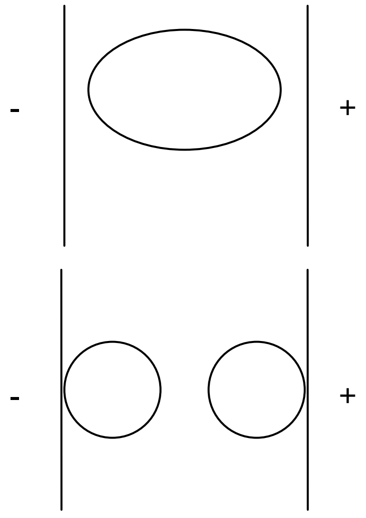
The final phase of the coalescence process is the collision of these small water droplets under the influence

3) An electrostatic field

to form layer drops which will settle faster



(a)



(b)

Tube Still Heater

Tube Still Heater

Tube 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.

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/ ^{o}F ft^2 hr at black body conditions.

T: absolute temperature of the surface , ^{o}F

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

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

$A_{cp=}$ Area of wall having tubes in front of it

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

A_{cp} = wall area
α 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)

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

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

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

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

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

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

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

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 ^{o} C . The heater is designed to burn 3500 kgs per hour of refinery off gases as fuel. The net heating value of fuel is $47.46x10^3$ 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,

Data α=0.88

Air fuel ratio= 25

Average Specific heat of stock=2.268 Kj/Kg ^{o} C.

Solution

Total heat liberated (Q) = m_{fuel} * NHV =$47.46*10^3$ * 3500

= $1.66*10^8$ Kj per hour

Projected area of one tube (L * D)=12x0.105

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

α A_{cp}=0.88* 120 * 0.105 * 2* 12=266 Sq. m.

$$\text{Heat absorption \%(R)} = \frac{1}{1+\frac{G\sqrt{Q/\alpha A_{cp}}}{S}}x100 = \frac{1}{1+\frac{25*\sqrt{\frac{1.66*10^8}{266}}}{14200}} = 44\%$$

Outlet temperature of the stock:

Q=m Cp Δt

$0.44*1.66*10^8$= 1200* 200* 0.8524* 2.268* Δt

Δt=157 ^{o} C

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

Example

A pipe still uses 7110 lb per hour of a cracked gas (Net Heating Value (NHV) 20560 Btu per 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?

Solution

Total heat liberated(Q)=m $_{fuel}$ * NHV=7110*20560=146000000 Btu/hr

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

A=1500

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

$A_{cp} = LN\frac{C}{12} =$ 40x90x10/12=3000

α A $_{cp}$=0.88x3000=2640 sq ft

Heat absorption %(R) $= \dfrac{1}{1+\dfrac{G*\sqrt{Q/\alpha A_{cp}}}{S}}x100 = \dfrac{1}{1+\dfrac{21*\sqrt{\dfrac{1.46x10^6}{2640}}}{4200}} = 45.8\%$

Heat absorption in radiant section = 0.458*146*10^6=66900000 Btu per hr

Heat absorbed per sq ft projected area = q= 66900000/1500=44500 Btu per hr

Example

A furnace is to be designed for a heat duty of 50x10^6 Btu/hr if the overall efficiency of the furnace is 80% and an oil fuel with a NHV=17130 Btu/lb is to be fired with 25% excess air (17.5 lb air/ lb fuel) with the air being preheated to 400 ^{o} F . Steam is used for atomizing at a rate of 0.3 lb/lb of fuel at 190 ^{0} F. Furnace tubes are of 5 in OD., 38.5 ft length and 10 in spacing arranged in a single row. 1500 ft^2 of projected area is available.

H$_{air}$ (400 ^{o} F) = 82 Btu/lb

H $_{steam}$ (190 ^{o} F) = 95 Btu/lb

H (flue gases at 1730 ^{o} F)=148 Btu/hr

Calculate :

1) The no. of tube required in radiation section.

2) % heat absorbed in convection section assuming wall losses of 5 %.

3) The heat rate available per unit projected area.

Solution

$$Q_{comb.} = \frac{heatduty}{efficiency} = \frac{50*10^7}{0.8} = 6.25*10^7\ Btu/hr$$

A=nxLxNxD/12

A= 1500 ft^2

1) N=1500*12/(1*38.5*5)

N= 94 tube/row

A $_{cp}$= L * C/12 * N =38.5*10/12*94=3015.8 ft^2

α A $_{cp}$=0.88*3015.8=2653.9 ft^2

Q $_{total}$= Q $_{comb.}$ + Q $_{steam}$ + Q $_{air}$

$Q_{comb.} = m_{fuel} * NHV$

$m_{fuel} = 6.25 * 10^7/17130 = 3.648 * 10^3$

0.3 lb steam / 1 lb fuel

$m_{steam} = 0.3 * m_{fuel}$

$m_{steam} = 0.3*3.648*10^3 = 1.0944*10^3$ lb/hr

$Q_{steam} = m_{steam} * H_{steam}$

$= 1.0944 * 10^3 * 95 = 1.03968 * 10^5$ Btu/hr

17.5 lb air / 1 lb fuel

$m_{air} = 17.5 * m_{fuel}$

$m_{air} = 17.5 * 3.648*10^3 = 6.384 * 10^4$ lb/hr

Excess air =25 %

$m_{air} = 1.25 * 6.384 * 10^4 = 7.98 * 10^4$ lb/hr

$Q_{air} = m_{air} \text{ x } H_{air}$

$Q_{air} = 7.98 * 10^4 * 82 = 6.5436 * 10^6$ Btu/hr

$m_{flue\ gases} = m_{fuel} + m_{air} + m_{steam}$

$m_{flue\ gases} = 3.648 * 10^3 + 7.98*10^4 + 1.0944*10^3 = 8.454 * 10^4$ lb/hr

$Q_{flue\ gases} = m_{flue\ gases} \text{ x } H_{flue\ gases} = 8.454 * 10^4 * 148 = 1.25 * 10^7$ Btu/hr

$Q_{total} = Q_{comb.} + Q_{steam} + Q_{air} = 6.25 * 10^7 + 1.03968 * 105 + 6.5436 * 10^6$

$= 6.9147 * 10^7$ Btu/hr

% stack loss = $Q_{flue\ gases} / Q_{total} * 100 = 1.25 * 10^7 / 6.9147 * 10^7 * 100 = 18$ %

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

$$= \frac{1}{1+\dfrac{17.5*\sqrt{\dfrac{6.9147\,x10^7}{2653.9}}}{4200}} = 59.88\%$$

2) % convection=100-%R-%stack loss-% wall loss

% convection = 100 - 59.88 – 18 – 5 = 17.12 %

3)$q = RQ/A = 0.5988 \text{ x } 6.78 \text{ x } 10^7/1500$

$q = 2.7 \text{ x } 10^4$ Btu/ hr ft^2

H.W (1)

A furnace is to be designed for a heat duty of 30 x 10^5 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.

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.

Fractionation Towers

After desalting, the crude oil is pumped through a series of heat exchanger and its temperature raised to about 550 °F (288 °C) by heat exchange with product and reflux streams. It is then further heated to about 750 °F (399 °C) in a furnace (i.e. direct fired heater or "pipe still") and charged to flash zone of atmospheric fractionators.

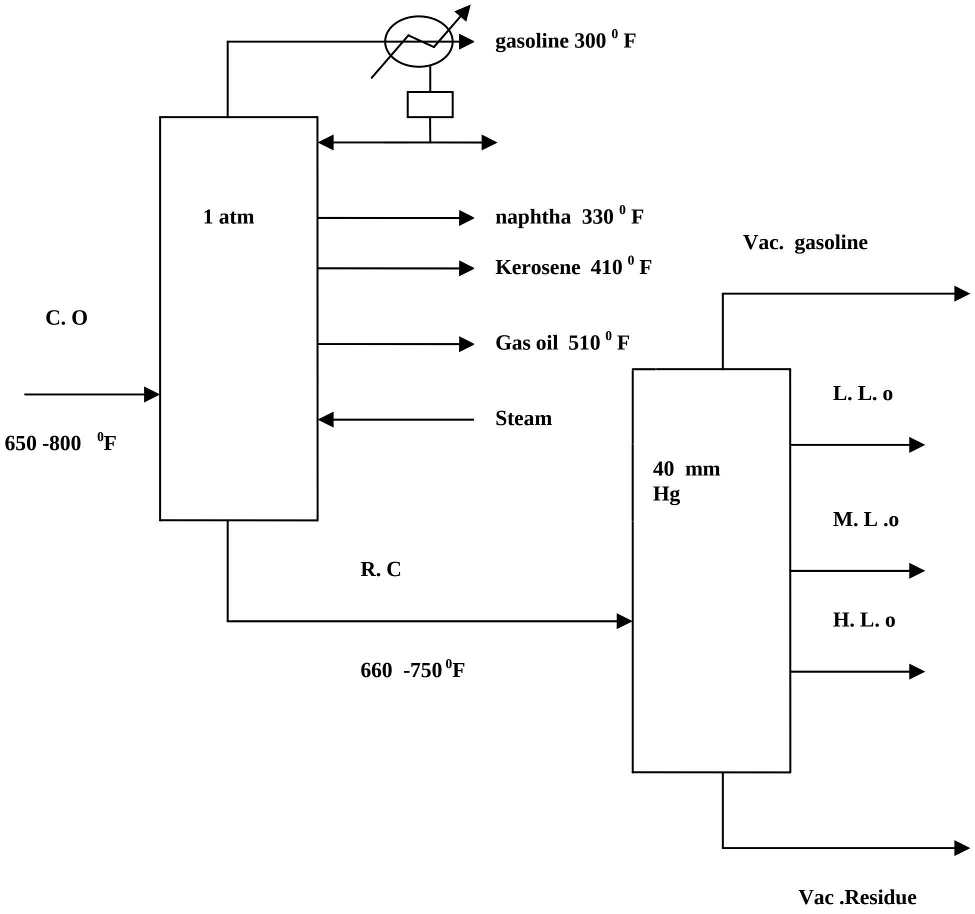
The furnace discharge temperature is sufficiently high to cause vaporization of all products with drawn above the flash zone + about 20% of the bottom product. The 20 % "over flash" allows some fractionation to occur on the trays just above the flashing zone by providing internal reflux in excess of side stream withdrawals.

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.

Bottom product of atmospheric column is now again routed through a furnace to reach a temperature of 350 to 400 °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.



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:

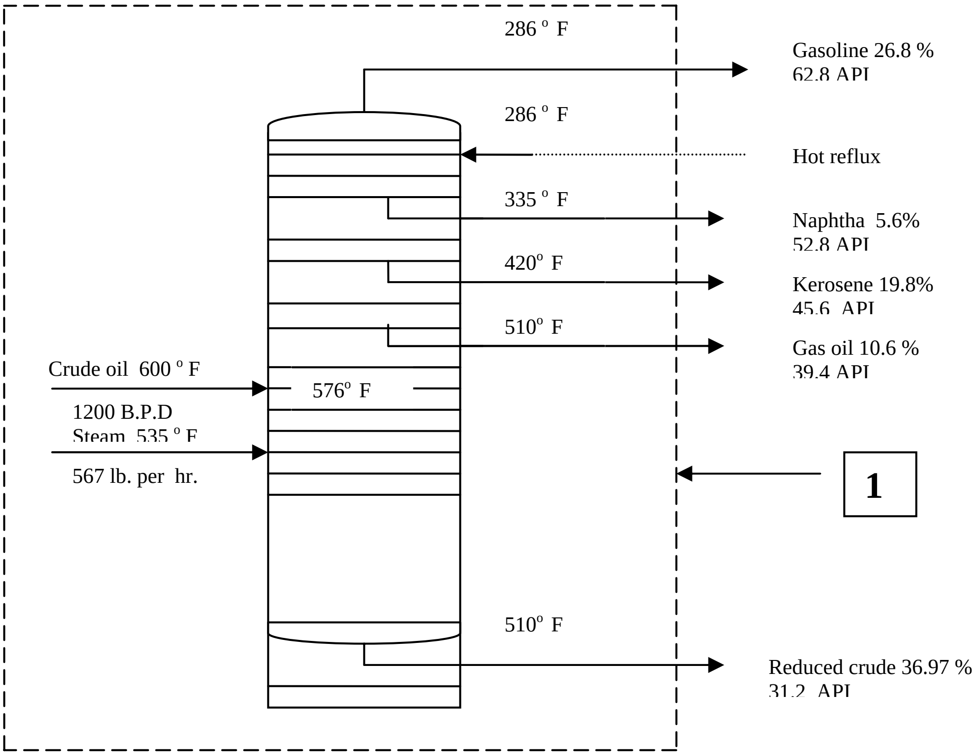
a)Cool each product from vaporizer temperature to its withdrawal temperature.

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.

	Volume, Percent	API	Lb per gal	Gal per hr	Lb per hr	50 per cent 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			



Solution :Energy Balance Basis =1hr

Sensible heat **Btu**

Gasoline (vapor) 3415x(576-286)x0.56 = 589000

Naphtha (vapor) 754x(576-335)x0.55 = 106000

Kerosene(vapor) 2765x(576-420)x0.57= 261000

Gas oil (vapor) 1530x(576-510)x0.59= 63000

Reduced crude (liquid) 5610x(576-510)x0.72=276000

1295000

Steam (vapor) 567x(535-286)x0.5= 70600

1365600

Latent heat **Btu**

Gasoline (withdraw as vapor)

Naphtha 754x113 = 85100

Kerosene 2765x100= 276500

Gas oil 1530x90= 138000

Total heat to be removed 1865200

Kinds of Reflux :

Ways of removing heat are indicated in Fig below , the types of 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

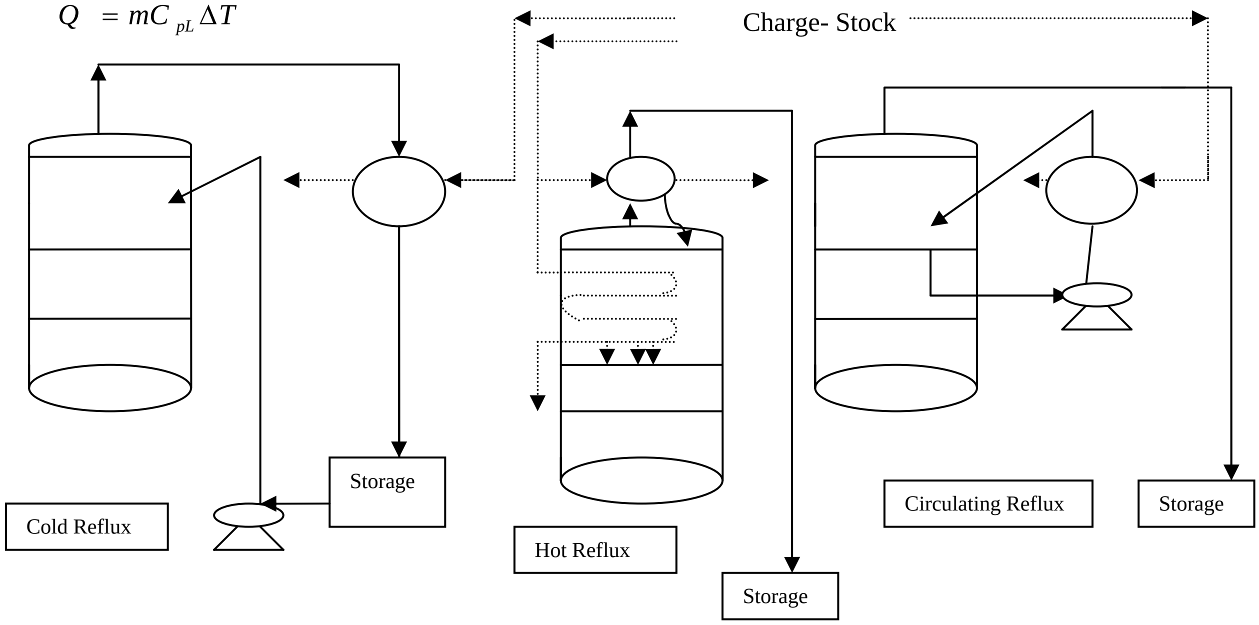
$$Q = m\lambda + mC_{pL}\Delta T$$

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

$$Q = m\lambda$$

2) 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.

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



<u>Example (2)</u> : (Quantity of Reflux)

A tower fractionating system is such that 18652000 Btu per 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?

<u>Solution</u>

<u>Hot reflux</u>:

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)x780 =660 mm Hg

(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/lb mole °R

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

T=284 °F

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

<u>Cold reflux</u> :

Assume storage tank at 80 °F

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

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

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

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

<u>Circulating reflux</u> :

When circulating reflux was used the top temperature was 244 °F. Assuming the reflux is cooled from 264 to 166 °F.

Mole gasoline	31
Mole steam	31.5
Total moles	62.5

Partial pressure $= \dfrac{31}{62.5} * 780 = 387$ mm Hg

Correction 296 to 387 mm pressure gives 253 °F

Lb circulating reflux $= \dfrac{18652000}{120+(264-166)*0.605} = 10403$

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**.

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.

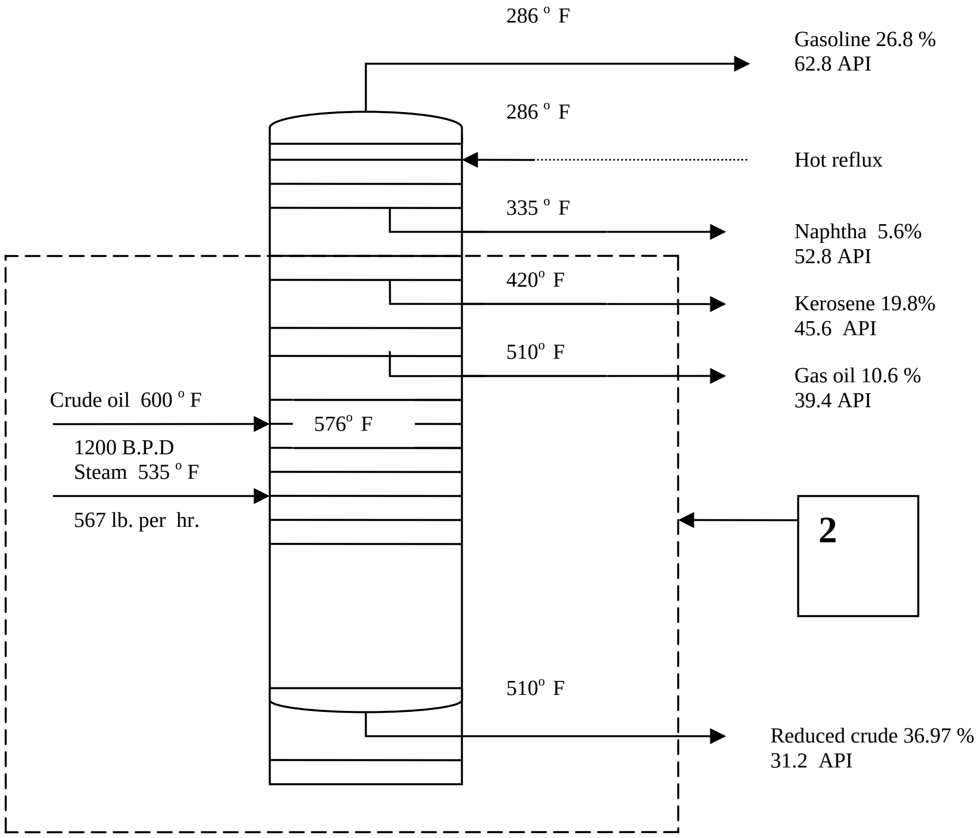
5) Arbitrarily, **the vapors materials that will be condensed at the second or higher draw plate above the plate under consideration may be considered to act as fixed gases.**

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.**

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

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

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 mm Hg

$P_i = P_T \text{ x } y_i$

Partial pressure $= \frac{78.6}{141.1} * 950 = 530$ mm Hg

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

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

$T = 414\ ^{o}F$

T actual $= 420\ ^{o}F$

H.W:

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

H.W :

Fraction	**Lb\hr**	**Mw**	**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	-	580
C.O.	121000	-	-	576

A)calculate the amount of Hot, Cold and circulating reflux if the storage temperature is 100 ^{o}F and $Cp_v = 0.6$ and $Cp_l = 0.7$ Btu/lb ^{o}F

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.

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 ^{o} F

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

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.

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

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

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

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 is ok

H.W:

120000 Lb/hr of 34 ^{o} API crude oil at 650 ^{o} F is fed to an atmospheric distillation unit. Steam at a rate of 600 lb/hr and 850 ^{o} F is used. The fraction obtained were 34000 lb/hr gasoline (MW=110,λ=120) at 310 ^{o} F; 12000 lb/hr kerosene (MW=185, λ=108) at 420 ^{o} F; 30000lb/hr gas oil (MW=270,λ=95) at 510 ^{o} F . The residue is withdrawn at 510 ^{o} F . Assume C_{PL}=0.7 ,C_{PV}=0.6 Btu/lb ^{o}F.

a) Check the top tower temperature if the dew point of gasoline is 296 ^{o} 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 .

The Petroleum Refinery

A small refinery : will take in ***2000 to 10000*** tons of crude oil/ day .

A large refinery : ***20000 to 40000*** tons/day and these are a few refineries larger than this up to ***60000*** tons/day. Refineries vary in ***complexity*** ;i.e. in the ***variety of processes operated*** and of ***products*** that are sent out.

Simple refinery : may make only ***gasoline, diesel fuel***, and ***heavy fuel***.

The crude oil is distilled into:

1) **Gaseous hydrocarbons**, which are burnt as refinery fuel

2) **Light gasoline** , which will need **sweetening, a simple chemical treatment**, and then use for automotive use except for its ***low octane number.***

3) **Naphtha of very low octane number**, perhaps 40 compared with a market of 90. It is **catalytically reformed**, by which ***octane number of 90 to 95*** can be obtained.

A simple refinery consist of a **crude oil distilling unit**, *a* **gasoline sweetening unit** *and a* ***catalytic reformer***. Refineries having just this usually small of **2000 to 4000** tons/day of crude oil.

Next stage of complexity is to added a ***desulphurization*** unit to treat the diesel fuel. Usually also the **growing refinery** will make **(LPG)** and some **low grade kerosene**. The **kerosene** will also need refining, at least ***sweetening*** to make it of **marketable odor.**

Large Complex Refinery: will have many more units representing more processes

a) Vacuum Distillation : To make a heavy distillate suitable for catalytic cracking or hydro-cracking or manufacture of lubricating oils , and a residue which may be blown or further distilled for bitumen.

b) Hydro-cracking : which makes more naphtha for catalytic reforming, more diesel fuel and low sulphur fuel.

c) Catalytic Cracking : which makes much gas, suitable for LPG ; olefinic hydrocarbons, the feed stock for many petroleum chemicals ; and high grade gasoline.

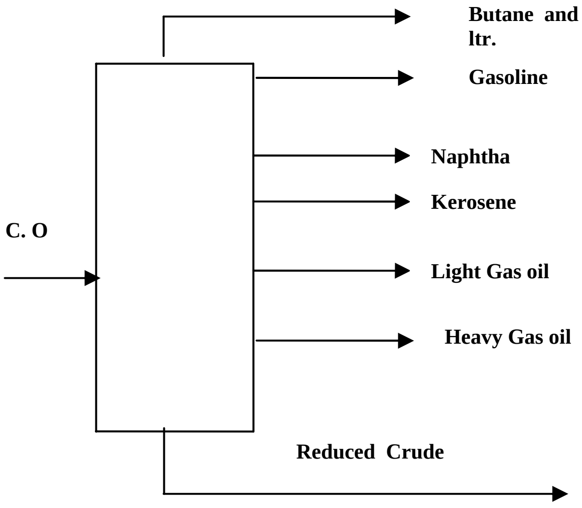
d) Wax Plant : de-waxing to get wax out of oil, then de oiling of the crude wax and final purification of the wax by hydrogenation.

e) Sweetening and Desulphurisation : for jet fuel.

f) Alkylation unit : to synthesize very high octane components for gasoline out of by product gases from processes (b) , (c) and the primary distillation of the crude oil.

g) Lubricating oil refining :special plant to remove resinous and solidifying materials from lubricating oil stocks and achieve the finished product by blending.

Butane and ltr → gas unit for refining and separation
Gasoline → Blending
Naphtha → Reforming
Kerosene → Hydrogenation
Light Gas oil → Gas Oil Blending
Heavy Gas oil → Catalytic Cracking
Reduced Crude → Vacuum Distillation Unit



Gas

Gas from petrolum is classified under several names

a) Natural gas : It is readily availble in nature, in almost as a finished product.It contains mainly methane It may be accompanied by other dry fractions like ethane and propane to a small extent. In addition to these combustibles some inerts like CO_2 ,N_2 , noble gases are also present. The proportion of methane ranges from 85% to 98%.

b) Associted gas : This is obtained from oil reservoirs and this exists as a separate gas cap over liquid phase. The proportion of CH_4, C_2H_4 , C_3H_8 vary depending on reservoir conditions. When the gas phase is taken out, it may still contain some liquid , hyrocarbons mainly of volatile range like butane and pentane which when condensed are treated as ***(Natural Gasoline).***

c) Disolved gas : Gas may be present in liquid HC mainly in the dissolved state depending upon the formation pressure. When the pressure dercreased, this dissolved gas comes out of the oil. This gas is separated before transportation in pipe lines or tankers . The remaining is first to come out of the distillation column because of higher temperature.

d) Refining off gas : In refinery , gas is formed in cracking and reforming operations due to the thermal degradation of liquid hydrocarbons. During stabilization of wild gasolines or prossessed gasolines, the gases are vented. This forms a major source of heat energy for refinery, as wall as feed stock for petrochemicals. All the gases contain impurities like CO_2 ,N_2 , mercaptans, H_2S, water vapour, suspended impurities. First three paraffins are gases at room temperature. The mixture of methane and ethane is called dry gas , propane and butane mixture is called wet gas.

e) Liquified Petroleum Gas (LPG) : Propane is frequently used as LPG after being mixed with butane. The most important property of this fuel is the vapour pressure. For factiliting leak detection, the gas is mixed with small amount of odourous mercaptans.

Gasoline

Most refiners produce gasoline in two grades, ***regular and premium*** and in addition supply a low-lead or non-lead gasoline to comply with antipollution requirments. The principal difference between regular and premium fuels is the antiknock performance. Gasoline is a complex mixture of hydrocarbons C_4-C_{12} having a boiling range from 100 to 400 ^oF as determined by ASTM method. Components are blended to promote : 1) high antiknock property. 2) ease of starting. 3) quick warm-up. 4) low tendency to vapour lock. 5) low engin deposits.

Normal butane is blended into gasoline to give the desired vapour pressure which is a compromise between high RVP to improve starting characteristics and a low RVP to prevevt vapour lock and reduce evaporation losses. As butane has a high blending octane number as much as vapour pressure limitation permits.

Gasoline specifications

The most important properties are :

1) Boiling Range :

This governs ease of starting, rate of acceleration, loss by crankcase dillution. and tendency towards vapour lock. **Engine warm-up time** ***is affected by the % distilled at 158 ^oF and the 90% ASTM distillation temperature.***

Warm up ***is expressed in terms of the miles of operation required to develop full power without excessive use of the choke.***

<u>Crankcase dilution</u> ***is controlled by the 90% ASTM distillation temperature and is also a function of outside temperature.***

Tendency to <u>vapour lock</u> is directly propotional to the RVP of the gasoline.

RVP is approximately the vapour pressure of the gasoline at 100 ^oF in Lb/in^2 absolute.

<u>2) Antiknock Properties :</u>

There are two types of octane numbers for gasoline engines : those determined by

- the motor method (MON)
- the research method (RON)

both methods use the same basic test engine but operate under different conditions. The RON represents the performance during low-speed driving when acceleration is relatively frequent, and the MON is aguide to engine performance and high speeds or under heavy load conditions. The difference between the RON & MON of gasoline is an indication of the change of performance under both city and highway driving and is known as the "sensivity" of the fuel.

Distillate Fuels

1) Jet Fuels : Commercial jet fuel is a material in the kerosine boiling range and must be clean burning. One of the critical specification of jet fuels is its **smoke point** and this limits the % of cracked products high in aromatic that can be incorporated. Specification limit **the aromatic conc. to 20%** . Hydrocracking saturates the aromatics in the cracked products and raise the smoke point.

The freeze point specification is very low **(-40 ^oF to -58 ^oF) max**. and hydrocracking is also used to isomerize paraffins and lower the freeze point. In addition the other limiting specification is **flash point (110 to 150 ^oF)**.

Naphtha jet fuel is produced for military and is a wide- boiling- range stock which extends through the gasoline and kerosene boiling range.

2) Diesel Fuels : The major performance characteristics of diesel fuels, some what in the order of importance are : (cleanlines, ignition quality, volatility, viscosity)

No.1 diesel fuel : is generally made from virgin stocks having cetane No. above 50 . It has a boiling range from 360 to 600 ^oF (250 to 320 ^oC) and is used in high- speed engines in trucks and buses, it is called some time super diesel.

No.2 diesel fuel : is similar to No.2 fuel oil, and has a wider boiling range (350 to 650 ^oF) than No.1. It is usually contains some cracked stocks and may be blended from naphtha, kerosene , and light cracked cycle oils.

<u>Limiting specifications are</u>

Flash point (120 to 125 ^oF min.)
5% 0.5% max
Dist. Range
Cetane No. (52 min.)
Pour point (-10 to +10 max.)

The ignition properties of diesel fuels are expressed in terms of cetane number which expressed the volume % of cetane ($C_{16}H_{34}$, high ignition quality) in a mixture with alpha-methl-naphthalene ($C_{11}H_{10}$, low ignition quality).

3) Heating Oils

No.1 fuel oil is very similar to kerosene but has a higher pour point and end point.

<u>Limiting specification are</u>

Distillation, pour point, flash point and sulfur content.

No.2 fuel oil is very similar to No. 2 diesel fuel, contains cracked stock, and is blended from naphth, kerosine,diesel and cracked- cycle oils.

Limiting specification are :

Sulfur content (0.25 to 0.5% max.)
Pour point (-10 to +5 max.)
Distillation
Flash point (120 °F min.)

Aviation Turbine Fuels , (ATF) , Jet Fuels

Modern jet engines use fuel similar to kerosene. It is a most flexible fuel in its boiling range (upto 300 °C)

Important properties

Pour point not higher than -30 °C
Smoke point high
Volatility
Water content

(HSR) Gasoline

Naphthas

These fractions are highly volatile and fall in the boiling range of motor spirits.

These are mostly used as **solvents** in paints, perfumery and other industries. Solvent grades are produced by distilling wide cut naphthas into small boiling range cuts.

Naphthas are not suitable for combustion because of the rapid flame propagation, resulting in explosions.

Cuts boiling below 80 °C donot have any aromatics, hence their solvent power is also less, such fractions are sent for cracking operations.

80-120 °C fraction is reformed to produce an improvrd octane No. and this goes as a blend into SRG.

Kerosenes

Approx. boiling point range 150-250 °C
Low viscosity
Good degree of refinement to be fairly stable.
Light in colour
Free from smoke
Used as illuminating oil.

Diesel Fuels

Boiling point range 250-320 °C

Mainly two types : classification of diesel oils is done according to speed and load of the engine as

1) high speed diesels
2) low speed diesels

Lube Oils

The principal source of lubricating oil is the fraction that is left after components, namely gasoline, kerosene, diesel oil during crude distillation.

Boiling point >350 °C

Otained from vacuum distillation units.

Residuums after precipitation of asphaltenes are known as bright stocks and form good source for lube oils.

Treating Processes

The essential purpose of the ***primary processes*** is to produce the required amounts of the various products from the available crude. The products obtained are, as a general rule, unsuitable as such for immediate use, for the following reasons :
1)Inadequate performance, 2) Instability in storage ,and 3) Objectionable odor and appearance and contamination with water or particulate matter.

Secondary refining processes (finishing or treating processes), are required to give the products acceptable with respect to the above criteria.

Main Finishing Processes

a) The removal of the objectionable gases (Acid gas removal).
b) The removal of the objectionable odors.
c) The improvement in storage stability.
d) The improvement in performance characteristics.
e) The removal of water and particulate matter.

a)The removal of the objectionable gases

Hydrogen sulphide : Has to be removed from products because :
a) toxic, b) foul smelling, c) corrosive, d) traces of it may seriously contaminate regenerative treating solvents such as a solutizer used for final sweetening of the products.

A) Scrubbing with caustic soda : It is still the most widely used process for the removal of H_2S , mainly because it simultaneously removes other constituents such as CO_2 , carbonyl sulphide, lower aliphatic mercaptans, phenols fatty acids and naphthenic acids.

The disadvantage of this processes is that there is no known cheap method of regenerating the spent soda, and if H_2S is present in gross amounts, as is frequently in crude gases, especially the C_2 -C_3 fractions , a regenerative method of extraction such as the girbotol method is more generally used.

This method is more economical than caustic washing but caustic washing may still be required as a final cleaning-up operation for the removal of the last traces of H_2S.

The combination of the two processes not only provides a very low H_2S content economically but also safe guards against high sulfur contents in the treated products should there be a temporary failure of the regenerative treating plant.

In the caustic washing of gases rather weak solutions of 2-10%wt NaOH have to be used to prevent the deposition of sodium sulphide crystals. The reaction proceeds almost to the complete conversion of NaOH to NaHS.

Traces of H_2S often appear in fractions much heavier than C_2 -C_3 fraction because of a slight breakdown of sulfur compounds owing to pyrolysis during re-distillation or a similar operation. Caustic soda may be employed for its removal.

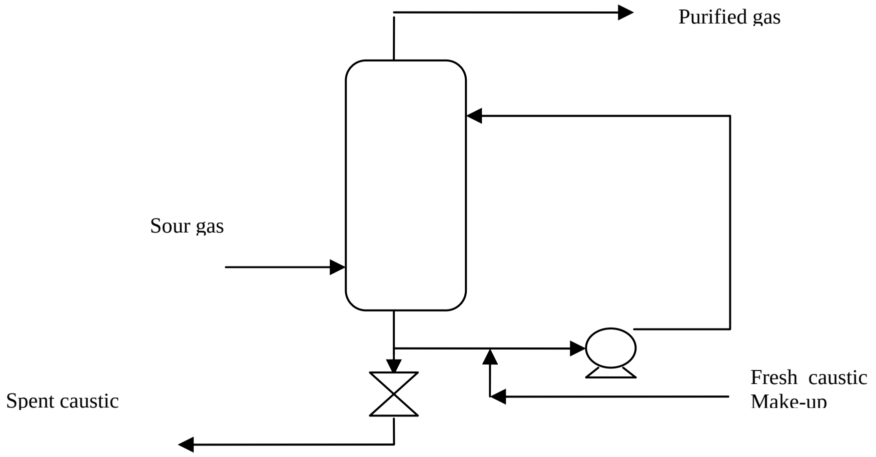


Fig ( ) H_2S removal from gases by caustic washing

B) Girbotol process :

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 °C .

The reaction with hydrogen sulphide is essentially

$$2\ RNH_2 + H_2S \rightleftharpoons (RNH_3)_2S$$

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 °C above the dew point of the gas to ensure that no hydrocarbons liquid condenses out of the plant.

The girbotal 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.

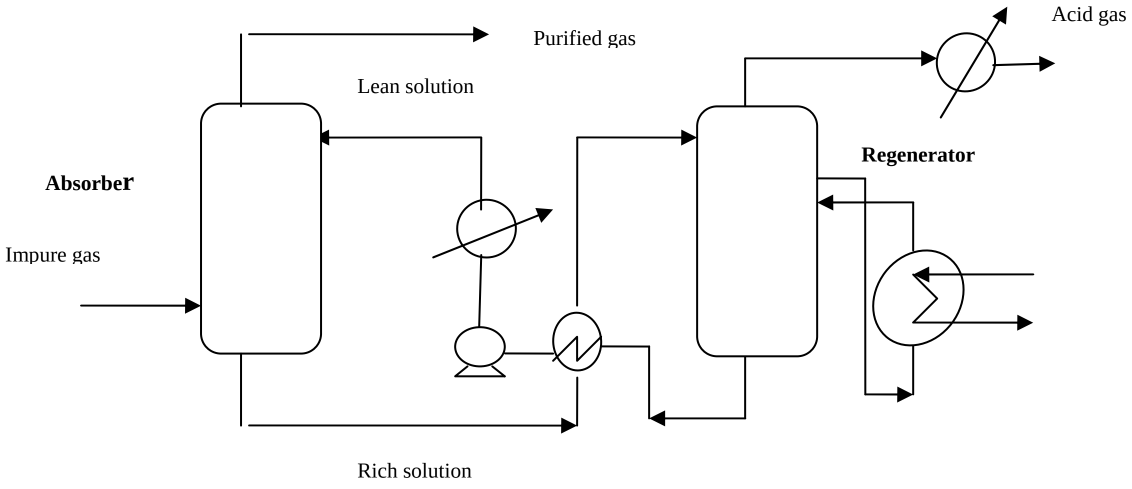


Fig ( ) Girbotol process

Carbon dioxide :

Carbon dioxide is frequently found in natural gas, and is also present in the products of catalytic crackers since regenerated catalyst always carries with it a small quantity of carbon dioxide. Its removal is rarely a direct aim but the major part of it will be removed by a caustic wash applied for the removal of H_2S.

When CO_2 removal is a direct aim one of the regeneration processes such as Girbotol process would normally be used.

b)The removal of the objectionable odors
(Sweetening Process)

The object of sweetening processes is to ensure that the finished products do not have objectionable odors. The objectionable odors are normally attributed to traces of mercaptans, and it is necessary either to remove them by extractive processes or by hydrodesulphurization , or to covert them into innocuous disulphides.

1)Copper Chloride Process

The copper chloride process is used to sweeten gasolines and kerosenes by the direct oxidation of mercaptans to disulphides, using cupric chloride as the oxidizing agent. The basic reactions of the process may be expressed as follows :

Sweetening

$$\underset{\text{Cupric chloride}}{CuCl_2} + \underset{\text{Mercaptan}}{2RHS} \longrightarrow \underset{\text{Cupric mercaptide}}{CU(SR)_2} + \underset{\text{Hydrochloric acid}}{2HCl}$$

$$Cu(SR)_2 + CuCl_2 \longrightarrow \underset{\text{Cupric chloride}}{Cu_2Cl_2} + \underset{\text{Disulphide}}{R\text{-}S\text{-}SR}$$

Regeneration

$$Cu_2Cl_2 + 2HCl \longrightarrow \underset{\text{Chlorocuprous acid}}{Cu_2Cl_2\ 2HCl}$$

$$Cu_2Cl_2\ 2HCl + \tfrac{1}{2} O_2 \longrightarrow 2CuCl_2 + H_2O$$

1)The sour charge is caustic washed to remove traces of hydrogen sulphide which would otherwise deactivate the cupric chloride.

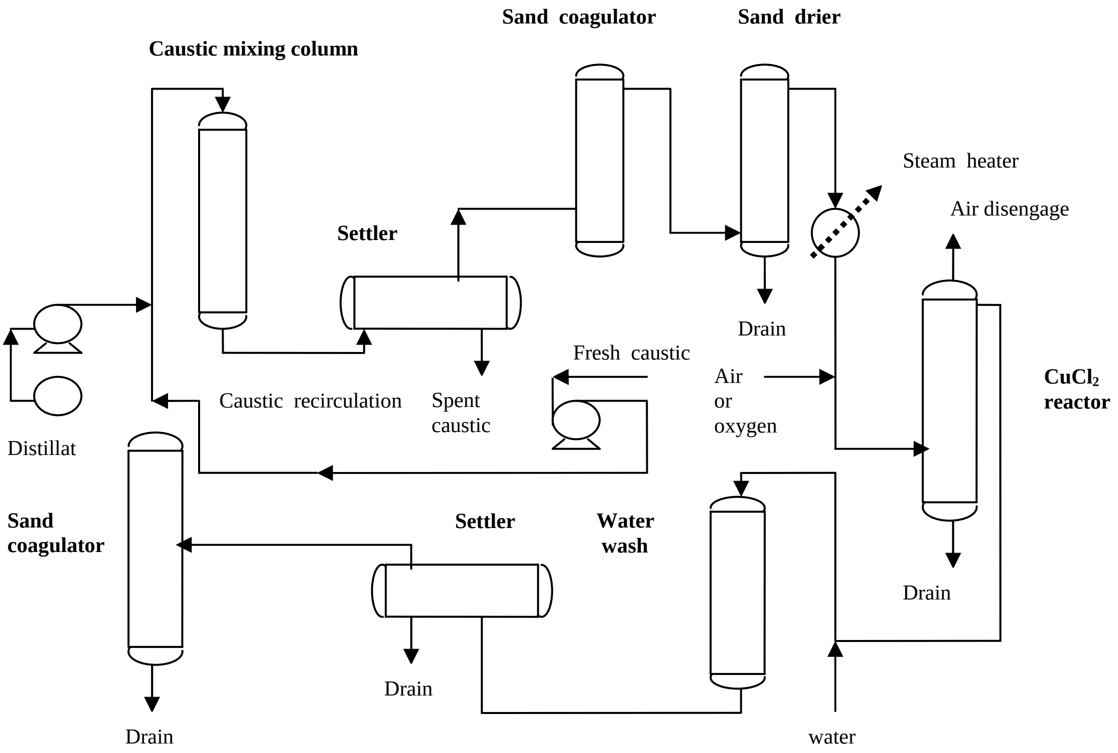
2) It then pass :

A) firstly through a sand coagulator to remove any caustic and / or water haze

B) secondly through a rock salt drying lower to ensure complete removal of free water, which would adversely affect the water balance in the reactor.

3)After passing through a pre-heater to raise the temperature sufficiently to dissolve the water formed during the process, air or oxygen is injected into the line, and the dried and oxygenated feed flows upwards through the reactor which contains a bed of fullers earth impregnated with cupric chloride.

4)The sweetened product is water washed to remove traces of acidity, clarified from water haze in an up-flow sand coagulator and passed to storage.



Copper Chloride Sweetening

2) Merox Process :

The Merox process, Developed by UOP (Universal Oil Products), is combination of mercaptan extraction and sweetening. The combined process is applicable to all gasoline and lighter boiling range fractions; the sweetening process is applicable to many jet fuel and kerosenes.

A) Merox Extraction:

1- The mercaptans are extracted by an aqueous solution of caustic soda according to the reaction :

$$\mathrm{RSH + NaOH} \rightleftharpoons \mathrm{NaSR + H_2O} \qquad \text{----------} \quad (1)$$

Since the reaction is reversible it is impossible to get complete removal of mercaptans by extraction without the use of an excessive amount of caustic soda solution. The forward reaction is favored by low temperature, low molecular weight of mercaptan and high caustic concentration. It is also promoted by the use of compounds that increase the solubility of the mercaptan in the aqueous phase, of these methanol, isobutyric acid and cresols.

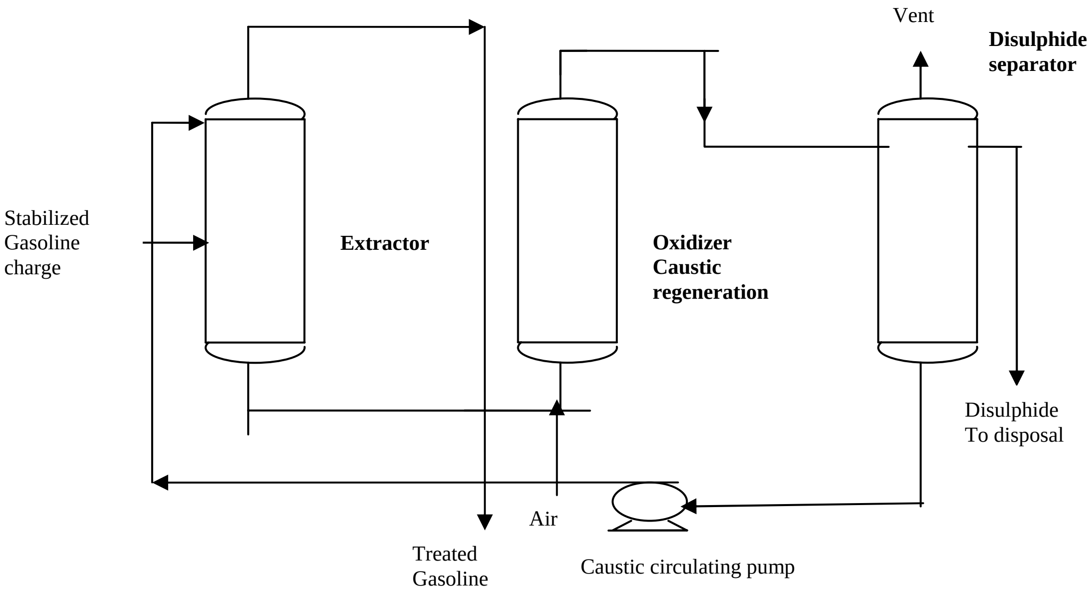
2- The caustic is generated ,after separation from hydrocarbons by blowing with air in the presence of a catalyst at ambient temperature the reaction proceeding according to the reaction :

$$\mathrm{2NaSR + 1/2\ O_2 + H_2O} \rightleftharpoons \mathrm{RSSR + 2\ NaOH} \qquad \text{---------} \quad (2)$$

The disulphide so formed are insoluble in caustic soda and are removed in a gravity separator, the caustic is being re-circulated for further use.

The catalyst which consists of an iron group metal chelate , may be in solution in the caustic, in which case the caustic and air are brought into contact in a reactor such as an orifice column, a mechanically stirred reactor or some other type of gas/liquid contactor.

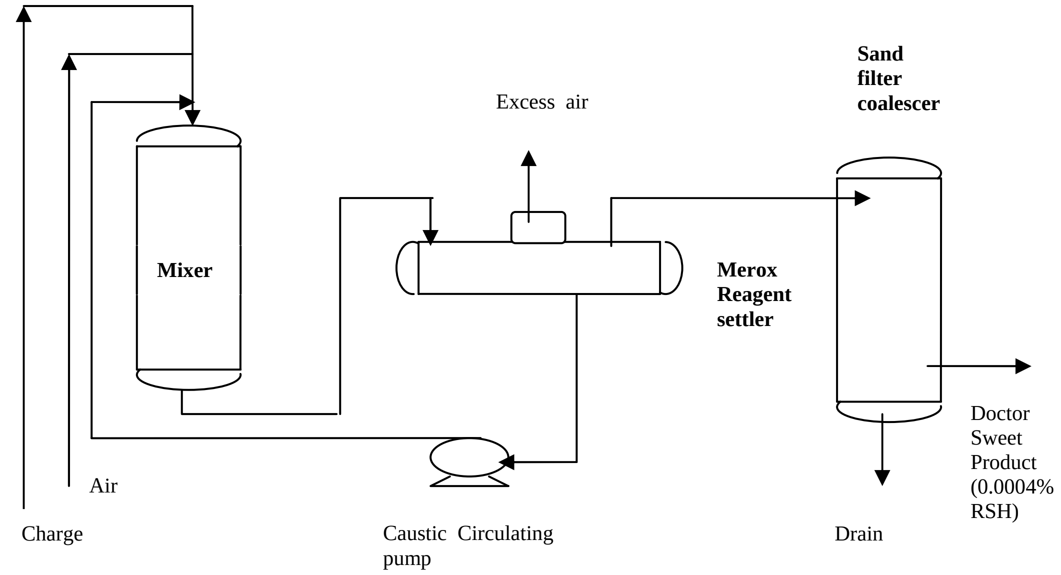
Alternatively the catalyst may be supported on a carrier, in which case the caustic and air are passed together over a packed bed.



Merox Extraction

B) Merox Sweetening

Sweetening is achieved by blowing a caustic hydrocarbon mixture with air in the presence of the catalyst where by disulphide are formed according to equation (2), and dissolve in the material being treated . As in the above mentioned regeneration process, the catalyst may be in solution in the caustic or held on carrier, and the process is carried out as described.



Merox Sweetening

C) Combined Operation

The combined extraction/ Sweetening operation is carried out by a combination of the extraction and sweetening processes.

c) Removal of Water and Particulate Matter In the Refinery

1) Water and particulate matter in the fuel can have disastrous effects on gas turbine blades.
2) Free water may cause corrosion through out a fuel distribution system.
3) Particulate matter may block filters or the fine orifices of fuel injection and burner.

Water may be removed by :

1) Physically 2) Chemically 3) Electro- statically

Particulate matter may be removed by:

1) Water washing 2) Filtration

Processes:

1) **Salt Dryers:** Used to remove water **from** water primary distillation products and to control the water content both before and after secondary processing. The product is passed through a vertical drum filled with suitably graded rock salt. Rock salts are not powerful desiccants; it will remove the free water but not dissolved water. If more dissolved water has to be removed it is usual to use calcium chloride in the dryer.

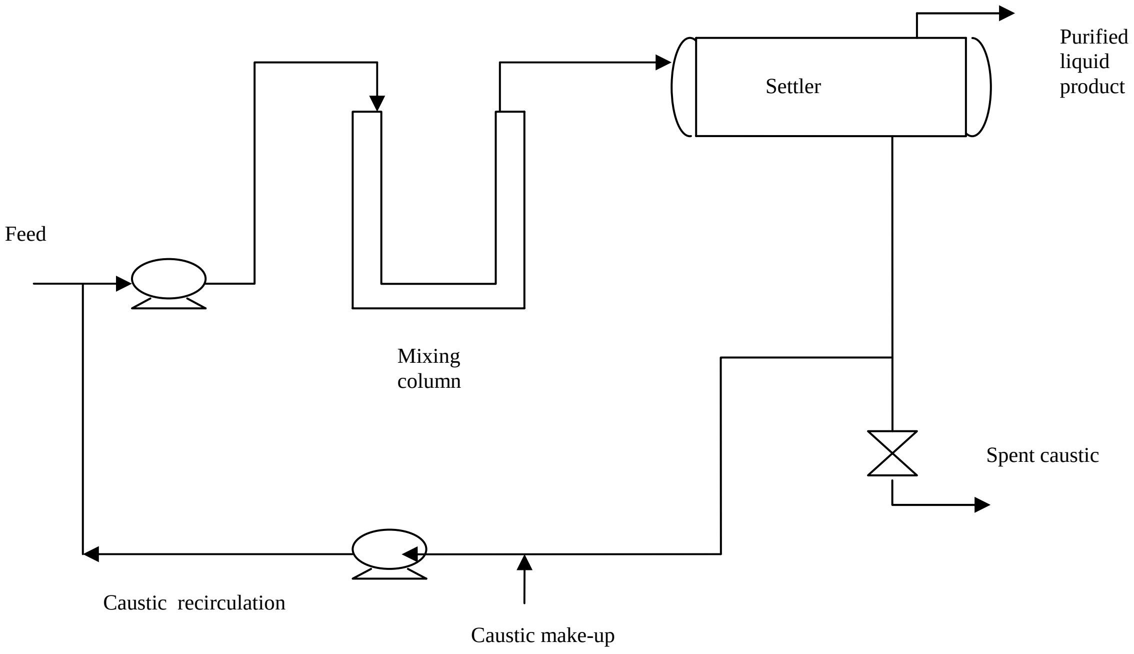
2) **Electrostatic Coalescers :** Uses electrical coalescing for the removal of free water and sodium chloride or calcium chloride for the removal of any residual traces of water. The process is used for the dehydration of heating oil, kerosene, jet fuel, diesel fuel and solvents. The dehydration product contains no free water but may contain some dissolved water.
3) **Sand Coagulators and Filters :** Vertical drums filled with fine sand are used for removal of particulate matter and water, this process have the advantage over salt dryers is not involving the use of chemicals. Down flow through the bed and up flow through a water separator will remove gross water but not haze. For this purpose the oil must pass upward through the bed with a bottom water drain so that it can emerge clear , and bright from the top of the drum, 5 micron peculator filter may be needed for turbo jet fuel.
4) **Vacuum Flashing :** Where difficulties might be met in the removal of water from high-boiling or viscous products by the previous methods, water may be removed by passing the product through a vessel at a sufficiently reduced pressure to cause the water to evaporates , it is used sometimes for the clarification of lubrication oil.

d) Improvement in Storage Stability

Owing to their complex composition and the presence of small amounts of N_2, S, organic acids, and oxygen, most petroleum products are subjected to deterioration in storage. This storage instability may be noticed by a darkening in color, the formation of gums, and in some cases a significant deterioration in those characteristics that control the performance of the products. Instability may be accompanied by a marked degree of corrosiveness due to the presence of organic and/ or inorganic acids.

Caustic Extraction

In addition to the use of caustic soda for the removal of acidic gases and malodorous compounds as described earlier , it is widely used for the removal of substances which cause instability and corrosion.



e) Improvement in Performance

The performance characteristics of products from primary refining processes are seldom in keeping with the demands of modern machinery and engines. It is therefore often necessary to subject the products to secondary refining processes to remove those compounds that have an adverse effect on performance.

Performance improvement processes

1) SO_2 Extraction : Liquid SO_2 is very selective solvent for removal of aromatic hydrocarbons . SO_2 treatment removes aromatics and some polar compounds, including sulfur , gum and color constituents , as well as olefins. The process is used in the manufacture of premium kerosene the removal of aromatics leads to better burning properties.

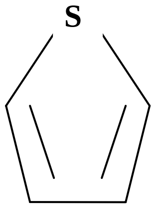
2) H_2SO_4 Treatment : This process is used for the removal of sulfur and thiophene from aromatic streams . It is less applicable now a days as other treating methods are available . This process may be applicable for the pretreatment of straight run naphtha that are to be reformed.

3) Hydrodesulphurization : Hydrodesulphurization is the most modern and effective processes for the removal of sulfur from oil products and for general improvement in the quality of refinery streams, including the pretreatment of catalytic reformer feed.

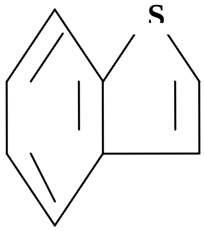
The process convert S to H_2S by reaction with hydrogen in the presence of catalyst. This process is used mainly for the processing of straight run and cracked medium and heavy distillates, while vapor phase hydro-treating is used for the processing of light distillates it operates at lower pressure.

Thiophen

Thiophen (XXII) and mono-methyl thiophens have been isolates from gasoline : alkyl-thiophens and benzo-hiophens (XXIII) have been isolates from kerosience. In gas oil range substituted thiophens, benzo-hiophens and higher polycyclic thiophens are present



(XXII)Thiophen



(XXII) Benzo thiophen

Two general methods of reducing the amount of sulfur have been developed, those which involve

1) solvent extraction of the sulfur compounds and

2) those by which most of the sulfur compounds are decomposed by the use of a catalyst into hydrogen sulfide and the remaining hydrocarbon part of the molecule. The solvent extraction processes are not cheap or effective as the catalytic processes in the removal of sulfur because they remove the entire sulfur bearing molecule and at the same time certain hydrocarbons , particularly those with aromatic rings.

This when the removal of aromatic hydrocarbons as well as sulfur is desirable , the solvent process may be superior.

H_2SO_4 , HF are an effective solvent, but SO_2 and furfural are more frequently used. The solvent process tends to raise the pour point and moderately improve the Diesel Index, but the catalytic processes of desulphurization do not materially affect either of these properties. Yields by the catalytic processes may exceed 100% especially if outside hydrogen is used.

By the addition of H_2 from outside sources more vigorous reaction (decomposition) and hydrogenation can be undertaken, and in the extreme, whole crude oils and residues can be desulphurization.

Desulphurization is a mild selective hydrogenation, so mild that aromatic are not usually hydrogenation to naphthenes. Sulfur is removed as H_2S and the remaining part of the molecule is hydrogenated.

Mild decomposition result in an evolution of hydrogen which can be recycled for hydrogenation reactions but if higher boiling or refractory stocks are being treated, extra H_2 must be introduced from outside sources to maintain a higher concentration of hydrogen during the reaction. The decomposition leads to products of slightly lower boiling range than that of the parent material slightly API gravities.

Efficiency of desulphurization depends upon the charge stock and severity of treatment, ranging from as low as 50 to 60 % for mild operation to 80 to 99 % and 95 to 98% is not uncommon.

Treating Equipment

The mechanical operations involved in treating are primarily those of ***mixing*** or ***contacting*** and ***settling*** or ***separating***.

Contacting method :

The design of mixing columns is normally based on the pressure drop that is available for mixing. A total pressure drop of 30 psi is sufficient to give effective mixing.

Among the type of mixers are ***square-angle bends***, ***orifice-plate***, ***baffle plate columns perforated buckets***, ***various mechanical mixers operated by motors***, ***jet and nozzle mixer*** and ***pumps***.

Orifice Column : is widely used for mixing

$$Q = 17.8 * D^2 * \sqrt{\Delta h}$$

Q= volumetric flow rate Bbl per hr
D= diameter of orifice hole, in
Δh= pressure drop across one plate, ft liquid

In general , the ratio of pipe area to the total orifice area may range from 3 to 10 .
The feet of liquid may be converted to pounds per square inch by

$$Psi = (\text{ft of fluid}) * (Spg) * (0.433)$$

Or

$$Psi = \frac{\text{Ft of fluid}}{2.148 + 0.01623\,(API)}$$

Example : Acid is to be mixed with 8000 Bbl per day of 53 API pressure distillate. A pressure drop of 25 psi is permissible. If pressure drop across one plate is 5.5 ft liquid, design the orifice mixer.

Given that the pipe area= 3 – 10 orifice area.

Solution:

$$\text{Bbl per hr} = \frac{8000 \text{ Bbl / day}}{24 \text{ hr/day}} = 334$$

$$\text{Bbl per hr} = 17.8 * D^2 * \sqrt{\Delta h}$$

$$334 = 17.8\, D^2 \quad \sqrt{5.5}$$

D = 2.83 in diameter of orifice hole

$$A = \frac{\pi}{4} D^2 = \frac{\pi}{4} (2.83)^2 = 6.3\ \text{in}^2$$

if 7/8 in holes is used how many holes required per plate

$$\underset{\text{per plate}}{\Delta\ \text{psi}} = \frac{\text{ft of fluid}}{2.148 + 0.01623\ (\text{API})}$$

$$= \frac{5.5}{2.148 + 0.01623 * (53)} = 1.83$$

$$\text{No. of plates} = \frac{25}{1.83} = 14\ \text{plates}$$

for 1 ft spacing, H = 16 ft

pipe area= 3 – 10 orifice area

pipe area = 5*6.3 = 31.5 in ^{2}

pipe diameter = 6.3 in

use standard pipe of 6 in with A= 28.9 in^2 , use clearance of 1/16 in

12 7/8 in holes total opening = 7.64 in ^{2}

Settlers or Separators : In general caustic and water mixtures are rapidly settles, 10-30 minutes are used as settling time. The settlers are usually 40 ft high and 2- 10 ft diameter. The velocity of the fluid in the settler should not exceed about 3 ft/ min. Stockes law governs the rate of settling.

Example : Design a settler to handle the separation of caustic from 12000 bbl of oil per day.

Solution:

Assume 30 min settling time

H= 40 ft

$$\text{Volume of oil per hr} = \frac{12000 * 42}{24 * 7.5}$$

$$= 2800\ \text{ft}^3$$

$$\frac{2800}{2} = 1400\ \text{ft}^3 \text{ handled in 30 min}$$

$$A = \frac{1400}{40} = 35\ \text{ft}^2$$

D = 6 ft = 10 in

If 40 ft tank are not convenient, use two 20 ft tanks connected in series

$$v = \frac{gD^2(\rho_s - \rho_l)}{18\mu}$$

Upgrading Processes

<u>Thermal cracking:</u> 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.

1) Coking

Coking are severe cracking operations designed to completely convert residual products such as pitch or tar into gas, naphtha, heating oil, gas oil, and coke.

The gas oil fraction represents the major product obtained used as a feed stock for catalytic cracking units. The C_5-220 °C naphtha may be used as a gasoline blending agent, although its octane no. quality from 65 to 80 RON (unleaded), is lower than the desirable, the coke is usually used as fuel.

After something like a ten year gap, there has been a renewed interest in coking; key reasons are the diminishing relative demand for fuel oils and the increasing concentration on reducing atmospheric pollution. For the later coking not only concentrated feed stock sulfur in the coke but yields products which can be readily desulfurized.

<u>The main uses of petroleum coke are as follows:</u>

1. Fuel
2. Manufacture of anodes 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, calcium carbide, and silicon carbide
5. Manufacture of graphite

<u>The major coking processes in use today:</u>

<u>1) Delayed Coking :</u> A semi- continuous process in which the heated charge is transferred to large soaking (or coking) drums which provide the long residence time needed to allow the cracking reactions to proceed to completion, the feed to these units is normally an atmospheric residue, although cracked tars and heavy catalytic cycle oils may be also used.

<u>Process Description — Delayed Coking</u>

Hot fresh liquid feed is charged to the fractionator two to four trays above the bottom vapor zone. This accomplishes the following:

1. The hot vapors from the coke drum are quenched by the cooler feed liquid thus preventing any significant amount of coke formation in the fractionator and simultaneously condensing a portion of the heavy ends which are recycled.
2. Any remaining material lighter than the desired coke drum feed is stripped (vaporized) from the fresh liquid feed.
3. The fresh feed liquid is further preheated making the process more energy efficient.

Vapors from the top of the coke drum return to the base of the fractionator.

These vapors consist of steam and the products of the thermal cracking reaction: gas, naphtha, and gas oils.

.

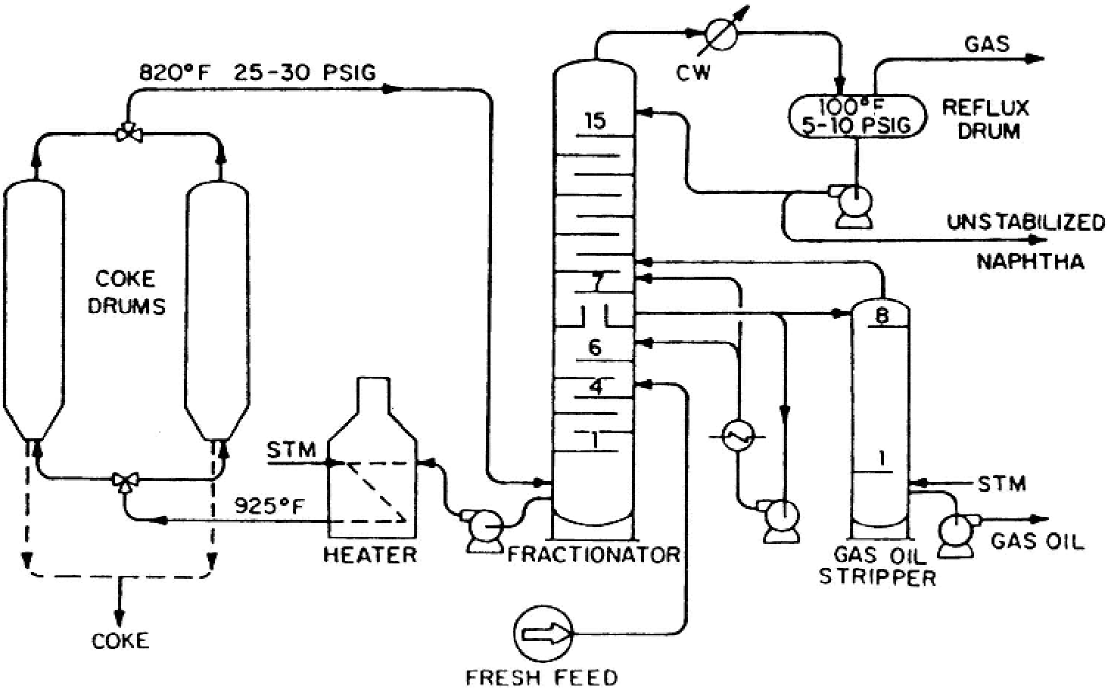


Fig 1: Delayed coking unit (From Gary and Handwerk, 2001)

2) Fluid Coking : 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; steam is used for fluidizing the bed.

Coke & liquid yields may be estimated by simple equations

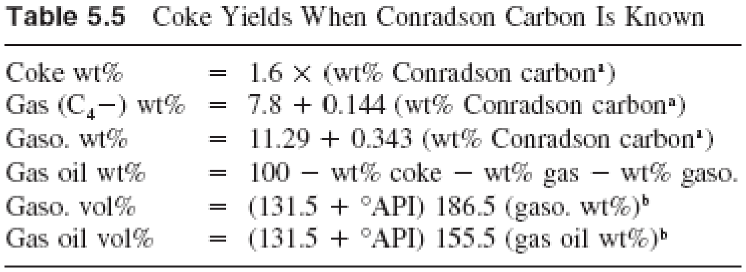


Table 5.5 Coke Yields When Conradson Carbon Is Known

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

Conradson carbon: A test used to determine the amount of carbon residue left after the evaporation and pyrolysis of an oil under specified conditions. Expressed as weight percent; ASTM D-189.

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	lb/ hr	wt% S	lb/hr S
			(348.56)			
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

H.W (1)

Feed RC of an 35.6 API gravity, C.O having 28.3 vol. % residuum with 8.4 % Conrad- son and 15.9 API, capacity 10000 BPD C.o. of 2.7 % Conrad son.

2) Visberaking

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 or to 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.

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 ^oF some cracking of naphthene rings.

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.

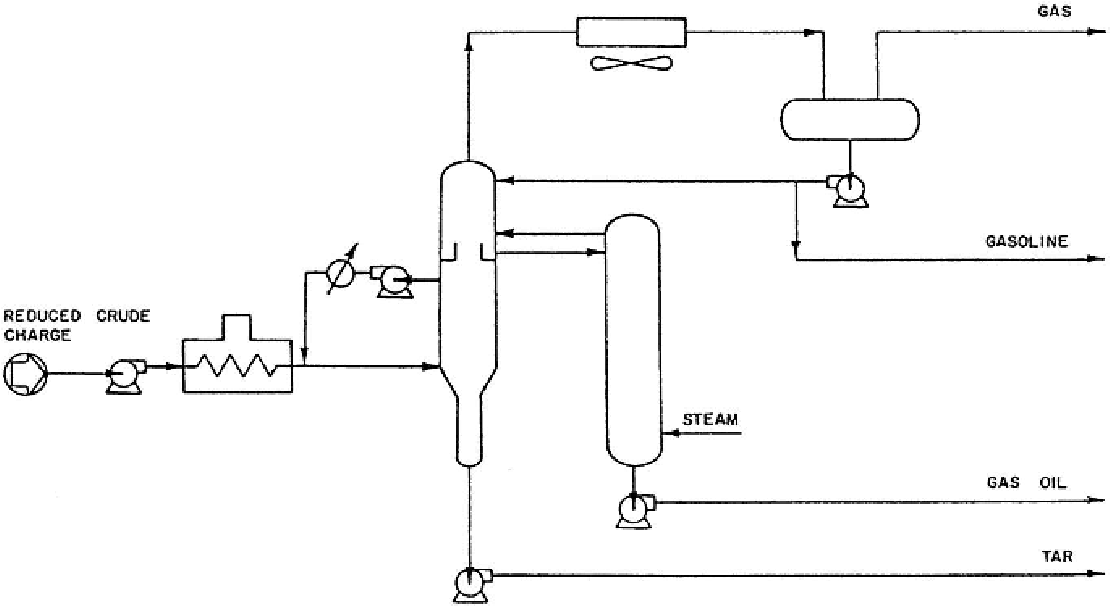


Fig 2 :Coil visbreaker (From Gary and Handwerk, 2001)

Catalytic Cracking

It has been the most important and widely used process for the production of gasoline from heavy distillates and hence the major means for increasing the ratio of light to heavy products from crude oil. **The catalytic-cracking processes in use today can all be classified as either moving-bed or fluidized-bed units:**

1) Moving Bed: In which the catalyst was allowed to fall slowly by gravity through the reactor and a regenerator vessels and was returned mechanically to the top.

2) Fluidized Bed: Is based on the fluidization propertied of fine powders, which enabled the catalyst to be transported continuously between the reactor and regenerator.

The fluidized system has been more widely used than the moving bed and now represents about 80 % of all cracking plants.

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.

Acid treated clays ground to a powder

Synthetic silica- alumina catalysts of higher activity (amorphous)

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.

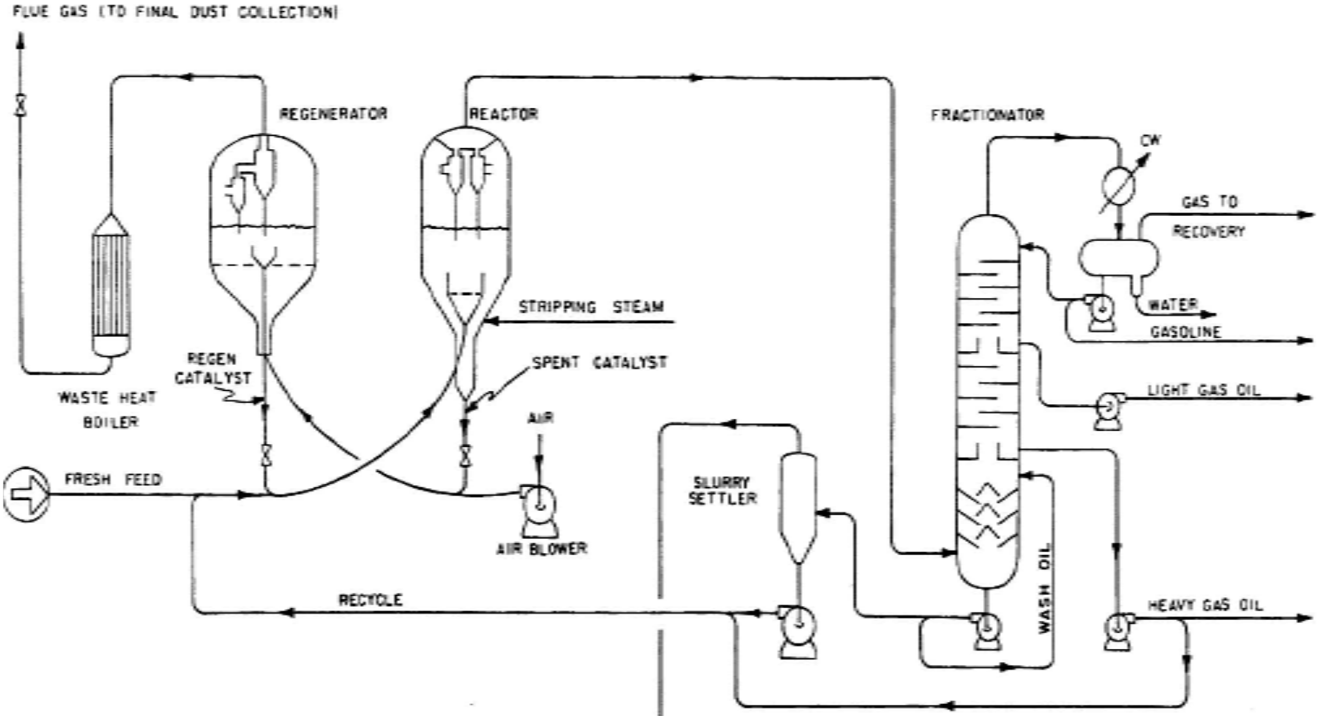


Fig 3: FCC unit (From Gary and Handwerk, 2001)

Catalytic Reforming

It is mainly used for the production of high- octane number hydrocarbons. In catalytic reforming the change in the boiling point of the feed stock passed through the unit is relatively small as the HC molecules are not cracked but their structures are rearranged to form higher octane aromatics. Thus catalytic reforming primarily increases the octane number of motor gasoline rather than increasing its yield. Typical feed stock is HSR gasoline and naphtha (180 to 375 ^{o}F).

<u>(PONA)</u> {Paraffin, Olefin, N**aphthene, 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.

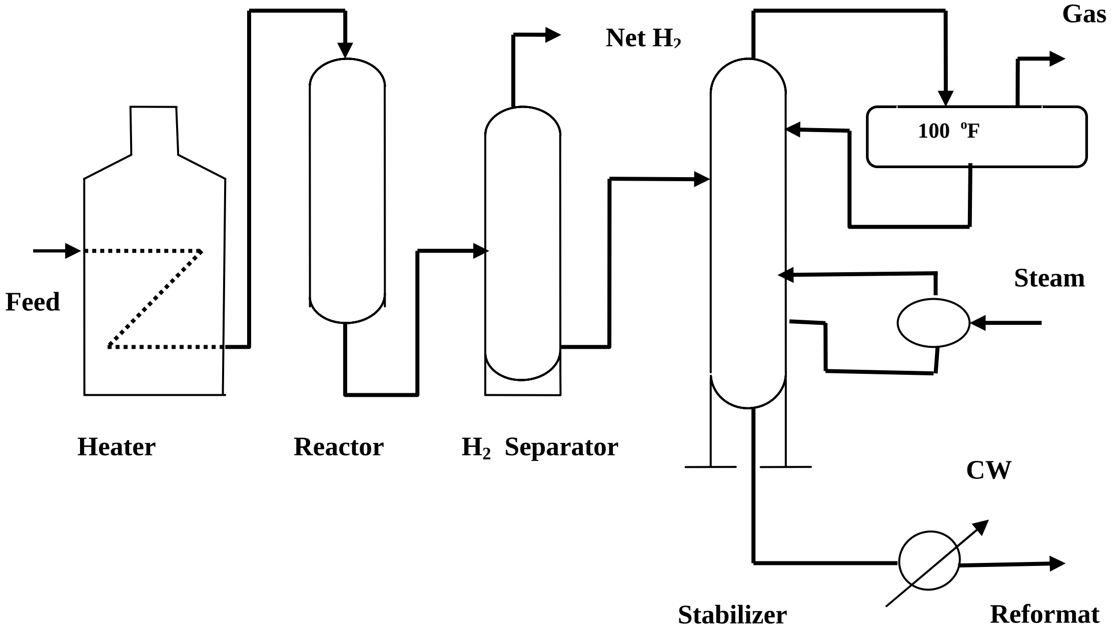
<u>Reforming are classified as :</u>

1) <u>Continuous :</u> Catalyst can be regenerated continuously and maintained at a high activity . ***(Higher capital cost)***.

2) <u>Semi- regeneration:</u> Regeneration is required at intervals 3 to 24 months depending on the severity of operation. ***(Low capital cost)***.

High H_2 recycle rates and operating pressure is utilized to minimize coke.

3) <u>Cyclic:</u> compromise between the two extremes having a swing reactor for regeneration.



Catalytic Reforming, semi- regeneration

<u>Reforming Catalyst :</u> 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.

Selectivity: The difference between the RON and MON of a given gasoline. Alkylate is an excellent low sensitivity and reformat a high sensitivity gasoline component.
Severity: The degree of intensity of the operating conditions of a process unit.

$$\text{Severity} = \frac{\text{(Cat. / oil) ratio (lb/lb)}}{\text{Space velocity}}$$

$$\text{Space velocity} = \frac{\text{lb oil /hr}}{\text{lb cat.}}$$

Space velocity: The volume or weight of gas and / or liquid passing through a given catalyst or reactor space per unit time, divided by the volume or (weight) of catalyst through which the fluid passes. High space velocity corresponds to short reaction time.
WHSV: Weight hour space velocity = weight of feed per hour per weight of catalyst.
LHSV: Liquid hour space velocity = volume of feed per hour per volume of catalyst.
Example (2):
Calculate the length of time between regeneration of catalyst in a reformer operation at the following conditions:
Liquid hourly space velocity (LHSV) = 3.0 v/hr/v
Feed rate = 5000 BPSD
Feed gravity = 55 API
Catalyst bulk density = 50 lb / ft^3
H_2 to feed ratio = 8000 scf /bbl (standard cubic feet, 14.7 psia, 60 ^oF)
No. of reactors = 3
Catalyst deactivates after processing 90 bbl 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 :
5000 BPSD = 5000 (bbl/day) * (day/ 24 hr) * (42 gal/bbl) * (0.13 ft^3/ 1 gal)
= 1170 ft^3/ hr

$$\text{LHSV} = \frac{\text{Oil volume /hr}}{\text{Catalyst volume}}$$

Total catalyst = 1170 / 3 =390 ft^3
Weight of catalyst = volume * density of catalyst
= 390 * 50 = 19500 lb catalyst

$$\text{Time between regeneration} = \frac{19500 \text{ lb}_{\text{catalyst}} * 90 \text{ bbl/ lb}_{\text{catalyst}}}{5000 \text{ bbl/day}} = 351 \text{ days}$$

Volume of catalyst per reactor = 390 / 3 =130 = 130 ft ^{3}
Inside area = 130 ft^3 / 6 ft
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
$m_{C5^+ \text{ gasoline}}$ = 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

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

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

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

$$D = \sqrt{\frac{4 * 21.17}{\Pi}} = 5.19 \text{ m}$$

$m_{catalyst}$ = 50000/0.7 = 71428 Kg
$V_{catalyst}$ = m/ ρ = 170 m^3

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

Alkylation or Polymerization

Propylene and butylenes can be polymerized to form a high-octane product boiling in the gasolineboiling range. The reactions involved are shown in Figure 5. In the first reaction two butylenesreact to form an octane. In the second reaction, two propylene molecules react to form a hexane.These reactions take place at 300-425°F and high pressures (400-1500 psi). The catalyst used is Phosphoric Acid on an inert support.

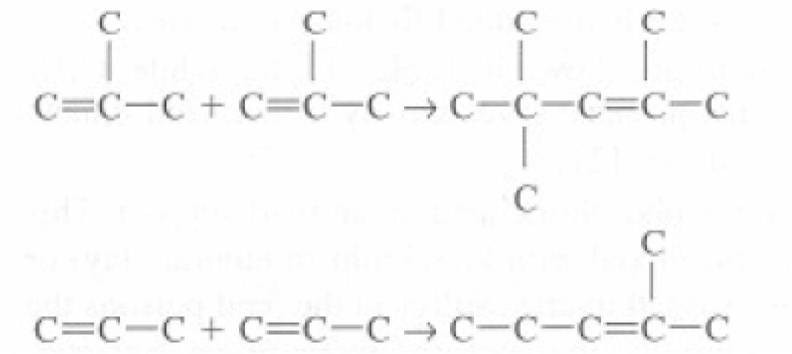


Figure 5: Polymerization reactions

Iso-merization

The rearrangement of ***straight chain*** HC molecules to form ***branched- chain*** products, pentanes and hexanes, which are difficult to reform, are iso-merized using aluminum chloride or precious metal catalyst to form gasoline- blending compounds of fairly high octane no.

The octane number of the LSR gasoline (C_5- 160 ^oF) can be improved by iso-merization to convert normal paraffins into their isomers. This results in a significant octane increase as n- pentane has an 61.7 RON and iso-pentane has 92.3 RON. In once through iso-merization the RON of LSR gasoline can be increased from 70 to about 82.

Reaction temperature of about 300-400 ^oF are preferred to higher temperature because the equilibrium conversion to isomers is enhanced at the lower temperature. Hence a very active catalyst is necessary to provide a reasonable reaction rate. Catalysts used contain platinum on various bases.

Process Variable

Activity: Ability to crack gas oil to lower boiling fractions.

Catalyst / oil ratio = C/ O = lb catalyst / lb feed.

$$\textbf{Conversion} = 100 * \left(\frac{\text{Volume of feed} - \text{Volume of cycle stock}}{\text{Volume of feed}} \right)$$

Cycle stock: portion of catalytic- cracker effluent not converted to naphtha and lighter products (generally the material boiling above 430 ^oF)

$$\textbf{Efficiency} = \left(\frac{\%\ \text{gasoline}}{\%\ \text{conversion}} \right) * 100$$

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 residence time in hours then

$$WHSV = \frac{1}{(t)} (C / O)$$

With in the limits of normal operation increasing:

1) **Reaction temperature.**
2) **C/O ratio**
3) **Catalyst activity.**
4) **Contact time.**

Results are an increase in conversion while a decrease in space velocity increases conversion. Increase in conversion does not necessarily mean an increase in gasoline yield, as an increase in temperature, above certain level can increase conversion coke and gas yields, and octane number of the gasoline but decrease gasoline yield.

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:

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

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:

$$ON_i = (MON_i + RON_i)/2 \qquad (2)$$

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 ^oF) with C_5 (193 ^oF) naphtha. The amount of n-butane required to give the needed RVP is calculated by

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

Where

M_t = total moles blended product

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

M_t = 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+52 M=21790 +10 M

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

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

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

$$A(VPBI)_a + B(VPBI)_b + C(VPBI)_c + \text{-------} + W(VPBI)_w = (Y+W)(VPBI)_m \qquad (5)$$

where

A= bbl of component a, etc

W= bbl of n- butane (w)

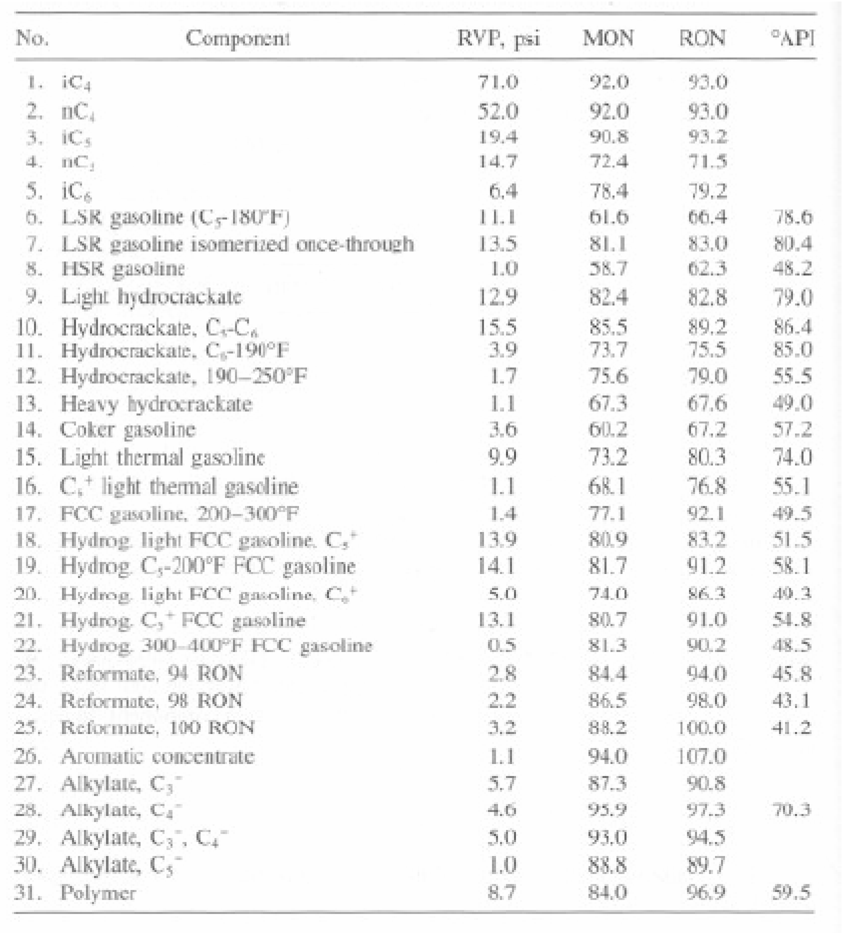
Y= A+B+C+ ----------- (all component except n- butane)

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

w= subscript indicating n- butane.

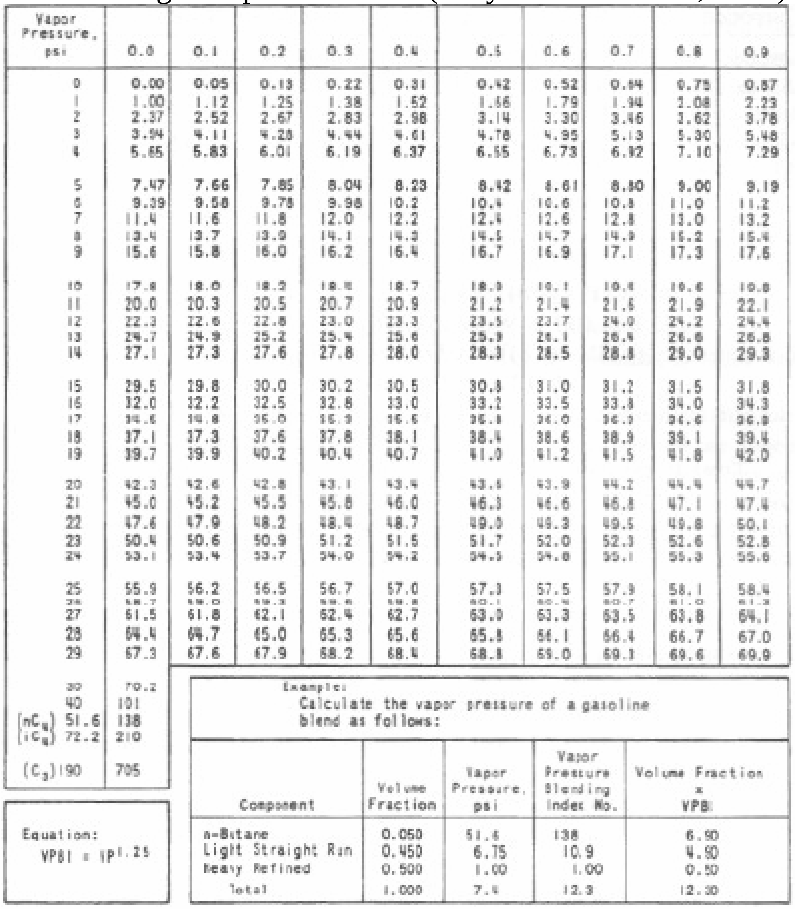
Table 11-1 and 11-2 show the blending component values for different blending streams and the blending indexes as a function of RVP values.

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_5^+ 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	18.2	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	29.8	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	35.5	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, $(VPBI)_m$ = 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)

Example (3): 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

Solution

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 :

1. Increase severity of reforming to produce a 98.8 to 100 RON clear reformate.
2. 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

$$P_t = \sum_{i=1}^{n} (v_i P_i) \qquad (7)$$

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

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, $(VPBI)_m$ = 17.6

Manufacturing of Lubricating Oils

The large number of natural lubricating and specialty oils today are produced by blending a small number of lubricating oil base stocks and additives.

The lube oil base stocks are prepared from selected crude oils by distillation and special processing to meet the desired qualifications. The additives are chemicals used to give the base stocks desirable characteristics which they lack or to enhance and improve existing properties.

The properties that considered important

1) Viscosity, 2) Viscosity index, 3) Pour point, 4) Oxidation resistance,
5) Flash point, 6) Boiling temperature, and 7) Acidity (Neutralization number)

Lubricating oil Processing

1) Separation of the individual fractions : according to viscosity and boiling range specifications in crude oil distillation units. The heavier lubricating oil row stocks are included in the vacuum fractionating tower bottoms with the asphaltenes resin, and other undesirable materials.

2) Removal of components which have undesirable characteristics

a) Reduce carbon- and sludge forming tendencies (***Solvent deasphalting***)
b) Improve viscosity index (***Solvent extractions + Hydrocracking***)
c) Lower Cloud and pour points (***Solvent De-waxing + Selective hydrocracking***)
d) Improve color and oxygen stability (***Hydrotreating***)
e) Lower organic acidity (***Hyrotreating***)

Although the main effects of the processes are as discussed, there are also secondary effects which are not shown . For example, ***although the main result of solvent dewaxing is the lowering of the cloud and pour points of the oil, solvent dewaxing also slightly reduces the viscosity index of the oil.***

For economic reasons as well as process ones, the process sequence is usually in the order of :1) deasphalting, 2) solvent extraction, 3) dewaxing, and 4)finishing.

Propane Deasphalting

The lighter feed stocks for producing lubricating oil stocks can be sent directly to the solvent extraction units.

The atmospheric and vacuum still residues require deasphalting to remove the asphaltenes and resins before undergoing solvent extraction.

In come cases highest boiling distillates also contain sufficient asphaltenes and resins and need deasphalting.

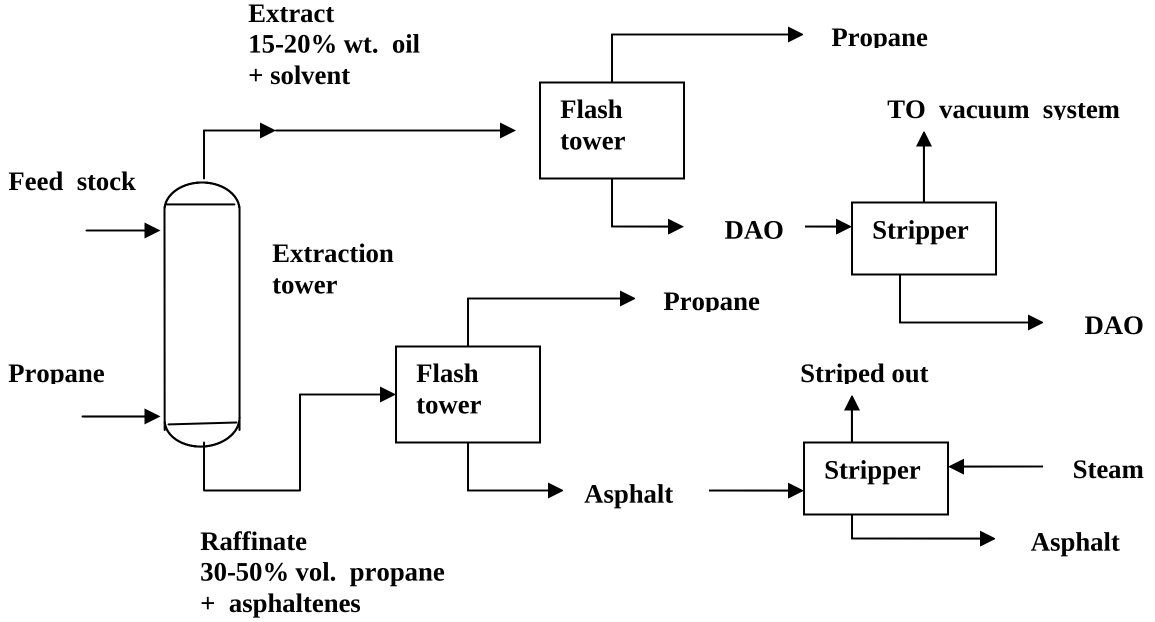
Propane : is usually used as the solvent in seasphalting but it may be used with ethane and butane in order to obtain the desired solvent properties.

(40- 60 ^{o}C) paraffins are very soluble in propane, the solubility decreases with increasing temperature, until the critical temperature (96.8 ^{o}C) all HC becomes insoluble.

(40 – 96.8 ^{o}C) the high molecular weight asphaltens and resins are largely insoluble in propane.

The feed stock is contacted with 4-8 volumes of liquid propane in a cylindrical tower, usually RDC (rotating disc contactor).

The asphalt recovered from the raffinate can be blended with other asphalts , into heavy fuels, or used as a feed to the coking unit. The heavy oil product from vacuum residuum is called ***bright stock***.



Propane deasphalting unit

Solvent Extraction

There are three solvents used for the ***extraction of aromatics*** from lubricating oil feed stocks and the solvent recovery portions of the system are different for each.

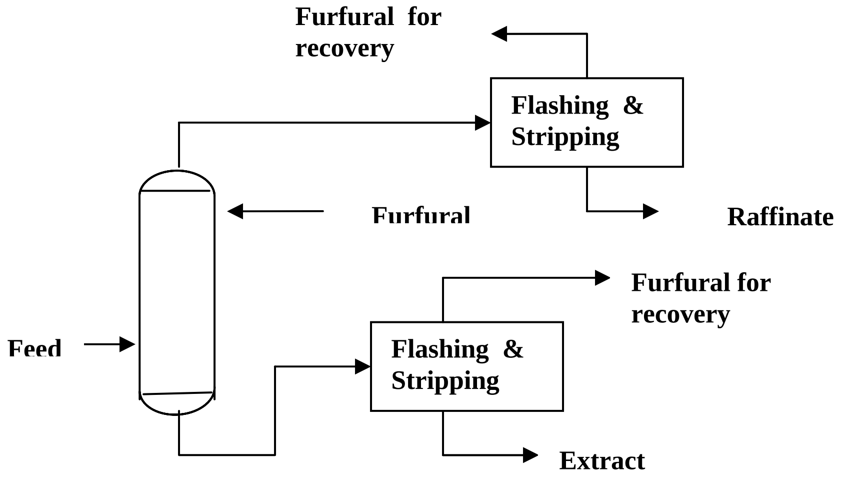
The solvents are : 1)Furfural, 2) phenol, 3) N- methyl 2- pyrrolidone (NMP).

The purpose of solvent extraction is :

1) Improve VI.
2) Improve oxidation resistance and color.
3) Reduce carbon and sludge forming tendencies of the lubricants by separating the aromatic portion from the naphthenic and paraffinice portion of the feed stock.

Furfural Extraction The most important operating variables are :

1) Furfural / oil ratio (F / O ratio) :It has the greatest effect on the quality and yield of the raffinate. Range 2:1 for light stocks to 4.5 : 1 for heavy stocks.
2) Extraction temperature : Is selected as a function of the viscosity of the oil and the miscibility temperature.
3) Extracted recycle ratio : Determines to some extent the rejection point for the oil and the sharpness of separation between the aromatics and naphthenes and paraffins.



Furfural Extraction Unit

Dewaxing

All the lubricating oil except those from a relatively naphthenic crude oils, must be dewaxed or they will not flow properly at ambient temperature. Dewaxing is one of the most important and most difficult processes in lubricating oil manufacturing.

There are two types of processes in use today :

1) Uses refrigeration to crystallize the wax and solvent to dilute the oil portion sufficiently to permit rapid filtration to separate the wax from the oil.
2) Uses selective hydrocracking process to crack the wax molecules to light HC.

<u>**Solvent dewaxing :**</u> The solvent used are

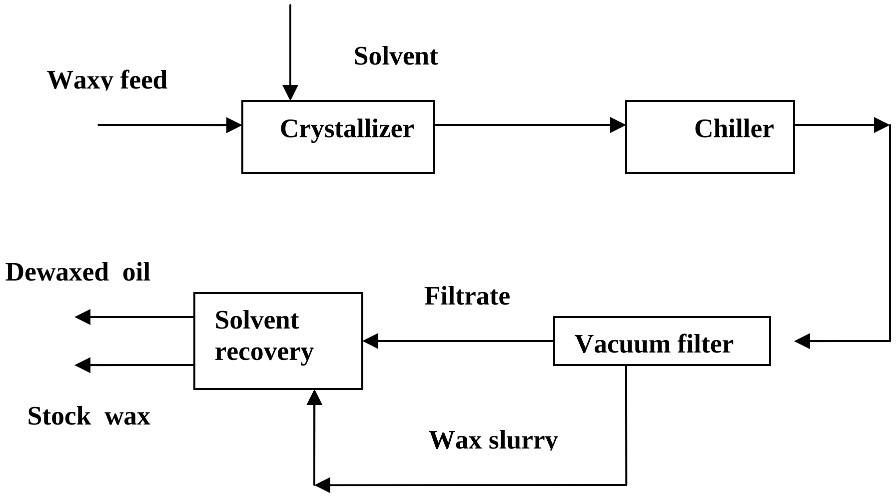
a) Propane

1) Readily available, less expensive and easier to recover
2) Direct chilling can be accomplished by vaporization of the solvent thus reducing the capital and maintenance costs of scraped- surface chiller.
3) High filtration rate can be obtained because of its low viscosity at very low temperature.
4) Requires use of a dewaxing aid.
5) Large difference between filtration temperature and pour point of finished oils (15 to 25 ^oC)

b) Ketone

1) Small differences between filtration temperature and pour point of dewaxing oil (5 to 10 ^oC).
2) Fast chilling rate.
3) Good filtration rate but lower than propane.

Lower pour point capability : Greater recovery of heat by heat exchanger lower refrigeration requirements.



Solvent Dewaxing Unit

The dewaxed oil next must go through a finishing step to improve its color and color stability.

The stock wax is used either for catalytic cracker feed or undergoes a de-oiling operation before sold as industrial wax.

Selective hydrocracking :

The feed to selective hydrocracking unit is solvent extracted oil from aromatic extraction units. The advantages over conventional solvent dewaxing unit

1) Production of very low pour and cloud oils from paraffinic stocks.
2) Lower capital investment.
3) Improved lubrication oils base stock yields.
4) A separate hydrofinishing operation is not necessary.

Hydrofinishing

This process is needed to remove chemically active compounds that affect the color stability of lubrication oils. Most hyderotreating operation use cobalt- molybdate catalysts. The removal of nitrogen compounds is a major requirement of the operation because it affect color, usually finished oil yields are approximately 98% of dewaxed oil feed.

Hydeotreating

Hydrotraeting: It is a relatively mild operation whose primary purpose is to saturate olefins and/ or reduce the sulfur and/ or nitrogen content (and not to change the boiling range) of the feed.

Hydrocracking : Processes whose primary purpose is to reduce the boiling range in which 100% of the feed is converted to product with boiling ranges lower than that of the feed.

Hydroteating and hydrocracking set the two ends of the spectrum and those processes with a substantial amount of sulfur and/ or nitrogen removal and a significant change in boiling range of the products versus the feed are called hydro- processing.

Hdrotreating is a process to catalytically stabilize petroleum products and/ or to remove objectionable from products or feeds stocks by reacting them with hydrogen.

Stabilization : Involves converting unsaturated hydrocarbons such as olefins and gum-forming unstable diolefines to paraffins, objectionable elements removed by hydrotreating include sulfur, nitrogen, oxygen , halides, and trace metals. Hydrotreating is applied to wide range of feeds stocks from ***naphtha*** to ***reduce crude*** . When the process is applied specifically for sulfur removal it is usually called ***hydrodesulfurization*** or ***HDS***.

1) The oil feed is mixed with hydrogen- rich gas either before or after it is preheated to the proper reactor inlet temperature, below 800 °F to minimize cracking in the presence of metal oxide catalyst.

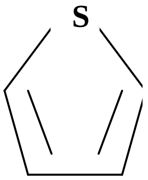
Reaction

1) Desulfurization

$RSH + H_2 \rightarrow RH + H_2S$
mercaptans

$R_2S + 2H_2 \rightarrow 2RH + H_2S$
sulfides

$(RS)_2 + 3H_2 \rightarrow 2RH + 2H_2S$
disulfides



$+ 4H_2 \longrightarrow C_4H_{10} + H_2S$

Thiophens

2) Denitrogenation

$C_4H_4NH + 4H_2 \rightarrow C_4H_{10} + NH_3$

Pyrrole

$C_5H_5N + 5H_2 \rightarrow C_5H_{12} + NH_3$

Pyridine

3) Deoxidation

$C_6H_5OH + H_2 \rightarrow C_6H_6 + H_2O$

Phenol

$C_7H_{13}00H + 3H_2 \rightarrow C_7H_{16} + 2H_2O$

Peroxides

4) Dehalogenation

$RCl + H_2 \rightarrow RH + HCl$

5) Hydrogenation

$C_5H_{10} + H_2 \rightarrow C_5H_{12}$

6) Hydrocracking

$C_{10}H_{22} \rightarrow C_4H_8 + C_6H_{14}$

Nitrogen removal requires more severe operating conditions than does desulfurization. The ease of desulfurization is dependent upon the type of compound. Lower boiling compounds are desulfurized more easily than higher boiling ones.