OIL REFINERY PROCESSES
1. Introduction
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5. Conversion of Heavy Residues
6. Treatment of Refinery Gas Streams
INTRODUCTION

• Oil refining is a key activity in the CPI.
• Over 600 refineries worldwide have a total annual capacity of more than $3500 \times 10^6$ tonnes.
• Goal of oil refining is twofold:
  i. production of fuels for transportation, power generation and heating; and
  ii. production of raw materials for the CPI.
• Oil refineries are complex plants but are relatively mature and highly integrated.
Overview

• After desalting and dehydration, crude is separated into fractions by distillation.
• The distilled fractions can not be used directly.
• The reason for such a complex set of processes is the difference between the crude oil properties and the needs of the market.
• Another reason for complexity is environmental. Legislation demands cleaner products and is the major drive for process improvement and development of novel processes.
Refining operations

Petroleum refining processes and operations can be separated into five basic areas:

• **Fractionation** (distillation) is the separation of crude oil in atmospheric and vacuum distillation towers into groups of hydrocarbon compounds of differing boiling-point ranges called "fractions" or "cuts."

• **Conversion Processes** change the size and/or structure of hydrocarbon molecules. These processes include:
  – Decomposition (dividing) by thermal and catalytic cracking;
  – Unification (combining) through alkylation and polymerization; and
  – Alteration (rearranging) with isomerization and catalytic reforming.

• **Treatment Processes** to prepare hydrocarbon streams for additional processing and to prepare finished products. Treatment may include removal or separation of aromatics and naphthenes, impurities and undesirable contaminants. Treatment may involve chemical or physical separation *e.g.* dissolving, absorption, or precipitation using a variety and combination of processes including desalting, drying, hydrodesulfurizing, solvent refining, sweetening, solvent extraction, and solvent dewaxing.
Refining operations

• **Formulating and Blending** is the process of mixing and combining hydrocarbon fractions, additives, and other components to produce finished products with specific performance properties.

• **Other Refining Operations** include:
  – light-ends recovery;
  – sour-water stripping;
  – solid waste, process-water and wastewater treatment;
  – cooling, storage and handling and product movement;
  – hydrogen production;
  – acid and tail-gas treatment;
  – and sulfur recovery.
PHYSICAL PROCESSES

- Desalting/dehydration
- How does distillation work?
- Crude distillation
- Propane deasphalting
- Solvent extraction and dewaxing
- Blending
Desalting/dehydration

• Crude oil often contains water, inorganic salts, suspended solids, and water-soluble trace metals.
• **Step 0** in the refining process is to remove these contaminants so as to reduce corrosion, plugging, and fouling of equipment and to prevent poisoning catalysts in processing units.
• The two most typical methods of crude-oil desalting are chemical and electrostatic separation, and both use hot water as the extraction agent.
• In chemical desalting, water and chemical surfactant (demulsifiers) are added to the crude, which is heated so that salts and other impurities dissolve or attach to the water, then held in a tank to settle out.
• Electrical desalting is the application of high-voltage electrostatic charges to concentrate suspended water globules in the bottom of the settling tank. Surfactants are added only when the crude has a large amount of suspended solids.
• A third (and rare) process filters hot crude using diatomaceous earth.
Desalting/dehydration

- The crude oil feedstock is heated to 65-180°C to reduce viscosity and surface tension for easier mixing and separation of the water. The temperature is limited by the vapor pressure of the crude-oil feedstock.

- In both methods other chemicals may be added. Ammonia is often used to reduce corrosion. Caustic or acid may be added to adjust the pH of the water wash.
Desalting/dehydration
How does distillation work?

- Distillation is defined as:
  - a process in which a liquid or vapour mixture of two or more substances is separated into its component fractions of desired purity, by the application and removal of heat.
How does distillation work?

- Distillation is based on the fact that the vapour of a boiling mixture will be richer in the components that have lower boiling points.
- Thus, when this vapour is cooled and condensed, the condensate will contain the more volatile components. At the same time, the original mixture will contain more of the less volatile components.
- Distillation is the most common separation technique and it consumes enormous amounts of energy, both in terms of cooling and heating requirements.
- Distillation can contribute to more than 50% of plant operating costs.
How does distillation work?

Distillation columns are classified by the manner in which they are operated:

1. Batch, in which the feed to the column is introduced batch-wise. That is, the column is charged with a 'batch' and then the distillation process is carried out. When the desired task is achieved, a next batch of feed is introduced.

2. Continuous columns process a continuous feed stream. No interruptions occur unless there is a problem with the column or surrounding process units. They are capable of handling high throughputs and are the most common of the two types.
Continuous distillation columns

Classified according to:

1. **Nature of the feed that they are processing:**
   - *binary* column - feed contains only two components;
   - *multi-component* column - feed contains more than two components.

2. **Number of product streams they have:**
   - *multi-product* column - column has more than two product streams.

3. **Where extra feed exits when used to help with the separation:**
   - *extractive* distillation - where the extra feed appears in the bottom product stream;
   - *azeotrop**ic* distillation - where the extra feed appears at the top product stream.

4. **Type of column internals:**
   - *tray column* - trays of various designs used to hold up the liquid to provide better contact between vapour and liquid;
   - *packed column* - packings are used to enhance vapour-liquid contact.
Main Components of Distillation Columns

- A vertical **shell** where separation of liquid components is done.
- Column internals *e.g.* **trays/plates** and/or **packings** which are used to enhance component separations.
- A **reboiler** to provide the necessary vaporization for the distillation process.
- A **condenser** to cool and condense the vapour leaving the top of the column.
- A **reflux drum** to hold the condensed vapour from the top of the column so that liquid (reflux) can be recycled back to the column.
Trays and plates

**Bubble cap trays**
A riser or chimney is fitted over each hole, and a cap covers the riser. The cap is mounted with a space to allow vapour to rise through the chimney and be directed downward by the cap, finally discharging through slots in the cap, and bubbling through the liquid on the tray.
Trays and plates

Valve trays
Perforations are covered by caps lifted by vapour, which creates a flow area and directs the vapour horizontally into the liquid.

Sieve trays
Sieve trays are simply metal plates with holes in them. Vapour passes straight upward through the liquid on the plate. The arrangement, number and size of the holes are design parameters.
Liquid and vapour flows in a tray column
Basic operation

- The **feed** is introduced somewhere near the middle of the column to a tray known as the **feed tray**.
- The feed tray divides the column into a top (enriching or **rectification**) and a bottom (stripping) section.
- The feed flows down the column where it is collected in the **reboiler**.
- Heat (usually as steam) is supplied to the reboiler to generate vapour.
- The vapour from the reboiler is re-introduced into the unit at the bottom of the column.
- The liquid removed from the reboiler is known as the **bottoms product** or simply, **bottoms**.
Basic operation

- Vapour moves up the column, exits the top, and is cooled in a **condenser**. The condensed liquid is stored in a holding vessel known as the **reflux drum**. Some of this liquid is recycled back to the top of the column and this is called the **reflux**. The condensed liquid that is removed from the system is known as the **distillate** or **top product**.
- Thus, there are **internal flows** of vapour and liquid within the column as well as **external flows** of feeds and product streams, into and out of the column.
Crude distillation

• **Step 1** in the refining process is the separation of crude oil into various fractions or *straight-run cuts* by distillation in *atmospheric* and *vacuum* towers. The main fractions or "cuts" obtained have specific boiling-point ranges and can be classified in order of decreasing volatility into gases, light distillates, middle distillates, gas oils, and residuum.

**Atmospheric distillation**

• The desalted crude feedstock is preheated using recovered process heat. The feedstock then flows to a direct-fired crude charge heater then into the vertical distillation column just above the bottom, at pressures slightly above atmospheric and at temperatures ranging from 340-370°C (above these temperatures undesirable thermal cracking may occur). All but the heaviest fractions flash into vapor.

• As the hot vapor rises in the tower, its temperature is reduced. Heavy fuel oil or asphalt residue is taken from the bottom. At successively higher points on the tower, the various major products including lubricating oil, heating oil, kerosene, gasoline, and uncondensed gases (which condense at lower temperatures) are drawn off.
Atmospheric distillation
Simple crude distillation
Vacuum distillation

- To further distill the *residuum* or *topped crude* from the atmospheric tower without thermal cracking, reduced pressure is required.
- The process takes place in one or more vacuum distillation towers.
- The principles of vacuum distillation resemble those of fractional distillation except that larger diameter columns are used to maintain comparable vapor velocities at the reduced pressures. The internal designs of some vacuum towers are different from atmospheric towers in that random packing and demister pads are used instead of trays.
- A typical first-phase vacuum tower may produce gas oils, lubricating-oil base stocks, and heavy residual for propane deasphalting.
- A second-phase tower operating at lower vacuum may distill surplus residuum from the atmospheric tower, which is not used for lube-stock processing, and surplus residuum from the first vacuum tower not used for deasphalting.
- Vacuum towers are typically used to separate catalytic cracking feedstock from surplus residuum.
Vacuum distillation
Solvent dewaxing unit

MAX-DEWAX

waxy feed to filters

lead chilling section

recycled cold solvent

membranes

solvent from recoveries

solvent recovery

dewaxed oil

slack wax mix to wax recovery
Blending

• Blending is the physical mixture of a number of different liquid hydrocarbons to produce a finished product with certain desired characteristics.
• Products can be blended in-line through a manifold system, or batch blended in tanks and vessels.
• In-line blending of gasoline, distillates, jet fuel, and kerosene is accomplished by injecting proportionate amounts of each component into the main stream where turbulence promotes thorough mixing.
• Additives including octane enhancers, anti-oxidants, anti-knock agents, gum and rust inhibitors, detergents, etc. are added during and/or after blending to provide specific properties not inherent in hydrocarbons.
THERMAL PROCESSES

When a hydrocarbon is heated to a sufficiently high temperature *thermal cracking* occurs. This is sometimes referred to as *pyrolysis* (especially when coal is the feedstock). When steam is used it is called *steam cracking*. We will examine two thermal processes used in refineries.

- Visbreaking
- Delayed coking
Visbreaking

- Visbreaking is a mild form of thermal cracking that lowers the viscosity of heavy crude-oil residues without affecting the boiling point range.
- Residuum from the atmospheric distillation tower is heated (425-510°C) at atmospheric pressure and mildly cracked in a heater.
- It is then quenched with cool gas oil to control over-cracking, and flashed in a distillation tower.
- Visbreaking is used to reduce the pour point of waxy residues and reduce the viscosity of residues used for blending with lighter fuel oils. Middle distillates may also be produced, depending on product demand.
- The thermally cracked residue tar, which accumulates in the bottom of the fractionation tower, is vacuum-flashed in a stripper and the distillate recycled.
Visbreaking
Visbreaking

- Alternatively, vacuum residue can be cracked. The severity of the visbreaking depends upon temperature and reaction time (1-8 min).
- Usually < 10 wt% of gasoline and lighter products are produced.
Delayed Coking

• Coking is a severe method of thermal cracking used to upgrade heavy residuals into lighter products or distillates.
• Coking produces straight-run gasoline (Coker naphtha) and various middle-distillate fractions used as catalytic cracking feedstock.
• The process completely reduces hydrogen so that the residue is a form of carbon called "coke."
• Three typical types of coke are obtained (sponge coke, honeycomb coke, and needle coke) depending upon the reaction mechanism, time, temperature, and the crude feedstock.
• In delayed coking the heated charge (typically residuum from atmospheric distillation towers) is transferred to large coke drums which provide the long residence time needed to allow the cracking reactions to proceed to completion.
Delayed Coking

Diagram showing a process flow for delayed coking, with labels for feed, coke drums, furnace, fractionator, gas oil stripper, gas, and unstabilized naphtha.
CATALYTIC PROCESSES

- Fluid Catalytic Cracking (FCC)
- Hydrotreating
- Hydrocracking
- Catalytic Reforming
- Alkylation
Catalytic Cracking

• Main incentive for catalytic cracking is the need to increase gasoline production.
• Feedstocks are typically vacuum gas oil.
• Cracking is catalyzed by solid acids which promote the rupture of C-C bonds. The crucial intermediates are carbocations (+ve charged HC ions) formed by the action of the acid sites on the catalyst.
• Besides C-C cleavage many other reactions occur:
  - isomerization
  - protonation and deprotonation
  - alkylation
  - polymerization
  - cyclization and condensation
Catalytic Cracking

• Catalytic cracking comprises a complex network of reactions, both intra-molecular and inter-molecular.
• The formation of coke is an essential feature of the cracking process and this coke deactivates the catalyst.
• Catalytic cracking is one of the largest applications of catalysts: worldwide cracking capacity exceeds 500 million t/a.
• Catalytic cracking was the first large-scale application of fluidized beds which explains the name fluid catalytic cracking (FCC).
• Nowadays entrained-flow reactors are used instead of fluidized beds but the name FCC is still retained.
Fluid Catalytic Cracking

**Diagram Description:**
- **Regenerator:** Feed → Regenerated catalyst → Reactor
- **Reactor:** Feed → Fluidized bed → 2-stage Cyclones → Flue gas
- **Cyclones:** 2-stage
- **Flue gas** temperature: 970 K
- **Fluidized bed** temperature: 775 K
- **Spent catalyst** recirculated
- **Steam** enters the riser
- **Riser** connects to the reactor
- **To fractionation** connection at the top
Fluid Catalytic Cracking
Hydrocracking

- Hydrocracking is a two-stage process combining catalytic cracking and hydrogenation, wherein heavier feedstock is cracked in the presence of hydrogen to produce more desirable products.

- The process employs high pressure, high temperature, a catalyst, and hydrogen. Hydrocracking is used for feedstock that are difficult to process by either catalytic cracking or reforming, since these feedstock are characterized usually by a high polycyclic aromatic content and/or high concentrations of the two principal catalyst poisons, sulfur and nitrogen compounds.

- The process largely depends on the nature of the feedstock and the relative rates of the two competing reactions, hydrogenation and cracking. Heavy aromatic feedstock is converted into lighter products under a wide range of very high pressures (70-140 bar) and fairly high temperatures (400°-800°C), in the presence of hydrogen and special catalysts.
Hydrocracking

• When the feedstock has a high paraffinic content, the primary function of hydrogen is to prevent the formation of polycyclic aromatic compounds.

• Another important role of hydrogen in the hydrocracking process is to reduce tar formation and prevent buildup of coke on the catalyst.

• Hydrogenation also serves to convert sulfur and nitrogen compounds present in the feedstock to hydrogen sulfide and ammonia.

• Hydrocracking produces relatively large amounts of isobutane for alkylation feedstock and also performs isomerization for pour-point control and smoke-point control, both of which are important in high-quality jet fuel.
Hydrocracking

• Preheated feedstock is mixed with recycled hydrogen and sent to the first-stage reactor, where catalysts convert sulfur and nitrogen compounds to \( \text{H}_2\text{S} \) and \( \text{NH}_3 \). Limited hydrocracking also occurs.

• After the hydrocarbon leaves the first stage, it is cooled and liquefied and run through a separator. The hydrogen is recycled to the feedstock.

• The liquid is charged to a fractionator.

• The fractionator bottoms are again mixed with a hydrogen stream and charged to the second stage. Since this material has already been subjected to some hydrogenation, cracking, and reforming in the first stage, the operations of the second stage are more severe (higher temperatures and pressures). Again, the second stage product is separated from the hydrogen and charged to the fractionator.
Catalytic Reforming

- Catalytic reforming is an important process used to convert low-octane naphthas into high-octane gasoline blending components called reformates.
- Reforming represents the total effect of numerous reactions such as cracking, polymerization, dehydrogenation, and isomerization taking place simultaneously.
- Depending on the properties of the naphtha feedstock (as measured by the paraffin, olefin, naphthene, and aromatic content) and catalysts used, reformates can be produced with very high concentrations of benzene, toluene, xylene, (BTX) and other aromatics useful in gasoline blending and petrochemical processing.
- Hydrogen, a significant by-product, is separated from the reformate for recycling and use in other processes.
Catalytic Reforming

- A catalytic reformer comprises a reactor and product-recovery section.
- There is a feed preparation section comprising a combination of hydrotreatment and distillation.
- Most processes use Pt as the active catalyst. Sometimes Pt is combined with a second catalyst (bimetallic catalyst) such as rhenium or another noble metal.
- There are many different commercial processes including platforming, powerforming, ultraforming, and Thermofor catalytic reforming.
- Some reformers operate at low pressure (3-13 bar), others at high pressures (up to 70 bar). Some systems continuously regenerate the catalyst in other systems. One reactor at a time is taken off-stream for catalyst regeneration, and some facilities regenerate all of the reactors during turnarounds.
THANK YOU