MANUFACTURE OF BITUMENS

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INTRODUCTION

- BITUMENS: Bitumens are black viscous mixture of hydrocarbons obtained naturally or a residue from petroleum distillation.
- It is used for road surfacing and roofing.
- Bitmens manufacture from crude oils have developed since 1900.
- Asphaltic crude oils were more suited to the production of heavy residues than others.
- Bitumens are derived from crude oils using distillation process not giving any degree of thermal cracking.

Selection of Crude Oil

- Bitumens can be economically manufactured only from specific crudes.
- Crude oils used for bitumen manufacture are chosen generally to yield 20 wt.% or greater of vacuum residue having the required properties to provide a full range of bitumens.
- Light crude oils give low viscosity vacuum residues.

- These could be used to produce satisfactory bitumens by giving essential extra processing and the use of additional components. Generally it would not be economical to do this.
- Very heavy crude oils yield 50 wt.% or more of vacuum residue. Such crude oils are highly viscous and difficult to move in pipelines.
- They find particular use in costal refineries by bitumen manufacturers or are blended with lighter crude oils.'

- The crude can be arranged as naphthenic, intermediate and paraffinic with respect to bitumin potentiality.
- The vacuum residue production at most refineries is much greater than the volume needed to make bitumens.
- Excess vacuum residue is used to produce heavy fuel oils either by visbreaking or bending with other oil components.
- The yield of vacuum residue and its properties for five crudes is given in the following table.

Characteristics of Crude Oils

Characterstics	North Rumaila (550°C)	Aghajari (550°C)	Basrah (530°C)	Dubai (550°C)	Bombay High (530°C)
Yeild , wt.% crude oil	20.5	17.5	20.6	19.0	6.2
Density at 15°C , gm/cc	1.031	1.017	1.019	1.046	1.0028
API gravity	5.8	7.6	7.3	3.72	9.51
Kinematic viscosity at 98.9°C , cSt	2943.7	1700	1043	5229	377.23
Softening point, °C	38.5	42.8	30.4	55.1	61.0
Penetration at 25°C, 100g,5 s , 1/10 mm	142	128	398	19	25
Ductility at 27°C , cm	130	100	56	130	7
Asphaltene, wt. %	7.2	4.8	3.3	15.5	7.1
Conradson carbon residue wt. %	21.5	20.8	21.4	28.9	19.2

Methods of Manufacture of Bitumens

- Bitumens are manufactured from carefully selected crude oils using a number of refining techniques.
- The type of process employed depends on
  -- the nature of crude oil
  -- the grade of bitumem desired
  -- product pattern of the refinery
- Different stages in processing to produce bitumens are shown in the following figure:

Distillation

- Atmospheric distillation of crude oils is conducted upto 300 – 370 degree celsius.
- This yields components for gasoline, kerosine and gas oils and atmospheric residue. With very high crude oils, the atmospheric residue is in some cases used for bitumen.
- The atmospheric residue can be further distilled to yield heavy gas oils, waxy distillates for lubricating oil manufacture and vacuum residue.
- Distillation is conducted under vacuum to allow lower distillation temperatures and prevents thermal cracking of the components of atmospheric residue

- Vacuum distillation of atmospheric residue removes lower boiling components.
- The removal of distillates leads to the preferential removal of saturates and the concentration of asphaltenes in vacuum residue.
- The vacuum residues of naphthenic crudes generally meet the specification of penetration bitumens which are referred to as ‘straight-run bitumens’.

Solvent Precipitation

- The high boiling components of some crudes are difficult to separate by distillation even when high vacuum is used.
- vacuum residue of some naphthenic and aromatic crude oils contains a good amount of oil which can be used for making lubricating oil base stocks and as catalytic cracker feedstock.
- This oil is recovered by extraction using liquid propane as solvent.
- The propane to feed ratio by volume is kept at a value of 3 to 5.

- The residues obtained by propane precipitation are also used to produce bitumens.
- Such residues have higher asphaltenes contents than vacuum residues but lower saturates contents than would be obtained by distillation of the vacuum residues.
- They have lower asphaltenes and saturates contents in comparison with penetration bitumens of similar penetration range.
- The propane precipitated asphalt has a low penetration and it is blended with suitable flux to get the desired penetration grade bitumens.

AIR BLOWING PROCESS FOR MANUFACTURE OF BITUMEN

AIR BLOWING

- This process gives the refiner a wide flexibility to produce bitumen which cannot be produced otherwise.
- Vacuum residues from particular crude oils meet the specification requirements for **penetration bitumens** or **viscosity graded asphalts.**
- For harder penetration bitumens however further processing is needed to obtain desirable properties for road or industrial uses. This is achieved by air blowing.
- In this process the aromatics and polar aromatics in the feed flux are condensed to form higher molecular weight species in the air-blown bitumen.
- The process doubles the asphaltenes levels while the levels of aromatics are reduced.

- **Limited air blowing** is only needed where it is necessary to produce penetration bitumens or viscosity graded asphalts from vacuum residue.

- It is possible to blow the vacuum to desired penetration range or to blow the vacuum residue to lower penetration value than needed.

- The latter can then be blended with the vacuum residue in a varying proportion to provide a range of bitumens.

- This second alternative can be referred to as over ***blowing and back blowing, semi blowing or partial blowing as only a part of the vacuum residue*** is blown.

- Oxidized bitumens, roofing asphalts or air-blown asphalts are produced using extended air blowing of vacuum residues or mixtures of vacuum residues and materials such as atmospheric residues or waxy distillates. Even, lubricating oil extracts are used to a limited extent.

- Catalysts in small concentrations such as ferric chloride (0-1%) and phosphorus pentaoxide (0-4%) are used to speed the reaction or modify the properties of the resultant bitumens.(***catalytic air blown bitumens***)

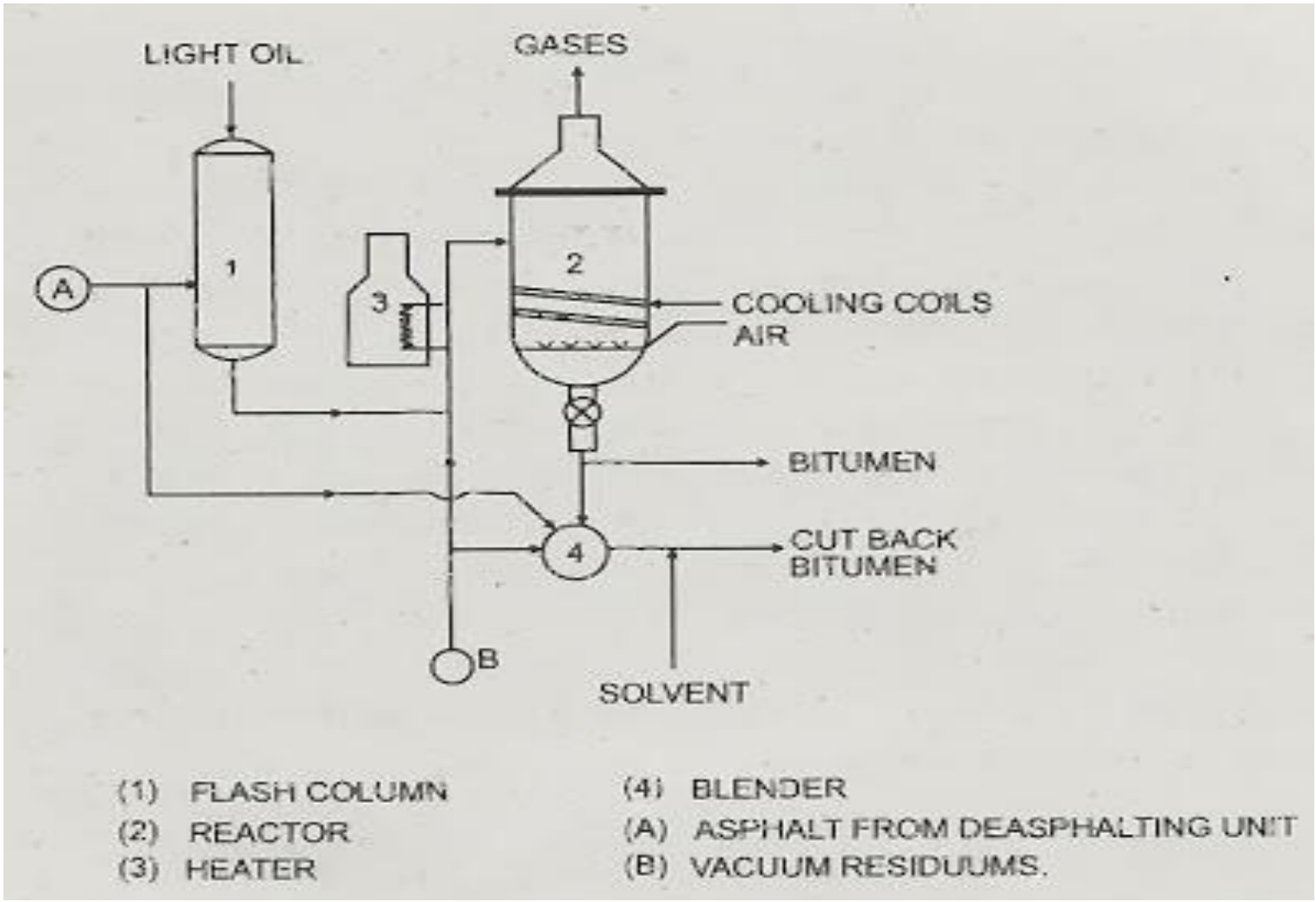
- The blowing processes give rise to noxious fumes. These are mixtures of sulphur compounds, light oils and steam. They are eliminated by water scrubbing and incinerated in a fume disposal furnace.

AIR BLOWING PROCESS

- ***Air blowing is a process in which hot liquid asphalt is contacted with air***. This process dehydrogenates the residues, resulting in oxidation and condensation polymerization, increases the overall molecular weight.

- This process provides products with properties that are unattainable by other means. These properties have made bitumen adaptable to roofing, waterproofing, adhesive and sealing applications.

- The asphalt is hardened as a result of air blowing and the properties of hard air blown bitumen are less susceptible to change with varying temperature and those of comparable asphalts from other processes.



Batch process for bitumen manufacture

Batch process for manufacture of bitumen:

•Air blowing of bitumen is mostly done in batch units.

•In this operation, asphalts from various sources are mixed and heated to a temperature of 200-210 degrees and sent to a reactor.

•The reactor may be horizontal or vertical type, usually made of mild steel , of a capacity to hold 1000 tons of charge stock .

•These reactors are fitted with air distributors at the bottom and also cooling and heating coils.

•During oxidation the temperature may increase rapidly, hence as a precautionary measure provision for cooling is made available.

•The reactor should be maintained at a temp. of 240 to 300 degrees.

•Blowing time lasts for 10 to 14 hours depending upon the required consistency of bitumen.

•Gases are allowed to escape into refinery flare up or combustion system after being stripped with water.

•The product, air blown bitumen is obtained from the bottom of the reactor.

PROCESS VARIABLES:

EFFLUX OF FLUX SOURCE OR COMPOSITION:

Flux source has significant effect on the following dependent variables:

- Softening point penetration relationship
- Composition of blown bitumen
- Rate of reaction
- Heat of reaction per degree of softening point rise.
- Process losses

The **composition** of the blown bitumen is known to change substantially during air blowing.

Asphaltenes always increase significantly while naphthene aromatics always decrease.

The process losses consist of:

•Condensable oils which are derived from the front end distillate fractions naturally present in the flux.

•Water which is the reaction product when flux hydrocarbons are hydrogenated.

•Non condensables consisting of gaseous reaction products.

EFFFLUX OF FLUX CONSISTENCY

Lower flux or consistency or viscosity yields blown bitumen with higher penetrations at the same softening point level. Flux consistency has only a slight effect on the other dependent variables.

EFFECT OF BLOWING TEMPERATURES

•Slightly higher penetration is observed when lower temperature are used.

•More asphaltenes are made when using higher blowing temperature.

•Reaction rate becomes greater as the temperature is increased.

•Product losses are always higher at high temperature undoubtedly due to distillation effect.

AIR RATE OR DEGREE OF DISPERSION

The higher the air rates and better degree of dispersion significantly increase the rate of reaction.

CATALYSTS

Catalysts significantly increase the penetration with **ferric chloride** being more effective than phosphorous pentaoxide.

When ferric chloride is added to the air blowing step the cyclo saturates are dehydrogenated.

TYPICAL OPERATING CONDITIONS:

Temperature °C	240-300
Air rate $m^3/h/kg$	0.025-0.050

Thanks