

The crude oil pretreatment environmental sciences essay



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A. CRUDE OIL PRETREATMENT (DESALTING)Crude oil often contains water, inorganic salts, suspended solids, and water-soluble trace metals. As a first step in the refining process, to reduce corrosion, plugging, and fouling of equipment and to prevent poisoning the catalysts in processing units, these contaminants must be removed by desalting (dehydration). The two most typical methods of crude-oil desalting, chemical and electrostatic separation use hot water as the extraction agent. In chemical desalting, water and chemical surfactant (demulsifiers) are added to the crude, heated so that salts and other impurities dissolve into the water or attach to the water, and then held in a tank where they 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. Both methods of desalting are continuous. A third and less-common process involve filtering heated crude using diatomaceous earth. The feedstock crude oil is heated to between 150° and 350°F 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. Wastewater and contaminants are discharged from the bottom of the settling tank to the wastewater treatment facility. The desalted crude is continuously drawn from the top of the settling tanks and sent to the crude distillation (fractionating) tower. ELECTROSTATIC DESALTING

FIGURE IV: 2-7. ELECTROSTATIC DESALTING. B. CRUDE OIL

DISTILLATION (FRACTIONATION)The first step in the refining process is the separation of crude oil into various fractions or straight-run cuts by

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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 Tower. At the refinery, the desalted crude feedstock is preheated using recovered process heat. The feedstock then flows to a direct-fired crude charge heater where it is fed into the vertical distillation column just above the bottom, at pressures slightly above atmospheric and at temperatures ranging from 650° to 700° F (heating crude oil above these temperatures may cause undesirable thermal cracking). 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. The fractionating tower, a steel cylinder about 120 feet high, contains horizontal steel trays for separating and collecting the liquids. At each tray, vapors from below enter perforations and bubble caps. They permit the vapors to bubble through the liquid on the tray, causing some condensation at the temperature of that tray. An overflow pipe drains the condensed liquids from each tray back to the tray below, where the higher temperature causes re-evaporation. The evaporation, condensing, and scrubbing operation is repeated many times until the desired degree of product purity is reached. Then side streams from certain trays are taken off to obtain the desired fractions. Products ranging from uncondensed fixed gases at the top to heavy fuel oils at the bottom can be taken continuously from a fractionating tower. Steam is often used in towers to lower the vapor

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pressure and create a partial vacuum. The distillation process separates the major constituents of crude oil into so-called straight-run products.

Sometimes crude oil is "topped" by distilling off only the lighter fractions, leaving a heavy residue that is often distilled further under high vacuum.

ATMOSPHERIC DISTILLATION

Align FIGURE IV: 2-8. ATMOSPHERIC DISTILLATION. product mix Vacuum Distillation Tower. In order to further distill the residuum or topped crude from the atmospheric tower at higher temperatures, reduced pressure is required to prevent thermal cracking. The process takes place in one or more vacuum distillation towers. The principles of vacuum distillation resemble those of fractional distillation and, except that larger-diameter columns are used to maintain comparable vapor velocities at the reduced pressures, the equipment is also similar. 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

Asia Pa FIGURE IV: 2-9. VACUUM DISTILLATION. Other Distillation Towers (Columns). Within refineries there are numerous other, smaller distillation towers called columns, designed to separate specific and unique products.
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Columns all work on the same principles as the towers described above. For example, a depropanizer is a small column designed to separate propane and lighter gases from butane and heavier components. Another larger column is used to separate ethyl benzene and xylene. Small "bubble" towers called strippers use steam to remove trace amounts of light products from heavier product streams.

C. THERMAL CRACKING

Because the simple distillation of crude oil produces amounts and types of products that are not consistent with those required by the marketplace, subsequent refinery processes change the product mix by altering the molecular structure of the hydrocarbons. One of the ways of accomplishing this change is through "cracking," a process that breaks or cracks the heavier, higher boiling-point petroleum fractions into more valuable products such as gasoline, fuel oil, and gas oils. The two basic types of cracking are thermal cracking, using heat and pressure, and catalytic cracking. The first thermal cracking process was developed around 1913. Distillate fuels and heavy oils were heated under pressure in large drums until they cracked into smaller molecules with better antiknock characteristics. However, this method produced large amounts of solid, unwanted coke. This early process has evolved into the following applications of thermal cracking: visbreaking, steam cracking, and coking.

VISBREAKING PROCESS.

Visbreaking, a mild form of thermal cracking, significantly lowers the viscosity of heavy crude-oil residue without affecting the boiling point range. Residual from the atmospheric distillation tower is heated (800°-950° F) 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

FIGURE IV: 2-12. VISBREAKING.

STEAM CRACKING PROCESS.

Steam cracking is a petrochemical process sometimes used in refineries to produce olefinic raw materials (e. g., ethylene) from various feedstock for petrochemicals manufacture. The feedstock range from ethane to vacuum gas oil, with heavier feeds giving higher yields of by-products such as naphtha. The most common feeds are ethane, butane, and naphtha. Steam cracking is carried out at temperatures of 1, 500°-1, 600° F, and at pressures slightly above atmospheric. Naphtha produced from steam cracking contains benzene, which is extracted prior to Hydrotreating. Residual from steam cracking is sometimes blended into heavy fuels. Coking Processes. 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 so completely reduces hydrogen that the residue is a form of carbon called " coke." The two most common processes are delayed coking and continuous (contact or fluid) coking. Three typical types of coke are obtained (sponge coke, honeycomb coke, and needle coke) depending

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upon the reaction mechanism, time, temperature, and the crude feedstock.

a) Delayed Coking - 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. Initially the heavy feedstock is fed to a furnace which heats the residuum to high temperatures (900°-950° F) at low pressures (25-30 psi) and is designed and controlled to prevent premature coking in the heater tubes. The mixture is passed from the heater to one or more coker drums where the hot material is held approximately 24 hours (delayed) at pressures of 25-75 psi, until it cracks into lighter products.

Vapors from the drums are returned to a fractionator where gas, naphtha, and gas oils are separated out. The heavier hydrocarbons produced in the fractionator are recycled through the furnace. After the coke reaches a predetermined level in one drum, the flow is diverted to another drum to maintain continuous operation. The full drum is steamed to strip out uncracked hydrocarbons, cooled by water injection, and decoked by mechanical or hydraulic methods. The coke is mechanically removed by an auger rising from the bottom of the drum. Hydraulic decoking consists of fracturing the coke bed with high-pressure water ejected from a rotating cutter.

b) Continuous Coking - Continuous (contact or fluid) coking is a moving-bed process that operates at temperatures higher than delayed coking. In continuous coking, thermal cracking occurs by using heat transferred from hot, recycled coke particles to feedstock in a radial mixer, called a reactor, at a pressure of 50 psi. Gases and vapors are taken from the reactor, quenched to stop any further reaction, and fractionated. The

reacted coke enters a surge drum and is lifted to a feeder and classifier

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where the larger coke particles are removed as product. The remaining coke is dropped into the preheater for recycling with feedstock. Coking occurs both in the reactor and in the surge drum. The process is automatic in that there is a continuous flow of coke and feedstock.

DELAYED COKING

FIGURE IV: 2-13. DELAYED COKING. D. CATALYTIC CRACKING

Catalytic cracking breaks complex hydrocarbons into simpler molecules in order to increase the quality and quantity of lighter, more desirable products and decrease the amount of residuals. This process rearranges the molecular structure of hydrocarbon compounds to convert heavy hydrocarbon feedstock into lighter fractions such as kerosene, gasoline, LPG, heating oil, and petrochemical feedstock. Catalytic cracking is similar to thermal cracking except that catalysts facilitate the conversion of the heavier molecules into lighter products. Use of a catalyst (a material that assists a chemical reaction but does not take part in it) in the cracking reaction increases the yield of improved-quality products under much less severe operating conditions than in thermal cracking. Typical temperatures are from 850°-950° F at much lower pressures of 10-20 psi. The catalysts used in refinery cracking units are typically solid materials (zeolite, aluminum hydro silicate, treated bentonite clay, fuller's earth, bauxite, and silica-alumina) that come in the form of powders, beads, pellets or shaped materials called extrudates. There are three basic functions in the catalytic cracking process:-

Reaction: Feedstock reacts with catalyst and cracks into different hydrocarbons;-

Regeneration: Catalyst is reactivated by burning off coke; and-

Fractionation: Cracked hydrocarbon stream is separated into

various products. The three types of catalytic cracking processes are fluid catalytic cracking (FCC), moving-bed catalytic cracking, and thermofor catalytic cracking (TCC). The catalytic cracking process is very flexible, and operating parameters can be adjusted to meet changing product demand. In addition to cracking, catalytic activities include dehydrogenation, hydrogenation, and isomerization. Fluid catalytic cracking

The most common process is FCC, in which the oil is cracked in the presence of a finely divided catalyst which is maintained in an aerated or fluidized state by the oil vapors. The fluid cracker consists of a catalyst section and a fractionating section that operate together as an integrated processing unit. The catalyst section contains the reactor and regenerator, which, with the standpipe and riser, forms the catalyst circulation unit. The fluid catalyst is continuously circulated between the reactor and the regenerator using air, oil vapors, and steam as the conveying media. A typical FCC process involves mixing a preheated hydrocarbon charge with hot, regenerated catalyst as it enters the riser leading to the reactor. The charge is combined with a recycle stream within the riser, vaporized, and raised to reactor temperature (900°-1,000° F) by the hot catalyst. As the mixture travels up the riser, the charge is cracked at 10-30 psi. In the more modern FCC units, all cracking takes place in the riser. The "reactor" no longer functions as a reactor; it merely serves as a holding vessel for the cyclones. This cracking continues until the oil vapors are separated from the catalyst in the reactor cyclones. The resultant product stream (cracked product) is then charged to a fractionating column where it is separated into fractions, and some of the heavy oil is recycled to the riser. Spent catalyst is regenerated to get rid of coke that collects on the catalyst during the process. Spent catalyst flows through the

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catalyst stripper to the regenerator, where most of the coke deposits burn off at the bottom where preheated air and spent catalyst are mixed. Fresh catalyst is added and worn-out catalyst removed to optimize the cracking process.

FLUID CATALYTIC CRACKING

FIGURE IV: 2-14. FLUID CATALYTIC CRACKING. Moving Bed Catalytic

Cracking The moving-bed catalytic cracking process is similar to the FCC process. The catalyst is in the form of pellets that are moved continuously to the top of the unit by conveyor or pneumatic lift tubes to a storage hopper, then flow downward by gravity through the reactor, and finally to a regenerator. The regenerator and hopper are isolated from the reactor by steam seals. The cracked product is separated into recycle gas, oil, clarified oil, distillate, naphtha, and wet gas. Thermofor Catalytic Cracking. In a typical thermofor catalytic cracking unit, the preheated feedstock flows by gravity through the catalytic reactor bed. The vapors are separated from the catalyst and sent to a fractionating tower. The spent catalyst is regenerated, cooled, and recycled. The flue gas from regeneration is sent to a carbon-monoxide boiler for heat recovery. E. HYDROCRACKING Hydrocracking is a two-stage process combining catalytic cracking and hydrogenation, wherein heavier feedstocks are 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 feedstocks that are difficult to process by either catalytic cracking or reforming, since these feedstocks are characterized usually by high polycyclic aromatic content and/or high concentrations of the two principal catalyst poisons, sulfur and

nitrogen compounds. The hydrocracking 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 (1,000-2,000 psi) and fairly high temperatures (750°-1,500° F), in the presence of hydrogen and special catalysts. 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. Hydrocracking also performs isomerization for pour-point control and smoke-point control, both of which are important in high-quality jet fuel.

Hydrocracking Process. In the first stage, preheated feedstock is mixed with recycled hydrogen and sent to the first-stage reactor, where catalysts convert sulfur and nitrogen compounds to hydrogen sulfide and ammonia. Limited hydrocracking also occurs. After the hydrocarbon leaves the first stage, it is cooled and liquefied and run through a hydrocarbon separator. The hydrogen is recycled to the feedstock. The liquid is charged to a fractionator. Depending on the products desired (gasoline components, jet fuel, and gas oil), the fractionator is run to cut out some portion of the first stage reactor out-turn. Kerosene-range material can be taken as a separate side-draw product or included in the fractionator bottoms with the gas oil. The fractionator bottoms are again mixed with a hydrogen stream and charged to the second stage. Since this material has

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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). Like the outturn of the first stage, the second stage product is separated from the hydrogen and charged to the fractionator.

TWO-STAGE HYDROCRACKING

FIGURE IV: 2-15. TWO-STAGE HYDROCRACKING. F. CATALYTIC

REFORMING Catalytic reforming is an important process used to convert low-octane naphtha 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 toluene, benzene, xylene, and other aromatics useful in gasoline blending and petrochemical processing. Hydrogen, a significant by-product, is separated from the reformates for recycling and use in other processes. A catalytic reformer comprises a reactor section and a product-recovery section. More or less standard is a feed preparation section in which, by combination of hydro treatment and distillation, the feedstock is prepared to specification. Most processes use platinum as the active catalyst. Sometimes platinum is combined with a second catalyst (bimetallic catalyst) such as rhenium or another noble metal. There are many different commercial catalytic reforming processes including platforming, powerforming, ultraforming, and thermofor catalytic reforming. In the platforming process,

the first step is preparation of the naphtha feed to remove impurities from the naphtha and reduce catalyst degradation. The naphtha feedstock is then mixed with hydrogen, vaporized, and passed through a series of alternating furnace and fixed-bed reactors containing a platinum catalyst. The effluent from the last reactor is cooled and sent to a separator to permit removal of the hydrogen-rich gas stream from the top of the separator for recycling. The liquid product from the bottom of the separator is sent to a fractionator called a stabilizer (butanizer). It makes a bottom product called reformate; butanes and lighter go overhead and are sent to the saturated gas plant. Some catalytic reformers operate at low pressure (50-200 psi), and others operate at high pressures (up to 1, 000 psi). Some catalytic reforming 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.

PLATFORMING PROCESS

FIGURE IV: 2-16. PLATFORMING PROCESS. G. CATALYTIC

HYDROTREATING Catalytic hydrotreating is a hydrogenation process used to remove about 90% of contaminants such as nitrogen, sulfur, oxygen, and metals from liquid petroleum fractions. These contaminants, if not removed from the petroleum fractions as they travel through the refinery processing units, can have detrimental effects on the equipment, the catalysts, and the quality of the finished product. Typically, hydrotreating is done prior to processes such as catalytic reforming so that the catalyst is not contaminated by untreated feedstock. Hydrotreating is also used prior to catalytic cracking to reduce sulfur and improve product yields, and to

upgrade middle-distillate petroleum fractions into finished kerosene, diesel fuel, and heating fuel oils. In addition, hydrotreating converts olefins and aromatics to saturated compounds. Catalytic Hydrodesulphurization Process Hydrotreating for sulfur removal is called hydrodesulphurization. In a typical catalytic hydrodesulphurization unit, the feedstock is deaerated and mixed with hydrogen, preheated in a fired heater (600°-800° F) and then charged under pressure (up to 1, 000 psi) through a fixed-bed catalytic reactor. In the reactor, the sulfur and nitrogen compounds in the feedstock are converted into H₂S and NH₃. The reaction products leave the reactor and after cooling to a low temperature enter a liquid/gas separator. The hydrogen-rich gas from the high-pressure separation is recycled to combine with the feedstock, and the low-pressure gas stream rich in H₂S is sent to a gas treating unit where H₂S is removed. The clean gas is then suitable as fuel for the refinery furnaces. The liquid stream is the product from hydrotreating and is normally sent to a stripping column for removal of H₂S and other undesirable components. In cases where steam is used for stripping, the product is sent to a vacuum drier for removal of water. Hydrodesulfurized products are blended or used as catalytic reforming feedstock. Other Hydrotreating Processes. Hydrotreating processes differ depending upon the feedstock available and catalysts used. Hydrotreating can be used to improve the burning characteristics of distillates such as kerosene. Hydrotreatment of a kerosene fraction can convert aromatics into naphthene, which are cleaner-burning compounds. Lube-oil hydrotreating uses catalytic treatment of the oil with hydrogen to improve product quality. The objectives in mild lube hydrotreating include saturation of olefins and improvements in color, odor, and acid nature of the oil. Mild lube

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hydrotreating also may be used following solvent processing. Operating temperatures are usually below 600° F and operating pressures below 800 psi. Severe lube hydrotreating, at temperatures in the 600°-750° F range and hydrogen pressures up to 3, 000 psi, is capable of saturating aromatic rings, along with sulfur and nitrogen removal, to impart specific properties not achieved at mild conditions. Hydrotreating also can be employed to improve the quality of pyrolysis gasoline, a by-product from the manufacture of ethylene. Traditionally, the outlet for pyrolysis gas has been motor gasoline blending, a suitable route in view of its high octane number. However, only small portions can be blended untreated owing to the unacceptable odor, color, and gum-forming tendencies of this material. The quality of pyrolysis gas, which is high in diolefin content, can be satisfactorily improved by hydrotreating, whereby conversion of diolefin into mono-olefins provides an acceptable product for motor gas blending.

DISTILLATE HYDRODESULFURIZATION

FIGURE IV: 2-17. DISTILLATE HYDRODESULFURIZATION. H.

ISOMERIZATION Isomerization converts n-butane, n-pentane and n-hexane into their respective isoparaffins of substantially higher octane number. The straight-chain paraffins are converted to their branched-chain counterparts whose component atoms are the same but are arranged in a different geometric structure. Isomerization is important for the conversion of n-butane into isobutane, to provide additional feedstock for alkylation units, and the conversion of normal pentanes and hexanes into higher branched isomers for gasoline blending. Isomerization is similar to catalytic reforming in that the hydrocarbon molecules are rearranged, but unlike catalytic

reforming, isomerization just converts normal paraffins to isoparaffins. There are two distinct isomerization processes, butane (C4) and pentane/hexane (C5/C6). Butane isomerization produces feedstock for alkylation. Aluminum chloride catalyst plus hydrogen chloride are universally used for the low-temperature processes. Platinum or another metal catalyst is used for the higher-temperature processes. In a typical low-temperature process, the feed to the isomerization plant is n-butane or mixed butanes mixed with hydrogen (to inhibit olefin formation) and passed to the reactor at 230°-340° F and 200-300 psi. Hydrogen is flashed off in a high-pressure separator and the hydrogen chloride removed in a stripper column. The resultant butane mixture is sent to a fractionator (deisobutanizer) to separate n-butane from the isobutane product. Pentane/hexane isomerization increases the octane number of the light gasoline components n-pentane and n-hexane, which are found in abundance in straight-run gasoline. In a typical C5/C6 isomerization process, dried and desulfurized feedstock is mixed with a small amount of organic chloride and recycled hydrogen, and then heated to reactor temperature. It is then passed over supported-metal catalyst in the first reactor where benzene and olefins are hydrogenated. The feed next goes to the isomerization reactor where the paraffins are catalytically isomerized to isoparaffins. The reactor effluent is then cooled and subsequently separated in the product separator into two streams: a liquid product (isomerate) and a recycle hydrogen-gas stream. The isomerate is washed (caustic and water), acid stripped, and stabilized before going to storage.

C4 ISOMERIZATION

FIGURE IV: 2-18. C4 ISOMERIZATION.

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C5 AND C6 ISOMERIZATION

FIGURE IV: 2-18. C5 AND C6 ISOMERIZATION. I. SWEETENING AND TREATING PROCESSES

Treating is a means by which contaminants such as organic compounds containing sulfur, nitrogen, and oxygen; dissolved metals and inorganic salts; and soluble salts dissolved in emulsified water are removed from petroleum fractions or streams. Petroleum refiners have a choice of several different treating processes, but the primary purpose of the majority of them is the elimination of unwanted sulfur compounds. A variety of intermediate and finished products, including middle distillates, gasoline, kerosene, jet fuel, and sour gases are dried and sweetened. Sweetening, a major refinery treatment of gasoline, treats sulfur compounds (hydrogen sulfide, thiophene and mercaptan) to improve color, odor, and oxidation stability. Sweetening also reduces concentrations of carbon dioxide. Treating can be accomplished at an intermediate stage in the refining process, or just before sending the finished product to storage. Choices of a treating method depend on the nature of the petroleum fractions, amount and type of impurities in the fractions to be treated, the extent to which the process removes the impurities, and end-product specifications. Treating materials include acids, solvents, alkalis, oxidizing, and adsorption agents. Acid, Caustic, or Clay Treating

Sulfuric acid is the most commonly used acid treating process. Sulfuric acid treating results in partial or complete removal of unsaturated hydrocarbons, sulfur, nitrogen, and oxygen compounds, and resinous and asphaltic compounds. It is used to improve the odor, color, stability, carbon residue, and other properties of the oil. Clay/lime treatment of acid-refined oil removes traces of asphaltic materials and other

compounds improving product color, odor, and stability. Caustic treating with <https://assignbuster.com/the-crude-oil-pretreatment-environmental-sciences-essay/>

sodium (or potassium) hydroxide is used to improve odor and color by removing organic acids (naphthenic acids, phenols) and sulfur compounds (mercaptan, H₂S) by a caustic wash. By combining caustic soda solution with various solubility promoters (e. g., methyl alcohol and cresols), up to 99% of all mercaptan as well as oxygen and nitrogen compounds can be dissolved from petroleum fractions. Drying and Sweetening. Feedstocks from various refinery units are sent to gas treating plants where butanes and butenes are removed for use as alkylation feedstock, heavier components are sent to gasoline blending, propane is recovered for LPG, and propylene is removed for use in petrochemicals. Some mercaptans are removed by water-soluble chemicals that react with the mercaptans. Caustic liquid (sodium hydroxide), amine compounds (diethanolamine) or fixed-bed catalyst sweetening also may be used. Drying is accomplished by the use of water absorption or adsorption agents to remove water from the products. Some processes simultaneously dry and sweeten by adsorption on molecular sieves.

MOLECULAR SIEVE DRYING AND SWEETENING

FIGURE IV: 2-23. MOLECULAR SIEVE DRYING AND SWEETENING.

SULFUR RECOVERY

Sulfur recovery converts hydrogen sulfide in sour gases and hydrocarbon streams to elemental sulfur. The most widely used recovery system is the Claus process, which uses both thermal and catalytic-conversion reactions. A typical process produces elemental sulfur by burning hydrogen sulfide under controlled conditions. Knockout pots are used to remove water and hydrocarbons from feed gas streams. The gases are then exposed to a

catalyst to recover additional sulfur. Sulfur vapor from burning and
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conversion is condensed and recovered. Hydrogen Sulfide

Scrubbing Hydrogen sulfide scrubbing is a common treating process in which the hydrocarbon feedstock is first scrubbed to prevent catalyst poisoning.

Depending on the feedstock and the nature of contaminants,

desulphurization methods vary from ambient temperature-activated charcoal absorption to high-temperature catalytic hydrogenation followed by zinc

oxide treating. J. HYDROGEN PRODUCTION High-purity hydrogen (95%-99%)

is required for hydrodesulphurization, hydrogenation, hydrocracking, and

petrochemical processes. Hydrogen, produced as a by-product of refinery

processes (principally hydrogen recovery from catalytic reformer product gases), often is not enough to meet the total refinery requirements,

necessitating the manufacturing of additional hydrogen or obtaining supply

from external sources. In steam-methane reforming, desulfurized gases are

mixed with superheated steam (1, 100°-1, 600° F) and reformed in tubes

containing a nickel base catalyst. The reformed gas, which consists of steam,

hydrogen, carbon monoxide, and carbon dioxide, is cooled and passed

through converters containing an iron catalyst where the carbon monoxide

reacts with steam to form carbon dioxide and more hydrogen. The carbon

dioxide is removed by amine washing. Any remaining carbon monoxide in

the product stream is converted to methane. Steam-naphtha reforming is a

continuous process for the production of hydrogen from liquid hydrocarbons

and is, in fact, similar to steam-methane reforming. A variety of naphtha in

the gasoline boiling range may be employed, including fuel containing up to

35% aromatics. Following pretreatment to remove sulfur compounds, the

feedstock is mixed with steam and taken to the reforming furnace (1, 250°-1, 500° F) where hydrogen is produced.

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CHAPTER - 2

GLOBAL REFINING SCENARIO

The growth in global demand for gasoline and diesel, and the regulatory actions that are requiring lower and lower sulfur content in these products, is creating a mismatch between the demand for clean products and the availability of refining capacity to produce the products from available crude oils. This 'capacity crunch' will change the historical playing field for international crude and product supply and trade, and create strong and sustained margins for refiners, higher prices and potentially supply shortfalls for consumers.

2. 1 Demands for Petroleum Products

Demand for petroleum products is increasing particularly in the larger developing countries such as India, China, and Brazil. Much of this demand is centered around gasoline and distillates as these countries industrialize and a growing middle class adding to demands for personal transportation.

Concurrently U. S. demand for products has also increased and, unchecked by government policy and regulations, is expected to keep rising. The growth in demand is a shift in the global product demand profile towards lighter products. Demand for gasoline and middle-distillates are growing, whereas that for heavier fuel oils is declining. Figure 1 shows the petroleum consumption profile for the world excluding the Former Soviet Union (FSU).

Table 1 shows the growth rates in refined product consumption with the final column showing the annualized growth rate over the last 25 years. The growth in demand for light products such as gasoline and diesel has been matched by the growth in concern over mobile source emissions and their

effects on the environment and public health. The last five years has seen increasingly stringent environmental restrictions on product specifications, particularly the sulfur content. The drive towards ever lower sulfur content in gasoline and diesels has spread to Japan and other countries of the Asia Pacific region. Figure 1: World Petroleum Products Consumption (ex FSU) (Thousand bbl/d) Table 1: Average Annual Growth Rates in World Refined Product Consumption (Ex FSU) The United States is the world's largest consumer of gasoline, consuming nearly 40 percent of the world's total gasoline in 2004. Distillates on the other hand are more evenly distributed throughout the world, with the United States consuming 22 percent of the world's distillate in 2004. The growth is particularly strong in low-sulfur diesel used primarily for on-road highway transportation. While the increase in total oil consumption in the 2001-2004 timeframe is 1.7 percent, the increase in gasoline and distillate on an absolute volume basis represents a growth of 3,748 thousand barrels per day. Table 2 shows the consumption and growth rates of gasoline and distillates in the United States, which indicates a growth of about 925 thousand barrels per day clean products (gasoline and distillate) from 2001 to 2004. Table 2: Refined Product Consumption and Growth Rates in the U. S. from 2000 to 2004 (M bbl/d) While gasoline demand in the United States is growing, in Europe it has actually declined since 2000. Europe is showing increasing preference for diesel as its automotive fuel and is moving away from gasoline. Currently diesel powered vehicles constitute the bulk of the new cars being sold in Europe. Consequently, gasoline demand in Europe has declined at an average 2.1 percent per year since 2000 and the diesel demand has increased by 2.0 percent. The decline in European demand for gasoline can be a boon for the United States as it

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makes more gasoline supplies available on the world market. However, the developing economies of the world (including Asian countries like India and China) are showing a strong demand for gasoline. With the recent economic growth in the Asian countries and increased wealth among the population, there is a growing demand for cars—resulting in a 3.9 percent increase in demand for gasoline since 2000. Moreover, the penetration of car ownership is a magnitude or two lower than in the United States giving ample opportunity for growth. On the other hand, the increasing demand for diesel in the European Union means that there is intense competition for this fuel on the world market. In the short term additional increased demand for diesel from the Asian developing countries imposes further pressures. In Asia, diesel demand has grown at the rate of 2.7 percent since 2000. The gasoline and diesel demand growth rates in Asia are much higher than the overall world average growth rates shown in Figure 2. Figure 2: Gasoline and Diesel Demand Trends in the U. S., Europe, and Asia (1995-2004)

2.2 Supply of Petroleum Products

On a macro level petroleum product supply depends on the availability of crude oil and refining capacity. More specifically, adequate supplies of clean products depend on the optimal alignment of types of crude oils and refinery complexity. Historically refining has been the low margin sector of the petroleum industry. Investment in refining, particularly upgrading existing simple refineries, has been conservative, especially so outside the United States. Figure 3 shows historic global capacity and throughput from 1980 to 2004. The key conclusion from this chart is that the 1980's and early 1990's resulted in the reduction of surplus global refinery capacity. This trend has

been reversed since the mid 1990's, with recent years showing some net capacity growth to keep pace with higher demands. The question of the hour is, however, can capacity continue to keep pace with demands, even as more and more pressure is placed on refiners to meet lower sulfur specifications worldwide? Figure 3: World Refinery Capacity, Throughput and Oil Consumption (Million bbl/d) During the period from 1990-2000, when the refining margins were less volatile and relatively low as compared to the period after 2000, the global refining capacity was on average 9 percent more than the global oil demand. Since 2000, this percentage has dropped to as low as 3 percent above global oil demand in 2004. The IEA estimates that the global oil demand in 2010 will be about 90 million barrels per day, an increase of nearly 8 million barrels per day over the 2004. This increase is about 30-40 world scale refineries, and the net impact on the marketplace, even if that much refinery capacity could be made operational by 2010, would simply be maintaining today's high margins and volatility. For the refining capacity to keep pace with this increase and also maintain the 9 percent surplus capacity over demand that occurred in 1990-2000, it would need an additional 13.9 million barrels per day capacity to be built between now and 2010. This would be 50-70 refineries of world scale size. According to the 2005 Oil & Gas Journal Worldwide Refining survey and Construction reports, the total new worldwide atmospheric crude distillation capacity under construction or engineering is about 250,000 bbl/d. Since that publication, there have been some announcements, including a large Saudi export refinery in Yanbu and other Saudi expansions, an ExxonMobil GTL facility and Condensate refinery in Qatar, and some China capacity.

However, it is clear that the number of new refineries needed, or major <https://assignbuster.com/the-crude-oil-pretreatment-environmental-sciences-essay/>

expansions, is significant, and, more critically, these additions should, right now, already be in the engineering phase to be operational by 2010. While some of that demand growth before 2010 may be met by capacity increment, and some could be met by upgrading existing refineries with lower current utilizations, the need for timely investment in capacity to sustain the demand outlook is essential. Table 3: Global Oil Demand and Refining Capacity (M bbl/d) As capacity growth follows demand, small events can have a grossly magnified effect. This leads to increased upward pressure on prices, refining margins, and volatility. Over the past year, refining margins in the United States have been very strong, with distillate in particular enjoying a sustained period of high margins versus WTI (See figure 4). The pull of higher global distillate demand and reduced diesel specifications are keeping margins high. High gasoline demands, and margins, are impacting the ability of refiners to swing to higher distillate production. These high margins are indicative of a tight market overall, and it is difficult to predict when this pattern will end. Note that Figure 4 shows a sustained high margin since mid-2004 as spare refinery capacity narrowed.

Figure 4: Price Spread between NYMEX Gasoline and NYMEX WTI

(cents/gal) Effect of Product Specifications

The outlook for capacity investment is hampered by the reality that the need to meet sulfur regulatory changes has been a primary pull on refiner's capital. Figure 5 shows clearly that hydro processing has been most significant processing investment over the past 5 years. The bulk of this growth is due to the continued pressure to meet lower sulfur specifications. Refiners have had to add secondary unit capacity and modify existing hardware and catalyst to

sustain and expand their capacity to meet lower sulfur standards with their
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historic crude slates. Reduced sulfur targets in global products, including potentially residual fuels and heating oil, will increase competition and premiums for sweet crude oils. Europe's base sweet crude refinery capability and the relatively weak sour refining ability in the Asia Pacific region will also pull sweet crude away from the United States. Figure 5: Change in World Refining Capacity Since 1999 (Million bbl/d) As the tighter specifications come into effect for both gasoline and distillates, and demand continues to grow, there will also be an increasing pressure on the system as both low-sulfur gasoline and ultra-low sulfur diesel compete for the best crude oils available. This will place a premium on the light sweet crude oils versus the heavy sour crude oils. Some refineries are adding coking, cracking and hydro treating capacity to increase their flexibility in handling heavier and more sour crude oils. However, these capacity additions may not have kept pace with the demand growth as evidenced by the high differentials between sweet and sour crude oils. Refiners who have not made the investment to upgrade will have no option other than to purchase the higher cost sweet crude oils. In some cases, even running sweet crude will not be enough to extract the required sulfur to meet low or ultra low sulfur specifications for some marginal refineries worldwide. Figure 6 shows the price spreads between West Texas Intermediate (Sweet) and Saudi Arabian (Sour) crude oils. It's assumed that the market will continue to reflect a much wider than historical premium for sweet crude's.

Figure 6: Price Spread between WTI and Saudi Arabian Crude Oils

2.3 The Capacity Crunch

Table 3 showed a trend of less and less surplus global refining capacity through 2004. Based on the forecast demands through 2010, an additional 8 million barrels per day of global refinery capacity is needed to maintain the same narrow surplus capacity as 2004. With IEA predicting another 17.6 million barrels per day demand by 2020, the refinery capacity need will grow even more. There will be some capacity increase every year, and some new refineries will be built and operational over the period, however there could also be some capacity lost as marginal refineries must either invest to make marketable clean products or be forced to close. The oil industry has worked to utilize surplus capacity since the mid 1980's that had depressed margins and profits, and industry obviously prefers a tighter ratio of capacity to demand. In cases where industry is evaluating or has announced capacity increases since the Oil & Gas Journal survey was released, the location of those projects are planned for China and the Middle East, and none are in the engineering stage. The Energy Bill provides some accelerated depreciation guidelines to encourage U. S. refining investment; however locations outside the United States may still be more economic due to costs of labor and environmental infrastructure needs. It is also significant that the Energy Bill contains provisions that are likely to accelerate the elimination of MTBE from the U. S. gasoline supply as refiners see inherent risk in blending MTBE on an economic basis versus a mandated need. This alone may reduce gasoline supply by as much as 140 M bbls/day or about the equivalent yield of gasoline from a 250 M bbls/day refinery. Moreover, the tighter product

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specifications in the United States versus the emerging Far East region will make it more cost effective for refiners with export capability in the Middle East, or even Europe, to manufacture and ship product to China or India. Where the product goes will depend on who is willing to ante-up to pay for the volume, and the ramifications for both the 'winner' and the 'loser' in that battle are significant.

2. 4 Infrastructure Needs

As demands increase and refinery capacity additions lag, the fragility of the distribution infrastructure will become more visible. In the Far East, the ability to import products is already there, but it likely will need to be expanded, and the downstream distribution systems will need extensive development. The United States also currently imports, but tankage for imports will need to be increased, and the strong existing product pipeline system will require investment to meeting growing demand and possibly integrate with new sources of imported supply. In addition, the globalization of products and phase out of single hull tankers will require larger investment in product vessels to handle the long range movement of products. Within the United States, several areas will likely show signs of infrastructure issues earlier than others. California is already tight on tankage and pipelines to import and move products. In other areas, the boutique fuels issue has tankage held captive that could be better used with a more fungible product mix. Reductions in tankage in markets such as Long Island can leave millions of consumers exposed, particularly in winter, despite having adequate supplies nearby in North Jersey and New York Harbor.

2.5 Refining Capacity

The global refining capacity utilization rate has increased substantially in recent years. In the 1980s, capacity utilization rates remained below 80 percent, implying that there was a large amount of idle refining capacity worldwide. But in the 1990s, utilization rates started to rise to meet growing demand for oil products. In 2004, the global refining capacity utilization rate reached 87 percent, while the utilization rates for major markets (US, Asia Pacific and Europe) exceeded 90 percent. The higher utilization rate for refining capacity indicates that surplus refining capacity is diminishing worldwide, particularly in major consuming markets of the world. The average annual increase of world oil demand from 1995 to 2003 was 1.5 percent; however, demand increased from 77.05 million barrels per day (B/D) in 2001 to 84 million B/D in 2005, an increase of close to 7 million B/D. Within this oil demand the fraction taken up by transportation fuels, namely gasoline and middle distillates (incl. aviation fuels) has shown phenomenal growth. Over the period 2001 to 2003 gasoline and middle distillate demand increased 1.35 million B/D from 47.04 million B/D to 48.39 million B/D, and accounted for 64 percent of total petroleum product demand increase. The average yearly growth rate of these petroleum products from 1995 is 1.8 percent, with gasoline at 1.4 percent and middle distillates at 2.1 percent. The increase in 2002 relative to 2001 was 529,000 B/D; however, in 2003 this increase was a massive 824,000 B/D. On the other hand, world refining capacity increased only 1.09 million B/D from 82.84 million B/D in 2001 to 83.93 million B/D in 2003, with the annual growth rate from 1995 being only 1.2 percent/year. Compared with the previous year in 2002 and 2003 the increase was 722,000 B/D and 368,000 B/D respectively. This has resulted

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in a world refining utilization rate rising from 84.2 percent in 2001 to 84.9 percent in 2003. Historically refining has been the low margin sector of the petroleum industry. Investment in refining, particularly upgrading existing simple refineries, has been conservative, especially so outside the United States. The key takeaway from the above statistics show that the 1980's and early 1990's resulted in the reduction of surplus global refinery capacity. This trend has been reversed since the mid 1990's, with recent years showing some net capacity growth to keep pace with higher demands (primarily capacity 'creep'). The question of the hour is, however, can capacity continue to keep pace with demands, even as more and more pressure is placed on refiners to meet lower sulfur specifications worldwide? During the period from 1990-2000, when the refining margins were less volatile and relatively low as compared to the period after 2000, the global refining capacity was on average 9 percent more than the global oil demand. Since 2000, this percentage has dropped to as low as 3 percent above global oil demand in 2004. The IEA estimates that the global oil demand in 2010 will be about 90 million barrels per day, an increase of nearly 8 million barrels per day over the 2004 number. This increase is about 30-40 world scale refineries, and the net impact on the marketplace, even if that much refinery capacity could be made operational by 2010, would simply be maintaining today's high margins and volatility. For the refining capacity to keep pace with this increase and also maintain the 9 percent surplus capacity over demand that occurred in 1990-2000, it would need an additional 13.9 million barrels per day capacity to be built between now and 2010. This would be 50-70 refineries of world scale size. According to the 2005 Oil & Gas Journal Worldwide Refining survey and Construction reports, the total new worldwide <https://assignbuster.com/the-crude-oil-pretreatment-environmental-sciences-essay/>

atmospheric crude distillation capacity under construction or engineering is about 250, 000 bbls/d. Since that publication, there have been some noteworthy announcements, including a large Saudi export refinery in Yanbu and other Saudi expansions, an Exxon Mobil GTL facility and Condensate refinery in Qatar and some China capacity. However, even with these announcements, it is clear that the number of new refineries needed, or major expansions, is significant, and, more critically, these additions should, right now, already be in the engineering phase to be operational by 2010. While some of that demand growth before 2010 may be met by capacity creep, and some could be met by upgrading existing refineries with lower current utilizations, the need for timely investment in capacity to sustain the demand outlook is compelling. As capacity growth lags demand, small events can have a grossly magnified effect. This leads to increased upward pressure on prices, refining margins, and volatility. Over the past year, refining margins in the United States have been very strong, with distillate in particular enjoying a sustained period of high margins versus WTI . The pull of higher global distillate demand and reduced diesel specifications are keeping margins high. High gasoline demands, and margins, are impacting the ability of refiners to swing to higher distillate production. These high margins are indicative of a tight market overall, and it is difficult to predict when this pattern will end.

2. 6 Effect of Product specifications

The outlook for capacity investment is hampered by the reality that the need to meet sulfur regulatory changes has been a primary pull on refiner's capital. Hydroprocessing has been far and away the most significant

processing investment over the past 5 years. The bulk of this extraordinary growth is the continued pressure to meet lower sulfur specifications. Refiners have had to add secondary unit capacity and modify existing hardware and catalyst to sustain and expand their capacity to meet lower sulfur standards with their historic crude slates. Reduced sulfur targets in global products, including potentially residual fuels and heating oil, will increase competition and premiums for sweet crude oils. Europe's base sweet crude refinery capability and the relatively weak sour refining ability in the Asia Pacific region will also pull sweet crude away from the United States. As the tighter specifications come into effect for both gasoline and distillates, and demand continues to grow, there will also be an increasing strain on the system as both low-sulfur gasoline and ultralow sulfur diesel compete for the best crude oils available. This will place a premium on the light sweet crude oils versus the heavy sour crude oils. Currently this can be seen in the historically high price spread between sweet and sour crude oils. Some refineries are adding coking, cracking and hydrotreating capacity to increase their flexibility in handling heavier and more sour crude oils. However, these capacity additions may not have kept pace with the demand growth as evidenced by the high differentials between sweet and sour crude oils. Refiners who have not made the investment to upgrade will have no option other than to purchase the higher cost sweet crude oils. In some cases, even running sweet crude will not be enough to extract the required sulfur to meet low or ultra low sulfur specifications for some marginal refineries worldwide. Based on the forecast demands through 2010, an additional 8 million barrels per day of global refinery capacity is needed to maintain the same narrow surplus capacity as 2004. With IEA predicting another 17.6 million barrels

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per day demand by 2020, the refinery capacity need will grow even more. There will be some capacity creep every year, and some new refineries will be built and operational over the period, however there could also be some capacity lost as marginal refineries must either invest to make marketable clean products or be forced to close. The oil industry has worked to wring out surplus capacity since the mid 1980's that had depressed margins and profits, and industry obviously prefers a tighter ratio of capacity to demand. The magnitude of the need for additional capacity over the next 5 years is, however in stark contrast to the relatively few significant projects currently underway to expand global refining capacity. In cases where industry is evaluating or has announced capacity increases since the Oil & Gas Journal survey was released, the location of those projects are planned for China and the Middle East, and none are in the engineering stage. The Energy Bill provides some accelerated depreciation guidelines to encourage U. S. refining investment; however locations outside the United States may still be more economic due to costs of labor and environmental infrastructure needs. It is also significant that the Energy Bill contains provisions that are likely to accelerate the elimination of MTBE from the U. S. gasoline supply as refiners see inherent risk in blending MTBE on an economic basis versus a mandated need. This alone may reduce gasoline supply by as much as 140 M bbls/day or about the equivalent yield of gasoline from a 250 M bbls/day refinery. Moreover, the tighter product specifications in the United States versus the emerging Far East region will make it more cost effective for refiners with export capability in the Middle East, or even Europe, to manufacture and ship product to China or India. Where the product goes will depend on who is

willing to ante-up to pay for the volume, and the ramifications for both the 'winner' and the 'loser' in that battle are significant.