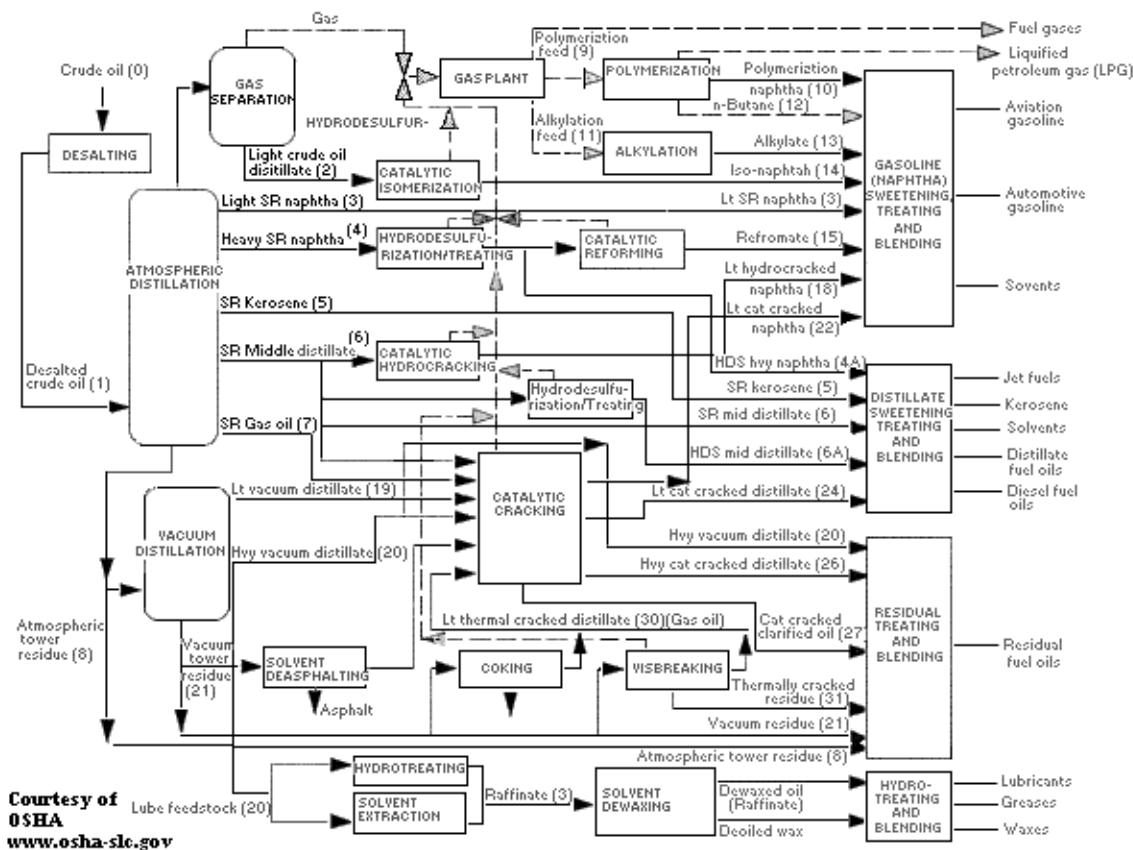


Students' Guide to Refining



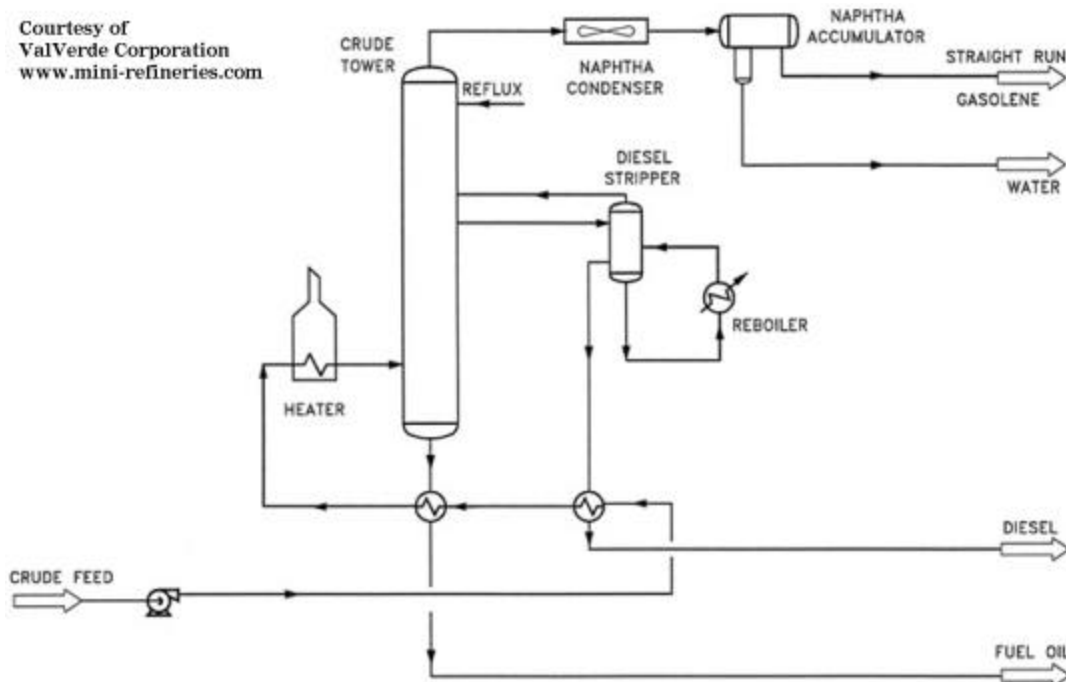
Crude Distillation

Distillation is the first step in the processing of crude oil and it takes place in a tall steel tower called a fractionation column. The inside of the column is divided at intervals by horizontal trays. The column is kept very hot at the bottom (the column is insulated) but as different hydrocarbons boil at different temperatures, the temperature gradually reduces towards the top, so that each tray is a little cooler than the one below.

The crude needs to be heated up before entering the fractionation column and this is done at first in a series of heat exchangers where heat is taken from other process streams which require cooling before being sent to rundown. Heat is also exchanged against condensing streams from the main column. Typically, the crude will be heated up in this way upto a temperature of 200 - 280 °C, before entering a furnace.

By: Hardeep Hundal, original editing by Jeroen Buren
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As the raw crude oil arriving contains quite a bit of water and salt, it is normally sent for salt removing first, in a piece of equipment called a desalter. Upstream the desalter, the crude is mixed with a water stream, typically about 4 - 6% on feed. Intense mixing takes place over a mixing valve and (optionally) as static mixer. The desalter, a large liquid full vessel, uses an electric field to separate the crude from the water droplets. It operates best at 120 - 150 °C, hence it is conveniently placed somewhere in the middle of the preheat train.



Part of the salts contained in the crude oil, particularly magnesium chloride, are hydrolysable at temperatures above 120 °C. Upon hydrolysis, the chlorides get converted into hydrochloric acid, which will find its way to the distillation column's overhead where it will corrode the overhead condensers. A good performing desalter can remove about 90% of the salt in raw crude.

Downstream the desalter, crude is further heated up with heat exchangers, and starts vaporising, which will increase the system pressure drop. At about 170 -200 °C, the crude will enter a 'pre-flashvessel', operating at about 2 - 5 barg, where the vapours are separated from the remaining liquid. Vapours are directly sent to the fractionation column, and by doing so, the hydraulic load on the remainder of the crude preheat train and furnace is reduced (smaller piping and pumps).

Just upstream the preflash vessel, a small caustic stream is mixed with the crude, in order to neutralise any hydrochloric acid formed by hydrolysis. The sodium chloride formed will leave the fractionation column via the bottom residue stream. The dosing rate of caustic is adjusted based on chloride measurements in the overhead vessel (typically 10 - 20 ppm).

At about 200 - 280 °C the crude enters the furnace where it is heated up further to about 330 - 370 °C. The furnace outlet stream is sent directly to the fractionation column. Here, it is separated into a number of fractions, each having a particular boiling range.

At 350 °C, and about 1 barg, most of the fractions in the crude oil vapourise and rise up the column through perforations in the trays, losing heat as they rise. When each fraction reaches the tray where the temperature is just below its own boiling point, it condenses and changes back into liquid phase. A continuous liquid phase is flowing by gravity through 'downcomers' from tray to tray downwards. In this way, the different fractions are gradually separated from each other on the trays of the fractionation column. The heaviest fractions condense on the lower trays and the lighter fractions condense on the trays higher up in the column. At different elevations in the column, with special trays called draw-off trays, fractions can be drawn out on gravity through pipes, for further processing in the refinery.

At top of the column, vapours leave through a pipe and are routed to an overhead condenser, typically cooled by air fin-fans. At the outlet of the overhead condensers, at temperature about 40 °C, a mixture of gas, and liquid naphtha exists, which is falling into an overhead accumulator. Gases are routed to a compressor for further recovery of LPG (C3/C4), while the liquids (gasoline) are pumped to a hydrotreater unit for sulfur removal.

A fractionation column needs a flow of condensing liquid downwards in order to provide a driving force for separation between light and heavy fractions. At the top of the column this liquid flow is provided by pumping a stream back from the overhead accumulator into the column. Unfortunately, a lot of the heat provided by the furnace to vaporise hydrocarbons is lost against ambient air in the overhead fin-fan coolers. A clever way of preventing this heat lost of condensing hydrocarbons is done via the circulating refluxes of the column. In a circulating reflux, a hot side draw-off from the column is pumped through a series of heat exchangers (against crude for instance), where the stream is cooled down. The cool stream is sent back into the column at a higher elevation, where it is been brought in contact with hotter rising vapours. This provides an internal condensing mechanism inside the column, in a similar way as the top reflux does which is sent back from the overhead accumulator. The main objective of a circulating reflux therefore is to recover heat from condensing vapours. A fractionating column will have several (typically three) of such refluxes, each providing sufficient liquid flow down the corresponding section of the column. An additional advantage of having circulating

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refluxes is that it will reduce the vapour load when going upwards in the column. This provided the opportunity to have a smaller column diameter for top sections of the tower. Such a reduction in diameter is called a 'swage'.

The lightest side draw-off from the fractionating column is a fraction called kerosene, boiling in the range 160 - 280 0C, which falls down through a pipe into a smaller column called 'side-stripper'. The purpose of the side stripper is to remove very light hydrocarbons by using steam injection or an external heater called 'reboiler'. The stripping steam rate, or reboiled duty is controlled such as to meet the flashpoint specification of the product. Similarly to the atmospheric column, the side stripper has fractionating trays for providing contact between vapour and liquid. The vapours produced from the top of the side stripper are routed back via pipe into the fractionating column.

The second and third (optional) side draw-offs from the main fractionating column are gasoil fractions, boiling in the range 200 - 400 0C, which are ultimately used for blending the final diesel product. Similar as with the kerosene product, the gasoil fractions (light and heavy gasoil) are first sent to a side stripper before being routed to further treating units.

At the bottom of the fractionation column a heavy, brown/black coloured fraction called residue is drawn off. In order to strip all light hydrocarbons from this fraction properly, the bottom section of the column is equipped with a set of stripping trays, which are operated by injecting some stripping steam (1 - 3% on bottom product) into the bottom of the column.

Hydrotreating

The objective of the Hydrotreating process is to remove sulfur as well as other unwanted compounds, e.g. unsaturated hydrocarbons, nitrogen from refinery process streams.

Until the end of World War 2, there was little incentive for the oil industry to pay significant attention to improving product quality by hydrogen treatment. However, soon after the war the production of high sulphur crudes increased significantly, which gave a more stringent demand on the product blending flexibility of refineries, and the marketing specifications for the products became tighter, largely due to environmental considerations. Furthermore, the catalyst used in the Platforming process can only handle sulfur in the very low ppm level, so hydrotreating of naphtha became a must. The necessity for hydrotreating of middle distillates (kerosene/gasoil) originates from pressure to reduce sulfur emissions into the environment. Overall, this situation resulted in an increased necessity for high sulphur removal capability in many refineries.

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As catalytic reforming gives hydrogen as a byproduct, it gave additional momentum to the development of sulphur removal process by hydrogen treatment. In this treatment, the sulphur compounds are removed by converting them into hydrogen sulphide by reaction with hydrogen in the presence of a catalyst. This results in high liquid product yields, since only sulphur is removed. Furthermore, the hydrogen sulphide produced can be easily removed from the product gas stream, for example by an amine wash. In this way, hydrogen sulphide is recovered as a highly concentrated stream and can be further converted into elemental sulphur via the "Claus" process.



Hydrodesulphurisation has been extensively used commercially for treating naphtha as feedstock for catalytic reformers to meet the very stringent sulphur specification of less than 1 ppm wt to protect the platinum catalyst. It has also been widely used for removal of sulphur compounds from kerosine and gasoils to make them suitable as blending components. In cases where products are from catalytic or thermal crackers, hydrogen treatment is used to improve product quality specifications like colour, smoke point, cetane index, etc.

For Hydrotreating, two basic processes are applied, the liquid phase (or trickle flow) process for kerosine and heavier straight-run and cracked distillates up to vacuum gas oil and the vapour phase process for light straight-run and cracked fractions.

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Both processes use the same basic configuration: the feedstock is mixed with hydrogen-rich make up gas and recycle gas. The mixture is heated by heat exchange with reactor effluent and by a furnace and enters a reactor loaded with catalyst. In the reactor, the sulphur and nitrogen compounds present in the feedstock are converted into hydrogen sulphide and ammonia respectively. The olefins present are saturated with hydrogen to become di-olefins and part of the aromatics will be hydrogenated. If all aromatics need to be hydrogenated, a higher pressure is needed in the reactor compared to the conventional operating mode.

The reactor operates at temperatures in the range of 300-380 °C and at a pressure of 10-20 bar for naphtha and kero, as compared with 30-50 bar for gasoil, with excess hydrogen supplied. The temperature should not exceed 380 °C, as above this temperature cracking reactions can occur, which deteriorates the colour of the final product. The reaction products leave the reactor and, after having been cooled to a low temperature, typically 40-50 °C, enter a liquid/gas separation stage. The hydrogen-rich gas from the high pressure separation is recycled to combine with the feedstock, and the low pressure off-gas stream rich in hydrogen sulphide is sent to a gas-treating unit, where hydrogen sulphide is removed. The clean gas is then suitable as fuel for the refinery furnaces. The liquid stream is the product from hydrotreating. It is normally sent to a stripping column where H₂S and other undesirable components are removed, and finally, in cases where steam is used for stripping, the product is sent to a vacuum drier for removal of water. Some refiners use a salt dryer instead of a vacuum drier to remove the water. The catalyst used is normally cobalt, molybdenum and nickel finely distributed on alumina extrudates. It slowly becomes choked by coke and must be renewed at regular intervals (typically 2-3 years). It can be regenerated (by burning off the coke) and reused typically once or twice before the breakdown of the support's porous structure unacceptably reduces its activity. Catalyst regeneration is, nowadays, mainly carried out ex-situ by specialised firms. Other catalysts have also been developed for applications where denitrification is the predominant reaction required or where high saturation of olefins is necessary.

A more recent development is the application of Hydrotreating for pretreatment of feedstock for the catalytic cracking process. By utilisation of a suitable hydrogenation-promoting catalyst for conversion of aromatics and nitrogen in potential feedstocks, and selection of severe operating conditions, hydrogen is taken up by the aromatic molecules. The increased hydrogen content of the feedstock obtained by this treatment leads to significant conversion advantages in subsequent catalytic cracking, and higher yield of light products can be achieved.

Hydrotreatment can also be used for kerosine smoke point improvement (SPI). It closely resembles the conventional Hydrotreating Process however an aromatic hydrogenation catalyst consisting of noble metals on a special carrier is used. The reactor operates at pressure range of 50-70 bar and temperatures of 260-320 °C. To restrict temperature rise due to the highly exothermic aromatics conversion reactions, quench oil is applied between the catalysts beds. The catalyst used is very sensitive to traces of sulphur and nitrogen in the feedstock and therefore pretreatment is normally applied in a conventional hydrotreater before kerosine is introduced into the SPI unit. The main objective of Smoke Point Improvement is improvement in burning characteristics as the kerosine aromatics are converted to naphthenes.

Hydrotreatment is also used for production of feedstocks for isomeration unit from pyrolysis gasoline (pygas) which is one of the byproducts of steam cracking of hydrocarbon fractions such as naphtha and gasoil.

A hydrotreater and a hydrodesulphuriser are basically the same process but a hydrotreater termed is used for treating kerosene or lighter feedstock, while a hydrodesulphuriser mainly refers to gasoil treating. The hydrotreatment process is used in every major refinery and is therefore also termed as the work horse of the refinery as it is the hydrotreater unit that ensures several significant product quality specifications. In most countries the Diesel produced is hydrodesulphurised before its sold. Sulphur specifications are getting more and more stringent. In Asia, countries such as Thailand, Singapore and Hong Kong already have a 0.05%S specification and large hydrodesulphurisation units are required to meet such specs.

The by-products obtained from HDT/HDS are light ends formed from a small amounts of cracking and these products are used in the refinery fuelgas pool. The other main by-product is Hydrogen Sulphide which is oxidized to sulphur and sold to the chemical industry for further processing.

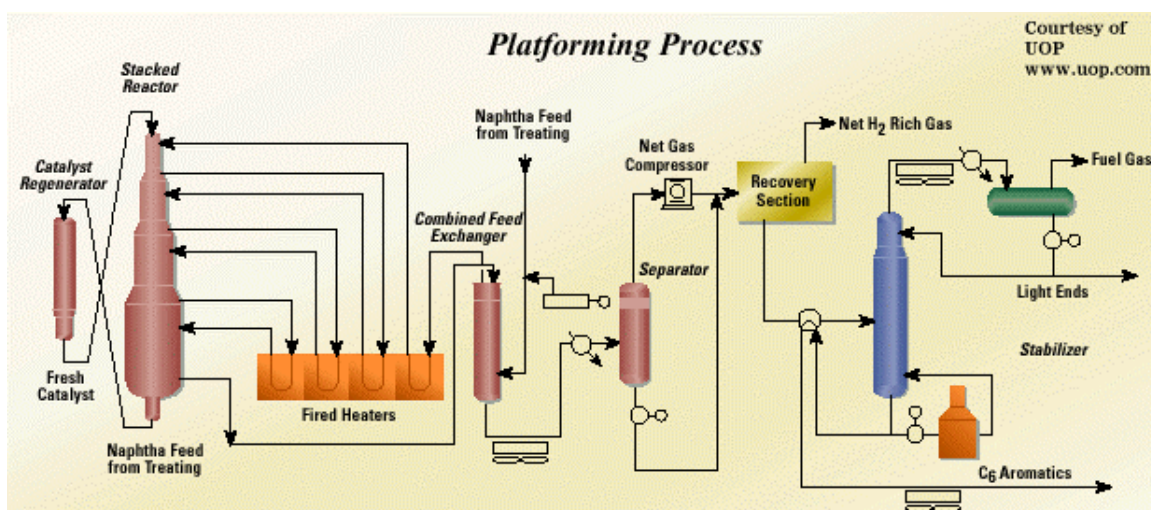
In combination with temperature, the pressure level (or rather the partial pressure of hydrogen) generally determines the types of components that can be removed and also determines the working life of the catalyst. At higher (partial) pressures, the desulphurisation process is 'easier', however, the unit becomes more expensive for instance due to larger compressors and heavier reactors. Also, at higher pressure, the hydrogen consumption of the unit increases, which can be a significant cost factor for the refinery. The minimum pressure required typically goes up with the required severity of the unit, i.e. the heavier the feedstock, or the lower levels of sulphur in product required.

Platforming

Motor gasoline (Mogas) production starts with the distillation of crude oil. One of the products out of that process is a fraction of low octane gasoline, normally referred to as naphtha, typically boiling in the range 100 - 160 °C. Other gasoline fractions are produced as a result of secondary processes like catalytic cracking, isomerisation, alkylation and platforming. Petrol is then produced by blending a variety of these gasoline components of different qualities to meet a series of product specifications.

One very important property of Mogas is the octane number, which influences "knocking" or "pinking" behaviour in the engine of cars. Traditionally lead compounds have been added to petrol to improve the octane number. Over the past years, in many countries legislation has been implemented aimed at reducing the emission of lead from exhausts of motor vehicles and this, calls for other means of raising the octane number.

The role of a platformer is to pave the way for this by a process which reforms the molecules in low octane naphtha to produce a high octane gasoline component. This is achieved by employing a catalyst with platinum as its active compound; hence the name Platformer. For many refinery catalyst applications, a promoter is used, and in the platforming process, it is a chloride promoter which stimulates the 'acidity' of the catalyst and thereby the isomerisation reactions. Often, a bimetallic catalyst is used, i.e. in addition to the platinum, a second metal, for instance Rhenium is present on the catalyst. The main advantage is a higher stability under reforming conditions. The disadvantage is that the catalyst becomes more sensitive towards poisons, process upsets and more susceptible to non-optimum regenerations.



Chemistry:

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The main reactions of platforming process are as follows:

- Dehydrogenation of naphthenes, yielding aromatics and hydrogen
- Dehydro-isomerisation of alkyl cyclopentanes to aromatic and hydrogen
- Isomerisation of paraffins and aromatics
- Dehydrocyclisation of paraffins to aromatics and hydrogen
- Hydrocracking of paraffins and naphthenes to lighter, saturated paraffins at the expense of hydrogen

The process literally re-shapes the molecules of the feed in a reaction in the presence of a platinum catalyst. Normally it is the hydrocarbon in the C6-C10 paraffins that get converted to aromatics.

The above reactions takes place concurrently and to a large extent also sequentially. The majority of these reactions, involve the conversion of paraffins and naphthenes and result in an increase in octane number and a nett production of hydrogen. Characteristic of the total effect of these reactions is the high endothermicity, which requires the continuous supply of process heat to maintain reaction temperature in the catalyst beds. That is why the process is typically done in four reactors in series with furnaces in between, in order to remain sufficiently high reactor temperatures.

The reactions takes place at the surface of the catalyst and are very much dependent, amongst other factors, on the right combination of interactions between platinum, its modifiers or activators, the halogen and the catalyst carrier. During operating life of the catalyst, the absolute and relative reaction rates are influenced negatively by disturbing factors like gradual coke deposition, poisons and deterioration of physical characteristic of the catalyst (surface area decline).

The process of platforming:

The feedstock of the platformer is drawn from the refinery's distillation units. This is first treated by passing the feedstock together with hydrogen over a catalyst, in a process called 'hydrotreating', to convert the sulphur and nitrogen compounds to hydrogen sulphide and ammonia, in order to prevent poisoning of the expensive platformer catalyst. After hydrotreating, the reactor effluent moves on through a stabiliser column to remove the gases formed (hydrogen sulphide, ammonia and fuel gas). In a second column, the C5 and some of the C6 is removed in a separate fraction called 'tops'. The reason to remove C5/C6 is that this component will crack in the platformer to produce fuel gas, while C6 gets converted into benzene, which can only be allowed in limited amount into the mogas because of its toxicity. From the bottom of the splitter column, the naphtha stream is produced, which is the feed for the Platforming section.

At the heart of the Platformer process are the four reactors, each linked to furnaces to sustain a sufficiently high reaction temperature, about 500 °C at the inlet of the reactors.

Over time, coke will build up on the catalyst surface area, which reduces the catalyst activity. The catalyst can be easily regenerated however, by burning the coke off with air. After coke burning, the catalyst needs to be reconditioned by a combined treatment of air and HCl under high temperature. This regeneration step is called 'oxy-chlorination'. After this step the catalyst is dried with hot nitrogen and subsequently brought in its active condition by reducing the surface with hot hydrogen. The refinery will therefore regularly have to take out one of the reactors to undergo this regeneration process. This type of process is therefore called semi-regen platforming.

During the regeneration process, the refinery will suffer production loss, which is the reason why UOP developed a major process enhancement by making the regeneration possible continuously, in a Continuous Catalytic Reformer, CCR. In the CCR unit, the reactors are cleverly stacked, so that the catalyst can flow under gravity. From the bottom of the reactor stack, the 'spent' catalyst is 'lifted' by nitrogen to the top of the regenerator stack. In the regenerator, the above mentioned different steps, coke burning, oxychlorination and drying are done in different sections, segregated via a complex system of valves, purge-flows and screens. From the bottom of the regenerator stack, catalyst is lifted by hydrogen to the top of the reactor stack, in a special area called the reduction zone. In the reduction zone, the catalyst passes a heat exchanger in which it is heated up against hot feed. Under hot conditions it is brought in contact with hydrogen, which performs a reduction of the catalyst surface, thereby restoring its activity. In such a continuous regeneration process, a constant catalyst activity can be maintained without unit shutdown for a typical runlength of 3 - 6 years. After 300 - 400 cycles of reaction/regeneration, the surface area of the catalyst will have dropped to a level (120 - 130 m²/g) that it becomes more difficult to maintain catalyst activity and at such a time normally the catalyst will be replaced by a fresh batch. The batch of 'spent' catalyst is then sent for platinum reclaim to recover the valuable precious metals.

For economic reasons, the design capacities of Platformer units vary from 1000 - 4500 t/d; operating pressures can vary over a wide range, units with from 3.5 barg up to 30 barg can be found, whereby the latest generation CCR's are typically at the lower pressure range. A lower pressure enhances the endothermic reactions, which gives less cracking reactions and thereby a higher liquid yield. However, at a lower reactor operating pressure, the hydrogen partial pressure will be lower as well, which favours coke formation. The reason why semi regen platformers will not operate at a too low pressure, otherwise the cycle length between regenerations becomes too short. A second disadvantage of operating at a lower pressure is that a larger compressor will be required to boost the pressure of the hydrogen up to the normal pressure of the hydrogen system (about 20 barg). Typical design reformat octane numbers are in the 95-104 range. The reactor temperature is in a region of 450-530 °C.

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At the outlet of the last reactor the product is still well above 400 °C. It is cooled down against cold feed in massive heat exchanger, either a so called 'Texas Tower' or a Packinox plate-pack heat exchanger. The special design of those heat exchangers ensures that minimum heat loss occurs in order to minimise the fuel consumption of the furnaces. After passing the feed/effluent exchanger, the reaction products are cooled in air/water coolers and routed to a product separator, where the hydrogen is the main gaseous product. Part of the hydrogen produced is recycled back (via a compressor) to the feed, in order to maintain a high enough hydrogen partial pressure in the reactors. The remainder of the gases are compressed and brought in contact again with the liquid from the product separator. This step is called 'recontacting' and is done in order to recover as much as possible hydrocarbons from the hydrogen produced. The reactor product, now in liquid form, goes on to the platformer stabiliser which removes Liquid Petroleum Gas (LPG) and other gases to leave a liquid high octane gasoline component called platformate, ready for blending into the refinery mogas pool. Summarising, the Platformer unit produces about 85% liquid platformate, 10% hydrogen and 5% LPG.

The Continuous Catalytic Reforming unit or better known as CCR Platformer is licensed by UOP, Universal Oil Products, based in USA. More recently, other technology vendors have copied the concept, one of the main competitors for UOP in this field is IFP from France.

Main Equipment in a CCR Platformer:

A CCR typically contains a feed/effluent heat exchanger (Texas Tower or Packinox), 4 furnaces, 4 reactors, a regenerator, overhead recontacting section, net gas compressor, recycle gas compressor and a stabiliser column.

Isomerization

The isomerisation process involves the transformation of one molecular structure into another (isomer) whose component atoms are the same but arranged in a different geometrical structure. Since isomers may differ greatly in physical and chemical properties, isomerisation offers the possibility of converting less desirable compounds into isomers with desirable properties, in particular to convert n-paraffins into iso-paraffins, thereby increasing the octane of the hydrocarbon stream. The main fields of application of isomerisation are:

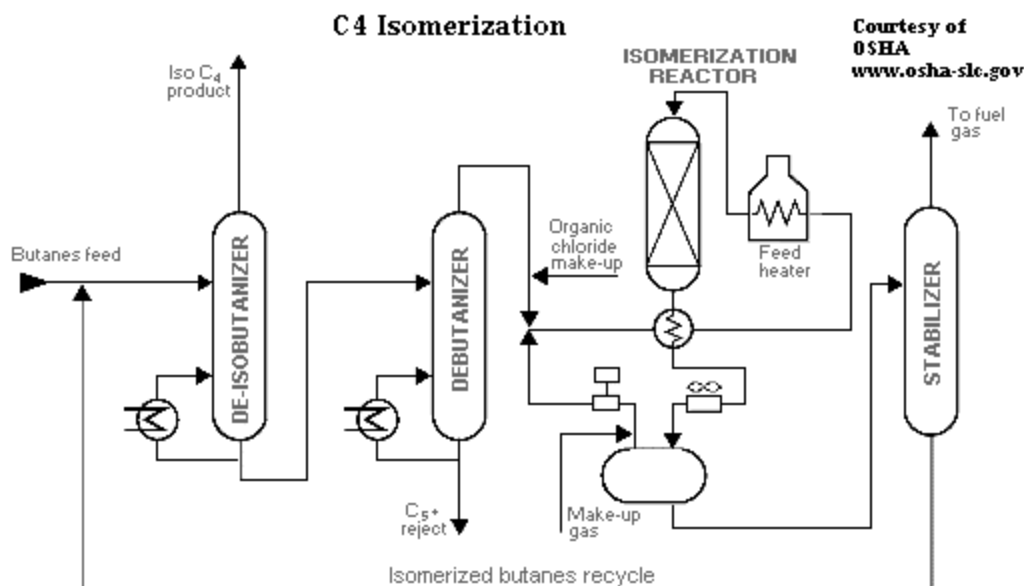
- ISOMERISATION of normal butane into isobutane
- ISOMERISATION of pentanes and hexanes into higher- branched isomers

Since branched isomers have a higher antiknock quality than the corresponding linear paraffins, this form of isomerisation is important for the production of motor fuels.

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In addition to the above applications, isomerisation is applied for the conversion of ortho-xylene and meta-xylene into para-xylene, used for the manufacturing of polyester fibres.

Isomerisation of low molecular weight paraffins has been commercially applied for many years. After extensive laboratory work had been carried out during the 1930s, World War 2 prompted the development of the laboratory processes into full-scale commercial units in order to meet the demand for isobutane necessary for the manufacture of large amounts of alkylate. While the first butane isomerisation unit went on stream in late 1941, by the end of the war nearly 40 butane isomerisation units were in operation in the USA and the Caribbean. Two pentane and two light naphtha isomerisation units also came on stream towards the end of the war to provide an additional source of blending aviation gasoline.



Though butane isomerisation has maintained its importance, present day interest in isomerisation is specially focussed on the upgrading of fractions containing C5 Pentane and C6 Hexane for use as motor gasoline components. This application has been prompted by the world drive to remove the lead additives gradually from motor gasoline in order to reduce air pollution. The octane loss caused by the removal or reduction of lead antiknock additives can be compensated for by isomerisation of pentane/hexane paraffin fraction of the light gasoline fractions.

Isomerisation technology has also improved substantially due to the hard work of many technologists. In order to achieve the low temperature necessary to obtain an acceptable yield of isomers, the catalyst systems used in the early units were based on aluminium chloride in some form. These catalyst systems, however, had the drawback of being highly corrosive and difficult to handle. In recent years, catalysts of a different type have come in use. These are solid catalysts consisting of a support having an acidic carrier and a hydrogenation function, frequently a noble metal. Modern isomerisation units utilise

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these dual- function catalysts and operate in the vapour phase and the presence of hydrogen. For these reasons, these process are called hydro- isomerisation processes.

The first hydro- isomerisation unit was introduced in 1953 by UOP, followed in 1965 by the first BP one, while in 1970 the first Shell hydro-isomerisation (HYSOMER) unit was started up. At present the following hydro-isomerisation processes are commercially available:

- UOP BUTAMER for butane isomerisation
- UOP PENEX for pentane/hexane isomerisation
- BP C4 isomerisation for butane isomerisation
- BP C5/C6 isomerisation for pentane/hexane isomerisation
- SHELL Hysomer for pentane/hexane isomerisation

All these processes take place in the vapour phase on a fixed bed catalyst containing platinum on a solid carrier.

As an example, the Shell Hysomer process will be briefly described. The liquid feedstock is pentane/hexane from light naphtha. Naphtha splitters are widely used to split light naphtha, heavy naphtha and also LPG. The light naphtha (C5/C6) is combined with the recycle gas/ fresh gas mixture. The resultant combined reactor feed is routed to a feed/ effluent heat exchanger, where it is heated and completely vaporised by the effluent of the reactor. The vaporised combined reactor feed is further heated to the desired reactor inlet temperature in the reactor charge heater. The hot charge enters the Hysomer reactor at the top and flows downwards through the catalyst bed, where a portion of normal and mono- branched paraffins is converted into higher branched (high octane) components. Temperature rise from the heat of reaction release is controlled by a cold quench gas injection into the reactor. Reactor effluent is cooled and subsequently separated in the product separator into two streams: a liquid product (isomerate) and a recycle gas stream returning to the reactor via the recycle gas compressor.

The catalyst is a dual function catalyst consisting of platinum on a zeolite basis, highly stable and regenerable.

Temperatures and pressure vary in a range of 230 - 285 °C and 13-30 bar, C5/C6 content in product relative to that in feed is 97% or better, and octane upgrading ranges between 8 and 10 points, depending on feedstock quality. The Hysomer process can be integrated with catalytic reformer, resulting in substantial equipment savings, or with iso-normal separation processes which allows for a complete conversion of pentane/hexane mixtures into isoparaffin mixtures. An interesting application in this field is the total isomerisation process (TIP) in which the isomerisation is completely integrated with a Union Carbide molecular sieve separation process or the naphtha IsoSiv Process by UOP.

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Highlights of TIP

The following are some of the highlights of the TIP process:

- A. TIP has been in commercial operation since 1975
- B. UOP manufacturers both the zeolite isomerisation catalyst and the IsoSiv Grade Molecular Sieve adsorbent.
- C. UOP's zeolite catalyst will tolerate sulfur and/or water upsets, the effects of which are usually reversible, either with time or by in situ regeneration (which minimises any down time).
- D. The expected life of the catalyst and adsorbent is 10 years or more.
- F. The combination of zeolite isomerisation and IsoSiv molecular separation is possible because each station has similar operating conditions of temperature, pressure and environment. This eliminates the need for a second compressor, intermediate stabilisation and the costs associated with cooling, purifying and reheating the recycle normal paraffins.
- G. TIP and IsoSiv separation permits maximum flexibility in changing the C5/C6 ratio and iso/normal ratio of the feed.

Conclusion:

Nowadays many refiners are looking into the isomerisation processes to add potential extra value and complimentary to the platforming process. Directly both the platforming and isomerisation process work hand in hand in several ways. C5 paraffins tend to crack away in the platformer, but give high upgrading in the isomerisation unit. C6 components convert nicely to benzene in the platformer, but nowadays the specs on aromatics and benzene are tightening, which makes conversion of these components to C6 isomers preferred. Furthermore, benzene is hydrogenated in the isomerisation unit. By adjusting the cutpoint between the light and heavy naphtha, i.e. the cutpoint between the feed to the isomerisation feed and the platformer feed, the refiner has the flexibility to control the benzene content of its gasoline pool.

Hydrocracking

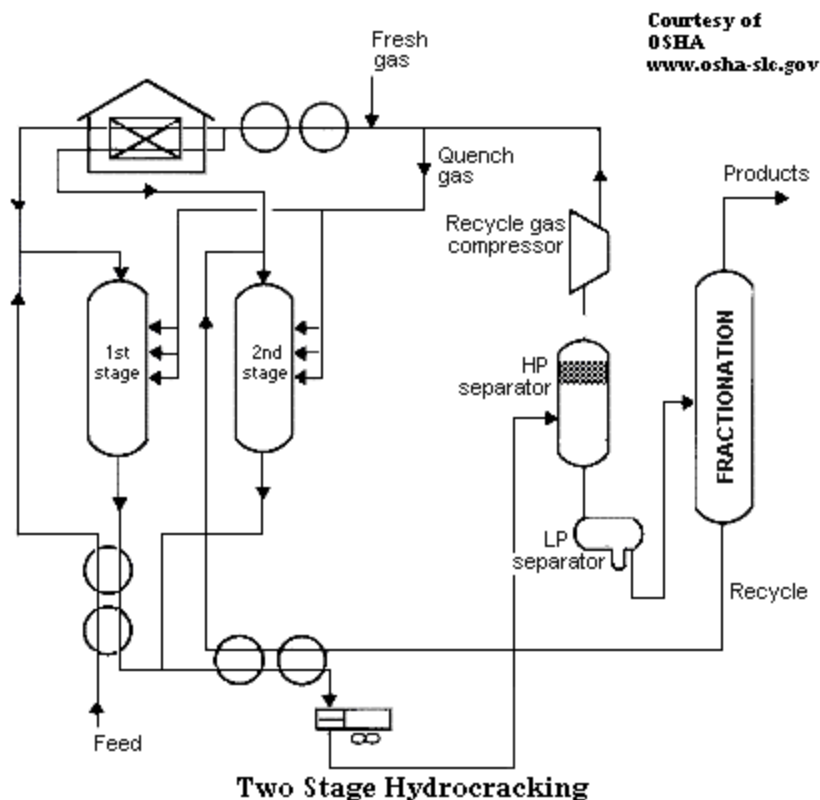
Introduction

The need for gasoline of a higher quality than that obtained by catalytic cracking led to the development of the hydrocracking process. The history of the process goes back to the later 1920s when a plant for the commercial hydrogenation of brown coal was commissioned at Leuna in Germany. Tungsten sulphide was used as a catalyst in this one-stage unit, in which high reaction pressures, 200-300 bar, were applied. The catalyst displayed a very high hydrogenation activity: the aromatic feedstock, coal and heavy fractions of oil, containing sulphur, nitrogen and oxygen, was virtually completely converted into paraffins and isoparaffins. The result of the Leuna plant - loss of octane number from aromatic hydrogenation of impurities in the feedstock, notably nitrogen compounds, followed by a hydrocracking step. In 1939, ICI developed the second-stage

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catalyst for a plant that contributed largely to Britain's supply of aviation gasoline in the subsequent years.

During World War II, two stage processes were applied on a limited scale in Germany, Britain and USA. In Britain, feedstock were creosote from coal tar and gas oil from petroleum. In the USA, Standard Oil of New Jersey operated a plant at Baton Rouge, producing gasoline from a Venezuelan kerosine/light gasoil fraction. Operating conditions in those units were comparable: approximate reaction temperature 400 °C and reaction pressures of 200-300 bar.



After the war, commercial hydrocracking was stopped because the process was too expensive. Hydrocracking research, however, continued intensively. By the end of the 1950s, the process had become economic, for which a number of reasons are identified.

The development of improved catalyst made it possible to operate the process at considerably lower pressure, about 70-150 bar.

This in turn resulted in a reduction in equipment wall thickness, whereas simultaneously, advances were made in mechanical engineering, especially in the field of reactor design and heat transfer. These factors, together with the availability of relatively low cost hydrogen from steam reforming process, brought hydrocracking back on the refinery scene. The first units of the second generation were built in USA to meet the demand for conversion of surplus fuel oil in the gasoline-oriented refineries.

Now, hydrocracking is well established process from many licensors.

Basis for the Choice of Conversion Route

Refiners are continuously faced with trends towards increased conversion, better product qualities and more rapidly changing product patterns. Various processes are available that can meet the requirements to a greater or lesser degree: coking, visbreaking/thermal cracking, catalytic cracking and hydrocracking.

The type of process applied and the complexity of refineries in various parts of the world are determined to a greater extent by the product distribution required. As a consequence, the relative importance of the above process in traditionally fuel-oil dominated refineries such as those in Western Europe will be quite different from those of gasoline-oriented refineries in, for instance, the USA.

An important aspect of the coking, thermal cracking and catalytic cracking process is that they operate at low pressures. This gives advantages in the fields of capital, metallurgy and engineering.

A particular feature of the hydrocracking process, as compared with its alternatives, is its flexibility with respect to product output and high quality of its products. In the areas where quantitative imbalance exists of lighter products, middle distillates and fuel, hydrocracking is a most suitable process for correction. Moreover, the hydrocracker does not yield any coke or pitch byproduct: the entire feedstock is converted into the required product range, an important consideration in a situation of limited crude oil availability. The development of the low-pressure catalytic reforming process, which produces relatively cheap, high quality hydrogen, has continued substantially to the economic viability of hydrocracking. On the whole, hydrocracking can handle a wider range of feedstock than catalytic cracking, although the latter process has seen some recent catalyst developments which narrowed the gap. There are also examples where hydrocracking is complementary rather than alternative to the other conversion process; an example, cycle oils, which cannot be recycled to extinction in the catalytic cracker, can be processed in the hydrocracker.

Notwithstanding many extensive comparisons between the various processes, the experience shows the generalisation with respect to the optimum conversion route still cannot be made.

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Process Description

All hydrocracking processes are characterised by the fact that in a catalytic operation under relatively high hydrogen pressure a heavy oil fraction is treated to give products of lower molecular weight.

Hydrocracking covers widely different fuels, ranging from C3/C4 production from naphtha, on the other hand, to lubeoil manufacture from deasphalted oils, on the other. Most hydrocrackers use fixed beds of catalyst with downflow of reactants. The H-Oil process developed by Hydrocarbon Research Corp and Cities Service R & D employs an ebullient bed reactor in which the beds of particulate catalyst are maintained in an ebullient or fluidised condition in upflowing reactants.

When the processing severity in a hydrocracker is increased, the first reaction occurring leads to saturation of any olefinic material present in feedstock. Next comes the reaction of desulphurisation, denitrogenation and de-oxygenation. These reactions constitute treating steps during which in most cases, only limited cracking takes place. When the severity is increased further, hydrocracking reaction is initiated. They proceed at various rates, with the formation of intermediate products (eg. saturation of aromatics), which are subsequently cracked into lighter products.

Process Configuration

When the treating step is combined with the cracking reaction to occur in one reactor, the process is called a SINGLE-STAGE PROCESS.

SINGLE-STAGE PROCESS: In this simplest of the hydrocracker configurations, the layout of the reactor section generally resembles that of a hydrotreating unit. This configuration will find application in cases where only a moderate degree of conversion (say 60% or less) is required. It may also be considered if full conversion, but with a limited reduction in molecular weight, is aimed at. An example is the production of middle distillates from heavy distillate oils. The catalyst used in a single-stage process comprises a hydrogenation function in combination with a strong cracking function. The hydrogenation function is provided by sulphided metals such as cobalt, molybdenum and nickel. An acidic support, usually alumina, attends to the cracking function. Nitrogen compounds and ammonia produced by hydrogenation interfere with the acidic activity of the catalyst. In the cases where high/full conversion is required, the reaction temperatures and run lengths of interest in commercial operation can no longer be adhered to. It becomes necessary to switch to a multi-stage process, in which the cracking reaction mainly takes place in an added reactor. With regard to the adverse effect of ammonia and nitrogen compounds on catalyst activity, two versions of the multi-stage hydrocracker have been developed: the TWO STAGE HYDROCRACKER and SERIES FLOW HYDROCRACKER.

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In the first type, the undesirable compounds are removed from the unconverted hydrocarbons before the latter are charged to the cracking reactor. This type is called the TWO STAGE PROCESS. The other variety is often referred to as SERIES FLOW HYDROCRACKER. This type uses a catalyst with an increased tolerance towards nitrogen, both as ammonia and in organic form.

TWO STAGE CONFIGURATION: Fresh feed is preheated by heat exchange with effluent from the first reactor. It is combined with part of a not fresh gas/recycle gas mixture and passes through a first reactor for desulphurisation/denitrogenation step. These reactions, as well as those of hydrocracking, which occurs to a limited extent in the first reactor, are exothermic. The catalyst inventory is therefore divided among a number of fixed beds. Reaction temperatures are controlled by introducing part of the recycle gas as a quench medium between beds. The ensuing liquid is fractionated to remove the product made in the first reactor. Unconverted, material, with a low nitrogen content and free of ammonia, is taken as a bottom stream from the fractionation section. After, heat exchange with reactor effluent and mixing with heated recycle gas, it is sent to the second reactor. Here most of the hydrocracking reactions occur. Strongly acidic catalyst with a relatively low hydrogenation activity (metal sulphides on, for example, amorphous silica-alumina) are usually applied. As in the first reactor, the exothermicity of the process is controlled by using recycle gas as quench medium the catalyst beds. Effluent from the second reactor is cooled and joins first stage effluent for separation from recycle gas and fractionation. The part of the second reactor feed that has remained unconverted is recycled to the reactor. Feedstock is thereby totally converted to the product boiling range.

SERIES FLOW CONFIGURATION: The principal difference is the elimination of first stage cooling and gas/liquid separation and the interstage ammonia removal step. The effluent from the first stage is mixed with more recycle gas and routed direct to the inlet of the second reactor. In contrast with the amorphous catalyst of the two-stage process, the second reactor in series flow generally has a zeolitic catalyst, based on crystalline silica-alumina. AS in the two stage process, material not converted to the product boiling range is recycled from the fractionation section.

Conclusion

Both two stage and series flow hydrocracking are flexible process: they may yield, in one mode of operation, only naphtha and lighter products and, in a different mode, only gasoil and lighter products. In the naphtha mode, both configurations have comparable yield patterns. In modes for heavier products, kerosine and gasoil, the two stage process is more selective because product made in the first reactor is removed from the second reactor feed, In series flow operation this product is partly overcracked into lighter products in the second reactor.

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Catalytic Cracking

Introduction

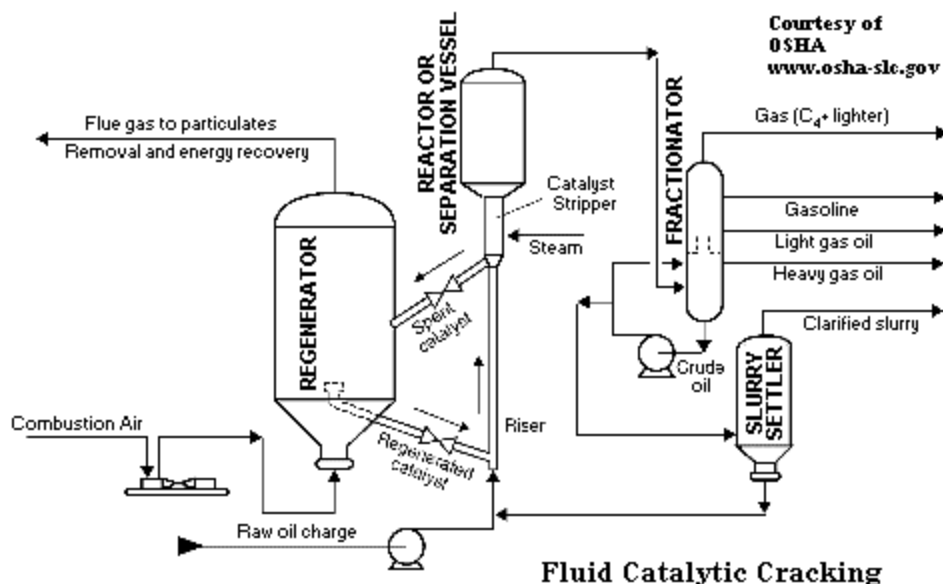
Already in the 30's it was found that when heavy oil fractions are heated over clay type materials, cracking reactions occur, which lead to significant yields of lighter hydrocarbons. While the search was going on for suitable cracking catalysts based on natural clays, some companies concentrated their efforts on the development of synthetic catalyst. This resulted in the synthetic amorphous silica-alumina catalyst, which was commonly used until 1960, when it was slightly modified by incorporation of some crystalline material (zeolite catalyst). When the success of the Houdry fixed bed process was announced in the late 1930s, the companies that had developed the synthetic catalyst decided to try to develop a process using finely powdered catalyst. Subsequent work finally led to the development of the fluidised bed catalytic cracking (FCC) process, which has become the most important catalytic cracking process.

Originally, the finely powdered catalyst was obtained by grinding the catalyst material, but nowadays, it is produced by spray-drying a slurry of silica gel and aluminium hydroxide in a stream of hot flue gases. Under the right conditions, the catalyst is obtained in the form of small spheres with particles in the range of 1-50 microns.

When heavy oil fractions are passed in gas phase through a bed of powdered catalyst at a suitable velocity (0.1-0.7m/s), the catalyst and the gas form a system that behaves like liquid, i.e. it can flow from one vessel to another under the influence of a hydrostatic pressure. If the gas velocity is too low, the powder does not fluidise and it behaves like a solid. If velocity is too high, the powder will just be carried away with the gas. When the catalyst is properly fluidised, it can be continuously transported from a reactor vessel, where the cracking reactions take place and where it is fluidised by the hydrocarbon vapour, to a regenerator vessel, where it is fluidised by the air and the products of combustion, and then back to the reactor. In this way the process is truly continuous.

The first FCC unit went on stream in Standard Oil of New Jersey's refinery in Baton Rouge, Louisiana in May 1942. Since that time, many companies have developed their own FCC process and there are numerous varieties in unit configuration.

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FCC Process Configuration:

Hot feed, together with some steam, is introduced at the bottom of the riser via special distribution nozzles. Here it meets a stream of hot regenerated catalyst from the regenerator flowing down the inclined regenerator standpipe. The oil is heated and vaporised by the hot catalyst and the cracking reactions commence. The vapour, initially formed by vaporisation and successively by cracking, carries the catalyst up the riser at 10-20 m/s in a dilute phase. At the outlet of the riser the catalyst and hydrocarbons are quickly separated in a special device. The catalyst (now partly deactivated by deposited coke) and the vapour then enter the reactor. The vapour passes overhead via cyclone separator for removal of entrained catalyst before it enters the fractionator and further downstream equipment for product separation. The catalyst then descends into the stripper where entrained hydrocarbons are removed by injection of steam, before it flows via the inclined stripper standpipe into the fluidised catalyst bed in the regenerator.

Air is supplied to the regenerator by an air blower and distributed throughout the catalyst bed. The coke deposited is burnt off and the regenerated catalyst passes down the regenerator standpipe to the bottom of the riser, where it joins the fresh feed and the cycle recommences.

The flue gas (the combustion products) leaving the regenerator catalyst bed entrains catalyst particles. In particular, it entrains "fines", a fine dust formed by mechanical rubbing of catalyst particles taking place in the catalyst bed. Before leaving the regenerator, the flue gas therefore passes through cyclone separators where the bulk of this entrained catalyst is collected and returned to the catalyst bed.

Normally modern FCC is driven by an expansion turbine to minimise energy consumption. In this expansion turbine, the current of flue gas at a pressure of about 2 barg drives a wheel by striking impellers fitted on this wheel. The power is then transferred to the air blower via a common shaft. This system is usually referred to as a "power recovery system". To reduce the wear caused by the impact of catalyst particles on the impellers (erosion), the flue gas must be virtually free of catalyst particles. The flue gas is therefore passed through a vessel containing a whole battery of small, highly efficient cyclone separators, where the remaining catalyst fines are collected for disposal.

Before being disposed of via a stack, the flue gas is passed through a waste heat boiler, where its remaining heat is recovered by steam generation.

In the version of the FCC process described here, the heat released by burning the coke in the regenerator is just sufficient to supply the heat required for the riser to heat up, vaporise and crack the hydrocarbon feed. The units where this balance occurs are called "heat balanced" units. Some feeds caused excessive amounts of coke to be deposited on the catalyst, i.e. much more than is required for burning in the regenerator and to have a "heat balanced" unit. In such cases, heat must be removed from the regenerator, e.g. by passing water through coils in the regenerator bed to generate steam. Some feeds cause so little coke to be deposited on the catalyst that heat has to be supplied to the system. This is done by preheating the hydrocarbon feed in a furnace before contacting it with the catalyst.

Main Characteristics

- A special device in the bottom of the riser to enhance contacting of catalyst and hydrocarbon feed.
- The cracking takes place during a short time (2-4 seconds) in a riser ("short-contact time riser") at high temperatures (500-540 0C at riser outlet).
- The catalyst used is so active that a special device for quick separation of catalyst and hydrocarbons at the outlet of the riser is required to avoid undesirable cracking after the mixture has left the riser. Since, no cracking in thereactor is required, the reactor no longer functions as a reactor; it merely serves as a holding vessel for cyclones.
- The regenerator takes place at 680-720 0C. With the use of special catalysts, all the carbon monoxide (CO) in the flue gas is combusted to carbon dioxide (CO₂) in the regenerator.
- Modern FCC includes a power recovery system for driving the air blower.

Equipment in FCC

- Large storage vessels for catalyst (fresh and equilibrium)
- Regenerator
- Reactor
- Main Fractionator
- Product Work Up section (several distillation columns in series)
- Product treating facilities

Feedstock & Yield

Before the introduction of residues, vacuum distillates were used as feedstock to load the Catalytic Cracker fully. These days, even residues are used to load the cracker. The term used for this type of configuration is Long Residue Catalytic Cracking Complex. The only modification or addition needed are a residue desalter and a bigger and more heat resistant reactor.

The yield pattern of an FCC unit is typically as follows:

Product	% weight on fresh feed
C3 & C4	15
Gasoline	40-50
Heavy Gas Oil	10
Coke	5

Conclusion

The FCC Unit can a real margin improver for many refineries. It is able to convert the residues into high value products like LPG , Butylene, Propylene and Mogas together with Gasoil. The FCC is also a start for chemical production (poly propylene). Many FCC's have 2 modes: a Mogas mode and a Gasoil mode and FCC's can be adapted to cater for the 2 modes depending on favourable economic conditions. The only disadvantage of an FCC is that the products produced need to be treated (sulfur removal) to be on specification. Normally Residue FCCs act together with Residue Hydroconversion Processes and Hydrocrackers in order to minimise the product quality give away and get a yield pattern that better matches the market specifications. Via product blending, expensive treating steps can be avoided and the units prepare excellent feedstock for eachother: desulfurised residue or hydrowax is excellent FCC feed, while the FCC cycle oils are excellent Hydrocracker feed.

In the near future, many refiners will phase the challenge how to desulfurise cat cracked gasoline without destroying its octane value. Catalytic distillation appears to be one of the most promising candidate processes for that purpose.

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Thermal Cracking

Introduction

Thermal cracking is the oldest and, in a way, the simplest cracking process. It basically aims at the reduction of molecular size by application of heat without any additional sophistication such as catalyst or hydrogen. At a temperature level of 450-500 C, the larger hydrocarbon molecules become unstable and tend to break spontaneously into smaller molecules of all possible sizes and types. By varying the time, temperature and pressure under which a particular feedstock remains under cracking conditions, the desired degree of cracking (conversion) can be controlled. Temperature and time (residence time) are important process variables pressure plays a secondary role.

Obviously, the cracking conditions to be applied and the amount and type of cracked products will depend largely on the type of feedstock. In practice, the feedstock for thermal cracking is a mixture of complex heavy hydrocarbon molecules left over from atmospheric and/or vacuum distillation of crude. The nature of these heavy, high molecular weight fractions is extremely complex and much fundamental research has been carried out on their behaviour under thermal cracking conditions. However, a complete and satisfactory explanation of these reactions that take place cannot be given, except for relatively simple and well-defined types of products. For instance, long chain paraffinic hydrocarbon molecules break down into a number of smaller ones by rupture of a carbon-to-carbon bond (the smaller molecules so formed may break down further). When this occurs, the number of hydrogen atoms present in the parent molecule is insufficient to provide the full complement for each carbon atom, so that olefins or "unsaturated" compounds are formed. The rupturing can take place in many ways, usually a free radical mechanism for the bond rupture is assumed.

However, paraffinic hydrocarbons are usually only a small part of the heavy petroleum residues, the rest being cyclic hydrocarbons, either aromatic or naphthenic in character. In these, the rupture takes place in the paraffinic side-chain and not in the ring. Other side reactions also take place. In particular, the condensation and polymerisation reactions of olefins and of the aromatics are of considerable practical importance, since they can lead to undesirable product properties, such as an increase in the sludge or tar content. Hence, in practice, it is very difficult to assess the crackability of various feedstocks without plant trials. The final products consist of gas, light hydrocarbons in the gasoline and gasoil range and heavier products. By selection of the type of unit, feedstock and operating conditions, the yields and quality of the various products can, within limits be controlled to meet market requirements.

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The maximum conversion that can be obtained will be determined by the quality of the bottom product of the thermal cracker, thermally cracked residue. This stream is normally routed to the fuel oil blending pool. When the cracking has taken place at a too high severity, the fuel can become 'unstable' upon blending with diluent streams (see below). Normally, the refinery scheduler will assess what the maximum severity is that the thermal cracking unit can operate on, without impacting on the stability of the refinery fuel blending pool.

When thermal cracking was introduced in the refineries some 80 years ago, its main purpose was the production of gasoline. The units were relatively small (even applying batch processing), were inefficient and had a very high fuel consumption. However, in the twenties and thirties a tremendous increase in thermal cracking capacity took place, largely in the version of the famous DUBBS process, invented by UOP. Nevertheless, thermal cracking lost ground quickly to catalytic cracking (which produces gasoline of higher octane number) for processing heavy distillates with the onset of the latter process during World War II. Since then and up to the present day, thermal cracking has mostly been applied for other purposes : cracking long residue to middle distillates (gasoil), short residue for viscosity reduction (visbreaking), short residue to produce bitumen, wax to olefins for the manufacture of chemicals, naphtha to ethylene gas (also for the manufacturing of chemicals), selected feedstocks to coke for use as fuel or for the manufacture of electrodes.

In modern oil refineries there are three major applications of the thermal cracking process:

- VISBREAKING
- THERMAL GASOIL PRODUCTION
- COKING

Visbreaking

Visbreaking (i.e. viscosity reduction or breaking) is an important application of thermal cracking because it reduces the viscosity of residue substantially, thereby lessening the diluent requirements and the amount of fuel oil produced in a refinery. The feed, after appropriate preheat, is sent to a furnace for heating to the cracking temperature, at about 450-460 degrees C. The cracking takes place to a small extent in the furnace and largely in a soaker (reaction chamber) just downstream of the furnace. At the soaker outlet, the temperature is lower than at the furnace outlet (soaker inlet) because the cracking reactions are endothermic. The products are quenched at the soaker outlet to stop the cracking reaction (to prevent excessive coke formation). After that, the products enter the fractionator at a temperature level of 300- 400 degrees C and from here onward the processing is similar to any normal distillation process. The products are separated into gas, gasoline, kero, gasoil and residue. The residue so obtained has a lower viscosity than the feed (visbreaking), which leads to a lower diluent requirement to make the fuel on specification for viscosity. The up-flow soaker provides for a prolonged residence time

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and therefore permits a lower cracking temperature than if the soaker was not used. This is advantageous as regards cost in furnace and fuel. Modern soakers are equipped with internals so as to reduce back mixing- effects , thus maximising the viscosity reduction. Since only one cracking stage is involved, this layout is also named one-stage cracking. The cracking temperature applied is about 440-450 degree C at a pressure of 5-10 barg in the soaker. The fractionator can be operated at 2-5 barg, depending on furnace constraints, condenser constraints and fuel cost.

Thermal Gasoil Production

This is a more elaborate and sophisticated application of thermal cracking as compared with visbreaking. Its aim is not only to reduce viscosity of the feedstock but also to produce and recover a maximum amount of gasoil. Altogether, it can mean that the viscosity of residue (excluding gasoil) run down from the unit is higher than that of the feed.

In the typical lay out is the first part of the unit quite similar to a visbreaking unit. The visbroken residue is vacuum-flashed to recover heavy distillates, which are then sent back to a thermal cracking stage, together with heavy distillate recovered from the fractionator, in a second furnace under more severe cracking conditions (temperature 500 degrees C; pressure 20-25 barg) . More severe conditions are necessary because the feedstock has a smaller molecular size and is therefore more difficult to crack than the larger residue molecules in the first stage. This layout is referred to as tow-stage cracking.

Delayed Coking

This is an even more severe thermal cracking application than the previous one. The goal is to make a maximum of cracking products - distillates - whereby the heavy residue becomes so impoverished in hydrogen that it forms coke. The term "delayed" is intended to indicate that the coke formation does not take place in the furnace (which would lead to a plant shutdown) but in the large coke drums after the furnace. These drums are filled/emptied batch-wise (once every 24 hours), though all the rest of the plant operates continuously. A plant usually has two coke drums, which have adequate capacity for one day's coke production (500-1500 m²). The process conditions in the coke drum are 450-500 degrees C and 20 - 30 bar. Only one coke drum is on-line; the other is off line, being emptied or standing by. Only the vapour passes from the top of the coke drums to the fractionator, where the products are separated into the desired fractions. The residue remains in the coke drum to crack further until only the coke is left. Often the heaviest part of the fractionator products is recycled to feed.

Product Quality

Thermally cracked products - distillates - are not suitable for commercial use as produced in other units; they require further refinement or treatment in order to improve their quality, particularly sulfur and olefins content. Formerly, wet treating processes, for example treatment with caustic or an other extraction medium, were applied to remove or "sweeten" the smelly sulfur products, but nowadays the catalytic hydrotreating is employed almost without exception, both for gasoline and for gas oil range products. Of course, the gases too have to be desulphurised before being used as fuel gas within the refinery.

The residual products from thermal cracking are normally not treated any further, except for coke, which may be calcined if the specifications require it to be treated. The cracked residue is normally disposed of as refinery or commercial fuel. Here a very important aspect of the process is the stability of the cracked residues or of the final fuels after blending with suitable diluents. Residue contains asphaltenes, which are colloiddally dispersed uniformly in the oil in a natural way. In the cracking process, the character of the asphaltenes as well as of the oil changes, and if the cracking is too severe the natural balance of the colloidal system can be affected to the extent that part of the asphaltenes precipitates in the equipment or in the storage tanks, forming sludge. If the sludge formation is excessive, i.e. above a certain specified limit, the product (fuel) is considered to be unstable.

Plant Operations/Decoking

A practical aspect of operation of thermal cracking units is that, in spite of good design and operating practice, furnaces, and sometimes also other equipment, gradually coke up, so that the unit has to be shut down and decoked. Furnaces can be decoked by "turbining" (using special rotary tools to remove coke from inside furnace pipes) or by steam-air decoking process. In the latter case, the coke is burnt off in a carefully controlled decoking process in which air and steam are passed through the tubes at elevated temperatures. Air serves to burn coke, where as the steam serves to keep the burning temperatures low so that they do not exceed the maximum tolerable temperatures.

More recently, a new decoking method using studded 'pigs' propelled with water, is getting more popular. The plastic pigs have a size slightly smaller than the tube inside diameter and are equipped with metal studs. When the pigs are pumped through the furnace pipes, they move around in a rotating fashion, thus scraping the cokes from the inside of the furnace tubes.

Other coked equipment is usually cleaned by hydrojetting techniques. Owing to these unavoidable stops for decoking, the on-stream time i.e. on stream days per annum, for thermal cracking units is slightly shorter than for most other oil processes.

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Vacuum Distillation

Introduction

To recover additional distillates from long residue, distillation at reduced pressure and high temperature has to be applied. This vacuum distillation process has become an important chain in maximising the upgrading of crude oil. As distillates, vacuum gas oil, lubricating oils and/or conversion feedstocks are generally produced. The residue from vacuum distillation - short residue - can be used as feedstock for further upgrading, as bitumen feedstock or as fuel component. The technology of vacuum distillation has developed considerably in recent decades. The main objectives have been to maximise the recovery of valuable distillates and to reduce the energy consumption of the units.

At the place where the heated feed is introduced in the vacuum column - called the flash zone - the temperature should be high and the pressure as low as possible to obtain maximum distillate yield. The flash temperature is restricted to about 420 °C, however, in view of the cracking tendency of high-molecular-weight hydrocarbons. Vacuum is maintained with vacuum ejectors and lately also with liquid ring pumps. Lowest achievable vacuum in the flash zone is in the order of 10 mbar.

In the older type high vacuum units the required low hydrocarbon partial pressure in the flash zone could not be achieved without the use of "lifting" steam. The steam acts in a similar manner as the stripping steam of crude distillation units. This type of units is called "wet" units. One of the latest developments in vacuum distillation has been the deep vacuum flashers, in which no steam is required. These "dry" units operate at very low flash zone pressures and low pressure drops over the column internals. For that reason the conventional reflux sections with fractionation trays have been replaced by low pressure-drop spray sections. Cooled reflux is sprayed via a number of specially designed spray nozzles in the column countercurrent to the up-flowing vapour. This spray of small droplets comes into close contact with the hot vapour, resulting in good heat and mass transfer between the liquid and vapour phase.

To achieve low energy consumption, heat from the circulating refluxes and rundown streams is used to heat up the long residue feed. Surplus heat is used to produce medium and/or low-pressure steam or is exported to another process unit (via heat integration). The direct fuel consumption of a modern high-vacuum unit is approximately 1% on intake, depending on the quality of the feed. The steam consumption of the dry high-vacuum units is significantly lower than that of the "wet" units. They have become net producers of steam instead of steam consumers.

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Three types of high-vacuum units for long residue upgrading have been developed for commercial application:

- FEED PREPARATION UNITS
- LUBOIL HIGH- VACUUM UNITS
- HIGH - VACUUM UNITS FOR BITUMEN PRODUCTION

Feed Preparation Units

These units make a major contribution to deep conversion upgrading ("cutting deep in the barrel"). They produce distillate feedstocks for further upgrading in catalytic crackers, hydrocrackers and thermal crackers. To obtain an optimum waxy distillate quality a wash oil section is installed between feed flash zone and waxy distillate draw-off. The wash oil produced is used as fuel component or recycled to feed. The flashed residue (short residue) is cooled by heat exchange against long residue feed. A slipstream of this cooled short residue is returned to the bottom of the high-vacuum column as quench to minimise cracking (maintain low bottom temperature).

Luboil High-Vacuum Units

Luboil high vacuum units are specifically designed to produce high-quality distillate fractions for luboil manufacturing. Special precautions are therefore taken to prevent thermal degradation of the distillates produced. The units are of the "wet" type. Normally, three sharply fractionated distillates are produced (spindle oil, light machine oil and medium machine oil). Cutpoints between those fractions are typically controlled on their viscosity quality. Spindle oil and light machine oil are subsequently steam- stripped in dedicated strippers. The distillates are further processed to produce lubricating base oil. Short residue is normally used as feedstock for the solvent de-asphalting process to produce deasphalted oil, an intermediate for bright stock manufacturing.

High-Vacuum Units for Bitumen Production

Special vacuum flashers have been designed to produce straight-run bitumen and/or feedstocks for bitumen blowing. In principle, these units are designed on the same basis as the previously discussed feed preparation units, which may also be used to provide feedstocks for bitumen manufacturing.

Vacuum Distillation

Asphaltic bitumen, normally called "bitumen" is obtained by vacuum distillation or vacuum flashing of an atmospheric residue. This is " straight run" bitumen. An alternative method of bitumen production is by precipitation from residual fractions by propane or butane- solvent deasphalting.

The bitumen thus obtained has properties which derive from the type of crude oil processed and from the mode of operation in the vacuum unit or in the solvent deasphalting unit. The grade of the bitumen depends on the amount of volatile material that remains in the product: the smaller the amount of volatiles, the harder the residual bitumen.

In most cases, the refinery bitumen production by straight run vacuum distillation does not meet the market product quality requirements. Authorities and industrial users have formulated a variety of bitumen grades with often stringent quality specifications, such as narrow ranges for penetration and softening point. These special grades are manufactured by blowing air through the hot liquid bitumen in a BITUMEN BLOWING UNIT. What type of reactions take place when a certain bitumen is blown to grade? Bitumen may be regarded as colloidal system of highly condensed aromatic particles (asphaltenes) suspended in a continuous oil phase. By blowing, the asphaltenes are partially dehydrogenated (oxidised) and form larger chains of asphaltenic molecules via polymerisation and condensation mechanism. Blowing will yield a harder and more brittle bitumen (lower penetration, higher softening point), not by stripping off lighter components but changing the asphaltenes phase of the bitumen. The bitumen blowing process is not always successful: a too soft feedstock cannot be blown to an on-specification harder grade.

The blowing process is carried out continuously in a blowing column. The liquid level in the blowing column is kept constant by means of an internal draw-off pipe. This makes it possible to set the air-to-feed ratio (and thus the product quality) by controlling both air supply and feed supply rate. The feed to the blowing unit (at approximately 210 °C), enters the column just below the liquid level and flows downward in the column and then upward through the draw-off pipe. Air is blown through the molten mass (280-300 °C) via an air distributor in the bottom of the column. The bitumen and air flow are countercurrent, so that air low in oxygen meets the fresh feed first. This, together with the mixing effect of the air bubbles jetting through the molten mass, will minimise the temperature effects of the exothermic oxidation reactions: local overheating and cracking of bituminous material. The blown bitumen is withdrawn continuously from the surge vessel under level control and pumped to storage through feed/product heat exchangers.