Chemical Composition of Petroleum

Petroleum, also known as crude oil, is a very complex mixture consisting of

- Paraffin,
- Naphthene (cyclo paraffin), and
- Aromatic hydrocarbon as well as
- Nitrogen-, oxygen-, sulfur-

containing compound and traces of a variety of metal-containing compounds, and inorganic compounds, over millennia.

The crude oil mixture is composed of the following groups:

1. Hydrocarbon compounds
2. Non-hydrocarbon compounds.
3. Organometallic compounds and
4. Inorganic salts (metallic compounds).

Chemical Composition

- Carbon 83.0 to 87.0%
- Hydrogen 10.0 to 14.0 %
- Sulphur 0.05 to 6.0 %
- Nitrogen 0.1 to 2.0 %
- Oxygen 0.05 to 1.5 %
- Metals 0.00 to 0.14 %

1. Hydrocarbon Compounds:

- The principal constituents of most crude oils are hydrocarbon compounds.
- All hydrocarbon classes are present in the crude mixture, except alkenes and alkynes.
- This may indicate that crude oils originated under a reducing atmosphere.

Alkanes (Paraffins)

Alkanes are saturated hydrocarbons having the general formula C_nH_{2n+2}.
The simplest alkane, methane (CH_4), is the principal constituent of natural gas. Methane, ethane, propane, and butane are gaseous hydrocarbons at ambient temperatures and atmospheric pressure. They are usually found associated with crude oils in a dissolved state.

. Normal alkanes (n-alkanes, n-paraffins) are straight chain hydrocarbons having no branches.
. Branched alkanes are saturated hydrocarbons with an alkyl substituent or a side branch from the main chain resulting in different isomers.

As the molecular weight of the hydrocarbon increases, the number of isomers also increases. Pentane (C_5C_{12}) has three isomers; hexane (C_6H_{14}) has five.

C_1-C_4 (Gases), C_5-C_{15} (Liquids) and C_{15}-C_{27} (Solids)

Cycloparaffins (Naphthenes).

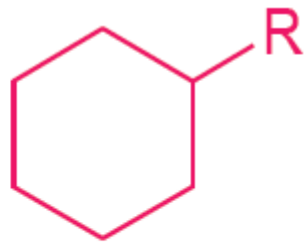
Saturated cyclic hydrocarbons, normally known as naphthenes, are also part of the hydrocarbon constituents of crude oils.

General Formula C_nH_{2n} for one ring compounds.

Cycloalkanes have similar properties to alkanes but have higher boiling points.

Cyclopentane

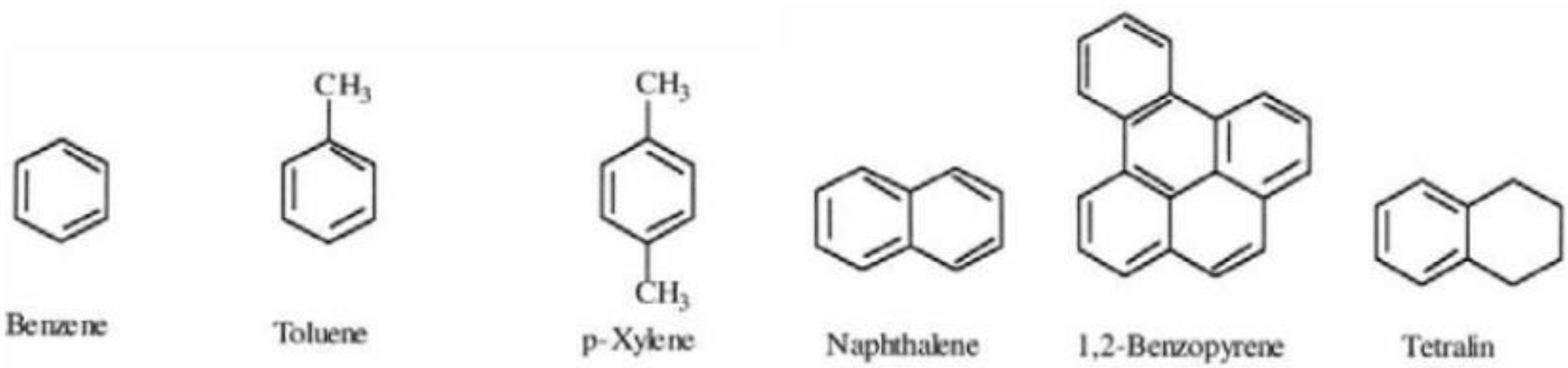
Cyclohexane



Alkylcyclohexane

Alkenes or Olefins
Unsaturated aliphatic hydrocarbon (e.g. ethylene or propylene) are rarely formed in crude oil, they are produced during cracking and conversion processes.

Aromatics hydrocarbon
(Cyclic and polyunsaturated hydrocarbons containing conjugated double bonds)
Alkyl aromatics have very high octane number.
Content in gasoline is limited by environmental regulations –health effects due to high toxicity.



The majority of crude oil is alkanes, cycloalkanes (naphthenes), aromatics, polycyclic aromatics, S-containing compounds, etc.

Gasoline: branched alkanes

Diesel: linear alkanes

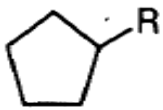
Alkanes

Normal $CH_3\text{-}CH_2\text{-}R$

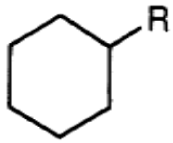
Branched $CH_3\text{-}CH_2\text{-}CH(CH_3)\text{-}R$

Cycloalkanes (Naphthenes)

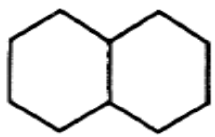
Alkylcyclopentanes



Alkylcyclohexanes

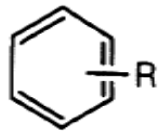


Bicycloalkanes

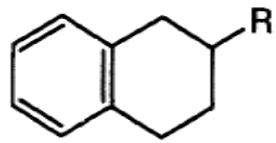


Aromatics

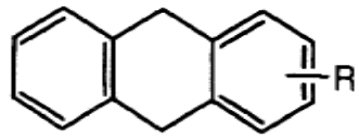
Alkylbenzenes



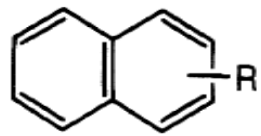
Aromatic-cycloalkanes



Fluorenes



Binuclear aromatics



Hetero Atom 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.

The presence of organic sulfur compounds, H_2S and elemental sulfur in petroleum can be accounted for in several ways. They might have formed by thermal reaction between elemental sulfur, or possibly H_2S, and the other organic components of the sediments including the hydrocarbons. These reactions may continue even after the oil has accumulated in the reservoir.

The crudes which contain more than 1% of sulfur are known as high sulfur bearing crudes (sour crude), but those that contain less than 1% sulfur are known as low sulfur bearing crudes (sweet crude).

Sulphur Compounds

Thiols

Sulphides

Cyclic sulphides

Disulphides

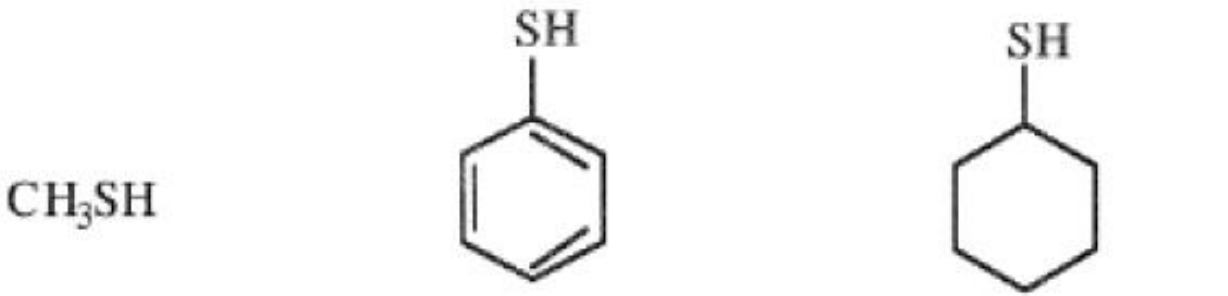
Thiophenes

Benzothiophenes

Dibenzothiophenes

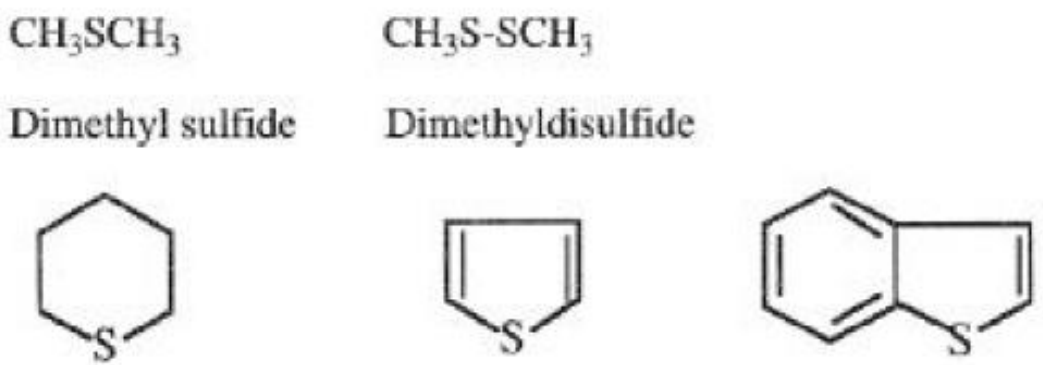
Naphthobenzothiophenes

Acidic Sulfur Compounds



Methyl mercaptan | Phenyl mercaptan | Cyclohexylthiol

Non-acidic Sulfur Compounds



Dimethyl sulfide | Dimethyldisulfide

Thiocyclohexane | Thiophene | Benzothiophene

Sour crudes contain a high percentage of hydrogen sulfide. Because many organic sulfur compounds are not thermally stable, hydrogen sulfide is often produced during crude processing.

Effect of Sulphur Compounds

- Great environmental concern, contribute to particulate matter, emission of obnoxious odoured sulphur oxide gases
- High-sulfur crudes are less desirable because treating the different refinery streams for acidic hydrogen sulfide increases production costs.
- Refining & Technology Focus shifted to sulphur removal from all petroleum products

Oxygen compounds

Oxygen compounds in crude oils are more complex than the sulfur types. However, their presence in petroleum streams is not poisonous to processing catalysts.

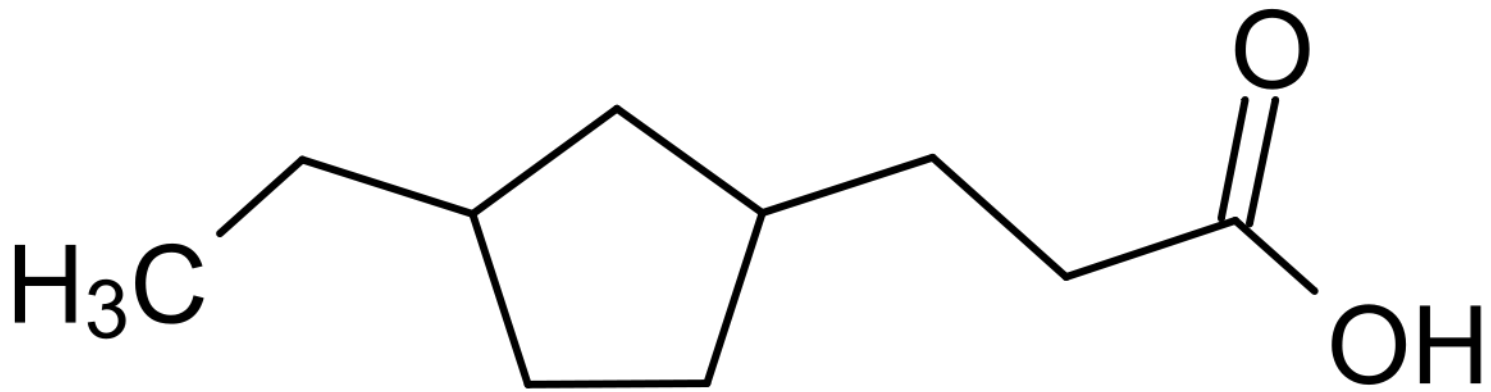
Many of the oxygen compounds found in crude oils are weakly acidic.

They are carboxylic acids, cresylic acid, and phenol.

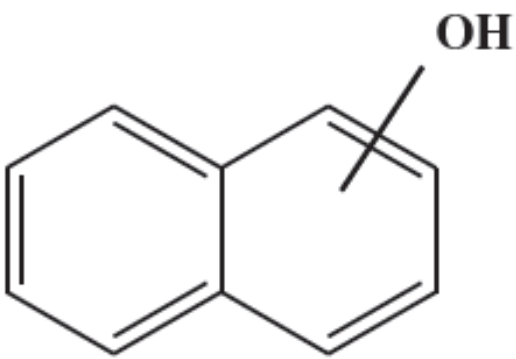
Naphthenic acids are cyclohexane or cyclopentane derivatives having a carboxy alkyl side chain.

Naphthenic acids in the naphtha fraction have a special commercial importance and can be extracted by using dilute caustic solution.

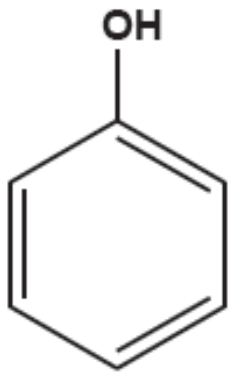
The total acid content of most crudes is generally low, but many reach as much as 3%, as in some California crudes.



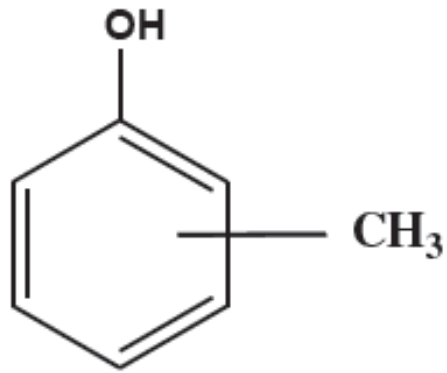
Naphthenic Acid



Naphthols



Phenol



Creasols

Oxygen compounds

- Alcohols/Ether/Cyclic ether/furan
- Carboxylic acids
- Naphthenic acids

  American crude oils : 0.006 to 0.35%wt

  Russian crudes oils : 0.2 to 1.05 %wt

  North Gujarat crude oil : 0.2%wt

- Increasingly High TAN Crude is being processed. Fractions that are rich in naphthenic acids can cause corrosion damage to oil refinery equipment; the phenomenon of naphthenic acid corrosion (NAC) has therefore been well researched. Crude oils with a high content of naphthenic acids are often referred to as high total acid number (TAN) crude oils or high acid crude oil (HAC).

Nitrogen Compounds

Pyrrole
Indole
Carbozole
Benzocarbozole

Pyridine
Quinoline
Indoline
Benzoquinoline

Effect:

Catalysts poison & Nitrogen oxide emission

Metals

- Present as inorganic salts & organic porphyrins (Ni, V, Mg etc.) in ppm
- Salts mostly removed in desalting operation
- Ni & V porphyrins are catalyst poisons

Crude Oil Characterization

- TRADING : Density, API Gravity
- TRANSPORTATION RVP, Pour Point, KV, Wax content
- CONTAMINATION: Salt content, BS&W
- PROCESSABILITY : Sulfur, Nitrogen, TAN, Asphaltene
- CRACKING POINT : ASTM Distillation
- LPG POTENTIAL : Light hydrocarbons (GC)
- CLASSIFICATION : Characterization factor

Classification of Crude Oil

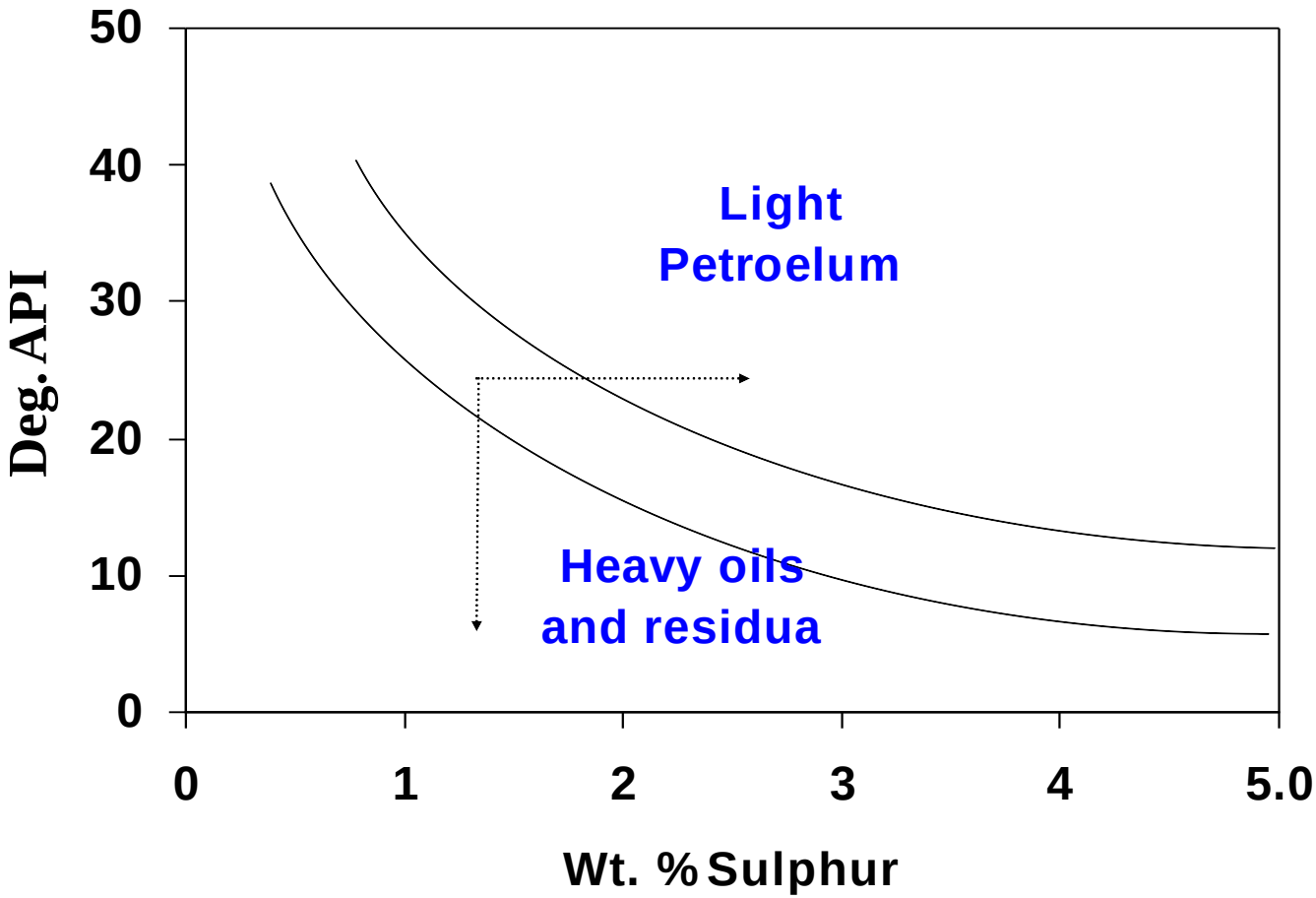
API Gravity

API = (141.5/sp.gravity)-131.5

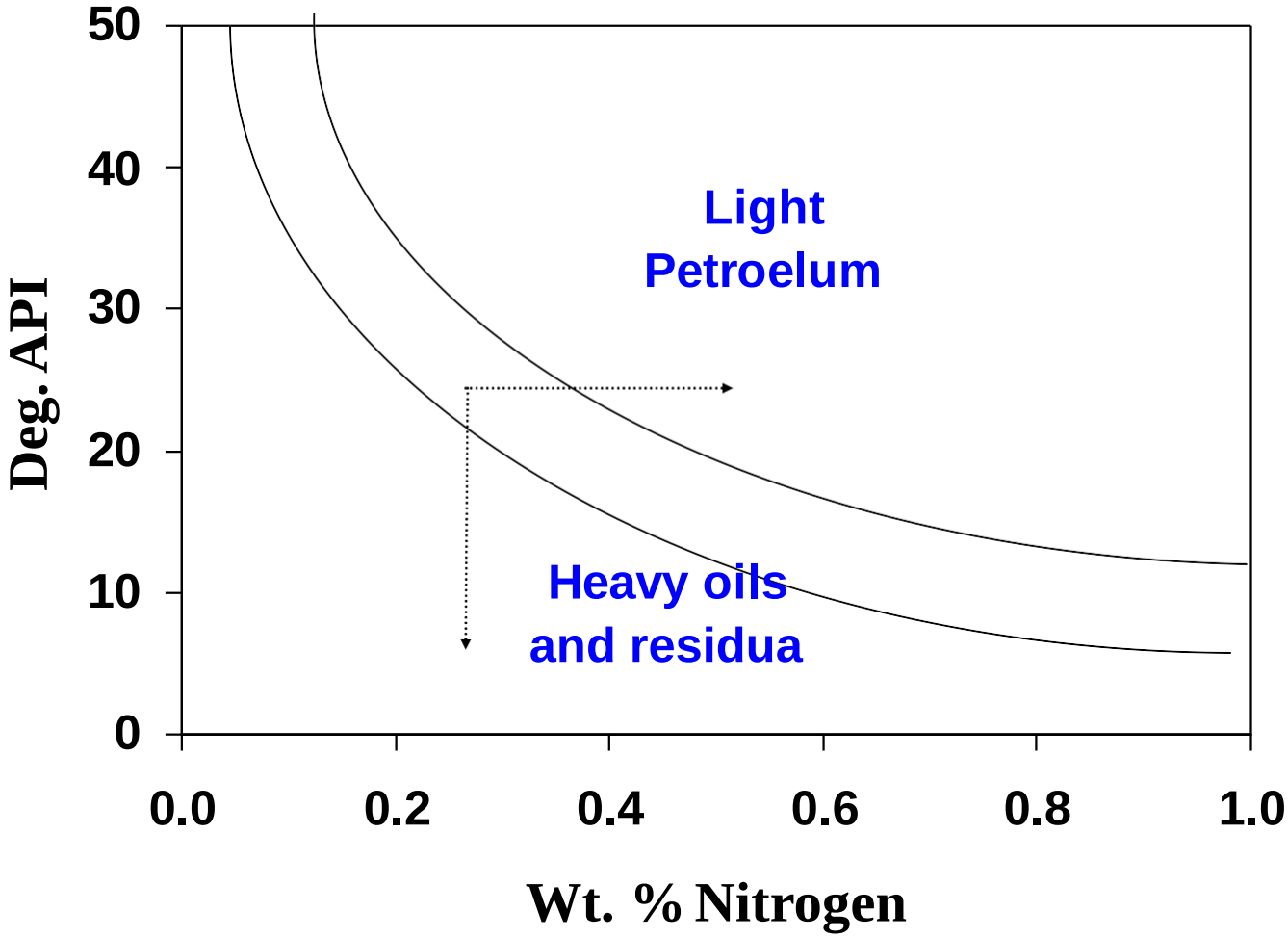
Light Crude Oil	>31
Mixed Based	22-31
Heavy crude	<22

API is a major factor for Crude pricing

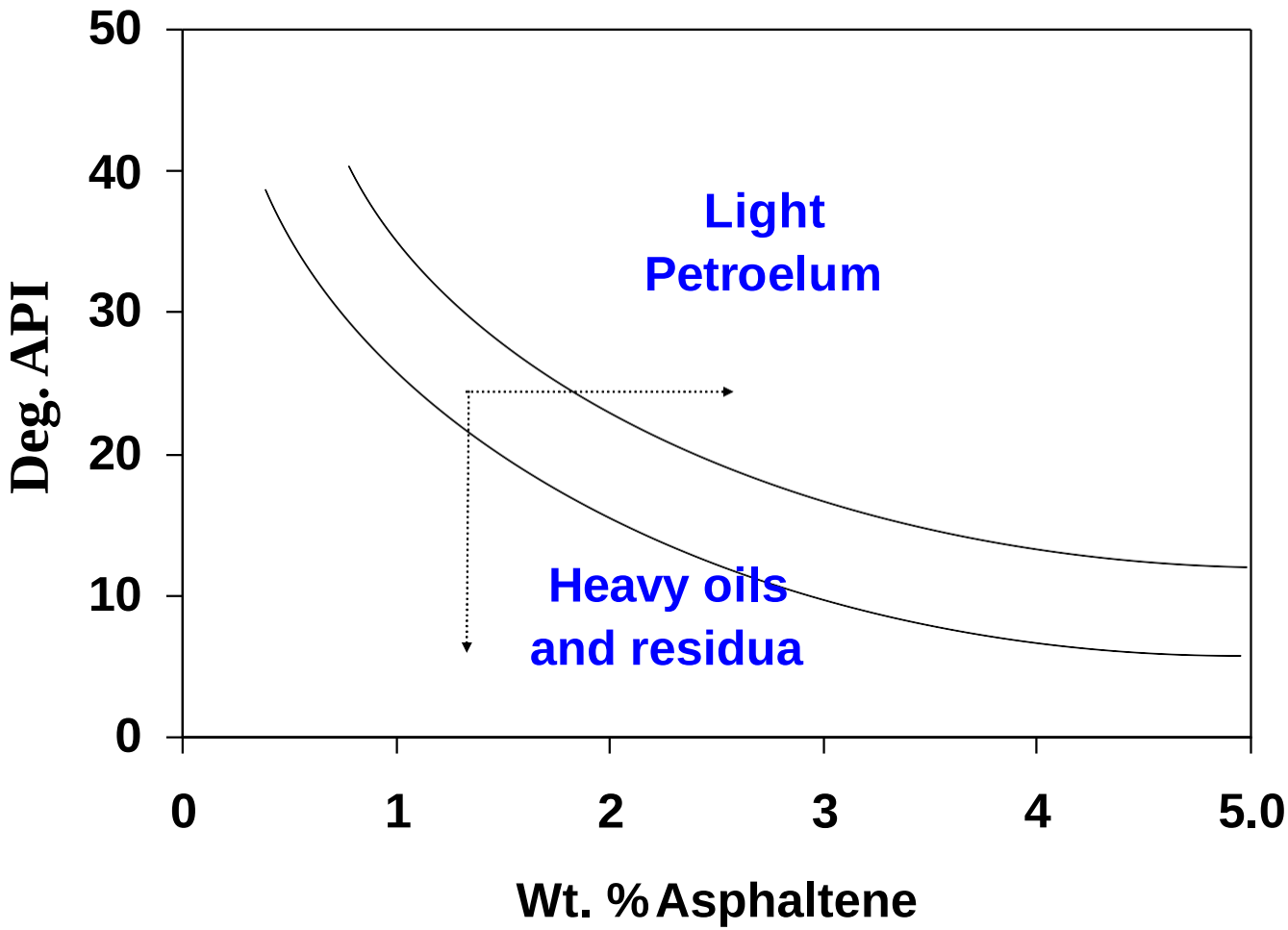
API & Sulphur


50
40
30
20
10
0
Deg. API
Light
Petroelum
Heavy oils
and residua
0
1
2
3
4
5.0
Wt. % Sulphur

API & Nitrogen



API & Asphaltene



Hydrocarbon Classification

- PARAFFINIC BASE

  WAXY, LESS ASPHALTIC, LOW SULPHUR, HIGH POUR

- NAPHTHENIC BASE

  NAPHTHENIC BASE STOCKS, LESS WAX, LESS ASPHALTIC, LOW POUR

- ASPHALTIC BASE

  HIGH SULPHUR, NITROGEN, SUITABLE FOR BASE OILS

Hydrocarbon Classification

UOP Characterization factor

K_{UOP} : Cube root of average boiling point(R) divided by specific gravity

- Paraffinic : >12.1
- Mixed based : 12.1 - 11.5
- Naphthenic :<11.5

Types of Crudes-Imported

- Low Sulphur Crudes
- High sulfur Crudes
  - Lube & Bitumen producing
    - Suitable for Lube producing refineries.
  - Non Lube Producing & Bitumen Producing
    - Suitable during Non Monsoon periods when Bitumen demand takes place
  - Non Lube / Non Bituminous
    - Suitable during Monsoon period when Bitumen production is not required.

World Crude Oil Quality

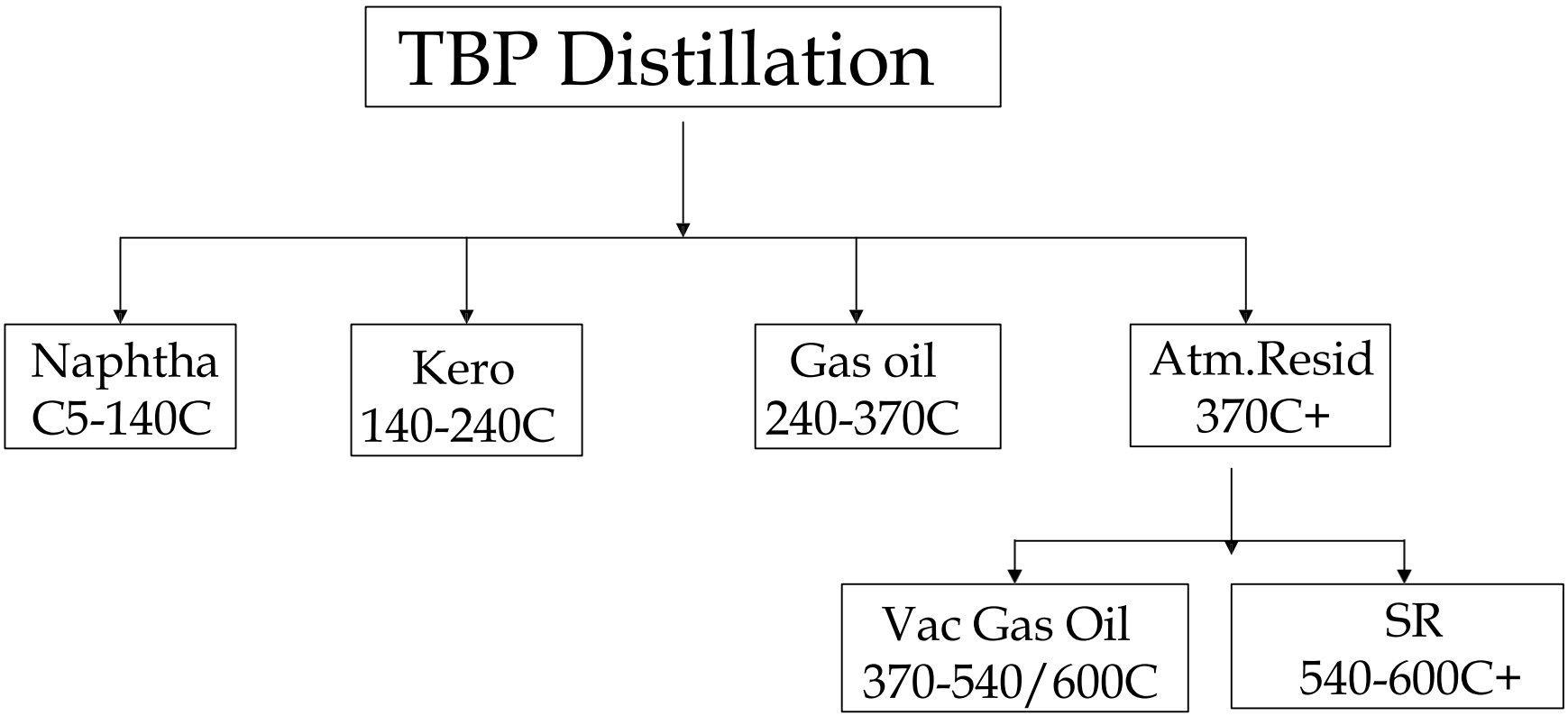
Properties of Crude Oil	**1985**	**1990**	**1995**	**2001**	**2010** (Proj)
'S' in crude Oil (wt%)	1.14	1.12	1.31	1.41	1.51
API Gravity of Crude oil	32.7	32.6	32.4	32.2	31.8
Metal in crude oil Residue (ppm wt)	275	286	297	309	320
Residue in crude (vol%)	19	19.4	19.8	20.2	21.3
'S' in crude oil residue (wt%)	3.07	3.26	3.61	3.91	4.0

Crude Oil Assay

- Crude assay is a detailed report which describes the properties of the whole crude, as well as the major fractions into which a crude is distilled at the refinery - gasoline, naphtha, kerosene, jet fuel, middle distillates, gas oils and resid

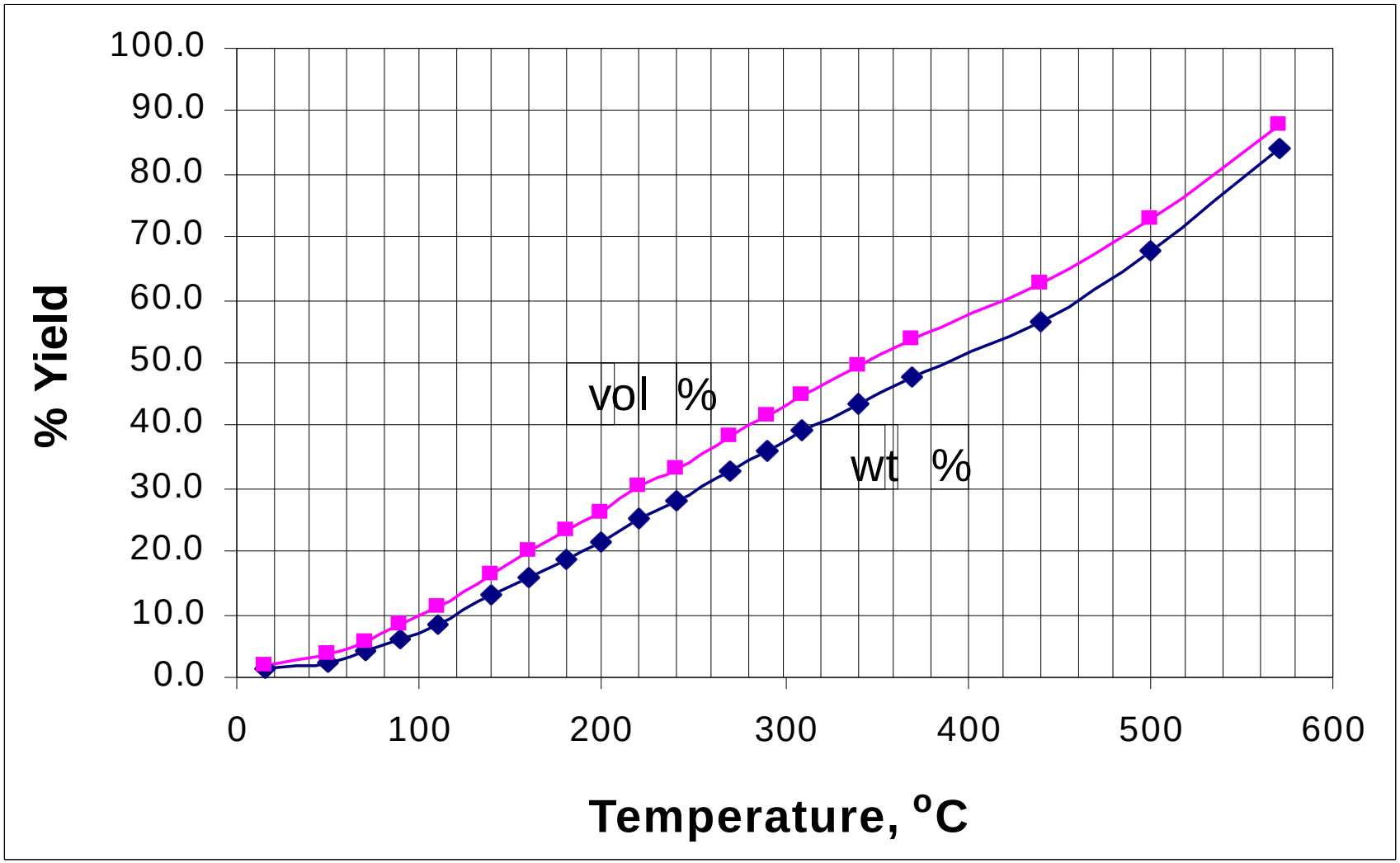
- Typically, the data contained in a crude assay includes yields generated from the physical distillation & distillate/residue properties

Crude Oil Evaluation Scheme



ALL TESTS ARE CONDUCTED AS PER STANDARD TEST METHODS : ASTM/IP/IS

Combined TBP curves of Basrah Light Crude oil



Properties of Crude oil

Characteristics	Basrah Light	Bombay High	Arab mix	Kuwait	North Gujarat
Density, gm/ml	0.8745	0.8200	0.8664	0.8741	0.8932
API gravity	30.3	41.0	31.6	30.3	26.8
Pour point, ^{o}C	-30	21	-24	-27	27
Kinematic Viscosity					
@40 ^{o}C	-	3.4	10.0	11.1	65.6
@50 ^{o}C	-	-	8.9	8.5	31.4
Water content, %wt	nil	nil	nil	nil	4.1
Salt content, ptb	10	-	L20	2.0	200
Sulphur, %wt	3.1	0.09	2.7	2.8	0.08
TAN, mgKOH/gm	-	0.1	0.14	0.14	1.93
CCR, %wt	5.9	1.1	6.4	5.4	2.5
Wax, %wt	1.2	12.7	2.5	6.0	5.9
Asphaltene, %wt	2.6	0.25	2.3	2.5	0.05
ASTMDistillation cracking point, ^{o}C	339	372	322	335	367
Metal content, ppm Nickel/vanadium	-	-	4/23	4/33	61/L10

Laboratory Distillation

- ASTM D86
- ASTM D1160
- TBP Distillation –ASTM D2892
- High vacuum Distillation, ASTM D5236
- Simulated Distillations based on gas chromatography principle

Test methods- Density

- Density is defined as the mass per unit volume of a substance. (Units:g/mL or g/cm^3 or kg/m^3). Density is temperature-dependent.
- Density is measured using an Anton Parr DMA 48/Kyoto digital density meter, and following ASTM method D 5002 - Density and Relative Density of Crude Oils by Digital Density Analyzer (ASTM, 1996a).
- Density of crude oils : 0.83 to 0.90 g/ml. Densities can be measured to 0.0001 g/ml with a repeatability of "0.0005 g/ml.

API Gravity

API Gravity

API =(141.5/sp.gravity)-131.5

- Light Crude Oil >31
- Mixed Based 22-31
- Heavy crude <22

API is a major factor for Crude pricing

BS&W

- Base sediments and Water determined by Karl Fischer titration using a Met Rohm 701 KF Automatic Titrator (ASTM D 4377) or by Distillation method, ASTM D4006

- Oils with significant water contents, (>5%), do not represent the properties of the "dry" oil.

- For 0.1%vol change, the cost implication

  For 10 MMT purchase at ~$420/MT

  US$420/MT x (0.1/100)x10 MMT

  ~US$4.20 million

Flash Point

- There are several ASTM methods for measuring flash points. The minimum flash point that can be determined by method D93/IP34 is 10^{o}C. Method D 56 is intended for liquids with a viscosity less than 9.5 cSt at 25^{o}C. The flash points and fire points of lubricating oils can be determined by ASTM method D 92/IP 36

- Many fresh crude oils have flash points below 10^{o}C and/or viscosities above 9.5 cSt at 25^{o}C

Pour Point

- The pour point of an oil is the lowest temperature at which the oil will just flow, under standard test conditions. The pour point of the oils is therefore an indication, and not an exact measure, of the temperature at which flow ceases.

- ASTM method D 97 - Standard Test Method for Pour Point of Petroleum Oils (ASTM, 1996a) for pour point determinations.

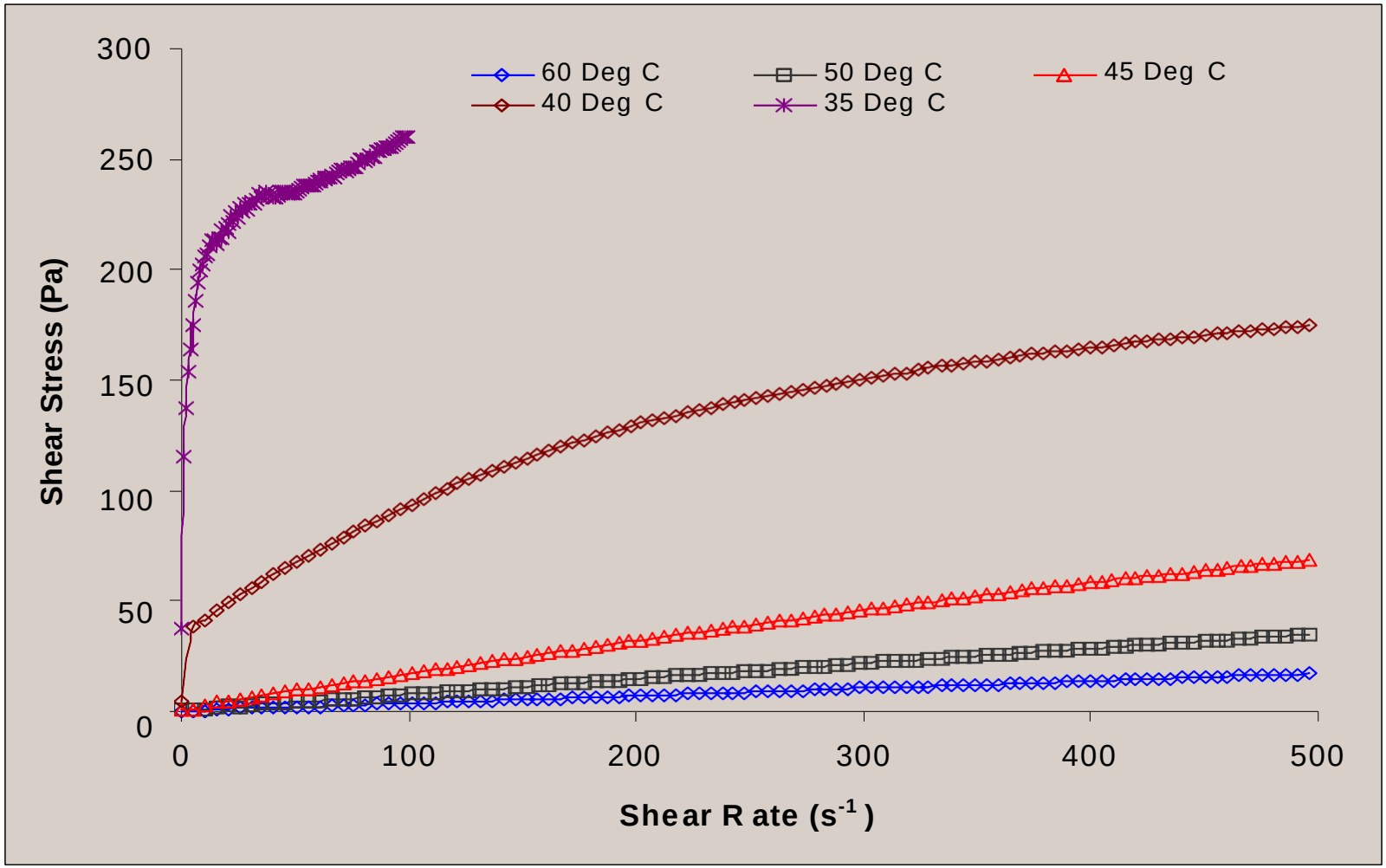
- Heavy & waxy oil transportation is a challenge

Viscosity

There are several ASTM Standard Methods for measuring the viscosity of oils. Of these, only methods D 445 - Standard Test Method for Kinematic Viscosity of Transparent and Opaque Liquids (the Calculation of Dynamic Viscosity) and D 4486 - Standard Test Method for Kinematic Viscosity of Volatile and Reactive Liquids, will yield absolute viscosity measurements (ASTM, 1996a).

Both of these methods make use of glass capillary kinematic viscometers and will produce absolute measurements in units of centistokes (cSt) only for oils that exhibit Newtonian flow behavior (viscosity independent of the rate of shear).

Flow curve of waxy crude at different temperatures



Factors Effecting the Selection of Crude oil

Choice of crude oil for a refinery depends on:

- Product mix
- Product quality
- Refinery configuration
- Product treatment facilities
- Refinery design spec- Metallurgy, desalter etc
- Environment stipulation for pollution control
- Pipeline design for inland refineries

- Proper crude selection is necessary for optimisation of refinery margin.

Refinery Constraints

- Refinery Configuration
- Refinery metallurgy
- Catalyst
- Down-stream treatment facilities
- Pipeline design constraints

Opportunity

- High S crude oil
- High Acid crude oils
- Beat the market by proper selection of crude
- Overcome refinery design constraints to widen crude basket
- Crude Blending Facility

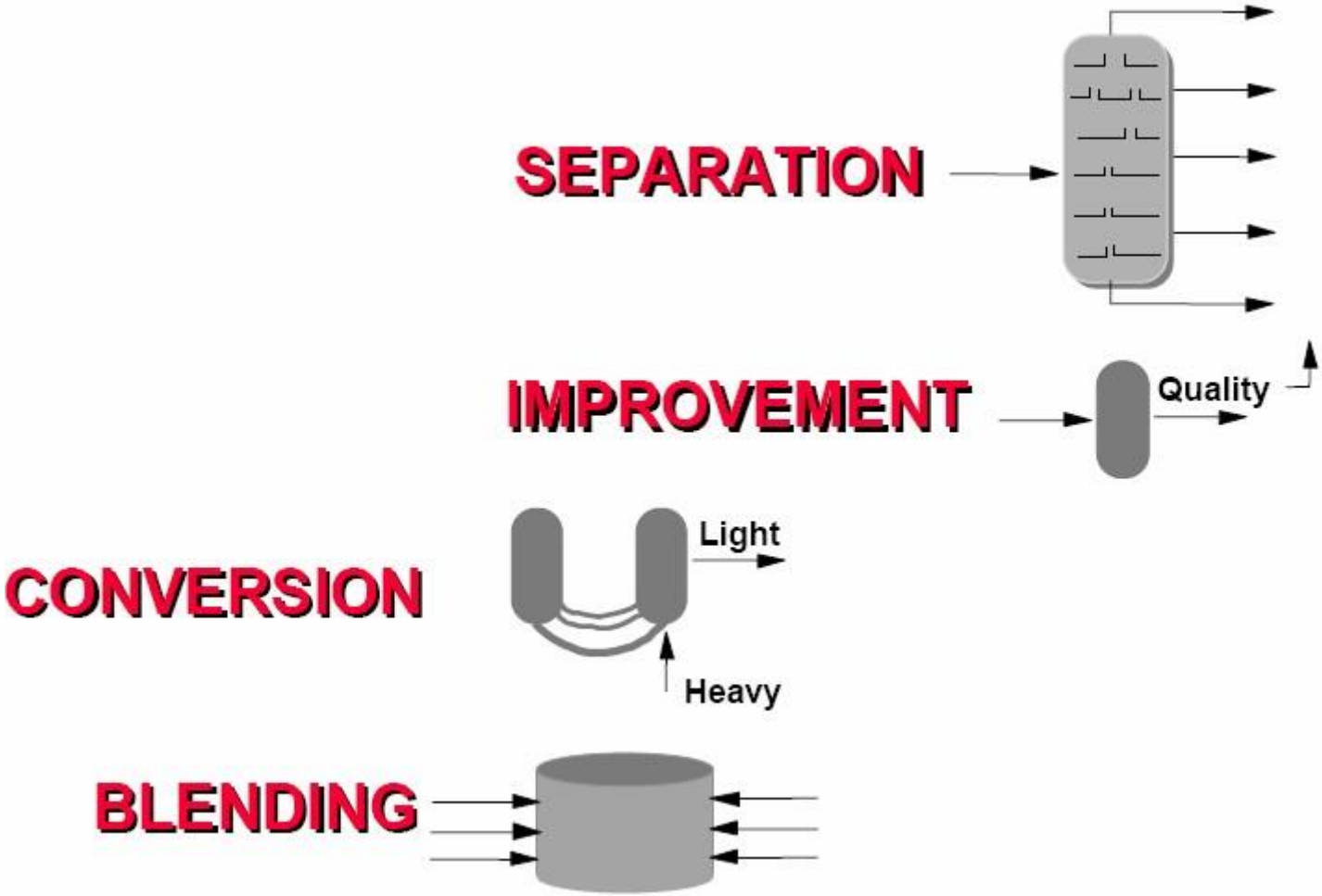
MAJOR THRUST BY OIL REFINERY

1	Optimise crude mix	: High or Low sulfur
2	Widening crude basket	: Increased No. of crudes
3	Ocean freight reduction	: Higher Cargo size
4	Demurrage control	: Minimise tanker waiting
5	Inventory control	: Min possible inventory
6	Ocean Loss reduction	: Proper controls
7	Reduce F&L	: Proper design,operation

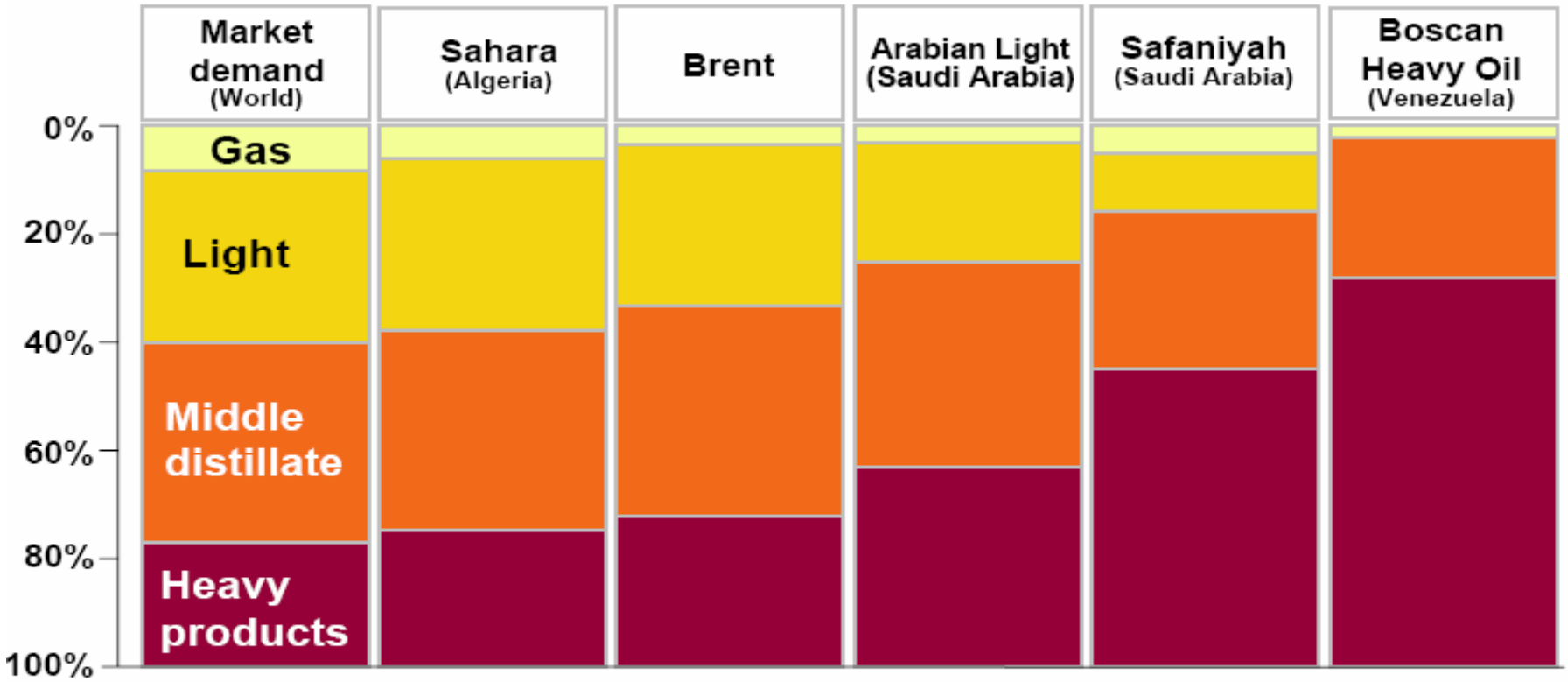
ELEMENTS OF IMPORTED CRUDE COST

	COST ELEMENT	%
1	FOB	90%
2	OCEAN FREIGHT	3.9%
3	DAUGHTER VESSEL FREIGHT	0.8%
4	INSURANCE	0.05%
5	OCEAN LOSS	0.2%
6	PORT CHARGES	0.08%
7	CUSTOM DUTY	5.0%
8	DEMURRAGE	0.002%
9	ENTRY TAX	0.09%
	TOTAL	100.0%

Refining

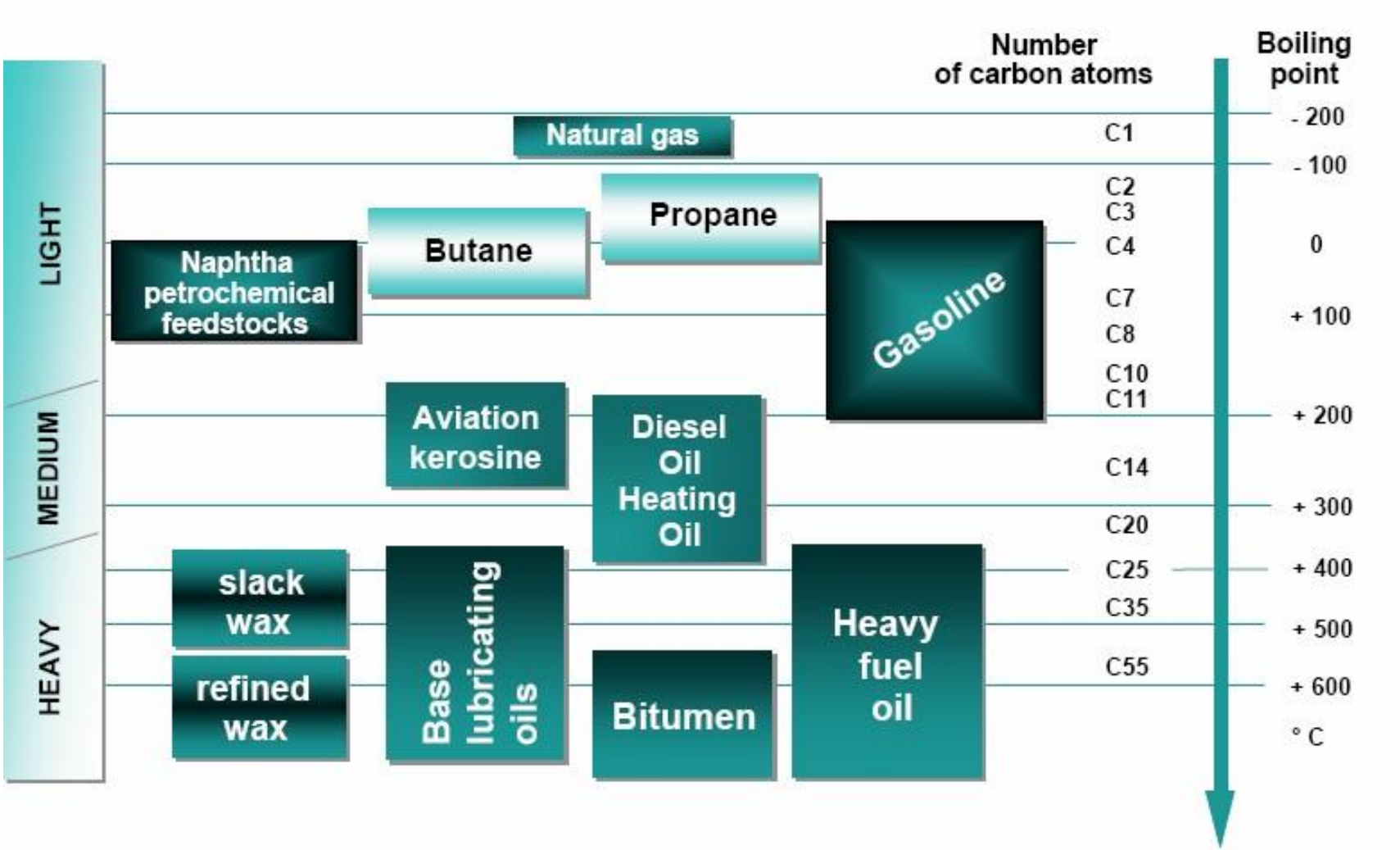

SEPARATION
IMPROVEMENT
Quality
CONVERSION
Light
Heavy
BLENDING

Yield Structure of Various Crudes



Density	0,806	0,837	0,855	0,893	0,995
° API	44	37,5	34	27	10,7
Sulfur content Wt %	0,2	0,3	1,7	2,8	5,3

Oil Products & Cut Points



Products

- LPG
- Naphtha
- Petrol (BS-II/BSIII)
- Kerosene
- ATF
- Diesel (BS-II/BS-III)
- LOBS
- Bitumen
- RPC
- Wax

- Fuel Oil (High S, Low S)
- Fuel Oil (High or low Viscosity)
- LSHS
- HPS
- Petrochemical feed stock
  - LABFS
  - HPL Naphtha
- Petrochemicals
  - pX, PTA
  - LAB etc

Gasoline Specification

	Euro I	Euro II	Euro III	Euro IV
RON	95	95	95	95
Sulphur, Wt%	0.05	0.05	0.015	0.005
Benzene %wt	5	5	1	1
Aromatics %wt	-	-	42	35
Olefins,Wt%	-	-	18	-

Properties of Kerosene

Characteristics Of kero from the Crude:	Basrah Lt.	MH	Arab mix	KEC	NG	ATF Spec
Density, gm/ml	0.783	0.7918	0.7902	0.787	0.7975	-
Smoke, mm	29	21	27	27	28	18
Sulphur, %wt	0.18	0.02	1.3	0.16	0.13	
RSH, ppm	30	nil	8.8	12.9	1	<30
H2S, ppm	nil	nil	nil	3.9	nil	nil
Freezing, ^{o}C	<-60	-54	-59	-53	-47	-47
Aromatics, %wt	18.1	27.7	20.6	20	9.2	20

Properties of Gas oil

Characteristics	Basrah Light	Mumbai High	Arab mix	KEC	NG	Diesel Spec
Density, gm/ml	0.8549		0.852	0.85	0.847	-
Pour point, ^{o}C	-15	6	-18	-6	3	-6/18
Sulphur, %wt	2.05	0.13	1.7	1.51	0.05	0.005
Cetane No.	48.8	59.5	54.9	56.8	60.6	53
Distillation , T95, C	-					340

Diesel Specification

	Euro I	Euro II	Euro III	EuroIV
Cetane Number	49	49	51	53
Sulphur,Wt%	0.2	0.05	0.035	0.005
Distillation T-95, ^{o}C	370	370	360	340

LOBS API classification

CLASS	COMPOSITION	SULPHUR % WT.	VISCOSITY INDEX
Group-I	<90% Saturates	>0.03	95-120
Group-II	>90% Saturates	<0.03	95-120
Group-III	>90% Saturates	<0.03	>120
Group-IV	Poly alpha olefin		
Group-V	Others		


THANK
YOU !!!