PETROLEUM TECHNOLOGY

The origin of oil

The origin of petroleum is not definitely known. Many theories have been advanced suggesting animals, vegetables, and even mineral Origins.

The commonly accepted Theory suggests Shallow seas rich in plant and animal life, both large and microscopically small e.g. Fish and other marine species, large plants, planktons etc.

Provided the seas were calm, the species will sink when dead, the species will sink to a muddy bottom where they will be covered by silt.

Quiet conditions could have been provided by a surrounding rock structure resembling a wall. The almost oxygen-free condition at the sea bed will have energy aroused the slow anaerobic decay of the constantly descending dead organic matter. The steady accumulation of mud above the buried and decayed organisms would have caused an increased of pressure and temperature. In these conditions, liquid oil, gaseous hydrocarbon and H_2S can in fact be produced.

Oil is usually found in the sedimentary basins (i.e. An area where water has flown) which were relatively shallow, acient seas and also in continental margins, foot hills, and lowlands boarding the main mountain ranges.

The pressure at the bottom of the well. In this way, a pressure gradient is created on the reservoir. Because of the pressure gradient, the fluid contained in the pore space begin to flow towards the well and are then evacuated to the surface.

OIL RECOVERY

An oil field is a natural hydrocarbon accumulation in the pores of the underground porous rocks which are called Reservoir Rocks or Reservoirs.

An oil field may contains several separate reservoirs

Primary recovery

Hydrocarbons are recovered from the field by means of wells drilled from the surface on to the Reservoir. The initial pressure in the fluids occupying the pore space in a reservoir is very often

higher than the hydrostatic pressure. By opening a well, therefore, the pressure at its bottom is reduced, thus driving Reservoir fluids towards the well.

If the natural pressure drops obtained by opening the well is too small it is possible to operate a pumping system which further decrease which further decreases the pressure

Diagram of an oil field x-sextion

Secondary recovery

To produce more oil, the pressure in the reservoir must be maintained by injecting another fluid. this second period of production is called secondary recovery

Fluid injection into the reservoir has two closely linked objectives:

    (i)   to maintain the Pressure in the reservoir

    (ii)   to push forward the oil contained in the reservoir towards the producing wells.

For a rather small oil field, the pressure may effectively be maintained by injecting water into the aquifer at the outer limit of the reservoir.

As shown in the above sketch,

It can be gas injection into the gas cap at the center of the reservoir as shown in the diagram below:

Diagram

For a large fluid, fluid injection only at the outer limit or only at the center is not an effective way of maintaining the pressure.

Very often, fluid injection must be distributed throughout the field. Injection then creates a water zone i.e. if the injected fluid is water or gas zone, if the injected fluid is gas around each injection well. These zones extend progressively and push the oil towards the production wells.

Diagram

After several years of secondary recovery, the injected fluid reaches the production well and makes up an increasing proportion of the extracted fluids. Finally, production is no longer cost effective. Hence, secondary recovery has reached its limit.

At this time, there are still some part of the reservoir that have not been swept by the displacing fluid, where the pore space may still contain a large proportion of oil.

Even in the part of the reservoir that has been swept by the injected fluid, a fraction of the oil initially in place may still remain, together with the injected fluid. Hence, by this excessive use of primary recovery and the secondary recovery; only a fraction (15 - 60%) of the oil initially in the field can be recovered.

Diagram

Distributed H_2O injection in a large field (horizontal projection)

Tertiary recovery

When a field has been exploited by primary and secondary recovery techniques, in some cases, an attempt is made to recover part of the remaining oil by using more sophisticated techniques. This is the tertiary recovery. such techniques aim at increasing the DISPLACEMENT EFFICIENCY. That is, it is aimed to produce the oil that remains in part of the reservoir already swept by displacing fluid. Other techniques are aimed at producing the oil that remains in the part of the reservoir not swept by the displacing fluid; i.e. aimed at increasing the SWEEP EFFICIENCY. However, some techniques can increase both displacement and sleep efficiency

THE DEVELOPMENT OF NIGERIA OIL INDUSTRY

Oil prospecting began in Nigeria as far back as 1908 through a German Company, in the Araromi area of Ondo State.

In 1937, oil prospecting continued with shell D'Achy (now shell petroleum Dev. Co. of Nigeria).

Shell started oil production and export from OLOIBIRI field in 1958.

By 1961, other Cos such as mobil, gulf, Agip, Satrap (now Elf), Tenneco and Amoseas (now Texaco and chevron) also began exploration activities for oil in the on-shore and off-shore areas.

Oil production and export from the Oloibiri field started at a production rate of 5,100 barrels of crude oil per day. The rate doubled the following year. By 1972, it rose to 2.0 million barrels per day. It reached its peak in 1979, at a rate of 2.4million barrels per day.

By 1972, Nigeria ranked as seventh world producer. Now Nigeria has been 6th largest oil producing country in the world.

OIL PROSPECTING EXPLOITATION

Petroleum is a mixture of hydrocarbon and oils obtained below the surface. In Nigeria, it generally occurs at depth below 1,500m.

The bulk of Nigeria's reserves occur between 2000 m and 3,000 meters (i.e. 1.25 to 2 miles) depth. Most of the exploratory work in Nigeria has been concentrated in the Niger Delta.

The search for oil involves 3 major stages:

(i)Geological/Geochemical surveys:

This involves geological mappings, rock sampling and rock analysis

(ii) Geologists and Geophysicists acquired the data from stage 1 and continue with the SEISMIC shooting. Here attempt is made to "look" into the earth with very sophisticated equipment in search of structural (e.g. faults, anticlines) and/or stratigraphic (e.g. pinchouts, sand lenses between shales) traps in which oil and gas could be found. These are also known as geophysical survey. The most prominent among this survey is the seismic method.

This seismic operation is carried out on the ground (on-shore) in marine areas (off-shores).

Seismic method

In this method, explosives are discharged into the ground. These generate artificial vibration (earthquakes) which travel down into the ground and back and picked up by highly sensitive detectors (SEISMOMETERS) arranged on the ground or floating a few meters below the sea surface. The seismometer then converts the vibration energy into electrical energy which is fed through cable store equipment where it is recorded as raw seismic data. This data is later processed with computers and interpreted by geophysicists to give valuable information on the sub-surface

structure from the results of this seismic surveys, possible areas of probable oil and gas accumulator can be selected for further investigation with the drill.

(iii)Drilling for oil

This is the third stage in oil exploration

Production facilities and the pipelines to evacuate the crude

FROM PRODUCTION WELL TO WHERE?

From all production wells, pipelines are installed to convey the oil to gathering stations nearby. There the separation of the component part of water, gas and oil takes place.

The gas is flared, the oil separated is passed through pumps to trunk line to oil terminal. There it undergoes further separation of water, from there the dry oil is exported through the terminal or pumped through pipelines to the refineries for refining.

NIGERIA'S MAJOR CRUDE AND PROPERTIES

	Crude Type	Spec. Gravity	% Sulphur	APIg
1	Bonny Light	0.8398	0.14	37°
2	Qua Iboc	0.8398	0.14	37°
3	Escravos	0.8448	0.14	36°
4	Brass River Oloibiri	0.8063	0.07	44°
5	Bonny Medium	0.8934	0.28	26°
6	Fircados	0.8708	0.2	31°
7	Pennington	0.8448	0.2	36°

NOTE:

	Crude Type	APIg	UOP(universal oil product) K-factor	Crude Class/Crude Base
1	Bonny Lighr	35.12	11.8	Mixed base 1 parrafinic - Naphthenic
2	Bonny Medium	24.41	11.40	Mixed base 1 parrafinic - Naphthenic
3	Brass Blend (Agip)	42.11	11.92	Mixed base 1 parrafinic - Naphthenic
4	Qua Iboe (Mobil)	35.13	11.75	Mixed base 1 parrafinic - Naphthenic
5	Escravos Light (Chevron)	35.4	11.85	Mixed base 1 parrafinic - Naphthenic
6	Eorcados (Shell)	28.12	11.54	Mixed base 1 parrafinic - Naphthenic
7	Antan Light	34.2	11.92 12 – 13 parrafinic (grand for cub oil)	Mixed base 1 parrafinic - Naphthenic
8	Pennington	36.21	11.79	Mixed base 1 parrafinic - Naphthenic
9	Oso Condensate	48		Mixed base 1 parrafinic - Naphthenic
10	Chevron Condensate	58		Mixed base 1 parrafinic - Naphthenic

Linear long chain hydrocarbon (n-paraffins) trend to coil and precipitate. as wax at low temperature; (high pour point).

High viscosity index is specified for good lube base oil – crude oil containing mostly paraffinic hydrocarbon. Ezeaniekwe et al. (1992).

Mixed based crudes – mixture of parafins, Naphthene and aromatic hydrocarbons.

$$API\left(g\right)\ Value\ =\ \frac{141.5}{sp.g.@\ ^{60}\!/_{60}\ ^{o}F}\ -\ 131.5$$

Geological considerations

The genesis and evolution of bio-organic material to KEROGEN and OIL are influenced by the nature of the operating geologic parameters within the sedimentary basin. After the early stages of diagenesis, where biological processes are very active, transformations of sedimentary organic matter are essentially controlled by the effect of increasing thermal regime with time.

CRUDE OIL COMPOSITION

crude oils are naturally occurring, normally free-flowing liquids which have specific gravities between

upper limit of approximately ~ 1.00 i.e. APIg 10°

lower limit of ~ 0.8 i.e. APIg 45°

This definition excludes

1. shale oil obtained only by strongly heating oil shale rocks
2. heavy, semi-solid bituminous oil deposits
3. Light liquid hydrocarbon mixtures (condensate) which are recovered from gas field containing no material of high molecular .weight and have specific gravity below ~ 0.78 i.e. API(g) > 50°

NOTE:

API(g): although a crude of high APIg (low Sp. Gr.) would normally be expected to yield more distillate and less residual fuel than one of lower APIg, there is no simple relationship between crude gravity and yield structure, partly because crudes vary. considerably in the relative proportions of distillates (gasoline, kerosene, gas oil) but of more important. Therefore crude gravity is also dependent on hydrocarbon composition. Aromatics and Naphthenes have higher specific gravities (lower APIg) than paraffin so that crudes of the same gravity, an aromatic/naphthenic crude yield more distillate than a Paraffinic crude of the same gravity.

Conversely, for the same yield structure, a paraffinic crude will have a lower specific gravity (higher APIg) than an aromatic/naphthenic crude.

Crude Composition

Crude oils are complex mixtures, each having a highly individual composition which cannot be matched exactly by any other crude oil.

The compounds in crude oil are essentially hydrocarbon or substituted hydrocarbon in which the major elements carbon (83-87%) and H_2 (10-14%) are combined with three minor elements – Sulphur (0.1 to 3%, rarely up to 7%), nitrogen (mostly below 0.1%, occasionally as high as 2%) and O_2 (up to $1\frac{1}{2}$ %).

Crude oils also generally contain traces of vanadium, nickel, sodium, iron and may also be contaminated with chlorine, arsenic and lead.

Recent analysis show that there is Chromium, vanadium, nickel, lead and magnesium in various concentrations of iron and may also have contamination such as chlorine, arsenic and lead.

The hydrocarbon compounds present in the crude oil can be classified as:

- Paraffins (alkanes)   -   subdivided into normal and isoparaffins
- Naphthenes(cycloparrafins
  or cycloalkanes)   -   cyclopentanes,   cyclohexanes   bicyclo paraffins, tricyclo paraffins
- Aromatics   -   alkylbenzenes,   naphthalenes,   anthracenes, phenanthrenes, etc.

The Non-hydrocarbon constituents are subdivided into:

- Sulphur compounds   -   hydrogen sulphide, mercaptans (thiols), monosulphides (thia alkanes), disulphides, cyclic sulphides (thiophenes), benzothiophenes, etc.
- Nitrogen Compounds   -   Pyridines, quinolines, carbazoles, etc.
- Oxygen compounds   -   Saturated fatty acids, naphthenic acids, phenols etc.

CRUDE ANALYSIS

Detailed analysis of crude samples which are thoroughly representative of average production of crude quality are essential for planning the most effective utilization of a crude oil in the refining system and for assessing its potential sales value in world markets.

More elaborate analysis are required to provide data for forward planning, studies and future plant construction, for assessing the suitability of a crude oil for the manufacture of specialty products (lubricants, bitumens, normal paraffins, chemicals, etc.).

The crude oil is separated into fractions for analysis by distillation in laboratory apparatus under atmospheric and reduced pressure.

Tests which are applied to the original crude oil and its fractions include:

a. Physical property measurements: - density or specific gravity, viscosity, etc.
b. Chemical analysis: - Sulphur, nitrogen, trace metals
c. Composition data: - individual saturates to C_3 like methane, ethane…etc. aromatics to C_{10}, n-paraffins to C_{30} or above
d. Semi-empirical tests – pour point, octane number

Some of the results of analysis include the indication of

1. Gravity:

There is no simple relationship between crude gravity and yield structure, partly because crudes vary considerably in the relative proportions of distillates (gasoline, kerosene, gas oil). However, it has been shown that crude gravity is dependent on hydrocarbon composition.

Note: Aromatics and naphthenes have higher specific gravities than paraffins so that for crudes of the same gravity, an aromatic/naphthenic crude will yield more distillate than a paraffinic crude of the same gravity. Conversely, a parrafinic crude will have a lower specific gravity than an aromatic/naphthemic crude.

2. Sulphur content

Successive fractions from crude show an increase in Sulphur content, and as a general rule about 80-90% of the Sulphur in crude is concentrated in the residue. Hence, crudes are normally classified as low, medium or high Sulphur crude relative to the amount of Sulphur in the residue.

- Low   Sulphur   content   crude
                crude contains < 1% in the residue
- Medium   Sulphur   content   crude
            crude contains between 1% to 3% in the residue
- High   Sulphur   content   crude
            crude contains > 3% in the residue

3. wax and Pour Point

wax contents of crude oil can range from less than 0.5% to as high as 40 to 50%. However, majority of the world crude contains about 5 to 7% wax. Crudes of high wax content and hence, a pour point cause handling problem. such require heating to discharge from the tanker and storage

WAX IN CRUDE OIL

Under the condition of temperature and pressure occurring underground, reservoir oil contains paraffin wax in suspension or solution in the crude. As the oil flows from the reservoir to the surface there is a reduction of temperature, pressure and the amount of dissolved gases contained in the oil.

Reduction of temperature of gas outbreak have shown to be factors causing reduced solubility of the paraffin in the crude.

Hence, as the oil flows up the well tubing, it cools and at some point, up the tubing, the tubing wall temperature is equal to the wax saturation. Temperature of the oil, at this point in the system the temperature falls below the oil cloud point and deposition of wax begins.

The Pour Point

The Pour Point is often used as a total indicator of a crude oil flow proportions.

waxy Crude: Crude that have tendency for deposition of paraffin and asphalt

Organic Deposit: deposit of paraffin and asphalt

Paraffin Deposits: Those materials insoluble in crude oil at the prevailing producing conditions of temperature and pressure.

Crude wax or paraffin deposit: consist small wax crystals that tends to agglomerate

Deposited paraffin: contains:

1. Gum
2. Resins
3. Asphaltic materials
4. Crude oil
5. Sand
6. Salt
7. Water

May also contains a variety of foreign materials such as:

1. Various metal oxides
2. Sulphate
3. Carbonate of iron
4. Barium and calcium
5. Amorphous wax
6. Gummy hydrocarbons with oil and inorganic

Paraffin deposits contain straight or branched chain hydrocarbons ranging from $C_{18}H_{38}$ to $C_{40}H_{82}$ C_nH_{2n+2}

C_{18} $\rightarrow$ C_{40}

Newberry 1984: stated that organic deposits comprises

PARAFFIN AND ASPHALTENES

waxy Crude oil:- oil laden with the paraffin and asphaltenes

The most prevalent type of crude oil in Nigeria is that Laden with Paraffin

By definition, paraffin deposits are those materials which are insoluble in crude oil at the prevailing producing conditions of temperature and pressure.

Paraffin deposits could form either downhole in where tubing or along surface flowlines, this interferes with production and therefore becomes an undesirable menace.

Reistle (1927) reported that the deposit of crude wax or paraffin consist of

   i.   very small wax crystals that tend to agglomerate

  ii.   gums

 iii.   Resin

 iv.   Asphaltic materials

  v.   crude oil

 vi.   sand

 vii.   salt

viii.   water

 ix.   foreign materials such as various

        a.   metal oxides, sulphates,

        b.   carbonate of iron, barium and calcium

  x.   gumming hydrocarbons mixed with oil and inorganic salt

In the refinery, when transported by pipeline to inland refineries, they must be diluted with less waxy crudes.

DISTILLATION IN PETROLEUM REFINERIES

Distillation of crude oil and of the fractions obtained from this primary step are among the most important operations in the petroleum refinery.

The various types of distillation operations involved are:

TYPES OF DISTILLATION

1. Crude oil Distillation
2. Vacuum Distillation
3. Light Oil Distillation
4. Special Product Distillation

1. CRUDE OIL DISTILLATION

This is the essential first step in any refinery which receives crude oil. This is to separate the crude into different fractions. The separation is made on the basis of boiling point – groups of hydrocarbons boiling within a certain range being produced. In some case some of these groups are used as feedstock for further processes such as catalytic reforming or isomerization.

The product distribution is somewhat variable, but a typical unit would distill crude oil to obtain – raw liquid petroleum gas (LPG), Straight run gasoline, Benzene, Naphtha, Kerosine, Light gas oil, Heavy gas oil and a residue.

CRUDE OIL DISTILLATION UNIT

Crude units are expensive to construct and operate.

Figure 1 shows a typical unit.

The crude oil is distilled in a primary tower giving an overhead product of gas and gasoline. The bottom product is then further distilled in the secondary tower to give normal atmosphere distillates up to heavy gas oil.

However, in figure 2 both major operations

- Separation of the light distillates (gasoline to gas itself) and other fractions (from benzene to heavy gas oil) are executed in a single column.

Comparing the two configurations, the latter trends is to be preferred.

i. Because only one furnace is required

ii. The after fractionator tower (re-run tower) is a smaller column than the fore flash column in the former configuration.

Subsequently, these two main factors tend to provide a cheaper unit.

COLUMN DIMENSIONS

The column height is governed by the number of trays, generally, heights could be expected to vary from about 110ft in column containing 30 trays (from which 4 products are withdrawn) to about 160ft for 50 tray columns from which the 6 products are withdrawn.

The diameter of the columns is determined from the vapor and liquid rates which they have to handle.

However, in many cases, particularly where circulating refluxes are removed, the vapor and liquid rates vary considerably from section to section. In this circumstance, two or more sections of different diameters are used, rather than to maintaining a diameter consistent with that required to handle the maximum vapor and liquid loads at a given point.

Plates

Bubble cap trays are still being used in certain sections of the columns where large change in vapor and liquid traffic may be encountered because they are relatively weep proof, but the presence of high liquid gradient in such cases makes suitably designed value trays preferable. The major disadvantage of sieve in such situation in its inflexibility. The holes through which the vapor passes are unshielded and at low vapor rates. There is little to prevent lig dropping through, the hence short-circuit, the down comer

DESALTING

Nowadays, a desalter is almost always included in a crude oil distillation complex.

Crude oil contains salt in varying quantities depending mainly on source, age of well etc. if the salt is allowed to pass through the unit without treatment for it's naturalization or removal it can cause severe hydrochloric (HCl) corrosion problems. Such things as complete disappearance of the top three trays of a column and extreme wear to the point of disintegration in overhead lines have been

known to occur. Hence, the importance of installing desalting facilities cannot be overemphasized. The desalter usually consists of a water/oil, mixing/settling arrangement.

The separation is often assisted by an electrical fuel from electrodes placed inside the separating vessels.

Sometimes systems based on the water/oil – mixing/settling arrangements.

Use of a demmrifying chemicals are used.

The water leaches out the salt and is then removed from the vessel. But since in complete separation of the water and oil takes place, some salt is left in the crude. further reduction can be achieved by two or more stages of mixing/settling.

Nevertheless, it is found that one stage is adequate for work purposes.

Difficult Crude - on occasions where a difficult crude is to be handled and desalting efficiency falls off, additional caustic soda solution is added downstream by the desalter to maintain a fairly neutral pH in the water drawn from the overhead receiving vessel.

Furthermore, Ammonia injection facilities are always provided to the top four trays in the column to neutralize any HCl which find its way through the system. This NH_3 addition also has the effect of forming ammonium sulphide from H_2S.

The combination of desalting, caustic soda addition and ammonia injection are the three main means of combatting corrosion in crude oil distillating unit

VACUUM DISTILLATION

Residue from the crude unit, that is, the stream drawn off below the vaporizing section can be sold directly as a fuel oil.

Normally other products such as vacuum residue, heavy gas oil etc. are blended in according to the product specifications. the distillates produced from this operation may be used as feedstock so, for example, a catalytic cracker, or may be further processed to produce lubricating oil base stocks.

A typical vacuum distillation unit is illustrated in figure 3.

Its operation is similar to crude oil distillation. The Essential differences are:

- The distillation is carried out under vacuum
- there is no overhead vapor product other than a small quantity of vacuum gas oil

Vacuum Distillation Process

Atmospheric residue is the starting point after further heating in a separate furnace with steam injection to the furnace coils to assist vaporization, the atmospheric residue enters the lower part of the distillation column operating under vacuum.

The vacuum at the top of the column is obtained by steam ejector discharging into water cooled condensers giving rise to a pressure of 60-80mm Hg absolute.

The pressure in the "flash zone" i.e. where the mixture of all hot vapours, steams and unvaporized liquid enter the column from the furnace, will be about 120-150mm Hg absolute.

To avoid thermal cracking of the field in the column, the maximum temperature to which the oil may be heated is restricted to about 400°C. This is to avoid the production of undesirable materials such as colored unstable compounds and material with low viscosity indices.

Laboratory distillation studies using "dry" vacuum (i.e. without steam injection) show that much lower pressures are required at the permitted distillation temperature to obtain the heaviest lubrication oil distillate.

In commercial distillation the hydrocarbon partial pressure in the flash zone to obtain the desired amount of vaporization is achieved by the injection of further quantities of steam near the base of the condom beneath the residue stripping trays. All the injected steam passes up the column and is condensed with the vacuum ejector steam.

Vacuum gas oil is taking off and the highest side stream and three other lubricating oil distillates of increasing viscosity are withdrawn from selected trays going down the column.

The court are finally steam stripped in separate strippers to improve the separation between the viscous streams.

The distillates havere than physical oil are solid at room temperature due to the presence of wax.

The black vacuum residue, although appearing to be solid at room temperature is very viscous liquid.

This residue, containing the highest viscosity lubricating oils namely bright stocks and cylinder oils is passed to the propane deasphalting units.

STEAM injection of pressure level required (crude oil notes)

LIQ TRAPOUT ARRANGMENT

NOTE: SOLVENT EXTRACTION

The vacuum distillates contain complex multi-ring aromatic compounds which are poor in oxidation stability and have poor viscosity temperature properties i.e. low viscosity index.

The undesirable aromatic compounds present in the raw lubricating stream are removed in counter-current liquid-liquid extraction process.

The two solvents which are most widely used are phenols and furfural.

The process described here is furfural extraction process.

Furfural is originally produced by the Quaker Oats Company from Oats husks in early 1920's but the major source of the world's supply is now corn cobs.

Furfural having a ring structure preferentially dissolves aromatic compounds because furfural has a higher density than the waxy feedstocks, it is pumped to the top of the extraction column and flows downwards against a rising stream of waxy distillate.

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                                              →  Raffinate phase to strippers
Furfural

                                                 Packed column

                                                 Inter phase

Waxy distillate

                                              →  Extract phase to stripper
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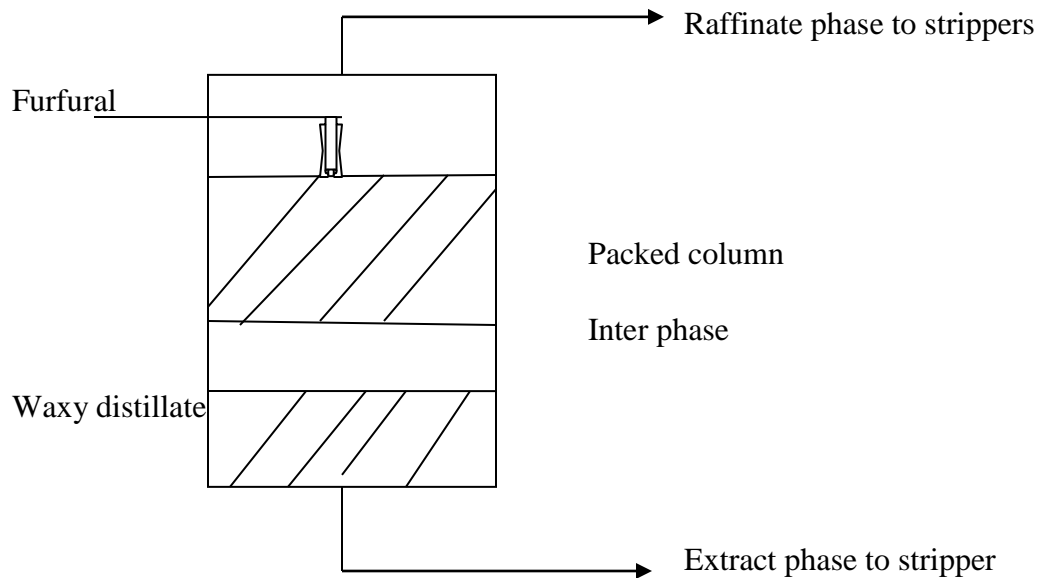
Diagram Solvent Extraction Column

Each stream use then passes through independent solvent recovery sections.

The heat supply is either by circulating hot oil or by direct fired heaters.

The raffinate and extract streams are finally steam stripped under vacuum to remove all the furfural. The furfural is then condensed, dried and recycled to the extraction tower.

But this removal process of the low-quality aromatic extract which may amount to 20% to 50% the wax originally presents is concentrated by a corresponding amount.

Solvent Dewaxing

At this stage, the wax is already out of solution but the viscosity of the mixture prevent direct filtration (except for the low viscosity spindle grade).

However, to separate the wax from the oil, a low viscosity solvent is used to dissolve the oil but not the wax and thus makes direct filtration possible.

Two forms of dewaxing solvents are applicable:

- Single-component dewaxing solvents (such as liquid propane and methyl iso-butyl ketone)
- Two-component dewaxing solvent such as benzine-acetone, toluene-methyl ethyl ketone, methylene chloride, dichlorethane

Most dewaxing plants use a two-component solvent. All solvent dewaxing processes operate in the same manner, although the actual process conditions vary depending on the solvent system used.

However, in this lecture the methyl ethyl ketone (MEK) - Toluene process is described

MEK $=$ $CH_3.CO.C_2H_5$ Boiling Point 79°C

Toluene $=$ $C_6H_5.CH_3$ Boiling Point 110°C

Toluene is the solvent for the oil and methyl ethyl ketone is the antisolvent MEK-Toluene is mixed with the hot oil and a complete solution of oil and wax is obtained.

The mixture is cooled in double pipe scrapped it exchanger and then chilled in double pipe scraped chillers (the scrapers prevent wax from adhering to the walls) down to about -20°C. The solid wax is then filtered out on rotary vacuum filters and the wax cake on the outside of the revolving drum is washed with cold solvent to ensure a good recovery of wax-free oil. The wax cake is dislodged from the filter cloth by a small gas pressure applied inside the drum, and the filtered wax-free oil in solvent solution is withdrawn. On a large dewaxing plant, fire rotary filters, each of 700-1000 square feet filtration area may be required. The solvent is recovered from the dewaxed oil and wax streams, using steam. It is usual to employ double effect evaporators to minimize utility requirements. The recovered solvent streams are recirculated to the hot incoming feed.

The total quantity of solvent required for the process

Dilution Solvent

This solvent used to watch the cake

- is 3 vols – 5 vols per volume of feedstock
- higher solvent dilution is required for higher viscosity oils in order to obtain a solution of suitable viscosity at filtration temperature.

The quantity of wax removed is of the order of about 20 – 25% by weight of waxy fuel.

Catalytic Cracking

The function of catalytic cracker is to convert fuel oil components to gasoline and middle distillate components.

Catalytic cracking developed from the discovery that natural silica alumina please catalyze the cracking of heavy oils to give good yields of gasoline.

Catalysts

All commercially used catalyst are based on silica alumina or silica magnesia. During normal operations, with continuous transfer through successive reaction and regeneration cycles, the physical and catalytic properties of the catalysts are degraded. Hence, intermittent or continuous addition of fresh and withdrawal of used catalyst is practiced to maintain a level of equilibrium activity.

There are four main divisions of the most widely used synthetic catalyst

1. Low alumina (13% wt Al_2O_3 /87% SiO_2) this is the original synthetics Products
2. High alumina (25-28% wt Al_2O_3), having increased activity for gasoline production than (1)
3. Silica magnesia (28% wt MgO), giving more light gas oil at the expense of light gasoline than (1).
4. Zeolite (aluminosilicate, molecular sieve) promoted silica alumina (5-25% wt zeolite). giving much greater activity and selectivity for gasoline production over (1-3)

The synthetic catalysts can be made in the form of micro-spheres, which are more resistant to breakdown by attrition and cost less corrosion of the plant equipment.

Operating Conditions

The Independent operating variables are:

1. reactor temperature

2. catalyst type and activity

3. recycle oil ratio

4. space velocity (level of catalyst in the reactor)

5. feedstocks

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6. feed preheat temperature

Normal practice is to operate with minimum reactor catalyst bed level and adjust the conversion level by means of the reactor temperature.

The temperature is changed by allowing more or less hot catalyst from the regenerator to mix with the entering feedstock

Riser Cracking

Originally, cracking was taught to occur substantially in the reactor, but it is now known that considerable conversion is obtained in the transfer line leading to the reactor. Consequently, plants are now designed for transfer line or riser cracking, thereby reducing the importance of the reactor almost to a settling and separation zone for catalyst.
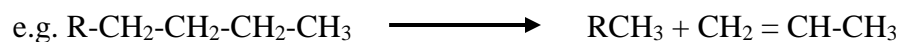
In modern riser cracker, contact line between the oil and catalyst is between 2 and 5 seconds in the riser, with some form of separation device at the end of the riser.

Short contact time riser cracking is carried out at temperature as high as 540 degrees centigrade using high activity zeolite catalysts to give high yield of gasoline.
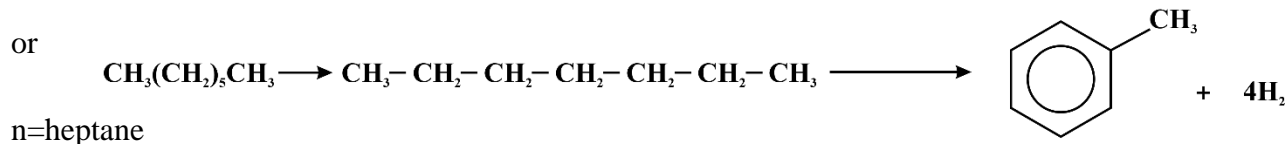
The Catalyst and operating conditions can, also, be selected to maximize middle distillate production if so required.

The major reaction in this process is C-C bond fission yielding products with 3 or 4 C atoms.

The main disadvantage of the process is the formation of coke on catalyst which is removable by combustion.

e.g. $R\text{-}CH_2\text{-}CH_2\text{-}CH_2\text{-}CH_3 \longrightarrow RCH_3 + CH_2 = CH\text{-}CH_3$

$$R-CH_2-CH_2-\underset{\underset{CH_3}{|}}{CH}-CH_3 \longrightarrow RCH_3 + CH_2=\underset{\underset{CH_3}{|}}{C}-CH_3$$
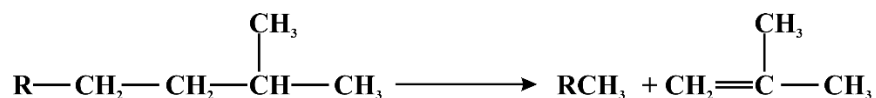
some dehydrocyclisation also occurs:

or

$$CH_3(CH_2)_5CH_3 \longrightarrow CH_3-CH_2-CH_2-CH_2-CH_2-CH_2-CH_3 \longrightarrow$$

 $+ \quad 4H_2$

n=heptane

Olefins are the most reactive hydrocarbons in catalytic cracking. they undergo rapid cracking and rapid isomerization, e.g.:

$$CH_3-CH_2-CH=CH_2 \rightleftharpoons CH_3.CH=CH.CH_3$$
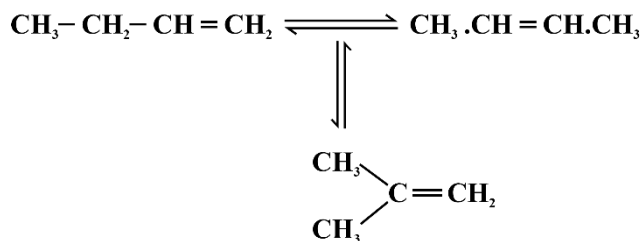
search branched-chain olefins then undergo hydrogen transfer with naphthenes, etc. to produce iso-paraffin e.g.
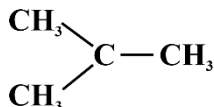
Other reactions taking place include:

1. olefins polymerize and condense to Aromatics to cokes
2. Naphthenes undergo ring and chain rupture to Olefin and paraffins

the main disadvantage is the formation of coke on catalyst which is removable by combustion.

Thermal Cracking

Heat and pressure are used to decompose hydrocarbons from crude oil fractions to produce lighter hydrocarbons.

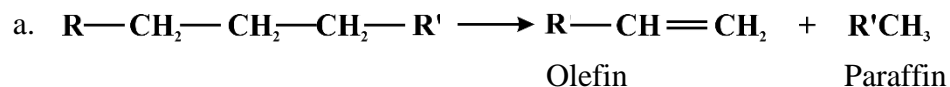This process is first used to improve gasoline yield from Petroleum.

Temperature of operation is $450°$ to $850°C$ pressure is within 1000 p.s.i
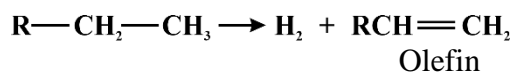
Reactions involve:

1. C-C Bond rupture and formation
2. dehydrogenation including organisation of naphthenes

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3. isomerization

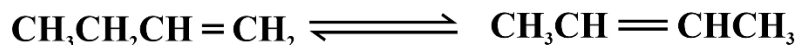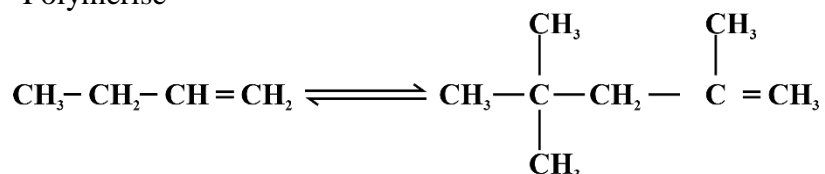4. polymerization

Examples of reactions involved

a. $R-CH_2-CH_2-CH_2-R' \longrightarrow R-CH=CH_2 + R'CH_3$

                                           Olefin   Paraffin

b. Dehydrogenation

  $R-CH_2-CH_3 \longrightarrow H_2 + RCH=CH_2$

                            Olefin

Olefin can now:

(i)   Isomerise

       $CH_3CH_2CH=CH_2 \rightleftharpoons CH_3CH=CHCH_3$

(ii)   Dehydrogenate

       $CH_3CH_2CH=CH_2 \rightleftharpoons H_2 + CH_2=CH-CH=CH_2$

(iii)   Polymerise

$$CH_3-CH_2-CH=CH_2 \rightleftharpoons CH_3-\overset{\overset{\textstyle CH_3}{|}}{\underset{\underset{\textstyle CH_3}{|}}{C}}-CH_2-\overset{\overset{\textstyle CH_3}{|}}{C}=CH_3$$

Naphthenes $\xrightarrow{\text{dehydrogenate}}$ Aromatics

C_6H_{14} $\xrightarrow{-H_2}$ ⬡ $\xrightarrow{-3H_2}$ ⬡
hexane   Cyclo hexane   benzene
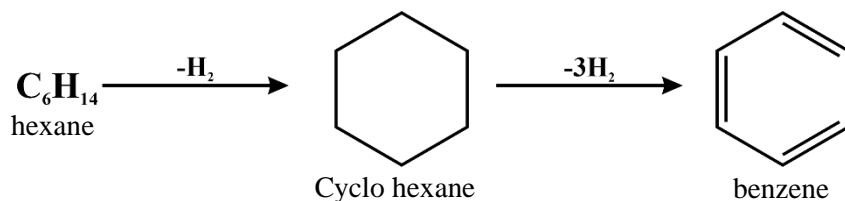
Thermal cracking is also used as a source of light hydrocarbons e.g. Cracking of ethane propane butane in natural gas and Petroleum to ethylene and propylene

Reforming processes

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catalytic reforming is one of the main processes for the production of motor gasoline taking straight sun naphthas in the boiling range of 70-190ºC as feed and raising octane number from about 40 to 95.

The main reactions are

1. dehydrogenation of naphthenes to Aromatics plus hydrogen
2. isomerisation of normal paraffin to isoparaffins
3. dehydrocyclisation of normal paraffin to Aromatics plus hydrogen
4. hydrocracking

The dehydrogenation

(1) is a very rapid reaction which is highly endothermic (2) and (4) are relatively slower reactions (2) is slightly exothermic (4) is highly exothermic (3) takes place in two stages first- cyclisation reaction to give a Naphthene (slow)