Presentation
On

CRUDE OIL CHARACTERISTICS AND REFINERY PRODUCTS

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GENERAL INFORMATION

Crude oils are formed by the action of geological processes on the remains of ancient marine life.

It is a complex mixture of hydrocarbons and over 16,000 compounds have been identified in one sample.

Composition varies widely:

- **By geographical location**
- **Mix of individual wells**
- **Variance of wells with time**

Crude Oil – Definition

Speight,1980

"A mixture of gaseous, liquid and solid hydrocarbon type chemical compounds that can be separated into a variety of different boiling point fractions and that occur naturally in sedimentary rock deposits through-out the world"

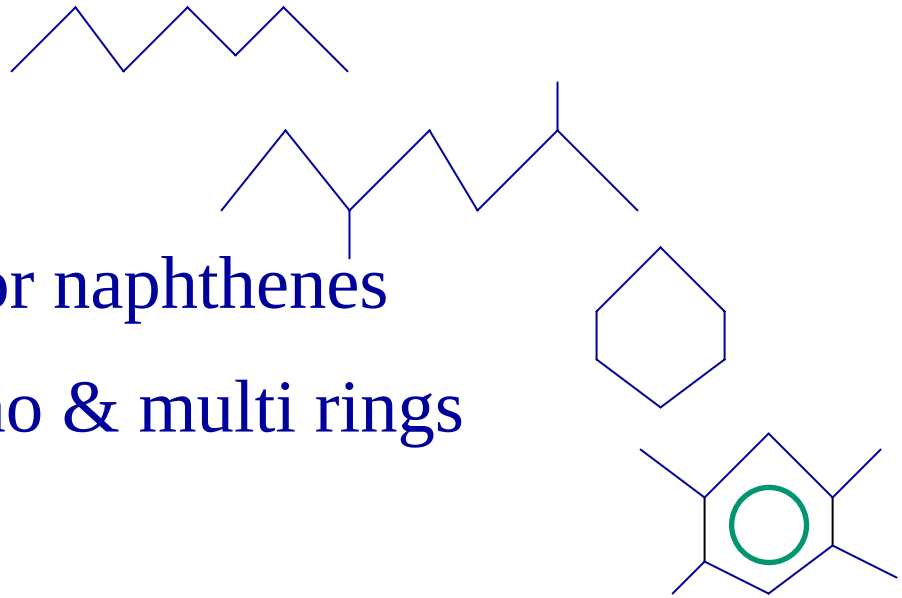
ASTM- D 288

- **"A naturally occurring mixture, consisting predominantly of hydrocarbons and/or of sulphur, nitrogen and/or oxygen derivatives of hydrocarbons, which is removed from the earth in a liquid state or is capable of being removed.**

Crude petroleum is commonly accompanied by varying quantities of extraneous substances such as water, inorganic matter, and gas. The removal of such extraneous substances alone does not change the status of the mixture as crude petroleum. If such removal appreciably affects the composition of the oil mixture, the resulting product is no longer crude petroleum"

Hydrocarbons in crude oil

- Paraffins
- Isoparaffins
- Cyclic alkanes or naphthenes
- Aromatics, Mono & multi rings
- Resins
- Asphaltenes



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

Gasoline: branched alkanes

Diesel: linear alkanes

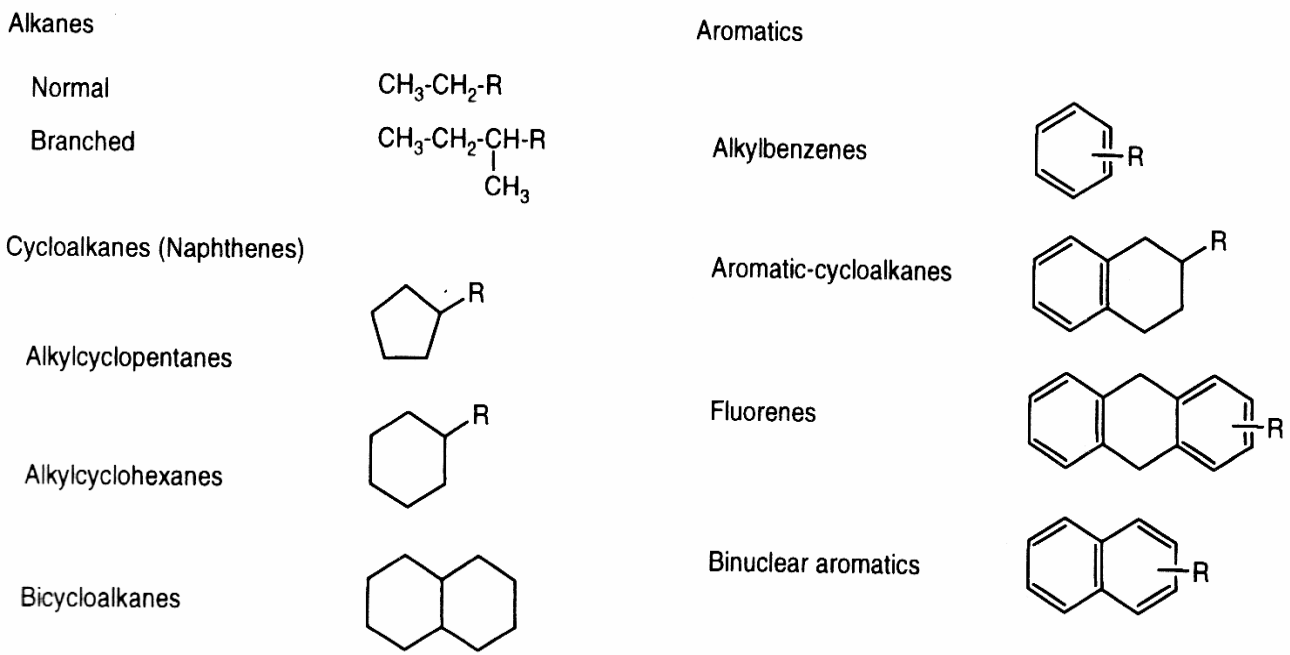


Figure 2.12 Examples of alkanes, cycloalkanes and aromatics present in crude oil.

Heavier crude contains more polycyclic aromatics Lead to carboneceous deposits called “coke”

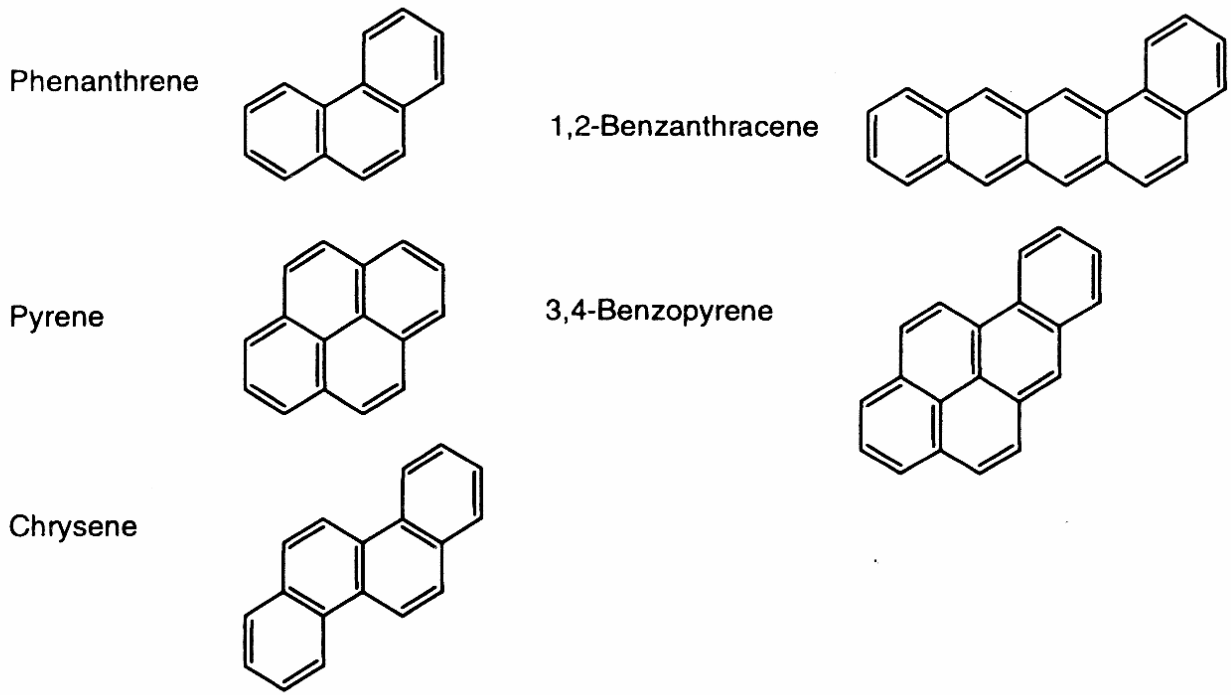


Figure 2.13 Examples of polycyclic, polynuclear aromatics in crude oil.

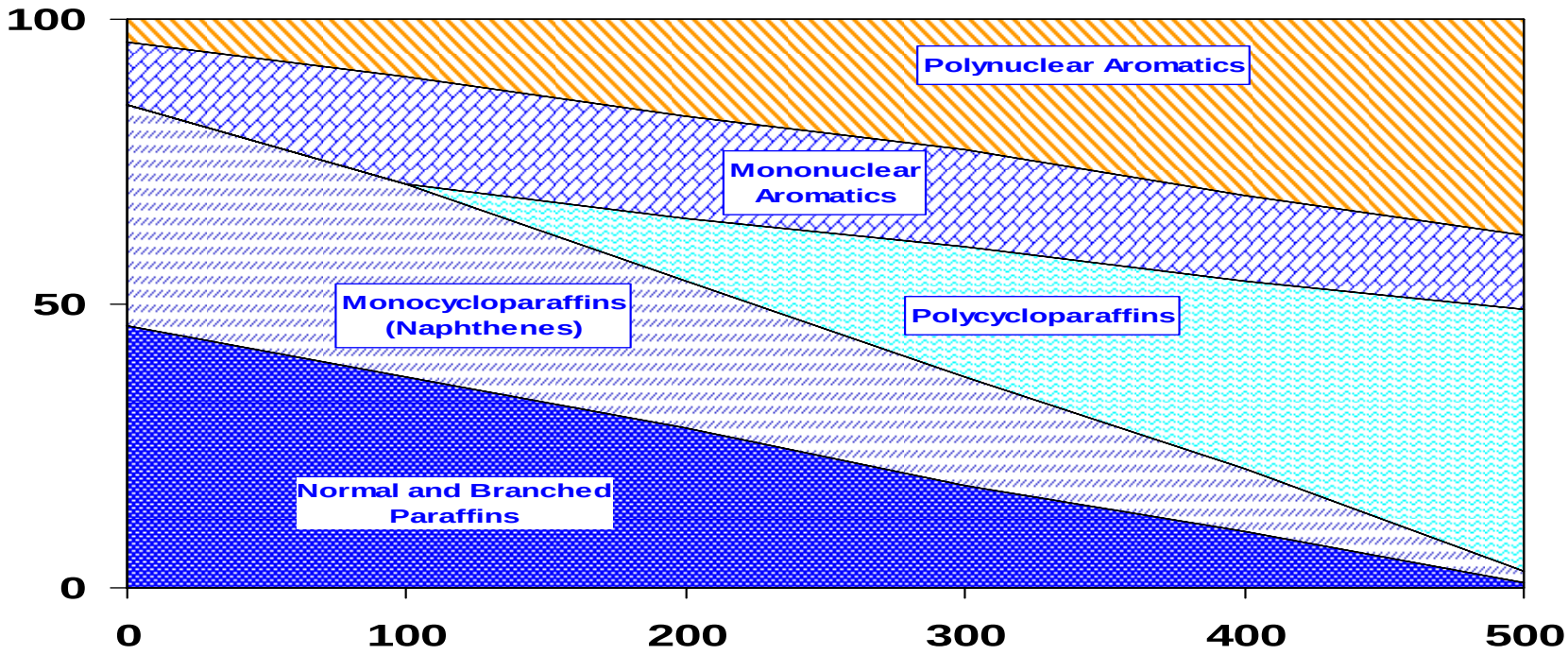
Crude Oil Composition

Elements	% Wt
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(Fe, Cu, Ni, V, Mg, Al, Cu)	0.00 to 0.14

Distribution of the hydrocarbon types in petroleum

Lighter oils → Heavier oils and Residue

→ Increasing Hetero-atom (N,O,S and Metals) content →



Origin of Petroleum

Theories broadly classified into non-biogenic & biogenic :

• Non-biogenic : from inorganic sources

Metal carbides + H2O…..> Hydrocarbons

CaCO3 --->CaC2--->Acetylene--->Petroleum hydrocarbons

Reaction of CO2, in presence of alkali and alkaline earth metals, with water is also postulated to form hydrocarbons

Theory did not receive much recognition

Origin of Petroleum

• Biogenic : from organics, by bacterial transformation :
Organic matter (carbohydrates/proteins//lipid/ lignin both from plant & animal origin -------->Decay in presence and/or absence of air into HC rich sediments which in presence of micro organism undergoes biological/physical and chemical alterations to form Kerogen (geopolymer) which may be coaly or sapropelic
Sapropelic Kerogen under high pressure and temperature further gets converted into Oil & Gas.

Widely accepted theory

Crude Oil Chemistry

A very complex mixture consisting of paraffins, naphthenes (cyclo paraffins), and aromatic hydrocarbons as well as nitrogen-, oxygen-, sulfur- containing compounds and traces of a variety of metal-containing organic and inorganic compounds.

Hydrocarbons:

- Saturated alkanes: (n-alkane and i-alkane)
- General formula CnH2n+2
- Boiling point and density increase with increasing no. of Carbon atoms.
- Branched alkanes (iso-alkanes) in relatively small quantities

Crude Oil Chemistry

- Boiling point of straight chains > iso-alkanes with the same no. of Carbon atoms

- Naphthenes or Cyclo paraffins (saturated cyclic hydrocarbons) -General formula CnH2n

- Alkenes or Olefins – unsaturated aliphatic hydrocarbon (i.e. ethylene or propylene) - Very small amounts found in crude oil – produced during refining

- Aromatics hydrocarbon (cyclic and polyunsaturated hydrocarbons containing conjugated double bonds) – CnH2n-6….

Crude Oil Chemistry

- Alkyl aromatics have very high octane no. but aromatics content in gasoline is limited by environmental regulations – health effects due to high toxicity.
- Di & polyaromatic Hydrocarbons – aromatics containing more than 2 and more aromatic ring
- Naphthalene – 2 rings
- Anthracene – 3 rings
- Pyrene – 4 rings (very toxic)
- Hydroaromatics or naphthenoaromatics – partially saturated PAHs
- Heteroatom compounds

Crude Oil Chemistry

- Sulfur compounds might be present in inorganic and organic forms. In crude oils sulfur concentration can range from 0.05 to more than 6 weight percent. dibenzylthiophene (2-benzene rings separated by 1 S atom) – is most difficult to release 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

Crude Oil Chemistry - Sulphur Compounds

- H2S (CO, SRP, CP)
- Aliphatic / mercaptans RSH(CO, SRP,CP)
- Aromatic thiols/mercaptans (CP)
- Sulphides R-S-R (CO,SRP,CP)
- Disulphides R-S-S-R (SRP)
- Cyclic : sulphides (SRP,CP) / disulphides (CP)
- Thiophenes & homologs: (CP)

(benzothiophenes,Dibenzothiophenes,Naphthobenzothiophenes)

NB CO- crude oil: SRP- straight run product; CP- cracked product

Crude Oil Chemistry

Why sulphur compounds are not desirable in crude/fuels?

- Great environmental concern, contribution to particulate matter, emission of obnoxious odoring sulphur oxide gases
- Reduction of sulphur level in all petroleum products mandated
- As a result refining technology focus shifted to sulphur removal from hydrocarbons

Crude Oil Chemistry - Oxygen compounds

May be present in different forms such as :

- 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 mix : 0.2%wt

  Effect: Corrosion

Crude Oil Chemistry - Nitrogen Compounds

Non-basic	Basic
Pyrrole	Pyridine
Indole	Quinoline
Carbozole	Indoline
Benzocarbozole	Benzoquinoline

Effects: Nitrogen oxide emissions & Catalysts poison

Crude Oil Chemistry - Metals

- Present as inorganic salts of organic acids and also as metallic Porphyrins (Ni, V, Fe) in ppm
- Salts mostly removed in desalting operation
- Ni & V Porphyrins are catalyst poisons

Effects of Contaminants in Crude Oil

H2S	acidity, corrosion, reduced ON, bad odor noxious combustion products
Alkyl mercaptans	- Do – (A)
Naphthenic acids	acidity, corrosion
Phenolic compds	possible increase in engine deposits
Aryl mercaptans	gum, engine deposits + A above
Total Sulphur	Same as ‘A’ above
Di-olefins	fuel instability, gum, engine deposits
Nitrogen bases	bad odor, cat poison, color formation, engine deposits
Trace metals	gum, engine deposits, cat deactivation

Crude Oil Classification

- **Paraffinic Base**
  - Waxy, High paraffins, less asphaltic, low sulphur, high pour, light crudes

- **Mixed Base**
  - Paraffinic- naphthenic, relatively Less Wax/ Less Asphaltic/ Low Pour

- **Naphthenic Base**
  - High sulphur/ high asphalt/ nitrogen- suitable for API – I base oils production, relatively heavy crudes

Empirical correlations/equations frequently used

Crude Oil Classification - Empirical Correlations

API Gravity

API =(141.5 / sp.gr.)-131.5

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

API is a major factor for Crude pricing

Characterization & classification of crude oils

-Purpose of classification is to provide gross compositional information based on simple measurable physical parameters like Density, Volatility etc.

- Characterisation of crude oil is an attempt to know its quality, directional help for processing and estimate of products availability.

Crude Oils are classified in various ways. Two simple methods are :

1.Qualitative Basis

Basis	Type
Predominant hydrocarbon	Paraffinic, mixed base, Naphthenic or asphaltic
Distillate Yield	Light, Heavy
Sulphur Content	Sour, Sweet

Characterization & classification of crude oils

2. Quantitative Basis

Approach based on determining the base of a crude oil by one of the following methods :

i) US Bureau of Mines Classification based on degree API:

Key Fraction	250 – 275 C	275 – 300 C
Paraffin	> 40	> 30
Intermediate	33 – 40	20 – 30
Naphthene	< 33	< 20

If cloud point is > 5 Deg F, it is wax bearing and if less, it is wax free crude oil

Characterization & classification of crude oils

ii) Bureau of Mines Correlation Index (BMCI):

BMCI = 48640 / mid BP in deg K) + 473.7 x G – 456.8

where K = Deg C + 273 and G = Sp. Gr. at 60/60 F

Key Fraction	Values
Paraffin	> 15
Mixed Base	15 - 50
Naphthene	< 50

iii) Kuop): Cubic root of average boiling point in deg Ranking (deg F + 460) divided by Sp. Gr.

Key Fraction	Values
Paraffin	> 12.1
Mixed Base	11.5 – 12.1
Naphthene	< 11.5

Objective of Crude Oil Characterisation / Crude Assay

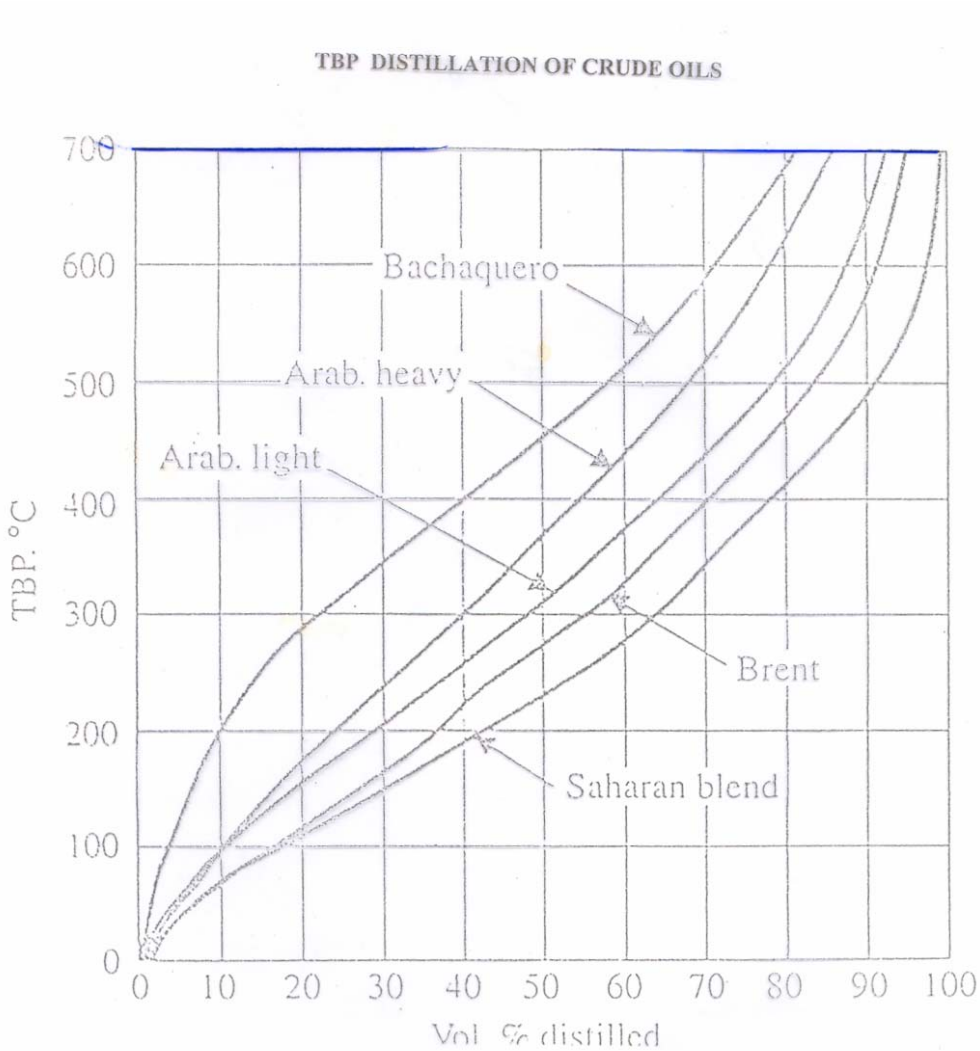
- Marketing / Pricing of Crude Oil
- Transportation of Crude Oil
- Design of Grass Root Refinery
- Processing of a new crude oil in an operating Refinery
- Expansion / Modification of an operating Refinery –Primary / Secondary operations
- Optimization of the product yields
- Value Addition

Types of Crude assays, their objectives and scope

Types	Objective	Scope
Preliminary Assay	•To Check consistency of a crude supply •To have a preliminary indication of quality of the new crude in exploration phase	•Characteristics of the crude oil •Non-fractionating distillation data
Short Assay	•Processing of new crude oil in a fuel refinery •To check the quality of a crude oil over a period of time •Pricing of a crude oil through bench marking	•Crude oil characteristics •Micro constituents (S, N, Trace Metals) •TBP Assay •Yields and Key characteristics of straight run products and residues

Types of Crude assays, their objectives and scope

Types	Objective	Scope
Detailed Assay	• Design basis for a new refinery • Optimization of product yields • Selection of secondary processes and treating units • Modeling and simulation data for the refinery units • Marketing Assay	• Base and detailed characteristics of crude oil • Micro-constituents (S, N trace metals) • TBP Assay in atmospheric and vacuum range • Yields and characteristics of broad distillate cuts in atmospheric and vacuum range (cuts prepared with variations in IBP and FBP) • Detailed component wise analysis of light distillates and hydrocarbon type composition of middle and vacuum distillates. • Detailed characterization of long and short residues



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Significance of Crude Characterization

- **Upstream Planning**
  - to determine the economic viability of new fields / discoveries
- **Supply Organizations/ Traders**
  - to assign crude value for individual grades
- **Refinery Operations**
  - to schedule crude receipts and determine product yields
- **Model Engineers**
  - to optimize refinery crude slates
- **Research & Development**
  - to design equipment and process planning

Need for Crude Characterization

- Because crude oil from different sources exhibit variation in composition, yield and properties, characterization is necessary to ascertain quality and product slate
- Assist refiner to select best processing routes
- Establishing theoretical potential & auditing/optimizing individual unit parameters
- Estimation of feedstock properties for optimizing process parameters
- Produce an optimal amount of finished products
- Meet product quality specifications
- To provide an economic assessment for margins from crude oils

Crude evaluation/assay widely known and practiced terminology

What does it means ?

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 namely:

- LPG
- naphtha
- gasoline
- kerosene
- jet fuel
- middle distillates/ diesel
- vacuum gas oils as :
- Feedstock for secondary processes
- VGO as LOBS

-long residue (AR/RCO) / short residue(VR/ SR) as feed-stock for RFO /Bitumen/RFCC etc

Laboratory Distillations- inter-conversion

Distillation

- True Boiling point (TBP) – D 2892
- ASTM Distillations:

1) D-86 for light fractions at atmospheric pressure
2) D-1160 for heavier fractions (>500°F) carried out in vacuum Equilibrium Flash Vaporization (EFV)

Crude oil evaluation for Lube Refinery

- Characterization of RCO
- High Vacuum Distillation of RCO
- Characterization of vacuum gas oil (VGO) cuts
- Dewaxing of VGO's
- Characterization of dewaxed oil, wax
- Elution chromatographic separation
- Characterization of LOBS
- Lube potential of SO, LO, IO & HO

Characteristics of Crude oil- Typical data

Characteristics	South Gujarat	Bombay High	Arab mix	Kuwait	North Gujarat	Rajasthan crude
Density, gm/ml	0.7906	0.8200	0.8664	0.8741	0.8932	0.8934
API gravity	47.3	41.0	31.6	30.3	26.8	26.9
Pour point, ^{o}C	12	21	-24	-27	27	42
Kinematic Viscosity						
@40 ^{o}C	1.7	3.4	10.0	11.1	65.6	-
@50 ^{o}C	1.5	-	8.9	8.5	31.4	-
Water content, %wt	nil	nil	nil	nil	4.1	-
Salt content, %wt	50	-	L20	2.0	200	-
Sulphur, %wt	0.02	0.09	2.7	2.8	0.08	0.08
TAN, mgKOH/gm	0.018	0.1	0.14	0.14	1.93	-
RCR, %wt	0.39	1.1	6.4	5.4	2.5	4.6
Wax, %wt	10.0	12.7	2.5	6.0	5.9	32
Asphaltene, %wt	0.07	0.25	2.3	2.5	0.05	-
ASTMDistillation						
cracking point, ^{o}C	340	372	322	335	367	-
Metal content, ppm						
Nickel/vanadium	0.3/-	-	4/23	4/33	61/L10	98/2

Indian Crude Basket

Indigenous

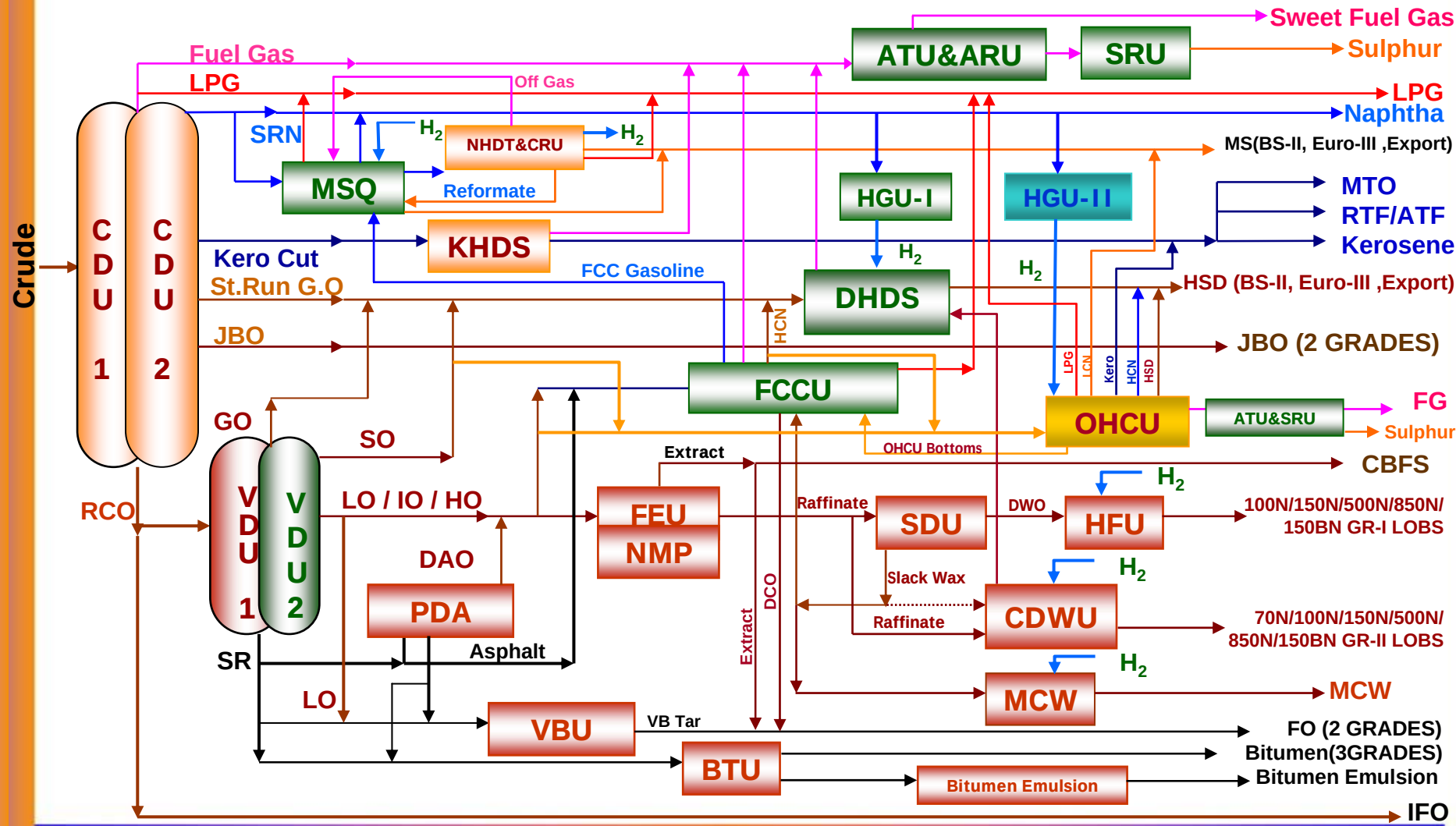
Bombay High	**API 38, S 0.2%wt, wax 10%wt, distillate yield 68%wt**
South Gujarat	API 48, S 0.1%wt. Wax 10%wt, Distillate yield 80%wt
North Gujarat	API 28, S 0.1%wt, Distillate yield 25%wt, resinous crude
Assam crude	API 31, S 0.3%wt, aromatic, waxy, Distillate yield 65%
KG basin-rava crude	API 36, S 0.1%wt, yield 61%wt
Cauvery basin crude	API 46, S 0.1%wt, yield 80%wt

Indian Crude basket
Imported

BITUMINOUS	NON-BITUMINOUS
Lube bearing	High sulphur
Arab mix, Lavan	Arab medium
Upper Zakum	Kuwait
Non-lube bearing	Low sulphur
Suez Mix	Qua I boe/Bonny Light/Forcados
Girrasol	
Dubai	Miri light

✓**Crude shopping based on Refinery configuration because at present only Selective crudes can be processed in Indian refineries**

Haldia Refinery – Block Flow Diagram



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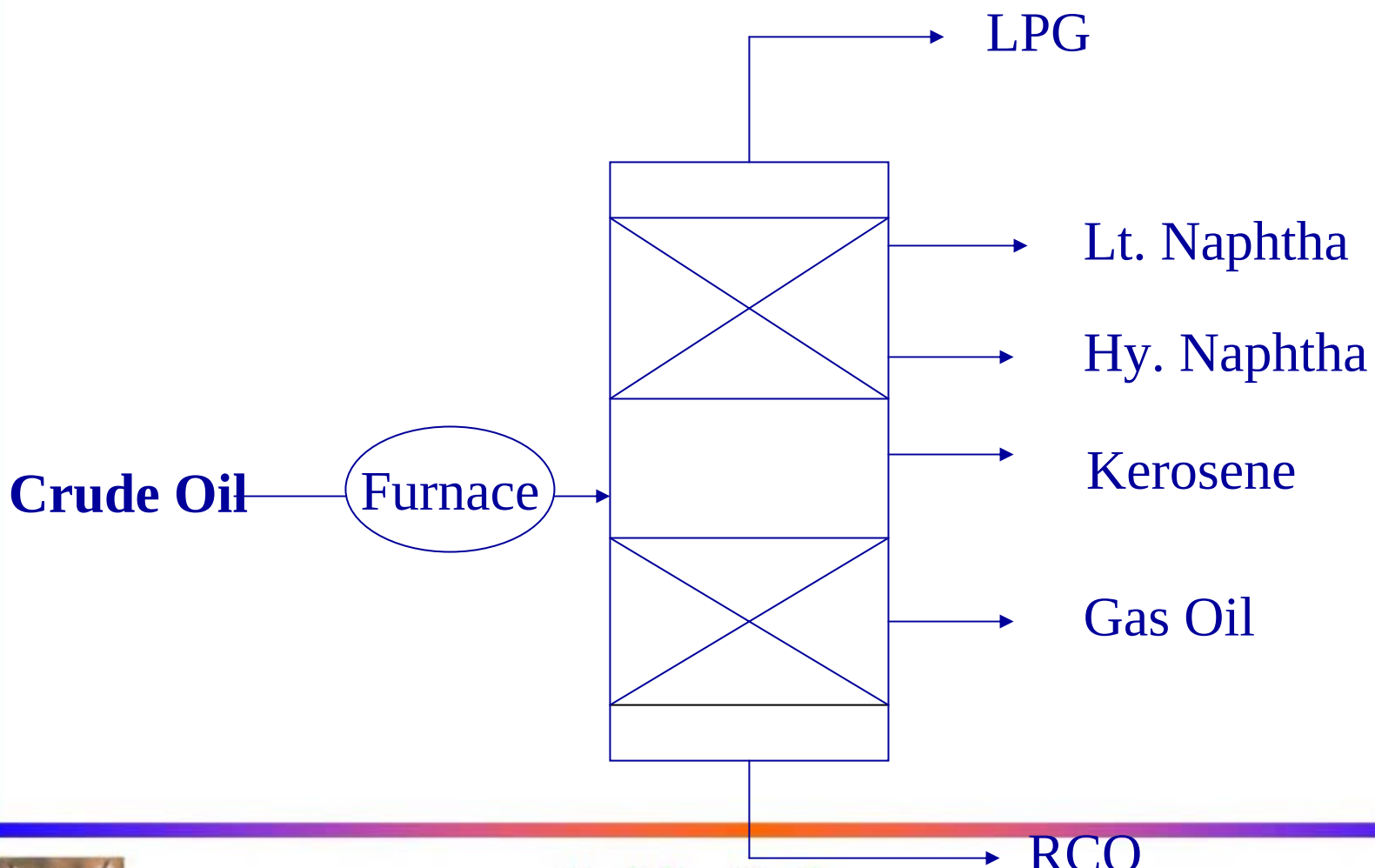
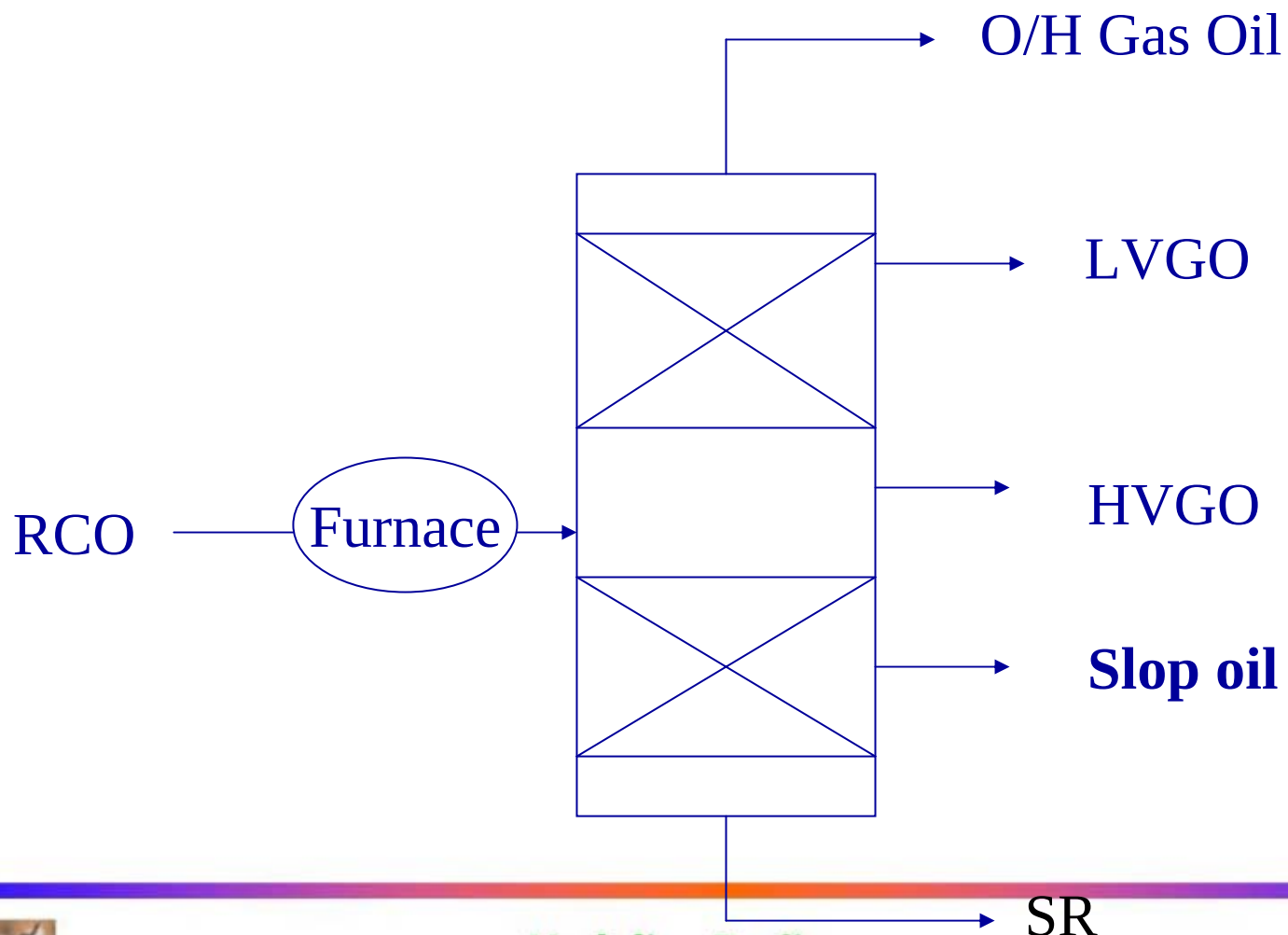
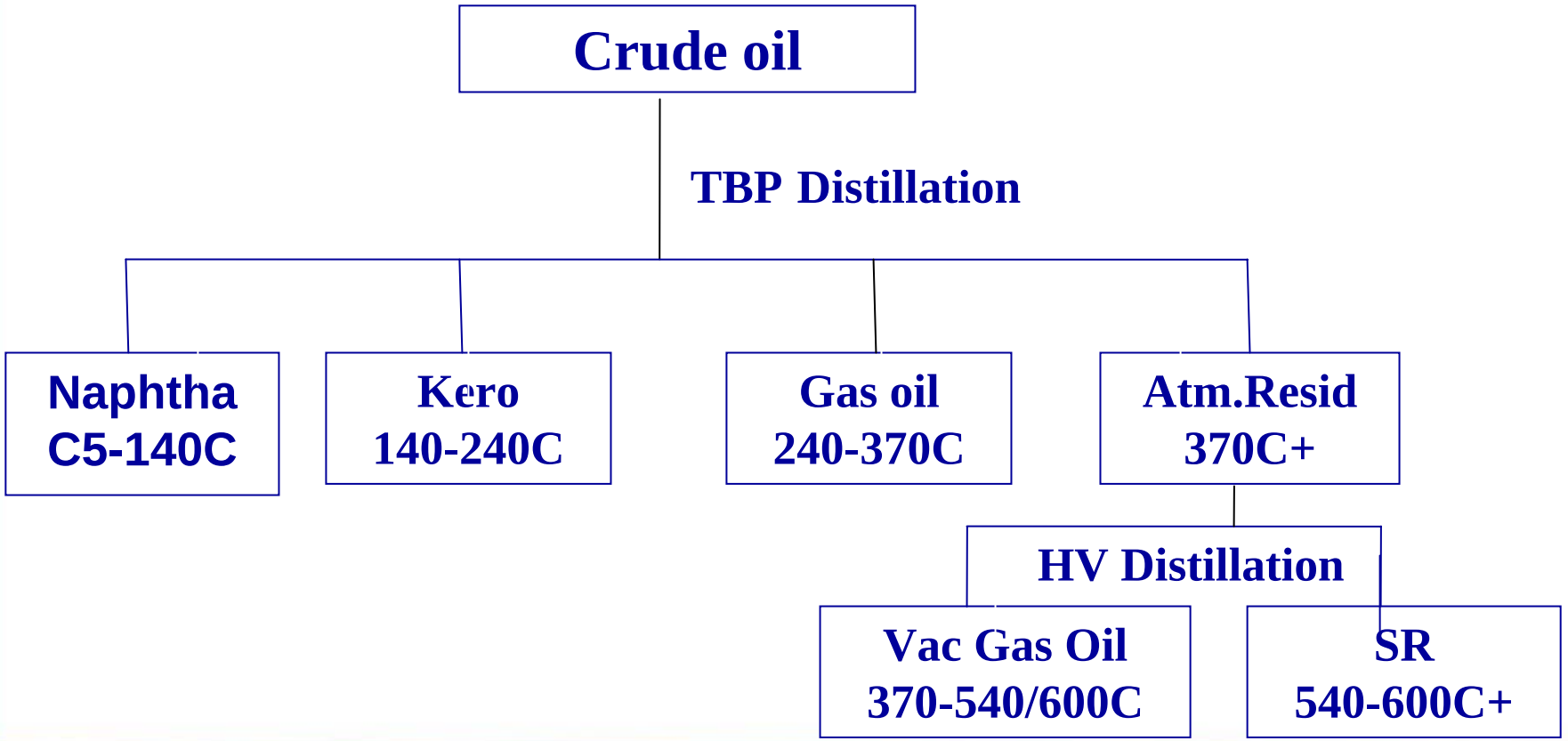
Crude or Atmospheric Distillation Unit



Vacuum Distillation Unit
FCC/HC Feed



Crude Oil - Distillation Scheme



Heavy Crudes

- High Sulphur
- High Asphaltic
- Waxy
- High TAN
- High Arsenic
- High Basic Nitrogen

High TAN Crudes

Crude oil	Crude TAN mgKOH/gm	Naphtha	Kero	AGO	LVGO	HVGO
Alba	1.42	0.0	0.1	0.8	1.9	2.2
Captain	2.4	0.1	0.4	1.3	2.4	2.9
Duri	1.27	0.1	0.8	2.5	2.7	1.8
Grane	2.2	0.03	0.03	1.5	2.5	3.9
Heidrum	2.6	0.03	0.19	3.9	4.2	3.5

High TAN Crudes

Parameters influencing Naphthenic Acid Corrosion

- Naphthenic Acid chemistry
- Sulphur
- Temperature
- Velocity
- Material of Construction

High TAN Crudes

Impact on Refinery Processes

- Furnace tubes and transfer lines
- Distillation units (Atm & Vac)
- Secondary Units
- Desalting operation
- Products quality

High TAN Crudes

Mitigation Methodologies

- Crude blending
- Corrosion inhibitors
- Suitable metallurgy
- Process changes

Characterisation of crude oil for value addition - Potential & composition is important

Naphtha	– Feed stock for petrochemicals through olefins – Feed stocks for petrochemicals through aromatics – Feed stocks for FGH – Potential of pure chemicals (Per tones & hexanes) – Potential of SBP solvents.
Kerosene	- Potential of n-paraffins (nC_{10}-nC_{14}) for linear alkye benzene – Detergents - Naphthalene precursors
Gas Oils	- Heavy gas oil can be studied for the potential of n-paraffins for synthetic fatty acids and higher alcohols.
VGOs	- Potential of lubes, waxes and microcrystalline waxes and feed stock for secondary conversion
Short Path / Deep Distillation Cuts	- Distillates for additional quantities of feed stock for secondary conversion - Potential of Microcrystalline waxes.

Summary

Characterization of crude oil provides vital information :

- Pricing/trading
- Pipeline transportation
- Production pattern
- Processing/refining
- Products quality
- Performance of products
- Profit making/value addition/ refinery margins etc...

Essential for configuring economically viable/ profitable refinery processing scheme

Summary

Crude quality effects its processing :

- Throughput/ plant capacity
- Change of products pattern/quality
- Change in processing scheme
- Material of construction
- Overall economics
- Effluent quality

Therefore, the crude assay data should be complete, consistent and accurate

Summary

- Crude oil needs to be understood before processing
- Selection of crude oil to be given top priority as it consumes more than 90% of the operating cost
- Lower the impurities easier the processing, higher the profit

Thank you

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